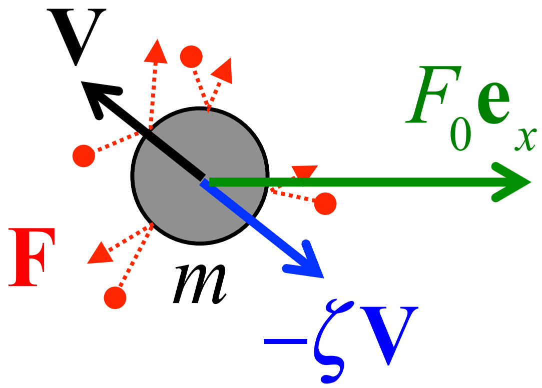
Brownian motion 1: basic theories

Linear response theory and the Green-Kubo formula

Linear response theory and the G-K formula

A Brownian particle under the external force $\mathbf{F}_{ext} = F_0 \mathbf{e}_x$



Langevin Equation:

$$m \frac{d\mathbf{V}}{dt} = -\zeta \mathbf{V} + \mathbf{F} + F_0 \mathbf{e}_x \qquad (41)$$

Linear response theory and the G-K formula

Steady state average under external force, $\lim_{t\to\infty}\langle\cdots\rangle_{ext}$

$$\lim_{t\to\infty}\left\langle\frac{d\mathbf{V}}{dt}\right\rangle_{ext}=(0,0,0)$$

$$\lim_{t\to\infty}\langle\mathbf{V}\rangle_{ext}=\left(\lim_{t\to\infty}\langle V_x\rangle_{ext},0,0\right)$$

$$\lim_{t\to\infty}\langle\mathbf{F}\rangle_{ext}=(0,0,0)$$

$$\lim_{t\to\infty}\langle F_0\mathbf{e}_x\rangle_{ext}=(F_0,0,0)$$

Linear response theory and the G-K formula

Thus, the steady drift velocity:

$$\lim_{t\to\infty}\left\langle V_x \right\rangle_{ext} = \frac{F_0}{\zeta} = \frac{DF_0}{k_B T} \qquad (42)$$

Here we used the Einstein relation Eq. (31) and finally:

$$D = \lim_{t\to\infty}\left\langle V_x \right\rangle_{ext} \frac{k_B T}{F_0} \qquad (43)$$

Linear response theory and the G-K formula

The linear response theory (LRT):

References:

- Barrat and Hansen “Basic concepts for simple and complex liquids” (Cambridge, 2003)
- Zwanzig “Non-equilibrium statistical mechanics” (Oxford, 2001)

Linear response theory and the G-K formula

The linear response theory (LRT):

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H_0 : Equilibrium Hamiltonian

$H_0 + H'(t)$: Hamiltonian under external force $F(t)$ conjugate with A , $H'(t) \equiv -AF(t)$

Linear response theory and the G-K formula

The linear response theory (LRT):

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$\langle B(t) \rangle_{H_0} \equiv B_0$: Average value of B at equilib. under H_0

$$\langle B(t) \rangle_{H_0+H'(t)} \equiv B_0 + \langle \Delta B(t) \rangle_{H_0+H'(t)}$$

: Average value of B at t under $H_0 + H'(t)$

Linear response theory and the G-K formula

For a small external force with $H'(t) = -AF(t)$, the time evolution of B is determined within LRT as:

$$\left\langle \Delta B(t) \right\rangle_{H_0+H'} = \int_{-\infty}^{t} ds\, \Phi_{BA}(t-s) F(s) \qquad (44)$$

Here $\Phi_{BA}(t)$ is the response function, which is defined as the cross correlation function of $\dot{A} \equiv \frac{dA}{dt}$ and B at equilibrium:

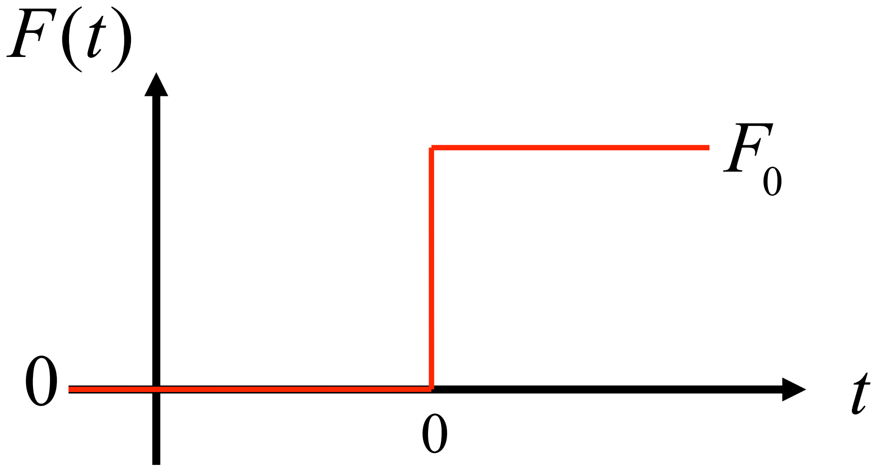
$$\Phi_{BA}(t) = \frac{1}{k_B T} \left\langle B(\tau + t) \dot{A}(\tau) \right\rangle_{H_0} \qquad (45)$$

Linear response theory and the G-K formula

Apply LRT to define self-diffusion constant D using equilibrium correlation function. We assume:

$$A(t) \equiv R_x(t)\,, \quad B(t) \equiv V_x(t)$$

$$F(t) = \Theta(t)\,, \quad H'(t) = -AF(t) = -R_x F_0 \Theta(t)$$

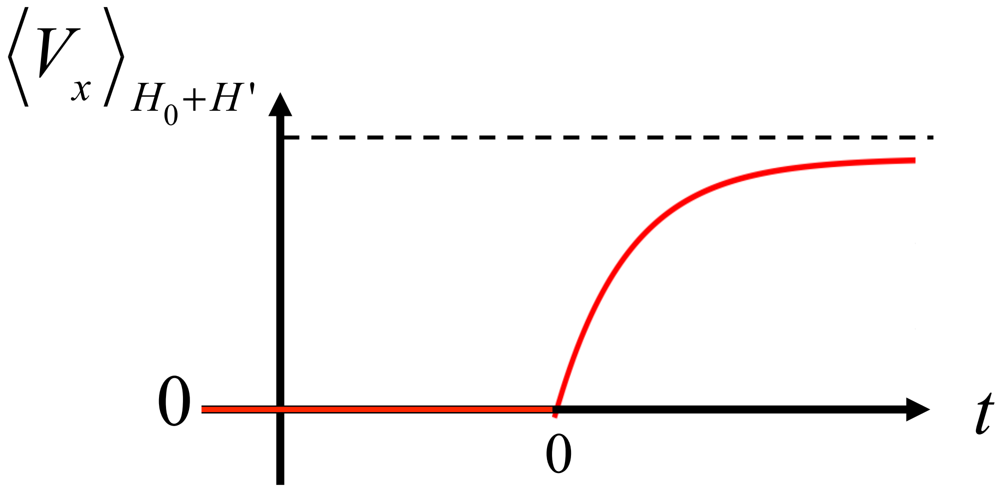


Linear response theory and the G-K formula

From LRT Eqs. (44) and (45):

$$\left\langle \Delta B(t) \right\rangle_{H_0+H'} = \left\langle V_x(t) \right\rangle_{H_0+H'} = \frac{F_0}{k_B T} \int_0^t ds \left\langle V_x(\tau+t-s) V_x(\tau) \right\rangle_{H_0}$$

$$= \frac{F_0}{k_B T} \int_t^0 dt' \frac{ds}{dt'} \left\langle V_x(\tau+t') V_x(\tau) \right\rangle_{H_0} = \frac{F_0}{k_B T} \int_0^t dt' \left\langle V_x(\tau+t') V_x(\tau) \right\rangle_{H_0}$$



$$= \frac{F_0}{3k_B T} \int_0^t dt' \left\langle \mathbf{V}(\tau+t') \cdot \mathbf{V}(\tau) \right\rangle_{H_0}$$

$$(t' \equiv t-s)$$

Linear response theory and the G-K formula

From Eqs. (43) and (46):

$$D = \lim_{t\to\infty} \langle V_x(t) \rangle_{H_0+H'(t)} \frac{k_B T}{F_0}$$

$$= \frac{1}{3} \int_0^\infty dt' \langle \mathbf{V}(\tau + t') \cdot \mathbf{V}(\tau) \rangle_{H_0}$$

$$\boxed{D = \frac{1}{3} \int_0^\infty dt \varphi_V(t)} \qquad (47)$$

(Green-Kubo formula for D)