CHAPTER II

INVESTIGATION OF THE THEORY OF BROWNIAN MOTION

An important phenomenon of statistical mechanics is called "Brownian Motion " which was investigated by the botanist Robert Brown in 1829. He observed a suspension of plant pollen dispersed in water under a microscope. The tiny particles executed an irregular fluctuating motion. The physical theory of Brownian motion was first described by Einstein and Smoluchowsky, and later further developed by Langevin and others. The aim of this section is to summarize some aspects of the theory of the Brownian motion, particularly, the classical case.

General Assumptions and Summary of Brownian Motion

It is well known that the Brownian motion is the phenomenon in which a particle, which we call a Brownian particle, moves through a stationary fluid. The Brownian particle is assumed to be large in comparison with the particles of the fluid and its motion is the result of the fluctuations in the collisions with the particles of the fluid. The frequency of the collisions is very high (about 10^{21} collisions per second). In the theory of this phenomenon the first concern has always been the calculation of the mean square value of the displacement of the Brownian particle, because this could be immediately observed. As is well known, this problem was first solved by Einstein [7],[10]-[15] in the case of a free Brownian particle, and he obtained the famous formula

$$\left\langle x^2 \right\rangle = 2Dt = \frac{2kT}{\eta} t \tag{2.1}$$

where η is the friction coefficient, T the absolute temperature and t the time. The influence of the surrounding medium or the particles of the fluid is characterized by the friction coefficient η as well as by the temperature T. For this Einstein used the formula of Stokes, because the Brownian particle is almost always immersed in the fluid as the liquid or gas at ordinary pressure. Furthermore in that case, the mean free path of the molecules of the surrounding medium is small when compared with the Brownian particle, and the surrounding medium may be considered as continuous, which allows us to use the results of hydrodynamics to calculate the friction coefficient for bodies of simple form (sphere, ellipsoid etc.). This will depend on the viscosity coefficient of the medium and is therefore independent of the pressure. But, in the other cases, as when the surrounding medium is a rarefied gas in which the mean free path of the molecules are great in comparison with the Browning particle, the friction will change in character. This friction coefficient may be proportional to the pressure.

The basis of Eq.(2.1), which, since Einstein, has been derived in various other ways, has been almost always the equation of motion of the so-called Langevin equation

$$m\dot{v} = -\eta v + F(t) \tag{2.2}$$

where $v = \dfrac{dx(t)}{dt}$ is the velocity of the Brownian particle. Characteristic of this equation is the influence of the surrounding medium to the Brownian particle being split into two parts:

(1) a systematic part $-\eta v$, which causes the friction and is important in determining the behavior of the Brownian particle over a long period of time.

(2) a fluctuating part $F(t)$, which is independent of velocity v and varies over a time scale that is much smaller than the time scale over which variation in the

velocity is noticeable, and its ensemble average value vanishes. We can write these assumptions more explicitly as

$$\begin{aligned} \langle F(t) \rangle &= 0 \\ \langle F(t)F(t') \rangle &= 2\eta kT\delta(t-t') \end{aligned} \tag{2.3}$$

One can say that Eq.(2.2) is a valid description of the motion in the limit that the motion can be described by two separate non-overlapping time scales. More generally Eq (2.2) is

$$m\dot{v} = f(t) - \eta v + F(t) \tag{2.4}$$

when the Brownian particle is acted upon by an external force f like the gravitational force.

One important notion is that of the probability distribution of any quantities like the displacement, velocity or force. Suppose that we have a quantity which is specified by g. This quantity cannot be specified more precisely as a function of time, but one just knows about its chance or probability with which any value of this quantity will occur, that is the function $W(g,g_0;t)$. For a given value g_0 of the quantity g at $t=0$ the probability $W(g,g_0;t)dg$ is a chance of this quantity if it has some value which lies between g and $g+dg$ in the later time t. It is clear that when we know $W(g,g_0;t)$, all mean values are determined. For instance,

$$\langle g^k \rangle = \int g^k W(g,g_0;t)dg. \tag{2.5}$$

In the case of the free Brownian particle (with no external force), the function $W(g,g_0;t)$ was already determined by Einstein as

$$W(x,x_0;t) = \left(\frac{1}{4\pi Dt}\right)^{1/2} \exp\left[-\frac{(x-x_0)^2}{4Dt}\right] \tag{2.6}$$

of which the first part of Eq.(2.1) is an immediate consequence. He derived this by finding for the function $W(x,x_0;t)$ a partial differential equation, which is the diffusion equation

$$\frac{\partial W}{\partial t}=D\frac{\partial^2 W}{\partial x^2} \tag{2.7}$$

and of which $W(x,x_0;t)$ is the so-called fundamental solution. It is clear from the definition of $W(x,x_0;t)$ that for $t=0$ there is certainty $x=x_0$. In other words, W is the solution of Eq.(2.7) for the initial condition $W(x,x_0;t)=\delta(x-x_0)$. There are boundary conditions which express the behavior of the particle at the wall. In the case of a completely free Brownian particle they are simply $W=0$ for $x=\pm\infty$. Einstein then derived the relation between the diffusion coefficient D and the friction constant η very simply, using the idea of the osmotic pressure. The connection between the probability distribution and the partial differential equation in the parabolic form like Eq.(2.7) has been generalized later by Smoluchowski, Fokker, Planck, Ornstein and others. The equation is generally called the Fokker-Planck equation. Especially for a particle under influence of an external force $f(t)$, Smoluchowski showed that the generalization of Eq (2.7) was

$$\frac{\partial W}{\partial t}=-\frac{1}{\eta}\frac{\partial}{\partial x}(fW)+D\frac{\partial^2 W}{\partial x^2}. \tag{2.8}$$

With the results (2.1), (2.6), (2.7) and (2.8) of Einstein and Smoluchowski, the problems seem completely solved. But there is one restriction, which was first stressed by Einstein, which says all of these results hold only when t is large when compared with m/η where m/η is a characteristic time constant of the system. The generalization of Eq.(2.1) for all times was given by Ornstein and Fürth, independently of each other. The result is

$$\langle x^2 \rangle = \frac{2mkT}{\eta^2}\left(\frac{\eta}{m}t - 1 + e^{-\eta t/m}\right). \tag{2.9}$$

For values of t large compared to m/η this becomes to Einstein formula (2.1). For very short time on the other hand, we get

$$\langle x^2 \rangle = \frac{kT}{m}t^2 \tag{2.10}$$

as one would expect, because in the beginning the motion must be uniform.

The Useful Methods on the Theory of the Brownian Motion

To study the Brownian motion in detail we have to deal with the theory of the so-called Gaussian random process. There are two approaches to the theory of the Gaussian process as follows:

i) **Fourier series method.** The attention of this method is focused on the actual random variation in time of the displacement, velocity, force or the other variables of the system. One usually develops this variable in term of a Fourier series in time. Any coefficients of the Fourier series can vary in a random fashion. A fundamental concept is the concept of the spectrum of the random process. The relation between the spectrum of the random process and the so-called correlation function of the random process is one of the basic theorems.

ii) Fokker-Planck method or diffusion method. Macroscopically, for an ensemble of particles or systems, the variations which occur are like a diffusion process. The distribution function of the random variables of the system will, therefore, satisfy a partial differential equation of the diffusion type.

The following sub-section describes some notions which are important to understand the theory of Brownian motion.

(1) The general random process

The meaning of a random process $q(t)$ is a process in which the variable q does not depend in a completely definite way on the independent variable t as in a casual process; instead one gets in different observations different function $q(t)$, so that only certain probability distributions are directly observable. Actually, the random process $q(t)$ is completely described by the following probability distribution:

$$w_n(q_n t_n, q_{n-1} t_{n-1}, \ldots, q_1 t_1) dq_n dq_{n-1} \ldots dq_1 \tag{2.11}$$

which is the joint probability of finding q in the range $(q_1, q_1 + dq_1)$ at time t_1, in the range $(q_2, q_2 + dq_2)$ at time t_2, in the range $(q_3, q_3 + dq_3)$ at time t_3, and so on. For the special case we have

$w_1(qt)dq \equiv$ probability of finding q in the range $(q, q + dq)$ at time t.
$w_2(q_2 t_2, q_1 t_1) \equiv$ joint probability of finding q in the range $(q_1, q_1 + dq_1)$ at time t_1, and in the range $(q_2, q_2 + dq_2)$ at time t_2. The joint probability w_n must fulfill the obvious conditions:

(a) $w_n \geq 0$

(b) $w_n(q_n t_n, \ldots, q_1 t_1)$ is a symmetric function in the set of variables $q_1 t_1, q_2 t_2, \ldots, q_n t_n$. This is clear since w_n is a joint probability.

(c) $w_k(q_k t_k, \ldots, q_1 t_1) = \int dq_n dq_{n-1} \ldots dq_{k+1} w_n(q_n t_n, \ldots, q_1 t_1)$ for $k < n$.

This is an example in which we are interested only in the joint probability at time $t_1, \ldots, t_k$ and then we sum (integrate) over all $q_{k+1}, q_{k+2}, \ldots, q_n$. Another interesting probability is that of finding the particle at time t_n at the position q_n and at time t_1 at position q_1, irrespective of the positions the particle may acquired at intermediate times. The probability for this case can be found by integrating w_n over all intermediate positions:

$$w_2(q_n t_n, q_1 t_1) = \int dq_{n-1} dq_{n-2} \ldots dq_2 w_n(q_n t_n, q_{n-1} t_{n-1}, \ldots, q_2 t_2, q_1 t_1) \qquad (2.12)$$

To determine the function w_n experimentally, it is clear that one needs a great number of records $q(t)$ obtained from a great number of experiments similarly prepared which is a so-called ensemble of observations. To find then, for instance, $w_1(qt)$, one determines at the definite time t how often in the definite experiment q occurs in a given interval $(q, q + \Delta q)$, etc. In most application (and especially for the Brownian motion problem) we can, however, make a simplification because the processes are stationary in time. This means that the underlying mechanism which causes the fluctuations does not change in cause of time. A shift of the t −axis will then not influence the function w_n, and as a result we can have

$w_1(q)dq \equiv$ probability of finding q between q and $q + dq$

$w_2(q_2, q_1; t) \equiv$ joint probability of finding a pair of values of q in the ranges dq_1 and dq_2, which are at time interval t apart from each other (t is therefore $= t_2 - t_1$).

And so on. These functions can now be experimentally determined from one record $q(t)$ taken over a sufficiently long time. One can then cut the record in pieces of length (where T is long in comparison with all periods occurring in the process), and one may consider the different pieces as the different records of an ensemble of observations. In computing average values one has, in general, distinguished between an ensemble average and time average. However, for a stationary process these two ways of averaging will always give the same result, and one can, therefore, use either of them.

The probability w_n leads immediately to a method of classifying the random process:

-We shall call a random process a purely random process when the successive values of q are not correlated at all. This means that:

$$w_n(q_n t_n, \ldots, q_1 t_1) = w_1(q_n t_n) w_1(q_{n-1} t_{n-1}) \ldots w_1(q_2 t_2) w_1(q_1 t_1) \tag{2.13}$$

It can be seen that all the information about the process is then completely contained in the first distribution function w_1. When t is discrete, it is easy to give examples, but for continuous t, the purely random process can only be considered as a kind of limiting case; in any actual example, the q_1 and q_2 will surely correlate when the time interval $t_2 - t_1$ is small enough.

-For a more complicated case, all the information about the process will be contained in w_2. Such processes are called Markoff processes. For the more precise definition it is useful to first introduce the concept of conditional probabilities. Let us now consider an experiment (a realization of the random process) in which the particle was found at times $t_1, \ldots, t_{n-1}$ at the corresponding position $q_1, \ldots, q_{n-1}$. We then ask what is the probability of finding it at time t_n at position q_n? We denote this conditional probability by

$$w(q_n t_n \mid q_{n-1} t_{n-1}, \ldots, q_1 t_1) \tag{2.14}$$

and the conditional probability is given by

$$w(q_n t_n \mid q_{n-1} t_{n-1}, \ldots, q_1 t_1) = \frac{w_n(q_n t_n, q_{n-1} t_{n-1}, \ldots, q_1 t_1)}{w_{n-1}(q_{n-1} t_{n-1}, \ldots, q_1 t_1)} \tag{2.15}$$

So far our consideration applies to any process. However, if we consider the special case in which the probability for the final position q_n depends only on the position at the time t_{n-1} and not on any earlier times, in the other words, the particle has lost its memory of the past, then the conditional probability depends only on the arguments at time t_n and t_{n-1}, so that we may write

$$w\left(q_n t_n \mid q_{n-1}t_{n-1},\ldots,q_1 t_1\right) = w\left(q_n t_n \mid q_{n-1}t_{n-1}\right). \tag{2.16}$$

If the conditional probability satisfies this condition, the corresponding process is called a Markoff process. The right hand side of Eq.(2.16) is often referred to as the transition probability. We can express the joint probability in term of the transition probability. In a first step we multiply Eq.(2.15) by $w_{n-1}\left(q_{n-1}t_{n-1},\ldots,q_1 t_1\right)$

$$w_n\left(q_n t_n, q_{n-1}t_{n-1},\ldots,q_1 t_1\right) = w\left(q_n t_n \mid q_{n-1}t_{n-1}\right)w_{n-1}\left(q_{n-1}t_{n-1},\ldots,q_1 t_1\right) \tag{2.17}$$

w_{n-1} can be written in terms of w_{n-2}, w_{n-2} can be written in terms of w_{n-3} and so on so that Eq.(4.17) becomes

$$w_n\left(q_n t_n, q_{n-1}t_{n-1},\ldots,q_1 t_1\right) = w\left(q_n t_n \mid q_{n-1}t_{n-1}\right)w\left(q_{n-1}t_{n-1} \middle| q_{n-2}t_{n-2}\right)\ldots \\ \times w\left(q_2 t_2 \mid q_1 t_1\right)w_1\left(q_1 t_1\right). \tag{2.18}$$

Thus the joint probability of a Markoff process can be obtained as a mere product of the transition probabilities. If we are not interested in all events between two times t_n and t_1 where $t_n > t_{n-1} > t_{n-2} > \ldots > t_1$, and we only want to know the probability of finding the particle at the position q_n at the final time t_n where at the beginning time t_1 we know its position is q_1, then we have to sum over all the position between the two end points, viz.,

$$w_2\left(q_n t_n, q_1 t_1\right) = \int dq_{n-1}dq_{n-2}\ldots dq_2 w\left(q_n t_n \mid q_{n-1}t_{n-1}\right)w\left(q_{n-1}t_{n-1} \middle| q_{n-2}t_{n-2}\right)\ldots \\ \times w\left(q_2 t_2 \mid q_1 t_1\right)w_1\left(q_1 t_1\right). \tag{2.19}$$

Now we wish to consider three arbitrary times subject to the condition $t_c > t_b > t_a$. We specialize Eq.(4.12) to this case as

$$w_2(q_c t_c, q_a t_a) = \int dq_b w_3(q_c t_c, q_b t_b, q_a t_a). \tag{2.20}$$

With the help of Eq.(2.17) and (2.18) we can write Eq.(2.20) in the form

$$w(q_c t_c | q_a t_a) = \int dq_b w(q_c t_c | q_b t_b) w(q_b t_b | q_a t_a) \tag{2.21}$$

which is the so-called Chapman-Kolmogorov equation or Smoluchowski equation. It is the basic equation for the theory of random processes.

(2) Relation between the spectrum and the correlation function

Suppose one considers for a very long time S a stationary random process $q(t)$ whose average value is zero. Taking $q(t)$ outside the time interval S, one can develop the resulting function in a Fourier integral:

$$q(t) = \int_{-\infty}^{\infty} d\omega\, p(\omega) e^{-2\pi i\omega t} \tag{2.22}$$

where $p(\omega) = p^*(-\omega)$ since $q(t)$ is real. By using the Parzeval theorem we shall have

$$\int_{-\infty}^{\infty} dt\, q^2(t) = \int_{-\infty}^{\infty} d\omega\, |p(\omega)|^2. \tag{2.23}$$

Using the fact that $|p(\omega)|^2$ is an even function of p and going to the limit $T \to \infty$, one can write this equation in the form

$$\langle q^2 \rangle = \lim_{S\to\infty} \frac{1}{S} \int_{-S}^{S} dt\, q^2(t) = \int_0^{\infty} d\omega\, I(\omega) , \tag{2.24}$$

$$I(\omega) = \lim_{S\to\infty} \frac{2}{S} \left| p(\omega) \right|^2, \tag{2.25}$$

where $I(\omega)$ is the spectral density. Consider next the average value

$$\langle q(t) q(t+s) \rangle = \lim_{S\to\infty} \frac{1}{S} \int_{-S}^{S} dt\, q(t) q(t+s) \; . \tag{2.26}$$

By introducing the Fourier expansion(4.22) and using the Fourier integral theorem, one shows easily

$$\langle q(t) q(t+s) \rangle = \int_0^{\infty} d\omega\, I(\omega) \cos 2\pi\omega s \tag{2.27}$$

from which follows by inversion

$$I(\omega) = 4 \int_0^{\infty} ds \langle q(t) q(t+s) \rangle \cos 2\pi\omega s \; . \tag{2.28}$$

The average $\langle q(t) q(t+s) \rangle$ is the so-called correlation function.

3) Some remarks on the theory of discrete random series

We will confine ourselves to Markoff processes. The problem will then always be to determine $w(n|m, s\tau)$ when one knows $w(n|m,\tau)$. Here $w(n|m, s\tau)$ is the analogue of the $w(q_2|q_1, t)$ where q_1, q_2 can only have discrete values m, n and the time t can also only have discrete values $s\tau$, $s = 1,2,3,\ldots$ From now on we will drop the τ and write also $W(n,m)$ for $w(n|m,\tau)$ in order to emphasize that it is the basic probability which must be given from the mechanism or the physical cause of the random process. To find $w(n|m,s)$ then one can try to make successive use of the Smoluchowski equation

$$w(n|m,s)=\sum_{l}w(n|l,s-1)W(l,m) \tag{2.29}$$

However, for large values of s this is usually not practicable, and one has to look for other methods. It is instructive to write (2.29) in a different way by using the conditions as

$$\sum_{m}W(l,m)=1 \tag{2.30}$$

or

$$W(l,l)+\sum_{m\neq l}W(l,m)=1 \tag{2.31}$$

Using this and dropping in Eq.(2.29) the initial value m, one can write Eq.(2.29) in the form

$$w(n,s)-w(n,s-1)=\sum_{l}W(n,l)w(l,s-1)-\sum_{l}W(l,n)w(n,s-1)\ . \tag{2.32}$$

One can interpret this by saying that the rate of change of $w(n,s)$ with the time is owing to the gains of w because of the transition from all possible l to n minus the losses of w because of the transition from n to all possible l. It is clear, therefore, that (2.29) is completely analoguous to the Boltzmann equation in the kinetic theory of gases. One must solve such an equation for a given initial condition distribution; in our case this is the way the variable m comes in since

$$w(n,0)=\delta_{mn}\ . \tag{2.33}$$

In many cases, the process has the property that the dependent variable l can change in one step by at most ± 1. This means that $W(n,l)=0$ except when $n=l,\ l\pm 1$, and Eq (4.29) or (4.30) then becomes a simple differential equation.

For example, we shall consider the discrete random walk problem in one dimension. This is the simplest possible case and very useful to study the Brownian motion problem. We assume that a particle can move on a straight line in steps of Δ and at each time moment s there is an equal chance that the particle moves a step Δ to the right or to the left. If at $s = 0$ the particle is at the position $m\Delta$, what is the probability $w(n|m,s)$ that at time s the point is at the positions $n\Delta$? It is clear that the basic transition probability $W(n,l)$ is given by

$$W(n,l) = \frac{1}{2}\delta_{n,l-1} + \frac{1}{2}\delta_{n,l+1} \tag{2.34}$$

Introducing this in Eq.(4.29) and dropping again initial state m, one obtains the discrete differential equation

$$w(n,s) = \frac{1}{2}w(n+1,s-1) + \frac{1}{2}w(n-1,s-1) \tag{2.35}$$

which has to be solved with the initial condition (4.33). The solution is very easy to obtain; with $\upsilon = |n-m|$ one gets:

$$w(n|m,s) = \frac{s!}{((\upsilon+s)/2)!\,((\upsilon-s)/2)!}(1/2)^{s}\,. \tag{2.36}$$

4) The Gaussian random process; method of Rice

The random process is characterized by the fact that all the basic distribution functions are Gaussian distributions, and one could take this fact as the defining property of the process. However since we shall see that the spectrum essential determines everything, it is more natural to start (following Rice) with the Fourier development of the Gaussian random function $q(t)$.

Consider again the stationary random function $q(t)$ over a long time T, and suppose that $q(t)$ is repeated periodically with the period T. One can then develop

$q(t)$ in a Fourier series

$$q(t) = \sum_{j=1}^{\infty} \left(a_j \cos 2\pi\,\omega_j t + b_j \sin 2\pi\,\omega_j t \right) \tag{2.37}$$

where $\omega_j = j/T$. There is no constant term, since we will assume that the average value of $q(t)$ is zero. The coefficient a_j and b_j are random variables, and we will assume that they are all independent of each other and Gaussian distributed with average values zero, so that one has for the probability that the a_j and b_j are in certain ranges da_j, db_j the expression

$$w(a_1 a_2 \ldots; b_1 b_2 \ldots) = \prod \frac{1}{\sigma_j \sqrt{2\pi}} \exp\left[-\left(a_j^2 + b_j^2 \right) / 2\sigma_j^2 \right] \tag{2.38}$$

where $\sigma_j^2 = \langle a_j^2 \rangle = \langle b_j^2 \rangle = I(\omega_j)/T$. $I(\omega)$ is again the spectral density, since:

$$\begin{aligned} \langle q^2(t) \rangle &= \sum_{j=1}^{\infty} \left(\langle a_j^2 \rangle \cos^2 2\pi\,\omega_j t + \langle b_j^2 \rangle \sin^2 2\pi\,\omega_j t \right) \\ &= \frac{1}{T} \sum_{j=1}^{\infty} I(\omega_j) \cong \int_0^{\infty} d\omega\, I(\omega) . \end{aligned} \tag{2.39}$$

With these assumptions one is now able to derive all possible distribution functions for the Gaussian random function $q(t)$.

5) Gaussian random process; method of Fokker-Planck

It is best to start with the discrete random series, say supposing that the basic transition probability $w(n|m,\tau)$ or $W(n,m)$ have the property that in the time τ n can only change by zero or by ± 1. This was, for instance, the case in the example of random walk problem. Consider now for this case the limit in which n and the time $s\tau$ becomes continuous. The Smoluchowski formula will then become a partial differential equation of the first order in the time coordinate and of the second order in the space coordinate. For instance, for the example of random walk problem, the Smoluchowski equation becomes

$$w(n,s) - w(n,s-1) = \frac{1}{2}\left[w(n+1,s-1) - 2w(n,s-1) + w(n-1,s-1)\right] . \qquad (2.40)$$

In the time that $s\tau = t$ and $n\Delta = x$ become continuous variables, and this clearly in the form

$$\frac{\partial w}{\partial t} = D\frac{\partial^2 w}{\partial q^2} \qquad (2.41)$$

when $D = \lim\limits_{\tau \to 0} \frac{\Delta^2}{2\tau}$. One gets, therefore, the well-known heat conduction or diffusion equation. This expression describes the behaviour of the free Brownian particle. In the same way one shows that in case the Brownian particle is acted on by the external forces like the gravitational force, one can get the equation

$$\frac{\partial w}{\partial t} = \beta \frac{\partial}{\partial x}(qw) + D\frac{\partial^2 w}{\partial q^2} \qquad (2.42)$$

where $\beta = \lim\limits_{\tau \to 0} \frac{1}{\tau R}$ and R is an integer.

In this limit the problem of finding the probability distribution $w(q,q_0,t)$ then becomes the problem of finding the fundamental solution of the partial differential equation of the diffusion type into which the Smoluchowski equation has degenerated. By this we mean the solution for which $t = 0$ becomes the Dirac delta function $\delta(q - q_0)$. This corresponds to the condition (2.33) in the discrete case and expresses again the fact that for $t = 0$ one is certain that $q = q_0$. For Eq.(2.41) this solution is given by

$$w\left(q\middle|q_0,t\right)=\frac{1}{\left(4\pi Dt\right)^{1/2}}\exp\left[-\left(q-q_0\right)^2/4Dt\right] \tag{2.43}$$

It is easy to show that this is the limit into which the solution (2.36) of the discrete case goes over. For Eq.(2.42) the fundamental solution is given by

$$w\left(q\middle|q_0,t\right)=\frac{1}{\left(2\pi\sigma^2\right)^{1/2}}\exp\left[-\left(q-\langle q\rangle\right)^2/4Dt\right]. \tag{2.44}$$

where $\langle q\rangle = q_0\exp(-\beta\, t)$ and $\sigma^2=\left\langle\left(q-\langle q\rangle\right)^2\right\rangle=\frac{D}{\beta}\left[1-\exp(-2\beta\, t)\right]$.

One should point out that one gets in the limit a diffusion equation only when $w\left(n\middle|m,\tau\right)$ is such that in the time τ n can only change by zero or ± 1, or, less precisely, when in small times the space coordinate can only change with small amounts. In the general case, the Smoluchowski equation will become in the limit an integro-differential equation which is of the same type as the Boltzman equation in the kinetic theory of gasses.

In the continuous case we will start from the Smoluchowski equation in the form

$$w\left(y\middle|x,t+\Delta t\right)=\int dz\, w\left(y\middle|z,t+\Delta t\right)w\left(z\middle|x,t\right). \tag{2.45}$$

This assume therefore that the process is a Markoff process. The moment of the change in the space coordinate in a small time Δt is given by

$$a_n(z,\Delta t)=\int dy\left(y-z\right)^n w\left(y\middle|z,\Delta t\right) \tag{2.46}$$

and we shall assume that for $\Delta t\to 0$ only the first and the second moments become proportional to Δt so that the limits

$$A(z) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} a_1(z, \Delta t), \tag{2.47}$$

$$B(z) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} a_2(z, \Delta t) \tag{2.48}$$

exist. This assumption expresses the fact that for these processes in small times the space coordinate can only change by small amounts. In the actual problems of the Brownian motion this assumption can be proved and the average values $A(z)$ and $B(z)$ can be calculated from the Langevin equations or the analogy from the circuit equations with thermal noise sources. Just as in the method of Rice, these equations are, therefore, the real basis for the theory of the Brownian motion.

To derive the Fokker-Planck equation we consider the integral $\int dy R(y) \frac{\partial w(y|x,t)}{\partial t}$, where $R(y)$ is an arbitrary function, which goes to zero sufficiently fast for $y \to \pm\infty$. Replacing the differential quotient by the limit of the difference quotient and using the Smoluchowski equation in the form of (2.45) one can write

$$\begin{aligned}\int dy R(y) \frac{\partial w(y|x,t)}{\partial t} &= \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int dy\, R(y)\left[w(y|x,t+\Delta t) - w(y|x,t)\right] \\ &= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\left[\int dy\, R(y) \int dz\, w(y|z,t+\Delta t) w(z|x,t) - \int dz\, R(z) w(z|x,t)\right].\end{aligned}$$

In the double integral, we interchange the order of integration and develop $R(y)$ in a Tayler series in $(z-y)$. Because of Eq.(2.47) and (2.48) one can stop at the term with $(z-y)^2$ and one gets

$$\int dy R(y) \frac{\partial w(y|x,t)}{\partial t} = \int dz\, w(z|x,t)\left[R'(z) A(z) + \frac{1}{2} R''(z) B(z)\right].$$

Integrating partially and writing y for z one obtains

$$\int dyR(y)\left[\frac{\partial w}{\partial t}+\frac{\partial Aw}{\partial y}-\frac{1}{2}\frac{\partial^2 Bw}{\partial y^2}\right]=0\,.$$

Since this must hold for any function $R(y)$, the expression in the square brackets must be zero, which gives the general Fokker-Planck equation

$$\frac{\partial w}{\partial t}=-\frac{\partial Aw}{\partial y}+\frac{1}{2}\frac{\partial^2 Bw}{\partial y^2} \qquad (2.49)$$

The Brownian Motion of a Free Particle

In this section we shall consider the Brownian motion in the case of free Brownian particle in detail. We assume that a free particle of mass M with velocity v satisfies the equation of motion as

$$M\frac{dv}{dt}+\eta v=F(t) \qquad (2.50)$$

where η is the friction coefficient, and $F(t)$ is the fluctuation force, of which the average value is zero and which has a very sharp correlation function and therefore, a practically white spectrum. The spectral density of $F(t)$ is $4\eta kT$ where k is the Boltzman constant and T the temperature of the surrounding medium. The analogous electrical problem is of course the $L-R$ circuit, and the circuit equation is

$$L\frac{di}{dt}+Ri=E(t) \qquad (2.51)$$

where $E(t)$ is a purely random fluctuation e.m.f. (the thermal noise source), which has the spectral density $4RkT$. We will combine these cases by writing (2.50) and (2.51) in the form

$$\frac{dy}{dt}+\gamma y=f(t) \tag{2.52}$$

and by taking $4D$ as the spectral density of the purely random $f(t)$. This means that we assume

$$\begin{aligned}\langle f(t)\rangle &= 0\\ \langle f(t_1)f(t_2)\rangle &= 2D\delta(t_2-t_1)\,.\end{aligned} \tag{2.23}$$

This means, however, besides being purely random, we must assume that $f(t)$ is Gaussian. This can be expressed in different ways. Either one can postulate the Gaussian distribution of the Fourier coefficients or one can assume the two properties

$$\left\langle f(t_1)f(t_2)\ldots f(t_{2j+1})\right\rangle = 0 \tag{2.54}$$

$$\left\langle f(t_1)f(t_2)\ldots f(t_{2j})\right\rangle = \sum_{allpairs}\langle f(t_k)f(t_l)\rangle.\langle f(t_m)f(t_n)\rangle\ldots \tag{2.55}$$

where the sum has to be taken over all the different ways in which one can divide the $2j$ time points $t_1 \ldots t_{2j}$ into j pairs. It is easy to show the equivalence of these two definitions.

Since $f(t)$ is Gaussian random process with a spectrum

$$G_y(\eta)=\frac{4D}{\gamma^2+(2\pi\eta)^2}\quad , \tag{2.56}$$

this corresponds to a correlation function $\rho(t)=\exp(-\gamma t)$ and the second probability distribution is, therefore, the two dimensional Gaussian distribution

$$w_2(y_2,y_1;t)=\frac{\gamma}{2\pi D(1-\rho^2)^{1/2}}\exp\left[\frac{\gamma}{2D(1-\rho^2)}\left(y_1^2+y_2^2-2\rho y_1y_2\right)\right] \tag{2.57}$$

since

$$\langle y^2 \rangle = \int_0^\infty d\omega\, G_y(\omega) = \frac{D}{\gamma} \tag{2.58}$$

Here $y(t)$ will be a Markoff process, so that $w_2(y_2, y_1; t)$ gives the complete description of the process.

Next, we can obtain the Fokker-Planck equation for this problem by using the general Fokker-Planck equation (2.49) of the previous section which the average values $A(y)$ and $B(y)$ can now be computed by means of Eq.(2.53) and one finds

$$A(y) = \gamma y, \qquad B(y) = 2D. \tag{2.59}$$

The proof is simple; integrating Eq.(2.52) over a short time interval Δt one gets

$$\Delta y = -\gamma y \Delta t + \int_t^{t+\Delta t} ds\, f(s). \tag{2.60}$$

Therefore

$$A(y) = \lim_{\Delta t \to 0} \frac{\langle \Delta y \rangle}{\Delta t} = -\gamma y \tag{2.61}$$

since $\langle f \rangle = 0$. Further

$$\langle \Delta y^2 \rangle = -\gamma^2 y^2 \Delta t^2 + \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} du\, \langle f(s) f(u) \rangle \tag{2.62}$$

and from the second equation of (2.53) leads to the value of the double integral is $2D\Delta t$, so that

$$B(y) = \lim_{\Delta t \to 0} \frac{\langle \Delta y^2 \rangle}{\Delta t} = 2D. \tag{2.63}$$

In the same way it follows from (2.54) and (2.55) that all the higher moments of Δy go to zero in the limit $\Delta t \to 0$. With the values given by (2.59) the Fokker-Planck equation becomes

$$\frac{\partial w}{\partial t} = \gamma \frac{\partial yw}{\partial y} + D \frac{\partial^2 w}{\partial y^2}. \tag{2.64}$$

The fundamental solution of this equation is given by (2.44). For $t \to \infty$ one gets

$$w_1(y) = \lim_{t \to \infty} w(y|y_0, t) = \left(\frac{\gamma}{2\pi D}\right)^{1/2} \exp\left(-\frac{\gamma y^2}{2D}\right)$$

in accordance with (2.58). For the second probability distribution

$$w_2(y_2, y_1, t) = w_1(y_1) w(y_2|y_1, t)$$

one gets again Eq.(2.57). That $y(t)$ is a Markoff process has now, of course, been assumed from the beginning.