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**Fourier's Heat Conduction Equation:
History, Influence, and Connections**

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FOURIER'S HEAT CONDUCTION EQUATION: HISTORY, INFLUENCE, AND CONNECTIONS

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ABSTRACT

The equation describing the conduction of heat in solids has, over the past two centuries, proved to be a very powerful tool for analyzing the dynamic motion of heat as well as for solving an enormous array of diffusion-type problems in physical sciences, biological sciences, earth sciences, and social sciences. This equation was formulated at the beginning of the nineteenth century by one of the most gifted scholars of modern science, Joseph Fourier of France. A study of the historical context in which Fourier made his remarkable contribution and the subsequent impact his work has had in the development of modern science is as fascinating as it is educational. This paper is an attempt to present a picture of how certain ideas initially led to the development of the heat equation by Fourier and how, subsequently, Fourier's work directly influenced and inspired others to use the heat diffusion model to describe other dynamic physical systems. Conversely, others concerned with the study of random processes, found that the equations governing such random processes reduced, in the limit, to Fourier's equation of heat diffusion. In the process of developing the flow of ideas, the paper also presents, to the extent possible, an account of the history and personalities involved.

INTRODUCTION

The equation describing the conduction of heat in solids occupies a unique position in modern mathematical physics. In addition to lying at the core of analyzing problems involving the dynamic transfer of heat in physical systems, the conceptual-mathematical structure of the heat conduction equation (also known as heat diffusion equation) has inspired the mathematical formulation of many other physical processes in terms of diffusion. As a consequence, the mathematics of diffusion has helped the transfer of knowledge relating to problem solving among diverse, seemingly unconnected disciplines. The transient process of heat conduction is described by a partial differential equation, familiarly referred to as a parabolic equation, which was first formulated by Jean Baptiste Joseph Fourier (1768-1830) in 1807 and presented as a manuscript to the Institut de France. At the time this manuscript was prepared, thermodynamics, potential theory, and differential equations were all in the initial stages of their formulation. Combining remarkable gifts in pure mathematics and insights into observational physics, Fourier opened up new areas of investigation in mathematical physics with his masterpiece, *Théorie de la propagation de la Chaleur dans les Solides* (Fourier, 1807).

Fourier's work was subjected to review by some of the most distinguished scientists of the time. However, it was not accepted as readily as one might have expected. It would be another fifteen years before this major contribution would be accessible to the general scientific community through publication of his classic monograph, *Théorie analytique de la Chaleur* (Fourier, 1822). Soon after this publication, the power and significance of Fourier's work was recognized outside of France. Fourier's method began to be applied to analyze problems in many fields besides heat transfer: electricity, chemical diffusion, fluids in porous media, genetics, and economics. It also inspired a great deal of research into the theory of differential equations. Nearly two centuries later, the heat conduction equation continues to constitute the conceptual foundation on which rest the analysis of many physical, biological, and social systems.

A study of the conditions that led to the articulation of the heat conduction equation and the reasons why that equation has had such a major influence on scientific thought over nearly two centuries is in itself very rewarding. At the same time, an examination of how the work was received and accepted by Fourier's peers and successors gives us a fascinating glimpse into the culture of science, especially as it prevailed during the nineteenth century in Europe. The present work has been

motivated both by the educational and historical importance of Fourier's work. Accordingly, the purpose of this paper is to explore how the framework of the heat conduction equation has come to help us understand an impressive array of seemingly disconnected natural processes. In so doing, the purpose also is to gain historical insights into the manner in which scientific ideas develop.

The paper starts with pertinent scientific developments during the eighteenth century that set the stage for Fourier's work on heat conduction. Following this, details are presented of Fourier himself and his contribution, especially the 1807 manuscript. Fourier's influence has occurred along two lines. Experimentalists in electricity, chemical diffusion and fluid flow in porous materials directly derived benefit by interpreting their experiments by analogy with the heat conduction phenomenon. Researchers in other fields such as statistical mechanics and probability theory indirectly established connections with the heat conduction equation by recognizing the similarities between the mathematical behavior of their systems and mathematical solutions of the heat conduction equation. These direct and indirect influences of Fourier's work are described next. The paper concludes with some reflections on the scientific atmosphere during the early nineteenth century, a comparison of the different facets of diffusion and a look beyond Fourier's solution strategy. A chronology of the important developments is presented in Table 1.

DEVELOPMENTS LEADING UP TO FOURIER

Before we describe the scientific developments of the eighteenth century that set the stage for Fourier's contribution, it is pertinent to briefly state the nature and content of the heat conduction process. The transient heat conduction phenomenon as embodied in Fourier's partial differential equation pertains to the conductive transport and storage of heat in a solid body. The body itself, of finite shape and size (e.g., a rod, a cylindrical annulus, a sphere, a cube), communicates with the external world by exchanging heat across its boundary. Within the solid body, heat manifests itself in the form of temperature, which can be measured accurately. Under these conditions, Fourier's differential equation mathematically describes the rate at which temperature is changing at any location in the *interior* of the solid as a function of time. Physically, the equation describes the conservation of heat energy per unit volume over an infinitesimally small volume of the solid centered at the point of interest. Crucial to such conservation of heat is the recognition that heat continuously

TABLE 1: A CHRONOLOGY OF SIGNIFICANT CONTRIBUTIONS ON DIFFUSION

Fahrenheit	1724	Mercury thermometer and standardized temperature scale
Abbé Nollet	1752	Observation of osmosis across animal membrane
Bernoulli	1752	Use of trigonometric series for solving differential equation
Black	1760	Recognition of latent heat and specific heat
Crawford	1779	Correlation between respiration of animals and their body heat
Lavoisier and Laplace	1783	First calorimeter; measurement of heat capacity, latent heat
Laplace	1789	Formulation of Laplace operator
Biot	1804	Heat conduction among discontinuous bodies
Fourier	1807	Partial differential equation for transient heat conduction in solids
Fourier	1822	Théorie Analytique de la Chaleur
Ohm	1827	Law governing current flow in electrical conductors
Dutrochet	1827	Discovery of endosmosis and exosmosis
Green	1828	Formal definition of a potential
Graham	1833	Law governing diffusion of gases
Thompson	1842	Similarities between equations of heat diffusion and electrostatics
Poiseuille	1846	Experimental studies on water flow through capillaries
Graham	1850	Experimental studies on diffusion in liquids
Fick	1855	Fourier's model applied to molecular diffusion
Darcy	1856	Law governing flow of water in porous media
Dupuit	1863	Potential theory applied to flow of groundwater in geological basins
Maxwell	1867	Diffusion equation for gases derived from dynamical theory
Pfeffer	1877	Investigations on osmosis in biological and inorganic membranes
Edgeworth	1883	Law of error and Fourier equation
Forchheimer	1886	Flownets for solving seepage problems using potential theory
van't Hoff	1887	Theory of osmotic pressure by analogy with gas laws
Nernst	1888	Interpretation of Fick's law in terms of forces and resistances
Lord Rayleigh	1894	Random mixing of sound waves as a diffusion process
Roberts-Austen	1896	Experimental measurement of solid diffusion
Bachelier	1900	Option pricing and diffusion of probability
Einstein	1905	Brownian motion and diffusion equation
Pearson	1905	The notion of random walk
Pearson	1906	Random migration of animals as a diffusion problem
Buckingham	1907	Diffusion of multiple fluid phases in soils
Langevin	1908	Framework for stochastic differential equation
Gardner	1922	Measurement of potential in a multi-fluid-phase porous medium
Fisher	1923	Inheritance of genes as a diffusion problem
Terzaghi	1924	Transient seepage in deformable clays as analogous to heat diffusion
Richards	1931	Non-linear diffusion of moisture in soils
Fermi	1936	Neutron diffusion in graphite as analogous to heat diffusion
Kolmogorov	1937	Traveling wave solution to non-linear diffusion
Chandrasekhar	1943	Generalization of Lord Rayleigh's stochastic differential equations
Taylor	1953	Advective dispersion as a diffusion process
Samuelson	1965	Warrant pricing and diffusion equation
Merton	1973	Stochastic calculus and theory of option pricing

moves across the surfaces bounding the infinitesimal element as dictated by the variation of temperature from place to place within the solid and that the change in temperature at a point reflects the change in the quantity of heat stored in the vicinity of the point.

It is clear from the above that the notions of temperature, quantity of heat, the relation between quantity of heat and temperature, and the notion of transport of heat are fundamental to the formulation of Fourier's equation. It is important to recognize here that these basic notions were still evolving at the end of the eighteenth century. Therefore, it is appropriate for us to begin by familiarizing ourselves with the evolution of these notions during the eighteenth century.

Since heat can be readily observed and measured only in terms of temperature, the development of a reliable thermometer capable of giving repeatable measurements was critical to the growth of the science of heat. Gabriel Daniel Fahrenheit (1686-1736), a German instrument maker and physicist, perfected the closed-tube mercury thermometer in 1714 and commercially produced them by 1717 (Middleton, 1966). By 1724 he had established what we now know as the Fahrenheit scale with the melting of ice at 32° and the boiling of water at 212° . Fahrenheit succeeded in calibrating his instruments carefully so that measurements were accurate and reliable.

The next developments of interest were qualitative and conceptual, and of great importance. Joseph Black (1728-1799), a pioneer in quantitative chemistry, was known for his lectures in chemistry at Glasgow and was also a practicing physician. Around 1760 he noticed that when ice melts it takes in heat without changing temperature. This observation led him to propose the term "latent heat" to denote the heat taken up by water as it changes its state from solid to liquid. He also noticed that equal masses of different substances needed different amounts of heat to raise their temperatures by the same amount. He coined the term "specific heat" to denote this type of heat. Although Black is said to have constructed an ice calorimeter, he never published his results. The precise measurement of latent heat and specific heat was left to Lavoisier and Laplace, some twenty years later. Another important development was the appearance of the book *Experiments and Observations of Animal Heat, and the Inflammation of Combustible Bodies* by Adair Crawford (1748-1795) in 1779. In this work, Crawford proposed that oxygen was involved in the generation of heat by animals during respiration and went on to discuss a method of measuring specific heat by a method of mixtures (Guerlac, 1982). Crawford's idea of measuring specific heat by the method of

mixtures would soon have a significant influence on Lavoisier and Laplace, although he himself was unable to measure these quantities accurately.

In the wake of the contributions of Black and Crawford, what must be considered as one of the most important papers of modern chemistry and thermodynamics appeared in 1783. This was the paper entitled *Mémoire sur la Chaleur* coauthored by Antoine Laurent Lavoisier (1743-1794), the central figure of the revolution in chemistry of the later eighteenth century, and Pierre Simon Laplace (1749-1827), one of the most influential mathematician and theoretical physicists of modern science. This paper provided detailed descriptions of an ice calorimeter with which they measured, for the first time, the latent heat of melting of ice and the specific heats of different materials. All the measurements were made relative to water, the chosen reference. They also showed experimentally that heat is released during respiration of animals, by placing a guinea pig within the calorimeter for several hours and measuring the quantity of ice melted. In a related set of experiments, they also demonstrated quantitatively that the process of respiration, in which oxygen is combined with carbon in the animal's body, is in fact combustion, resulting in the release of heat. During the late nineteenth century when this work was done, the nature of heat was still a matter of debate among scientists. Some believed that heat was a fluid diffused within the body (referred to as "caloric") while others believed that heat was a manifestation of vibrations or motions of molecules. Although Lavoisier and Laplace preferred the latter concept, they interpreted and presented their results in such a way that the experiments stood by themselves, independent of any hypothesis concerning the nature of heat. In so far as Fourier's heat conduction equation is concerned, the significance of the Lavoisier-Laplace work is that it provided the notion of specific heat, which is fundamental to the understanding of time-dependent changes of temperature. Nonetheless, the significance of the work far transcends Fourier's equation. By experimentally quantifying latent heat and heats of reactions, the Lavoisier-Laplace work constitutes an essential component of the foundations of thermodynamics.

We now consider the process of transfer of heat in solids, that is, the process of heat conduction. The best known work in this regard is that of Jean Baptiste Biot (1774-1862), a versatile scientist who made important contributions in magnetism, optics, and celestial mechanics. Biot (1804) addressed the problem of heat conduction in a thin bar heated at one end (Grattan-Guinness, 1972). In the bar, heat was not only conducted along the length but it was also lost to the exterior

atmosphere transverse to the direction of conduction. His starting point to analyze this problem was Newton's law of cooling, according to which the rate at which a body loses heat to its surroundings is proportional to the difference in temperature between the bar and the exterior atmosphere. Biot, who was a student of Laplace's mechanistic school, believed in the philosophy of action at a distance between bodies. Accordingly, the temperature at a point in the heated rod was perceived to be influenced by all the points in the vicinity of the point. Essentially then, the mathematical problem of heat conduction came to be considered as one of a class of many-body problems. As pointed out by Grattan-Guinness (1972), Biot's idealization of action at a distance involved only the difference in temperature between points and did not involve the distance between the points. As a consequence, Biot's approach did not involve a temperature gradient, so necessary to the formulation of the differential equation. However, Biot did articulate the underlying concepts clearly by stating that when the heat content of the bar changes at each instant, the net accumulation of heat at a point causes a change in temperature. Biot also asserted that he experimentally found Newton's law concerning the loss of heat to be rigorous. It is not quite clear how Biot chose to work on the heat conduction problem. A footnote in his paper refers to earlier experiments of Count Rumford, but no other details are given.

Apart from these foundational developments pertaining to heat, two other major topics of the eighteenth century are pertinent to Fourier's work: potential theory and differential equations. The theory of potentials arises in many branches of science such as electrostatics, magnetostatics, irrotational movement of perfect fluids, and so on. Potential theory involves problems describable in terms of a partial differential equation in which the dependent variable is the appropriate potential (defined as energy per unit mass, charge, etc.) and the sum of the second spatial derivatives of the potential in three principal directions is equal to zero. This equation was first formulated by Laplace in 1789, although the term potential would be coined later by George Green (1793-1841), a self-educated mathematician, in a classic essay on electricity and magnetism (Green, 1828). Laplace formulated the equation in the context of the problem of the stability of Saturn's rings (Laplace, 1789). The mathematical operator denoting the sum of the second spatial derivatives of the potential is therefore known as the Laplacian and the equation itself is known as Laplace's equation in his honor.

The eighteenth century also saw very active developments in the theory of ordinary and partial differential equations through the contributions of Daniel Bernoulli (1700-1782), Jean le Rond d'Alembert (1717-1783), Leonhard Euler (1707-1783), John-Louis Lagrange (1736-1813), and others. For the partial differential equation describing a vibrating string, Daniel Bernoulli had suggested, on physical grounds, a solution in terms of trigonometric series. Similar usage of trigonometric series was also made a little later by Euler and Lagrange. Yet, d'Alembert, Euler, and Lagrange were not particularly satisfied with the trigonometric series. Their concerns were purely mathematical in nature, consisting of issues of convergence and algebraic periodicity of such series (Grattan-Guinness, 1972).

It is pertinent here to dwell a little on the atmosphere of scientific philosophy that existed in Europe at the turn of the nineteenth century. Two views of the physical world prevailed at the time: the mechanistic school of Isaac Newton (1642-1727) and the dynamic school of Gottfried Wilhelm Leibniz (1646-1716). During the eighteenth and nineteenth centuries, a number of the most gifted thinkers from France were fully committed to the mechanistic view and devoted their efforts to describing the physical world with grater and greater detail in terms of Newton's laws. At the same time, his contemporary Leibniz also had a major influence on the development of scientific thought. At the foundation of physics were the notions of force, momentum, work and action. Although these notions are all related, Newton and Leibniz pursued two parallel, but distinct avenues to understanding the physical world. Newton's approach was based on the premise that by knowing the forces and momenta at every point or particle, one could completely describe a physical system. Leibniz, on the other hand pursued the approach of understanding the total system in terms of work and action. One of the leading figures of Newton's mechanistic school was Laplace. Laplace, in turn, had many ardent followers, including Biot and Poisson. Among those who followed Leibniz's philosophy were Lagrange, Euler and Hamilton. Although, ultimately, both approaches proved equivalent, the mathematics associated with them are very different. While the mechanistic school relied on the use of vector fields to describe the physical system, the dynamic school of Leibniz could, remarkably, realize the same results through the use of energy and action, which are scalar quantities. Additionally, the thinking of the mathematical physicists of the late eighteenth century was also influenced by their intense interest in celestial mechanics, a field which had greatly captivated Galileo,

Newton and Kepler.

It was under these circumstances that observational data on heat, electricity, chemical reactions, and physiology of animals were being collected and great efforts were being made to rationally understand them in terms of force, momentum, energy and work. As should be expected, opposing views were pursued and tested before concepts and ideas could evolve into forms that we now take for granted. When Fourier commenced his work on heat conduction at the turn of the nineteenth century, the nature of heat was still unresolved. Those of the mechanistic school, including Biot, believed that heat was a permeating fluid. On the other hand, those of the dynamic school believed that heat was essentially motion, rapid molecular vibrations. Those of the mechanistic school also believed that a cogent theory of heat should be rigorously built from a detailed description of motion at the level of individual particles. This approach, it appears, governed the work of Biot (1804) and his use of action at a distance.

FOURIER'S CONTRIBUTION

As we have seen, the science of heat, the theory of potentials and the theory of differential equations were all in their early stages of development by the time Fourier started his work on heat conduction. Opinions were still divided about the nature of heat: whether it was an all-pervading fluid or it was related to molecular motion. However, heat conduction due to temperature differences and heat storage and the associated specific heat of materials had been experimentally established. Potential theory had already been formulated, and both the Laplace equation and the Laplace operator were well established. Finally, the representation of dynamic problems in continuous media with the help of partial differential equations (e.g., the problem of a vibrating string) and their solution with the help of trigonometric series were also known. This is the context in which Fourier began working on the transient heat conduction problem.

Fourier's life and contributions are so unusual that a brief sketch of his career and the conditions under which he worked are very worthwhile. For a comprehensive account, the reader is referred to Grattan-Guinness (1972). Joseph Fourier was born in 1768 in Auxerre in Burgundy, now the capital of Yonne Département in central France. In 1789, about the time his mathematical talents began to blossom, the French Revolution intervened. In his native Auxerre he was socially

and politically active, being a forceful orator. His outspoken criticism of corruption almost took him to the guillotine in 1794; he was saved mainly by the public outcry in the town and a deputation of local people on his behalf. Following this he taught mathematics for a few years at the Ecole Polytechnique in Paris. In 1798, Napoleon Bonaparte (1769-1821) was leading an expedition to Egypt and Fourier was made Secrétaire Perpétuel of the newly formed Institut d'Egypte. In Egypt he held many important administrative and judicial positions, and in 1799 was made leader of a scientific expedition investigating monuments and inscriptions in Upper Egypt. In November 1801 Fourier returned to France upon the withdrawal of French forces from Egypt. However, his hopes for resuming his teaching duties at Ecole Polytechnique were ended when Bonaparte made him Prefect of the Département of Isère near the Italian border, with its capital at Grenoble.

During his tenure as Prefect, a demanding job that lasted many years, Fourier embarked on two very different major scholarly efforts. On the one hand he started his leadership role on a multi-volume work on Egypt, which would later form the foundation for the science of Egyptology. On the other, he began working on the problem of heat diffusion. It appears that Fourier started work on heat conduction sometime between 1802 and 1804 (Grattan-Guinness, 1972), probably for no other reason than that he saw it as one of the unsolved problems of his time. Between 1802 and 1807, he conducted his researches into Egyptology and heat diffusion whenever he could find spare time from his prefectural duties.

Just as Biot before him, Fourier initially formulated the heat conduction problem as an n-body problem, stemming from the Laplacian philosophy of action at a distance. During this early investigations, he was aware of Biot's work, having received a copy of Biot's paper from the author himself. For some reason that is not quite clear, Fourier abandoned the action at a distance approach around 1804 and made a bold departure from convention, which eventually led to his masterpiece, the transient heat conduction equation.

Essentially, what Fourier did was to move away from discontinuous bodies and towards continuous bodies. Instead of starting with the basic equations of action at distance, Fourier took an empirical, observational approach to idealize how matter behaved macroscopically. In this way he also avoided discussion of the nature of heat. His observational approach (like that of Lavoisier and Laplace before him), was independent of what the fundamental nature of heat was. Rather than

assuming that the behavior of temperature at a point was influenced by all points in its vicinity, Fourier assumed that the temperature in an infinitesimal lamina or element was dependent only on the conditions at the lamina or element immediately upstream and downstream of it. He thus formulated the heat diffusion problem in a continuum.

In formulating heat conduction in terms of a partial differential equation and developing the methods for solving the equation, Fourier initiated many innovations. He visualized the problem in terms of three components: heat transport in space, heat storage within a small element of the solid, and boundary conditions. The differential equation itself pertained only to the interior of the flow domain. The interaction of the interior with the exterior across the boundary was handled in terms of "boundary conditions", conditions assumed to be known a priori. The parabolic equation devised by Fourier was a linear equation in which the parameters, conductivity and capacitance were independent of time or temperature. This attribute of linearity enabled Fourier to draw upon the powerful concept of superposition to combine many particular solutions and thereby create general solutions (Grattan-Guinness, 1972). The superposition artifice offered such promise in solving problems that mathematicians who followed Fourier resorted to linearizing differential equations so as to facilitate their subsequent solution.

Perhaps the most powerful and most daunting aspect of Fourier's work was the method of solution. Fourier was clearly aware of the earlier work of Bernoulli, Euler, and Lagrange relating to solutions in the form of trigonometric series. He was also aware that Euler, D'Alembert and Lagrange viewed trigonometric series with great suspicion. Their opposition to the trigonometric series stemmed from reasons of pure mathematics: convergence and algebraic periodicity. Lagrange, in fact had a particular preference for solutions expressed in the form of Taylor series (Grattan-Guinness, 1972). Yet, Fourier, who was addressing a well-defined physical problem with physically realistic solutions, did not allow himself to be held back by the concerns of his illustrious predecessors. He boldly applied the method of separation of variables and generated solutions in terms of infinite trigonometric series. Later, he would also generate solutions in the form of integrals that would come to be known as Fourier integrals. In the last part of his 1807 work, Fourier also presented some results pertaining to heat conduction in a cylindrical annulus, a sphere and a cube.

Fourier submitted his manuscript to the French Academy in December 1807. As was the

practice, the secretary of the Academy appointed a committee of reviewers consisting of four of the most renowned mathematicians of the time, Laplace, Lagrange, Monge, and Lacroix. The manuscript was not well received, particularly by Laplace and Lagrange, for the mathematical reasons alluded to above. Although Laplace would later become sympathetic to Fourier's method, Lagrange would never change his mind. Because of the lack of approval by his peers, the possible publication of Fourier's work by the French Academy was getting delayed indefinitely. In the end, Fourier took it upon himself to expand the work and publish it on his own in 1822 under the title, *Théorie Analytique de la Chaleur*, which is now an avowed classic.

THE HEAT CONDUCTION EQUATION

It is appropriate to introduce here the transient heat conduction equation of Fourier. In modern notation, this parabolic partial differential equation may be written as,

$$(1) \quad \nabla \cdot K \nabla T = c \frac{\partial T}{\partial t} ,$$

where K is thermal conductivity, T is temperature, c is specific heat capacity of the solid per unit volume and t is time. The dependent variable T is a scalar potential while thermal conductivity and specific heat capacity are empirical parameters. Physically, the equation expresses the conservation of heat per unit volume over an infinitesimally small volume lying in the interior of the flow domain. The exchange of heat with the external world is to be taken into account with the help of either temperature or thermal fluxes prescribed on the boundary. Also, it is assumed that the distribution of temperature over the domain is known at the initial time $t = 0$.

For the particular case when the temperature over the flow domain does not change with time and is steady, (1) reduces to the Laplace equation,

$$(2) \quad \nabla \cdot K \nabla T = 0 .$$

The left hand sides of (1) and (2) are the Laplacian or the Laplace operator referred to earlier.

It is appropriate here to pay attention to the physical parameters of the above equations. The thermal conductivity K is a constant of proportionality, which relates the quantity of heat crossing a unit surface area in unit time to the spatial gradient of temperature perpendicular to the surface. This relationship is now known as Fourier's law in his honor. However, in his 1807 manuscript Fourier formulated thermal conductivity mathematically rather than experimentally. As pointed out by Grattan-Guinness (1972), Fourier arrived at this concept gradually, as he was making the transition from discontinuous bodies to a continuous body. The concept of specific heat capacity, proposed experimentally by Lavoisier and Laplace in 1783, is an essential part of the transient heat diffusion process. It helps convert the rate at which heat is accumulating in an elemental volume to an equivalent change in temperature. Thermal conductivity and thermal capacity are two fundamentally different attributes of a solid, one governing transport in space and the other governing change in storage in the vicinity of a point. Together, these two parameters govern the ability of the solid to respond in time to forces that cause the thermal state of the solid to change. Sometimes, it is found mathematically convenient to combine the two parameters into a single parameter known as thermal diffusivity, $\eta = K/(\rho c)$. The higher the diffusivity, the faster the tendency of the material to respond to externally imposed perturbations.

INFLUENCE AND CONNECTIONS

Soon after the publication of the *Analytic Theory of Heat* in 1822, the general scientific community became aware of the significance of Fourier's work, not merely for the science of heat, but in general as a rational framework for conceptualization for other branches of science. Within a few years, the heat conduction analogy was brought to the study of electricity and later to the analysis of molecular diffusion in liquids and solids. The dynamical theory of gases directly led to the analogy between diffusion of gases and diffusion of heat. The investigation of the flow of blood through capillary veins and the flow of water through porous materials led to the adoption of Fourier's heat conduction model to the flow of fluids in geologic media. The study of random motions of particles led to the interpretation of Fourier's equation in terms of stochastic differential equations.

Simultaneously, Fourier's work began also to be recognized by the establishments of the intellectual world (Grattan-Guinness, 1972). He was made a foreign member of the Royal Society in 1823, and in 1827 he was elected to the Académie Française and the Académie de Médecine. He succeeded Laplace as the president of the Council of Prefects of Ecole Polytechnique. He also became the Secrétaire Perpétuel of the Académie des Sciences.

For the sake of completeness, it is pertinent here to allude to the fate of Fourier's political career. In 1815, with the fall of Napoleon at Waterloo, Fourier's political career came to an end. His pension was refused and, close to fifty years old, he was virtually without an income. But, thanks to a former student of his at the Ecole Polytechnique in 1794 who was a prefect of the department of Seine, Fourier was given the directorship of the Bureau of Statistics in Paris. Later, in 1817, he was elected to a vacancy in physics in the Académie des Sciences. With these, Fourier had a secure income for the rest of his life and he could find plenty of time for conducting research. During the 1820s Fourier also had an influential and distinguished following: Sturm, Navier, Sophie Germain, Dirichlet, and Liouville.

To gain an understanding of Fourier's influence over the past nearly two centuries, it is convenient to organize the discussions into the following subheadings: electricity, molecular diffusion, flow in porous materials, random walk, and economics.

ELECTRICITY

The nature of electricity and its relation to magnetism were not completely understood at the time Fourier published his Analytic Theory, nor were the relations between electrostatics and electrodynamics (galvanic electricity). Becquerel and Barlow, and Davy (Dictionary of Scientific Biography, vol 10, p. 186-194) had been studying the electrical conductivity of metals in the context of materials with different lengths and cross sectional areas. Quantities such as current strength and intensity were not precisely defined. At this time, Georg Simon Ohm of Germany (1789-1854) set himself the task of removing the ambiguities about galvanic electricity with mathematical rigor, supported by experimental data. He published four papers on galvanic current between 1825 and 1827, of which the most well-known is his 1827 pamphlet, "*Die galvanische Kette, mathematisch bearbeitet*." Ohm's work, which is considered to be one of the most important fundamental

contributions to electricity, was largely inspired by Fourier's heat conduction model. It was thus a combination of inductive reasoning as well as an empirical idealization of the phenomenon of electricity. Ohm started with three "laws" (Ohm, 1827). According to his first law, the communication of electricity from one particle only takes place directly to the particle next to it, so that no immediate transition from that particle to any other situated at a greater distance occurs. Recall that Fourier made this important idealization when making the transition from action at a distance to the continuous medium. The second law was that of Coulomb relating to the effect of a charge at a distance in a dielectric medium. The third law was that when dissimilar bodies touch one another, they constantly maintain the same difference of potential at the surface of contact. This assumption is quite important because it points to a significant difference between the processes of heat conduction and conduction of electricity. In the case of heat conduction, temperature is *continuous* at material interfaces, whereas in the case of galvanic electricity the potential, namely, voltage, is *discontinuous*, as implied by this assumption of Ohm.

By means of carefully controlled experiments, Ohm showed that the current in a galvanic circuit did not vary with time (steady flow), the intensity of the electric current was directly proportional to the drop in voltage along the conductor in the direction of flow and inversely proportional to the resistance of the conductor. In turn, the resistance of the conductor was a function of the material of which the conductor is made of and its form (that is, shape and size). Equally important, Ohm showed that the resistance of the conductor was independent of the magnitude of the current itself or the magnitude of the voltage drop (the electromotive force), or the absolute value of the potential at which the conductor is maintained. In addition to giving precise meaning to current, electromotive force and resistance, Ohm's work provided a link between electrostatics (from which the notion of a potential or voltage is derived) and electrodynamics or galvanic electricity. Following Ohm's work, the measurement of the electrical resistance of various materials with great precision became a fundamental task in physics (Maxwell, 1881).

In his classic 1827 work Ohm took the analogy with heat conduction much further. In fact, he treated the flow of electricity as being exactly analogous to the flow of heat and wrote a transient equation of the form similar to (1)¹,

¹ Unless otherwise stated, the notations used in this paper are those of the referenced authors.

$$(3) \quad \gamma \frac{du}{dt} = \chi \frac{d^2 u}{dx^2} - \frac{bc}{\omega} u ,$$

where γ is a quantity analogous to heat capacity, which, according to Ohm, was not experimentally proven, u is the electric potential (voltage), χ is electrical conductivity, b is a transfer coefficient associated with the atmosphere to which electricity is being lost by the conductor according to Coulomb's Law, c is the circumference of the conductor, and ω is the area of cross section of the conductor along the x direction. Ohm was not confident about this equation and admitted that no experimental evidence for γ was as yet forthcoming.

Maxwell (1881) derived the same equation in a different context and showed that Ohm was in error in proposing (3) the way he did. Maxwell considered a long conducting wire (such as a transoceanic telegraph cable) surrounded by an insulator. In this case, the insulator, which is a dielectric material, functions as a condenser and possesses the electrical capacitance property analogous to heat capacitance. Moreover, if the insulator is not perfect, some amount of electricity would be lost to the surroundings, as indicated by the second term on the right-hand side of (3). Maxwell expressed Ohm's error thus (Maxwell, 1881, p. 422): "Ohm, misled by the analogy between electricity and heat, entertained an opinion that a body when raised to a high potential becomes electrified throughout its substance, as if electricity were compressed into it, and was thus by means of an erroneous opinion led to employ the equations of Fourier to express the true laws of conduction of electricity through a long wire, long before the real reason of the appropriateness of these equations had been suspected." Indeed it is fundamental to the nature of electricity that capacitance is an electrostatic phenomenon and only insulators possess that property. Electricity, as Maxwell pointed out (Maxwell, 1881, p. 336), behaves like an incompressible fluid, and hence conductors do not possess the property of capacitance.

It is of interest to take note of the particular way Ohm formulated his mathematical ideas. Fourier's law of heat conduction is expressed as: heat flux in the x direction = $-K(dT/dx)A$, where A is the area of cross section through which heat is flowing. That is, heat flux is expressed in such a way that the material property, K , is kept distinct from the geometric attributes of cross sectional area and distance. However, Ohm expressed current as being equal to the difference in voltage

divided by resistance. The resistance in Ohm's law is an integral which combines the material property as well as the geometry of the conductor of finite size through which current is flowing. Ohm conceptualized in terms of *potential difference* whereas Fourier conceptualized in terms of *potential gradient*. Fourier's method of separating material property from geometry was of the right mathematical form to pose the problem as a differential equation. As we shall see later on, while discussing Fick's work on molecular diffusion, Ohm's approach of dealing with resistance may prove to be quite advantageous for problems in which the domain of flow is characterized by curvilinear flow paths and the domain lacks simple symmetry.

Ohm's work is now accepted as one of the most important contributions in the science of electricity. Yet, recognition did not come to him readily. Although physicists such as Theodor Fechner, Heinrich Lenz, Wilhelm Weber, Friederich Gauss, and Moritz Jacobi drew upon Ohm's work in their own research soon after Ohm published "Die galvanische Kette", Ohm's work came under criticism from an unexpected quarter. His experimental approach to finding order in nature was heavily criticized by Georg Poul (Dictionary of Scientific Biography, 1981), a physicist who was a follower of Hegel's philosophy of pure reason. However, due recognition came to Ohm after a few years when he was elected to the Academies at Berlin and Munich and the Royal Society conferred on him the Copley Medal in 1841. Ohm moved to Cologne and went on to occupy the Chair of Physics at that University.

William Thompson (1824-1907) was greatly influenced by Fourier's work even when he was in his teens. Thomson's first two articles, written at ages 16 and 17, were in defense of Fourier's mathematical approach. Later he demonstrated the similarities between the mathematical structures of Fourier's heat conduction equation and the equations of electrostatics stemming from the works of Laplace and Poisson (Thompson, 1842). For example, potential was analogous to temperature, a tube of induction was analogous to a tube of heat flow, the electromotive force was in the direction of the gradient of potential and the flux of heat was in the direction of temperature gradient.

While physical analogies serve a useful purpose, Maxwell (1888, pp. 52-53) emphasized that caution was in order so that the analogies are not carried too far. Maxwell pointed out that the analogy with electric phenomena applied only to the steady flow of heat. Even here differences exist between electricity and heat. For steady flow, heat must be kept up by a continuous supply,

accompanied by its continuous loss. However, in electrostatics, a set of electrified bodies placed in a perfectly insulating medium might remain electrified forever without any supply from external sources. And, there is nothing in the electrostatic system that can be described as flow. Another limitation of the analogy is that the temperature of a body cannot be altered without altering the physical state of the body, such as density, conductivity, or electrical properties. However, the electrical potential is merely a scientific concept. Bodies may be very strongly electrified without undergoing any physical change.

We saw earlier that Ohm had attempted unsuccessfully to formulate a time-dependent electrical flow problem by direct analogy with Fourier's equation. Later work, stemming from Maxwell's equations, established that transient heat conduction and transient electricity flow are very different in nature. Transient flow of electricity typically arises in the case of alternating current as opposed to the steady state direct current with which Ohm was concerned. In the case of alternating current, the change in electric field is intrinsically coupled with an induced magnetic field in a direction perpendicular to the direction in which current is flowing. The nature of the coupled phenomena is such that when the frequency of the alternating current is low, Maxwell's electromagnetic equations may be described in the form of an equation which looks mathematically similar to the heat conduction equation, in that one side of the equation involves the Laplace operator (second derivative in space) and the other involves the first derivative in time. However, the resemblance is only superficial because the dependent variable in this equation is a vector potential, whereas the dependent variable in the heat conduction equation is a scalar potential.

MOLECULAR DIFFUSION

Molecular diffusion is the process by which molecules of matter migrate within solids, liquids and gases. The phenomenon of diffusion was observationally known to chemists and biologists by the eighteenth century. In the early nineteenth century, experimental chemists began paying serious attention to molecular diffusion, and the publication of Fourier's Analytical Theory in 1822 provided the chemists with a logical framework with which to interpret and extend their experimental work. The following discussion on molecular diffusion starts with diffusion in liquids, followed by solids and gases.

Diffusion in Liquids

Among the earliest observations which attracted the attention of chemists to diffusion in liquids is the phenomenon of osmosis. In 1752, Jean Antoine (Abbé) Nollet (1700-1770) observed and reported selective movement of liquids across an animal bladder (semipermeable membrane). Between 1825 and 1827, Joachim Henri René Dutochet (1776-1847) made pioneering contributions in the systematic study of osmosis. A physiologist and medical doctor by training, Dutochet spent most of his career in the study of the physiology of animals and plants. About this time, Poisson had attempted to explain osmosis in terms of capillary theory. In his paper, Dutochet (1827) strongly disagreed with Poisson and, based on experimental evidence, argued that two currents (solute and solvent) simultaneously occur in opposite directions during osmosis, one of them being stronger than the other, and that the understanding of osmosis required something more than a simple physical mechanism such as capillarity. He speculated on the possible role of electricity in the osmotic phenomenon. He also coined the terms “endosmosis” for the migration of the solvent towards the solution and the term “exosmosis” for the reverse process.

The next major work on liquid diffusion was that of Thomas Graham (1805-1869). Graham's experimental work on liquid diffusion led to the distinction between crystalloids (such as common salt) having high diffusibility and colloids (such as gum arabic) having low diffusibility. Graham's detailed observations on the diffusibility of a variety of chemical substances would later give him the distinction of being considered by some to be the father of colloid chemistry. In 1850 he presented data on the diffusibility of a variety of solutes and solvents in his Bakerian Lecture of the Royal Society.

Despite the wealth of data he collected, Graham did not attempt to elicit from them a unifying fundamental statement of the process of diffusion in liquids. That Graham restricted himself essentially to the collection of experimental data on diffusion in liquids proved to be a catalyst for one of the most influential papers of molecular diffusion, that of Fick (1855). Adolf Fick (1829-1901) was a Demonstrator in Anatomy at the University of Zurich and, despite his professional training in medicine, had a sound background in mathematics and physics. Barely twenty five years old, Fick started by expressing regret that Graham had failed to identify any fundamental law of diffusion from his substantial experimental data and set himself the task of remedying the situation. Fick saw a direct

analogy between the diffusion of heat in solids and the diffusion of solutes in liquids, and his starting point was Fourier's heat conduction equation.

By direct analogy with Fourier, Fick wrote down the parabolic equation for transient diffusion of solutes in liquids in one dimension thus:

$$(4) \quad D \left(\frac{\delta^2 c}{\delta x^2} + \frac{1}{Q} \frac{dQ}{dx} \frac{\delta c}{\delta x} \right) = \frac{\delta c}{\delta t} ,$$

where D is the diffusion coefficient, c is aqueous concentration, and Q is the area of cross section.

It is of particular interest to note that Fick made a novel departure from Fourier in writing the one-dimensional equation. Note that the second term on the left hand side of (4) accounts for the variation of the area of cross section along the flow path (the x axis). Intrinsically, therefore, Fick's equation is valid for a flow tube of arbitrary shape involving a curvilinear x axis. Indeed, Fick (1855) presented data from a diffusion experiment in an *inverted funnel shaped vessel*, solved (4) for the particular cone-shaped vessel and found that his mathematical solution compared favorably with the steady state observations made at different locations within the vessel. For a flow tube with constant area of cross section, (4) simplifies to Fourier's equation, and one can readily verify that (4) leads also to the appropriate differential equations for radial and spherical coordinates. Upon reflection, it becomes apparent that integration of (4) along curvilinear flow tubes leads to the evaluation of resistances within finite segments of flow tubes and that the evaluation of resistances thus provides a link between the approaches of Fick and Ohm.

According to Fick, concentration is analogous to temperature, heat flux is analogous to solute flux and thermal diffusivity is analogous to chemical diffusivity. If concentration in the aqueous phase is defined as mass per unit volume, then specific chemical capacity (analogous to specific heat) equals unity and chemical diffusivity is equal to chemical conductivity.

In the second part of his paper, Fick (1855) went on to analyze flow across a semipermeable membrane by idealizing the membrane as a collection of cylindrical pores of radius ρ . As suggested

earlier by Dutrochet (1827), two simultaneous currents will occur through the capillaries; the solute current will occur towards the solvent and the solvent current will occur towards the solution. Fick reasoned that because of the affinity of water to the material comprising the membrane, the water current will be organized more toward the walls of the pores and the solute towards the axis of the pores. Incidentally, a remarkably similar reasoning was employed by Taylor (1953), who studied solute diffusion in capillary tubes with moving water. When the radius of the pore becomes sufficiently small, the flow of the solute will be arrested and osmosis will involve one current, that of the solvent. Interestingly, Fick did not address the issue of the forces causing the movement of water, that is, why the solute should move in the direction of concentration gradient. He simply asserted that in a diffusion vessel, as the solute moves one way, a certain amount of water will move in the opposite direction. Fick went on to publish a year later what probably is the first text book in biophysics under the title, *Die medizinische Physik* (1856).

The study of liquid diffusion was soon to take a very important place in the field of biophysics through the investigations of Wilhelm Pfeffer (1845-1920). After receiving a doctoral degree in chemistry from Göttingen when he was twenty years old, Pfeffer grew interested in the study of biological processes and brought his experimental and analytical skills to bear on the study of mass transfer in plant cells. Broadly, the outer layer of the cell was treated as a semipermeable membrane, and Pfeffer devised sophisticated techniques to measure osmotic pressure within cells, and went on to develop and test several hypotheses concerning the diffusion of nutrients within and across cells.

Pfeffer found osmosis experiments on plant cells to be quite limiting and sought to conduct measurements on controlled inorganic membranes. Along these lines he pioneered the use of thin layers of ferrocyanide deposited on ceramic substrates as semipermeable membranes. Using such membranes he went on to measure osmotic pressure of various solutions as a function of concentration as well as temperature. Pfeffer's data, published in his 1877 classic, *Osmotische Untersuchungen*, would later help van't Hoff to lend credibility to his theory of osmotic pressure. Dutrochet, Pfeffer, Fick and other biophysicists of the time strongly supported the view that physiological processes must be elucidated and understood in terms of inorganic (nonbiological) processes. Dutrochet (1827) eloquently articulated this view thus: "The physical processes of living and inorganic matter merge in endosmosis and exosmosis. The further we advance in our

understanding of physiology, the more reasons we will have to revise our opinion--whose major proponent is Monsieur Bichat--that life and physical phenomena are essentially different. It is undoubtedly false."

By the time Pfeffer published his book on cell mechanics, a wealth of data had been collected on osmosis, both from physiological and inorganic materials. Many hypotheses were in vogue and a rational description of osmosis in terms of known principles of physics and chemistry was lacking. Jacobus Henricus van't Hoff (1852-1911), one of the most influential physical chemists of the second half of the nineteenth century, filled this gap by providing a theoretical foundation for osmotic pressure based on well-established laws of chemistry. Van't Hoff (1887) started with and justified the proposition that the physical behavior of solutions and the associated osmotic pressure can be rationally understood by treating solutions as analogous to gases and by applying Boyle's law, Gay-Lussac's law, and Avogadro's law to solutions. He formally defined osmotic pressure as the excess pressure that would develop in a solution contained in a vessel that communicates with a reservoir of a solvent across a perfect semipermeable membrane. By using the aforesaid laws and the second law of thermodynamics, van't Hoff was able to draw many inferences about relationships between the magnitude of osmotic pressure on the one hand and the nature of the solute concentration and temperature on the other. He demonstrated that the experimental data of previous workers, especially Pfeffer (1877), substantially justified his theoretical framework.

In osmosis, as we have seen, two opposing currents of flow are involved and each current is driven by its own force--the solvent by spatial variations in its fluid potential and the solute by the spatial variations of osmotic pressure. Therefore, it is convenient to conceptualize the total pressure in the solution as a sum of the water phase pressure and the osmotic pressure. Thus, in the solution, the pressure in the water phase $p_w = p_{\text{total}} - p_{\text{osmotic}}$. The stronger the concentration of the solution, the lesser is the water phase pressure and the stronger will be the solvent current towards the solution should the solution communicate with the solvent across a semipermeable membrane. Analogously, the solute will be driven in the opposite direction because osmotic pressure decreases in the direction of the solvent.

Closely following van't Hoff, Walther Hermann Nernst (1864-1941) examined the process of solute diffusion in the context of osmotic pressure as defined by the former. Nernst (1888) pointed

out that the diffusion of solutes in the direction of decreasing concentration had been suggested earlier by Berthollet (1803) and that Fick established it rigorously with mathematics, supported by experimental data. Nernst found Fick's approach to be formal and lacking in the elucidation of the forces which impelled the solute diffusion process. To overcome this deficiency, he looked at diffusion in terms of impelling forces and resistive forces, the former stemming from spatial variations of osmotic pressure and the latter stemming from the collision of molecules with the solvent molecules and even among the solute molecules themselves.

Nernst (1888) considered the force due to osmotic pressure acting on a molecule of the solute and defined a coefficient of resistance K representing the force required to move 1 gram-molecule of the solute through the solvent at a velocity of 1 cm/sec. Combining these, he expressed the flux of solute in terms of the gradient of the osmotic pressure and the reciprocal of the resistance coefficient K . He then recognized that for dilute solutions, osmotic pressure is linearly related to concentration by a simple relation, $p = p_0 c$, where p_0 is the osmotic pressure in a solution containing a gram molecular weight of the solute and c is concentration. As a result, for dilute solutions, the ratio p_0/K becomes part of the diffusion coefficient and flux becomes proportional to the gradient of concentration, as proposed by Fick (1855). By extending the analysis to concentrated solutions, Nernst pointed out that in such solutions the solute will encounter greater resistance to flow because of mutual collision among the solute molecules in addition to the solvent molecules. Therefore, in concentrated solutions the diffusion coefficient will be a function of concentration. As a consequence, the relevant differential equation of diffusion becomes non linear.

In analyzing the process of diffusion, Nernst gave consideration to electrolytes in which individual ions will migrate separately. In this case, in order that the ions composing a given solute may migrate at the same velocity, he suggested that the differences in ion velocities induced by osmotic pressure will be compensated by electrostatic forces.

Solid Diffusion

An early documented observation of solid diffusion is attributed to Robert Boyle (Barr, 1997) who succeeded in 1684 in making zinc diffuse into one of the faces of a copper farthing, leading to the formation of brass. By carefully filing the face, Boyle showed that zinc had indeed diffused into

the body of copper. Yet, controlled diffusion measurements would not become possible until two hundred years later.

The first measurements of the diffusion of one solid metal into another was made by William Roberts-Austen (1843-1902) who was Chemist and Assayer of the British Mint. He started his career at the Mint as an assistant to Thomas Graham, who was the Master of the Mint from 1855 to 1869, and extended the scope of his diffusion studies to metals and alloys. Roberts-Austen thus took up the challenge of extending Graham's work on liquid diffusion to metals. However, his progress was considerably hampered because of difficulties in accurately measuring the temperature at which diffusion was taking place in the solid state. Finally, he succeeded by adopting Le Chatelier's platinum-based thermocouples and was able to study the diffusion of gold in solid lead at different temperatures. The results were analyzed in terms of Fourier's model of one-dimensional diffusion (Roberts-Austen, 1896).

The discussion of solid diffusion would not be complete without a mention of the work of Enrico Fermi (1901-1954). He was the first to successfully achieve, in 1942, a sustained release of energy from a source other than the sun by bombarding and splitting uranium atoms with the help of neutrons slowed down in a matrix of solid graphite. Critical to the design of the experiment was the calculation of the slowing down of neutrons and the absorption of thermal neutrons by the carbon host. The slowing down of the neutrons was described as a diffusion process (Anderson and Fermi, 1940) and the corresponding diffusion constants were calculated based on experimental data. The approach was one Fermi had already perfected earlier (Fermi, 1936). The diffusion theory developed by Fermi would later be known as the "age theory."

Diffusion of Gases

The earliest experimental work on the diffusion of gases was by Graham (1833). When two or more gases are mixed together in a closed vessel, the natural tendency is for the gases to redistribute themselves by diffusion in such a way that the mixture has a uniform composition everywhere. Graham showed experimentally that the rate at which each of the gases diffuses is inversely proportional to the square root of its density. This observation was stated as a law by Graham (1833) and is known as Graham's law. When we compare gas diffusion with liquid diffusion

or heat conduction or the conduction of electricity, we find that in these latter cases we are concerned with conductive transport in different materials, whereas in the case of gas diffusion we are concerned with the conduction of gas in free space. In the case of nongaseous conduction, the transport coefficient (conductivity or diffusivity) is experimentally estimated for different materials on the basis of Fourier's equation. The conductivity of different materials pertains to the ability of the materials to inhibit or resist the flow of the permeant. In contrast, in the case of pure gaseous diffusion, diffusivity is a property that stems solely from the attributes of the permeating fluid, the gas.

With the advances that were taking place in molecular physics and chemistry during the middle of the nineteenth century, a great deal of effort was being made by researchers to directly estimate the properties of gases such as viscosity, specific heat, thermal conductivity, Diffusion coefficient and diffusivity by starting with force, momentum and energy at the molecular level and statistically integrating these quantities in space and time to estimate the macroscopic properties of interest. Among the earliest researchers in this regard was Maxwell (1831-1879), whose work on the dynamical theory of gases is of fundamental importance. In this work, Maxwell (1867) assumed molecules to be small bodies or groups of small bodies which possess forces of mutual repulsion varying inversely as the fifth power of distance. Macroscopically, he described the diffusion of a mixture containing two gases in terms of an equation which has the same form as Fourier's transient heat conduction equation. In this case, the diffusion coefficient is describable by Dalton's Law of partial pressures and densities of the two gases and is inversely proportional to the total pressure. Maxwell generated a solution of this equation for the case of a particular column experiment conducted by Graham involving carbonic acid and air and found some agreement with the diffusion coefficient independently estimated by Graham.

Brownian Motion

About the same time osmosis was being recognized as an important physical process by Dutrochet, Robert Brown (1773-1858), a renowned British Botanist discovered that pollen and other fine particles suspended in water exhibited continuous and permanent random motions. During the second half of the nineteenth century, physicists became very interested in the mechanisms and forces responsible for these continuous motions. It was soon recognized through the investigations of

Delsaux, Gouy and others (Fürth, 1926) that the random motions were sustained by the impacts of the molecules of the liquid on the suspended by particles. Subsequently, the theory of Brownian movement was placed on formal physical-mathematical foundations by Albert Einstein (1879-1955) in one of his celebrated papers (Einstein, 1905). In this paper Einstein set out to establish the validity of the molecular-kinetic theory of heat rather than attempting to explain Brownian motion. His goal was to show that because of the molecular-kinetic nature of heat, bodies of microscopically observable particles suspended in liquids will perform movements of such magnitude as are observable under a microscope.

Einstein started with the proposition that colloidal particles suspended in liquids exert osmotic pressure, just as dissolved solute molecules and that an equal number of suspended colloidal particles and nonelectrolyte solute molecules exert the same osmotic pressure in dilute solutions. Such osmotic pressure arises from the random motion of the particles as they are impelled by their random collisions with the vibrating liquid molecules. The kinetic energy transferred in the process is directly related to the temperature of the liquid (analogous to Nernst's idealization of osmotic pressure in solutes). In their random movement, the particles are decelerated by the viscous resistive forces of the liquid. By analogy with van't Hoff's equation for osmotic pressure for nonelectrolytic solutes, the osmotic pressure associated with suspended particles is given by,

$$(5) \quad p = \frac{RT}{N} v ,$$

where p is the osmotic pressure, R is the universal gas constant, T is temperature, N is Avogadro's Number, and v is the number of suspended particles per unit volume of the liquid. Also, the resistive force offered by the particles suspended in a unit volume of the liquid is given, according to Stokes formula by,

$$(6) \quad v K = v 6 \pi k P u ,$$

where K is the resistive force per particle of radius P , k is viscosity and u is particle velocity. Noting that the particles are macroscopically impelled by spatial gradient of osmotic pressure and that under dynamic equilibrium, impelling forces and resistive forces must balance, Einstein derived a macroscopic flux law (analogous to Fourier's law for thermal conduction) for the flux of particles crossing a unit area in unit time,

$$(7) \quad D \frac{\partial v}{\partial x} = \frac{v K}{6\pi k P},$$

where D , the diffusion coefficient is given by $D = RT/(6\pi k P N)$, in which N is Avogadro's Number.

In view of (7), it would have been trivial for Einstein to have derived a partial differential equation for colloid diffusion in a manner analogous to Fick's derivation. However, Einstein had a far more fundamental goal and followed a different path. He proceeded to derive the partial differential equation for the distribution of particles at time $t + \tau$, given that the distribution at time t is $v = f(x, t)$. During a time interval τ there exists a finite probability $\phi(\Delta)d\Delta$ that the x coordinate of a single particle will change by an amount Δ . This leads to the recursive relation,

$$(8) \quad f(x, t + \tau) = \int_{-\infty}^{\infty} f(x + \Delta, t) \phi(\Delta) d\Delta.$$

For small values of τ , the left-hand side of (8) can be approximated by $f(x, t + \tau) \approx f(x, t) + \tau (\partial f / \partial t)$. Also, $f(x + \Delta, t)$ can be approximately expanded into a Taylor's series,

$$(9) \quad f(x + \Delta, t) = f(x, t) + \Delta \frac{\partial f}{\partial x} + \frac{\Delta^2}{2} \frac{\partial^2 f}{\partial x^2}.$$

Einstein assumed the function ϕ to be such that $\phi(\Delta) = \phi(-\Delta)$ and that ϕ differs from zero only for small values of Δ . Under such assumptions, $\int \Delta \phi(\Delta) d\Delta = 0$ and $\int \Delta^2 \phi(\Delta) d\Delta = 1$. Thus, substitution of (9) into (8) leads to the one-dimensional diffusion equation,

$$(10) \quad \frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2},$$

where $D = (1/\tau) \int_{-\infty}^{\infty} (\Delta^2/2) \phi(\Delta) d\Delta$. The distribution function $f(x,t)$, which is a solution to the diffusion equation (10), is a symmetric function with a mean value of zero.

Einstein extended $f(x,t)$ to represent the probability that n particles, each with its own coordinate system, will have displacements between $x + \Delta x$ after time t and showed that the function can be expressed as,

$$(11) \quad f(x, t) = \frac{n}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}.$$

He recognized the similarity between this function and that representing the distribution of random error by stating, "The probability distribution of the resulting displacements in a given time t is therefore the same as that of fortuitous error, which was to be expected." We will see later that this line of reasoning had been used by Edgeworth in 1883 to derive the diffusion equation relating to the Law of Error.

Einstein's 1905 paper is considered a landmark in physics. It provided a strong impetus to experimentally establish the veracity of the molecular-kinetic theory of Brownian motion as well as to determine Avogadro's Number more precisely.

Soon thereafter, Paul Langevin (1872-1946) developed an alternate approach to describing Brownian movement. Rather than devoting attention to the distribution of particles in space (as Einstein did), Langevin (1908) started with the forces acting on a single particle. A Brownian particle is impelled by the momentum transferred to it by the molecules that collide with it. In turn, the particle is retarded by the viscous resistance offered to it by the molecules of the liquid. Thus the net force on the particle equals the sum of a "systematic" drag force and a stochastic force (Langevin's complementary force),

$$(12) \quad F(t) = -6\pi\mu a u + X(t) ,$$

where μ is viscosity, a is the radius of the spherical particle, u is velocity, and X is the stochastic force. Langevin showed that after a “relaxation” time τ of the order of $m/(6\pi\mu a)$, where m is the mass of the particle, the diffusion equation of Einstein (1905) is valid. Langevin’s equation soon became, among physicists, the starting point for formulating stochastic differential equations. In particular, Fokker, Planck and others showed that Langevin’s equation can be used to represent the diffusion process in terms of the probability $W(u+\Delta u)$ that the velocity of a particle is in the interval u and $u+\Delta u$ at the end of an interval of time τ , given that it had a velocity u at time zero. This has led to the equation describing diffusion in the velocity space, known as the Fokker-Planck equation (Chandrasekhar, 1943, p. 33),

$$(13) \quad \frac{\partial W}{\partial t} = \beta \frac{\partial (uW)}{\partial u} + q \frac{\partial^2 W}{\partial u^2} ,$$

where $\beta = m/(6\pi\mu a)$ and $q = \beta k t/m$, in which k is Boltzman’s constant, t is absolute temperature and m is the mass of the particle. In (13) the first term on the right-hand side is known as “drift.” As we shall see later, Bachelier (1900) had independently developed this type of stochastic differential equation in developing the theory of speculation in connection with the pricing of options in the French stock market.

The Fokker-Planck equation is considered to be a more general representation of the stochastic process of diffusion than Einstein’s equation. The basis for this consideration is the notion of a Markoff Process, which is a random process without “memory”. In applying Langevin’s equation to Brownian movement, it is assumed that velocity is assumed to be a Markoff process. Note that the position x of the Brownian particle is an integral of velocity. Strictly speaking, if velocity is a Markoff process, position will have some memory and so it cannot be a Markoff process (Gillespie, 1996). Therefore, to enable stochastic analysis of position, the derivation of the Fokker-Planck equation has to start with a multivariate form of the Langevin equation in which velocity and position together constitute a stochastic process. In this framework, Einstein’s equation arises when

the time interval chosen is sufficiently large. If, however, the time interval is small, the mean value of the probability distribution will “drift” away from zero and is accounted for by the first term on the right hand-side of (13). Additionally, drift could also arise from the presence of external forces such as gravity. The equation is then referred to as Smoluchowski’s equation.

FLOW OF WATER IN POROUS MATERIALS

Fourier’s heat conduction equation has had an enormous influence in the study of fluid flow processes in the earth, especially water and petroleum in porous media. In applying the equation to these processes, the following analogies can be made: temperature corresponds to scalar fluid potential, heat corresponds to mass of water, thermal conductivity corresponds to hydraulic conductivity and heat capacity corresponds to hydraulic capacity. However, unlike electricity, heat, and solutes, the potential of water has a very special attribute, namely, gravity. This attribute renders the extension of heat analogy to the earth sciences particularly interesting.

Steady Flow of Water

By the time of Fourier’s work, fluid mechanics was a well developed science and the concept of a fluid potential, defined as energy per unit mass of water was already established through the seminal contribution of Daniel Bernoulli in hydrodynamics, early in the eighteenth century. The flow of water in open channels was being rigorously studied by civil engineers. In addition to civil engineers, many physiologists were also interested in the study of water flow through capillary tubes to better understand, by analogy, the flow of blood through narrow vessels.

Among the earliest experimentalists to study the slow motion of water through capillary tubes was Jean Leonard Marie Poiseuille (1799-1869), a physician and a physiologist who had studied under Ampère at the École Polytechnique. He was not satisfied with the contemporary state of understanding of blood circulation in veins and therefore embarked on a study of the flow of water in narrow capillary tubes under carefully controlled conditions. Using a sophisticated laboratory setup, Poiseuille studied the flow of water in horizontal capillary tubes varying in diameter from about 50 to about 150 microns and measured fluxes as low as 0.1 cc over several hours. In the absence of gravity, he found that water flux was directly proportional to the pressure difference

between the inlet and the outlet and inversely proportional to the length of the capillary. These observations were very similar to those made by Ohm in the case of galvanic current. Although the work was completed in 1842, it was not published until a few years later (Poiseuille, 1846). Similar observations had been made earlier in Germany by Hagen (1839)

One of the most influential works on the flow of water in porous media during the nineteenth century was that of Darcy (1856). Henry Darcy (1803-1858) was a highly recognized civil engineer who is credited with designing and completing the first ever protected town water supply system in the world. Dissatisfied with the unhealthy sources of drinking water available in his native town of Dijon, he helped bring and distribute water from a perennial spring located several kilometers away from the town. The project was completed in 1840. Later, presumably to build a water purification system, Darcy conducted a series of experiments in vertical sand columns to develop a quantitative relationship for estimating the rate of flow of water through sand filters. Darcy's experiment was novel in that it included gravity and it involved a natural material (sand) rather than an engineered material such as a capillary tube. He too, like Ohm and Poiseuille before him, found that the flux of water through the column was directly proportional to the drop in potentiometric head, $h = z + \psi$, where z is elevation with reference to datum and ψ is pressure head, directly proportional to the area of cross section and inversely proportional to the length of the column. Darcy's law plays a fundamental role in many branches of earth sciences such as hydrogeology, geophysics, petroleum engineering, soil science, and geotechnical engineering.

The middle of the nineteenth century witnessed many developments in the earth sciences, among which was the discovery of artesian groundwater basins in France and elsewhere in Europe. It was apparent that the deep circulation of groundwater driven by gravity could be rationally understood within the context of potential theory. Soon, the heat conduction model of Fourier began to be used for analyzing circulation of water in groundwater basins. The earliest studies in this regard restricted themselves to the steady motion of groundwater. Unlike the problems of electricity and molecular diffusion, the problems of groundwater involved large spatial scales (many tens or even hundreds of kilometers laterally and hundreds of meters vertically). Two of the most distinguished engineers of this era were Jules-Juvenal Dupuit (1804-1866) in France and Philipp Forchheimer (1852-1933) in Austria. Dupuit (1863) developed the basic theoretical framework for analysis of

flow in groundwater systems and of the flow of water to wells. Forchheimer (1886) formally stated the steady seepage of water in terms of the Laplace equation and initiated the use of complex variable theory to the solution of two-dimensional problems in flow domains of complicated geometry that occur in the vicinity of dams and other engineering structures. He also pioneered the use of flow nets as practical, graphical means of solving seepage problems in complex flow domains.

Flow of Multiple Fluid Phases

A significant development in the study of flow in porous media was the work of Edgar Buckingham (1867-1940), a distinguished thermodynamicist of his time. From 1902-1905 he was an Assistant Physicist with the Bureau of Soils, U.S. Department of Agriculture. In this brief period, he not only introduced himself to a totally new field, the science of soils, but made one of the most important contributions to soil physics in particular as well as to the general study of multiphase fluid flow. Soon after, he moved to the National Bureau of Standards and became well known for, among other achievements, for his π -theorem of dimensional analysis.

In soils close to the land surface where plant roots thrive, both water and air coexist. An understanding of the dynamics of the occurrence and movement of water in the soil is critical to agricultural management. When water and air coexist in soils, the contacts between air and water in the minute pores are curved menisci in which energy is stored. As a result, the pressure in the water phase is less than that in the air phase and the difference is the capillary pressure. The physics and the mathematics of capillarity had been enunciated a hundred years earlier by Laplace and by Thomas Young. Buckingham brought together the work on capillary pressure with that of Fourier and Ohm on diffusion, and defined the capillary potential in the water phase as a sum of work to be done per unit mass against gravity and fluid pressure. He stated that moisture moves in soils in response to spatial variations in potential and that moisture flux density is directly proportional to the gradient of capillary potential, the proportionality constant being hydraulic conductivity. Although this statement resembles the laws of Fourier, Ohm, and Darcy, there exists a very important difference. In soils which contain water and air, the capillary potential is directly related to water saturation. And, as water saturation decreases, the flow paths available for moisture movement decrease. Therefore, the conductivity parameter is strongly dependent on capillary potential, instead of being constant or

nearly so as is the case with the laws of Fourier, Ohm, or Darcy. Because Buckingham rigorously defined the capillary potential, his flux law encompasses Darcy's law as a special case of full water saturation. The strong dependence of hydraulic conductivity on capillary potential renders the study of moisture diffusion in soils a very difficult mathematical problem. For the first time, Buckingham also experimentally measured the relation between capillary potential and water saturation in different soils. In an earlier work, Buckingham (1904) also applied the diffusion equation to the migration of gas in soils and analyzed the dynamic vertical migration of air from the land surface to the water table in response to fluctuating atmospheric pressure. Buckingham's work helped resolve a contemporary paradox in agriculture. In arid regions where evaporation rates are very high, the soils are found to be wetter and hold their moisture for much longer periods than do the soils of humid areas in dry seasons. Part of the reason for this counter-intuitive observation is to be found in the dependence of hydraulic conductivity on capillary potential, or, equivalently, water saturation. In arid areas, as evaporation rapidly desaturates the uppermost soil, the hydraulic conductivity drops practically to zero and further evaporative loss from deeper zones is virtually eliminated.

Note that specific heat, originally defined and measured by Lavoisier and Laplace (1783), is an extremely important physical attribute of materials and occupies an important position in the heat conduction equation. It plays a crucial role in dictating the rapidity with which a material will thermally respond to externally imposed perturbations: the smaller the capacitance, the faster the response. Analogously, in the phenomenon of fluid flow in porous media, hydraulic capacitance plays a very important role. It so happens that the slope of the variation of water saturation as a function of capillary potential contributes to the hydraulic capacitance of a soil. As a consequence, Buckingham's work lies at the foundation of the dynamics of multiple fluid phases in porous media.

Although Buckingham theoretically defined a capillary potential, he could only measure it indirectly in vertical columns in which water moves down solely by gravity. He recognized that new instruments would have to be developed to measure capillary potential under dynamic conditions of flow. Such an instrument was invented over a decade later by Willard Gardner (1883-1964). This ingenious instrument is called the tensiometer. The key component of this device is a porous ceramic cup that is completely saturated with water. Such a porous cup acts like a semipermeable membrane, allowing the flow of water from the soil into the cup, but not allowing the flow of air. The cup is

connected to a long tube filled with water which is connected to a manometer. The tensiometer is set into a natural soil and, through exchange of water between the soil and the cup and, fluid pressure inside of the cup is allowed to attain equilibrium with that in the soil. The equilibrium pressure represents the capillary potential. The first measurements from this instrument were reported by Gardner et al. (1922). Subsequent measurements of the relation between water saturation and capillary potential on many soils have shown that the relation is not unique and is characterized by hysteresis. Thus, the hydraulic capacitance of the soil introduces a strong non-linearity into the differential equation.

Deformable Porous Media

The attribute of hydraulic capacitance of a naturally occurring porous material such as a soil or a rock arises also for reasons other than the rate of change of saturation with potential. Earth materials are deformable in response to changes in the stresses which act on the porous skeleton. The ensuing rate of change of pore volume (which is occupied by water) in response to changes in fluid potential also contributes to hydraulic capacitance. The measurement of pore volume as a function of fluid potential was elucidated through the work of Karl Terzaghi (1883-1963), who founded the discipline of soil mechanics. In presenting his experimental results on the deformation of water saturated clays, Terzaghi (1925) postulated that in water saturated earth materials volume change is to be related to the difference between skeletal stresses and water pressure. Thus, when skeletal stresses remain unchanged, volume change is directly attributable to the change in fluid pressure or, equivalently, the fluid potential. Extensive experimental work following Terzaghi has shown that earth materials invariably exhibit nonelastic deformation behavior.

Hydraulic Capacitance

In addition, a third component also contributes to hydraulic capacitance of porous materials: the compressibility of the fluid itself. Thus, hydraulic capacitance in natural geological materials arises from the ability of the porous medium to deform due to changing fluid pressure, the ability of the fluid to dilate, and the desaturation of the pores due to changing capillary pressure. Whereas the specific heat capacity of most known materials does not vary by more than a factor of a hundred it

is not uncommon for the hydraulic capacitance of soils and rocks to vary by a factor of a million.

If we now look at Fourier's diffusion equation as the basis for the flow of water in soils and rocks, we see at once that hydraulic conductivity may vary significantly as a function of fluid potential, as does also the hydraulic capacitance. Thus, unlike the heat problem which is characterized by a linear differential equation, the diffusion equation pertaining to flow of water in soils and rocks is characterized by a highly nonlinear differential equation. Drawing upon the contribution of Buckingham and Gardner, Lorenzo Richards (1904-1993) presented, in 1931, the transient capillary conduction of water in porous media,

$$(14) \quad \nabla \cdot K(\psi) \nabla (\phi + \psi) = \rho_s A \frac{\partial \psi}{\partial t} ,$$

where $\phi = gz$ is the potential in the gravity field (in which g is gravitational acceleration and z is elevation above datum), $\psi = \int dp/\rho$ is capillary potential (in which p is pressure in the water phase and ρ is density of water), ρ_s is dry bulk density of the soil and, A is the rate of change of moisture content with respect to capillary potential, which is referred to as the capillary capacity of the medium.

Hydrodynamic Dispersion

Geoffrey Taylor (1886-1975) who studied the advective transfer (transport by the bulk movement of water) of dissolved solutes by water in thin capillary tubes made an interesting conceptual-mathematical addition to Fourier's diffusion equation. In a tube through which water is flowing, the velocity of water is practically zero at the walls and is at a maximum along the central axis of the tube. Thus, although we may be satisfied with an average velocity to quantify the total flux of water in the tube, we cannot ignore the velocity variation within the tube if we wish to understand the migration of a solute dissolved in water. The process is complicated by molecular diffusion which will cause the solute to spread perpendicular to the direction of advective transport. By an elegant mathematical analysis of the problem, Taylor (1953) showed that after a sufficient period of time the distribution of the solute will exhibit a diffusion-like profile along the direction of

flow and that the effective diffusion coefficient is a function of the average velocity as well as the geometrical attributes of the capillary tube. Recall that Fick (1855) considered, in a similar fashion, the variation of concentration as a function of capillary radius in osmotic membranes.

Taylor's work has inspired the concept of hydrodynamic dispersion, which is widely used to analyze the migration of contaminant plumes in groundwater systems. Hydrodynamic dispersion is a macroscopic diffusion-like process by which contaminants dissolved in water in a porous medium such as sand spreads (principally along the general flow direction) due to random variations in flow velocity at a microscopic scale.

In considering the migration of solutes with moving water in porous materials, it is important to focus on another attribute of these systems which has direct relevance to the heat diffusion equation. Many solutes which occur in groundwater also have affinities for the solid surface. Hence, they tend to partition themselves between the aqueous phase and the solid surface by a process of adsorption. Adsorption, in turn, is proportional to aqueous phase concentration. When one writes the molecular diffusion equation only for the aqueous phase in such systems, the portion of the solute taken up by the solid surface is accommodated in the form of a chemical capacitance term, usually referred to as the retardation factor. In the mathematics of diffusion, the retardation factor plays the same role as specific heat in the heat diffusion equation.

RANDOM WALK

In 1905, Karl Pearson (1857-1936), a biometrician, sought the help of the journal *Nature* with the request, "Can any one of your readers refer me to a work wherein I should find a solution of the following problem, or failing the knowledge of any existing solution provide me with an original one? I should be extremely grateful for aid in this matter. A man starts from a point O and walks L yards in a straight line; he then turns through any angle whatever and walks another L yards in a second straight line. He repeats this process n times. I require the probability that after these n stretches he is at a distance between r and $r + \delta r$ from his starting point, O" (Pearson, 1905, p. 242). Within a couple of weeks there were several responses to his request. One of them provided a solution in the form of elliptic integrals for $n = 3$. And another, Lord Rayleigh, brought to Pearson's attention his own work (Rayleigh, 1894) on a problem in sound, which gave a simple solution for very large n.

Pearson thanked the correspondents and stated, "I ought to have known it, but my reading of late years has drifted into other channels, and one does not expect to find the first stage in a biometric problem provided in a memoir on sound" (Pearson, 1905, p. 342). He ended his response by stating, "The lesson of Lord Rayleigh's solution is that in open country the most probable place to find a drunken man who is at all capable of keeping on his feet is somewhere near his starting point!" Pearson was probably the earliest to formally state the problem of random walk or random flight. By analogy, however, the representation of the random walk problem in the form a diffusion equation for very large n goes back to Lord Rayleigh.

In 1880, Lord Rayleigh (1842-1919) addressed the problem of the intensity of the resultant of a large number of vibrations of the same period and amplitude but of arbitrarily chosen phase. He solved this problem and then in the second edition of his classic, *Theory of Sound*, Rayleigh (1894) solved the same problem by a different method, in which the distribution function of the random flight problem was shown to satisfy Fourier's heat conduction equation.

Rayleigh (1880) started with a simple case in which only two phases were possible, positive and negative. In this instance, if all the n cases had the same phase, the resulting intensity would be n^2 , but, if half of them had one phase and the other the opposite phase, the resultant intensity will be 0. Rayleigh investigated the question: what is the probability of expectation that the intensity will be between x and $x + \delta x$, given n is large? Clearly, the solution involves the study of a very large number of independent combinations in order to deduce the required probability. This question lead him first to a difference equation involving x and n , which was then identified with the following equation, Rayleigh (1894, p. 39),

$$(15) \quad \frac{df}{dn} = \frac{1}{2} \frac{d^2f}{dx^2} .$$

In this equation f is a probability function, dependent on x and n . Note that Rayleigh did not use the now widely used symbol for the partial differential. He then proceeded to consider the more general case in which the phases of the vibration are distributed randomly over the entire period. In such a

case, two quantities have to be considered, the resultant amplitude and resultant phase. For mathematical convenience, Rayleigh converted the two quantities in polar coordinates (magnitude and phase angle) to Cartesian equivalents. This then led to the “two-dimensional” diffusion equation,

$$(16) \quad \frac{df}{dn} = \frac{1}{4} \left(\frac{d^2f}{dx^2} + \frac{d^2f}{dy^2} \right) .$$

It is worth noting here that Lord Rayleigh’s equation is defined in the sample space rather than in time.

Pearson (1906) applied the random walk approach to the idealized problem of dispersal of species in homogeneous habitats. His “fundamental problem” of species dispersal involved the average distance r through which an individual of a species moves from habitat to habitat (referred to as the flight). Let there be n such flights to a breeding ground, or from one breeding ground to another if the species reproduces more than once. Given these the question is, what would be the distribution after n random flights of N individuals departing from a central point? In this classic work on dispersion, Pearson addressed cases ranging from n being small to n being very large. Later, the random walk approach was applied by Ronald Aylford Fisher (1890-1962) to the problem of transmission of a finite number of genetic mutations among successive generations of a given species (Fisher, 1923).

During the 1930s, the Russian mathematician Andrei Nikolaevich Kolmogorov (1903-1987) known for his major contributions to the theories of probability and diffusion, addressed the two dimensional linear diffusion equation with a source-sink term dependent on the potential itself ,

$$(17) \quad \frac{\partial v}{\partial t} = k \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + F(v) .$$

This is a differential equation with a nonlinear source term, and Kolmogorov showed (1937) that this equation had solutions of the traveling wave type. He embarked on this problem with the idea of contributing to the field of genetics in such areas as the advancing profile of a recessive gene or the

study of the behavior of an island populated by carriers of a dominant gene (such an island will “dissolve” if it is too small, or will grow indefinitely if it is too large). Although this work did not receive the anticipated attention in biology, it did prove to be quite influential in the fields of combustion and gas dynamics.

We now consider the connection between Fourier’s heat conduction equation and stochastic problems in physics. Drawing upon the earlier work of Rayleigh and generalizing the results, Chandrasekhar (1943) provided a detailed development of the three-dimensional stochastic differential equation stemming from random flight. He first derived an expression, based on arguments similar to those of Rayleigh, for the probability $W(R)$ that a single particle, starting from a center and undergoing n random displacements in a unit of time in three dimensions, each displacement having a magnitude r , will find itself in an element of space between R and $R + dR$. In this development he accounted for absorbing and reflecting boundaries. From the form of this solution he inferred, “... that the solutions perhaps correspond to solving a partial differential equation with appropriate boundary conditions.” The solution he had obtained in fact resembled the continuous point source solution of the heat conduction problem (Carslaw, 1921). Chandrasekhar (1943) then extended the result to a slightly different problem involving a large number of particles (instead of a single particle), all starting from the same initial position. He then asked: what fraction of the total number of particles will be found in an element between $R+dR$? The answer to this question led to the partial differential equation for the function $W(x,y,z,t)$,

$$(18) \quad \frac{\partial W}{\partial t} = D \left(\frac{\partial^2 W}{\partial X^2} + \frac{\partial^2 W}{\partial Y^2} + \frac{\partial^2 W}{\partial Z^2} \right) ,$$

where $D = n \langle r^2 \rangle / 6$, in which $\langle r^2 \rangle$ is the mean square displacement that is to be expected on any given occasion. This equation is physically closer to the heat conduction equation because W now denotes particle density; hence, we can think of this equation in terms of mass conservation, which is analogous to energy conservation.

ECONOMICS

During the eighteenth century, Pascal, Bernoulli, Laplace and others made great strides in the application of the calculus and the theory of differential equations to the solution of a variety of problems in the physical sciences. Simultaneously, these natural philosophers were also developing the foundations of probability and statistics to help understand the behavior of biological and social systems which are intrinsically subject to uncertainties of observation and quantification. Thanks to these pioneering contributions, the application of probability and statistics in the fields of ethics, morality, psychology, and economics was well under way by the middle of the nineteenth century.

Francis Ysidro Edgeworth (1845-1926) was a statistician of distinction who played a major role in the development of mathematical economics by incorporating probability and statistics into the analysis of social economic data (Stigler, 1978). In an early analysis of the law of error, Edgeworth (1883) provided a derivation of Fourier's diffusion equation for the probability density of the sum of many random variables. Let u_x be the probability density of u evaluated at x of the sum of s independent random variables, each with density $f(x)$ symmetric about 0. Edgeworth started with the recursive relation,

$$(19) \quad u_{x,s+1} = \int_{-\infty}^{\infty} f(z) u_{x+z,s} dz ,$$

with $\int f(z) dz = 1$ and $\int zf(z) dz = 0$. The left-hand side of (19) is approximated by, $u_{x,s+1} = u_{xs} + du_{xs}/ds$, and $u_{x+z,s}$ is expanded into an approximate Taylor series,

$$(20) \quad u_{x+z,s} = u_{x,s} + z \frac{du_{xs}}{dx} + \frac{z^2}{2} \frac{d^2u_{xs}}{dx^2} .$$

Substituting (20) into (19) and recognizing that $\int z^2 f(z) dz = 1$ and $\int zf(z) dz = 0$, we get,

$$(21) \quad \frac{\partial u}{\partial s} = \frac{c^2}{4} \frac{\partial^2 u}{\partial x^2} ,$$

where, $c^2 = 2 \int z^2 f(z) dz$. The implication is that (21) provides an approximate asymptotic solution to the recursive equation (19). Note that Edgeworth too, like Lord Rayleigh, dealt with the distribution function in terms of samples rather than time and that Einstein's (1905) line of reasoning is very similar to that of Edgeworth.

About the same time that Lord Rayleigh (1894) derived the stochastic differential equation involving a random mixing of acoustic waves, Louis Bachelier (1870-1946) independently laid the foundation for the application of stochastic calculus to the continuous time economics of derivatives-security pricing. A student of Henri Poincaré at the Sorbonne, Bachelier (1900) presented a dissertation entitled "*Theory of Speculation*" in which he applied evolving notions of stochastic calculus to economic problems of option pricing. In this work, Bachelier provided a derivation of the Fourier partial differential equation for the probability density of what is known as a Wiener process, or Brownian motion (a symmetric normal distribution with zero mean). He pursued an approach similar to that of Lord Rayleigh (1894) with discrete difference equations and introduced the notion of "radiation of probability" which is conceptually analogous to Fourier's law of heat conduction. Thus Bachelier states, "Each price x during an element of time radiates towards its neighboring price an amount of probability proportional to the difference of their probabilities." Accordingly, the probability p of price x at moment t is given as,

$$(22) \quad p = - \frac{dP}{dx},$$

where P is the probability that the price exceeds x . Using this to evaluate the "probability exchanged through x during the period Δt ", Bachelier wrote down the Fourier equation,

$$(23) \quad c^2 \frac{\partial P}{\partial t} - \frac{\partial^2 P}{\partial x^2} = 0.$$

Bachelier's stochastic treatment of option pricing was ahead of its time. And the work would receive little recognition for nearly half a century.

In the field of mathematical economics, the importance of Bachelier's approach was recognized by Paul Anthony Samuelson (1915-), who used it to develop a theory of warrant pricing. Samuelson (1965) pointed out that Bachelier's derivation, just as Einstein's derivation of the diffusion equation for Brownian motion, assumed that the mean of the distribution function to be always zero. From practical considerations of warrant pricing he found this assumption too restrictive. He then showed that the introduction of a bias in the instantaneous rate of growth introduced a drift term, leading a more general Fokker-Planck equation analogous to (13).

Meanwhile, Bachelier's approach had also influenced the work of Kiyoshi Itô (1915-) in stochastic processes. Itô's work, in turn, formed the basis of the introduction of stochastic calculus to the theory of finance by Robert C. Merton (1944-). Introducing the notion of Continuous Time Finance in which stock-pricing is treated as a continuous process in time, he employed Ito's stochastic theory to establish rules for portfolio management and rational option pricing (Merton, 1971, 1973). Based on the derivations of Merton, Black and Scholes (1973) proposed a diffusion model for option pricing which has proved to be extremely influential in guiding the pricing of stock options and evaluating corporate assets over the past two decades.

The problem of option pricing arises when an investor trades in stocks through a combination of actual stocks held and stock options. The purpose of combining stocks owned and stock options is to hedge or protect the investment portfolio from risk in an environment where stock prices are intrinsically volatile, that is, subject to random changes in price. Merton (1973) showed that if one could continuously trade in call options by maintaining a dynamic balance between the stocks held in the hedge and the quantity of options in the hedge, the investment would be risk-free, regardless of the volatility of the stock prices.

Let option price w be a function of time and stock price, S . In turn, S is a random variable in time. That is, $w = w(t, S(t))$. If S were to be a non-random variable, the total derivative of w is equal to the sum of the partial derivatives of w with reference to t and S , multiplied respectively by dt and dS . However, a fundamental attribute of the Itô process is that if $F = F(t, X(t))$, where X is a random variable, the total derivative of F will include an extra term involving the second derivative of X with reference to X . That is,

$$(25) \quad dF = \frac{\partial F}{\partial t} dt + \frac{\partial F}{\partial X} dX + \frac{1}{2} \sigma^2 \frac{\partial^2 F}{\partial X^2} dt ,$$

where, σ^2 is the variance. This property, when applied to the change in call price dw and subjected to the condition that the stocks held in hedge and the quantity of call options are continuously balanced, leads to the diffusion equation,

$$(26) \quad \frac{\partial w}{\partial t} = r w - r S \frac{\partial w}{\partial S} - \frac{1}{2} S^2 \sigma^2 \frac{\partial^2 w}{\partial S^2} ,$$

where σ^2 is the instantaneous variance rate of the stock price. In (26) r is the riskless return rate on investments, such as treasury bills. The reasoning is that if the option price is perfectly hedged and riskless, the return from the portfolio must be equal to the riskless return rate. Note that the Black-Scholes equation (26) a form of the Fokker-Planck equation.

REFLECTIONS

Having surveyed the development and influence of Fourier's heat conduction equation over the past two centuries, it is appropriate to reflect on what we may learn from this type of historical, integrated survey of a broad topic. It is clear that we have gained valuable insights into the atmosphere that prevailed at a time when most of the foundations of modern science were being laid down. We have also learned something about how some of the most distinguished figures of modern science developed their ideas, communicated with each other and collectively contributed to the advancement of knowledge. The process of knowledge advancement continues, although the scientific atmosphere of today is different from that which prevailed at the time of Fourier. It is remarkably noteworthy that the many fundamental laws which we use to solve problems of modern day science and technology were enunciated over a hundred years ago. It is therefore useful to step back, and reflect on the atmosphere of the eighteenth and nineteenth centuries, comparing and

contrasting ideas relating to diffusion processes.

THE SCIENTIFIC ATMOSPHERE

Although Fourier made his heat conduction model independent of the nature of heat, he departed from convention and took a macroscopic approach based on empirically defined laws. Interestingly, this approach of developing workable models of nature based on empirical laws was followed with great fervor by others who followed. Many set for themselves the goal of finding “laws” and often presented their results as laws, although supporting experimental data were not quite perfect. Ohm (1827), Graham (1833), Fick (1855), and Darcy (1856), all described their experimental observations as laws. However, departures were made from this empiricism by Maxwell (dynamical theory of gases, 1867), Nernst (osmotic pressure and chemical diffusion, 1888) and Einstein (Brownian motion, 1905) who derived the diffusion coefficient by starting with mechanics at the molecular level and integrating the results to the macroscopic scale. Following this tradition, modern physicists are attempting to calculate properties of material starting from the atomic level, taking advantage of the power of modern computers.

During the late eighteenth century and early nineteenth century, great contributions were being made to physical sciences by physiologists, physicians, and biologists. Notable among these were Black, Crawford, Berthollet, Dulong, Poiseuille, Fick, and Pfeffer. Science was advancing due both to the intuitive genius of experimentalists and the talents of the mathematical physicists for the abstract. James Clerk Maxwell, one of the most distinguished personalities of modern science, had a flair not only for generating scientific ideas of remarkable originality but also for reflecting, with fascination, on how the creative minds of his time enriched science. A great admirer of Michael Faraday (1791-1867), he recognized that Faraday made his greatest discoveries in electricity by mental imagery and used practically no mathematics at all. Writing about Faraday, (Maxwell, 1873) states, “The way in which Faraday used his lines of force in co-ordinating the phenomena of magneto-electric induction shews him to have been in reality a mathematician of a very high order--one from whom the mathematicians of the future may derive valuable and fertile methods.”

The fact that Newton's laws of motion provided a single foundation for all of physical

sciences led to the demonstration in the early nineteenth century that all forms of energy--heat, electricity, magnetism, and mechanical-- are equivalent and are mutually convertible. Maxwell demonstrated the unity of electromagnetism and light. Because of the underlying unity of these various phenomena, the major figures of nineteenth century exhibited remarkable breadth of interests and made simultaneous contributions in celestial mechanics, electricity, magnetism, optics, fluid mechanics, and mathematics. Some notable names that come to mind are Laplace, Biot, Poisson, Fourier, Thompson, and Maxwell. Others such as Fourier went beyond science and made contributions in history, linguistics, archeology, and so on. It is evident that in the advancement of scientific knowledge, intuition, and rigor are equally important, as are the talents for meticulous detail and the flair for sweeping synthesis.

The science of the early nineteenth century was largely natural philosophy. Surprisingly, a good deal of communication existed among scholars in diverse fields. The espousal of Fourier's heat conduction equation in so many different disciplines within a few years of its publication attests to the ability and willingness of contemporary researchers to freely borrow ideas from other disciplines.

In contrast, an argument could be made that present-day scientists tend to focus attention on narrow questions at the expense of broader knowledge. One may be tempted to rebut this by stating that scientists of that era could afford to be broad because they were dealing with far fewer complexities than what we are forced to deal with in modern science.

SIMILARITIES AND DIFFERENCES AMONG DIFFUSION PROCESSES

Fourier's single mathematical equation has helped us look at and understand a remarkable array of physical processes. Yet, as Maxwell (1888) so thoughtfully cautioned us, analogies should not be taken too far. Because nature is complex and our ability to describe it is limited, we must idealize it to a form that is convenient for analysis with mathematical tools. Therefore, in dealing with physical systems, mathematical results have to be tempered by the unique feature of the human mind; intuition. Therefore, the scientific enterprise requires that we have the ability to combine mathematics with due consideration of the physical traits that are peculiar to different natural systems. With this view in mind, it is useful to look at the similarities and differences of the systems which we have examined under the unifying role of the heat diffusion equation.

For our purposes, it is useful to identify two broad classes of scientific problems which involve the diffusion process. The first are those in which we like to have control over the materials we are studying. We engineer materials possessing great purity or possessing attributes tailored to our specifications. The second involves the study of materials as they exist. We have to study them in their native state, often with very limited ability to probe their attributes. The first class of problems arise in physical sciences and engineering. The second class of problems arises in what we call the natural sciences, such as earth sciences and biological sciences. The sciences of electricity, magnetism, molecular diffusion, and fluids in permeable media are used by us in both modes. Electricity and magnetism, for example, are used in the study of semiconductors, in the study of neural signals in animals, and the study of the Earth's response to electrical storms. So also, molecular diffusion may be studied either in living cells or as the diffusion of chemicals in contaminant plumes. How rationally we use the diffusion equation to understand the process of diffusion is influenced by the traits of the particular class of problems we are concerned with.

If we go back to Fourier, we find two empirical concepts that are fundamental to the heat diffusion equation: conductivity and capacitance. Conductivity is associated with transport in space. Heat is impelled by thermal forces and, at a particular flux, the impelling forces and resistive forces balance each other, leading to the definition of conductivity. Capacitance, on the other hand, relates to the change of state of mass of material at a given location over an interval of time. The way Lavoisier and Laplace (1783) defined it, the mass in question changes from one thermostatic state to another as temperature changes. By thermostatic, we mean no movement of heat and hence the temperature within the mass in question is uniform everywhere, in the beginning and after the change has occurred. Although conductivity and capacity require, for their definition, finite masses of materials, Fourier mathematically posed the diffusion problem in terms of the limiting case of gradients at a "point," and his limiting model has helped us to reasonably understand diffusion as observed in nature. Therefore, it is reasonable to use conductivity and capacitance as factors for comparing different diffusion processes.

In heat conduction, all materials possess the ability to transmit as well as store the permeant. However, in electricity the materials with the ability to conduct (conductors) and those with the ability to store electricity (dielectrics) form two distinct classes. The flow of electricity in the former

leads to electrodynamics while the storage of electricity in the latter leads to electrostatics. Essentially, the diffusivity of a conductor is infinite whereas the diffusivity of a dielectric is zero. Thus, in the case of a conductor, only the steady state diffusion equation is realistic and the non-steady equation will be meaningful only in heterogeneous situations where conductors and capacitors are arranged in parallel. With modern advances in instrumentation and the ability to probe the dynamic behavior of materials at picosecond and femtosecond intervals, one may ask whether the diffusivity of conductors is very large, although finite. If so, do materials exist between the extremes of conductors and capacitors whose diffusivity is moderate enough so that they can be observed with fast devices and also analyzed with the transient diffusion equation? Should Maxwell's statement that electricity is analogous to an "incompressible fluid" be modified to a "very slightly compressible fluid?" Another important difference between heat and electrodynamics is that electric potential may jump sharply at the junction between materials whereas temperature remains continuous at material interfaces.

Maxwell (1881, p. 334) stresses the importance of Ohm's law by noting that the resistance of a conductor is a very unique physical property which changes only when the nature of the conductor is changed. The magnitude of resistance of a conductor, for example, is independent of the electric potential at which the conductor is maintained or the intensity of the current. Because of this, if the conductor has a uniform cross sectional area, we can assert that the gradient of potential is the same everywhere within the conductor. Hence, as Maxwell (1881, p. 334) states, "The resistance of a homogeneous conductor may be measured to within one ten thousandth or even one hundred thousandth part of its value." Now, compare this with heat conduction. The thermal conductivity of a material is a function of its temperature, although in general the dependence is not very strong. Therefore, if the heat conduction experiment is conducted on a uniform bar with small temperature differences between the inlet and the outlet, we may reasonably *assume* that the gradient everywhere within the rod is the same. Nonetheless, this is only an assumption. If in fact thermal conductivity is a function of temperature, then in principle one cannot interpret the experimental data unless an a priori assumption is made about the dependence of conductivity on temperature.

The phenomenon of molecular diffusion in liquids is more complex than portrayed by Fick's equation, which only considers solute movement. Van't Hoff's (1887) analogy between gases and

solutions implies that the pressure in the water phase of an aqueous solution and the osmotic pressure are additive, just as partial pressures in gases. As a result, in a solution where spatial concentration variations exist, water will be driven towards areas of higher solute concentration where the water phase pressure is smaller and the solutes will be driven in the opposite direction. Thus, in general, solute migration is intrinsically a multispecies problem involving more than one current.

As we have seen, Maxwell (1867) derived an expression for the diffusion coefficient of one gas in another starting from molecular collisions and found that his theoretical estimates reasonably agreed with experimental data. Similar attempts could probably be made with success in the case of pure solvents or solids. However, such theoretical estimation of hydraulic conductivity or hydraulic capacitance is almost impossible in the case of natural geologic materials. These materials are in fact heterogeneous mixtures of solids and fluids with grain size and grain geometry showing enormous spatial variations. In geologic materials, one uses the heat conduction model purely in an empirical sense. Conductivity and capacity are empirically determined parameters. Ideally, these will be experimentally estimated on a spatial scale that is of relevance to a given problem on hand.

Unlike in heat conduction where thermal conductivity and thermal capacity are both weak functions of temperature, in geologic materials with migrating fluids these parameters may vary significantly in space and in time. For example, consider the advancing wetting front in a soil following rain, in which the hydraulic diffusivity in the vicinity of the front may change by a factor of a million or more. Combined with the fact that geological materials are very heterogeneous, such systems are characterized by a profoundly non-linear form of the diffusion equation, a non-linearity that is seldom encountered in heat diffusion or perhaps, any other diffusion process.

Capacitance, Random Walk and Error Function

If we take a panoramic view of the development of thought related to diffusion, we notice two fundamentally different lines which converge to the same mathematical statement. As shown below, we also notice that these two lines are linked together by a remarkable mathematical function.

Consider the simple and fundamental problem of instantaneous point source of heat. This problem is described by Fourier's equation in spherical coordinates and consists of the release of a finite quantity of heat Q instantaneously at time 0 at a point within a homogeneous solid extending

to infinity in all directions. For convenience, we choose the point of release to be the origin. We now ask the question, what will the distribution of change of temperature $v(r,t)$ be in the vicinity of the point?

We may qualitatively visualize the solution to this problem as follows. Because the solid is homogeneous in all directions, the distribution of change in temperature will be symmetrical along any line passing through the origin at all times. Also, since quantity of heat and temperature are uniquely related through heat capacity, the maximum temperature change along any profile will be at the origin at all times, although the maximum value will decay with time. The symmetry at origin requires that the spatial gradient of temperature be zero there at all times. Finally, the temperature at infinite distance from the origin will always be zero. Intuitively, one can visualize that this curve must have a bell shape. It turns out that mathematical function which satisfies these requirements is the integrand of the well-known error function. Thus, the mathematical solution to this problem is (Carslaw, 1921),

$$(27) \quad v(r, t) = \frac{Q}{8 [\pi \kappa t]^{\frac{3}{2}}} e^{-\frac{r^2}{4 \kappa t}},$$

where, κ is thermal diffusivity and r is distance from origin.

Interestingly, this function which describes an observable physical process, also describes the probability density of random variables such as measurement errors, Brownian movement of particles in suspension or the random walk of a drunken man, except for scaling factors. It was this connection that induced Edgeworth (1883, Law of Error), Lord Rayleigh (1894, random mixing of acoustic waves), Bachelier (1900, theory of speculation) and Einstein (1905, Brownian movement) to establish the links of stochastic processes with Fourier's diffusion equation.

The mathematical similarity between a deterministic physical process and the statistical representation of the gross behavior of a random process is intriguing and merits some attention. We note that in setting up the diffusion equation, Fourier moved away from the philosophy of action at a distance and assumed that ".....each general section of infinitesimal width dx would be influenced

only by the adjacent sections...” Curiously, this assumption resembles the basic attribute of the Markoff process, namely, short memory. In the case of the instantaneous point source problem, the bell shape of the temperature profile at any given time arises because materials possess the important ability to store heat with changing temperature. As heat moves away from the point at which heat was introduced, part of it is absorbed by the solid and the quantity of heat moving through declines with increasing distance from the origin. Remarkably, in the case of fortuitous error the same bell shaped curve arises due to a collection of random events. Why is it that a deterministic process involving change of storage exhibits a mathematical similarity to a random process for which the notion of storage has no relevance? Or could it be that an abstract notion of storage is associated with random processes and that by contriving a notion of capacitance for these processes one may facilitate the solution of problems involving random processes?

BEYOND LINEAR PROBLEMS

Perhaps the most important reason for Fourier's success is that he was able to provide credible methods for solving the differential equation he had formulated. Without the solution techniques, his equation would merely have remained a curiosity. In order for him to obtain the solutions, the differential equation had to be linear. The linearization of the heat diffusion equation remains to this day one of the first steps to enable solvability of that equation. The nature of partial differential equations is such that even so linearized, solutions can be obtained only when the domain of flow has reasonably simple geometry and when simple heterogeneities are involved. Experience, however, shows that problems of practical interest, especially in geological and biological systems, are characterized by nonlinearities, heterogeneities, and flow domains with complicated geometry. These systems were clearly beyond the reach of the methods pioneered by Fourier and remained so until the advent of digital computers. Digital computers opened up a new avenue of solving problems by numerical methods.

During the 1940s and 1950s, von Neumann and others initiated the solution of the heat diffusion equation by approximating the spatial and temporal derivatives by difference equations. Within a decade thereafter, new numerical methods were developed in which the parabolic differential equation was transformed into an integro-differential equation in which the conservation statements

were posed over finite subdomains of space rather than points. These integro-differential equations were then solved numerically. Although these integro-differential equations were initially developed by ad hoc reasoning, it was soon realized that they could in fact stem from variational calculus, which dates back to Lagrange and Euler. It is of interest to us therefore to look at the variational approach.

Recall that Leibniz provided a philosophy of looking at mechanical systems in terms of the scalar quantities, energy and action. Mechanical systems possess energy in two forms, potential energy and kinetic energy. It is a postulate of the Leibniz approach that such systems, when impelled to change by external forces, would respond by redistributing the two forms of energy in some optimal way. This line of reasoning was pursued by Lagrange and was applied to dynamic systems by William Rowan Hamilton (1805-1865). Hamilton enunciated the principle that as a dynamic system changes in time, it tends to minimize the difference between kinetic energy and potential energy, integrated over the system. That difference, expressed in generalized coordinates, is known as the Lagrangian. Hamilton's principle is a variational principle for dynamic systems. The nature of the variational principle is such that it will, upon minimization, lead to the differential equation appropriate to the particular problem. Thus, the variational principle and the corresponding differential equation are two independent ways of describing the same problem. As it turns out, the choice of the differential equation as the basis of problem solving leads to vector calculus which is convenient to use with rectilinear coordinate systems. However, when the system involves complex geometrical patterns that are better described in curvilinear coordinates, the use of vector calculus becomes cumbersome, even with the help of tensors.

The variational approach, which involves global integrals and evaluation of scalars such as energy and action, is better suited to general curvilinear coordinate systems. Therefore, if we have the ability to handle the geometric information pertaining to curvilinear coordinate systems, then we may solve the problem of interest by directly minimizing the variational integral, without being concerned with the equivalent differential equation. Until the advent of computers, we did not have such an ability to handle a large amount of geometric information and, in the absence of such ability, we reduced the variational integral to an integro-differential equation and solved it with the help of techniques developed for vector calculus. The limitation of this approach is that one is still constrained by the drawbacks of handling curvilinear coordinates with vector calculus.

With the availability of increasingly powerful computers, we are now in a position to handle very large amounts of geometric information and process them with great speed. As a result, we should now be able to pursue the philosophical approach of Leibniz, Lagrange, and Hamilton with renewed interest. Fourier's approach of analytic solutions provided the only practical avenue for problem solving in the absence of the powerful tool we now have, the computer. Additionally, analytic solutions to simple problems have provided us with enormous insights into the potential behavior of physical systems. Perhaps the best way to improve upon Fourier's work would be to go beyond the differential equation and look at dynamic systems of diffusion in terms of variational integrals that are directly minimized with the help of the digital computer. This should help us tackle problems which were clearly beyond Fourier's reach.

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