Part 4 Nonequilibrium states and processes in nonequilibrium environments

Nonequilibrium steady states (NESS)

Relaxation to NESS

Linear response relations

Reciprocal relations

Inequality between current and dissipation

Improved Shiraishi-Saito inequality

No free-pumping theorem

Trade-off relation between power and efficiency in a heat engine

<nonequlibrium steady states (NESS)> 1

§ general setting and typical models

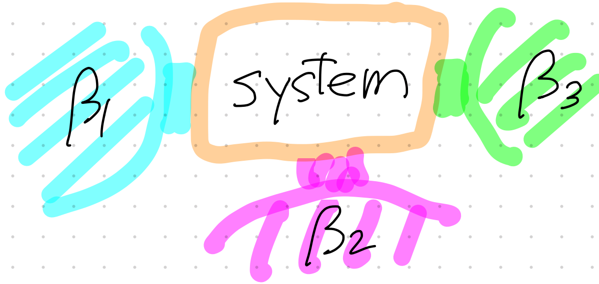
may be large or small

- physical system with almost stable states $j = 1, 2, \cdots, \Omega$
  - E_j energy (free energy) of state j
- case1 : the system is in touch with mulitple heat baths $\alpha = 1, 2, \cdots$ with different inverse temperatures $\beta_1, \beta_2, \cdots$
- case2 : the system is in touch with a single heat bath with β, but is subject to a non-conservative force

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

- basic assumption all states are "connected" through nonzero $W_{k \to j}$

(iii) local detailed balance condition (case ?)



heat baths $\alpha = 1, 2, \cdots, n_B$

with inverese temperatures β_α

assumption for any j, k ($j \neq k$) s.t. $w_{k\to j} \neq 0$ (and hence $w_{j\to k} \neq 0$),

there is a unique bath $\alpha(j,k) = \alpha(k,j)$ that causes the transitions $j \rightleftarrows k$

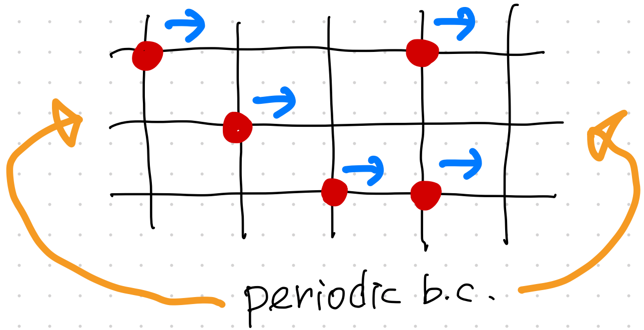
local detailed balance condition

for any j, k ($j \neq k$) s.t. $w_{k\to j} \neq 0$ we have

(1) $$\frac{w_{k\to j}}{w_{j\to k}} = e^{\beta_{\alpha(k,j)}(E_k - E_j)}$$

"proved" from
a mechanical model
+
equlibrium stat. mech.
part 1 - p38

(iii) local detailed balance condition (case 2)



a non-conservative force f is acting on the particles

local detailed balance condition

"proved" from a mechanical model + equlibrium stat. mech. part 1 - p40

for any j, k $(j \neq k)$ s.t. $w_{k\to j} \neq 0$ we have

$$(1) \quad \frac{w_{k\to j}}{w_{j\to k}} = e^{\beta(E_k - E_j) + \beta f J_{k\to j}}$$

(2) $J_{k\to j} = -J_{j\to k}$ the displacement of particles in the direction of the force

(there is no potential V_j such that (3) $f J_{k\to j} = V_k - V_j$)

§ relaxation to nonequilibrium steady state (NESS)

the condition for the convergence theorem (part2 p.34) is satified:

- there is a unique probability distribution $\mathbb{P}^S = (p^S_j)_{j=1,\dots,\Omega}$ that satisfies (1) $R\mathbb{P}^S = 0$
- it holds that $p^S_j > 0$ for any j
- for any initial distribution $\mathbb{P}(0)$ it holds that (2) $\boxed{\lim_{t\uparrow\infty} \mathbb{P}(t) = \mathbb{P}^S}$

$\mathbb{P}^S$ the probability distribution of the nonequlibrium steady state (NESS)

no general results for the precise form of $\mathbb{P}^S$ → part 2 p35

- H-thorem (3) $H(\mathbb{P}) := D(\mathbb{P}|\mathbb{P}^S)$ is well-defined, and $H(\mathbb{P}(t))$ is non-increasing in t and converges to zero as $t\uparrow\infty$

BUT we do not know almost anything about $H(\mathbb{P})$ → "free energy" for NESS??

III expectation value in NESS (part 2 p45)

- asymmetric jump quantity $\hat{g}$ → takes value (1) $g_{j\to k} = -g_{k\to j}$ $(j \neq k)$

expectation value of $\hat{g}$ (per unit time) (2) $\langle \hat{g} \rangle_{\mathbb{P},\mathbb{W}} := \sum_{\substack{j,k=1 \\ (j\neq k)}}^{\Omega} p_j w_{j\to k} g_{j\to k}$

path quantity $\hat{g}(t)$ → takes value (3) $g(t,\gamma) = \sum_{m=1}^{n} g_{j_{m-1}\to j_m} \delta(t - t_m)$

in path $\gamma = (j_0, \cdots, j_n; t_1, \cdots, t_n)$

$t_0 = 0,\ t_{n+1} = \tau$

- integrated path quantity

(4) $\hat{G} = \int_0^{\tau} dt\, \hat{g}(t)$ → takes value (5) $G(\gamma) = \sum_{m=1}^{n} g_{j_{m-1}\to j_m}$

path average

(6) $\langle\!\langle \hat{G} \rangle\!\rangle_{\mathbb{P}(0),\tilde{\mathbb{W}}} = \int_0^{\tau} dt \langle\!\langle \hat{g}(t) \rangle\!\rangle_{\mathbb{P}(0),\tilde{\mathbb{W}}} = \int_0^{\tau} dt \langle \hat{g} \rangle_{\mathbb{P}(t),\mathbb{W}}$

since

(7) $\lim_{t\nearrow\infty} \langle \hat{g} \rangle_{\mathbb{P}(t),\mathbb{W}} = \langle \hat{g} \rangle_{\mathbb{P}^S,\mathbb{W}}$ we have (8) $\boxed{\lim_{\tau\nearrow\infty} \frac{1}{\tau} \langle\!\langle \hat{G} \rangle\!\rangle_{\mathbb{P}(0),\tilde{\mathbb{W}}} = \langle \hat{g} \rangle_{\mathbb{P}^S,\mathbb{W}}}$

for any $\mathbb{P}(0)$

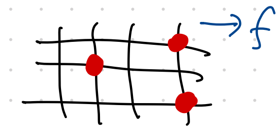
§ linear response relations

▷ nonequilibrium environments very close to equilibrium

- case 1 $\quad$ bath 1 $\beta+\varepsilon$ $\quad$ system $\quad$ β bath 2 $\quad$ (remark $\quad \beta+\frac{\varepsilon}{2}$ $\quad$ system $\quad \beta-\frac{\varepsilon}{2}$ $\quad$ is essentially the same)

  ε is small

- case 2 $\quad$ weak non-conservative force $\quad$ $\varepsilon = \beta f$ is small



▷ notations and goal

- transition rates $\mathbb{W}^{\varepsilon} = (w^{\varepsilon}_{j\to k})_{j\neq k}$
- stationary distribution $\mathbb{P}^{S,\varepsilon} \xrightarrow{\varepsilon=0} \mathbb{P}^{S,0} = \mathbb{P}^{\mathrm{can},\beta}$
- corresponding expectation value $\quad$ (1) $\langle \hat{g} \rangle_{\mathbb{P}^{S,\varepsilon},\mathbb{W}^{\varepsilon}} \xrightarrow{\text{abbreviate}} \boxed{\langle \hat{g} \rangle_{\varepsilon}}$

(2) $\langle \hat{g} \rangle_{\varepsilon} = L\varepsilon + O(\varepsilon^2)$ $\quad$ $\boxed{\text{what is the coefficient } L \text{ ?}}$

(i) basic lemma

chose $w^{\varepsilon}_{j\to k}$ to be real analytic in ε

- examples
  - case 1
$$w^{\varepsilon}_{k\to j} = \begin{cases} A_{j,k}\, e^{(\beta+\varepsilon)E_k} & \text{if } \alpha(j,k)=1 \\ A_{j,k}\, e^{\beta E_k} & \text{if } \alpha(j,k)=2 \end{cases} \tag{1}$$
  - case 2
$$w^{\varepsilon}_{k\to j} = A_{j,k}\, e^{\beta E_k + \varepsilon J_{k\to j}/2} \tag{2}$$

Lemma: the expectation value $\langle \hat{g} \rangle_\varepsilon$ is real analytic in $\varepsilon \in (-\varepsilon_0, \varepsilon_0)$ for some ε_0

proof $\mathbb{P}^{S,\varepsilon}$ is the unique solution of $R^{\varepsilon}\mathbb{P}^{S,\varepsilon} = 0$.

$p_j^{S,\varepsilon}$ is real analytic in ε.

one can simply "solve" this and normalize

$$\langle \hat{g} \rangle_\varepsilon = \sum_{\substack{j,k \\ (j\neq k)}} p_j^{S,\varepsilon}\, w^{\varepsilon}_{j\to k}\, g_{j\to k} \tag{3}$$

remark: this simple proof is valid only for a finite system.

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III detailed fluctuation theorem

part2 p47

entropy production (1) $\theta_{k\to j} = \log \frac{w^{\varepsilon}_{k\to j}}{w^{\varepsilon}_{j\to k}}$ (if $w^{\varepsilon}_{k\to j} \neq 0$)

(2) $\gamma = (j_0, \cdots, j_n, t_1, \cdots, t_n)$

total entropy production (3) $\Theta(\gamma) = \sum_{m=1}^{n} \theta_{j_{m-1}\to j_m}$

- case 1 (4) $\theta_{k\to j} = \beta_{\alpha(k,\ell)}\{E_k - E_j\} = \beta\{E_k - E_j\} + \varepsilon J_{k\to j}$

  p2-(1)

  (5) $J_{k\to j} := \begin{cases} E_k - E_j & \alpha(k,j) = 1 \\ 0 & \alpha(k,j) = 2 \end{cases}$ ⇐ heat current into bath 1

- case 2 (6) $\theta_{k\to j} = \beta\{E_k - E_j\} + \varepsilon J_{k\to j}$

  p3-(1)

- in both cases (7) $\Theta(\gamma) = \beta\{E_{j_0} - E_{j_n}\} + \varepsilon Q(\gamma)$

  with

  (8) $Q(\gamma) := \sum_{m=1}^{n} J_{j_{m-1}\to j_m}$ (9) $Q(\gamma^{\dagger}) = -Q(\gamma)$

part 2 p49-(4)

$\gamma = (j_0, \cdots, j_n, t_1, \cdots, t_n)$

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(1) $$\mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma)\, e^{-\Theta(\gamma)} = \mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma^\dagger)$$

(2) $$\frac{e^{-\beta E_{\gamma_{init}}}}{Z(\beta)} \mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma)\, e^{\beta E_{j_0} - \Theta(\gamma) - \beta E_{j_n}} = \frac{e^{-\beta E_{\gamma^\dagger_{init}}}}{Z(\beta)} \mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma^\dagger)$$

$\gamma_{init} = j_0$, $\gamma^\dagger_{init} = j_n$

$\beta E_{j_0} - \Theta(\gamma) - \beta E_{j_n} = -\varepsilon Q(\gamma) = \varepsilon Q(\gamma^\dagger)$

$\Downarrow$

- basic symmetry

(3) $$\boxed{p^{can,\beta}_{\gamma_{init}} \mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma) = e^{-\varepsilon Q(\gamma^\dagger)}\, p^{can,\beta}_{\gamma^\dagger_{init}} \mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma^\dagger)}$$

path average (4) $$\boxed{\langle\langle \hat{F} \rangle\rangle_{p^{can,\beta}, \tilde{\omega}\varepsilon} = \int \mathcal{D}\gamma\, p^{can,\beta}_{\gamma_{init}} \mathcal{J}_{\tilde{\omega}\varepsilon}(\gamma)\, F(\gamma)}$$

$\langle\langle \hat{F} \rangle\rangle_\varepsilon$ abbreviate

start from equilibrium and evolve in a weakly nonequilibrium environment

linear response relation

since (1) $g_{k\to j} = -g_{j\to k}$ and (2) $G(\gamma) = \sum_{m=1}^{n} g_{j_{m-1}\to j_m}$

(3) $G(\gamma^\dagger) = -G(\gamma)$

(4) $$\langle\!\langle \hat{G} \rangle\!\rangle_\varepsilon = \int D\gamma \, p^{\mathrm{can},\beta}_{\gamma_{\mathrm{init}}} \, J_{\tilde{\omega}^\varepsilon}(\gamma)\, G(\gamma)$$

pq-(3)

$$= \int D\gamma \, e^{-\varepsilon Q(\gamma^\dagger)} p^{\mathrm{can},\beta}_{\gamma^\dagger_{\mathrm{init}}} J_{\tilde{\omega}^\varepsilon}(\gamma^\dagger) \{-G(\gamma^\dagger)\}$$

$D\gamma = D\gamma^\dagger$

$$= -\langle\!\langle \hat{G}\, e^{-\varepsilon \hat{Q}} \rangle\!\rangle_\varepsilon \quad \left(\xrightarrow{\varepsilon=0} (5)\ \langle\!\langle \hat{G} \rangle\!\rangle_0 = -\langle\!\langle \hat{G} \rangle\!\rangle_0 \right)$$

$$\langle\!\langle \hat{G} \rangle\!\rangle_0 = 0$$

exact relation

$$\langle\!\langle \hat{G} \rangle\!\rangle_\varepsilon = \frac{1}{2} \langle\!\langle \hat{G} (1 - e^{-\varepsilon \hat{Q}}) \rangle\!\rangle_\varepsilon$$

$$= \frac{\varepsilon}{2} \langle\!\langle \hat{G} \hat{Q} \rangle\!\rangle_\varepsilon + O(\varepsilon^2) = \frac{\varepsilon}{2} \langle\!\langle \hat{G} \hat{Q} \rangle\!\rangle_0 + O(\varepsilon^2)$$

$$\langle\!\langle \hat{G} \hat{Q} \rangle\!\rangle_\varepsilon = \langle\!\langle \hat{G} \hat{Q} \rangle\!\rangle_0 + O(\varepsilon)$$

formal expansion

(the range of ε may depend on τ)

since (1) $\langle \hat{g} \rangle_\varepsilon = \lim_{\tau \to \infty} \frac{1}{\tau} \langle\langle \hat{G} \rangle\rangle_\varepsilon$ is real analytic in ε,

(2) $\hat{Q} = \int_0^\tau ds\, \hat{J}(s)$ ← p8-(8)

(3) $\langle \hat{g} \rangle_\varepsilon = L\varepsilon + O(\varepsilon^2)$

with

(4) $L = \lim_{\tau \to \infty} \frac{1}{\tau} \frac{1}{2} \langle\langle \hat{G} \hat{Q} \rangle\rangle_0 = \lim_{\tau \to \infty} \frac{1}{2\tau} \int_0^\tau dt \int_0^\tau ds \langle\langle \hat{g}(t) \hat{J}(s) \rangle\rangle_0$

where (5) $\langle\langle \hat{F} \rangle\rangle_0 = \langle\langle \hat{F} \rangle\rangle_{P^{can,\beta}, \tilde{\omega}^0} = \int D\gamma\, P^{can,\beta}_{\gamma_{init}} J_{\tilde{\omega}^0}(\gamma) F(\gamma)$

start from equilibrium and evolve in an equlibrium environment

quantity $\langle \hat{g} \rangle_\varepsilon$ in the nonequlibrium steady state is expresed in terms of the time-dependent correlation function $\langle\langle \hat{g}(t) \hat{J}(s) \rangle\rangle_0$ in equlibrium set $\hat{g}$ to be $\hat{J}$ in P.11-(2),(3) → (fluctuation)^2 of $Q(\gamma)=\int_0^\tau dt\, J_\gamma(t)$

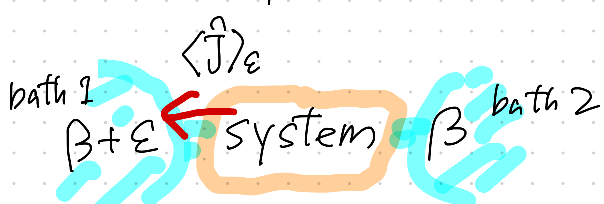
$\langle\langle \hat{Q} \rangle\rangle_0 = 0$

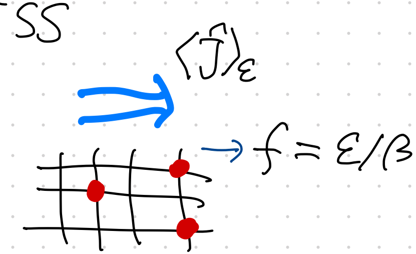
$$
\boxed{
\begin{aligned}
(1)\quad \langle \hat{J} \rangle_\varepsilon &= \left\{ \lim_{\tau\to\infty} \frac{1}{2\tau} \langle\langle \hat{Q}^2 \rangle\rangle_0 \right\} \varepsilon + O(\varepsilon^2) \\
&= \left\{ \lim_{\tau\to\infty} \frac{1}{2\tau} \int_0^\tau dt \int_0^\tau ds \, \langle\langle \hat{J}(t)\, \hat{J}(s) \rangle\rangle_0 \right\} \varepsilon + O(\varepsilon^2)
\end{aligned}
}
$$

fluctuation-response relation

(a.k.a. fluctuation-dissipation relation of the 1st kind)

- case 1 $\langle \hat{J} \rangle_\varepsilon$ heat current into bath 1 in NESS
- case 2 $\langle \hat{J} \rangle_\varepsilon$ total particle current in NESS





remark: fluctuation-response relation in equlibrium statistical mechanics

example Ising model under uniform magnetic field h

lattice Λ lattice sites $x, y, \ldots \in \Lambda$ spin variable $\sigma_x = \pm 1$

Hamiltonian (1) $H_h = H_0 - h\mathcal{M}$

Hamiltonian without magnetic field (2) $H_0 = -J \sum_{\langle x,y \rangle} \sigma_x \sigma_y$ (for example)

total magnetization (3) $\mathcal{M} = \mu_0 \sum_{x \in \Lambda} \sigma_x$

expectation value (4) $\langle \cdots \rangle^{\mathrm{can}}_{\beta,h} = Z(\beta,h)^{-1} \sum_{\substack{\sigma_x = \pm 1 \\ (x \in \Lambda)}} (\cdots)\, e^{-\beta H_h}$

(assume $T > T_c$, $\langle \mathcal{M} \rangle^{\mathrm{can}}_{\beta,0} = 0$)

(5) $\langle \mathcal{M} \rangle^{\mathrm{can}}_{\beta,h} = \chi\, h + O(h^2)$

(6) $\chi = \left.\frac{\partial}{\partial h} \langle \mathcal{M} \rangle^{\mathrm{can}}_{\beta,h} \right|_{h=0} = \beta \langle \mathcal{M}^2 \rangle^{\mathrm{can}}_{\beta,0}$

response of $\mathcal{M}$ to the magnetic field h

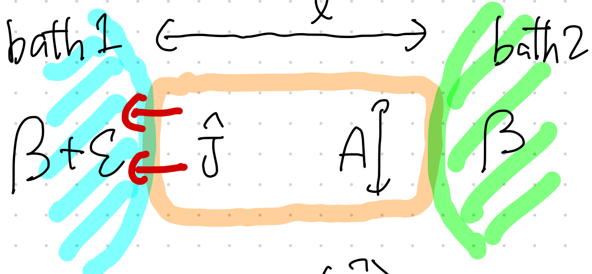
$(\text{fluctuation})^2$ of $\mathcal{M}$

remark: standard transport coefficients

general relation (1) $\langle \hat{J} \rangle_\varepsilon \simeq \boxed{L}\, \varepsilon$ with (2) $L = \lim_{\tau \to \infty} \frac{1}{2\tau} \iint dt\, ds \langle\langle \hat{\hat{J}}(t)\, \hat{\hat{J}}(s) \rangle\rangle_0$

case 1 thermal conductivity $\boxed{\kappa}$ (3) $\dot{j} \simeq -\kappa \operatorname{grad} T$ (Fourier's law)

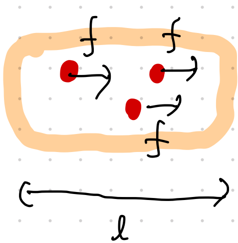
heat flux density; temperature gradient



(1) corresponds to the standard relation (3) if the baths are coupled to the system efficiently enough

(4) $\dot{j} = \dfrac{\langle \hat{J} \rangle_\varepsilon}{A}$ (5) $\operatorname{grad} T \simeq -\dfrac{\varepsilon}{k_B \beta^2 \ell}$ (6) $\kappa = \dfrac{k_B \beta^2 \ell}{A} L$

case 2 resistance $\boxed{R}$ voltage V Joule heat (7) $W_J = \dfrac{V^2}{R}$



(8) $W_J = f \langle \hat{J} \rangle_\varepsilon$ (9) $V = \dfrac{f\ell}{q}$ ← charge (10) $R = \dfrac{\ell^2}{q^2 \beta} \dfrac{1}{L}$

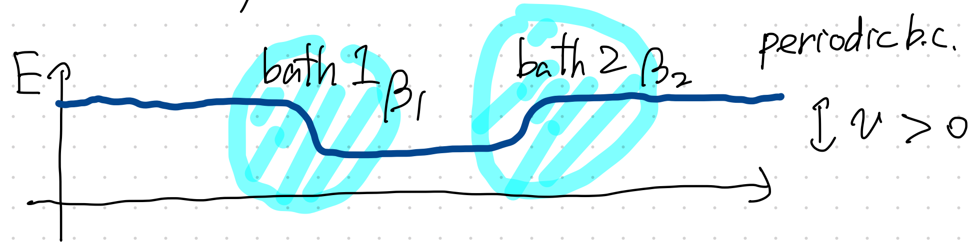
§ reciprocal relations

▷ thermoelectric effects → Seebeck effect, Peltier effect, Thomson effect

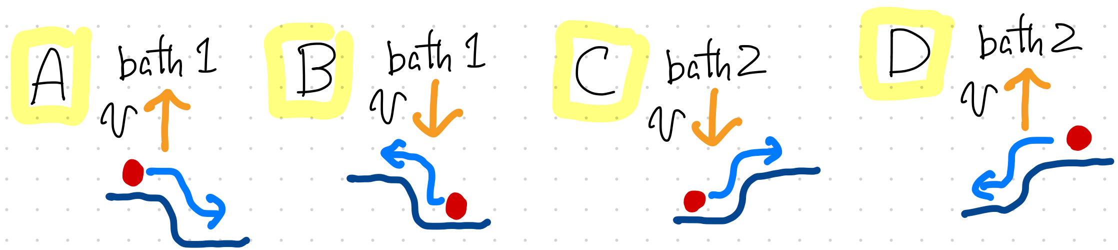
heat current and particle current may couple with each other!

simple example → (see problem 4-1)

Brownian particles in a potential with two steps



energy exchange with the baths



- $\beta_1 > \beta_2$, $f=0$: heat flow from bath 2 to bath 1 → $N_A > N_B$, $N_C > N_D$ → → particles move to the right!
- $f>0$, $\beta_1 = \beta_2$: particles move to the right → $N_A > N_B$, $N_C > N_D$ → → heat flow from bath 2 to bath 1!

J_h heat current $\quad J_p$ particle current

- $\beta_1 > \beta_2,\ f=0$ → particles move to the right!

(1) $J_h \simeq L_{hh}(\beta_1-\beta_2)$ (2) $\boxed{J_p \simeq L_{ph}(\beta_1-\beta_2)}$ ← new!

- $f>0,\ \beta_1=\beta_2$ → heat flow from bath 2 to bath 1!

(3) $J_p \simeq L_{pp}\,\beta f$ (4) $\boxed{J_h \simeq L_{hp}\,\beta f}$

Onsager's reciprocal relation (5) $L_{ph} = L_{hp}$

(Thomson (Kelvin) 1854)

Onsager 1931

Surprising (or even miraculous) symmetry

there must be some structure behind the symmetry!

(cf. Maxwell relations in equlibrium thermodynamics

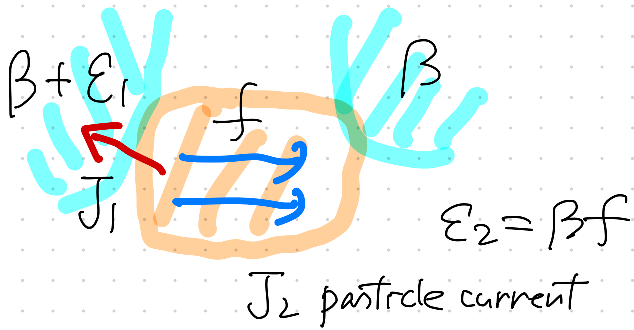
(6) $$\frac{\partial^2 F[T;V,N]}{\partial N\,\partial V} = \frac{\partial^2 F[T;V,N]}{\partial V\,\partial N} \Rightarrow \text{(7)}\ \frac{\partial P(T;V,N)}{\partial N} = -\frac{\partial \mu(T;V,N)}{\partial V}$$)

iii) general setting

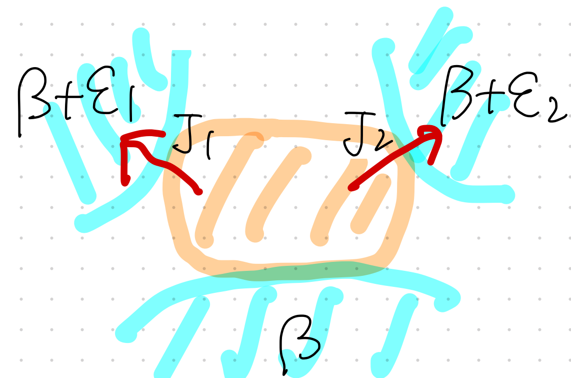
- two nonequilibrium parameters $\varepsilon_1, \varepsilon_2$
- the corresponding currents J_1, J_2

examples

- thermoelectric effect



- multiple heat currents



$\langle \cdots \rangle_{\varepsilon_1, \varepsilon_2}$ expectation value in the corresponding NESS (p6-(1))

① derivation

basic relation p11-(3),(4)

(1) $\langle \hat{g} \rangle_\varepsilon = L\varepsilon + O(\varepsilon^2)$ (2) $L = \lim_{\tau \nearrow \infty} \frac{1}{2\tau} \int_0^\tau dt \int_0^\tau ds \langle\langle \hat{\hat{g}}(t) \hat{\hat{J}}(s) \rangle\rangle_0$

(3) $\langle \hat{J}_1 \rangle_{0,\varepsilon_2} = \boxed{L_{12}} \varepsilon_2 + O(\varepsilon_2^2)$

(4) $L_{12} = \lim_{\tau \nearrow \infty} \frac{1}{2\tau} \int_0^\tau dt \int_0^\tau ds \langle\langle \hat{\hat{J}}_1(t) \hat{\hat{J}}_2(s) \rangle\rangle_0$

(5) $\langle \hat{J}_2 \rangle_{\varepsilon_1,0} = \boxed{L_{21}} \varepsilon_1 + O(\varepsilon_1^2)$

(6) $L_{21} = \lim_{\tau \nearrow \infty} \frac{1}{2\tau} \int_0^\tau dt \int_0^\tau ds \langle\langle \hat{\hat{J}}_2(t) \hat{\hat{J}}_1(s) \rangle\rangle_0$

clearly (7) $L_{12} = L_{21}$

a remarkable symmetry which can be explained by linear response relations

<inequality between current and dissipation>

operations in a nonequilibrium environment

§ Improved Shiraishi-Saito inequality

setting　general Markov jump process

- transition rates (1) $\tilde{\mathbb{W}} = (\mathbb{W}(t))_{t\geq 0}$, $\mathbb{W}(t) = (W_{j\to k}(t))_{j,k=1,\cdots,\Omega\ (k\neq j)}$

  (assume $W_{j\to k}(t) \neq 0 \Longleftrightarrow W_{k\to j}(t) \neq 0$ for $\forall j\neq k,\ t\geq 0$)

- transition rate matrix $R(t)$

  $\lambda_j(t)$ escape rate

  (2) $R_{kj}(t) = W_{j\to k}(t)$　(3) $R_{jj}(t) = -\boxed{\sum_{k=1}^{\Omega}{}' W_{j\to k}(t)}$

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

- asymmetric jump quantity $g_{j\to k}(t) = -g_{k\to j}(t)$　$(j\neq k)$

(5)　$\langle \hat{g}(t)\rangle_{\mathbb{P}(t),\mathbb{W}(t)} := \sum_{j,k\ (j\neq k)}{}' P_j(t) W_{j\to k}(t)\, g_{j\to k}(t)$

$\langle \hat{g}(t)\rangle_t$ abbreviation

☐ lower bound for entropy production rate

entropy production (in the baths) (1) $\theta_{j\to k}(t) := \log \dfrac{W_{j\to k}(t)}{W_{k\to j}(t)} = \log \dfrac{R_{kj}(t)}{R_{jk}(t)}$

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

total entropy production rate at time t

(2) $\boxed{\sigma(t)} := \underbrace{\dfrac{d}{dt} S(\mathbb{P}(t))}_{\text{change in the entropy of the system}} + \langle \hat{\theta}(t) \rangle_t$

(3) $S(\mathbb{P}) = -\sum_{j=1}^{\Omega} P_j \log P_j$

basic lower bound for $\sigma(t)$

(4) $\sigma(t) \geq \sum_{\substack{j,k \\ (j\neq k)}} \dfrac{\{R_{kj}(t)P_j(t) - R_{jk}(t)P_k(t)\}^2}{R_{kj}(t)P_j(t) + R_{jk}(t)P_k(t)} \geq 0$

(Shiraishi-Saito-Tasaki 2016)

part 2 - p.32

(cf. probability current from j to k (5) $J_{j\to k}(t) = R_{kj}(t)P_j(t) - R_{jk}(t)P_k(t)$

(4) $\Longrightarrow$ nonzero $J_{j\to k}(t)$ implies $\sigma(t)$ is nonzero)

proof :

(1) $$\frac{d}{dt} S(\mathbb{P}(t)) = -\frac{d}{dt}\sum_{k=1}^{\Omega} P_k(t)\log P_k(t) = -\sum_k \dot{P}_k(t)\log P_k(t) - \overbrace{\sum_k P_k(t)\frac{\dot{P}_k(t)}{P_k(t)}}^{0\,=}$$

$$= -\sum_{j,k=1}^{\Omega} R_{kj}(t)P_j(t)\log P_k(t) = \sum_{j,k=1}^{\Omega} R_{kj}(t)P_j(t)\log\frac{P_j(t)}{P_k(t)}$$

$$\sum_k R_{kj}(t) = 0$$

(2) $$\langle \hat{\Theta}(t)\rangle_t = \sum_{j,k\ (j\neq k)} P_j(t)W_{j\to k}(t)\log\frac{R_{kj}(t)}{R_{jk}(t)}$$

$$= \sum_{j,k\ (j\neq k)} R_{kj}(t)P_j(t)\log\frac{R_{kj}(t)}{R_{jk}(t)} = \sum_{j,k=1}^{\Omega} R_{kj}(t)P_j(t)\log\frac{R_{kj}(t)}{R_{jk}(t)}$$

(3) $$\sigma(t) = \sum_{j,k=1}^{\Omega} R_{kj}(t)P_j(t)\log\frac{R_{kj}(t)P_j(t)}{R_{jk}(t)P_k(t)} = \sum_{\substack{j,k\\(j\neq k)}} R_{kj}(t)P_j(t)\log\frac{R_{kj}(t)P_j(t)}{R_{jk}(t)P_k(t)}$$

$$= \frac{1}{2}\sum_{\substack{j,k\\(j\neq k)}} \{R_{kj}(t)P_j(t) - R_{jk}(t)P_k(t)\}\log\frac{R_{kj}(t)P_j(t)}{R_{jk}(t)P_k(t)}$$

well-known expression

(1) $$\sigma(t) = \frac{1}{2}\sum_{\substack{j,k \\ (j\neq k)}} \{R_{kj}(t)P_j(t) - R_{jk}(t)P_k(t)\} \log \frac{R_{kj}(t)P_j(t)}{R_{jk}(t)P_k(t)}$$

$$\geq \sum_{\substack{j,k \\ (j\neq k)}} \frac{\{R_{kj}(t)P_j(t) - R_{jk}(t)P_k(t)\}^2}{R_{kj}(t)P_j(t) + R_{jk}(t)P_k(t)}$$

(2) $\frac{1}{2}(a-b)\log\frac{a}{b} \geq \frac{(a-b)^2}{a+b}$ for any $a, b > 0$

invariance under $a \leftrightarrow b$

we can assume $a \geq b > 0$

(2) $\Longleftrightarrow$ (3) $\log\frac{a}{b} \geq \frac{2(a-b)}{a+b} = \frac{2(\frac{a}{b}-1)}{\frac{a}{b}+1}$

write $\frac{a}{b} = 1 + x$

with $x \geq 0$

(4) LHS of (3) $= \log(1+x) \simeq x - \frac{x^2}{2} + \frac{x^3}{3}$

(5) RHS of (3) $= \frac{2x}{x+2} \simeq x\left(1+\frac{x}{2}\right)^{-1} \simeq x - \frac{x^2}{2} + \frac{x^3}{4}$

proof (6) $f(x) := \log(1+x) - \frac{2x}{x+2}$

(7) $f(0) = 0$, (8) $f'(x) = \frac{x^2}{(x+1)(x+2)^2} \geq 0$ $\quad$ $f(x) \geq 0$ for $\forall x \geq 0$

improved Shiraishi-Saito inequality

general asymmetric jump quantity

(1) $g_{j\to k}(t) = -g_{k\to j}(t) \quad (j\neq k)$

(2)
$$\langle \hat{g}(t)\rangle_t = \sum_{j,k\,(j\neq k)} p_j(t)\, w_{j\to k}(t)\, g_{j\to k}(t) = \sum_{j,k\,(j\neq k)} R_{kj}(t)\, p_j(t)\, g_{j\to k}(t)$$

$$= \frac{1}{2} \sum_{j,k\,(j\neq k)} \{R_{kj}(t)\,p_j(t) - R_{jk}(t)\,p_k(t)\}\, g_{j\to k}(t)$$

$$= \frac{1}{2} \sum_{\substack{j,k\\(j\neq k)}} \frac{R_{kj}(t)\,p_j(t) - R_{jk}(t)\,p_k(t)}{\sqrt{R_{kj}(t)\,p_j(t) + R_{jk}(t)\,p_k(t)}} \sqrt{R_{kj}(t)\,p_j(t) + R_{jk}(t)\,p_k(t)}\; g_{j\to k}(t)$$

thus

(3)
$$\left|\langle \hat{g}(t)\rangle_t\right| \leq \sqrt{\underbrace{\sum_{\substack{j,k\\(j\neq k)}} \frac{\{R_{kj}(t)\,p_j(t) - R_{jk}(t)\,p_k(t)\}^2}{R_{kj}(t)\,p_j(t) + R_{jk}(t)\,p_k(t)}}_{\leq\, \sigma(t)}\; \underbrace{\frac{1}{4} \sum_{\substack{j,k\\(j\neq k)}} \{R_{kj}(t)\,p_j(t) + R_{jk}(t)\,p_k(t)\}\left(g_{j\to k}(t)\right)^2}_{=:\, \Xi_g(t)}}$$

Schwartz ineq

$$\left|\sum_\ell a_\ell b_\ell\right| \leq \sqrt{\sum_\ell a_\ell^2 \sum_\ell b_\ell^2}$$

improved Shiraishi-Saito inequality

$$\boxed{(1)\quad \left|\langle \hat{g}(t)\rangle_t\right| \le \sqrt{\sigma(t)\,\Xi_g(t)}}$$

$$(2)\quad \Xi_g(t) = \frac{1}{4}\sum_{\substack{j,k\\(j\neq k)}}{}' \{R_{kj}(t)P_j(t) + R_{jk}(t)P_k(t)\}\{g_{j\to k}(t)\}^2$$

$$= \frac{1}{2}\sum_{\substack{j,k\\(j\neq k)}}{}' R_{kj}(t)P_j(t)\{g_{j\to k}(t)\}^2 = \langle \hat{g}(t)^2\rangle_t$$

finite (in general)

if (3) $|g_{j\to k}(t)| \le g_0$ (4) $\lambda_j(t) \le \lambda_0$

$$(5)\quad 0 \le \Xi_g(t) \le \frac{g_0^{\,2}}{2}\sum_{\substack{j,k\\(j\neq k)}}{}' R_{kj}(t)P_j(t) = \frac{g_0^{\,2}}{2}\sum_j{}' \lambda_j(t)P_j(t) \le \frac{\lambda_0 g_0^{\,2}}{2}$$

$$\boxed{(6)\quad \sigma(t) \ge \frac{\left(\langle \hat{g}(t)\rangle_t\right)^2}{\Xi_g(t)}}$$

entropy increases whenever $\langle \hat{g}(t)\rangle_t \neq 0$

(improvement of the well-known inequality $\sigma(t) \ge 0$)

Time-averaged version

(1) $\langle \hat{g}(t) \rangle_t \leq \sqrt{\sigma(t)\, \Xi_g(t)}$

Schwartz $\int_a^b dx\, f(x) g(x) \leq \sqrt{\int_a^b dx\, f(x)^2 \int_a^b dx\, g(x)^2}$

(2) $\frac{1}{\tau}\int_0^\tau dt \langle \hat{g}(t) \rangle_t \leq \sqrt{\frac{1}{\tau}\int_0^\tau dt\, \sigma(t) \quad \frac{1}{\tau}\int_0^\tau dt\, \Xi_g(t)}$

(3) $\frac{1}{\tau}\int_0^\tau dt\, \sigma(t) \overset{\text{P20-(2)}}{=} \frac{1}{\tau}\{S(P(\tau)) - S(P(0))\} + \frac{1}{\tau}\int_0^\tau dt \langle \hat{\Theta}(t) \rangle_t$

vanishes if we let $\tau \nearrow \infty$

averaged entropy production in the baths

||

mean dissipation

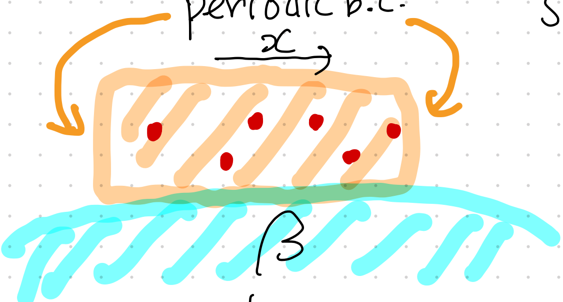
(4) $\overline{\Xi}_g := \lim_{\tau \nearrow \infty} \frac{1}{\tau}\int_0^\tau dt\, \Xi_g(t) \left(\leq \frac{\lambda_0 g_0^2}{2} \right)$

(5) $(\overline{\Xi}_g)^{-1} \left\{ \lim_{\tau \nearrow \infty} \frac{1}{\tau}\int_0^\tau dt \langle \hat{g}(t) \rangle_t \right\}^2 \leq \lim_{\tau \nearrow \infty} \frac{1}{\tau}\int_0^\tau dt \langle \hat{\Theta}_t \rangle_t$

nonzero in general

nonzero averaged current implies nonzero mean dissipation

§ no free-pumping theorem (a trivial example)



system in touch with an equilibrium environment

(1) $\log \dfrac{w_{j\to k}(t)}{w_{k\to j}(t)} = \beta\{E_j(t) - E_k(t)\}$

(2) $\theta_{j\to k}(t) = \beta(E_j(t) - E_k(t))$

(3) $\langle \hat{\theta}(t)\rangle_t = \beta \boxed{J(t)}$ ← heat current to the bath

we set

(4) $g_{j\to k}$ = total displacement of particles (in the x-direction)

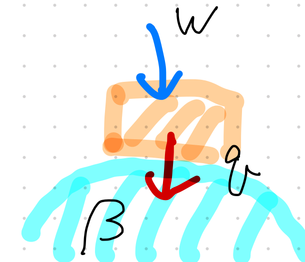
pumping choose appropriate $\tilde{w} = (w(t))_{t\geq 0}$ to have

(5) $\bar{g} = \lim_{\tau\to\infty} \dfrac{1}{\tau}\displaystyle\int_0^\tau dt\, \langle \hat{g}\rangle_t \neq 0$

NO WORK IS DONE TO THE PARTICLE ??

what is the minimum energy cost for pumping? zero??

time-averaged Shiraishi-Saito inequality (p25-(5))



(1) $$\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt\,\langle\hat{\Theta}(t)\rangle_t \geq \left(\bar{\Xi}_g\right)^{-1}\bar{g}^2 \neq 0$$

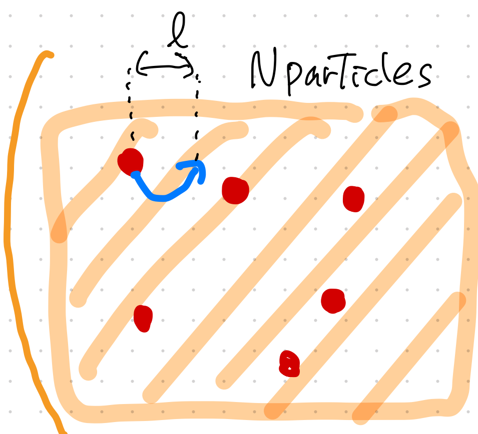
$= \beta q \rightarrow$ q averaged heat current to the baths

W averaged power input to the system

since (2) $W = q$

(3) $$\boxed{W \geq \frac{\bar{g}^2}{\beta\,\bar{\Xi}_g} \neq 0}$$

no free-pump!



p24-(5)

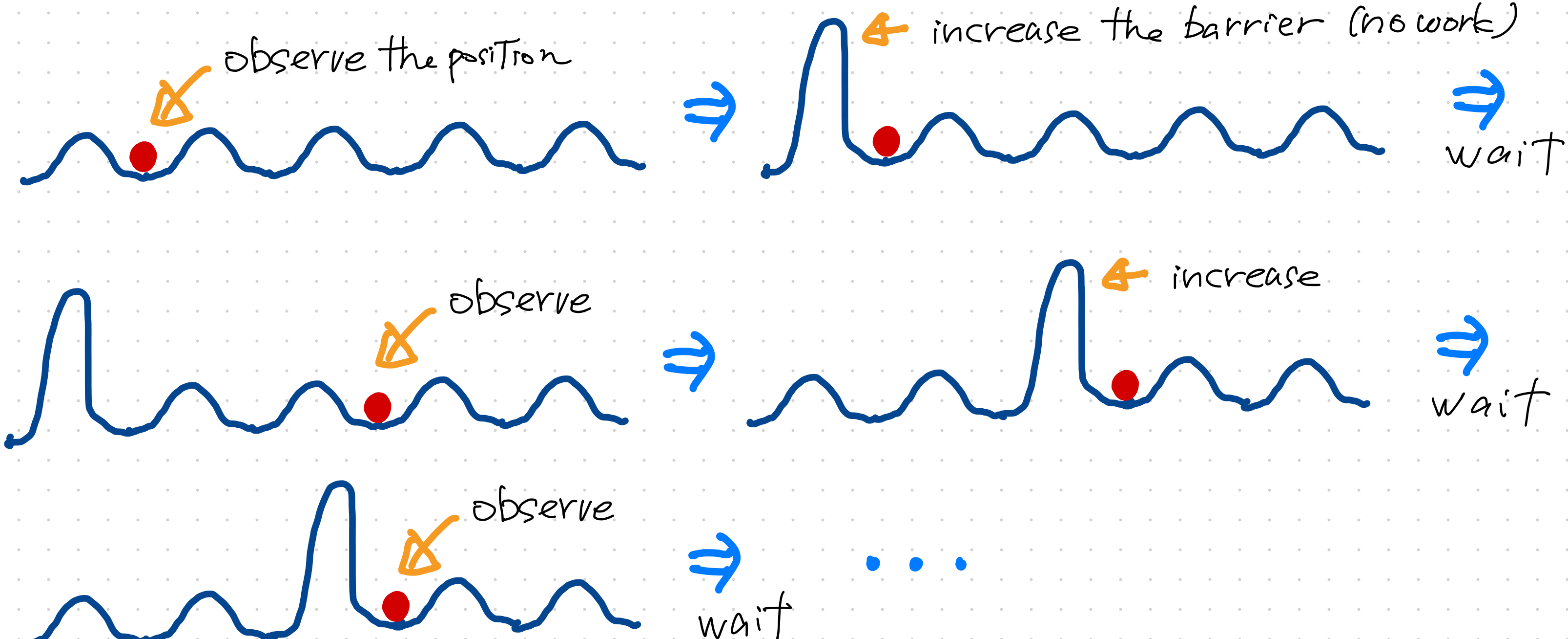
(4) $\bar{\Xi}_g \leq \frac{1}{2}\lambda_0 l^2$

(5) $$W \geq \frac{2\bar{g}^2}{\beta\lambda_0 l^2}$$

(6) $\lambda_0 = O(N)$ if (7) $\bar{g} = O(N)$ (8) $W \geq O(N)$

remark: free-pumping with measurement + feedback

small system where fluctuation is dominant



directional motion is generated without any work

(a kind of Maxwell daemon)

§ Trade-off relation between power and efficiency of a heat engine

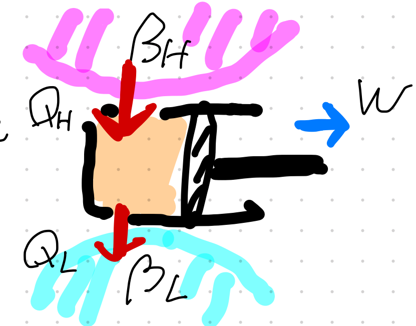
Shiraishi, Saito, Tasaki 2016

efficiency and power of a heat engine

heat engine (external combustion engine)

Q_H heat absorbed from the hot heat bath
Q_L heat expeled to the cold heat bath
$W = Q_H - Q_L$ extracted work

} in a single cycle



efficiency $\eta = \boxed{\dfrac{W}{Q_H}} \boxed{\leq} \eta_C := 1 - \dfrac{\beta_H}{\beta_L} < 1$

→ Carnot's theorem ⇐ starting point and the essence of thermodynamics

power $\boxed{\dfrac{W}{\tau_0}}$

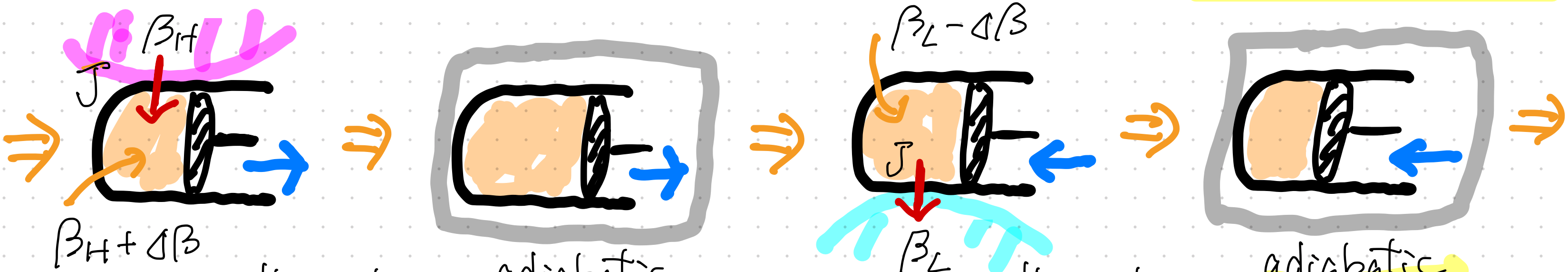
in thermodynamics there is no fundamental limitation on the power of a heat engine

τ_0 : period of the cycle

(i) **Carnot cycle** attains the maximum efficiency η_c
but realized only for $\tau_0 \nearrow \infty$ $\Rightarrow$ $\boxed{\text{power } \frac{W}{\tau_0} \text{ is zero}}$

(ii) **near Carnot cycle** induce nonzero current $J \simeq K \Delta\beta$
by temperature differences

K: constant describing thermal conduction



near isothermal $\Rightarrow$ adiabatic $\Rightarrow$ near isothermal $\Rightarrow$ adiabatic $\Rightarrow$

efficiency (1) $\eta \simeq 1 - \dfrac{\beta_H + \Delta\beta}{\beta_L - \Delta\beta} \simeq \eta_c - \left(\dfrac{1}{\beta_L} + \dfrac{\beta_H}{(\beta_L)^2}\right)\Delta\beta$

minimum period (2) $\tau_0 \simeq \dfrac{Q_H + Q_L}{J} \simeq \dfrac{Q_H + Q_L}{K\Delta\beta}$

thus (3) $\tau_0 \simeq \dfrac{(Q_H + Q_L)^2}{K \beta_L Q_H} (\eta_c - \eta)^{-1}$ $\Rightarrow$ $\boxed{\tau_0 \uparrow \infty \text{ as } \eta \uparrow \eta_c}$

question and main conclusion

near Carnot cycle

$$\tau_0 \simeq \frac{(Q_H + Q_L)^2}{K \beta_L Q_H} (\eta_C - \eta)^{-1} \Rightarrow \boxed{\tau_0 \uparrow \infty \text{ as } \eta \uparrow \eta_C}$$

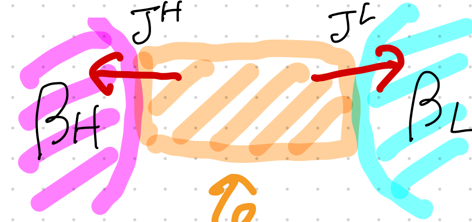
power $\frac{W}{\tau_0} = \frac{Q_H - Q_L}{\tau_0}$ must vanish as the efficiency η approaches the Carnot efficiency

- is this a general (or an inevitable) feature? $\Rightarrow$ yes!
  we prove a univeral bound
- are there heat engines with nonzero power that attains the Carnot efficiency? $\Rightarrow$ no!!

There exists an inevitable loss when the engine exchanges heat with the baths

fundamental limitation of external combustion engines!

Setting



operation = protocol

- system in touch with two heat baths $\alpha = H, L$

  Markov jump proces with $w_{j\to k}(t)$ and $E_j(t)$

  determined by a protocol (may be periodic in t)

  local detailed balance (1) $\log \dfrac{w_{j\to k}(t)}{w_{k\to j}(t)} = \beta_{\alpha(j,k)}\{E_j(t) - E_k(t)\}$ (if $w_{k\to j}(t) \neq 0$)

  $\alpha(j,k) = H$ or L

  master equation (2) $\dot{\mathbb{P}}(t) = R(t)\,\mathbb{P}(t)$

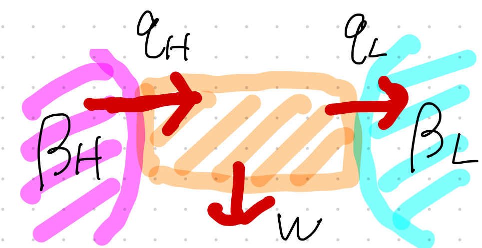
- heat current to bath $\alpha = H, L$

  (3) $J^{\alpha}_{j\to k}(t) = \begin{cases} E_j(t) - E_k(t) & \text{if } \alpha(j,k) = \alpha \\ 0 & \text{otherwise.} \end{cases}$

- entropy production (in the baths)

  (4) $\theta_{j\to k}(t) = \beta_{\alpha(j,k)}\{E_j(t) - E_k(t)\} = \beta_H J^H_{j\to k}(t) + \beta_L J^L_{j\to k}(t)$

averaged quantities



assumption valid when a heat engine operates periodically

the following limits exist and are positive

$$q_H = -\lim_{\tau\nearrow\infty}\frac{1}{\tau}\int_0^\tau dt\,\langle\hat{J}^H(t)\rangle_t > 0$$

$$q_L = \lim_{\tau\nearrow\infty}\frac{1}{\tau}\int_0^\tau dt\,\langle\hat{J}^L(t)\rangle_t > 0$$

averaged power $W = q_H - q_L$ averaged efficiency $\eta = \dfrac{W}{q_H}$

averaged entropy production

$$\boxed{\lim_{\tau\nearrow\infty}\frac{1}{\tau}\int_0^\tau dt\,\langle\hat{\Theta}(t)\rangle_t} = -\beta_H q_H + \beta_L q_L = -\beta_H q_H + \beta_L q_H - \beta_L W$$

$$= \beta_L q_H\left\{-\frac{\beta_H}{\beta_L} + 1 - \frac{W}{q_H}\right\} = \beta_L q_H(\eta_c - \eta)$$

vanishes as $\eta\nearrow\eta_c$!!

iii) the main inequality

set (1) $g_{j\to k}(t) = J^{L}_{j\to k}(t) - J^{H}_{j\to k}(t)$

time-averaged Shiraishi–Saito inequality (p25-(5))

$$(2)\quad \left\{ \underbrace{\lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} dt \, \langle \hat{g}(t)\rangle_t}_{=(q_H+q_L)^2} \right\}^2 \le \bar{\Xi} \underbrace{\lim_{\tau\to\infty} \frac{1}{\tau}\int dt \, \langle \hat{\Theta}_t \rangle_t}_{=\beta_L q_H(\eta_c-\eta)}$$

with (3) $\bar{\Xi} = \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} dt \, \frac{1}{2}\sum_{\substack{j,k\\(j\neq k)}} R_{kj}(t)\, p_j(t) \{E_j(t) - E_k(t)\}^2$

$$(4)\quad \boxed{(q_H+q_L)^2 \le \bar{\Xi}\, \beta_L q_H (\eta_c - \eta)}$$

inequality between thermodynamic quantities and $\bar{\Xi}$

p30-(3)

near Carnot cycle (5) $(q_H+q_L)^2 \simeq K \beta_L q_H (\eta_c - \eta)$, $q_H = Q_H/\tau_0$, $q_L = Q_L/\tau_0$

it can be shown that $\bar{\Xi} \simeq K$ when the system is near equilibrium

the main inequality (4) is optimal!

III) efficiency and power

the main inequality

$$(1)\quad \boxed{(q_H+q_L)^2 \le \bar{\Xi}\,\beta_L\, q_H\,(\eta_c-\eta)}$$

$$(2)\quad \bar{\Xi}\,\beta_L(\eta_c-\eta) \ge \frac{(q_H+q_L)^2}{q_H} \ge q_H+q_L, \qquad q_H\ge 0,\ q_L\ge 0$$

$$(3)\quad \eta \nearrow \eta_c \rightarrow q_H, q_L \to 0, \quad W\to 0$$

the power w must vanish when η attains the maximum η_c

an explicit bound

$$(4)\quad w \le \bar{\Xi}\,\beta_L \frac{q_H}{(q_H+q_L)^2}(\eta_c-\eta)\,w \qquad w = \eta\, q_H$$

$$(5)\quad \boxed{w \le \bar{\Xi}\,\beta_L\left(\frac{q_H}{q_H+q_L}\right)^2 \eta(\eta_c-\eta) \le \bar{\Xi}\,\beta_L\,\eta(\eta_c-\eta)}$$

tradeoff relation between power and efficiency

$$\boxed{W \leq \bar{\Xi}\, \beta_L\, \eta(\eta_C - \eta)} \quad (1)$$

- an engine with high power inevitably has a low efficiency η

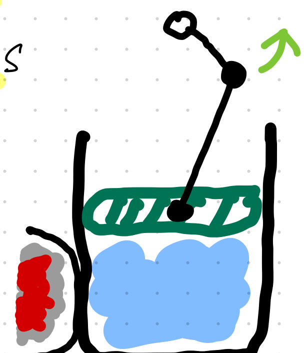
  the bounds are univeral ← apply to any heat engine
  small or large
  close to or far from equlibrium

  $\bar{\Xi}$ is system dependent

- there are extensions to more realistic models (Kramers equation) → part 5

- there is an inevitable dissipation associated with heat current between the engine and the heat baths

fundamental limitation of external combustion engines!



internal combustion engine

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