Fourth application of path integral : fluctuation theorems.

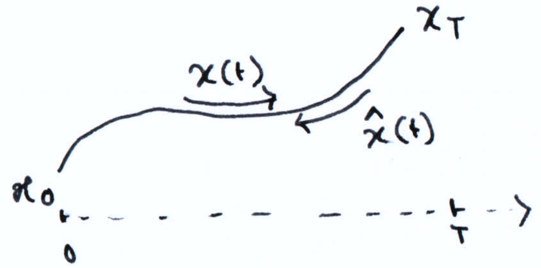
Ref : ① Chernyak et. al. J. stat mech (2006) P08001.
② Lecture note of Udo Seifert on fluctuation theorem.

What we will learn : quantifying breaking of time reversal invariance in an example outside equilibrium and how that ~~lead to a new "thermodynamic~~ leads to an extension of the second law of thermodynamics.

Reminder : time reversed process. (dynamics)

(A) In Newtonian mechanics, a particle in a potential follows

$$\ddot{x}(t) = -U'(x(t))$$



Let $\hat{x}(t) = x(T-t)$ be the time reversed trajectory.

We see that, the backward evolution is described by the same dynamics

$$\ddot{\hat{x}}(t) = -U'(\hat{x}(t))$$

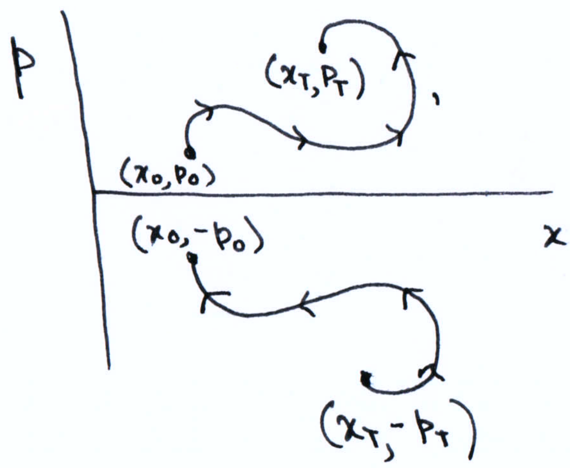
This means, Newtonian dynamics is time ~~reversible~~ reversal invariant.

(B) In Hamilton's ~~picture~~ description

$$\dot{p}(t) = -\frac{\partial H}{\partial x(t)} = -U'(x(t))$$

$$\dot{x}(t) = \frac{\partial H}{\partial p(t)} = \frac{p(t)}{m}$$

for $H = \frac{p^2}{2m} + U(x)$



Corresponding time reversed trajectory

$$\{\hat{x}(t), \hat{p}(t)\} = \{x(T-t), -p(T-t)\}$$

note the -ve sign

follows the same dynamics

$$\dot{\hat{p}} = -U'(\hat{x}(t))$$

$$\dot{\hat{x}} = \frac{\hat{p}(t)}{m}$$

This means, Hamiltons dynamics is time reversible.

(c) Quantum mechanics: A probabilistic description

$$i\hbar \frac{\partial \psi_t(x)}{\partial t} = -\frac{\hbar^2}{2m}\psi_t''(x) + V(x)\psi_t(x)$$

$$= H \cdot \psi_t(x) \qquad \text{...... (1)}$$

Rather than deterministic paths, we think about evolution of state $\psi_t(x)$.

Given initial $\psi_0(x)$, schrödinger eqution gives an evolution of $\psi_t(x)$.

Time reversed evolution is constructed by

$$\hat{\psi}_t(x) = \psi^*_{T-t}(x)$$

(change of sign of t, plus complex conjugation)

We see (using $H^\dagger = H$)

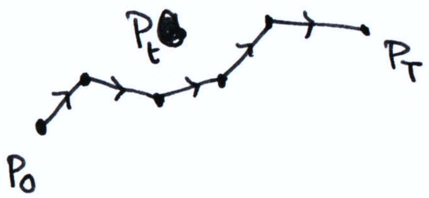
$$i\hbar \frac{\partial \hat{\psi}_t(x)}{\partial t} = H\hat{\psi}_t(x) \qquad \text{...... (2)}$$

This means, schrödinger evolution is time reversible.

In words, if $\psi_t(x)$ for $0 \le t \le T$ ~~with initial~~ is the evolution by forward schrödinger equation $^{(1)}$ with initial condition $\psi_0(x)$, then $\hat{\psi}_t(x) = \psi^*_{T-t}(x)$ is the time reversed path and is a solution of time reversed equation (2) with initial condition $\hat{\psi}_0(x) = \psi^*_T(x)$.

(D) For classical stochastic evolution we follow ~~the same~~ a similar idea.

(a) <u>Discrete Markov process</u> :



Let P_t be the forward evolution of probability starting with P_0 and following

$$P_{t+dt} = M \cdot P_t$$

Let $\boxed{\hat{P}_t = P_{T-t}}$ be the time reversed evolution starting with $\hat{P}_0 = P_T$

We showed earlier, the $\hat{P}_t$ follow a dynamics (Markovian)

$$\hat{P}_{t+dt} = \hat{M} \cdot \hat{P}_t \qquad \text{with} \qquad \boxed{\hat{M}(c',c) = P_{ss}(c')\, M(c,c')\, \frac{1}{P_{ss}(c)}}$$

[* when P_0 is in stationary state]

$$\Rightarrow \boxed{\hat{M} = [P_{ss}] \cdot M^t \cdot [P_{ss}^{-1}]}$$

$$P_{ss} = \begin{pmatrix} P & & 0 \\ & \ddots & \\ 0 & & \ddots \end{pmatrix}$$

* $\hat{M}$ is markovian matrix $\Rightarrow$ column sum = 1.

* In general, $\hat{M} \neq M$.

Only in equilibrium (detailed balance), $\hat{M} = M \Rightarrow$ dynamics is time reversal invariant.

(b) Langevin equation: If we follow the standard proceedure

discret Master eq^n $\longrightarrow$ cont Master eq^n

$\downarrow$ Kramer's Moyale expansion

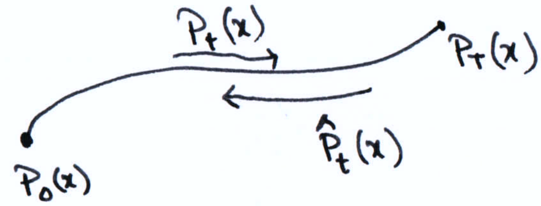
FP equation

We can show the following analoge.

$F(x) \equiv$ force

let $$\frac{\partial}{\partial t} P_t(x) = \mathcal{L} \cdot P_t(x) = \left(D \frac{d^2}{dx^2} - \frac{d}{dx} F(x) \right) \cdot P_t(x)$$

give forward evolution starting with $P_0(x)$.



Then the time reversed dynamics *

$$\frac{\partial}{\partial t} \hat{P}_t(x) = \hat{\mathcal{L}} \cdot \hat{P}_t(x) \quad \text{with } \hat{\mathcal{L}} := P_{ss}(x) \cdot \mathcal{L}^{\dagger} \cdot \left(P_{ss}(x)\right)^{-1}$$

with $\hat{P}_0(x) = P_T(x)$ gives the ~~same~~ backward evolution such that $\hat{P}_t(x) = P_{T-t}(x)$.

Here, $$\mathcal{L}^{\dagger} := D \frac{d^2}{dx^2} + F(x) \cdot \frac{d}{dx}$$ [use the definition $\langle \mathcal{L}^{\dagger} \ell | r \rangle = \langle \ell | \mathcal{L} r \rangle$ and integration by parts]

(*) Because of $\mathcal{L}^{\dagger}$, the time reversed evolution is also called adjoint dynamics.

Simplest example: $F(x) = -U'(x)$. gradiant force.

$$P_{ss}(x) = \frac{e^{-\frac{U(x)}{D}}}{Z}$$ ← normalization.

The stationary state is in equilibrium.

It is easy to check that

$$\hat{\mathcal{L}} := e^{-\frac{U(x)}{D}} \cdot \mathcal{L}^{+} \cdot e^{\frac{U(x)}{D}} = \left(D\frac{d^2}{dx^2} - \frac{d}{dx}F \right) \equiv \mathcal{L}.$$

This means Langevin equation in a potential is time reversal invariant.

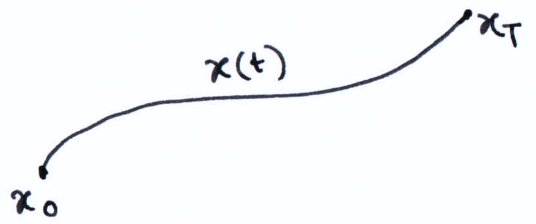
It means:

$\boxed{\text{If } \dot{x}_t = -U'(x_t) + \eta(t) \text{ is forward Langevin equation, then } \dot{\hat{x}}_t = -U'(\hat{x}_t) + \eta(t) \text{ is the time reversed equation, such that a forward path } x_t \text{ with initial distribution } P(x_0) \propto e^{-\frac{U(x_0)}{D}} \text{ has the same probability of a time reversed path } \hat{x}_t \text{ with initial distribution } P(\hat{x}_0) \propto e^{-\frac{U(\hat{x}_0)}{D}} \text{, and } \hat{x}_0 = x_T.}$

[non-trivial: note the time reversal is not just definining $t \to T-t$, which would have given $\dot{\hat{x}}_t = U'(\hat{x}_t) - \eta_t$]

Remark: the time reversibility here is a result of ~~much general property that~~ detailed balance and we have shown this earlier for Markov process explicitly.

This result is easy to see using path integral (and generalizable, as we will see soon).



From $\dot{x} = -U'(x) + \eta$

$$\text{Prob}\left[x(t) \,\middle|\, P(x_0) \propto e^{-\frac{U(x_0)}{D}}\right] = e^{-\frac{1}{4D}\int_0^T dt\,\left(\dot{x}(t) + U'(x(t))\right)^2 + \frac{1}{2}\int_0^T dt\, U''(x)} \times \frac{e^{-\frac{U(x_0)}{D}}}{Z}$$

From $\dot{\hat{x}} = -U'(\hat{x}) + \eta$

$$\text{Prob}\left[\hat{x}(t) \,\middle|\, P(\hat{x}(0)) \propto e^{-\frac{U(\hat{x}(0))}{D}}\right] = e^{-\frac{1}{4D}\int_0^T dt\,\left(\dot{\hat{x}}(t) + U'(\hat{x}(t))\right)^2 + \frac{1}{2}\int_0^T dt\, U''(\hat{x})} \times \frac{e^{-\frac{U(\hat{x}(0))}{D}}}{Z}$$

If indeed $\hat{x}(t) = x(T-t)$ follows $\dot{\hat{x}} = -U'(\hat{x}) + \eta$ then the two probabilities should be equal. To see this, we write

$$-\frac{1}{4D}\int_0^T dt\,\left(\dot{\hat{x}}(t) + U'(\hat{x}(t))\right)^2 \xrightarrow{t \to T-t} = -\frac{1}{4D}\int_0^T dt\,\left(-\dot{x}(t) + U'(x(t))\right)^2$$

$$= -\frac{1}{4D}\int_0^T dt\,\left(\dot{x}(t) + U'(x(t))\right)^2 + \frac{1}{D}\int_0^T dt \cdot \dot{x}(t) \cdot U'(x(t))$$

The last term

$$\frac{1}{D}\int_0^T dt\cdot\dot{x}(t)\cdot U'(x(t)) = \frac{1}{D}\int_{x_0}^{x_T} dx\cdot U'(x) = \frac{U(x_T)-U(x_0)}{D}.$$

Continuing the analysis for rest of the terms, we see

$$\text{Prob}\left[\hat{x}(t)\,\middle|\,P(\hat{x}(0))\propto e^{-\frac{U(\hat{x}(0))}{D}}\right]$$

$$= e^{-\frac{1}{4D}\int_0^T dt\left(\dot{x}(t)+U'(x(t))\right)^2+\frac{1}{2}\int_0^T dt\cdot U''(x(t))}$$

$$\times\, e^{\frac{\cancel{U(x_T)}-U(x_0)}{D}} \times \frac{e^{-\cancel{\frac{U(x_T)}{D}}}}{Z_n} \qquad \hat{x}(0)=x_T$$

$$= \text{Prob}\left[x(t)\,\middle|\,P(x(0))\propto e^{-\frac{U(x(0))}{D}}\right]$$

This confirms the time reversed dynamics.

Now consider a non-trivial case where $U_t(x)$ is changing with time. Clearly this is a <u>non-equilibrium</u> situation and time reversal invariance would <u>not</u> hold any more.

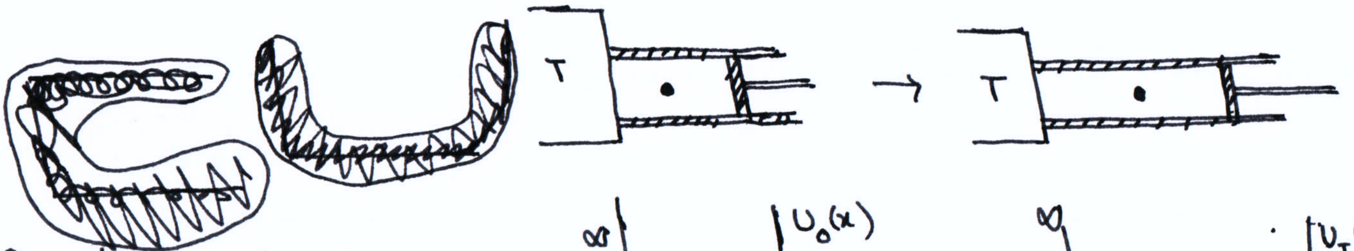
<u>Q</u>. how much it deviates from reversal invariance?

Precise formulation :

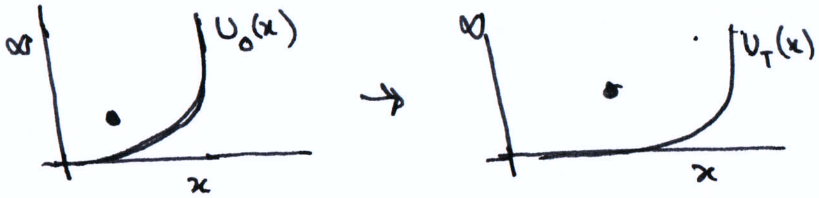
Consider a Langevin particle at $t=0$ in equilibrium in potential $U_0(x)$.

$$P_0(x) \equiv P_{eq}(x) = \frac{e^{-\frac{U_0(x)}{D}}}{Z_0}$$

The potential is changed following protocol $U_t(x)$ upto time $t=T$, where the potential is $U_T(x)$. One such realistic scenario is moving piston of the box containing a Brownian particle



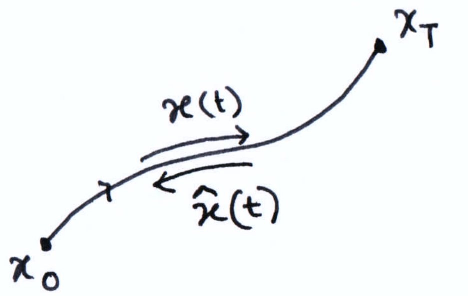
Can be thought of a 1-d Brownian particle in a moving potential



$U(x)$ is the piston-wall potential.

Consider a trajectory of the particle, that follows

$$\dot{x}(t) = -U_t'(x(t)) + \eta(t)$$



Probability of such a path

$$\mathrm{Prob}\left[x(t) \,\middle|\, P_{eq}(x_0); U_0\right] = e^{-\frac{1}{4D}\int_0^T dt\left[\dot{x}(t) + U_t'(x(t))\right]^2 + \frac{1}{2}\int_0^T dt \cdot U_t''(x(t))} \times \frac{e^{-\frac{U_0(x_0)}{D}}}{Z_0}$$

Corresponding time reversed path $\hat{x}(t) = x(T-t)$ has probability (by definition)

$$\mathrm{Prob}\left[\hat{x}(t) \,\middle|\, P_T(\hat{x}(0))\right] = \mathrm{Prob}\left[x(t) \,|\, P_{eq}(x(0)); U_0\right]$$

From this we could construct the Action for $\hat{x}(t)$ and the dynamics it satisfies.

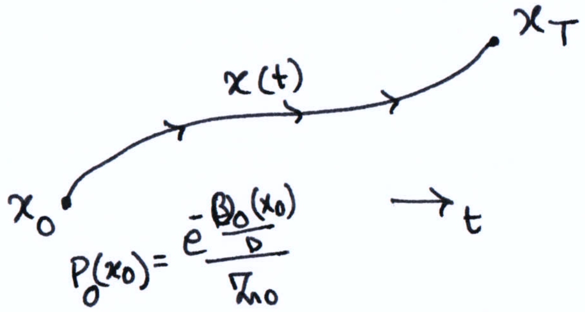
$$e^{-\hat{S}[\hat{x}(t)]} \cdot P_T(\hat{x}(0)) = e^{-\frac{1}{4D}\int_0^T dt\left[-\dot{\hat{x}}(t) + U'_{T-t}(\hat{x}(t))\right]^2 + \frac{1}{2}\int_0^T dt\, U''_{T-t}(\hat{x}(t))} \times \frac{e^{-U_0(\hat{x}(T))}}{Z_0}$$

However, the trouble is, we don't know $P_T(\hat{x}(0)) = P_T(x_T)$.

This makes very hard to determine the time reversed dynamics.

But, we can say that the time reversed dynamics is not same as the original dynamics!

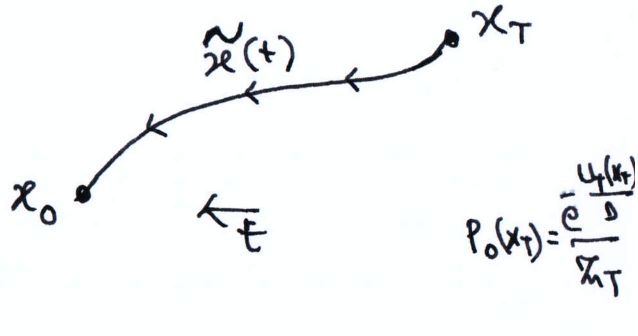
Let's look at the problem differently. (we shall see that it will give us an important insight)



Forward protocol.

$t=0$ is in eq with $U_0(x)$.

Then change U_t from $U_0 \to U_T$



Backward protocol.

at $t=0$ is in eq with $U_T(x)$,

Then change U ~~from~~ $U_T \to U_0$.

* The dynamics is still the forward dynamics!

time moves forward, and $\tilde{x}(t)$ follows the forward Langevin equation

$$\dot{\tilde{x}}(t) = - U'_{T-t}\big(\tilde{x}(t)\big) + \eta(t)$$

What is the probability that $\tilde{x}(t) = x(T-t)$?

$$\mathrm{Prob}\Big[\tilde{x}(t) \,\Big|\, P_{eq}(\tilde{x}(0)) ; U_T\Big]$$

$$= e^{-\frac{1}{4D}\int_0^T dt \left\{ \cancel{-}\dot{\tilde{x}}(t) + U'_{T-t}(\tilde{x}(t)) \right\}^2 + \frac{1}{2}\int_0^T dt \cdot U''_{T-t}(\tilde{x}(t))} \times \frac{e^{-\frac{U_T(\tilde{x}(0))}{D}}}{Z_T}$$

$\tilde{x}(t) = x(T-t)$

$$= e^{-\frac{1}{4D}\int_0^T dt \left\{ -\dot{x}(t) + U'_t(x(t)) \right\}^2 + \frac{1}{2}\int_0^T dt \cdot U''_t(x(t))} \times \frac{e^{-\frac{U_T(x_{\cancel{f}})}{D}}}{Z_T}$$

$$= e^{-\frac{1}{4D}\int_0^T dt \left\{ \dot{x}(t) + U'_t(x(t)) \right\}^2 + \frac{1}{2}\int_0^T dt \, U''_t(x(t))} \times e^{+\frac{1}{D}\int_0^T dt \cdot \dot{x}(t) \cdot U'_t(x(t))} \times \frac{e^{-\frac{U_T(x_T)}{D}}}{Z_T}$$

$$\int_0^T dt \cdot \dot{x} \cdot U'_t(x(t)) = \int_0^T dt \cdot \frac{d}{dt} U_t(x(t)) - \int_0^T dt \cdot \frac{\partial}{\partial t} U_t(x(t))$$

$$\hookrightarrow U_T(x_T) - U_0(x_0)$$

Substituting and cancelling terms we get

$$\mathrm{Prob}\left[\tilde{x}(t) \,\middle|\, P_{eq}(\tilde{x}(0)); U_T\right]$$

$$= e^{-\frac{1}{4D}\int_0^T dt \left\{\dot{x}(t) + U_t'(x(t))\right\}^2 + \frac{1}{2}\int_0^T dt \cdot U_t''(x(t))}$$

$$\times \frac{e^{-\frac{U_0(x_0)}{D}}}{Z_0} \times \left\{ \frac{Z_0}{Z_T} \times e^{-\frac{1}{D}\int_0^T dt \cdot \frac{\partial}{\partial t} U_t(x(t))} \right\}$$

$$= \mathrm{Prob}\left[x(t) \,\middle|\, P_{eq}(x(0)), U_0\right]$$

$$\times e^{\frac{F_T - F_0}{D} - \frac{W_T}{D}}$$

<u>Here we denote</u>

$F_T = -D \log Z_T$ the equilibrium free energy

$$W_T = \int_0^T dt \cdot \frac{\partial}{\partial t} U_t(x(t))$$

Notice that $W_T[x(t)]$ depends on trajectory and a fluctuating quantity. But F_0 and F_T are specified by the initial and final equilibrium state.

Noting that there is one-to-one correspondence between $\tilde{x}(t)$ and $x(t)$, we see that

$$1 = e^{\frac{F_T - F_0}{D}} \cdot \left\langle e^{-\frac{W_T}{D}} \right\rangle$$

giving

$$\boxed{\left\langle e^{-\frac{W_T}{D}} \right\rangle = e^{-\frac{F_T - F_0}{D}}}$$

This is the famous <u>Jarzynski equality</u>. (more general).

<u>Interpretation</u>: what is W_T?

$$dU_t(x(t)) = dx(t) \cdot U_t'(x(t)) + dt \cdot \frac{\partial}{\partial t} U_t(x(t))$$

Integrating between 0 to T,

$$U_T(x_T) - U_0(x_0) = \int_0^T dt \cdot \dot{x}(t) \cdot U_t'(x(t)) + \int_0^T dt \cdot \frac{\partial}{\partial t} U_t(x(t))$$

$$\Rightarrow \boxed{\Delta E = \Delta Q + W_T}$$

change in energy of the system.

non-zero even for constant potential.

coming because we are changing potential. Would be zero otherwise. ~~work~~

Therefore, comparing with first law of thermodynamics, we see that

$W_T = \int_0^T dt \cdot \frac{\partial}{\partial t} U_t(x(t))$ is the work done on the system in one history $x(t)$.

$\Delta Q = \int_0^T dt \cdot \dot{x}(t) \cdot U_t'(x(t))$ is the heat ~~into~~ flown into the system from the surrounding bath.

Another way of recognizing the heat term.

$$m\ddot{x} = -U_t'(x) - \dot{x} + \eta(t) \qquad [\text{we set } \gamma = 1]$$

$$\Rightarrow \quad m\cdot\dot{x}\cdot\ddot{x} = \frac{d}{dt}\left(\frac{1}{2}m\dot{x}^2\right) = -\dot{x}\cdot U_t'(x) + \left(\eta(t) - \dot{x}\right)\cdot\dot{x}$$

$$\Rightarrow \quad \int_0^T dt\left[\dot{x}\cdot U_t'(x) + \frac{d}{dt}\left(\frac{1}{2}m\dot{x}^2\right)\right] = \int_0^T dt\cdot\dot{x}\cdot\left(\eta(t) - \dot{x}\right)$$

$$= \int_0^T dx\cdot\left(\eta - \dot{x}\right)$$

net energy flow into the system from surrounding bath (input by the noise, and dissipation back by viscous drag $\dot{x}$)

= heat flown into the system.

Then, for overdamped limit, ignoring the intertial term $\frac{1}{2}m\dot{x}^2$, we see that

$$\int_0^T dt\cdot\dot{x}\cdot U_t'(x) = \Delta Q$$

= heat flown into the system.

Then, the equality $\langle e^{\frac{W_T}{D}}\rangle = e^{\frac{F_T - F_0}{D}}$ says that if we take a system in equilibrium with free energy F_0, then do work W_T on the system (~~move~~ change the potential) up to time T, and then let the system equilibrate with the new potential $U_T(x)$ such that it equilibrates ~~to~~ with free energy F_T, then

$$\langle e^{-\frac{W_T}{D}}\rangle = e^{-\frac{F_T - F_0}{D}} \qquad (\text{here } D = k_B \text{Temp})$$