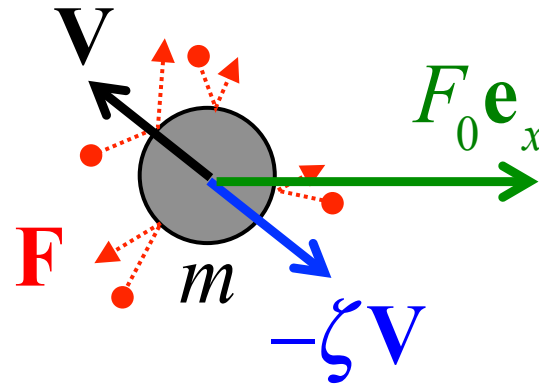


# Brownian motion 1: basic theories

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:

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

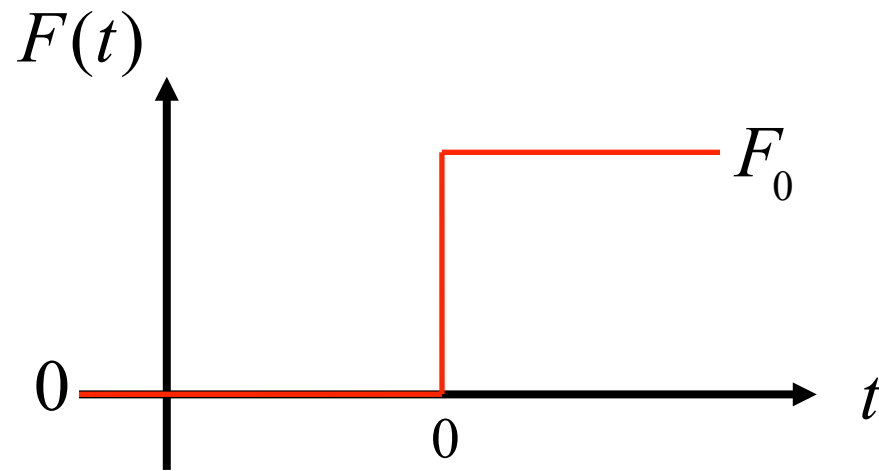


# Linear response theory and the G-K formula

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

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

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



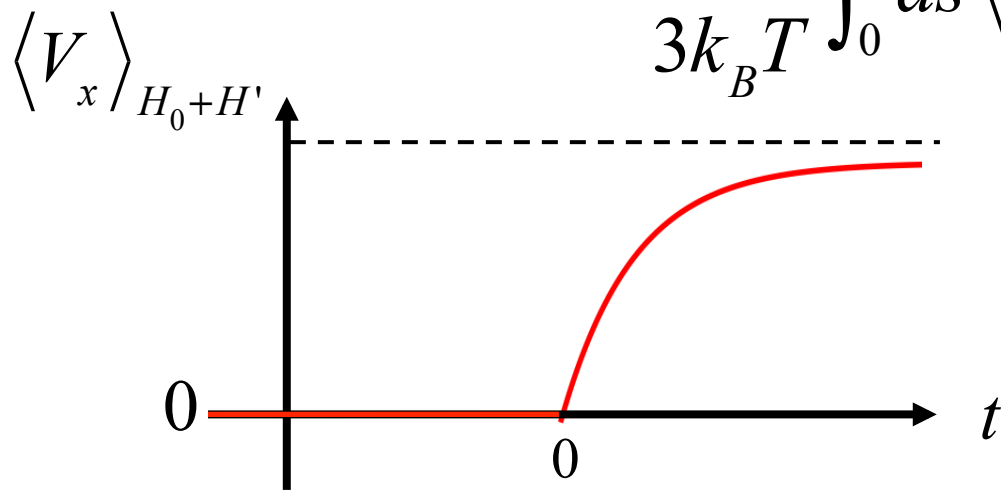
# Linear response theory and the G-K formula

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

$$\langle \Delta B(t) \rangle_{H_0+H'} = \langle V_x(t) \rangle_{H_0+H'}$$

$$= \frac{F_0}{k_B T} \int_0^t ds \langle V_x(\tau+t) V_x(\tau) \rangle_{H_0}$$

$$= \frac{F_0}{3k_B T} \int_0^t ds \langle \mathbf{V}(\tau+t) \cdot \mathbf{V}(\tau) \rangle_{H_0} \quad (46)$$



# 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  $D$ )