Quantum thermodynamical approach to work-extraction

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Outline

Revisiting some standard problems in thermodynamics starting from quantum mechanics.

- How much work can be extracted from a given non-equilibrium system ?

- What are the features of the maximal work ?

- Are adiabatically slow (reversible) processes always optimal ?

- Summary/Outlook.

Setup for work-extraction

- A thermally isolated quantum system interacts with an external macroscopic work-source.
- $\Rightarrow$ Time-dependent Hamiltonian $H(t)$.
- A non-equilibrium initial state: $\rho_0 \equiv \rho(0)$.
- Cyclic processes: $H(\tau) = H(0) = H$.
- von Neumann eq. of motion: $i\hbar\dot{\rho} = [H(t), \rho(t)]$.
- Work is the energy added to the system:

  $\frac{\mathrm{d}W}{\mathrm{d}t} = \mathrm{tr}\left(\rho(t)\,\frac{\mathrm{d}H}{\mathrm{d}t}\right).$

  $W = E_{\mathrm{f}} - E_{\mathrm{i}} = \mathrm{tr}\,(\,\rho(\tau)\,H\,) - \mathrm{tr}\,(\,\rho_0 H\,),$
- $W < 0$ means work-extraction.
- $W_{\mathrm{m}} = min\ W$; with H and ρ_0 being fixed.

The standard answer

- $W = E_\mathrm{f} - E_\mathrm{f} \Rightarrow$ minimize E_f.

- 2'nd law: $S[\rho(\tau)] \geq S[\rho_0] \equiv -\mathrm{tr}\rho_0 \ln \rho_0$.

- <u>Postulate</u>: $\rho(\tau) \equiv \rho_\mathrm{f} = \exp[-\beta_\mathrm{f} H]/Z_\mathrm{f}$.

- $\mathrm{d}S_\mathrm{f}/\mathrm{d}E_\mathrm{f} = \beta_\mathrm{f} \geq 0$

  $\Rightarrow \beta_\mathrm{f}$ to be found from $S[\rho(\tau)] = S[\rho_0]$.

- $W_\mathrm{th}[\rho_0] = -T_\mathrm{f} \ln Z_\mathrm{f} + T_\mathrm{f} S[\rho_0] - E[\rho_0]$.

- Comparing initial states ρ_0 and σ_0, $E[\rho_0] = E[\sigma_0]$.

  $W_\mathrm{th}[\rho_0] \leq W_\mathrm{th}[\sigma_0] \quad \Leftrightarrow \quad S[\rho_0] \leq S[\sigma_0]$

  $\Leftrightarrow \quad W_\mathrm{th}[\rho_0 \otimes \omega_0] \leq W_\mathrm{th}[\sigma_0 \otimes \omega_0] \qquad$ for any ω_0.

- $\Rightarrow$ Entropy measures activity.

- $\Rightarrow$ Resources act additively.

L.D. Landau & E.M. Lifshitz, *Statistical Physics, I.*
H.B. Callen, *Thermodynamics.*
I. Prigogine & R. Defay, *Chemical Thermodynamics.*

Direct solution of the problem.

$$i\hbar\dot{\rho} = [H(t), \rho(t)] \quad \Rightarrow \quad \rho(\tau) = U^\dagger \rho_0 U, \quad U^\dagger U = 1.$$

$$\Rightarrow \qquad S[\rho(\tau)] = S[\rho_0],$$

$$\Rightarrow \quad \text{Eigenvalues}[\,\rho(\tau)\,] = \text{Eigenvalues}[\,\rho_0\,].$$

$$\rho_0 = \sum_{j\geq 1} r_j |r_j\rangle\langle r_j|, \quad H = \sum_{k\geq 1} \lambda_k |\lambda_k\rangle\langle\lambda_k|,$$

$$r_1 \geq r_2 \geq \ldots, \qquad \lambda_1 \leq \lambda_2 \leq \ldots.$$

- Find the optimal U.
- Construct a smooth, cyclic $H(t)$ realizing U.

Ergotropy:

$$min\ W \equiv W_{\mathrm{m}} = \sum_{j,k} r_j \lambda_k \,(\,\delta_{jk} - |\langle r_j|\lambda_k\rangle|^2).$$

- $\rho(\tau) = \sum_j r_j |\lambda_j\rangle\langle\lambda_j|$ (completely exhausted).

- In general: $W_{\mathrm{th}} \leq W_{\mathrm{m}}$.

Entropy and activity.

Cases where $W_{\rm th} = W_{\rm m}$, and the entropy criterion holds:

- Two level systems.
- Gaussian states of harmonic oscillator.
- Several classes of macroscopic systems.

- More work is possible from larger entropy state.

Three-level example: $\lambda_1 = 1, \quad \lambda_2 = 0, \quad \lambda_3 = -1.$

$$\rho_0 = \sum_{j=1}^{3} r_j |r_j\rangle\langle r_j|, \qquad \sigma_0 = \sum_{j=1}^{3} s_j |s_j\rangle\langle s_j|,$$

$$|r_{1,3}\rangle = |s_{1,3}\rangle = \frac{1}{\sqrt{2}}(|\lambda_1\rangle \mp |\lambda_3\rangle), \qquad |r_2\rangle = |s_2\rangle = |\lambda_2\rangle,$$

$$\Rightarrow \qquad E(\rho_0) = E(\sigma_0) = 0.$$

$$\{r_j\} = \{0.90, 0.08, 0.02\}, \quad \{s_j\} = \{0.91, 0.05, 0.04\},$$

$$S[\rho_0] \simeq 0.375 \qquad > \qquad S[\sigma_0] \simeq 0.364.$$

$$W_{\rm th}[\rho_0] \simeq -0.882 \;>\; W_{\rm th}[\sigma_0] \simeq -0.887.$$

$$W_{\rm m}[\rho_0] = -0.88 \;<\; W_{\rm m}[\sigma_0] = -0.87.$$

Adding a resources of work.

- Thermodynamics predicts:

$$W_{\rm th}[\rho_0] \; > \; W_{\rm th}[\sigma_0] \;\; \Rightarrow \;\; W_{\rm th}[\rho_0 \otimes \omega_0] \; > \; W_{\rm th}[\sigma_0 \otimes \omega_0]$$

- Is it possible ? Yes.

$$W_{\rm m}[\rho_0] \; > \; W_{\rm m}[\sigma_0] \;\; \Rightarrow \;\; W_{\rm m}[\rho_0 \otimes \omega_0] \; < \; W_{\rm m}[\sigma_0 \otimes \omega_0].$$

Example: ρ_0 and σ_0 are 4-level; ω_0 has 2 levels.

Energy levels: $(0 < x < 1)$

$$\lambda_4 = 1, \qquad \lambda_3 = 1 - x, \qquad \lambda_2 = -1 + x, \qquad \lambda_4 = -1$$

Eigenstates:

$$|r_{1,4}\rangle = |s_{1,4}\rangle = \tfrac{1}{\sqrt{2}}(|\lambda_1\rangle \pm |\lambda_4\rangle),$$
$$|r_{2,3}\rangle = |s_{2,3}\rangle = \tfrac{1}{\sqrt{2}}(|\lambda_2\rangle \pm |\lambda_3\rangle), \qquad E(\rho_0) = E(\sigma_0) = 0.$$

Eigenvalues:

$$\{r_j\} = \tfrac{1}{(1+\phi)^2}\left\{\phi(\phi+3),\, \tfrac{1-\phi}{2},\, \tfrac{1-\phi}{2},\, 0\right\}, \qquad \tfrac{1}{2} < \phi < \tfrac{1}{\sqrt{2}}.$$

$$\{s_j\} = \tfrac{1}{(1+\phi)^2}\left\{2\phi,\, 2\phi,\, \phi(1-\phi)^2,\, (1-\phi)^3\right\}.$$

$$\omega_0 = \sum\nolimits_{j=1}^{2} \omega_j |\omega_j\rangle\langle\omega_j|, \qquad \{\omega_j\} = \{\phi, 1-\phi\}.$$

Thermodynamic domain for finite systems.

- Definition of majorization:

$$\rho_0 \succ \sigma_0 \quad \underline{\text{iff}} \quad \sum_{j=1}^{k} r_j \geq \sum_{j=1}^{k} s_j, \quad \text{for} \quad k \geq 1.$$

$$\{1, 0, 0, ...\} \succ \text{all states} \succ \{\tfrac{1}{d}, \tfrac{1}{d}, ...\}$$

- More major states are more active.

$$\boxed{\rho_0 \succ \sigma_0, \quad E[\rho_0] = E[\sigma_0] \quad \Rightarrow \quad W_{\rm m}[\rho_0] \leq W_{\rm m}[\sigma_0].}$$

- $\rho_0 \succ \sigma_0, \quad \Rightarrow \quad S[\rho_0] \leq S[\sigma_0].$
- $\rho_0 \succ \text{diag}(\rho_0) \quad \Rightarrow \quad W_{\rm m}[\rho_0] \leq W_{\rm m}[\text{diag}(\rho_0)].$
- $\rho_0 \succ \sigma_0 \quad \Rightarrow \quad \rho_0 \otimes \omega_0 \succ \sigma_0 \otimes \omega_0$

$$\Rightarrow \quad W_{\rm m}[\rho_0 \otimes \omega_0] \leq W_{\rm m}[\sigma_0 \otimes \omega_0].$$

- However, there are cases, where $\rho \not\succ \sigma, \quad \rho \not\prec \sigma.$

Ruch, Schlögl, Mead, Uhlmann, Wehrl: 70s-80s.
Marshall & Olkin, *Theory of Majorization.*
Bhatia, *Matrix Analysis.*

Minimal work principle.

- An equilibrium initial state: $\rho(0) = \exp[-\beta H_{\rm i}]/Z_{\rm i}$, prepared, e.g. via a thermal bath.

- Non-cyclic processes: $H_{\rm f} \neq H_{\rm i}$.

- Duration of the process is τ.

- Adiabatic process: $\tau \to \infty$; $H_{\rm f}$ and $H_{\rm i}$ are fixed.

- Minimum work principle: $W \geq W_{\rm adiabatic}$.

- Exact theorem:

  $$W \geq \Delta F \equiv T \ln {\rm tr}\,[\exp -\beta H_{\rm i}] + T \ln {\rm tr}\,[\exp -\beta H_{\rm f}]$$

  QM: Bochkov & Kuzovlev, Kurchan, Partovi, H. Tasaki, S. Mukamel.
  CM: Sekimoto & Sasa, Jarzynski, C. Maes.

Level crossing.

- It can happen $W_{\text{ad}} > \Delta F$

  $\Rightarrow$ the theorem provides no information.

- We proved: No-crossings of the eigenvalues of $H(t)$

  $\Rightarrow$ then the minimum work principle holds.

- A single crossing is enough for $W < W_{\text{ad}}$.

- Examples of level crossings observed in experiment: Yarkony, Rev. Mod. Phys. 1996

- No crossing rule: Level crossings for a real and smooth Hamiltonian $H(t)$ are unstable with respect to small perturbations, if only one parameter is varied in time.

  Wigner & Neumann, Longuet-Higgins, Mead.

- No work from an equilibrium system by making a cycle.

  Pucz & Woronowich; Lenard

Summary

- The program of quantum thermodynamics:
  Derivation of thermodynamical laws from QM.

- General solution to the maximal work problem.

- Entropically more disordered states can give more work. Resources can act anti-additively.

- The proper measure of order is majorization.
  It defines the "thermodynamic domain" for finite systems.

- Minimum work principle:
  the proof and counterexamples.

Outlook

- Microscopic approaches to thermodynamics of small classical systems

  Jarzynski; Sekimoto; Sasa; Parrondo;

- Related approaches in quantum thermodynamics:

  Scully, Zubairy....; Bender, Brody,.....:

  quantum heat engines.

  Kurchan; Maes; S. Mukamel:

  quantum fluctuation theorems.

- Second law(s) in quantum thermodynamics:

  Lenard,

  Partovi,

  H. Tasaki,

  Gemmer, Otte, Mahler

- Limits of some formulations of the second law:

  - Clausius inequality
  - H-theorem
  - Minimum work principle