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1 Brownian motion and Langevin equations

This is the lecture note on Apr. 15, 2024 introducing Brownian motion as an introduction to the stochastic phenomena using Langevin equation. This part of the text is based mainly on Ref.[1].

1.1 Langevin equation and the Fluctuation-Dissipation theorem

Consider the one-dimensional classical motion of a spherical particle of radius a, mass m, position x, velocity $v = \frac{dx}{dt}$, immersed in a fluid medium of viscosity η, which is assumed to be in thermal equilibrium at temperature T. The size a and mass m of the particle is assumed to be much larger than that of the molecules constituting the fluid. Newton's equation of motion for the particle is

$$m\frac{dv}{dt} = F_{\text{total}}(t), \tag{1}$$

where $F_{\text{total}}(t)$ is the total instantaneous force exerted on the particle at time t. If there are no external forces applied to the particle, our experience teaches us that this force is dominated by a frictional force $-\zeta v$, proportional to the velocity v of the particle. The friction coefficient ζ (> 0) is given by the Stokes' law, $\zeta = 6\pi\eta a$.

If this is the whole story, the equation of motion for the particle becomes

$$m\frac{dv}{dt} \sim -\zeta v. \tag{2}$$

Since this is a linear first-order differential equation, its solution can be easily obtained as

$$v(t) = e^{-\frac{\zeta t}{m}} v(0), \tag{3}$$

starting from an arbitrary initial velocity $v(0)$. If we wait for a long time, the total system made of the fluid and the particle becomes thermal equilibrium with temperature T (assuming the fluid is macroscopic and we can neglect the change of its temperature by the dynamics of the particle). According to Eq. (3), the velocity of the particle is predicted to decay to zero after a long time.

However, this cannot be strictly true because the mean squared velocity of the particle at thermal equilibrium with temperature T is proportional to T:

$$\left\langle \frac{1}{2}mv^2 \right\rangle_{\text{eq}} = \frac{m}{2}\left\langle v^2 \right\rangle_{\text{eq}} = \frac{k_{\text{B}}T}{2}, \tag{4}$$

which is the **equipartition theorem** where k_{B} is the Boltzmann's constant.[1] Hence, the actual velocity cannot remain zero for a finite temperature T. Here, $\langle \bullet \rangle_{\text{eq}}$ means the statistical average over an equilibrium state. Evidently, the assumption that $F_{\text{total}}(t)$ is dominated by the frictional force must be modified. In fact, in 1827, Robert Brown had observed by a microscope a random motion of particles from a pollen of the plant Clarkia pulchella immersed in water. This is the **Brownian motion** or a **random walk**.

[1] For a molecular particle constituting the fluid of a mass $m_{\text{mol}} \ll m$, the same equipartition theorem is applied and $\frac{m_{\text{mol}}}{2}\left\langle v_{\text{mol}}^2 \right\rangle_{\text{eq}} = \frac{k_{\text{B}}T}{2}$, where v_{mol} is the velocity of the fluid molecules. This shows that $\left\langle v_{\text{mol}}^2 \right\rangle_{\text{eq}} \gg \left\langle v^2 \right\rangle_{\text{eq}}$, the fluid molecules are moving much faster than the particle in average.

The appropriate modification, suggested by the observed randomness of an individual motion, is to add a "random" and "fluctuating" force $\delta F(t)$ to the frictional force, so that the equation of motion becomes

$$m\frac{dv}{dt} = -\zeta v + \delta F(t). \tag{5}$$

This is the **Langevin equation** for a Brownian particle without external field. Here, in the following for simplicity, we assume that the effect of the fluctuating force can be summarized by giving its first and second moments, as time averages over an infinitesimal time interval dt (*coarse graining*) represented by the bracket $\langle \bullet \rangle$,

$$\langle \delta F(t) \rangle = 0, \quad \langle \delta F(t) \delta F(t') \rangle = 2B\delta(t-t'). \tag{6}$$

B (>0) is a measure of the strength of the fluctuating force which is characterized later. The delta function in time indicates that there is no correlation between impacts in any distinct time intervals $[t, t+dt]$ and $[t', t'+dt]$. The remaining mathematical specification of this dynamical model is that the fluctuating force has a **Gaussian distribution** determined by these moments.

The Langevin equation, (5), which is a linear, first-order, inhomogeneous differential equation, can be solved for $t(>0)$ to give (This can be solved with setting $v(t) = e^{-\frac{\zeta t}{m}} g(t)$ with an auxiliary function $g(t)$.)

$$v(t) = e^{-\frac{\zeta t}{m}} v(0) + \int_0^t dt' e^{-\frac{\zeta(t-t')}{m}} \frac{\delta F(t')}{m}. \tag{7}$$

The first term gives the exponential decay of the initial velocity, and the second term gives the extra velocity produced by the random force. Let us use this to get the mean squared velocity. After using the properties of the Gaussian distribution, Eq. (6) and partial integration, the result is (Show this !)

$$\langle v^2(t) \rangle = e^{-\frac{2\zeta t}{m}} v^2(0) + \frac{B}{\zeta m}\left(1 - e^{-\frac{2\zeta t}{m}}\right). \tag{8}$$

In the long time limit, the exponentials drop out, and this quantity approaches $B/\zeta m$. As discussed above, in the long time limit, the mean squared velocity must approach its equilibrium value $k_{\mathrm{B}}T/m$. Consequently we find

$$B = \zeta k_{\mathrm{B}} T. \tag{9}$$

This result is known as the **Fluctuation-dissipation theorem**. It relates the strength B of the random noise or *fluctuating force* to the magnitude ζ of the friction or *dissipation*. It expresses the balance between friction, which tends to drive any system to a completely **"dead" state**, and noise, which tends to keep the system **"alive"**. This balance is required to keep a thermal equilibrium state for a long time.

It is evident from Eq. (7) that the velocity of the particle at time t, $v(t)$, is a **random (statistical) variable**, which is connected to a real physical quantity either when we consider a particular trajectory (realization) or when we consider its statistical average of it over some ensemble. In fact, we can assume two sources of the statistical features. One is the probability distribution of the initial velocity of the particle at time $t=0$, $v(0)$. Another is the random fluctuating forces $\delta F(t)$. In the following, various examples of this statistical treatment of them are introduced.

1.2 Velocity correlation functions

The second equation of Eq. (6) is the first example of time correlation function of fluctuating forces at times t and t'. Here we discuss the time correlation function of the velocity, the **velocity correlation function** of a single particle in a fluid, $\langle v(t)v(t') \rangle_{\mathrm{ens}}$, where $v(t)$ is the velocity of that particle at time t and $\langle \bullet \rangle_{\mathrm{ens}}$ means a statistical average of a physical quantity $\bullet$ over some ensemble. One reason for interest in this time correlation function is its connection with the **self-diffusion coefficient**, D. If there are no time-dependent external forces and the system is in thermal equilibrium, which is the situation considered in this lecture almost all the cases, we may expect that this correlation function only depends on the relative time $t-t'$ (This property should be carefully analyzed since this is only expected after a long time passed from a certain initial condition.)

There are many ways to show this connection. A particularly easy one starts with the one-dimensional diffusion equation for the space (x) and time (t) dependence of the concentration $W(x,t)$ of a tagged particle,[2]

$$\frac{\partial}{\partial t}W(x,t) = D\frac{\partial^2}{\partial x^2}W(x,t). \tag{10}$$

The function $W(x,t)$ represents the statistics of the (single) particle concentration over an *ensemble* of huge amount of trials starting from a given initial condition. The definition of the concentration suggests the normalization condition $\int_{\mathcal{V}} dx W(x,t) = 1$ for $\forall t$, which means that you can find exactly one particle at any time if you search for all region $\mathcal{V} : -\infty < x < \infty$. Using this function, ensemble average of an arbitrary physical function of the space x, $f(x)$, is obtained by $\langle f \rangle_{\text{ens}}(t) \equiv \int_{\mathcal{V}} dx f(x) W(x,t)$.

Suppose that the tagged particle starts out at an initial time $t = 0$ from the origin $x = 0$. Then the concentration will change from an initial delta function peaked at $x = 0$ to a spread out distribution (in fact it becomes a Gaussian function of x). By symmetry, $W(x,t) = W(-x,t)$ and the ensemble average of the displacement $\langle x \rangle_{\text{ens}}(t) \equiv \int_{\mathcal{V}} dx\, xW(x,t)$ is zero. The mean squared displacement defined as $\langle x^2 \rangle_{\text{ens}}(t) = \int_{\mathcal{V}} dx\, x^2 W(x,t)$ is equivalent to the variance of the distribution, which is zero at time $t = 0$ since $W(x,0) = \delta(x)$. The mean squared displacement at a finite time t can be found by multiplying the diffusion equation by x^2 and integrating over x. Then its change is

$$\frac{\partial}{\partial t}\langle x^2 \rangle_{\text{ens}}(t) = \int_{\mathcal{V}} dx\, x^2 \frac{\partial}{\partial t}W(x,t) = D\int_{\mathcal{V}} dx\, x^2 \frac{\partial^2}{\partial x^2}W(x,t) = 2D. \tag{11}$$

(This can be shown by making use of integration by parts and boundary conditions $\lim_{|x|\to\infty} W(x,t) = 0$ and $\lim_{|x|\to\infty} \partial_x W(x,t) = 0$ for finite t, which are required from the normalization condition.) On integrating over time, this result leads to the well-known **Einstein formula** for a diffusion in one dimension, $\langle x^2 \rangle_{\text{ens}} = 2Dt$.

Now we construct a statistical mechanical theory of the same quantity. The net displacement of the particle's position during the time interval from 0 to t is,

$$x(t) = \int_0^t ds\; v(s), \tag{12}$$

where $v(s)$ is the velocity of the particle at time s. The ensemble average of the mean squared displacement is

$$\langle x^2 \rangle_{\text{ens}}(t) = \left\langle \int_0^t ds_1 v(s_1) \int_0^t ds_2 v(s_2) \right\rangle_{\text{ens}} = \int_0^t ds_1 \int_0^t ds_2 \langle v(s_1) v(s_2) \rangle_{\text{ens}}. \tag{13}$$

Note that the integral contains the velocity correlation function at times s_1 and s_2. Next, take the time derivative and combine two equivalent terms on the right-hand side,

$$\frac{\partial}{\partial t}\langle x^2 \rangle_{\text{ens}}(t) = 2\int_0^t ds\, \langle v(t)v(s) \rangle_{\text{ens}} = 2\int_0^t du\, \langle v(u)v(0) \rangle_{\text{ens}}, \tag{14}$$

where as noted above, the velocity correlation function is assumed to depend only on the time difference $t - s = u$ except for very short initial times. The diffusion equation (10) is expected to be valid only at times much longer than a molecular time. In the limit of large t, the left-hand side approaches $2D$, and the right-hand side approaches a time integral from zero to infinity since the velocity correlation function generally decays to zero in a short time difference; in simple liquids, this may be of the order of picosecond. Therefore, we have derived the simplest example of the relation of a transport coefficient D to the velocity correlation function $\langle v(t)v(0) \rangle_{\text{ens}}$,

$$D = \int_0^\infty dt\, \langle v(t)v(0) \rangle_{\text{ens}}. \tag{15}$$

[2] This equation will be derived microscopically in the lecture of next week.

1.3 Correlation functions and Brownian motion

The Langevin equation and the fluctuation-dissipation theorem can be used to find expressions for various time correlation functions. The first example is to obtain the velocity correlation function of a Brownian particle introduced in the previous subseciton. In this example, it is instructive to calculate both the equilibrium ensemble average and the long-time average.

As explained before, calculating the equilibrium ensemble average involves both an average over noise and an average over the initial velocity. Using the solution of the Langevin equation (7), the noise average leads to

$$\langle v(t)\rangle = e^{-\frac{\zeta t}{m}} v(0). \tag{16}$$

Now we multiply by $v(0)$ and average over initial velocity under equilibrium,

$$\langle v(t)v(0)\rangle_{\text{eq}} = \frac{k_{\text{B}}T}{m} e^{-\frac{\zeta t}{m}}. \tag{17}$$

This holds only for $t > 0$ because the Langevin equation is valid only for positive times.

We expect that the velocity correlation function is actually a function of the absolute value of the time-difference t, but to see this from the Langevin equation we have to go to the long time average. This calculation starts with a record of the time dependence of the velocity $v(t)$ over a very long time interval τ. Then the velocity correlation function can be obtained from the long time average,

$$\langle v(t)v(t')\rangle_{\text{time}} \equiv \frac{1}{\tau}\int_0^\tau ds\ \langle v(t+s)v(t'+s)\rangle\,. \tag{18}$$

The instantaneous velocity at time t is determined by its initial value and by an integral over the noise as shown in Eq. (7). For large τ, we can assume that the initial value of the velocity has decayed to zero, and the instantaneous velocity is determined only by the noise. Then with a slight rearrangement of the time integral ($t' = t - u$) and approximating the upper limit t of the integral to infinity assuming no any change because of the factor $e^{-\zeta u/m}$ for large u, we obtain

$$v(t) \sim \frac{1}{m}\int_0^\infty du e^{-\frac{\zeta u}{m}} \delta F(t-u). \tag{19}$$

Now the velocity correlation function is the triple integral,

$$\langle v(t)v(t')\rangle_{\text{time}} = \int_0^\infty du_1 \int_0^\infty du_2 e^{-\frac{\zeta(u_1+u_2)}{m}} \frac{1}{\tau}\int_0^\tau ds \frac{1}{m^2}\langle \delta F(t-u_1+s)\delta F(t'-u_2+s)\rangle = \frac{B}{m\zeta} e^{-\frac{\zeta|t-t'|}{m}}. \tag{20}$$

(Exercise I: derive this relation.) The product of two random force factors has been replaced by its average. The integral over s can be done immediately. The delta function removes another integral, and the last one can be done explicitly. Note that when the time correlation function is calculated this way, the absolute value of the time difference comes in automatically. On using the fluctuation-dissipation theorem, this leads to the final expression for the velocity correlation function,

$$\langle v(t)v(t')\rangle_{\text{time}} = \frac{k_{\text{B}}T}{m} e^{-\frac{\zeta|t-t'|}{m}}. \tag{21}$$

The time average of the product of two velocities Eq. (21) is the same as the equilibrium ensemble average Eq. (17). This is what one expects for an ergodic system. One point of this derivation is to show that observation of time dependent fluctuations over a long time interval can be used to learn about friction. Putting this result in the definition of diffusion constant Eq. (15), D,

$$D = \int_0^\infty dt\ \frac{k_{\text{B}}T}{m} e^{-\frac{\zeta t}{m}} = \frac{k_{\text{B}}T}{\zeta}. \tag{22}$$

1.3.1 Mean squared displacement

Another application of the general solution of the Langevin equation is to find the mean squared displacement of the Brownian particle. As shown in (12), the actual displacement is

$$x(t) = \int_0^t dt' v(t'). \tag{23}$$

To find $\langle x^2(t)\rangle_{\rm eq}$, we start with Eq. (7)

$$v(t) = e^{-\frac{\zeta t}{m}} v(0) + \frac{1}{m}\int_0^t dt' e^{-\frac{\zeta(t-t')}{m}} \delta F(t') \tag{24}$$

and then do the averages both for initial equilibrium distribution of $v(0)$ and $\delta F(t)$, and the result is

$$\langle x^2(t)\rangle_{\rm eq} = \int_0^t ds \int_0^t ds' \, \langle v(s)v(s')\rangle_{\rm eq} = 2\frac{k_{\rm B}T}{\zeta}\left[t - \frac{m}{\zeta} + \frac{m}{\zeta}e^{-\frac{\zeta t}{m}}\right]. \tag{25}$$

with using the result of fluctuation-dissipation theorem: $B/m\zeta = k_{\rm B}T/m$. (Exercise II: derive this relation.) At short times, the mean squared displacement increases quadratically with time, namely for $t \ll \frac{m}{\zeta}$,

$$\langle x^2(t)\rangle_{\rm eq} = 2\frac{k_{\rm B}T}{\zeta}\left[t - \frac{m}{\zeta} + \frac{m}{\zeta}\left(1 - \frac{\zeta t}{m} + \frac{1}{2}\left(\frac{\zeta t}{m}\right)^2 + \cdots\right)\right] \sim \frac{k_{\rm B}T}{m}t^2. \tag{26}$$

This is the inertial behavior that comes from the initial velocity. At long times, the effects of the noise are dominant, and the mean squared displacement increases linearly with time,

$$\langle x^2(t)\rangle_{\rm eq} \to 2\frac{k_{\rm B}T}{\zeta}t. \tag{27}$$

Einstein's formula for the mean squared displacement of a diffusing particle is $2Dt$ as shown below Eq. (11). Thus we obtain again the Einstein's expression for the self-diffusion coefficient,

$$D = \frac{k_{\rm B}T}{\zeta}. \tag{28}$$

When Stokes' law is used for the friction coefficient, the result is called the Stokes-Einstein formula.

1.4 Conclusions

We discussed a classical one-dimensional Brownian particle in the Langevin equation formalism. Velocity correlation function and mean squared displacement are explicitly evaluated. Fluctuation-dissipation relation and diffusion constant are given. We had introduced four types of average, $\langle \bullet \rangle$ (coarse graining), $\langle \bullet \rangle_{\rm eq}$ (equilibrium ensemble average), $\langle \bullet \rangle_{\rm ens}$ (ensemble average, in general) and $\langle \bullet \rangle_{\rm time}$ (time average).

When an external field (or more generally an affinity, for example, potential difference or temperature gradient *etc.*), the Langevin equation can also treat non-equilibrium situations. In the next lecture, we introduce Fokker-Planck equation, which in equilibrium, describes the same physics as the Langevin equation. In the following lectures, we will learn the framework of (quantum) master equation, which can in principle treat arbitrary non-equilibrium situations.

References

[1] Robert Zwanzig, "Nonequilibrium Statistical Mechanics", Oxford University Press, 2001.