Computer simulation of Brownian motion

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Summary

1) Stochastic process

Consider a steady stochastic process $Y(t)$ with $\langle Y(t) \rangle = 0$.

Fourier transformation

$$\tilde{Y}_T(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} Y_T(t) \tag{1}$$

Inverse Fourier transformation

$$Y_T(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} \tilde{Y}_T(\omega), \tag{2}$$

where

$$\begin{aligned} Y_T(t) &= Y(t) \quad && (|t| \le T/2) \\ Y_T(t) &= 0 && (|t| > T/2) \end{aligned} \tag{3}$$

The following equations can be derived.

I) Spectral density:

$$S_Y(\omega) = \lim_{T\to\infty} \frac{1}{T} \left| \tilde{Y}_T(\omega) \right|^2 \tag{4}$$

II) Auto-correlation function:

$$\varphi_Y(t) = \lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{\infty} d\tau\, Y_T(\tau) Y_T(\tau + t) \tag{5}$$

III) Wiener–Khinchin theorem:

$$S_Y(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \varphi_Y(t) \tag{6}$$

$$\varphi_Y(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} S_Y(\omega) \tag{7}$$

2) Brownian motion and the Langevin equation

Suppose a Brownian spherical particle of radius a and mass m is moving in a liquid of viscosity η at a temporal velocity $\mathbf{V}(t)$ under the influence of the random force $\mathbf{F}_R(t)$ due to thermal fluctuation and the external force $\mathbf{F}_{ext}(t)$ acting on the particle. The equation of motion for the Brownian particle can be given by

$$m\frac{d\mathbf{V}}{dt} = -\gamma\mathbf{V} + \mathbf{F}_R + \mathbf{F}_{ext}, \tag{8}$$

where $\gamma = 6\pi\eta a$ (Stokes friction) and $\mathbf{V} = \frac{d\mathbf{R}}{dt}$. Assuming that the particle motion is over dumped $\frac{d\mathbf{V}}{dt} = 0$, one yields the Langevin equation of the form

$$\frac{d\mathbf{R}(t)}{dt} = \frac{1}{\gamma}\mathbf{F}_R + \frac{1}{\gamma}\mathbf{F}_{ext} \tag{9}$$

with

$$\langle \mathbf{F}_R(t) \rangle = 0, \quad \langle \mathbf{F}_R(t)\mathbf{F}_R(t') \rangle = 2\tilde{D}\mathbf{I}\delta(t-t'). \tag{10}$$

When the system is in equilibrium $\mathbf{F}_{ext} = 0$, the following results can be derived.

I) Auto-correlation function for $\mathbf{V}(t)$:

$$\varphi_V(t) = \frac{3\tilde{D}}{\gamma m}\exp\left(-\frac{\gamma}{m}t\right) \tag{11}$$

II) Fluctuation dissipation theorem:

$$\tilde{D} = k_B T\gamma \tag{12}$$

III) Einstein relation, Stokes-Einstein relation:

$$D = \frac{k_B T}{\gamma} = \frac{k_B T}{6\pi\eta a} \tag{13}$$

When the particle is driven by an external force in x-direction $\mathbf{F}_{ext} = F_0\mathbf{e}_x$, the following results can be derived.

IV) Steady drift velocity:

$$\lim_{t\to\infty}\langle V_x(t) \rangle = \frac{F_0}{\gamma} = \frac{DF_0}{k_B T} \tag{14}$$

$$\therefore D = \lim_{t\to\infty}\langle V_x(t) \rangle \frac{k_B T}{F_0} \tag{15}$$

3) Linear response theory and the Green-Kubo formula

I) Linear response theory (LRT):

$$H(t) = H_0, \qquad \langle B \rangle_{H_0} = B_0 \qquad (t < 0) \tag{16}$$

$$\downarrow$$

$$H(t) = H_0 + H'(t), \quad \langle B \rangle_{H_0+H'} = B_0 + \langle \Delta B(t) \rangle_{H_0+H'} \qquad (t \geq 0) \tag{17}$$

When $H'(t) = -AF(t)$,

$$\langle \Delta B(t) \rangle_{H_0+H'} = \int_{-\infty}^{t} ds\, \Phi_{BA}(t-s) F(s) \tag{18}$$

$$\Phi_{BA}(t) = \frac{1}{k_B T} \langle B(\tau + t) \dot{A}(\tau) \rangle_{H_0} \tag{19}$$

II) Application of LRT to drift velocity:

$A \equiv R_x(t), \quad B \equiv V_x(t)$, and $H'(t) = -AF(t) = R_x F_0 \theta(t)$

$$\begin{aligned} \langle \Delta B(t) \rangle_{H_0+H'} &= \langle V_x(t) \rangle_{H_0+H'} \\ &= \frac{F_0}{k_B T} \int_0^t ds\, \langle V_x(\tau + t) V_x(\tau) \rangle_{H_0} \\ &= \frac{F_0}{3k_B T} \int_0^t ds\, \langle \mathbf{V}(\tau + t) \bullet \mathbf{V}(\tau) \rangle_{H_0} \end{aligned} \tag{20}$$

$$\therefore D = \lim_{t \to \infty} \langle V_x(t) \rangle_{H_0+H'} \frac{k_B T}{F_0} = \frac{1}{3} \int_0^{\infty} ds\, \varphi_V(t) \quad \text{(Green-Kubo Formula)} \tag{21}$$