Part 1 Foundation

What do we get from mechanics and equilibrium statistical mechanics?

Classical Hamiltonian mechanics

Jarzynski equality

Fluctuation theorem

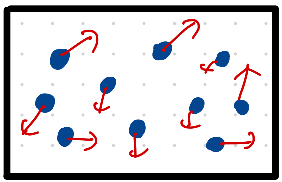
Detailed balance condition

< classical Hamiltonian mechanics >

1

§ phase space and Hamilton's equation

Λ



a system of N classical particles in d-dimensions → $d = 1, 2, 3 \dots$

position of the j-th particle $\mathbb{r}_j \in \Lambda \subset \mathbb{R}^d$

momentum of the j-th particle $\mathbb{p}_j \in \mathbb{R}^d$

phase space point (microscopic state)

(1) $X = (\mathbb{r}_1, \dots, \mathbb{r}_N, \mathbb{p}_1, \dots, \mathbb{p}_N) \in \Gamma = \Lambda^N \times \mathbb{R}^{Nd}$ → phase space

time-dependent Hamiltonian $H(t, X)$

general form ($d=3$)

(2) $$H(t,X) = \sum_{j=1}^{N} \left\{ \frac{(\mathbb{p}_j - q_j A(t,\mathbb{r}_j))^2}{2m_j} + q_j \varphi(t,\mathbb{r}_j) \right\} + V(t, \mathbb{r}_1, \dots, \mathbb{r}_N)$$

kinetic energy + electromagnetic forces

interaction + external force

Hamilton's equations

a trajectory (1) $X(t) = (\mathbb{q}_1(t), \cdots, \mathbb{q}_N(t), \mathbb{p}_1(t), \cdots, \mathbb{p}_N(t))$ with $t \in \mathbb{R}$

is a solution of Hamilton's equation

generally one cannot solve this

$$
(2) \quad \begin{cases} \dot{\mathbb{q}}_j(t) = \left. \dfrac{\partial H(t, X)}{\partial \mathbb{p}_j} \right|_{X = X(t)} \\[2ex] \dot{\mathbb{p}}_j(t) = - \left. \dfrac{\partial H(t, X)}{\partial \mathbb{q}_j} \right|_{X = X(t)} \end{cases}
$$

$\mathcal{J}_t : \Gamma \to \Gamma$ time-evolution map from 0 to t $(t \in \mathbb{R})$

determined by the Hamiltonian $H(t, X)$

i.e. (3) $\mathcal{J}_t(X(0)) = X(t)$ for any initial state $X(0)$

▷ we assume $\mathcal{J}_t$ is one-to-one for each $t \in \mathbb{R}$

this is always the case for usual Hamiltonians

§ Time-reversal symmetry

phase space point (1) $X = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N)$

time-reversal (2) $X^* = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, -\boldsymbol{p}_1, \ldots, -\boldsymbol{p}_N)$ flip all momenta

▷ time-independent Hamiltonian with time-reversal symmetry

(3) $\boxed{H(X) = H(X^*)}$

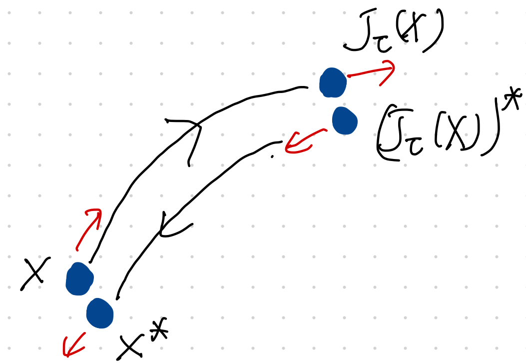
example (4) $H(X) = \sum_{j=1}^{N} \frac{(\boldsymbol{p}_j)^2}{2m_j} + V(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ no magnetic field

$\mathcal{T}_t$ the corresponding time-evolution map

then we have (5) $\left(\mathcal{T}_\tau\left((\mathcal{T}_\tau(X))^*\right)\right)^* = X$

or (6) $\mathcal{T}_\tau\left((\mathcal{T}_\tau(X))^*\right) = X^*$

for any $X \in \Gamma$ and $\tau > 0$

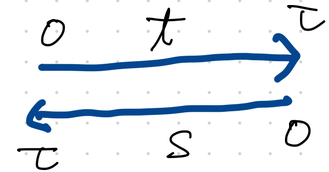


proof

a solution of Hamilton's eq. (1) $X(t) = (q_1(t), \cdots, q_N(t), p_1(t), \cdots, p_N(t))$, $t \in [0, \tau]$

(2) $\dot{q}_j(t) = \left.\dfrac{\partial H(X)}{\partial p_j}\right|_{X=X(t)}$, $\dot{p}_j(t) = -\left.\dfrac{\partial H(X)}{\partial q_j}\right|_{X=X(t)}$

time-reversed trajectory (3) $\tilde{X}(s) = (X(\tau - s))^*$, $s \in [0, \tau]$



$\quad \parallel$

(4) $(\tilde{q}_1(s), \cdots, \tilde{q}_N(s), \tilde{p}_1(s), \cdots, \tilde{p}_N(s))$

(5) $\tilde{q}_j(s) = q_j(\tau - s)$, $\tilde{p}_j(s) = -p_j(\tau - s)$

(6) $\dfrac{d}{ds}\tilde{q}_j(s) = -\dot{q}_j(\tau - s) = -\left.\dfrac{\partial H(X)}{\partial p_j}\right|_{X=X(\tau-s)} = \left.\dfrac{\partial H(\tilde{X})}{\partial \tilde{p}_j}\right|_{\tilde{X}=\tilde{X}(s)}$

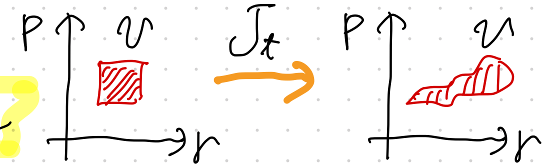
(7) $\dfrac{d}{ds}\tilde{p}_j(s) = \dot{p}_j(\tau - s) = -\left.\dfrac{\partial H(X)}{\partial q_j}\right|_{X=X(\tau-s)} = -\left.\dfrac{\partial H(\tilde{X})}{\partial \tilde{q}_j}\right|_{\tilde{X}=\tilde{X}(s)}$

where $\underset{\substack{\parallel \\ X^*}}{\tilde{X}} = (\tilde{q}_1, \cdots, \tilde{q}_N, \tilde{p}_1, \cdots, \tilde{p}_N)$, $\tilde{q}_j = q_j$, $\tilde{p}_j = -p_j$, $H(X) = H(\tilde{X})$

$\tilde{X}(s)$ obeys the same Hamilton's equation determined by H. //

§ Liouville's theorem

the map $\mathcal{J}_t$ preserves the phase space volume

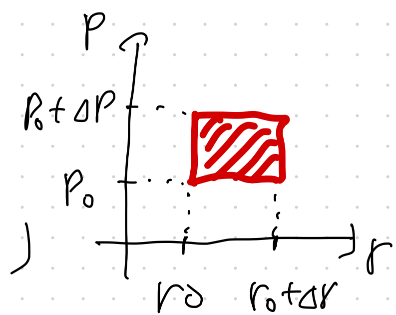


simple example (1) $\dot{r}(t) = \frac{p(t)}{m}$ (2) $\dot{p}(t) = f(r(t)) - \gamma p(t)$

time evolution by Δt (only the 1st order in Δt) (3) $f_0 = f(r_0)$

(4) $\Delta f = f(r_0+\Delta r) - f_0$

(5) $(r_0, p_0) \to \left(r_0 + \Delta t \frac{p_0}{m},\ p_0 + \Delta t(f_0 - \gamma p_0)\right) \eqqcolon (r_0', p_0')$



(6) $(r_0+\Delta r, p_0) \to \left(r_0+\Delta r+\Delta t\frac{p_0}{m},\ p_0 + \Delta t(f_0+\Delta f - \gamma p_0)\right)$

$= (r_0', p_0') + (\Delta r, \Delta t \Delta f) \eqqcolon a$

(7) $(r_0, p_0+\Delta p) \to \left(r_0 + \Delta t \frac{p_0+\Delta p}{m},\ p_0+\Delta p+\Delta t(f_0 - \gamma(p_0+\Delta p))\right)$

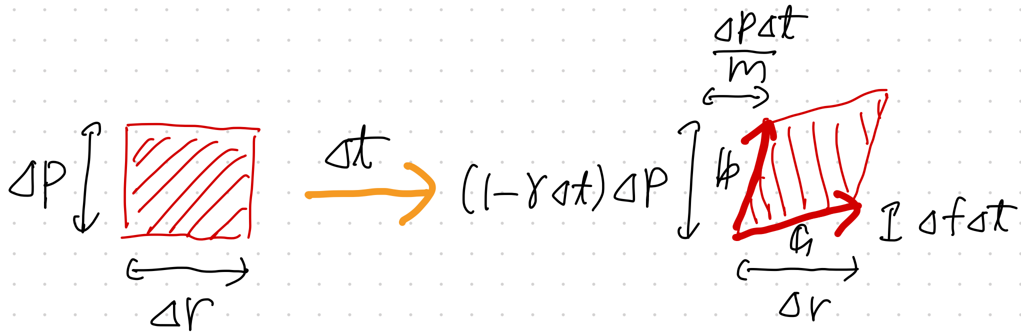
$= (r_0', p_0') + \left(\Delta t \frac{\Delta p}{m},\ \Delta p - \gamma \Delta p \Delta t\right) \eqqcolon b$

(8) $(r_0+\Delta r, p_0+\Delta p) \to \left(r_0+\Delta r+\Delta t\frac{p_0+\Delta p}{m},\ p_0+\Delta p+\Delta t(f_0+\Delta f-\gamma(p_0+\Delta p))\right)$

$= (r_0', p_0') + \left(\Delta r + \Delta t \frac{\Delta p}{m},\ \Delta p + \Delta t(\Delta f - \gamma \Delta p)\right)$

$= a + b$

Simple example (1) $\dot{r}(t) = \frac{p(t)}{m}$ (2) $\dot{p}(t) = f(r(t)) - \gamma p(t)$



area $\boxed{\Delta r \Delta p}$ area $\big((\underbrace{\Delta r, \Delta f \Delta t, 0}_{a}) \times (\underbrace{\tfrac{\Delta p \Delta t}{m}, (1-\gamma\Delta t)\Delta p, 0}_{b})\big)_z$

$$= \boxed{(1-\gamma\Delta t)\Delta r \Delta p} - \underbrace{\frac{\Delta f \Delta p}{m}(\Delta t)^2}_{\text{higher order}} \qquad (3)$$

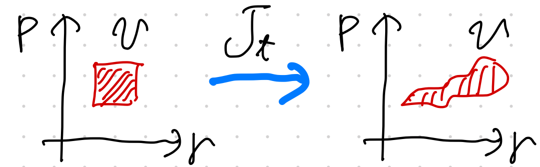
The area is preserved if and only if $\gamma = 0$

$\Leftrightarrow$ (1), (2) follow from a Hamiltonian

Liouville's theorem

the map $\mathcal{J}_t$ preserves the phase space volume

determined by a Hamilton's equation



* useful consequence

phase space point $X = (\mathbb{r}_1, \cdots, \mathbb{r}_N, \mathbb{p}_1, \cdots, \mathbb{p}_N)$ (1)

integration measure $dX = d^d\mathbb{r}_1 \cdots d^d\mathbb{r}_N \, d^d\mathbb{p}_1 \cdots d^d\mathbb{p}_N$ (2)

change of variable $\boxed{X' = \mathcal{J}_\tau(X)}$ (with fixed τ)

phase space point $X' = (\mathbb{r}_1', \cdots, \mathbb{r}_N', \mathbb{p}_1', \cdots, \mathbb{p}_N')$ (3)

integration measure $dX' = d^d\mathbb{r}_1' \cdots d^d\mathbb{r}_N' \, d^d\mathbb{p}_1' \cdots d^d\mathbb{p}_N'$ (4)

then $\boxed{dX = dX'}$ (5) $\longleftrightarrow$ $\boxed{\text{volume preservation}}$

(Jacobian is 1)

§ Liouville's equation and a proof of Liouville's theorem (optional)

→ indirect, but standard and illuminating proof

- arbitrary probability density $\rho_0(X)$ on the phase space Γ

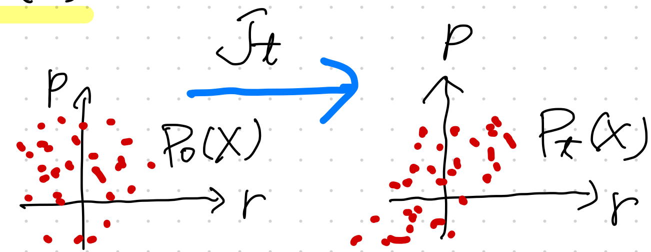
(1) $\rho_0(X) \geq 0$, (2) $\int_{X\in\Gamma} dX\, \rho_0(X) = 1$

(for any $S \subset \Gamma$, (3) $\int_{X\in S} dX\, \rho_0(X)$ is the probability to find X in S)

- initial state $X(0)$ is distributed according to $\rho_0(X)$

$\rho_t(X)$ the probability distribution of $X(t)$

(3) $\rho_t(X) = \int_{Y\in\Gamma} dY\, \delta(X - J_t(Y))\, \rho_0(Y)$



Liouville's theorem

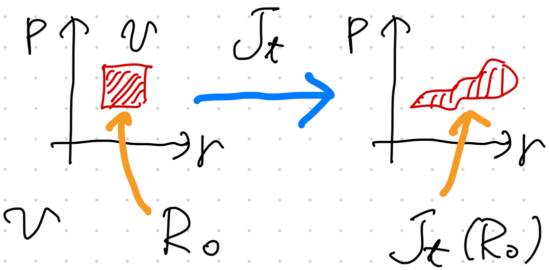
$H(t, X)$

any Hamiltonian mechanics → $X(t)$, J_t, $\rho_t(X)$

- for any solution $X(t)$ (4) $\rho_t(X(t)) = \rho_0(X(0))$ for any t
- (5) $\rho_t(J_t(X)) = \rho_0(X)$ for any $X \in \Gamma$ and any t

Liouville's theorem

- (1) $P_t(J_t(X)) = P_0(X)$ for any $X \in \Gamma$



this implies volume preservation

- arbitrary region $R_0 \subset \Gamma$ with volume v
- probability density (2) $P_0(X) = \begin{cases} \frac{1}{v} & X \in R_0 \\ 0 & X \notin R_0 \end{cases}$

from (1), (3) $P_t(X) = \begin{cases} \frac{1}{v} & X \in J_t(R_0) \\ 0 & X \notin J_t(R_0) \end{cases}$

(4) $\underbrace{\int dX\, P_t(X)}_{\parallel \atop 1} = \frac{1}{v} \times \underbrace{(\text{volume of } J_t(R_0))}_{\parallel \atop v}$

Liouville's theorem

for any solution $X(t)$ of the eq. of motion, (1) $P_t(X(t)) = P_0(X(0))$

proof

▷ new notation (2) $X = (x_1, \cdots, x_D)$ $D = 2dN$

write Hamilton's equations (p.2-(2)) as

(3) $\dot{x}_j(t) = v_j(t, X(t))$ $(j = 1, \cdots, D)$

with

$$(4)\quad v_j(t,X) = \begin{cases} \dfrac{\partial H(t,X)}{\partial x_{j+\frac{D}{2}}} & j = 1, \cdots, \dfrac{D}{2} \\[2ex] -\dfrac{\partial H(t,X)}{\partial x_{j-\frac{D}{2}}} & j = \dfrac{D}{2}+1, \cdots, D \end{cases}$$

velocity field

(3) is also written as

$$(5)\quad \frac{\partial}{\partial t} J_t(X) = \left(v_1(t, J_t(X)), \cdots, v_D(t, J_t(X)) \right)$$

▷ $P_t(X)$ satisfies the continuity equation

$$(1) \quad \frac{\partial}{\partial t} P_t(X) = -\sum_{j=1}^{D} \frac{\partial}{\partial x_j} \{ \underbrace{v_j(t,X)\, P_t(X)}_{\text{j-th component of the probability current}} \}$$

one can even declare that (1) is the definition of $P_t(X)$

proof p8-(3)

$$(2) \quad P_t(X) = \int_{Y\in\Gamma} dY\, \delta(X - J_t(Y))\, P_0(Y)$$

(3)

$$\frac{\partial}{\partial t} P_t(X) = \frac{\partial}{\partial t} \int dY \left\{ \prod_{k=1}^{D} \delta(x_k - (J_t(Y))_k) \right\} P_0(Y)$$

$$= \sum_{j=1}^{D} \int dY \left\{ \prod_{k\neq j} \delta(x_k - (J_t(Y))_k) \right\} \left\{ - v_j(t, J_t(Y))\, \delta'(x_j - (J_t(Y))_j) \right\} P_0(Y)$$

$$= -\sum_{j=1}^{D} \boxed{\frac{\partial}{\partial x_j}} \int dY\, v_j(t, \underbrace{J_t(Y)}_{X}) \underbrace{\left\{ \prod_{k=1}^{D} \delta(x_k - (J_t(Y))_k) \right\}}_{= \delta(X - J_t(Y))} P_0(Y) = -\sum_{j=1}^{D} \frac{\partial}{\partial x_j} \{ v_j(t,X) P_t(X) \}$$

(1) $$\frac{\partial}{\partial t}P_t(X) = -\sum_{j=1}^{D}\frac{\partial}{\partial x_j}\{v_j(t,X)\,P_t(X)\}$$

continuity

$$= -\left(\sum_{j=1}^{D}\frac{\partial v_j(t,X)}{\partial x_j}\right)P_t(X) - \sum_{j=1}^{D} v_j(t,X)\frac{\partial}{\partial x_j}P_t(X)$$

BUT

P10-(4)

(2) $$\sum_{j=1}^{D}\frac{\partial v_j(t,X)}{\partial x_j} = \sum_{j=1}^{\frac{D}{2}}\frac{\partial H(t,X)}{\partial x_j\,\partial x_{j+\frac{D}{2}}} - \sum_{j=\frac{D}{2}+1}^{D}\frac{\partial H(t,X)}{\partial x_j\,\partial x_{j-\frac{D}{2}}} = 0$$

we thus have

(3) $$\frac{\partial}{\partial t}P_t(X) + \sum_{j=1}^{D} v_j(t,X)\frac{\partial}{\partial x_j}P_t(X) = 0$$ ← Liouville's equation

Then, for any solution $X(t)$

(4) $$\frac{d}{dt}\{P_t(X(t))\} = \frac{\partial}{\partial t}P_t(X)\Big|_{X=X(t)} + \sum_{j=1}^{D} v_j(t,X(t))\frac{\partial}{\partial x_j}P_t(X)\Big|_{X=X(t)} = 0$$ //

for (5) $$H(X) = \sum_{n=1}^{N}\frac{(\mathbf{p}_n)^2}{2m} + V(\mathbf{r}_1,\cdots,\mathbf{r}_N)$$

(3) ⇒ (6) $$\frac{\partial}{\partial t}P_t(X) = -\sum_{n=1}^{N}\left\{\frac{\mathbf{p}_n}{m}\cdot\frac{\partial}{\partial \mathbf{r}_n} - \frac{\partial V(\mathbf{r}_1,\cdots,\mathbf{r}_N)}{\partial \mathbf{r}_n}\cdot\frac{\partial}{\partial \mathbf{p}_n}\right\}P_t(X)$$

<equlibrium statistical mechanics>

a system with phase space $\Gamma \ni X$

- probability density $P(X)$ (1) $P(X) \geq 0$ (2) $\int_{X\in\Gamma} dX\, P(X) = 1$

  $S \subset \Gamma$ (3) $\int_{X\in S} dX\, P(X)$ probability to find X in S

- canonical distribution

  if a system described by a time-independent Hamiltonian $H(X)$ is in touch with a heat bath at temperature β^{-1} and in equlibrium its behavior is described by

  ($\beta = (k_B T)^{-1}$, $k_B = 1$)

$$\boxed{P_{can,\beta}(X) = \frac{e^{-\beta H(X)}}{Z(\beta)}} \quad (4)$$

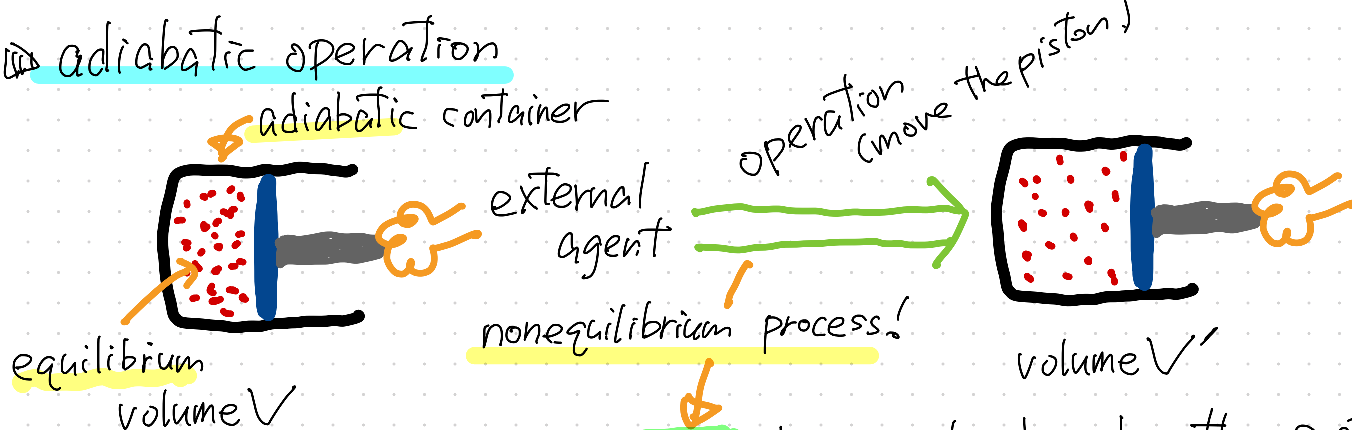
$$\boxed{Z(\beta) = \int dX\, e^{-\beta H(X)}} \quad (5)$$

Helmholtz free energy (6) $\boxed{F(\beta) = -\beta^{-1} \log Z(\beta)}$

⟨Jarzynski equality and the second law of thermodynamics⟩

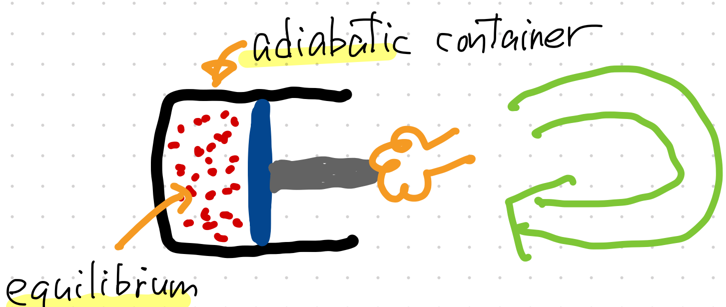
§ motivation from thermodynamics

(i) adiabatic operation



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

(ii) Planck's principle



$V = V'$

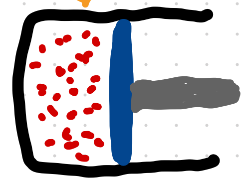
in any cyclic adiabatic operation,

$$\boxed{W \le 0}$$

a form of the 2nd law

§ setting (adiabatic system)

adiabatic container

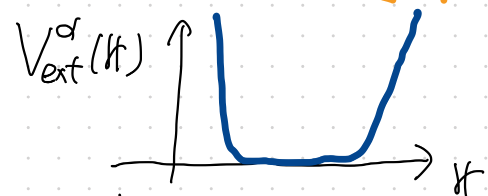


System of N classical particles → microscopic state

(i) phase space point (1) $X = (\mathbf{r}_1, \cdots, \mathbf{r}_N, \mathbf{p}_1, \cdots, \mathbf{p}_N) \in \Gamma$

(ii) Hamiltonian $H_\alpha(X)$ with control parameter $\alpha \in \mathbb{R}^\nu$

the volume can be controlled by varying the external potential



(2) $$H_\alpha(X) = \sum_{j=1}^{N} \left\{ \frac{(\mathbf{p}_j)^2}{2m} + V_{ext}^{\alpha}(\mathbf{r}_j) \right\} + V_{int}(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

(iii) the external agent varies α according to a fixed protocol $\alpha(t)$ $(0 \le t \le \tau)$

final time

initial value $\alpha = \alpha(0)$, final value $\alpha' = \alpha(\tau)$

(iv) time-dependent Hamiltonian $H_{\alpha(t)}(X)$ $(0 \le t \le \tau)$

(v) $J_\tau : \Gamma \to \Gamma$ time evolution map from 0 to τ determined by $H_{\alpha(t)}(X)$

in general one can never compute this explicitly

- time-dependent Hamiltonian $H_{\alpha(t)}(X)$ $(0 \leq t \leq \tau)$
- $\mathcal{J}_\tau : \Gamma \to \Gamma$ time evolution map from 0 to τ determined by $H_{\alpha(t)}(X)$
- the work done by the system to the agent during the operation (from 0 to τ) when the initial state is X

$$\begin{cases} \alpha = \alpha(0) \\ \alpha' = \alpha(\tau) \end{cases}$$

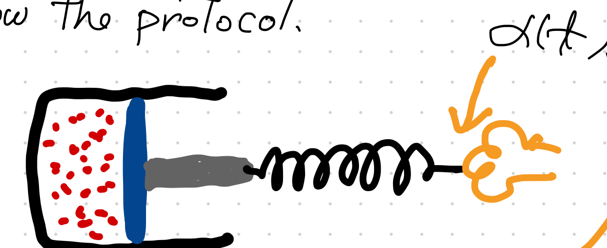
$$(1)\quad \boxed{W(X)} = \underbrace{H_\alpha(X)}_{\text{initial energy}} - \underbrace{H_{\alpha'}(\mathcal{J}_\tau(X))}_{\text{final energy}}$$

energy conservation

(it may be unrealistic to assume that the agent can perfectly control, e.g., the position of the piston to follow the protocol.

$\Downarrow$

we can insert an intermediate mechanical system



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§ Jarzynski equality

initial state X is distributed according to the canonical distribution

(1) $$P_0(X) = \frac{e^{-\beta H_\alpha(X)}}{Z_\alpha(\beta)}$$

(2) $$Z_\alpha(\beta) = \int \underbrace{dX}_{= d^d r_1 \cdots d^d r_N \, d^d p_1 \cdots d^d p_N} e^{-\beta H_\alpha(X)} = e^{-\beta F_\alpha(\beta)}$$

(3) $$W(X) = H_\alpha(X) - H_{\alpha'}(J_\tau(X)) \qquad (\alpha = \alpha(0),\ \alpha' = \alpha(\tau))$$

(4) $$\langle e^{\beta W(\hat{X})} \rangle_0 = \int dX \, P_0(X) e^{\beta W(X)} = \int dX \frac{e^{-\beta H_\alpha(X)}}{Z_\alpha(\beta)} e^{\beta \{H_\alpha(X) - H_{\alpha'}(J_\tau(X))\}}$$

$$= \int dX \frac{e^{-\beta H_{\alpha'}(J_\tau(X))}}{Z_\alpha(\beta)} = \frac{\int dX' \, e^{-\beta H_{\alpha'}(X')}}{Z_\alpha(\beta)} = \frac{Z_{\alpha'}(\beta)}{Z_\alpha(\beta)}$$

$$= e^{\beta\{F_\alpha(\beta) - F_{\alpha'}(\beta)\}}$$

$$\begin{cases} X' = J_\tau(X) \\ dX = dX' \quad (\text{Liouville's theorem}) \end{cases}$$

Jarzynski equality

(1) $$\boxed{\left\langle e^{\beta W(\hat{X})} \right\rangle_0 = e^{\beta\{F_a(\beta) - F_{a'}(\beta)\}}}$$

- exact equality which is valid for $\left\{ \begin{array}{l} \text{any system} \to \text{large or small} \\ \text{any process} \to \text{slow or fast} \end{array} \right.$

  (the final state is in general NOT the equilibrium state at β^{-1})

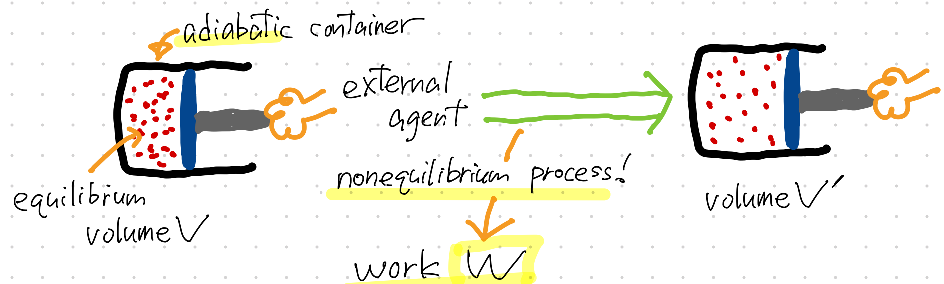
  very far from equilibrium

- represents a nontrivial property of the work that holds universally in nonequlibrium processes

- the assumption that the ininitial state is canonical is essential

- there are various extensions

  see Part-3-p10



§ the second law of thermodynamics

(inequalities that can be interpreted as the second law)

from Jensen's inequality (part 2-p4) — Jarzynski equality

$$(1)\quad e^{\beta\langle W(\hat{X})\rangle_0} \leq \langle e^{\beta W(\hat{X})}\rangle_0 = e^{\beta\{F_\alpha(\beta)-F_{\alpha'}(\beta)\}}$$

thus

$$(2)\quad \boxed{\langle W(\hat{X})\rangle_0 \leq F_\alpha(\beta) - F_{\alpha'}(\beta)}$$

☆ Planck's principle

the work done by a thermodynamic system in any cyclic adiabatic operation is not positive

(β,α) $\rightarrow$ (β',α)

set $\alpha=\alpha'$ in (2)

$$(3)\quad \boxed{\langle W(\hat{X})\rangle_0 \leq 0}$$

passivity

majorization

(remark: (3) is proved for a much more general initial probability

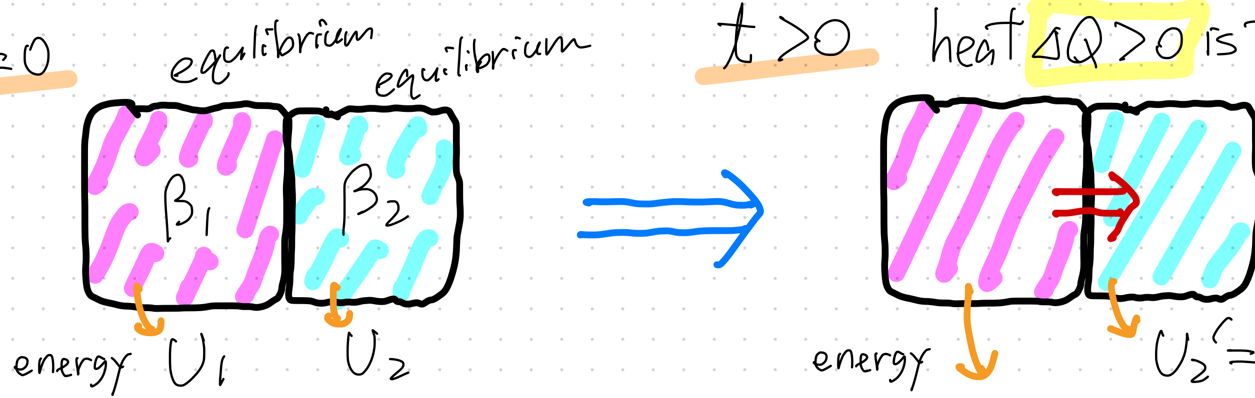
(4) $P_0(X) = f(H_\alpha(X))$ with any non-increasing function $f(E)$ (Lenard 78))

<heat conduction and the fluctuation theorem>

§ motivation from thermodynamics

two thermodynamic systems at temperatures β_1^{-1} and β_2^{-1} $\quad \beta_1 < \beta_2$

$t=0$ $\qquad\qquad\qquad\qquad$ $t>0$ heat $\boxed{\Delta Q > 0}$ is transfered from left to right



$U_2' = U_2 + \Delta Q$

$U_1' = U_1 - \Delta Q$

change in entropy (entropy production)

$$\Delta S = S_t - S_{\text{initial}} = \beta_1(U_1' - U_1) + \beta_2(U_2' - U_2) \tag{1}$$

$$= (\beta_2 - \beta_1)\Delta Q \; \boxed{> 0}$$

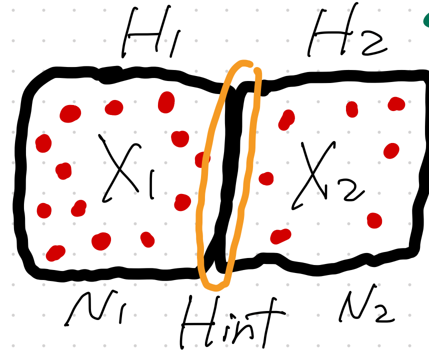
entropy increases!

§ setting

two systems of classical particles

(1) $X_1 = (\mathbf{r}_1, \ldots, \mathbf{r}_{N_1}, \mathbf{p}_1, \ldots, \mathbf{p}_{N_1})$

(2) $X_2 = (\mathbf{r}_{N_1+1}, \ldots, \mathbf{r}_{N_1+N_2}, \mathbf{p}_{N_1+1}, \ldots, \mathbf{p}_{N_1+N_2})$



we write (3) $X = (X_1, X_2)$

▷ Hamiltonian (4) $H(X) = H_1(X_1) + H_2(X_2) + H_{int}(X)$

J_t time evolution by H (5) $J_t(X) = ([J_t(X)]_1, [J_t(X)]_2)$

▷ entropy production during $[0, t]$ when the initial state is X

(6) $\Delta S_t(X) = \beta_1 \{H_1([J_t(X)]_1) - H_1(X_1)\} + \beta_2 \{H_2([J_t(X)]_2) - H_2(X_2)\}$

$$\left((7)\ \Delta S_t(X) = \beta_1 (U_1' - U_1) + \beta_2 (U_2' - U_2) \simeq (\beta_2 - \beta_1) \Delta Q \right)$$

we don't assume this if H_{int} is "small"

time-reversal symmetry

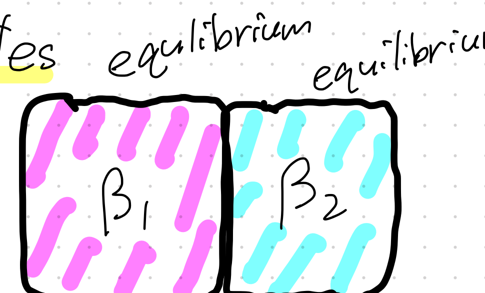
we assume (1) $H_1(X_1^*) = H_1(X_1)$, $H_2(X_2^*) = H_2(X_2)$, $H_{int}(X^*) = H_{int}(X)$

write (2) $X' = (J_t(X))^*$ then (3) $J_t(X') = X^*$ (p3-(6))

(4)
$$\begin{aligned}
\Delta S_t(X') &= \beta_1\{H_1([J_t(X')]_1) - H_1(X'_1)\} + \beta_2\{H_2([J_t(X')]_2) - H_2(X'_2)\} \\
&= \beta_1\{H_1(X_1^*) - H_1([J_t(X)]_1^*)\} + \beta_2\{H_2(X_2^*) - H_2([J_t(X)]_2^*)\} \\
&= \beta_1\{H_1(X_1) - H_1([J_t(X)]_1)\} + \beta_2\{H_2(X_2) - H_2([J_t(X)]_2)\} \\
&= -\Delta S_t(X)
\end{aligned}$$

initial state

two systems are in independent equlibrium states



(5)
$$P_0(X) = \frac{e^{-\beta_1 H_1(X_1)}}{Z_1(\beta_1)} \frac{e^{-\beta_2 H_2(X_2)}}{Z_2(\beta_2)}$$

§ fluctuation theorem

(1) $$\Delta S_t(X) = \beta_1 \{ H_1([J_t(X)]_1) - H_1(X_1) \} + \beta_2 \{ H_2([J_t(X)]_2) - H_2(X_2) \}$$
$$= \beta_1 \{ H_1(X_1') - H_1(X_1) \} + \beta_2 \{ H_2(X_2') - H_2(X_2) \}$$

(2) $$X' = (J_t(X))^*$$

basic relation

(3) $$P_0(X) = \frac{1}{Z_1(\beta_1) Z_2(\beta_2)} e^{-\beta_1 H_1(X_1) - \beta_2 H_2(X_2)}$$

$$-\Delta S_t(X') = \Delta S_t(X)$$

$$= \frac{1}{Z_1(\beta_1) Z_2(\beta_2)} e^{-\beta_1 H_1(X_1') - \beta_2 H_2(X_2')} \quad e^{\Delta S_t(X)}$$

$$= P_0(X') \, e^{-\Delta S_t(X')}$$

- the probability density that the entropy production $\Delta S_t(X)$ is $s \in \mathbb{R}$

(1) $P(s) = \int dX\, P_0(X)\, \delta(\Delta S_t(X) - s)$

by using

(2) $dX = dX'$ Liouville's theorem

(3) $P_0(X) = P_0(X')\, e^{-\Delta S_t(X')}$

(4) $X' = (J_t(X))^*$

(5) $\Delta S_t(X) = -\Delta S_t(X')$

(6) $P(s) = \int dX'\, P_0(X')\, e^{-\Delta S_t(X')}\, \delta(-\Delta S_t(X') - s)$

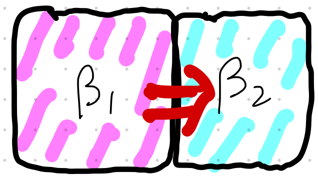
$\delta(-\Delta S_t(X') - s) = \delta(\Delta S_t(X') + s)$

$= e^{s} \int dX'\, P_0(X')\, \delta(\Delta S_t(X') + s)$

$= e^{s}\, P(-s)$

▷ fluctuation theorem

$P(s)$: the probabilty density that $\Delta S_t(X)$ is s



$$\boxed{(1) \quad P(s) = e^{s} P(-s)}$$

heat flows from hot to cold!

▷ when $s \gg 1$ (2) $P(s) \gg P(-s)$

the entropy production is mostly positive

$P(-s)$ can be nonzero $\rightarrow$ but small

$\Uparrow$ / $\Downarrow$ irreversibility

(3) $\mathrm{Prob}(\Delta S_t(X) \leq -\xi) \leq e^{-\xi}$ for $\forall \xi > 0$

$\Vert$

this is built into the initial state.

$$\left(\because (\mathrm{LHS}) = \int_{-\infty}^{-\xi} ds\, P(s) = \int_{-\infty}^{-\xi} ds\, e^{s} P(-s) \leq e^{-\xi} \right) \quad (4)$$

heat sometimes flows from cold to hot!!

▷ $P(s)$ satisfies nontrivial symmetry (1)

this is in general NOT the case.

if (5) $P(s) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(s-s_0)^2/(2\sigma^2)}$

(6) $\sigma^2 \doteq 2 s_0$

<detailed balance condition for effective stochastic processes> 26

① canonical distribution
+
② Hamiltonian time-evolution

$\Rightarrow$

- Jarzysnki equality
- fluctuation theorem

did we learn new nonequilibrium "physics"?

yes or not really

theses are universal relations for nonequilibrium processes!

the relations are too general. after all they follow from ① + ②

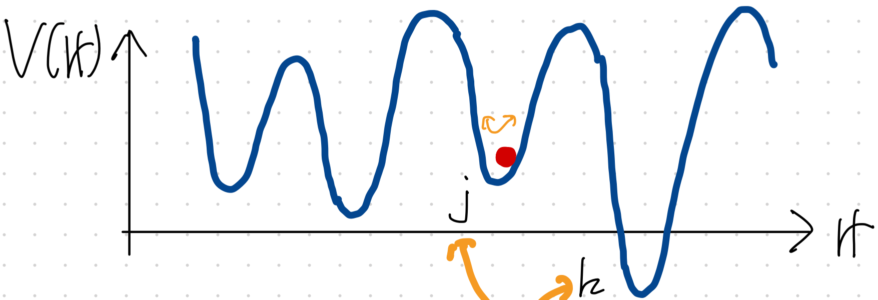
① + ② $\Rightarrow$ detailed balance condition

essential constraint on effective descriptions of nonequilibrium processes

$\rightarrow$ parts 3 and 4

§ motivation — a Brownian particle in a potential

a particle in a potential with multiple sharp local minima



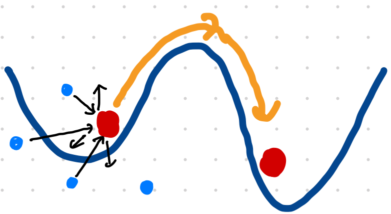
the particle is mostly trapped in one of the local minima and moves there

labels for the minima

a plastic bead trapped by an optical tweezer

water molecules

the particle interacts with surrounding small particles in thermal equilibrium



with some small but nonzero probability, the particle may "tunnel" the potential barrier and "jump" to a neighboring potential minimum

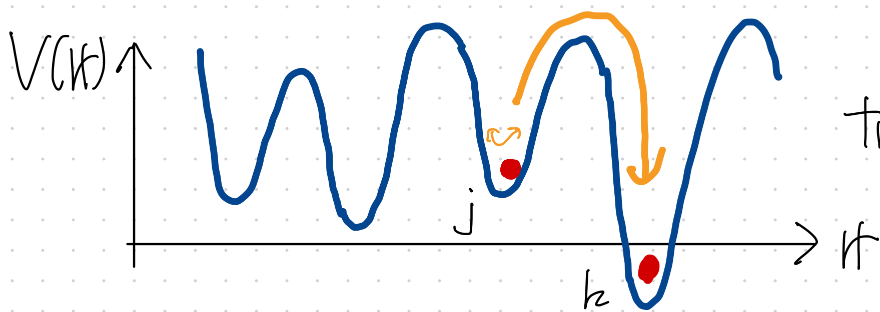
effective stochastic process for the particle

- the particle stays mostly near one of the potential minima and is (almost) in equilibrium with the surrounding particles
- from time to time, it jumps to a different minimum in a stochastic manner

any universal rule for the transition probability ?

Yes! detailed balance condition.

the picture should be valid if $\begin{pmatrix}\text{potential}\\ \text{barrier}\end{pmatrix} \gg \beta^{-1}$



transition $j \to k$

§ detailed balance condition

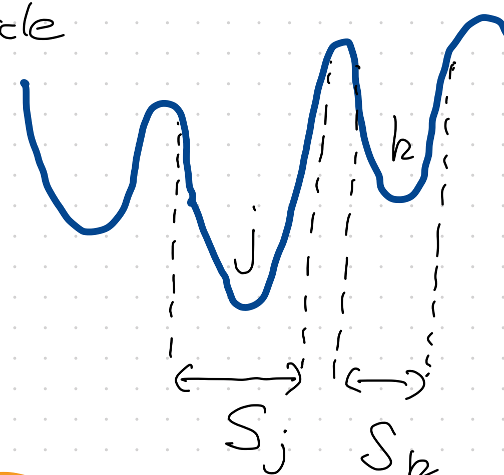
formulation

$(\mathbb{r}, \mathbb{p})$ the position and the momentum of the particle

(1) $\mathbb{r} \in \Lambda \subset \mathbb{R}^d$, $\mathbb{p} \in \mathbb{R}^d$

a finite box

$V(\mathbb{r})$ potential with multiple minima $j = 1, 2, \cdots$



$S_j \subset \Lambda$ a sufficiently large region including the potential minimum j

no overlaps

(2) $S_j \cap S_k = \phi$ if $j \neq k$

X_s state of all other (small) particles

(3) $X = (\mathbb{r}, \mathbb{p}, X_s)$ state of the whole system

$$(4) \quad \chi_j(X) = \begin{cases} 1 & \mathbb{r} \in S_j \\ 0 & \mathbb{r} \notin S_j \end{cases}$$

note that $\chi_j(X^*) = \chi_j(X)$

total Hamiltonian

$$(1)\quad H(X) = \frac{p^2}{2m} + V(x) + \underbrace{H_s(X_s) + V_{int}(x, X_s)}_{= \tilde{H}_s(X)}$$

we assume $(2)\quad H(X^*) = H(X)$

$\mathcal{J}_\tau$ time-evolution map determined by $H(X)$

constrained canonical distribution at inv. temp. β

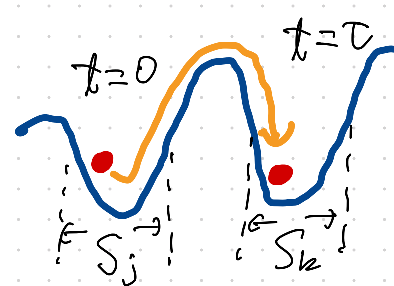
$$(3)\quad P_j(X) := \frac{1}{Z_j(\beta)} \chi_j(X) e^{-\beta H(X)}$$

the standard canonical distribution WITH the constraint that the particle is near the minimum j

$$(4)\quad Z_j(\beta) := \int dX\, \chi_j(X) e^{-\beta H(X)}$$

$$(5)\quad F_j(\beta) := -\frac{1}{\beta} \log Z_j(\beta)$$

the transition probability



(1) $$p^{(\tau)}_{j\to k} := \int dX\ \chi_k(J_\tau(X))\ P_j(X)$$

the probability to find the particle near the minimum k at time τ provided that it is near the minimum j at time 0.

$p^{(\tau)}_{j\to k} \xrightarrow{\tau\nearrow\infty}$ equilibrium probability that depends only on k

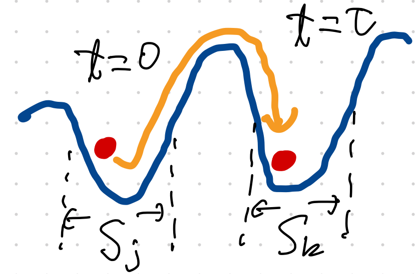
if $\tau>0$ is small and $0<p^{(\tau)}_{j\to k}\ll 1$ $(j\neq k)$

we can interpret $p^{(\tau)}_{j\to k}$ as the transition probability from j to k

We assumed that the surrounding particles are in thermal equlibrium before the transition.

may be justified if there are sufficiently many small particles.

III symmetry



(1) $P_j(X) = \frac{1}{Z_j(\beta)} \chi_j(X)\, e^{-\beta H(X)}$

(2) $p^{(\tau)}_{j\to k} = \int dX\, \chi_k(J_\tau(X))\, P_j(X)$

$= \frac{1}{Z_j(\beta)} \int dX\, \chi_k(J_\tau(X))\, \chi_j(X)\, e^{-\beta H(X)}$

energy conservation

$\boxed{(3)\ X' = (J_\tau(X))^* \rightarrow (4)\ dX' = dX \quad (5)\ X^* = J_\tau(X') \quad (6)\ H(X) = H(X')}$

$= \frac{1}{Z_j(\beta)} \int dX'\, \chi_k(X')\, \chi_j(J_\tau(X'))\, e^{-\beta H(X')}$

$= \frac{Z_k(\beta)}{Z_j(\beta)} \frac{1}{Z_k(\beta)} \int dX'\, \chi_j(J_\tau(X'))\, \chi_k(X')\, e^{-\beta H(X')}$

$= \frac{Z_k(\beta)}{Z_j(\beta)}\, p^{(\tau)}_{k\to j}$

(1) $$p^{(\tau)}_{j\to k} = \frac{Z_k(\beta)}{Z_j(\beta)}\, p^{(\tau)}_{k\to j}$$ ← symmetry between the transitions $j\to k$ and $k\to j$

(2) $$\frac{p^{(\tau)}_{j\to k}}{p^{(\tau)}_{k\to j}} = \frac{Z_k(\beta)}{Z_j(\beta)} = e^{\beta\{F_j(\beta)-F_k(\beta)\}}$$

an essential symmetry of the transition probabilities

in a special setting this can be simplifed to

(3) $$\boxed{\frac{p^{(\tau)}_{j\to k}}{p^{(\tau)}_{k\to j}} = e^{\beta(E_j-E_k)}}$$ for suitable E_j

detailed blance condition

(iii) simplification

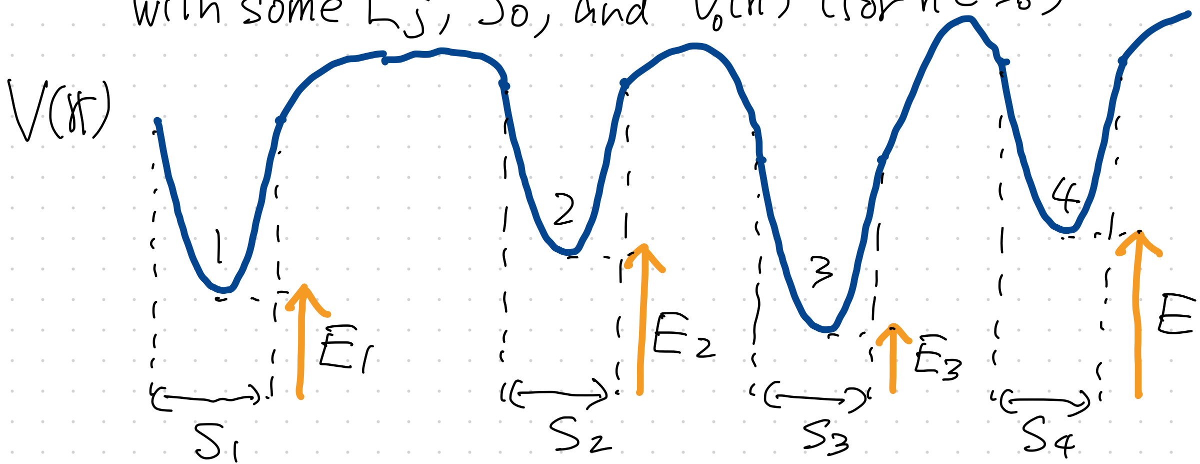
the whole system is in a box Λ with periodic boundary conditions

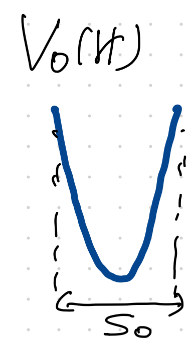
$H_S(X_S)$ and $V_{int}(\mathbf{r}, X_S)$ are translationally invariant

$\mathbf{r}_j^{(0)}$ the center of the potential minium j

assume for all j
$$\begin{cases} (1)\ S_j = S_0 + \mathbf{r}_j^{(0)} \\ (2)\ V(\mathbf{r}) = V_0(\mathbf{r} - \mathbf{r}_j^{(0)}) + E_j \quad (\mathbf{r} \in S_j) \end{cases}$$

with some E_j, S_0, and $V_0(\mathbf{r})$ (for $\mathbf{r} \in S_0$)





then

(1) $$Z_j(\beta) = \int dX\, \chi[\mathbb{r} \in S_j]\, e^{-\beta\left\{\frac{\mathbb{p}^2}{2m} + V(\mathbb{r}) + \tilde{H}_s(X)\right\}}$$

(shift all the position coordinates by $\mathbb{r}_j^{(0)}$ $\Rightarrow$ $\mathbb{r}_{new} = \mathbb{r}_{old} - \mathbb{r}_j^{(0)}$)

$$= \int dX\, \chi[\underline{\mathbb{r} \in S_0}]\, e^{-\beta\left\{\frac{\mathbb{p}^2}{2m} + V_0(\mathbb{r}) + \boxed{E_j} + \tilde{H}_s(X)\right\}}$$

$$= e^{-\beta E_j}\, Z_0(\beta)$$

thus

(2) $$\frac{Z_k(\beta)}{Z_j(\beta)} = e^{\beta(E_j - E_k)}$$

(characteristic function
$$\begin{cases} \chi[\text{true}] = 1 \\ \chi[\text{false}] = 0 \end{cases}$$
)

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§ Generalization

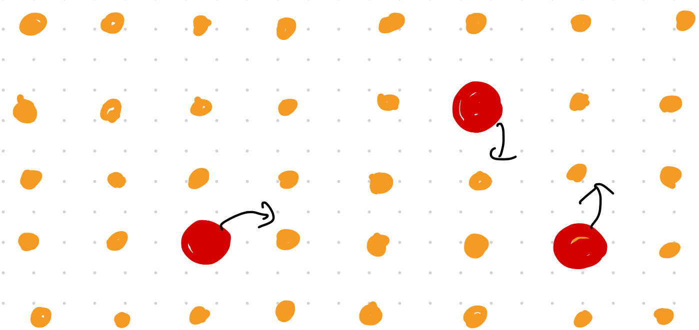
(1) $X = (X_0, X_s)$

X_s: huge surrounding environmental system which is in equilibrium

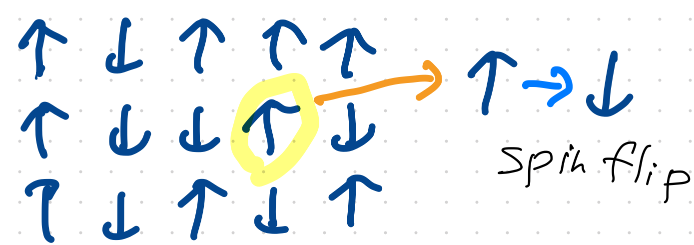
X_0: smaller system (not necesarilly a single particle) with multiple local minima $j = 1, 2, \cdots$ of the potential

we are interested in the behavior of this system

examples
- ionic conductor
- a system of molecules with multiple stable states
- (classical spin system)



X_0 is mostly close to one of the minima and jumps to a different minimum stochastically frome time to time



constrained canonical distribution

(1) $$P_j(X) := \frac{1}{Z_j(\beta)} \chi[X \in \mathcal{S}_j] \, e^{-\beta H(X)}$$

with some simplifying assumptions

(2) $$Z_j(\beta) := \int dX \, \chi[X \in \mathcal{S}_j] \, e^{-\beta H(X)} = e^{-\beta E_j} Z_0(\beta)$$

$\mathcal{S}_j$: the set of states in which X_0 is near the j-th minimum

transition probabity (τ should be small enough)

(3) $$p^{(\tau)}_{j \to k} := \int dX \, \chi[\mathcal{T}_\tau(X) \in \mathcal{S}_k] \, P_j(X)$$

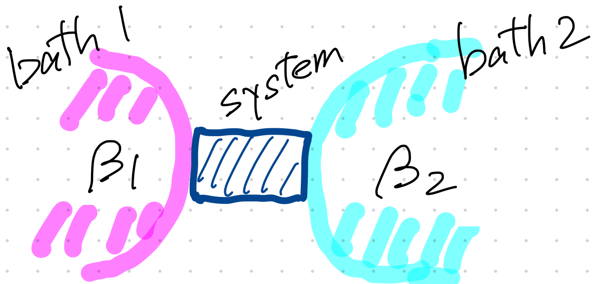
detailed balance condition

(4) $$\boxed{\frac{p^{(\tau)}_{j \to k}}{p^{(\tau)}_{k \to j}} = e^{\beta(E_j - E_k)}}$$

§ extentions to nonequilibrium environments

detailed balance condition $\rightarrow$ local detailed balance condition

▷ a system in contact with multiple heat baths

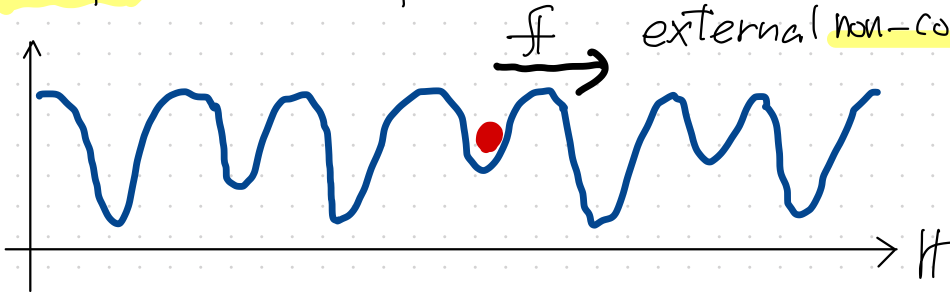


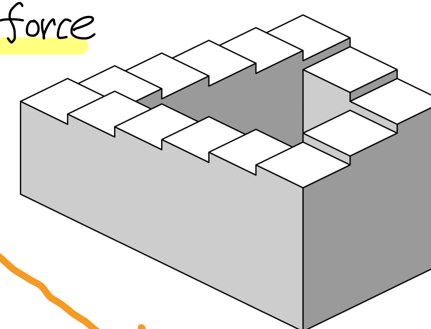
if the transition $j \to k$ (in the system) is triggered by the interaction with the bath α, then

$$\frac{p^{(\tau)}_{j\to k}}{p^{(\tau)}_{k\to j}} = e^{\boxed{\beta_\alpha}(E_j - E_k)} \qquad (1)$$

(iii) a system of particles under non-conservative force

example a Brownian particle in a box with periodic b.c. under a constant external non-conservative force





equation of motion

$$(1)\quad m\frac{d^2}{dt^2}\mathbf{x}(t) = -\mathrm{grad}\,V(\mathbf{x}) - \mathrm{grad}_{\mathbf{x}}\,V_{int}(\mathbf{x}, X_s(t)) + \boxed{\mathbf{f}}$$

standard force in the Hamiltonian dynamics

can never be described by a potential!

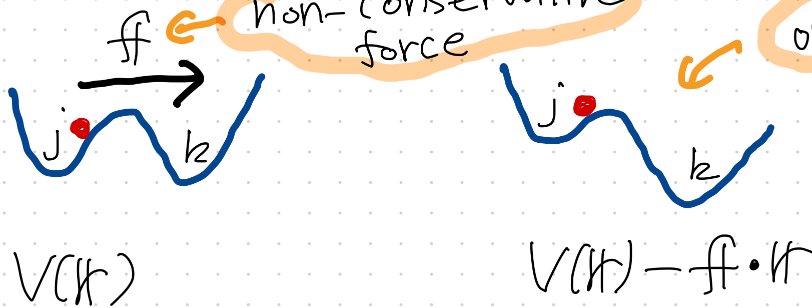
an utterly unphysical setting, often used to study the current induced by external (electric) field without being bothered by complicated physics at boundaries local detailed balance condition

$$(1) \quad \frac{p^{(\tau)}_{j\to k}}{p^{(\tau)}_{k\to j}} = e^{\beta(E_j - E_k) - \beta \mathbf{f}\cdot(\mathbf{r}_j^{(0)} - \mathbf{r}_k^{(0)})}$$

non-conservative force

only conservative forces!

derivation



when we examine a local transition $j \to k$ in a short time τ, the dynamics given by p-39 (1) is the same as that follows from a potential which is $V(\mathbf{r}) - \mathbf{f}\cdot\mathbf{r}$ near j and k.

(the same extension in multi-particle systems)

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