15

Fluctuations and Nonequilibrium Statistical Mechanics

In this course we have been mostly concerned with the evaluation of *statistical averages* of the various physical quantities; these averages represent, with a high degree of accuracy, the results expected from relevant measurements on the given system *in equilibrium*. Nevertheless, there do occur *deviations* from, or *fluctuations* about, these mean values. Even though they are generally small, their study is of great physical interest for several reasons.

First, such a study enables us to develop a mathematical scheme with the help of which the magnitude of the relevant fluctuations, under a variety of physical situations, can be estimated. Not surprisingly, we find that while in a single-phase system the fluctuations are thermodynamically negligible but they can assume considerable importance in multiphase systems, especially in the neighborhood of a critical point. In the latter case, we obtain a rather high degree of *spatial correlation* among the molecules of the system which, in turn, gives rise to phenomena such as *critical opalescence*.

Second, it provides a natural framework for understanding a class of phenomena that come under the heading "Brownian motion"; these phenomena relate properties such as the mobility of a fluid system, its coefficient of diffusion, and so on, with temperature through the so-called *Einstein relations*. The mechanism of Brownian motion is vital in formulating, and in a certain sense answering, questions as to how "a given physical system, which is not in a state of equilibrium, finally approaches such a state" while "a physical system, which is already in a state of equilibrium, persists to stay in that state."

Third, the study of fluctuations, as a function of time, leads to the concept of certain "correlation functions" that play a vital role in relating the dissipative properties of a system, such as the viscous resistance of a fluid or the electrical resistance of a conductor, with the microscopic properties of the system in a state of equilibrium; this relationship (between irreversible processes on one hand and equilibrium properties on the other) manifests itself in the so-called *fluctuation–dissipation theorem*. At the same time, a study of the "frequency spectrum" of fluctuations, which is related to the time-dependent correlation function through the fundamental theorem of Wiener and Khintchine, is of considerable value in assessing the "noise" met with in electrical circuits as well as in the transmission of electromagnetic signals.

Statistical Mechanics. DOI: 10.1016/B978-0-12-382188-1.00015-3

15.1 Equilibrium thermodynamic fluctuations

We begin by deriving a *probability distribution law* for the fluctuations of certain basic thermodynamic quantities pertaining to a given physical system; the *mean square fluctuations* can then be evaluated, in a straightforward manner, with the help of this law. We assume that the given system, which may be referred to as 1, is embedded in a reservoir, which may be referred to as 2, such that a mutual exchange of energy, and of volume, can take place between the two; of course, the overall energy E and the overall volume V are supposed to be fixed. For convenience, we do not envisage an exchange of particles here, so the numbers N_1 and N_2 remain individually constant. The equilibrium division of E into $\overline{E}_1$ and $\overline{E}_2$, and of V into $\overline{V}_1$ and $\overline{V}_2$, must be such that parts 1 and 2 of the composite system $(1+2)$ have a *common* temperature T^* and a *common* pressure P^*; see Sections 1.2 and 1.3, especially equations (1.3.6). Of course, the entropy of the composite system will have its largest value in the equilibrium state; in any other state, such as the one characterized by a fluctuation, it must have a lower value. If ΔS denotes the deviation in the entropy of the composite system from its equilibrium value S_0, then

$$\Delta S \equiv S - S_0 = k \ln \Omega_f - k \ln \Omega_0, \tag{1}$$

where Ω_f (or Ω_0) denotes the number of distinct microstates of the system $(1+2)$ in the presence (or in the absence) of a fluctuation from the equilibrium state; see equation (1.2.6). The probability that the proposed fluctuation may indeed occur is then given by

$$p \propto \Omega_f \propto \exp(\Delta S/k); \tag{2}$$

see Section 3.1, especially equation (3.1.3). In terms of other thermodynamic quantities, we may write

$$\Delta S = \Delta S_1 + \Delta S_2 = \Delta S_1 + \int_0^f \frac{dE_2 + P_2 dV_2}{T_2}; \tag{3}$$

note that the pressure P_2 and the temperature T_2 of the reservoir may, in principle, vary during the build-up of the fluctuation! Now, even if the fluctuation is sizable from the point of view of system 1, it will be small from the point of view of 2. The "variables" P_2 and T_2 may, therefore, be replaced by the constants P^* and T^*, respectively; at the same time, the increments dE_2 and dV_2 may be replaced by $-dE_1$ and $-dV_1$, respectively. Equation (3) then becomes

$$\Delta S = \Delta S_1 - (\Delta E_1 + P^* \Delta V_1)/T^*. \tag{4}$$

Accordingly, formula (2) takes the form

$$p \propto \exp\{-(\Delta E_1 - T^* \Delta S_1 + P^* \Delta V_1)/kT^*\}. \tag{5}$$

Clearly, the probability distribution law (5) does not depend, in any manner, on the peculiarities of the reservoir in which the given system was supposedly embedded. Formula (5), therefore, applies equally well to a system that attained equilibrium in a statistical ensemble (or, for that matter, to any macroscopic part of a given system itself). Consequently, we may drop the suffix 1 from the symbols $\Delta E_1, \Delta S_1$, and ΔV_1, and the star from the symbols P^* and T^*, and write

$$p \propto \exp\{-(\Delta E - T\Delta S + P\Delta V)/kT\}. \tag{6}$$

In most cases, the fluctuations are exceedingly small in magnitude; the quantity ΔE may, therefore, be expanded as a Taylor series about the equilibrium value $(\Delta E)_0 = 0$, with the result

$$\begin{aligned}\Delta E = {} & \left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \left(\frac{\partial E}{\partial V}\right)_0 \Delta V \\ & + \frac{1}{2}\left[\left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2\right] + \cdots \end{aligned} \tag{7}$$

Substituting (7) into (6) and retaining terms up to second order only, we obtain

$$p \propto \exp\{-(\Delta T \Delta S - \Delta P \Delta V)/2kT\}; \tag{8}$$

here, use has been made of the relations

$$\left(\frac{\partial E}{\partial S}\right)_0 = T, \quad \left(\frac{\partial E}{\partial V}\right)_0 = -P, \tag{9}$$

and of the fact that the expression within the square brackets in (7) is equivalent to

$$\Delta\left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \Delta\left(\frac{\partial E}{\partial V}\right)_0 \Delta V = \Delta T \Delta S - \Delta P \Delta V. \tag{10}$$

With the help of (8), the mean square fluctuations of various physical quantities and the statistical correlations among different fluctuations can be readily calculated. We note, however, that of the four Δ terms appearing in this formula only two can be chosen independently; the other two must assume the role of "derived quantities." For instance, if we choose ΔT and ΔV to be the *independent variables*, then ΔS and ΔP can be written as

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V = \frac{C_V}{T}\Delta T + \left(\frac{\partial P}{\partial T}\right)_V \Delta V \tag{11}$$

and

$$\Delta P = \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \left(\frac{\partial P}{\partial V}\right)_T \Delta V = \left(\frac{\partial P}{\partial T}\right)_V \Delta T - \frac{1}{\kappa_T V}\Delta V, \tag{12}$$

κ_T being the *isothermal compressibility* of the system. Substituting (11) and (12) into (8), we get

$$p \propto \exp\left\{-\frac{C_V}{2kT^2}(\Delta T)^2 - \frac{1}{2kT\kappa_T V}(\Delta V)^2\right\}, \tag{13}$$

which shows that the fluctuations in T and V are *statistically independent, Gaussian variables*! A quick glance at (13) yields the results

$$\overline{(\Delta T)^2} = \frac{kT^2}{C_V}, \quad \overline{(\Delta V)^2} = kT\kappa_T V, \tag{14a}$$

while

$$\overline{(\Delta T \Delta V)} = 0. \tag{14b}$$

Similarly, if we choose ΔS and ΔP as our *independent variables*, we are led to the distribution law

$$p \propto \exp\left\{-\frac{1}{2kC_P}(\Delta S)^2 - \frac{\kappa_S V}{2kT}(\Delta P)^2\right\}, \tag{15}$$

which gives

$$\overline{(\Delta S)^2} = kC_P, \quad \overline{(\Delta P)^2} = \frac{kT}{\kappa_S V}, \tag{16a}$$

while

$$\overline{(\Delta S \Delta P)} = 0; \tag{16b}$$

here, κ_S denotes the *adiabatic compressibility* of the system.

We note that, in general, the mean square fluctuation of an extensive quantity is directly proportional to the size of the system while that of an intensive quantity is inversely proportional to the same; in either case, the *relative, root-mean-square fluctuation* of any quantity is inversely proportional to the square root of the size of the system. Thus, except for situations such as the ones met with in a critical region, normal fluctuations are thermodynamically negligible. This does not mean that fluctuations are altogether irrelevant to the physical phenomena taking place in the system; in fact, as will be seen in the sequel, the very presence of fluctuations at the *microscopic* level is of fundamental importance to several properties of the system displayed at the *macroscopic* level!

With the help of the foregoing results, we may evaluate the mean square fluctuation in the energy of the system. With T and V as independent variables, we have

$$\Delta E = \left(\frac{\partial E}{\partial T}\right)_V \Delta T + \left(\frac{\partial E}{\partial V}\right)_T \Delta V. \tag{17}$$

Squaring this expression and taking averages, keeping in mind equations (14), we get

$$\begin{aligned}\overline{(\Delta E)^2} &= kT^2 C_V + kT\kappa_T V \left\{\left(\frac{\partial E}{\partial V}\right)_T\right\}^2 \\ &= kT^2 C_V + kT\kappa_T \left(\frac{N^2}{V}\right)\left\{\left(\frac{\partial E}{\partial N}\right)_T\right\}^2. \end{aligned} \tag{18}$$

Now, the results derived in the preceding paragraphs determine the fluctuations of the various physical quantities pertaining to *any macroscopic subsystem* of a given system, provided that the number of particles in the subsystem remains fixed. The expression (14b) for $\overline{(\Delta V)^2}$ may, therefore, be used to derive an expression for the mean square fluctuation of the variable v (the volume per particle) and the variable n (the particle density) of the subsystem. We readily obtain

$$\overline{(\Delta v)^2} = kT\kappa_T V/N^2, \quad \overline{(\Delta n)^2} = \frac{1}{v^4}\overline{(\Delta v)^2} = kT\kappa_T N^2/V^3; \tag{19}$$

note that the last result obtained here is in complete agreement with equation (4.5.7), which was derived on the basis of the grand canonical ensemble. A little reflection shows that this result applies equally well to a subsystem with a fixed volume V and a fluctuating number of particles N. The mean square fluctuation in N is then given by

$$\overline{(\Delta N)^2} = V^2\overline{(\Delta n)^2} = kT\kappa_T N^2/V. \tag{20}$$

Substituting (20) into (18), we obtain once again the grand canonical result for $\overline{(\Delta E)^2}$, namely

$$\overline{(\Delta E)^2} = kT^2 C_V + \overline{(\Delta N)^2}\{(\partial E/\partial N)_T\}^2, \tag{21}$$

as in equation (4.5.14).

In passing, we note that the first part of expression (21) denotes the mean square fluctuation in the energy E of a subsystem for which both N and V are fixed, just as we have in the canonical ensemble (N, V, T). Conversely, if we assume the energy E to be fixed, then the temperature of the subsystem will fluctuate, and the mean square value of the quantity ΔT will be given by $(kT^2 C_V)$ divided by the square of the thermal capacity of the subsystem. The net result will, therefore, be (kT^2/C_V), which is the same as in (14a).

15.2 The Einstein–Smoluchowski theory of the Brownian motion

The term “Brownian motion” derives its name from the botanist Robert Brown who, in 1828, made careful observations on the tiny pollen grains of a plant under a microscope. In his own words: “While examining the form of the particles immersed in water, I observed many of them very evidently in motion. These motions were such as to satisfy me ... that they arose neither from currents in the fluid nor from its gradual evaporation, but belonged to the particle itself." We now know that the real source of this motion lies in the incessant, and more or less random, bombardment of the *Brownian particles*, as these grains (or, for that matter, any colloidal suspensions) are usually referred to, by the *molecules* of the surrounding fluid. It was Einstein who, in a number of papers (beginning in 1905), first provided a sound theoretical analysis of the Brownian motion on the basis of the so-called "random walk problem" and thereby established a far-reaching relationship between the irreversible nature of this phenomenon and the mechanism of molecular fluctuations.

To illustrate the essential theme of Einstein's approach, we first consider the problem in *one* dimension. Let $x(t)$ denote the position of the Brownian particle at time t, given that its position coincided with the point $x = 0$ at time $t = 0$. To simplify matters, we assume that each molecular impact (which, on an average, takes place after a time τ^*) causes the particle to jump a (small) distance l — of *constant* magnitude — in either a positive or negative direction along the x-axis. It seems natural to regard the possibilities $\Delta x = +l$ and $\Delta x = -l$ to be *equally likely*; though somewhat less natural, we may also regard the successive impacts on, and hence the successive jumps of, the Brownian particle to be *mutually uncorrelated*. The probability that the particle is found at the point x at time t is then equal to the probability that, in a series of $n (= t/\tau^*)$ successive jumps, the particle makes $m (= x/l)$ more jumps in the positive direction of the x-axis than in the negative, that is, it makes $\frac{1}{2}(n+m)$ jumps in the positive direction and $\frac{1}{2}(n-m)$ in the negative.[1] The desired probability is then given by the binomial expression

$$p_n(m) = \frac{n!}{\left\{\frac{1}{2}(n+m)\right\}!\left\{\frac{1}{2}(n-m)\right\}!}\left(\frac{1}{2}\right)^n, \tag{1}$$

with the result that

$$\overline{m} = 0 \quad \text{and} \quad \overline{m^2} = n. \tag{2}$$

Thus, for $t \gg \tau^*$, we have for the net displacement of the particle

$$\overline{x(t)} = 0 \quad \text{and} \quad \overline{x^2(t)} = l^2 \frac{t}{\tau^*} \propto t^1. \tag{3}$$

Accordingly, the root-mean-square displacement of the particle is proportional to the square root of the time elapsed:

$$x_{\text{r.m.s.}} = \sqrt{\left(\overline{x^2(t)}\right)} = l\sqrt{(t/\tau^*)} \propto t^{1/2}. \tag{4}$$

It should be noted that the proportionality of the *net* overall displacement of the Brownian particle to the *square root* of the total number of elementary steps is a typical consequence

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[1] Since the quantities x and t are *macroscopic* in nature while l and τ^* are microscopic, the numbers n and m are much larger than unity; consequently, it is safe to assume that they are *integral* as well.

of the random nature of the steps and it manifests itself in a large variety of phenomena in nature. In contrast, if the successive steps were fully coherent (or else if the motion were completely predictable and reversible over the time interval t),[2] then the net displacement of the Brownian particle would have been proportional to t^1.

Smoluchowski's approach to the problem of Brownian motion, which appeared in 1906, was essentially the same as that of Einstein; the difference lay primarily in the mathematical procedure. Smoluchowski introduced the *probability function* $p_n(x_0|x)$, which denotes the "probability that, after a series of n steps, the Brownian particle, initially at the point x_0, reaches the point x"; the number x here denotes the distance traveled by the Brownian particle in terms of the length of the elementary step. Clearly,

$$p_n(x_0|x) = \sum_{z=-\infty}^{\infty} p_{n-1}(x_0|z)p_1(z|x) \quad (n \geq 1); \tag{5}$$

moreover, since a single step is equally likely to take the particle to the right or to the left,

$$p_1(z|x) = \frac{1}{2}\delta_{z,x-1} + \frac{1}{2}\delta_{z,x+1}, \tag{6}$$

while

$$p_0(z|x) = \delta_{z,x}. \tag{7}$$

Equation (5) is known as the *Smoluchowski equation*. To solve it, we introduce a *generating function* $Q_n(\xi)$, namely

$$Q_n(\xi) = \sum_{x=-\infty}^{\infty} p_n(x_0|x)\xi^{x-x_0}, \tag{8}$$

from which it follows that

$$Q_0(\xi) = \sum_{x=-\infty}^{\infty} p_0(x_0|x)\xi^{x-x_0} = \sum_{x=-\infty}^{\infty} \delta_{x_0,x}\xi^{x-x_0} = 1. \tag{9}$$

Substituting (6) into (5), we obtain

$$p_n(x_0|x) = \frac{1}{2}p_{n-1}(x_0|x-1) + \frac{1}{2}p_{n-1}(x_0|x+1). \tag{10}$$

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[2] The term "reversible" here is related to the fact that the Newtonian equations of motion, which govern this class of phenomena, preserve their form if the direction of time is reversed (i.e., if we change t to $-t$, etc.); alternatively, one would expect that if at any instant of time we reverse the velocities of the particles in a given mechanical system, the system would "retrace" its path exactly. This is *not* true of equations describing "irreversible" phenomena, such as the *diffusion equation* (19), with which the phenomenon of Brownian motion is intimately related.

Multiplying (10) by ξ^{x-x_0} and adding over all x, we obtain the recurrence relation

$$Q_n(\xi) = \frac{1}{2}[\xi + (1/\xi)]Q_{n-1}(\xi), \tag{11}$$

so that, by iteration,

$$Q_n(\xi) = \left\{\frac{1}{2}[\xi + (1/\xi)]\right\}^n Q_0(\xi) = (1/2)^n[\xi + (1/\xi)]^n. \tag{12}$$

Expanding this expression binomially and comparing the result with (8), we get

$$p_n(x_0|x) = \begin{cases} \left(\dfrac{1}{2}\right)^n \dfrac{n!}{\{\frac{1}{2}(n+x-x_0)\}!\{\frac{1}{2}(n-x+x_0)\}!} & \text{for } |x-x_0| \le n \\ 0 & \text{for } |x-x_0| > n. \end{cases} \tag{13}$$

Identifying $(x - x_0)$ with m, we find this result to be in complete agreement with our previous result (1).[3] Accordingly, any conclusions drawn from the Smoluchowski approach will be the same as the ones drawn from the Einstein approach.

To obtain an asymptotic form of the function $p_n(m)$, we apply Stirling's formula, $n! \approx (2\pi n)^{1/2}(n/e)^n$, to the factorials appearing in (1), with the result

$$\begin{aligned} \ln p_n(m) \approx \left(n + \frac{1}{2}\right)\ln n - \frac{1}{2}(n+m+1)\ln\left\{\frac{1}{2}(n+m)\right\} \\ - \frac{1}{2}(n-m+1)\ln\left\{\frac{1}{2}(n-m)\right\} - n\ln 2 - \frac{1}{2}\ln(2\pi). \end{aligned}$$

For $m \ll n$ (which is generally true because $\overline{m} = 0$ and $m_{\text{r.m.s.}} = n^{1/2}$, while $n \gg 1$), we obtain

$$p_n(m) \approx \frac{2}{\sqrt{(2\pi n)}} \exp(-m^2/2n). \tag{14}$$

Taking x to be a continuous variable (and remembering that $p_n(m) \equiv 0$ either for even values of m or for odd values of m, so that in the distribution (14), $\Delta m = 2$ and not 1), we may write this result in the *Gaussian* form:

$$p(x)dx = \frac{dx}{\sqrt{(4\pi Dt)}} \exp\left(-\frac{x^2}{4Dt}\right), \tag{15}$$

where

$$D = l^2/2\tau^*. \tag{16}$$

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[3] It is easy to recognize the additional fact that if n is even, then $p_n(m) \equiv 0$ for odd m, and if n is odd, then $p_n(m) \equiv 0$ for even m.

Later on, we shall see that the quantity D introduced here is identical to the *diffusion coefficient* of the given system; equation (16) connects this quantity with the microscopic quantities l and τ^*. To appreciate this connection, one has simply to note that the problem of Brownian motion can also be looked on as a problem of "diffusion" of Brownian particles through the medium of the fluid; this point of view is also due to Einstein. However, before we embark on these considerations, we would like to present here the results of an actual observation made on the Brownian motion of a spherical particle immersed in water; see Lee, Sears, and Turcotte (1963). It was found that the 403 values of the net displacement Δx of the particle, observed after successive intervals of 2 seconds each, were distributed as follows:

Displacement Δx, in units of $\mu (= 10^{-4}\text{cm})$	*Frequency of occurrence n*
less than -5.5	0
between -5.5 and -4.5	1
between -4.5 and -3.5	2
between -3.5 and -2.5	15
between -2.5 and -1.5	32
between -1.5 and -0.5	95
between -0.5 and $+0.5$	111
between $+0.5$ and $+1.5$	87
between $+1.5$ and $+2.5$	47
between $+2.5$ and $+3.5$	8
between $+3.5$ and $+4.5$	5
greater than $+4.5$	0

The mean square value of the displacement here turns out to be: $\overline{(\Delta x)^2} = 2.09 \times 10^{-8}\text{cm}^2$. The observed frequency distribution has been plotted as a "block diagram" in Figure 15.1. We have included, in this figure, a Gaussian curve based on the observed value of the mean square displacement; we find that the experimental data fit the theoretical curve fairly well. We can also derive here an experimental value for the diffusion coefficient of the medium; we obtain: $D = \overline{(\Delta x)^2}/2t = 5.22 \times 10^{-9}\text{cm}^2/\text{s}$.[4]

We now turn to the study of the Brownian motion from the point of view of diffusion. We denote the number density of the Brownian particles in the fluid by the symbol $n(\boldsymbol{r}, t)$ and their current density by $\boldsymbol{j}(\boldsymbol{r}, t)\{= n(\boldsymbol{r}, t)\boldsymbol{v}(\boldsymbol{r}, t)\}$; then, according to Fick's law,

$$\boldsymbol{j}(\boldsymbol{r}, t) = -D\nabla n(\boldsymbol{r}, t), \tag{17}$$

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[4] In the next section we shall see that, for a *spherical* particle, $D = kT/6\pi\eta a$ where η is the coefficient of viscosity of the medium and a the radius of the Brownian particle. In the case under study, $T \simeq 300\,\text{K}$, $\eta \simeq 10^{-2}$ poise, and $a \simeq 4 \times 10^{-5}$ cm. Substituting these values, we obtain for the Boltzmann constant: $k \simeq 1.3 \times 10^{-16}\text{erg/K}$.

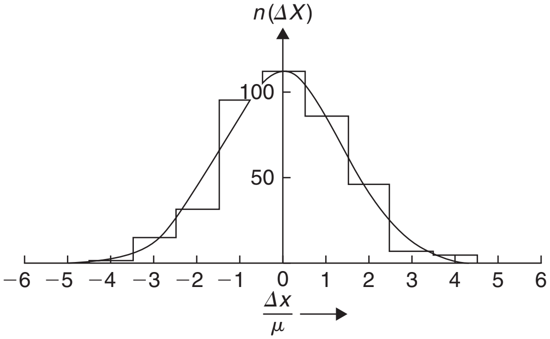

FIGURE 15.1 The statistical distribution of the successive displacements, Δx, of a Brownian particle immersed in water: $(\Delta x)_{\text{r.m.s.}} \simeq 1.45\mu$.

where D denotes for the *diffusion coefficient* of the medium. We also have here the equation of continuity, namely

$$\nabla \cdot \boldsymbol{j}(\boldsymbol{r}, t) + \frac{\partial n(\boldsymbol{r}, t)}{\partial t} = 0. \tag{18}$$

Substituting (17) into (18), we obtain the diffusion equation

$$\nabla^2 n(\boldsymbol{r}, t) - \frac{1}{D} \frac{\partial n(\boldsymbol{r}, t)}{\partial t} = 0. \tag{19}$$

Of the various possible solutions of this equation, the one relevant to the present situation is

$$n(\boldsymbol{r}, t) = \frac{N}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \tag{20}$$

which is a spherically symmetric solution and is already normalized:

$$\int_0^\infty n(\boldsymbol{r}, t) 4\pi r^2 dr = N, \tag{21}$$

N being the total number of (Brownian) particles immersed in the fluid. A comparison of the (three-dimensional) result (20) with the (one-dimensional) result (15) brings out most vividly the relationship between the random walk problem on one hand and the phenomenon of diffusion on the other.

It is clear that in the last approach we have considered the motion of an "ensemble" of N Brownian particles placed under "equivalent" physical conditions, rather than considering the motion of a single particle over a length of time (as was done in the random walk approach). Accordingly, the averages of the various physical quantities obtained here will be in the nature of "ensemble averages"; they must, of course, agree with the long-time averages of the same quantities obtained earlier.

Now, by virtue of the distribution (20), we obtain

$$\langle \boldsymbol{r}(t)\rangle = 0; \quad \langle r^2(t)\rangle = \frac{1}{N}\int_0^\infty n(\boldsymbol{r},t)4\pi r^4 dr = 6Dt \propto t^1, \tag{22}$$

in complete agreement with our earlier results, namely

$$\overline{x(t)} = 0; \quad \overline{x^2(t)} = l^2 t/\tau^* = 2Dt \propto t^1. \tag{23}$$

Thus, the "ensemble" of the Brownian particles, initially concentrated at the origin, "diffuses out" as time increases, the nature and the extent of its spread at any time t being given by equations (20) and (22), respectively. The diffusion process, which is clearly *irreversible*, gives us a fairly good picture of the statistical behavior of a single particle in the ensemble. However, the important thing to bear in mind is that, whether we focus our attention on a single particle in the ensemble or look at the ensemble as a whole, the ultimate source of the phenomenon lies in the incessant, and more or less random, impacts received by the Brownian particles from the molecules of the fluid. In other words, the irreversible character of the phenomenon ultimately arises from the random, fluctuating forces exerted by the fluid molecules on the Brownian particles. This leads us to another systematic theory of the Brownian motion, namely the theory of Langevin (1908). For a detailed analysis of the problem, see Uhlenbeck and Ornstein (1930), Chandrasekhar (1943, 1949), MacDonald (1948–1949), and Wax (1954).

15.3 The Langevin theory of the Brownian motion

We consider the simplest case of a "free" Brownian particle, surrounded by a fluid environment; the particle is assumed to be free in the sense that it is not acted on by any other force except the one arising from the molecular bombardment. The equation of motion of the particle will then be

$$M\frac{d\boldsymbol{v}}{dt} = \boldsymbol{\mathcal{F}}(t), \tag{1}$$

where M is the particle mass, $\boldsymbol{v}(t)$ the particle velocity, and $\boldsymbol{\mathcal{F}}(t)$ the force acting on the particle by virtue of the impacts received from the fluid molecules. Langevin suggested that the force $\boldsymbol{\mathcal{F}}(t)$ may be written as a sum of two parts: (i) an "averaged-out" part, which represents the *viscous drag*, $-\boldsymbol{v}/B$, experienced by the particle (accordingly, B is the *mobility* of the system, that is, the drift velocity acquired by the particle by virtue of a unit "external" force)[5] and (ii) a "rapidly fluctuating" part $\boldsymbol{F}(t)$ which, over long intervals of

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[5] If Stokes's law is applicable, then $B = 1/(6\pi\eta a)$, where η is the coefficient of viscosity of the fluid and a the radius of the particle (assumed spherical).

time (as compared to the characteristic time τ^*), averages out to zero; thus, we may write

$$M\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{B} + \boldsymbol{F}(t); \quad \overline{\boldsymbol{F}(t)} = 0. \tag{2}$$

Taking the ensemble average of (2), we obtain[6]

$$M\frac{d}{dt}\langle\boldsymbol{v}\rangle = -\frac{1}{B}\langle\boldsymbol{v}\rangle, \tag{3}$$

which gives

$$\langle\boldsymbol{v}(t)\rangle = \boldsymbol{v}(0)\exp(-t/\tau) \quad (\tau = MB). \tag{4}$$

Thus, the mean drift velocity of the particle decays, at a rate determined by the *relaxation time* τ, to the ultimate value zero. We note that this result is typical of the phenomena governed by *dissipative* properties such as the viscosity of the fluid; the *irreversible* nature of the result is also evident.

Dividing (2) by the mass of the particle, we obtain an equation for the *instantaneous* acceleration, namely

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} + A(t); \quad \overline{\boldsymbol{A}(t)} = 0. \tag{5}$$

We now construct the scalar product of (5) with the *instantaneous* position $\boldsymbol{r}$ of the particle and take the ensemble average of the product. In doing so, we make use of the facts that (i) $\boldsymbol{r}\cdot\boldsymbol{v} = \frac{1}{2}(dr^2/dt)$, (ii) $\boldsymbol{r}\cdot(d\boldsymbol{v}/dt) = \frac{1}{2}(d^2r^2/dt^2) - v^2$, and (iii) $\langle\boldsymbol{r}\cdot\boldsymbol{A}\rangle = 0$.[7] We obtain

$$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2\langle v^2\rangle. \tag{6}$$

If the Brownian particle has already attained thermal equilibrium with the molecules of the fluid, then the quantity $\langle v^2\rangle$ in this equation may be replaced by its *equipartition value* $3kT/M$. The equation is then readily integrated, with the result

$$\langle r^2\rangle = \frac{6kT\tau^2}{M}\left\{\frac{t}{\tau} - (1 - e^{-t/\tau})\right\}, \tag{7}$$

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[6] The process of "averaging over an ensemble" implies that we are imagining a large number of systems similar to the one originally under consideration and are taking an average over this collection at *any* time t. By the very nature of the function $\boldsymbol{F}(t)$, the ensemble average $\langle\boldsymbol{F}(t)\rangle$ must be zero at all times.

[7] This is so because we have no reason to expect a statistical correlation between the position $\boldsymbol{r}(t)$ of the Brownian particle and the force $\boldsymbol{F}(t)$ exerted on it by the molecules of the fluid; see, however, Manoliu and Kittel (1979). Of course, we do expect a correlation between the variables $\boldsymbol{v}(t)$ and $\boldsymbol{F}(t)$; consequently, $\langle\boldsymbol{v}\cdot F\rangle \neq 0$ (see Problem 15.7).

where the constants of integration have been so chosen that at, $t = 0$, both $\langle r^2 \rangle$ and its first time-derivative vanish. We observe that, for $t \ll \tau$,

$$\langle r^2 \rangle \simeq \frac{3kT}{M} t^2 = \langle v^2 \rangle t^2, \tag{8}$$[8]

which is consistent with the reversible equations of motion whereby one would simply have

$$\boldsymbol{r} = \boldsymbol{v}t. \tag{9}$$

On the other hand, for $t \gg \tau$,

$$\langle r^2 \rangle \simeq \frac{6kT\tau}{M} t = (6BkT)t, \tag{10}$$[9]

which is essentially the same as the Einstein–Smoluchowski result (15.2.22); incidentally, we obtain here a simple, but important, relationship between the coefficient of diffusion D and the mobility B, namely

$$D = BkT, \tag{11}$$

which is generally referred to as the *Einstein relation*.

The irreversible character of equation (10) is self-evident; it is also clear that it arises essentially from the viscosity of the medium. Moreover, the Einstein relation (11), which connects the coefficient of diffusion D with the mobility B of the system, tells us that the ultimate source of the viscosity of the medium (as well as of diffusion) lies in the random, fluctuating forces arising from the incessant motion of the fluid molecules; see also the fluctuation–dissipation theorem of Section 15.6.

In this context, if we consider a particle of charge e and mass M moving in a viscous fluid under the influence of an external electric field of intensity E, then the "coarse-grained" motion of the particle will be determined by the equation

$$M\frac{d}{dt}\langle \boldsymbol{v} \rangle = -\frac{1}{B}\langle \boldsymbol{v} \rangle + e\boldsymbol{E}; \tag{12}$$

compare this to equation (3). The "terminal" drift velocity of the particle would now be given by the expression $(eB)\boldsymbol{E}$, which prompts one to define (eB) as the "mobility" of the system and denote it by the symbol μ. Consequently, one obtains, instead of (11),

$$D = \frac{kT}{e}\mu, \tag{13}$$

which, in fact, is the original version of the Einstein relation; sometimes this is also referred to as the *Nernst relation*.

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[8] Note that the limiting solution (8) corresponds to "dropping out" the second term on the left side of equation (6).

[9] Note that the limiting solution (10) corresponds to "dropping out" the first term on the left side of equation (6).

So far we have not felt any *direct* influence of the rapidly fluctuating term $\boldsymbol{A}(t)$ that appears in the equation of motion (5) of the Brownian particle. For this, let us try to evaluate the quantity $\langle v^2(t)\rangle$ which, in the preceding analysis, was assumed to have already attained its "limiting" value $3kT/M$. For this evaluation we replace the variable t in equation (5) by u, multiply both sides of the equation by $\exp(u/\tau)$, rearrange and integrate over du between the limits $u=0$ and $u=t$; we thus obtain the formal solution

$$\boldsymbol{v}(t) = \boldsymbol{v}(0)e^{-t/\tau} + e^{-t/\tau}\int_0^t e^{u/\tau}\boldsymbol{A}(u)du. \tag{14}$$

Thus, the drift velocity $\boldsymbol{v}(t)$ of the particle is also a fluctuating function of time; of course, since $\langle \boldsymbol{A}(u)\rangle = 0$ for all u, the *average* drift velocity is given by the first term alone, namely

$$\langle \boldsymbol{v}(t)\rangle = \boldsymbol{v}(0)e^{-t/\tau}, \tag{15}$$

which is the same as our earlier result (4). For the mean square velocity $\langle v^2(t)\rangle$, we now obtain from (14)

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + 2e^{-2t/\tau}\left[\boldsymbol{v}(0)\cdot\int_0^t e^{u/\tau}\langle \boldsymbol{A}(u)\rangle du\right] \\ + e^{-2t/\tau}\int_0^t\int_0^t e^{(u_1+u_2)/\tau}\langle \boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_2)\rangle du_1 du_2. \tag{16}$$

The second term on the right side of this equation is identically zero, because $\langle \boldsymbol{A}(u)\rangle$ vanishes for all u. In the third term, we have the quantity $\langle \boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_2)\rangle$, which is a measure of the "statistical correlation between the value of the fluctuating variable $\boldsymbol{A}$ at time u_1 and its value at time u_2"; we call it the *autocorrelation function* of the variable $\boldsymbol{A}$ and denote it by the symbol $K_A(u_1,u_2)$ or simply by $K(u_1,u_2)$. Before proceeding with (16) any further, we place on record some of the important properties of the function $K(u_1,u_2)$.

(i) In a stationary ensemble (i.e., one in which the overall macroscopic behavior of the systems does not change with time), the function $K(u_1,u_2)$ depends only on the time interval (u_2-u_1). Denoting this interval by the symbol s, we have

$$K(u_1,u_1+s) \equiv \langle \boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_1+s)\rangle = K(s), \text{ independently of } u_1. \tag{17}$$

(ii) The quantity $K(0)$, which is identically equal to the mean square value of the variable $\boldsymbol{A}$ at time u_1, must be *positive definite*. In a stationary ensemble, it would be a constant, independent of u_1:

$$K(0) = \text{ const.} > 0. \tag{18}$$

(iii) For any value of s, the magnitude of the function $K(s)$ cannot exceed $K(0)$.

Proof: Since

$$\begin{aligned}\langle|\boldsymbol{A}(u_1)\pm\boldsymbol{A}(u_2)|^2\rangle &= \langle A^2(u_1)\rangle+\langle A^2(u_2)\rangle\pm 2\langle\boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_2)\rangle\\ &= 2\{K(0)\pm K(s)\}\geq 0,\end{aligned}$$

the function $K(s)$ cannot go outside the limits $-K(0)$ and $+K(0)$; consequently,

$$|K(s)|\leq K(0)\quad\text{for all } s. \tag{19}$$

(iv) The function $K(s)$ is symmetric about the value $s=0$, that is,

$$K(-s)=K(s)=K(|s|). \tag{20}$$

Proof:

$$\begin{aligned}K(s)&\equiv\langle\boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_1+s)\rangle=\langle\boldsymbol{A}(u_1-s)\cdot\boldsymbol{A}(u_1)\rangle\ ^{10}\\ &=\langle\boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_1-s)\rangle\equiv K(-s).\end{aligned}$$

(v) As s becomes large in comparison with the characteristic time τ^*, the values $\boldsymbol{A}(u_1)$ and $\boldsymbol{A}(u_1+s)$ become *uncorrelated*, that is

$$K(s)\equiv\langle\boldsymbol{A}(u_1)\cdot\boldsymbol{A}(u_1+s)\rangle\xrightarrow[s\gg\tau^*]{}\langle\boldsymbol{A}(u_1)\rangle\cdot\langle\boldsymbol{A}(u_1+s)\rangle=0. \tag{21}$$

In other words, the "memory" of the molecular impacts received during a given interval of time, say between u_1 and u_1+du_1, is "completely lost" after a lapse of time large in comparison with τ^*. It follows that the magnitude of the function $K(s)$ is significant only so long as the variable s is of the same order of magnitude as τ^*.

Figures 15.7 through 15.9 later in this chapter show the s-dependence of certain typical correlation functions $K(s)$; they fully conform to the properties listed here.

We now evaluate the double integral appearing in (16):

$$I=\int_0^t\int_0^t e^{(u_1+u_2)/\tau}K(u_2-u_1)du_1du_2. \tag{22}$$

Changing over to the variables

$$S=\frac{1}{2}(u_1+u_2)\quad\text{and}\quad s=(u_2-u_1), \tag{23}$$

the integrand becomes $\exp(2S/\tau)K(s)$, the element (du_1du_2) gets replaced by the corresponding element $(dSds)$ while the limits of integration, in terms of the variables S and s,

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[10] This is the only crucial step in the proof. It involves a "shift," by an amount s, in both instants of the measurement process; the equality results from the fact that the ensemble is supposed to be stationary.

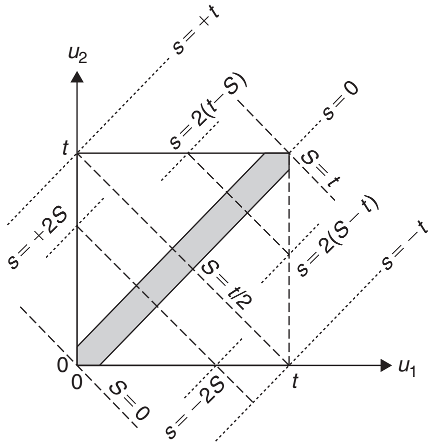

FIGURE 15.2 Limits of integration, of the double integral I, in terms of the variables S and s.

can be read from Figure 15.2; we find that, for $0 \le S \le t/2$, s goes from $-2S$ to $+2S$ while, for $t/2 \le S \le t$, it goes from $-2(t-S)$ to $+2(t-S)$. Accordingly,

$$I = \int_0^{t/2} e^{2S/\tau} dS \int_{-2S}^{+2S} K(s) ds + \int_{t/2}^{t} e^{2S/\tau} dS \int_{-2(t-S)}^{+2(t-S)} K(s) ds. \tag{24}$$

In view of property (v) of the function $K(s)$, see equation (21), the integrals over s draw significant contribution only from a very narrow region, of the order of τ^*, around the value $s = 0$ (i.e., from the shaded region in Figure 15.2); contributions from regions with larger values of $|s|$ are negligible. Thus, if $t \gg \tau^*$, the limits of integration for s may be replaced by $-\infty$ and $+\infty$, with the result

$$I \simeq C \int_0^t e^{2S/\tau} dS = C \frac{\tau}{2} (e^{2t/\tau} - 1), \tag{25}$$

where

$$C = \int_{-\infty}^{\infty} K(s) ds. \tag{26}$$

Substituting (25) into (16), we obtain

$$\langle v^2(t) \rangle = v^2(0) e^{-2t/\tau} + C \frac{\tau}{2} (1 - e^{-2t/\tau}). \tag{27}$$

Now, as $t \to \infty$, $\langle v^2(t) \rangle$ must tend to the equipartition value $3kT/M$; therefore,

$$C = 6kT/M\tau \tag{28}$$

and hence

$$\langle v^2(t)\rangle = v^2(0) + \left\{\frac{3kT}{M} - v^2(0)\right\}(1 - e^{-2t/\tau}). \tag{29}$$[11]

We note that if $v^2(0)$ were itself equal to the equipartition value $3kT/M$, then $\langle v^2(t)\rangle$ would always remain the same, which shows that statistical equilibrium, once attained, has a natural tendency to persist.

Substituting (29) into the right side of (6), we obtain a more representative description of the manner in which the quantity $\langle r^2\rangle$ varies with t; we thus have

$$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2v^2(0)e^{-2t/\tau} + \frac{6kT}{M}(1 - e^{-2t/\tau}), \tag{30}$$

with the solution

$$\langle r^2\rangle = v^2(0)\tau^2(1 - e^{-t/\tau})^2 - \frac{3kT}{M}\tau^2(1 - e^{-t/\tau})(3 - e^{-t/\tau}) + \frac{6kT\tau}{M}t. \tag{31}$$

Solution (31) satisfies the initial conditions that both $\langle r^2\rangle$ and its first time-derivative vanish at $t = 0$; moreover, if we put $v^2(0) = 3kT/M$, it reduces to solution (7) obtained earlier. Once again, we note the *reversible* nature of the motion for $t \ll \tau$, with $\langle r^2\rangle \simeq v^2(0)t^2$, and its *irreversible* nature for $t \gg \tau$, with $\langle r^2\rangle \simeq (6BkT)t$.

Figures 15.3 and 15.4 show the variation, with time, of the ensemble averages $\langle v^2(t)\rangle$ and $\langle r^2(t)\rangle$ of a Brownian particle, as given by equations (29) and (31), respectively. All important features of our results are manifestly evident in these plots.

Brownian motion continues to be a topic of contemporary research nearly 200 years after Brown's discovery and over 100 years after Einstein and Smoluchowski's analysis and early measurements by Perrin. The renewed interest is due to the growth in the technological importance of colloids across a wide range of fields and the development of digital video and computer image analysis. An interesting example is the detailed observation and analysis of rotational and two-dimensional translational Brownian motion of ellipsoidal particles by Han et al. (2006) in a thin microscope slide. The case of rotational Brownian motion was first analyzed by Einstein (1906b) and first measured by Perrin (1934, 1936). Both rotational and translational modes diffuse according to Langevin dynamics but the translational diffusion is coupled to the rotational diffusion since the translational diffusion constant parallel to the longer axis is larger than the diffusion constant perpendicular

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[11] One may check that

$$\frac{d}{dt}\langle v^2(t)\rangle = \frac{2}{\tau}\left[v^2(\infty) - \langle v^2(t)\rangle\right] = -\frac{2}{\tau}\Delta\langle v^2(t)\rangle,$$

where $v^2(\infty) = 3kT/M$ and $\Delta\langle v^2(t)\rangle$ is the "deviation of the quantity concerned from its equilibrium value." In this form of the equation, we have a typical example of a "relaxation phenomenon," with *relaxation time* $\tau/2$.

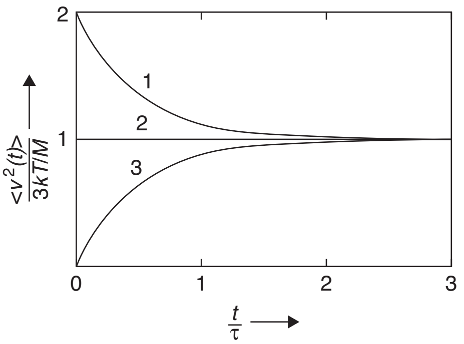

FIGURE 15.3 The mean square velocity of a Brownian particle as a function of time. Curves 1, 2, and 3 correspond, respectively, to the initial conditions $v^2(0) = 6kT/M, 3kT/M$, and 0.

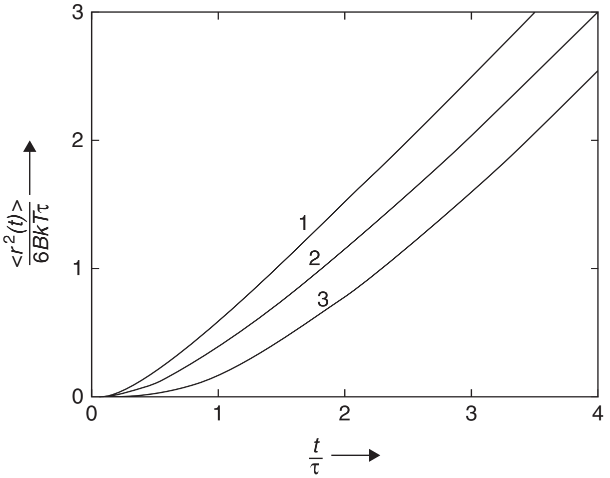

FIGURE 15.4 The mean square displacement of a Brownian particle as a function of time. Curves 1, 2, and 3 correspond, respectively, to the initial conditions $v^2(0) = 6kT/M, 3kT/M$, and 0.

to that axis. The rotational diffusion and both long-axis (a) and short-axis (b) body-frame diffusions are all Gaussian:

$$p_\theta(\Delta\theta, t) = \frac{1}{\sqrt{4\pi D_\theta t}} \exp\left(-\frac{(\Delta\theta)^2}{4D_\theta t}\right), \tag{32a}$$

$$p_{\mathrm{a}}(\Delta x_{\mathrm{a}}, t) = \frac{1}{\sqrt{4\pi D_{\mathrm{a}} t}} \exp\left(-\frac{(\Delta x_{\mathrm{a}})^2}{4D_{\mathrm{a}} t}\right), \tag{32b}$$

$$p_{\mathrm{b}}(\Delta x_{\mathrm{b}}, t) = \frac{1}{\sqrt{4\pi D_{\mathrm{b}} t}} \exp\left(-\frac{(\Delta x_{\mathrm{b}})^2}{4D_{\mathrm{b}} t}\right), \tag{32c}$$

with diffusion constants D_θ, D_a, and D_b. Experiments have observed the complex two-dimensional spatial diffusion at short times ($t \lesssim \tau_\theta = 1/(2D_\theta)$), as predicted by the Langevin theory. The long-time ($t \gg \tau_\theta$) spatial diffusion is isotropic with diffusion constant $\overline{D} = (D_\mathrm{a} + D_\mathrm{b})/2$.

15.3.A Brownian motion of a harmonic oscillator

An analysis similar to the one for a diffusing Brownian particle can also be performed for a particle in a harmonic oscillator potential that prevents the particle from diffusing away from the origin and allows a more general analysis of the relationship between the position and velocity response functions and the power spectra of the fluctuations; see Kappler (1938) and Chandrasekhar (1943). The one-dimensional equation of motion for a Brownian particle of mass M in a harmonic oscillator potential with spring constant $M\omega_0^2$ is

$$\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \omega_0^2 x = \frac{F(t)}{M}, \tag{33}$$

where $\gamma\,(= 6\pi\eta a/M)$ is the damping coefficient of a spherical particle in a fluid with viscosity η. Just as in the case of diffusive Brownian motion, the force $F(t)$ can be a time-dependent external force designed to explore the response function or a time-dependent random force due to collisions with molecules in the fluid to analyze the equilibrium fluctuations. Assuming the system was in equilibrium in the distant past, the position at time t is given by

$$x(t) = \int_{-\infty}^{t} \chi_{xx}(t-t')F(t')dt', \tag{34}$$

where

$$\chi_{xx}(s) = \frac{1}{M\omega_1}e^{-\frac{\gamma s}{2}}\sin(\omega_1 s) \tag{35}$$

is the xx response function and $\omega_1 = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$.[12] The velocity response is given by

$$v(t) = \int_{-\infty}^{t} \chi_{vx}(t-t')F(t')dt', \tag{36}$$

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[12] This form of the response function assumes that the oscillator is underdamped. The notation χ_{xx} refers to the notation used in Section 15.6.A in which the response of the position coordinate x depends on the applied field F that couples to the Hamiltonian via a term $-F(t)x(t)$.