Fluctuation Theorems for classical and quantum systems

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Fluctuation Theorems

What?

- Exact results relating nonequilibrium fluctuations to equilibrium quantities
- Example: Jarzynski Equality (1997)

$$< e^{-W/k_B T} >= e^{-\Delta F/k_B T}$$

Why?

- Fluctuations are relevant for small systems (nanoscale physics)
- Fluctuations are not just noise
- Microscopic understanding of thermodynamics laws
- Compute equilibrium properties from nonequilibrium measurements

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Incessant motion of pollen grains suspended in water (Brown, 1827)

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Einstein explanation (1905)

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Relation between thermal fluctuation D and response to perturbation μ

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- Linear Response theory: Fluctuation-Dissipation theorem

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What about system arbitrarily far from thermal equilibrium?

A model study: single thermal bath

Start at thermal equilibrium (reservoir at temperature T)

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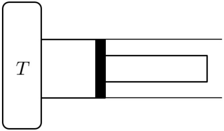

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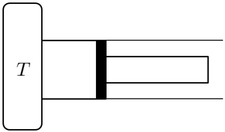

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System driven away from equilibrium, protocol $\lambda : [0, \tau] \longrightarrow R$, with hamiltonian $H(\mathbf{z}, \lambda_t)$

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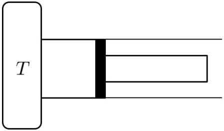

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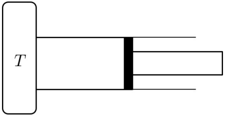

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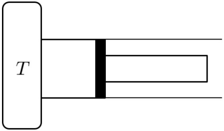

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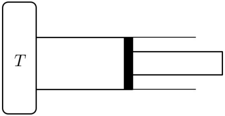

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Let it thermalize $\longrightarrow W \geq \Delta F$ (equality if reversible)

Fluctuation Theorems: Classical Physics

Microscopic viewpoint: $\forall \mathbf{z}_0 \longrightarrow W[\mathbf{z};\lambda] = H(\mathbf{z}_\tau;\lambda_\tau) - H(\mathbf{z}_0,\lambda_0)$
Work is a RANDOM quantity ($p[W;\lambda]$)

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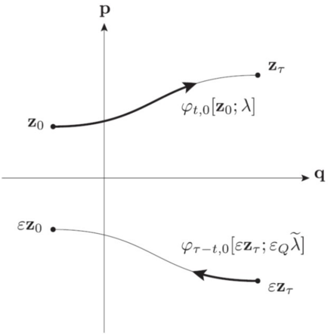

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Two ingredients

- Dynamical microreversibility
- Initial Gibbs state

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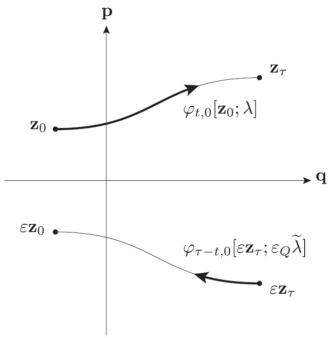

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Results

Crooks (1999)

$$\frac{p[W;\lambda]}{p[-W;\tilde{\lambda}]} = e^{\beta(W-\Delta F)}$$

Follows the Jarzynski equality

$$< e^{-\beta W} >_\lambda = e^{-\beta \Delta F}$$

Relation to second principle of thermodynamics

Using Jensen Inequality $< e^{-\beta W} >_\lambda = e^{-\beta \Delta F} \longrightarrow < W >_\lambda \geq \Delta F$
In particular for $\Delta F = 0$, $< W >_\lambda \geq 0$ (Kelvin Formulation)

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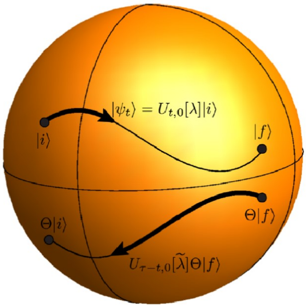
Fluctuation relation for entropy:

$$< e^{-\Delta(\beta E) + \int dQ/T} >_\lambda = e^{-\Delta(\beta \Delta F)}$$

Follow Clausius formulation $\Delta S \geq < \int dQ/T >$



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Substitutions

$$H(\mathbf{z}, \lambda_t) \longrightarrow \mathcal{H}(\lambda_t)$$

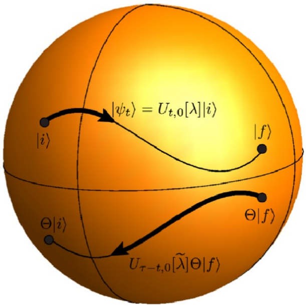
$$\rho(\mathbf{z}, \lambda_t) \longrightarrow \varrho(\lambda_t) = \frac{e^{-\beta\mathcal{H}(\lambda_\tau)}}{\mathcal{Z}(\lambda_t)}$$

$$Z(\lambda_t) \longrightarrow \mathcal{Z}(\lambda_t) = \mathrm{Tr}\ e^{-\beta\mathcal{H}(\lambda_\tau)}$$

$$\phi_{t,0}[z_0; \lambda] \longrightarrow U_{t,0}[\lambda] = \mathcal{T}\ \mathrm{e}^{-\frac{i}{\hbar}\int_0^t ds\mathcal{H}(\lambda_s)}$$

$$W \longrightarrow ???$$

Fluctuation Theorem: Quantum Physics



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$$W \longrightarrow ???$$

What is quantum work?

- Work is NOT a quantum observable, $\nexists \mathcal{W}$ hermitian operator
- Work it is not a state variable, characterize a process

Fluctuation Theorem: Quantum Physics

Two projective measurements definition

Measure the energy at times $t = 0$ and $t = \tau$

$$W[\mathbf{z}; \lambda] \longrightarrow w = E_m^{\lambda_t} - E_n^{\lambda_0}$$

where

$$\mathcal{H}(\lambda_t)|\psi_{n,\lambda}^{\lambda_t} >= E_n^{\lambda_t}|\psi_{n,\lambda}^{\lambda_t} >$$

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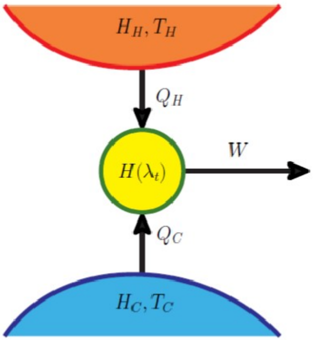
Microreversibility+Gibbs Distribution

The same fluctuation relations apply! Tasaki(2000) and Kurchan (2000)

$$\frac{p[w; \lambda]}{p[-w; \tilde{\lambda}]} = e^{\beta(w - \Delta F)} \; , \; < e^{-\beta w} >_{\lambda} = e^{-\beta \Delta F}$$

An application: efficiency of a Quantum Heat Engine

$$\mathcal{H}(t) = H(\lambda_t) + H_H + H_C + c_t V_C + h_t V_H$$



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$$\rho_0 = \frac{e^{-\beta_C H(\lambda_0)}}{Z_0(\beta_C)} \otimes \frac{e^{-\beta_C H_C}}{Z_C} \otimes \frac{e^{-\beta_H H_H}}{Z_H}$$

$$\frac{P(\Delta E, Q_H, Q_C)}{\tilde{P}(-\Delta E, -Q_H, -W)} = e^{(\beta_C - \beta_H) Q_H - \beta_C W}$$

$$< e^{(\beta_C - \beta_H) Q_H - \beta_C W} >= 1$$

$$< \eta >= \frac{< W >}{< Q_H >} \leq 1 - \frac{T_C}{T_H}$$

Efficiency smaller than Carnot!!!

Conclusions

Fluctuations Theorems

- Rely on microreversibility of motion and initial thermal state
- Hold unaltered in classical and quantum physics
- Deeper understanding of thermodynamics laws

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