

Classical and Quantum Fluctuation Theorems for Heat Exchange

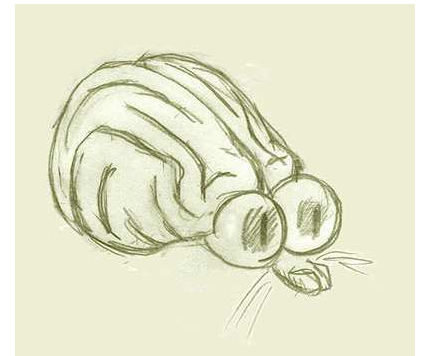
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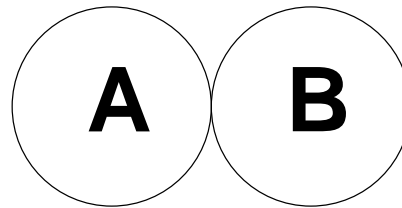


Imaginary experiment

Consider a simple experiment: put two bodies A and B at different temperatures T_A and T_B



in contact for a short time τ (too short for equilibration)



What can you say about the energy exchange?



Assumptions

- Hamiltonian, time reversible evolution
- “Small” coupling

Assumptions again

We assume:

- At times $t < 0$ and $t > \tau$:

$$H = H_A(\mathbf{z}_A) + H_B(\mathbf{z}_B)$$

- For $0 \leq t \leq \tau$:

$$H = H_A(\mathbf{z}_A) + H_B(\mathbf{z}_B) + h_{\text{int}}(\mathbf{z}_A, \mathbf{z}_B, t)$$

- Time reversal invariance:

$$H^i(\mathbf{z}_i) = H^i(\mathbf{z}_i^*), \quad h^{\text{int}}(\mathbf{y}) = h^{\text{int}}(\mathbf{y}^*)$$

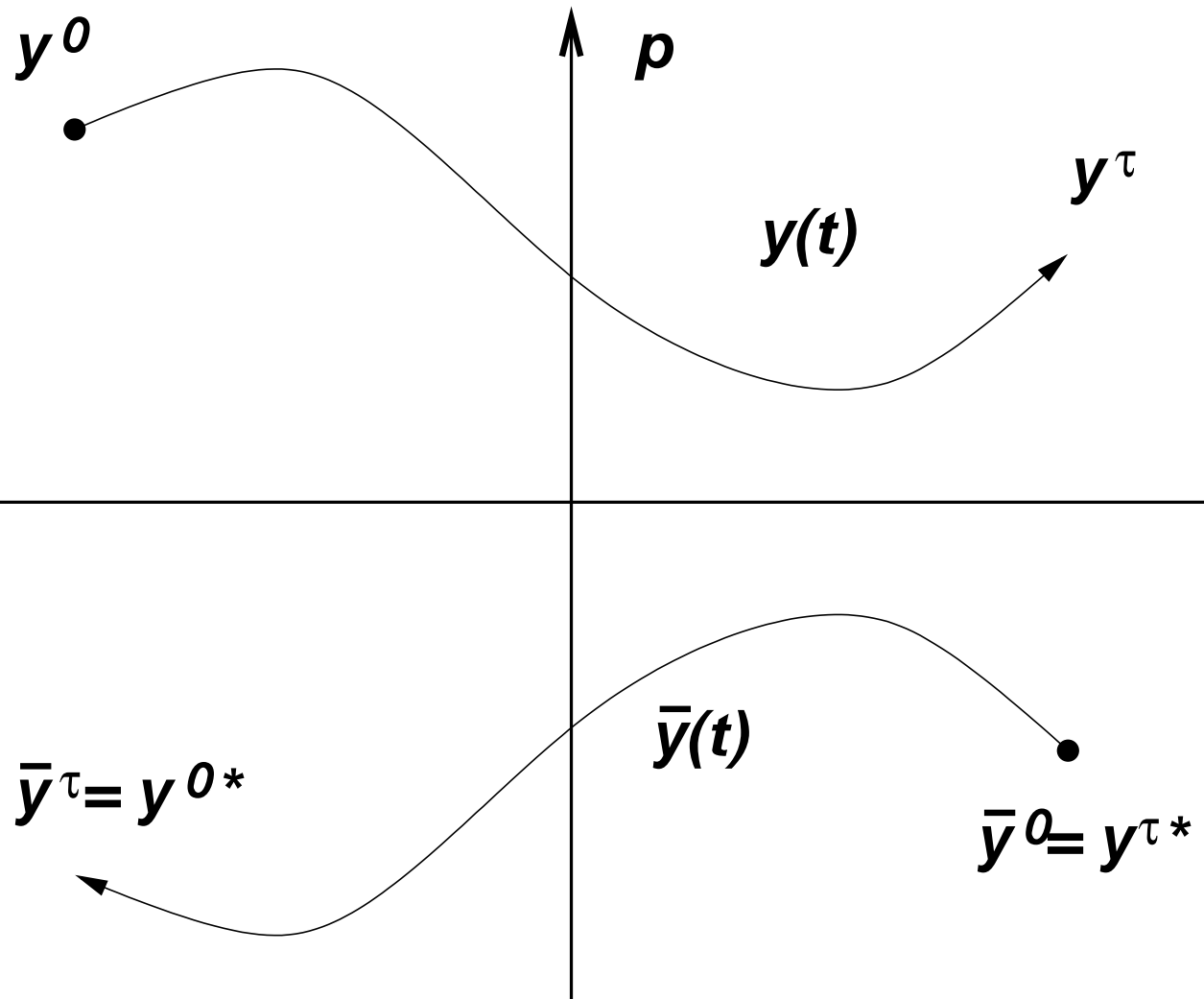
where (*) denotes time-reversal operation, usually the reversal of momenta: $(\mathbf{q}, \mathbf{p})^* = (\mathbf{q}, -\mathbf{p})$; $\mathbf{y} = (\mathbf{z}_A, \mathbf{z}_B)$.

Twin trajectories

To every trajectory there corresponds another one

$$\bar{y}(t) = y^*(\tau - t)$$

Thus with every point y^0 we can uniquely (given τ) associate another point \bar{y}^0



Initial state

Initially, the systems are at temperatures T_A, T_B .

The probability that at $t = 0$ the coupled system will start its evolution at $\mathbf{y}^0 = (\mathbf{z}_A^0, \mathbf{z}_B^0)$ is

$$P(\mathbf{y}^0) = \frac{1}{Z_A Z_B} e^{-H^A(\mathbf{z}_A^0)/T_A} e^{-H^B(\mathbf{z}_B^0)/T_B}$$

Probability of observing twin trajectory is

$$P(\bar{\mathbf{y}}^0) = \frac{1}{Z_A Z_B} e^{-H^A(\bar{\mathbf{z}}_A^0)/T_A} e^{-H^B(\bar{\mathbf{z}}_B^0)/T_B}$$

Ratio

Therefore,

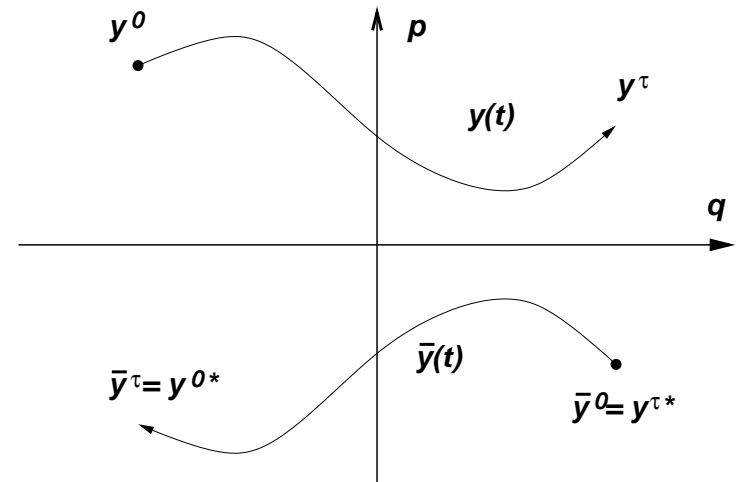
$$\frac{P(\mathbf{y}^0)}{P(\bar{\mathbf{y}}^0)} = e^{-\beta_A(H^A(\mathbf{z}_A^0) - H^A(\bar{\mathbf{z}}_A^0))} e^{-\beta_B(H^B(\mathbf{z}_B^0) - H^B(\bar{\mathbf{z}}_B^0))}$$

But $\bar{\mathbf{z}}_A^0 = \mathbf{z}_A^{\tau*}$, thus

$$H_A(\bar{\mathbf{z}}_A^0) = H_A(\mathbf{z}_A^{\tau*}) = H_A(\mathbf{z}_A^\tau)$$

It follows that

$$\frac{P(\mathbf{y}^0)}{P(\bar{\mathbf{y}}^0)} = e^{-\beta_A(H^A(\mathbf{z}_A^0) - H^A(\mathbf{z}_A^\tau))} e^{-\beta_B(H^B(\mathbf{z}_B^0) - H^B(\mathbf{z}_B^\tau))}$$



Conservation of energy

Since we assumed h_{int} “small”, the initial and final total energy are approximately equal

$$H_A(\mathbf{z}_A^0) + H_B(\mathbf{z}_B^0) \approx H_A(\mathbf{z}_A^\tau) + H_B(\mathbf{z}_B^\tau)$$

The change of the energy of system B in time is the heat transferred from A to B . Define

$$Q := H_B(\mathbf{z}_B^\tau) - H_B(\mathbf{z}_B^0) \approx H_A(\mathbf{z}_A^0) - H_A(\mathbf{z}_A^\tau)$$

Put it together

Substituting

$$Q = H_A(\mathbf{z}_A^0) - H_A(\mathbf{z}_A^\tau) \approx H_B(\mathbf{z}_B^\tau) - H_B(\mathbf{z}_B^0)$$

in

$$\frac{P(\mathbf{y}^0)}{P(\bar{\mathbf{y}}^0)} = e^{-\beta_A(H^A(\mathbf{z}_A^0) - H^A(\mathbf{z}_A^\tau))} e^{-\beta_B(H^B(\mathbf{z}_B^0) - H^B(\mathbf{z}_B^\tau))}$$

we obtain

$$\frac{P(\mathbf{y}^0)}{P(\bar{\mathbf{y}}^0)} = e^{(\beta_B - \beta_A)Q} = e^{\Delta\beta \cdot Q}$$

Classical heat exchange fluctuation theorem

Let $p_\tau(Q)$ be the probability of transfer of heat Q from A to B

$$p_\tau(Q) = \int d\mathbf{y}^0 P(\mathbf{y}^0) \delta[Q - \hat{Q}(\mathbf{y}^0)]$$

where $\hat{Q}(\mathbf{y}^0)$ is trajectory dependent amount of energy transferred from A to B . Clearly,

$$\hat{Q}(\mathbf{y}) = -\hat{Q}(\bar{\mathbf{y}})$$

Thus we have

$$\begin{aligned} p_\tau(Q) &= \int d\mathbf{y}^0 P(\bar{\mathbf{y}}^0) e^{\Delta\beta \cdot \hat{Q}(\mathbf{y}^0)} \delta[Q - \hat{Q}(\mathbf{y}^0)] \\ &= e^{\Delta\beta \cdot Q} \int d\bar{\mathbf{y}}^0 P(\bar{\mathbf{y}}^0) \delta[Q + \hat{Q}(\bar{\mathbf{y}}^0)] = e^{\Delta\beta \cdot Q} p_\tau(-Q), \end{aligned}$$

Classical heat exchange fluctuation theorem

Thus we have proved

Classical exchange fluctuation theorem

$$\ln \frac{p_{\tau}(+Q)}{p_{\tau}(-Q)} = \Delta\beta \cdot Q$$

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<http://www.arxiv.org/abs/cond-mat/0404475>; to appear in Phys Rev Lett

Modifications for the quantum case

- Assume systems A and B have equilibrated. At time $t = 0^-$ we separate them from reservoirs and *measure* their energies. As a result, each system i is projected onto a pure state $|n_i\rangle$ with probability $e^{-\beta_i E_{n_i}^i} / Z_i$
- We then allow the systems to interact through a weak coupling term h^{int} over time τ

$$\mathcal{H} = H^A \otimes I^B + I^A \otimes H^B + h^{\text{int}}$$

- The combined system then reaches entangled state $|\Psi\rangle$. We separate the two systems and again measure their energies. The state $|\Psi\rangle$ is thus projected onto a product state $|m_A m_B\rangle$.

Additional assumptions

- Total energy is almost preserved

$$E_n^A + E_n^B \approx E_m^A + E_m^B$$

- Time reversibility:

$$\Theta H = H \Theta$$

Transition probabilities

Let $P_\tau(|n\rangle \rightarrow |m\rangle)$ denote the probability of observing a transition from $|n\rangle \equiv |n_A n_B\rangle$ to $|m\rangle \equiv |m_A m_B\rangle$. Then

$$P_\tau(|n\rangle \rightarrow |m\rangle) = |(\langle m|, U_\tau |n\rangle)|^2 \frac{e^{-\beta_A E_{n_A}^A - \beta_B E_{n_B}^B}}{Z_A Z_B},$$

where $U_\tau = e^{-i\tau\mathcal{H}}$ is the quantum evolution operator.

Similarly, the probability of observing the time-reversed transition from $\Theta|m\rangle$ to $\Theta|n\rangle$ is

$$P_\tau(\Theta|m\rangle \rightarrow \Theta|n\rangle) = |(\langle \Theta|n\rangle, U_\tau \Theta|m\rangle)|^2 \frac{e^{-\beta_A E_{m_A}^A - \beta_B E_{m_B}^B}}{Z_A Z_B}.$$

Ratio

Since Θ is anti-unitary, and $U_\tau\Theta = \Theta U_{-\tau}$, we have

$$\begin{aligned}(\Theta|n\rangle, U_\tau\Theta|m\rangle) &= (\Theta|n\rangle, \Theta U_{-\tau}|m\rangle) \\ &= (U_{-\tau}|m\rangle, |n\rangle) \\ &= (|m\rangle, U_\tau|n\rangle),\end{aligned}$$

therefore

$$\frac{P_\tau(|n\rangle \rightarrow |m\rangle)}{P_\tau(\Theta|m\rangle \rightarrow \Theta|n\rangle)} = e^{-\beta_A(E_{n_A}^A - E_{m_A}^A)} e^{-\beta_B(E_{n_B}^B - E_{m_B}^B)}.$$

Conservation of energy

Since we assumed that the interaction is weak, we expect the energy of the total system to be almost preserved:

$$E_n^A + E_n^B \approx E_m^A + E_m^B.$$

It follows that the energy changes in the two systems are approximately equal

$$Q_{n \rightarrow m} := E_m^B - E_n^B \approx E_n^A - E_m^A.$$

We interpret Q as the heat exchange between the systems A and B . Thus,

$$\frac{P_\tau(|n\rangle \rightarrow |m\rangle)}{P_\tau(\Theta|m\rangle \rightarrow \Theta|n\rangle)} \approx e^{\Delta\beta \cdot Q_{n \rightarrow m}}.$$

Quantum heat exchange fluctuation theorem

Since every eigenstate has a corresponding time-reversed twin, the net probability of the heat transfer Q in time τ is

$$\begin{aligned} p_\tau(Q) &= \sum_{n,m} P_\tau(|n\rangle \rightarrow |m\rangle) \delta(Q - Q_{n \rightarrow m}) \\ &= e^{\Delta\beta \cdot Q} \sum_{\Theta n, \Theta m} P_\tau(\Theta|m\rangle \rightarrow \Theta|n\rangle) \delta(Q + Q_{\Theta m \rightarrow \Theta n}) \\ &= e^{\Delta\beta \cdot Q} p_\tau(-Q) \end{aligned}$$

Quantum heat exchange fluctuation theorem

We have proved

Quantum exchange fluctuation theorem

$$\ln \frac{p_{\tau}(+Q)}{p_{\tau}(-Q)} = \Delta\beta \cdot Q$$

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