Brownian Motion Problem: Random Walk and Beyond

Shama Sharma and Vishwamittar

A brief account of developments in the experimental and theoretical investigations of Brownian motion is presented. Interestingly, Einstein who did not like God's game of playing dice for electrons in an atom himself put forward a theory of Brownian movement allowing God to play the dice. The vital role played by his random walk model in the evolution of non-equilibrium statistical mechanics and multitude of its applications is highlighted. Also included are the basics of Langevin's theory for Brownian motion.

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Introduction

Brownian motion is the temperature-dependent perpetual, irregular motion of the particles (of linear dimension of the order of $10^{-6}m$) immersed in a fluid, caused by their continuous bombardment by the surrounding molecules of much smaller size (*Figure* 1). This effect was first reported by the Dutch physician, chemist and engineer Jan Ingenhousz (1785), when he found that fine powder of charcoal floating on alcohol surface exhibited a highly random motion. However, it got the name Brownian motion after Scottish botanist Robert Brown, who in 1828-29 published the results of his extensive studies on the incessant random movement of tiny particles like pollen grains, dust and soot suspended in a fluid (*Box* 1). To begin with when experiments were performed with pollen immersed in water, it was thought that ubiquitous irregular motion was due to the life of these grains. But this idea was soon discarded as the observations remained unchanged even when pollen was subjected to various killing treatments, liquids other

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Brownian motion, Langevin's theory, random walk, stochastic processes, non-equilibrium statistical mechanics.

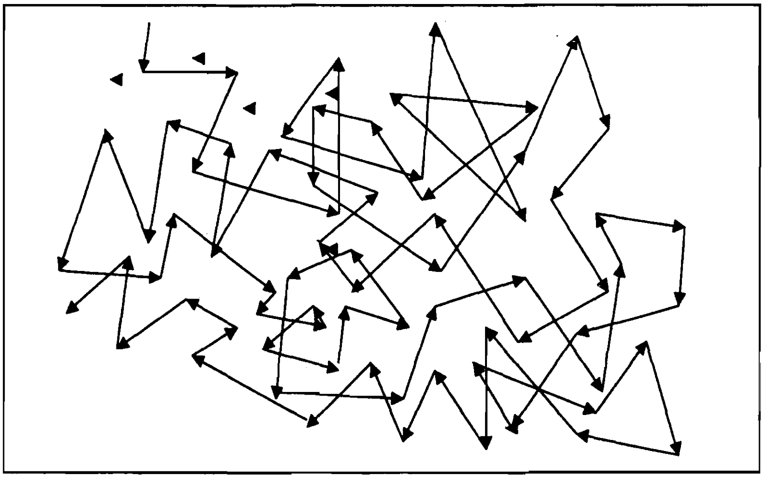

Figure 1. Brownian motion of a fine particle immersed in a fluid.

than water were used and fine particles of glass, petrified wood, minerals, sand, etc were immersed in various liquids. Furthermore, possible causes like vibrations of building or the laboratory table, convection currents in the fluid, coagulation of particles, capillary forces, internal circulation due to uneven evaporation, currents produced by illuminating light, etc were considered but were found to be untenable.

An early realization of the consequences of the studies on Brownian motion was that it imposes limit on the precision of measurements by small instruments as these are under the influence of random impacts of the surrounding air.

Box 1. Observing the Brownian Motion

One can observe Brownian movement by looking through an optical microscope with magnification 10^3 10^4 at a well illuminated sample of some colloidal solution (say milk drops put into water) or smoke particles in air. Alternately, we can mount a small mirror (area 1 or 2 mm^2) on a fine torsion fiber capable of rotation about a vertical axis (as in suspension type galvanometer) in a chamber having air pressure of about 10^{-2} torr and note the movement of the spot of light reflected from the mirror. The trace of the light spot is manifestation of angular Brownian motion of the mirror.

It may be pointed out that movement of dust particles in the air as seen in a beam of light through a window is not an example of Brownian motion as these particles are too large and the random collisions with air molecules are neither much imbalanced nor strong enough to cause Brownian movement.

In 1863, Wiener attributed Brownian motion to molecular movement of the liquid and this viewpoint was supported by Delsaux (1877-80) and Gouy (1888-95). On the basis of a series of experiments Gouy convincingly ruled out the exterior factors as causes of Brownian motion and argued in favour of contribution of the surrounding fluid. He also discussed the connection between Brownian motion and Carnot's principle and thereby brought out the statistical nature of the laws of thermodynamics. Such ideas put Brownian motion at the heart of the then prevalent controversial views about philosophy of science. Then, in 1900 Bachelier obtained a diffusion equation for random processes and thus, a theory of Brownian motion in his PhD thesis on stock market fluctuation. Unfortunately, this work was not recognized by the scientific community, including his supervisor Poincaré, because it was in the field of economics and it did not involve any of the relevant physical aspects.

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Eventually, Einstein in a number of research publications beginning in 1905 put forward an acceptable model for Brownian motion[1]. His approach is known as 'random walk' or 'drunkards walk' formalism and uses the fluctuations in molecular collisions as the cause of Brownian movement. His work was followed by an almost similar expression for the time dependence of displacement of the Brownian particle by Smoluchowski in 1906, who started with a probability function for describing the motion of the particle. In 1908, Langevin gave a phenomenological theory of Brownian motion and obtained essentially the same formulae for displacement of the particle. Their results were experimentally verified by Perrin (1908 and onwards)[2] using precise measurements on sedimentation in colloidal suspensions to determine the Avogadro's number. Later on, more accurate values of this constant and that of Boltzmann constant k were found out by many workers by performing similar experiments.

[1] These are collected in the book *Albert Einstein Investigations on the theory of Brownian Movement* edited with notes by R Furth (Dover Publications, New York,1956).

[2] Review article entitled 'Brownian Movement and Molecular Reality' based on his work has been translated into English by F Soddy and published by Taylor & Francis,London in 1910.

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The correctness of the random walk model and Langevin's theory made a very strong case in favour of molecular kinetic model of matter and unleashed a wave of activity for a systematic development of dynamical theory of Brownian motion by Fokker, Planck, Uhlenbeck, Ornstein and several other scientists. As such, during the last 100 years, concerted efforts by a galaxy of physicists, mathematicians, chemists, etc have not only provided a proper mathematical foundation to the physical theory but have also led to extensive diverse applications of the techniques developed.

The two basic ingredients of Einstein's theory were: (i) the movement of the Brownian particle is a consequence of continuous impacts of the randomly moving surrounding molecules of the fluid (the 'noise'); (ii) these impacts can be described only probabilistically so that time evolution of the particle under observation is also probabilistic in nature. Phenomena of this type are referred to as stochastic processes in mathematics and these are essentially non-equilibrium or irreversible processes. Thus, Einstein's theory laid the foundation of stochastic modeling of natural phenomena and formed the basis of development of non-equilibrium statistical mechanics, wherein generally, the Brownian particle is replaced by a collective property of a macroscopic system. Consequently, the techniques developed for the theory of Brownian motion form cornerstones for investigating a variety of phenomena (in different branches of science and engineering) that have their origin in the effect of numerous unpredictable and may be unobservable events whose individual contribution to the observed feature is negligible, but collective impact is observed in the form of rather rapidly varying stochastic forces and damping effect (see *Box* 2).

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The main mathematical aspect of the early theories of Brownian motion was the 'central limit theorem', which am- ounted to the assumption that for a sufficiently large

Box 2. Brownian Motors

One of the topics of current research activity employing these techniques is referred to as Brownian motors. This phrase is used for the systems rectifying the inescapable thermal noise to produce unidirectional current of particles in the presence of asymmetric potentials. Their study is relevant for understanding the physical aspects involved in the movement of motor proteins, the design and construction of efficient microscopic motors, development of separation techniques for particles of micro- and nano-size, possible directed transport of quantum entities like electrons or spin degrees of freedom in quantum dot arrays, molecular wires and nano-materials; and to the fundamental problems of thermodynamics and statistical mechanics such as basing the second law of thermodynamics on statistical reasoning and depriving the Maxwell demon type devices of their mystique and the trade-off between entropy and information.

number of steps, the distribution function for random walk is quite close to a Gaussian. However, since the trajectory of a Brownian particle is random, it grows only as square root of time[3] and, therefore, one cannot define its derivative at a point. To handle this problem, N Wiener (1923) put forward a measure theory which formed the basis of the so-called stable distributions or Levy distributions. As a follow-up of these and to give a firm footing to the theory of Brownian motion, Ito (1944), developed stochastic calculus and an alternative to Brownian motion – the Geometrical Brownian motion. This, in turn, led to extensive modeling for the financial market, where the balance of supply and demand introduces a random character in the macroscopic price evolution. Here the logarithm of the asset price is governed by the rules for Brownian motion. These aspects have enlarged the scope of applicability of theoretical methods far beyond Einstein's random walks. These concepts have been fruitfully exploited in a multitude of phenomena in not only physics, chemistry and biology but also physiology, economics, sociology and politics.

[3] This result will be obtained in the next section of this article; see equation (8).

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The Random Walk Model for Brownian Motion

While tottering along, a drunkard is not sure of his steps; these may be forward or backward or in any other direction. Besides, each step is independent of the one taken. Thus, his motion is so irregular that nothing can be predicted about the next step. All one can talk about is the probability of his covering a specific distance in given time. Such a problem was originally solved by Markov and therefore, such processes are known as Markov processes. Einstein adopted this approach to obtain the probability of the Brownian particle covering a particular distance in time t. The randomness of the drunkard's walk has given this treatment the name 'random walk model' and in the case of a Brownian particle, the steps of the walk are caused by molecular collisions.

To simplify the derivation, we consider the problem in one-dimension along x-axis, taking the position of the particle to be 0 at $t = 0$ and $x(t)$ at time t and make the following assumptions.

1. Each molecular impact on the particle under observation takes place after the same interval $\tau_0(10^{-8}s)$ so that the number of collisions in time t is $n = t/\tau_0$ (of the order of 10^8).

2. Each collision makes the Brownian particle jump by the same distance δ which turns out, we will see, to be about $1nm$, for a particle of radius $1\mu m$ in a fluid with the viscosity of water, at room temperature along either positive or negative direction with equal probability and δ is much smaller than the displacement $x(t)$ which we resolve through the microscope only on the scale of a μm of the particle.

3. Successive jumps of the particle are independent of each other.

4. At time t, the particle has net positive displacement $x(t)$ (it could be equally well taken as negative) so that out of n jumps, $m(= x(t)/\delta$, of the order of 10^3) extra jumps have taken place in positive direction. Since n and m are quite large, these are taken as integers.

In view of the four assumptions above, the total number of positive and negative jumps, respectively, is $(n+m)/2$ and $(n-m)/2$. Since the probability that n independent jumps, each with probability 1/2, have a particular sequence is $(1/2)^n$, the probability of having m extra positive jumps is given by

$$P_n(m) = (1/2)(1/2)^n\{n!/[(n+m)/2]![(n-m)/2]!\}, \quad (1)$$

where the factor (1/2) comes from normalization $\Sigma_m P_n(m) = 1$. While writing this expression, we have not used any restriction on n and m except that both are integers. So it holds good even for small n and m. Note that both n and m are either even or odd. As an illustration, if we consider 8 jumps, then the probabilities for $m = 0, 2, 4$ and 8 are 35/256, 7/64, 7/128 and 1/512, respectively.

For large n we can use the approximation $n! = (2\pi n)^{1/2} (n/e)^n$, so that for large n and m, equation(1) finally becomes

$$P_n(m) = (1/2n)^{1/2}\exp(-m^2/2n). \quad (2)$$

Substituting $m = x/\delta$ and $n = t/\tau_0$, this yields the probability for the particle to be found in the interval x to $x + dx$ at time t as

$$P(x)dx = (1/4\pi Dt)^{1/2}\exp(-x^2/4Dt)dx, \quad (3)$$

with $D = \delta^2/2\tau_0$. It may be mentioned that taking m to be large mathematically means that δ is infinitesimally small for a finite value of x. This aspect has enabled us to switch over from discrete step random walk to a continuous variable x in the above expression.

In order to understand the physical significance of the symbol D, recall that if the linear number density of suspended particles in a fluid is $N(x,t)$ and their concentration is different in different regions, diffusion takes place. This is governed by the diffusion equation

$$D_0(\partial^2 N(x,t)/\partial x^2) = \partial N(x,t)/\partial t, \tag{4}$$

where D_0 is the diffusion coefficient. Equation (4) has one of the solutions as

$$N(x,t) = (N_{\text{tot}}/\sqrt{\{4\pi D_0 t\}})\exp(-x^2/4D_0 t) \tag{5}$$

Here,

$$N_{\text{tot}} = \int_{-\infty}^{\infty} N(x,t)dx \tag{6}$$

is the total number of particles along the x-axis. Obviously, $N(x,t)/N_{\text{tot}}$ corresponds to $P(x)$ if we identify D as D_0 , i.e, $\delta^2/2\tau_0$ as diffusion coefficient. In other words, $P(x)$ is a solution of the diffusion equation meaning thereby that the random walk problem is intimately related with the phenomenon of diffusion. In fact, the random walk model is a microscopic phenomenon of diffusion.

A look at (3) shows that the probability function describing the position of the particle at time t is Gaussian with dispersion $2Dt$ (*Figure* 2) implying spread of the peak width as square root of t. Furthermore, mean values of $x(t)$ and $x^2(t)$ turn out to be

$$\langle x(t)\rangle = 0 \quad \text{and} \quad \langle x^2(t)\rangle = 2Dt. \tag{7}$$

The proportionality of root mean square displacement of the Brownian particle to the square root of time is a typical consequence of the random nature of the process.

Since $\langle x(t)\rangle = 0$, the physical quantity of interest is $\langle x^2(t)\rangle$. So what one measures experimentally is the root mean square displacement of the Brownian particle given by

$$x_{\text{rms}} = \langle x^2(t)\rangle^{1/2} = (2Dt)^{1/2} \tag{8}$$

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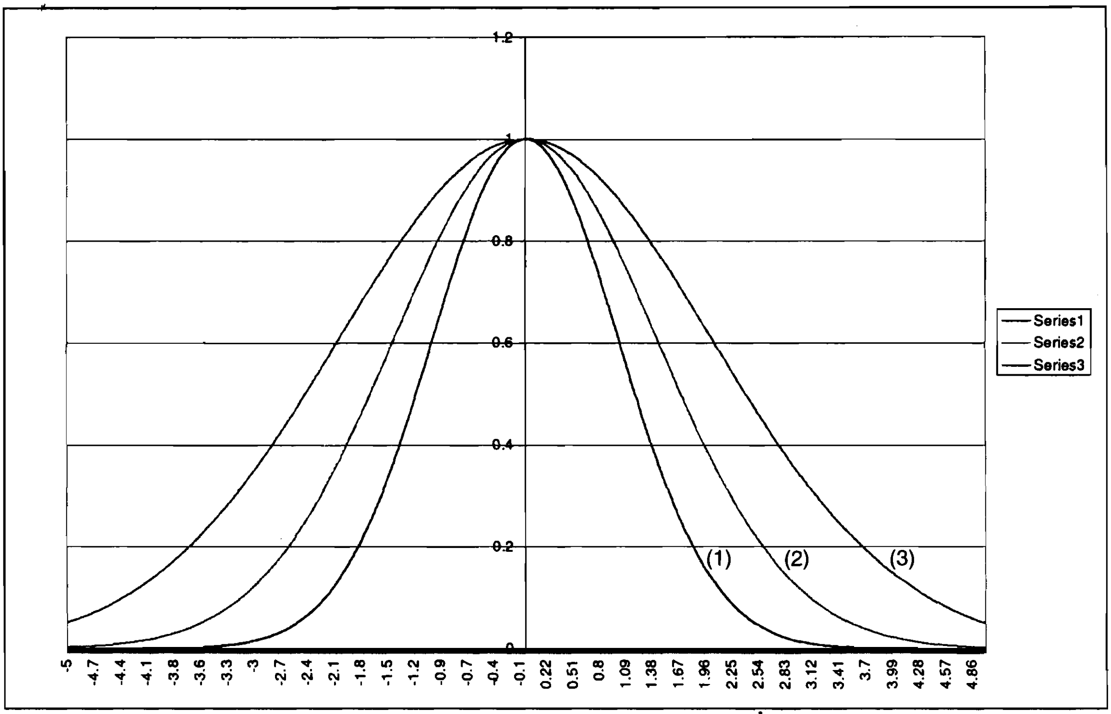

Figure 2. Plot of $(4\pi Dt)^{1/2} P(x)$ (equation(3)) versus x for $D = 5.22 \times 10^{-13}\, m^2 s^{-1}$ and x varying from 5.0 mm to 5.0 mm corresponding to t values 1s (the innermost curve), 2s (the middle curve), and 4s (the outermost curve).

and is in contrast with the result of usual mechanical predictable and reversible motion where displacement varies as t. For three dimensional motion, the above expression becomes

$$\langle r^2(t)\rangle = \langle x^2(t)\rangle + \langle y^2(t)\rangle + \langle z^2(t)\rangle = 6Dt. \quad (9)$$

From equation (7), we have

$$D = \langle x^2(t)\rangle / 2t, \quad (10)$$

which connects the macroscopic quantity diffusion constant D or D_0 with the microscopic quantity the mean square displacement due to jumps. It gives us a direct relationship between the diffusion process, which is irreversible, and Brownian movement that has its origin in random collisions. In other words, irreversibility has something to do with the random fluctuating forces acting on the Brownian particle due to impacts of the molecules of the surrounding fluid.

[4] One such well-investigated topic is that of quantum random walks – a natural extension of classical random walks. Though the main emphasis in these studies has been on bringing out the differences in their behaviour as compared to the classical analogs, it is believed that this knowledge will be helpful in developing algorithms that can be run on a quantum computer as and when it is practically realized.

The successful use of the concept of random walk in the theory of Brownian motion encouraged physicists to exploit it in different fields involving stochastic processes.[4]

Langevin's Theory of Brownian Motion

The intimate relationship between irreversibility and randomness of collisions of the fluid molecules with the Brownian particle (mentioned above) prompted Langevin (1908) to put forward a more logical theory of Brownian movement. However, before proceeding further, we digress to consider the motion of a hockey ball of mass M being hit quickly by different players. Its motion is governed by two factors. The frictional force $\mathbf{f}_d$ between the surface of ball and the ground tends to slow it down, while the impact of the hit with the stick by a player increases its velocity. The effect of the latter, of course, is quite random as its magnitude as well as direction depend upon the impulse of the hit. Since a hit lasts for only a very short time, we represent the magnitude f_j of corresponding force at time t_j by a Dirac delta function (*Box* 3) of strength C_j

$$f_j(t) = C_j \delta(t - t_j), \tag{11}$$

and write the equation of motion pertaining to this force as

$$M|d\mathbf{v}/dt| = f_j. \tag{12}$$

To find the effect of the hit in changing the velocity, we substitute (11) into (12), integrate on both the sides with respect to time over a small time interval around t_j and use the property of delta function to get

$$M|\Delta \mathbf{v}_j| = C_j. \tag{13}$$

Here, $\Delta \mathbf{v}_j$ is the change in velocity brought about by the hit at time $t = t_j$. Now, the hits applied by different players can be in any direction, the total force exerted

Box 3. The Dirac Delta Function

Many times we come across problems in which the sources or causes of the observed effects are nearly localized or almost instantaneous. Some such examples are : point charges and dipoles in electrostatics; impulsive forces in dynamics and acoustics; peaked voltages or currents in switching processes; nuclear interactions, etc. To handle such situations, we use what is known as Dirac delta function. It represents an infinitely sharply peaked function given, for one-dimensional case, by

$$\delta(x - x_0) = \begin{cases} 0 & x \neq x_0 \\ \infty & x = x_0 \end{cases}$$

but such that its integral over the whole range is normalized to unity :

$$\int_{-\infty}^{\infty} \delta(x - x_0)dx = 1.$$

Its most important property is that for a continuous function f(x)

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0)dx = f(x_0).$$

Thus, $\delta(x - x_0)$ acts as a sieve that selects from all possible values of $f(x)$ its value at the point x_0, where the δ function is peaked. Accordingly, the above result is sometimes called sifting property of δ function.

on the ball in a finite time interval will be obtained by summing up the above expression over a sequence of hits made taking into account the directions of the hits. This force can be written as

$$\mathbf{f}_r(t) = \Sigma_j C_j \phi_j \delta(t - t_j), \qquad (14)$$

where ϕ_j is unit vector in the direction of hit at time $t = t_j$. The subscript r in (14) has been used to indicate the randomness of the force vector. Thus, the total force acting on the ball at any time t will be $\mathbf{f}_d + \mathbf{f}_r$ and its equation of motion will read

$$M d\mathrm{v}/dt = \mathbf{f}_d + \mathbf{f}_r. \qquad (15)$$

Furthermore, if a very large number of hits are applied quickly over a long time interval as compared to the impact time, all possible directions ϕ_j will occur completely randomly with equal probability. Accordingly,

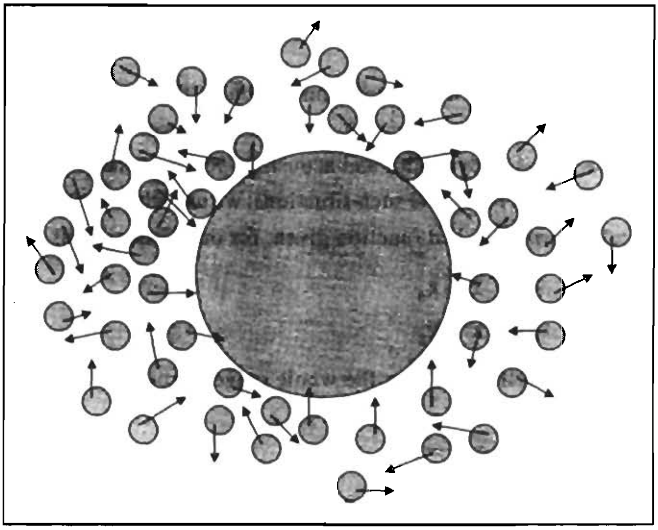

Figure 3. A large Brownian particle surrounded by randomly moving relatively smaller molecules of the fluid.

average value of $\mathbf{f}_r$ will be zero, i.e.,

$$\langle \mathbf{f}_r(t) \rangle = 0.$$

Reverting to the Langevin's theory, we consider Brownian particle in place of the hockey ball in the above illustration and make the following simplifying assumptions.

1. The Brownian particle experiences a time-dependent force $\mathbf{f}(t)$ only due to molecular impacts from the surrounding particles (*Figure* 3) and there is no other external force (such as gravitational, Coulombic, etc.) acting on it.

2. The force $\mathbf{f}(t)$ is made up of two parts: $\mathbf{f}_d$ and $\mathbf{f}_r(t)$. The former is an averaged out, systematic or steady force due to frictional or viscous drag of the fluid, while the latter is a highly fluctuating force or noise arising from the irregular continuous bombardment by the fluid molecules. The equation of motion of the particle is given by (15).

3. The steady force $\mathbf{f}_d$ is governed by the Stokes formula (*Box* 4) so that

$$\mathbf{f}_d = -\gamma \mathbf{v}. \tag{16}$$

Box 4. Stokes Formula

Following Stokes we assume that a perfectly rigid body (say, a sphere) with completely smooth surface and linear dimension l is moving through an incompressible, viscous fluid (viscosity η, density ρ) having an infinite extent in such a manner that there is no slip between the body and the layers of the fluid in its contact, with such a speed v that the motion is streamlined and the Reynolds number R ($= vl\rho/\eta$) is very small (strictly speaking vanishingly small), then the viscous drag force $\mathbf{f}_d$ on the body is proportional to velocity **v**, i.e. $\mathbf{f}_d = -\gamma\mathbf{v}$; and the constant γ depends on the geometry of the body. For example, it is $6\pi\eta a$ for a sphere of radius a and is 16 ηa for a plane circular disc of radius a moving perpendicular to its plane.

Here, γ is viscous drag coefficient and

$$1/\gamma = |\mathbf{v}|/|\mathbf{f}_d| \qquad (17)$$

is mobility of the Brownian particle. The drag coefficient depends upon viscosity η of the fluid, geometry as well as size of the Brownian particle. For a spherical particle of radius a,

$$\gamma = 6\pi\eta a. \qquad (18)$$

4. The coefficient of viscous drag γ is a constant, having the same value in all parts of the fluid and at all times.

5. The random force $\mathbf{f}_r(t)$ is independent of $\mathbf{v}(t)$ and varies extremely fast as compared to it so that over a long time interval (much larger than the characteristic relaxation time τ), the average of $\mathbf{f}_r(t)$ vanishes (as elaborated above for a hockey ball), i.e.,

$$\langle \mathbf{f}_r(t) \rangle = 0. \qquad (19)$$

This essentially amounts to saying that the collisions are completely independent of each other or are uncorrelated.

Substituting (16) into (15), we get

$$M(d\mathbf{v}/dt) = -\gamma\mathbf{v} + \mathbf{f}_r(t), \qquad (20)$$

where $\mathbf{f}_r(t)$ satisfies the condition given in (19).This is the celebrated Langevin equation for a free Brownian particle. $\mathbf{f}_r(t)$ is usually referred to as 'stochastic force'; (20) is the stochastic equation of motion and is the basic equation used for describing a stochastic process. The solution to (20) reads

$$\mathbf{v}(t) = \mathbf{v}(0)\exp(-t/\tau) + \exp(-t/\tau)\int_0^t \exp(u/\tau)\mathbf{A}(u)du, \tag{21}$$

and gives us the drift velocity of the Brownian particle. Here,

$$\tau = M/\gamma \tag{22}$$

is the relaxation time of the particle and

$$\mathbf{A}(t) = \mathbf{f}_r(t)/M \tag{23}$$

is the stochastic force per unit mass of the Brownian particle and is generally called 'Langevin force'.

It may be mentioned that the first term in (21) is the damping term and it tries to exponentially reduce the value of $\mathbf{v}(t)$ to make it essentially dead. On the other hand, the second term involving Langevin force or noise creates a tendency for $\mathbf{v}(t)$ to spread out over a continually increasing range of values due to integration and, thus, keeping it alive. Consequently, the observed value of drift velocity at any time t is an outcome of these two opposing tendencies.

From (19) and (23), it is clear that $\langle \mathbf{A}(t) \rangle = 0$ so that the average value of drift velocity in (21) becomes

$$\langle \mathbf{v}(t) \rangle = \mathbf{v}(0)\exp(-t/\tau). \tag{24}$$

Obviously, average drift velocity of the Brownian particle decays exponentially with a characteristic time τ till it becomes zero. This is a typical result for dissipative or irreversible processes. But, this is physically not acceptable as ultimately the particle must be in thermal equilibrium with its surroundings at ambient temperature and, therefore, cannot be at rest. So we consider $\langle v^2(t)\rangle = \langle \mathbf{v}(t).\mathbf{v}(t)\rangle$. Substituting for $\mathbf{v}(t)$ from (21) and using the fact that $\langle \mathbf{A}(t)\rangle = 0$, we have

$$\langle v^2(t)\rangle = v^2(0)\exp(-2t/\tau) + \exp(-2t/\tau)\times$$

$$\int_0^t \int_0^t \exp(u_1 + u_2)/\tau) K(u_2 - u_1) du_1 du_2, \qquad (25)$$

where

$$K(u_2 - u_1) = \langle \mathbf{A}(u_1).\mathbf{A}(u_2)\rangle. \qquad (26)$$

It is called autocorrelation function for the Langevin force $\mathbf{A}(u)$ and involves $u_2 - u_1$ to emphasize the fact that for Brownian motion it depends upon the time interval $u_2 - u_1$ rather than actual values of u_1 and u_2. We assume that $K(u_2 - u_1)$ is an even function of its argument and is significant only for u_2 almost equal to u_1. Using these ideas when the double integral in (25) is evaluated, we get[5]

$$\langle v^2(t)\rangle = v^2(0) + [v^2(\infty) - v^2(0)][1 - \exp(-2t/\pi)]. \qquad (27)$$

[5] For details of this step see *Statistical Mechanics* by R K Pathria listed at the end.

Here, $\langle v^2(\infty)\rangle$ is the mean square velocity of the Brownian particle for infinitely large value of t and is expected to be the value corresponding to the situation when the system is in equilibrium at temperature T Thus, from equipartition theorem

$$(1/2)Mv^2(\infty) = (3/2)kT \qquad (28)$$

As a special case if $v^2(0)$ equals the equipartition value $3kT/M$, then $\langle v^2(t)\rangle = v^2(0) = 3kT/M$ implying that if the system has attained statistical equilibrium then it would continue to be so throughout.

It may be noted that multiplying (20) with $\mathbf{r}(t)/M$, where $\mathbf{r}(t)$ is the instantaneous position of the Brownian particle, we finally get

$$d^2\langle r^2\rangle/dt^2 + (1/\tau)(d\langle r^2\rangle/dt) = 2\langle v^2(t)\rangle; \tag{29}$$

here $\langle v^2(t)\rangle$ is given by (27). This second order differential equation, on being solved, gives

$$\langle r^2(t)\rangle = v^2(0)\tau^2\{1-\exp(-t/\tau)\}^2 - (3kT/M)\tau^2\times$$

$$\{1-\exp(-t/\tau)\}\{1-\exp(-t/\tau)\} + (6kT\tau/M)t. \tag{30}$$

For t very small as compared to τ it yields

$$\langle r^2(t)\rangle = v^2(0)t^2, \tag{31}$$

so that root mean square displacement $r_{\mathrm{rms}} = \langle r^2(t)\rangle^{1/2}$ is proportional to t as for a reversible process. On the other hand, for $t \gg \tau$, we get

$$\langle r^2(t)\rangle = (6kT\tau/m)t = (6kT/\gamma)t \tag{32}$$

implying that

$$r_{\mathrm{rms}}(t) = (6kT/\gamma)^{1/2}t^{1/2}. \tag{33}$$

Expression (32) becomes identical to (9) if we take

$$D = kT/\gamma, \tag{34}$$

which in view of (18) reads

$$D = kT/6\pi\eta a \tag{35}$$

for a spherical Brownian particle. Equation (34) is usually known as 'Einstein relation' Obviously, it gives a relationship between the diffusion coefficient and mobility of the particle and hence the viscosity of the fluid. Thus, viscosity of a medium is a consequence of fluctuating forces arising from their continuous and random motion and is an irreversible phenomenon.

The Einstein relation gives a relationship between the diffusion coefficient and mobility of the particle and hence the viscosity of the fluid. Thus, viscosity of a medium is a consequence of fluctuating forces arising from their continuous and random motion and is an irreversible phenomenon.

At this stage it is in order to mention one of the experimental observations by Perrin and Chaudesaigues. They studied the mean square displacement of gamboge particles of radius 0.212 μm in a medium with viscosity 0.0012 Nm^{-2}s and maintained at a temperature of 186 K. The values found along the x-axis at times 30, 60, 90 and 120 seconds, respectively, were 45, 86.5, 140, 195 $\times 10^{-12} m^2$. These give the mean value of squared displacement for 30 seconds as $48.75 \times 10^{-12} m^2$. Now, from (7) and (35), we have

$$\langle x^2(t)\rangle = (kTt/3\pi\eta a), \quad (36)$$

which on substituting the above listed values yields $k = 1.36 \times 10^{-23} JK^{-1}$. Clearly, it is quite close to the accepted value of the Boltzmann constant except that the deviation is reasonably large.

It may be mentioned that the Langevin equation (equation (20)) was based on the assumptions enumerated in the beginning of this section. However, in a real system being used for the observation of Brownian motion, some external force $\mathbf{f}_{\text{ext}}(t)$ may be present; the viscous drag force $\mathbf{f}_d$ may be a function of higher powers of velocity or some other function of $\mathbf{v}(t)$; the drag coefficient may not be a constant and rather may depend upon $\mathbf{v}$, t or even position. In such a case this equation is modified to a general form

$$M(d\mathbf{v}/dt) = -\gamma(\mathbf{v}, x, t)F(\mathbf{v}) + \mathbf{f}_r(t) + \mathbf{f}_{\text{ext}}(t). \quad (37)$$

It is worthwhile to point out that the Langevin equations can also be obtained by assuming the Brownian particle to be interacting bilinearly with a large number of harmonic oscillators constituting a heat bath[6]. This approach yields explicit expressions for the drag force $\mathbf{f}_d$ as well as the stochastic force or noise $\mathbf{f}_r(t)$ and, thus, provides better insight into their mechanism but still does not make the theory very rigorous[7]. The latter task is achieved by using the so called master equation

[6] This derivation is given, e.g., in article 1.6 in *Nonequilibrium Statistical Mechanics* by R Zwanzig (Oxford University Press, Oxford, 2001).

[7] See R Zwanzig, *J. Stat. Phys.*, Vol.9, p.215, 1973.

for the time rate of variation of probability distribution function and its simplified version – the Fokker–Planck equation.[8] However, we do not propose to go into these details here.

[8] See H Risken, *The Fokker-Planck Equation: Methods of Solution and Applications*, Springer, 1996.

Suggested Reading

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[8] D Ruelle, Conversations on Nonequilibrium Physics with an Extraterrestial, *Physics Today*, Vol. 57, No. 5, pp.48-53, 2004.

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Sir Isaac Newton had a theory of how to get the best outcomes in a courtroom. He suggested to lawyers that they should drag their arguments into the late afternoon hours. The English judges of his day would never abandon their 4 o'clock tea time, and therefore would always bring down their hammer and enter a hasty, positive decision so they could retire to their chambers for a cup of Earl Grey.

This tactic used by the British lawyers is still recalled as 'Newton's Law of Gavel Tea' in legal circles.