3) The Fokker-Planck operator

$$\partial_t P = \frac{\partial}{\partial x}\left[kT\frac{\partial}{\partial x} - F(x)\right] P(x,t) \quad (1) \iff \partial_t P = -H_{FP} P \text{ where}$$

$$H_{FP} = -\frac{\partial}{\partial x}\left[kT\frac{\partial}{\partial x} - F(x)\right]$$ which acts on the Hilbert space of functions

$\mathcal{H}(P)$ that depends on the dimensions & boundary conditions of the problem.

3.1) Relaxation towards equilibrium

Q: How does a system relax towards equilibrium?

Tentative ansatz: $P(x,t) = e^{-\lambda t} P_0(x)$

(1) $\partial_t P = -H_{FP} P_0(x) e^{-\lambda t} = -\lambda P_0 e^{-\lambda t} \iff H_{FP} P_0(x) = \lambda P_0(x)$

$\to P_0(x)$ is an eigenfunction of H_{FP} & λ is the corresponding eigenvalue.

If H_{FP} is diagonalizable in $\mathcal{H}(P)$, there is a basis $\varphi_\alpha(x)$ of eigenfunctions of H_{FP}, with associated eigenvalues λ_α, such that $H_{FP}\varphi_\alpha(x) = \lambda_\alpha \varphi_\alpha(x)$

Evolution of P

Since φ_α is a basis, any $P(x,t)$ can be written as $P(x,t) = \sum_\alpha c_\alpha(t)\varphi_\alpha(x)$

then $\partial_t P = -H_{FP}\sum_\alpha c_\alpha(t)\varphi_\alpha(x) = -\sum_\alpha c_\alpha(t) H_{FP}\varphi_\alpha(x)$

$$= -\sum_\alpha c_\alpha(t)\lambda_\alpha \varphi_\alpha(x)$$

but also $\partial_t P = \partial_t \sum_\alpha c_\alpha(t)\varphi_\alpha(x) = \sum_\alpha \dot{c}_\alpha(t)\varphi_\alpha(x)$

Since φ_α is a basis, this implies $\dot{c}_\alpha(t) = -\lambda_\alpha c_\alpha(t)$ & $c_\alpha(t) = e^{-\lambda_\alpha t} c_\alpha(0)$

① Take $P_0(x)$

② Expand it as $P_0(x) = \sum_\alpha c_\alpha(0)\, \varphi_\alpha(x)$

③ For all times t, $P(x,t) = \sum_\alpha c_\alpha(0)\, e^{-\lambda_\alpha t}\, \varphi_\alpha(x)$

If you can diagonalize H_{FP} $\Rightarrow$ problem solved!

Comment: . $\mathrm{Re}(\lambda_\alpha) \geq 0$ is required, otherwise $P(x,t)$ blows up as $t \to \infty$.
. The existence of a steady state requires $\mathrm{Inf}(\lambda_\alpha) = \lambda_0 = 0$

Equilibrium dynamics with a confining potential $V(x)$

The Perron Frobenius theorem states that, for a confining potential,

(i) H_{FP} is diagonalizable with $\lambda_\alpha \in \mathbb{R}^+$

(ii) There is a unique ground state such that $\lambda_0 = 0$.

As $t \to \infty$, the contribution of excited states decay exponentially and the system equilibrates: $P(x,t) = \sum_\alpha c_\alpha^0\, e^{-\lambda_\alpha t} \varphi_\alpha(x) \to c_0\, \varphi_0(x)$

Gapped spectrum and relaxation rate

Consider $P(x,0) = c_1 \varphi_1(x) + c_2 \varphi_2(x)$ with $\mathrm{Re}(\lambda_1) < \mathrm{Re}(\lambda_2)$, then

$$P(x,t) = c_1 \varphi_1 e^{-\lambda_1 t} + c_2 \varphi_2 e^{-\lambda_2 t} = c_1 e^{-\lambda_1 t}\Big[\varphi_1 + \underbrace{\frac{c_2}{c_1}\varphi_2 e^{-(\lambda_2-\lambda_1)t}}_{\substack{\to 0 \\ t \gg 1/\lambda_2-\lambda_1}}\Big]$$

φ_2 is forgotten at a typical rate which is $\dfrac{1}{\lambda_2 - \lambda_1}$.

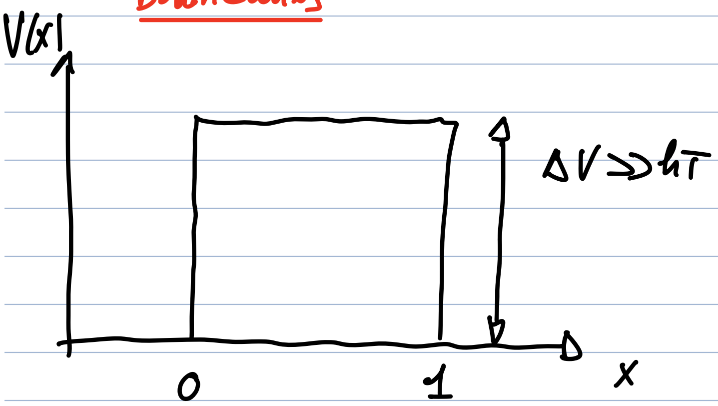
$\Rightarrow$ the typical time scales of the system can be read in the spectrum of H_{FP}.

$\Rightarrow$ can be used to define metastability and reaction path.

[Tanase-Nicola, Kurchan, J. Stat. Phys. 116, 1201 (2004)]

$\Rightarrow$ For systems with N degrees of freedom, one may end up with a continuous spectrum as $N \to \infty$ $(\lambda_2 - \lambda_1 \to 0)$. The relaxation can then become very slow as in glassy materials. $t \to \infty$ & $N \to \infty$ do not necessarily commute.

3.2) Example of diagonalization of H_{FP}: diffusion with absorbing boundaries



If the particle exits $[0,1]$, then it cannot come back.

$\Rightarrow$ random walk in $[0,1]$ with absorbing boundary conditions.

Q: how much time until absorption?

This is the simplest form of a question frequently encountered: how does a diffusive molecule reach a target? (Here, target $x = 0, 1$)

More generally:

Starting from x_0 in $(0,1)$, how does the probability to remain in $[0,1]$ evolve in time? $\Rightarrow P(x,t|x_0,0)$ conditioned to having stayed in $[0,1]$ $\Rightarrow$ $P(x,t|x_0,0) = 0$ for $x \leq 0$ & $x \geq 1$.

In practice, solve $\partial_t P(x,t) = kT\, \partial_{xx} P(x,t)$ with $P(x=0,t) = P(x=1,t) = 0$.

Survival probability: $Q(t) = \int_0^1 dx\, P(x,t)$ is the probability that the system is still in $[0,1]$ at time t.

Solution: Consider $H_{FP} = -D\frac{\partial^2}{\partial x^2}$ and look for a basis of eigenfunctions satisfying the boundary conditions:

$$H_{FP}\varphi = \lambda\varphi \iff \varphi''(x) = -\frac{\lambda}{D}\varphi(x)$$

$$\Rightarrow \varphi(x) = A e^{i\sqrt{\frac{\lambda}{D}}x} + B e^{-i\sqrt{\frac{\lambda}{D}}x}$$

Boundary conditions $\varphi(0) = 0 \Rightarrow A = -B$ & $\varphi(x) = 2iA\sin\left(\sqrt{\frac{\lambda}{D}}x\right)$

$$\varphi(1) = 0 \Rightarrow \sqrt{\frac{\lambda}{D}} = k\pi\,;\; k \in \mathbb{Z}^+$$

$$\Rightarrow \varphi_k(x) = \sin(k\pi x) \;\&\; \lambda_k = Dk^2\pi^2 \qquad \text{(Fourier basis)}$$

$$t=0 \quad P(x,0) = \sum_{k=1}^{\infty} c_k \sin(k\pi x)\;;\quad c_k = 2\int_0^1 dx\, \sin(k\pi x)\, P(x,0)$$

$$\Rightarrow P(x,t) = \sum_{k=1}^{\infty} c_k \sin(k\pi x)\, e^{-D\pi^2k^2t}$$

Example: $P(x,0) = \delta(x-x_0) \Rightarrow c_k = 2\sin(k\pi x_0)$

$$P(x,t) = \sum_{k=1}^{\infty} 2\sin(k\pi x)\sin(k\pi x_0)\, e^{-D\pi^2k^2t}$$

$$\underset{t\to\infty}{\sim} 2\sin(\pi x)\sin(\pi x_0)\, e^{-D\pi^2 t}$$

$$Q(t) \sim \frac{4}{\pi}\sin(\pi x_0)\, e^{-D\pi^2 t}$$

$\Rightarrow$ late-time absorption rate $\kappa = \frac{1}{D\pi^2}$ with a position-dependent modulation of the survival probability.

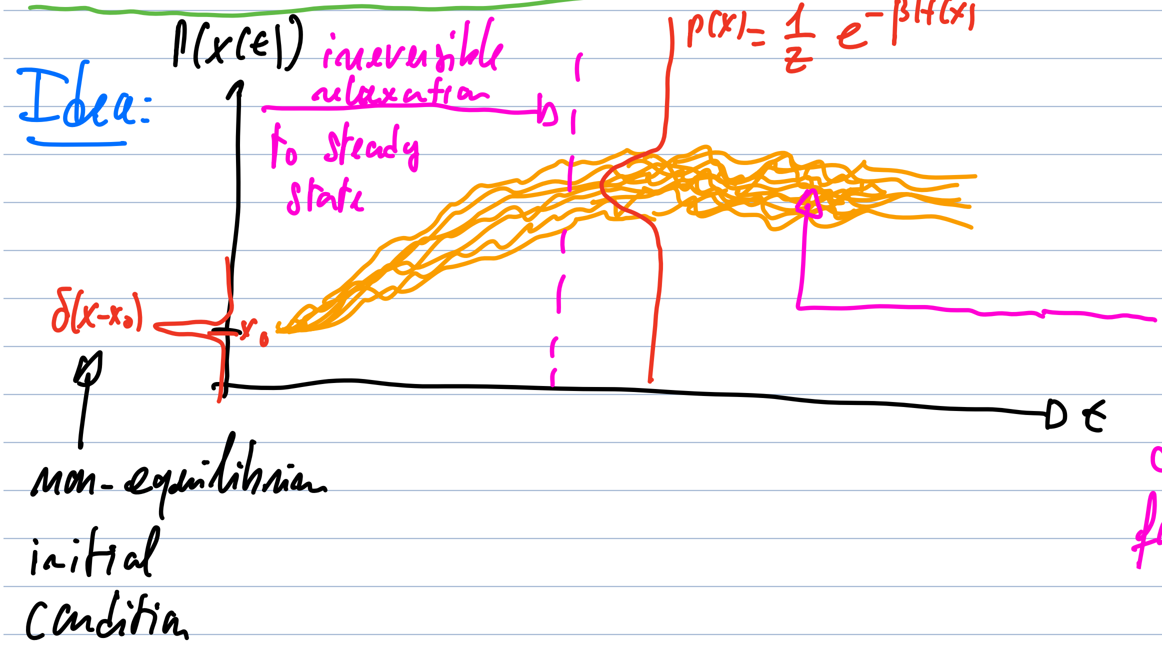
Chapter 4) Time Reversal Symmetry

Historically, equilibrium corresponds to $P(x) = \frac{1}{Z} e^{-\beta H(x)}$ (8.333)
(8.044)

Modern perspective on statistical mechanics puts an emphasis on dynamics & characterize equilibrium by a statistical time reversal symmetry in the steady state.

Q: What does it mean & how do we characterize that?

Idea:



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

1) Propagator & Dirac Bra-ket notation

Remember quantum mechanics: $P(x)$ lives in a Hilbert space, which is a vector space. We can denote the corresponding vector as $|P\rangle$.

Scalar product: $\langle f|g\rangle = \int dx\, f^*(x)\, g(x)$

Adjoint operator: $\langle f|Mg\rangle = \langle M^\dagger f|g\rangle$

E.g. $\langle f|\partial_x g\rangle = \int dx\, f^*(x)\, \partial_x g = -\int dx\, \partial_x f^* \cdot g = \langle -\partial_x f|g\rangle \Rightarrow \frac{\partial}{\partial x}^\dagger = -\frac{\partial}{\partial x}$

$= \langle \frac{\partial}{\partial x}^\dagger f|g\rangle$

Position operator & representation

$|x\rangle$ such that $\hat{x}|x\rangle = x|x\rangle$, $|x\rangle$ position basis

position operator

Observable: $O(x) \to$ operator $\hat{O}$ such that $\hat{O}|x\rangle = O(x)|x\rangle$

e.g. $\hat{P}|x\rangle = P(x)|x\rangle$

Scalar product: $\langle x|$ such that $\langle x|x'\rangle = \delta(x-x')$

Flat measure: $|-\rangle = \sum_x |x\rangle$

Representation of probability distribution:

$$\hat{P}|-\rangle \equiv |P\rangle = \hat{P}\int dx\, |x\rangle = \int dx\, \hat{P}|x\rangle = \int dx\, P(x)\, |x\rangle$$

component — basis vector

Probabilities

$$\langle x|P\rangle = \int dx'\, P(x') \underbrace{\langle x|x'\rangle}_{\delta(x-x')} = P(x)$$ different from QM.

Average of observables:

$$\langle O(x)\rangle = \int dx\, O(x)\, P(x) = \int dx\, dx'\, \delta(x-x')\, O(x')\, P(x') = \int dx\, dx' \langle x|x'\rangle O(x') P(x')$$
$$= \langle -|\hat{O}|P\rangle$$

$$= \langle -|\hat{O}|P\rangle$$

Fokker-Planck equation:

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

Formal solution: $|P(t)\rangle = e^{-tH_{FP}}|P_0\rangle$

Initial condition $x = x_0$:

Any observable $\mathcal{O}$ such that $\langle \mathcal{O}(t=0)\rangle = \mathcal{O}(x_0) = \int dx\, \delta(x-x_0)\, \mathcal{O}(x_0)$

$\Rightarrow P(x,t=0) = \delta(x-x_0) \Rightarrow |P(t=0)\rangle = |x_0\rangle \Rightarrow$

$$\Rightarrow \boxed{|P(t)\rangle = e^{-tH_{FP}}|x_0\rangle}$$

Note that $\int dx\, \delta(x-x_0) = 1$ so that P is normalized

Propagator:

The probability to go from x_0 to x in a time t is called a "propagator":

$$P(x,t|x_0,0) = \langle x|\, e^{-tH_{PF}}\, |x_0\rangle$$

measure the probability in x — evolve — 2 start here

2) Detailed balance & time-reversal symmetry

Statistical time reversibility: a succession of events is as likely to occur as the time reversed sequence.

E.g. $P(x,t;x_0,t_0) = P(x_0,t;x,t_0)$ for $t_0 < t$ (1)

Claim: At large times $(t_0 \to \infty)$, the evolution induced by H_{FP} leads to a steady-state that is time-reversal symmetric.

Q: Can we read directly in H_{FP} this property?

(ie without having to solve for $P(x,t;x_0,t_0)$)

Since $P(a,b) = P(a|b)\,P(b)$, (1) can be rewritten as:

$P(x,t|x_0,t_0)\ P(x_0,t_0) = P(x_0,t|x,t_0)\ P(x,t_0)$ (8)

$\Leftrightarrow \langle x| e^{-(t-t_0)H_{FP}} |x_0\rangle P(x_0,t) = \langle x_0| e^{-(t-t_0)H_{FP}} |x\rangle P(x,t_0)$ (2)

If $t_0 \to -\infty$, $P(x_0,t) \to P_s(x_0)$ the stationary state

Since $\langle x_0| e^{-(t-t_0)H_{FP}} |x\rangle \in \mathbb{R}$,

$$\langle x_0| e^{-(t-t_0)H_{FP}} |x\rangle = \left[\langle x_0| e^{-(t-t_0)H_{FP}} |x\rangle\right]^{+} = \langle x| e^{-(t-t_0)H_{FP}^{+}} |x_0\rangle$$

$$(2) \Leftrightarrow \langle x| e^{-(t-t_0)H_{FP}} |x_0\rangle = P_s(x) \langle x| e^{-(t-t_0)H_{FP}^{+}} |x_0\rangle P_s^{-1}(x_0)$$
$$= \langle x| P_s\, e^{-(t-t_0)H_{FP}^{+}} P_s^{-1} |x_0\rangle$$

Expand for small $t-t_0$: $e^{-uH_{FP}} = \mathbb{I} - u H_{FP}$

$(**) \Leftrightarrow \langle x|x_0\rangle - (t-t_0)\langle x|H_{FP}|x_0\rangle = \langle x|x_0\rangle - (t-t_0)\langle x|P_s H_{FP}^{+} P_s^{-1}|x_0\rangle$

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

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

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

(ii) The converse is also true $H_{FP}^{+} = P_s^{-1} H_{FP} P_s \Rightarrow \forall x, x_0, t, t_0\ P(x,t;x_0,t_0) = P(x_0,t;x,t_0)$

Proof: $e^{-tH_{FP}^{+}} = \sum_k \frac{(-t)^k}{k!} (H_{FP}^{+})^k = \sum_k \frac{(-t)^k}{k!} \underbrace{P_s^{-1} H_{FP} P_s \cdot P_s^{-1} H_{FP} P_s \cdot P_s^{-1} H_{FP} P_s \cdots}_{k \text{ times}}$

$$= P_s^{-1} \sum_k \frac{(-t)^k}{k!} H_{FP}^k \cdot P_s = P_s^{-1} e^{-tH_{FP}} P_s$$

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 $\frac{\partial}{\partial x}\left(g(x) f(x)\right) = g'(x) f(x) + g(x) \frac{\partial}{\partial x} f(x)$ (9)

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

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

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

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

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

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

For the Brownian equilibrium dynamics, one thus has

$P_s(x_0)\, P(x,t|x_0,0) = P_s(x)\, P(x_0,t|x,0)$, which can be

summarized as $P_s(x_0)\, P(x_0 \to x, t) = P_s(x)\, P(x \to x_0, t)$ (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 matrix.

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 function

Take two observables $A(x)$ & $B(x)$, and the corresponding operators $A|x\rangle = A(x)$ & $B|x\rangle = B(x)$. Take $t > t'$

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

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

Since the system is in the steady state at t', $C_{AB}(t,t') = C_{AB}(t-t')$ due to time translational invariance, 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

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

$\Rightarrow$ 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