

Brownian motion

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Brownian motion describes the erratic motion of a big particle suspended in fluids. Irregular or erratic motion of the big particle (which we call as Brownian particle) is due to the continuous random collision of surrounding fluid particles. Theoretical explanation of Brownian motion was pioneered by Einstein and Smoluchowsky and latter it was developed by Langevin and others. Here we discuss the Langevin approach of Brownian motion.

I. LANGEVIN DESCRIPTION

To write down the Langevin equation for Brownian particle, we consider that mass of Brownian particle is m , and velocity is denoted by $u(t)$ at time t . The force acting on the Brownian particle is assumed to be given by sum of two terms. The first term is frictional force which is proportional to the velocity and acts on opposite direction. This term is deterministic part of the equation. The second term is the stochastic or random force $\xi(t)$. The stochastic force results due to the random collision of surrounding particle. Now we write down the Langevin equation:

$$m \frac{du}{dt} = -\zeta_0 u + \xi(t). \quad (1)$$

In the above equation we have ignored the effect of interaction field term which is also a deterministic part of the equation. The above equation is in the form of first order ordinary differential equation. Next, to solve Eq. (1), we multiply both sides of the equation with the factor $e^{\zeta_0 t}$ and write it as (For simplicity we take mass $m = 1$)

$$\frac{d}{dt}(u(t)e^{\zeta_0 t}) = e^{\zeta_0 t}\xi(t). \quad (2)$$

Integrating the above equation from t_0 to t we obtain:

$$u(t)e^{\zeta_0 t} = u_0 e^{\zeta_0 t_0} + \int_{t_0}^t e^{\zeta_0 \tau} \xi(\tau), \quad (3)$$

where we take initial value of velocity $u(t_0) = u_0$. We write Eq. (3) for the velocity of the particle as

$$u(t) = u_0 e^{-\zeta_0(t-t_0)} + \int_{t_0}^t e^{-\zeta_0(t-\tau)} \xi(\tau) d\tau. \quad (4)$$

To proceed further, we assume, on the basis of the nature of random force (or noise), that noise does not create any net force. Therefore, we write

$$\langle \xi(t) \rangle = 0. \quad (5)$$

Using the above assumption, the average velocity of the particle is obtained as

$$\langle u(t) \rangle = \langle u_0 \rangle e^{-\zeta_0(t-t_0)}. \quad (6)$$

Average velocity at time t decays exponentially from its initial value. The initial directions of the velocity in thermal equilibrium is randomly distributed, i.e., $\langle u_0 \rangle = 0$. Therefore the average velocity, $\langle u(t) \rangle = 0$, for all times. This implies that in thermal equilibrium, there is no net motion for a collection of Brownian particles.

Next to compute the velocity autocorrelation function defined by, $C(t, t') = \langle u(t)u(t') \rangle$, we need to identify the correlation of noise at different times. In the description of Brownian motion, we assume that fluctuating force or noise varies very fast in short time interval in comparison to the velocity of the Brownian particle. In the simplest form, we consider delta correlated white noise defined by

$$\langle \xi(t)\xi(t') \rangle = \bar{D}\delta(t-t'), \quad (7)$$

where \bar{D} is a constant to be determined. Further, we consider that random force $\xi(t)$ does not affect the velocity $u(t')$ of the Brownian particle, where $t > t'$, which is the causality condition. Thus we write

$$\langle \xi(t)u(t') \rangle = 0. \quad (8)$$

The velocity correlation function at two different time is given by

$$\begin{aligned} C(t, t') &= \langle v_0^2 \rangle e^{-\zeta_0(t-t'-2t_0)} \\ &+ \int_{t_0}^t d\tau \int_{t_0}^{t'} d\tau' e^{-\zeta_0(t-\tau)} e^{-\zeta_0(t'-\tau')} \langle \xi(\tau)\xi(\tau') \rangle. \end{aligned} \quad (9)$$

Using Eq. (7) we obtain

$$\begin{aligned} C(t, t') &= C(t_0, t_0) e^{-\zeta_0(t-t'-2t_0)} \\ &+ \bar{D} \int_{t_0}^t d\tau \int_{t_0}^{t'} d\tau' e^{-\zeta_0(t-\tau)} e^{-\zeta_0(t'-\tau')} \delta(\tau - \tau'), \end{aligned} \quad (10)$$

evaluating the τ, τ' intergal (evaluation is done in Appendix A), we obtain the following reation

$$C(t, t') = \frac{\bar{D}}{2\zeta_0} e^{-\zeta_0|t-t'|} + e^{-\zeta_0(t+t'-2t_0)} \left[C(t_0, t_0) - \frac{\bar{D}}{2\zeta_0} \right]. \quad (11)$$

If we assume that Brownian particle system is in equilibrium at temperature T , initial velocity distribution follow Maxwell-Boltzmann statistics. Thus we obtain the equal time velocity-correlation function as

$$C(t_0, t_0) = \langle v_0^2 \rangle = k_B T, \quad (12)$$

where mass m is taken to be unity. To obtain the equal time velocity correlation, we write Eq. (11) for the case $t = t'$ as

$$C(t, t) = \frac{\bar{D}}{2\zeta_0} + e^{-2\zeta_0(t-t_0)} \left[k_B T - \frac{\bar{D}}{2\zeta_0} \right]. \quad (13)$$

In equilibrium state, $C(t, t)$ should be time independent satisfying the following condition

$$k_B T - \frac{\bar{D}}{2\zeta_0} = 0. \quad (14)$$

Using the above condition we obtain \bar{D} as

$$\bar{D} = 2\zeta_0 k_B T. \quad (15)$$

Therefore noise correlation (7), using the relation (15), is given by

$$\langle \xi(t)\xi(t') \rangle = 2\zeta_0 k_B T \delta(t - t'). \quad (16)$$

In the long time limit (for large t and t'), Brownian particle equilibrates at temperature T and Eq. (11) becomes independent of the initial time t_0 giving the following relation for the velocity autocorrelation function as

$$C(t, t') = k_B T e^{-\zeta_0|t-t'|}. \quad (17)$$

The above equation depends on time difference between t and t' and hence is time translation invariant.

II. THE ROOT MEAN SQUARE DISPLACEMENT AND STOKES-EINSTEIN RELATION

The root mean square (rms) displacement of the Brownian particle can be obtained by integrating the velocity correlation function defined in Eq. (17) with respect to time. Now using the definition of velocity $u = dx/dt$, we write Eq. (17) in the following form

$$\left\langle \frac{d}{dt}x(t) \frac{d}{dt'}x(t') \right\rangle = k_B T e^{-\zeta_0 |t-t'|}. \quad (18)$$

Next, we Integrate the above equation at time t and t' obtaining the following relation

$$\langle \Delta(t) \Delta(t') \rangle = k_B T \int_{t_0}^t d\tau \int_{t_0}^{t'} d\tau' e^{-\zeta_0 |\tau-\tau'|}, \quad (19)$$

where we have defined $\Delta(t) = (x(t) - x(t_0))$. Integral on the right hand side of the above equation is evaluated in the Appendix A, we obtain rms displacement of the particle as

$$\begin{aligned} \langle \Delta(t) \Delta(t') \rangle = k_B T \zeta_0^{-1} & \left[t + t' - |t - t'| - 2t_0 + \right. \\ & \left. \zeta_0^{-1} \left(e^{-\zeta_0(t-t_0)} + e^{-\zeta_0(t'-t_0)} - e^{-\zeta_0(t'-t)} - 1 \right) \right]. \end{aligned} \quad (20)$$

For the equal time case $t = t'$, we obtain

$$\langle \Delta^2(t) \rangle = 2k_B T \zeta_0^{-1} \left[t - t_0 \zeta_0^{-1} \left(e^{-\zeta_0(t-t_0)} - 1 \right) \right]. \quad (21)$$

Now we discuss two limiting cases of the above equation:

Case-I: Assume the very short time such that $\zeta_0^{-1}(t - t_0) \ll 1$, the rms displacement of the particle is obtained as

$$\langle (x(t) - x(t_0))^2 \rangle^{1/2} = (k_B T)^{1/2} (t - t_0) = u_0 (t - t_0). \quad (22)$$

The above relation shows that the rms displacement is linearly proportional to time. This implies that at very short times of motion of the particle corresponds to free particle behavior.

Case-II: Next, if we take long-time limit such that $\zeta_0^{-1}(t - t_0) \gg 1$, we obtain

$$\langle (x(t) - x(t_0))^2 \rangle = 2k_B T \zeta_0^{-1} (t - t_0) = 2D_0 (t - t_0), \quad (23)$$

which indicates that the mean square displacement has linear dependence with time. We call this the Einstein relation. The relation between diffusion coefficient D_0 and frictional

coefficient ζ_0 is given as $D_0 = k_B T \zeta_0^{-1}$. Now using Stokes' law $\zeta_0 = 6\pi r \eta_0$, where r is the radius of the Brownian particle and η_0 is the shear viscosity of the surrounding liquid, we obtain the relation between viscosity and the diffusion coefficient D_0 as

$$D_0 = \frac{k_B T}{6\pi r \eta_0}, \quad (24)$$

which is termed as the Stokes-Einstein relation. This relation indicates that Diffusion coefficient \bar{D} and the viscosity η_0 are inversely proportional to each other. .

Appendix A: velocity-correlation integral evaluation

We evaluate here the integral (here we denote it by ϕ_B) in the Eq. (9).

$$\begin{aligned}
\phi_B &= \bar{D} \int_{t_0}^t d\tau \int_{t_0}^{t'} d\tau' e^{-\zeta_0(t-\tau)} e^{-\zeta_0(t'-\tau')} \delta(\tau - \tau') \\
&= \bar{D} \left\{ \theta(t-t') \int_{t_0}^{t'} d\tau' e^{-\zeta_0(t+t'-2\tau')} + \theta(t'-t) \int_{t_0}^t d\tau e^{-\zeta_0(t+t'-2\tau)} \right\} \\
&= \frac{\bar{D}}{2\zeta_0} e^{-\zeta_0(t+t')} \left\{ \theta(t-t') (e^{2\zeta_0 t'} - e^{2\zeta_0 t_0}) + \theta(t'-t) (e^{2\zeta_0 t} - e^{2\zeta_0 t_0}) \right\} \\
&= \frac{\bar{D}}{2\zeta_0} \left\{ e^{\zeta_0|t-t'|} + e^{-\zeta_0(t+t'-2t_0)} \right\}. \tag{A1}
\end{aligned}$$

Here $\theta(t)$ the Heaviside step function.

Next, we take the integral defined in Eq. (19)

$$\begin{aligned}
\langle \Delta(t)\Delta(t') \rangle &= \int_{t_0}^t d\tau \int_{t_0}^{t'} d\tau' e^{-\zeta_0|\tau-\tau'|} \\
&= \theta(t-t') \int_{t_0}^{t'} d\tau \left\{ \int_{t_0}^{\tau} d\tau' e^{-\zeta_0(\tau-\tau')} + \int_{\tau}^{t'} d\tau' e^{-\zeta_0(\tau'-\tau)} \right\} \\
&\quad + \theta(t'-t) \int_{t_0}^t d\tau \left\{ \int_{t_0}^{\tau} d\tau' e^{-\zeta_0(\tau-\tau')} + \int_{\tau}^{t'} d\tau' e^{-\zeta_0(\tau'-\tau)} \right\} \\
&= \theta(t-t') \left[\zeta_0^{-1} \left\{ e^{-\zeta_0(t-t_0)} + e^{-\zeta_0(t'-t_0)} - e^{\zeta_0|t-t'|} - 1 \right\} + 2(t'-t_0) \right] \\
&\quad + \theta(t'-t) \left[\zeta_0^{-1} \left\{ e^{-\zeta_0(t-t_0)} + e^{-\zeta_0(t'-t_0)} - e^{\zeta_0|t-t'|} - 1 \right\} + 2(t-t_0) \right] \\
&= 2t'\theta(t-t') + 2t\theta(t'-t) - 2t_0 \\
&\quad + \zeta_0^{-1} \left\{ e^{-\zeta_0(t-t_0)} + e^{-\zeta_0(t'-t_0)} - e^{\zeta_0|t-t'|} - 1 \right\} \\
&= (t+t'-|t-t'| - 2t_0) \\
&\quad + \zeta_0^{-1} \left(e^{-\zeta_0(t-t_0)} + e^{-\zeta_0(t'-t_0)} - e^{-\zeta_0(t'-t)} - 1 \right) \tag{A2}
\end{aligned}$$

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- [1] Investigations on the theory of the Brownian movement. A. Einstein edited by R. Furth translated by A. D. Gowper
- [2] S. Chandrasekhar, Rev. Mod. Phys. **21**, 383 (1949).