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Diffusion Processes and Brownian Motion

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Abstract. This theoretical paper was written motivated by measurements of diffusion of metals (Pt, Ag and Au) in polymers performed in the Thin Films Laboratory (LFF) of the IFUSP. This is a didactical article about *diffusion laws* of particles in a material medium. It was written to graduate and postgraduate students of physics and engineering. The calculations are performed in a simple way, but, as rigorously as possible.

Key words: diffusion equation; stochastic processes; Langevin equation; Brownian motion.

(I)Introduction.

Today at the LFF of the IFUSP we are investigating diffusion of metals like Pt, Ag and Au in PMMA. "While metal diffusion in polymers is very interesting from the fundamental point of view, research into the fields has been triggered off by technologically important applications of polymers in microelectronics. Large-scale integration of devices necessitates the use of multilayer metallization structures on the chip level and for packing. In these structures, which are mainly made up of alternate metal and insulating layers, ceramics are increasingly replaced by high-temperature polymers".[1] Since this paper was written to graduate and postgraduate students of Physics we intend to explain as simple as possible, didactically, the diffusion of metals in PMMA. In this way, as processes of *diffusion of particles* and *heat conduction* are mathematically described by the Diffusion Equation we present in **Section 1** a brief review about the main aspects of this equation. In **Section 2** is seen the diffusion of particles or Brownian Motion. In **Section 3** is obtained the Diffusion Equation using the Stochastic Approach and the Statistical Approach. In **Section 4**, is used Langevin´s Equation. In **Section 5** is analyzed the diffusion due to the osmotic pressure. In **Section 6 is** shown the Smoluchowsky model. Finally, in **Section 7** are analyzed the diffusion of particles in an homogeneous medium using the basic diffusion equations presented in **Sections 3** and **4.**

(1) Diffusion of Heat.

According to basic texts[2]of Physics the flux of heat **J** per unit of time and area that passes by an infinitesimal slab of matter with thickness ds maintained at a difference of temperature dθ is given by

$$\mathbf{J} = -\,\kappa\,(d\theta/ds)\mathbf{n} = -\kappa\,\mathrm{grad}(\theta) \qquad (1.a.1),$$

where κ is the *thermal conductivity* of the matter and **n** the unit vector normal to the slab surface. If a body has volume V, *specific heat capacity* c and density ρ one can show that the quantity of heat dQ/dt changed per unit of time by this body with the environment is given by

$$dQ/dt = \int_{(s)} \mathbf{J}.d\mathbf{A} = \int_{(v)} c\rho(\partial\theta/\partial t)dV \qquad (1.a.2),$$

where S and V are, respectively, the surface and volume of the body. As, by the Stokes theorem, $\int_{(s)} \mathrm{grad}(f).d\mathbf{A} = \int_{(v)} \mathrm{lapl}(f)\, dV$ we verify that from (1.a.2) we conclude that

$$\partial\theta(\mathbf{r},t)/\partial t = D\ \mathrm{lapl}[\theta(\mathbf{r},t)] \qquad (1.a.3),$$

called *heat diffusion equation* and D = κ/cρ is the *diffusion coefficient.*

(2)Diffusion of Particles or Brownian Motion.

As will be shown in what follows, the motion of a dissolved solute or suspension in gases or liquids obeys a diffusion equation similar to (1.a.3). This motion is historically known as **Brownian Motion**. In Figure 1 are reproduced from the book of Jean Baptiste Perrin, *Les Atomes*,[3,4]three tracings of the motion of colloidal particles of radius 0.53 μm, as seen under the microscope, are displayed. Successive positions every 30 seconds are joined by straight line segments (the mesh size is 3.2 μm).[4]

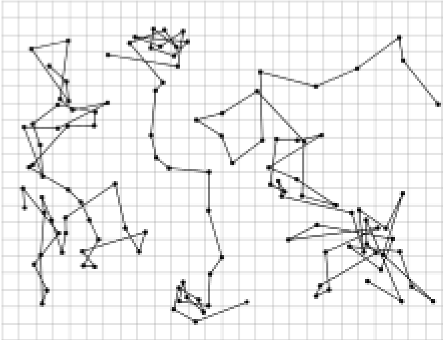

Figure 1. Three tracings of the motion of colloidal particles.[4]

This random phenomenon, however, is intrinsically different from the heat diffusion; it obeys, from the mathematical point of view, to *stochastic laws*.[5] This phenomenon was described in verses[4] by the Roman poet Lucretius(~ 60 BC). He uses this as a proof of the existence of atoms:

"Observe what happens when sunbeams are admitted into a building and shed light on its shadowy places. You will see a multitude of tiny particles mingling in a multitude of ways... their dancing is an actual indication of underlying movements of matter that are hidden from our sight... It originates with the atoms which move of themselves [i.e., spontaneously]. Then those small compound bodies that are least removed from the impetus of the atoms are set in motion by the impact of their invisible blows and in turn cannon against slightly larger bodies. So the movement mounts up from the atoms and gradually emerges to the level of our senses, so that those bodies are in motion that we see in sunbeams, moved by blows that remain invisible."

Although the mingling motion of dust particles is caused largely by air currents, the glittering, tumbling motion of small dust particles (or pollen grains) is, indeed, caused chiefly by true Brownian dynamics.

While Jan Ingenhousz described in 1785 the irregular motion of coal dust particles on the surface of alcohol, the discovery of this phenomenon is often credited to the botanist Robert Brown (botanist, born 1773) in 1827. Brown was studying pollen grains of the plant *Clarkia pulchella* suspended in water under a microscope when he observed minute particles, ejected by the pollen grains, executing a jittery motion. By repeating the experiment with particles of inorganic matter he was able to rule out that the motion was life-related, although its origin was yet to be explained. The first person to describe the mathematics behind Brownian motion was Thorvald N. Thiele in a paper on the method of least squares published in 1880. This was followed independently by Louis Bachelier in 1900 in his PhD thesis "The theory of speculation", in which he presented a stochastic analysis of the stock and option markets. Brown in1827, while looking through a microscope at particles trapped in cavities inside pollen grains in water, noted that the particles moved through the water; but he was not able to determine the mechanisms that caused this motion. Atoms and molecules had long been theorized as the constituents of matter, and Albert Einstein published a paper in 1905 that explained in precise detail how the motion that Brown had observed was a result of the pollen being moved by individual water molecules, making one of his first big contributions to science. This explanation of Brownian motion served as convincing evidence that atoms and molecules exist, and was further verified experimentally by Jean Perrin in 1908. Perrin was awarded the Nobel Prize in Physics in 1926 "for his work on the discontinuous structure of matter". The direction of the force of atomic bombardment is constantly changing, and at different times the particle is hit more on one side than another, leading to the seemingly random nature of the motion.[4]

(3) Diffusion Equation.

Liquid and gases are composed by particles - atoms and molecules - that are free to move. Let us consider a subset of particles, such as a dissolved solute or a suspension, characterized by a number density[3]

$$n(x,y,z,t) = \Delta N/\Delta V \qquad (3.1).$$

Suppose that these (Brownian) particles of mass M are surrounded by lighter particles of mass *m* which are traveling at a speed *u*. Then, in any collision between a surrounding and Brownian particles, the velocity transmitted to the latter will be *mu*/*M*. This ratio is of the order of 10^{-7} cm/s. But we also have to take into consideration that in a gas there will be more than 10^{16} collisions in a second, and even greater in a liquid where we expect that there will be 10^{20} collision in one second. Some of these collisions will tend to accelerate the Brownian particle; others will tend to decelerate it. If there is a mean excess of one kind of collision or the other to be of the order of 10^{8} to 10^{10} collisions in one second. Thus, even though there are equal probabilities for forward and backward collisions there will be a net tendency to keep the Brownian particle in a random, chaotic, motion. The direction of the force of atomic bombardment is constantly changing, and at different times the particle is hit more on one side than another, leading to the seemingly random nature of the motion. The many-body interactions that yield the Brownian pattern cannot be solved by a model accounting for every involved molecule. In other words, Classical Mechanics is unable to determine this displacement because of the enormous number of these bombardments. In consequence only probabilistic models applied to molecular populations can be employed to describe it. Two such models of the statistical mechanics, due to Einstein and Smoluchowski are presented elsewhere.[4] Another, pure probabilistic class of models is the class of the *stochastic process* models that can be seen, for instance, in references.[5]

(3.1)Stochastic Approach.

As these particles are moving randomly, one model used to describe such a process is the *random walk*[4,5] also called "drunkard´s walk". In one dimension it looks like this: a clock ticks at intervals δt; at each tick, the particle moves one step to the left (with probability α), one step to the right (with probability β) or remains where it is x (with probability 1-α-β). Thus, the probability to find the particle in the interval x+δx at time t+δt is

$$p(x, t+\delta t) = \alpha\, p(x+\delta x,t) + \beta\, p(x-\delta x,t) + (1-\alpha-\beta)\, p(x,t) \qquad (3.1.1).$$

Supposing that left and right dislocations are equally probable, putting $\alpha = \beta$ we obtain from (3.1.1), for $\delta x << 1$ and $\delta t << 1$, since the first order terms $\partial p/\partial x$ given a null contribution and taking only terms up to the second order $\partial^2 p/\partial x^2$:

$$\partial p/\partial t = \alpha\, (\partial^2 p/\partial x^2)\, (\delta x)^2/\delta t \equiv D\, (\partial^2 p/\partial x^2)\, , \qquad (3.1.2)$$

where the *diffusion constant* D is defined by $D = \alpha\, (\delta x)^2/\delta t$. Extending the same idea to 3-dimension we derive the *diffusion equation*

$$\partial p(\mathbf{r},t)/\partial t = D\ \mathrm{lapl}[p(\mathbf{r},t)] \qquad (3.1.3).$$

Since $p(\mathbf{r},t) = n(\mathbf{r},t)/N$ we see that (3.1.3) can written as

$$\partial n(\mathbf{r},t)/\partial t = D\ \mathrm{lapl}[n(\mathbf{r},t)] \qquad (3.1.4).$$

Taking into account that the number of particles is conserved, that is, $\partial n(\mathbf{r},t)/\partial t + \mathrm{div}(\mathbf{j}) = 0$ we see that the flux of particles $\mathbf{j} = n\mathbf{v}$ is given by

$$\mathbf{j} = - D\ \mathrm{grad}(n) \qquad (3.1.5).$$

(3.2)Statistical Approach.

In the statistical approach, Einstein[4] in one unrestricted dimensional domain (x) assumed that, in a time interval τ, the increment of particle positions as a random variable Δ with some probability density function $\varphi(\Delta)$, so that

$$n(x, t + \tau) = \int_{-\infty}^{+\infty} n(\mathbf{x} + \mathbf{\Delta}, t)\, \varphi(\Delta)\, d\Delta \qquad (3.2.1).$$

For small time intervals τ the left side of (3.2.1) becomes,

$$n(x, t + \tau) = n(x, t) + \tau\, \partial n(x,t)/\partial t + ... \qquad (3.2.2).$$

The right side of (3.2.1), for small increments Δ becomes given by,

$$\int_{-\infty}^{+\infty} n(\mathbf{x} + \mathbf{\Delta}, t)\, \varphi(\Delta)\, d\Delta = n(\mathbf{x},t) \int_{-\infty}^{+\infty} \varphi(\Delta)\, d\Delta +$$

$$(\partial n/\partial x) \int_{-\infty}^{+\infty} \Delta\, \varphi(\Delta)\, d\Delta + (\partial^2 n/\partial x^2) \int_{-\infty}^{+\infty} (\Delta^2/2)\, \varphi(\Delta)\, d\Delta + ...$$

$$= n(\mathbf{x},t).1 + 0 + (\partial^2 n/\partial x^2) \int_{-\infty}^{+\infty} (\Delta^2/2)\, \varphi(\Delta)\, d\Delta +..... \qquad (3.2.3)$$

substituting (3.2.2) and (3.2.3) into (3.2.1) we get, for $\Delta \ll 1$ and $\tau \ll 1$,

$$\partial n(x,t)/\partial t = D\,(\partial^2 n/\partial x^2) \qquad (3.2.4),$$

where $D \equiv \int_{-\infty}^{+\infty} (\Delta^2/2\tau)\,\varphi(\Delta)\,d\Delta$.

Extending the same idea to 3-dimension systems we obtain the *diffusion equation* (3.1.3).

Estimation of $< x >$ and $< (x - < x >)^2 >$.

If N is the number of independently moving particles and $n(\mathbf{r},t)$ density of these particles the probability to find a particle in the element of volume $\delta V = \delta x\delta y\delta z$ is given by

$$p(\mathbf{x},y,z,t) = n(\mathbf{r},t)/N \qquad (3.2.5).$$

Defining $q(x,t) = \iint dy\,dz\,p(x,y,z,t)$ we see that

$$< x(t) > = \int_{-\infty}^{+\infty} dx\,x\,q(x,t)$$

and that, according to (3.1.2), $\partial q(x,t)/\partial t = D\,(\partial^2 q/\partial x^2)$. Consequently,

$$d< x>/dt = D \int_{-\infty}^{+\infty} dx\,x\,(\partial^2 q/\partial x^2) = 0, \quad \text{an so,} \quad < x > = \textbf{constant} \qquad (3.2.6),$$

that is, the average position of a diffusion particle does not change.

Let us estimate dVar(x)/dt of the **variance** Var[x(t)] defined by

$$\mathrm{Var}[x(t)] \equiv < (x - < x >)^2> = \int_{-\infty}^{+\infty} dx\,x\,(x - < x >)^2\,q(x,t) \qquad (3.2.7).$$

So, using (4.3) and $\partial q(x,t)/\partial t = D\,(\partial^2 q/\partial x^2)$ and that $< x > =$ constant we get,

$$d\mathrm{Var}(x)/dt \equiv D \int_{-\infty}^{+\infty} dx\,(x - < x >)^2(\partial^2 q/\partial x^2) = 2D \qquad (3.2.8),$$

or

$$\mathrm{Var}(x) = 2Dt \qquad (3.2.9).$$

So, the *diffusive distance d* $=\sqrt{<x^2>} = \sqrt{2D}\sqrt{t}$ increases proportionally to $\sqrt{t}$.

(4)Stochastic Differential Equation or Langevin Equation.

Let us see another approach, proposed by Langevin,[5]to the random walk by analyzing the motion of a particle subjected to a time-dependent random force f(t). According to Langevin a particle that performs a random motion, called Brownian motion, is submitted to two kinds of forces. One dissipative admitted to be proportional to its velocity (Stokes force), and another f(t) which has a random (or stochastic) character due to myriads impacts of the particles with molecules of medium. Supposing the simplest case of the motion of a particle with mass m along the x axis we have

$$m\,(d^2x/dt^2) = -\,\alpha(dx/dt) + f(t) \qquad (4.1).$$

The first term of (4.1) is a dissipative force being α the dissipative coefficient and f(t) is the stochastic force, *impossible to be represented analytically,* characterized by the following time average properties

$$< f(t) > = 0 \qquad (4.2)$$

because in average the value of the stochastic forces due to collisions is expected to be zero and

$$< f(t)f(t') > = B\,\delta(t - t') \qquad (4.3),$$

supposing that the molecular impacts are independents, where B is a constant. Eq.(4.1) supplemented by properties (4.2) and (4.3) is named **Langevin Equation**. Dividing (4.1) by m results,

$$dv/dt = -\,\gamma v + \zeta(t) \qquad (4.4),$$

where $\gamma = \alpha/m$ and $\zeta(t) = f(t)/m$. The *noise function* ζ(t) is a stochastic variable, that is, a time dependent random variable with the properties, putting $\Gamma = B/m^2$,

$$< \zeta(t) > = 0 \qquad (4.5),$$

and

$$< \zeta(t)\,\zeta(t') > = \Gamma\,\delta(t - t') \qquad (4.6).$$

(4.1)Quadratic Average Velocity $< v^2 >$.

To obtain the generic solution of (4.4) we begin writing $v(t) = u(t)\exp(-\gamma t)$ where u(t) is a function of t to be determined. Substituting this in (4.4) we verify that it satisfy the following equation $(du/dt) = \exp(\gamma t)\,\zeta(t)$ whose solution is

$$u(t) = u_o + \int_o^t \exp(\gamma t') \zeta(t')dt' \quad (4.7).$$

Consequently,

$$v(t) = v_o \exp(-\gamma t) + \exp(-\gamma t) \int_o^t \exp(\gamma t') \zeta(t')dt' \quad (4.8),$$

where v_o is the particle velocity at t = 0. Taking into account (4.5) we get

$$< v(t) > = v_o \exp(-\gamma t) \quad (4.9).$$

In this way,

$$v(t) - < v > = \exp(-\gamma t) \int_o^t \exp(\gamma t') \zeta(t')dt' \quad (4.10).$$

From (4.10) we have

$$(v(t) - < v >)^2 = \exp(-2\gamma t) \int_o^t \int_o^t \zeta(t') \zeta(t'') \exp[\gamma(t'+ t'')] dt'dt'' \quad (4.11).$$

Taking into account (4.6) the above equation becomes

$$< (v(t) - < v >)^2 > = \exp(-2\gamma t) \int_o^t \Gamma \exp(2\gamma t') dt' \quad (4.12).$$

So,

$$<v^2(t)> - < v >^2 = (\Gamma/2\gamma)[1 - \exp(-2\gamma t)] \quad (4.13),$$

that, for **long times**, that is, in the stationary regime, < v > = 0 gives,

$$< v^2(t) > = < v^2 > = (\Gamma/2\gamma) \quad (4.14).$$

Remembering that $m < v^2 >/2 = k_B T/2$ from (4.14) we obtain,

$$\Gamma = \gamma k_B T/m \quad (4.15).$$

(4.2)Average Quadratic Displacement or Variance.

Now, let us determinate the *average quadratic displacement* or *variance* of the particle position defined by $< (x - < x >)^2 >$. To this, we begin calculating x(t), using (4.8), given by

$$x(t) = x_o + \int_o^t v(t') dt' = x_o + v_o \exp(-\gamma t) + \exp(-\gamma t) \int_o^t \exp(\gamma t') \zeta(t')dt' \quad (4.16).$$

Performing similar calculations seen in Section (4.1) one can see that[5]

$$< x^2 > - < x > = 2Dt \quad (4.17),$$

where $D = \Gamma/2\gamma^2$, that is, as $\gamma = \alpha/m$ and $\Gamma = \gamma k_B T/m$, according to (4.15)

$$D = k_B T/\alpha \qquad (4.18),$$

obtained first by Einstein.[4] According to (4.17) (see also Eq.(3.2.9))

$$\mathrm{Var}(x) = 2Dt$$

that is, the *diffusive distance d* increases proportionally to $\sqrt{t}$. In spite of equation (4.17) been deduced to the 1-dimensional case it is also valid to 2 and 3 dimensions.

To spherical particles with radius a, immersed in a liquid with viscosity η, at a temperature T, the coefficient α is given by $\alpha = 6\pi\eta a$.[6-8] In this case (4.18) becomes

$$D = k_B T/6\pi\eta a \qquad (4.19).$$

The observation of the Brownian motion of a particle (dust, colloid,...) is possible because they are much larger than the liquid molecules with which they collide. The estimation of D by measuring the variance and the parameters a and η permit us to determine the Boltzmann constant k_B. This was done by Perrin in 1913.[3,4]

(5)Osmotic Pressure or Thermal Force Approach.

Einstein´s starting point for derivation[3,4] of (5.3) was somewhat different from that given in Section 5. He used the fact that the osmotic pressure P of a solute in a dilute solution is given by empirical van´t Hoff law (1887), where n(**x**) is density of the solute:

$$P(\mathbf{x}) = n(\mathbf{x})\, k_B T \qquad (5.1).$$

To show how osmotic pressure is measured let us consider a *semi-permeable membrane* separating two parts of a solution (see **Figure 2**).This is a membrane that permits the passage of solvent molecules from one side to another but blocks the passage of the solute molecules.

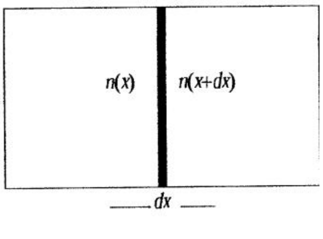

Figure 2. Semi-permeable membrane.

Suppose that $n(x)$ and $n(x+dx)$ are the solute densities in two sides of a thin membrane slab with area A and thickness dx. Einstein proposed that the net thermodynamic force acting F_x on the thin slab would be given by

$$F_x = A\,P(x) - A\,P(x+dx) = A\,k_BT\,[n(x) - n(x+dx)] = -\,k_BT(\partial n/\partial x)A dx \quad (5.2),$$

that is,

$$F_x = -\,k_BT(\partial n/\partial x)\;dV \quad (5.3).$$

In this slab there are dN particles, that is, $dN = n(x)dV$; *each particle* is submitted to a dissipative $f_x = -\alpha\, v_x$, so $F_x = dN\, f_x = n(x)dV\, f_x$. This implies that $F_x/dV = n(x)\, f_x$. In this way (5.3) becomes written as

$$n(x)\, f_x = -\,k_BT(\partial n/\partial x) \quad (5.4),$$

or more generically

$$n\,\mathbf{f} = -\,k_BT\ \mathrm{grad}(n) \quad (5.5).$$

As, $\mathbf{f} = -\,\alpha < \mathbf{v} >$ the corresponding particle flux $\mathbf{j}$,using (6.5), is given by

$$\mathbf{j} = n < \mathbf{v} > = n\,\mathbf{f}/\alpha = -\,(k_BT/\alpha)\ \mathrm{grad}(n) \quad (5.6),$$

in agreement with (3.15) and (4.18) with $D = k_BT/\alpha$.

(6)Smoluchowsky Model.

Smoluchowsky estimated[4] Var(x) assumed that the Brownian particles suffer random displacements along the x-direction due to the molecular collisions. Supposing that rear and forward directions are equally probable (**which is not rigorously valid**) he found that Var(x) = (64/27) Dt where D is given by (4.18).

(7)Basic Equations for Diffusion of Brownian Particles.

According to Sections (3)-(5) the diffusion of particles in an homogeneous medium is described by the equations

$$\partial c(\mathbf{r},t)/\partial t = D\ \mathrm{lapl}[c(\mathbf{r},t)] \quad (7.1),$$

and

$$\mathbf{j}(\mathbf{r},t) = c(\mathbf{r},t) < \mathbf{v} > = -\,D\ \mathrm{grad}[c(\mathbf{r},t)],$$

where $c(\mathbf{r},t) \equiv \rho(\mathbf{r},t) \equiv n(\mathbf{x},t)$ is the *concentration* or *density* of particles (number of particles per unit of volume) and $< \mathbf{v} >$ is the average velocity of the particles. The diffusion coefficient D depends of the Brownian particle and of the medium but is independent of the concentration c(**r**,t).

In a typical diffusion experiment[F] a thin layer of the diffusant is deposited onto the surface of semi-infinite sample prior to the diffusion run. Subsequently the sample is quickly *heated or chilled* up to the diffusion temperature and kept at this temperature for a certain time t. If the initial deposited layer is thin enough to be approximated by a Dirac δ-function the resulting concentration profile is a Gaussian[1] (**Appendix A**):

$$c(x,t) = (C/\sqrt{\pi Dt})\exp(-x^2/4Dt) \qquad (7.2),$$

where C is the initial concentration of particles deposited on the surface.

If the tracer is deposited onto the hot sample at the beginning of the diffusion run at a constant deposition during a certain *deposition* time t_{dep} which is a fraction of the total annealing time t, Eq.(7.2)has to be replaced by [1]

$$c(x,t) = (C/t_{dep}\sqrt{\pi D}) \int_o^{tdep} (1/\sqrt{t-\tau})\exp[-x^2/4D(t-\tau)]\, d\tau \qquad (7.3).$$

In the case of solubility limited diffusion the concentration profile is described by the complete *error function*

$$c(x,t) = c_o\, \mathrm{erfc}\{x/2\sqrt{Dt}\} = c_o\Big\{1-(2/\sqrt{\pi}) \int_o^{x/2\sqrt{Dt}} \exp(-u^2)du\Big\} \qquad (7.4),$$

where c_o is the constant surface concentration given by the solubility limit.

APPENDIX A. Solution of the Diffusion Equation.

Let us first solve the diffusion equation (1.a.3) in 1- dimension case x in the finite interval (-ℓ, ℓ), that is, $\partial F(x,t)/\partial t = D\, \partial^2 F(x,t)/\partial t^2$. Using the separation of variables method[9] we know that the general solution of this equation, for a given parameter ω, is given by

$$F(x,t) = [a\cos(\omega x) + b\sin(\omega x)]\exp[-D\omega^2 t] \qquad (A.1),$$

where A,D and ω will be determined using initial and boundary conditions. Supposing that for *any time* F(0,t) = F(ℓ,t) = 0 we see that $\omega\ell = n\pi$ (n = 0,1,2,...) which implies that $\omega_n = n\pi/\ell$ and, consequently,

$$F(x,t) = \sum\nolimits^{\infty}_{n=1} b_n \sin(\omega_n x)]\exp(-D\omega_n^2 t) \qquad (A.2).$$

If at t = 0 $F(x,0) = f(x)$ from (A.2) we get

$$f(x) = \sum^{\infty}_{n=1} b_n \sin(n\pi x/\ell) \qquad (A.3),$$

from which b_n can be determined using the orthogonality property of the Fourier series.[9] On the other hand, if for any time $F(0, t) = F_1$ and $F(\ell,t) = F_2$ the general solution of *linear* diffusion equation will be written as

$$F(x,t) = \sum^{\infty}_{n=1} b_n \sin(\omega_n x)] \exp(-D\omega_n^2 t) + x(F_2-F_1)/\ell + F_1 \qquad (A.4).$$

When $\ell \to \infty$ the $\omega_n = n\pi/\ell$ values becomes closer and closer, that is, $\Delta\omega = \omega_{n+1} - \omega_n = \pi/\ell \to 0$, ω becoming a continuous variable. So, in the general case of a continuous summation over wave numbers we have

$\sum^{\infty}_{n=1} u(\omega_n) = (\ell/\pi) \sum^{\infty}_{n=1} (\pi/\ell)\, u(\omega_n) = (\ell/\pi) \sum^{\infty}_{n=1} \Delta\omega\, u(\omega_n)$,

that is, when $\ell \to \infty$ we get $\sum^{\infty}_{n=1} u(\omega_n) = (\ell/\pi) \int_o^{\infty} u(\omega)\, d\omega$.

Thus, for continuous ω values the solution of the diffusion equation we have F(x,t), instead of (A.1), according to the Fourier Integral method[9]

$$F(x,t) = \int_o^{+\infty} [a(\omega) \cos(\omega x) + b(\omega) \sin(\omega x)] \exp(-D\omega^2 t)\, d\omega \qquad (A.5).$$

If for $t = 0 \to F(x,0) = f(x) = \int_o^{+\infty} [a(\omega) \cos(\omega x) + b(\omega) \sin(\omega x)]\, d\omega$ where[9]

$a(\omega) = (1/\pi) \int_{-\infty}^{+\infty} f(\xi) \cos(\omega\xi) d\xi$
and (A.6),
$b(\omega) = (1/\pi) \int_{-\infty}^{+\infty} f(\xi) \sin(\omega\xi) d\xi$

supposing that $f(x) \to 0$ when $|x| \to \infty$.

Substituting (A.6) in (A.5) we obtain

$$F(x,t) = (1/\pi) \int_{-\infty}^{+\infty} f(\xi)\, d\xi \int_o^{+\infty} \cos[\omega(x-\xi)] \exp(-D\omega^2 t)\, d\omega$$
(A.7).

Now, it is possible to integrate in ω obtaining,[9]

$$F(x,t) = (1/2\sqrt{\pi D t}) \int_{-\infty}^{+\infty} f(\xi) \exp[-(x-\xi)^2/4Dt]\, d\xi \qquad (A.8).$$

In the limit $t \to 0$ we can show that[9] $F(x,0) = f(x)$ which was assumed to be the *initial condition* of F(x,t).

(A.1)Particular Solution for $f(x) = F_o\delta(x-b)$.

In this case putting $f(\xi) = F_o\delta(\xi-b)$ in (A.8) we have,

$$F(x,t) = (1/2\sqrt{\pi Dt}) \int_{-\infty}^{+\infty} F_o\delta(\xi-b)\ \exp[-(x-\xi)^2/4Dt]\, d\xi$$

$$= (F_o/2\sqrt{\pi Dt}) \exp[-(x-b)^2/4Dt] \qquad (A.9),$$

shown in **Figure 3** for times $t_1 \approx 0$, $t_1 > t_2 > t_3 >$

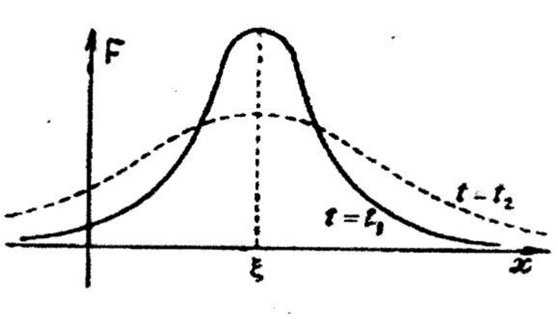

Figure 3. Temporal diffusion between the physical quantity F along the x-axis.

Note that the areas between x and the curves 1,2,3,.. are equal since

$$\int_{-\infty}^{+\infty} F(x,t)\, dx = (F_o/2\sqrt{\pi Dt}) \int_{-\infty}^{+\infty} \exp[-(x-b)^2/4Dt]\, dx = F_o,$$

that is, the "physical quantity" diffused along the x-axis is constant.

Heat Conduction along a Bar.

We know[9] that the heat conduction along a solid with heat conductivity χ obeys a diffusion equation $\partial\theta(\mathbf{r},t)/\partial t = D\ \mathrm{lapl}[\theta(\mathbf{r},t)]$, where $\theta(x,t)$ is the temperature, the diffusion coefficient $D = \chi/c\rho$, χ the heat conductivity, ρ the density and c the specific heat of the solid, respectively. The heat flux $\mathbf{J}(\mathbf{r},t)$ is given by $\mathbf{J} = -\chi\ \mathrm{grad}[\theta(\mathbf{r},t)]$.

In the particular case of an infinite bar with cross section A supposing, for instance, that $\theta(x) = \theta_o\delta(x-b)$, verify that the total quantity of heat diffused along this bar is constant given by

$$Q = \int_{-\infty}^{+\infty} Q(x,t)\, dx = \int_{-\infty}^{+\infty} c\rho\ \theta(x,t)\ A\, dx = c\rho A\theta_o = \text{constant},$$

as it must be.

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