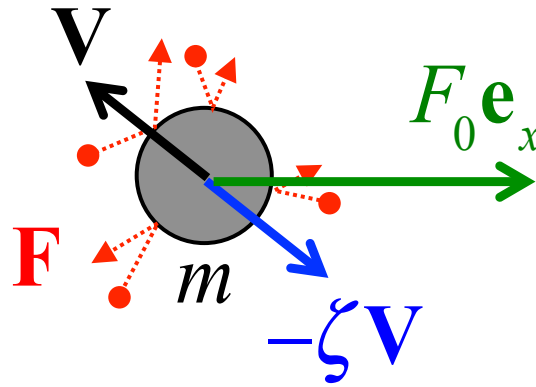


Brownian motion 1: basic theories

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:

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

Linear response theory and the G-K formula

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

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

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

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

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

Linear response theory and the G-K formula

Thus, the steady drift velocity:

$$\lim_{t \rightarrow \infty} \langle V_x \rangle_{ext} = \frac{F_0}{\zeta} = \frac{DF_0}{k_B T} \quad (42)$$

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

$$D = \lim_{t \rightarrow \infty} \langle V_x \rangle_{ext} \frac{k_B T}{F_0} \quad (43)$$

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):

References:

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

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):

References:

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

H_0 : Equilibrium Hamiltonian

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

$\langle B(t) \rangle_{H_0} \equiv B_0$: 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:

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

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:

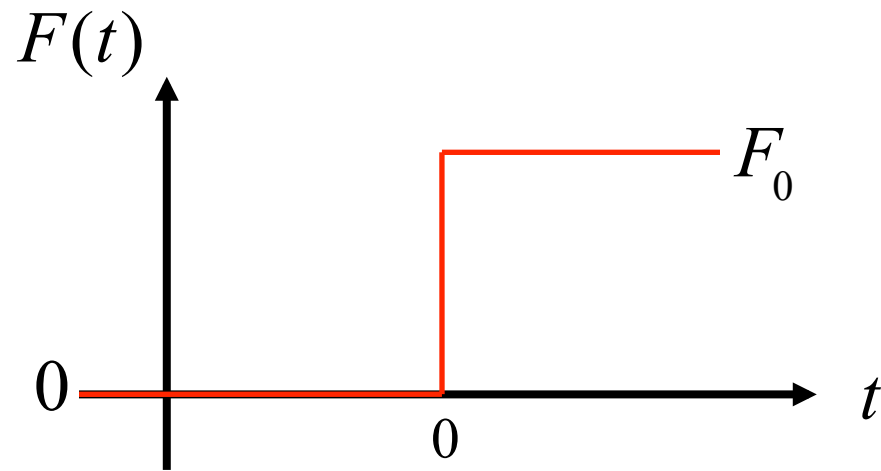
$$\Phi_{BA}(t) = \frac{1}{k_B T} \langle B(\tau+t) \dot{A}(\tau) \rangle_{H_0} \quad (45)$$

Linear response theory and the G-K formula

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

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

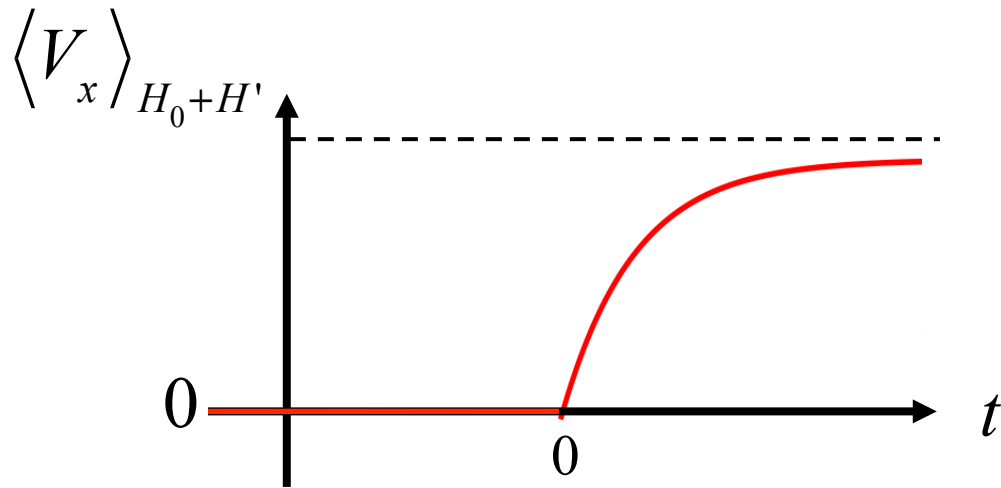
$$F(t) = \Theta(t), \quad H'(t) = -AF(t) = -R_x F_0 \Theta(t)$$



Linear response theory and the G-K formula

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

$$\begin{aligned}\langle \Delta B(t) \rangle_{H_0+H'} &= \langle V_x(t) \rangle_{H_0+H'} = \frac{F_0}{k_B T} \int_0^t ds \langle V_x(\tau + t - s) V_x(\tau) \rangle \\ &= \frac{F_0}{k_B T} \int_t^0 dt' \frac{ds}{dt'} \langle V_x(\tau + t') V_x(\tau) \rangle = \frac{F_0}{k_B T} \int_0^t dt' \langle V_x(\tau + t') V_x(\tau) \rangle_{H_0}\end{aligned}$$



Linear response theory and the G-K formula

From Eqs. (43) and (46):

$$\begin{aligned} D &= \lim_{t \rightarrow \infty} \left\langle V_x(t) \right\rangle_{H_0 + H'(t)} \frac{k_B T}{F_0} \\ &= \frac{1}{3} \int_0^\infty dt' \left\langle \mathbf{V}(\tau + t') \cdot \mathbf{V}(\tau) \right\rangle_{H_0} \end{aligned}$$

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

(47)

(Green-Kubo formula for D)