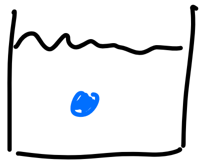
Recap so far



colloidal particle in a fluid ⓘ

(I) Equation of motion

Generalized Langevin eq°: $M\dot{x} = p$; $\dot{p} = -V'(x) - \int^{t} ds\, K(t-s)\,\dot{x}(s) + \xi(t)$

where $\xi(t)$ is a Gaussian noise with $\langle \xi(t)\xi(t')\rangle = k_BT\, K(t-s)$

White noise limit when fluid relaxation time << colloid

$M\dot{x} = p$; $\dot{p} = -V'(x) - \gamma\dot{x} + \xi(t)$, where $\xi(t)$ is a Gaussian white noise with $\langle \xi(t)\rangle = 0$ & $\langle \xi(t)\xi(t')\rangle = 2\gamma k_BT\,\delta(t-t')$

Overdamped limit In viscous fluid, inertia is negligible &

$\dot{x} = -\mu V'(x) + \eta(t)$, with $\mu = \frac{1}{\gamma}$ the particle mobility

& $\langle \eta(t)\eta(t')\rangle = 2\mu k_BT\,\delta(t-t')$

(II) Path probability

$$P[\eta(t)] \propto \frac{1}{Z}\, e^{-\int dt\, \eta(t)^2}$$

For an α discretization $x(t+dt) - x(t) = F(x^{\alpha}(t)) + \int_t^{t+dt} ds\, \eta(s)$

$$P[\{x(t)\}] \propto \frac{1}{\tilde{Z}}\, e^{-\int dt \left\{ \frac{[\dot{x} - F(x)]^2}{4k_BT} + \alpha F'(x) \right\}}$$

(III) Probability distribution of $x(t)$

$$\partial_t P(x,t|x_0,0) = \frac{\partial}{\partial x}\left[-F(x) + k_BT \frac{\partial}{\partial x} \right] P(x,t|x_0,0)$$

When $F(x) = -V'(x)$, $P(x) = \frac{1}{Z} e^{-\beta V(x)}$ is a time independent solution of the Fokker Planck equation.

Comment: For $P(x)$ to be normalizable, we need $\int dx\, e^{-\beta V(x)} < +\infty$

$\Rightarrow V(x)$ has to diverge fast enough.

If $V(x) \underset{x \to \pm\infty}{\sim} \varepsilon \log|x|$, $e^{-\beta V(x)} \underset{x \to \pm\infty}{\sim} \frac{1}{|x|^{\beta\varepsilon}}$ not integrable for $\varepsilon\beta \leq 1$

$\Leftrightarrow kT \geq \varepsilon$

$\Rightarrow$ at high temperature, the system does not equilibrate.

The potentials that diverge faster than logarithmically are called confining potentials.

Today: (I) N dimensional Fokker-Planck eq°

(II) Spectral theory of the Fokker-Planck eq°

(III) Study time-reversal symmetry in the steady state

2) The N-dimensional Fokker-Planck equation

Let's consider $\dot{x}_i = F_i(x_1, \dots, x_N) + \eta_i$ where η_i are GWN s.t. $\langle \eta_i \rangle = 0$

and $\langle \eta_i(t) \eta_k(s) \rangle = B_{ik}\, \delta(t-s)$

numbers

$$P(x_1, \dots, x_N; t) = \Big\langle \prod_i \delta(x_i - g_i(t)) \Big\rangle_{\vec{g}}$$

stochastic processes

$$\frac{\partial P}{\partial t} = \sum_k \underbrace{\Big\langle \frac{\partial}{\partial g_k} \Big(\prod_i \delta(x_i - g_i) \Big) \dot{g}_k \Big\rangle_{\vec{g}}}_{\text{Itô } \left\langle \frac{\partial}{\partial g_k} \left(\prod_i \delta(x_i - g_i) \right) F_k \right\rangle_{\vec{g}}} + \sum_{j,k} \Big\langle \frac{B_{jk}}{2} \frac{\partial^2}{\partial g_j \partial g_k} \prod_i \delta(x_i - g_i) \Big\rangle_{\vec{g}}$$

$$= \int \Big(\prod_i dg_i \Big) \Big\{ \sum_k \frac{\partial}{\partial g_k} \Big[\prod_i \delta(x_i - g_i) \Big] F_k P + \sum_{j,k} \frac{\partial^2}{\partial g_j \partial g_k} \Big[\prod_i \delta(x_i - g_i) \Big] \frac{B_{jk}}{2} P \Big\}$$

$$\overset{\text{IBP}}{=} \int \prod_i dg_i \cdot \Big[\prod_i \delta(x_i - g_i) \Big] \Big\{ \sum_k - \frac{\partial}{\partial g_k} \big[F_k P \big] + \sum_{j,k} \frac{\partial^2}{\partial g_j \partial g_k} \Big[\frac{B_{jk}}{2} P \Big] \Big\}$$

leading to the Fokker planck equation

$$\frac{\partial P(x_1, \dots, x_N, t)}{\partial t} = \sum_k \frac{\partial}{\partial x_k} \Big[- F_k - \sum_j \frac{\partial}{\partial x_j} \frac{B_{jk}}{2} \Big] P(x_1, \dots, x_N, t)$$

Conservation of probability:

This can again be written as

$$\partial_t P = - \sum_k \frac{\partial}{\partial x_k} \cdot J_k = - \vec{\partial} \cdot \vec{J}\,,$$ where the probability

current is given by $$J_k = \underbrace{F_k P}_{\text{advection}} - \underbrace{\sum_j \frac{\partial}{\partial x_j} \frac{B_{jk}}{2} P}_{\text{diffusion}}$$

B_{jh} tells us how noise along $\hat{j}$ leads to a diffusive current along $\hat{h}$.

Application: Underdamped Langevin equation & the Kramers equation

$m\dot{q} = p$; $\dot{p} = -\gamma \frac{p}{m} - V'(q) + \sqrt{2\gamma kT}\,\eta(t)$ with $\langle \eta(t) \rangle = 0$ $(m=1)$

and $\langle \eta(t)\,\eta(s) \rangle = \delta(t-t')$. As before, we can understand this equation as experiencing noise on both q & p, but with $B_{qq} = B_{qp} = B_{pq} = 0$ & $B_{pp} = 2\gamma kT$. Then the equation for $P(q,p,t)$ reads

$$\boxed{\partial_t P(\vec{q},\vec{p},t) = -\frac{\partial}{\partial q}\left(\frac{p}{m}P\right) + \frac{\partial}{\partial p}\left(\left(\frac{\gamma}{m}p + V'(q)\right)P + \gamma kT \frac{\partial^2}{\partial p^2}P\right)}$$

This is called the Kramers equation.

Steady state solution in the presence of a confining potential

$H = \frac{p^2}{2m} + V(q) \Rightarrow \partial_q\left(e^{-\beta H}\right) = -\beta V'(q)\, e^{-\beta H}$ & $\partial_p e^{-\beta H} = -\beta \frac{p}{m} e^{-\beta H}$.

Let's show that the steady-state solution is $Z^{-1} e^{-\beta H}$.

$$-\frac{\partial}{\partial q}\left(\frac{p}{m}e^{-\beta H}\right) + \frac{\partial}{\partial p}\left(\cancel{\frac{\gamma p}{m} e^{-\beta H}} + V'(q)\, e^{-\beta H} + \cancel{\gamma kT \underbrace{\left(-\frac{\beta p}{m} e^{-\beta H}\right)}_{\frac{\partial}{\partial p} e^{-\beta H}}}\right)$$

$$= -\frac{p}{m}\left[-\beta V'(q)\, e^{-\beta H}\right] + V'(q)\left[-\frac{\beta p}{m} e^{-\beta H}\right] = 0$$

Again, the steady state corresponds to the Boltzmann weight.

Comment: The steady state is independent from γ, which is a purely kinetic parameter and plays no role in the thermodynamics of equilibrium systems. It, however, controls the relaxation rate of the system towards steady-state.

Comment: The same result holds for a space-dependent viscosity $\gamma(\vec{q})$, but not for $T(\vec{q})$, which leads to a nonequilibrium steady state.

Recap so far:

Stochastic dynamics: $\dot{\vec{r}} = -\mu \vec{\nabla} V + \sqrt{2\mu k T}\, \vec{\eta}$

→ clear physical picture of the dynamics

→ simulations

→ stochastic calculus → evolution of observables

→ correlation functions

Fokker-Planck equation: $\partial_t P = -\vec{\nabla} \cdot [-\mu \vec{\nabla} V P - \mu k T \vec{\nabla} P]$

→ hard to simulate

→ statistical information/intuition through $P(\vec{r})$

e.g. Show that $P_s(\vec{r}) \propto e^{-\beta H}$

→ Now: very powerful operator calculus

3) The Fokker-Planck operator

$\partial_t P = \frac{\partial}{\partial x}\left[kT\frac{\partial}{\partial x} - F(x)\right]P(x,t)$ (1) $\Leftrightarrow$ $\partial_t P = -H_{FP}P$ 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) $\partial_t P = -H_{FP}P_0(x)e^{-\lambda t} = -\lambda P_0 e^{-\lambda t} \Leftrightarrow H_{FP}P_0(x) = \lambda P_0(x)$

$\rightarrow P_0(x)$ 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 $\inf_\alpha(\lambda_\alpha) = \lambda_0 = 0$

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

The Perron Froebenius 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

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

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

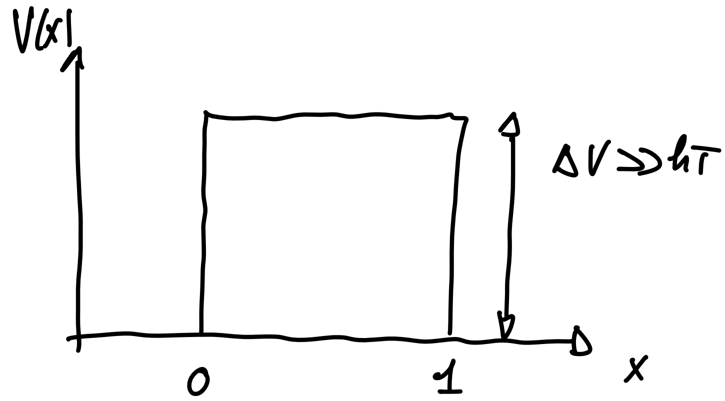
$\Rightarrow$ the typical time scales of the system can be read in the spectrum of H_{FP}.

$\Rightarrow$ 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.

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

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

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

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

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

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

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

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

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

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

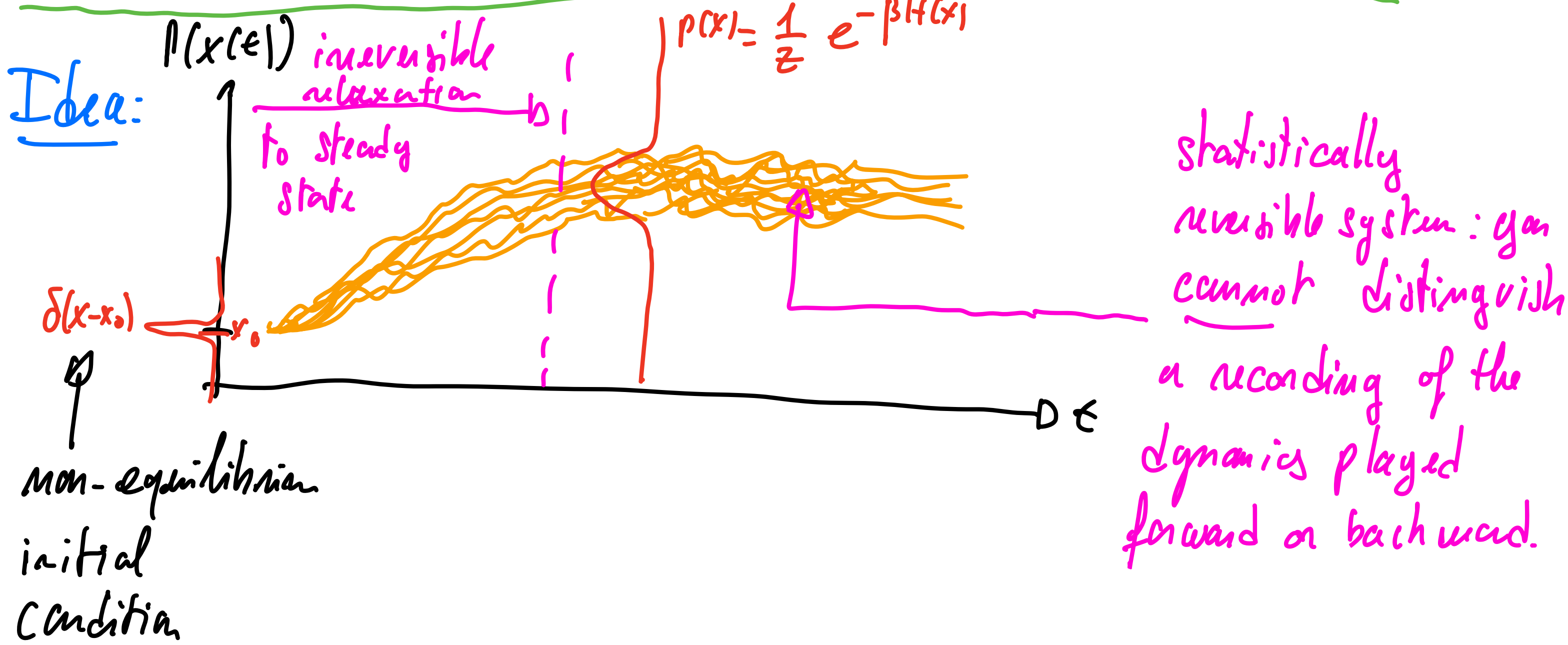
Chapter 4) Time Reversal Symmetry

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:



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

$\hat{x}$ 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: $|-\rangle = \int dx\, |x\rangle$

Representation of probability distribution:

$$\hat{P}|-\rangle \doteq |P\rangle = \hat{P}\int dx\, |x\rangle = \int dx\, \hat{P}|x\rangle = \int dx\, \underbrace{P(x)}_{\text{component}}\, \underbrace{|x\rangle}_{\text{basis vector}}$$

Probabilities

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

Average of observables:

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

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 O such that $\langle O(t=0)\rangle = O(x_0) = \int dx\, \delta(x-x_0)\, O(x_0)$

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

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

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 for a time t

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 long 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:

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

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

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

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

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

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

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

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

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