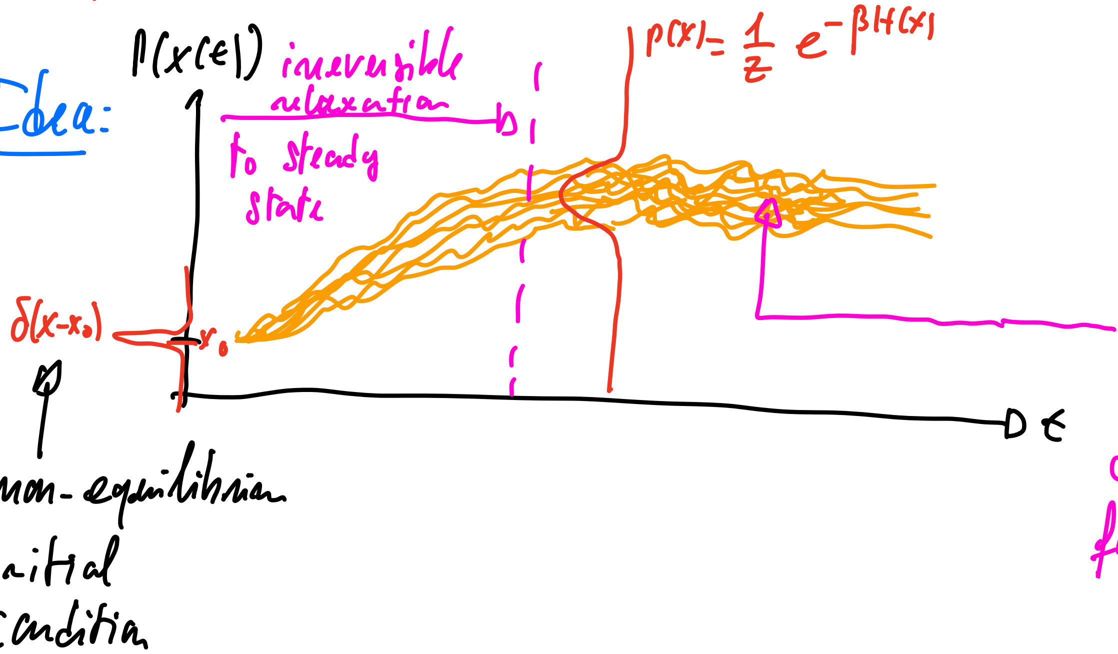
Chapter 4) Time Reversal Symmetry

Idea:



statistically reversible system: you cannot distinguish a recording of the dynamics played forward or backward.

TRS implies $P(x,t;x_0,t_0) = P(x_0,t;x,t_0)$ for $t_0 < t$ (1)

If $\partial_t P = -HP$ then $P(x,t|x_0,0) = \langle x| e^{-tH} |x_0\rangle$ (2)

measure the probability in x — evolve for a time t — start here

then (1) $\Leftrightarrow$ $\langle x| e^{-(t-t_0)H} |x_0\rangle P(x_0,t_0) = \langle x_0| e^{-(t-t_0)H} |x\rangle P(x,t_0)$

Holds $\forall x, x_0$, so that TRS $\Rightarrow$ $\boxed{H_{FP} = P_s H_{FP}^\dagger P_s^{-1} \quad \text{or} \quad H_{FP}^\dagger = P_s^{-1} H_{FP} P_s}$ (3)

Comments: This is an operator equality, it means that, $\forall f(x)$

$$H_{FP} f(x) = P_s H_{FP}^\dagger P_s^{-1} f(x)$$

Overdamped Brownian dynamics

Let us show that (3) holds for $H_{FP} = -\frac{\partial}{\partial x}\left[kT \frac{\partial}{\partial x} + V'(x)\right]$ and

$P_{st}(x) = \frac{1}{Z} e^{-\beta V(x)}$. Let's use that $\frac{\partial}{\partial x}\left(g(x) f(x)\right) = g'(x) f(x) + g(x) \frac{\partial}{\partial x} f(x)$

$$= \left(g'(x) + g(x)\frac{\partial}{\partial x}\right) f(x) \quad (4)$$

$$P_s^{-1} H_{FP} P_s f = \frac{P_s^{-1}}{Z} \frac{\partial}{\partial x}\left[kT \frac{\partial}{\partial x} + V'(x)\right] \underbrace{e^{-\beta V(x)}}_{g} f(x)$$

$$\overset{(4)}{=} \frac{P_s^{-1}}{Z} \frac{\partial}{\partial x} \underbrace{e^{-\beta V}}_{g} \left[\cancel{\overbrace{-V'(x)}^{kT g'/g}} + kT \frac{\partial}{\partial x} + \cancel{V'(x)}\right] f(x)$$

$$= \underbrace{\frac{P_s^{-1}}{Z} e^{-\beta V}}_{1} \left[-\beta V'(x) + \frac{\partial}{\partial x}\right] kT \frac{\partial}{\partial x} f(x)$$

$$= \left[V' - kT \frac{\partial}{\partial x}\right]\left(-\frac{\partial}{\partial x}\right) f(x) = \left[V'(x) + kT\frac{\partial}{\partial x}\right]^{\dagger} \left[\frac{\partial}{\partial x}\right]^{\dagger} f(x)$$

$$= \left[\frac{\partial}{\partial x}\left(kT \frac{\partial}{\partial x} + V(x)\right)\right]^{\dagger} f(x) \Rightarrow \boxed{P_s^{-1} H_{FP} P_s = H_{FP}^{\dagger}}$$

For the Brownian equilibrium dynamics, one thus has

$$\rho_s(x_0)\, P(x,t|x_0,0) = \rho_s(x)\, P(x_0,t|x,0),$$

which can be summarized as $P_s(x_0)\, P(x_0 \to x, t) = \rho_s(x)\, P(x \to x_0, t)$ (ΔΔΔ)

(1) is often called a detailed balance relation. (3) is its operatorial form for a Langevin dynamics.

Mapping to Schrödinger's equation:

Let us note that (1) implies that a change of basis can be H_{FP} into a Hermitian form.

$H^h \equiv P_{st}^{-1/2} H_{FP} P_{st}^{1/2}$ is such that

$$(H^h)^\dagger = P_{st}^{1/2} H_{FP}^\dagger P_{st}^{-1/2} = P_{st}^{1/2} P_{st}^{-1} H_{FP} P_{st} P_{st}^{-1/2} = H^h$$

Direct algebra shows that $H^h = -kT\frac{\partial^2}{\partial x^2} + \left[\frac{V'(x)^2}{4kT} - \frac{V''(x)}{2}\right]$, which looks like a Schrödinger operator $H_s = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_s(x)$ up to $\frac{\hbar^2}{2m} = kT$ and $V_s(x) = \frac{V'(x)^2}{4kT} - \frac{V''(x)}{2}$

Proof: $H^h = -\frac{P_s^{-1/2}}{\sqrt{Z}}\frac{\partial}{\partial x}\left[kT\frac{\partial}{\partial x} + V'(x)\right]e^{-\beta\frac{V(x)}{2}} = -\frac{P_s^{-1/2}}{\sqrt{Z}}\frac{\partial}{\partial x}e^{-\beta\frac{V(x)}{2}}\left[-\beta\frac{kT}{2}V'(x) + kT\frac{\partial}{\partial x} + V'(x)\right]$

$$= -\left[-\beta\frac{V'}{2} + \frac{\partial}{\partial x}\right]\left[kT\frac{\partial}{\partial x} + \frac{V'}{2}\right] = -kT\frac{\partial^2}{\partial x^2} + \frac{1}{2}V'\frac{\partial}{\partial x} - \underbrace{\frac{\partial}{\partial x}\frac{V'}{2}}_{\frac{V'}{2}\frac{\partial}{\partial x} + \frac{V''}{2}} + \frac{\beta}{4}(V')^2$$

$$= -kT\frac{\partial^2}{\partial x^2} - \frac{V''(x)}{2} + \frac{\beta}{4}\left[V'(x)\right]^2$$

Consequences for H_{FP} spectrum

H^h is Hermitian $\Rightarrow$ diagonalizable in an orthonormal basis, with a real spectrum.

H^h is H_{FP} in another basis $\Rightarrow$ H_{FP} has a real spectrum & it is also diagonalizable but not in an orthonormal basis.

Comment: All this can be generalized to the case with inertia but it's much more subtle and difficult.

Diagonalization of H_{FP}:

* Eigenbasis $|\psi_R^\alpha\rangle$ such that $H_{FP}|\psi_R^\alpha\rangle = \lambda_\alpha |\psi_\alpha^R\rangle$

  & $\langle\psi_\alpha^L|$ s.t. $\langle\psi_\alpha^L|H_{FP} = \lambda_\alpha \langle\psi_\alpha^L|$ (*)

* Since H_{FP} is not Hermitian $\langle\psi_\alpha^L| \neq |\psi_\alpha^R\rangle^\dagger$

(*) $\Rightarrow H_{FP}^\dagger|\psi_\alpha^L\rangle = \lambda_\alpha^*|\psi_\alpha^L\rangle = \lambda_\alpha|\psi_\alpha^L\rangle$ since $\lambda_\alpha \in \mathbb{R}$

$\Leftrightarrow P_s^{-1} H_{FP} P_s |\psi_\alpha^L\rangle = \lambda_\alpha |\psi_\alpha^L\rangle$

$\Leftrightarrow H_{FP}\underbrace{P_s|\psi_\alpha^L\rangle}_{|\psi_\alpha^R\rangle} = \lambda_\alpha \underbrace{P_s|\psi_\alpha^L\rangle}_{|\psi_\alpha^R\rangle}$

$\Rightarrow |\psi_\alpha^R\rangle = P_s|\psi_\alpha^L\rangle$ & $|\psi_\alpha^L\rangle = P_s^{-1}|\psi_\alpha^R\rangle$

Important example: $|\psi_0^R\rangle = \frac{1}{Z}|e^{-\beta V(x)}\rangle \Rightarrow |\psi_0^L\rangle = |-\rangle$

$\Rightarrow \langle -|H_{FP} = 0$

Conservation of probability $\forall x$ $\int dx\, P(x,t) = 1 = \langle -|P(x)\rangle$

$$\partial_t \int dx\, P(x,t) = \partial_t \langle -|P(x,t)\rangle = -\langle -|H_{FP}|P(x,t)\rangle = 0$$

$\langle -|H_{FP} = 0 \Rightarrow \int dx\, P(x,t)$ is conserved

$\Rightarrow$ mathematical encoding of physical laws.

Symmetry of two-times correlation functions

Take two observables $A(x)$ & $B(x)$, and the corresponding operators

$A|x\rangle = A(x)|x\rangle$ & $B|x\rangle = B(x)|B\rangle$. Take $t > t'$

$$C_{AB}(t,t') = \langle A(t)\, B(t')\rangle = \int dx\,dx'\, A(x)\, B(x')\, P(x,t;x',t')$$
$$= \langle -|\, A\, e^{-(t-t')H}\, B\, e^{-t'H}\, |P_{initial}\rangle$$

Take t' very large $e^{-t'H}|P_{initial}\rangle = |P_s\rangle$

Since the system is in the steady state at t', we expect that time translational invariance imposes $C_{AB}(t,t') = C_{AB}(t-t')$, which can be read in

$$C_{AB}(t,t') = \langle -|\, A\, e^{-(t-t')H}\, B\, |P_s\rangle = C_{AB}(t-t')$$

$A(x), B(x) \in \mathbb{R} \Rightarrow C_{AB} \in \mathbb{R} \Rightarrow C_{AB}^{\dagger} = C_{AB}$

$\Rightarrow C_{AB}(t-t') = \langle P_s|\, B^{\dagger}\, e^{-(t-t')H^{\dagger}}\, A^{\dagger}\, |-\rangle$ using $\left(e^{uH}\right)^{\dagger} = \left(\sum_k \frac{u^k}{k!} H^k\right)^{\dagger} = \sum_k \frac{u^k}{k!} (H^{\dagger})^k$

Since $\langle P_s| = \langle -|\, P_s$, we get

$$C_{AB} = \langle -|\, \underbrace{P_s\, B\, P_s^{-1}}_{\substack{\text{commute}\\ = B P_s P_s^{-1}}}\, e^{-(t-t')H}\, \underbrace{P_s\, A}_{\text{commute}}\, |-\rangle = \langle -|\, B\, e^{-(t-t')H}\, A\, |P_s\rangle$$
$$= C_{BA}$$

$\Rightarrow$ Measuring B and then A or A and then B leads to the same result.

Idea for a numerical project: check this? And its departure from equilibrium?

3) Fluctuation dissipation theorem

Einstein relation $\quad K(t-t') = 2\gamma k_B T\, \delta(t-t')$ (2)

has thus enforced ① the Boltzmann weight
② time-reversal symmetry

For the overdamped Langevin equation, $\dot{x} = \mu f(x) + \sqrt{2\mu kT}\,\eta$, we have

① $f = f_0 \Rightarrow \langle v \rangle = \mu f_0$. The mobility $\mu = \frac{\langle v \rangle}{f_0}$ measures the response of the system to a force f_0

② $f = 0 \Rightarrow \langle x^2 \rangle = 2Dt$ with $D = \mu kT$. The diffusivity characterizes the fluctuations of the system.

$D = \mu kT$ is thus a relation between fluctuations and response.

Let us now show that an equilibrium dynamics admits a much more general relation between fluctuations & response.

Take a small perturbation of the energy of the system.

$E(t) = E - h(t)\,A(x)$; $h(t)$: time-dependent amplitude of the perturbation

Q: What is the consequence for $\langle B(t) \rangle$ where B is any other observable

Response function $R(t-t')$

$$\langle B(t) \rangle_h = \langle B(t) \rangle_{h=0} + \int dt'\, R(t-t')\, h(t') + o(h)$$

Why is this true ??

$\langle B(t) \rangle$ is a functional of $h(t) \Rightarrow$ functional Taylor expansion

$$\langle B(t) \rangle_h \simeq \langle B(t) \rangle_{h=0} + \int dt' \frac{\delta \langle B(t) \rangle}{\delta h(t')} h(t') \quad \text{(functional Taylor)}$$

Morally $t = n\,dt = t_n$

$$\langle B(t_n)\rangle_h \simeq \langle B(t_n)\rangle_{h=0} + \text{"}\sum_{t_p} \frac{\partial \langle B(t_n)\rangle}{\partial h(t_p)} h(t_p)\text{"} + \mathcal{O}(h^2)$$

(Taylor expansion up to $\frac{\delta}{\delta h(n\,dt)} = \frac{1}{dt}\frac{\partial}{\partial h(t_n)}$)

Again equivalent to

"$d\langle B\rangle = \nabla\langle B\rangle \cdot dh$" in a functional space

Note that $\nabla\langle B\rangle$ is independent of dh

$$R(t-t') = \frac{\delta \langle B(t)\rangle}{\delta h(t')}$$ is also independent of h.

$\Rightarrow$ Compute $R(t-t')$ once & predict $\langle B(t)\rangle_h$ for <u>any</u> small $h(t)$.

<u>Comment</u>: Since we neglect correction of order h^2, we speak about linear response.

<u>Q</u>: How can we compute $R(t-t')$? Just have to do it for a wisely chosen $h(t)$!

Take $\left.\begin{array}{ll} h(t) = h_0 & \text{for } t < t' \\ \quad\;\; = 0 & \text{for } t > t' \end{array}\right\}$ ①

$$\langle B(t)\rangle_h = \langle B(t)\rangle_0 + \int_{-\infty}^{t'} ds\, h_0\, R(t-s)$$; we note $\langle\;\rangle_0 = \langle\;\rangle_{h=0}$

$$\frac{\partial}{\partial t'} \langle B(t) \rangle_h = 0 + h_0 R(t-t') \Rightarrow \text{need to compute } \frac{\partial}{\partial t'}\langle B(t)\rangle_h \text{ for (1)}$$

By definition $\langle B(t)\rangle = \langle -| B\, e^{-(t-t')H_{FP}^{0}} |P(t')\rangle$ (Δ) $\leftarrow h=0$

when $H_{FP}^{(0)}$ corresponds to the evolution after t', with $h(s>t')=0$

What is $|P(t')\rangle$? If $t,t' \to \infty$ with $t>t'$, $|P(t')\rangle$ has relaxed to its equilibrium steady state with an energy $E-h_0A$

$$\Rightarrow P(t') = \frac{1}{Z_{h_0}}\, e^{-\beta(E-h_0A)}$$

Small h:
$$\begin{aligned} Z_{h_0}^{-1} &= \left[\int dx\, e^{-\beta(E-h_0A)}\right]^{-1} \simeq \left[\int dx\, e^{-\beta E}(1+\beta h_0 A)\right]^{-1} \\ &= \left[Z_0 + \beta h_0 \frac{Z_0}{Z_0}\int dx\, A e^{-\beta E}\right]^{-1} \quad \text{where } Z_0 = Z(h_0=0) \\ &= Z_0^{-1}\left[1+\beta h_0\langle A\rangle_0\right]^{-1} \quad \text{with } \langle\ldots\rangle_0 \Leftrightarrow \langle\ldots\rangle \text{ with } h_0=0 \\ &\simeq Z_0^{-1}(1-\beta h_0\langle A\rangle_0) \end{aligned}$$

$$\begin{aligned} \Rightarrow P(t') &= Z_0^{-1}(1-\beta h_0\langle A\rangle_0)(1+\beta h_0 A)\, e^{-\beta E} \\ &\simeq P_0(x)\left[1+\beta h_0(A-\langle A\rangle_0)\right] \end{aligned}$$

Back to $\langle B(t)\rangle$ and Eq. (Δ)

$$\begin{aligned} \langle B(t)\rangle &= \langle -|B\, e^{-(t-t')H_{FP}^0}\left[1+\beta h_0(A-\langle A\rangle_0)\right]|P_0\rangle \\ &= \underbrace{\langle -|B\, e^{-(t-t')H^0_{FP}}|P_0\rangle}_{\langle B(t)\rangle_0} + \beta h_0\Big\{\langle -|B\, e^{-(t-t')H^0_{FP}} A|P_0\rangle \\ &\qquad - \langle A\rangle_0 \underbrace{\langle -|B\, \underbrace{e^{-(t-t')H^0_{FP}}|P_0\rangle}_{|P_0\rangle}}_{\langle B\rangle_0}\Big\} \end{aligned}$$

$$\langle B(t)\rangle = \langle B(t)\rangle_0 + \beta h_0 \langle B(t)A(t')\rangle_0 - \beta h_0 \underbrace{\langle B(t)\rangle_0 \langle A(t')\rangle_0}_{=\langle B\rangle\langle A\rangle \text{ steady state}}$$

$$\frac{\partial}{\partial t'}\Big($$

$$h_0 R(t-t') = \beta h_0 \frac{\partial}{\partial t'}\langle B(t)A(t')\rangle = \frac{1}{k_B T} h_0 \frac{\partial}{\partial t'} C_{BA}(t-t') = -\frac{h_0}{k_B T}\frac{\partial}{\partial t} C_{BA}(t-t')$$

Fluctuation-dissipation theorem:

$$\boxed{R_{BA}(t) = -\frac{1}{k_B T}\frac{\partial}{\partial t} C_{BA}(t)} \qquad (\circ)$$

Remarkably: This holds for any pairs of observables A & B

$\Rightarrow$ can be used to measure $k_B T$!

Comment: ① In many non equilibrium systems, people have measured that, for some A & B, $R_{BA} \propto -\frac{\partial}{\partial t} C_{BA}$ and used that to define some effective temperature through

$$R_{BA}(t) = -\frac{1}{k_B T_{eff}}\frac{\partial}{\partial t} C_{BA}(t)$$

In general, T_{eff} is different for different choices of A & B $\Rightarrow$ not universal!