Detailed Balance and Fluctuation Relations in Quantum Thermodynamics

Ali Rezakhani

Department of Physics
Sharif University of Technology
Tehran, IRAN
thermodynamics

Quantum mechanics

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what is all this “quantum thermodynamics” about?

• revisiting cornerstones of thermodynamics & stat. mech. (ergodic hypothesis, ...)
• reformulating the laws of thermodynamics (1st and 2nd laws)
• employing quantum information ideas (e.g., entanglement, quantum correlations, typicality ...) in studying thermodynamics of quantum systems
• approach to thermalization and equilibrium (e.g., eigenstate thermalization, manybody localization, ...)
• quantum heat engines (e.g., quantum Carnot machines, ...)

it’s not about bosons/fermions (another story: “quantum stat. mech.”)
2nd law of thermodynamics: nature is irreversible (for macroscopic systems)

entropy of nature during any process never decreases
2nd law also implies thermalization of open systems (equilibrium state)

Key questions in q. thermodynamics:

- When do systems equilibrate?
- When do systems thermalize?
but: macro-irreversibility $\leftrightarrow$ micro-reversibility (fundamental laws of nature)

time reversal:

classical $(q, p) \rightarrow (q, -p)$

quantum $(|q\rangle, |p\rangle) \rightarrow (|q\rangle, | - p\rangle)$

$$\Theta q \Theta^\dagger = q \quad \Theta p \Theta^\dagger = -p$$

more on $\Theta$:

$$|\tilde{v}\rangle \equiv \Theta(|v\rangle)$$

(antiunitary)

$$\Theta(\alpha_1|v_1\rangle + \alpha_2|v_2\rangle) = \alpha_1^*\Theta(|v_1\rangle) + \alpha_2^*\Theta(|v_2\rangle)$$

$$\langle\tilde{v}_2|\tilde{v}_1\rangle = \langle v_1|v_2\rangle$$

$$\Theta j \Theta^\dagger = -j \quad (\tilde{j} = \tilde{I} + \tilde{s}) \quad \Theta = e^{-i\pi jyC} \quad \Theta^2 = (-1)^j\mathbb{I}$$

$q$. microreversibility: $[H, \Theta] = 0$ or $\mathcal{T}[H] = H$
detailed balance condition:

configurations of the system: \( \{ i \} \)

probability of configuration \( i \) at time \( \tau \): \( p_i(\tau) \)

Markovian dynamics

\[ \frac{d}{d\tau} p_i(\tau) = \sum_{j \neq i} \left( w_{j \rightarrow i} p_j(\tau) - w_{i \rightarrow j} p_i(\tau) \right) \]

jump/transition rates
(calculated, e.g., from Fermi’s golden rule)

sufficient condition for having a "stationary state" or an "equilibrium state":

\[ p_i^{(eq)} w_{i \rightarrow j} = p_j^{(eq)} w_{j \rightarrow i} \quad \forall i, j \]

a shorthand:

\[ \frac{d}{d\tau} |p(\tau)\rangle = -W |p(\tau)\rangle \]

\[ |p(\tau)\rangle = e^{-\tau W} |p(0)\rangle \]

\[ W_{ij} = \begin{cases} -\sum_{k \neq i} w_{i \rightarrow k} ; & i = j \\ w_{j \rightarrow i} ; & i \neq j \end{cases} \]
**fluctuation theorem**: how probable is the 2nd law

how irreversibility develops in time from a completely time-reversible system at short times to an irreversible system at long times

precise statement of the 2nd law derived from dynamical laws

\[
\frac{P(\text{process})}{P(-\text{process})} = e^{f(\text{process})}
\]

- **process**: a physical event (in forward time)
- \(-\text{process}\): time-reversed version of an event (in backward time)
- **\(f(\text{process})\)**: some thermodynamical function of the system

(transient & equilibrium versions)

Crooks
Jarzynski
Evans
Searles
Bochkov
Gallavotti
Kurchan
...

forward-backward

relaxation

time
examples:

1- entropy exchange

\[
\frac{P_f(+\Delta S)}{P_b(-\Delta S)} = e^{\Delta S} \quad \langle e^x \rangle \geq e^{\langle x \rangle} \quad \langle \Delta S \rangle \geq 0
\]

2- work exchange

\[
\frac{P_f(+W)}{P_b(-W)} = e^{\beta(W-\Delta F)} \quad \langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \quad \langle W \rangle \geq \Delta F
\]

(Jarzynski equality)

3- heat exchange

\[
\frac{P_f(+Q)}{P_b(-Q)} = e^{\Delta \beta Q} \quad \Delta \beta = \beta_S - \beta_B \quad \beta = 1/(k_B T)
\]

\[
\begin{align*}
T_B & \quad T_B \\
T_S & \quad 0 \\
\tau & \quad Q
\end{align*}
\]
quantum detailed balance condition

reversibility

thermalization/equilibration

quantum fluctuation theorem
question: how are detailed balance & fluctuation theorems connected?
sufficient conditions for thermalization:

a system interacting with a large thermal bath

\[
E_D^{(0)} \quad E_1^{(0)}
\]

\[ H_0|m\rangle = E_m^{(0)}|m\rangle \]

Markovian dynamics (Lindblad equation)

\[
\frac{d}{dt} \rho = -i[H, \rho] + \sum_a \gamma_a \left( L_a \rho L_a^\dagger - \frac{1}{2} \{ L_a^\dagger L_a, \rho \} \right)
\]

quantum jump rates \( \gamma_a > 0 \)

quantum jump operators \( L_a \)

\[ E_1^{(0)} < E_2^{(0)} < \ldots < E_D^{(0)} \]

(nondegeneracy)

\[ H = \sum_m E_m|m\rangle\langle m| \]

(modification of energies)

\[ \gamma_{mn} = C_{mn} e^{-\beta_B (E_m^{(0)} - E_n^{(0)})/2} \quad \& \quad C_{mn} = C_{nm} > 0 \]

detailed balance condition:

\[ \sum_n \gamma_{mn} e^{-\beta_B E_n^{(0)}} = \sum_n \gamma_{nm} e^{-\beta_B E_m^{(0)}} \]
\[ g(\tau) = \sum_{nm} \varepsilon_{nn}(0) \langle m| e^{-\tau W_{mn}|n}\rangle \langle m|n\rangle + \sum_{m \neq n} e^{-(i\omega_{mn} + \sigma_{mn})\tau} \varepsilon_{mn}(0) \langle m|n\rangle \]

\[ W_{mn} = \begin{cases} \sum_{j \neq m} \varepsilon_{jm}; & m = n \\ -\varepsilon_{mn}; & m \neq n \end{cases} \]

(reminiscent of the transition matrix)

\[ \omega_{mn} = E_m - E_n \]
\[ \sigma_{mn} = (1/2) \sum_j (\varepsilon_{jm} + \varepsilon_{jn}) \geq 0 \]

\[ \lim_{\tau \to \infty} g(\tau) \to g^{(eq)} \approx e^{-\beta B H_0} \quad \forall g(0) \]

thermal/equilibrium/Gibbs state
system initially in a thermal state with $\beta_S \neq \beta_B$

$$P_f(+Q, \tau) = \sum_{mn} p_m p(n, \tau|m, 0) \delta(Q - [E_n^{(0)} - E_m^{(0)}])$$

**theorem:**

$$\frac{P_f(+Q, \tau)}{P_f(-Q, \tau)} = e^{\Delta \beta Q}$$  
(forward-forward version)
proof: \[
\frac{p(n, \tau|m, 0)}{p(m, \tau|n, 0)} = \frac{\langle n | e^{-\tau W} | m \rangle}{\langle m | e^{-\tau W} | n \rangle} = \ldots = e^{\beta B Q}
\]

key observation:

sufficient condition for the fluctuation relation:
\[
e^{-\beta B E_m^{(0)}} p(n, \tau|m, 0) = e^{-\beta B E_n^{(0)}} p(m, \tau|n, 0)
\]

implication on the 2nd law of thermodynamics:
\[
\int_{-q}^q P(Q, \tau) \, dQ = \int_{-q}^q P(-Q, \tau) e^{Q \Delta \beta} \, dQ \leq e^{q \Delta \beta}
\]

now if \( q = -|q| \leq 0 \) \& \( \Delta \beta > 0 \)

total probability of a heat transfer of amount \( \geq |q| \)
from a cold system to a hot bath

violation of the 2nd law (Clausius statement): only exponentially negligibly possible
question: how general is this?

(consider more general dynamics)
the most general open-system quantum dynamics:

\[ \rho(\tau) = \mathcal{G}_\tau[\rho(0)], \; \tau \geq 0 \]

\[ \mathcal{G}_\tau[\cdot] = \sum_j \mathcal{G}^{(j)}_\tau \cdot \mathcal{G}^{(j)\dagger}_\tau \]

\[ \sum_j \mathcal{G}^{(j)\dagger}_\tau \mathcal{G}^{(j)}_\tau = \mathbb{1} \]

(CPTP map)

special case: (quantum version of a classical Markovian dynamics)

\[ \partial_\tau \rho(\tau) = \mathcal{L}[\rho(\tau)] \]

\[ \mathcal{L}[\cdot] = -i[H, \cdot] + \sum_{k,l=1}^{d^2-1} C_{kl}(F_k \cdot F_l^\dagger - (1/2) \{ F_l^\dagger F_k, \cdot \}) \]

\[ \mathcal{G}_\tau = e^{\tau \mathcal{L}} \]

\[ \mathcal{G}_{\tau_1} \mathcal{G}_{\tau_2} = \mathcal{G}_{\tau_1+\tau_2} \]

(Lindblad generator)

thermalizing dynamics:

\[ \rho(\infty) = \lim_{\tau \to \infty} \mathcal{G}_\tau[\rho(0)] \propto e^{-\beta H} \]
reminding from literature:

**Heisenberg picture** or dual dynamics: \( \text{Tr}[\mathcal{G}_\tau[\sigma]A] = \text{Tr}[\sigma \mathcal{G}^\#_\tau[A]] \)

the most general form of a **quantum detailed balance condition**

take:

\[
\begin{bmatrix}
  s \in [0, 1] \\
  \Sigma & \text{a reference state (full-rank); e.g., thermal state}
\end{bmatrix}
\]

\[\langle \langle A, B \rangle \rangle_s = \text{Tr}[\Sigma^{1-s} A^\dagger \Sigma^s B] \quad \text{(inner product)}\]

\[\langle \langle A, \mathcal{O}[B] \rangle \rangle_s = \langle \langle \mathcal{O}^*[A], B \rangle \rangle_s \quad \text{(adjoint)}\]

\[\langle \langle A^\dagger, \mathcal{G}^\#_\tau[B] \rangle \rangle_s = \langle \langle \mathcal{T}[B^\dagger], \mathcal{G}^\#_\tau[\mathcal{T}[A]] \rangle \rangle_s\]

special case: for dynamical semigroups \( \mathcal{L}^\#[A] - \mathcal{L}^{\#\ast}[A] = 2i[H, A] \)
The Hamiltonian is symmetric under time-reversal:

$$P_f(+\mathcal{E}, \tau) = \sum_{mn} p_m(\beta_S) p(n, \tau|m, 0) \delta(\mathcal{E} - [E_n - E_m])$$

Theorem:

- Hamiltonian is symmetric under time-reversal: $[H, \Theta] = 0$ or $\mathcal{T}[H] = H$
- Dynamics is thermalizing
- Quantum detailed balance holds

Proof: Technical ...
bottomline:

quantum detailed balance condition $\rightarrow$ quantum fluctuation theorem

we have found counterexample for the converse (relatively technical)

**question:** how are detailed balance & fluctuation theorems connected?

partially answered ...