

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 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 on 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 Fourier's development of the heat equation 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.

1. 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 the analysis of problems involving the transfer of heat in physical systems, the conceptual-mathematical structure of the heat conduction equation (also known as the 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, described by a partial differential equation, was first formulated by Jean Baptiste Joseph Fourier (1768–1830) and presented as a manuscript to the Institut de France in 1807. At that time, thermodynamics, potential theory, and the theory of 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 1807 masterpiece, *Théorie de la Propagation de la Chaleur dans les Solides*.

Fourier's work was subjected to review by some of the

most distinguished scientists of the time and was not accepted as readily as one might have expected. It would be another 15 years before this major contribution would be accessible to the general scientific community through publication of his classic monograph, *Théorie Analytique de la Chaleur* (Analytic Theory of Heat) [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 2 centuries later, the heat conduction equation continues to constitute the conceptual foundation on which rests 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 2 centuries is in itself instructive. At the same time, an examination of how the work was received and accepted by Fourier's peers and successors gives us a glimpse into the culture of science, especially during the nineteenth century in Europe. The present work has been motivated both by the educa-

TABLE 1. Chronology of Significant Contributions on Diffusion

	<i>Year</i>	<i>Contribution</i>
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 heat conduction in solids
Fourier	1822	<i>Théorie Analytique de la Chaleur</i>
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
Thomson	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 diffusion in liquids
Darcy	1856	law governing flow of water in porous media
Dupuit	1863	potential theory applied to flow in groundwater 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	flow nets 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	notion of random walk
Buckingham	1907	diffusion of multiple fluid phases in soils
Langevin	1908	framework for stochastic differential equation
Gardner	1922	measurement of potential in a multiple-fluid-phase porous medium
Terzaghi	1924	seepage in deformable clays as analogous to heat diffusion
Richards	1931	nonlinear diffusion of moisture in soils
Fermi	1936	neutron diffusion in graphite as analogous to heat diffusion
Bullard	1949	thermal gradient probe for the ocean floor
Taylor	1953	advective dispersion as a diffusion process

tional 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 unconnected natural processes and, in so doing, to gain historical insights into the manner in which scientific ideas develop. The focus of this paper is on the connections of concepts and ideas. An in-depth treatment of Fourier's 1807 manuscript can be found in the work of *Grattan-Guinness and Ravetz* [1972], and critical treatment of Fourier the man and the physicist, including important Fourier correspondence, can be found in the work of *Herivel* [1975].

The paper starts with 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 from 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 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.

2. DEVELOPMENTS LEADING UP TO FOURIER

Before we describe the scientific developments of the eighteenth century that set the stage for Fourier's con-

tribution, it is useful to briefly state the nature and content of the heat conduction process. The transient heat diffusion equation pertains to the conductive transport and storage of heat in a solid body. The body itself, of finite shape and size, 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 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, and transport of heat, as well as the relation between quantity of heat and temperature, are fundamental to Fourier's heat conduction model. It is important to recognize here that these basic notions were still evolving when Fourier developed his equation. Therefore it is appropriate 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 was producing it commercially 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°.

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 20 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 latter half of eighteenth century, and Pierre Simon Laplace (1749–1827), one of the more influential mathematicians and theoretical physicists of modern science. *Lavoisier and Laplace* [1783] 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 animals release heat during respiration 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. 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 matter at the atomic level. 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. The significance of the Lavoisier-Laplace contribution to Fourier's equation 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 pre-Fourier work in this regard is that of Jean Baptiste Biot (1774–1862) 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. In the bar, heat not only

was conducted along the length but was also lost to the exterior atmosphere transverse to the direction of conduction. Biot's starting point 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 its vicinity. Essentially, then, the mathematical problem of heat conduction came to be considered as one of a class of many-body problems. As was pointed out by *Grattan-Guinness and Ravetz* [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. Consequently, 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. Similar inferences of a qualitative nature had been drawn by *Lambert* [1779], who had experimentally studied heat conduction in a rod [*Herivel*, 1975].

Apart from these foundational developments relating to heat, developments relating to potential theory and differential equations during the nineteenth century deserve notice. The theory of potentials arises in many branches of science, such as electrostatics, magnetostatics, and fluid mechanics. Potential theory involves problems describable in terms of a partial differential equation in which the dependent variable is the appropriate potential (defined as a quantity whose gradient is force) 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* [1789], although the term potential would be coined later by *George Green* (1793–1841), a self-educated mathematician, [*Green*, 1828]. *Laplace* [1789] formulated the equation in the context of the problem of the stability of Saturn's rings.

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, *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 particu-

larly 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 and Ravetz*, 1972; *Herivel*, 1975].

In nineteenth-century Europe, two philosophical views of the physical world prevailed: 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 leading thinkers from France were fully committed to the mechanistic view and devoted their efforts to describing the physical world with greater detail in terms of Newton's laws. At the same time, Newton's 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 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 both approaches ultimately proved equivalent, the mathematics associated with each of 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*, remarkably, realized 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 that 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 understand them rationally in terms of force, momentum, energy, and work. As was already noted, 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, consisting of 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, influenced the work of *Biot* [1804] and his use of action at a distance.

3. FOURIER'S CONTRIBUTION

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. 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. 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. In this setting, 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 is worthwhile. For a comprehensive account, the reader is referred to *Grattan-Guinness and Ravetz* [1972] and *Herivel* [1975]. Fourier was born in 1768 in Auxerre in Burgundy, now the capital of Yonne department 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'Égypte. 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 the Ecole Polytechnique were ended when Napoleon made him prefect of the department of Isère, near the Italian border, with its capital at Grenoble.

During his tenure as prefect, Fourier embarked on two very different major scholarly efforts. On the one hand, he played a leadership role on a multivolume 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, 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.

Like Biot before him, Fourier initially formulated heat conduction as an n -body problem, stemming from the Laplacian philosophy of action at a distance. During

these early investigations he was aware of Biot's work, having received a copy of the paper from Biot 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, Fourier moved away from discontinuous bodies and towards continuous bodies. Instead of starting with the basic equations of action at a 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. 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 and Ravetz*, 1972]. The superposition artifice offered such promise for 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 and Ravetz*, 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 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*; it is now an avowed classic.

4. 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,

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

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 K is independent of temperature, (1) reduces to Laplace's equation.

In (1), thermal conductivity K is physically 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 1807 manuscript, Fourier formulated thermal conductivity mathematically rather than experimentally. As was pointed out by *Grattan-Guinness and Ravetz* [1972] and *Herivel* [1975], Fourier arrived at this concept gradually, as he was making the transition from discontinuous

bodies to a continuous body. The notion of heat flux was yet a new concept, and Fourier would fully clarify it only in 1810, in a letter to an unknown correspondent [*Herivel*, 1975].

The concept of specific heat capacity, proposed experimentally by *Lavoisier and Laplace* [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 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, $\eta = K/(\rho c)$, where ρ is density of the solid. The higher the diffusivity, the faster the tendency of the material to respond to externally imposed perturbations.

5. 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 it was applied 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 adaption 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 and Ravetz*, 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 the Ecole Polytechnique. He also became the Secrétaire Perpétuel of the Académie des Sciences.

For the sake of completeness it may be mentioned here that Fourier's political career came to an end with the fall of Napoleon at Waterloo in 1815. His pension was refused and, close to 50 years old, he was virtually without an income. However, 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 appointments, 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 2 centuries, it is convenient to organize the discussions into the following general subheadings: electricity, molecular diffusion, flow in porous materials, and stochastic diffusion.

5.1. 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). Quantities such as current strength and intensity were not precisely defined. At this time, Georg Simon Ohm of Germany (1787–1854) 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. Ohm [1827] started with three "laws." According to his first law, the communication of electricity from one particle takes place only 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 is implied by this assumption of Ohm.

Ohm's careful experiments showed that the current in a galvanic circuit did not vary with time (steady flow), the intensity of the electric current (measured with a torsion magnetometer) was directly proportional to the drop in "electrostatic force" (measured with an electroscope) 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 and of its

form (resistance was found to be inversely proportional to the cross-sectional area of the conductor). Equally important, Ohm showed that the resistance of the conductor was independent of the magnitude of the current itself or the magnitude of the electrostatic force. Ohm gave a precise meaning to flux (current) and resistance. However, he erred in his use of electrostatic force, which he considered to be the quantity of electricity contained in an unit volume. Although electrostatic force so defined is an intensive quantity, it was left to Kirchhoff [1849] to establish that Ohm's law should properly be expressed in terms of potential (voltage) difference rather than difference in electrostatic force [Archibald, 1988]. Following Ohm's work, the measurement of the electrical resistance of various materials with great precision became a fundamental task in physics [Maxwell, 1881].

Ohm took the analogy with heat conduction farther and considered the flow of electricity to be exactly analogous to the flow of heat and wrote a transient equation of the form similar to (1),

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

where γ is a quantity analogous to heat capacity, u is the electrostatic force, 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. (Unless otherwise stated, the notations used in this paper are those of the referenced authors.) Ohm was not confident about this equation and admitted that no experimental evidence for γ was as yet forthcoming.

James Clerk Maxwell (1831–1879) derived the same equation in a different context and showed that Ohm was in error in proposing (2) the way he did. Maxwell [1881] 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 is indicated by the second term on the right-hand side of (2). Maxwell [1881, p. 422] expressed Ohm's error thus: "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* [1881, p. 336] pointed out, behaves like an incompressible fluid, and hence conductors do not possess the property of capacitance.

It is interesting to note that Ohm formulated his flux law in terms of a difference in potential and a resistance, rather than in terms of the infinitesimal notion of a gradient as was done by Fourier. The resistance, in Ohm's law is an integral that combines the material property as well as the geometry of the conductor of finite size through which current is flowing. Fourier's method of separating material property from geometry was of the right mathematical form to pose the problem as a differential equation. In contrast, Ohm's approach of dealing with resistance and potential difference is more naturally suited for appreciating the diffusion problem directly in terms of integrals involving work, energy, and action.

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 Fechner, Lenz, Weber, Gauss, and 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 [*Gillispie*, 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.

William Thomson (1824–1907), also known as Lord Kelvin, was greatly influenced by Fourier's work. 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 [*Thomson*, 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 to prevent the analogies from being carried too far. He 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. Moreover, there is nothing in the electrostatic system that can

be described as flow. Note also that the temperature of a body cannot be altered without altering the physical state of the body, such as density, conductivity, or electrical properties. On the contrary, bodies may be strongly electrified without undergoing any physical change.

It is pertinent here to mention a major geological controversy of the nineteenth century in which Lord Kelvin and the heat conduction model played a part. Fourier himself had maintained on more than one occasion [*Herivel*, 1975] that the phenomenon of terrestrial heat motivated him to develop a theory for heat conduction in solids. On the basis of geological observations, contemporary geologists were of the opinion that the Earth was very old. For example, Charles Darwin had estimated that the age of the Earth was about 300 million years, based on assumed erosional rates of sediments. Kelvin analyzed the problem from a different basis, assuming that the Earth was initially a solid sphere at a high uniform temperature which gradually lost heat by conduction to reach the present state. Accordingly, he estimated that the Earth cannot be older than about 100 million years [*Hallam*, 1983]. Based on this he severely criticized Darwin and other geologists for grossly overestimating the age of the Earth. However, Kelvin's cooling Earth model was eventually invalidated by with the discovery of radiogenic heat in the Earth's crust. The radioactive heat source of the Earth enabled Earth scientists to extend the age of the Earth to many billion years during the early twentieth century.

Despite his erroneous estimate of the age of the Earth, Kelvin's conceptualization of global heat transport was very perceptive. It drew the attention of Earth scientists to the fact that the Earth is a heat engine and that observations of temperature and heat flow near the Earth's surface are essential for understanding the internal structure and the evolution of the Earth. Prior to the 1950s, however, few heat flow measurements were available from continental boreholes, and practically nothing was known about the natural loss of heat from the oceanic floors occupying over 70% of the Earth's surface. The prevalent untested view was that because the oceanic crust was known to have very low content of radioactive minerals (compared to the high content of the continental granitic rocks), heat loss from the floors of the oceans must be significantly smaller than that of the continental surface.

A major breakthrough in the field of terrestrial heat flow studies was the design and development of a probe to measure temperature gradients on the deep ocean floor by Edward Crisp Bullard (1907–1980) in the summer of 1949 [*Bullard et al.*, 1956]. This device produced the first set of heat flow data from the Pacific Ocean in 1952 and the Atlantic Ocean in 1954. Surprisingly, the data showed that the heat loss from beneath the oceans was comparable in magnitude to that from the continents, and it became necessary for Earth scientists to rethink their fundamental notions about the thermal

structure of the Earth. These initial observations provided a major impetus to marine geophysicists to the measurement of heat flow beneath the deep oceans.

This was also the period during which the notion of plate tectonics was taking root in the Earth sciences on the basis of diverse field observations: magnetic reversals, young ages of oceanic crust, patterns of submarine seismicity and volcanism. Within a decade of the first heat flow measurements by Bullard and his coworkers, by the mid 1960s, several hundred heat flow measurements became available from the Atlantic, the Pacific and the Indian Oceans. The spatial patterns of heat flow on the ocean floors revealed by these measurements contributed greatly to the emerging notions of plate tectonics. Fundamental to the new view was the hypothesis that the oceanic crust is created at the mid-oceanic ridges by molten rock welling up from the Earth's interior and that upon cooling, the rigid oceanic plate spreads away from the ridges with time. Thus the rocks of the seafloor become older with distance away from the ridge.

To analyze this problem, *McKenzie* [1967] considered the oceanic crust to be a plate of finite thickness (about 50 km), in which conductive heat transport occurred in two dimensions. The bottom (550°C) and the top of the plate (0°C) were treated as constant temperature boundaries. The lateral spread of the plate away from the ridge at a finite velocity of a few centimeters per year was handled with the help of an advection (linear translation) term. Heat flow observations from the Atlantic, the Pacific and the Indian Oceans agreed reasonably well with the estimates based on the solutions of this advection-diffusion problem. The fact that the spatial heat flow patterns from the ocean floors were consistent with a spreading seafloor with vertical heat conduction through the rigid crust was an important corroborative factor in the establishment of plate tectonics as a viable theory.

We saw earlier that Ohm had attempted unsuccessfully to formulate a time-dependent electrical flow equation 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.

5.2. 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 during the eighteenth century. In the early nineteenth century, experimental chemists began paying serious attention to molecular diffusion, and the publication of Fourier's work 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.

5.2.1. Diffusion in liquids. Among the earliest observations that 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 Dutrochet (1776–1847) made pioneering contributions in the systematic study of osmosis. A physiologist and medical doctor by training, Dutrochet 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. *Dutrochet* [1827] strongly disagreed with Poisson and, on the basis of 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 toward 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* [1850] 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* [1855a, b]. Adolf Fick (1829–1901) was a Demonstrator in Anatomy at the University of Zurich and, in addition to his professional training in medicine, had a sound background in mathematics and physics. Fick expressed regret that Graham failed to identify any fundamental law of diffusion from his substantial experimental data. In seeking to remedy the situation, Fick saw a direct analogy between the diffu-

sion of heat in solids and the diffusion of solutes in liquids.

By direct analogy with Fourier, *Fick* [1855b] wrote down the parabolic equation for transient diffusion of solutes in liquids in one dimension thus:

$$D \left(\frac{\delta^2 c}{\delta x^2} + \frac{1}{Q} \frac{dQ}{dx} \frac{\delta c}{\delta x} \right) = \frac{\delta c}{\delta t}, \quad (3)$$

where D is the diffusion coefficient, c is aqueous concentration, and Q is the area of cross section. Note that Fick made a novel departure from Fourier in writing the one-dimensional equation. The second term on the left-hand side of (3) accounts for the variation of the area of cross section along the flow path (the x axis). Intrinsically, Fick's equation is valid for a flow tube of arbitrary shape involving a curvilinear x axis. Indeed, *Fick* [1855a, b] presented data from a diffusion experiment in an inverted-funnel-shaped vessel, solved (3) for the geometric attributes of the particular cone-shaped vessel, and found that his mathematical solution compared favorably with the steady state concentrations at different locations within the vessel. For a flow tube with constant area of cross section, (3) simplifies to Fourier's equation. One can readily verify that (3) leads also to appropriate differential equations for radial and spherical coordinates. Upon reflection, it becomes apparent that integration of (3) 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* [1855a, b] went on to analyze flow across a semipermeable membrane by idealizing it as a collection of cylindrical pores of radius ρ . As was suggested earlier by *Dutrochet* [1827], two simultaneous currents will occur through the capillaries; the solute current will occur toward the solvent and the solvent current will occur toward the solution. Fick reasoned that because of the affinity of water to the material composing the membrane, the water current will be organized more toward the walls of the pores and the solute will be organized toward 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.

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 the University of Göttingen when he was 20 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, treating the outer layer of the cell as a semipermeable membrane, 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 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 measured 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.

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 Hendricus van't Hoff (1852–1911), an influential physical chemist 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, two opposing currents of flow are involved, each being 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 the water phase pressure and the stronger will be the solvent current toward the solution should the solution communicate with the solvent. 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 that 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 s^{-1} . Combining these, he expressed the flux of solute in terms of the gradient of the osmotic pressure and the reciprocal of the 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 was proposed by *Fick* [1855a, b]. 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 nonlinear.

For electrolytes in which individual ions will migrate separately, Nernst suggested that in order that the ions composing a given solute may migrate at the same velocity, the differences in ion velocities induced by osmotic pressure will be compensated by electrostatic forces.

5.2.2. Solid diffusion. An early documented observation of solid diffusion is attributed to Robert Boyle (1627–1691) [*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

filig the face, Boyle showed that zinc had indeed diffused into the body of copper. Yet controlled diffusion measurements would not become possible until 200 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 took up the challenge of extending *Graham's* work on liquid diffusion to metals. His progress was considerably hampered by difficulties in accurately measuring the temperature at which diffusion was taking place in the solid state. By adopting *Le Chatelier's* platinum-based thermocouples, he succeeded in studying 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].

Solid diffusion is a process of great importance in many natural and industrial processes. In the lithosphere of the Earth it influences the genesis of minerals, ores, and rocks. As an illustration, we consider the role of solid diffusion in metamorphism, one of three major rock-forming processes. Metamorphism constitutes the physical, chemical, and structural adjustments undergone by solid rocks in response to temperature, pressure, and other environmental changes consequent to burial at depths within the Earth's crust. Metasomatism is a metamorphic process by which a new mineral may grow in the body of an old mineral or mineral aggregate, often occurring at constant volume, with little disturbance of original texture or structure of the mineral (palimpsest textures).

Many geologists of the first half of this century, especially from Europe, were persuaded by field evidence to believe that solid diffusion must have been responsible for the genesis of large bodies of granite and granite-looking rocks, which were previously thought to have solidified from a molten magma. Although their inference was justified qualitatively, the magnitude of the role of solid diffusion in the genesis of large rock masses could not be gauged reliably. This was due to a lack of instruments to observe the effects of diffusion on the microscopic scale at which solid diffusion occurs within mineral grains. Fortunately, the 1950s saw rapid developments in the field of X-ray spectrometry, leading to the development of the "electron-microprobe." This remarkable instrument enabled quantitative chemical analysis in situ within a mineral grain, in the immediate vicinity of a location. By the mid-1960s, mineralogists were able to quantitatively study variations of chemical composition within a single mineral grain at a spatial resolutions of $\leq 1 \mu\text{m}$. New possibilities opened up in the application of the diffusion equation to address fundamental questions related to the age of rocks and their thermal history.

Over the past 3 decades, diffusion-based mathematical models have been used to decipher the history of certain potassium-rich minerals such as feldspars using

the decay of radioactive ^{40}K to ^{40}Ar . Similarly, techniques have also been developed to analyze the decay of uranium in naturally occurring zircon to lead. In both cases the assumption is that the radioactive clock starts to count when the mineral of interest (feldspar or zircon) begins to crystallize from a melt at a certain critical temperature. Once the crystal has formed, the decay process will release the daughter product, as dictated by the appropriate half-life. For different chemical reasons, the daughter products will tend to be excluded from the lattice structure and diffuse out of the crystal, at a rate that depends on the geometry of the crystal (sheet, sphere, cylinder), the diffusion coefficient, and the thermal environment. In minerals, diffusion coefficient is an exponential function of temperature (the Arrhenius relationship), and diffusion will become practically negligible below some threshold temperature. Thus solid diffusion in these minerals is constrained to a temperature window. Consequently, the measurement of diffusion profiles within a single mineral grain may provide valuable information about the thermal history of the mineral and its environment, that is, whether it cooled rapidly or very slowly. In quantitatively interpreting observed diffusion profiles, it is customary to use solutions to Fourier's heat diffusion equation for assumed simple geometries of the mineral grains (sheet, sphere, cylinder), initial conditions and boundary conditions.

Although looking at minerals at extremely fine spatial resolution is of great value, rocks and their origin have to be understood on a much larger field scale, on the scale of rock masses. On a large scale, one may wish to look at metasomatism as a macroscopic solid diffusion process. Intuitively, this may be reasonable because the porosity of rocks is extremely small, comprising microfissures and grain boundaries. However, such a macroscale idealization may lead to quantitatively inaccurate inferences because the fluids in the micropores and grain boundaries may have diffusivities that are many orders of magnitude larger than the corresponding diffusivities of the solid minerals. Thus, in these larger bodies, diffusion over long distances may be dictated by the fluids in the fine pores, and solid diffusion may occur locally, within the mineral grains on the small scale. This entails the application of Fourier's diffusion equation to systems with interpenetrating continua (e.g., fractures on the one hand, and the solid on the other) with radically different diffusion properties.

We may end this discussion on solid diffusion with the work of Enrico Fermi (1901–1954) on neutron diffusion. Fermi 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 corre-

sponding diffusion constants were calculated on the basis of 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."

5.2.3. 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 is known as Graham's law. When we compare gas diffusion with liquid diffusion or the conduction of heat or electricity, we find that in these latter cases we are concerned with conductive transport of the permeant in different host materials, whereas in this 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 law. Thus conductivity is a property of the material rather than 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 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 whose work on the dynamical theory of gases is of fundamental importance. 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 with 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.

5.3. 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 fluid, 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.

5.3.1. 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 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 Léonard Marie Poiseuille (1799–1869), a physician and physiologist. Not satisfied with the contemporary understanding of blood circulation in veins, he 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 $\sim 50 \mu\text{m}$ to $\sim 150 \mu\text{m}$ and measured fluxes as low as 0.1 cm^3 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, in 1840, the first ever protected town water supply system in the world. Dissatisfied with the unhealthy sources of drinking water in his native town of Dijon, he helped bring and distribute water from a perennial spring located several kilometers away from the town. 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 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 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.

During the middle of the nineteenth century, potential theory was recognized as providing a useful conceptual-mathematical basis for understanding artesian wells and other manifestations of deep groundwater circulation in France and elsewhere in Europe.

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.

5.3.2. Flow of multiple fluid phases. A significant development in the study of flow in porous media was the work of Edgar Buckingham (1867–1940). From 1902 to 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 also made one of the most important contributions to soil physics in particular and the study of multiphase fluid flow in general. Soon after, he moved to the newly formed National Bureau of Standards (now National Institute of Standards and Technology) and became well known for, among other achievements, 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 moisture in the soil is critical to judicious 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 (1773–1829). Buckingham [1907]

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 that 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. The strong dependence of hydraulic conductivity on capillary potential renders the study of moisture diffusion in soils a very difficult mathematical problem. 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 counterintuitive 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 transient heat conduction equation. It influences the rapidity with which a material will respond thermally 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. Indeed, 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 defined a capillary potential theoretically, he could measure it only 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, water-filled tube, 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, 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]. This strong dependence capacitance on capillary potential introduces a strong nonlinearity into the differential equation of moisture movement in soils.

5.3.3. Hydraulic capacitance. 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, change in pore volume 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 change in fluid pressure or, equivalently, the fluid potential. Extensive experimental work following Terzaghi has shown that earth materials invariably exhibit nonelastic deformation behavior.

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 as a result of 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 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 the hydraulic capacitance. Thus, unlike the heat problem, which is generally 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 the transient capillary conduction of water in porous media [Richards, 1931],

$$\nabla \cdot K(\psi) \nabla (\phi + \psi) = \rho_s A \frac{\partial \psi}{\partial t}, \quad (4)$$

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 (where 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, referred to as the capillary capacity of the medium.

5.3.4. 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 [1855a, b] considered, in a similar fashion, the variation of concentration as a function of capillary radius in osmotic membranes.

Taylor's work inspired the concept of hydrodynamic dispersion, widely used to analyze the migration of contaminants in groundwater systems. Hydrodynamic dispersion is a macroscopic diffusion-like process by which contaminants dissolved in water in a porous medium spread (principally along the general flow direction) owing to random variations in flow velocity on 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 that has direct relevance to the heat diffusion equation. Many solutes that 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 concentration in the aqueous phase. 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 because this process effectively slows down spreading caused by the advective process. In the mathematics of diffusion, the retardation factor plays the same role as specific heat in the heat diffusion equation.

5.4. Stochastic Diffusion

5.4.1. Random walk. It is evident from the foregoing discussion that the analyses of the flow of electric current; diffusion in liquids, solids, and gases; and the flow of fluids in porous materials were all directly influenced by Fourier's heat conduction model during the nineteenth century. In these analyses, Fourier's model was used in an empirical way, to interpret experimental data from macroscopic systems. In marked contrast to this empirical transfer of concept, the second half of the nineteenth century saw the extension of the heat diffusion equation to problems of a more theoretical nature, involving the gross manifestation of random processes. During the early twentieth century this extension would lead to the development of a new field of considerable interest, namely, stochastic processes. The beginnings of stochastic diffusion were latent in the work of four quite different workers: the theory of sound of Lord Rayleigh, the law of error of Edgeworth, the theory of speculation of Bachelier, and the theory of Brownian motion of Einstein. The appellation "random walk" to denote these processes was coined by Karl Pearson (1857–1936), a biometrician. The transition from random walk to stochastic differential equations would be catalyzed by the work of Langevin. It is now of interest to consider in some detail, the conceptual-mathematical developments that led to the theoretical view of the heat conduction equation as an ensemble manifestation of fine-scale random processes.

Pearson [1905, p. 242] 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 ." 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 $n = 3$. In another, Lord Rayleigh (John W. Strutt, 1842–1919) 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 [Pearson, 1905, p. 342]. "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." 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 of a diffusion equation for very large n goes back to Lord Rayleigh.

5.4.2. Theory of sound. *Rayleigh* [1880] addressed the problem of estimating the amplitude and intensity of the resultant of the mixing of n vibrations of the same period and amplitude but of arbitrarily chosen phase. He solved this problem using Bernoulli's theorem on probability and obtained an expression in terms of the exponential of $-x^2/2n$ for the probability that the resultant amplitude would be between x and $x + \delta x$ after a large number of trials. Recognizing the similarity of this solution to that of Fourier's heat equation, *Rayleigh* [1894] solved the same problem by a different method, obtained the same results, and showed that the resultant of random mixing satisfies Fourier's heat conduction equation on an average after a large number of trials.

Rayleigh 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 half had the other phase, the resultant intensity will be 0. Rayleigh investigated the question: What is the expectation that the amplitude will be between x and $x + \delta x$, given n is large? Here, "expectation" denotes the mean value that can be expected from a large number N of such experiments, with the number of waves mixed in each case being n . Let $f(n, x)$ denote the number of combinations in which the resultant amplitude is x . Suppose the number of waves mixed is increased to $n + 1$. What is the number of combinations in which the resultant is x ? If the phase is restricted to $+1$ or -1 , the number of combinations that can have a value x after mixing $n + 1$ will depend on $f(n, x - 1)$ and $f(n, x + 1)$. In fact, if the choice is purely random, we must have,

$$f(n + 1, x) = \frac{1}{2}f(n, x - 1) + \frac{1}{2}f(n, x + 1). \quad (5)$$

By subtracting $f(n, x)$ from both sides of (5),

$$\begin{aligned} f(n + 1, x) - f(n, x) &= \frac{1}{2}f(n, x - 1) + \frac{1}{2}f(n, x + 1) \\ &\quad - f(n, x). \end{aligned} \quad (6)$$

Note that (6) is the classical finite difference form of the diffusion equation. Thus for large n , (6) reduces to,

$$\frac{df}{dn} = \frac{1}{2} \frac{d^2f}{dx^2}. \quad (7)$$

Subject to the condition that $f(0, 0) = 0$, the solution to this is the probability density function,

$$f(n, x) = \frac{1}{\sqrt{(2\pi n)}} \exp\left(-\frac{x^2}{2n}\right). \quad (8)$$

The arithmetic mean of the intensity of a large number of trials is given by,

$$\frac{1}{\sqrt{2\pi n}} \int_{-\infty}^{\infty} x^2 \exp\left(-\frac{x^2}{2n}\right) dx = n. \quad (9)$$

Rayleigh now relaxed the assumption of allowing only two phases, positive and negative, and let the phases take all values from 0 to 2π . By using suitable transformations between polar coordinates and cartesian coordinates, he then showed that the appropriate equation takes on the two-dimensional form of Fourier's equation,

$$\frac{df}{dn} = \frac{1}{4} \left[\frac{d^2f}{dx^2} + \frac{d^2f}{dy^2} \right]. \quad (10)$$

5.4.3. Law of error. Francis Ysidro Edgeworth (1845–1926) was a statistician 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]. *Edgeworth* [1883] derived the differential equation governing the behavior of compound error, which he termed the law of error. He started by assuming that compound error is a linear function of indefinitely numerous elements, each element being sampled from facility function $f(z)$ assumed to be symmetric. Let $u_{x,s}$ be the function describing the compound error where x is the extent of the error and s is the number of elements. Given this definition of u , Edgeworth expressed $u_{x,s+1}$ in terms of $u_{x,s}$ as,

$$u_{x,s+1} = \int_{-\infty}^{\infty} f(z)u_{x+z,s} dz. \quad (11)$$

The left-hand side of (11) may be expressed as, $u + du/ds$. The right hand side of (11) may be expanded into a Taylor series. Therefore (11) leads to

$$\begin{aligned} u_{x,s+1} &= u_{x,s} \int_{-\infty}^{\infty} f(z) dz + \frac{du_{x,s}}{dx} \int_{-\infty}^{\infty} zf(z) dz \\ &\quad + \frac{1}{2} \frac{d^2u_{x,s}}{dx^2} \int_{-\infty}^{\infty} z^2f(z) dz. \end{aligned} \quad (12)$$

Noting that the middle term on the right-hand side of (12) is equal to zero, (11) leads to

$$\frac{du}{ds} = \frac{c^2}{4} \frac{d^2u}{dx^2}, \quad (13)$$

where $c^2 = 2 \int z^2 f(z) dz$. Equation (13) is referred to as the law of error and provides an approximate asymptotic solution to the recursive relation (11). Note that the time dimension of Fourier's equation is replaced by the number of samples in the equations of Rayleigh (equation (7)) and Edgeworth (equation (13)).

5.4.4. Theory of speculation. At the turn of the twentieth century, Louis Bachelier (1870–1946) showed that probable values of stock option prices could be described in terms of a diffusion equation by making some assumptions about the randomness of stock prices. A student of Henri Poincaré at the Sorbonne, *Bachelier* [1900] presented a dissertation entitled “*Theory of Speculation*” in which he applied principles of probability to economic problems of stock option pricing. Pursuing an approach very similar to that of *Rayleigh* [1894] involving discrete difference equations, he introduced the notion of “radiation of probability,” which is conceptually analogous to Fourier's law of heat conduction. Thus *Bachelier* (p. 39 of 1964 translation) 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,

$$p = -d\mathcal{P}/dx, \quad (14)$$

where \mathcal{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 diffusion equation,

$$c^2 \frac{\partial \mathcal{P}}{\partial t} - \frac{\partial^2 \mathcal{P}}{\partial x^2} = 0. \quad (15)$$

Bachelier's work remained unnoticed for over half a century, until its relevance to warrant pricing was demonstrated by *Samuelson* [1965]. Since then it has been very influential in the development of econometric models based on stochastic calculus, which are widely used to rationally price stock options and corporate assets subjected to highly volatile stock market conditions.

5.4.5. Brownian motion. The fourth paper of historical interest that inspired the development of stochastic differential equations was that on Brownian motion by Albert Einstein (1879–1955). During the 1820s, Robert Brown (1773–1858), a renowned British botanist, discovered that pollen and other fine particles suspended in water exhibited continuous and permanent random motions. It was soon recognized by physicists that the random motions were sustained by the impacts of the molecules of the liquid on the suspended particles.

Unlike Rayleigh, Edgeworth, and Bachelier, who devoted attention to the mathematics of randomness, *Einstein* [1905] saw in Brownian motion an opportunity to test the validity of the molecular-kinetic theory of heat. He started with the proposition that colloidal particles suspended in liquids exert osmotic pressure, just as dissolved solute molecules do, 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* [1887] equation for osmotic pressure for nonelectrolytic solutes, the osmotic pressure associated with suspended particles is given by

$$p = \frac{RT}{N} \nu, \quad (16)$$

where p is the osmotic pressure, R is the universal gas constant, T is temperature, N is Avogadro's number, and ν is the number of suspended particles per unit volume of the liquid. Combining (16) with Stokes' law for viscous resistance, 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,

$$D \frac{\partial \nu}{\partial x} = \frac{\nu K}{6\pi k P}, \quad (17)$$

where D , the diffusion coefficient, is given by $D = RT/(6\pi k P N)$, in which k is coefficient of viscosity and P is radius of the particle.

Following a procedure similar to that of *Edgeworth* [1883], Einstein then proceeded to derive the partial differential equation for the distribution of particles at time $t + \tau$, given that the distribution at time t is $\nu = f(x, t)$. 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 similar to (11),

$$f(x, t + \tau) = \int_{-\infty}^{\infty} f(x + \Delta, t) \phi(\Delta) d\Delta. \quad (18)$$

Upon using Taylor series expansion, this leads to the one-dimensional diffusion equation,

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}, \quad (19)$$

where $D = (1/\tau) \int_{-\infty}^{\infty} (\Delta^2/2) \phi(\Delta) d\Delta$.

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

$$f(x, t) = \frac{n}{\sqrt{4\pi D}} \frac{\exp(-(x^2/4Dt))}{\sqrt{t}}. \quad (20)$$

The implication of (20) is that $f(x, t)$ represents the mean value of $\phi(\Delta, t)$ after a very large number of trials.

Einstein [1905] (p. 16 of 1926 translation) recognized the similarity between this function and that representing the distribution of random error by stating, "The probable distribution of the resulting displacements in a given time t is therefore the same as that of fortuitous error, which was to be expected."

Finally, Einstein integrated (20) and obtained the following expression for the arithmetic mean of the squares of displacement of a large number of particles,

$$\begin{aligned}\bar{x}^2 &= \frac{1}{n} \int_{-\infty}^{\infty} x^2 f(x, t) dx \\ &= \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} x^2 \exp\left(-\frac{x^2}{4Dt}\right) dx = 2Dt.\end{aligned}\quad (21)$$

Note that Einstein's equation (20) and (21) are the same as Rayleigh's equations (8) and (9) if we set $D = 0.5$.

Soon thereafter, Paul Langevin (1872–1946) developed an alternate approach to obtain (21), the mean of the square of displacements. Rather than solving the differential equation (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 liquid molecules that collide with it. In turn, the particle is retarded by the viscous resistance offered to it by the liquid. Thus the net force on the particle equals the sum of a "systematic" drag force and a stochastic force (Langevin referred to it as complementary force),

$$F(t) = -6\pi\mu a u + X(t), \quad (22)$$

where μ is viscosity, a is the radius of the spherical particle, u is velocity, and X is the stochastic force. Recognizing that for a large number of particles the stochastic component will cancel out, Langevin obtained the same result as (21) by equating force expressed as mass times acceleration with the first term on the right-hand side of (22). He also showed that after a "relaxation" time τ of the order of $m/(6\pi\mu a)$, where m is the mass of the particle, Einstein's diffusion equation is valid. Langevin's elegant separation of the deterministic and the stochastic components of the force was soon recognized by physicists to be a strong foundation for handling randomness. Thus Langevin's short paper catalyzed the subsequent development of stochastic calculus.

6. REFLECTIONS

It is now useful to reflect on what we have gained from this historical, integrated survey of a broad topic of interest. This reflection should enable us to understand the manner in which ideas pertaining to the foundations of modern science evolved during the nineteenth cen-

tury and the manner in which some of the leading thinkers of modern science communicated with each other in making their contributions. Revisiting some of the original contributions from a broad perspective should also help us become better aware of the intent and the content of the many equations we routinely use in our day-to-day scientific work.

6.1. Scientific Atmosphere

Many of the leading thinkers of the eighteenth and nineteenth century were natural philosophers, who did not limit their work by disciplinary boundaries. Lagrange, Euler, Laplace, Biot, Poisson, Thomson, Maxwell and others made simultaneous contributions in mechanics, electricity, magnetism, optics, fluid mechanics, and celestial mechanics. Others such as Fourier, went beyond the sciences and made contributions in the humanities. Major contributions in the physical sciences were made by biologists and men of medicine, notable among them being Black, Crawford, Dutrochet, Poiseuille, Fick, and Pfeffer. The difficulties that Fourier encountered in the acceptance of his ideas by Lagrange and Laplace or the difficulties Ohm encountered in the acceptance of his work by his contemporaries in Germany show that even these distinguished scientists arrived at their final results only in stages, as the ideas became progressively clarified. Despite the remarkable talents in pure mathematics that were being brought to the analysis of physical problems by Laplace, Lagrange, Fourier, and others, empirical observations and their intuitive interpretation (e.g., heat capacity, osmosis, heat conduction, electrical conduction) provided much impetus for mathematical innovation. Although intricate mathematical developments tend to overshadow the importance of more descriptive contributions in science, *Maxwell* [1873, p. 398] spoke eloquently about the importance of intuition and its relation to mathematics in his praise of Faraday, who made his greatest discoveries through mental imagery and used practically no mathematics at all: "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."

It is interesting that nineteenth century science was noted for its eagerness to discover new "laws" of nature. The laws of Ohm, Fick, and Darcy were experimental observations that showed that measured fluxes could be approximately described, on the observed scale, by a simple, linear mathematical relation. Despite the limited set of experiments, all these authors daringly used the word "law" in their papers. These empirical laws were then used as justification for developing mathematical solutions to problems of complexity in terms of domain geometry, heterogeneity, and forcing functions. Although the mathematical solutions themselves may be very precise, the value of the solutions for understanding

the physical problems on hand must necessarily depend on the faithfulness with which the mathematical idealization represents the mundane problem of interest. This is true especially in the Earth sciences, where Fourier's model is used to solve problems of fluid flow, chemical diffusion, and electrical resistivity on field scales that are often extremely large in comparison with the laboratory scale on which the laws are based. In these situations, the ultimate value of Fourier's equation depends on our ability to make intuitive judgements on the reasonableness of the mathematical idealization to represent the empirically describable field system.

6.2. Similarities and Differences Among Diffusion Processes

Despite the similarity of mathematical form of heat diffusion, electrical conduction, molecular diffusion and flow in porous media, it is necessary to recognize that in practical application of mathematics to solve particular problems proper consideration must be accorded to the physical traits peculiar to the particular system. To this end it useful to recognize some of the similarities and differences among the phenomena unified by Fourier's heat conduction equation.

The parameters conductivity and capacity are intrinsic to Fourier's diffusion model. How well these critical parameters may be known in the practical use of the Fourier model depends on the type of system of interest. Physicists and engineers who deal with engineered materials may be able to fabricate materials whose conductivity or capacity may be controlled with great confidence by manipulating the purity of the materials and their structural arrangement. However, a very different situation exists in the Earth sciences and in the biological sciences, in which one has to work with materials in place in their natural heterogeneous state, whose geometry and structure may be known only in sketchy detail. Therefore the fundamental parameters of the diffusion model can only be estimated empirically, accompanied by uncertainty. In these systems, consequently, the connection between the mathematics and the physics has to be tempered by intuition and judgement.

Maxwell [1881, p. 334] stressed the importance of Ohm's law by noting that the electrical resistance of a conductor can be measured with great precision because the physical nature of the conductor is unaffected by the potential difference or the absolute value of the potential. Thus if the conductor is made of a homogeneous material and the area of cross section is constant, the potential drop will be as perfectly linear, as one may expect in a natural system. However, in the case of thermal conduction, molecular diffusion, and flow in porous media, the physical properties of the host are subject to modification by the magnitude of temperature, chemical concentration, or fluid pressure. Thus, in these cases, even when a single homogeneous material of uniform cross section is involved, the profile of potential within the body cannot, in principle, be truly

linear, and one has to make a priori assumptions about the functional relation between conductivity and potential before experimental data can be interpreted. This problem becomes especially severe in multifluid phase Earth systems in which hydraulic conductivity and capacitance become very strong functions of capillary potential.

During the nineteenth century, materials were essentially divided into conductors, which had no ability to hold charge; and insulators, which offered infinite resistance and had the ability to hold charge. Because conductors by definition did not hold charge, *Maxwell* [1881] faulted Ohm for literally extending Fourier's equation to galvanic current by inventing an electrical capacitance term (γ in (2) above). However, no material can be either a perfect conductor or a perfect insulator. If so, is it reasonable to expect that conductors possess extremely small but finite capacitances? If they do, is it reasonable to infer that Ohm's transient equation is valid on extremely small timescales?

Looking at liquid diffusion, it is common practice in science and engineering to use Fick's law, essentially assuming that the liquid is stationary. However, the work of van't Hoff and Nernst suggests that in a solution, the solute is driven in one direction by differences in osmotic pressure, while the solvent is driven in the opposite direction by spatial variations in fluid potential. Thus transport in solutions should involve consideration of two migrating phases, salt and solvent. Under what conditions may we approximate this by restricting consideration only to the solute?

6.2.1. Capacitance, random walk, and error function. It seems rather remarkable that the macroscopic empirical view of heat conduction and the abstract notion of the random walk phenomenon should both lead to the same mathematical equation of diffusion. What may we learn from this similarity?

Consider the fundamental problem of an instantaneous plane source of heat [*Carslaw*, 1945] released at a point on a line extending to infinity on either side of the point. The homogeneous medium is initially in a thermodynamic state. Because the specific heat of the medium is finite, temperature at the point of release (taken to be the origin) will instantly jump by a finite amount. Following this, the temperature will gradually decrease with time at the point, as heat moves away with equal facility in both directions. In order that heat may move away from the origin, heat must initially be taken into storage to raise the temperature, as governed by specific heat. Qualitatively, it is easy to see that the temperature profile should be symmetrical about and have a maximum value at the origin. Moreover, because of symmetry, the gradient of temperature is zero at the origin. Far away from the origin there will be no flow of heat and the temperature gradient will be zero. Consequently, at any instant in time, the symmetric temperature profile will have a bell shape. It turns out that the shape of this bell-shaped curve is describable [*Carslaw*, 1945] by,

$$T(x, t) = \frac{Q}{\sqrt{4\pi\kappa t}} \exp\left(-\frac{x^2}{4\kappa t}\right), \quad (23)$$

where T is temperature and κ is thermal diffusivity, which is thermal conductivity divided by volumetric specific heat. Note that this solution is mathematically the same as that of Rayleigh (equation (8)) and Einstein (equation (20)). Yet in Rayleigh's problem the notions of resistance and capacitance are irrelevant, while in Einstein's model, the notion capacitance does not enter. While much has been written about diffusion being a manifestation of random processes, is there a rationale for reversing the question and looking at random processes in terms of suitably contrived notions of conductivity, capacitance, and diffusivity?

6.2.2. Foundations of the diffusion equation.

Clearly, Fourier's heat conduction equation continues to serve us well after nearly two centuries. Yet it has limitations, the chief one being that the linear heat conduction equation can be rigorously solved only for flow domains with simple geometry and heterogeneity. Systems with complicated geometry, heterogeneity, and material properties that are dependent on time can be solved only approximately. With the advent of the digital computer, these problems are now being integrated numerically to obtain approximate solutions. In numerically integrating Fourier's equation, the common practice is to either approximate the spatial and temporal gradients with finer and finer discretization of space and time, or evaluate the integrals with approximate weighting functions for the space and time domains. Current wisdom is to treat the differential equation as the truth and assume that the numerical solution will approximate the solution of the differential equation more and more closely as the discretization becomes finer and finer.

Be that as it may, it seems reasonable to pose a question from a different perspective. Is there an integral form of Fourier's differential equation? If so, can that integral be evaluated directly, as accurately as one may please? It turns out that for the special case of steady state diffusion, where the time derivative in Fourier's equation is zero, an integral statement of the problem does exist in the form of a variational principle. For the problem of steady state porous media flow, it is fairly straightforward to derive the variational integral by starting with the law of least action and postulating that under steady conditions of flow, the system will maximize work where the boundary potentials are prescribed or that it will minimize work to achieve a set of prescribed fluxes on the boundary.

However, for the transient diffusion problem for which Fourier's equation is valid, no physically realistic variational principle has as yet been formulated. In other words, no extension of a statement such as the principle of least action is available to describe why a transient diffusion system will choose a particular optimal way of evolving in time, given set of initial conditions and forcing functions. This issue of an integral statement of

Fourier's equation is of fundamental importance because we cannot confidently integrate the equation over arbitrary domains of time and space unless we know what the exact form of the integral is.

While mathematicians may approach this important issue in one way, it is of value to speculate on this issue from an intuitive perspective. Note that in Fourier's equation, conductivity is defined as a parameter that relates flux and potential gradient under steady conditions of flow, when potentials are not changing with time. On the other hand, capacitance is defined as a parameter that relates change in quantity of the permeant over a domain, however small, and the corresponding change in potential, as the small domain jumps from jumps in time from one static state to another. The fact that we have used Fourier's equation successively for so long may suggest that in the infinitesimal limit the system can in fact be considered to simultaneously be steady and nonsteady. However, the intriguing question arises, what happens when we consider finite domains, which are not infinitesimal? Can the system be simultaneously steady and nonsteady?

As we try extend Fourier's equation to heterogeneous domains of complicated geometry and time-dependent material properties with the help of integral equations, it behooves us to examine the foundations of the heat conduction equation and try to understand intuitively as well as mathematically how we may formulate a physically meaningful and mathematically tractable integral statement of the diffusion process.

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