CHAPTER III

THE MODERN THEORY

We have known from the preceding chapter that Brownian motion are concerned with the perpetual irregular motions exhibited by small grains or particles of colloidal size immersed in a fluid, which motions are the phenomenon of molecular agitation on a reduced scale by particles very large on the molecular scale-so large as to be readily visible in an ultramicroscope. The perpetual motions of the particles are maintained by fluctuations in the collisions with the molecules of the surrounding fluid. Under normal conditions, in a liquid, a Brownian particle will suffer about 10^{21} collisions per second and this is so frequent that we cannot really speak of separate collisions. Since each collision can be thought of as producing a kink in the path of the particle,so we cannot hope to follow the path in any detail-indeed, to our senses the details of the path are impossibly fine.

The modern theory of the Brownian motion discussed is about Langevin equation, Fokker-Planck equation and Ford-Kac-Mazur model.

3.1.Langevin Equation

3.1.1 The derivation of Langevin equation (8)

We shall treat the problem of Brownian motion in one dimension. Consider a particle of mass m whose center-of-mass coordinate at time t is designated by x(t) and whose corresponding velocity is $u = dx/dt$. This particle is immersed in a liquid at the absolute temperature T. It would be a hopelessly complex task (collision rate on the particle is too high) to describe in detail the interaction of the center-of-mass coordinate x with all the many degrees of freedom (i.e., those describing the motion of the molecules in the surrounding liquid). But these degrees of freedom can be regarded as a heat reservoir at some temperature T, and their interaction with x can be lumped into some net force $A'(t)$ effective in determining the time dependence of x. In addition, the particle may also interact with some external systems, such as gravity or electromagnetic fields, through a force denoted by K(t). The velocity u of the particle may, in general, be appreciably different from its mean value in equilibrium.

Focusing attention on the center-of-mass coordinate x, Newton's second law of motion can then be written in the form

$$m\frac{du}{dt} = K(t) + A'(t) \tag{1}$$

Here very little is known about the force $A'(t)$ which describes the interaction of x with the many degrees of freedom of the system. Basically, $A'(t)$ depends on the positions of many atoms which are in constant motion. Thus $A'(t)$ is some rapidly fluctuating function of the time t and varies in a highly irregular fashion. Indeed, one cannot specify the precise functional dependence of A' on t. So, one has to formulate the problem in statistical terms. One must, therefore, envisage an ensemble of many similarly prepared systems, each of them consisting of a particle and the surrounding medium. For each of these the force $A'(t)$ is some random function of t (see Fig.1). One can then attempt to make statistical statements about this ensemble.

The rate at which $A'(t)$ varies can be characterized by "correlation time" τ^* which is roughly the mean time between two successive maxima (or minima) of the fluctuating function $A'(t)$. This time τ^* is quite small on a macroscopic scale. (It is roughly of the order of a mean intermolecular separation divided by a mean molecular velocity, e.g., about 10^{-13} sec, if $A'(t)$ describes

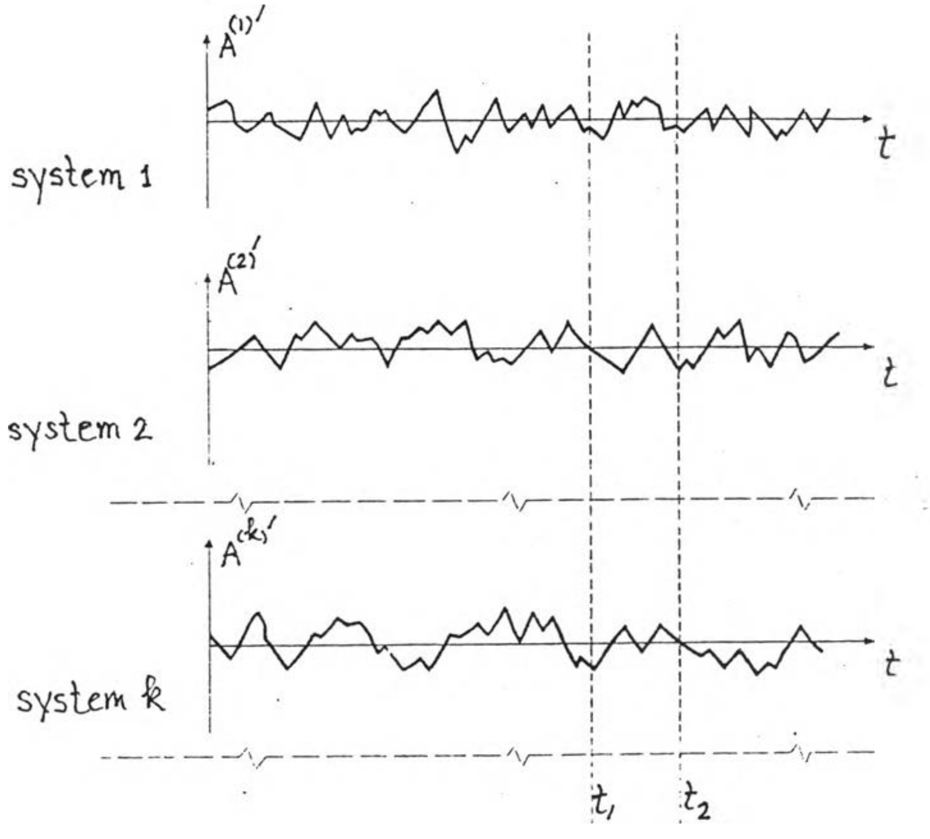

Fig.1 Ensemble of systems illustrating the behavior of the fluctuating force $A'(t)$ acting on a stationary particle.

interactions with molecules of the surrounding liquid.) Furthermore, if one contemplates a situation where the particle is imagined clamped so as to be stationary, there is no preferred direction in space; then $A'(t)$ must be as often positive as negative so that the ensemble average $A'(t)$ vanishes.

Equation (1) holds for each member of the ensemble, and our aim is to deduce from it statistical statements about u. Since $A'(t)$ is a rapidly fluctuating function of time, it follows by Eq. (1) that u also fluctuates in time. But, superimposed upon these fluctuations, the time dependence of u may also exhibit a more slowly varying trend. For example, one can focus attention on the ensemble average $\overline{u}$ of the velocity, which is a much more slowly varying function of the time than u itself, and write

$$u = \overline{u} + u' \qquad (2)$$

where u' denotes the part of u which fluctuates rapidly (although less rapidly than $A'(t)$, since the mass m is appreciable) and whose mean value vanishes. The slowly varying part $\overline{u}$ is of crucial importance (even if it is small) because it is of primary significance in determining the behavior of the particle over long periods of time. To investigate its time dependence, let us integrate Eq. (1) over some time interval τ which is small on a macroscopic scale, but large in the sense that $\tau \gg \tau^*$. Then one gets

$$m\{u(t+\tau) - u(t)\} = K(t)\tau + \int_t^{t+\tau} A'(t')\,dt' \tag{3}$$

where we have assumed that the external force K is varying slowly enough that it changes by a negligible amount during a time τ. The last integral in Eq.(3) ought to be very small since $A'(t)$ changes sign many times in the time τ. Hence one might expect that any slowly varying part of u should be due only to the external force K, i.e., one might be tempted to write

$$m\frac{d\bar{u}}{dt} = K \tag{4}$$

But this order of approximation is too crude to describe the physical situation. Indeed, the interaction with the environment expressed by $A'(t)$ must be such that it tends to restore the particle to the equilibrium situation. Suppose that the external force $K = 0$. The interaction expressed by A' must then be such that, if $\bar{u} \neq 0$ at some initial time, it causes $\bar{u}$ to approach gradually its ultimate equilibrium value $\bar{u} = 0$. But (4) fails to predict this kind of trend of $\bar{u}$ toward its equilibrium value. The reason is that we were too careless in treating the effects of A' in Eq.(3). We did not consider that the interaction force A' must actually be affected by the motion of the particle in such a way that A' itself contains a slowly varying part $\bar{A}$ tending to restore the particle to equilibrium. Hence we shall write, analogously to Eq.(2)

$$A' = \bar{A} + A \tag{5}$$

where A is the rapidly fluctuating part of A' whose average value vanishes. The slowly varying part $\overline{A}'$ must be some function of $\overline{u}$ such that $\overline{A}'(\overline{u})=0$ in equilibrium when $\overline{u} = 0$. If $\overline{u}$ is not too large, $\overline{A}'(\overline{u})$ can be expanded in a power series in $\overline{u}$ whose first nonvanishing term must then be linear in $\overline{u}$. Thus $\overline{A}'$ must have the general form

$$\overline{A}' = -\beta\overline{u} \tag{6}$$

Where β is some positive constant (called the "friction constant") and the minus sign indicates explicitly that the force $\overline{A}'$ acts in such a direction that it tends to reduce $\overline{u}$ to zero as time increases. Our present arguments do not permit us to make any statements about the actual magnitude of β . We can, however, surmise that β must in some way be expressible in terms of A' itself, since the frictional restoring force is also caused by the interactions described by $A'(t)$.

In the general case the slowly varying part of Eq.(1) becomes then

$$m\frac{d\overline{u}}{dt} = K + \overline{A}' = K - \beta\overline{u} \tag{7}$$

If one includes the rapidly fluctuating parts u' and A of Eq.(2) and Eq.(5), Eq. (1) can be written

$$m\frac{du}{dt} = K - \beta u + A(t) \tag{8}$$

where we have put $\beta\overline{u} \approx \beta u$ with negligible error (since the rapidly fluctuating contribution $\beta u'$ can be neglected compared to the predominant fluctuating term A(t). Equation (8) is called the "Langevin Equation" It differs from equation (1) by decomposing the force $A'(t)$ into a slowly varying part $-\beta u$ and into a fluctuating part A(t) which is "purely random," i.e., such that its mean value always vanishes irrespective of the velocity or position of the particle. The Langevin equation (8) describes the behavior of the particle at all later times if its initial conditions are specified.

3.1.2 The theory of the Brownian motion of a free particle.

Consider the Brownian motion of a free particle (no field of force) the Langevin equation for this case is

$$d\vec{u}/dt = -\beta\vec{u} + \vec{A}(t) \tag{9}$$

According to this equation, the influence of the surrounding medium on the motion of the particle can be split up into two parts: first, a systematic part $-\beta\vec{u}$ representing a dynamical friction experienced by the particle and second, a fluctuating part $\vec{A}(t)$ which is characteristic of the Brownian motion.

Regarding the frictional term $-\beta\vec{u}$ it is assumed that this is governed by Stokes' law. Hence

$$\beta = 6\pi a\eta/m \tag{10}$$

As for the fluctuating part $\vec{A}(t)$ the following principal assumptions are made:

(i) $\vec{A}(t)$ is independent of $\vec{u}$

(ii) $\vec{A}(t)$ varies extremely rapidly compared to the variations of $\vec{u}$

The second assumption implies that time interval Δt exist such that during Δt the variations in $\vec{u}$ are expected to be very small while during the same interval $\vec{A}(t)$ may undergo several fluctuations. Alternatively, we may say that though $u(t)$ and $u(t+\Delta t)$ are expected to differ by a negligible amount, no correlation between $\vec{A}(t)$ and $\vec{A}(t+\Delta t)$ exists.

The problem is to solve the stochastic differential equation (9) subject to the restrictions on $\vec{A}(t)$ stated in the preceding. But "Solving" a stochastic differential equation (6) is not the same as solving any ordinary differential equation. For one thing, Eq (9) involves the function $\vec{A}(t)$ which has only statistically defined properties. Consequently, "solving" the Langevin Eq (9) has to be understood in the sense of specifying a probability distribution $W(\vec{u}, t; \vec{u}_0)$.
$W(\vec{u}, t; \vec{u}_0)$ which governs the probability of occurrence of the velocity $\vec{u}$ at time t given that $\vec{u} = \vec{u}_0$ at t = 0. Of this function $W(\vec{u}, t; \vec{u}_0)$ we require that, as $t \rightarrow 0$,

$$W(\vec{u}, t; \vec{u}_0) \rightarrow \delta(u_x - u_{x,0})\,\delta(u_y - u_{y,0})\,\delta(u_z - u_{z,0}) \tag{11}$$

where the δ's are Dirac's δ functions (8). Further, the physical circumstances of the problem require that we demand of W that it tend to a Maxwellian distribution for the temperature T of the surrounding fluid, independently of $\vec{u}_0$ as $t \rightarrow \infty$:

$$W(\vec{u}, t; \vec{u}_0) \rightarrow \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-m|\vec{u}|^2/2kT) \tag{12}$$

This demand on $W(\vec{u}, t; \vec{u}_0)$ conversely requires that $\vec{A}(t)$ satisfy certain statistical requirements. According to the Langevin equation we have the formal solution

$$\vec{u} - \vec{u}_0 e^{-\beta t} = e^{-\beta t}\int_0^t e^{\beta \xi} \vec{A}(\xi)\, d\xi \tag{13}$$

Consequently, the statistical properties of

$$\vec{u} - \vec{u}_0 e^{-\beta t} \tag{14}$$

must be the same as

$$e^{-\beta t} \int_0^t e^{\beta \xi} \vec{A}(\xi)\, d\xi \tag{15}$$

As $t \to \infty$ the quantity (14) tends to $\vec{u}$; hence the distribution of

$$\lim_{t\to\infty} \left\{ e^{-\beta t} \int_0^t e^{\beta \xi} \vec{A}(\xi)\, d\xi \right\} \tag{16}$$

must be the Maxwellian distribution

$$(m/2\pi kT)^{3/2} \exp(-m|\vec{u}|^2/2kT) \tag{17}$$

One of our principal assumptions concerning $\vec{A}(t)$ is that it varies extremely rapidly compared to any other quantities which enter into our discussion. Further, the fluctuating acceleration experienced by the particles is statistical in character in the sense that the particles having the same initial coordinates and/or velocities will suffer accelerations which will differ from particle to particle both in magnitude and in their dependence on time. However, on account of the rapidity of these flutuations, we can always divide an interval of time which is long enough for any of the physical parameters like the position or the velocity of a Brownian particle to change appreciably, into a very large number of subintervals of duration Δt such that during each of these subintervals we can treat all functions of time except $\vec{A}(t)$ which enter in our formulae as constants. Thus, the quantity on the right - hand side of Eq (13) can be written as

$$e^{-\beta t} \sum_j e^{\beta j \Delta t} \int_{j\Delta t}^{(j+1)\Delta t} \vec{A}(\xi)\, d\xi \tag{18}$$

Let

$$\vec{B}(\Delta t) = \int_t^{t+\Delta t} \vec{A}(\xi)\, d\xi \tag{19}$$

$\vec{B}(\Delta t)$ represents the net acceleration which the particle may suffer on a given occasion during Δt. Equation(13) becomes

$$\vec{u} - \vec{u}_0 e^{-\beta t} = \sum_j e^{\beta(j\Delta t - t)} \vec{B}(\Delta t) \tag{20}$$

We require that as $t \rightarrow \infty$ the quantity on the right-hand side tends to the Maxwellian distribution. We now assert that this requires the probability of occurrence of different values for $\vec{B}(\Delta t)$ be governed by the distribution function

$$w[\vec{B}(\Delta t)] = \frac{1}{(4\pi q \Delta t)^{3/2}} \exp\left(-|\vec{B}(\Delta t)|^2 / 4q\Delta t\right) \tag{21}$$

where

$$q = \beta k T/m \tag{22}$$

To prove this assertion we have to show that $W(\vec{u}, t; \vec{u}_0)$ derived on the basis of Eqs (20) and (21) does in fact tend to the Maxwellian distribution as $t \rightarrow \infty$.

The expression for $w[\vec{B}(\Delta t)]$ is valid only for times Δt large compared to the average period of a single fluctuation of $\vec{A}(t)$. Now, the period of fluctuation of $\vec{A}(t)$ is clearly of the order of the time between successive collisions between the Brownian particle and the molecules of the surrounding fluid; in a liquid this is generally of the order of 10^{-21} sec.

We now proceed to prove our assertion concerning Eqs.(20), (21), and (22)

We first prove the following lemma:

Lemma I. Let

$$\vec{R} = \int_0^t \psi(\xi)\vec{A}(\xi)\,d\xi \tag{23}$$

Then, the probability distribution of $\vec{R}$ is given by

$$W(\vec{R}) = \frac{1}{\left[4\pi q\int_0^t \psi^2(\xi)\,d\xi\right]^{3/2}} \exp\left(-|\vec{R}|^2/4q\int_0^t \psi^2(\xi)\,d\xi\right) \tag{24}$$

In order to prove this, we first divide the interval (0,t) into a large number of subintervals of duration Δt . We can then write

$$\vec{R} = \sum_j \psi(j\Delta t)\int_{j\Delta t}^{(j+1)\Delta t} \vec{A}(\xi)\,d\xi \tag{25}$$

Refer to the definition of $\vec{B}(\Delta t)$ [Eq.(19)] we can express $\vec{R}$ in the form

$$\vec{R} = \sum_j \vec{r}_j \tag{26}$$

where

$$\vec{r}_j = \psi(j\Delta t)\vec{B}(\Delta t) = \psi_j \vec{B}(\Delta t) \tag{27}$$

According to Eq (21) the probability distribution of $\vec{r}_j$ is governed by

$$\tau(\vec{r}_j) = \frac{1}{(2\pi l_j^2/3)^{3/2}} \exp\left(-3|\vec{r}_j|^2/2l_j^2\right) \tag{28}$$

where we have written

$$l_j^2 = 6q\psi_j^2 \Delta t \tag{29}$$

A comparison of Eqs.(26) and (28) with Eqs.(A-1) and (A-23) shows that we have reduced our present problem to the special case in the theory of random flights. Hence from Eqs.(A-25) and (A-28)

$$W(\vec{R}) = \frac{1}{(2\pi \Sigma l_j^2/3)^{3/2}} \exp(-3|\vec{R}|^2/2\Sigma l_j^2) \tag{30}$$

But

$$\Sigma l_j^2 = 6q \sum_j \psi_j^2 \Delta t = 6q \sum_j \psi^2(j\Delta t)\Delta t$$

$$\lim_{\Delta t \to 0} \Sigma l_j^2 = 6q \int_0^t \psi^2(\xi)\, d\xi \tag{31}$$

We therefore have

$$W(\vec{R}) = \frac{1}{[4\pi q \int_0^t \psi^2(\xi) d\xi]^{3/2}} \exp\left(-|\vec{R}|^2/4q\int_0^t \psi^2(\xi)d\xi\right) \tag{32}$$

which proves the lemma.

Returning to Eq.(13) we can express the right-hand side of this equation in the form

$$\int_0^t \psi(\xi)\vec{A}(\xi)\, d\xi \tag{33}$$

if

$$\psi(\xi) = e^{\beta(\xi - t)} \tag{34}$$

We therefore apply lemma I and the definition of $\psi(\xi)$, Eq.(32) governs the probability distribution of

$$\vec{u} - \vec{u}_0 e^{-\beta t} \tag{35}$$

Since,

$$\int_0^t \psi^2(\xi)\,d\xi = \int_0^t e^{2\beta(\xi - t)}\,d\xi = \frac{1}{2\beta}(1 - e^{-2\beta t}) \tag{36}$$

According to Eq. (22) $$q/\beta = kT/m \tag{37}$$

From Eqs.(32), (36) and (37) we obtain

$$W(\vec{u},t;\vec{u}_0) = \left[\frac{m}{2\pi kT(1-e^{-2\beta t})}\right]^{3/2} \exp\left[-m|\vec{u}-\vec{u}_0 e^{-\beta t}|^2 / 2kT(1-e^{-2\beta t})\right] \tag{38}$$

Then for $t \to \infty$

$$W(\vec{u},t;\vec{u}_0) \to \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-m|\vec{u}|^2/2kT\right) \tag{39}$$

which is the Maxwellian distribution. This proves the assertion we made with the statistical properties of $\vec{B}(\Delta t)$ implied in Eqs.(21) and (22), Eq.(20) leads to a distribution $W(\vec{u},t;\vec{u}_0)$ which tends to be Maxwellian independent of $\vec{u}_0$ as $t \to \infty$.

We shall now show how with the assumptions made concerning $\vec{B}(\Delta t)$ to derive $W(\vec{r},t;\vec{r}_0,\vec{u}_0)$, the distribution of the displacement $\vec{r}$ of a particle at time t given that the particle is at $\vec{r}_0$ with a velocity $\vec{u}_0$ at time t = 0.

Since

$$\vec{r} - \vec{r}_0 = \int_0^t \vec{u}(t)\,dt \tag{40}$$

Substituting Eq(13) into Eq(40), therefore, gives

$$\vec{r} - \vec{r}_0 = \int_0^t d\eta \left\{ \vec{u}_0 e^{-\beta\eta} + e^{-\beta\eta} \int_0^\eta d\xi\, e^{\beta\xi} \vec{A}(\xi) \right\} \tag{41}$$

or

$$\vec{r}-\vec{r}_0-\beta^{-1}\vec{u}_0(1-e^{-\beta t}) = \int_0^t d\eta\, e^{-\beta\eta}\int_0^\eta d\xi\, e^{\beta\xi}\vec{A}(\xi) \tag{42}$$

By integrating by parts of the right-hand side of Eq.(42), we find that

$$\vec{r}-\vec{r}_0-\beta^{-1}\vec{u}_0(1-e^{-\beta t}) = -\beta^{-1}e^{-\beta t}\int_0^t e^{\beta\xi}\vec{A}(\xi)\,d\xi + \beta^{-1}\int_0^t \vec{A}(\xi)\,d\xi \tag{43}$$

We can reduce Eq.(43) to the form

$$\vec{r}-\vec{r}_0-\beta^{-1}\vec{u}_0(1-e^{-\beta t}) = \int_0^t \psi(\xi)\vec{A}(\xi)\,d\xi \tag{44}$$

by defining

$$\psi(\xi) = \beta^{-1}(1-e^{\beta(\xi-t)}) \tag{45}$$

Thus lemma-I can be applied and with the definition of $\psi(\xi)$ Eq.(32) governs the probability distribution of

$$\vec{r}-\vec{r}_0-\beta^{-1}\vec{u}_0(1-e^{-\beta t}) \tag{46}$$

Since,

$$\begin{aligned}\int_0^t \psi^2(\xi)\,d\xi &= \frac{1}{\beta^2}\int_0^t (1-e^{\beta(t-\xi)})^2\,d\xi \\ &= \frac{1}{2\beta^3}(2\beta t-3+4e^{-\beta t}-e^{-2\beta t})\end{aligned} \tag{47}$$

we have from lemma I, therefore

$$W(\vec{r},t;\vec{r}_0,\vec{u}_0) = \left\{\frac{m\beta^2}{2\pi kT(2\beta t-3+4e^{-\beta t}-e^{-2\beta t})}\right\}^{3/2} \exp-\left\{\frac{m\beta^2|\vec{r}-\vec{r}_0-\vec{u}_0(1-e^{-\beta t})/\beta|^2}{2kT(2\beta t-3+4e^{-\beta t}-e^{-2\beta t})}\right\} \tag{48}$$

For intervals of time long compared to β^{-1}, we can ignore the exponential and the constant terms as compared to $2\beta t$. Further, as we shall presently show, $\langle|\vec{r}-\vec{r}_0|^2\rangle$ is of order t [cf. Eq.(51)] ; hence we can also neglect $\vec{u}_0(1-e^{-\beta t})\beta^{-1}$ compared to $\vec{r}-\vec{r}_0$, Eq (48) thus reduces to

$$W(\vec{r},t;\vec{r}_0,\vec{u}_0)=\frac{1}{(4\pi Dt)^{3/2}}\exp(-|\vec{r}-\vec{r}_0|^2/4Dt)\;;(t\gg\beta^{-1}) \quad (49)$$

where we have introduced the " diffusion coefficient " D defined by

$$D=kT/m\beta = kT/6\pi a\eta \quad (50)$$

In Eq.(50) we substituted for β according to Eq.(10).

From Eq.(49) we obtain for the mean square displacement along any given direction (say, the x-direction)

$$\langle(x-x_0)^2\rangle=\frac{1}{3}\langle|\vec{r}-\vec{r}_0|^2\rangle=2Dt=(kT/3\pi a\eta)t \quad (51)$$

This is Einstein's result(1). Equation (51) has been verified by Perrin(6) to lead to consistent and satisfactory values for the Boltzmann constant k by observation of $\frac{\langle(x-x_0)^2\rangle}{t}$ over wide ranges of T, η and a.

The law of distribution of displacements (49) has been tested by observation. Perrin gives the following sets of counts of the displacements of a grain of radius 2.1×10^{-5} cm at 30 sec intervals. Out of a number N of such observations the number of observed values of x displacements between x_1 and x_2 should be

$$\frac{N}{\pi^{1/2}}\int_{x_1}^{x_2}\exp(-x^2/4Dt)\frac{dx}{(4Dt)^{1/2}}$$

The agreement is in satisfactory. See Table I(6).

Table -I Observations and calculations of the distribution of the displacements of a Brownian particle.

Range $X \times 10^4$ cm	1 st set Obs.	1 st set Calc.	2 nd set Obs.	2 nd set Calc.	Total Obs.	Total Calc.
0 - 3.4	82	91	86	84	168	175
3.4 -6.8	66	70	65	63	131	132
6.8 -10.2	46	39	31	36	77	75
10.2 - 17.0	27	23	23	21	50	44

From Eq.(48), we have

$$\langle|\vec{r}-\vec{r}_0|^2\rangle = \frac{|\vec{u}_0|^2}{\beta^2}(1-e^{-\beta t})^2 + \frac{kT}{m\beta^2}(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}) \tag{52}$$

Averaging this equation again and from $\langle|\vec{u}_0|^2\rangle = \frac{3kT}{m}$ we obtain

$$\langle\langle|\vec{r}-\vec{r}_0|^2\rangle\rangle = \frac{2kT}{m\beta^2}(\beta t - e^{-\beta t} + e^{-2\beta t}) \tag{53}$$

For $t \to \infty$, Eq (53) is in agreement with our result (51) while for $t \to 0$ we have

$$\langle\langle|\vec{r}-\vec{r}_0|^2\rangle\rangle = \frac{3kTt^2}{m} = \langle|\vec{u}_0|^2\rangle t^2 \tag{54}$$

So far we have only the law of distributions of $\vec{u}$ and $\vec{r}$ separately. But we can ask for the distribution $W(\vec{r},\vec{u},t;\vec{u}_0,\vec{r}_0)$ governing the probability of the simultaneous occurrence of the velocity $\vec{u}$ and the position $\vec{r}$ at time t, given that $\vec{u}=\vec{u}_0$ and $\vec{r}=\vec{r}_0$

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$$F = q\beta^{-3}(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}); \quad G = q\beta^{-1}(1 - e^{-2\beta t}) \tag{61}$$

and

$$H = 2q\beta^{-1}\int_0^t e^{\beta(\xi - t)}(1 - e^{\beta(\xi - t)})\, dt = q\beta^{-2}(1 - e^{-\beta t})^2 \tag{62}$$

3.1.3 The theory of the Brownian motion of a particle in a field of force. [The harmonically bound particle] (5,6)

In the presence of an external field of force, the Langevin Eq.(9) is

$$d\vec{u}/dt = -\beta\vec{u} + \vec{A}(t) + \vec{K}(\vec{r}, t) \tag{63}$$

where $\vec{K}(\vec{r}, t)$ is the acceleration produced by the field. The method of solution is illustrated sufficiently by a one-dimensional harmonic oscillator describing Brownian motion. The appropriate stochastic equation is

$$\frac{du}{dt} = -\beta u + A(t) - \omega^2 x \tag{64}$$

where ω denotes the circular frequency of the oscillator. We can write Eq.(64) alternatively in the form

$$d^2x/dt^2 + \beta\, dx/dt + \omega^2 x = A(t) \tag{65}$$

What we seek from this equation are, the probability distributions $W(x, t; x_0, u_0)$, $W(u, t; x_0, u_0)$ and $W(x, u, t; x_0, u_0)$. To obtain these distributions we first find the formal solution of Eq.(65) regarded as an ordinary differential equation. The method of solution most appropriate for our present purposes is that of the variation of the parameters.

Therefore from Eq.(65)

$$x = a_1 \exp(\mu_1 t) + a_2 \exp(\mu_2 t) \tag{66}$$

where μ_1 and μ_2 are the roots of

$$\mu^2 + \beta\mu + \omega^2 = 0 \tag{67}$$

i.e.,

$$\mu_1 = -\frac{1}{2}\beta + \left(\frac{1}{4}\beta^2 - \omega^2\right)^{1/2} ; \mu_2 = -\frac{1}{2}\beta - \left(\frac{1}{4}\beta^2 - \omega^2\right)^{1/2} \tag{68}$$

We assume that the solution of Eq.(65) is of the form (66) where a_1 and a_2 are functions of time restricted to satisfy the equation

$$\exp(\mu_1 t)\,(da_1/dt) + \exp(\mu_2 t)(da_2/dt) = 0 \tag{69}$$

and

$$\mu_1 \exp(\mu_1 t)(da_1/dt) + \mu_2 \exp(\mu_2 t)(da_2/dt) = A(t) \tag{70}$$

Solving Eqs.(69) and (70) we obtain

$$a_1 = \frac{+1}{\mu_1 - \mu_2} \int_0^t \exp(-\mu_1 \xi) A(\xi)\, d\xi + a_{10}$$

$$a_2 = \frac{-1}{\mu_1 - \mu_2} \int_0^t \exp(-\mu_2 \xi) A(\xi)\, d\xi + a_{20} \tag{71}$$

where a_{10} and a_{20} are constants. Substituting Eq.(71) in Eq. (66) we have

$$x = \frac{1}{\mu_1 - \mu_2} \left\{ \exp(\mu_1 t) \int_0^t \exp(-\mu_1 \xi) A(\xi)\, d\xi - \exp(\mu_2 t) \times \int_0^t \exp(-\mu_2 \xi) A(\xi)\, d\xi \right\} + a_{10} \exp(\mu_1 t) + a_{20} \exp(\mu_2 t) \tag{72}$$

From the foregoing equation we obtain the velocity $u = \frac{dx}{dt}$ the formula

$$u = \frac{1}{\mu_1-\mu_2}\Big\{\mu_1 \exp(\mu_1 t)\int_0^t \exp(-\mu_1\xi)A(\xi)d\xi$$

$$-\mu_2 \exp(\mu_2 t)\int_0^t \exp(-\mu_2\xi)A(\xi)d\xi\Big\} + \mu_1 a_{10}\exp(\mu_1 t) + \mu_2 a_{20}\exp(\mu_2 t) \tag{73}$$

The constants a_{10} and a_{20} can now be determined from the conditions that $x = x_0$ and $u = u_0$ at $t = 0$. We find

$$a_{10} = -\frac{x_0\mu_2 - u_0}{\mu_1-\mu_2}\;;\quad a_{20} = +\frac{x_0\mu_1 - u_0}{\mu_1-\mu_2} \tag{74}$$

Thus, we have from Eqs.(72), (73) and (74)

$$x + \frac{1}{\mu_1-\mu_2}\Big[(x_0\mu_2-u_0)\exp(\mu_1 t) - (x_0\mu_1-u_0)\exp(\mu_2 t)\Big] = \int_0^t A(\xi)\psi(\xi)d\xi \tag{75}$$

and

$$u + \frac{1}{\mu_1-\mu_2}\Big[\mu_1(x_0\mu_2-u_0)\exp(\mu_1 t) - \mu_2(x_0\mu_1-u_0)\exp(\mu_2 t) = \int_0^t A(\xi)\phi(\xi)d\xi \tag{76}$$

where

$$\psi(\xi) = \frac{1}{\mu_1-\mu_2}\Big[\exp[\mu_1(t-\xi)] - \exp[\mu_2(t-\xi)]\Big] \tag{77.1}$$

and

$$\phi(\xi) = \frac{1}{\mu_1-\mu_2}\Big[\mu_1\exp[\mu_1(t-\xi)] - \mu_2\exp[\mu_2(t-\xi)]\Big] \tag{77.2}$$

It is now seen that the quantities on the right-hand sides of Eqs.(75) and (76) are of the forms considered in lemmas I and II. Accordingly, we can at once write down the distribution functions $W(x,t;x_0,u_0)$, $W(u,t;x_0,u_0)$ and $W(x,u,t;x_0,u_0)$ in terms of the integrals

$$\int_0^t \psi^2(\xi)d\xi\;;\quad \int_0^t \phi^2(\xi)d\xi\;,\quad \int_0^t \psi(\xi)\phi(\xi)d\xi \tag{78}$$

With $\psi(\xi)$ and $\phi(\xi)$ defined as in Eqs.(77.1) and (77.2), therfore

$$\int_0^t \psi^2(\xi)d\xi = 1/(\mu_1-\mu_2)^2\Big[(\mu_2 \exp(2\mu_1 t) + \mu_1 \exp(2\mu_2 t))/2\mu_1\mu_2 - 2/(\mu_1+\mu_2)(\exp[(\mu_1+\mu_2)t]-1) - (\mu_1+\mu_2)/2\mu_1\mu_2\Big] \quad (79)$$

$$\int_0^t \phi^2(\xi)d\xi = 1/(\mu_1-\mu_2)^2\Big[\tfrac{1}{2}(\mu_1 \exp(2\mu_1 t) + \mu_2 \exp(2\mu_2 t)) - 2\mu_1\mu_2/(\mu_1+\mu_2)(\exp[(\mu_1+\mu_2)t]-1) - \tfrac{1}{2}(\mu_1+\mu_2)\Big] \quad (80)$$

and

$$\int_0^t \psi(\xi)\phi(\xi)d\xi = \{1/2(\mu_1-\mu_2)^2\}(\exp(\mu_1 t) - \exp(\mu_2 t))^2 \quad (81)$$

According to Eq.(68). The quantities on the left-hand sides of Eqs.(75) and (76) become, respectively,

$$x - x_0 e^{-\beta t/2}\cosh\tfrac{1}{2}\beta_1 t - \frac{x_0\beta + 2u_0}{\beta_1} e^{-\beta t/2}\sinh\tfrac{1}{2}\beta_1 t \quad (82)$$

and

$$u - u_0 e^{-\beta t/2}\cosh\tfrac{1}{2}\beta_1 t + \frac{2x_0\omega^2 + \beta u_0}{\beta_1} e^{-\beta t/2}\sinh\tfrac{1}{2}\beta_1 t \quad (83)$$

where

$$\beta_1 = (\beta^2 - 4\omega^2)^{1/2} \quad (84)$$

Similarly, we find

$$\int_0^t \psi^2(\xi)d\xi = \frac{1}{2\omega^2\beta} - \frac{e^{-\beta t}}{2\omega^2\beta_1^2\beta}(2\beta^2\sinh^2\tfrac{1}{2}\beta_1 t + \beta\beta_1\sinh\beta_1 t + \beta_1^2) \quad (85)$$

$$\int_0^t \phi^2(\xi)d\xi = \frac{1}{2\beta} - \frac{e^{-\beta t}}{2\beta_1^2\beta}(2\beta^2\sinh^2\tfrac{1}{2}\beta_1 t - \beta\beta_1\sinh\beta_1 t + \beta_1^2) \quad (86)$$

and

$$\int_0^t \psi(\xi)\phi(\xi)d\xi = 2\beta_1^{-2} e^{-\beta t}\sinh^2\tfrac{1}{2}\beta_1 t \quad (87)$$

It is seen that all the foregoing expressions remain finite and real even when β_1 is zero or imaginary. Thus, while all the expressions remain valid in the "overdamped" case (β_1 real) the formulae appropriate for the periodic (β_1 imaginary) and the aperiodic (β_1 zero) cases can be obtained by replacing

$$\cosh \tfrac{1}{2}\beta_1 t \ , \ \beta_1^{-1} \sinh \tfrac{1}{2}\beta_1 t \ \text{ and } \ \beta_1^{-1} \sinh \beta_1 t \tag{88}$$

repectively, by

$$\cos\omega_1 t \ , \ \frac{1}{2\omega_1}\sin\omega_1 t \ \text{ and } \frac{1}{2\omega_1}\sin 2\omega_1 t \ ; \ \omega_1 = \left(\omega^2 - \tfrac{1}{4}\beta^2\right)^{\frac{1}{2}} \tag{89}$$

in the periodic case, and by

$$1 \ , \ \tfrac{1}{2}t \ \text{ and } \ t \tag{90}$$

in the aperiodic case

We can immediately obtain the distribution functions for the quantities on the left-hand sides of the Eqs.(75) and (76), i.e., the quantities(82) and (83) according to lemmas I and II. Thus,

$$W(x,t;x_0,u_0) = \left[\frac{m}{4\pi\beta kT\int_0^t \psi^2(\xi)\,d\xi}\right]^{1/2} \exp - \frac{\left(x - x_0 e^{-\beta t/2}\left[\cosh\tfrac{1}{2}\beta_1 t + \frac{\beta}{\beta_1}\sinh\tfrac{1}{2}\beta_1 t\right] - \frac{2}{\beta_1}u_0 e^{-\beta t/2}\sinh\tfrac{1}{2}\beta_1 t\right)^2}{\frac{2kT}{m\omega^2}\left\{1 - e^{-\beta t}\left(\frac{2\beta^2}{\beta_1^2}\sinh^2\tfrac{1}{2}\beta_1 t + \frac{\beta}{\beta_1}\sinh\beta_1 t + 1\right)\right\}} \tag{91}$$

We have similar expressions for $W(u,t;x_0,u_0)$ and $W(x,u,t;x_0,u_0)$ (the physical meaning of these probability distributions is similar to the meaning mentioned in section (3.1.2))

The quantities of greatest interest are the moments(6) $\langle x\rangle$, $\langle u\rangle$, $\langle x^2\rangle$ and $\langle u^2\rangle$. We find

$$\langle x\rangle = x_0 e^{-\beta t/2}\left(\cosh\tfrac{1}{2}\beta_1 t + \frac{\beta}{\beta_1}\sinh\tfrac{1}{2}\beta_1 t\right) + \frac{2u_0}{\beta_1} e^{-\beta t/2}\sinh\tfrac{1}{2}\beta_1 t \tag{92.1}$$

$$\langle u \rangle = u_0 e^{-\beta t/2}\left(\cosh \tfrac{1}{2}\beta_1 t - \frac{\beta}{\beta_1}\sinh \tfrac{1}{2}\beta_1 t\right) - \frac{2x_0\omega^2}{\beta_1} e^{-\beta t/2} \sinh \tfrac{1}{2}\beta_1 t \tag{92.2}$$

$$\langle x^2 \rangle = \langle x \rangle^2 + \frac{kT}{m\omega^2}\left\{1 - e^{-\beta t}\left(2\frac{\beta^2}{\beta_1^2}\sinh \tfrac{1}{2}\beta_1 t + \frac{\beta}{\beta_1}\sinh \beta_1 t + 1\right)\right\} \tag{92.3}$$

$$\langle u^2 \rangle = \langle u \rangle^2 + \frac{kT}{m}\left\{1 - e^{-\beta t}\left(2\frac{\beta^2}{\beta_1^2}\sinh^2 \tfrac{1}{2}\beta_1 t - \frac{\beta}{\beta_1}\sinh \beta_1 t + 1\right)\right\} \tag{92.4}$$

The foregoing expressions are the average values of the various quantities at time t for assigned values of x and u (namely, x_0 and u_0) at time t = 0. We see that

$$\left.\begin{array}{ll} \langle x \rangle \to 0; & \langle u \rangle \to 0 \\ \langle x^2 \rangle \to kT/m\omega^2; & \langle u^2 \rangle \to kT/m \end{array}\right\} t \to \infty \tag{93}$$

By averaging the various moments over all values of u_0 and remembering that $\langle u_0 \rangle = 0$; $\langle u_0^2 \rangle = kT/m$

we obtain from Eq(92) that

$$\langle\langle x \rangle\rangle = x_0 e^{-\beta t/2}\left(\cosh \tfrac{1}{2}\beta_1 t + \frac{\beta}{\beta_1}\sinh \tfrac{1}{2}\beta_1 t\right) \tag{94.1}$$

$$\langle\langle u \rangle\rangle = -\frac{2x_0\omega^2}{\beta_1} e^{-\beta t/2} \sinh \tfrac{1}{2}\beta_1 t \tag{94.2}$$

$$\langle\langle x^2 \rangle\rangle = \frac{kT}{m\omega^2} + \left(x_0^2 - \frac{kT}{m\omega^2}\right) e^{-\beta t}\left(\cosh \tfrac{1}{2}\beta_1 t + \frac{\beta}{\beta_1}\sinh \tfrac{1}{2}\beta_1 t\right)^2 \tag{94.3}$$

$$\langle\langle u^2 \rangle\rangle = \frac{kT}{m} + \frac{4\omega}{\beta_1^2}\left(x_0^2 - \frac{kT}{m\omega^2}\right) e^{-\beta t} \sinh^2 \tfrac{1}{2}\beta_1 t \tag{94.4}$$

where $\langle y \rangle$ and $\langle\langle y \rangle\rangle$ stand for $\dfrac{\int_{-\infty}^{\infty} y\, W(y)\, dy}{\int_{-\infty}^{\infty} W(y)\, dy}$; $\dfrac{\int_{-\infty}^{\infty} \langle y(u_0)\rangle W(u_0)\, du_0}{\int_{-\infty}^{\infty} W(u_0)\, du_0}$