Part 3 Nonequilibrium processes in an equilibrium environment

Relaxation process in an equilibrium environment

Approach to thermal equilibrium

Fluctuation theorem

Operations in an equilibrium environment

Jarzynski equality and the second law of thermodynamics

No pumping theorem

<relaxation process in an equilibrium environment>

1

may be large or small, the system parameters are time-independent

- physical system with almost stable states $j = 1, 2, \cdots, \Omega$

  E_j energy (free energy) of state j

- the system is in touch with a heat bath = a larger system (e.g., surrounding water) in equilibrium with inverse temperature β
- The interaction with the bath causes the system to "jump" from a state another, frome time to time, in a stochastic manner

$\Downarrow$

effective theory a Markov jump process with time-independent transition rates $\mathbb{W} = (W_{k \to j})_{k,j=1,\cdots,\Omega,\ k \neq j}$

☞ more or less faithful description of some systems (ionic conductors, trapped beads, ...)

☞ a theoretical playground for developing nonequlibrium statistical mechanics

(iii) basic assumptions on W

"proved" from a mechanical model + equlibrium stat. mech.
part 1 - p33 - (3)

- W satisfies detailed balance condition

$$(1) \quad \frac{W_{k\to j}}{W_{j\to k}} = e^{\beta(E_k - E_j)}$$

for any k, j with $k \neq j$ and $W_{k\to j} \neq 0$

part 2 p.34

- all states are "connected" through nonzero $W_{k\to j}$ → R is irreducible

(for $\forall j, k$, $\exists n > 0$ and $i_0, i_1, \cdots, i_n$ s.t. $i_0 = j$, $i_n = k$, and
$W_{i_{\ell-1}\to i_\ell} \neq 0$ for $\ell = 1, \cdots, n$)

(remark (1) implies

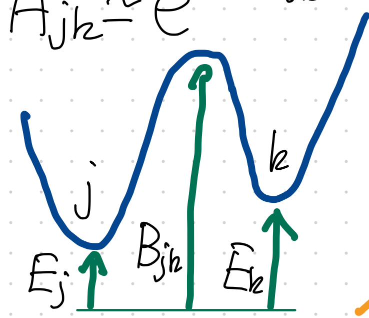
$$(2) \quad W_{k\to j} = e^{\beta E_k} \boxed{A_{jk}}$$ for any j, k

with $A_{jk} = A_{kj} \geq 0$

characterizes the barrier between j and k

example

$$(3) \quad A_{jk} \simeq e^{-\beta B_{jk}}$$



)

§ approach to thermal equilibrium

corresponding transition rate matrix (1) $R_{jk} = w_{k\to j} \quad (j \neq k)$

R is irreducible → unique $\mathbb{P}^S$ s.t. (2) $R\mathbb{P}^S = 0$ ⇐ part 2 - p34

detailed balance condition (3) $w_{k\to j}\, e^{-\beta E_k} = w_{j\to k}\, e^{-\beta E_j}$

(4) $R_{jk}\, p_k^{(can,\beta)} = R_{kj}\, p_j^{(can,\beta)}$ with (5) $p_j^{(can,\beta)} = \dfrac{e^{-\beta E_j}}{Z(\beta)}$

(5) $\sum_{k=1}^{\Omega} R_{jk} p_k^{(can,\beta)} = R_{jj} p_j^{(can,\beta)} + \sum_{k(\neq j)} \underbrace{R_{jk} p_k^{(can,\beta)}}_{= R_{kj} p_j^{(can,\beta)}} = \left(\sum_{k=1}^{\Omega} R_{kj}\right) p_j^{(can,\beta)} = 0$

(6) $R\mathbb{P}^{(can,\beta)} = 0 \xrightarrow{\text{niqueness}}$ (7) $\mathbb{P}^S = \mathbb{P}^{(can,\beta)}$

Theorem: let $\mathbb{P}(t)$ be the solution of (1) $\dot{\mathbb{P}}(t) = R\,\mathbb{P}(t)$ with arbitrary initial distribution $\mathbb{P}(0)$ then (2) $\lim_{t \nearrow \infty} \mathbb{P}(t) = \mathbb{P}^{(\mathrm{can},\beta)}$

the minus first law of thermodynamics has been proved!!
(within the effective Markov jump process)

fluctuation in small systems is also precisely described by $\mathbb{P}^{(\mathrm{can},\beta)}$

(iii) H-theorem

part 2 – p35

(3) $H(\mathbb{P}) = D(\mathbb{P} \| \mathbb{P}^{(\mathrm{can},\beta)}) = \beta\,\{F(\mathbb{P}) - F(\beta)\}$

(4) $F(\mathbb{P}) = \langle \hat{E} \rangle_{\mathbb{P}} - \beta^{-1} S(\mathbb{P})$

part 2 – p17

"Helmholtz free energy" for general probability distribution $\mathbb{P}$

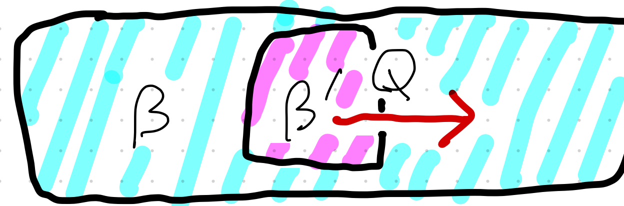
(5) $F(\beta) = -\beta^{-1} \log Z(\beta)$ ← the standard Helmholtz free energy

Theorem $F(\mathbb{P}(t))$ is non-increasing in t and converges to $F(\beta)$

§ relaxation to equilibrium from a different temperature : a fluctuation theorem 5

chose $\mathbb{P}(0) = \mathbb{P}^{(\mathrm{can},\beta')}$ with $\beta \neq \beta'$

then $\mathbb{P}(t) \xrightarrow{t\uparrow\infty} \mathbb{P}^{(\mathrm{can},\beta)}$



part 2
P47–(2) entropy production

detailed balance

(1) $\Theta_{k\to j} = \log \dfrac{W_{k\to j}}{W_{j\to k}} = \underbrace{\beta(E_k - E_j)}_{\text{heat transfered to the bath}}$

path in the time interval $[0,\tau]$ (2) $\gamma = (j_0, \cdots, j_n ; t_1, \cdots, t_n)$

(3) $\Theta(\gamma) = \sum_{m=1}^{n} \Theta_{j_{m-1}\to j_m} = \beta \sum_{m=1}^{n} \beta(E_{j_{m-1}} - E_{j_m}) = \beta(E_{j_0} - E_{j_n}) = \beta(E_{\gamma_{init}} - E_{\gamma_{fin}})$

part 2
P51–(1)

(4) $\Psi(\gamma) = \Theta(\gamma) + \overbrace{\log P_{\gamma_{init}}(0)}^{-\beta' E_{\gamma_{init}} - \log Z(\beta')} \overbrace{- \log P_{\gamma_{fin}}(0)}^{\beta' E_{\gamma_{fin}} + \log Z(\beta')} = (\beta - \beta')\underbrace{(E_{\gamma_{init}} - E_{\gamma_{fin}})}_{\text{total heat transfered from the system to the bath } Q(\gamma)}$

(1) $P(s) = \left\langle \delta((\beta-\beta')\hat{Q} - s) \right\rangle_{\mathbb{P}(0),\tilde{\omega}}$

probability density that $(\beta-\beta')Q(\Upsilon)$ equals $s \in \mathbb{R}$

part2-p51-(4)

fluctuation theorem (2) $\boxed{P(s) = e^{s} P(-s)}$

▷ $(\beta-\beta')\hat{Q}$ is more likely to be positive = heat flows from hot to cold

$\hat{Q}$ is likely to be positive if $\beta-\beta'>0$

$\hat{Q}$ is likely to be negative if $\beta-\beta'<0$

we know this since $\mathbb{P}(t) \to \mathbb{P}^{(\mathrm{can},\beta)}$

▷ there is a small chance that $(\beta-\beta')\hat{Q}$ becomes negative

heat may flow from cold to hot!!

part1-p25-(3)

(3) $\mathrm{Prob}[(\beta-\beta')\hat{Q} \le -\xi] \le e^{-\xi}$ for any $\xi>0$

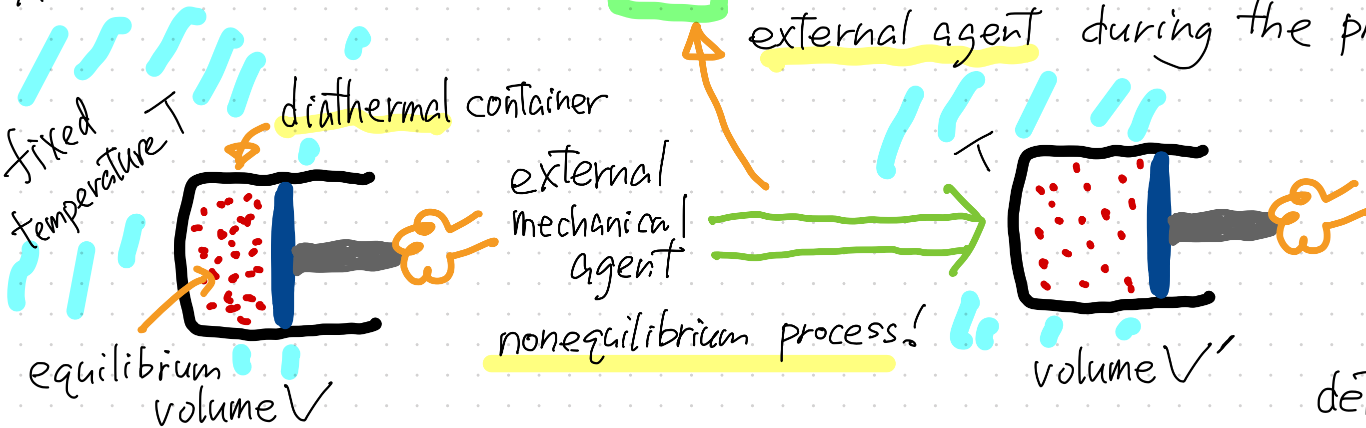
▷ the probability density $P(s)$ exhibits nontrivial symmetry (2)

meaningful in small system + small $\beta-\beta'$ + small τ

⟨operations to systems under an equilibrium environment⟩

▷ typical situation isothermal operation

$\boxed{W}$ the work done by the system to the external agent during the process



▷ a system with controllable parameter $\alpha \in \mathbb{R}^\nu$

energy E_j^α transition rate $W^\alpha = (w_{j\to k}^\alpha)_{j\neq k}$

detailed balance condition

$$\frac{w_{k\to j}^\alpha}{w_{j\to k}^\alpha} = e^{\beta(E_k^\alpha - E_j^\alpha)} \quad (\text{if } w_{k\to j}^\alpha \neq 0)$$

the external agent controls α according to a fixed protocol $\alpha(t)$ $t \in [0, \tau]$

fixed functions

we write $E_j^{\alpha(t)} \to E_j(t)$ $w_{k\to j}^{\alpha(t)} \to w_{k\to j}(t)$ $\tilde{w} = (w_{k\to j}(t))_{k\neq j, t\geq 0}$

▷ heat and work

master equation (1) $\dot{\mathbb{P}}(t) = R(t)\,\mathbb{P}(t)$

$$\begin{cases} (2) & R_{jk}(t) = w_{k\to j}(t) \\ (3) & \dfrac{R_{jk}(t)}{R_{kj}(t)} = e^{\beta(E_k(t)-E_j(t))} \end{cases}$$

the energy expectation value at time t

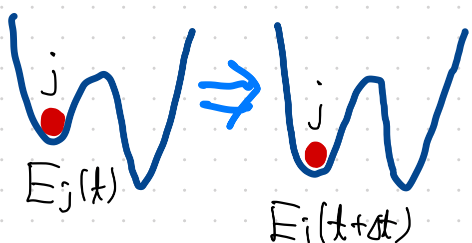
(4) $$\langle \hat{E}(t)\rangle_{\mathbb{P}(t)} = \sum_{j=1}^{\Omega} E_j(t)\, p_j(t)$$

(5) $$-\frac{d}{dt}\langle \hat{E}(t)\rangle_{\mathbb{P}(t)} = \boxed{-\sum_{j=1}^{\Omega} \dot{E}_j(t)\, p_j(t)}\ \boxed{-\sum_{j=1}^{\Omega} E_j(t)\, \dot{p}_j(t)}$$

the change of energy caused directly by the change in the parameter $\alpha(t)$

=

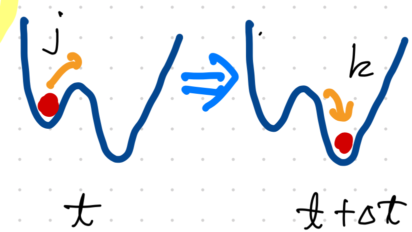
the work done in unit time by the system on the agent = power



the change of energy caused by the change in the probability distribution

=

the heat transfered in unit time from the system to the bath = heat current



(1) $-\frac{d}{dt}\langle \hat{E}(t)\rangle_{P(t)} = -\sum_{j=1}^{\Omega} \dot{E}_j(t)\, P_j(t) - \sum_{j=1}^{\Omega} E_j(t)\, \dot{P}_j(t)$

power heat current

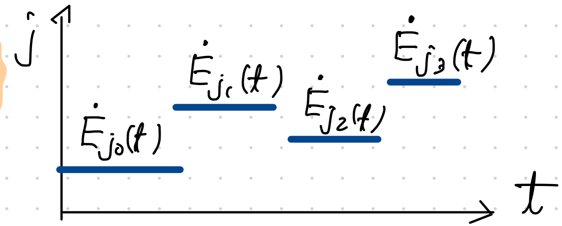
- total work

(2) $W_{tot} = -\int_0^{\tau} dt \sum_{j=1}^{\Omega} \dot{E}_j(t) P_j(t) = \langle\langle \hat{W} \rangle\rangle_{P(0),\tilde{\omega}}$

- the work done in a path $\gamma = (j_0, \cdots, j_n; t_1, \cdots, t_n)$, $t_0 = 0$, $t_{n+1} = \tau$

(3) $W(\gamma) = -\sum_{m=0}^{n} \int_{t_m}^{t_{m+1}} dt\, \dot{E}_{j_m}(t)$

state quantity part 2 p44



- total heat and the heat in a path γ

(4) $Q_{tot} = -\int_0^{\tau} dt \sum_{j=1}^{\Omega} E_j(t) \dot{P}_j(t) = \int_0^{\tau} dt \sum_{\substack{j,k \\ (j\neq k)}} P_j(t)\, w_{j\to k}(t) \{E_j(t) - E_k(t)\} = \langle\langle \hat{Q} \rangle\rangle_{P(0),\tilde{\omega}}$

(5) $Q(\gamma) = \sum_{m=1}^{n} \{E_{j_{m-1}}(t_m) - E_{j_m}(t_m)\}$

jump quantity part 2 p45

work $W(\gamma)$ and heat $Q(\gamma)$ are defined for each γ (Sekimoto 97), Jarzynski 97

§ Jarzynski equality

operation in an equilibrium environment from $t=0$ to $t=\tau$

energy $E_j(t)$ initial energy $E_j = E_j(0)$ final energy $E_j' = E_j(\tau)$

transition rates $w_{k\to j}(t)$ (1) $\dfrac{w_{k\to j}(t)}{w_{j\to k}(t)} = e^{\beta(E_k(t)-E_j(t))}$

when $w_{k\to j}(t)\neq 0$

entropy production (2) $\theta_{k\to j}(t) = \log \dfrac{w_{k\to j}(t)}{w_{j\to k}(t)} = \beta(E_k(t)-E_j(t))$

choose initial distribution as $\mathbb{P}(0) = \mathbb{P}^{can,\beta}$ (3) $p_j^{can,\beta} = \dfrac{e^{-\beta E_j}}{Z(\beta)}$, $F(\beta) = -\frac{1}{\beta}\log Z(\beta)$

set $\mathbb{q} = \mathbb{P}^{can',\beta}$ (4) $p_j^{can',\beta} = \dfrac{e^{-\beta E_j'}}{Z'(\beta)}$, $F'(\beta) = -\frac{1}{\beta}\log Z'(\beta)$

integrated fluctuation theorem (part 2 p50-(2))

(5) $\left\langle\!\left\langle \exp\left[\underbrace{-\hat{\hat{\Theta}} - \log p_{\gamma_{init}}(0) + \log q_{\gamma_{fin}}}_{=(\ast)}\right]\right\rangle\!\right\rangle_{\mathbb{P}(0),\tilde{w}} = 1$

path (1) $\gamma = (j_0, \cdots, j_n ; t_1, \cdots, t_n)$, $t_0 = 0$, $t_{n+1} = \tau$

total entropy production

(2) $\textcircled{H}(\gamma) = \sum_{m=0}^{n-1} \theta_{j_m \to j_{m+1}}(t_{m+1}) = \beta \sum_{m=0}^{n-1} \{ E_{j_m}(t_{m+1}) - E_{j_{m+1}}(t_{m+1}) \}$

(3) $\log p_{\gamma_{init}}(0) = \log p_{j_0}^{can, \beta} = -\beta E_{j_0}(0) - \log Z(\beta) = -\beta E_{j_0}(0) + \beta F(\beta)$

(4) $\log q_{\gamma_{fin}} = \log p_{j_n}^{can', \beta} = -\beta E_{j_n}(\tau) - \log Z'(\beta) = -\beta E_{j_n}(\tau) + \beta F'(\beta)$

(5)
$$(*) = \beta \left\{ E_{j_0}(0) - \sum_{m=0}^{n-1} \left(E_{j_m}(t_{m+1}) - E_{j_{m+1}}(t_{m+1}) \right) - E_{j_n}(\tau) - F(\beta) + F'(\beta) \right\}$$

$$= \beta \left\{ \boxed{\sum_{m=0}^{n} \left(E_{j_m}(t_m) - E_{j_m}(t_{m+1}) \right)} - F(\beta) + F'(\beta) \right\} = \beta \{ W(\gamma) - F(\beta) + F'(\beta) \}$$

$\|$

(6) $$-\sum_{m=0}^{n} \int_{t_m}^{t_{m+1}} dt \, \dot{E}_{j_m}(t) = W(\gamma)$$ the work in path γ !!

Jarzynski equality

Jarzyski 97

(1) $(*) = \beta\{W(\gamma) - \Delta F\}$, (2) $\Delta F = F(\beta) - F'(\beta)$

(3) $\langle\!\langle e^{(*)} \rangle\!\rangle_{\mathbb{P}(0),\tilde{\omega}} = 1$ integrated fluctuation theorem

(4) $$\boxed{\langle\!\langle e^{\beta \hat{W}} \rangle\!\rangle_{\mathbb{P}(0),\tilde{\omega}} = e^{\beta \Delta F}}$$

exact equality that holds for any operation in any system !!

slow or fast

large or small

corresponding fluctuation theorem

Crooks 99

(5) $$\boxed{p^{\tilde{\omega}}(W) = e^{\beta(-W+\Delta F)}\, p^{\tilde{\omega}^\dagger}(-W)}$$

starts from $\mathbb{P}^{\mathrm{can},\beta}$

$p^{\tilde{\omega}^\dagger}(W)$ the probability distribution of work in the inveres process

The second law of thermodynamics

Jensen's inequality (1) $e^{\beta\langle\langle \hat{W} \rangle\rangle_{P(0),\tilde{w}}} \le \langle\langle e^{\beta\hat{W}} \rangle\rangle_{P(0),\tilde{w}} = e^{\beta\Delta F}$

(2) $W_{tot} = \langle\langle \hat{W} \rangle\rangle_{P(0),\tilde{w}} \le \Delta F = F(\beta) - F'(\beta)$

maximum work principle

essentially no fluctuation in a macroscopic system

"violation" of the second law in a small system

probability that $\hat{W} \le \Delta F$ is "violated"

(3) $\mathrm{Prob}[\hat{W} \ge \Delta F + \xi] \le e^{-\beta\xi}$ for any $\xi > 0$

$\Big(\because$ (4) $\mathrm{LHS} = \langle\langle \chi[\hat{W} - \Delta F - \xi \ge 0] \rangle\rangle_{P(0),\tilde{w}} \le \langle\langle e^{\beta\{\hat{W} - \Delta F - \xi\}} \rangle\rangle_{P(0),\tilde{w}} \le e^{-\beta\xi}$

(5) $\chi[\mathrm{true}] = 1$, $\chi[\mathrm{false}] = 0$ $\quad (\chi[x \ge 0] \le e^{x})$ $\Big)$

(6) $e^{-\beta\xi} \ll 1$ if $\xi \gg kT$ $\Rightarrow$ no macroscopic violation

Simple example system of N independent spins

no magnetic field

suddenly apply magnetic field h at $\frac{\tau}{2}$ $\quad h \neq 0$

state (1) $\sigma = (\sigma_1, \dots, \sigma_N)$ (2) $\sigma_j = \pm 1$

energy (3) $E_\sigma(t) = \begin{cases} 0 & t \in [0, \frac{\tau}{2}) \\ E_\sigma = -h \sum_{j=1}^{N} \sigma_j & t \in [\frac{\tau}{2}, \tau] \end{cases}$

(4) $Z(\beta) = 2^N \qquad Z'(\beta) = (e^{\beta h} + e^{-\beta h})^N = \{2\cosh(\beta h)\}^N$

(5) $\Delta F = F(\beta) - F'(\beta) = \frac{N}{\beta} \log \frac{Z'(\beta)}{Z(\beta)} = \frac{N}{\beta} \log \cosh(\beta h) > 0$

$\simeq \frac{N\beta h^2}{2}$ if $\beta |h| \ll 1$

work (6) $W_\sigma = 0 - E_\sigma = h \sum_{j=1}^{N} \sigma_j$

all σ appears with equal probability 2^{-N} at time $\frac{\tau}{2}$

(7) $\langle W_\sigma \rangle = 0$ (8) $\langle (W_\sigma)^2 \rangle = N h^2$

(9) $\langle W_\sigma \rangle \leq \Delta F$ is of coures valid.

15

work (1) $W_\sigma = 0 - E_\sigma = h\sum_{j=1}^{N}\sigma_j$ (all σ appears with equal probability 2^{-N})

N=1

(2) $W_\sigma = \begin{cases} h \gneq \Delta F = \frac{1}{\beta}\log\cosh(\beta h) & \text{with probability } 1/2 \\ -h \lneq \Delta F & \text{with probability } 1/2 \end{cases}$

$\boxed{\text{the second law is "violated" with probability } 1/2}$

N ≫ 1

W_σ is distributed according to (3) $P(W) = \frac{1}{\sqrt{2\pi N h^2}}\, e^{-\frac{W^2}{2Nh^2}}$

(4) $\mathrm{Prob}[W_\sigma \geq \Delta F] \sim e^{-\frac{(\Delta F)^2}{2Nh^2}} \sim e^{-\frac{1}{2}\left(\frac{\log\cosh(\beta h)}{\beta h}\right)^2 N}$

very small

essentially no violation of the 2nd law
even $W \simeq \Delta F$ is impossible

irreversible process

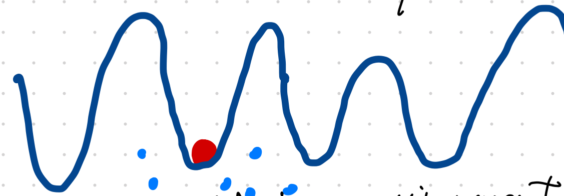
§ no pumping theorem

(mainly for small systems)

Rahav, Horowitz, Jarzynski 2008

motivation

a Brownian particle in a one-dimensional ring
periodic b.c.

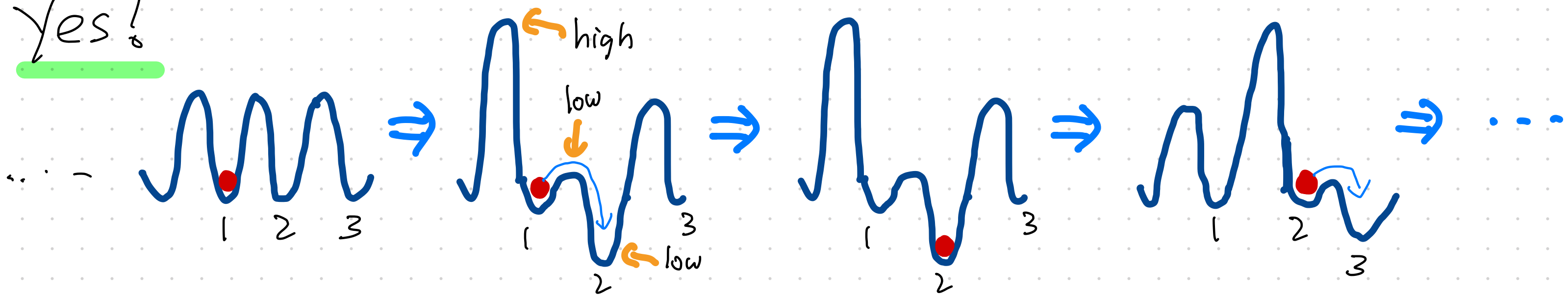


equilibrium environment

Can one generate a directed current of the particle (or particles) by modifying the potential periodically in time?

transport in biological systems, nano-machines, ...

Yes!



we need to change both the potential depths E_j and the barrier B_{jk} see p2 (3)

can we "pump" by only modifying the potential depths E_j ??

setting and results

P2-(2)

this assumption can be removed

- Markov jump process with (1) $W_{k\to j}(t) = \boxed{e^{\beta E_k(t)} A_{kj}}$

  (2) $A_{kj} = A_{jk} \geq 0$ time-independent, all states are connected by nonzero A_{jk}'s

  control $E_k(t)$ according a periodic protocol (3) $E_k(t+\tau_0) = E_k(t)$

- $\mathbb{P}(t)$ solution of the master equation (4) $\dot{\mathbb{P}}(t) = R(t)\,\mathbb{P}(t)$

- probability current (5) $J_{k\to j}(t) = P_k(t)W_{k\to j}(t) - P_j(t)W_{j\to k}(t)$ $(k \neq j)$

part2-p32

$$\boxed{\text{Theorem} \quad (6) \quad \lim_{T\uparrow\infty} \frac{1}{T}\int_0^T dt\, J_{k\to j}(t) = 0 \quad \text{for any } k, j \ (k \neq j)}$$

no net probability current $\rightarrow$ pumping is impossible!

Rahav, Horowitz, Jarzynski 2008

proof Maes, Netočný, Thomas 2010

set (1) $v_k = \sum_{j(\neq k)} A_{jk}$ (2) $T_{jk} = \begin{cases} \dfrac{A_{jk}}{v_k} & \text{for } j \neq k \\ 0 & \text{for } j = k \end{cases}$

(3) $T_{jk} \geq 0$ and (4) $\sum_{j=1}^{\Omega} T_{jk} = 1$ → T is a stochastic matrix

Lemma T has eigenvalue 1, and it is nondegenerate → direct consequence of the Perron-Frobenius theorem part 2 - p.25

(proof let (5) $R = T - I$, which is an irreducible transition rate matrix. then use the convergence theorem (part 2 - p34))

$v = (v_k)_{k=1,\dots,\Omega}$ is the corresponding eigenvector

(proof (5) $T_{jk} v_k = A_{jk} = A_{kj} = T_{kj} v_j$

detailed balance condition!

and hence (6) $\sum_{k=1}^{\Omega} T_{jk} v_k = v_j$)

escape rate (1) $\lambda_k(t) = \sum_{j(\neq k)} W_{k\to j}(t) = e^{\beta E_k(t)} \sum_{j(\neq k)} A_{jk} = e^{\beta E_k(t)} \nu_k$

$j \neq k$

transition rate (2) $W_{k\to j}(t) = e^{\beta E_k(t)} A_{jk} = e^{\beta E_k(t)} \nu_k \frac{A_{jk}}{\nu_k} = \lambda_k(t)\, T_{jk}$

probability current (3) $j_{k\to j}(t) = P_k(t)\, W_{k\to j}(t) - P_j(t)\, W_{j\to k}(t)$

$$= T_{jk}\lambda_k(t) P_k(t) - T_{kj}\lambda_j(t) P_j(t)$$

long-time averages (4) $\nu_{k\to j} := \lim_{T\nearrow\infty} \frac{1}{T}\int_0^T dt\, j_{k\to j}(t)$ (5) $\rho_k := \lim_{T\nearrow\infty} \frac{1}{T}\int_0^T dt\, \lambda_k(t) P_k(t)$

periodicity (p17 (3)) is only used to guarantee the existence of the limits

(3) $\Rightarrow$ (6) $\boxed{\nu_{k\to j} = T_{jk}\rho_k - T_{kj}\rho_j}$

(7) $\dot{P}_k(t) + \sum_{j(\neq k)} j_{k\to j}(t) = 0$ continuity equation part 2 - p32 - (4)

since

(8) $\lim_{T\nearrow\infty} \frac{1}{T}\int_0^T dt\, \dot{P}_k(t) = 0$ (9) $\boxed{\sum_{j(\neq k)} \nu_{k\to j} = 0}$

from (1) $\nu_{k\to j} = T_{jk} P_k - T_{kj} P_j$

(2) $\displaystyle \sum_{j(\neq k)}{}' \nu_{k\to j} = 0$

we see (3) $\displaystyle \underbrace{\sum_{j(\neq k)}{}' T_{jk}}_{=1} P_k - \sum_{j(\neq k)}{}' T_{kj} P_j = 0$

(4) $\displaystyle \sum_{j=1}^{\Omega}{}' T_{kj} P_j = P_k \xRightarrow{\text{Lemma in p.18}}$ (5) $P_k = c\, v_k$

p18-(6) $\left(T_{jk} v_k = T_{kj} v_j \right)$

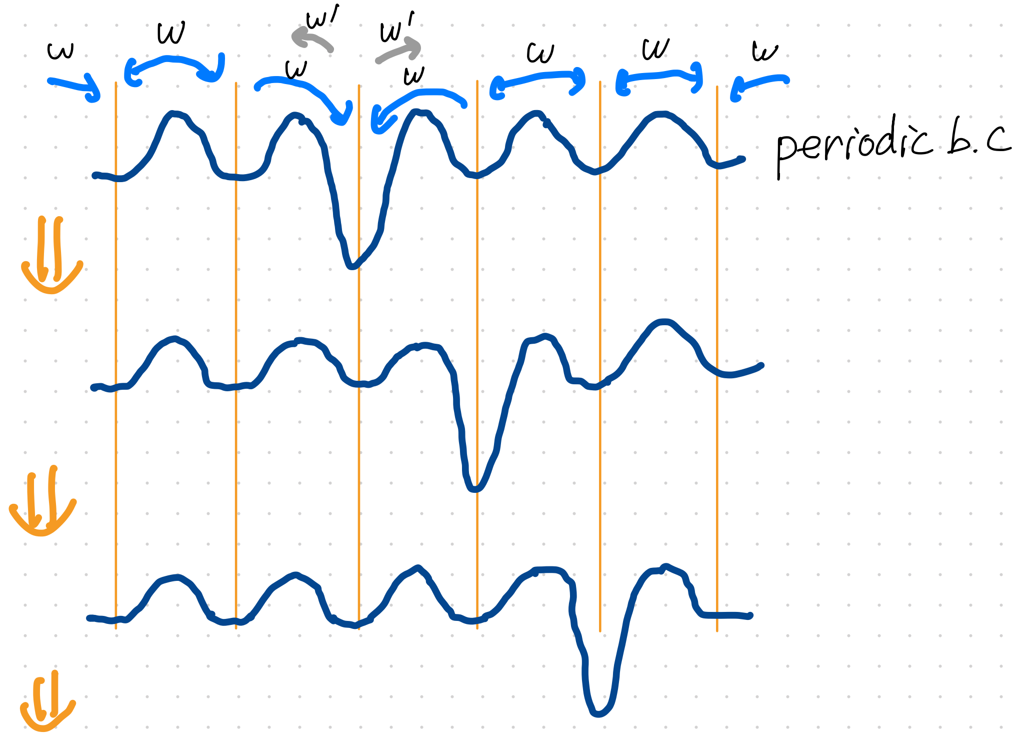
then (6) $\displaystyle \underbrace{\nu_{k\to j}}_{= \lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, \dot{j}_{k\to j}(t)} \overset{(1)}{=} c\, T_{jk} v_k - c\, T_{kj} v_j = 0$

Why doesn't the following "pump" work ??

a single particle

in the potential

$w' \ll w$



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No pumping theorem

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