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Ph.D. Thesis

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**The Influence of Ambient Medium Density
on Laser Ablation Processes**

Marvin Moses Kilgo III
Ph.D. Thesis

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and

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November 1995

MASTER

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Table of Contents:

LIST OF FIGURES	vi
LIST OF TABLES	ix
ACKNOWLEDGEMENTS	x
1. INTRODUCTION	1
2. PHILOSOPHY OF ENGINEERING	5
ENGINEERING EPISTEMOLOGY	7
MICROSCALE ENERGY TRANSPORT PROCESSES	15
BAYESIAN ANALYSIS IN ENGINEERING	21
3. LASER-MATERIAL INTERACTIONS	28
ABSORPTION OF RADIATION BY A SOLID	28
THERMAL CONDUCTION: SELECTION OF A CONSTITUTIVE EQUATION	34
LMI REGIMES	40
<i>Linear heating</i>	41
<i>Laser induced phase change problems</i>	48
<i>Radiative ablation</i>	51
LASER-FLUID INTERACTIONS	66
4. THE BEHAVIOR OF REAL FLUIDS	71
THERMODYNAMICS OF REAL FLUIDS	71
<i>Ideal fluid behavior</i>	72
<i>Phase equilibria</i>	76
<i>Real fluid behavior and selection of an equation of state</i>	81
<i>Interfacial phenomena</i>	92
<i>Interpretations of thermodynamic concepts</i>	94

CRITICAL PHENOMENA IN FLUID SYSTEMS	96
<i>Introduction</i>	96
<i>Characteristics of second-order phase changes</i>	100
<i>Behavior of thermodynamic potentials near critical points</i>	101
<i>Critical point opalescence</i>	101
<i>Phenomenology of near critical fluid systems</i>	104
THERMALLY INDUCED CONVECTION	105
<i>Continuum formulation of convective flow</i>	106
<i>Teleological considerations in convection</i>	111
<i>The initiation of natural convection</i>	114
<i>Convection in the melt pool of the target</i>	116
5. EXPERIMENTAL ABLATION SYSTEM	125
THE PICOSECOND Nd:YAG LASER	125
<i>General description</i>	125
<i>Q-switching and passive mode locking</i>	127
<i>Active mode locking</i>	129
<i>Oscillator alignment</i>	132
CONTROL OF AMBIENT CONDITIONS	142
SAMPLE PREPARATION, SYSTEM ALIGNMENT AND DATA COLLECTION	146
TEMPORAL STABILITY OF LASER OUTPUT	149
6. EXPERIMENTAL RESULTS	152
VARIATION OF CRATER MORPHOLOGY	152
<i>Variation of crater dimensions with ambient density</i>	153
<i>Exterior thermal affected zone</i>	155
<i>Optical caustics as a diagnostic tool for plasma formation</i>	156
<i>Rim deformation</i>	156
<i>Crater descriptions</i>	157
TRANSMISSION OF LIGHT AS A FUNCTION OF DENSITY	176

TEMPORAL STABILITY OF PULSE ENERGY OF THE LASER	178
7. CONCLUSIONS	185
EXPERIMENTAL RESULTS: LASER ABLATION IN NONIDEAL FLUIDS	185
THEORETICAL RESULTS: ANALYSIS OF HIGH FLUX TRANSPORT PROCESSES	186
DIRECTIONS FOR FUTURE RESEARCH	189
REFERENCES	193

Appendices:

A. MATHEMATICAL CONSIDERATIONS	231
GENERALIZED FUNCTIONS	231
MEASURE THEORY AND LEBESGUE INTEGRATION:	235
NONSTANDARD ANALYSIS	235
CATASTROPHE THEORY	242
ALTERNATIVE INTERPRETATIONS OF FAMILIAR TOPICS	246
B. CONSTANTS, PHYSICAL PROPERTIES, AND NOMENCLATURE	254
C. STOCHASTIC AND FRACTAL ELEMENTS IN ENGINEERING ANALYSIS	264
STOCHASTIC ANALYSIS	266
SIMILARITY ANALYSIS	277
FRACTAL ANALYSIS	285
D. ERROR ANALYSIS	296
E. OPTICAL EFFECTS	306
OPTICAL ANALYSIS OF GAUSSIAN BEAMS	306
NONLINEAR OPTICAL EFFECTS	317
THE LORENTZ-LORENZ EQUATION	323
ANOMALOUS DISPERSION IN METALS	324

List of Figures

FIGURE 3-1. PROCESSES ASSOCIATED WITH LASER ABLATION	29
FIGURE 3-2: RAYLEIGH CURVE FOR HEAT TRANSFER TO A COMPRESSIBLE FLOW.	56
FIGURE 3-3. INITIATION OF CAUSTIC STRUCTURE.....	63
FIGURE 3-4. RESULTANT CAUSTIC FOR AN INTERNALLY DISPLACED SOURCE.....	64
FIGURE 3-5. CAUSTIC RESULTING FROM AN EXTERNALLY DISPLACED SOURCE.	65
FIGURE 3-6: INITIAL CRATER MORPHOLOGY	66
FIGURE 3-7: EARLY STAGES OF CAUSTIC DEVELOPMENT.....	66
FIGURE 4-1 : NORMALIZED LENNARD-JONES POTENTIAL.	87
FIGURE 4-2: SIMULATION OF INTERMOLECULAR CORRELATION FOR A=10.....	89
FIGURE 4-3: SIMULATION OF INTERMOLECULAR CORRELATION FOR A=14.....	90
FIGURE 4-4: SIMULATION OF INTERMOLECULAR CORRELATION FOR A=12.....	91
FIGURE 4-5: SIMULATION OF INTERMOLECULAR CORRELATION FOR A=7.....	92
FIGURE 4-6: CONFIGURATION OF HELE-SHAW FLOW.....	116
FIGURE 4-7. ORIGIN OF MARANGONI FORCES. (A) SPATIAL DEPENDENCE OF IRRADIATION; (B) SPATIAL VARIATION OF T AND Σ	122
FIGURE 5-1. SCHEMATIC VIEW OF EXPERIMENTAL SYSTEM	126
FIGURE 5-2: MODELOCKING OF SIMPLE COSINUSOIDS.....	131
FIGURE 5-3. OPTICAL CONFIGURATION OF THE CONTINUUM YG601C LASER.....	133
FIGURE 5-4. BUILD-UP TIME EVALUATION.....	135
FIGURE 5-5. INFLUENCE OF ACOUSTO-OPTIC MODE LOCKING ON FREE RUNNING STATE.	136
FIGURE 5-6. "STAIRCASE" APPEARANCE DURING FREE RUNNING OPERATION.....	137
FIGURE 5-7. THE EFFECT OF DYE ADDITION ON SIGNAL RESPONSE.....	138
FIGURE 5-8. Q SWITCHING OF THE LASER.....	139
FIGURE 5-9. SIGNAL AFTER BEAM DUMPING TO THE AMPLIFIER.....	140
FIGURE 5-10. TYPICAL BEAM PROFILE.....	141
FIGURE 5-11: THERMAL CYCLING OF CARBON DIOXIDE DURING AUTOCLAVE FILL PROCESS.	145
FIGURE 5-12. LOCATION OF REFLECTIONS FROM DUAL LENS SYSTEM.	146
FIGURE 5-13. AUTOCLAVE POSITION AS A FUNCTION OF DENSITY.	149
FIGURE 5-14: EXPERIMENTAL LAYOUT FOR MEASUREMENT OF PULSE ENERGY FLUCTUATIONS	151
FIGURE 5-15: A REPRESENTATIVE REAL-TIME SEQUENCE OF PULSE ENERGIES.	151
FIGURE 6-1: CRATER RIM DEPENDENCE ON FLUID DENSITY.....	154
FIGURE 6-2. DEPENDENCE OF DENSITY ON PRESSURE	157

FIGURE 6-3: SAMPLE 940714.3-A	159
FIGURE 6-4. SAMPLE 940714.3C.....	159
FIGURE 6-5. SAMPLE 940714.3B.....	160
FIGURE 6-6. SAMPLE 940930.1A.....	161
FIGURE 6-7: SAMPLE 940717.6-A	162
FIGURE 6-8. SAMPLE 941006.4A.....	162
FIGURE 6-9. SAMPLE 940717.6B.....	163
FIGURE 6-10. SAMPLE 940717.6C.....	163
FIGURE 6-11. SAMPLE 940717.4A.....	164
FIGURE 6-12. SAMPLE 940717.3A.....	164
FIGURE 6-13. SAMPLE 940717.5A.....	165
FIGURE 6-14. SAMPLE 941006.4B.....	165
FIGURE 6-15. SAMPLE 941006.3A.....	166
FIGURE 6-16. SAMPLE 940717.9B.....	167
FIGURE 6-17. SAMPLE 940717.9A.....	167
FIGURE 6-18. SAMPLE 940717.9C.....	168
FIGURE 6-19. SAMPLE 940809.1A.....	168
FIGURE 6-20. SAMPLE 940809.1B.....	169
FIGURE 6-21. SAMPLE 940809.2A.....	169
FIGURE 6-22. SAMPLE 940809.2B.....	170
FIGURE 6-23. SAMPLE 940809.3A.....	171
FIGURE 6-24. SAMPLE 940809.3B.....	171
FIGURE 6-25. SAMPLE 941006.9B.....	172
FIGURE 6-26. SAMPLE 941006.9A.....	172
FIGURE 6-27. SAMPLE 941011.5A.....	173
FIGURE 6-28. SAMPLE 940808.3A.....	173
FIGURE 6-29. SAMPLE 940808.3B.....	174
FIGURE 6-30. SAMPLE 940808.3C.....	174
FIGURE 6-31. SAMPLE 940808.2D.....	175
FIGURE 6-32: REPRESENTATIVE PULSE ENERGY SEQUENCES.	181
FIGURE 6-33: UNSTABLE PULSE SEQUENCE, PRIOR TO DELAY LINE MANIPULATION	182
FIGURE 6-34: MODERATE IMPROVEMENT OF PULSE ENERGY STABILITY.....	182
FIGURE 6-35: A GOOD PULSE ENERGY SEQUENCE.....	183
FIGURE 6-36: A SECOND GOOD SEQUENCE	183
FIGURE 6-37: R/S BEHAVIOR FOR A BAD SEQUENCE	184

FIGURE 6-38: R/S BEHAVIOR FOR A GOOD SEQUENCE.....	184
FIGURE A-1. A SIMPLE CAUSTIC	235
FIGURE A-2: THE GEOMETRY OF A CUSP.....	245
FIGURE C-1 . ITERATIVE CREATION OF A SIMPLE FRACTAL.....	286
FIGURE D-1: SKEWNESS FOUND THROUGH MONTE CARLO ANALYSIS.....	303
FIGURE E-1. SCHEMATIC DESCRIPTION OF MODELOCKING FOR WAVES OF CONSTANT PHASE.....	320

List of Tables

TABLE 2-1. REPRESENTATIVE ABLATION TIME AND LENGTH SCALES.	17
TABLE 2-2. LINEAR CONSTITUTIVE RELATIONS FOR TRANSPORT PROCESSES.	19
TABLE 3-1: FLUENCE RANGES ASSOCIATED WITH LASER MATERIAL INTERACTIONS	40.
TABLE 3-2: REGIMES OF LASER INDUCED PLASMAS	58
TABLE 3-3 OPTICAL REGIMES OF LASER INTERACTION WITH FLUIDS.	67
TABLE 4-1: MONTE CARLO SIMULATION PARAMETERS	89
TABLE 4-2 : CRITICAL SYSTEMS AND THEIR ORDER PARAMETERS	97
TABLE C-1. KINETIC PROPERTIES OF 1 CM ³ OF ARGON AT STP (P= 1 BAR, T = 273.2 K)	267.
TABLE C-2: SELECTED DIMENSIONLESS GROUPS	283
TABLE D-1: UNCERTAINTY OF SPECIFIC VOLUME	302
TABLE D-2: PROCESS SETTINGS FOR HIGH DENSITY EXAMPLE	303
TABLE D-3: ERROR PROPAGATION CALCULATIONS FOR HIGH DENSITY CARBON DIOXIDE	304
TABLE E-1: REPRESENTATIVE ABCD MATRICES.	311

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1. INTRODUCTION

Interest in high flux transport processes has grown in recent years along with the ability and need to manipulate systems with microscopic length and time scales. These systems present unique engineering challenges. Because the time and length scales associated with these problems are very small, assumptions of local equilibrium, physical and mathematical smoothness of boundaries and the unambiguous definition of thermodynamic fields can not be automatically made, even though they may ultimately be acceptable. Furthermore, the observations are made on macroscopic or integrated scales. The large difference in scales between the temporal evolution of the process and the observation requires careful consideration of the claims made regarding the system's microscopic, temporal behavior. In particular, consistency of a proposed model with observed results does not guarantee uniqueness, or predictive accuracy for the model. For these reasons, microscale heat transfer systems demand a careful consideration of the framework within which the experimentation and analysis are conducted.

This dissertation presents an engineering perspective on the investigation of high flux transport processes. Its purpose is two-fold. First, the specific intent is to investigate the performance of high power pulsed laser ablation processes in the presence of an ambient fluid. Second, a more general objective is to use laser ablation as a paradigm for high flux, small scale transport processes. These processes (hereafter denoted HFTP) are of practical and philosophical importance. Their practical importance is obvious: new technologies have ever smaller length and time scales, and technologically significant high flux processes range from the cooling of new computer

chips to the operation of inertially confined fusion plasmas. The philosophical issues associated with HFTP are less apparent, but also of vital importance to the development of appropriate analytical tools.

This dissertation also presents an observationally biased approach to engineering which is integrated throughout the analysis. This perspective has been discussed in numerous contexts previously, particularly in Bayesian statistical techniques, in the maximum entropy methods used in statistical physics, and in design methodologies. However, its use in thermal engineering is not common, and its implementation is not trivial. These facts justify its explicit consideration here.

Overview of this research

The basis of this work is established in chapter 2, which focuses on the philosophical foundations of engineering analysis and clearly defines the regime of HFTP. The process of gathering and analyzing information is shaped – often implicitly – by the paradigm within which the observer is working. The purpose of this chapter is to present the assumptions made regarding the epistemology and the inferential structure which support the remainder of the work. This is not a detailed review of the philosophy of science; rather, this discussion is included to clarify the nature of the conclusions which are presented.

The remainder of this dissertation focuses on the mathematical and physical analysis of microscale HFTP, and on the application of these techniques to laser ablation of metals.

In Chapter 3, the interaction of lasers and materials is discussed in depth. The nature of such interactions is highly dependent on material properties and pulse fluence;

this chapter studies the approximations appropriate to several of these regimes, and evaluates the numerous attempts to solve various aspects of the problem. This chapter also discusses *a fortiori* the nature of microscale thermal conduction and of surface melting and vaporization.

Chapter 4 presents an analysis of the behavior of real fluid systems. The first two sections discuss nonideal classical thermodynamics and the phenomenological behavior of fluids in the region of phase space near a critical point. This topic is of considerable interest for two reasons. First, the experimental work discussed in later chapters is strongly dependent on the behavior of the ambient medium surrounding the ablation site. Second, many of the techniques developed in the statistical mechanics of fluids during the last few decades can be readily adapted to the study of HFTP.

The third component discussed in Chapter 4 is convective flow, particularly that resulting from the ablation process. The coupling of thermofluid transport processes to the energy dissipation at the surface plays an important role in the development of surface morphology and system behavior. Natural convective flows are also an appropriate component of this chapter because their structure arises from internal dissipative processes, rather than from external forces. The resulting flow can thus show strong deviations from idealized models.

For engineering applications, experimental confirmation of a theory is necessary, for two reasons. First, the theory can not be complete. As proven earlier this century by Gödel, given any axiomatic system, formally undecidable questions exist. For engineering purposes, the inability to derive an analytical solution demands experimentation to provide an empirical basis for future work. Second, understanding the implications of a model is far different from understanding a physical system. Birkhoff

[1] emphatically presents this case by reviewing paradoxes in fluid mechanics, in which real fluid behavior would not have been predicted by – or actually contradicted – otherwise satisfactory theories. Thus, the next two chapters are devoted to the application of the theory developed previously to an experimental laser ablation system. Chapter 5 provides a description of the experimental system and serves as an operating manual for the laser, while Chapter 6 provides the experimental results.

Finally, Chapter 7 presents the conclusions of this study and suggests potential avenues for further study. The appendices contain a substantial body of material which was not appropriate in any of the above chapters, but which is important for placing this research in perspective. As a result, several topics are considered in depth which are only peripherally related to the analysis of laser ablation. Among these are the mathematics and physics associated with HFTP, techniques for error analysis, and nonlinear optical phenomena which played a role in this research.

2. PHILOSOPHY OF ENGINEERING

Processes such as laser ablation present considerable experimental, theoretical and analytical challenges. Some of the specific difficulties for this system are considered in detail in subsequent chapters. Priority is given in this chapter, however, to general concerns for high flux transport processes (HFTP):

In most technical literature, a brief statement of the physical and mathematical assumptions is conventional and sufficient. However, microscale heat transfer, like other HFTP, has incredibly small time and length scales. The typical assumptions of local equilibrium, physical and mathematical smoothness of boundaries, and the unambiguous definition of thermodynamic fields can not be blithely made, even though they may ultimately be acceptable. Furthermore, the large difference in time scales between the evolution of the process and the observation requires careful consideration of the claims made regarding the system's microscopic, temporal behavior. In particular, consistency of a proposed model with observed results guarantees neither uniqueness nor predictive accuracy for the model beyond the experimental region. For these reasons, HFTP demand a careful consideration of the framework within which the experimentation and analysis are conducted.

As is often the case in thermal engineering, the analysis of HFTP is essentially an inverse problem. Such problems are characterized by the availability of limited data, which represent the evolution of a dynamic system. The objective of the analysis is to determine the values of the parameters of the system, which is typically represented by a set of differential equations. Such analyses usually assume a form for these equations,

and the problem is then overconstrained. Inversion of the data, using techniques such as the method of least squares, leads to estimates of the parameter values [2 – 11]. Typical parameters of interest in thermal problems include physical properties such as the conductivity and heat capacity, and boundary conditions such as surface temperatures and surface fluxes [12 – 26].

Of course, the quality of these results depends heavily on the appropriateness of the system of equations. This caveat is particularly important in cases where extrapolation of the data is attempted. Testing for adequacy of the model is an important and difficult task, which is discussed extensively in the applied statistics literature. [27 – 34]. Across a limited range, several models might give acceptable results. The art of engineering analyses is thus building a model which incorporates the salient physical features of the problem. This is discussed in more detail below.

As an example, a “typical” thermal inverse problem might be to evaluate the internal surface temperature of a kiln, given temperature observations from thermocouples at several locations throughout the kiln wall [35].¹ In this case, observation and experience conclusively demonstrate that the ‘standard’ energy equation is appropriate for the temperatures and fluxes to be expected. For this problem, therefore, lack of fit of the model is of little concern from an engineering perspective. The desired temperature can be found by jointly considering the temporal behavior of the thermocouples. This is relatively simple for a steady state problem, and quite difficult for arbitrary fluctuations of the temperature.

¹This is not an artificial problem. Placement of thermocouples in the wall rather than the internal surface might be necessary if the kiln environment was too harsh thermally or chemically for the thermocouples.

The philosophical implications of HFTP are less obvious than the analytical difficulties, but equally important. As length and time scales shrink, physical and mathematical objections to the continuum hypothesis become more urgent. As fluxes increase, nonlinearities play a more significant role in system evolution. To address these concerns, an epistemology of engineering systems is presented in this chapter. In addition, a review of the scales associated with laser ablation is presented, and the chapter concludes with a discussion of the role of Bayesian inference for the incorporation of stochastic elements into engineering theories.

Engineering Epistemology

The process of gathering and analyzing information is shaped – often implicitly and unconsciously – by the perspective of the observer [36–38]. The purpose of this section is to present the assumptions regarding the epistemology of thermal engineering and the nature of acceptable inference which underlay the remainder of the work. This discussion specifies the nature of the conclusions which are presented throughout the thesis; it is not a comprehensive review of the philosophy of science.

The next section stresses the importance of thinking clearly about the implications of continuity for HFTP. The more general role of continuity in models of physical reality also deserves consideration. As the following quote from Roger Penrose explains, the concept is very useful, but ultimately physically artificial [39]:

[there is a] “lack of a firm foundation for assigning any physical reality to the conventional continuum concept....[U]ltimately, physical laws should find their most natural expression in terms of essentially

combinatorial principles, that is to say, in terms of finite processes such as counting....

“If one is to accept the physical reality of the continuum, then one must accept that there are as many points in a volume of diameter 10^{-13} cm, or 10^{-33} cm or 10^{-1000} cm as there are in the entire universe.

“The concepts of open and closed sets, for example, depend vitally on the continuum of points, and are essentially meaningless in strictly physical terms, but such concepts can be used to great advantage when mathematical theory is applied to physics....”

As thermal engineering begins to focus more carefully on HFTP, we enter a realm much like that discussed by Penrose. The traditional analytical tools used by engineers remain useful, but we have to consider more carefully what our models are telling us, and in what way they are “true.”

In philosophy, the development of a theory of knowledge is known as epistemology. This has been an active field, particularly in the philosophy of science [40]. The perspective of Newton and Laplace, in which everything was ultimately knowable – the “clockwork Universe” – was destroyed early in the twentieth century by the development of quantum mechanics and relativity theory. More recently, chaos theory has demonstrated that even in a deterministic system, absolute predictability may be chimeric. Within this context, the epistemological basis for science has been widely debated.

Engineers, however, have largely avoided these concerns because engineering is teleological in nature; that is, questions of “why” a system behaves as it does are typically answered by describing “how” it works. In such a perspective, the emphasis is on

making a model of the system as simple as possible, while retaining the observed features. This approach encourages the use of heuristic formulations, and its application is responsible for great technological successes. As engineering research focuses more closely on HFTP, however, the interpretation of results and the definition of problems requires developing a more general perspective on the nature of the problem being analyzed.

The study of HFTP is still a developing field, and therefore presents a good opportunity to consider epistemological concerns within the structure of a rapidly growing area of study. Several approaches have been used in conducting HFTP research, and the field has yet to be axiomatized in the manner in which thermodynamics or quantum mechanics have been reformulated. To initiate this study, it is reasonable to consider the range of philosophies within which such models could be made, and then speculate on the type of formulation which is likely to be appropriate for engineering analyses of HFTP.

As discussed by Rescher [41], scientific epistemologies can be loosely placed into three categories: *instrumentalism*, *realism*, and *approximationism*.

- Instrumentalism is the belief that the theoretical components of a model do not actually exist, but merely serve as ‘thought-fictions.’ Within this perspective, the components help an investigator to visualize the processes by which observable changes occur, but are not thought of as real in any tangible sense. This is the view of science as a “black box”, in which the sole value of theory is as a method of making verifiable predictions, and in which questions of the truth of the model are irrelevant, and unanswerable. Many practical applications of engineering effectively adopt this approach.

•Realism is the opposing perspective that the items of our theories exist and have, in fact, all of the important features which we ascribe to them. Within this view, the assertion is that theory is true, *as stated*. Taking this approach makes the acceptance of radical changes to an accepted theory extremely difficult. Examples in which the emergence of a new theory was begrudgingly accepted are easy to find². Adoption of an absolute realism in this sense effectively limits the range of investigations which a scientist or engineer might consider. (For example, see the discussion in Chapter 3 of the confounding of thermal and mechanical effects.)

The dichotomy between these two and their weaknesses are stressed here. The middle ground of approximationism is the choice suggested by Rescher in a more general setting, and by this thesis for HFTP in particular. Within this category, the belief is that current theories are in some sense reasonable approximations, but that they are not true in an absolute sense. This perspective seems natural from an engineering perspective, in which a long tradition of realizing the limitations of available information exists. We therefore are describing things that *do* exist, even if we remain unable to precisely and absolutely define them.

Several important points remain to be considered. Among the most important of these is whether our field of study is converging. Such a convergence would suggest that ultimately approximationism would be replaced by realism, as we come closer and closer to understanding the areas that we study. This was clearly the view of Richard Feynman [41], who wrote that:

² The imprisonment of Galileo for averring that the Earth revolves around the sun, and the suicide of Ludwig Boltzmann as a result of the rejection of his statistical mechanical models are two well known examples.

“Science cannot keep on going so that we are always going to discover more and more new laws....It is like the discovery of America — you only discover it once. The age in which we live is the age in which we are discovering the fundamental laws of nature, and that day will never come again.”

Although this perspective seems reasonable, it in essence implies that, ultimately, a realistic epistemology is possible. An alternative view is that the “age” referred to by Feynman has seen a growth in the range and precision of empirical observations, and that theories adequate to cover them have been developed. To claim that all possible future observations must fit this structure is quite optimistic³. Furthermore, even if the framework of the theory is correct, as the precision of observation improves, there will always be further levels of detail to be explored and explained in processes for which we have models at a coarser level.

Another way of responding to Feynman, and for justifying an approximationist epistemology arises by consideration of Wigner’s classic commentary “On the unreasonable effectiveness of mathematics in the natural sciences” [42]. Wigner expressed amazement at the utility of mathematics, often abstract and derived for other purposes, as a tool for explaining scientific observations. The physical sciences and engineering are reductionist in nature, and not ideal. This means that these fields rely on observation of physical and chemical processes, followed by logical analysis of these

³ Note that this does not imply that we know nothing: for example, we now know that the earth is roughly spheroidal, and can measure its dimensions repeatably, and this will not change. Nor are we talking about whether the sensory experiences of different observers are identical. Rather we are acknowledging that our basis of observations will always be finite, and therefore, our theories are neither complete nor final.

observations, rather than deduction from an abstract logically derived set of assumptions or axioms. That mathematics *does* describe nature was viewed as a wonderful coincidence.

An alternative view [43], however, recognizes the anthropomorphic nature of a human activity such as science. Our conclusions are intertwined with our observations, which in turn depend on the methods used to gather them. Since we have mathematics as a tool, we tend to define the problems that we can attack in terms of this tool. Problems which can not be unambiguously defined within this structure are referred to as “ill-posed,” even though these may be important problems, and it is our tools that are ill suited to the problem! An example of a field which has blossomed recently as new tools have become available has direct bearing on HFTP. The introduction by Mandelbrot [44, 45, 46] of fractal concepts to science greatly simplified the study of multiscale physical processes. These methods are discussed in detail with relation to laser ablation in succeeding chapters, and their absence would make description of ablation a much less defined process.

Thus, the claim of Wigner can be modified, and remain valid. The definition of a problem as ‘important’ tends to lead to the development of new tools, or the modification of old ones. The surprising aspect of the success of these tools is how well they can be made to fit within the existing framework of mathematics. This is a testament to the precision and rigor with which mathematicians have developed their theories, and to the surprising degree of structure imposed by relatively simple physically “intuitive” axioms.

The need to consider these issues is emphasized by two case studies in the development of scientific theories. The older of the two involves studies of optics by Newton and Goethe [47]. Newton’s pioneering work on optics included explaining the

separation of white light into its components by a prism. Newton designed a clever experiment to demonstrate that the formation of the spectrum was due to the presence of light of different wavelengths, rather than to the prism changing the light. This process was characteristic of Newton's emphasis on objectivity in the analysis of physical systems. Goethe, by comparison, was more interested in the perception of color by an observer, and was inclined to believe in the inseparability of "Nature." Working a century after Newton, his initial work was looking through the prism, rather than at its projected beams. His observations did not agree with Newton's theories, and by coincidence, his subsequent work was confounded by a physiological optical effect unknown at the time. The resulting controversy effectively drove Goethe from the physical sciences. Although there were certainly other factors involved in this imbroglio, at its foundation is a difference in perspective on the nature of light.

A second case involves Albert Einstein and Henri Poincaré, both of whom were noted philosophers of science as well as scientists. Both men also focused on fundamental physics at the turn of the twentieth century, and both greatly influenced current physical thinking. The differences in their areas of influence, however, can be directly attributed to the differences in their epistemological perspectives. Poincaré emphasized the role of sensory observations and empirical data in his theories, and furthermore felt that two innate rules of thought, mathematical induction and the concept of continuous groups, guided their organization⁴ [37]. He felt that the role of Euclidean geometry, while a matter of convention, was important because it was the most natural

⁴ Poincaré believed that in this sense it was the relation between objects that was important and objectively measurable. Thus physical theory serves to organize observations. Also, the concept of continuous groups, while consistent with Lie theory, is in this context less formal and more intuitive.

structure within which to observe the world. Thus, while he was willing to alter the laws of physics to account for relative motion, his view of the world as Euclidean remained firm. Today his influence is strongest in the developing area of chaos theory, in which inherently unpredictable systems evolve on manifolds embedded in a larger dimensional Euclidean space.

By comparison, Einstein was less firmly committed to the retention of a Euclidean geometry, and this led to his theory of relativity, and to his work on the photoelectric effect, within which photons are seen to exhibit both wave and particle features. Einstein, while guided by empirical observations, felt that theories were not discovered, but invented [37]. This distinction allowed him to freely suggest nonintuitive and unconventional ideas when they helped to explain observed behavior.

Parenthetically, the ubiquity of epistemological concerns can be noted by considering the work of the late W. Edwards Deming in the study of quality management issues. Deming was famous for his fourteen points for quality improvement, and for the influence that he had on the development of Japanese manufacturing processes after the Second World War. The *specific* statistical and management techniques which Deming advocated can be readily implemented, and yet many companies found Deming's full methodology difficult to adopt. The primary reason for this difficulty is explained by the significant differences in epistemology between most American businesses and Deming's theory. He referred to it as the development of a "theory of profound knowledge," and relied heavily on the work of an American philosopher, C.I. Lewis. Dramatically simplified, the view of Lewis and Deming is that it is virtually impossible to know enough about specific, individual cases to make an informed decision. Both systematic and unique causes influence all activity. Therefore, one must seek to understand the system within which people and processes work, and control the system. Based on this

perspective, Deming advocated the use of statistical control techniques, and the elimination of arbitrary numerical goals, whether for personnel evaluation or production planning⁵.

In a qualitative sense, therefore, it seems evident that epistemological concerns must be addressed in the analysis of complex systems, be they in manufacturing or basic research⁶. To provide an explicit basis for the remainder of this investigation, an approximationist epistemology will be assumed. Investigation of microscale HFTP must assume that science provides more than a black box, and yet, over-reliance on the conventional formulations used in microscale physics represents a dangerous blinkering of the study. The tools that we have, both physical and theoretical, are sufficient to allow probing of HFTP, but are coarse enough that we must consider the influence of the measurement process on the observations. In the next section some of the specific technical aspects of this interaction of HFTP and their observation are examined in detail.

Microscale energy transport processes

To set the experimental ablation process in a proper perspective, several of the length and time scales involved should be considered. The ablation is caused by pulses from a frequency doubled pulsed Nd:YAG laser, $\lambda = 532$ nm, incident on a copper

⁵ Deming's philosophy was also at odds with the academic world. As a professor at Columbia and New York University, he refused to grade students.

⁶ . These concerns are particularly important in modern research, where the complexity of experimentation and the use of indirect measurement requires trust in the abilities and judgement of others. It is virtually impossible for a single person to solely manage all observations, calibrations, and computations in state-of-the-art physical research, and thus modern scientists must trust the work of others in the development of their theories [92].

surface. Some representative time and length scales for this process are listed in Table 2-1.

The specific concerns raised above can now be considered in greater depth:

- *Local thermodynamic equilibrium*: this assumption implies that the relevant time scale is long enough to allow relaxation of most molecular processes. The use of equilibrium values for physical properties may not be appropriate if any kinetically controlled processes are taking place (i.e., dissolution, precipitation, phase changes, etc.). [49 – 60]
- *Physical and mathematical smoothness of boundaries*: obviously, the adequacy of an assumption of “smooth boundaries” depends on the specific question asked, even for the following ablation experiments: Surface morphology is actually quite rough compared to the radiative skin depth and the within pulse thermal diffusion length; it is negligible compared to the crater depth and diameter, and the interpulse thermal diffusion length.[61 – 67] Thus, an assumption of smooth boundaries is quite acceptable for consideration of the post-pulse conductive transport from the surface, and may pose problems in analysis of the coupling of the pulse or a resultant plasma to the surface. If, however, this coupling is nearly linear, it may also be possible to utilize an effective surface in the model.
- *Definition of thermodynamic fields*: speaking of fields such as temperature is only useful when they can be expressed as smooth, unique functions. This may not be the case during the pulse[68 – 72]. The difficulties raised by this problem are considered in greater depth in the next chapter, “Laser Ablation Models.”

Ablation parameter	Magnitude
Pulse duration, τ_p	$3\text{E}(-11) \text{ s}$
Pulse length, $\tau_p c$	$\sim 9 \text{ nm}$
Photon energy, $h\nu$	$3.7\text{E}(-19) \text{ J}$
Pulse energy, $E_p = N_p h\nu$	30 mJ
Number of photons per pulse, N_p	$8\text{E}(16)$
Focal spot effective diameter, D	$\sim 50 \text{ }\mu\text{m} = 50,000 \text{ nm}$
Radiation skin depth, l_{rad}	$\sim \lambda/16 = 33 \text{ nm}$
Thermal diffusion length, l_{th}	56 nm
Typical crater depth, Z	$10\text{'s of } \mu\text{m}$
Typical surface roughness, σ_r	$3 \text{ }\mu\text{m}$

Table 2-1. Representative ablation time and length scales.

These three issues arise from considerations of the meaning of “continuity” in the modeling of physical systems. The concept of continuity appears deceptively simple as it is initially presented in an introductory calculus course. Indeed, an intuitive sense of continuity is sufficient for most engineering analysis. Engineers and scientists, however, are often unaware that several centuries elapsed between the initial development of the calculus by Newton and Leibnitz and firm theoretical justification of the subject in the

nineteenth century. One of the primary difficulties that arose in this effort was the clarification of the concept of continuity [73]. The relevance to engineering analysis of several mathematical topics — including the use of generalized functions, nonstandard analysis, measure theory, group theory, and fractal geometry — is discussed in greater detail in appendices A and C.

To understand the practical significance of these issues on the consideration of HFTP, the foundation of traditional transport process analysis must be considered. The study of transport processes is quintessentially an engineering subject. Although the motion of fluids and energy transport have intrigued philosophers, artists and scientists for millennia⁷, the growth of practical tools for predicting the behavior of transport processes has been driven by applications. Thus, engineers have made a distinguished contribution by carefully studying transport phenomena and developing heuristic tools. In most cases, these tools preceded theoretical understanding of the mechanisms driving the processes. The developers of these tools typically realized the limitations inherent in such methods, which nonetheless allowed straightforward and accurate prediction of the behavior of transport processes across parameter regions of practical interest. Even now, the use of these “engineering” methods within their range of applicability is typically preferred from a design perspective over more rigorous — but significantly more complicated — methods.

The development of the study of transport phenomena as a coherent field resulted from the application of some basic concepts to physical systems. The resulting

⁷ Recall Leonardo da Vinci’s sketches of turbulent eddies, Archimede’s investigations of hydrodynamics, and Aristotle’s inclusion of fire and water as two of the four elements of the universe.

Conserved Quantity	Area of Study	Typical Driving Force	Linear Constitutive Relation
Momentum	Fluid mechanics, convective transport	Velocity gradient	Newtonian fluid, $\tau_{xy} = \mu \frac{\partial u_x}{\partial y}$
Energy	Heat transfer	Temperature gradient	Fourier's Law, $\mathbf{q} = -k\nabla T$
Chemical species	Mass transfer	Concentration gradient	Fick's Law, $\mathbf{j}_A = -\rho D \nabla \omega_A$

Table 2-2. Linear constitutive relations for transport processes

formulation is deeply ingrained within the subject because of its intuitive appeal and the ubiquity of its presentation. The transport of energy and matter, both in bulk and in relative motion, is presented as merely the application of three conservation laws.

In the approach used in virtually every text on the subject, conservation of mass, energy, and momentum is postulated to hold for an arbitrary body under consideration. Appropriate constitutive relations (typically linear) are chosen between the conserved quantity and the gradient of a potential which is assumed to act as a driving force (see Table 2-2). Finally, an appeal is made to Stoke's theorem to replace boundary fluxes with a volumetric density⁸. This removes explicit consideration of the volume element; as a result, the arbitrary body is thus allowed to shrink to "infinitesimal" size, effectively

⁸ See the appendix for a discussion of the development of Stokes theorem as an application of the calculus of differential forms.

replacing the macroscopic balance equations with differential equations. The *continuum hypothesis* is that any length scale of interest is longer than the scales on which atomic or molecular fluctuations might be important, and thus the transition to a differential equation from an integral balance is justifiable.

(Within Table 2-2, τ_{xy} is the shear stress, μ is the viscosity, u_x is the x-direction velocity, q is the heat flux, k is the thermal conductivity, T is the temperature, j_A is the mass flux of A with respect to the bulk velocity, ρ is the mass density, D is the mass diffusivity, and ω_A is the mass fraction of A.)

For most traditional applications of transport processes, quibbling over this procedure would be pedantic and irrelevant⁹. However, as noted above, for HFTP, these considerations can become important. The rationale for referring to such processes as “high flux” rather than “small scale” now becomes apparent: it is only when the fluxes and their rates of change become high that assumptions regarding constitutive relations and field definition become important. As a specific instance, consider steady state heat flux in a circumferentially insulated rod, with a constant imposed temperature difference across its ends. The temperature field can be readily defined, even at extremely small length scales. In this case, observation – that is, temperature measurement – is equivalent

⁹ For instance, in consideration of turbulent flow, the scales of the smallest eddies – beyond which viscous dissipation is the controlling mechanism – is still substantially larger than the scale of molecular fluctuations. The Navier–Stokes equations are still valid, if almost impossible to solve [93]!

to formation of an appropriate local ensemble which admits solutions to the standard formulation of the energy equation.¹⁰

Engineering applications of HFTP serve as a prototype for the approach referred to as “mesoscopic” by van Kampen [74]. This perspective recognizes that the actual behavior of the system is controlled by the microscopic equations relating its constituents, but stresses the fact that the behavior of these unique constituents can not be known and is not important in and of itself. Therefore, the quantities in which we are interested — and which can both be measured and predicted — are the stochastic properties of the system: namely, appropriately defined averages. This class of problems is distinct from truly *microscopic* systems, where the behavior of individual entities is important, and from *macroscopic* systems, where behavior is readily determined from bulk properties and directly measurable motions. Specific applications of stochastic techniques to HFTP are discussed in chapters 3 and 4; however, a general interpretation of these methodologies is presented in the next section.

Bayesian Analysis in Engineering

Like other mesoscopic systems, HFTP are implicitly stochastic processes. These physical processes have random elements, and modeling of even their deterministic elements is often most effectively done by the introduction of probabilistic concepts. The development of the statistical tools needed to analyze these processes depends on the

¹⁰ This holds even for molecular length scales, where the discrete nature of the flux leads to a statistical mechanical approach and, ultimately, the Boltzmann equation. When the flux is low, the departure from equilibrium is small and the temperature gradient can be meaningfully discussed.

assumed structure of the probability space. Most often in applied efforts such as engineering or the physical sciences, a classical formulation is used. An alternative formulation deserves consideration for both philosophical and technical reasons. This formulation is known as *Bayesianism*. Its acceptance has grown rapidly in the foundations and philosophy of probability and statistical inference [75], but the use of strictly Bayesian methods is still rather uncommon.

The equation known as Bayes' rule was published (posthumously) by an English clergyman, Thomas Bayes, in the eighteenth century[76]. It expresses the relationship between conditional and marginal probabilities,

$$p(\theta|y) = \frac{p(\theta, y)}{p(y)} = \frac{p(y|\theta) \cdot p(\theta)}{p(y)} \quad (2.1)$$

where $p(\theta|y)$ is the probability of ' θ ' occurring given that ' y ' is true. When the constituent probabilities on the right-hand side are clearly defined, this relationship is trivial and its use is noncontroversial. An alternate interpretation, however, has been the subject of contentious debate[77 – 81].

If y represents the experimental outcome and θ represents the parameters to be estimated after experimentation¹¹, then the two marginal probabilities in equation 2.1 deserve closer scrutiny. The term $p(\theta)$ is referred to as the "prior" probability. It represents the incorporation of previous knowledge regarding the parameters being estimated, and the application of equation 2.1 then amounts to revising a 'prior' belief about the values of the parameter. The second term in the numerator, $p(y|\theta)$, can be viewed as a function of θ ; it is then known as the 'likelihood' in classical statistics.

¹¹Note that both θ and y may be vectors.

Finally, the probability in the denominator, $p(y)$ is the integral (or sum) of the likelihood across all possible values of θ , and it normalizes the desired probability.

The use of Bayes' rule as a basis for statistical inference is attractive from an engineering perspective, because it allows explicit incorporation of information from diverse sources or of a qualitative nature. This structure leads, for example, to a "Maximum Entropy" formulation and a rational interpretation of many formulae in statistical mechanics. Unfortunately, the use of Bayesian methods has been attacked for two perceived flaws. These problems are significant, and deserve consideration before the application of Bayes rule to thermal problems is attempted.

The first concern regarding Bayesian inference is that the results depend on the prior distribution chosen, and therefore these techniques are more subjective than classical statistical methodology. Since the intent of any statistical technique is to provide a rational interpretation of typically noisy data, this is an important concern. Although this debate has raged in the mathematical statistics community for several decades, from an engineering perspective, this problem can be resolved rather readily. In practice, it is not objectionable that experimenters with different experience might draw different conclusions from identical results.

A specific example of this concept is provided by Box and Tiao[82]. Two physicists attempting to estimate a physical constant analyze the same data set. If both incorporate their prior beliefs about the system, the one with the greatest knowledge of the system will give less weight to the current observations, if they differ modestly from her expectations. In other words, an experimenter with substantial experience is unlikely to alter her beliefs based on an isolated result. Conversely, this same observer is more

likely to identify, and be affected by, results which are truly different than previous expectations.

As the amount of information contained in an experiment increases, the relative importance of the prior decreases. In the context of the example above, as the number of measurements increases, the differences between the observers' conclusions vanish. This situation, in which the likelihood is said to dominate, is typical in experimentation in engineering and the physical sciences. For such studies, the issue of subjectivity in prior selection can be dismissed, and typically a locally noninformative prior is assumed. The phrase "locally noninformative" means exactly that: it is the local shape of the prior — in particular its flatness — rather than its value that is important when the posterior probability is dominated by the likelihood [83, 84].

The second objection to Bayesian methods is not of great importance in engineering, but relates to how probabilities are to be interpreted. In the classical – or frequentist – view, experiments represent samples from a hypothetically unlimited population, and the probabilities then represent the expectation across the possible outcomes. The Bayesian perspective is more biased toward the observed quantities; construction of artificial populations is not necessary. Although this debate is interesting, it is somewhat irrelevant for engineering applications. In most practical instances, the distinction is unimportant¹²; if necessary, the interpretation used will be explicitly stated.

The main connection of Bayesian techniques to thermal engineering is through the use of "maximum entropy" methods. These methods arose after the development of the

¹² In fact, most engineers use classical methods but unwittingly interpret such quantities as confidence intervals from a Bayesian perspective[77].

development of information theory by Claude Shannon in 1948 [85]. Shortly thereafter, E.T. Jaynes recognized the functional similarity of the information theoretic entropy and the traditional thermodynamic entropy, and worked to reformulate many of the traditional problems of physical science in terms of information theoretic ideas. The central idea in these formulations is that the best estimate for a physical parameter is the one which is the most likely given the data. Such a process uses the data to restrict the space of possible estimates, and selects the one which maximizes the entropy calculated in an information theoretic sense. This approach seems reasonable, since this entropy is measuring the degree of randomness in the remaining space. If there is a measurable degree of nonrandomness in the space, then all of the available information has not been used to restrict the space. This approach has been successfully used in fields ranging from image reconstruction and geophysics to evaluation of the temperature of radiatively participating surfaces[12, 24]. Application in traditional thermodynamics is discussed in more detail in chapter 4.

While the methodology of Maximum Entropy – like the standard form of Bayes theorem – is widely used, the premise on which it rests has been hotly debated. Jaynes and his followers go beyond noting a similarity between the two forms of “entropy,” and claim that they are identical. This has produced responses ranging from strenuous rejection [87, 88] to fervent agreement [23] to attempts at compromise [85]. The primary objection to equating information theoretic entropy with thermodynamic entropy is that the former is dependent on the prior information of the observer [88]. Such prior information may be subjective, or qualitative, and the opponents of Jaynes’ techniques have steadfastly rejected the idea of entropy as a subjective quantity.

A subtle issue arises at this point. Opponents of the maximum entropy formalism are certainly not opposed to the idea that the system evolves to a state that maximizes the

thermodynamic entropy. Rather, they disagree with equating the two forms of entropy, since the information theoretic entropy explicitly considers the entropy in terms of the process of observation. That is, they feel that a state function of a system, such as the entropy, should not depend in any manner on the observer or the process of observation. They reject the epistemic position of the Maximum Entropy formalism that measurement of a thermodynamic process is essentially an act of receiving a "message" from the system, which can be treated as any other transmission of information. To these opponents this claim borders on anthropomorphism of the system, and is imprecise at best. The Maximum Entropy school of thought on the other hand, insists that the measurement process is inherently contained in any observation, and that though the system is not consciously sending a message, our collection of data amounts to the reception of information, which should be treated as such.

As discussed in Robertson [85], the conflict between these positions is more apparent than real. Just as in the measurement example discussed above, two experimenters who have the same prior information should reach the same estimate. The development of Maximum Entropy techniques which assure such a result seems desirable. In such a case, the disagreement becomes mainly semantic, as relevant prior information in a thermodynamic sense is likely to be quantifiable, and no "subjectivity" remains in calculating the entropy.

For HFTP, these techniques may provide an important methodology for solving problems in a consistent fashion. Their role in the stochastic elements of specific aspects of the ablation process is discussed in chapters 3 and 4. This importance is underscored by the realization that a Bayesian inferential structure is effectively a quantification of "Occam's razor." This principle, first articulated by an English Monk in the thirteenth century, stipulates that physical theories should be kept as simple as possible. Recent

work has shown that this traditional precept is consistent with the use of Bayesian methods [90, 91].

3. LASER-MATERIAL INTERACTIONS

Lasers are useful as intense, readily manipulated energy sources. As a result, they are applied in a wide variety of situations in which their interactions with matter are of great importance. The study of laser-material interactions spans all states of matter, and includes numerous interesting physicochemical phenomena, as seen in Figure 3-1.

This chapter discusses and extends the thermal models used in studying laser-material interaction. The primary emphasis is on the behavior of metallic solids upon irradiation by laser beams of various intensities. The next three sections discuss these phenomena. Potential nonlinear responses of fluids to intense beams are also important and are discussed in the final section of the chapter.

Absorption of radiation by a solid

The coupling of energy into solids has been an area of intense interest since the invention of the laser [94,95]. As intensity is increased, a variety of modes of interaction can be seen. At very low intensity, simple linear heating occurs. As fluence increases, phase changes in the target material are induced. These changes include structural rearrangements, melting and vaporization [96]. Increased rates of chemical reaction at the surface are also noted in this regime[97]. Most industrial applications of lasers for material modification fall into this range of moderate intensities[98 – 101]. If the intensity is increased further, ablation occurs. Ablative processes are far from

Figure 3-1. Processes associated with laser ablation

equilibrium, even locally; it is this extreme departure from thermal equilibrium that differentiates ablation from less complex laser evaporation processes.¹

A general balance of the radiant energy accounts for energy absorption by the material, reflection at the surface, and emission from the surface[102,103]. For an

¹This also differentiates ablation from sublimation, in which material also goes directly from a solid to a vapor. Sublimation occurs when the local pressure is less than the material's vapor pressure for surface temperatures below the triple point. As substantial latent heat is absorbed during this first order phase change and the surface temperature is assumed to equal that of the adjacent boundary layer, departures from equilibrium are typically much smaller than those encountered during ablation.

optically thick body, no transmission of radiation is expected; thus, the incident energy is partitioned into two components, absorbed energy and reflected energy. The relative proportion of the beam in each component is dependent on the beam's wavelength and angle of incidence, and on the temperature and composition of the body. For the system under study, the beam is effectively monochromatic, highly directional and typically incident normal to the surface. The reflection from the metallic surface is therefore also assumed to be normal to the surface.² Unlike this specular reflection, emission from the surface is diffuse, and a common assumption is that the surface acts as a gray body. The net radiative energy flux into the body is therefore equal to the incident radiation minus the radiative surface loss, which is the sum of reflected energy and emitted energy. If, for this initial analysis, convective losses at the surface are ignored, no phase changes are considered, and the radiative flux is assumed to be absorbed at the surface, the radiative balance equation simplifies to yield a net surfacial heat flux, q :

$$q = (1 - \rho)I - \epsilon\sigma T^4 \quad (3.1)$$

where ρ is the reflectivity of the surface, $(1-\rho) = \alpha$ is the absorptivity, σ is the Stefan Boltzmann constant, and ϵ is the emissivity of the surface. Since the absorbed radiation is at a fixed wavelength and the emitted radiation is broad band in nature, α and $\epsilon(T)$ need not be identical [104].

²Consideration of other angles of incidence would expand the generality of this analysis; however, allowing for an angular dependence of reflectivity would only change the partitioning of energy into reflected and absorbed components, without affecting the physical processes discussed. Also, due to surface roughness, some of the specular reflection will be seen as "speckle," which is interference between rays reflected at slightly different angles. This effect, although irrelevant to the radiative balance at the surface may play a role in processes occurring above the surface.

The penetration depth of optical radiation into a metal is very small, and in many cases, the approximation of a surface flux is acceptable. When greater precision is required, the intensity of the radiation is assumed to decay exponentially with depth in the material [102]. This relation is known as Beer's law and is related to the imaginary component of the index of refraction. In this case, the flux effectively becomes a volumetric energy source, and is no longer imposed as a boundary condition. The source term can be written as:

$$g(r, \theta, z, t) = -\frac{dI_a}{dz} = a \cdot I_o(r, \theta, t) \cdot (1 - \rho) \cdot \exp(-az) \quad (3.2)$$

where g is the source term, written in cylindrical coordinates, I_o is the radiative flux incident on the surface, and a is the optical absorption coefficient³. Although g is generally a function of the polar angle, symmetry of the beam around the origin is often assumed. As noted in chapter 2, the optical skin depth for copper irradiated by green light ($\lambda = 532$ nm) is on the order of 35 nm. Thus, for a macroscopic analysis, the assumption of surface absorption is quite good for laser interactions with metals.

A first approximation — which is particularly good for metals at low and moderate intensities — is that absorption by metals is due to the presence of free electrons. These are valence electrons which are not strongly localized, but move relatively freely through the lattice⁴ of metal “ions.” Since the electrons are not strongly bound, they are able to undergo a wide range of transitions, which accounts for the

³ Note that a is a dimensional quantity whose unit is a reciprocal length. Thus, this is a different quantity than α , the absorptivity defined by equation 3.1, which is dimensionless.

⁴ In this context, the term “lattice” refers to an actual physical arrangement, rather than to an algebraic structure.

broadband nature of metallic absorption and emission [102, 105]. The ensemble of these free electrons is assumed to equilibrate internally very quickly ($\sim 10^{-12}$ s), and then transfer energy to the lattice structure through interactions with phonons, which are quasiparticles representing quantized modes of lattice vibration [106 – 112].

Because the intensities available in focused laser beams cover an extremely broad range, consideration of the limitations of this model of absorption is appropriate. At the lowest level of approximation, the free electron model represents an attempt to rewrite the very complex Hamiltonian for the electron ensemble in more tractable terms. The full Hamiltonian contains terms corresponding to the motion of each electron in the field induced by the radiation as well as terms representing interactions among electrons and between the metallic atoms in the lattice. The free electron model assumes that the only contribution of the lattice is to jointly contribute a uniform background field, and that interactions among electrons can be effectively ignored. The result is a Hamiltonian which is functionally equivalent to that for an ideal gas — which is well understood and easily manipulated. The excitation of this “cloud” of electrons facilitates energy and charge transport as well as radiative absorption [106, 107,].

An interesting interpretation arises here. The “standard” textbook interpretation is that quantities, such as mean free path, calculated from this model correspond closely to physical reality. An alternative perspective, presented by Gitterman and Halpern [114], is that under this approach, the entire electronic structure has, in effect, been re-indexed, and that the “motion” of the free electrons makes sense only in the ensemble sense. This perspective is attractive, since electrons are indistinguishable particles and the free electron gas model only holds at relatively high electron densities. This interpretation considers “free electrons” as a class of elementary excitations, and the full ensemble of

“free electrons” thus corresponds to quantized modes of excitation of the “true” electronic structure of the solid.

Successively more detailed models are available as the nonideality of the interacting system increases. The refinements to the model include allowing for Coulombic interactions among the electrons, and for spatial inhomogeneity of the lattice charge structure. These enhancements of the system Hamiltonian can be best represented by their corresponding Feynman diagrams [106 – 108, 116, 117]. The diagrams were initially developed in quantum electrodynamics (QED) and specific components represent the types of interactions considered in each of the models. As they are typically drawn, straight lines represent electron motion and wavy lines represent photons. Time is assumed to be the vertical axis. Then, the diagram represent a form of continued fraction, and thus provides an approach for calculating ensemble behavior in a many body system.

These Feynman diagrams serve two purposes. The first is as a mnemonic device to facilitate the organization of the calculation of the electronic interactions. The second role is related: the diagrams show explicitly the assumptions made for each calculation regarding the nature of the behavior of the ensemble. Thus, the diagrams become progressively more complicated as more types of interactions are assumed to be important.

As discussed in appendix E, path integral techniques and Feynman integrals are intimately related, but this level of detail is not necessary for most LMI studies.

For thermal analyses of laser-material interactions, a semiclassical approach for radiative absorption is often appropriate, since interest is focused on energy dissipation on long length and time scales [118 – 122]. The more complicated models arising from

QED are useful primarily as a basis for qualitatively understanding the physical basis of the interaction and for inherently nonlinear surface optical processes.

In addition to radiative absorption, nonlinear interactions are also important in several electro-optic phenomena associated with pulse generation and second harmonic generation. These are discussed in more detail in appendix E.

Thermal conduction: selection of a constitutive equation

For most problems involving thermal conduction, it is assumed that the continuum hypothesis is valid; that is, all length scales of interest are substantially larger than those of atomic or molecular fluctuations. Hence, as discussed in Chapter 2, integral mass and energy balances representing empirically postulated conservation laws are valid for arbitrary bodies and can be written in a differential form. The standard formulation of the energy equation for a rigid solid with no internal energy sources then becomes [123]:

$$\rho \frac{de}{dt} = -\nabla \cdot \mathbf{q}. \quad (3.3)$$

The solution of this problem depends on the nature of the boundary conditions and the nature of the constitutive relation between the energy field and the heat flux vector. The relation used in almost all cases is Fourier's "law," in which the heat flux vector, $\mathbf{q}$, is proportional to the temperature gradient,

$$\mathbf{q} = -k\nabla T \quad (3.4)$$

The proportionality 'constant,' k , is known as the thermal conductivity. It is positive by convention, and thus the negative sign in equation 3.4 reflects the fact that energy transport is in the direction of decreasing temperature. The thermal conductivity is a

function of temperature, although this dependence is typically weak and is often neglected.

Substitution of this relation into the energy balance, and incorporation of the heat capacity by use of the chain rule connecting temperature to the internal energy, results in the standard diffusion equation:

$$\frac{dT}{dt} = \alpha \nabla^2 T. \quad (3.5)$$

This reduction assumes constant thermal conductivity, and introduces the thermal diffusivity, $\alpha = k/(\rho C)$. (Unfortunately, the same symbol is conventionally used for the diffusivity and the absorptivity. They are usually distinguished by context.)

The energy equation incorporating Fourier's law shows both quantitative and qualitative agreement with experimental observation in a wide variety of situations. This diffusion equation, however, is a parabolic partial differential equation, and therefore predicts an aphysical instantaneous response arbitrarily far away from an excitation. This is often referred to as an infinite speed of propagation for energy. This situation is theoretically interesting, and leads to deviation of observed behavior from Fourier's law in two situations. The first of these is in cryogenic systems, where the occurrence of a thermal wave, occasionally called "second sound," has been observed [67]. The second situation is found in microscale systems such as laser ablation.

Interestingly, the nature of the failure of Fourier's law differs for the two systems mentioned above. In cryogenic systems, thermal wave propagation becomes noticeable because low absolute temperatures enhance experimental ability to identify deviations of the temperature field from that predicted by the parabolic equation. On the other hand, in microscale systems, the departure of the observed values from the predictions appears to

be due to failure of the assumptions underlying the model. Specifically, the continuum hypothesis is questionable, ambiguity may exist in the definition of the temperature field, and the assumption of a local form of the equation may no longer be appropriate.

As discussed above, thermal conduction in a metal is primarily due to “free” electrons, whose mobility is responsible for the high thermal and electrical conductivities of metals. The lattice temperature is in turn raised as the energetic electrons are scattered by phonons. The focus of this section, however, is on the development of alternative continuum models rather than on the quantum physics of thermal conduction. This approach is taken for two reasons:

- (1) For engineering purposes, analysis of the system requires linking widely varying length scales. This is greatly facilitated if appropriate differential equations can be used.
- (2) For any real system, the simplifying assumptions made in the tractable quantum models are likely to be inappropriate. Since the analysis will be largely empirical regardless of the approach used, a semiclassical approach is desirable for its (relative) simplicity⁵.

The use of Fourier’s law to analyze the conduction of energy into the substrate during laser ablation is of dubious validity. Unfortunately, little consensus exists as to the appropriate resolution of the problem. Several excellent reviews have studied the

⁵A pertinent comparison is to the analysis of lasers, in which the radiation field is assumed to follow classical electromagnetic theory, through Maxwell’s equations, while the lasing medium is analyzed from a quantum mechanical perspective.

varied approaches which have been taken to attempt to resolve this problem[124 – 126].⁶ Although a complete discussion of this topic is beyond the scope of this dissertation, several pertinent efforts merit consideration because of their potential for application to ablation systems.

Three primary approaches have been taken in the development of hyperbolic conduction equations. The first approach is to simply postulate an additional term in the constitutive equation, and solve for the associated parameter. The heuristic justification — often unstated — is the belief that the heat flux “is” a function of the temperature field, and that a better representation of reality should be found by including additional terms in a Taylor series approximation [126]. This methodology can generate an equation which fits the experimental observations used in the estimation, and which facilitates data reduction and analysis for related experiments. Such *ad hoc* techniques are difficult to extend or generalize and lend little insight into the problem as they are based on a questionable epistemic assumption.

The second method uses results from thermal physics to postulate the nature of the modification required. For example, recent work has focused on the use of multiple temperature scales, recognizing that the system of electrons in a metal will equilibrate internally long before energy can be transferred to the lattice [127]. By considering the lattice and electron temperatures separately, a good approximation of physical observations can be attained. Another application of thermal physics to conduction problems is the use of nonequilibrium thermodynamics to model the behavior of the

⁶ A brief, enjoyable article by Swenson [140] provides a concise discussion of the problem of incorporating nonparabolic features.

system[128 – 130]. An appropriate form of the Boltzmann equation is derived, in which the standard parabolic equation is obviously retrieved as a limiting case. In this methodology, the unstated epistemological assumption is that the models of thermal physics, which are typically derived for steady state or near equilibrium systems will suffice to describe higher flux processes.

The third method for studying nonparabolic behavior of conduction systems focuses on the relationship between the observation scales and the assumptions made in generating the equations[131,132]. In such analyses, it is recognized that the standard formulation is local in nature. Thus, extension to situations where “interesting” phenomena occur on the same scale as observation require a relativistic view of the system [133]. In such an appraisal, hyperbolic terms naturally arise. Similar results are seen when the possibility of nonlocal effects is allowed [134 – 138]. Temporal or spatial nonlocal effects seem difficult to explain in an intuitive, causal sense, but they directly introduce nonparabolic features into the heat equation. An interesting abstract formulation is to take the Fourier transform of the energy equation, and allow the conductivity to be a function of frequency[137, 140]. Thus, the response of a system to an impulse thermal load (which has a broad frequency spectrum) is expected to differ from its response to a gradually modulated heating, which has a much narrower spectrum. This frequency dependence can be understood as resulting from possible resonance of electron-phonon interactions.

Parenthetically, the method discussed in the preceding paragraph demonstrates the danger of applying concepts and methods from thermal physics to an engineering analysis of HFTP. The use of the Fourier transform to examine the frequency dependence of the conductivity is appealing. Such an approach may be of limited validity, however, since most discussions of the evaluation of transport coefficients focus, as the thermal physics

models above, on systems either near equilibrium, or in steady state, where temporal fluctuations are unimportant. In fact, this is implicit in the use of the Fourier transform. A better approach would be to use a joint time-frequency analytical method, such as the Gabor transform or a wavelet decomposition [141].

Another epistemological factor which arises in thermal engineering is seldom discussed in the literature. If one assumes that since energy deposition is due to radiative absorption, the resulting energy dissipation is “obviously” thermal in nature, then the use of a hyperbolic formulation is required to fit observation. This “obvious” assumption is a large step. As discussed below, research by Shannon has indicated that in high flux situations, the energy dissipated by stress power can approach that dissipated thermally [142]. Unambiguous separation of energy transport due to mechanical waves from that due to thermal waves could be rather difficult to demonstrate experimentally. Furthermore, in systems of practical interest, true hyperbolic effects might well be masked by thermal resistances due to impurities, inclusions or grain boundaries [143 – 145]. A heuristic interpretation of many of the non-Fourier conduction models is thus that they represent the lumping of all energy dissipation processes occurring within the solid substrate.

Regardless of the source of the equation, hyperbolic conduction equations present serious computational and analytical challenges. The investigation of these effects is currently an active research field [146 – 153].

The problem of selecting a thermal constitutive equation for laser materials interactions is interesting and challenging, and this problem is magnified by the qualitative dependence of the material’s response on the flux. The range of phenomena that can be seen are discussed in the next section.

LMI regime	Typical fluence, Wcm^{-2}
Simple heating	$< 10^4$
Induced phase changes	$10^5 - 10^8$
Ablation	$> 10^9$
Laser induced fusion	$> 10^{15}$

Table 3-1: Fluence ranges associated with laser material interactions.

LMI Regimes

Approximate ranges corresponding to these various regimes are presented in Table 3-1. Before discussing the ablation process in more detail, it is appropriate to consider simpler laser induced thermal problems first. Linear heating and heating with phase change highlight some features of the problem, without the competing effects which can mask thermal dissipation during ablation. Furthermore, although these topics have been discussed in detail since the laser was first invented (and soon thereafter focused onto a solid target), much is still unknown about the dynamics and kinetics of these processes. These less intense processes thus provide a good basis for the study of laser material interactions.⁷

⁷ Since irradiation in the experimental system is 'only' on the order of 100 GWcm^{-2} , laser driven nuclear fusion processes will not be discussed. The value of the flux in Table 3-1 is based typical values given in the literature.

Linear heating

The prototypical problem in simple laser heating is the determination of the temperature increase in a semi-infinite body due to a point heat source. This problem has been widely discussed in the literature[154 – 159], but deserves special consideration since it provides a limiting case for low intensity laser material interactions, and since several interesting aspects of microscale transport processes can be readily examined.

An assumption of constant thermophysical properties is typically satisfactory for simple laser heating, because the temperature increases are often moderate, and in those cases where the property values do change, the Kirchoff transformation can be used to determine an effective value [22]. The inaccuracies introduced by such an approximation are often irrelevant, particularly when the target is macroscopic and polycrystalline, and effective or mean values of the properties are therefore used.

When the variable of interest is the temperature at macroscopic distances from the laser irradiated spot, the assumption of a surface source is quite acceptable, as the radiation skin depth is only on the order of the wavelength of the radiation. Assumptions regarding the distribution of the source across the surface depend greatly upon the system being analyzed and the objective of the analysis. When the surface is near the focal plane of the beam, the beam can be analytically considered as a point source. If, however, the beam is unfocused, and length scales of interest in the problem are comparable to the beam diameter, the specification of the power density across a finite sized source is necessary. Furthermore, the need to consider lateral conduction effects can be evaluated by considering the Fourier number, $Fo = \alpha t / L^2$, where α is the thermal diffusivity, t is the time of interest and L is a relevant length, such as spot size [161]. When Fo is less than unity, relatively little energy is transported across the face of the irradiated region, and the

geometry of the problem is essentially one dimensional. As Fo grows substantially larger than unity, the geometry can be assumed to exhibit some azimuthal or radial symmetry. In the intermediate region where Fo is of the order of unity, a full three dimensional formulation is necessary to adequately describe heat flux within the target material.

Analysis of linear heating.

The assumptions discussed above lead to the following system:

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + (1 - R) Q_0(t) \frac{\exp(-x/l_{rad})}{l_{rad}} \quad (3.6)$$

$$T(x, 0) = \text{const.} = T_\infty \quad (3.7)$$

$$T(\infty, t) = T_\infty$$

$$\left. \frac{\partial T}{\partial x} \right|_{x=0} = 0 \quad (3.8)$$

The laser flux is here assumed as a volumetric source term, where R is the surface reflectivity, and $Q_0(t)$ is the nominal fluence at the surface. The radiation skin depth is l_{rad} . The solid is assumed to be initially at a constant temperature, and to be thermally semi-infinite. Since the flux is written as a volumetric source, and convection and radiation are ignored, the surface, $x = 0$, is assumed to be adiabatic. Radiation is ignored because, even at $T=1500K$, the blackbody radiative emission is only $q = \sigma T^4 < 30 \text{ Wcm}^{-2}$. This is negligible compared to the laser flux, which is typically several orders of magnitude greater. (This estimate is *extremely* conservative, since the peak temperature for simple heating would almost certainly be below 1500 K. Given the quartic dependence of flux on temperature, ignoring the radiation is quite reasonable for many real systems.). Convection and conduction into the ambient medium are neglected for convenience; such an assumption is typically acceptable for heating of metals in a

reduced pressure environment. Experimentally, control of conduction and convection is important, particularly if the target's thermal diffusivity is close to that of the ambient fluid [142]. Ignoring these effects also yields an upper limit to the expected temperature profiles.

The variables can be nondimensionalized by assuming l_{rad} as a length scale and l_{rad}^2/α as a time scale. This transformation yields appreciable⁸ numbers centered around the spatial scale associated with radiative absorption. (An alternative normalization would utilize the pulse length, t_p , and the related thermal diffusion length. Such an approach would focus on the temporal scale associated with the incident radiation, and would be less concerned with the local, short time distribution of energy.) In addition, the dependent variable – the temperature – is normalized relative to the initial temperature and the melting temperature, T_m :

$$\begin{aligned}\chi &= x/l_{\text{rad}} \\ \tau &= \alpha t / l_{\text{rad}}^2 \\ \theta &= \frac{(T - T_\infty)}{(T_m - T_\infty)}\end{aligned}\quad (3.9)$$

This normalization also affects the source term. The resulting quantity, $\phi(\tau)$, expresses the flux in terms of an effective maximum flux for the single phase solution:

$$\phi(\tau) = \left(\frac{k(T_m - T_\infty)}{l_{\text{rad}}} \right)^{-1} (1 - R) Q_0(\tau) \quad (3.10)$$

The solution of this system can be readily found by taking the Laplace transform of the simplified equations to yield an ordinary differential equation in the normalized

⁸ "Appreciable" numbers are those that can be observed, i.e., both x and $1/x$ are limited.

spatial variable[22]. After inversion, the temperature field for the entire body can be described. The most interesting aspect of the solution is consideration of the surface temperature variation as a function of time. As expected, the initial temperature rise can be found by simply integrating the normalized source term, $\phi(\tau)$, over $\{0, t\}$, $\tau \ll 1$. This effectively ignores any diffusion away from the deposition region [162]. At the other extreme, the surface temperature rise due to a laser pulse shows a decay proportional to $t^{-1/2}$, as would be expected for a diffusive system, for times much longer than the pulse length [162].

As a specific example, consider the irradiation of a semi-infinite copper target by a 30 ps, 30 mJ pulse from a frequency-doubled Nd:YAG laser. If the beam is either expanded and collimated, or otherwise attenuated by an order of magnitude, the fluence is roughly $10 \text{ mJ}\cdot\text{cm}^{-2}$. The integration of $\phi(\tau)$ over the pulse period leads to a temperature increase of over 800 K, as follows:

$$\Delta T = \frac{(E / A)}{l_{\text{rad}} \rho c} = \frac{(0.01 \text{ J cm}^{-2})}{(3 \cdot 10^{-6} \text{ cm} \cdot 3.46 \text{ J cm}^{-3} \text{ K}^{-1})} \approx 840 \text{ K} \quad (3.11)$$

This example demonstrates the impact of high power levels, even when the energies involved are small, and the stringent restrictions on using a linear heating model with pulsed lasers. This approximation of the temperature rise is valid within the limits of the linear heating model, since $\tau = 0.03 \ll 1$, but the model itself is not acceptable. First, the use of a constant property model is not apt to be satisfactory for increases of hundreds of Kelvin. More importantly, assuming the target is initially at room temperature, an increase of this magnitude would raise the surface temperature to nearly the melting point. The onset of phase changes and material removal adds significant difficulty to the analysis of thermal problems. These complications are discussed in greater detail below.

(It is important to note that the fluence cited in this example is several orders of magnitude less than that used in the experiments described in chapter 5.)

Algebraic consideration of diffusion equations.

The response of a semi-infinite body to a thermal excitation is diffusive in nature, and assuming an initial temperature distribution, the homogeneous energy equation can be written in operator format as :

$$H[T(\mathbf{x}, t)] = \left(\frac{\partial}{\partial t} - \nabla^2 \right) T = 0, \quad (3.12)$$

where T is the normalized temperature, $\mathbf{x}$ represents spatial position, and t is the time. Specification of the system is completed by inclusion of initial conditions. The important point that this formulation expresses is that the rate of change of energy is identically equal to the local second derivative of the temperature field. Therefore, as expected, diffusive change is greatest at points of rapid spatial variation of the temperature distribution.⁹ Furthermore, this operator implicitly defines a heat kernel, $K_t(\mathbf{x})$, which defines temperature by convolution with the initial temperature distribution and which acts as a semigroup[163]. Considering the one dimensional form for clarity, this kernel is:

$$T(x, t) = K_t * T(x, 0) \quad (3.13)$$

$$K_t = \frac{1}{\pi \sqrt{t}} \exp\left(-x^2/t\right) \quad (3.14)$$

⁹ A subtle difference exists between the definition of flux through Fourier's law, $q = -k\nabla x$, and the consideration of the rate of heat loss discussed here. Based on Fourier's law, maximal *heat flux* occurs at the point of the steepest *gradient*. Maximal local *heat loss*, i.e., temperature change, occurs at the extrema of the *divergence*, or second derivative of the temperature.

The kernel can be seen to be a semigroup when convolution is taken as the semigroup's operation, and the subscripted index is the argument:

$$K_a * K_b = K_{a+b} \quad (3.15)$$

(The identity element of the semigroup is obviously K_0 . Since the system is causal and dissipative, and thus evolves forward in time, unique inverse elements are not defined for members of the kernel. Therefore, the kernel is not a group. This argument is physically plausible because all initial temperature distributions for a given energy addition will evolve to the same final distribution¹⁰. Therefore, a unique inverse can not exist on physical grounds.)

The behavior of the heat kernel even for simple conduction dominated homogeneous heat transfer suggests an analytical concern regarding transient problems. The temperature distribution is assumed to belong to $L^2(\mathcal{R}^3)$, the space of square integrable functions defined in a three dimensional Euclidean space. In many standard applications, Fourier analysis is used to convert the difficult system of differential equations to a more tractable algebraic system [164 – 166]. This can be done because the frequency space of the Fourier transform provides a complete orthonormal basis for the temperature field. Unfortunately, while the Fourier transform provides precise information on the frequency content of the analyzed signal, it provides no time localization. If the system is in steady state, this presents no problem; however, for transient problems a better basis is needed. Among the techniques available to provide

¹⁰ This discussion is particularly important for the case of pulsed laser material interactions. As shown in the previous section, energy deposited on a time scale shorter than tens of nanoseconds will appear to the bulk material as an initial condition with very steep, nearly discontinuous, gradients.

both time and frequency resolution is the use of wavelet transforms, where dilated and translated copies of a given “wavelet” provide the basis for the space. Of particular value for diffusion problems is the Marr wavelet, which was developed in studies of edge detection¹¹, and is related to the temperature distribution through the heat loss function, $R(x, t^{1/2})$ [167]:

$$R(x, \sqrt{t}) = \frac{\partial}{\partial t} T(x, t) \quad (3.16)$$

$$R(x, \sqrt{t}) = g_{\sqrt{t}} * T_0(x) \quad (3.17)$$

$$g(\tau) = \frac{1}{\pi} (\tau^2 - 1) \exp(-\tau^2) \quad (3.18)$$

$$g_a(t) = \frac{1}{a} g\left(\frac{t}{a}\right) \quad (3.19)$$

In these equations, the basic wavelet is $g(t)$, while $g_a(t)$ defines the family of dilations that provide the basis for the evolution of the temperature distribution in time.

Although these more complex procedures are superfluous for traditional thermal problems, this setting provides a well understood situation for studying their use and development [168 – 171].

The geometry of conduction dominated heat transfer is as interesting as its analytical properties. Although most pedagogical problems have idealized boundary conditions in which either temperature or heat flux is held constant at an essentially smooth interface, more realistic boundary conditions may be needed to adequately

¹¹ The analytical similarity between edge detection and thermal diffusion suggests that, as in thermodynamics, maximum entropy ideas may be useful. This is discussed in the context of convection by Bejan [249].

describe microscale thermal processes [172]. This is an area in which the application of fractal concepts would seem to be appropriate.

Laser induced phase change problems

As the flux increases, laser irradiation causes phase changes, and the nature of the thermal problem changes qualitatively. The appearance of a moving phase front adds significant analytical difficulties to the problem. Such problems are generically known as Stefan problems. Physically, the addition of a phase change presents several problems. First, the presence of multiple phases requires the partitioning of the physical space, and typically introduces distinct thermophysical properties for each of the zones [142, 173]. Second, the motion of the interface is implicitly defined by the inclusion of a latent heat into the energy balance at the front. Explicit determination of the front position is possible only in highly idealized cases. Furthermore, the choice of a coordinate system for the problem is an important concern in cases where the front motion is unsteady or a significant change in specific volume occurs during phase change.

A common formulation for melting problems assumes that physical properties differ between phases but are constant within each phase, and that the change in specific volume is negligible. Furthermore, a distinct transition temperature is assumed, and the process is assumed to be slow enough that no superheating occurs. Then the boundary conditions for a planar interface are [104]:

$$k_s \frac{\partial T_s}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{dX}{dt} \quad (3.20)$$

$$T_s(X(t), t) = T_l(X(t), t) = T_m \quad (3.21)$$

where $X(t)$ is the interface position, the subscripts s and l refer to the solid and liquid respectively, L is the latent heat, and ρ is the density of the solid phase (This would imply

that the coordinate system is fixed in the solid phase if $\rho_l \neq \rho_s$). Furthermore, equation 3.21 holds for all time t . Although this assumption provides very desirable simplification, it is quite tenuous for very rapid front motion, where some superheat may be needed to drive the process, and in the melting of amorphous materials, where the phase change temperature may be ill defined, and melting takes place across an extended so-called “mushy zone.”[174]

For a temporally varying surface flux, the thickness of the liquid layer varies with time, and interesting fluctuations of the temperature field may occur. In particular, the temperature and diffusive flux at the surface vary dramatically depending on the assumed geometry of the source. This feature was used by Shannon [142] to indirectly identify the onset of melting. Of equal importance, this demonstrates that even rather simple physical systems can exhibit interesting topological features.

The dimensionless parameter which best describes the melting process is the Stefan number, N_{st} , which is the ratio of the sensible heat required to raise an element of the target to its melting point to the latent heat of fusion, ΔH_f ,

$$N_{st} = \frac{c \cdot (T_m - T_\infty)}{\Delta H_f}. \quad (3.22)$$

The process of melting the target is, of course, transient and the propagation of the front is a primary concern in diverse material processing applications. The maximum velocity attainable is readily seen to be the ratio of the effective fluence to the sum of the latent and sensible heats. In particular, if the absorbed fluence is normalized against the latent heat, the limiting front velocity is seen to be:

$$v_{m,max} = \frac{(1 - R) \cdot Q_0 / \Delta H_f}{1 + N_{st}} \quad (3.23)$$

In practice, the front velocity is typically reduced as the liquid layer thickens and the temperature gradient at the front lessens. It is also interesting to note that the motion of the front lags behind the temporal structure of the pulse. This is *not* due to a physical inertia, but to diffusive transfer of energy stored in the liquid phase.

The growth of the liquid layer is affected by both the motion of the front, and by the rate of removal of the liquid. This removal can be due to either mechanical means, such as flushing of the surface by an imposed flow, or thermal processes, in particular evaporation. Furthermore, for pulsed lasers, the front ultimately stops and then recedes. The same energy balance holds, and a negative velocity merely implies recrystallization of the molten metal. Since the free surface of the metal is assumed to be adiabatic, and the liquid region is strictly above the melt temperature, the velocity of the freezing front is determined by the thermal diffusivity of the solid, which now acts as a heat sink.

The addition of evaporation to a laser melting problem is conceptually similar to the formulation of the initial Stefan problem, although the computational difficulties are more extreme. In this case, an energy balance, analogous to the melting front, is performed at the liquid-vapor interface to account for motion of the vaporization front. The primary difference is that material removal is nearly total for the case of vaporization. This change is due to the increased mobility of the vapor phase, and the likelihood of its dispersal in the ambient medium. Although the vapor may influence the properties of the ambient medium, it is quite unlikely that total recondensation will occur in a practical system. This complete removal is also characteristic of sublimation processes, although in this case only one interface exists. (As discussed in the next section, vaporization differs dramatically from ablation.)

Numerically, Stefan problems pose many difficult challenges. A large body of literature on laser induced melting and solidification exists, but its detailed consideration is beyond the scope of this thesis [175, 173 – 183].

Radiative ablation

The regime in which material is explosively removed from the surface is referred to as “ablation.” Radiatively driven ablation differs dramatically from the more commonly known phenomenon of *convective* ablation, a thermal process in which the heating of a solid body by a fluid stream of high relative velocity leads to evaporation and immediate removal of material. In *radiative* ablation, material is also removed at a high rate, but the removal mechanisms include substantial nonthermal contributions. Furthermore, the mechanisms responsible for carrying away removed materials differ dramatically. In convective ablation, this is done by the externally imposed fluid stream which causes the phase change. (Ironically, the formulation of the energy equation for convective ablation is simpler than for the case of a physically less intense two-stage Stefan process, in which vaporization follows melting, and two fronts must be tracked.) In radiative ablation, material is carried away by processes induced by the irradiation. These processes include the ejection of particles from the surface, and motion of the ambient fluid due to surface recoil or thermally induced density gradients. Furthermore, since radiative ablation tends to occur in small areas, local condensation or redeposition may significantly reduce net material loss. The investigation of radiative ablation is the basis of the experimental portion of this work.

Ablation presents unique opportunities for applications and significant difficulties in analysis [184 – 189]. Among the most commonly cited applications are the creation of

thin films¹², analytical material sampling, destruction or modification of biological materials, and surface modification of metals and semiconductors [190 – 204]. The intensity of energy transport leads to mechanical and thermal dissipation processes which are of comparable magnitude, typically resulting in substantial material removal from the surface and formation of a plasma above the target. The following discussion considers these aspects of ablation systems separately. For simplicity, the interactions of these subprocesses are ignored, although in practice the interactions often control system evolution.

Mechanical processes

Interesting mechanical phenomena occur both in the target material and in the ambient medium in which the target material is immersed. Within the substrate, radiative absorption occurs within a small volume, and thus substantial thermal expansion can occur locally. The large resulting stress gradient leads to stress power waves within the solid which can remove large amounts of energy from the irradiated region. Above the surface, both motion due to the thermal expansion and recoil due to material removal can lead to the formation of shock waves above the surface. The interaction of these waves with the surface as they collapse leads to substantial morphological variation of the ablation site.

Stress power

¹² A particularly important example is the creation of thin film high temperature superconductors. These materials are typically rare earth oxides.

Stress power, P , arises in continuum mechanical analysis as the scalar product of the stress tensor, T , and the velocity gradient tensor, L , [205]

$$P = T:L \quad (3.24)$$

As noted by Shannon [142], it is the presence of high stress power, rather than high values of stress alone that lead to substantial dissipation of energy. First order approximations of the magnitudes of both T and L yield values of the stress power that suggest that this mechanical dissipation mechanism can transport a substantial fraction of the deposited energy away from the ablation zone.

The physics of the mechanical processes associated with ablation is interesting. Substantial pressure increases are caused above an ablation zone by momentum conservation, due to the large recoil associated with the rapid removal of material (in numerous forms, as discussed below). The pressures associated with this recoil have been estimated to be on the order of 10^9 Pa, and the point loading of the substrate with this pressure causes the initiation of both elastic and dissipative waves in the solid material. The partitioning of energy among these waves has been a topic of considerable research[94 , 206].

The large ablation induced stress power can also be seen through its influence on failure mechanisms within the substrate. These mechanisms vary from ductile to brittle, depending on the intensity of the incident radiation. The role of these phenomena in material removal is discussed below in the context of ejection processes.

Although the research discussed in succeeding chapters is concerned with metallic substrates, dielectric materials also exhibit a variety of mechanic failure processes. These are of great practical importance, since one of the limiting factors for application of laser material processing is the optically induced damage to optical components. For such

transparent dielectrics, catastrophic thermal damage can occur when absorption centers develop in the material, and dielectric breakdown or substantial thermal absorption occurs [143, 207, 208, 209, 210].

Shock waves

The occurrence of a large recoil pressure at the surface also affects the ambient medium. Ablation processes are invariably associated with audible shock waves. These shocks are important indicators of the strength of the coupling between the laser and the substrate [211 – 215].

The evolution of shocks in an ablation system is typically modeled by assuming that the system is either one dimensional or radially symmetric, and that the shock is propagating into an ideal ambient medium¹³. Assumption of an ideal gas ambient allows the use of a simple equation of state to relate pressure and density and to thus simply express the sonic velocity in terms of state variables. The sonic velocity is determined by applying the integral form of the conservation laws to flow across a moving wavefront. For a weak sonic wave, the changes of pressure, density, and velocity are infinitesimal, and the passage of the wave is isentropic[216]. Substitution and simplification yields:

$$a^2 = \left(\frac{\partial p}{\partial \rho} \right)_{s=const.} \quad (3.25)$$

where a is the sonic velocity. Along isentropes, the quantity $p \cdot \rho^\gamma$ is invariant (γ is the ratio of heat capacities at constant pressure and volume, $\gamma = c_p/c_v$)[217]. Further

¹³ This “ideal” medium may be a vacuum. For clarity of description, an ideal gas is assumed as the ambient for this section.

substitution of this relation and the ideal gas EOS into equation 3.25 yields the familiar relation

$$a = \sqrt{\gamma RT} . \quad (3.26)$$

For an ablation system, it is typical to consider the shock processes as unsteady waves, similar to explosions, and to therefore use the sonic velocity in the undisturbed ambient [218]. The shock Mach number is then defined as the ratio of the shock speed to this ambient sonic velocity[219]. The motion of the shock wave and the contact surface are controlled by the pressure ratio and the thermophysical properties of the fluid. Generally, the shock front precedes the initial contact front, that is, the shock compresses and heats the initially quiescent ambient fluid. This induces motion of the ambient following the shock. The separation between the ambient and the material evolved from the surface is referred to as the contact surface, and it moves at the velocity induced in the ambient. This velocity may be supersonic, and is a function of both time and space for three dimensional flows.

The evolution of a shock wave can be explained by considering finite amplitude and nonlinear effects in the motion of longitudinal waves in a material. As noted above, the approximation used for acoustic theory is that the amplitude of temperature, pressure and density differences in an acoustic wave are vanishingly small. If, however, the density perturbation is assumed to be finite and the system is at local equilibrium, the changes in temperature, and the local sonic velocity also are finite and positive. As a result, the local mass velocity is increased in this region of initially higher density. This process thus results in a steepening of the density and temperature profile until initially distinct wavefronts coalesce, and the system collapses into a shock wave, which is a region of nearly discontinuous change in temperature, pressure, density, and most

importantly, entropy. The structure of the shock is such that the large gradients induced as described above lead to the rapid increase of entropy due to viscous and conductive effects. The thickness of this zone is on the order of several molecular mean free paths.

As a parenthetical note, the potential for the application of catastrophe theory to compressible flows seems promising¹⁴. This can be seen by considering the so-called Rayleigh curve which shows that the heating of a compressible flow always drives the flow toward its sonic velocity [217]. When this curve is projected on a Mollier diagram, the dependence on initial conditions of the qualitative nature of the curve strongly suggests the presence of an analytical catastrophe. (A sketch of a Rayleigh curve is seen in Figure 3-2). Of further interest is the coalescence of separate wavefronts into the shock wave. This process is driven by entropy increases, but presents a qualitative change in

the nature of the flow. In particular, when considered in an $x-t$ diagram, characteristics of the flow show a cusp at the point of shock generation [219]. An investigation of the nature of the topology of these curves would be interesting.

Ejection processes

Figure 3-2: Rayleigh curve for heat transfer to a compressible flow.

The term "ejection

¹⁴ Catastrophe theory is discussed in Appendix A and other applications are discussed in this chapter and in chapter 4.

processes” represents several phenomena which occur during ablation. Among these are ejection of photoelectrons and thermoelectrons from the ablating surface, the removal of liquid and vapor from thermal phase changes occurring at the surface and surface spalling at the surface due to mechanical stresses. The nature of these processes changes qualitatively as the intensity of irradiation increases, and these changes are the subject of much current research [220 – 222]. As discussed below, the ejection of electrons from the surface is one of the mechanisms leading to plasma formation, and understanding the distribution of the energy in the electrons and the dynamics of their ejection is therefore important for many applications of laser plasmas [223 – 226].

Physical ejection processes are also important in determining energy partitioning in ablation. Spalling, the flaking of macroscopic masses of material from the surface, is typically considered a brittle failure process and is indicative of the intensity of mechanical forces in the irradiated region [227 – 230]. This spalled material, which may have a fractal size distribution [231], is often found in the region surrounding ablation craters, particularly when the ablation occurs at low pressures. This surface debris leads to difficult cleaning problems and is one of the factors restricting applications of high precision ablation processes [201, 233].

As will be noted in chapter 6, the appearance of the solidified melt ejected from the crater onto the surrounding surface shows remarkable similarity to patterns seen in viscous fingering in Hele-Shaw flows. At first this similarity was rather surprising since in Hele-Shaw flows, a more viscous fluid is displaced by the injection of a less viscous fluid into a bounded volume. For these rim structures, molten liquids are flowing across a solid surface in the presence of a much lighter, less viscous fluid, in an essentially semi-infinite space. The key to resolving this paradox is to recognize that the temperature

Regime	Typical Irradiance, MW·cm ⁻²
Laser Supported Combustion (LSC)	< 10
Laser Supported Detonation (LSD)	10 – 100
Laser Supported Radiation (LSR)	> 1000

Table 3-2: Regimes of laser induced plasmas

gradients across the flowing metal serve to establish an increasing viscosity, and control the evolution of the structure. This process is considered in greater detail in chapter 4.

Plasma processes

The final category of phenomena occurring during ablation are associated with plasma formation. Among these are formation of plasmas due to inverse *Bremstrahlung* and due to multiphoton ionization, plasma shielding of the surface, plasma reradiation to the surface, and plasma induced distortion of the incident beam. The occurrence of a plasma above the surface during a short laser pulse typically reduces the direct coupling of energy into the surface, and lengthens the period of interaction. As a result, the occurrence of a plasma is generally undesirable in applications where an intense, short pulse is important.

Laser induced plasmas, like other aspects of laser material interactions, have been the subject of intense research for the past three decades. These plasmas show a wide range of characteristics, depending on the medium involved, and the wavelength, intensity and duration of the laser pulse [234, 235]. An understanding of these plasmas allows better prediction of laser material interactions. Phenomenologically, laser induced

plasmas can be classified into three regimes. The limits of these regimes, seen in Table 3-2, are approximate, and depend on the laser wavelength and pulse length, the substrate material, and the ambient atmosphere. These models assume that the incident radiation is driving force in the evolution of the plasma, and therefore an initial approximation as a one dimensional system is used. Assuming that the pulse is long enough to interact with the plasma, the regimes can be readily described [236]:

1. **Laser Supported Combustion (LSC)** occurs at the lowest irradiances, typically below $10 \text{ MW}\cdot\text{cm}^{-2}$. This phenomenon is named for its resemblance to chemical combustion waves. The plasma near the surfaces causes the propagation of a shock into the ambient. The passage of this “precursor” shock obviously raises the temperature and pressure of the medium into which it moves, but the material remains transparent. Thus, a region of high pressure gas exists between the shock and the expanding plasma.

2. **Laser Supported Detonation (LSD)** occurs for irradiances on the order of $100 \text{ MW}\cdot\text{cm}^{-2}$. In such systems, the shock is sufficiently strong that the shocked gas becomes strongly absorbing of incident radiation, and the effect is similar to a chemical detonation. The absorption of incident laser radiation raises the energy and velocity of the gas to its sonic point, and the propagation of the front is driven entirely by this source. As a result the trailing plasma is effectively uncoupled from the front.

3. **Laser Supported Radiation (LSR)** occurs at higher irradiances, typically those greater than $1000 \text{ MW}\cdot\text{cm}^{-2}$. Within this regime, the radiation from the plasma is sufficiently strong that the ambient medium becomes absorbing *before* the arrival of the shock. Therefore, there is no density profile associated with this process, but significant temperature and pressure gradients caused by the localized heating of the gas.

For “long” pulse or even continuous lasers, all of these regimes can be observed and have found important applications. These applications range from well developed spectrochemical analytic techniques to potential use in thermonuclear fusion and high impulse rocket engines [236]. Thus, these systems are certainly important examples of HFTP.

The experimental ablation system which is the focus of this thesis, however utilizes ~30 ps pulses. Because these pulses are so short, they have little direct influence on the evolution of the plasmas which they generate. The simplified regimes discussed above are thus not directly applicable, but many of the features which they exhibit can be seen. The primary problem with these models is that the convenient restriction to one dimension that they permit is not satisfactory for the shorter pulse case. More generally, the generation and evolution of a plasma is typically represented by a master equation. The important independent variable is the number of free electrons in the plasma, which is related to the degree of ionization of the constituent matter.¹⁵

For a gas, the normal range of energies described by the Maxwell-Boltzmann distribution includes a very small fraction of molecules at energies high enough to be ionized. Thus, for a gas close to equilibrium, the extent of ionization is described by the Saha equation:

$$\frac{n_e n_i}{n} = \frac{2Q_i}{Q_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \exp(-E_i / kT) \quad (3.27)$$

¹⁵ Although plasmas are often thought of as occurring in gaseous materials, breakdown can also be induced in solids and liquids [250].

where n_e is the number of electrons, n_i is the number of ions, n is the number of neutral atoms, Q_x is the appropriate partition function, T is the temperature, m_e is the mass of an electron, and k and h are respectively Boltzmann's and Planck's constants. This equation can be generalized for higher degrees of ionization, but the important physical insight can be gleaned from this simpler equation. For a gas near equilibrium, the degree of ionization is fixed by temperature. Thus, the use of dynamic master equations is not necessary for such systems. Furthermore, this equation implies the existence of ionized particles in any fluid medium; even though their number density may be extremely small. A material which has a substantial degree of ionization is approximately in equilibrium is known as a "thermal plasma." Laser ablation plasmas will seldom be completely in equilibrium, however, and if the departure is extreme, the distribution of energies can lead to misleading estimates of temperatures for the components of the plasma.

More generally, if the plasma is transient in nature, equations relating the various ionization and recombination mechanisms must be developed. These "master equations" ultimately lead to an equilibrium distribution such as the Maxwell-Boltzmann distribution if the system is closed to further energy or mass transfer¹⁶. For short pulse laser ablation systems, breakdown mechanisms would include inverse Bremsstrahlung, multiphoton ionization, and electron cascade breakdown. Several excellent reviews and text discuss these processes [105, 237 – 243], so they are not considered here in depth, beyond the observation that the breakdown process is an extremely important example of a naturally occurring fractal process[239, 245].

¹⁶ This implies that when considered in an operator sense, the master equation must have a semi-group character, as was discussed for thermal conduction earlier in this chapter. These systems are generally considered as reaction diffusion equations, and the addition of the "reaction" term increases the complexity and generality of the system.

Plasma induced caustics

One of the primary novel observations of the experiments associated with this work is the presence of crater cross sections resembling optical caustics. Since the optical system is axisymmetric and was kept clean, the asymmetry observed in these forms is believed to be due to plasma interactions with the surface. The hypothetical mechanism proposed is that during initial pulses a very shallow circular crater is formed. Its rim, also very shallow initially, acts as a mirror for any radiation toward the plane of the target. It is assumed that this rim is also circular. The resulting caustic within the crater then becomes the primary locus for thermal effects. This zone will experience the highest redeposition of energy from the plasma formed above the target.

If the plasma remains centered above the crater, the resulting crater will obviously be circular as the pattern of reflections from the rim is trivially axisymmetric. However, when the plasma is displaced away from the center of the target, the caustic will become nontrivial, and an investigation of its shape will allow diagnostic investigation of the plasma behavior.

A caustic formed by reflection is simply a locus of singularity in which multiple rays pass through a given curve [246, 247]. The prototypical example is the bright ring that is seen on the surface of a coffee cup when it is held at an angle to a light. This curve can be found by tracing rays from the source as they reflect off of the surface, but this is tedious, and does not provide the ability to determine the location of the source for a given observed caustic.

Figure 3-3. Initiation of caustic structure

It is much more useful to analytically derive the relationship. This is done for a general mirror shape in [248]. If the location of the source, S , is given, and it is distinct from the mirror curve, M , it can be seen that the family of first reflections from the surface is given by the envelope of curves generated by the normals to the orthotomic curve of M . An orthotomic curve is the collection of points generated by reflecting S

across the tangent line to M at all points of M . The benefit of this complicated construction is that the physical reflections of S from M are now identical to the normals of the orthotomic of M . Thus, only straight lines need to be evaluated, rather than calculating the angles of incidence and reflection for arbitrary rays. Furthermore, as the orthotomic of M represents the reflected optical rays, the caustic can be determined by evaluating the evolute, or locus of centers of curvature, for the orthotomic. This lengthy series of calculations simplifies dramatically when the mirror is smooth rather than arbitrary. It can be shown that the procedure simplifies to finding a conic section whose

Figure 3-4. Resultant caustic for an internally displaced source.

contact¹⁷ with M is equal to the degree of contact of their respective orthotomics. This again simplifies if M is itself a conic section, preferably a circle.

The locations of the cusps of the caustic then depend only on the relative location of the source to the center of M when it is circular. This is expected since any location of S will place it on a diameter of M. Representative caustics for varying source positions are shown in Figure 3-4 and Figure 3-5.

If the rim is assumed to have vertical walls, the caustic and source can be projected into the same plane for analysis, which is considerably simpler than the more general three dimensional case. For the internally displaced caustic shown in Figure 3-4, the source was displaced by sixty percent of the rim radius. The resulting caustic has three pronounced cusps inside the crater. In practice, the sharp corners associated with

¹⁷ Two curves are said to have k-point contact at a point if they have the same tangent, curvature, and the first (k-3) derivatives of curvature. Thus: 0-point, the curves do not intersect, 1-point; they meet but do not have the same slope; 2-point, they have the same tangent, but different curvature; 3-point, they have the same tangent and curvature, etc.

Figure 3-5. Caustic resulting from an externally displaced source.

the outer two would be expected to promote rapid evaporation, and the net effect of this would be to reduce the curvature of the crater on the side away from the source. This analysis is consistent with the experimental observations as discussed in chapter 6.

The case where the source is displaced beyond the rim is the more interesting case. This situation suggests a higher degree of coupling between the plasma and the ambient medium, and the resultant caustic is more readily identifiable. For the caustic shown in Figure 3-5, the source was assumed to be centered twice the radius of the initial rim from the center of the crater. The resulting symmetric form of two overlapping circular regions is clearly seen in a sample ablated at 50 bar (sample 941006.9, seen in chapter 6). Further confirmation of the hypothesis that this shape is due to displacement of the plasma away from the center of the crater is provided by the highly directional nature of the “bright” region around the crater.

Figure 3-6: Initial crater morphology

Figure 3-7: Early stages of caustic development

The analysis of caustics and the role they play in other fields are discussed further in chapter 4 and in Appendix A.

Experimental support for the proposed crater formation mechanism can be seen in Figure 3-6, which shows the initial formation of a crater ablated at ~70 bar. This is a large crater ($>100\text{ }\mu\text{m}$), and it exhibits a low rim structure. In Figure 3-7, the early stages of the development of a caustic pattern can be seen at the bottom of the crater.

Laser-Fluid Interactions

The interaction of laser beams with fluids exhibits a broad range of features. Several of the germane optical aspects of laser interaction with fluids are presented and discussed in this section. The physicochemical processes induced by this interaction are discussed in detail in the next chapter.

The experiments described in chapters 5 and 6 occur in an ambient medium of carbon dioxide. This fluid is a polarizable

LMI Regime	Example from this research
Linear absorption	CO ₂ transmission study
Saturable absorption	Bleaching of Q-switch I
Solute multiphoton ionization	Ionization of ejected Cu neutral atoms
Fluid breakdown by multiphoton ionization	Plasma formation in ambient carbon dioxide
Fluid breakdown by inverse Bremsstrahlung	Plasma formation in ambient carbon dioxide

Table 3-3 Optical regimes of laser interaction with fluids.

potential fluid properties, it is difficult to provide meaningful bounds on the range of fluences which correspond to a given phenomenon.)

The low intensity limiting behavior is linear absorption, as was described previously for solids. Most dielectric fluids are transparent, and thus their optical density is quite low. When Beer's law is applied, the resulting optical penetration depth is thus very long for most of these fluids. For example, consider neat water illuminated at low intensity at $\lambda = 532$ nm. Assuming that the predominant mechanism for energy loss is absorption, the decay of intensity is given by Beer's law [103]:

dielectric, and thus the following discussion emphasizes the behavior of dielectric fluids. (Electrolytic solutions and liquid metals would behave differently.) The various regimes of behavior are shown in Table 3-3, with representative applications from the experiments which were performed as a part of this research. (Because of the broad range of

$$\frac{I(x)}{I(0)} = \exp(-a_\lambda x) \quad (3.28)$$

where a_λ is the absorption coefficient; for water at ~ 550 nm, a_λ is 0.000045 cm^{-1} [102]. Thus the intensity falls by approximately 64% over a distance of 2.2×10^4 cm. This is roughly twelve orders of magnitude greater than the skin depth of the copper target described above! This example is slightly extreme, since the minimum absorption coefficient for water is at 550 nm. Water absorbs both infrared and ultraviolet light much more quickly, but the absorption lengths are still much longer than the skin depth of copper ($\delta_{\text{rad, water}} = 60$ cm at $\lambda = 250$ nm; $\delta_{\text{rad, water}} = 2.8$ cm at $\lambda = 1$ mm.).

The approximation of exponential decay in intensity implicitly assumes that the relaxation time for an excited molecule is fast enough that the majority of the molecules in a sample of liquid are in their ground state at all times. The relaxation processes may be thermal or radiative in nature, and for many systems of interest this assumption is quite good. If, however, a liquid is exposed to intense radiation over a time scale in which the excited molecules can not relax, the effective absorption coefficient becomes a strong function of time. If the liquid is initially a very strong absorber at the wavelength of illumination, transparency can be quickly induced if the intensity is high enough to “saturate” the absorption states of the molecule. This process is known as bleaching, and is the basis for passive Q-switching in lasers. In most systems, the excited molecule is an organic dye in solution at low concentrations. This regime is known as “saturable absorption.” Details of the specific system used in these experiments are discussed in chapter 5.

The remaining three regimes of behavior correspond to ionization of either a solute or the liquid itself. This is an important issue in the study of ablation processes in

particular, where an additional nonoptical plasma generation mechanism – shock heating – also exists. The generation of a plasma is of considerable interest since its presence can affect the transport of energy within the system, and even qualitative influences are difficult to predict *a priori*. As discussed in the previous section, if a plasma forms on the time scale of the pulse it can absorb significant amounts of the incident radiation, and effectively shield the surface. Much of this energy, however, may be reradiated to the surface over the longer lifetime of the plasma, and thus affect a much larger area than the initial ablation zone [236].

The primary factor determining the formation of the plasma is its initiation mechanism [105]. As shown in table 2, there are three optical sources for ionization. The first is ionization of neutral solute atoms or clusters. Thus, copper evaporated or ablated away during a previous pulse may be within the region of maximal irradiation and become ionized on a subsequent pulse. This serves as a “seeding” mechanism, and an avalanche ionization may follow.

The second mechanism is known as inverse *Bremsstrahlung* (IB). *Bremsstrahlung* is a German term meaning “braking radiation.” It is a process well known in plasma physics, whereby radiation is emitted by charged particles as they are decelerated. The inverse of this procedure is the absorption of radiation by particles to bring them to an excited state.

The third mechanism is the direct ionization of the fluid molecules by the radiation field. This typically is a multiphoton event.

It is important to note that the three ionization mechanisms listed above all are directly driven by nonlinear optical effects. They are inherently quantum mechanical in

nature, as the number of photons required for multiphoton events and the radiation absorption of IB are given by allowed quantum mechanical changes in energy levels of the molecules.

4. THE BEHAVIOR OF REAL FLUIDS

At the end of chapter 3, the interaction of an intense optical field with a fluid was considered. Of equal importance for an ablation system are the thermophysical processes that occur in a fluid on longer scales than the pulse itself. These processes include phase changes, bulk flows within the melt pool of the target, induced convective flows in the ambient medium, and the occurrence of shocks in the ambient due to interaction with the target. This chapter considers such phenomena by loosely grouping them into three categories. These three areas are nonideal classical thermostatics, the behavior of systems near a critical point, and the occurrence of induced convective flows. All three of these topics exhibit nonideal and nonlinear effects which are interesting and which dramatically affect the ablation processes discussed in chapters 5 and 6. Furthermore, the joint consideration of these topics is a paradigm for HFTP in thermofluid systems.

Thermodynamics of real fluids

Although transport processes, by definition, are the result of a system's departure from equilibrium, the limiting thermodynamic behavior of a system provides a basis for understanding its evolution. In this section, some pertinent aspects of the thermodynamics of real fluids are discussed as they apply to the ablation system being studied. In addition, several calculations are presented to provide a qualitative understanding of processes occurring in real fluids away from the critical point. Beyond this phenomenological material, the analytical framework discussed in chapter 2 is extended to investigate the role of epistemological concerns in a practical setting.

Ideal fluid behavior

The first — and often only — approximation made in the analysis of transport processes occurring in fluids is that the fluid is “ideal.” An understanding of the implications of such an assumption is important, because many of the most useful methods of accounting for real fluid behavior express results in relation to ideal systems.

Ideal gases

The study of the behavior of ‘ideal’ gases provided a significant impetus to much of physics throughout the nineteenth century, and the techniques developed for this readily visualized system have been used successfully in other applications¹. Most gases at atmospheric pressures follow ideal gas relations quite closely. These relations arise from the adoption of several empirical physical “axioms.” These principles can be easily stated, but have profound influence on the types of behavior that a system can exhibit.

Among the first relations to be noted was that the pressure and volume of a closed system are inversely related at a given temperature. Furthermore, there is no additive constant in this relation: extrapolation of either quantity to zero causes the other to grow without bound. Thus, the product of pressure and volume is invariant for a given system and temperature. Next, the temperature is directly proportional to both pressure and volume whenever one of the latter is held constant. Again, there is no additive constant in this relation. Finally, the mass of the system is assumed to be proportional to the volume and the temperature, and inversely proportional to its temperature. All of these effects can be seen by compressing an inflated balloon — or the contents of a piston,

¹ I.e., the Fermi gas of free electrons uses an ideal gas Hamiltonian.

which is the example used in most thermodynamics texts and exemplifies the practical importance of ideal gas thermodynamics to the development of the steam engine.

When these relationships are combined to yield a single equation, the ideal gas equation of state (EOS) results[251]:

$$\frac{pV}{nT} = \text{const.} = R = kN_A \quad (4.1)$$

In this equation, p , V , T , and n represent the pressure, volume, temperature, and number of moles of gas, respectively. R is the universal gas constant, $8.314 \text{ m}^3 \cdot \text{Pa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. It is equal to the product of the Boltzmann constant k and Avogadro's number, which is the number of items in a mole, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$. (The use of the system's mole number is a 'chemical engineering' convention. An alternative convention common in mechanical engineering is to use mass rather than mole number. This results in a unique gas constant for each substance, determined by multiplying R by the molecular weight. The choice is simply a matter of convenience and preference.)

For a multicomponent ideal gas, it is assumed that the constituents are isothermal, and that the partial pressure due to each is proportional to its relative preponderance [252]. For example, air at 300 K is observed to be saturated with water when it contains $0.018 \text{ (kg H}_2\text{O) / (kg dry air)}$. Given molar weights of $18 \text{ g} \cdot \text{mol}^{-1}$ for water and $29 \text{ g} \cdot \text{mol}^{-1}$ for dry air, the molar proportion of water is given by:

$$\frac{.018/18}{.018/18 + 1/29} = \frac{n_{\text{water}}}{n_{\text{total}}} = y_{\text{water}} = 0.028 \quad (4.2)$$

Since the total atmospheric pressure is 101.325 kPa, the ideal gas estimate of the partial pressure of water is:

$$p_{\text{water}} = y_{\text{water}} \cdot p_{\text{tot}} = 2.8 \text{ kPa.} \quad (4.3)$$

This is, as expected, in agreement with the vapor pressure of water which is 2.81 kPa at 300 K [161].

Ideal liquids

The definition of an ideal liquid is less precise than that of an ideal gas. Several features, however, are important for HFTP in general, and the laser ablation system in particular. First, one typically assumes that liquids are effectively incompressible. Thus, any mechanical work done on the liquid is dissipated through the effects of the viscosity, rather than through compression work. This is important because viscous dissipation is a nonconservative process, and obviously irreversible. Unlike compressible fluids, the potential energy stored in a fixed container of a liquid can not be dramatically increased². The sudden release of pressure on a liquid may cause some vaporization, but since there is no change of volume and evaporation is endothermic, such a pressure release is not typically catastrophic [253]. The resultant flow is driven by the pressure gradient while it exists. By comparison, rapid pressure relief of a compressible fluid causes a large conversion of potential to kinetic energy and a significant increase in volume. Such a release of energy is desirable for many processes, but can also be quite dangerous.

The second assumption typically made regarding liquids is that there are no chemical interactions among the constituents of the liquid, and thus its properties can be estimated additively from those of the constituents. For example, the specific volume of a mixture is assumed to be the molar average of the specific volumes of the individual components, and the other thermodynamic functions are calculated in a similar manner.

² Of course, the potential energy can be raised by raising the entire system in a gravitational field.

As discussed in the next section, the primary importance of these assumptions is in the determination of the phase equilibrium behavior, in which a liquid is assumed to be in equilibrium with a vapor phase above it.

This second feature is so attractive that most models of real liquid behavior are expressed relative to the ideal model [254]. Thus, if the volume of a mixture of two components differs from the composition weighted sum of their individual volumes, the difference is referred to as the mixing volume. The mixing volume can then be determined as a function of concentration, and the resulting map can be used to model the fluid. Obviously, as either of the components vanishes, so does the mixing volume, and thus its boundary conditions are;

$$\Delta V_{mix}|_{x=0} = \Delta V_{mix}|_{x=1} = 0 \quad (4.4)$$

where x is the molar concentration of one of the components.

As noted above, the remaining thermodynamic functions can be evaluated in a similar manner, and mixing rules can be generated by fitting experimental data to a functional relationship. The determination and use of such mixing rules is extremely empirical, but a few general statements can be made about their formulation. First, these relations are invariably smooth. This is expected, because small differences in concentration can not be expected to lead to divergent behavior. Second, in the limits $x \rightarrow 0$ and $x \rightarrow 1$, the curves are expected to become linear, and deviation from the ideal behavior is expected to become small in an absolute sense. Given these guidelines, the mixing rules can often be expressed as low order polynomials. Interestingly, such curves can even predict the occurrence of azeotropic mixtures, in which the composition of the vapor and liquid phases are identical.

Phase equilibria

The term 'phase equilibria' refers to two situations of interest in HFTP. The first, which is discussed in detail in the next several sections is the transition of a material from one state to another: sublimation, evaporation and melting of a pure substance fall into this category. These changes may be desired, in the case of micromachining processes, or undesired, in the case of catastrophic thermal damage of microsensors. The second situation is the equilibrium between two multicomponent phases in contact. This is discussed briefly in this section.

The thermodynamic equation governing such a system is Gibb's phase rule. The number of degrees of freedom of a thermodynamic system is determined by:

$$F = C - P + 2 \quad (4.5)$$

where F is the number of degrees of freedom, P is the number of coexisting phases, and C is the number of components [255]. If, for simplicity, a binary ($C=2$), two phase ($P=2$) system is considered, the number of degrees of freedom of the system is $F = C - P + 2 = 2$. The composition of a liquid and vapor in equilibrium is therefore fixed when the common experimental variables of either temperature and pressure or temperature and volume are set. The movement of the phases towards equilibrium is the basis for physical separations processes such as distillation [256, 257]. For macroscopic applications, a phase map can be prepared showing the corresponding equilibrium concentrations of the phases as a function of one component's concentration. The importance of the ideal phase behavior now becomes apparent: if the phases behave ideally, it is relatively easy to relate the temperature and pressure of the system to the phase composition, and therefore to predict the behavior of the system [254]. Typical

calculations would then allow determination of the number of stages necessary to cause the desired separation.

As noted in chapter 3 for thermal processes, however, for HFTP such an approach may be unsatisfactory. Two specific problems deserve explicit consideration. First, the use of Gibb's phase rule, the basis for the entire procedure, may not be appropriate. This problem arises because the phase rule is essentially a macroscopic rule, and does not consider the molecular scale fluctuations which occur within the realm of HFTP. Thus, while a large system will evolve to the limit described by the phase rule, such a limitation places very loose restrictions on microscale fluctuations likely to dominate the behavior of a HFTP.

The second aspect of the evolution of multiphase HFTP that must be considered is the constitutive equation controlling the kinetic behavior of the system. In macroscopic separations calculations, the equilibrium behavior is considered as a limiting idealized reference point, and the kinetics of the separation are assumed to be controlled by Fick's law³. Thus, the evaporation of water in a glass is assumed to be driven by the presence of a concentration gradient of water in the air over the liquid. The surface of the liquid and the adjacent mass transfer boundary layer are assumed to be in equilibrium at the composition described by the phase rule, and the ideal gas laws. Continuing the example cited earlier, if the glass of water is at 300 K, the mass fraction of water in the layer adjacent to the surface is $y = 0.028$. If the glass is covered, no further *net* evaporation occurs once the mass fraction of water in the enclosed vapor reaches this value (of course,

³ Of course, in practice, the approach to equilibrium would be enhanced by the use of forced convection and the promotion of turbulence. Both of these mechanisms enhance the concentration gradient at the phase interface, and—ideally—increase surface area as well

localized evaporation and condensation will still occur, but they will be balanced.). If, however, the top of the glass is open, a concentration gradient can be established, and the flux from the liquid phase is calculated by solving a diffusion equation using Fick's law.

Fick's law is a phenomenological relation which holds for a wide variety of situations [104]. However, the gradient involved is of the local mass fraction of a component. As discussed in chapters 2 and 3, diffusive processes are driven by gradients of a potential. This distinction leads to the suspicion that a more fundamental quantity must be causing mass transfer. This is indeed the case, and this source can be readily identified by considering the grand canonical formulation of a system. For such a system, which is open to material and energy transfer, a mechanical potential can be identified with a pressure gradient. This causes bulk flows. A thermal potential is identified with the temperature gradient, and is responsible for thermal conduction. The remaining potential is the chemical potential, and the gradients of this quantity are ultimately responsible for mass transfer.

The concentration gradient corresponds to the chemical potential gradient in the majority of cases of engineering interest. Such an assumption is inherent in calculations of the fugacity of fluids, and since concentration can be readily measured and understood, this relation allows the design of separations processes [254, 258]. The instances where the chemical potential and the concentration gradients are not equal for macroscopic systems are so unusual that they are 'named' relations and are expressed in terms of their deviation from Fick's law – i.e., the "Soret effect" and "double diffusion," in which transverse or opposed temperature and concentration gradients give rise to mass transfer that is not expected based on the concentration gradient alone [259 – 262]. Such effects are generally of secondary importance.

A consistent formulation of HFTP, however, requires recognition of the fact that the definition of a concentration gradient may be as problematic as the definition of the temperature gradient discussed in chapter 3. Evolution of the system at microscopic time and length scales will be much more influenced by kinetic processes and local fluctuations than by the global equilibria. Again, as in chapter 3, the approaches to this problem can be placed at – or between – two extremes:

- Statistical mechanical kinetic equations can serve as a basis for the system.
- The continuum formulation can be modified by the ad hoc addition of terms to the governing equations to yield effective potentials and fluxes.

The use of the latter in specific cases is undoubtedly the most effective method, but is of little generality, and requires the explicit incorporation of observed data to provide a fit for the model. The former method requires careful derivation, since HFTP are generally nonstationary processes, and may be far from local equilibrium. Thus, the approach that seems the most promising is a middle ground which recognizes that the scale of observations is much larger than the scale of the process, and that therefore, the observations should be expressible in terms of a system of differential equations. Meanwhile, the influence of the molecular level fluctuations should be recognized, and the structure of such evolution equations should guide the development of the system of equations. It might be hoped that since mass transfer involves the motion of real particles of substantial mass, a damping of the departure from equilibrium will occur. If this is in fact the case, deviations from the classical equations would be minimized after thermal effects are considered.

A specific example of a multiphase, multicomponent HFTP is laser ablation of alloys or mixtures. One specific system which has been studied extensively is the

ablation of brass [263]. The preferential ablation of zinc over copper has presented interesting theoretical problems, as well as a significant practical problem. Such laser ablation systems are used for material evaluation techniques, and as a spatially very precise source of material for spectroscopic methods, such as ICP–AES (Inductively Coupled Plasma — Atomic Emission Spectroscopy). The intent of such systems is to use laser ablation as a method for sampling very small specifically chosen volumes of material for analytical purposes. If, however, preferential ablation occurs, the value of the technique is lessened by the need for the development of standards.

For this system, the two extremes discussed in the preceding paragraph would require either *ab initio* calculation of the behavior of a large ensemble of atoms — which would be prohibitively difficult — or the assumption of local phase equilibrium as the temperature and pressure change dramatically during the ablation process — which seems unlikely. A more tractable approach might be to consider that:

- the long term behavior as the thermally affected zone cools should approach equilibrium behavior, but requires explicit consideration of temperature gradients to incorporate Soret effects.
- mass transfer involves the motion of metallic atoms (or clusters, or ions), and that the initial kinetic stages should show inertial effects and slightly lag the rapid change of local temperature and pressure.
- since the observed signal represents an integration of the total mass flux, departures of observations from equilibrium partitioning should be expected.

Further analysis of this system is beyond the scope of this thesis. (An important distinction should be noted between this preferential vaporization problem and a related procedure known as MALDI (Matrix Assisted Laser Desorption Ionization). MALDI is

a thermal process in which a laser is used to heat a substrate, whose localized thermal behavior drives an analyte from the surface. Thus, local equilibrium is assumed between the matrix and the analyte, even though temperatures in the irradiated zone may be far above the ambient temperature.)

Real fluid behavior and selection of an equation of state

The natural assumption in considering laser ablation in the presence of an ambient fluid is that a single component fluid is present. The reason for this assumption is that very little of the material removed during ablation will be dissolved in the fluid. The removal processes are physical, rather than chemical in nature, and, in any event, even local concentrations are expected to be so low that the fluid's properties are not appreciably altered. Furthermore, away from regions of phase separations, even multicomponent mixtures often behave effectively as if they had only one component. (For this reason, air is often treated as a single component gas.)

Unfortunately, to further assume ideal fluid behavior for ablation systems may be less acceptable. The behavior of such systems is typically manifested in the equation of state (EOS) relating temperature, pressure, and density⁴. In accordance with Gibb's phase rule, a single phase, single component fluid has two degrees of freedom. An EOS thus specifies the third variable after a pair is specified among T , P , and ρ . As noted above, for ideal gases, the EOS is a simple relation,

$$P = \rho RT. \quad (4.6)$$

⁴ In some applications, it is conventional to work with the specific volume, $v = 1/\rho$, rather than the density.

Obviously, the "ideal gas" behavior that occurs in the limit of low density occurs for high specific volume, *i.e.*, $\rho \rightarrow 0 \Leftrightarrow v \rightarrow \infty$. Thus, the choice of variable, though arbitrary, can depend on the type of limiting process preferred.

In general, the form of an EOS is more complicated, and depends on the range of the process variables under consideration, and on the degree of accuracy required. The EOS also is severely restricted if multiphase behavior must be modeled.

The first nonideal EOS was developed by van der Waals in 1873, and accounts for molecular influences by incorporating two constants and transforming the ideal gas EOS into a cubic equation [264]. The most commonly cited form of the equation is then:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (4.7)$$

where v is the molar volume, a accounts for the reduction of pressure due to interactions between pairs of molecules, and b is an estimate of the volume occupied by the molecules. When the appropriate restrictions are placed on the equation, the constants can be expressed in terms of the critical properties of the fluid, rather than as arbitrary empirical values [258, 265, 266]. These restrictions arise from the topological properties of the critical isotherm. As discussed below in the context of catastrophe theory, at the critical point, the first and second derivatives of the isotherm must vanish. Given these two restraints, the constants are therefore⁵:

$$a = \frac{27}{64} \cdot \frac{R^2 T_c^2}{P_c} \quad (4.8)$$

$$b = \frac{RT_c}{8P_c} \quad (4.9)$$

⁵ Despite the relative simplicity of these parameters, they were successfully used to predict the critical point, and thus the temperature required to condense “noncondensable” gases during the late nineteenth century. [286]

Careful analysis of equation 4.7 reveals that as the specific volume of a gas increases, the van der Waals equation approaches the ideal gas equation. The behavior of isotherms near the coexistence curve is more interesting, however.

At temperatures below the critical temperature, T_c , liquid and vapor phases can coexist. These phases have dramatically different volumes, and the experimentally observed isotherms then have a gap in the range of allowed volumes between $v_{liq}(T)$ and $v_{vap}(T)$. Analytically, the vdW EOS also changes as the temperature decreases past T_c . Above T_c it shows no extremum, at T_c it has an inversion point (at v_c), and below T_c it has two extrema. Identification of the saturation pressure is then achieved by placing the tie line between the phases at a pressure, p_{sat} such that the integral of $p - p_{sat}$ over (v_{liq}, v_{vap}) vanishes.

Curiously, the extension of the isotherms into the two phase regions is also physically important, since it provides an estimate of the extent of possible superheating of the liquid or supercooling of the vapor which can be achieved before spontaneous phase separation [267]. The so-called spinodal limits occur at the extrema of the EOS, between which the slope of the isotherms is positive (i.e., $dp/dv > 0$). This is a mechanically unstable solution, and the existence of a single fluid phase in this region is not possible. The region between the coexistence curve and the curve defined by the locus of upper and lower spinodal volumes is thus "metastable." If phase separation occurs, the system evolves to the volumes defined by the coexistence curves, but it is possible to drive a system well into the metastable region before the process occurs spontaneously [268]. In fact, the separation is almost invariably caused by a heterogeneous nucleation process, which requires a smaller driving force than homogeneous nucleation [269]. The initiation of the process at a position different from

its equilibrium value is one of the “fingerprints” of a catastrophe [270], and is discussed further in the topological analysis of thermodynamics below.

Although the van der Waals equation exhibits almost all of the interesting qualitative features seen in real systems, and although it is quantitatively more accurate than the ideal gas EOS, for many practical applications, a more accurate EOS is needed. Of particular importance are the EOS used for hydrocarbons separations and other industrial distillations. The development of these equations is a bridge between statistical mechanics and empiricism. Efforts at defining new equations of state fall into several distinct categories [258, 271, 272]:

- Two parameter, or corresponding states, models. Here it is assumed that the behavior of a gas is determined by its critical temperature and pressure. Then, the compressibility, $Z = pv/RT$, represents departure from ideal gas behavior, and is expressed graphically in terms of the reduced pressure and temperature. This approach allows rapid estimates of nonideal behavior, but only models gases and is unsatisfactory for associating or highly polar molecules.

- Three parameter models attempt to extend the concept of corresponding states models by adding a term to account for molecular configurational effects. Then, the compressibility factor is defined as $Z = Z^{(0)} + \omega Z^{(1)}$, where ω is the “acentric factor” and $Z^{(0)}$ and $Z^{(1)}$ are tabulated as functions of reduced pressure and temperature.

- Viral equation expansions. These equations arise from statistical mechanical analyses, and express the pressure as a power series in density, or reciprocal volume,

$$P = RT \left(\frac{1}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \dots \right) \quad (4.10)$$

These methods are attractive because there is a physical basis for the virial constants, which are functions of temperature, but have two weaknesses that limit their use. First, although the constants are directly related to the intermolecular potential, calculating higher terms is usually not possible. Second, because of their functional form, and the nonanalyticity of the critical point, they are generally not useful at volumes less than twice the critical volume.

- Cubic equations of state. This group includes the vdW equation as a special case, and is the simplest analytical form capable of providing a qualitatively correct model of the critical behavior of the isotherms. Furthermore, these equations can model behavior of the liquid as well as the vapor phase. Among other well known cubic EOS are the Redlich–Kwong, the Soave, and the Peng–Robinson.
- Analytically more complicated models. This class of models arises from attempts to fit experimental data more closely, and generally provide very good results at the expense of significant computational difficulty. One of the earliest attempts at such a model is the Benedict–Webb–Rubin (BWR) model which extends a virial type equation by including the acentric factor, and exponential terms

Two equations of state were used to model the carbon dioxide ambient contained within the ablation system discussed in chapters 5 and 6. For trials run at $p \leq 50$ bar, the densities were estimated using the van der Waals equation. For trials at higher pressures, a modified Lee Kessler equation was used, in accordance with the recommendations of recently published experimental data [273 – 276]. This fit is quite good for reduced temperatures on the order of $T_r \approx 0.01$, which was the typical operational value. Because the system was operated above the critical temperature, inversion of the EOS to determine density, given temperature and pressure, was possible. (For two phase

operation, selection of an EOS in which the volume rather than the pressure can be explicitly derived can become a difficult analytical issue. This difficulty was avoided by operating at positive reduced temperatures.)

One important point that must be stressed is that, contrary to several discussions in the literature, the processes associated with metallic liquids and vapors during ablation can *in no way* be considered as occurring near the metal's critical point. This conclusion seems self evident after a careful analysis of the process, but should be carefully noted to avoid confusion⁶. As discussed in the next section, processes operated at vanishingly small reduced pressures and temperatures exhibit numerous nonintuitive features, and the ability of lasers to generate liquid and vapor phases of a metallic target has lead to speculation that the metallic fluid was near the critical point. Although the critical parameters for metals are poorly known, this possibility can be dismissed by considering the operation of ablation as projected into a p-v plane. The system originates in the solid region of the phase diagram, and the absorption of optical energy leads to significant departure from thermal equilibrium. Locally, therefore the temperature and pressures are dramatically increased, and have large gradients. As discussed in chapter 3, these gradients lead to substantial energy fluxes. The pulse has a rapid time scale, however, and atomic motion is retarded by inertia. Therefore, there is no mechanism by which the original solid would be expected, even locally, to melt and expand to the critical point, at which a vapor and liquid phase would become indistinguishable. The large pressure and temperature gradients lead to ablation instead: as a fluid phase is generated, it is

⁶ The material which is removed from the surface may reach temperatures and pressures well above critical values, but this is irrelevant. The path taken by the fluid does not pass through the critical point. A related discussion is given in [340]

Figure 4-1 : Normalized Lennard-Jones potential.

immediately removed from the interaction zone. Furthermore, as discussed below, the heterogeneous nature of this process will not even allow the establishment of interfacial equilibrium around bulk thermodynamic values.

All equations of state represent the macroscopic averaging of intermolecular forces, and ultimately, the balance between attractive and repulsive forces[277 – 279]. Many models of the intermolecular potential have been developed, and many of these produce very good quantitative results over their range of applicability [258, 272]. Although the details of intermolecular attraction and repulsion can be very complex, the important qualitative features can be seen by considering a common, easily analyzed model, the Lennard–Jones (L-J) “6-12” potential. Under this model, attractive forces

vary proportionally to r^{-6} , while repulsive forces vary proportionally to r^{-12} , where r is the intermolecular distance between a pair of molecules. Analytically, this potential can therefore be expressed as:

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (4.11)$$

where σ and ε are the characteristic distance and energy, respectively⁷. Although this equation is not quantitatively correct, it does show the existence of large repulsive forces for spacings of molecular proportions, and weaker attractive forces decaying as the separation increases. When integrated over a large ensemble of molecules, such an interaction potential can provide estimates of bulk thermodynamic and transport properties.

Property estimates and equations of state are macroscopic manifestations of the interactions between molecules. A determination of the extent of these interactions is given by the two point correlation integral. This integral provides an estimate of the strength of intermolecular forces and of the average spatial density variation around a given molecule. Typically, one assumes that the system is effectively infinite in extent, and is homogeneous. The structure of the correlation function is then the primary measure of local structure, and is extremely important in the analysis of fluids near their critical points [280].

⁷ The values of ε and σ must be mutually estimated from the same data set. Since a fit is empirical, many sets of (ε, σ) provide comparable fits to the data, but the values of the parameters themselves may vary widely [265].

Figure	Size of cube, L/σ	Number Density
4-2	10	2.2×10^{18}
4-3	12	1.3×10^{18}
4-4	14	8.1×10^{17}
4-5	7	6.5×10^{19}

Table 4-1: Monte Carlo simulation parameters

Several examples of the simulation of correlation functions for carbon dioxide at 308 K and various densities can be seen in Figures 4-2 through 4-5. These simulations were conducted by placing 125 molecules into cubes of varying sizes. Periodic boundary

Figure 4-2: Simulation of intermolecular correlation for $a=10$.

Figure 4-3: Simulation of intermolecular correlation for $a=14$

conditions were assumed, and movement of the molecules was performed using a Metropolis algorithm (This algorithm has a Bayesian character as was recently discussed, [281]). A 'hot' start was achieved by randomly placing the molecules prior to the simulation, and each simulation was run for 800 steps per molecule. The sizes of the cubes and their corresponding densities are given in Table 4-1.⁸

The resulting correlation functions exhibit several interesting features. First, as expected, there is almost complete exclusion of molecules from an area corresponding to the molecular diameter. (Some alternative choices for intermolecular potentials consider

⁸ For reference, number density at STP is $\sim 2.6 \times 10^{19}$.

Figure 4-4: Simulation of intermolecular correlation for $a=12$

the molecules to be rigid, and result in absolute exclusion.). Second, the relative density experiences a maximum for separation distances slightly greater than unity. This is to be expected, since the average relative density must equal one, and the region nearer to the molecule is inaccessible. Finally, there is relatively little evidence of long term structure as the separation distance grows. This result is also expected, given the hypothesis of molecular chaos.

Finally, the difference between the simulation at the highest density simulated (Figure 4-5) and the lower density simulations shows the anticipated tendency for denser fluids to exhibit longer range correlations, and to take longer to converge to a solution.

Figure 4-5: Simulation of intermolecular correlation for $a=7$

Interfacial phenomena

When multiple bulk phases are present in a system, the region separating the phases is typically a spatially well defined locally smooth surface of negligible thickness embedded in the volume occupied by the system. The physics of these interfaces provides a good model for the study of HFTP because many of the issues which arise in HFTP have also been of concern for interfacial transport processes.

The study of interfacial phenomena provides a good example of the relation between the object of the analysis and the nature of the tools used. For most engineering applications, it is sufficient to divide the problem into three components, namely, the two phases and the interfacial region. Then, it is assumed that the interface exists and can be treated as a membrane. This membrane is assumed to have an array of physical

properties, such as stiffness, strength, and resistance to mass flux. The behavior of the interface is then modeled using standard membrane theory developed in the study of plates and shells [282].

A more detailed analysis, however, recognizes that this “membrane” does not truly exist. When localized fluctuations are important, or when the objective of the study is to develop more qualitatively detailed constitutive equations, the structure within the interface region must be considered. Such an analysis involves rigorous consideration of the intermolecular chemical and physical forces which allow discrete jumps in concentrations across an interface, and lead to effective surface tensions along the interfacial surface.

This dissonance between models of the system due to the objectives of the investigation serves as an apt analogy for the study of HFTP. The distinction between these models is considered in depth in [283]. Several of the methodologies which have proven useful in the study of interfacial transport processes can be expected to also be important for HFTP.

The significance of this model for HFTP in general arises because many such processes will be effectively confined to surfaces by virtue of the short time scales involved, and therefore will be dramatically influenced by local topology and resultant free energy variations. Among the many techniques developed in the study of interfacial processes are density functional theory and the use of variational analysis to account for localized fluctuations in free energy density. These fluctuations are especially important in the analysis of laser material interactions, because they may limit the effectiveness of simpler models.

Interfacial effects may also directly influence the energy coupling at a surface in ways that would be difficult to predict analytically. First among these is the early onset of melt, due to local free energy maxima. This phenomenon is known as surface melting, and could lead to a reduction in the effective surface temperature required for melting to occur. Since the optical properties of materials can change substantially upon melt, an early onset of melt would lead to a dramatic change in the coupling of incident radiation. Also of importance are surface chemical effects. The presence of either surface oxide layers or of adsorbed molecules on the surface will also affect energy coupling.

The study of interfacial phenomena thus serves as a paradigm for analysis of HFTP, because it demonstrates that abstract tools and mesoscopic analysis can indeed lead to an increased understanding of the macroscopic behavior of a complex system. It is also encouraging that this qualitatively related field has proven to be an experimentally tractable area for demonstrating some effects which might be difficult to observe in faster HFTP, such as pattern formation away from equilibrium [284], the emergence of fractal structures [285], and the successful application of methods from differential geometry and topology [283].

Interpretations of thermodynamic concepts

The study of thermodynamics – more properly called “thermostatistics” by Tribus [23] – includes a wide array of subjects. The standard pedagogical approach is based on using phenomenological, intuitive results to introduce and justify a set of axioms. From these axioms, the behavior of systems near equilibrium can be predicted with impressive precision. The typical perspective of this structure is that it is an objective codification of the behavior of real systems. The purpose of this section is to present two concepts

which, though not new, are often ignored. Both of these connect the study of thermodynamics to the concerns raised in chapter 2.

The first concept is the use of an information theoretic approach to formulating the laws of thermodynamics. This approach is consistent with the empirical Bayesian perspective discussed earlier, and is particularly important in considerations of irreversible thermodynamics (which typically focuses on steady state processes).

The controversy over this formulation was briefly noted in chapter 2. As far as engineering applications are concerned, however, the debate is academic, because Tribus [23] has demonstrated that the results of classical thermodynamics can be recovered using this approach. Its primary significance for this research is its role in the interpretation of HFTP. As noted elsewhere, the presence of nonlinearities and the extreme departure from equilibrium require consideration of the measurement process in conjunction with the observed process. It is reassuring to know that a thermodynamic formalism which explicitly considers the measurement process leads to identical results in the thermodynamic limit.

The second idea involves analyzing the thermodynamic behavior of fluids using catastrophe theory. This analysis is rather abstract in its initial formulation, but it provides a natural link between statistical physics and macroscopic thermodynamics. It also suggests a rationale for the restrictions on the types of behavior which can be expected for an arbitrary system. Thus, the form of some relationships is shown not to be coincidental, but determined implicitly by the properties desired of the final formulation. (This important tool for understanding thermodynamic systems is discussed in more depth in appendix A.) The significance of this methodology lies in its ability to transform

difficult algebraic problems into topological or geometric problems [270]. For example, catastrophe theory provide a link between classical continuum thermodynamics and statistical thermodynamics, using a small parameter expansion in a path integral. The exposition of such a connection helps to provide a justification for other heuristic tools, such as variational methods, and allows a clearer understanding of the role of assumptions about the nature of the system.

This perspective is even more important for the analysis of HFTP, since these processes are far from equilibrium, and thermodynamic results provide a limiting envelope for system behavior.

Critical phenomena in fluid systems

Introduction

Many of the trials conducted in this investigation occur near the critical point of the ambient carbon dioxide. The nonideal condition of the ambient atmosphere has a profound influence on the resulting ablation. The purpose of this section is to study the behavior of systems near a thermodynamic critical point in order to make predictions regarding laser material interactions. A secondary purpose is to review the techniques used in the study of near critical systems with the hope of being able to apply these tools to other multiscale problems.

Although this dissertation focuses on the liquid–vapor critical point, several other types of systems exhibit critical behavior. As discussed below, all of these systems have an order parameter which is related to the thermodynamic potentials of the material through a power law dependence. Furthermore, the same exponents seem to apply for all

System	Order Parameter
Ferromagnetic/paramagnetic	Instantaneous mean magnetization
Liquid–vapor	Difference between local density and gas density at same temperature and pressure
Binary liquid two phase	Difference of molar density of one component from equilibrium
Helium I / Helium II	Quantum amplitude to find a Bose particle as a spatial function
Superconductor / nonsuperconductor	Quantum amplitude to find a Cooper pair as a spatial function

Table 4-2 : Critical systems and their order parameters

of these systems. This remarkable fact suggests strongly that there is a universal character to near– critical behavior [280]. Some of the more commonly studied critical systems and their order parameters are noted in Table 4-2.. Order functions, which are denoted by $\phi(x,t)$, disappear in a thermally averaged sense at temperatures above the critical point and diverge continuously from zero as temperature drops from the critical point. Selection of order parameters incorporates the physics of the system, and allows comparison of a wide variety of systems [286].

For fluid systems, the exponents used relate some function of the order parameter to perturbations of the temperature and pressure around their critical values. The six commonly used exponents express these relationships, and, amazingly, the experimental values of these quantities agree to within experimental error for most of the systems noted in Table 1. Among the first of these relationships to be noted experimentally was the divergence of the heat capacity of a fluid system with decreasing temperature as the critical point is approached from above. This relationship can be expressed as:

$$c \sim \frac{1}{\alpha} \cdot \left(\left| \frac{T - T_c}{T_c} \right|^{-\alpha} - 1 \right). \quad (4.12)$$

For a system at the critical pressure, as the temperature approaches the critical point from below, the vapor phase becomes progressively denser, while the liquid phase expands due to strengthening repulsive intermolecular forces. As a result, the difference in the densities of the two phases gradually vanishes, until at the critical point the phases become indistinguishable. This relationship is also a power law:

$$\rho_{liq} - \rho_{gas} \sim (T_c - T)^{\beta}. \quad (4.13)$$

The *isothermal* compressibility of a two-phase fluid system is infinite due to the ability of the phases to respond to pressure fluctuations by evaporation or condensation. Thus, as the critical point is approached from above, the isothermal compressibility diverges as a function of the difference between the system temperature and the critical temperature,

$$\kappa_T \sim (T - T_c)^{-\gamma}. \quad (4.14)$$

For a system at the critical temperature, the nonanalytic nature of the equation of state implies that system the density is a nonlinear function of the pressure. Therefore, along the critical isotherm, density fluctuations and pressure fluctuations are related as:

$$\rho \sim (P - P_c)^{1/6} \quad (4.15)$$

The importance of the correlation function, $G^{(2)}(r)$, and the correlation length, ξ , is discussed elsewhere; however, the rate of decay of the correlation function at the critical point with distance is given by

$$G^{(2)}(r) \sim r^{-(d-2+\eta)}, \quad (4.16)$$

while the correlation length's temperature dependence is

$$\xi \sim |T - T_c|^{-\nu}. \quad (4.17)$$

Many of the anomalous properties of near critical systems can be well explained by these 'simple' relations.

These scaling laws also provide a qualitative link to the identification of fractal behavior in near critical systems because of their high degree of self-similarity.

Although exponential relations are also dimensionless, they do not possess the degree of self similarity seen in power laws [280]. This is shown by noting that if $f_1(x) \sim x^a$ is a power law, and $f_2(x) \sim \exp(bx)$ is an exponential function, then:

$$f_1(2x)/f_1(x) = 2^a, \quad (4.18)$$

which is independent of the value of x , whereas

$$f_2(2x)/f_2(x) = \exp(2bx - bx) = \exp(bx). \quad (4.19)$$

Equation 4.19 obviously depends on the value of x . Therefore, although the arguments of exponential functions are nondimensional and these relationships are well suited for

scaling of physically similar systems, they do not exhibit the fractal behavior seen in power laws.

Characteristics of second-order phase changes

An early attempt by Ehrenfest to categorize phase change phenomena [280] is based on the relative smoothness of thermodynamic potentials as the phase change occurs.⁹ “First order” changes are those in which finite changes in macroscopic quantities occur, and for which a latent heat exists. For “second-order” phases changes, no macroscopic changes occur, but there may be discontinuities in the thermodynamic potentials. Since no macroscopic changes occur, there is no latent heat associated with these “continuous” phase changes.

For the experimental system studied, the presence of a first-order phase change is clearly seen in the filling of the autoclave. As the temperature of the system is reduced, gaseous carbon dioxide initially cools to its saturation temperature and then begins to condense. While an effective heat sink is available, the fluid continues to condense at a constant temperature,¹⁰ and the latent heat could *hypothetically* be determined by comparing the rate of condensation and the temperature rise of the water in the cooling loop. Thus, as the system crosses the coexistence curve in the P–T plane, a substantial energy change accompanies an infinitesimal change in the control variable.

⁹This classification is slightly different from Ehrenfest’s original suggestion, which allowed an indefinite number of categories based on the topology of the chemical potential. For fluid systems, the distinction is irrelevant.

¹⁰ Note that the use of a constant saturation temperature implies that the system is isobaric, and open to mass transfer.

Continuous phase changes are qualitatively different. As discussed below, the topology of the thermodynamic potentials is nonanalytic near the critical point. The disappearance of the latent heat thus allows large physical fluctuations to occur in response to vanishingly small perturbations of the control parameters.

Behavior of thermodynamic potentials near critical points

While the PVT relation is well-defined even as the critical point is approached, the divergence of the correlation length leads to nonanalyticity of this relation. This is an important, but somewhat subtle point. As was discussed in the previous section, the van der Waals equation (vdW EOS) can predict qualitatively the occurrence of a critical point, but as it is a cubic equation, and thus analytic, its quantitative predictions are rather poor in the vicinity of the critical point. A famous data reduction by Guggenheim [265], in which normalized data for many gases fall on the same coexistence curve, confirmed the principle of “corresponding states,” namely, that the behavior of fluids is essentially universal if the variables are reduced relative to their critical values. The observed coexistence curve is much flatter than that predicted by the vdW EOS.

The occurrence of the singularity in such systems is quite interesting. For physical systems, experimental observation at extremely small reduced parameters confirms the power law structure and universal nature of the exponents.

Critical point opalescence

The presence of a fluid near its critical point is useful in ablation processes for several reasons. First, a wide range of densities and pressures is readily achievable, which allows analysis of the influence of mechanical coupling of the ambient to the target

material. Second, since the equilibrium optical characteristics of the fluid are very dependent on the density [287, 288], numerous nonlinear optical effects can be studied across a relatively small range of experimental conditions. Furthermore, the possibility of generating interesting physicochemical processes is exciting.

One significant problem arises in such a setting, however. As discussed above, near the critical point, the correlation function diverges [289]. This means that clusters of molecules exist on all scales. Rather than separating as would happen with finite density differences, these clusters are found throughout the fluid, and result in substantial light scattering. The resulting phenomenon is known as critical opalescence [290], and it places limitations on how close to the critical point ablation experiments can be conducted.

Critical opalescence has fascinated observers since it was initially reported by Andrews in 1869. It is readily created by passing a closed system of average density $\rho_{\text{avg}} = \rho_c$ through the critical temperature, and was demonstrated several times in the course of these experiments. As T_c is approached from below, the meniscus separating the two phases becomes less stable, and appears to thicken. The instability is observed by the rapid growth of perturbations, and is due to the fact that as the densities of the two phases converge to ρ_c , the gravitational stabilization of the interface lessens. As the reduced temperature, $T_r = (T - T_c)/T_c$, vanishes, the interface ultimately becomes indistinct, and then vanishes. The fluid gradually becomes somewhat brown as the light transmitted through the fluid experiences more and more scattering. As the scattering increases further, the fluid becomes murkier until it finally becomes opaque. At this point, scattering is so intense that the majority of incident light is rapidly reflected, and

the fluid has a milky, bluish appearance.¹¹ If heating continues through the critical point, this milky appearance slowly disappears, and the fluid is now a single, transparent phase. It should be emphasized that these observations, using the experimental system described in chapter 5, although readily repeatable, are qualitative only. Much more careful control of the apparatus would be needed to use scattering data to evaluate system behavior quantitatively. Furthermore, because of the high compressibility of the fluid near its critical point and the relatively large height of the autoclave, gravitationally induced spatial inhomogeneities are certain to exist, and would make any such data difficult to interpret.

The benefit of observing this opalescence is twofold. First, its occurrence is a clear indication that the density of the material in the autoclave is close to the critical density. This was a valuable independent check for those trials where this was the desired density, and verified that the filling procedure used was acceptable. Second, and more importantly, the disappearance of the opalescence was taken as an indication that the system had passed far enough away from the critical point to allow the ablation process to proceed.

The qualitative explanation for opalescence is that near the critical point the range of cluster sizes grows rapidly, and that a substantial proportion of these cluster sizes are of the order of the wavelength of the light. This explains the brownish appearance of the autoclave as the critical point is approached: the blue end of the spectrum is scattered away from the propagation direction more strongly than longer wavelengths, and the

¹¹ The "brownish" and "bluish" colors described are common to all initially transparent systems. Indeed, with the proper interpretation of the scattering, similar behavior is seen for neutrons scattered by ferromagnetic systems near their critical points.

transmitted light is therefore red shifted. As the intensity of the scattering increases, the effective extinction coefficient of the fluid rises dramatically. Thus, the majority of the light is scattered quickly, and a substantial proportion will be backscattered. Again, the blue light is scattered more intensely, and thus the system appears bluish-white.

The quantitative description of critical point opalescence is far more challenging, because of the long range structure of the fluid. It is well established that near the critical point, multiple scattering makes a substantial contribution to the total intensity of the observed scattered light. A diagrammatic approach to this problem has been presented, and such efforts involve analysis of multiple scattering events [290].

Phenomenology of near critical fluid systems

Fluid systems near either a liquid-vapor or binary critical point exhibit other interesting features in addition to opalescence. These features have been studied in great detail, both experimentally and theoretically. They merit mention here because they exhibit multiple scale dependence which in some ways is similar to HFTP.

Because the singular behavior near critical points is due to the presence of molecular clusters of many sizes, fluids near a critical point have unusual and practically important chemical features. The strength of solvents is greatly enhanced near their critical points [291]. This is due to the ability of solvent molecules to effectively "collapse" around a solute molecule, resulting in tremendous negative partial molar volumes. This effect is widely used in chromatographic and industrial separations processes [292 – 296].

The thermodynamic and transport properties are also of both intrinsic and practical interest [135, 298 – 304]. The expected divergences in these properties affect the behavior of the system, and make computation extremely difficult. Numerous heat

and mass transfer studies have been reported [305 – 309]. Among applications currently considered are the use of supercritical fuels to cool aerospace systems and materials modifications as well as the chemical systems referred to above. Based on the extensive body of work reported in the literature, the theoretical scaling exponents discussed above seem universal. Experimentally, however, near-critical systems are extremely difficult to manipulate. Two features provide interesting examples of the sensitivity of these systems:

- Near critical fluids are extremely compressible. As a result, real systems can exhibit substantial vertical density gradients due to hydrostatic forces [310]. Such loading reduces the volume of the fluid that is at critical conditions, and leads to a substantial refractive index gradient in the fluid. This, of course, makes optical observations of a system more difficult to analyze.
- When a system is in reduced gravity, the expected critical slowing down of thermal diffusion is not seen. This phenomenon, called the “piston effect,” is the result of dissipation brought on by damping of an acoustic wave launched when a boundary temperature is impulsively raised [311 – 314].

(The experimental system discussed in chapter 5 is operated at reduced temperatures above 0.01, and thus these difficulties are not expected to be seen.)

Thermally induced convection

The convection of energy from the ablation site is one of the most important macroscale physical processes associated with ablation in the presence of a fluid. When this fluid is nonideal some rather interesting modifications of the standard analysis of convective flows arise. The notation “thermally induced” is nonstandard, but was chosen

in an attempt to include such effects as Marangoni flows and other physicochemically driven flows with the more commonly studied “free” or “natural” convective flows. This section briefly discusses the analysis of two such flows. The first of these is the motion of the ambient fluid past the target material. It has length scales much larger than the ablation site, and is idealized as a boundary layer flow with periodic excitation which is sharply localized in both time and space. The second flow of interest occurs in the melt pool of the thermally affected zone. This novel flow is driven by surface tension and pressure transients in the bounding ambient medium. The resulting structure is fractal in nature, and is preserved as the melt resolidifies.

Continuum formulation of convective flow

Convection is the process of energy or species transport by bulk flow of a fluid. This process can either be driven by an externally imposed flow (forced convection) or by a gradient of either energy or chemical potential (natural convection). The typical approach to both processes is to assume that a continuum formulation is appropriate.¹² For this case, with minimal additional assumptions, the governing equations used are:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (4.20)$$

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \rho \mathbf{b} + \nabla(\lambda \nabla \cdot \mathbf{u}) + \nabla \cdot (2\mu \mathbf{D}) \quad (4.21)$$

¹² The alternative is to use a kinetically based approach. This methodology, referred to as “rarefied gas dynamics” was initially developed for situations in which the fluid density was low enough that length scales of interest are of comparable magnitude to the mean free path of the molecules. A similar correspondence of length scales has arisen in recent years with the development of micro- and nano- scale mechanical devices [62].

$$\rho \frac{De}{Dt} = -\nabla \cdot \mathbf{q} + \rho r + \mathbf{T} : \mathbf{D} - \nabla \cdot (\sum_j \gamma_j e_j \nabla m_j) \quad (4.22)$$

$$= \nabla \cdot (k \nabla T) + \rho r - p \nabla \cdot \mathbf{u} + \mu_b (\nabla \cdot \mathbf{u})^2 + \mu \Phi - \nabla \cdot (\sum_j \gamma_j e_j \nabla m_j)$$

$$\frac{\partial m_j}{\partial t} + \nabla \cdot (\mathbf{n}_j) = R_j \quad (4.23)$$

Each of these equations is a differential expression of a balance equation, and the use of the substantial derivative, $D/Dt = \partial/\partial t + \mathbf{u} \cdot \nabla$, indicates a Lagrangian formulation. Equation 4.20 is referred to as the “continuity equation” and is a statement of mass conservation; $\mathbf{u}$ is the velocity vector and ρ is the mass density. Equation 4.21, the momentum equation, is a vector valued equation, and is written here in a very general form. In practice, this equation would typically be simplified before use. The pressure field is defined to be an isotropic scalar, and is denoted by p . The sum of body forces (i.e., gravitational or electromagnetic forces) is denoted by $\mathbf{b}$, and λ and μ are viscosity coefficients. (The divergence of the velocity occurs with λ which is thus irrelevant for incompressible flows. The existence and interpretation of λ —also known as the dilational viscosity—was a topic of discussion in both statistical and continuum mechanics [315, 85]. Recent work has linked this parameter to departure from equilibrium between various modes of energy storage for polyatomic molecules in dilational flows [316, 317].) The deformation tensor, $\mathbf{D}$, accounts for surface forces and is defined as the sum of the velocity gradient and its transpose. Its components are therefore:

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (4.24)$$

Together, equations 4.20 and 4.21 are often referred to as the Navier–Stokes equations and they are the basis for most fluid dynamics problems.

Equation 4.22 describes the conservation of energy. This is a scalar equation, and a distinction should be made between the temperature, T , which is a scalar field, and $\mathbf{T}$, which is the stress tensor. In the second equality, $\mathbf{T}$ is replaced through an assumption of a Newtonian constitutive equation relating the stress to the velocity gradients. The thermal conductivity is denoted by k , r represents a volumetric energy source, μ_b is the bulk viscosity, and Φ is the viscous dissipation function. The final term accounts for energy flux due to mass diffusion.

Finally, equation 4.23 represents species conservation, where R_j represents a source or sink of component j . Although this is a scalar equation, it is repeated for each of the constituents of the flow; their sum, representing the total mass of the system, yields the continuity equation. Thus, for a system of k components, the continuity equation and species conservation equations yield only k independent equations.

Substantial insight into the challenges associated with convective flows can be gained by studying the form of the equations and by evaluating the simplifying assumptions often made. For forced convection in some simple geometries, closed form solutions can be found. More often, however, numerical solutions of the flow fields must suffice. This is particularly true for natural convective flows, which are inherently rotational and in which the energy equation and the momentum equation can not be decoupled.

Since simulations will often be the only (nonexperimental) source of information about the structure of these flows, the discretization of the flow field must be done with care. Thus, in order to gain the maximum amount of information from these simulations, careful analysis of possible scaling relations is beneficial.

The first step in an analysis of these flows is the realization that the primary physical process by which a fluid exchanges energy or mass¹³ with its surroundings is diffusion. If a force – either externally or internally imposed – exists which is sufficient to drive a bulk flow, the energy added at a surface can then be rapidly dispersed by the underlying flowfield. Thus, the increased efficiency of convection over conduction alone is the result of the modification of the temperature field near the surface.

Of particular interest in the study of laser ablation is a second mechanism for energy deposition in a fluid. In this case, the flux occurs due to volumetric absorption of radiation. Such a source is fundamentally different from the surface flux discussed above. It appears as a separate local source term in the energy equation rather than as a boundary condition. As a result, it leads directly to internal energy and density gradients, and thus inextricably couples the energy and momentum equations. Therefore, except in trivial cases, the velocity field is rotational, and considerably more complicated. In order to examine the nature of the full set of equations, however, this contribution will be initially overlooked. Physically, this can be justified, since for an ablation system, one would typically use an ambient medium which is transparent to the incident radiation. (When heating of the surface is sufficient to cause substantial thermal radiation or when a plasma is formed in the fluid, broadband illumination of the fluid occurs. This can lead to absorption by a fluid which is effectively transparent at the frequency of the laser.)

Returning briefly to forced convection, the prototypical problem is the flow of an incompressible, viscous fluid past a boundary whose temperature differs from that of the

¹³ For clarity, the remainder of this discussion will focus on energy transport. The argument can be applied in a virtually identical manner for species transport.

bulk fluid. Subtleties arise depending on the geometry of the boundary, and whether the flow is external – i.e., past an object immersed in the fluid, with the remaining fluid boundaries effectively “at infinity” – or internal – fully bounded flow through an enclosure. (Obviously, this distinction is dependent on the length scales of interest for any laboratory scale experiment.) For clarity, consider steady external flow past an extensive flat surface. The continuity equation thus becomes:

$$\nabla \cdot (\rho \mathbf{u}) = \rho \nabla \cdot \mathbf{u} + \mathbf{u} \cdot \nabla \rho = 0. \quad (4.25)$$

This equation can often be simplified further by assuming constant fluid density. In that case, the divergence of the velocity vanishes, and occasionally, the problem may be simplified by introducing a vector valued potential, ϕ , such that $\mathbf{u} = \nabla \times \phi$.¹⁴

The distinction between incompressibility and constant density, and the validity of assuming constant density in real flows both deserve consideration. Incompressibility is the weaker of the two claims and is a property of the flow, not of the fluid. In such a flow, the pressure gradients are insufficient to cause appreciable local changes of fluid density. Spatial variation of the density due to other, e.g. thermal or gravitational, effects may occur. The distinction between flow properties and fluid properties represents an important and subtle abstraction from the physical system to the corresponding model. The influence of compressibility becomes important as the speed of the flow, $v = |\mathbf{u}|$, approaches, and exceeds, the sonic velocity, a , of the fluid. This can be expressed quantitatively by assuming incompressibility for flows where the Mach number is less than unity, that is,

$$M = v/a < 1 \quad (4.26)$$

¹⁴ The result follows immediately from a vector identity that $\nabla \cdot \nabla \times \phi = 0$ for any vector ϕ .

For most boundary layer flows, this relationship is easily satisfied; however, during ablation, material ejected from the surface is hypersonic, and generates short-lived shocks. Also, if the fluid is near its critical point, the divergence of the fluid's compressibility leads to dramatic reductions in the sonic velocity, and the need to carefully consider any assumption of incompressibility.

As noted above, the assumption of constant density is more restrictive. Since the density is a fluid property, determined by its equation of state, an assumption of constant density effectively assumes that the system operates along an isochore. Since such a coupling of temperature and pressure variation would be difficult to control for an open system, a more realistic requirement is that the temperature and pressure gradients in the system must be small enough that the resulting density changes are negligible:

$$\left(\frac{\partial \rho}{\partial \phi} \cdot \frac{\partial \phi}{\partial x} \right)_{\max} \cdot \Delta x \cdot \frac{1}{\rho} \ll 1, \quad \phi = T, P \quad (4.27)$$

where Δx corresponds to the length scale of the system. For the small length scales and relatively moderate driving forces associated with laminar boundary layers, such an assumption is often quite good. An alternative method of expressing the result of equation 4.27 is as " $X \approx 0$ " rather than " $X \ll 1$." Such a formulation is in the spirit of NSA, and the interpretation would be that any density changes are incommensurate with the proper choice of scale for the problem.

Teleological considerations in convection

As noted above, diffusion is the physical mechanism by which energy and mass are transferred in convective flows. The nature of the enhancement caused by bulk fluid

motion is most easily seen by considering the phenomenon known as Taylor dispersion. This paradoxical flow was first noted by Griffiths in 1911, but was not fully explained until the work of Taylor and Aris in the 1950s [318 – 322]. The problem arises in the dispersion of a miscible tracer inserted into a laminar tube flow. It is observed that this tracer diffuses symmetrically relative to a cross-sectional plane moving with the average velocity, U . This motion can be used to measure diffusion coefficients [323]. The paradox of this system arises because the “slug” of the tracer is approached from behind by neat solvent with an axial velocity twice the mean speed. This velocity profile is maintained through the slug, of course, and yet the front edge of the tracer does not move with this velocity. Instead, the plug broadens at a rate proportional to $t^{1/2}$, where t is a convective time scale relating the longitudinal position and the velocity, $t = x/U$. A more detailed analysis shows that the behavior of the system is defined by its Peclet number, $Pe = (U \cdot r_0)/D$, and the relative magnitude of axial and radial length scales, L/r_0 . In these relations, r_0 is a length scale for radial concentration gradients (i.e., on the order of the tube radius), L is length scale associated with axial gradients, and D is the diffusion coefficient. Thus, for high velocities ($Pe > 1$) and small axial length scales ($L/r_0 \gg Pe$), diffusion does not appreciably affect the concentration profiles induced by convection. As the system evolves and L/r_0 increases, diffusion plays an increasingly important role, and the Taylor dispersion results.

The importance of this flow for convective processes in general arises when one considers self diffusion. As a first order approximation, the Schmidt number for self diffusion is of the order of unity, and thus kinematic viscosity can be used as an approximate diffusion coefficient [265]. A time scale for diffusion of molecules out of an initially defined control volume can be estimated by solving a diffusion equation. For an axial diffusion problem, the time scale is proportional to δ^2/ν , where δ is the initial

thickness of the control volume, and ν is the viscosity. For example, for carbon dioxide at STP, $\nu = 7.6 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$. If an initial control volume width of $1 \text{ } \mu\text{m}$ is used, this time scale is $\sim 100 \text{ ns}$. Thus, the intuitive notion of a set control volume is an abstraction: the net, measurable motion of the control volume, over a finite period of time, does not refer to the motion of a specific mass of material in a molecular sense, as is the case of a deforming solid. Rather, as discussed previously in chapter two, the use of continuum equations absolutely invokes the existence of local thermodynamic equilibrium. The flow field is thus concretely defined because the molecular length scales are extremely different from the observational scale, and there is thus no ambiguity in defining this abstract quantity. In the case of HFTP, where extreme departure from local equilibrium is typical, the definition of abstract fields such as density, temperature, and velocity is influenced by nonlocal events.¹⁵

The continuum approach to convection also presents an opportunity to investigate the meaning of the term “function” for engineering systems. Any quantitative knowledge of such a system is based on measurement processes which are themselves subject to small errors. If the measurement process (for both the dependent and independent variables) is taken as the physical representation of a test function, then the “true” variable can not, and need not, be independently measured.¹⁶ As a result, the use of generalized functions rather than standard functions is appropriate. This is extremely important, since it leads to two results which are often assumed, but seldom stated:

- arbitrary smoothness assumptions can be made, and

¹⁵ It has been argued in a recent review [49] that the stress field is inherently nonlocal, even for more general flows.

¹⁶ see the discussion of generalized functions in Appendix A.

- for reasonable test functions, the problem can be transformed into Fourier space

It is interesting to note that this result arises based on the objective of an analysis, and on the measurement process, and not solely on the system! As discussed in chapter 2, the breakdown of the linear continuum approach therefore is closely correlated with the emergence of significant nonlinear processes on length scales comparable to the measurement scale of the system. For example, in evaluating compressible flow, a shock can be approximated as surface of discontinuity, and the relevant functions can be assumed to be piecewise continuous for macroscopic analyses, but if dissipation processes in the shock itself are of interest, then the continuum relations are unlikely to suffice. (It should also be emphasized that the measurement scale need not correspond to an actual physical measurement, but, for example, to the minimal scales needed for a hypothetical measurement. Thus, for determining a temperature, the measurement length scale corresponds to the ensemble used for evaluating thermal averages, even if such a measurement is physically impractical. Within the context of HFTP discussed in this thesis, this measurement scale can be taken as a molecular or atomic length scale.)

The initiation of natural convection

For the experimental investigation of ablation systems, convective flows of the ambient medium are driven by several mechanisms, including energy deposited in the target and bulk temperature gradients in the autoclave. From the perspective of the flow inside the autoclave, the dimensions of the crater are quite small, and the convection can be considered to be arising from a point source located on a wall. This is of course a tremendous simplification which neglects for now any mechanical coupling due to the presence of shock waves and any magnetohydrodynamic effects due to plasma ignition in the fluid. The final aspect of the convective process which deserves consideration is that

while ablation is occurring, the laser is pulsing at 10 Hz. This periodic behavior could be expected to have a substantial influence on the behavior of the flow field. An initial investigation of this specific problem is assisted by considering in detail the behavior of natural convective flows in a simpler steady state.

A common analysis of natural convective flows proceeds by adopting the Oberbeck–Boussinesq approximations [324]. For this analysis, one assumes that the flow is incompressible, and that the fluid has constant property values, except for temperature dependence of the density in the buoyancy term of the momentum equation. If the temperature variation is small enough that the density variation is roughly linear, the momentum equation can be written as:

$$\frac{D\mathbf{u}}{Dt} = -\frac{\nabla p}{\rho} + \nu \nabla^2 \mathbf{u} - \mathbf{g}\alpha \cdot \Delta T, \quad (4.28)$$

where $\mathbf{g}$ is the gravity vector, α is the thermal expansion coefficient, and ΔT is the driving temperature difference relative to a reference temperature. As discussed in [325], this approximation is acceptable for many experimental conditions. While the simplification of the equations makes them much more tractable, it also introduces additional symmetry to the system, compared to the general form of the Navier Stokes equations. As a result, very small departures of the system from the assumed restrictions may lead to symmetry breaking [284]. It is therefore possible that even in a case where each aspect of the Boussinesq approximation seems satisfactory when considered separately, the system fails to follow equation 4.28.

Convection in the melt pool of the target

As noted in chapter 6, the variation of rim morphology with changes in ambient density presents clear qualitative evidence of thermal coupling of the ambient and the target. The optical and mechanical aspects of crater shape and formation are discussed in detail in chapter 3. This section discusses an interesting observation of two types of fractal structures in the resolidified melt ejected from the crater. It is argued that these structures represent (1) a novel convective flow, namely a free surface, single component thermal analogue to Hele-Shaw flow, and (2) evidence of dense branching morphology (DBM). The modifications that these distinctions impose on the flow are discussed after a brief review of the formulation of Hele-Shaw flows, with special emphasis on their fractal behavior. DBM is contrasted with diffusion limited aggregation (DLA) in appendix C.

Hele-Shaw flows

A ready example of the occurrence of fractal behavior in fluid systems is seen in the class of flows known as Hele-Shaw flows. This is a simple system in which a thin layer of a viscous fluid is displaced by the injection of a less viscous, immiscible fluid. A typical system, as seen in Figure 4-6, consists of an oil as the more viscous fluid, and air

Figure 4-6: Configuration of Hele-Shaw flow

as the less viscous fluid. As the air is injected, it displaces the oil. Since the system is bounded by plates above and below, this two phase system is constrained to be a quasi-two dimensional flow. As the fluids are immiscible, a sharp interface between them arises. As the less viscous fluid advances, any instabilities in the interface will be magnified, and the shape of the interface becomes tortuous, as these instabilities are magnified, and grow. The lobes, or dendrites, of the lighter fluid also branch as they become large enough to encounter such instabilities, and the continued branching and growth of the interface exhibit complex variation that ranges between spatially fractal forms, and dense dendritic branches of a characteristic length.

The occurrence of this shape is obviously dependent on the relative viscosity's of the two phases. If the more viscous phase were injected into the lighter phase, no branching would occur, and the shape of the advancing interface would be roughly circular. In fact, this advancing front is may well show fractal variation at length scales much shorter than the radius of the front's envelope. Thus, three complex forms can be seen to arise for various parameter ranges for Hele-Shaw geometries [326]:

- Fractal viscous fingering, similar to DLA.
- Dense dentritic branching, with characteristic dendrite sizes.
- Stable envelope formation, with fractal substructure.

All three of these forms are seen in craters ablated for this study, indicating that the qualitative variations seen in these craters are evidence of fractal behavior of the thermal processes associated with melting and solidification in the target's thermally affected zone.

To express the details of this flow quantitatively, several assumptions are typically made. First, a two-dimensional geometry is assumed.¹⁷ This is considered acceptable, since the spacing of the plates, d , is much less than the length scales of interest in the problem. All body forces, such as gravity, are assumed to act on the normal to the plane of the fluid, and are thus ignored. Second, the geometry of the system is assumed to be azimuthally symmetric around the point of injection. This effectively eliminates any boundary influences on the initially present, or expelled, fluid. Third, the system is assumed to be isothermal, so that the energy equation is decoupled from the momentum equation, and the resulting flow is driven solely by the imposed pressure on the injected fluid.

Under these conditions, the flow can effectively be described using a Darcy's law formulation as used for flow in porous media. The velocity of the interface can thus be expressed as [319]:

$$\bar{U} = -\frac{k}{\mu} \nabla p = -M \nabla \phi, \quad (4.29)$$

where the overscore indicates that this is the mean interface velocity, k is the "permeability," in this case $k = d^2/12$, and $M = k/\mu$ is known as the "mobility." In the second equality, p is replaced by ϕ to allow generalization to the case of additional potential sources. Assuming that both fluids are incompressible, the divergence of the velocity must disappear, and equation 4.29 simplifies to a potential problem, whose solution is determined by the specification of boundary conditions. Capillary forces at

¹⁷ The primary resistance to flow occurs due to viscous shear at the plates, but this can be replaced with an effective force in the plane of the fluid.

the interface will obviously influence the pressure field locally, and thus the shape of the interface can become the dominant factor controlling its motion. These capillary forces lead to a pressure jump whose magnitude is [269]

$$\Delta p = \sigma \cdot (r_x^{-1} + r_z^{-1}), \quad (4.30)$$

where σ is the surface tension, and r_x and r_z are the radii of curvature in the plane and vertically, respectively. (This relationship is known as the Young–LaPlace equation, and the radii are assumed positive as seen from the nonwetting fluid.) If the plate spacing is small, the vertical radius of curvature is roughly $d/2$. Thus, $r_z \ll r_x$ and the pressure difference between the phases is primarily due to the vertical curvature. However, r_z is also quite insensitive to local variations in r_x . As a result the local fluctuations in the pressure are due to r_x . In this case, the evolution of the interface is controlled primarily by the in-plane radius of curvature.

As the front advances, and is exposed to infinitesimal perturbations, it is easily shown that for very short wavelengths, the surface tension forces will stabilize the front, since they require a larger driving pressure to propagate. Above a critical value, though, the surface tension can no longer restore the interface, and the front begins to distort. The wavelength corresponding to maximum growth of the fingers in the front is:

$$\lambda_{\max} = \pi \cdot d \cdot Ca^{-1/2}, \quad (4.31)$$

where Ca is the capillary number, $Ca = (U\mu)/\sigma$. As discussed in Feder [326], the behavior of such fingering cells is dependent on Ca . For small values of Ca , the critical wavelength is large, and relatively large fingers, with well defined branch points are observed. As Ca grows, it begins to resemble DLA more closely. As this corresponds to very small surface tension, the width of the fingers can become comparable to the plate

separation, d , and the connected path of the invading fluid is decidedly fractal in nature; several experimental studies have generated fractal exponents ~ 1.7 .

The range of small and moderate values of Ca are of most interest in relation to the ablation experiments described in chapter 6. For these ranges in Hele–Shaw cells, the front typically exhibits between five and seven fingers. Such an observation is consistent with the ablation experiments. Also, the statement of the number of fingers does not specify a power law dependence on the radius. At this early point in the evolution of the front, therefore, the finger growth is highly patterned but is not fractal. As the front continues to move, some fractal subfeatures do develop, however, which indicates shifts in the governing mechanisms for front propagation.

Melt pool convection

The dynamics of the thermally induced fluid motion have been intensely studied in connection with numerous applications including welding, laser heating and laser ablation [221, 329 – 337]. Such pools can exhibit a range of features, depending on the pulse length and intensity of the energy source. Of particular interest for the experimental work reported in this thesis are the melt pools formed during laser ablation processes, where the pulse length is negligible compared to the time scales of the thermal processes occurring in the liquid material.

Initially, the dynamics of the melt pool of an ablation process would seem to have little in common with a Hele–Shaw flow. Only one constituent is present. The flow is not bounded above, and the depth of the pool is not specified. Furthermore, the pool experiences large temperature gradients.

The photographs shown in chapter 6, however, show remarkable similarities to the experimental and computational results associated with viscous fingering, and with

DBM. Therefore, an investigation of the source of these similarities seems appropriate. First, the issue of heat flux in the system can be readily accommodated. An interesting subset of DLA/DBM experiments has studied the solidification of alloys, particularly Ge–Al. Although these experiments have generally occurred in closed, carefully controlled systems, they show similarities to the ejecta solidification patterns seen in ablation studies.

A somewhat more subtle set of problems is associated with the geometric and boundary considerations. In the ablation case, substantial lateral and vertical temperature gradients exist. During the period of irradiation, the energy deposited is highly localized, and therefore, a large surfacial gradient of surface tension exists. Since the cooling and resolidification will have much larger time scales, the liquid pool is expected to deform due to Marangoni effects. The parameter associated with such flows, naturally known as the Marangoni number, is given by [284]:

$$Ma = \frac{\Delta T \cdot d}{\rho \cdot \alpha \cdot \nu} \cdot \left(\frac{-\partial \sigma}{\partial T} \right), \quad (4.32)$$

where ΔT is the representative temperature difference, d is the corresponding length scale, ρ is the density, α is the thermal diffusivity, ν is the kinematic viscosity, and $\partial \sigma / \partial T$ expresses the temperature dependence of the surface tension.

The surface tension gradient across the surface will tend to lead to rim formation around the crater. As the density of the ambient atmosphere increases, however, the coupling of the collapse of the ablation driven shock will lead to a stagnation point near the center of the crater, and thus result in a large pressure transient on this growing rim structure. If the time scale of the resolidification is comparable to that of this pressure transient, the net lateral pressure, and shear from the resulting flow in the ambient would be expected to lead to distortion of the rim. In particular, if the rim is still largely molten, the pressure loading and shear serve to drive the less viscous material in the center toward the more viscous outer material. Such a flow, although it arises from different forces than

Figure 4-7. Origin of Marangoni forces. (a) Spatial dependence of irradiation; (b)

Spatial variation of T and σ

Hele–Shaw flows, should show a similar susceptibility to the Taylor instabilities that gave rise to the DBM patterns noted above. Thus, while the two families of flow fields are not identical, they are closely related, and the more easily visualized Hele–Shaw flows serve as useful analogues for ablation flows. (It is also instructive to note that the occurrence of Rayleigh–Taylor instabilities is a problem of interest in the implosion associated with laser–driven inertially confined fusion experiments. These occur at substantially higher intensities than those discussed here, and are not considered further.)

Based on these arguments, several predictions can be made. First, for craters which are small, and which therefore have a large superheat, the expected morphology is one of strict DBM, where the bulk of the liquid metal flow is confined to a smooth envelope, and distortions of the surface from the plane of the target are expected to be large. This is exactly the pattern seen in several figures in chapter 6, namely:

- Figure 6-6: Very pronounced dendritic structures are seen at the edge of the structure, but only at length scales much below the crater size. Furthermore, the bulk of the crater rim is, indeed, smooth and shows considerable distortion.
- Figures 6-8 and 6-14: Similarly, this crater shows a nearly smooth profile, with substantial fine surface features at smaller length scales.
- Figure 6-15: This crater, ablated at 30 bar, also shows the separation of scales between the smooth envelope of the rim and the imposed fine structure.

A second type of evolution is also expected. For cases where the degree of superheat is not as pronounced, and therefore local fluctuations of physical properties are relatively more important, the expectation is that a degree of fingering should be seen as well as the development of the envelope. (Note that this formation mechanism is much different than expulsion of droplets, which have been observed in other ablation work,

and which may not remain connected with the bulk of the liquid flowing from the crater.) Structures of this sort were also observed:

- Figures 6-7, 6-9, and 6-10: These figures show the same crater at different magnifications, and the multiple features discussed above can be easily seen. Eight large localized “bumps” exist within the rim structure itself. Beyond the bumps are large “threads,” with large fingers between them. In particular, in figure 6-10, the fractal nature of these surfaces can be seen as there are small irregularities and threads at many different dimensions.

- Figure 6-12: This sample also shows the tendency for the development of fingering in addition to motion of the envelope.

- Figure 6-17: In this sample the tendency toward fingering is reduced, as the superposed structures here are much smaller, and are beginning to dominate the envelope growth noted with the first series of samples.

Finally, figure 6-31 presents an interesting look at the leading edge for a large crater ablated at 70 bar. The branching of the filaments at the leading edge is quite different from the appearance of the imposed structure on the smaller craters discussed above.

The analysis of these craters confirms that the evolution of the crater is a highly transient process, and is strongly influenced by fluctuations in boundary conditions. Further study of these rims would benefit from stability analysis [338]. An approach which seems likely to be fruitful is the variational formulation advocated by Straughan and his coworkers [339] for studying convective flows, in which an energy functional is defined for the flow.

5. EXPERIMENTAL ABLATION SYSTEM

The experimental arrangement used to evaluate the processes discussed above consists of a high power laser, focused onto copper samples contained in a small, temperature-controlled pressure vessel. A schematic view of the system is shown in Figure 5-1. Each of the components in the system influences the nature of the observations, and is discussed in greater detail below. This chapter is also intended to serve as an operating manual for the Continuum YG-601C laser used in this research.

The picosecond Nd:YAG laser

General description

The laser used in these experiments is a cavity dumped, Q-switched Nd:YAG laser, Continuum model YG601C. The lasing medium is neodymium-doped yttrium-aluminum-garnet. The oscillator is both actively and passively mode locked. Extraction of a single pulse from the pulse train is achieved using a Pockels cell, which dumps the pulse to the amplifier. The single pass amplifier is a larger Nd:YAG crystal; after amplification, the beam is passed through a KD*P crystal which doubles the frequency, yielding a wavelength of 532 nm. Frequency doubling and the Pockel's effect are discussed in greater detail in appendix E.

The Nd:YAG laser is one of the most common solid state lasers. The crystal is formed by substituting neodymium for a portion of the yttrium in crystals of $Y_3Al_5O_{12}$. Due to considerations of strain in the cubic lattice structure, doping is limited to

Figure 5-1. Schematic view of experimental system

approximately one percent on an atomic basis. This yields a neodymium density of about $1.4 \times 10^{20} \text{ cm}^{-3}$.

For modeling of electronic transitions, the neodymium is considered to be triply ionized, Nd^{3+} . The primary lasing transition is from the $^4\text{F}_{3/2}$ state to $^4\text{I}_{11/2}$, which results in emission at 1064 nm in the near infrared. Excitation is caused by a flash lamp which excites electrons to states above the upper lasing level. The upper level has a fluorescence lifetime of 255 μs , while the lower level decays to the ground state with a

lifetime of ~ 30 ns. Thus, the rapid depletion of the lower level allows the generation of a substantial population inversion.

The laser operates at a fixed repetition rate of 10 Hz. The primary reason for operating at a single frequency is to minimize thermal fluctuations in the cavity. The lasing process is no more than five percent efficient. Much of the remaining energy is dissipated thermally through the crystal, and the resulting gradients can cause beam distortion. (The principle behind this phenomenon is discussed in appendix E; it also provides the basis for optical beam deflection techniques.) The selection of a fixed repetition rate allows corrections to be made through the polishing of the ends of the crystal. Operation at any other frequency leads to different thermal and density gradients in the crystal, and hence to suboptimal performance. For any experiments requiring a single pulse, the pulse selection should be performed outside of the cavity.

Q-switching and passive mode locking

The pulse length of the laser is shortened by the use of a flowing dye passive Q-switch, which also serves as a passive mode locking device. The Continuum YG-601C can be operated with either of two dyes, commonly known as "Q-switch I" and "Q-switch V." In practice, the primary difference between these dyes is that Q-switch I yields a pulse length of approximately 30 ps, while Q-switch V yields a pulse length of 20 ps. For the experiments discussed in this thesis, Q-switch I was used exclusively. The dye is sold as a powder, and is dissolved in spectroscopic grade 1,2-dichloroethane. The solution is prepared by dissolving approximately 10 mg of the powder in 50 ml of solvent. During cavity tuning, this dark purple concentrate is slowly added to a reservoir

of neat solvent.¹ The resulting solution is continuously pumped through the dye cell. This cell is bounded by a window and the rear mirror of the cavity, and has a nominal width of 0.5 mm. The assembly is adjusted as necessary to maintain cavity alignment.

Q-switch I is a benzopyrilium. Its CAS number is 2106-19-3, and its molecular formula is $C_{49}H_{43}ClO_6$. As a saturable absorber, its absorption is a function of intensity of the incident light. It serves as a Q-switch by absorbing incident photons early in an arriving pulse, and spoiling the gain of the cavity. This prevents lasing, and thus inversion depletion, by raising the lasing threshold until the solution has absorbed enough photons that it becomes transparent. Such saturable absorbers act very quickly, and effectively shorten pulses by preferentially absorbing the leading edge of a pulse. The center of the pulse then is preferentially amplified upon passage through the crystal, due to stimulated emission resulting from the large inversion relative to the threshold. The trailing edge of the pulse then passes through after much of the inversion is depleted, and is therefore amplified less than the earlier portions of the pulse. This pulse shortening mechanism is controlled by the degree of excess inversion achieved and the kinetics of the dye bleaching, which explains differences between the performance of different dyes. The recovery time of Q-switch I is 9.3 ps, and its saturation threshold is 56 MW/cm^2 at a wavelength of 1064 nm [342].

Although other methods can be used to place the absorber in the cavity, the use of a flowing dye solution enhances performance for two reasons. First, because the period

¹Since the amount of dye added to the laser is affected by numerous factors and the final addition is dropwise, the precise concentration of the prepared solution is unimportant. The dissolution process can be quite slow; although stirring and swirling of the solution are helpful, several hours should be allowed for complete dissolution. Filtration of the solution prior to use is good practice, as is the use of spectroscopic grade solvent.

between pulses is 100 ms, the dye cell is flushed and fresh solution is present for each pulse. This extends the lifetime of the dye, which ultimately oxidizes and must be replaced.² Second, as a result of constant circulation, energy which is thermalized in the solution is convected away. Thus, the dye cell can maintain a constant temperature close to that of its surroundings, which minimizes optically problematic temperature gradients.

Active mode locking

Mode-locking of the Continuum YG601C is performed by an acousto-optic modulator (AML), which is driven at a frequency near 70 Mhz. Mode-locking is a phenomenon which allows the formation of short pulse by selectively amplifying radiation at harmonically related frequencies. This section focuses on longitudinal mode-locking. It is typically assumed that this laser operates in the lowest order transverse mode, TEM_{00} , which corresponds to a Gaussian spatial profile. When the laser is optimized correctly, this is a very good approximation.

In a heuristic sense, mode-locking performs a function that is similar to Q-switching; in fact, the flowing dye cell serves as passive mode locker as well as a Q-switch. The primary difference is that, while Q-switching operates in the time domain, mode-locking works in the frequency domain. (Passive modelocking occurs because the dye's recovery time (~ 10 ps) is much less than the round-trip period of the cavity (~ 7 ns),

²Exposure to light causes the dye to turn first brown, and then yellow. This slow process is wavelength dependent, and is much faster for UV light. The dye should be replaced *before* noticeable degradation occurs. As a rule of thumb, it should be replaced every two weeks when the laser is used regularly, and prior to any realignment after periods of inactivity.

and the dye can effectively serve as a shutter for the cavity during the period when it is not bleached.)

For any real lasing system, the output is not truly monochromatic, but rather occurs across a small, finite frequency window. This window is due to broadening of the frequency associated with a radiative transition due to quantum mechanical considerations. For a laser cavity of length L , the frequencies which can resonate within the cavity are those defined by

$$\nu = \frac{k \cdot c}{2L} \quad (5.1)$$

where k is a positive integer and c is the speed of light. The spacing of these frequencies, $\Delta\nu = c/2L$, is the separation for adjacent longitudinal modes. Typically, many such modes fall within the gain envelope of the excitation, and can lase. (It is important to note that while the spacing seems large, it is quite small relative to the absolute frequency. For a laser with a cavity length of 1 m,

$$\Delta\nu = \frac{c}{2L} = \frac{3 \times 10^8 \text{ ms}^{-1}}{2 \cdot 1 \text{ m}} = 1.5 \times 10^8 \text{ s}^{-1} = 150 \text{ MHz} \quad (5.2)$$

By comparison, at $\lambda = 1064 \text{ nm}$, $\nu = 280 \text{ THz}$; thus, $\Delta\nu/\nu \sim 5 \times 10^{-7}$.) Since the relative spacing of these modes is very small, as is the relative width of the gain envelope, the approximation of monochromatic emission in the semiclassical laser equations is justifiable.

In typical operation, the allowed modes oscillate at arbitrary relative phases, and the average output is thus relatively low. If, however, an element is placed in the cavity which forces all of the modes to operate at a constant phase, the output then becomes a pulse of substantial power. This is precisely what is done by the acousto-optic modulator

in the Continuum YG601-C. Acousto-optic modulation is performed, as its name implies, by using an acoustic field to control an optical element in the cavity.

For this laser, the active element is a quartz crystal which is excited ultrasonically by a radio frequency driver at ~ 70 MHz. This excitation causes the formation of a standing longitudinal density wave across the crystal, which is oriented perpendicularly to the beam path. This density variation causes a refractive index variation, which in turn diffracts energy away from the beam path, except at two points in its temporal cycle. As a result, only those components passing through the AML at these times can resonate and be amplified.

The presence of the multiple longitudinal modes is important to pulse formation, since, as is known from elementary Fourier analysis, numerous frequencies must be present to allow sharp changes in a temporal signal. This is seen in Figure 5-2, which

Figure 5-2: Modelocking of simple cosinusoids.

shows the result of locking together ten cosinusoids, $y_n = \cos(2\pi nt/T)$ for $n = 1$ to 10 , and $-.25 < t/T < 0.75$. The basis for the time, T , is the period of the fundamental frequency, and all of the phases are set to zero for convenience. The net intensity is the square of the sum of the component waveforms, scaled to give a maximum pulse height of unity. Thus, by “locking” adjacent longitudinal modes onto a constant phase, active modelocking allows formation of sharp well-defined pulses in the time domain.

Oscillator alignment

Although the Continuum laser used in this investigation is a commercially available instrument, it is notoriously difficult to align and maintain. Attempts to resolve electronic and alignment problems consumed over a third of the period during which experimentation was conducted. This section provides a detailed description of the procedure for aligning the oscillator.

The layout of components inside the laser is shown in Figure 5-3. The majority of the components in the oscillator are considered fixed³. Only the mirrors, delay line, half wave plate, and the acousto-optic mode locker should be moved. Prior to beginning the alignment, the dye solution in the dye reservoir is drained and discarded into the proper hazardous waste container (If the dye filter is to be changed, it is replaced at this point. It too is hazardous waste, and must be discarded properly!). The reservoir is then filled to about half of capacity with neat 1,2-dichloroethane. With the AML off, the laser is now in the “free running state.” This means that the laser is oscillating with no restrictions on the relative phases of resonating modes, and the cavity loss is not modulated.

³ For routine tuning, adjusting any of the fixed components is not recommended, due to the increase in the number of cavity degrees of freedom. Adjustment of these components should be left to the manufacturer.

Figure 5-3. Optical configuration of the Continuum YG601C laser

Prior to subsequent optimization steps, the proper physical alignment of the components in the cavity is verified by running the beam of a He-Ne laser down the center of the cavity. By centering the beam through the etalon at the rear of the cavity and the pinhole near the dye cell and then tracing reflections from various surfaces in the cavity, an assessment of the degree of misalignment is possible.

All of the remaining steps require the use of a fast oscilloscope. Two configurations are used; for both, a fast photodiode is positioned to pick off a reflection from one of the quarter-wave plates. This set-up is advantageous because the photodiode can be permanently mounted outside of the laser to enhance repeatability of these measurements. The two oscilloscope settings are:

1. Triggered by the laser power supply; signal from the photodiode terminated into an impedance of $1\text{ M}\Omega$, with a bandwidth of at least 400 MHz. The acquisition is continuous, with no averaging of the signal. The temporal scale is $100\text{ }\mu\text{s}$ per division. The vertical scale is determined by the signal intensity and hence by the exact position of the photodiode, but it should be about 10 mV per division.
2. Triggered by the photodiode signal which is terminated into an impedance of 50Ω , with a bandwidth of at least 400 MHz. The acquisition is again continuous with no averaging. The time scale is 50 ns per division, and, again, the vertical scale is adjusted based on signal intensity. It is very important that the main record length of the scope be adjusted to 512 points so that the sampling is performed in "real time," rather than "equivalent time."

The radio frequency (RF) driver for the AML is turned off and the BNC leading to the Pockels cell is disconnected for the next step in the alignment (The amplifier flashlamps can also be turned off to minimize undesired reflections.). The mirrors, delay line, and the AML are adjusted to yield the maximum signal and the minimum build-up time (BUT) using oscilloscope set-up 1. The BUT can be calculated by setting one cursor at an edge of the trigger and the other at the peak of the photodiode signal, as shown in Figure 5-4.

The next step is the fine tuning of the AML. To maximize the attenuation of the signal by the AML, the cavity length should be changed slightly from the optimum found in the previous step. The RF driver is now turned on and the AML is rotated to minimize the signal. The position should be verified by turning the RF driver off and observing the

Figure 5-4. Build-up time evaluation

Figure 5-5. Influence of acousto-optic mode locking on free running state.

return of the larger signal (Figure 5-5). This step is necessary to insure that the minimum found is due to acousto-optic diffraction, and not to clipping of the beam by the crystal's aperture.

An additional test for proper positioning of the AML is to place a mirror behind the dye cell to reflect the HeNe beam out of the cavity and onto a screen. This beam should show a classic Fresnel diffraction pattern of successively dimmer concentric rings around a bright central spot. If a small hole in the screen is set to pass the central spot,

Figure 5-6. “Staircase” appearance during free running operation

then the temporal attenuation of the outer rings by the AML can be seen in a darkened room⁴.

When the oscillator is well aligned in the free running state, the signal seen using setup 1 should look like a stable “staircase,” as shown in Figure 5-6. The signal should be free of jitter, and its amplitude should fluctuate by only a few percent from its mean value.

⁴The amplifier flashlamps should also be turned off to enhance visibility of this pattern.

Figure 5-7. The effect of dye addition on signal response

After the AML is appropriately positioned, dye is added to the system. The concentrated dye solution is made by dissolving approximately 10 mg of the dye in about 50 ml of 1,2-dichloroethane. As the dye is light sensitive and will oxidize over time, any remaining solution should be stored in a sealed container in a dark place. As dye is added to the reservoir, the characteristic notched appearance of the free running signal will change from the "staircase" into a single smooth step (Figure 5-7). At this point, the scope is switched to set-up 2. The shape of the observed signal changes dramatically because of the reduction of the time scale and the impedance, and represents the real time output of the photodiode, rather than its response to impulsive loading.

Figure 5-8. Q switching of the laser

The signal will now show Q-switching due to the dye (Figure 5-8). A sequence of pulses separated by about 7 ns will be appear on the scope. This is easier to see if the “pan–zoom” feature of the scope is used to magnify the horizontal scale. *The sampling should be done only in the real time mode!* As more dye is added to the reservoir, the saturation intensity increases and the growth of the pulse energy will be therefore occur more quickly. Thus, fewer pulses are seen on the trace, and the threshold voltage required for lasing will increase. Optimization of the laser is achieved by keeping the flashlamp voltage 40 V above threshold but less than 1040 V while dye is added. The specified level of performance is attained when there are about eight pulses per train that

Figure 5-9. Signal after beam dumping to the amplifier

have an amplitude greater than a quarter of the largest pulse. The use of signal averaging is not recommended at this point, but acquisition can be briefly stopped if desired to allow observation of the pulse train.⁵

Pulse selection is the next step. The BNC to the Pockels cell is reconnected to the internal photodiode, and pulse dumping is observed on the oscilloscope using set-up 2 (Figure 5-9). The energy in the pulse grows as it passes through the cavity as long as the

⁵Averaging of the signal obscures small jitter in the signal, and makes optimization more difficult.

inversion in the crystals is sufficient to overcome the assorted loss mechanisms, such as diffraction and partial reflections. Ultimately, the energy of the pulse begins to decrease, as the loss mechanisms predominate. The pulse should be at its maximum energy when it is dumped. This point in time is selected by changing the optical path length in front of the photodiode with small strips of paper and by adjusting the delay of the trigger to the Pockels cell.

The energy of the dumped pulse should be between three and five millijoules, and the next step of laser optimization is to steer the beam into the center of the amplifier rod. Compared to the oscillator tuning, this is an easy task. The beam should be round, and its shape can be verified after each of the steering mirrors using burn paper and IR detector cards. Also, the beam must pass through a small pinhole ($5\text{ }\mu\text{m}$) which severely limits its position. Since the beam is focused to get through the pinhole, its intensity is high enough to cause audible ablation if it is misaligned.

If the beam is round and passing through the center of the rod, the amplifier

Figure 5-10. Typical beam profile

should deliver pulses at 10 Hz with an average energy of about 75 mJ in its fundamental frequency. (A typical beam profile can be seen in Figure 5-10.) If the second harmonic (532 nm) or fourth harmonic (266 nm) is desired, the beam must be steered through the appropriate doubling crystals. The efficiency of the conversion is strongly dependent on the rotation of the K*DP crystals; these are easily adjusted by turning their flywheels to maximize output.

If the laser is properly aligned, average energies of over 30 mJ can be achieved in the green, with a pulse energy standard deviation of less than 7%. The energy is measured using a Molelectron joulemeter attached to a beamsplitter. The signal from this pyroelectric device is processed through a Stanford Research Systems boxcar, and saved on the oscilloscope. This arrangement allows real-time recording of pulse energy sequences. Details of the analysis of pulse energy sequences are presented elsewhere.

Control of ambient conditions

One of the primary purposes of this investigation is to study the influence of ambient medium density on the ablation process. The thermodynamic significance of varying the densities is discussed elsewhere; however, the degree of experimental control available for these experiments deserves careful consideration.

The autoclave as a closed system

The autoclave containing the samples is considered closed to mass transfer and open to energy transfer during the ablation process. Thus, in particular, it is assumed that if the autoclave is allowed to reach a steady temperature before ablation, and if the temperature gradients are small, that the density is essentially uniform across the fluid, and that it is a function solely of temperature and pressure. Thus, careful measurement of these two intensive parameters allows density to be determined. Although the compressibility diverges near the critical point, most of this experimentation took place at 3 K above the critical point, and the increased compressibility is not a concern.

Thermal cycling of carbon dioxide

The density of the carbon dioxide within the autoclave is determined by the loading of the fluid. Loading was achieved by manipulating the chamber pressure and temperature. For most of these experiments, the fluid was provided by a cylinder of bone dry carbon dioxide (minimum 99.8% purity). Such cylinders contain a saturated vapor over its liquid at common temperatures. As the gas is bled from the cylinder, liquid evaporates and cylinder pressure is thus held constant for a given temperature until all of the liquid has evaporated.⁶ The cylinder is connected to the autoclave, which was purged prior to each run by filling it to 20 bar and bleeding to 0 bar gauge at least three times. The autoclave effluent valve was then closed, and the temperature of the cooling system was reduced. As the temperature of the interior of the autoclave fell below the dew point of the cylinder, the carbon dioxide supply valve was opened, and the fluid would condense in the autoclave. The process was monitored through the window, and when the appropriate liquid level was reached for the desired final density, the supply valve was closed.

The system was then heated to the target temperature for the run, typically 308 K (35° C). Minor downward adjustments to the density could be made by venting a small amount of fluid. An important observation is that this heating is an isochoric process. If the mean density is substantially below the critical density, the quantity of liquid in the autoclave is reduced as it warms up, and the interior will eventually “dry out.”

⁶The flow rate is low enough and the thermal mass of the system is large enough that cooling due to Joule-Thompson expansion can be neglected. At higher flow rates, such as those experienced on venting the autoclave, cooling can be sufficient to cause valves to ice if even trace amounts of water vapor are present.

Conversely, if the mean density is greater than the critical density, the meniscus gradually rises to the top of the autoclave, and a single liquid-like phase results. When the density is close to its critical value, however, the meniscus remains at roughly the midline of the autoclave. For such a system, as the temperature rises, the liquid density falls and the vapor density grows, and both approach the critical density. Based on the well-known “law of rectilinear diameters,” this critical density is approximately half that of the saturated liquid at temperatures well removed from the critical point; this can be shown as follows:

$$\rho = \frac{1}{2 \cdot V_{tot}} (V_{liq} \cdot \rho_{liq} + V_{vap} \cdot \rho_{vap}) = \frac{\rho_{liq}}{2 \cdot V_{tot}} \left(V_{liq} + V_{vap} \cdot \frac{\rho_{vap}}{\rho_{liq}} \right). \quad (5.3)$$

For a system near its critical density, $V_{liq} \approx V_{vap} \approx V_{tot}/2$, and when the vapor is essentially an ideal gas, its density is roughly three orders of magnitude less than the liquid density, yielding the desired approximation.

A schematic drawing of the thermal process used to load the autoclave is shown in

Figure 5-11. In this drawing, **a** represents the initial state of the autoclave at ambient temperature (~298 K) and atmospheric pressure (~101 kPa). The first stage, from **a** to **b**, is the connection of the autoclave to the cylinder, which is at the vapor pressure of CO₂ at room temperature. The step from **b** to **c** is the cooling of the autoclave. The path follows the coexistence curve, and the temperature reduction speeds the filling by establishing a slight pressure gradient from the tank to the cylinder, and providing a thermal sink to drive the condensation within the autoclave.

Figure 5-11: Thermal cycling of carbon dioxide during autoclave fill process.

When the autoclave was filled to the desired level, it was closed, and the autoclave was heated, $c \rightarrow d$. This process follows the isochore, which itself follows the coexistence curve until the specific volume of one of the phases matches the average specific volume of the fluid in the autoclave, at which point the two curves diverge. For most of these experiments, the final temperature at point d was 308 K, and thus T_f was ~ 0.01 .

Sample preparation, system alignment and data collection

Sample preparation

The samples used are research grade copper. Specimen dimensions are approximately 12 mm x 12 mm x 2 mm. To ensure consistency between samples, and to provide a flat surface, the samples were initially polished on a sequence of papers from 240 grit to 600 grit. Samples were polished wet and rotated between papers to successively reduce the magnitude of surface scratches. The preparation technique was refined during the course of the experiment; the final samples were polished using a sequences of alumina powders down to 1 micron. Use of the powder also allowed an orbital motion of the sample on later stages, eliminating the straight scratches seen on earlier samples.

System alignment

The distance between the laser and the autoclave is approximately 5 meters. As shown in Figure 5-1, a high power, monochromatic mirror is used to turn the beam onto the axis of the autoclave. To avoid optical damage of the windows or lenses due to high power densities from the pulse or reflections, a pair of lens is used to expand and refocus

Figure 5-12. Location of reflections from dual lens system.

the beam as shown in Figure 5-12. The focused reflections, denoted by **a**, **b**, and **c**, must be kept out of the window and the lenses. This requirement places some limitations on the range of magnifications which can be used. These lenses and the autoclave are placed on an optical rail to maintain alignment while allowing motion of the autoclave to account for variation of the optical path length through the fluid as density is changed. As discussed in the appendices, several methods can be used for the design of the optical system.

Regardless of the methodology used, the calculations used to determine the appropriate positions of the lenses and the autoclave assume that the medium is homogeneous or, at worst, that the density varies smoothly as a function of depth. Density fluctuations are specifically neglected since the resulting variation of the optical path is stochastic and can not be incorporated as a controllable parameter. (The phenomenon of critical point opalescence can cause almost total scattering of incident light. Its occurrence is discussed in detail in Chapter 4.) If the lens are assumed to be fixed, then only two components of the optical path vary as the fluid density changes. Since it is desired to maintain a constant beam diameter at the target surface, the product of the two component matrices must remain invariant as the autoclave position and the density of the fluid in the autoclave change. As shown in appendix E, this requirement is equivalent to:

$$d_3 + \frac{74.6}{n} = \text{const.} \quad (5.4)$$

where d_3 is the distance in mm between the converging lens and the front surface of the window, and n is the refractive index of the fluid. If the position of the autoclave is referenced to that used for the experiments at atmospheric pressure, the relationship can be written as:

$$\Delta d_3 = \frac{74.6}{n_0} \cdot \left(1 - \frac{n_0}{n_1} \right) \quad (5.5)$$

where Δd_3 is the change of position required when the refractive index is n_1 .

The variation of carbon dioxide's refractive index as a function of density is well described by the Lorentz-Lorenz equation (see appendix E on optical effects for details),

$$\frac{n^2 - 1}{n^2 + 2} = L\rho. \quad (5.6)$$

For temperatures near 30°C, the constant in equation 5.6 is $L=6.7$ cc/mol. The highest densities used are near the critical density of 0.468 kg/l $\approx$ 0.01 mol/cc. Thus the largest value of $L\rho$ is less than 1, and the inversion of equation 5.6 is well defined as:

$$n = \sqrt{\frac{1 + 2L\rho}{1 - L\rho}} \quad (5.7)$$

Substitution of this relationship into equation 5.5 yields position of the autoclave as a function of density, as shown in Figure 5-13.

As the maximum index of refraction for these experiments was less than $n = 1.2$, the full range of autoclave positions, $\Delta d_{3,\max} \approx 8$ mm. It should also be noted that, although the position varied nearly linearly with density, its relation to the pressure would show the same nonlinearity as the equation of state.

Figure 5-13. Autoclave position as a function of density.

Temporal stability of laser output

The laser alignment procedure provides clear evidence that significant fluctuations in the laser's pulse energy occur. This problem has been addressed both operationally and analytically. First, from an operational point of view, it is imperative that the energy be measured in real time during the experiments. Thus, a beam splitter and joulemeter were installed into the beam path prior to the turning mirror. This pick-

off reduces transmitted energy by about eight percent, but allows normalization of the results to energy levels and permits verification of laser performance during ablation.

The analytical aspects of the problem are much more intriguing. Numerous reports in the literature suggest that Q-switched lasers can exhibit chaotic behavior. Repeated sequences of pulse energies were gathered and analyzed to verify this proposition.

For the purpose of data collection, the 1 M Ω output of the joule meter was fed to a boxcar gated integrator. The gate width was set to 300 ns, and the resulting value was transmitted to the oscilloscope as a step function with a 100 ms step width. The oscilloscope was set to capture ten points per second; a record length of 8192 points then allowed the recording of pulse energies over a period in excess of fifteen minutes. The results of both the fractal analysis and of more typical Fourier analysis are presented in chapter 6.

The duration of most of the ablation experiments was 10 seconds. Since the ablation was the result of only 100 pulses, knowledge of the pulse energies was essential. For these sequences, a beam block was placed in front of the beamsplitter, and the laser's shutter was opened. The time scale for the oscilloscope was set for 2 seconds per division, and it was set for single shot acquisition. After the oscilloscope was triggered, the block was removed from the beam path for ten seconds and then replaced. A representative sequence of pulses obtained in this manner is shown in **Error! Reference source not found.**

Figure 5-14: Experimental layout for measurement of pulse energy fluctuations

Figure 5-15: A representative real-time sequence of pulse energies.

6. EXPERIMENTAL RESULTS

This chapter presents the results of four experimental aspects of the laser ablation studies described above. Two of these are related to the craters which resulted from the ablation, and two are related to optical aspects of the system. The experimentation described in this chapter represents the ablation of several hundred samples; however, the majority of the reproducible results were generated during the summer and fall of 1994. Earlier effort was devoted to developing an appropriate experimental protocol, and to tuning the ps laser used for the ablation.

Variation of crater morphology

The most interesting aspect of the ablation investigation is the morphological changes in the craters as the density of the ambient fluid is increased. Previous work by Chan and Mao showed the emergence of a crater rim as the ambient pressure increased from vacuum to atmospheric pressure. Their work demonstrates that the nature of the zone affected by the ablation is substantially altered as the density of the ambient fluid increases from a rarefied gas into the low density area of ideal gas behavior observed at atmospheric pressures. The current study extends the range of observation for ablation processes.

This section is devoted to presenting the observed dependence of the ablation process on the ambient density, as the pressure of the carbon dioxide ambient is raised from 1 bar to the critical pressure of CO_2 near 72 bar. The first four subsections provide an overview of the type of quantitative and qualitative observation that can be made for

these samples; the final portion of this section is a discussion of representative craters at densities across the entire experimental range.

Variation of crater dimensions with ambient density

The most obvious criterion for evaluating laser ablation systems is the analysis of the crater dimensions to assess crater volumes and rim heights. Unfortunately, although these measurements are frequently reported in the literature, meticulous care must be taken to generate reproducible results, and reported results are often imprecise.

A typical method for making these measurements is to use a diamond tipped scanning profilometer. This method was tried for the samples generated in this experiment, but was not pursued. Significant operator error in sample placement and positioning caused difficulty in generating reproducible results. Furthermore for the crater diameters and depths common in these trials, the ability of the tip to accurately track surface features was suspect.

An alternative method of crater measurement was the use of a scanning white light interferometer. This instrument, made by Zygo, measures the entire sample simultaneously, and is a noncontact technique. Resolution is enhanced by the very small depth of field, and the full range of features is measured by moving the part along the optical axis of the system. Two instruments were used; one is at the Zygo facility in Santa Clara, California, and the other is in the Computer Mechanics Laboratory at the University of California. The output from these scans is valuable because it allows careful selection of the diameter of interest for profile measurements, and measures surface texture characteristics as well as gross crater dimensions.

All of the craters generated in this study were examined under an optical microscope. Photographs were taken of representative samples; some of these are

Figure 6-1: Crater rim dependence on fluid density

presented and discussed in the next section.¹ A coarse estimate of the crater depth was obtained by noting the travel of the microscope objective as the focus was moved from the surface to the bottom of the crater. This estimate and a measurement of the primary diameter allowed order of magnitude estimation of the crater volume. The volume estimate and diameter were used primarily to confirm that the system was properly positioned, and not as a quantitative result, since density fluctuations induced by the thermal processes in both the substrate and in redeposited material preclude direct correlation of mass removal with crater volume.

¹ Scanning electron microscopy was also tried. Because most of the craters were large — diameters $\sim 100 \mu\text{m}$ — low magnification was needed. Optical microscopy generally yielded better results than the SEM.

Apparent crater volumes were held as close to constant as practicable during these runs. As a result, the most useful physical measurement for discussing changes caused by variation of the ambient density was the rim height. This was measured directly from the Zygo scans, and was measured relative to the unaltered background surface. As shown in Figure 6-1, the mean height of the rim decreased with increasing pressure and density. The error bars on these estimates are set at $\pm 2 \mu\text{m}$, which represents the approximate range of rim heights observed for a given operating pressure.

Initially, this observation was puzzling, since, as noted above, the appearance of a crater rim has been shown to occur with an increase of pressure from low vacuum to atmospheric pressure. An interpretation of these results is presented in the more general discussion of crater morphology in the next section.

Exterior thermal affected zone

Lasers are valuable as materials processing and analysis tools because of the precise localization possible for energy deposition. Although the potential for thermal damage to areas surrounding the interaction zone is greatly reduced compared to other techniques, laser processing of materials does cause heating of the target. This region is referred to below as the *exterior thermal affected zone* to emphasize the fact that the effects seen in this region are not due to direct laser material interaction, but rather to thermal and mechanical processes induced by the absorption of laser energy at the point of irradiation. Investigation of these areas is a quintessential inverse problem, but the consideration of the morphology of the surfaces in these exterior zones beyond the crater rims provides clues to the partitioning of energy between various modes of propagation.

Optical caustics as a diagnostic tool for plasma formation

One of the most common applications of catastrophe theory has been in the description of optical caustics. As discussed in appendix A, these caustics represent singularities in the optical intensity field.² Explicit consideration of caustics is not common in much of the study of laser material interactions, since optical systems are designed to minimize aberrations and to generate smooth, continuous illumination fields. In this set of experiments, however, an intentional search for the presence of caustics was conducted. The presence of caustics was considered to be important for several reasons:

- as a manifestation of a real physical process, such phenomena serve as diagnostic tools;
- physical indications of caustics identify limitations of the typical first order optical design approach used in this ablation system.

This study clearly shows that optical caustics can play a substantial role in laser material interactions, and that variations in the shape of the crater can be used to understand the nonlinear optical processes occurring in the ambient medium.

Rim deformation

One of the most interesting distinctions in craters generated in different environments was the substantial density dependent variation of the form of the crater rim. Although, as noted above, the rim height varies with ambient density, equally interesting changes occur in the *shape* of the rim. These changes are closely correlated with the changes in the exterior thermal affected zone and indicate changes in the

² In fact, the term "caustic" is used because, under ordinary illumination, the high intensities along these curves can burn paper.

coupling of the target's surface with the ambient medium. Some of the changes to be discussed below are quantitative, as is the case for rim heights and widths, and some are qualitative, as is the case for the topology of the flow field of the ejected melt.

Crater descriptions

A detailed analysis of the ablation craters is presented in this section. The temperature was held constant throughout these trials, and therefore pressure and density of the fluid are uniquely related through the equation of state. Pressure is the experimentally measurable quantity used to classify the trials. As discussed in chapter 4, this relationship is monotonically increasing but nonlinear. This is seen in Figure 6-2,

Figure 6-2. Dependence of density on pressure

which shows portions of three isotherms based on published data. The highest curve is 300 K, the central curve is 307 K, and the lowest curve is 320 K.

Several important points should be noted about these curves. First, the central isotherm –which represents typical system operation – is tightly bounded by the other curves for pressures below 5 MPa. This behavior is expected, since extrapolation to low pressure leads to a limiting case of ideal gas behavior, for which the ratio of the densities is expected to be the reciprocal of the temperature ratio. In this case,

$$\rho_2/\rho_1 = T_1/T_2 = 300/320 = 0.9375 \quad (6.1)$$

The anticipated region across which the ideal gas approximation is expected to be satisfactory can also be estimated by looking at this figure, and noting that it remains nearly linear for pressures near 4 Mpa (~40 bar).

Also, the system shows extreme density fluctuations for small pressure differences near the critical point. In these experiments, this is not a severe problem, since the ultimate density is set during the vessel charging procedure. Nonetheless, relatively small pressure differences for a given temperature correspond to substantial density differences which would cause extreme experimental difficulties for operation in a pressure controlled regime. As these experiments follow an isochore, slight pressure and temperature fluctuations will be correlated until the autoclave has stabilized internally, and the final pressure inside the vessel is determined by the point at which the appropriate isochore crosses the isotherm for 308 K.

The remainder of this section is devoted to the analysis of craters generated at several pressures. Unless stated otherwise, all of these craters were formed using the protocol described in chapter 5, and are the result of approximately 100 pulses at $\lambda = 532$ nm. The pulse length was 35 ps, and pulse energy was ~35 mJ at a 10 Hz repetition rate.

Figure 6-3: Sample 940714.3-a **Figure 6-4. Sample 940714.3c**

Atmospheric pressure

Trials were conducted using air and carbon dioxide at atmospheric pressure to evaluate the presence of any specific chemical effects, such as absorption or scattering, and to provide a baseline for the study. (The next section discusses the evaluation of density dependent linear optical effects.) Craters generated in air and in CO₂ at atmospheric pressure were virtually indistinguishable, and all showed characteristic features of ablation at $P=1$ bar. A typical appearance is shown by sample 940714.3, seen in Figure 6-3 at 100x, Figure 6-4 at 200x, and Figure 6-5 at 400x. (Diameter ~ 100 μ m)

The lowest magnification shows some important features of macroscopic scale. First, the darkened area surrounding the crater was seen in almost every crater at every density. This region is symmetric around a nearly vertical axis through the crater. The

axis is tilted slightly toward the head of a sample retaining screw which is 5 mm from the crater³. This pattern is indicative of long time scale processes within the chamber, and appears to be associated with the primary flow across the face of the sample.

Another macroscopic feature of these samples is the bright circular region centered around the crater. The size of this region and its contrast with the outer dark zone varies among samples, but it is almost always concentric with the crater. As seen at 200x, this zone also shows substantial surface structure. The radial symmetry and the spacing of these features is indicative of a process of melting and resolidification. This conclusion is supported by the absence within the bright zone of the small polishing scratches which are visible in Figure 6-3 in the undisturbed region away from the crater.

Figure 6-5. Sample 940714.3b

The rim structure is visible in Figure 6-4 and in greater detail in Figure 6-5. The rim is noted to be relatively thin and to extend well above the surface. This structure is consistent with previous experimental observations. They have a “tulip” shape near the

³ The long axis of this picture is rotated about 20 degrees from the vertical of the sample. The darkened region opens toward both the screw and the vertical axis.

Figure 6-6. Sample 940930.1a

top, and tend to curve outward. The gaps in the rim are less common in smaller craters, indicating the possibility of Rayleigh–Taylor instabilities in the formation dynamics. These rims rise smoothly from the crater, and little structure is seen inside the crater itself.

Another sample ablated at 1 bar is seen in Figure 6-6, which is shown at 400x. The crater had a diameter of $\sim 80\ \mu\text{m}$, and was similar in structure to the sample observed above. The important feature to notice in this photograph is the fine feathering at the edge of the molten zone.

Similar structure can be seen in Figure 6-4, also near the edges of the molten area. This type of dendritic, or branching, structure provides support for the hypothesis of fractal solidification dynamics presented in Chapter 4.

This figure is also interesting because of the larger scale topological features of the rim which it shows. At this magnification, the depth of field is very small, and some perspective of the rim is lost; however, the trans-rim channel mentioned above can be seen just below the center of the picture, as well as the flow field behind the rim.

Twenty bar

As seen in Figure 6-2, carbon dioxide is still essentially an ideal gas at 20 bar for temperatures near 308 K. Therefore, differences seen between the previously discussed

Figure 6-7: Sample 940717.6-a

Figure 6-8. Sample 941006.4a

samples and those ablated at 20 bar are assumed to be due solely to the twenty-fold increase of the density, but not to nonlinearities of the fluid system. Thus, comparison of the resulting craters allows a way to study the increased mechanical and thermal coupling inherent in the increased density. This coupling is expected to be potentially important in two distinct ways. First, the thermal coupling is expected to be better, as the thermal mass of the fluid in contact with the surface is higher. Second, mechanical coupling is expected to become even stronger. At higher densities, the increased fluid inertia is expected to alter the behavior of shocks from the surface, and the collapse of these waves is anticipated to change rim creation mechanisms and crater flushing dynamics.

Some of these changes can, in fact, be seen in Figure 6-7 and Figure 6-8. Both of these samples were ablated with 100 pulses at a pressure of 20 bar. At the scale of these photographs, the widening of the rim and the coarsening of the external flow field

Figure 6-9. Sample 940717.6b

Figure 6-10. Sample 940717.6c

can be clearly seen. Also, the nascent asymmetry in the “bright” region outside the rim and inside the darkened area is indicative of potential modifications of the thermal coupling of the fluid to the surface on a macroscopic time scale.

At higher magnifications, more detail of the craters can be seen, and the modification of the rim is more apparent. Figure 6-9 is a magnification of the sample seen in Figure 6-7. The large dimpled structures around the rim are visible, and the long threads of ejected liquid are also easily seen.

Further magnification shows the fine structure associated with this surface (Figure 6-10). This view is of the lower right quadrant of the previous figure. It is interesting to note that although the flow field shows some large scale features (i.e., the large “threads,” and the gap in the crater rim) – and significant small scale features (the roughness of the surface) there appears to be a gap between these

two scales. In other words, this solidification surface does not seem to show an affine scaling linking these two scales. Such a finding is interesting, as it helps to place bounds on the time scales associated with solidification. This suggests a quicker freezing at the elevated pressure, which seems to be a reasonable trend.

Another aspect of these samples that confirms this conclusion is the appearance of the polishing scratches within the "bright zone." These scratches were obliterated in the ablation at 1 bar, but remain visible here, indicating that the thermal affected zone is smaller, and the region across which melting occurs is smaller.

Additional samples ablated at 20 bar are shown in Figure 6-11, Figure 6-12, and Figure 6-13. Although these craters differ slightly in diameter, similarities exist among them. In these craters, we again see a relatively broad rim structure, with detail

Figure 6-11. Sample 940717.4a

Figure 6-12. Sample 940717.3a

Figure 6-13. Sample 940717.5a

Figure 6-14. Sample 941006.4b

at two distinct length scales. Another difference which these samples demonstrate by comparison with the ablation at 1 bar is that the craters now have straighter walls above the target surface. The outward curved "tulip" shape has been replaced with a more vertical inner surface. Also, although the camera was focused at the surface, hints of some structure within the crater can be seen in Figure 6-12. The amplitude of this structure is much smaller than the depth of the crater, and is smooth. This is further indication of the presence of surface instabilities in the molten liquid on time scales much longer than the original pulse.

A final view of craters ablated at 20 bar is seen in Figure 6-14. This is a magnified view of a small crater (diameter $\sim 80 \mu\text{m}$). This crater also shows the same separation of scales and rim broadening noted previously. Also, the tendency for smaller craters to lack large scale gaps is observed once again, although several protrusions on the exterior of the rim are

visible. These features may, in fact, be the early stage of the more noticeable circumferential structure which is more often seen in larger diameter craters.

Thirty bar

Relatively few trials were conducted at thirty bar, where fluid behavior is still anticipated to be nearly ideal. The crater seen in Figure 6-15 is significant primarily because it tends to confirm some observations made previously. The diameter of the crater is roughly 80 μm , and a high degree of symmetry is seen in both the crater and the rim structure. Compared to the samples ablated at 20 bar, the rim is broader and slightly lower. Both of these trends are expected based on earlier results. Also, the structures associated with liquid ejection are once again rather large, and little evidence of bifurcations can be seen in the associated flow field.

Figure 6-15. Sample 941006.3a

Fifty bar

The samples ablated at an ambient pressure of 50 bar show a considerable degree of variety. Some of these samples indicate the incipient influence of fluid nonidealities, while others continue trends seen at lower ablation pressures. The range of crater diameters seen in these samples is also somewhat greater than would be expected based

on the reproducibility of the autoclave position and the degree of density control in the system. This variability is suspected to be the result of the greater likelihood of fluid breakdown as density increases. Such breakdown would obviously significantly alter the laser material interaction.

Figure 6-16, Figure 6-17, and Figure 6-18 are photographs of an early sample ablated at 50 bar, seen at various scales. This is a large crater, with a diameter in excess of 100 μm . The darkened arc and symmetric bright zone are seen around the crater as noted in samples at lower pressures. (Figure 6-16 is rotated about 60 degrees. The arc opens nearly vertically.)

More detail of the crater and rim can be seen in Figure 6-17. The rim is broader and flatter than seen in previous samples, and the crater itself has steep, smooth walls and a flat bottom. The shape of the crater and its size suggest that some

Figure 6-16. Sample 940717.9b

Figure 6-17. Sample 940717.9a

Figure 6-18. Sample 940717.9c

Figure 6-19. Sample 940809.1a

of the material removal is due to coupling of the target and a plasma above the target.

The presence of radial splatters indicates that vigorous liquid expulsion occurred. Furthermore, a sheet of the ejecta is now seen to exist, as shown in Figure 6-18. This layer differs from the melt ejected in previous samples in several important ways. First, its leading edge shows fingers with a variety of widths, but the main layer seems to have uniformly advanced.

Second, the surface of the layer is smooth, whereas the melt ejecta at lower pressures showed considerable random roughness.

The next three samples discussed show features common to many samples ablated at 50 bar. These samples comprise Figure 6-19 through Figure 6-24, and are the first samples to show some evidence of caustics in their slightly cusped cross section. Once again, the crater is flat bottomed, has steep walls, and the rim is

relatively broad with a quasi-periodic circumferential structure.

These craters provide some evidence that the caustics arise from interactions with the plasma above the surface. First, the direction of the cusp is in the direction of the predominant bright region, and away from the minimal "darkened" zone. Both of these trends are consistent with reflective and refractive interaction of the plasma with the crater.

Furthermore, as clearly seen in Figure 6-20, the rim is thickest in the direction the cusp. If the rim is considered to be the result of physicochemical processes in the melt pool, the time scale for its formation would be comparable to that for a plasma, and the observed asymmetry would be expected.

Figure 6-21 shows the ability to duplicate this effect. In this picture, the cusp occurs in the right hand edge of the

Figure 6-20. Sample 940809.1b

Figure 6-21. Sample 940809.2a

crater, and again this coincides with the largest extent of the bright zone.

The cusps seen in these samples are small, but their appearance is quite important. As discussed in Chapter 3 and in Appendix A, the shapes seen here are indicative of a source of illumination which is not axisymmetric with the bulk of the crater, and their occurrence is clearly a diagnostic tool for evaluating the strength of coupling of the induced plasma to the surface. It is also extremely important to note that these asymmetries *are not* the result of an external optical effect. Several dozen samples ablated at lower densities showed no indications of asymmetry in the crater cross section, even when the rims were distorted.

Figure 6-22. Sample 940809.2b

Figure 6-22 focuses on the rim structure in sample 940809.2. This sample shows clearly the asymmetry of the rim development, and it broadening in the direction of the crater asymmetry. The sheet structure of the flow field is again visible as is the fingering structure of its leading edge.

Figure 6-23. Sample 940809.3a

As discussed in chapter 3, the cusping associated with these slight distortions corresponds to the displacement of the source by a fraction of the crater radius. Thus, the slight asymmetry of these craters suggests that a plasma is formed, and is centered over the crater, but off the craters axis. This observation is consistent with the shape of the darkened area and bright zone.

Figure 6-24. Sample 940809.3b

A much more exciting result is seen in the crater of sample 941006.9. The cross section of this crater, as well as its orientation relative to the bright zone, unequivocally demonstrates the appearance of caustics in these experiments. Again, this appearance was not due to a problem with the optics or the laser. Symmetric samples were generated at lower densities preceding and following this sample. The lenses and window were clean, and the beam profile was circular. This shape, which appears almost as the overlap of two craters of $\sim 80 \mu\text{m}$ diameter, is a classic optical caustic, suggesting illumination from above, in the frame of reference suggested by Figure 6-25. This figure also shows the expected asymmetry in the bright zone and the ejecta.

The asymmetry of the rim structure is seen in more detail in Figure 6-26. The fine structure associated with flow of the melt is seen above the crater, and differs

Figure 6-25. Sample 941006.9b

Figure 6-26. Sample 941006.9a

significantly from the limited flow and rim broadening seen to the left of the crater.

Finally, Figure 6-27 presents evidence for the need for caution in the use of crater volumes in evaluating craters. Although the crater itself is unremarkable, the area outside of the bright zone shows a porosity which would be difficult to quantify in any estimate of mass loss.

Overall, the craters evaluated at 50 bar suggest two conclusions. First, the density dependent trends in rim formation noted at lower pressures seem to continue at 50 bar. Second, the elevated density is expected to lower the breakdown potential of the fluid. This reduced potential is expected to lead to more frequent plasmas, and to stronger coupling of plasmas to target materials. This enhanced coupling has been seen in the appearance of optical caustics left in crater cross sections.

Near critical pressure (~70 bar)

The most difficult set of experiments involved operation “near” the critical point. Although this proximity to the critical point

Figure 6-27. Sample 941011.5a

Figure 6-28. Sample 940808.3a

made replication of experiments difficult, it was far enough away that the extraordinary effects seen very near the critical point were not expected to interfere with the experiments. The reduced temperature, $T_r = \Delta T/T_c$, was held at $T_r = 0.0098$. This is small enough to see dramatic dependence of the pressure on the density, but large enough to avoid the singularities in transport and optical properties which occur nearer to the critical point.

The appearance of caustics for samples ablated at 50 bar leads to the expectation of similar coupling at 70 bar, and this is indeed the case.

The craters ablated at an ambient pressure of 70 bar were uniformly larger than those attainable at lower pressures. However, several very interesting effects were observed. First, as seen in Figure 6-28, the relative size of the dark region is reduced, and the bright region around the crater is virtually gone. Second, the most obvious feature of this crater is the

Figure 6-29. Sample 940808.3b

Figure 6-30. Sample 940808.3c

complex internal crater structure seen in Figure 6-29 and Figure 6-30..

Two aspects of this structure are noteworthy. The most obvious is the series of concentric rings which appear almost like a diffraction pattern. Their spacing, however, does not seem consistent with an optical effect, and their cause is uncertain. Another interesting feature of these craters is the cross shaped region in the center of the crater. This was the deepest part of the crater, and like the forms seen at 50 bar, this shape is consistent with an optical caustic due to plasma coupling to the surface.

Evolution of the rim structure is inferred from Figure 6-31. As mentioned above, the rim is broad and relatively low, and extends directly into the dark region surrounding the crater. Furthermore, its leading edge exhibits similar fingering characteristics as were previously noted for samples ablated at 50 bar.

Above critical pressure

Since the autoclave was filled using a thermal cycling process, and since the critical density is approximately half the liquid volume, the density could only be increased – at most – by a factor of two above the critical density. Furthermore, this isochore intercepted the 308 K isotherm at a prohibitively high pressure. Since this density increase was relatively small compared to that covered by previous experiments, this region was not

Figure 6-31. Sample 940808.2d

extensively covered. An important set of experiments, however, evaluated performance at roughly the critical density and elevated temperature ($T > 323$ K). For these samples, the temperature was increased substantially above that used for the other experiments. The purpose of these efforts was to separate the effects of temperature and density. The appearance of the samples generated in this experiment differed insignificantly from the sample discussed in detail in the preceding section. This confirms that the effect seen is due to the elevation of the density, and not to proximity to the critical point, a point suggested in connection with the discussion of ablation at 70 bar.

Transmission of light as a function of density

A very brief set of experiments was conducted to investigate the source of nonlinearities observed in preliminary ablation studies. Of particular concern was the difficulty of generating small craters during ablation at high ambient densities. Two potential optical problems were considered: the occurrence of substantially increased absorption or scattering near the critical point, and intensity dependent, nonlinear laser-fluid interaction. An experiment to resolve these two possibilities was therefore conducted.

If the enlargement of the crater was due primarily to blooming of the beam due to fluid nonidealities, it was hypothesized that similar behavior would be seen at much lower light intensities. Therefore, a mirror was mounted inside the chamber, and a green He-Ne laser was directed into the autoclave. With the room darkened, the reflected beam was then attenuated by a neutral density filter and the beam was directed through a pinhole onto a photodiode. To facilitate measurement, the beam was modulated using a chopper from Stanford Research Systems. The photodiode was positioned several meters

away from the autoclave, so that any deflection of the beam would be recorded by a drop in the signal to the oscilloscope.

The equilibration of the system was readily observed by this technique. The density gradients associated with convective flow caused displacements of the beam, which gradually died away as the system reached a constant temperature. This set of experiments also conclusively demonstrated the need to insulate the rear of the autoclave. When the metal plug at the back of the autoclave was uncovered, the thermally induced density gradients persisted indefinitely for temperatures more than 8°C above room temperature.

A simple Styrofoam cover placed over the rear of the autoclave substantially improved the stability of the fluid. Thermally induced density gradients died away rapidly even for temperature differences as great as 12°C. These gradients were no longer noticeable within five minutes after the thermocouple reached a constant temperature. This period was therefore adopted as an "equilibration" interval prior to ablation trials.

A second, more important observation concerned the optical properties of the fluid at elevated densities: no measurable reduction in transmission was seen as density increased. This is not a claim that absorption and scattering of light were unchanged across this range of densities. Rather, the autoclave is optically thin for visible wavelengths at low intensities since the optical path length in the autoclave ($2 \times n \times \text{length}$) is small, as is the proportion of light scattered and absorbed. As the acceptance angle for the photodiode was small, its source of illumination is effectively restricted to the reflected beam. Since this signal did not exhibit a dependence on density, a reasonable conclusion is that any anomalous behavior seen in subsequent experiments is not due

solely to fluid nonidealities. This was expected, since the typical operation temperature was 3°C above the critical point. This temperature difference is large enough that density fluctuations should not cause opalescence, as they would for temperatures nearer the critical point. Accurate measurement of the density dependence of the optical properties of carbon dioxide was not a part of this research and could not be done with the available equipment. The qualitative results did indicate, however, that changes in optical performance of the system are due to intensity dependent effects.⁴

Temporal stability of pulse energy of the laser

A major concern in the analysis of laser material interactions is the consistency of the energy emitted by the laser. A series of experiments was conducted to evaluate the performance of the Continuum picosecond Nd:YAG used in these ablation experiments. Using the experimental arrangement described at the end of chapter 5, sequences of pulse energies were obtained. Because the boxcar gated integrator acted as an amplifier, the absolute magnitude of the signal is irrelevant. The same set-up was used for all trials, however, and the signals from various runs can be honestly compared.

In order to facilitate FFT analysis, the record length was required to be a power of two. Furthermore, rescaled range analysis looks for correlation across a broad range of time scales, and the longest record possible was therefore used. As a result, the standard

⁴ That the optical *nonlinear* effects exhibit a density dependence is shown in later experiments.

record length for these analyses was 8192 points. As the laser operates at 10 Hz, the time required to gather a record was approximately fourteen minutes.⁵

The output of Q-switched lasers is well known to exhibit signs of chaotic behavior. Among the potential control parameters is loss within the cavity. In a parametric study of laser behavior, a quantitative measure of the loss would be important; however, for this study, the intention was to optimize the output, and the cavity was not instrumented in such a way that a quantitative loss parameter could be defined. In the course of cavity optimization, the observation was made that the tilt of the delay line — which is not normally varied intentionally — acted as an effective loss parameter. This fact was discovered when the weight of a finger on the linear translation screw was observed to affect the pulse energy stability in real time. Active manipulation of this angle was then conducted by adjusting one of the three set screws holding the spring-loaded base in place.

Numerous sequences were recorded; several representative records are shown in Figure 6-1. These plots show several interesting features of the laser's temporal output. First, long quasicycles appear in most sequences, suggesting the presence of thermal instabilities in the cavity. These quasicycles have a period of nearly two minutes; however, this spacing is not exact, and as a result, harmonic analysis does not indicate the presence of a single component in that frequency range. The idea that these trends are thermal in nature is supported by the fact that the relative magnitude of the "cycles" is substantially larger when the laser is cold or when room temperature is changing rapidly.

⁵ i.e., $8192 \text{ pulses} \times 0.1 \text{ s/pulse} \approx 820 \text{ s} = 13 \text{ minutes}, 40 \text{ seconds}$.

A second observation is that infrequent “dropouts” in the sequences occur. These dropouts are intervals when the pulse energy essentially vanishes, and were observed to last for as long as five minutes. Several “obvious” causes for this phenomena, such as physical obstruction of the beam and drift of the gating trigger, were explored and do not appear to be responsible. These occurrences were typically preceded and followed by a relatively brief (~20 seconds) interval in which pulse energies fluctuated wildly between zero and the typical mean value. This intermittent problem typically disappeared as rapidly as it arose, and has not been satisfactorily explained. It does, however, support the decision to utilize an in-line monitor of energy during the ablation process.

Figure 6-1: Representative pulse energy sequences.

An Unstable Pulse Sequence

Figure 6-2: Unstable pulse sequence, prior to delay line manipulation

Finally, the influence of the tilt of the delay line can be readily seen in Figure 6-2–Figure 6-5. All of these sequences were recorded on the same morning, with no adjustments to the cavity except the delay line tilt, and with no tuning of the amplifier or

Figure 6-3: Moderate improvement of pulse energy stability

Figure 6-4: A good pulse energy sequence

power supply. Because the intent of this project is to study laser ablation, it was decided that a full investigation of the parameter space would be imprudent; rather, the best performance achieved by the laser was considered acceptable, and the laser was used in that state for the remaining ablation studies.

The fractal nature of these series, particularly the suboptimal ones, can be seen by evaluating the dependence of the average value of R/S upon sample size. For this analysis, the minimum subgroup size was eight. In order to yield even spacing on a log-log plot, sample sizes were doubled between successive evaluations, up to a maximum of

Figure 6-5: A second good sequence

R/S Dependence on Sample Size: Unstable Sample **Figure 6-6: R/S behavior for a bad sequence****R/S Dependence on Sample Size: Stable Performance** **Figure 6-7: R/S behavior for a good sequence**

4096. (Details of the procedure are discussed in Appendix C.)

Representative plots of R/S variation are shown in Figure 6-6 and Figure 6-7. It is interesting to note that even the best sequence shows nonGaussian behavior, with a slope greater than the 0.5 predicted for pure Brownian motion. This fact is not surprising given the presence of the long period fluctuations, and the asymmetry of the distribution, which seems to have a long tail on the high side.

7. CONCLUSIONS

This thesis summarizes experimental and theoretical work focused in two areas. The system of specific concern was the ablation of metallic samples in a nonideal fluid environment; it is of interest both intrinsically and as an archetype of the rapidly growing field of high flux transport process analysis. The more general investigation was the analysis of these high flux transport processes, and their physical, mathematical and epistemological foundations. Both lines of inquiry led to novel results, and both suggest avenues for future research.

Experimental results: Laser ablation in nonideal fluids

The experiments discussed in preceding chapters clearly demonstrated a strong effect of ambient medium density on the behavior of a laser ablation process. As the density increases, the apparent rim height decreases as a result of more energetic coupling of the fluid to processes occurring at the surface. The resulting interactions lead to flow of material across the surface in patterns which clearly demonstrate a fractal structure. Furthermore, at the highest densities studied, the interaction of the fluid with the incipient beam becomes important, and this is readily seen by the appearance of caustic patterns within the craters. Their identification was made for the first time in these experiments. This pattern of coupling acts as a potentially very useful diagnostic tool for plasma interactions with material surfaces, regardless of the source of the plasma.

Also of interest, the pulse to pulse stability of the laser used in these experiments was shown to exhibit temporally fractal behavior. A unique application of an analytic

technique known as R/S analysis allowed clear demonstration that sequences of pulse energies showed a long term dependence characteristic of fractal processes. Also, this long term process served as a model for the behavior of smaller, faster components within the ablation system which are assumed to also be fractal.

Theoretical results: Analysis of high flux transport processes

The primary conclusion drawn from the analysis in this thesis is that high flux transport processes are qualitatively different from their macroscopic, locally equilibrated counterparts, and that these differences influence the nature of observations which can be made, and the conclusions that can be drawn from these observations. Traditional transport processes are assumed to be in local equilibrium throughout their domains, and are often expressible in relation to a limiting steady state process. The analysis of such a physical process can be legitimately derived either by application of symmetry principles and empirically observed axioms or as the evolution limit of stationary stochastic processes. HFTP, on the other hand, occur when systems are locally very far from equilibrium, and are highly transient. Thus, the temporal observation of the system is difficult at best, and the underlying stochastic system is not stationary. This difference is tremendously important, as it allows the simultaneous development of processes at a variety of scales, and allows the system to evolve into patterns which do not correspond to the thermodynamic global equilibrium. Furthermore, such systems show an extreme sensitivity to initial conditions. Since each stage of the process alters the system and since the intra-event evolution is the object of study, consideration of the behavior of a long sequence of events does not resolve the difficulties associated with the diverging variance of the nonstationary process. In terms of the ablation experiment, each pulse

experiences a different surface, and therefore will be expected to give rise to differing phenomena within and adjacent to the target.

The presence of nonstationary stochastic elements, although challenging, is very exciting because this is the linkage that introduces the concepts of fractal and multifractal processes into the evolution of HFTP. These techniques are widely used as descriptive tools in many fields, but this inclusion in HFTP provides an impetus to expand the range of what is considered a "thermal" problem.

Given the analytical difficulties of analyzing such processes, it was shown in chapter 2 that an approximationist epistemology is appropriate for considering these phenomena. Because we are able to reproducibly and objectively operate these systems, the assumption that they are "real" is natural from an engineering perspective but an assertion that they exist, in detail, as our models claim is simply hubris. One of the most valuable skills cultivated in engineers is the use of models which are appropriate for the level of investigation. In this spirit, we simply claim that we are modeling a real system, which has many of the features which we have incorporated into our model. Thus, where HFTP differ philosophically from traditional transport processes is in understanding the subtle implications of the assumptions made. The definitions of continuity, equilibrium, physical fields, and the relation of the measurement process to the experimental system must all be carefully considered. In systems such as HFTP which are highly nonlinear, an apparently innocuous assumption may, in fact, lead to an unacceptably restricted manifold of evolution. It has been the intent of this thesis to examine the implications of some of the more common assumptions used in transport processes and to suggest alternatives where appropriate.

Several existing analytic techniques were also applied to these problems in a novel manner. Traditional thermal engineering does not require, and therefore does not incorporate nonstandard analysis, functional analysis, catastrophe theory and Bayesian statistics. Although each of these areas is well developed in its own field, this thesis is believed to be the initial attempt to integrate them into a coherent application in an engineering analysis. The common feature which these disparate topics share is an emphasis on careful, explicit definition of elements of the model. Thus, considering the measurement process in relation to the HFTP itself, an empirical bias arises and Bayesian statistics are incorporated. Likewise, statistical physics assumes that all processes of importance to HFTP are ultimately discrete; moving from a large set of inexpressible, insoluble equations to differential equations arises from the application of symmetry considerations and the use of nonstandard analysis. Given a model, its representation ultimately involves functional analysis, and in the case of nonstationary processes, the consideration of bases other than Fourier space: the use of wavelets is thus included. Finally, given a set of equations, the evolution of the system may show instabilities. Some of these are discovered as fractal components, mentioned above. Other instabilities, however, are connected with specific singularities. The analysis of these occurrences is the province of catastrophe theory.

Thus, HFTP present an opportunity to explore the boundaries of thermal engineering, and in the process develop a better understanding of the foundations of the subject. It is important to realize that these novel tools are topological in nature, and thus focus on the qualitative structure of the system. This emphasis on qualitative features should not be construed as a lack of precision; rather, it represents an important avenue of addressing HFTP which is complementary to more traditional computational methods.

Directions for future research

As is true of most investigations, this study raises as many questions as it answers. The potential for further research in both laser ablation and HFTP is substantial. Among the many open questions, the most difficult – and perhaps the most important – ones concern the construction of appropriate models for microscale HFTP. This problem has been attacked from two extreme perspectives, both of which have significant weaknesses. The ad hoc extension of continuum models is unsatisfactory because of its need for empirical input to find parameters so that the model fits the data. At the other extreme, the use of statistical physical techniques based on assumptions of stationarity can not be expected to reasonably model nonstationary events occurring in HFTP.

The perspective recommended throughout the thesis is to adopt a third approach. First, the scale of observation typically differs from that of the processes' evolution, and since the quantity to be modeled and predicted is future observations, it seems reasonable to try to maintain a continuum formulation for these quantities. This is acceptable in the spirit of nonstandard analysis and distribution theory, because the observation scale represents a smoothed average over a range of space and time. This observation is therefore expected to vary smoothly as a function of space and time, and the use of differential equations to model its behavior seems reasonable. Second, the presence of nonstationary elements in the process's evolution suggests that the system of equations may well incorporate stochastic elements. The use of stochastic differential equations was not considered in this thesis, but is an important avenue for future investigation.

The third factor of this recommended approach is to explicitly look for the “fingerprints” of catastrophes and fractal behavior. The series of experiments with one system — laser ablation of copper — showed ample signs of both. Qualitative analysis

of a system of equations can indicate the range of parameters for which these phenomena can occur. If the system of equations under consideration is not susceptible to their occurrence, then the system is almost certainly unacceptable, no matter how reasonable it seems analytically. Fractals and catastrophes *do occur physically*; they must be allowed by the model!

The general study of HFTP, therefore suggests several general lines of inquiry. These are fundamental in nature, and require careful analysis of the system. They expand the range of what is typically considered to be a “thermal” problem, and, indeed, what is considered to be “engineering” mathematics. This is a difficult and exciting challenge. Among the specific topics worth pursuing are the following:

- For a system whose initial evolution is defined by a nonstationary process, how can invariants be identified?
- For what subprocesses do conservation laws provide sharp bounds, i.e. equalities?
- How can fractal processes and procedures be introduced into engineering as analytical and not merely descriptive tools?
- Can nonstandard analysis play an important role in engineering systems?
- What formulation is appropriate for microscale thermal problems? Does the intuitive advantage of embedding a system in one time and three spatial dimensions justify the difficulties of tracing evolution across manifolds, or should a different embedding space be used?
- Are any difficult problems in traditional thermal analysis simplified by recasting in terms of catastrophe theory? (In particular, can phase change problems – especially boiling – be better explained at a quantitative level using catastrophe theory ?)

- How can the use of geometric algebra be incorporated into convective flow problems?

Just as this thesis benefited from the joint consideration of theory and experimental observations, ongoing HFTP research must also be motivated and justified by experimental results. In this regard, several extensions of the laser ablation experiments merit further study:

- The evolution of the rim morphology provides an interesting case study in the growth of macroscopic fractal structures. Numerical work is needed to study the range of possible structures.
- The influence of the orientation of the optical axis of the autoclave could be studied. In all of the current experiments, this axis was horizontal. Rotating it into a vertical position would modify any convective flows across the sample, and allow decoupling of plasma and convective effects.
- The use of fluids other than carbon dioxide as the ambient medium would allow separation of chemical and physical effects. Use of a heavier fluid further from its critical point would also allow further investigation of the relative importance of fluid density and nonideality.
- The use of other target materials would broaden the nature of the observations. In addition to metals, the ablation of dielectrics and particularly semiconductors is of immense practical importance. Also, the ablation of multicomponent targets would allow incorporation of chemical potential effects into the models
- The observation of caustics in ablated craters suggested a method for diagnosing the coupling of a plasma to a surface. Can these caustics be replicated in a more controlled fashion, using another, longer lived plasma source?

The many theoretical and experimental challenges presented by high flux transport processes generally, and laser ablation particularly, provide many avenues for further experimentation. A natural extension to the field of thermal engineering thus arises, and the flexibility and complexity of techniques for process analysis grows as the physical scale of the problems considered shrinks.

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A. Mathematical Considerations

Because of the short length and time scales often involved in high flux transport processes, careful consideration needs to be given to the structure of the mathematical models which are used. This appendix presents some results from contemporary mathematics which allow models to more closely match the behavior of complex physical processes than traditional techniques. Incorporation of these techniques also facilitates consideration of the nature of the physical approximations made in modeling.

The first three sections consider the basis of functional relationships. Three different concepts of the idea of “function” exist. Each has a role within engineering analysis, and each arises from a subtly different generalization of concepts from introductory calculus. These considerations would be pedantic for traditional thermal engineering, but raise important considerations for high flux processes.

The subsequent two sections present some interesting ideas which focus predominantly on local behavior of systems. The first discusses catastrophe theory, which is a method of investigating the structure of singularities, and which has been applied successfully both in thermodynamics and optics. The second presents different perspectives on two standard topics in engineering analysis, Stokes theorem and vector calculus. Although the results discussed in this section are well established, this change of perspective is valuable for the increased insight it yields.

Generalized functions

In engineering applications, it is often convenient to approximate the occurrence of thermal or mechanical loading as an instantaneous event. The use of this impulse signal, $(\delta(x-x_0))$, often referred to as a “Dirac delta function”) simplifies the problem by

neglecting the details of the fields at the origin at the time of the loading, and focusing on the long term, far field response of the system. This procedure is considered in more detail in the discussion on Green's functions which follows.

The Dirac delta "function" is in fact not a function in the traditional sense because it is singular at the origin; rather, it is classified as a *generalized function* or distribution. The remainder of this section reviews a few of the pertinent properties of such distributions, and provides a basis for understanding the development of Green's functions and for justifying attempts at harmonic analysis of poorly characterized physical fields arising in HFTP.

Generalized functions represent the first of three interpretations of "functions." They are linear transforms over a space of test functions,

$$\langle T, \phi \rangle = \int T(x) \phi(x) dx \quad (\text{A.1})$$

where T is the operator of interest and $\phi(x)$ is an arbitrary test function. By requiring ϕ to meet some fairly stringent conditions, distributions can be readily defined even for 'functions' which are not piecewise continuous [141]. Physically, this process is appealing since the test function can be interpreted as a sampling window, which allows for uncertainty of the function on a small scale, and recognizes that our perception of reality is actually filtered through our measurement system. This is academic on large scales, but extremely important as scales drop to microscopic levels. For this reason, generalized functions play a large role in quantum mechanics [343].

The significance of this approach to function definition is that for properly chosen test functions, distributions have Fourier transforms, which greatly facilitates the analysis of differential systems [164].

The three most common classes of test functions are:

- D: the class of infinitely differentiable (C_∞) functions which vanish outside a finite interval, known as the “support of the distribution.
- S: the Schwartz class of C_∞ functions which decay at least exponentially outside some region.
- E: the class of all C_∞ functions.

Of course, $D \subset S \subset E$. Distributions based on test functions in S are known as “tempered distributions.” This class is useful as it is closed under the Fourier transform. Thus, a tempered distribution in S will have a Fourier transform in S as well. Because of this result, the continuity as well as the existence of the transform is established *a priori* when the domain of investigation is restricted to S. (It is interesting to note that the only function in D whose transform is also in D is the zero function, $f(x) = 0$. Thus, a nontrivial signal with finite support in time must have illimited bandwidth, while a limited bandwidth signal is not limited in time. Since any real measurement is effectively – if not precisely – limited in both time and frequency, the Schwartz class is obviously the one of the most practical interest.)

Green’s functions:

One of the tools justified through the application of generalized functions to linear problems with singularities is the method of Green’s functions. The following notes are based on a discussion in Greenberg (1971) [Greenberg, M.D. (1971) Applications of Green’s Functions in Science and Engineering, Prentice-Hall, Englewood Cliffs.].

If a linear differential equation is represented by an operator, L , and the boundary conditions are represented by B_j over the range x_1 to x_2 the problem can be expressed as:

$$Lu = \phi(x) \quad (\text{A.2})$$

$$B_j(u) = c_j, j = 1, 2, \dots, n \quad (\text{A.3})$$

The Green's function is defined by taking the inner product of an undefined generalized function, G , with the product Lu . Integration by parts yields

$$\langle G, Lu \rangle = \langle u, L^*G \rangle + \text{boundary terms} \quad (\text{A.4})$$

In the second inner product, L^* is known as the adjoint of the operator L . To generate the solution, choose $G(\zeta)$ such that L^*G is $\delta(\zeta - x)$. The second inner product now becomes $u(x)$, which is the desired solution. If Lu is replaced by $\phi(x)$ in the first inner product and the boundary conditions are incorporated into the equation, an expression for $u(x)$ is obtained.

Obviously, the most difficult portion of this task is determining G . This is done by applying homogeneous boundary conditions on G and solving the differential equation with the adjoint as the operator.

Physically the Green's function (GF) for a given problem is typically viewed as the system's response to a unit impulse applied as the only nonhomogeneous boundary or initial condition. Thus in conduction problems, the GF is assumed to be the response to a unit impulsive point source.

Measure theory and Lebesgue integration:

Measure theory represents a second perspective for considering the evaluation of a function. In this case, a function known as a measure is defined which represents, simplistically speaking, the relative proportion of the space at which the function assumes a given value. This can be done in a number of ways, including the use of sequences of step functions. The use of measure theory leads directly to Lebesgue integration [344].

A function which is integrable in the familiar Riemannian sense is also Lebesgue integrable. The converse of this statement is not true. This explains the usefulness of measure theory and Lebesgue integration in statistical practice and the theory of fractals: the requirement of piece-wise continuity which applies to Riemann integrals is not needed for Lebesgue integrals.

Initially, consideration of measure theory in the analysis of thermal problems might seem unnecessary. Microscale processes, however, present several concerns which require this level of analysis. First, when the length scales associated with a problem are less than a micron, ordinarily reasonable assumptions of spatial homogeneity of a target material or of local flatness of a boundary become suspect. Similar problems arise when the temporal nature of the radiative source is considered. The utility of Lebesgue integration is that it allows the direct use of fractal models. These models and other issues of self affinity are discussed in greater detail in Appendix C.

Nonstandard analysis

The third approach to defining functions is on a pointwise basis. This framework of point set topology was the structure within which the previously heuristic theorems of

calculus were first proved in the 19th century. This approach uses limits of sequences to define continuity and differentiability; under this rubric, the consideration of “differentials” and “infinitesimals” is considered imprecise and unacceptable [345 – 348]¹. Although this structure is mathematically and logically consistent, it discounts physical and geometric intuition and seems excessively abstract from an engineering perspective.

The field of real analysis *is* rather abstract, but it provides the traditional justification of the tools of the calculus which engineers routinely use. The initial development of the calculus by Liebnitz and Newton in the seventeenth century was driven strongly by intuition, but its justification was rather heuristic. Over the succeeding two centuries, the efforts of numerous mathematicians to provide a rigorous foundation for the calculus lead to refinements in the understanding of the concept of numbers. The final proof of the veracity of the calculus rested on the invention of the real numbers as an algebraic closure of the rational numbers.² The development of this theory also pointed out many difficulties with the concepts of continuity and infinity. Among the more obvious is the existence of a proper subset of a larger set that contains “as many” elements as the set which contains it (consider the integers and the even integers, or the ability to map any given closed interval onto a larger or smaller interval).

¹ The dogmatism of this approach can be seen in particular in [347] and in an essay by Bertrand Russell in vol. 3 of [346].

² Although the reals are required logically to prove the theorems of calculus, it is worth noting that *all* calculations are ultimately done with a finite portion of the rational numbers.

Relatively recently, however, an alternative approach to the derivation of differential calculus has been developed, known as nonstandard analysis [349 – 352]. This methodology relies on a class of numbers, called “nonstandard,” to create quantities that are either “infinitely large” or “infinitely small.” These nonstandard numbers can be logically proven to exist, as was done with over fifty pages of mathematical logic by Abraham Robinson, or merely postulated to exist.

The qualitative justification for the existence of nonstandard numbers begins by noting that the natural numbers are defined by induction. From their additive closure, the negative integers are created. Consideration of multiplication and division leads to the rational numbers. From considering the limits of all possible sequences of rational numbers, the real numbers emerge. Thus the complete algebraically closed system of real numbers arises from the natural numbers by a set of logical extensions. However, since the natural numbers are defined by induction –which must have a starting point – and since they can be scaled by multiplication, any real number for which we can give an expression must be finite. Furthermore, the *very* desirable property of ordering of elements of the reals also implies the finiteness of all standard real numbers. However, if we are willing to allow the existence of numbers with which we can not *explicitly* work, it becomes immediately obvious that numbers must exist which are larger than any element of the traditionally defined real numbers. In addition, their multiplicative inverses are still positive, but are less than any positive real number.³

³ This argument is rather heuristic and qualitative and, but it represents the essence of the construction of this structure of nonstandard numbers.

For applications, the most important aspect of this system arises by considering infinitesimally small numbers. The definition and use of these quantities is in the tradition of Euler and Liebnitz, without the necessity of the ad hoc procedures used in the early applications of the calculus.. No results from standard analysis need to be changed, but a firm theoretical basis for the use of infinitesimals is provided. (This is a good thing since engineers are going to use them regardless!) By allowing translations of the infinitesimals, a monoid, or “cloud,” of infinitesimals can be located around every point in the real numbers. These collections of infinitesimals are monoids and handling the composite number of real and infinitesimal numbers is accomplished following standard algebraic techniques. Powers of infinitesimals and any real multiple of them is also nonstandard, and therefore can be neglected in the final real expression of the result. Thus the standard part of a number is taken to be equal to its real component. The standard portion of the number is always the quantity of interest in the final result, although the nonstandard numbers are useful in intermediate steps.

One of the most interesting applications of nonstandard analysis to date has no direct use in engineering, but illustrates the power of the method. Zeno’s paradox⁴ has, since the time of the ancient Greeks, been used to illustrate the difficulties associated with the concept of continuity. Recent work has used NSA to resolve the paradox without the arduous limiting process associated with standard ϵ - δ analytic techniques [353].

Manipulation of nonstandard numbers is initially rather intimidating. For example, If x is a nonstandard integer, then it is larger than any number which can be

⁴Zeno’s paradox involves a race between Achilles and a tortoise. Simply stated, if the tortoise is given a handicap and starts in front of Achilles, and both start at the same time, when Achilles gets to where the tortoise was, it has moved. By induction he can never catch or pass the tortoise – an obviously incorrect result.

named. Furthermore, if x is nonstandard, so is $x-1$. Based on such recursive considerations, it is easy to see that there is no lower bound on the nonstandard numbers, just as there is no upper bound on the standard numbers. An apt analogy is the simplification of the Navier–Stokes equations in boundary layer theory: partial derivatives in the streamwise direction are discarded because they are ‘much less’ than those in the transverse direction[51]. It is impossible –and irrelevant –to specify exactly how large the difference must be for this simplification to be satisfactory. Using a similar argument, the nonstandard numbers are simply considered ‘much greater than’ standard integers.

Application of nonstandard analysis rests on three primary axioms [349]:

- *Idealization*: for classical binary relations, $R(x,y)$, for any finite standard set F , there is an x such that $R(x,F)$ is true. Thus, when $R(x,y)$ is an ordering relation, this axiom implies the existence of numbers larger than any integer, since any integer can be named as part of a finite set.
- *Standardization*: for any standard set E and any property P , there exists a standard subset, $A_p \subset E$, whose standard elements are the standard elements of E for which $P(x)$ is true.
- *Transfer*: if all the parameters of a classical formula have standard values, then if the formula holds for all standard values, it holds for all values of x , including nonstandard values.

The implications of these axioms in conjunction with set point topology are both subtle and fascinating. The nonstandard numbers can be shown to be an extension of the real numbers. From the perspective of engineering application, one startling result concerning continuity may prove to be quite important.

In standard topology, a function is called continuous if for every $\varepsilon > 0$ there exists a $\delta > 0$, such that whenever $|x - x_0| < \delta$, then $|f(x) - f(x_0)| < \varepsilon$. The common interpretation of this is that a small change in x results in a small change in $f(x)$. This latter concept is referred to as S -continuity; that the two are not the same can most readily be seen by looking at the function $f(x) = x^2$ and using nonstandard values of the argument. If X is a nonstandard integer, then $\delta = 1/X$ is smaller than any positive real number, and thus $(X + \delta)$ and X can be made arbitrarily close. However,

$$f(X + \delta) - f(X) = (X^2 + 2X\delta + \delta^2) - X^2 = 2X(1/X) + \delta^2 = 2, \quad (\text{A.5})$$

which implies that this continuous function is not S -continuous for nonstandard values of the argument. Likewise, examples of functions which are S -continuous, but not continuous for nonstandard arguments can be easily developed. Therefore, it is a surprising and fortuitous result that for a standard function and standard values of the arguments, the concepts of continuity and S -continuity are equivalent.

This result is important for physical applications, because it provides a firmer logical foundation for the approximation of fluxes of discrete quantities by continuous functions. To make this argument more concrete, consider the flow of a gas at atmospheric pressure through an arbitrary hypothetical surface. The mass flux is caused by the motion of discrete molecules, and thus the flux is also a discrete quantity. However, since every cubic millimeter contains in excess of 10^{16} molecules, fluctuations in the number of molecules passing the surface in a given interval are small relative to the average number. This argument leads to the use of S -continuity as an approximation for real physical systems. Thus the equivalence of continuity and S -continuity for standard arguments justifies the use of the machinery developed in standard analysis in the study of transport processes. Furthermore, relying on S -continuity to define densities and

fluxes provides a natural interpretation for the continuum hypothesis: the use of smooth functions to represent densities and potentials is appropriate not because the smooth function is a good approximation of an unknown real function, but because it is the closure of the real behavior, and is thus truly logically equivalent. Thus, the *approximation enters the model due to the fact that the molecular scale of events, although very small, is standard*. Thus, the quality of the analysis increases as the gap between molecular and modeled length scales grows.

(To belabor this point, it is important to note that the same conclusion has been reached as in the standard continuum formulation using a dramatically different approach. This new perspective is in the empirical spirit of the engineering development of the analysis of transport processes. Ironically, the use of a more complex mathematical structure provides a logically more satisfying explanation of the role of the continuum hypothesis.)

An additional benefit of nonstandard analysis for microscale thermal engineering is that it provides a bridge between standard analysis and the use of generalized functions[352]. This linkage arises, for example, by taking the support of a delta function to be nonstandard. Then the distribution is simply defined by relating the magnitude of the function (which is nonstandard) with its support (which is also nonstandard) and considering the distribution as an S -continuous function with a nonstandard range of definition. Application of the transfer axiom completes the analysis.

Finally, another important connection exists between nonstandard methods and transport processes. Substantial work has been done to apply these ideas to stochastic processes [355]. Two applications which have proven particularly fruitful are the analysis of Brownian motion, and the study of the Boltzmann transport equation. This

success might be expected, because in both cases, the observed quantities represent averages of many indistinguishable and untrackable particles. Thus the evolution of the system is driven by interactions between particles on scales which are negligible compared to those of the system itself. Applying this material still further, a recent text on stochastic fluid mechanics derives its results using NSA [356].

Catastrophe Theory

In numerous areas of engineering interest, analyses are complicated by the presence of singularities in the models used. Although these singularities present computational difficulties, they typically represent observable physical phenomena and must be retained. Careful study of the nature of the behavior of the system near these singularities can lead to a deeper appreciation of the physical processes involved.

Areas relevant to this investigation where these phenomena arise include laser stability analysis, refractive optical caustic generation, and thermodynamic phase changes. The family of techniques used to analyze such phenomena is known as "catastrophe theory." This theory restricts itself to the study of the local behavior of systems governed by a potential. Although this initially seems rather restrictive, in practice, many systems of experimental and theoretical interest can be modeled quite well using such theories.[270,357, 358]

Three types of points are studied. The first type consists of points where the gradient of the potential is not zero. These noncritical points correspond to physical nonequilibrium. At the second type of point, known as a Morse, or isolated, critical point, the gradient is zero, but the determinant of the system's Hessian matrix is nonzero. These points correspond to physical equilibrium. Finally, the third type is the non-

Figure A-1. A simple caustic

Morse, or degenerate critical point, at which the gradient of the potential is zero and the determinate of the Hessian is zero.⁵

The intent of catastrophe theory is thus to express the system in a canonical form and to investigate the *qualitative* behavior of the system as parameter values are perturbed. Generally speaking, critical points are then found to be local maxima or minima, which change in a quantitative sense as the parameters change, but whose local

form changes slowly. Non-Morse critical points are then the separatrix across which the *qualitative* shape of the potential changes for small perturbations of parameter values.

The simplest example of a catastrophe to visualize is the reflection of parallel rays of light from a semicircular mirror. (A very similar form can be seen by tilting a coffee cup to the light, and looking at the reflection in the surface of the liquid.) Such a caustic is seen in Figure A-1. The creation of this caustic is similar to that discussed in chapter 3 and seen experimentally in chapter 6. The rays reflected from the mirror intersect, and the locus of their intersection, particularly the cusp on the mirror's center line, is a singular surface.

The techniques of catastrophe theory have an importance beyond the study of singularities. This can be seen by recognizing the role that path integrals play in the

⁵Unfortunately, the term critical point is used differently in mathematics and physics. Physical critical points correspond to the nonMorse critical points of this theory.

calculations of catastrophe theory. Thus, as pointed out by Gilmore [270], it is possible to develop classical mechanics, geometric optics, and classical thermodynamics as the small parameter versions of quantum mechanics, wave optics, and statistical thermodynamics, respectively. This linkage is useful from a pedagogical perspective, and is of vital importance in the study of HFTP. In HFTP, the presence of small length and time scales suggests that the systems under investigation may show behavior intermediary between the traditional classical limits and the more detailed quantum statistical models. The use of catastrophe theory provides a bridge between these limits that is not ad hoc, and within which the other mathematical techniques discussed in this appendix (particularly NSA) can more readily be brought to bear.

Several common clues regarding the existence of catastrophes and singularities exist. These have been referred to as “fingerprints of catastrophes” [270], and they arise in many contexts within thermal engineering. These signals are:

- Modality: multiple distinct physical states exist for parameter values in certain portions of parameter space
- Inaccessibility: Solutions of the equation exist which are physically unattainable.
- Sudden jumps: An envelope exists within parameter space across which discrete jumps in the state variable are caused by small changes in the control parameter.
- Divergence: This is similar to the technical definition of chaotic behavior, namely, there is a sensitive dependence on initial conditions, and initially neighboring states diverge exponentially as the process evolves.
- Hysteresis: The process is not reversible, and jumps occur at different locations in parameter space depending on the direction of the evolution.

Figure A-2: The geometry of a cusp.

•Critical slowing down and anomalous variance: These phenomena are found in the physics of near critical systems, where the approach to equilibrium is very slow, and long term correlations exist. One physical manifestation of this is critical opalescence.

All of these phenomena correspond to physically observed processes within thermal systems, and these connections are discussed further in chapter 4.

The catastrophes discussed in relation to the van der Waals equation are of the cusp type. Under Thom's classification, this structure is named A_{+3} . It is a manifold embedded in a three dimensional Euclidean space, $\mathbb{R}^1 \times \mathbb{R}^2$. This is the product of a single variable, x , and a plane corresponding to values of two parameters, a and b . Then,

the manifold corresponds to the null space of the gradient of a function F , which is defined as:

$$A_{43} = F(x, a, b) = \frac{1}{4}x^4 + \frac{1}{2}ax^2 + bx \quad (\text{A.6})$$

As seen in Figure A-2, if the manifold $\nabla F = 0$ is projected into the $\{a, b\}$ plane, an interesting phenomenon is observed. The majority of the plane is single valued; thus for a given value of (a, b) , there is a unique value of x for which $\nabla F = 0$. However, there is a region of the plane for which three solutions exist, and the regions are separated by curves for which two solutions exist. Note that this implies that there are significant qualitative differences in the behavior of $F(x)$ in these various areas, and it is seen in chapter 4 that the van der Waals equation can be written in a canonical form equivalent to equation 6. Thus by studying the topology of this form, predictions regarding the thermodynamic behavior of a fluid can be made. Furthermore, since these observations are topological in nature, the results are expected to be useful even in regions where the VDW EOS is not quantitatively accurate.

Alternative interpretations of familiar topics

Two topics which arise repeatedly in engineering analysis are application of vector algebra and vector calculus and the invocation of Stoke's theorem. Often, these applications are mechanistic and tedious. However, consideration of the structure of the equations can occasionally lead to increased physical insight or reduced computational effort. In this section, several aspects of the algebraic structure of engineering analysis are discussed

Modern algebra and group theory

As noted in several preceding sections, the nature of the results which an analysis yields is directly tied to the structure within which the analysis is performed. For ease of reference, this section presents a brief glossary of the structures which are of importance in engineering analysis, and concludes with a few comments on the significance of the distinction between different structures.

- *Relational structure*: an arbitrary binary relation between elements of a set is denoted by $R(a,b)$, or more suggestively as aRb , for $a,b \in A$. Relations can be further categorized as follows (for all definitions, the domain is assumed to be a set A):

reflexive: aRa for all $a \in A$

irreflexive: aRa for no $a \in A$

symmetric: $aRb \Rightarrow bRa$ for $a,b \in A$

antisymmetric: aRb and bRa together imply $a = b$, $a,b \in A$

transitive: aRb and bRc together imply aRc , $a,b,c \in A$

A relation which is reflexive and transitive is known as a *preorder*. A symmetric preorder is known as an *equivalence*, while an antisymmetric preorder is an *order*.

- *Chain*: a set which is totally ordered by a relation; i.e., $a \leq b$ or $b \leq a$ holds for all a,b .
- *Lattice*: A chain is a lattice if every pair of elements have both a greatest lower bound and a least upper bound.
- *Semigroup*: A set with an associative binary operation, $(A, \oplus)$. The operation is typically referred to as addition, although it need not be –and often is not – arithmetic addition. By definition, the set is closed under the operation.

- *Monoid*: A semigroup with an identity element, u , such that $a \oplus u = u \oplus a = a$ for all $a \in A$
- *Group*: A monoid with an inverse; that is for all $a \in A$, there is $b \in A$ s.t. $a \oplus b = u$
- *Abelian group*: a group for which the operation is commutative.
- *Quotient group*:
- *Ring*: A set with two operations, $(A, +, \cdot)$, such that:
 - a.) $(A, +)$ is an Abelian group with identity “0”
 - b.) $(A, \cdot)$ is a semigroup.
 - c.) The product is distributive over the sum.

If $(A, \cdot)$ is a monoid, the identity element is denoted as “1.” Commutivity is not required for $(A, \cdot)$; if it does hold, then it is known as a commutative ring.

- *Integral domain*: a commutative ring with a cancellation law for multiplication; i.e., for $a, b, c \in D$ and $c \neq 0$, $a \cdot c = b \cdot c$ implies $a = b$.
- *Ideal*: a subset, I , of an integral domain D that is closed under addition, and is also closed under multiplication with any element of D .
- *Field*: an integral domain, $\mathcal{F}$, with multiple elements, for which all elements of $\mathcal{F} \setminus \{0\}$ have a multiplicative inverse. Thus, $(\mathcal{F}, +)$ and $(\mathcal{F} \setminus \{0\}, \cdot)$ are both Abelian groups, with unique identity and inverse elements.
- *Vector space*: a triple (V, F, f) where V is an additive Abelian group, F is a field, and f is a function from $F \times V$ to V known as “scalar multiplication.” Furthermore, it is associative with respect to multiplication, and is distributive both for scalar and vector addition. Scalar multiplication is typically denoted by juxtaposition of arguments.

- *Inner product space*: a vector space with a function, f , from $V \times V$ into F with the following properties:

i) $f(u,v)$ and $f(v,u)$ are complex conjugates.

ii) $\lambda f(u,v) = f(\lambda u,v)$.

iii) $f(u+w,v) = f(u,v) + f(w,v)$.

iv) $f(u,u) \geq 0$ and $f(u,u) = 0$ implies $u = 0$.

Here, f is known as an inner product. It is linear in its first argument and conjugate linear in its second argument (thus $f(u,u)$ is real). The inner product is also known as a “dot product,” and is written as such. The length of a vector is the positive square root of the dot product of the vector with itself. This corresponds to the concept of length defined in a Euclidean space.

Although numerous examples could be provided of the importance of using the appropriate structure in the modeling of physical phenomena, only one is presented. This example is particularly pertinent to this investigation, and the mathematical structure is of direct physical relevance. It has to do with the renormalization group, or RG, techniques used to analyze near critical systems. Actually, the name is something of a misnomer, since the RG is actually a semigroup because it is not uniquely invertible. This technique involves repeated rescaling of the problem to reduce the number of degrees of freedom of the Hamiltonian, and the intent is to extract the relevant thermodynamic properties of the system. Since this involves smoothing out the stochastic behavior of the many particles, a structure which actually was invertible would be of no use.

Furthermore, the properties of the semigroup are actually necessary. If the operation was not associative, the determination of invariants of the system would be impossible. Of course, closure is necessary.

In many engineering operations, the structure used is a real, (locally) Euclidean vector space. Such a space has many structural properties that may not be necessary for the problem under analysis. It is a Lie group, a field, and a topological manifold [359, 360]. A careful study of the problem under consideration is needed to determine the level of restriction that must be placed on solutions of the problem, to avoid making overly broad claims of the applicability of the solution. For instance, the existence of an unique solution within the space of C_∞ functions does not preclude solutions of broader classes of functions. This is the basis for so-called weak solutions to a set of equations.

Geometric algebra

Geometric algebra is alternatively known as Clifford algebra, or Grassman algebra. This structure creates a single entity for analytical purposes by combining scalar, vector, bivector, and trivector components into multivectors. (Bivectors represent directed areas, and trivectors represent directed volumes.) These dimensionally different quantities are thus components of a number, in an analogous sense to the real and imaginary components of complex numbers. Addition is thus done on a componentwise basis. By carefully defining multiplication of these multivectors, the standard equations of vector analysis can be recovered. The objective is not to find a difficult way to express a known relationship, however, but to enhance geometric interpretation of otherwise algebraic expressions. One curious result is that i , commonly interpreted as $\sqrt{-1}$, arises in this theory as the unit bivector or trivector. This provides a less mysterious interpretation for the appearance of imaginary numbers in the development of vector relationships [361, 362].

The basic rules for manipulation of multivectors are [363 – 366]:

- Addition is componentwise and commutative.

- Multiplication is associative, distributive, and linear under multiplication by scalars, but it need not be commutative.
- The product of two multivectors is the sum of an inner product and an outer product:

$$ab = a \cdot b + a \wedge b$$

In Clifford algebras of arbitrary dimension, an outer product generally is of higher grade than the constituents, while the inner product is lower grade. For algebras of fixed dimensions – such as Euclidean space – this generalization is modified to ensure that the resulting structure is closed. Specifically, the product of the a trivector with vectors or bivectors is defined to be zero for a three dimensional Euclidean space.

- Specific rules for calculating the product can be written out for each combination of components, and these products often have a physical significance. For purposes of manipulation, the algebra is often simplified by considering the product as a single entity, as is done in complex analysis, and “collecting terms” only at the end of a calculation..
- The combination of scalars and either the trivectors or the bivectors is algebraically equivalent to the field of complex numbers, since – as noted above – i arises as the unit bivector or trivector.

Just as vector algebra is a generalization of the algebra of real numbers, geometric algebra contains vector algebra, spinor algebra, the complex numbers, and tensor algebra as subalgebras. All of the traditional results still hold in their respective restrictions, but in many cases, results are more readily generated in the expanded superalgebra. By analogy, note that many results in the real numbers are more readily generated in the manipulation of the field of complex numbers, which contains $\mathbb{R}$ as a subalgebra [367, 368].

Although geometric algebra has been applied in quantum mechanics and electrodynamics, it does not seem to have been widely introduced into continuum mechanics. It is unclear if this is due to problems within the structure or merely to lack of familiarity of the engineering community with these techniques. The possibility of such applications in the analysis of convective flows is briefly presented in chapter 4. Extension beyond this point seems likely to be an interesting and challenging area of investigation.

Differential forms

An interesting approach to advanced calculus is through the use of differential forms⁶. Essentially this is the study of local mappings from one space to another [369 – 371]. The study of these transforms leads immediately to Stokes theorem for arbitrary dimensions. This is not introduced as a “new” result, but rather as a simple interpretation of a result that is often belabored in other derivations. It is also in this form that the introduction of geometric algebra into thermal problems can be most easily achieved, although the results are primarily of academic interest.

Differential forms provide a simple way to prove existence and uniqueness results for the heat equation, for example, and provide a natural setting for the introduction of variational methods into engineering analysis [370]. The abstract structure that results is

⁶ Differential forms can be shown to be a sub-algebra of the Clifford algebra discussed above.

thus implied by seemingly simple assumptions about the nature of the thermodynamic and material fields. If density and temperature can be considered well defined and unique, then these results follow from a simple statement of conservation laws.

B. Constants, Physical Properties, and Nomenclature

Pertinent Physical Constants

Constant	Source	Value	Unit
Planck's constant, h	[373]	6.6262×10^{-34}	J·s
Boltzmann constant, k	[373]	1.3806×10^{-23}	J/K
Stefan–Boltzmann constant, σ	[373]	5.6696×10^{-8}	W/(m ² K ⁴)
Avogadro's number	[373]	6.023×10^{23}	mol ⁻¹
Universal gas constant, R	[251]	8.314	J·mol ⁻¹ ·K ⁻¹
Standard atmospheric pressure, p_{atm}	[251]	101.325	kPa

Physical Properties of Copper

Property	Source	Relation/Value
Molecular weight	[374]	$8.94 \text{ g}\cdot\text{mol}^{-1}$
Density	[375]	$63.55 \text{ g}\cdot\text{cm}^{-3}$
Heat Capacity	[161]	$5.88 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 25 °C, 6.9 at 1000 K
Thermal Conductivity	[374]	$4 \text{ W}\cdot\text{cm}^{-1}\cdot^{\circ}\text{C}^{-1}$ at 25 °C, 3.5 at 1100 K
Index of Refraction	[376]	$1.07 + 2.6i$
Emissivity	[102]	0.03
Melting point	[374]	1083.4 °C
Normal boiling point	[374]	2567 °C
Latent heat of fusion	[161]	$3110 \text{ cal}\cdot\text{mol}^{-1}$
Latent heat of vaporization	[161]	$72,810 \text{ cal}\cdot\text{mol}^{-1}$
Surface tension	[374]	$1282 - 0.15(T - T_m) \text{ mN}\cdot\text{mm}^{-1}$

These properties are functions of temperature; the values provided are for order of magnitude estimation.

Physical Property Estimation for Carbon Dioxide

Property	Source	Relation/Value
Molecular weight	[374]	44.01 g
Critical temperature	[374]	304.1 K
Critical pressure	[374]	73.8 bar
Critical volume	[374]	93.9cm ³ mol ⁻¹
Lennard Jones parameters: ϵ/k σ	[258]	205 K 0.407 nm

Transport and thermodynamic functions exhibit strong dependence on temperature and pressure. Recommendations of Reid, Prausnitz, and Poling [265] were used as needed.

Nomenclature*Latin and German Symbols:*

A	beam cross sectional area
$\Re$	field of the reals
$\Re^3$	Euclidean 3-space
a	scale parameter in Weierstrass function
α	optical absorption coefficient
a	sonic velocity
a, b	van der Waals constant
a, b, c	focal points of reflections
B, C	virial coefficients
b	frequency parameter in Weierstrass function
$\mathbf{b}$	body forces
b_i	estimated parameter values
C	heat capacity
C	number of components in mixture
c	speed of light
c_p	heat capacity
$\mathcal{D}$	mass diffusion coefficient
D	effective beam diameter
D	mass diffusivity
$\mathbf{D}$	deformation tensor
D/Dt	substantial derivative operator
Δd_3	displacement of autoclave
d	plate spacing for Hele-Shaw cell
E	effective pulse energy

$E[\bullet]$	expectation operator
e	specific internal energy
F	thermodynamic degrees of freedom
f	right eigenvector of P
$f(x)$	generic assumed functional relationship
$G^{(2)}$	two point correlation function
g	gravitational acceleration
g	volumetric energy source
$g(t)$	wavelet basis function
$g_a(t)$	dilations of $g(t)$
H	Hurst exponent
$H[\bullet]$	heat operator
ΔH_f	latent heat of fusion
h	heat transfer coefficient
h	Planck's constant
h	Planck's constant
I	radiation intensity
i	imaginary unit/ unit bivector
i, j, k	dummy indices
$\mathbf{j}_A$	mass flux of A with respect to the bulk velocity
$K_t(\mathbf{x})$	heat kernel
k	thermal conductivity
k	Boltzmann's constant
k	permeability
L	length dimension

L	length scale
$\mathbf{L}$	velocity gradient tensor
L	cavity length
L	Lorentz-Lorenz constant
L^2	space of square integrable functions
l_{rad}	radiation skin depth
l_{th}	thermal diffusion length
M	mass dimension
M	mirror curve for caustic generation
M	mobility
m_e	mass of an electron
N_A	Avogadro's number
N_p	number of photons per pulse
n	number of neutral atoms
n	mole number
n	simple index of refraction
n_e	number of electrons
n_i	number of ions
$v_{m,max}$	front velocity
P	stress power
P	number of phases in equilibrium
$P = \parallel P_{ij} \parallel$	Markov chain transition matrix
$p(\theta y)$	conditional probability
p_x	partial pressure of x
Q_x	partition function for x
$\mathbf{q}$	heat flux vector

APPENDIX B: CONSTANTS, PHYSICAL PROPERTIES, AND NOMENCLATURE

R	universal gas constant
R_j	source of species
r	radial distance
r_x	radius of curvature
S	location of source for caustic generation
T	time dimension
T	temperature
T	stress tensor
ΔT	temperature difference
Δt	time interval
t	time
U	velocity scale
u	velocity vector
u_x	x-direction velocity
v	molar volume
v	flow speed
$W(k)$	Weierstrass function
X_t	stochastic process, indexed by time t
x	position vector
x	mole fraction in condensed phase
Y_t	conditioning process for martingale
y_x	mole fraction of x in vapor
Z	crater depth
Z	compressibility factor
z	axial distance from ablation site

Greek Symbols:

α	thermal diffusivity
α	absorption coefficient
α	thermal expansion coefficient
$\alpha, \beta, \gamma, \delta, \eta, \nu$	critical exponents
β	thermal expansion coefficient
β_i	true values of statistical model parameters
γ	heat capacity ratio
$\delta(x)$	Dirac delta function
ε	random component of a model
ε	emissivity
ε	Lennard-Jones energy scale
η	similarity transformation variable
Θ	temperature dimension
θ	temperature scale or normalized temperature
θ	unknown statistical parameters
θ	polar angle
λ	eigenvalue of Markov transition probability matrix
λ	wavelength
λ	dilational viscosity coefficient
$\lambda_{\max}$	wavelength of maximum growth
μ	kinetic viscosity
ν	dynamic viscosity
ν	frequency
$\Delta\nu$	mode spacing
ξ	correlation length
ρ	mass density

APPENDIX B: CONSTANTS, PHYSICAL PROPERTIES, AND NOMENCLATURE

ρ	reflectivity
σ	surface tension
σ	Stefan–Boltzmann constant
σ	Lennard-Jones distance scale
σ_r	surface roughness
σ_x^2	variance of x
τ	normalized time
τ_p	pulse length
τ_{xy}	shear stress
Φ	viscous dissipation function
$\Phi(x_1, x_2, \dots)$	similarity reduction function
ϕ	order function
ϕ	velocity potential
$\phi(\tau)$	normalized energy source
φ	intermolecular potential
$\varphi(x)$	test function
χ	normalized length
ω	acentric factor
ω_A	mass fraction of A

Subscripts:

∞	far field
0	standard, reference, or initial
c	critical
l	liquid
liq	liquid phase
p	isobaric

APPENDIX B: CONSTANTS, PHYSICAL PROPERTIES, AND NOMENCLATURE

r	reduced
s	solid
sat	saturation
v	isochoric
vap	vapor phase

C. Stochastic and Fractal Elements in Engineering Analysis

The art of engineering analysis is the construction of simplified models of physical systems. These models must have sufficient complexity to capture the interesting aspects of observed behavior, while remaining computationally tractable. This task is made even more difficult by the availability of limited, noisy data, of limited precision. Thus, any useful engineering model must differentiate between insignificant fluctuations and true lack of fit between the model and experimental data. Two methods for developing models in the presence of such noise are discussed in this appendix. These methods, stochastic analysis and fractal analysis, address the same problem — i.e., the presence of fluctuations in the observed data. The differences in the nature and objectives of these two methods have led to substantial confusion and misapplication in the literature. The purpose of the following sections is to attempt to provide a clear basis for the analysis contained in chapters 3 and 4.

When careful consideration is given to their respective strengths, stochastic and fractal concepts can serve complementary roles in the development of models of physical systems [377 – 382]. Unfortunately, both fractal and stochastic elements are used in models in two very different ways. A blurring of the distinction between these two uses is the apparent source of much of the confusion surrounding the selection of model components. The first use is purely descriptive, while the second is as a dynamic component of the system itself.

Both methodologies work very well as descriptive techniques. For nearly three centuries, since the groundbreaking work by Gauss and Laplace, statistical techniques have been used to reduce data and to define ‘best’ models [27, 383 – 385]. The importance of this probabilistic perspective on the development of modern physics and

chemistry is virtually impossible to overstate. The use of statistical methodology allows an analysis to focus on a linearization of the problem, and to identify and study invariants of the system. Much more recently, the development of fractal methodologies has allowed description of systems which are inherently nonlinear and expanded the range of scales across which a physical analysis can be reasonably applied. Both techniques inarguably provide good descriptions of physical processes.

The controversy over the use of fractal and stochastic techniques relates to their role in the evolution of the system. The typical claim is that stochastic elements represent the presence of “randomness” in the system, while fractals arise from complexities of purely deterministic evolution equations. This statement somewhat exaggerates the gap between the two methodologies. As discussed below, and in chapters 2 – 4, stochastic elements can arise in deterministic systems where the available information is incomplete, or the model is too simple to exhibit all of the features of the real system. Thus, the presence of a stochastic element in a model does not imply that the underlying process is inherently random.

Likewise, fractals arise when there is coupling between length and time scales, and these links do indeed have a profound effect on system evolution. However, claims that the entire system is therefore deterministic are poorly supported by such linkages alone. Particularly for engineering analysis, such claims are irrelevant. The important contribution to analysis made by fractal methodologies is the ability to simplify the descriptions and models of many extremely complex phenomena which previously defied rigorous analysis.

Both laser ablation and , more generally, HFTP provide interesting opportunities to apply both stochastic and fractal techniques. This appendix discusses first the relevant

portions of stochastic analysis, and then the role of similarity and self similarity in applied engineering analysis. That discussion, of course, leads directly to consideration of the role of fractals in HFTP.

Stochastic Analysis

The term *stochastic analysis* refers to the study of processes in which random variation plays an important role. As mentioned above, the source of the observed variation may be either inherent randomness in a process or incomplete experimental information. The study of stochastic processes allows the identification of invariants of a system, and thus focuses analytical attention on the “important” (i.e., measurable) aspects of the process [74, 386]. For application of these techniques to HFTP, several specific topics deserve consideration; these are presented from the perspective of statistical mechanics.

Statistical mechanics occupies an interesting intersection between the fields of physics and statistics. It emerged late in the nineteenth century, and provided a framework within which the then controversial concept of the existence of molecules and atoms was shown to influence behavior of material on vastly larger length and time scales [258]. This gap of scales can be seen by considering 1 cm^3 of a monatomic gas, say argon, at standard temperature and pressure ($T = 273\text{ K}$, $p = 101.325\text{ kPa}$). Some pertinent quantities are shown in Table C-1. Since an enormous number of molecules are contained in even small volumes, statistical estimates of the properties become quite sharp [387]. This is a result of the central limit theorem. This theorem asserts that as the number of items in a sample rises, the distribution of the sample averages tends to a normal, or gaussian distribution, centered around the true parameter value, and the variance of the estimate is equal to that of the underlying process, divided by the number

Quantity	unit	Approximate value
Number of atoms	—	2.7×10^{19}
Weight of sample	g	1.8×10^{-3}
Mean speed	$\text{cm} \cdot \text{s}^{-1}$	3.8×10^4
Collision frequency	s^{-1}	5×10^9
Mean free path	cm	7×10^{-6}
Atomic diameter	cm	3×10^{-8}

Table C-1. Kinetic properties of 1 cm^3 of argon at STP ($p = 1 \text{ bar}$, $T = 273.2 \text{ K}$).

of items in the sample [388]. Thus, when the density of molecules is $\sim 10^{19} \text{ cm}^{-3}$, fluctuations of the averaged, *observed* quantity could be reduced by *nineteen* orders of magnitude, compared to the variance of the individual probability distribution function (pdf).

(This assumes that all of the molecules in the volume effectively contribute to the average. This assumption is usually reasonable, and can be slightly relaxed under a more detailed analysis. It is important to distinguish between fluctuations in the measurements, which depend on the ensemble used in the measurement process, and the (abstract) field, which is uniquely defined. Too often this distinction is blurred. An experimental perspective is effectively Bayesian: the quantity of interest is the measurable value, which is then used as an estimate of the field variable. Furthermore, as discussed in appendix A, the measurement process defines the physical analog of a test function, and, therefore, the true distribution of the field is convolved with the measurement process.)

The use of the central limit theorem in this case requires some additional assumptions and justifications; these revolve around the ergodicity of the system and are discussed below. Before that discussion, however, a sketch of the proof of the central limit theorem is useful. All probability distributions are uniquely defined by their Fourier transforms, which are referred to in statistics as characteristic functions [389]. This uniqueness arises because probability distributions are bounded, square integrable, and decay rapidly¹. As discussed in appendix A, these conditions guarantee the existence and uniqueness of the Fourier transform. The next relevant observation is that the distribution of the averages of n independent items is defined as n -fold convolution in the probability space. In Fourier space, such a convolution is simply multiplication of the component transforms[165]. The central limit theorem is found in two more steps. First, it is assumed that the observations arise from the same, fixed distribution. As a result, the Fourier transform of the average can be replaced by the n^{th} power of the constituent Fourier transform through a change of variables. Then, taking the limit as n grows without bound, and using a Taylor series approximation truncated at the second term, it is readily seen that the characteristic function of the average converges to a Gaussian form. Since this is the (unique) characteristic function for the Gaussian pdf, the theorem follows immediately. (The variance is found by scaling so that the pdf for the average is normalized.)

Stationarity and ergodicity

The primary objective of stochastic analysis is to isolate a “signal” from the noise associated with a process. As a result, the statistical fluctuations around the deterministic

¹ These properties result from the fact that the (Lebesgue) integral of the pdf equals unity.

component of the signal are typically assumed to have constant properties. Thus, although the signal itself will probably drift over time, the random components are assumed to be *stationary* in some properly scaled frame. This assumption of stationarity facilitates the use of Fourier methods in statistics, and is often a physically reasonable assumption. A process, X_t , is said to be stationary if for any set of times, $\{t_i\}$, and any positive constant h , the joint distributions of groups of observations at $\{t_i\}$ and $\{t_i + h\}$ are identical. These groups can be written as:

$$(X_{t_1}, X_{t_2}, X_{t_3}, \dots, X_{t_i}, \dots) \text{ and } (X_{t_1+h}, X_{t_2+h}, X_{t_3+h}, \dots, X_{t_i+h}, \dots) \quad (\text{C.1})$$

A slightly less restrictive form often cited is *covariance stationarity*, in which the covariance of two observations depends only on their relative positions, not their absolute positions.

Stationarity is assumed in the solution of an equilibrium distribution of variables. This is intuitive, since the properties of the equilibrium distribution should not change with time, even though the observable properties of the system are functions of underlying molecular chaos. In fact, much of statistical mechanics relies on a further assumption of *ergodicity*. This assumption means that the long term behavior of a system is equivalent to the behavior of many identical systems, evaluated at a given instant [74]. This assumption allows the useful notion of ensembles: in order to determine a system's properties, an imaginary collection of identically prepared systems is compared. Computation of the behavior of these ensembles is much easier than for the infinite time

limit. The behavior of the physical system is expected to reside within the envelope defined statistically by this ensemble.²

From a physical perspective, this ergodic hypothesis effectively requires that all points on a closed energy surface be accessible, and equally likely. Thus, the observed macrostate of a system will be that corresponding to the most microstates. As noted above for the application of the central limit theorem, the presence of a large number of particles leads to an overwhelming probability that rare events will not be seen. A famous example of this effect is seen by considering the Ehrenfest “dog—flea” model [85]. If two dogs share a given number of fleas, what is the probability that all of the fleas will be on one dog at a later point in time? If 100 fleas are initially on the first dog, and the fleas make among them 1,000,000 jumps per second, the expected waiting time for the reoccurrence of the initial condition is $\sim 2^{100}$ jumps — more than 10^{16} years! Thus, even for this small number of fleas, an observation corresponding to a unique microstate is extremely unlikely, although not forbidden.³

² Technically, this formulation implies a microcanonical ensemble, but with slight modifications, the canonical and grand canonical formulations can be accommodated.

³ This concept is the basis for the manufacturing engineering specialty known as *statistical process control (SPC)*, in which processes are analyzed to identify excursions beyond those predicted for a stable operation. The distinction is referred to as “common cause” variation versus “assignable cause” variation. Thus, if one dog gets a flea collar, all (or most) of the fleas may well end up on the other dog! This occurrence is taken as a signal that the underlying probability structure has changed (the dogs are now different). Although it is conceivable that an unusual distribution might occur even without any such changes, it is so unlikely that other causes are assumed to have become important. The major difficulty in the implementation of SPC is the estimation of the appropriate common cause variances.

Martingales and Markov processes

Two additional stochastic structures which are important for understanding the probabilistic analysis of transport processes are martingales and Markov processes. This section briefly defines these terms and presents an overview of their importance for the evolution of physical systems.

A stochastic process, X_t , is referred to as a *martingale* with respect to a process Y_t , if its expected value is finite for all times, and is equal to the observed value at the previous time [386]. The sequence, Y_t , may be identically X_t or an alternate function which incorporates the history of the process and other relevant information (in some cases, where it is obvious from context, Y_t is suppressed). These restrictions can be written as:

$$E[|X_n|] < \infty \tag{C.2}$$

$$E[X_{n+1}|Y_0, \dots, Y_n] = X_n \tag{C.3}$$

where $E[\bullet]$ represents the expectation operator (averaging with respect to the pdf), the solidus precedes prior information upon which the calculation is dependent, and the index indicates observation order. The term ‘martingale’ refers to an old betting stratagem of doubling the stake at each loss, and playing until a victory. For a process such as a random walk, the concept is similar: at each step, the process ‘starts over’, centered on its current location. Since steps in all directions are possible, and equally likely, the expected value for the next step is the current location.

Markov processes are in a sense generalizations of Poisson processes⁴, in that they are nearly memoryless. Thus, the probabilities associated with the subsequent observation are conditional only on the current state of the process, and not on prior values [386]. The implications of this are subtle and important. They represent a form of localization of the probability of transitions between different states. To be more specific, a Markov process is assumed to be defined by its state. The probability of going from state i to state j is solely a function of i and j , and not of the previous values of the sequence. The number of states in a Markov process may be finite, countable, or uncountable (i.e. continuous). When the number of states is finite or denumerable, the probabilities associated with the transitions between states can be expressed as a matrix, and the process is known as a *Markov chain*. When the state space of the process is composed of continuous functions, the process is known as a *diffusion process*; this name obviously foreshadows the important role that Markov processes play in transport analysis.

From their definitions, it is apparent that martingales and Markov processes are closely related. In particular, if Y_t is a Markov chain with transition matrix $P = \| P_{ij} \|$, then, if a right eigenvector, f , and eigenvalue, λ , can be found for this matrix, such that

$$\lambda f(i) = \sum_j P_{ij} f(j) \quad (C.4)$$

a corresponding martingale, X_n can be easily defined as:

⁴ For a Poisson process, if X corresponds to the occurrence of an event, $P[X=t+h | X=t] = P[X=h]$, and the probability of multiple simultaneous occurrences is negligible. This models fits many physical processes, including reliability analysis, reasonably well and leads to an exponential distribution of interevent times. The first feature in the definition is known as "memorylessness," since it implies that the history prior to observation is irrelevant for predicting future behavior. For such a process, there is no limit on the inter-event time.

$$X_n = \lambda^{-n} f(Y_n). \quad (C.5)$$

The importance of moving between these structures is that, although the specification of Markov processes is often easier, martingales are more readily analyzed. Numerous inequalities and limits are known for martingales, and therefore the probabilistic behavior of the process can be readily defined.

Brownian motion

The premiere model for Markov processes and martingales in physics is Brownian motion. Because it is also an important example in fractal analysis and provides a microscopic basis for diffusion processes, it is discussed briefly here. For clarity, the discussion focuses on standard Brownian motion, with no drift, and no unusual boundary conditions. This obviously corresponds to diffusion in an unlimited domain. Imposed drift (i.e., convection) and absorbing or reflecting boundaries can be treated in a similar, albeit more laborious, manner.

Brownian motion is named in honor of the British botanist who first described it. It is the irregular motion of a small, but macroscopic particle suspended in a fluid. The phenomenon was first described in 1827, but was not satisfactorily explained analytically until early in the twentieth century when Einstein, among others, published results of the analysis of such processes. The success of these analyses served as the 'final' proof of the atomic theory of matter, since the irregular motion of the particle is due to the net effect of collisions of many fluid molecules with the particle. The path of a Brownian particle is defined by the common diffusion equation discussed in chapter 3. If the experimentally determined value of the diffusivity is compared with the value theoretically derived from Einstein's analysis, Avogadro's number may be determined, by the ratio of the universal gas constant, R , and the Boltzmann constant, k .

Brownian motion can be classified as a Markov process with both continuous argument (time), and continuous state space. The particle drifts through the fluid slowly, and thus the process defined by position of the particle is not stationary. Fortunately, the *difference* between successive positions is both stationary, and Markovian for a fixed sampling interval. Physically this means that the direction and magnitude of the net motion between two observations are both random. The distributions of these quantities must be normalized and unbounded (this implies rapid decay). Furthermore, as the time interval between observations vanishes, the displacement must also approach zero. These considerations yield a unique solution: namely, the motion between observations follows a multivariate Gaussian distribution. By scaling, the diffusion coefficient can be taken as $1/2$. Then, for a process starting at $(\mathbf{x}_0, t_0)$, the expected position at a future time is $\mathbf{x}_0$ and the variance is $(t - t_0)$. The connection to diffusive transport processes is now complete. Energy or mass is assumed to be transported by an enormous number of particles, each of which experiences localized, random perturbations to its velocity. Each of these particles, taken individually, traces a highly irregular, erratic path through the host medium. However, taken as a whole, the measurable properties of the ensemble are seen to evolve smoothly. The highest concentration of particles remains near the origin, and the diffusing material evolves to a Gaussian distribution whose variance has a well known proportionality to $t^{1/2}$. This formulation also explains why diffusive phenomena do not show a sharp "wavefront," or leading edge. Since the probability associated with a large displacement is unbounded, albeit rapidly decaying, no sharp upper bound on the position of a particle can be given. Rather, very sharp bounds can be given for the *aggregate* behavior of the ensemble. Fortunately, this is often the quantity of interest in engineering applications of diffusive processes.

Regression and time series analysis

The analysis of time series is typically done in one of two ways. These are based on the equivalence discussed earlier in this appendix between the real space and Fourier space representations of a probability distribution function. The most intuitive procedure performs the analysis in real space, while spectral methods investigate the behavior of the process in frequency space.

Real space analysis methods of time series analysis are sophisticated extensions of the ideas of linear regression originated by Galton [391, 392]. In these techniques, a plausible stochastic structure for the process is assumed, and the data are analyzed to evaluate the unknown parameter values. The simplest nontrivial case, of a single predictor, x , and a single response, y , can be expressed as:

$$y_i = f(x) + \varepsilon = \beta_0 + \beta_1 x_i + \varepsilon \quad (\text{C.6})$$

where $f(x)$ represents the assumed functional relation between the variables — here simple linearity. The random component of the model is given by ε , and the parameters β_i are assumed to be constants. The convention assumed in statistics is that Greek letters are used for unknown values, while the corresponding Latin letters are used for their estimates. Numerous techniques are available for generating estimates of the parameters, but the most widely used criterion is the minimization of the squared error in the observations.⁵ The resulting parameter estimates, b_i , then provide the “best” fit of a model of this form to the data. Obviously, $f(x)$ may assume functional forms of arbitrary

⁵ It should be stressed that the use of the term error in this context is not pejorative: it does not imply a mistake, or imprecision. Rather, it merely refers to the magnitude of the random component of the model. It should also be noted that different estimates are generated if the predictor variables contain any uncertainty [31, 9]

complexity; the analysis cited here remains “linear” so long as the parameters enter into the equation linearly, regardless of the form of $f(x)$ relative to x .

For time series analysis, it is often the case that the value at a future point is influenced either by the value at the current time, or by the error at the current time. A general model for such problems is referred to as the ARIMA structure (Auto-Regressive Integrated Moving Average). These models were developed and thoroughly explored by Box and Jenkins in the seminal book on real space time series analysis. Parameters are allowed for regression on both the observations, and the assumed error. Although algebraically complex, these models have great flexibility. Often heuristic or qualitative rationales can be found for using a given structure, and, especially in these cases, ARIMA modeling can be very illuminating.

ARIMA modeling is exemplified in the development and interpretation of a SPC technique which uses geometric averages rather than sample means. The geometric average is also known as an “exponentially weighted moving average”(EWMA), because the current value of the EWMA is found by forming a weighted average of the current observation and the previous value of the EWMA. Thus, the most important single observation is the current one, and the influence of prior observations on the EWMA is slowly damped away. Thus trends in the underlying process are readily differentiated from isolated outliers. These tools are widely used in the process industries, where diffusive, and especially thermal, process upsets are typically seen as gradual drifts from a set point.

Real space methods have the advantage of yielding models which are congruent with the observed values, and are sensitive to a broad range of signals. However, the selection of the appropriate model requires considerable insight. An alternative method

of analyzing time series is to work in frequency space. Then, the Fourier transform of the observations can be used to provide a clue as to the nature of the process. As is well known (see appendix A), transition into Fourier space effectively provides an alternative basis for the function. If one assumes that the random part of the process is stationary, and ideally Gaussian, then it should contribute a smooth structure to the Fourier transform. Therefore, any significant structure in the frequency space representation is assumed to be due to the presence of a deterministic component in the model. The combination of these components allows reconstruction of the signal.

These methods are compared to fractal tools in the final section of this appendix.

Similarity analysis

The reduction of complex systems to appropriate differential equations is the first step of an engineering analysis. The next step is often to further reduce the problem by identifying the symmetries and possibly universal aspects of these equations. In this section, several complementary approaches to similarity analysis are discussed, as are the differences between “similarity” and “self-similarity.”

When the behavior of a physical system is described mathematically by a set of differential or difference equations, the material properties enter as parameters of the equations. Geometric, kinematic and dynamic constraints enter through the boundary and initial conditions. Thus, whenever a given equation is applicable, the behavior of the system is controlled entirely by the parameters and the boundary and initial conditions. As discussed in appendix A, when the manifold exhibits critical points, the qualitative changes associated with catastrophes is seen. For regions where the manifold is single valued, the qualitative shape of the response curve is constant, which suggests that by a proper change of variables, curves from within this region can be collapsed into a single

curve. This is indeed the case, under some regularity conditions for the boundary conditions.

Three approaches to similarity analysis merit comparison, and are discussed below. Because their objectives and results differ slightly, they should be considered complementary, rather than competing methods. The first is the analytical approach, in which the equation is directly manipulated to identify an appropriate similarity variable, and to reduce a partial differential equation to an ordinary differential equation. This reduction is extremely useful, since the ODE can be easily numerically integrated to yield the desired result. Extreme caution must be used in this method that symmetries of interest are not lost. Also, since the system of equations is being reformulated, restrictions exist on allowable boundary conditions.

The second approach is more directly based on physical intuition and considerations. Under the name of "dimensional analysis" this approach attempts to identify appropriate scalings, and to provide dimensionless parameters which can be used to index the problem. This method works well in cases where imposed dimensional scales exist.

The third approach is based on a group theoretical analysis of the system. An attempt is made to find a continuous transformation parameter. This method is more abstract than the other two. This added abstraction is unnecessary in some situations, but can provide a structure to the investigation of new systems.

Analytical similarity

The first set of techniques mentioned above are derived from basic analysis of the equations. An example of this approach is the so-called 'free parameter' method. The reformulation of the equations is highly dependent on the boundary conditions, and in

general, a similarity solution exists only for constant or homogeneous boundary conditions. Qualitatively, this method precedes by assuming that the dependent variable is expressible as the product of two functions. The first of these is a function of all but one of the independent variables. Then, the other is assumed to be a function of an unknown 'free' parameter. This parameter itself is a function of the variable excluded from the previous function, as well as the other independent variables. The transformed variables are inserted into the equation, and the first subfunction is restricted as necessary to allow the equation to be expressed as an ordinary differential equation in the free parameter. This now becomes the similarity parameter. If $f(x_1, x_2, \dots, y)$ is the dependent variable, and $\{x_1, x_2, x_3, \dots, y\}$ is the set of independent variables, the separation of the dependent variable can be written as:

$$f(x_1, x_2, x_3, \dots, y) = \Phi(x_1, x_2, x_3, \dots) \cdot F(\eta) \quad (C.7)$$

where η is the free parameter, $\eta = \eta(y, x_1, x_2, x_3, \dots)$.

Similarity and group theory

The search for a similarity parameter also provides an opportunity to investigate the topological structure of the system. This approach searches for continuous transformation groups, i.e. Lie groups, and then analyzes the invariants of these groups. The search for these invariants arises from an analysis of the differential forms arising in the analysis and discussed in appendix A and chapter 4. This method was pioneered by Birkhoff [1], and discussed in detail by Hansen [393], who identifies five steps in the analysis. His description of these steps is paraphrased below.

1. Select an appropriate one parameter transformation group.

2. Find an absolute invariant of the group which is a function of only the independent variables
3. Find a second invariant involving the dependent variable.
4. Express the second invariant as a function of the first, and use this function as the new dependent variable.
5. Substitute these transformations into the equations to reduce the number of independent variables by one.

The primary advantage of this approach is that it provides a structured approach to deducing the transformation, without requiring luck, or great physical intuition. Also, it does not require the introduction of the boundary conditions during the development of the problem. Of course, there is no guarantee that a similarity solution will exist.

Buckingham's Pi-theorem

While the method described above is usually ineffective for problems with imposed time and length scales, many problems of interest do have such scales. Therefore, a method for identifying appropriate parameters without focusing on the solution of the equation is needed. The technique known as dimensional analysis is used for precisely this purpose.

When a mathematical model is developed for a physical process, the numbers used are imbued with an additional characteristic. They represent magnitudes of physical quantities, and thus they have physical dimensions and are expressed in a standard unit of measure. Although an enormous variety of units are defined by convention and for convenience, all of them are expressible in terms of a set of primitive variables. The

choice of these primitive variables is also a matter of convention, and the (nearly) universal set of them is mass (M), length (L), time (T), temperature (Θ).⁶

The dimensional quantities generated relative to this basis of primitive variables have an intuitively acceptable arithmetic:

- only quantities of identical dimension and unit of expression can be added or subtracted. The resulting number, of course, has the same dimension as the two constituent values. This requirement implies dimensional homogeneity in an equation since all terms can be brought to one side of an expression.
- any two values may be multiplied, and the dimensions and units of the resulting number are found by multiplying the units of the factors together.
- since differentiation and integration are expressible as sums, products, differences, and quotients using nonstandard analysis, the above rules apply directly to derivatives and integrals.
- The argument of transcendental functions must be dimensionless, and thus the physical argument must be scaled by an appropriate magnitude before insertion.

Using these simple rules, the search for parameters which make the model appropriate for a wide range of conditions and materials relies on the Buckingham Pi theorem. Paraphrased, this theorem asserts that in a dimensionally homogeneous equation involving n quantities, expressed in r primitive variables, $(n-r)$ dimensionless

⁶ Electric current and luminous intensity are also conventionally taken as 'fundamental' but are rarely needed for thermal problems.

parameters can be found. Some of the more important dimensionless parameters which arise in thermal analysis are given in Table C-2.

(Notation used in the table is standard: U is a velocity, L is a length scale, ρ is the density, μ is the kinetic viscosity, ν is the dynamic viscosity, α is the thermal diffusivity, k is the thermal conductivity, h is the heat transfer coefficient, $\mathcal{D}$ is the diffusion coefficient, θ is the temperature, β is the thermal expansion coefficient, σ is the surface tension, c_p is the heat capacity, g is the acceleration of gravity, and ΔH_f is the latent heat of fusion.)

Often these parameters represent scaling of the features of the model relative to reference scales. A commonly cited example is to consider the Reynolds number to be the ratio of inertial to viscous forces in a flow. An interesting alternative interpretation is offered by Bejan [249], who is troubled by the large value of Re at the transition from laminar to turbulent flow. His belief is that if the number represents the relative magnitude of competing forces, that the transition should occur on the order of unity. Instead, he feels that the parameter of interest is $Re^{1/2}$, which is then interpreted as a geometric factor comparing the boundary layer thickness to the dimensions of the flow.

Regardless of the interpretation of these parameters, they provide a method for comparing different systems, and for consolidating experimental data. For example, one of the most important uses of the Nusselt number is in the presentation of correlations for convective heat transfer experiments.

NAME	SYMBOL	DEFINITION	USE
Reynolds	Re	$UL\rho/\mu$	Transition to turbulence
Prandtl	Pr	$\nu/\alpha = \mu c_p/k$	Relative diffusivities for viscous and thermal processes
Nusselt	Nu	hL/k	Convective flux correlation
Peclet	Pe	$UL/\alpha = \text{RePr}$	Thermal boundary layer development
Marangoni	Ma	$L\Delta\sigma/k\rho\nu$	Influence of surface tension forces
Fourier	Fo	$k\theta/\rho c_p L^2$	Magnitude of thermal transients
Stefan	Ste	$c_p\Delta\theta/\Delta H_f$	Comparison of latent and sensible heat
Grashof	Gr	$gb\Delta\theta L^3\rho^2/\mu^2$	Strength of natural convection
Schmidt	Sc	ν/D	Relative diffusivities for viscous and mass transfer processes
Mach	M	U/c	Onset of compressibility
Brinkman	Br	$\mu U^2/k\Delta\theta$	Influence of viscous dissipation
Biot	Bi	hL/k	Evaluation of flux limiting mechanism

Table C-2: Selected dimensionless groups

These parameters are also intimately related to the qualitative topological analysis discussed in other sections of this thesis. For almost all of the named numbers listed in Table C-2, significant qualitative change accompanies large difference in the parameter values. Two obvious examples of this are the transition of a flow from laminar to

turbulent at a critical Reynolds number, and the change in the relative thicknesses of thermal and momentum boundary layers as the Prandtl number passes through unity.

Similarity versus self-similarity

In many of the situations where a traditional search for a similarity parameter is successful, a natural scale exists, but is a function of time and space. Thus, there is a single boundary layer thickness at a given point along a flat plate, but the boundary layer is observed to grow proportionally to $x^{1/2}$. Thus the meaning of a 'similarity solution' is that the functional form of a relation is invariant, and when properly scaled this form holds for a broad range of times and locations. As an example, solutions of a diffusion equation spread slowly in time, but if the initial distribution is gaussian, it will remain gaussian for all future times. Scaling to normalize this distribution provides the appropriate similarity parameter. This example also suggests why similarity solutions are uncommon: maintenance of a functional form over time places inherently very strict limitations on the allowable forms, and the perturbations they can withstand through boundary conditions.

One of the situations for which a standard similarity solution can not exist is for problems where the local length scales are not unique. When these systems exhibit multiple length scales, and related behavior is seen across these ranges, the system is said to be *self* similar. The analysis of these structures leads immediately to fractals, and their well known apparent similarity when viewed at different scales. This is the topic of the next section.

Fractal analysis

The use of fractal geometry to characterize objects and processes has developed rapidly since the publication of Benoit Mandelbrot's book, *The Fractal Geometry of Nature* [44]. Despite the skepticism that many of his early efforts drew, the idea of utilizing scale independent similarity to simplify difficult looking problems has great appeal. Unfortunately for practicing engineers, while these methods are easily explained at a qualitative level, their application is much more difficult. Furthermore, the appearance of the same few examples in most review and expository articles suggests to some that the use of fractal concepts is not immediately practical.

Perhaps the most ubiquitous example of a fractal is the Koch curve, which was first described in 1906. It was created as an abstract mathematical object, and although it has several rather unusual properties, its significance as a model for physical processes was unrecognized for several decades. It is created in an iterative manner, as seen in Figure C-1, starting from an equilateral triangle. At each stage, every line segment in the curve is replaced by a curve constructed by replacing the middle third of the segment by two segments of equal length. These new segments are rotated outward 60 degrees from the parent segment. The full Koch curve is the limit of this process.

(a.) Similarity operation for the Koch curve

(b) The first two iterations towards the Koch curve

Figure C-1 . Iterative creation of a simple fractal.

As noted above, this is an unusual curve. It is clearly continuous, by its construction, and yet it is nowhere differentiable. Furthermore, at each iteration, the perimeter of the curve increases by a factor of $4/3$. Its area, however is easily shown to be bounded above (A simple bound is the circle which circumscribes the original triangle). Furthermore, if only a portion of the curve is examined, it is impossible to determine any scale information, as exact similarity across all length scales is built into this curve.

The issue of differentiability of continuous curves was initially prompted by the creation of the Weierstrass function in the late nineteenth century. This function is also the limit of an iterative process,

$$W(k) = \sum_{n=0}^{\infty} a^{-n} \cos(b^n k), \quad (\text{C.8})$$

where $1 < a < b$. A generalized form of this relation, the Mandelbrot–Weierstrass function, has been studied extensively [395, 396, 397]. The unusual structure of $W(k)$ can be seen by noting that for a unit increase of n , the frequency of the cosine increases by a factor of b , while the amplitude associated with this term is a factor of a smaller than that of the preceding term. It is this linkage between the terms that prevents convergence, and makes differentiation impossible. When the argument, k , represents time the resulting function is a model for deterministic fractal time series; when it represents a spatial variable, and is multiplied by a copy of itself, it generates a surface embedded in Euclidean 3-space $\mathbb{R}^3$ and is used to model fractal surfaces.

As noted above, the Koch curve and the Weierstrass function appear in almost all discussions of fractals, because they are relatively easily visualized and explained. In engineering applications, however, two difficulties arise with the use of fractals. First, the use of iteratively defined functions to describe a real system seems counterintuitive to many engineers. Perhaps more importantly, modeling of real systems requires generalizing the concept of similarity from strict geometric similarity to statistical similarity across a (perhaps finite) range of scales. Inclusion of these properties increases the difficulty of the analysis, and thus, while fractal concepts are often invoked in qualitative descriptions, or used for data reduction, they are less often used for quantitative modeling of engineering systems. The purpose of this section is to

summarize some of the more important definitions associated with fractal geometry from the perspective of applications to transport processes.

Defining fractals

Fractals can be defined in a popular sense as objects that show similarity across a range of scales. Defining the nature of this similarity and the scales across which it applies can be very difficult, but if this generic definition is used, it is obvious that fractals should be useful in many areas of engineering. Some of these applications are discussed in the following two sections; the focus of this section is to provide a glossary for those discussions, as well as the specific applications considered in the body of the text.

A rigorous definition of fractals requires careful consideration of the concept of ‘dimension’, which in turn relies heavily on topological measure theory. Since several excellent references exist [398, 399], it is inappropriate to go into detail regarding the subtleties of selecting an appropriate dimension. However, the conceptual issues are important, and can be briefly sketched in a qualitative manner. A partial justification for this approach is the primary value of fractal analysis is not in finding an ‘exact’ or ‘true’ dimension for a process, but rather in providing an understanding of the qualitative and topological aspects of the problem.⁷ The most easily explained dimension is referred to as the box counting dimension [400]. This is based on the limit of a process of considering the number of boxes of a given size that are necessary to “cover” the

⁷ In this context, it is amazing to note that for processes with limited available data, that is *experimentally observed* fractals, human “eyeball” estimation of fractal dimension is at worst comparable, and in many cases far superior, to numerical estimation! [430]

observed function. In other words, all of the data is initially contained in a box of a given size. If the size of the box is reduced, the number of boxes need to cover the data rises also. If the data is a smooth curve, then the number of boxes needed grows linearly ($n_1/n_0 \sim L_1/L_0$) with the reduction of the dimension, and if the data comprise a smooth surface, the number of boxes needed grows as the square of the reduction ($n_1/n_0 \sim (L_1/L_0)^2$).

These correspond to our idea of Euclidean dimensions of space. If however, the object has significant structure, it is possible that this exponent will assume nonintegral values in the limit, and the object is then declared to be “fractal”

Spatial fractals

Spatial fractals occur in many disciplines, and range from analytical constructions to descriptive tools. For the theory discussed in chapter 4, the spatial fractals of most concern correspond to the branching morphology seen in melt ejection. The behavior of these fractals ranges from the fine threads associated with diffusion limited aggregation, in effect a representation of a Brownian martingale, to dense branching, which shows fine structure developing within a well defined envelope of evolution. These structures are discussed in the context of melt ejection processes in chapter 3.

Temporal fractals

Although similar theoretical concepts are used in their description, temporal fractals differ from spatial fractals in practice. The observations correspond to necessarily discrete time series, and although multiple characteristics may evolve together and influence each other, the primary independent variable is the time. Thus, strictly speaking, temporal fractals are self affine, rather than self similar, since time is fundamentally (and dimensionally) distinct from the observed sequence of points. In

contrast, in considering spatial fractals, the function is embedded in a space in which all of the orthogonal coordinates are dimensionally the same⁸.

The most important temporal fractals from an experimental point of view are those which are statistically similar. Sequences of observed points from such fractal processes show fluctuations in the observed sequence which depend on the time scale. By definition, fractal processes possess variances which must grow with the observation scale, and are therefore unbounded. Direct analysis of these processes is possible when their fractal nature is explicitly considered. Thus, for Brownian motion, the position of the particle, rather than its incremental step, is the object of study. Compared to stochastic analysis, therefore, fractal analysis focuses on the local structure of the process, and allows the features of a particular occurrence of a process to be readily summarized. This information is not available through standard stochastic analysis, which focuses instead on the invariants of the system, and in particular, the martingale structure defined by a single variance for a given time increment.

Using R/S to study temporal fractals

One of the most useful methods for analyzing potentially fractal time series is rescaled range, or R/S, analysis. This method looks at the scale dependent behavior of the ratio of the range of a process to its standard deviation. The variance of the process under analysis must be unbounded as the observation time grows, and thus for a process which has a fixed scale, the quantity used in calculations is the sum of consecutive

⁸ In general, therefore, a temporal fractal resides in $\mathfrak{R}^n \times \mathfrak{R}$, while a spatial fractal resides in $\mathfrak{R}^m$.

observations. If the process, for example, is gaussian with a constant variance, the sum of consecutive observations corresponds to standard Brownian motion, which does indeed have an unbounded variance as the observation time grows. (In fact, the functional dependence of the variance's growth is known in this case, and is $\sim \Delta t$.)

The scaling behavior of R/S can now be investigated. The initial use of R/S predates the development of fractal theory, as it was initially used by Hurst, a civil engineer studying flood records of the Nile. The statistic is assumed to have a power law dependence on the magnitude of the time interval:

$$y(t) \sim t^H, \quad (C.9)$$

where $y(t)$ represents the average value of the R/S statistic for a given spacing between observations, and H is known as the Hurst exponent. This methodology requires a data set spanning several orders of magnitude in time, but its implementation is quite simple, as seen in chapter 6.

If the steps in a process are uncorrelated, and Gaussian, the integrated process is standard Brownian motion, and the Hurst exponent is $1/2$. Two alternatives exist. If negative correlation exists between steps in the process, then $H < 1/2$, while if positive correlation exists, then $H > 1/2$.

In chapter 6, R/S analysis is applied to sequences of laser pulse energies. This application allows several salient points to be addressed. First, as with all such data sets, there is some experimental error associated with the observation process.. Second, any deterministic structure in the relationship would not scale with the sample size, and could therefore be identified and removed prior to analyzing the structure of the variability. Based on physical considerations, one would expect that temporal variations in oscillator conditions (primarily uncontrolled, irregular loss modulation in the cavity) would lead to

a degree of positive correlation in the sequence of observed values. In fact, this is what was observed. Therefore, the magnitude of the Hurst exponent provides an objective measure of the consistency of the pulse energy

In addition to Hurst's application, and the use of R/S analysis in chapter 6, several very interesting successes of this methodology have been published. Most notable among these is the work by Feder and colleagues[326, 401], who have studied long sequences of wave height data.

It is interesting to note the truth of the adage that the available analytical tools shape one's perspective on a physical process. From the perspective of traditional stochastic analysis, Brownian motion is first converted to a "well behaved" martingale by looking at the variation of the steps [386, 402]. The invariants associated with the process are determined, and the resulting diffusion process is the paragon of a smooth process. The small fluctuations are deemed to be of little importance. By contrast, a fractal analysis of the same process focuses on these fluctuations, and looks at Brownian motion as the paradigm for statistically similar fractal behavior[403, 404, 326]. In a sense, both of the approaches are correct, since they focus on different *aspects* of the same process. The lesson for HFTP is twofold. First, the definition of the specific problem to be studied can dramatically alter the choice of modeling techniques. Second, and perhaps more important, interesting behavior may found in processes that are assumed to be well known.

Wavelet analysis

The occurrence of fractal structure in a physical process often results in difficulty in analysis. This difficulty arises because there is structure across a broad range of scales, and therefore traditional methods of representing the process, such as Fourier analysis, do

not result in simplification of the process. An alternative method of representation which has been developed rapidly over the past decade is the use of wavelet bases. The basic approach is to represent the function by translations and dilations or contractions of a given wavelet. These functions are referred to as wavelets because they are rapidly decaying – or have compact support – and they integrate to zero. Thus, they have some wave-like properties, but are of limited extent.

The important point to note regarding the use of this alternative base is that Fourier analysis relies on cancellation between terms to generate the observed features, and thus a broad band transform is required to generate a sharp feature. (This is the source of Gibb's phenomenon, the ringing which is observed around a Fourier series representation of a step change [405].) By comparison, the wavelet base determines structure using addition. Thus, for an edge or discontinuity in an analyzed function, the wavelet basis approximates the change by using only those wavelets which are localized in position and frequency around the point of interest [406]. This simplifies the form of the resulting transform.

Wavelets are intimately related to fractals and to spline representation of data; these links, and the application of wavelets to physical problems are currently areas of active research [407 – 412].

Renormalization

Renormalization is a technique which is related to fractal analysis, and which incorporates algebraic analysis of a mathematical system of equations. The analysis can be conducted either in real space, or in Fourier space. The essence of the technique is that if a physical process is described by a very detailed Hamiltonian, and if the number of degrees of freedom can be reduced by an appropriate rescaling of the system, then a

semigroup, known as the renormalization group (RG), may exist, which can be applied indefinitely to the system to determine its invariants. RG methods have been widely used in numerous areas where a large, essentially indefinite system exhibits behavior which shows a degree of self similarity. Among these applications are critical phenomena, turbulent flow, and quantum electrodynamics[280, 413 – 429,]. The common feature of all of these systems is that they are composed of many elements which interact across a wide range of scales, and that the number of degrees of freedom is effectively unlimited. The identification of a semigroup operation which reduces the number of degrees of freedom, and can be applied in an iterative fashion is therefore of enormous importance.

To clarify the idea, a simple application of RG methods to a two dimensional Ising lattice would proceed as follows. For a given number of particles, the free energy of the system is influenced by the relative positions of the particles, whose possible locations are laid out on a square lattice. In order to reduce the number of sites involved in the summation, an imaginary reduced grid is introduced. This grid would have a larger spacing between sites, but otherwise be geometrically identical. For example, the spacing might be increased by a factor of three, and thus, each site of the new lattice would correspond to $3^2 = 9$ sites of the old lattice. The new site would therefore be defined as “occupied” if the majority of the original sites were occupied, and unoccupied otherwise. The effective particles defined for this larger grid must exhibit the same free energy as the original grid, and therefore the Hamiltonian must be scaled to preserve this value. If it is possible to do this in such a manner that the functional form of the Hamiltonian is also invariant, then a RG has been found, and by repeated application, the invariants of the system can be found. It is interesting to note that such calculations can show the onset of critical point opalescence, phase separation, and the evolution of turbulent eddies (whose RG analysis is typically conducted in a frequency space where wave number corresponds

to eddy size). Thus RG techniques tend to emphasize the fact that if the small scale structure of a physical process is important, and if an imposed scale is not present, fractal behavior is likely to exist. Therefore, the important aspect of the analysis of any such process is the identification of the points at which it is appropriate to focus on the smooth evolution of the invariants, and when it is necessary to consider the more complicated fine structure of the process. This is the defining difficulty of HFTP. 430

D. Error analysis

In most engineering work, systematic errors arise in predicted values due to the use of approximate relations and imprecisely known or inaccurate data. Careful analysis of experimental data therefore requires an evaluation of the influence of errors in the settings of the predictors on the behavior of the response variables [431 – 435]. This chapter discusses computer based methods for evaluation of error propagation by calculating the uncertainty in the density or pressure of a fluid. These methods are significant because they allow rapid estimation of the influence of predictor variables on experimental response. The first two of these techniques are based on the traditional analytical method for evaluating error propagation. The third technique uses direct simulation to evaluate error propagation. An advantage that these methods share is that they utilize the readily available power of desktop computers and make the procedure less tedious.

Analytical error propagation

Engineers are often faced with the need to estimate the influence of errors in independent variables on a calculated quantity[286]. For generality, consider the calculated, or response, variable to be an arbitrary function of a number of independent variables:

$$Y = f(x_1, x_2, \dots) \tag{D.1}$$

The traditional approach to this problem uses a Taylor series expansion of the system's response function to relate variability in the predictors to variability in the response. The expression can be written as [436 – 438]:

$$\sigma_y^2 = \sum \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2, \quad (D.2)$$

where σ_y^2 is the variance of the response function and σ_i^2 is the variance of the i^{th} predictor. Evaluation of this expression is trivial when the function, $f(x_1, x_2, \dots)$ is a linear relation, but can become rather tedious when the functional relationship is highly nonlinear. Unfortunately, this is when information regarding error propagation is most important.

Two potential difficulties arise in the evaluation of equation D.2. First, the variances of the predictors must be estimated if they are not known *a priori*. This can be an interesting problem; however, for the system under consideration, the predictor variances are assumed from knowledge of the equipment. Second, the more difficult obstacle is the evaluation of the derivatives of the response with respect to the predictors. An approach which has been used in the past is the linearization of the response in the range of interest [439]. The skill and effort required to either perform the linearization or to directly evaluate the derivatives analytically often deter an experimentalist from making the calculation.

Numerical techniques

Fortunately, the advent of powerful personal computers has greatly simplified the analysis of error propagation. In this section, three methods for conducting this analysis using a personal computer are presented.

Symbolic evaluation

The first computer intensive method is perhaps the most obvious: the use of symbolic manipulation software to perform calculations which would be too tedious to do

by hand [440]. These programs, such as *Mathematica*, *MathCAD*, *Maple*, and *Macsyma*, can quickly and accurately evaluate partial derivatives for virtually any relationship which can be expressed in closed form. When the software is available, this method allows the evaluation of equation 2 for almost all problems. (For the present problem, the Macintosh version of *Mathematica* was used.)

Two situations exist, however, which necessitate other approaches. The first of these occurs when a relationship can not be readily expressed in a closed form. This might be the case in a complicated spreadsheet calculation. Although the reduction to a single formula might be possible, it is unlikely to be done in practice.

The second reason for looking at other procedures deserves careful consideration. As noted above, equation D.2 is based on a truncated Taylor series approximation. Therefore, any calculation which exactly uses that equation is subject to the limits of the approximation. In particular, the resulting estimate is essentially a scale factor; it contains no information on the shape of the distribution of the variation of the response. This is a problem in particular near the critical point, where asymmetry in the resulting error distribution might be expected to arise.

Numerical estimation of derivatives

When the function can not be expressed in closed form, the derivatives can be estimated numerically. For the examples considered below, central finite differences yield good estimates of the partial derivatives required for the evaluation of equation 2 [437, 442]. Higher order finite differences were not used because in the cases where first order differences are not good estimates, the form of equation D.2 is unlikely to be appropriate, as discussed above.

Calculation in this case is straight forward. The spreadsheet is evaluated for perturbations of each independent variable, x_i , by an amount Δx_i . The resulting estimate of the partial derivative is:

$$\frac{\partial f}{\partial x_i} \equiv \frac{f(x_i + \Delta x_i) - f(x_i - \Delta x_i)}{2\Delta x_i} \quad (\text{D.3})$$

Values of the partial derivatives are then substituted directly into equation D.2 to yield the estimate of the variance of the response. For the problem considered below, these calculations were performed on an *Excel* spreadsheet.

Simulation of experimental results

The third technique for evaluation of error propagation is inherently different from the other two. Previously, we were concerned with numerical and analytical difficulties associated with the evaluation of a deterministic equation. The approach we take now is to reconsider the problem in a probabilistic sense. This approach has not been used for error propagation calculations, but is the foundation of statistical mechanics. In that case, the behavior of an ensemble of molecules is believed to be deterministic, but is treated statistically because of the huge number of particles being considered. The current application is much more pedestrian, but also benefits from the change of perspective.

The procedure used is essentially a Monte Carlo simulation of the experimental response function. Appropriate random deviates of the independent variables are selected and inserted into equation D.1, which yields y_i as an estimate of Y . This process is repeated many times, and the variance of Y is directly estimated from the values of y_i .

This method has one obvious disadvantage: it takes longer to perform than the two preceding techniques. However, the simulation has two distinct advantages which

will make it very useful in a number of situations. The first advantage is that since the simulation works directly with the response function, it is not limited by the approximations inherent in equation D.2. Thus, this approach is the method of choice in those cases when approximation by a second order Taylor series proves to be unsatisfactory.

The second advantage of the simulation occurs for all experimental situations. Because each simulation yields an estimate of the response, it is possible to accumulate these results and gain an approximate shape for the distribution of errors. As shown in one of the examples below, the distribution of errors in a response can be highly skewed or bimodal. This information is not available in an estimate which is based on equation D.2.

This technique is a variant of the "bootstrap methods" developed and used in applied statistics [443 – 449]. The selection of the random variates is a nontrivial consideration, particularly when the response function has numerous independent variables. For the example considered below, the simulations were performed on a spreadsheet program; the deviates were generated based on suggestions made by Abramowitz and Stegun [450].

Error analysis using an equation of state

These techniques are now applied to the determination of the properties of a fluid using a nonideal equation of state. This is an important calculation for the ablation system studied in this thesis. As discussed elsewhere, the density of the fluid directly influences the coupling of incident radiation into the target as well as the dissipation mechanisms which dominate thermal processes at the surface. Furthermore, the index of refraction is related to the density through the Lorentz–Lorenz equation, and thus

uncertainty in the fluid density can lead to mis-estimation of refractive index and hence to improper placement of optics.

The van der Waals equation and a modified form of the Lee Kessler equation are the equations of state used in the following examples.

The van der Waals equation

The van der Waals equation is a cubic equation of state [265, 387]

$$(P + aV^{-2})(V - b) = RT, \quad (D.4)$$

where R is the universal gas constant. The constants “ a ” and “ b ” account for repulsive and attractive intermolecular forces respectively. When the pressure and temperature are assumed to be known, this equation can be solved for the specific volume. Analytical solution of the equation requires selection of the appropriate root [265].

Modified Lee-Kesler Equation

A modified form of the Lee-Kesler equation of state was also used in the experimental work to estimate the density of carbon dioxide at various temperatures and pressures. This equation [276] contains 15 parameters, and is conveniently expressed in terms of the compressibility factor, Z :

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^4} + \frac{E}{V_r^5} + \frac{F}{V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp\left(\frac{-\gamma}{V_r^2}\right) \quad (D.5)$$

where the coefficients B – F are functions of the reduced temperature and the parameter values.

$$\begin{aligned}
 B &= a_1 + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3}, \\
 C &= a_4 + \frac{a_5}{T_r^2} + \frac{a_6}{T_r^3}, \\
 D &= a_7 + \frac{a_8}{T_r^2} + \frac{a_9}{T_r^3}, \\
 E &= a_{10} + \frac{a_{11}}{T_r^2} + \frac{a_{12}}{T_r^3}, \\
 F &= \frac{\alpha}{T_r^3}
 \end{aligned}
 \tag{D.6}$$

An analytical solution of this example was readily determined using *Mathematica*. This problem was also solved using the other two techniques discussed above.

Uncertainty estimates

The first example is estimation of the specific volume of dichlorodifluoromethane using the van der Waals equation. The process parameters were assumed to be $T = 408 \text{ K}$ and $p = 50 \text{ bar}$. Because of the need to choose among roots of the equation, the analytical solution was not calculated. The remaining two methods were used and yielded comparable results as seen in Table D-1. As discussed in [451], however, the more interesting result is that the Monte Carlo simulation is able to detect significant skewness in the distribution of the estimated quantity. (The Monte Carlo result is based on 8000 samples.) This example is somewhat unusual, because the system operation is near its

Method	Standard deviation of $\hat{v}$, $\text{cm}^3 \text{mol}^{-1}$
Numerical derivatives	55.0
Monte Carlo simulation	48.2

Table D-1: Uncertainty of specific volume

critical point. For such a system, however, this skewness of the estimate is expected, and can not be determined except through the simulation.

Figure D-1: Skewness found through Monte Carlo analysis.

The second example uses the modified Lee-Kessler equation, and assumes that temperature and mass are known, in order to evaluate the pressure of the system. Such a calculation might have industrial importance, for example, in evaluating conditions inside a closed process vessel. The settings of the

process variables are shown in Table D-2. This is at a very high density, and therefore requires the use of a sophisticated EOS. The expected value of the pressure is ~1900 bar.

The resulting error propagation estimates are seen in Table D-3. As expected all yield comparable results. (The Monte Carlo result is based on 1000 simulations). Further simulations demonstrate the expected convergence of this estimate as $n^{-1/2}$, where

Property	Nominal Value	Standard Deviation
Temperature, K	320	1.0
Volume, l	25	---
Mass, kg	30	0.1

Table D-2: Process settings for high density example

Evaluation method	Standard deviation of pressure, bar
Symbolic evaluation	44.5
Numerical derivatives	44.6
Monte Carlo simulation	42.7

Table D-3: Error propagation calculations for high density carbon dioxide

n is the sample size [451]

Discussion and conclusions

An evaluation of the uncertainty in calculated quantities is an important component of engineering analyses. Three methods have been presented above for estimating the propagation of error through a calculation; each can be a useful tool for the practicing engineer.

The first two methods are computer assisted applications of the traditional error propagation formula. An analytical solution is preferable when it is possible as it is readily invertible, and can be quickly performed. The use of numerical derivatives becomes useful in those instances when developing a closed form for the relationship is impractical.

The final method considered is direct simulation of the error propagation. This technique avoids the assumptions inherent in the previous methods. Furthermore, it provides an estimate of the shape of the error distribution's shape as well as its mean and

variance. Although running the simulations takes slightly longer than the previous methods, the additional information generated may prove quite useful

As noted by Tibirishani and Efron[452], the nature of statistical analysis can be expected to change significantly as computing power becomes more readily available and less expensive. For error propagation calculations, that change is painless, as is exemplified by this analysis.

E. Optical effects

In an experimental program involving high power pulsed lasers, numerous optical phenomena must be considered. This appendix provides pertinent background material for the optical issues discussed in the body of the thesis.

Optical analysis of gaussian beams

The most obvious optical calculation needed for this work is the design of the optical system for focusing the beam onto the sample. Because of the high intensities involved, and the need to focus to a small spot on the sample without damaging the optics, this calculation was important; however, the validity of common simplifying assumptions was uncertain. This section presents several approaches to beam propagation calculations, and discusses their relative merits.

Geometric optics

A first order approach to the problem of laser optics design is the use of geometric optics, or ray tracing. This method has serious limitations; however, it is intuitively appealing and generally provides satisfactory estimates of a system's real behavior away from focal regions[453,454].

In geometric optics, the particle nature of light is exclusively considered. This assumption is equivalent to analyzing limiting behavior as the wavelength vanishes. Such an approach is typically valid when all length scales of the problem are much larger

than the wavelength.¹ As a result, all diffraction and interference effects are ignored. It is assumed that aberration-free beams can be focused to an infinitesimal spot at the system's focal point. Furthermore, the paths of individual rays are determined by local refractive index variation through a generalization of Snell's law to allow continuous changes in refractive index as well as step changes [455,456].²

Snell's "law" states the product of refractive index and the component of a ray's path which is tangential to a surface of interaction is invariant, that is,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2, \quad (1)$$

where θ_1 and θ_2 are the angles of incidence and refraction, measured from the normal to the surface. The quantities n_1 and n_2 are the simple indices of refraction for the two media. Several steps must be taken to apply this concept to the performance of a simple lens [457 – 461]:

1. A set of rays representing the anticipated incident beam must be chosen. For each ray, the angle of incidence and point of incidence on the lens surface is determined.
2. Snell's law is applied to each ray to calculate the angle of refraction.
3. The rays are assumed to propagate in a straight line through the lens medium, until the back surface is encountered.

¹ This approach of allowing a physically important term to vanish also plays a large role in the catastrophe theory formulations of mechanics and thermodynamics, and is discussed in that context in the mathematical appendix.

² This principle has been used to develop optical beam deflection spectroscopic techniques by numerous researchers, including the group led by R.E. Russo at the Lawrence Berkeley Laboratory. References for this technique include [271, 391, 501]. The phenomenon, which also leads to mirages, is more elegantly demonstrated using a Hamiltonian formulation, and is discussed in a subsequent section..

4. Snell's law is applied a second time to determine the trajectory of each ray as it leaves the lens.
5. The rays are again assumed to propagate in a straight line as they traverse the medium behind the lens.

The variety of effects which can be seen depending upon the shape of the lens is a common topic in undergraduate physics courses and is not belabored here; however, it should be emphasized that more complex systems can be treated in the same conceptual manner. Thus, a train of lenses, media with a given refractive index gradient, mirrors, and other optical elements can be combined by considering the behavior of each ray as it proceeds through the system. A curious, and surprising, caveat at this point is that the occurrence of unstable behavior in beam intensity can be found by taking partial reflections and multiple surfaces into account [462].

The application of geometric optics is greatly simplified if the "paraxial" approximation is used. This model assumes that the beam is close to the axis of the optical elements, and that the divergence of the beam is small. As a result, the problems associated with chromatic and spherical aberrations can be ignored, and the behavior of the beam can be readily traced through a system; a particularly successful methodology is discussed in the next section. Using this approach, if a beam is assumed to be collimated (that is, all rays are parallel) as it hits a focusing lens and coaxial with the lens, all of the rays cross the axis at the focal point of the lens. This estimation presents the greatest limitation to the use of ray tracing, and leads directly to the need for the use of Gaussian optics in the design of laser manipulation optics, as real beams can not be focused to a point.

An alternative interpretation of ray tracing is available, however, which allows the extension of these methods for use with coherent sources such as lasers. For such sources, the rays are considered to represent the local normal to the wavefront [457, 463]. For many solid state and gas lasers, the energy distribution is assumed to have a two-dimensional Gaussian distribution. It is important to note, however, that this refers to the energy distribution across the coherent wavefront, which is a spherical wave with a large radius of curvature [464, 465]. Thus, by considering the evolution of the normal of the wave front at the centerpoint and a marginal location, the propagation of the beam can be evaluated using the matrix methodology discussed below with only minor modifications. As a result, the experimentally observable beam waist at a focal point is determined by paraxial techniques.

Using the general formulation of geometric optics, spherical aberrations, astigmatism, and chromatic aberrations can be determined. Even the state of polarization can be described [466]. Determination of diffraction effects, however, requires more detailed analysis of wave propagation through the system. The purpose of the optical system used in these experiments was to generate a (repeatably) focused spot; as a result, the level of detail required to assess higher order aberrations was deemed unnecessary. Furthermore, the aperture of the system was kept as large as possible to minimize diffraction effects; therefore, they are not discussed further. For many such systems, the simple application of ray tracing techniques is satisfactory, and for rough calculations, numerous simple graphical techniques have been developed [461, 467].

“ABCD” matrix formulation

An interesting observation can be made regarding the use of ray tracing. If the rays under consideration are paraxial (close to the axis, and with small angles relative to

the optical axis of the lens), the equations arising from the ray tracing procedure can be written in a matrix formulation. The general form is then:

$$\begin{bmatrix} r_2 \\ r_2' \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \bullet \begin{bmatrix} r_1 \\ r_1' \end{bmatrix}, \quad (2)$$

where r is the distance from the axis at a given point, and r' is the slope relative to the axis. The useful feature of this observation is that the matrix corresponding to each element of the system can be determined separately. The net effect of the system on a beam is the product of all of the constituent element's matrices. As always, order of the matrices is important; subsequent elements are left multiplied onto the matrices of preceding elements. Several representative matrices are given in Table E-1.

The determinant of all of these matrices is unity, and the overall system matrix is generated by left multiplying the matrices of sequential optical components. The composite matrix is used as written in (2) when geometric optics is sufficient. As demonstrated by Kogelnik and Li [468, 469], when the Gaussian character of the beam is important, the elements of the matrix are used to transform the complex beam parameter, $q(z)$:

$$q_0 = \left(\frac{\pi w_0^2}{\lambda} \right) \cdot i \quad (3)$$

$$q_2 = \frac{Aq_1 + B}{Cq_1 + D}, \quad (4)$$

Propagation through a homogeneous medium	$\begin{bmatrix} 1 & d/n \\ 0 & 1 \end{bmatrix}$
Propagation through a lens	$\begin{bmatrix} 1 & 0 \\ -1/f & 1 \end{bmatrix}$
Propagation through a region of quadratic refractive index variation: $n(r,z) = n_0(z) + (n_2(z) \cdot r^2) / 2$	$\begin{bmatrix} \cos(d\sqrt{n_1/n_0}) & \sqrt{n_0 n_2} \sin(d\sqrt{n_1/n_0}) \\ -\sqrt{n_0 n_2} \sin(d\sqrt{n_1/n_0}) & \cos(d\sqrt{n_1/n_0}) \end{bmatrix}$

Table E-1: Representative ABCD matrices.

where q_0 is the value of the beam parameter at the location of the beam waist, w_0 . The values of the beam parameter at the entrance and exit of the system are denoted by q_1 and q_2 , respectively. It is conventional, although not necessary, to define the system relative to the waist, so that $q_1 = q_0$. It is also important to note that a system can have multiple waists, and that these waists can be virtual as well as real.

For the experimental laser ablation system described in chapter 5, seven components are considered:

1. M_I : Propagation between the laser and the diverging lens ($n \approx 1.0$).
2. M_{II} : Passage between the principal surfaces of the diverging lens ($f = -50$ mm).
3. M_{III} : Propagation between the two lens.
4. M_{IV} : Passage through the converging lens ($f = 150$ mm).

5. M_V : Propagation between the converging lens and the autoclave window.
6. M_{VI} : Passage through the window ($d = 25.4$ mm; $n = 1.460079$).
7. M_{VII} : Passage through the autoclave ($d = 74.6$ mm; $1.0 \leq n \leq 1.2$).

The net matrix for the entire system is thus:

$$M_{tot} = M_{VII} M_{VI} M_V M_{IV} M_{III} M_{II} M_I \quad (5)$$

In a similar fashion, the waist of the reflection from the first surface of the window is found by multiplying matrices M_I — M_V and noting the beam reflects at the front surface. Therefore, the position of the reflected focus is at

$$d_r = 2 \cdot d_3 - d_{III} \quad (6)$$

where d_r is the distance between the lens and the waist, d_3 is the distance between the lens and the window, and d_{III} is the nominal waist position. For given lens positions, d_{III} is a constant, and d_r is linearly related to d_3 .

The position of the reflection from the back surface of the window is calculated in an analogous manner. For the optical system and the range of fluid densities used, the waist of both reflections occurred between the window and the converging lens. No optical damage to the lenses was anticipated, and none was observed after this arrangement was adopted.³

³ A large, catastrophic flaw was induced in a lens in a preliminary layout which used a single plano-convex lens. Also, several windows ultimately showed signs of optical damage. This damage did not threaten the mechanical integrity of the window, but manifested itself as a "strand" of small bubbles within the fused silica. The window was inspected daily and replaced at the first appearance of such flaws.

Path integral formulation

The design of a simple optical system, such as that discussed in this thesis, is easily accomplished using standard matrix optics, and thus the investigation of alternative formulations might seem unnecessary. Optics, however, provides an intuitive paradigm for consolidating alternative perspectives which is useful in the study of HFTP. This value arises in two forms. First, the specific tools developed for handling optical systems may be used with slight modification for other microphysical applications. More importantly, the facility developed in incorporating alternative theories into the interpretation of observed results translates directly to the study of HFTP.

One approach to optics which fits both of the above criteria is the use of Feynman's path integral approach to develop optics[470 – 472]. While no one would use this highly theoretical approach to decide where to place a lens, this perspective on the propagation of light is of immense importance. The tools which can be explained intuitively in this setting are directly useful in such diverse areas as QED, critical point phenomena, electron optics, and statistical mechanics. Also of particular interest in this study is the fact that path integrals can be used to describe scattering and the appearance of caustics. [470]

The typical presentation of the path integral is that the time varying Green's function for the intensity of a point x , given a source at y is:

$$G(x, t; y) = C \sum_{x(\cdot)} \exp\left(\frac{iS(x(\cdot))}{\hbar}\right), \quad (7)$$

where $x(\cdot)$ represents paths going from y to x . In this formulation, $S(x)$ is the action, and the use of Planck's constant assumes an application in a quantum mechanical system

[470]. Also note that in this case, the summation is used to emphasize the fact that the space of paths has an improper measure, and therefore integration is poorly defined. Traditional mechanics can be derived as resulting from the limit $\hbar \rightarrow 0$. (As $\hbar$ is a constant, this might seem illogical, but as the dimensions of the problem grow, the relative magnitude of $\hbar$ decreases. This is precisely the situation in which classical mechanics becomes valid, and the wave nature of objects can be neglected.) As discussed by Schulman [470], geometric optics can be recovered in a similar manner if the scalar form of Maxwell's equations is solved using a reparametrized spatial variable. The rescaling is accomplished by noting that the characteristic distances of systems where geometric optics is appropriate are significantly longer than the wavelength of the light. Thus, setting $\lambda = c/\omega$,

$$x' = By' \cdot \left(\frac{c}{\omega} \right), \quad (8)$$

where x' is the physical distance, and y' is the new argument of order unity. As B grows, the geometric optics limit is recovered by writing an "integral" as above. The net result is that the primary contribution occurs from those paths for which the integral

$$T = \int_0^s c(x') ds' \quad (9)$$

is stationary, where $c(x)$ is the local speed of light, and the integration is over paths of arbitrary length starting at y and ending at x . This is, of course, one formulation of Fermat's principle; deriving it in this fashion unfortunately requires a substantial amount of work. The interesting point, however, is that one can consider the propagation of light from a very abstract perspective, and generate the familiar heuristic equations by making appropriate approximations. Further work in this direction would be to then integrate

over a range of source positions to investigate local intensities resulting from diffraction effects leading to the appearance of caustics.

Hamiltonian optics: a Lie algebraic formulation

The Hamiltonian formulation of optics is an interesting, abstract perspective, which also utilizes an assumption of vanishing wavelength. It is interesting because it allows the formulation of optical problems in similar terminology to mechanical problems, and is useful in the context of HFTP because it provides an intuitive setting for studying the impact of algebraic methods on physical systems. In a qualitative sense, it falls between the use of ray tracing methods and the path integral techniques discussed above. Because the wavelength is typically assumed to be negligible, diffraction effects are ignored by this formulation. The approach relies on visualizing the system in terms of an appropriate Lie algebra. Although some of the terminology is intimidating, the resulting system provides an elegant approach to the propagation of light through continuously varying media [473 – 477].

If a ray propagating through an arbitrary medium is parameterized by s , its path can be described by the vector $\mathbf{q}(s) \in \mathbb{R}^3$. Furthermore, its tangent vector can also be expressed in terms of s , $\mathbf{p}(s)$. The assumptions of two postulates now allows the introduction of a Hamiltonian approach [475]:

- (1) Geometric postulate: $\mathbf{q}(s)$ is continuous and at least piecewise differentiable;
- (2) Dynamic postulate: $\mathbf{p}(s)$ is dependent on the gradient of the refractive index, $n(\mathbf{q})$.

In the simplest case, where $n(\mathbf{q})$ is smooth, the equations become:

$$\frac{d\mathbf{q}}{ds} = \frac{\mathbf{p}}{|\mathbf{p}|} \tag{10}$$

$$\frac{d\mathbf{p}}{ds} = \frac{\partial n}{\partial \mathbf{q}} \quad (11)$$

The use of these two equations implies the existence of an invariant, the Hamiltonian function $H = |\mathbf{p}| - n(\mathbf{q})$. For convenience, it is often assumed that $H = 0$; in this case, the magnitude of the tangent vector equals the local value of the refractive index. The behavior of these equations is well known from classical mechanics, where $\mathbf{q}(t)$ is the position and $\mathbf{p}(t)$ is the momentum. The correspondence between optical systems and mechanical systems here is stronger than merely analogy. Although the parametrization is not by time in the optical case, the postulates, which seem intuitive and are confirmed by experiment, require this structure.

It should be noted that this formulation becomes more problematic if the refractive index has surfaces of discontinuity. Although the gradient, ∇n , does not exist at these points, the cross product of the surface with the optical momentum is readily shown to be a conserved quantity. Taken together with the continuity of $\mathbf{q}$, behavior at surfaces of finite refraction can be determined, and the beam path can be calculated in a piecewise manner.

This approach is abstract, and directly introduces Lie algebraic techniques into the solution of optical problems. As discussed elsewhere, the structure is a curve embedded in a three dimensional Euclidean space. Thus, the objects of interest are the tangent space as a function of the parameter, as well as the curve itself. The benefit of this less concrete formulation is the ability to work with a single parameter which controls evolution of the curve. Of course, if the problem is restricted to small deviations of the beam and essentially parallel gradient fields – i.e., the paraxial case – this approach is not needed. Where substantial benefit should be seen is in situations where the refractive index gradient is a strong function of position. In OBD applications this might be expected to

occur where the refractive index is a highly nonlinear function of density (or concentration, temperature, etc.).

In general, the Hamiltonian formulation requires the use of differential forms and careful analysis since the “motion” is constrained to an embedded manifold. However, it should be noted that the “volume” of an element of the $\{q,p\}$ phase space is conserved in transformation. Thus, as discussed by Sekiguchi and Wolf [479],

“Points in phase space (light rays) move as specks of dust in an incompressible fluid....By means of an optical device, we may ...produce a smaller image dq' , but at the cost of a larger spread dp' in ray directions....”

This realization provides a strong foundation for many of the heuristic tools used in optical design. Given this perspective, it is understandable that the primary role of Lie optics has been as a design tool for complex optics for both light and for charged particles.

Nonlinear optical effects

The preceding section discussed the propagation of the beam under the assumption that its interactions with the medium were limited to refraction. In this section, some important interactions of the beam and the medium through which it passes are considered. Some of these effects are utilized in the laser to allow pulse formation while others influence the behavior of the beam in the small pressure vessel used for experimentation.

Thermal blooming and lensing

Thermal blooming and lensing are experimental manifestations of the same phenomenon; namely, the passage of light through a region of variable refractive index. If the refractive index increases away from the center of the beam, the beam's radius increases, or blooms. If, however, the refractive index decreases away from the axis of the beam, the beam effectively sees a focusing lens, and its radius decreases. If these phenomena occur because of thermally induced refractive index gradients, they are then known, respectively, as "thermal blooming" and "thermal lensing." [480 – 485]

For clarity, this section focuses on thermal lensing which is of more practical importance for the experimental ablation system. Thermal blooming, which is particularly useful for the study of turbulence [486 – 489], is essentially the inverse of this process.

The dependence of the refractive index on ambient density is discussed in detail below. For the remainder of this section, this dependence is taken as a given. The presence of a plasma leads to a substantial number of free electrons and ionized molecules; this can also serve as a source for refractive index gradients.

The equations governing thermal lensing are readily developed from considerations of geometric optics. The ABCD matrix associated with a fixed gradient index element is given in the bottom row of Table E-1 where the refractive index is assumed to vary quadratically around the axis of the beam.

More generally, the deflection of a ray by a thermally induced refractive index gradient is given by:

$$\theta = \int_{\text{ray path}} \frac{1}{n} \frac{\partial n}{\partial T} ds \times \nabla T \quad (12)$$

In practice, if the deflections are small, the integration is conducted over an appropriate spatial coordinate rather than the beam path. (Interestingly, this expression blurs the distinction between traditional geometric optics and the Lie optics approach.)

In typical occurrences of thermal lensing, however, the refractive index field is neither temporally nor spatially fixed, and its gradient may be quite large. Thus, the propagation of a beam can change catastrophically if a thermal lens develops in a material during irradiation, and *ab initio* calculation of the beam's behavior may be necessary to evaluate the possibility of unanticipated focal points within the system.

Two particularly interesting situations exist in which thermal lensing (or blooming) occurs during laser processing. The first of these is when the absorptivity of the material changes nonuniformly during the interaction period. Notable examples include the development of flaws in excimer laser optics after millions of pulses, and spectroscopy based on the distortion of a probe beam due to the influence of a pump beam on a material [490, 491, 492]. The second instance is the deformation of the beam due to plasma formation. Because of the high intensities associated with such processes, the resulting changes in the beam are very nonlinear, and phenomena such as beam filamentation may occur. Filamentation is the aptly named phenomenon whereby a beam is broken down into many small beamlets, whose distribution is often fractal in nature [56, 239, 494 – 496]. This process of splitting nearby rays from each other presents an interesting example of extreme dependence on initial conditions which is the hallmark of processes which are chaotic in the technical, as well as the colloquial sense.

Acousto-optic effects: mode locking

The formation of very short pulses from a laser is generally accomplished through *mode locking* and *Q-switching*. Mode locking relies on the superposition of emission

(a) Superposition of sinusoids of constant phase **(b) Modelocking of Ten Sinusoids**

Figure E-1. Schematic description of modelocking for waves of constant phase

temporal process.

As shown in Figure E-1, modelocking occurs when frequencies with a constant spacing are brought into a common phase. In a laser, the spacing of resonant frequencies is $\Delta\nu = 2c/L$, where L is the length of the laser cavity, and c is the speed of light.

from numerous frequencies oscillating in phase to form a pulse[497, 498], while Q-switching is a process for spoiling the cavity gain for most of the period of the pulse to allow the population inversion in the lasing medium to grow above normally achievable levels[498]. The techniques used in practice often exhibit both effects, but it is important to realize that the mode locking is occurring in frequency space, while Q-switching refers to a

Because this spacing is so small⁴, numerous resonant frequencies can be expected to exceed the lasing threshold under the gain envelope, particularly for inhomogeneously broadened systems.

The occurrence of these frequencies is fortuitous, as the presence of multiple frequencies is required to generate a sharp pulse. Figure E-1-b shows the effect of adding together ten components of equal amplitude.

The laser used in these experiments was both passively and actively mode locked. The passive mode locking was accomplished by the flowing saturable absorber as a part of its primary role as a Q-switching agent. The active mode locking was achieved by an acousto-optic modulator. Acousto-optic mode locking relies on the generation of standing density waves in a quartz crystal by radio frequency excitation. The resulting density profile acts as a grating, and diffracts energy away from the resonator, except for brief intervals during each cycle of the excitation [499]. Both the passive and active mode locking techniques are discussed further in chapter 5.

Electro-optic effects: the Pockels cell

The selection of a single pulse from the Continuum YG-601C is performed by triggering a Pockels cell. The Pockels effect, also known as the DC Kerr effect, is an electro-optic phenomenon: an electric field is used to alter the optical behavior of the system. This effect is caused in a nonlinear crystal by changing the voltage drop across

⁴For reference, mode spacing for a HeNe laser is approximately 100 MHz, while the lasing frequency is 500 THz. The relative spacing is thus $\Delta\nu/\nu_0 \sim 10^{-7}$.

the crystal transverse to the direction of propagation. This change in the bias changes the birefringence of the crystal, which in turn alters the polarization of the transmitted beam.

Just beyond the cell is a quarter waveplate. It is well known that such a waveplate transmits strongly at one polarization, and reflects strongly for a polarization rotated 90° with respect to the transmitting orientation. The effect of triggering the Pockels cell is therefore to change the orientation of a the pulse when it reaches it maximum amplitude. The pulse now is reflected out of the cavity and into the amplifier.

Second harmonic generation

In the experimental laser ablation system, the amplified output of the laser can be frequency doubled using a KD*P crystal. This process, known as *second harmonic generation* (SHG), was among the first nonlinear optical effects utilized after the invention of the laser. The ability to generate powerful output at shorter wavelengths has proven to be of enormous technological importance.

SHG relies on the birefringence of crystals whose structure does not possess inversion symmetry [465]. Therefore, the induced field within an illuminated crystal causes asymmetric restoring forces on displaced electrons. When the crystal is oriented properly relative to the beam's polarization, so that phases can be matched, Fourier analysis shows that the wave propagating from the crystal can be expressed as the sum of three components:

- (1) A wave with the frequency of the incident wave,
- (2) A wave with a frequency twice that of the incident wave, and
- (3) A constant, or bias term (frequency = 0).

SHG is merely the simplest example of a phenomenon known as sum frequency generation. These are three wave processes, in which the participating waves must

conserve energy and momentum, and the sum of the frequencies of two of the waves equals that of the third. In SHG, two waves at ω_0 participate, and thus $\omega_1 = 2\omega_0$.

One of the simplifying assumptions typically made for the analysis of SHG is that the pump beam changes slowly. Such an assumption is inaccurate for high conversion efficiencies, and also for very fast pulses. In particular, when the pulse length is shorter than the crystal length – as is the case for this ablation experiment – nonlinearity induced varies as a function of position. As a result efficiency can be reduced. This is exacerbated when there is a significant velocity dispersion, and the fundamental and second harmonic pulses can separate. This separation would normally be expected to broaden the resultant pulse. If the group velocities are the same for both frequencies, then the upshifted pulse never is never influenced directly by the rapid spatial fluctuation of the pump pulse, and the stationary approximation can be used with caution.

The Lorentz–Lorenz Equation

Empirically, refractive index is known to vary with the density of a fluid medium. As noted elsewhere, this effect has been used to great advantage in numerous optical beam deflection experiments [15, 501, 502]. The most commonly used relation between the refractive index and fluid density is the Lorentz–Lorenz equation [373]:

$$\frac{1}{\rho} \left(\frac{n^2 - 1}{n^2 + 2} \right) = L(T) \quad (13)$$

In this equation, $L(T)$ is a weak function of temperature; for carbon dioxide under the conditions used in this thesis, $L(T) \approx 6.6$ [503]. This relation was published independently by both Lorentz and Lorenz in 1880, based on an analysis of the implications of Maxwell's equations for electrical fields oscillating at optical frequencies. Qualitatively, the incident optical field induces a dipole in the molecules of the material.

The index of refraction is a relative measure of the propagation speed of the wave, $n = c_0/c$, where the subscript 0 indicates the speed of light in a vacuum. Thus, consideration of the dimensional quantities in Maxwell's equations immediately leads to:

$$n^2 = \varepsilon \quad (14)$$

where ε is the permittivity of the material. Because of the random orientation of molecules in a liquid, spherical symmetry and an effective permittivity can be assumed. The reduction of the phase velocity due to these molecules is then assumed to be proportional to their number density. The combination of these two assumptions — effective spherical symmetry and linear density dependence — leads immediately to the Lorentz–Lorenz equation, equation 13.

Anomalous dispersion in metals

In real absorbing media, the refractive index assumes complex values to account for the reduction of energy as the beam propagates [216]. The complex index is then written as:

$$\tilde{n} = n + ik, \quad (15)$$

where n is the common index of refraction and k is the extinction coefficient. For metals and other conducting materials, the value of n is often less than unity. At first glance, this would appear to indicate superluminal velocities, but this is not the case. For these materials, the value of c implied by equation 14 is the phase velocity of the wave, which is not bound by relativistic concerns to be less than c_0 .