BROWNIAN MOTION

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Abstract

This is a brief discussion of Brownian motion. The concept of a stochastic, Markovian process is introduced, and the Fokker-Plank equation is derived. The statistical nature of Brownian motion is then explored by means of the Langevin equation and the Fokker-Planck equation. For more details, see R. E. Wilde and S. Singh, *Statistical Mechanics: Fundamentals and Modern Applications*, and C. Kittel, *Elementary Statistical Physics*.

I. INTRODUCTION

In 1827 the English botanist Robert Brown noticed that pollen grains suspended in water jiggled about under the lens of the microscope, following a zigzag path. The motion of pollen grains and the random walk represent what are known as *stochastic processes*. That is, in time some variable such as the position of the pollen grain traces out an irregular path that can be treated by statistical methods. This irregular motion, called *Brownian motion*, has served as a model for treating a host of irreversible processes that occur in nature.

In the case of pollen grains suspended in water, the water molecules are constantly in motion, bombarding the pollen grains from all sides with very high frequency. The grains respond to the net effect of bombardment by behaving in a seemingly erratic manner. However, the very fact that there are a very large number of water molecules colliding with the pollen grains per unit time means that the problem of understanding the random motion is susceptible to a statistical treatment. In this way, it should be possible to relate macroscopic properties such as viscosity to random displacements of a Brownian particle. Einstein was one of the first scientists to derive such relations.

II. MARKOVIAN PROCESS

By a *random process* or *stochastic process* $x(t)$ we mean a process in which the variable x does not depend in a completely definite way on the independent variable t, which may denote time. In observations on the different systems of a representative ensemble, we find different $x(t)$. All we can do is to study certain *probability distributions* because we cannot obtain the functions $x(t)$ themselves for the members of the ensemble. We can determine, for example, $p_1(x_1, t_1)dx_1$, the probability of finding x in the range $(x_1, x_1 + dx_1)$ at time t_1; $p_2(x_2, t_2; x_1, t_1)dx_1dx_2$, the probability of finding x in $(x_1, x_1 + dx_1)$ at time t_1 *and* in the range $(x_2, x_2 + dx_2)$ at time t_2. Proceeding similarly we can form $p_3(x_3, t_3; x_2, t_2; x_1, t_1)$, $p_4(x_4, t_4; x_3, t_3; x_2, t_2; x_1, t_1)$, $\cdots$. In many important cases p_2 contains all information we need. When this is true, the random process is called a *Markovian process.*

It is useful to introduce the *conditional probability* $P_2(x_2, t_2|x_1, t_1)dx_2$ for the probability that given x_1 at time t_1 one finds x in dx_2 at x_2 at time t_2 later. Then it is obvious that

$$p_2(x_2, t_2; x_1, t_1) = P_2(x_2, t_2|x_1, t_1)p_1(x_1, t_1).$$

Similarly, it is obvious that

$$p_3(x_3, t_3; x_2, t_2; x_1, t_1) = P_2(x_3, t_3|x_2, t_2)p_2(x_2, t_2; x_1, t_1),$$

from which we have

$$p_2(x_3, t_3; x_1, t_1) = \int dx_2 p_3(x_3, t_3; x_2, t_2; x_1, t_1) = \int dx_2 P_2(x_3, t_3|x_2, t_2)p_2(x_2, t_2; x_1, t_1),$$

and

$$P_2(x_3, t_3|x_1, t_1) = \int dx_2 P_2(x_3, t_3|x_2, t_2)P_2(x_2, t_2|x_1, t_1).$$

The last equation is known as the Smoluchowski equation.

III. FOKKER-PLANCK EQUATION

The Fokker-Planck equation describes the time development of a Markovian process. It is useful in the study of the approach to statistical equilibrium.

We start from the Smoluchowski equation

$$P(z,t+\Delta t|x,0) = \int dy P(z,t+\Delta t|y,t)P(y,t|x,0) = \int dy P(z,\Delta t|y,0)P(y,t|x,0).$$

where $P(x_2,t_2|x_1,t_1)dx_2 = P(x_2,t_2-t_1|x_1,0)dx_2$ is the conditional probability that given x_1 at time t_1 one finds x in dx_2 at x_2 at time t_2 later. Consider the integral $\int dz R(z)\frac{\partial}{\partial t}P(z,t|x,0)$ where $R(z)$ is an arbitrary function vanishing at $z=\pm\infty$ sufficiently rapidly. We write the integral as

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

in which the order of integration has been interchanged in the double integral. Expanding $R(y)$ in a power series about $R(z)$:

$$R(y) = R(z) + (y-z)R'(z) + \frac{1}{2}(y-z)^2R''(z) + \cdots,$$

we have

$$\begin{aligned}
&\int dy R(y)P(y,\Delta t|z,0) \\
\simeq\ &R(z) + R'(z)\int dy(y-z)P(y,\Delta t|z,0) + R''(z)\int dy\frac{(y-z)^2}{2}P(y,\Delta t|z,0).
\end{aligned}$$

where $\int dy P(y,\Delta t|z,0) = 1$ has been used. Let a and b denote the moments

$$a(z,\Delta t) = \int dy(y-z)P(y,\Delta t|z,0);$$

$$b(z,\Delta t) = \int dy\frac{(y-z)^2}{2}P(y,\Delta t|z,0).$$

Now assume that in the limit $\Delta t \to 0$ the moments a and b are proportional to Δt, and we introduce

$$A(z) = \lim \frac{1}{\Delta t} a(z, \Delta t);$$
$$B(z) = \lim \frac{1}{\Delta t} b(z, \Delta t).$$

Then,

$$\int dy R(y) P(y, \Delta t|z, 0) \simeq R(z) + R'(z)a(z, \Delta t) + R''(z)b(z, \Delta t),$$

and

$$\begin{aligned}
& \int dz R(z) \frac{\partial}{\partial t} P(z, t|x, 0) \\
= \ & \lim \frac{1}{\Delta t} \left[\int dz \left[\int dy R(y) P(y, \Delta t|z, 0) \right] P(z, t|x, 0) - \int dz R(z) P(z, t|x, 0) \right] \\
= \ & \lim \frac{1}{\Delta t} \left[\int dz \left[R(z) + R'(z)a(z, \Delta t) + R''(z)b(z, \Delta t) \right] P(z, t|x, 0) - \int dz R(z) P(z, t|x, 0) \right] \\
= \ & \int dz \left[R'(z)A(z) + R''(z)B(z) \right] P(z, t|x, 0).
\end{aligned}$$

Integrating by parts, we obtain

$$\int dz R(z) \left[\frac{\partial}{\partial t} P(z, t|x, 0) + \frac{\partial}{\partial z} \left(A(z) P(z, t|x, 0) \right) - \frac{\partial^2}{\partial z^2} \left(B(z) P(z, t|x, 0) \right) \right] = 0,$$

which hold for all functions $R(z)$, and so

$$\frac{\partial}{\partial t} P(z, t|x, 0) = -\frac{\partial}{\partial z} \left[A(z) P(z, t|x, 0) \right] + \frac{\partial^2}{\partial z^2} \left[B(z) P(z, t|x, 0) \right].$$

This is the Fokker-Planck equation. Using

$$p_1(z, t) = \int dx p_2(z, t; x, 0) = \int dx P(z, t|x, 0) p_1(x, 0),$$

we can apply the Fokker-Planck equation to the probability density $p_1(z, t)$ as well:

$$\frac{\partial}{\partial t} p_1(z, t) = -\frac{\partial}{\partial z} \left[A(z) p_1(z, t) \right] + \frac{\partial^2}{\partial z^2} \left[B(z) p_1(z, t) \right].$$

IV. BROWNIAN MOTION

A. Langevin equation

By Brownian movement we mean the movement of a body arising from thermal agitation. We consider the motion of a particle suspended in a fluid. For simplicity, we consider the one-dimensional equation of motion:

$$m\frac{dv}{dt} = -\gamma v + \zeta(t),$$

where $-\gamma v$ represents the viscous drag on a particle moving with velocity v, and $\zeta(t)$ is a stochastic force of average value zero representing the effects of molecular bombardment by the surrounding fluid. This equation is the Langevin equation in one dimension. It can be solved directly:

$$v(t) = v_0 e^{-\gamma t/m} + \frac{1}{m} e^{-\gamma t/m} \int_0^t e^{\gamma\tau/m}\zeta(\tau)d\tau.$$

We now take an ensemble average of this solution. This averaging can be done in two ways. Either one consider a large number of independent Brownian particles and average over them, or one take a time average of the motion of a single particle over widely separated intervals. (Each interval is microscopically long enough to allow a time average, but macroscopically short enough to allow a time resolution.) We assume for the random force that

$$\langle\zeta(t)\rangle = 0;$$

$$\langle\zeta(t_2)\zeta(t_1)\rangle = \Gamma\delta(t_2 - t_1).$$

where Γ is a time-independent constant and the delta function ensures that collisions are uncorrelated. Taking the average of $v(t)$ we obtain

$$\langle v(t)\rangle = v_0 e^{-\gamma t/m},$$

because $\langle\zeta(\tau)\rangle$ vanishes. Similarly, taking the average of $v^2(t)$ we obtain

$$\begin{aligned}\langle v^2(t)\rangle &= v_0^2 e^{-2\gamma t/m} + \frac{1}{m^2} e^{-2\gamma t/m} \int_0^t d\tau_2 \int_0^t d\tau_1 \exp\left[\frac{\gamma(\tau_2+\tau_1)}{m}\right] \langle\zeta(\tau_2)\zeta(\tau_1)\rangle \\ &= v_0^2 e^{-2\gamma t/m} + \frac{\Gamma}{m^2} e^{-2\gamma t/m} \int_0^t d\tau_2 \exp\left[\frac{2\gamma\tau_2}{m}\right] \\ &= v_0^2 e^{-2\gamma t/m} + \frac{\Gamma}{2\gamma m}\left[1 - e^{-2\gamma t/m}\right],\end{aligned},$$

where the cross terms involving $\langle\zeta(\tau)\rangle$ vanish. For $t \gg m/\gamma$, $\langle v^2(t)\rangle$ approaches

$$\left\langle v^2(\infty)\right\rangle = \frac{\Gamma}{2\gamma m},$$

By equipartition $\frac{1}{2}\langle v^2(\infty)\rangle = \frac{1}{2}k_B T$, we obtain

$$\Gamma = 2\gamma k_B T,$$

which relates the coefficient of friction to the fluctuating force.

Based on the above results, a Fokker-Planck equation can be obtained for the velocity of a Brownian particle. Now the stochastic variable is the velocity of the particle, and

$$a(v_0, t) = \int dv (v - v_0) P(v, t|v_0, 0) = \langle v(t)\rangle - v_0;$$
$$b(v_0, t) = \int dv \frac{(v - v_0)^2}{2} P(v, t|v_0, 0) = \frac{\langle v^2(t)\rangle - v_0^2}{2}.$$

From the short time behaviors:

$$\langle v(t)\rangle - v_0 \simeq -\frac{\gamma t}{m} v_0;$$
$$\langle v^2(t)\rangle - v_0^2 \simeq \frac{\Gamma t}{m^2},$$

we have

$$A(v) = -\frac{\gamma}{m} v;$$
$$B(v) = \frac{\Gamma}{2m^2},$$

and the corresponding Fokker-Planck equation

$$\frac{\partial}{\partial t} p_1(v, t) = \frac{\gamma}{m}\frac{\partial}{\partial v}[v p_1(v, t)] + \frac{\Gamma}{2m^2}\frac{\partial^2}{\partial v^2} p_1(v, t) = \frac{\gamma}{m}\left[\frac{\partial}{\partial v}[v p_1(v, t)] + \frac{k_B T}{m}\frac{\partial^2}{\partial v^2} p_1(v, t)\right].$$

The equilibrium velocity distribution $p_1 \propto \exp\left(-\frac{mv^2}{2k_B T}\right)$ may be derived from the stationary solution of the Fokker-Planck equation, which satisfies

$$v p_1(v, t) + \frac{k_B T}{m}\frac{\partial}{\partial v} p_1(v, t) = 0.$$

B. Diffusion of a Brownian particle

The Langevin equation can also be used to investigate the diffusion of a Brownian particle in real space. Multiplying the Langevin equation by q yields

$$mq\frac{d^2 q}{dt^2} = -\gamma q\frac{dq}{dt} + q\zeta(t),$$

which may be rewritten as

$$m\left[\frac{1}{2}\frac{d^2}{dt^2}q^2-\left(\frac{dq}{dt}\right)^2\right]=-\frac{\gamma}{2}\frac{d}{dt}q^2+q\zeta(t).$$

Taking the time average, we have

$$m\left[\frac{1}{2}\frac{d^2}{dt^2}\langle q^2\rangle-\left\langle\left(\frac{dq}{dt}\right)^2\right\rangle\right]=-\frac{\gamma}{2}\frac{d}{dt}\langle q^2\rangle+\langle q\zeta(t)\rangle.$$

Using $\langle(dq/dt)^2\rangle = k_BT/m$ (equipartition) and $\langle q\zeta(t)\rangle = \langle q\rangle\langle\zeta(t)\rangle = 0$ (q and ζ uncorrelated), we have

$$\frac{1}{2}\frac{d^2}{dt^2}\langle q^2\rangle-\frac{k_BT}{m}=-\frac{\gamma}{2m}\frac{d}{dt}\langle q^2\rangle.$$

Let $D=\frac{1}{2}\frac{d}{dt}\langle q^2\rangle$, then

$$\frac{dD}{dt}-\frac{k_BT}{m}=-\frac{\gamma D}{m},$$

whose solution is given by

$$D=\frac{k_BT}{\gamma}+Ce^{-\gamma t/m},$$

where C is a constant. We are not interested in the transient period. For $t \gg m/\gamma$, $D = k_BT/\gamma$ and

$$\langle q^2\rangle = 2Dt=\frac{2k_BT}{\gamma}t.$$

For a sphere of radius R, Stokes' law gives

$$\gamma = 6\pi\eta R,$$

where η is the viscosity of the fluid, and correspondingly,

$$\langle q^2\rangle = 2Dt=\frac{k_BT}{3\pi\eta R}t,$$

as given originally by Einstein.

C. Connection with the diffusion equation

If $\mathbf{J}_n$ is the particle current density and n the particle concentration, diffusion is described by Fick's law

$$\mathbf{J}_n = -D\nabla n,$$

where D is the *diffusivity*. The conservation equation

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J}_n = 0$$

then leads to the diffusion equation

$$\frac{\partial n}{\partial t} = D\nabla^2 n,$$

which becomes

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}.$$

in one dimensional space.

Consider the initial condition $n(x,0) = N\delta(x)$ in an infinite medium: there are N particles concentrated at $x = 0$ when $t = 0$. Solving the one-dimensional diffusion equation subject to this initial condition gives

$$n(x,t) = \frac{N}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right),$$

from which the mean square displacement is obtained as

$$\langle x^2 \rangle = \frac{1}{N}\int x^2 n(x,t)dx = 2Dt.$$

Comparing this equation with $\langle q^2 \rangle = 2k_B Tt/\gamma$ derived from the Langevin equation, we obtain the diffusivity for the Brownian particle:

$$D = \frac{k_B T}{\gamma},$$

which is known as the Einstein relation.

In the presence of an external force field, there is a drift velocity

$$\mathbf{v}_d = -\frac{1}{\gamma}\nabla V,$$

which is attained when the external force is balanced by the frictional force: $-\gamma\mathbf{v}_d - \nabla V = 0$, where V is the external potential. (For a particle of mass m, the time required to reach $\mathbf{v}_d$ is m/γ.) Taking into account this drift velocity, we write the particle current density as

$$\mathbf{J}_n = \mathbf{J}_D + \mathbf{J}_d = -D\nabla n + n\mathbf{v}_d = -D\nabla n - \frac{n}{\gamma}\nabla V,$$

where $\mathbf{J}_D = -D\nabla n$ represents the diffusive current and $\mathbf{J}_d = n\mathbf{v}_d$ represents the contribution due to drift. Given this $\mathbf{J}_n$, the conservation equation leads to

$$\frac{\partial n}{\partial t} = D\nabla^2 n + \frac{1}{\gamma}\nabla \cdot (n\nabla V) \, .$$

This is actually the Fokker-Planck equation for the position of a Brownian particle:

$$\frac{\partial}{\partial t} p_1(\mathbf{r}, t) = -\nabla \cdot [\mathbf{A}(\mathbf{r}) p_1(\mathbf{r}, t)] + B\nabla^2 p_1(\mathbf{r}, t),$$

with $\mathbf{A}(\mathbf{r}) = \mathbf{v}_d$ and $B = D$. The equilibrium distribution $n_e(\mathbf{r}) \propto \exp\left[-\frac{V(\mathbf{r})}{\gamma D}\right]$ is easily derived from the condition $\mathbf{J}_n = -D\nabla n - \frac{1}{\gamma} n\nabla V = 0$. Comparing $n_e(\mathbf{r})$ with the canonical distribution $\exp\left[-\frac{V(\mathbf{r})}{k_B T}\right]$, the relation $\gamma D = k_B T$ is recovered.

D. A remark

Both $\Gamma = 2\gamma k_B T$ and $D = k_B T/\gamma$ show that physical quantities describing fluctuation and dissipation are related. This is not surprising because fluctuation and dissipation effects both arise from the random force exerted by the fluid molecules on the Brownian particle. The viscous drag, as a dissipation effect, may be regarded as the average effect of the random force, and the fluctuating part of the random force causes the diffusion of the Brownian particle. Both ought to be related, because they are both rooted in the random bombardment of the Brownian particle by the fluid molecules.

E. Overdamped harmonic oscillator

Consider a harmonic oscillator governed by the equation of motion:

$$m\frac{d^2 q}{dt^2} + \gamma\frac{dq}{dt} + m\omega_0^2 q = 0,$$

in the presence of the damping force $-\gamma\frac{dq}{dt}$ and the potential force $-m\omega_0^2 q$. If $q \sim e^{-i\omega t}$, then ω is given by

$$\omega = -\frac{i\gamma}{2m}\left(1 \pm \sqrt{1 - \frac{4m^2\omega_0^2}{\gamma^2}}\right) .$$

In the overdamped regime, $\frac{\gamma}{m} \gg \omega_0$, then the two solutions of ω are

$$\omega_p \simeq -i\frac{\gamma}{m}, \quad \omega_q = -i\frac{m\omega_0^2}{\gamma},$$

with $|\omega_p| \gg |\omega_q|$. These two imaginary frequencies correspond to two damping rates $|\omega_p| = \tau_p^{-1}$ and $|\omega_q| = \tau_q^{-1}$, respectively. The first damping rate, τ_p^{-1}, is very large, representing a rapidly decaying transient; the second damping rate, τ_q^{-1}, is very small, representing a slow, relaxational process in which the damping force $-\gamma\frac{dq}{dt}$ and the potential force $-m\omega_0^2 q$ are balanced, with inertia playing an insignificant role. Physically, $\tau_p = \frac{m}{\gamma}$ is the characteristic time for the relaxation of particle momentum p, derived from $\frac{dp}{dt} = -\frac{\gamma}{m}p$; $\tau_q = \frac{\gamma}{m\omega_0^2}$ is the characteristic time for the relaxation of particle position q, derived from $\gamma\frac{dq}{dt} = -m\omega_0^2 q$. Given the very large difference between the two characteristic time scales, we can neglect the rapidly decaying transient associated with momentum relaxation and use $\gamma\frac{dq}{dt} = -m\omega_0^2 q$ to describe the slow particle motion.

F. Two Fokker-Planck equations

We can derive two Fokker-Planck equations. The first one is given by

$$\frac{\partial}{\partial t}p_1(v,t) = \frac{\gamma}{m}\left[\frac{\partial}{\partial v}\left[vp_1(v,t)\right] + \frac{k_B T}{m}\frac{\partial^2}{\partial v^2}p_1(v,t)\right],$$

which describes the fast relaxation of velocity distribution toward the equilibrium distribution $\exp\left(-\frac{mv^2}{2k_B T}\right)$. The second one is given by

$$\frac{\partial}{\partial t}n(q,t) = \frac{1}{\gamma}\frac{\partial}{\partial q}\left[n(q,t)\frac{\partial V(q)}{\partial q}\right] + D\frac{\partial^2}{\partial q^2}n(q,t),$$

which describes the slow relaxation of space distribution toward the equilibrium distribution $\exp\left[-\frac{V(q)}{\gamma D}\right]$, where $V(q)$ is the external potential and $\gamma D = k_B T$. It corresponds to the overdamped Langevin equation

$$\gamma\frac{dq}{dt} = -\frac{\partial V(q)}{\partial q} + \zeta(t),$$

with $\langle\zeta(t_2)\zeta(t_1)\rangle = 2\gamma k_B T\delta(t_2 - t_1)$.

G. Generalization to multi-dimensional space

Consider a system described by the generalized coordinates $\mathbf{q} = \{q_i\}$, $i = 1, 2, \cdots, N$, and governed by the overdamped Langevin equation

$$\gamma \frac{dq_i}{dt} = -\nabla_i V(\mathbf{q}) + \zeta_i(t), \tag{1}$$

where γ is the frictional coefficient, $\nabla_i = \partial/\partial q_i$, and $\zeta_i(t)$ is a white noise satisfying $\langle \zeta_i(t)\zeta_j(t')\rangle = 2\gamma k_B T \delta_{ij}\delta(t-t')$. The Fokker-Planck equation corresponding to the N-dimensional overdamped Langevin equation is given by

$$\frac{\partial n}{\partial t} = -\nabla \cdot \mathbf{J}_n = \frac{1}{\gamma}\nabla \cdot (n\nabla V) + \frac{k_B T}{\gamma}\nabla^2 n,$$

where the current $\mathbf{J}_n$ is of the form

$$\mathbf{J}_n = \mathbf{J}_d + \mathbf{J}_D = n\mathbf{v}_d - D\nabla n = -\frac{n}{\gamma}\nabla V - \frac{k_B T}{\gamma}\nabla n,$$

in which $\mathbf{J}_d = n\mathbf{v}_d$ represents the contribution due to the potential force, $\mathbf{J}_D = -D\nabla n$ represents the diffusive current caused by the random force.