$v = \dot{x} = \mu f(x) + \sqrt{2\mu T}\,\eta(t)$

Stratonovich convention

$$\frac{\dot{x}f}{T} = \frac{d}{dt}\left(\frac{Q_f}{T}\right) = \frac{d}{dt} S_f \Rightarrow \text{variation of entropy of the fluid.}$$

Variation of entropy of the fluid along a trajectory: $\boxed{\Sigma = \int_0^t ds\, \frac{\dot{x}f}{T}}$

$\boxed{\bar{\Sigma} = \left\langle \log \frac{P[x]}{P[x^R]} \right\rangle = \langle \Sigma \rangle}$ is the average variation of entropy of the system.

entropy production rate $\boxed{\sigma = \lim_{t\to\infty} \frac{1}{t}\bar{\Sigma}(t) = \lim_{t\to\infty} \frac{1}{t}\left\langle \log \frac{P[x]}{P[x^R]} \right\rangle}$

$$\sigma = \lim_{t\to\infty} \left\langle \frac{1}{t}\int_0^t ds\, \frac{\dot{x}f}{T} \right\rangle_{\text{path}} \underset{\substack{\text{ergodicity}\\ \text{\& steady state}}}{=} \frac{1}{T}\langle \dot{x} f \rangle_{ss}$$

* Fluctuation theorem $\quad \langle e^{-\Sigma} \rangle = 1$

$$\Rightarrow \langle \Sigma \rangle \geq 0$$

Many generalizations of the fluctuation theorem

We have shown $\quad \Sigma = \log \frac{P[x(t)]}{P[x^R(t)]} \Leftrightarrow P[x]\, e^{-\Sigma} = P[x^R] \quad (*)$

9

Sum over all $x(t)$ with the same Σ $\Rightarrow \sum_{x|\Sigma(x)=\Sigma} P[x] \equiv P(\Sigma)$

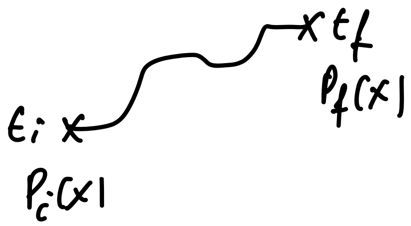
Since $\Sigma(x^R) = -\Sigma(x)$, $(*)$ leads to $\boxed{P(\Sigma)\, e^{-\Sigma} = P(-\Sigma)}$

this extends to the case with $\lambda(t)$ up to

$$\boxed{P_F(\Sigma)\, e^{-\Sigma} = P_R(-\Sigma) \quad \text{when } P_F(x) = P(x) \text{ with } \lambda(t) \ \& \ P_R(x) = P(x) \text{ with } \lambda(t_f - t)}$$

[Crooks 1999, PRE 60, 1063]

This can be used to characterize the system during transformations $\lambda(t): \epsilon_i \to \epsilon_f$



The most famous result is Jarzynski equality:

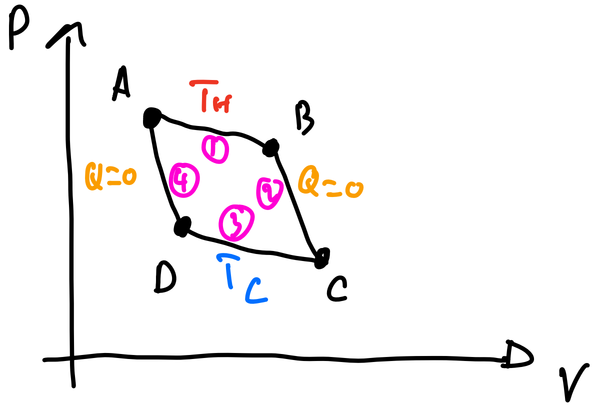
$$\boxed{\langle e^{-W} \rangle = e^{-\beta \Delta F}}$$

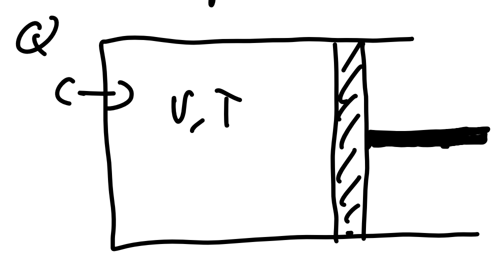
Chapter V: From Brownian ratchet to molecular motor

Q: If equilibrium is contagious (Chapter 2) and leads to Boltzmann weight (chap. 4) and time-reversal symmetry, how can one produce microscopic motors & persistent motion, as commonly observed in biology?

1) Carnot cycle & the lack of equilibrium isothermal motor

Hypothesis: macroscopic system subject to the laws of thermodynamics





A→B: isothermal spontaneous expansion.
Produces work
Requires heat to maintain temperature

B→C: isolate the engine & let the expansion continue.
Adiabatic cooling ($Q = \Delta S = 0$) & $w > 0$

C→D: isothermal compression, produces heat, cost work.

D→A: adiabatic compression to close the cycle.

1st law of thermodynamics: $dE = TdS - pdV$ since $\Delta Q = 0$

$$\oint_{cycle} dE = 0 = \underbrace{\int TdS}_{\text{Heat}} - \underbrace{\int pdV}_{\text{work}} \Rightarrow \text{Work } W = \int_{①} TdS + \underbrace{\int_{②} TdS}_{=0} + \int_{③} TdS + \underbrace{\int_{④} TdS}_{=0}$$

①: $Q_H = T_H (S_B - S_A)$

③: $Q_C = T_C (S_D - S_C) = T_C (S_A - S_B)$

$\Big\}$ $W = (T_H - T_C)(S_B - S_A) > 0$

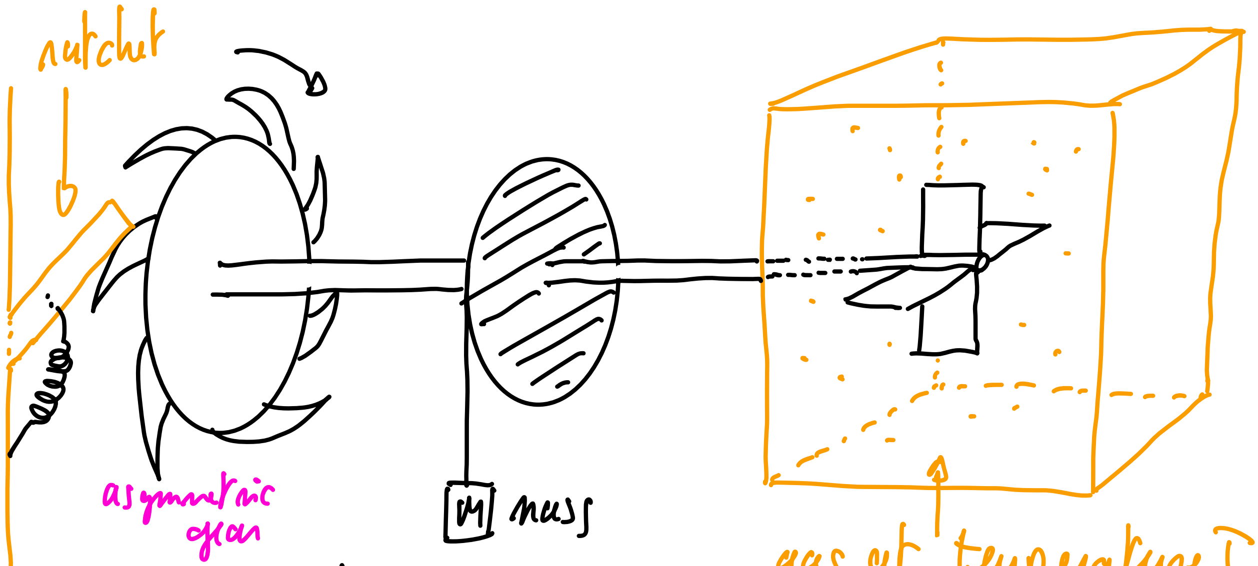
Cost: $Q_H > 0$; Efficiency $\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$

When $T_C \to T_H$, $\eta \to 0$ and one cannot extract energy from a single temperature macroscopic motor ruled by equilibrium thermodynamics.

Idea: Maybe, in a small system, fluctuations can help?

2) Thermal Ratchets

* Smolluchowsky, Phys. Z. 13, 1069 (1912)
* Feynman, Mecanics, Chap. 46, lectures on Physics



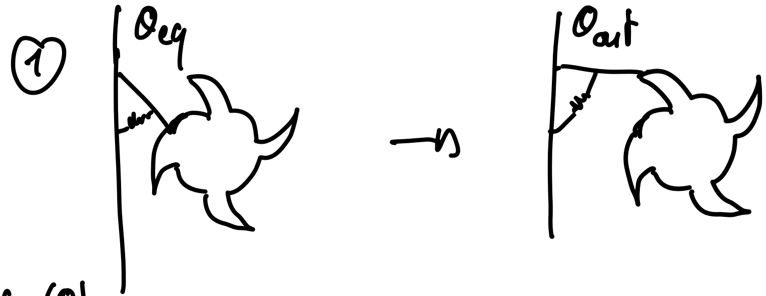
Idea: The gas molecules randomly collide with the paws, which promotes clockwise (cw) & counterclockwise (ccw) rotations of the axis.

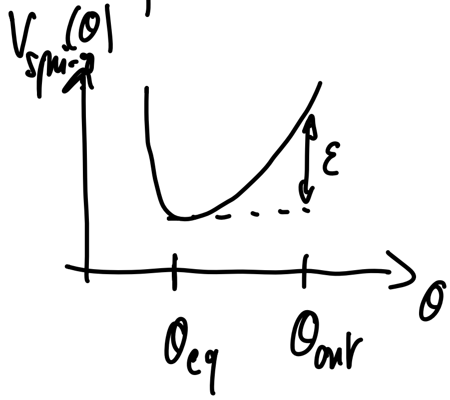
The ratchet allows for the cw rotations of the gear, but prevents its counterclockwise rotation.

The overall system should thus rectifies the motion of the gear, leading to an isothermal stochastic motor that can exert work & lift the mass M.

Problem: it does not work. Why?

To make the gear rotate, we need to lift the ratchet from its rest angle θ_{eq} up to the angle θ_{out} which releases the wheel.





This requires an increase of energy of the spring, which is then dissipated once the wheel has rotated $\Rightarrow$ heats up the spring.
$\Rightarrow$ The whole system equilibrates at temperature T.

Then, the probability that the ratchet opens spontaneously is $e^{-\beta\varepsilon}$, which is the same as the probability that the gas particles make the wheel rotate. The mass then makes the gear go CCW on average $\Rightarrow$ no motor, except if $T_{spring} < T$

[Parrondo, Español, Am. J. Phys. 64, 1125 (1996)]

Conclusion: No isothermal motor in equilibrium.

Symmetry: breaking $\theta \to -\theta$ symmetry, as the asymmetric gear does, is not sufficient $\Rightarrow$ need to break time reversal symmetry to allow for a non-vanishing steady-state J_θ current

Several different strategies:

(i) Non isothermal systems.

(ii) Two-state systems, with transition rates between states that drive

3) Fluctuating drive: not treated in class

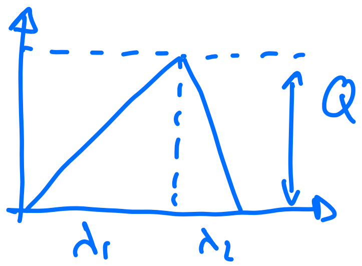
[Magnasco, Phys. Rev. Lett. 71, 1477 (1993)]

See also [C. R. Acad. Sci. Paris, t. 315, p. 1635-1639, (1992)]

Model: * Brownian particle in an asymmetric potential

$\lambda \equiv \lambda_1 + \lambda_2$

$\Delta\lambda \equiv \lambda_1 - \lambda_2$

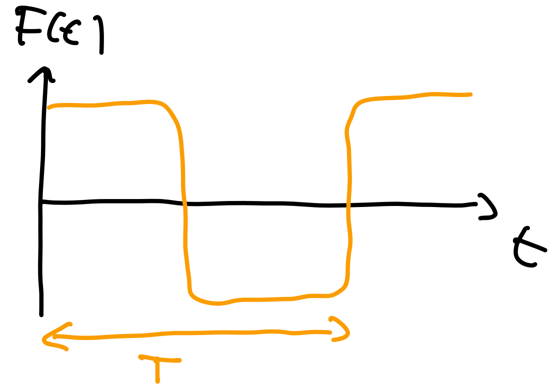


$\dot{x} = -V'(x) + \xi(t) + F(t)$

$\xi(t)$ a GWN $\langle \xi \rangle = 0$

$\langle \xi(t)\xi(t') \rangle = 2kT\delta(t-t')$

* $F(t)$ is a symmetric fluctuating force of zero mean



* Periodic boundary conditions.

Question: can there be a nonzero current?

3.1) Constant force F

FPE: $\partial_t P = kT\,\partial_{xx}P + \partial_x\left[V'(x)P - FP\right] = -\partial_x J; \quad J = -kT\partial_x P + FP - V'(x)P(x)$ (1)

Steady-state: $\partial_t P = 0 \Rightarrow J$ constant

$\Rightarrow$ Solve (1) $\Leftrightarrow \partial_x P = -\beta J + \beta F P - \beta P \partial_x V$

for constant J & use $P(L) = P(0)$ & $\int_0^L dx\, P(x) = 1$

Homogeneous solution: $P_H(x) = \alpha\, e^{\beta[Fx - V(x)]}$

Look for $P_J(x) = \alpha(x)\, e^{\beta[Fx - V(x)]} \Rightarrow \alpha'(x) = -\beta J\, e^{-\beta[Fx - V(x)]}$

General solution:

$$\boxed{P(x) = P(0)\, e^{\beta[Fx - V(x)]} - \beta J \int_0^x du\, e^{-\beta[V(x)-Fx]}\, e^{\beta[V(u)-Fu]}}$$

where: $x \le \lambda_1$; $V(x) = \frac{Qx}{\lambda_1}$

$\lambda_1 \le x \le \lambda$; $V(x) = \frac{\lambda - x}{\lambda_2} Q$

Two unknowns J & $P(0)$ $\to$ two equations $P(\lambda) = P(0)$ & $\int_0^\lambda dx\, P(x) = 1$

$$P(\lambda) = 0 \Rightarrow J = \frac{2P(0)\sinh\left(\beta \frac{\lambda F}{2}\right)}{\frac{\lambda_1}{Q - \lambda_1 F}\left(e^{\beta(Q - \frac{\Delta F}{2})} - e^{\beta\frac{\lambda F}{2}}\right) + \frac{\lambda_2}{Q + \lambda_2 F}\left(e^{\beta(Q - \frac{\Delta F}{2})} - e^{-\beta\frac{\lambda F}{2}}\right)}$$

Proof:

$$P(0) = P(0) e^{\beta\lambda F} - \beta J e^{\beta F\lambda}\left[\int_0^{\lambda_1} du\, e^{\beta\left[\frac{Q}{\lambda_1} - F\right]u} + \int_{\lambda_1}^{\lambda} du\, e^{\beta\frac{\lambda}{\lambda_2}Q}\, e^{-\beta\left[\frac{Q}{\lambda_2}+F\right]u}\right]$$

$$P(0)\left[1 - e^{\beta\lambda F}\right] = -\cancel{\beta} J e^{\beta F\lambda}\left\{\frac{e^{\beta[Q - F\lambda_1]} - 1}{\cancel{\beta}\left[\frac{Q}{\lambda_1} - F\right]} + e^{\beta\frac{\lambda}{\lambda_2}Q}\, \frac{e^{-\beta\left[\frac{Q}{\lambda_2}+F\right]\lambda} - e^{-\beta\left[\frac{Q}{\lambda_2}+F\right]\lambda_1}}{-\cancel{\beta}\left[\frac{Q}{\lambda_2}+F\right]}\right.$$

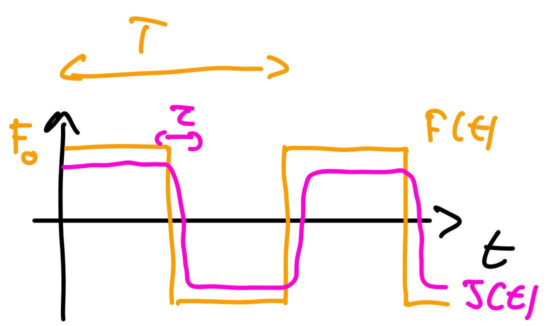
$$= -J\left\{\lambda_1 \frac{e^{\beta[Q+F\lambda_2]} - e^{\beta\lambda F}}{Q - \lambda_1 F} - \lambda_2 \frac{1 - e^{\beta F\lambda_2 + \beta Q}}{Q + \lambda_2 F}\right\}$$

$\times e^{-\frac{\lambda F}{2}}$

$$2P(0)\sinh\left(\beta\frac{\lambda F}{2}\right) = J\left\{\lambda_1 \frac{e^{\beta[Q - \frac{\Delta F}{2}]} - e^{\beta\frac{\lambda}{2}F}}{Q - \lambda_1 F} + \lambda_2 \frac{e^{\beta[Q - \frac{\Delta F}{2}]} - e^{-\beta\frac{\lambda F}{2}}}{Q + \lambda_2 F}\right\}$$

3.2) The limit of large T

$$\bar{J} = \frac{1}{T}\int_0^T ds\, J(F(s))$$



As $F(t)$ flips, so does $J(t)$, with some relaxation time τ.

When $T \gg \tau$; $\bar{J} \simeq \frac{1}{2}\left[J(F_0)+J(-F_0)\right]$

Q: Under what conditions is $\bar{J} \neq 0$?

① $\lambda_1=\lambda_2$, $J(F) \equiv \frac{N(F)}{D(F)}$

* symmetric potential $\Rightarrow P_0(F)=P_0(-F)$; $\sinh\left(\beta\frac{\lambda F}{2}\right)$ is odd

$\Rightarrow N(F) = 2P_0 \sinh(\beta\lambda F)$ is odd

* $$D(F,\Delta=0) = \underbrace{\frac{\lambda}{2Q-\lambda F}\left(e^{\beta Q}-e^{\beta\frac{\lambda F}{2}}\right)}_{f(F)} + \underbrace{\frac{\lambda}{2Q+\lambda F}\left(e^{\beta Q}-e^{-\beta\frac{\lambda F}{2}}\right)}_{f(-F)} \qquad (*)$$

$= f(F) + f(-F) \Rightarrow$ even

overall $J(F)$ is odd & $\bar{J}=\frac{1}{2}\left(J(F)+J(-F)\right)=0$

Because of the left-right symmetry, the system cannot "choose" a direction and $\bar{J}=0$.

② $\lambda_1 \neq \lambda_2$. In principle, need to compute $P_0(F)$, as in Magnasco's PRL.

Work to leading order for small Δ & F.

$$N(F) \simeq P_0^0 \beta F \lambda \quad \text{where} \quad P_0(\Delta,F) = P_0^0 + o(\Delta,F)$$

$$D(F) = \frac{\lambda+\Delta}{2Q-(\lambda+\Delta)F}\left[e^{\beta Q}\left(1-\beta\frac{\Delta F}{2}\right) - e^{\beta\frac{\lambda F}{2}}\right] + \frac{\lambda-\Delta}{2Q+(\lambda-\Delta)F}\left[e^{\beta Q}\left(1-\beta\frac{\Delta F}{2}\right) - e^{-\beta\frac{\lambda F}{2}}\right]$$

$$D(F) = \frac{(\lambda+\Delta)}{2Q-\lambda F}\cdot\left(1+\frac{\Delta F}{2Q-\lambda F}\right)\left[e^{\beta Q} - e^{\beta\frac{\lambda F}{2}} - \beta e^{\beta Q}\frac{\Delta F}{2}\right]$$
$$+ \frac{(\lambda-\Delta)}{2Q+\lambda F}\left(1+\frac{\Delta F}{2Q+\lambda F}\right)\left[e^{\beta Q} - e^{-\beta\frac{\lambda F}{2}} - \beta e^{\beta Q}\frac{\Delta F}{2}\right]$$

$D(F) = D_0(F) + D_1(F)\Delta$

$D_0(F) = (*) \Rightarrow$ even

$$D_1(F) = \frac{1}{2Q-\lambda F}\left(e^{\beta Q} - e^{\beta\frac{\lambda F}{2}}\right) - \frac{1}{2Q+\lambda F}\left(e^{\beta Q} - e^{-\beta\frac{\lambda F}{2}}\right)$$

$$+ \frac{\lambda F}{(2Q-\lambda F)^2}\left(e^{\beta Q} - e^{\beta\frac{\lambda F}{2}}\right) - \frac{-\lambda F}{(2Q+\lambda F)^2}\left(e^{\beta Q} - e^{-\beta\frac{\lambda F}{2}}\right)$$

$$\underbrace{- \frac{\beta\frac{\lambda F}{2}}{2Q-\lambda F} e^{\beta Q}}_{} + \frac{-\beta\frac{\lambda F}{2}}{2Q+\lambda F} e^{\beta Q}$$

$$D_1(F) = g(F) - g(-F) \Rightarrow \text{odd}$$

$$J(F) \simeq \frac{N(F)}{D_0(F) + \Delta D_1(F)} \simeq \frac{N(F)}{D_0(F)}\left(1 - \Delta\frac{D_1(F)}{D_0(F)}\right) = \underbrace{\frac{N(F)}{D_0(F)}}_{\text{odd in } F} - \Delta \underbrace{\frac{N(F)D_1(F)}{D_0(F)^2}}_{\text{even in } F}$$

$$\Rightarrow \bar{J}(F) = -\Delta \frac{N(F)D_1(F)}{D_0(F)^2} \neq 0 \text{ whenever } \Delta \neq 0$$

Here, breaking left-right symmetry suffice to generate a current.

(ii) Breakdown of FDR: We can recast this problem into

$$\dot{x} = -V'(x) + \tilde{\eta}(t) \quad ; \text{ where } \tilde{\eta}(t) = \sqrt{2T}\,\eta(t) + F(t)$$

$$\langle \tilde{\eta}(t)\tilde{\eta}(t')\rangle = \underbrace{2T\,\delta(t-t')}_{\text{FDR abiding noise}} + \underbrace{\langle F(t)F(t')\rangle}_{\text{non equilibrium driving}}$$

the system out of equilibrium (of molecular motor).

(iii) Break FDR with temporal correlations

$$\dot{p}(t) = -\int_{-\infty}^{t} ds\, \gamma(t-s)\, p(s) - V'(x(t)) + \sqrt{2\gamma k_B T}\, \eta(t) \quad \text{with}$$

$$\langle \eta(t)\eta(t')\rangle \neq \gamma(t-t')$$ [Magnasco, Phys. Rev. Lett. 71, 1477 (1993)]

4) Molecular motors

4.1) Introduction

Molecular motors are proteins capable of exerting a non-zero average work.

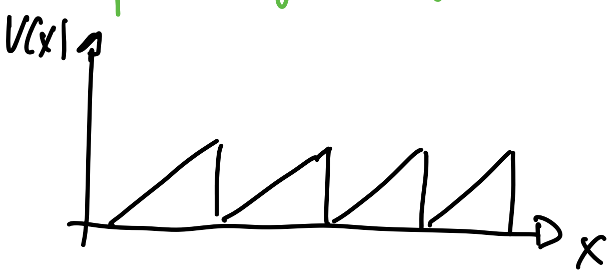
Ex: . kinesin & dynein transport vesicles along microtubules

. Myosin exert forces on actin filaments

Q: how is it possible?

At the scale of molecular motors, temperature equilibrates in μs while motors step $\sim 1ms$ ⇒ isothermal motion.

① Spatial symmetry is broken because filaments are polar



⇒ left-right asymmetry.

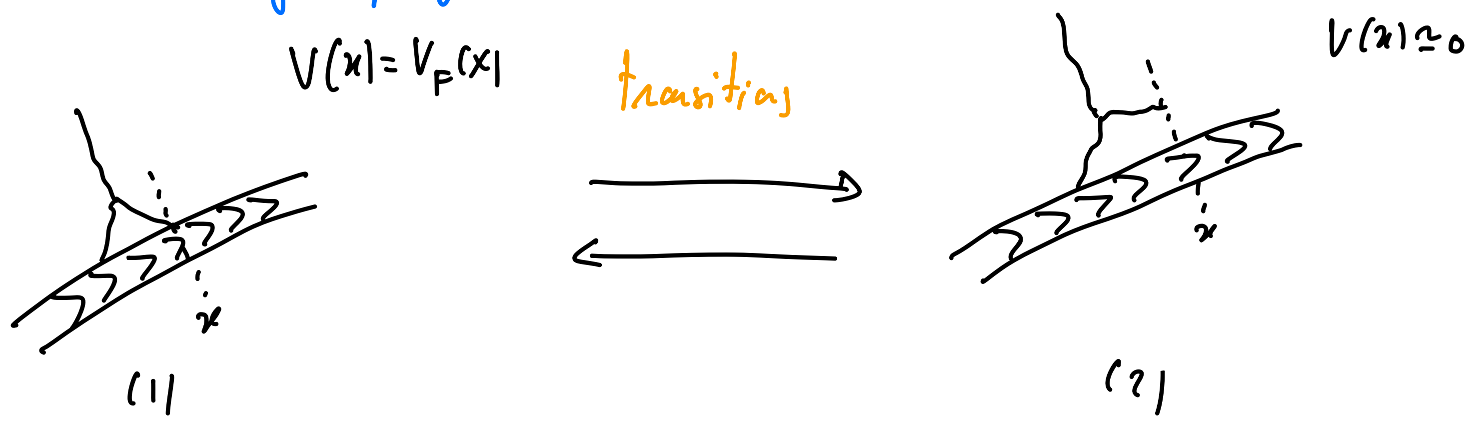
But if $P \propto e^{-\beta V(x)}$

then $J(x) = T\partial_x P + V' P = 0$

⇒ NOT SUFFICIENT

② Two-state model breaks detailed balance

State 1: strong coupling — State 2: weak coupling



Idea: In each state, the dynamics would relax to $e^{-\beta V(x)}$ and thus leads to vanishing current, but the transitions between the states prevents that. $\Rightarrow$ How?

4.2) Model and dynamics

We consider Brownian dynamics in each state and transitions at rates ω_1 and ω_2 from (1) to (2) and (2) to (1), respectively.

$P_i(x,t)$: probability to find the system in state i and at position x at time t.

$P(x,t) = P_1(x,t) + P_2(x,t)$ the proba to find the system at x at time t, whatever its state.

Q: time evolution of $P_i(x,t)$?

Idea: $\partial_t P_i(x,t) = \lim_{dt \to 0} \dfrac{P_i(x,t+dt) - P_i(x,t)}{dt}$ $\Rightarrow$ compute $P_i(x,t+dt) - P_i(x,t)$ to order dt.

rates ω_i: proba to go from $1 \to 2$ in $[t, t+dt]$ $\underset{dt \to 0}{=} \omega_1 \, dt$

Two state changes $\propto (\omega_1 dt) \times (\omega_2 dt) \sim dt^2 \Rightarrow$ no need to consider

* $P(i,x,t+dt \mid j,y,t)$ the proba to find the system in state i & position x at time $t+dt$ given that it was in state j & position y at t. 8

$$\boxed{P(1,x,t+dt) = \int dy\, P_1(y,t)\, P(1,x,t+dt \mid 1,y,t) + \int dy\, P_2(y,t)\, P(1,x,t+dt \mid 2,y,t)}$$

$\Rightarrow$ we need to compute the conditional probabilities (a.k.a. "propagators")