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Authors
Vogel, Alfred
Venugopalan, Vasan

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Kinetics of phase transitions in pulsed IR laser ablation of biological tissues

Alfred Vogel*[1], and Vasan Venugopalan[2]

1) Medizinisches Laserzentrum Lübeck, 23562 Lübeck, Germany
2) Department of Chemical Engineering and Materials Science and Laser Microbeam and Medical Program, Beckman Laser Institute, University of California, Irvine, USA

ABSTRACT

We review the mechanisms underlying material ejection in pulsed laser ablation of biological tissues, with special emphasis on the thermodynamics and kinetics of phase transitions and their modifications arising from the presence of a tissue matrix.

Key words: Pulsed laser tissue ablation, phase diagrams, surface vaporization, normal boiling, explosive boiling, phase explosion, vapor explosion, tissue matrix, stress confinement

1. INTRODUCTION

It is known that efficient laser ablation of biological tissues using pulsed IR laser irradiation is always associated with material ejection. Nevertheless, soft tissue ablation is mostly described as surface vaporization and/or normal boiling of the tissue, and until recently no systematic presentation of the mechanisms underling material ejection was available. This article summarizes part of a comprehensive analysis of the mechanisms of pulsed laser tissue ablation that was recently published by the authors[1] and adds new aspects related to nanosecond laser ablation using moderate and high radiant exposures. Special emphasis is laid on the thermodynamics and kinetics of phase transitions and their modifications arising from the presence of a tissue matrix. The results presented here will be used in two other articles of this proceedings volume to analyze the dynamics of free-running and Q-switched Er:YAG laser ablation, respectively.[2, 3]

In our analysis of phase transitions, tissue is viewed as material consisting of cells that reside in and attach to an extracellular matrix (ECM). In "cell-continuous" tissue such as liver and epithelia, the ECM fraction is quite small and consists mostly of cell adhesion proteins. By contrast, "matrix-continuous tissues" that include the corneal stroma, dermis, cartilage, and tendon have a very small cellular fraction and are almost entirely ECM. In matrix-continuous tissues, the ECM consists largely of collagen, with the collagen content being as high as 35%. Both cells and ECM contain large amounts of water that is the main chromophore for IR laser irradiation. Phase transitions of the tissue water are, in most cases, the driving force for IR laser ablation. However, these phase transitions are strongly modified by the ECM, depending on the mechanical strength of this matrix. The mechanical strength correlates positively with collagen content.

2. PHASE DIAGRAMS

The pressure vs. temperature projection of the phase diagram for liquid and gaseous water shown in Figure 1 and the pressure vs. specific volume projection of the thermodynamic phase diagram in Figure 2 will be used to discuss the kinetics of phase transitions. The solid curve *A-C* on Figure 1 represents those pressure/temperature pairs where liquid and gaseous water are in equilibrium with one another and is known as the "binodal". The curve *B-C-D* ("spinodal") denotes a locus of states representing the intrinsic stability limit of the liquid or vapor phase (i.e., $(\partial T/\partial s)_p = 0$ and $(\partial p/\partial v)_T = 0$). At the spinodal the superheated liquid phase or subcooled vapor phase is no longer stable with respect to the random density fluctuations that occur in all materials at nonzero temperatures. The region between the segment

* vogel@mll.mu-luebeck.de; phone: xx49-451-500-6504, fax: xx49-451-505 486; http://www.mll.mu-luebeck.de;
Medizinisches Laserzentrum Lübeck, Peter-Monnik-Weg 4, 23562 Lübeck, Germany.

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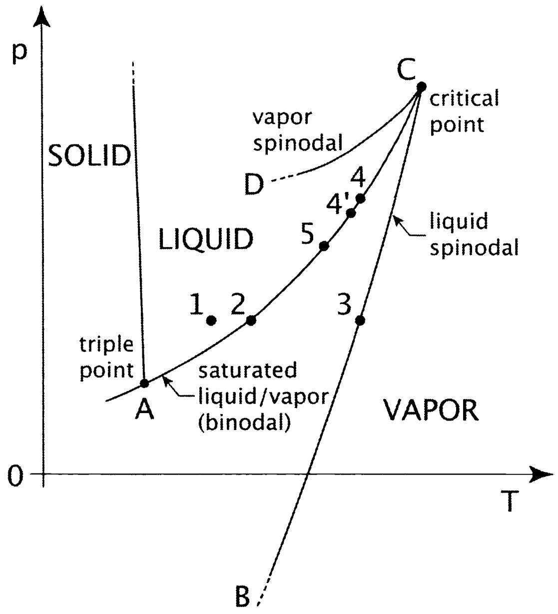

Fig. 1: Pressure vs temperature projection of the thermodynamic phase diagram including the stability limits (spinodal curves) for superheated liquid and subcooled vapor. Specific states of interest are (1) ambient temperature and pressure (25°C and 101 kPa), (2) boiling temperature under ambient pressure (100°C), (3) spinodal temperature under ambient pressure (305°C), and (4) saturated conditions corresponding to the ambient spinodal temperature (305°C and 9.2 Mpa). Points 4' and 5 serve to illustrate the process of a phase explosion and are explained in the text.

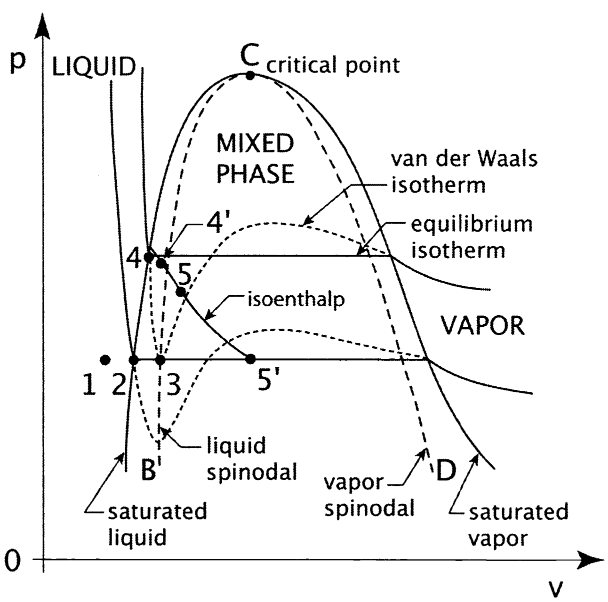

Fig. 2: Pressure vs specific volume projection of the thermodynamic phase diagram including the spinodal curve along with equilibrium and van der Waals isotherms. Points 1-5 correspond to those shown in Figure 1. The importance of the isoenthalp and of point 5' are explained in the text.

A-C of the binodal and *B-C* of the spinodal represents metastable states of the superheated liquid in which free surfaces or bubble nuclei are required to initiate vaporization. The binodal and spinodal curves intersect at the critical point *C* above which no thermodynamic distinction can be made between liquid and vapor phases.

In the *p-V* diagram in Figure 2, the liquid, vapor, and mixed phase regions are clearly demarcated. The boundary of the mixed phase region is the binodal, and the area it encloses specifies the range of specific volumes in which liquid and gaseous phases coexist for a given pressure and temperature. The apex of the binodal (point *C)* denotes the critical point which for water is located at T_c = 374.14 °C and p_c = 22.09 MPa. The dashed curve provides the spinodal where the segment *B-C* represents the stability limit of superheated liquid and segment *C-D* represents the stability limit of subcooled vapor.

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3. SURFACE VAPORIZATION

Equilibrium vaporization at a liquid-vapor interface is associated with an increase of specific volume at constant temperature that requires the latent heat of vaporization. This process is depicted as point on the binodal in the *p-T* diagram in Figure 1, and in the *p-V* diagram in Figure 2 it is represented by a path following an equilibrium isotherm from a state of saturated liquid to a state of saturated vapor. Equilibrium vaporization can occur when the liquid is in any thermodynamic state lying on the binodal. Thus vaporization does not occur at a pre-determined temperature and theoretical models that adopt a fixed "vaporization temperature"[4] violate the basic physics of the process.[5] The actual surface temperature is dictated by the vaporization rate required to equilibrate the rate of energy supplied to the system.

Enhanced rates of vapor formation from the free surface of a liquid are achieved at the start of pulsed laser when the vapor pressure above its surface has not yet reached the saturation vapor pressure corresponding to the surface temperature. This non-equilibrium condition results in an increased mass transfer from the liquid to the gaseous phase.[6, 7]

For laser parameters leading to efficient tissue ablation, surface vaporization cannot equilibrate the rate of energy supplied to the system, and ablation progresses via *volumetric* processes.

4. NORMAL BOILING

Normal boiling refers to a volumetric process that occurs at ambient pressure on the binodal as indicated by point 2 in Figures 1 and 2. Thus, for a given pressure within the liquid, the binodal defines the "boiling temperature." For water at atmospheric pressure, the boiling temperature is 100°C, but it is higher during an ablation process with a high rate of mass removal. The recoil pressure associated with mass removal increases the pressure at the target surface beyond the ambient pressure, and the corresponding boiling point exceeds 100°C.

Normal boiling relies on the presence of cavities of dissolved gas or other heterogeneities within the liquid that catalyze the nucleation and growth of vapor bubbles. The transition from saturated liquid to saturated vapor occurs in a finite layer of mixed phase at the sample surface. The thickness of this 'vapor-liquid' layer is comparable to the optical penetration depth of the incident radiation and its composition varies from that of saturated liquid at the base to saturated vapor at the surface. As a result, the surface temperature is fixed to the saturation conditions corresponding to the pressure at the target surface and there is no temperature gradient within the vapor-liquid layer.

When vaporization nuclei are present, the presence of volumetric energy densities infinitesimally higher than that corresponding to the saturation temperature immediately results in the growth of vapor bubbles. Thus the concept sometimes found in biomedical ablation papers that vaporization only occurs once the entire latent heat of vaporization is deposited is not correct. Nevertheless, normal boiling plays a negligible role for pulsed laser ablation because the high rates of energy deposition can only be balanced if the bubbles move to the target surface on a time scale set by the propagation velocity of the ablation front. Bubble diffusion must take place within a time span shorter than that during which the ablation front propagates through the original vapor-liquid layer. Miotello and Kelly[8] showed that this is not possible for irradiation of pure water with submicrosecond laser pulses. With microsecond pulses, it will be possible in pure water only for radiant exposures very close to the ablation threshold. In tissue, the mobility of vapor bubbles is further inhibited by the presence of the ECM, and boiling does hardly contribute to ablation.

We must conclude that surface vaporization and normal boiling alone cannot produce a phase transition sufficiently vigorous to constitute an efficient ablation process – in contrast to the assumptions made in many theoretical ablation studies. Efficient ablation is always accompanied by material ejection based on superheating of the target material followed by an explosive phase transition or phase separation.

5. PHASE EXPLOSIONS AND EXPLOSIVE BOILING

When the rate of volumetric energy deposition provided by laser radiation is more rapid than the rate of energy consumed by vaporization and normal boiling, the tissue water is driven to a metastable superheated state. The liquid can remain metastable until the spinodal limit (line B-C in Figure 1) is reached. At the spinodal limit, the liquid

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undergoes 'spinodal decomposition'; a spontaneous process by which an unstable liquid relaxes towards equilibrium by separating into a mixture of saturated vapor and saturated liquid.[9, 10] The spinodal temperature of water at atmospheric pressure is ≈305°C, and the corresponding saturation vapor pressure is 9.2 MPa. Thus spinodal decomposition involves an impressive pressure rise resulting in the violent emission of saturated liquid droplets by the expanding vapor.

For the phase diagram shown in Figure 1, the heating phase corresponds to the path 1→3, and the spinodal decomposition results in a nearly isochoric transition from point 3 on the spinodal to point 4' in the mixed phase region possessing the same enthalpy. In pure water and in mechanically weak tissues the thermodynamic state will during the explosive expansion of this mixture follow approximately the curve of constant enthalpy (isoenthalp) as shown on Figure 2 until it reaches atmospheric pressure at point 5'. During the expansion 4'→5', the temperature of the mixture drops to 100°C, and about half of the liquid is transformed into vapor. This fraction is related to the volumetric energy density of the superheated liquid at the spinodal limit that amounts to about half of the vaporization enthalpy of the entire liquid volume at atmospheric pressure.

To provide a complete description of the phase transformation process, we must also consider the contribution of homogenous nucleation as the liquid is heated to the spinodal limit. For a superheated liquid, "homogenous nucleation" refers to the spontaneous formation of vapor embryos in the bulk liquid that arise solely from thermodynamic fluctuations and is not catalyzed by the presence of impurities or dissolved gas. While the formation of vapor nuclei is spontaneous, their growth is not ensured and depends strongly on superheat temperature. Growth of the vapor bubbles requires energy to overcome the barrier posed by surface tension. Because surface tension disappears at the critical point, the energy barrier that must be overcome for the conversion from the liquid to vapor phase decreases when the temperature approaches the critical temperature. This is accompanied by a dramatic increase of the rate of homogeneous nucleation as shown in Figure 3.

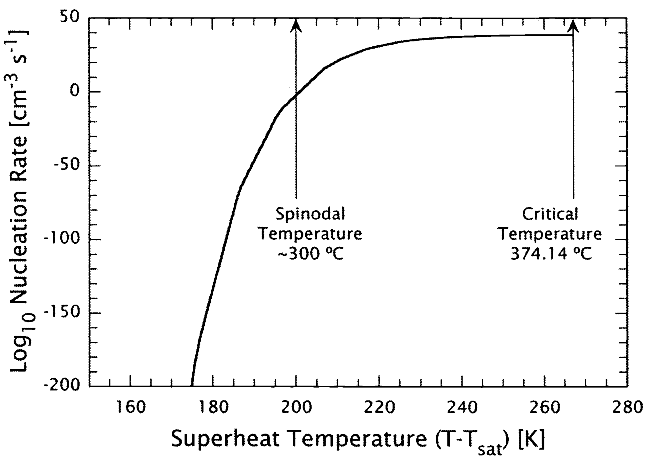

Fig. 3: Variation of homogeneous vapor bubble nucleation rate with superheat temperature.

The transformation of superheated liquid to an equilibrium state of mixed phase involves both bubble nucleation (formation of large density fluctuations of small spatial extent) and spinodal decomposition (rapid spontaneous growth of small density fluctuations that extend over large spatial scales). The collective phase transition process is commonly termed "phase explosion".

Thus far we have focused on processes tracing a path indicated by 1→3→4'→5→5' in Figures 1 and 2. This path corresponds to a case in which no vapor nuclei are present in the liquid and the heating occurs relatively slowly such that the pressure in the liquid remains near atmospheric pressure. When the heating occurs very rapidly, the liquid experiences a recoil pressure from surface vaporization that can be fairly high due to the nonequilibrium conditions at the beginning of the laser pulse (see section 3). Thus spinodal conditions are reached somewhere between point 3 and the critical point *C*. The resulting phase explosion occurs at elevated temperature and pressure but the pressure jump associated with the phase separation is less severe. The elevated temperature corresponds to a higher volumetric energy of the superheated liquid, and therefore more than half of the liquid will be transformed into vapor during the phase

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separation process. Cases where the recoil pressure is sufficiently strong to drive the liquid into a supercritical state are discussed in section 7.

When vapor nuclei are present in the liquid and the heating occurs on a time scale such that a significant fraction of the incident laser energy (but not the entire energy flux) contributes to the growth of heterogeneous and homogeneous vapor nuclei, the resulting process is again intermediate to the path 1→3→4 and normal boiling. The heating phase is accompanied by a finite pressure rise, and spinodal conditions are reached between point 3 and the critical point. Such intermediate processes are termed "explosive boiling."

Since in phase explosion and explosive boiling part of the target material is ejected in liquid phase, the latent heat of vaporization must not be supplied for the entire ablated mass. Therefore, the ablation efficiency (mass removed by a given amount of laser energy) is higher than in surface vaporization and normal boiling.

6. MODIFICATION OF PHASE TRANSITIONS BY THE TISSUE MATRIX

In pulsed laser ablation of tissues, the phase transition processes are altered by the presence of the ECM. For a boiling process within tissue, the vapor pressure necessary to drive bubble growth must not only exceed the hydrostatic pressure and the pressure due to surface tension but also overcome the elastic restoring forces in the tissue matrix. Therefore, bubble growth requires a higher internal pressure than in pure liquids, and the elevated pressure is coupled to an increase in the boiling (saturation) temperature. The pressure build-up that occurs during the boiling process continues until it exceeds the ultimate tensile strength of the ECM and results in explosive tissue ablation.[11] We term this process "confined boiling". On the *p-T* phase diagram in Figure 4, the confined boiling process corresponds to a path 1→2→6 that is coincident with the binodal and terminates where the saturated vapor pressure equals the ultimate tensile strength of the tissue. In the presence of a tissue matrix, explosive material ejection will thus occur regardless of the rate of energy deposition. Therefore, it is not surprising that explosive material ejection due to confined boiling has also been reported to occur in continuous wave laser ablation.[12, 13]

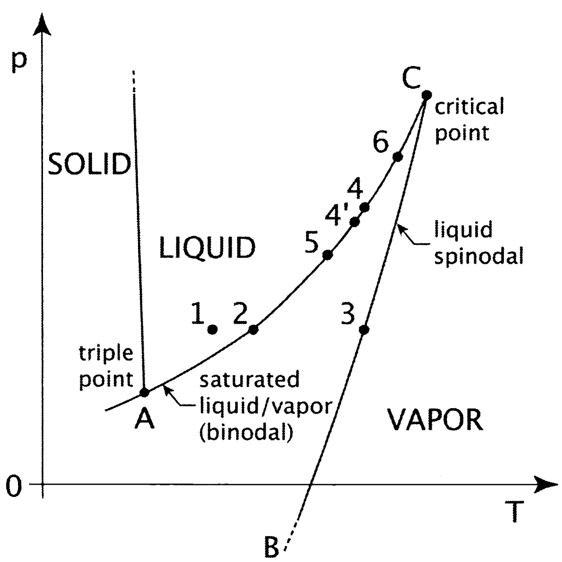

Fig. 4: Path taken through the *p-T* phase diagram for boiling confined by a tissue matrix (1→2→6) and for tissue ablation involving a phase explosion (1→2→3→4'→5 or 1→2→3→4'→5→6. The actual path followed depends on the rate of energy deposition, number density of heterogeneous nuclei, and the mechanical strength of the tissue matrix relative to the saturation vapor pressure corresponding to the ambient spinodal temperature).

In the above scenario, little vaporization occurs prior to the onset of ablation because of the impediment of bubble growth by the tissue matrix. For mechanically weak tissues, the ablation enthalpy can thus be considerably smaller than the vaporization enthalpy of water. However, for tissues containing a strong matrix, such as skin, temperatures of 400°C to 700°C are required to produce a saturation vapor pressure equaling the ultimate tensile strength of the tissue and to initiate ablation.[14] Under these conditions, the ablation enthalpy becomes comparable to or exceeds the vaporization enthalpy of water.

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The tissue matrix probably remains mechanically largely intact even for a temperature rise of several hundred degrees during a nanosecond or microsecond laser exposure because the temperatures required to disintegrate the matrix increase strongly with decreasing duration of the heat exposure. Moreover, it is known that the application of tensile stresses to collagen fibrils stabilizes the helical architecture and results in a significant increase in the denaturation temperature. Thus the generation of tensile stresses resulting from pulsed laser heating is expected to further stabilize a collagen ECM with respect to possible collagen denaturation. In fact, the ultimate tensile strength of the tissue matrix is likely higher in pulsed laser ablation than literature values for native tissues because those values have been acquired at slow strain rates while during a pulsed laser ablation process tissue is subjected to enormously high strain rates; on the order of 10^5-10^7 s^{-1}. Available data on the variation of UTS with strain rate over the range 0.3-170 s^{-1} demonstrate that the UTS increases in proportion to the logarithm of the strain rate.[15, 16]

For cases in which the rate of volumetric energy deposition is slow and the number density of heterogeneous nuclei is high, the nature of the ablation process is largely independent of the mechanical tissue properties. The tissue will initially be heated under equilibrium conditions at constant pressure (1→2) and then continue on the binodal until the ultimate tensile strength of the tissue is reached and results in explosive material removal. However if the tissue is heated rapidly and/or a small number density of heterogeneous nuclei are present, the tissue water will be driven into a metastable state and a phase explosion will be induced when the spinodal limit is reached (1→2→3→4'→5). The continuation of the process now depends on the mechanical properties of the tissue. Ablation will result for tissues that are unable to withstand the stresses and deformations associated with the phase explosion. However, for tissues possessing high collagen content, the tensile strength of the tissue matrix is higher than the stresses resulting from the phase explosion. In this case the process continues as confined boiling (5→6) as indicated in Figure 4 until the tissue ruptures at higher vapor pressures resulting in material removal. For the ablation of skin surface temperatures of 400-750°C have been measured[14] indicating that the dynamic tensile strength of the tissue matrix is higher than the pressure at the critical point.

7. VAPOR EXPLOSION AND PHOTOTHERMAL DISSOCIATION OF THE TISSUE MATRIX

When nanosecond laser pulses are used for ablation, volumetric energy densities may be achieved in the tissue water that exceed the vaporization enthalpy of water at constant pressure. Under these conditions, the liquid water is completely transformed into vapor in a process termed "vapor explosion." Moreover, at temperatures exceeding 1000 °C the constituent molecules of the ECM can be thermally dissociated into volatile fragments. Energetically, these processes are not as favorable as a phase explosion or confined boiling because they do not involve the ejection of condensed material. Therefore, the corresponding ablation enthalpy is higher than the vaporization enthalpy of water. More details about the ablation efficiency as a function of radiant exposure can be found in section VII of Ref. [1].

An important factor contributing to the high volumetric energy densities achieved in nanosecond laser ablation is the recoil pressure produced by rapid non-equilibrium surface vaporization at the beginning of the laser pulse (see section 3). The recoil pressure prevents ablation of deeper tissue layers until the volumetric energy density is sufficiently high to result in a phase transition that can overcome the recoil pressure. When the recoil pressure is sufficiently high, it can drive the thermodynamic state of the tissue water into the supercritical regime because energy dissipation by phase explosion or explosive boiling is largely suppressed.[17] The phase transition of subsurface tissue layers will due to the larger volumetric energy density be more vigorous than the initial surface vaporization and produce a higher recoil pressure that impedes ablation in deeper tissue layers until even higher volumetric energy densities are reached. At any given depth and time, ablation starts as soon as the vapor pressure exceeds the recoil pressure resulting from the explosive removal of more superficial layers. The volumetric energy density and pressure values corresponding to the onset of ablation increase as long as the laser irradiance increases. After the intensity peak of the laser pulse has been reached, the volumetric energy density and pressure at the target surface will decrease while the ablation front continues to propagate into the target. Because the evolution of thermodynamic states within the target is determined both by the incident laser irradiation and by hydrodynamic phenomena arising from the ablation plume, ablation may continue well beyond the end of the laser pulse.[1, 3] When the volumetric energy density in the target drops below the value required to produce thermal dissociation of the tissue matrix, the ejection of particulate tissue fragments sets in.[3] When the energy density becomes smaller than the vaporization enthalpy of water, the superheated tissue water starts to decompose into

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saturated vapor and liquid in a phase explosion, and the ejected material is composed of tissue fragments and liquid droplets.[3] Ablation ceases when the vapor pressure falls below the value corresponding to the ultimate tensile strength of the tissue matrix.

When the radiant exposure is sufficiently high for plasma production in front of the target, the pressure within the plasma will enhance and prolong the action of the recoil pressure.[18] This will further delay the ejection of particulate tissue fragments.

The explosive character of nanosecond laser ablation and the fact that particulate ejecta are observed only late during the laser pulse or after the end of the pulse have suggested a description of nanosecond ablation as "blow-off" process.[1] In this model it is assumed that material removal commences only after the end of the laser pulse when the entire optical energy has been deposited into the target. Moreover, it is assumed that ablation occurs everywhere simultaneously and in the same way. The wide acceptance of this simple heuristic model has, unfortunately, inhibited researchers from developing mechanistic models that would provide a description of the complex dynamics during nanosecond laser ablation of biological tissues at moderate and high radiant exposures.

8. ABLATION UNDER STRESS CONFINEMENT

Rapid heating of tissue by pulsed laser radiation leads to a thermoelastic expansion of the heated tissue volume, and thus to the generation of thermoelastic stress. Thermoelastic stresses are most prominent when the laser pulse duration is shorter than the time required for the stress wave to propagate across the heated volume during the pulse ("stress confinement"). While thermal expansion of a heated volume results in the generation of compressive stresses, the resulting stress wave propagation results in transients that contain both compressive and tensile components. Tensile stresses arise from the reflection of the compressive stress waves at a boundary to a medium with lower acoustic impedance (tissue- air, tissue-water) or from the three-dimensional characteristics of acoustic wave propagation. Conservation of momentum demands that the stress transient emitted from a heated tissue volume of finite size must contain both compressive and tensile components such that the integral of the stress over time vanishes.[1, 19]

The tensile thermoelastic stress waves can for liquids with heterogeneous vapor/cavitation nuclei and for mechanically weak tissues such as liver produce material ejection at temperatures less than 100°C. This phenomenon is known as "spallation" and has been investigated in numerous studies. Nevertheless, it plays very little role in tissue ablation because usually temperatures above 100 °C are necessary to initiate efficient tissue removal. The important influence of tensile stress waves at temperatures above 100 °C has only recently attracted attention.[1, 19] Figure 5 shows the path

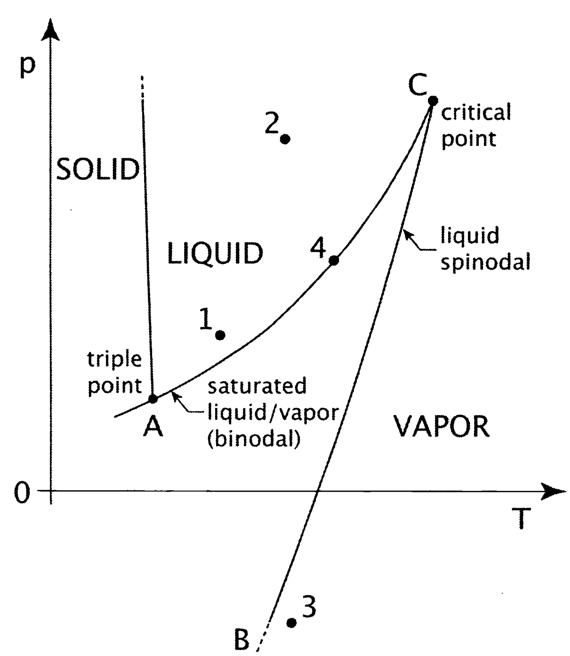

Fig. 5: Path taken through the *p-T* phase diagram for a temperature rise above 100 °C under stress confinement conditions. The transition 1→2 corresponds to the heating phase that is coupled with the generation of compressive stress. The transition 2→3 corresponds to the passage of the tensile stress wave that leads to a crossing of the spinodal limit, resulting in phase separation. After the passage of the stress wave, the system reaches point 4 that corresponds to explosive boiling into the large number of bubbles produced shortly before.

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taken through the *p-T* phase diagram for a temperature rise above 100 °C under stress confinement conditions. A heating phase (1→2) that is coupled with the generation of compressive stress is followed by the passage of a tensile stress wave (2→3) that leads to a crossing of the spinodal limit, resulting in phase separation. The passage of the stress wave is followed by explosive boiling into the large number of bubbles produced shortly before (point 4) resulting in vigorous material ejection. This ejection occurs at temperatures far below the spinodal limit at atmospheric pressure (305°C) that must be exceeded in ablation without stress confinement to produce a similar effect (see sections 5 and 6).

At volumetric energy densities exceeding the spinodal limit, triggering of explosive boiling is not an issue any more. However, in this regime the thermoelastic stresses may reach values where the compressive stress wave evolves into a shock wave. Shock wave propagation together with the energy dissipation at the shock front serves as a form of convective heat transport[18, 20, 21] that may extend the ablated volume beyond the range that can be achieved by radiative energy transport into the tissue and heat diffusion (heat diffusion plays hardly any role in stress confined tissue ablation). In the volume heated by energy dissipation at the shock front, the interplay of compressive and tensile stress in the thermoelastic transients may again serve to enhance ablation.

The amplitude of thermoelastic transients produced by a given temperature rise under conditions of stress-confinement is much larger than the saturation vapor pressure resulting from the same temperature rise. Stress confinement thus results in a considerable lowering of the ablation threshold. This holds not only for the "spallation" regime but also for T > 100 °C where the tensile stresses support the ablation process both by direct tissue rupture and by triggering an explosive boiling process. For temperatures above the spinodal limit, an extension of the ablation depth by thermoelastically produced convective heat transfer into the tissue will also increase the ablation efficiency.

9. CONCLUSIONS

The kinetics of phase transitions in the field of pulsed laser ablation of biological tissues is much more complex than previously assumed, and theoretical descriptions for important aspects of the ablation process and relevant parameter regimes are still lacking. This is a hindrance for the optimization of biomedical applications, and a challenge for future research.

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