CHAPTER 1

THE MATHEMATICS OF DIFFUSION
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1.1 Introduction

This chapter represents a sound structure in logical manner to provide knowledge of wide concept of diffusion. Diffusion is very useful to engineers, chemists, life scientists and to our daily lives. This chapter deals also with definition and brief discussion of fundamental laws introduced by: (1) Fourier, (2) Ohm, (3) Thomas Graham, (4) Adolf Fick and (5) Darcy. In addition, it contains some useful information about the rheological development of these laws. The wonders of diffusion are in general represented by the partial differential equations.

1.2 History

Fourier’s Law:

The Mathematics of diffusion 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. Firstly the 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. Secondly
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 topic concludes with some reflections on the scientific atmosphere during the nineteenth century, a comparison of the different facet of diffusion, and a look beyond Fourier’s solution strategy. Before we describe the scientific developments of the eighteenth century that set the stage for Fourier’s contribution, 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 [1]. By 1724 he had established what we now know as the Fahrenheit scale with the melting of ice at 32°F and the boiling of water at 212°F.

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. 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 [2]. 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 [2]. 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.

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,

\[ \nabla \cdot K \nabla T = c \frac{\partial T}{\partial t} \]  
(1.2.1)
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, (1.2.1) reduces to Laplace's equation. In (1.2.1), 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:

“A rate equation, that allows determination of the conduction heat flux from knowledge of the temperature distribution in a medium”.

Heat always conducts from warmer objects to cooler objects. The composition of a material affects its conduction rate. If a copper rod and an iron rod are joined together end to end, and the ends placed in heat sources, the heat will conduct through the copper end more quickly than
the iron end because copper has a $K$ value of 92, whereas, iron has a $K$ value of 11.

Fourier (1768-1830) considered the above properties and summarized them in Fourier's law of heat conduction.

$$\phi = -k \frac{\partial T}{\partial x}$$ (1.2.2)

which states that the heat flux ($\phi$) is proportional to the temperature difference per unit length. The proportionality constant is the Thermal conductivity $K$.

Substituting Fourier's law into the conservation of heat law, the following is obtained by

$$\int_a^b \left( c(x) \rho(x) \frac{\partial T(x,t)}{\partial t} + \frac{\partial}{\partial x} \left( K \frac{\partial T}{\partial x} \right) - Q \right) dx = 0$$ (1.2.3)

This is the integral form of the heat equation. This can be written as

$$\int_a^b \left( c(x) \rho(x) \frac{\partial T(x,t)}{\partial t} - Q \right) dx - \left[ K \frac{\partial T}{\partial x} \right]_{x=b} + \left[ K \frac{\partial T}{\partial x} \right]_{x=a} = 0$$ (1.2.4)

In order to complete the model, some boundary conditions must be specified at each end of the rod, and an initial state of the temperature distribution is also required. The side conditions can take several forms.

The value of the temperature or the value of the flux can be specified.

**Ohm’s Law:**

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 [3] 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 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 (1.2.1),

\[
\gamma \frac{du}{dt} = \chi \frac{d^2 u}{dx^2} - \frac{bc}{\omega} u
\]

where \( \gamma \) is a quantity analogous to heat capacity, \( u \) is the electrostatic force, \( \chi \) 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 \( \omega \) is the area of cross section of the conductor along the \( x \) direction. Ohm was not confident about this equation and admitted that no experimental evidence for \( \gamma \) was as yet forthcoming. 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 for finding order in nature was heavily criticized by Georg Poul, (Gillispie [4]) 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 [5]. For example, potential was analogous to temperature, a tube of induction was analogous to a tube of heat flow, the
electro-motive force was in the direction of the gradient of potential and the flux of heat was in the direction of temperature gradient.

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 [6] that the phenomenon of terrestrial heat motivated him to develop a theory for heat conduction in solids.

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.

Thomas Graham:

Our modern ideas on diffusion are largely due to two scientists, Thomas Graham and Adolf Fick. In 1855, Adolf Fick first reported (Smith [7]) his well known laws governing the transport of mass through diffusive means.

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 next major work on liquid diffusion was that of Thomas Graham (1805–1869). Graham [8] 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 [9,10].

The earliest experimental work on the diffusion of gases was by Graham [11]. 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. Experimental studies of diffusion were probably performed for the first time by Thomas Graham.
Graham was born on December 21, 1805. Graham’s father was a successful textile manufacturer. At the age of 13, he entered the University of Glasgow with the intention of becoming minister and there his interest in science was stimulated by Thomas Thomson. Graham’s main research was on the diffusion of gases, the apparatus shown in the figure (1.2.1). This apparatus, a diffusion tube, consists of a straight glass tube, one end of which is closed with a dense stucco plug. The tube is filled with hydrogen, and the end is sealed with water, as shown, hydrogen diffuses through the plug and out of the tube while air diffuses back through the plug and into the tube. Because the diffusion of hydrogen is faster than the diffusion of the air, the water level in this tube will rise during the process; Graham saw that this change of water level would lead to a pressure gradient that in turn would alter the diffusion. To avoid this pressure gradient, he continually lowered the tube so that the water level stayed constant. Graham’s original experiment was unusual because the diffusion took place at constant pressure, not at
constant volume. Graham also performed important experiments on liquid diffusion using the equipments shown in the figures (1.2.2) and (1.2.3).

In these experiments, he worked with dilute solutions. In one series of experiments, he connected two bottles that contained solutions at different concentrations. He waited several days and then separated the bottles and analyzed their contents as in the figure (1.2.2). In another series of experiments, he placed a small bottle containing solution of known concentration in a large jar containing only water. After waiting several days, he removed the bottle and analyzed its contents as in the figure (1.2.3).

He concluded that diffusion in the liquid is much slower than the diffusion in gases; diffusions must necessarily follow a diminishing progression according to Graham’s flux caused by diffusion is
proportional to the concentration (Cussler [12]). In one of his articles he explicitly stated what we now call Graham’s law: “The diffusion or spontaneous intermixture of two gases is effected by an interchange in position of indefinitely minute volume of gases, which volumes are not of equal magnitude, being in the case of each gas, inversely proportional to the square root of the density of that gas.”

**Adolf Fick:**

The next major advance in the field of the diffusion came from the work done by Adolf Fick (1829–1901). Adolf Fick was born in Kassel, Germany, as the youngest of five siblings. His father, a civil engineer, was a superintendent of buildings. During his secondary schooling, Fick was delighted by Mathematics, especially by the work of Fourier. He entered the University of Marburg with the intention to specialize in Mathematics, but switched to medicine on the advice of an elder brother, a professor of anatomy. After finishing his doctorate, he joined the University of Zurich as a demonstrator in anatomy. 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 diffusion of heat in solids and the diffusion of solutes in liquids. By direct analogy with Fourier, Fick [10] wrote down the following parabolic equation for transient diffusion of solutes in liquids in one dimension.
\[ D \left( \frac{\partial^2 u}{\partial x^2} + \frac{1}{A} \frac{\partial A}{\partial x} \frac{\partial u}{\partial x} \right) = \frac{\partial u}{\partial t} \]  

where \( D \) is the diffusion coefficient, \( u \) is aqueous concentration, and \( A \) 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 (1.2.3) 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 [9, 10] presented data from a diffusion experiment in an inverted-funnel-shaped vessel, solved (1.2.3) 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, (1.2.3) simplifies to Fourier's equation. One can readily verify that (1.2.3) leads also to appropriate differential equations for radial and spherical coordinates. Upon reflection, it becomes apparent that integration of (1.2.3) 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 [9, 10] went on to analyze flow across a semi permeable membrane by idealizing it as a collection of cylindrical pores of radius $r$.

**Fick’s First law**: The most fundamental Fick’s law of diffusion uses a diffusion coefficient. Fick’s law is commonly cited in description of diffusion. The second mathematical form which has no formal name involves a mass transfer coefficient a type of reversible rate constant. Fick’s law leads to description common to Physics, Physical Chemistry and Biology. Fick’s first law relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient in one dimension [7], this is

$$ J = -D \frac{\partial \phi}{\partial x} \quad (1.2.7) $$

where $J$ is the diffusion flux, $J$ measures the amount of substance that will flow through a small area during a small time interval, $D$ is the diffusion coefficient, $\phi$ (for ideal mixture) is the concentration, and $x$ is the position. $D$ is proportional to the squared velocity of the diffusing
particles, which depends on the temperature viscosity of the fluid and the size of the particles according to the Stokes–Einstein relation [7].

In two or more dimensions we must use \( \nabla \), the del or gradient operator, which generalized the first derivative, obtaining,

\[
J = -D \nabla \phi
\]  
(1.2.8)

**Fick’s Second Law:** Fick’s Second Law predicts low diffusion causes the concentration field to change with time [7],

\[
\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}
\]  
(1.2.9)

where \( \phi \) is the concentration, \( t \) is time, \( D \) is the diffusion coefficient, and \( x \) is the position.

It can be derived from Fick’s First Law and the mass balance

\[
\frac{\partial \phi}{\partial t} = -\frac{\partial J}{\partial x}
\]  
(1.2.10)

Using (1.2.7) in (1.2.10), we have,

\[
\frac{\partial \phi}{\partial t} = -\frac{\partial}{\partial x} \left( -D \frac{\partial \phi}{\partial x} \right)
\]

\[
\therefore \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \phi}{\partial x} \right)
\]  
(1.2.11)

Assuming the diffusion coefficient \( D \) to be a constant, we can exchange the order of the differentiation,

\[
\frac{\partial}{\partial x} \left( D \frac{\partial \phi}{\partial x} \right) = D \frac{\partial}{\partial x} \frac{\partial \phi}{\partial x} = D \frac{\partial^2 \phi}{\partial x^2}
\]  
(1.2.12)

And thus, obtain the form of the Fick’s equation as stated above.
For the case of diffusion in two or more dimensions, Fick’s Second Law becomes,

\[ \frac{\partial \phi}{\partial t} = D \nabla^2 \phi \]  

(1.2.13)

This equation is analogous to the Heat Equation.

The driving force for the one dimensional diffusion is the quantity \(-\frac{\partial \phi}{\partial x}\), which for ideal mixture as is the concentration gradient. In chemical system, other than ideal solution or mixtures, the driving force diffusion of each species is the gradient of chemical potential of this species. Than Fick’s First Law (one dimensional case) can be written as,

\[ J_i = -\frac{D c_i}{R T} \frac{\partial \mu_i}{\partial x} \]  

(1.2.14)

where the index \(i\) denotes the \(i^{th}\) species, \(c\) is the concentration, \(R\) is the universal gas constant, \(T\) is the absolute temperature, and \(\mu\) is the chemical potential.

**Darcy’s Law:**

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. 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. One of the most influential works on the flow of water in porous media during the nineteenth century was that of Darcy. (Whitaker [13]). 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 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 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 $c$ is pressure head, directly proportional to the area of cross section and inversely proportional to the length of the column. Darcy's law plays a fundamental role in many branches of Earth sciences such as hydrogeology, geophysics, petroleum engineering, soil science, and geotechnical engineering. The subject of homogeneous flow has many technical and engineering applications, in which the law of Darcy is valid. Darcy performed a classical experiment on which the theory of flow through the homogeneous porous media is based. The differential form of Darcy’s basic theory is the process of filtration.

The experiment of Darcy and the other workers give a law of flow. The review on fluid dynamics in “industrial and engineering Chemistry” also contains much information on the advance in the theory of flow through porous media. Due to the fact the shape of the internal pore geometry, the boundary conditions are unknown; the problem of fluid flow through porous media is difficult to treat by the fundamental Navier-Stokes equations. If boundary conditions are known, they are very complex, so it is difficult to solve by the Navier-Stokes equation directly. It can be studied by the Statistical Mechanics. A natural porous medium is disordered and irregular. Here we discuss Darcy’s experiment as it was
originally performed by Darcy for making the law of flow through porous media more clear. The Darcy’s law, actually first finding by Darcy; is based on his experimental study of water through horizontal beds of sands and subsequently confirmed by number of other investigators.

The first attempt to study the flow phenomena of fluid through homogeneous and porous media was means by Darcy’s law, which is an empirical linear relation between the velocity ($v$) and the slope ($-\frac{dh}{ds}$):

$$v = -k' \frac{dh}{ds}$$  \hspace{1cm} (1.2.15)

where $k'$ is a proportionality coefficient, called the filtration coefficient, which depends upon properties of both fluid and porous medium [14].

If $k'$ is to be replaced by the specific permeability $k$, then according to dimensional analysis, the relation between $k'$ and $k$ is,

$$k = \frac{\mu}{\rho g} k'$$  \hspace{1cm} (1.2.16)

where, $\mu$ is the viscosity of the fluid, $\rho$ is the density of the fluid, and $g$ is the gravity acceleration. Darcy’s law then can be written as [14];

$$v = -\frac{k}{\mu} \frac{d}{ds} (p + \rho g z)$$  \hspace{1cm} (1.2.17)

In case of one-dimensional horizontal flow, this can be written as,

$$v = -\frac{k}{\mu} \frac{dp}{ds}$$  \hspace{1cm} (1.2.18)
1.3 The Diffusion Process

Diffusion is one of several “transport processes” that occur in nature. Diffusion plays a key role in many processes as diverse as intermixing of gases and liquids, permeation of atoms or molecules through membranes, evaporation of liquids, drying of timber, doping silicon wafers to make semiconductor devices, and transport of thermal neutrons in nuclear power reactors. Rates of important chemical reactions are limited by how fast diffusion can bring reactants together or deliver them to reaction sites on enzymes or other catalysts.

It is usually illustrated by the classical experiment in which a droplet of ink is placed without stirring at the bottom of a bottle filled with water, the colour will slowly spread through the bottle. At first, it will be concentrated near the bottom. After a few days, it will penetrate upwards a few centimeters. After several days, the solution will be coloured homogeneously. The process responsible for the movement of the coloured material is diffusion. Diffusion is caused by the Brownian motion (Brownian motion is the presumably random moving of particles suspended in a fluid (a liquid or a gas) resulting from their bombardment by the fast moving atoms or molecules in the gas or liquid.) of atoms or molecules that leads to complete mixing. In gases, diffusion progresses at a rate of centimeters per second; in liquids, its rate is typically fractions of
millimeters per second; in solids, diffusion is a fairly slow process and the rate of diffusion decreases strongly with decreasing temperature: near the melting temperature of a metal a typical rate is about one micrometer per second; near half of the melting temperature it is only of the order of nanometers per second. A distinguishing feature of diffusion is that it results in mixing or mass transport without requiring bulk motion. Thus, diffusion should not be confused with convection or dispersion, which is other transport mechanisms that use bulk motion to move particles from one place to another. Diffusion is as central to our daily lives as it is used to the chemical industry. It is a spontaneous mixing process basic to such diverse phenomena as transport in living cells, the efficiency of distillation and the dispersal of pollutants. It is a transport process with originates from molecular activity [15]. The diffusion can be altered by tortuous path. Its speed may be affected by the size and the chemistry of the pores. A solute will diffuse faster through a larger straight pore than through a small crooked one. It may diffuse differently if it absorbs on the pore’s wall and then scouts along the wall at a faster rate than it moves in the bulk. If the pores are not straight, diffusion takes place only through the cramped and tortuous pores of the composite. The diffusion effectively occurs over a longer distance that it would in a homogeneous material. If the solid is impermeable diffusion occurs over a smaller cross-section area than that available in a homogeneous material.
If $D_{eff}$ is the effective diffusion coefficient, then

$$D_{eff} = \epsilon \frac{D}{\varphi}$$  \hspace{1cm} (1.3.1)

where, $D$ is the diffusion coefficient within the pores, $\varphi$ is the tortousity and $\epsilon$ is the valid fraction.

The effects of the longer pores and smaller areas often lumped together. For the longer distance traversed in the pores, the tortousity is count. Tortousities usually range between two and six, averaging about six. The solute diffuse is in three directions instead of one. So, solute diffuses three times as far as tortousity measured by diffusion [15]. The description of diffusion is generally useful to engineers, chemist and scientist. It is a fascinating subject as central to our daily lives as it is to the chemical industry; it describes the transport in living cells, the efficiency of distillation and the dispersal of pollutants. It is responsible for gas absorption, for the fog form by the rain on snow, for the dying of wool. It has the reputation of being a difficult subject, much harder than say, fluid mechanics or solution of hydrodynamics in gases, diffusion processes at the rate of about 10 cm in a minute, its rate in liquid is about 0.5 cm in a minute, and its rate in solid is only about 0.0001 cm in a minute. In general it varies less with temperature than do many other phenomena. It can be slow process. This slow rate of diffusion is responsible for its importance. In many cases diffusion occurs
sequentially with other phenomena when it is the slowest step in the sequence; it limits the overall rate of the process. For example, diffusion often limits the efficiency of commercial distillation and the rate of industrial reaction using porous catalysts. It limits the speed with which acid and the base react and the speed with which the human intestine absorbs nutrients. It controls the growth of micro organizations producing penicillin and the rate of the corrosion of steel and release the flavor from food.

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.

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 permeate 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 non-steady. However, the intriguing question arises, what happens when we consider finite domains, which are not infinitesimal? Can the system be simultaneously steady and non-steady? 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.

The description of the diffusion involves of Mathematical model, based on the fundamental hypothesis or law. Interestingly, there are two common choices for such a law. The more fundamental, Fick’s law of diffusion uses a diffusion coefficient. This is the law that is commonly cited in description of diffusion. The second, which has no
formal name, involves a mass transfer coefficient, a type of reversible rate, constant choosing Fick’s law leads to descriptions common to Physics, Physical Chemistry, Biology, choosing mass transfer coefficients produces correlation develop explicitly in Chemical kinetics and in medicine.

1.4 The measurement of diffusivity coefficient

Measuring diffusion coefficients is reputed to be very difficult. Thomas Graham worked on diffusion coefficients [8]. Measurement of diffusion coefficients are rarely routine, usually can be determined to within about five or ten percent accuracy without excessive effort because such accuracy is sufficient for most situations, we should always consider measuring the coefficient accurate 10%, we want 2%, when we achieve 2%, we want 5%, we shall consider only those method of measuring diffusion that are reasonably accurate, that are easy to use, or that have some special advantage.

The subject of the diffusion problem arises in fluid mechanics and heat transfers hold an exciting and special position in Mathematics. The diffusion equation is a large undertaking and falls into several areas of Mathematics.
1.5 Mathematical Formulation of Diffusion

In this section the Mathematical formation of Diffusion equation by Fick’s law is briefly discussed [8]. Thus, the physical phenomena of the diffusion are represented by the partial differential equation. The description of diffusion in porous media involves a mathematical model based on Darcy’s law. Fick’s law of diffusion uses a diffusion coefficient. Fick’s law is the law that is commonly in descriptions of diffusion. Also, Fick’s law leads to description common to Physics, Physical Chemistry and Biology etc. The major advance in the theory of diffusion came from the work of Adolf Fick. Fick’s introduction of his basic idea is almost casual. In other words, diffusion can be described on the same Mathematical basic as Fourier’s law for heat. The analogy remains a useful pedagogical tool. In 1856, Fick understood the difference between a true equilibrium and a steady state possibly as a result of his studies with muscles. Fick quickly developed the law of diffusion by mean of analogies with Fourier’s work done in 1822. He defined a total one dimensional flux \( J \) as [8]

\[
J = -AD \frac{\partial u}{\partial x}
\]  
(1.5.1)

where \( A \) is an area across which diffusion occurs, \( J \) is the flux per unit area, \( u \) is the concentration, \( x \) is the position.
This is the first suggestion of what is now known as Fick’s law. The quantity $D$, which is called the constant depending on the nature of the substance is the diffusion coefficient. Fick also determined the more general conservation equation [8];

$$\frac{\partial u}{\partial t} = D \left( \frac{\partial^2 u}{\partial x^2} + \frac{1}{A} \frac{\partial A}{\partial x} \frac{\partial u}{\partial x} \right)$$

(1.5.2)

when the area $A$ is constant, the equation (1.5.1) becomes basic equation for one-dimensional unsteady-state diffusion. It is called Fick’s second law. Thus, one-dimensional unsteady-state diffusion equation is,

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2}$$

(1.5.3)

### 1.6 References


