MARKOV CHAINS:

Convergence to the stationary distribution $\vec{w}^{(1)}$

$$W \vec{w}^{(1)} = \vec{w}^{(1)}$$

general initial condition $\vec{p}(0) = \sum_k \alpha_k \vec{w}^{(k)}$

right eigenvectors

$$\vec{p}(t) = W^t \vec{p}(0) \xrightarrow[t \to \infty]{} \alpha_1 \vec{w}^{(1)}$$

$$\underline{\alpha_1 = 1} \qquad \alpha_k = \vec{w}_e^{(k)} \cdot \vec{p}(0) = \underline{\underline{\sum_i (w_{e,i}^{k})^* p_i(0)}}$$

left eigenvectors

$$\boxed{\vec{w}_e^{(k)} \cdot w^{(j)} = \delta_{kj}}$$

— orthonormalization for vectors

$\vec{w}^{(1)}$ is a stochastic vector $\longrightarrow \sum_i w_i^{(k)} = 1$

For $\lambda^{(1)} = 1 \to \boxed{w_{e,i}^{(1)} = 1}$

$$\sum_i w_{e,i}^{(1)} W_{ij} = w_{e,j}^{(1)}$$

$$\parallel$$

$$\sum_i W_{ij} = 1$$

$$\sum_i \underbrace{(w_{e,i}^{(1)})^*}_{=1} \cdot w_i^{(1)} = \sum_i w_i^{(1)} = 1$$

$$\underline{\alpha_1 = \sum_i p_i(0) = 1}$$

Detailed balance ⟷ microscopic reversibility ⟷ thermodyn. equilibrium

in the context of:

Langevin eq. with an ext. potential $U(x)$

$$m\ddot{x}(t) = -U'(x) - \tilde{\gamma}\,\dot{x}(t) + \tilde{\eta}(t) \qquad \left(\begin{array}{c}\text{Einstein relation} \\ \hat{\Gamma} = 2\tilde{\gamma}T \end{array} \right)$$

$$\langle \tilde{\eta}(t) \rangle = 0 \; ; \; \langle \tilde{\eta}(t)\,\tilde{\eta}(t') \rangle = \tilde{\Gamma}\,\delta(t-t')$$

Discrete state space ; continuous time

Generalized DB: $\vec{p} \to -\vec{p}$ under time reversal

state $\alpha \to (x, p)$ $\qquad \alpha^* = (x, -p)$

state $\beta \to (x', p')$ $\qquad \beta^* = (x', -p')$

$$\boxed{p_\alpha W_{\beta\alpha} = p_{\beta^*} W_{\alpha^*\beta^*}}$$

$dt \ll 1$

$$\longrightarrow \left\{ \begin{array}{l} x(t+dt) = x(t) + p/m\, dt \\ p(t+dt) = p(t) - U'(x)\,dt - \tilde{\gamma}/m\, p(t) + dW \end{array} \right.$$

$$dW = \int_t^{t+dt} \tilde{\eta}(t)\,dt \qquad \text{Wiener process}$$

dW is Gaussian stoch. var. with zero average and variance $\tilde{\Gamma}\,dt$

$$W_{\beta\alpha} = \delta\left(x' - x - p/m\, dt\right) \cdot \frac{1}{\sqrt{2\pi\tilde{\Gamma}\, dt}}\, \exp\left(-\frac{\big(\overbrace{p' - p + U'(x)\,dt + \tilde{\gamma}\frac{p}{m}\,dt}^{dW}\big)^2}{2\tilde{\Gamma}\, dt}\right)$$

forward transition ($\alpha \to \beta$)

$$W_{\alpha^*\beta^*} = \delta\left(x - x' + p'/m\, dt\right) \cdot \frac{1}{\sqrt{2\pi\tilde{\Gamma}\, dt}}\, \exp\left(-\frac{\left(p' - p + U'(x')\,dt - \tilde{\gamma}\frac{p'}{m}\,dt\right)^2}{2\tilde{\Gamma}\, dt}\right)$$

backward transition ($\beta^* \to \alpha^*$)

$$x' - x \sim dt \quad ; \quad p' - p' \sim \sqrt{dt} \quad (\sim dW)$$

$$\frac{W_{\beta\alpha}}{W_{\alpha^*\beta^*}} \left(= \frac{P_{\beta^*}}{P_\alpha} \,?\right) = \exp\left\{\frac{\tilde{\gamma}}{\tilde{\Gamma}}\left(\underbrace{\frac{p^2 - p'^2}{2m}}_{\sim\sqrt{dt}} - \frac{2p}{m}U'(x)\,dt + \dots\right)\right\}$$

neglecting terms $\mathcal{O}(dt^{3/2})$

$$\frac{p}{m}U'(x)\,dt$$

$$\parallel$$

$$\cancel{\frac{p}{m}}\, \frac{U(x+dx) - U(x)}{\cancel{dx}}\, \cancel{dt} = U(x') - U(x)$$

$$\boxed{E(\alpha) = p^2/2m + U(x)} \qquad \left(\begin{array}{l} E(\alpha^*) = E(\alpha) \\ E(\beta^*) = E(\beta) \end{array}\right)$$

$$\frac{W_{\beta\alpha}}{W_{\alpha^*\beta^*}} = \exp\left\{\frac{2\tilde{\gamma}}{\tilde{\Gamma}}\big(E(\alpha) - E(\beta)\big)\right\} = P_{\beta^*}/P_\alpha$$

Boltzmann distrib. $\to P_\alpha(x,p) \propto \exp\left(-\frac{E(\alpha)}{k_B T}\right) \to \boxed{k_B T = \frac{\tilde{\Gamma}}{2\tilde{\gamma}}}$

Fluctuation-dissipation theorem and linear response theory

Transport coefficients ⟶ current-current equilibrium auto-correlation function

diffusion coeff. ⟶ particle current
thermal conductivity ⟶ energy (heat) current
magnetic susceptibility ⟶ magnetization current
viscosity ⟶ momentum current

- general thermodynamic formalism for thermal noise (Langevin, Fokker-Planck)

hydrodynamics (continuity equations & conserved quantities)

- Linear response to small perturbations

Response to small perturbations = response to thermal fluctuations in equilibrium

⟶ Globally out-of-equilibrium but locally always equilibrium

KUBO relation (1st example of F-D relation involving a current)

Brownian particle (D as vel-vel correl. function)

FP for free Brownian particle (d = 1)

$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2}{\partial x^2} \rho(x,t)$$

$$\langle x^2(t)\rangle - \langle x\rangle^2 \xrightarrow[t\to\infty]{} 2Dt$$

$$\frac{\partial}{\partial t}\int_{-\infty}^{+\infty} x^2 \rho(x,t)\, dx = D\int_{-\infty}^{+\infty} x^2 \frac{\partial^2 \rho(x,t)}{\partial x^2}\, dx$$

by parts ; $x^2 \frac{\partial \rho}{\partial x} \xrightarrow[x\to\pm\infty]{} 0$

$x \frac{\partial \rho}{\partial x} \xrightarrow[x\to\pm\infty]{} 0$

$$\frac{\partial}{\partial t}\langle x^2(t)\rangle = 2D\int_{-\infty}^{+\infty} \rho(x,t)\, dx$$

$$\Rightarrow \boxed{\frac{\partial}{\partial t}\langle x^2(t)\rangle = 2D}$$

(exact result: $\langle x^2(t)\rangle = \langle x^2(0)\rangle + 2Dt$)

$$x(t) = \int_0^t dt'\, v(t') \rightarrow x^2(t) = \int_0^t dt'\, v(t')\int_0^t dt''\, v(t'')$$

$$\frac{\partial x^2(t)}{\partial t} = 2\int_0^t dt'\, v(t')\, v(t)$$

$\langle \cdot \rangle$ = eq. therm. average

$$\frac{\partial}{\partial t}\langle x^2(t)\rangle = 2\int_0^t dt' \langle v(t')\, v(t)\rangle$$

at equilib. → time translation invariance

$$= 2\int_0^t dt' \langle v(0)\, v(t-t')\rangle$$

$$\boxed{\frac{\partial}{\partial t}\langle x^2(t)\rangle = 2\int_0^t d\tau \,\langle v(\tau)\, v(0)\rangle} \qquad \tau = t - t'$$

$$\boxed{D = \lim_{t\to\infty} \int_0^t d\tau \,\langle v(\tau)\, v(0)\rangle} \rightarrow \text{holds for F-P for Langevin eq.}$$

(↳ estimate of D from numerical simulations

KUBO relation

Generalized Brownian motion (F.P. or L. formalism)

(thermal) fluctuation driven time evolution of

(any macroscopic thermodynamic observable X

at or "close" to thermal eq. at T

$X(t)$ fluctuates in time around eq. value X^*

Equilibrium → interactions with large number of microscopic degrees of freedom

Fluctuations vanish in the thermodyn. limit

$(N_A \approx 10^{23})$ independent stochastic variables

$$\Delta X = |X - X^*| \sim 1/\sqrt{N}$$

Central limit theorem

⇒ Generalized Brownian motion is possible only for finite systems!