Relativistic fluctuation relation

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Outline of the course

Part I — Thermodynamics

- The classical fluctuation relations.
- The quantum fluctuation relations.

Part II — Relativity

- Why General Relativity?
- A simple introduction to the theory.

Outline of the course

Part III — Relativistic thermodynamics

- A quantum system living in a curved spacetime.
- The relativistic fluctuation theorem.
- A simple example: How is the life of a harmonic oscillator in an expanding universe.

Quantum what???

What is Pequi?

What is Pequi used for?



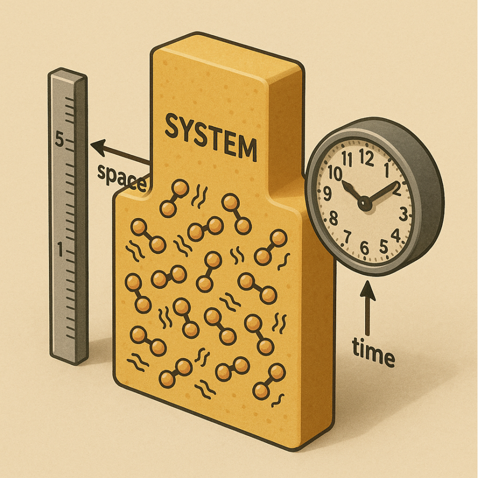


The classical world

The rise of thermodynamics

Macroscopic measurements

Space and time measurements are averages. Our macroscopic instruments cannot see the fast dynamics of the microscopic world. From this set of measurements, the **time-independent** thermodynamic variables emerge. This is a *subjective ignorance*.



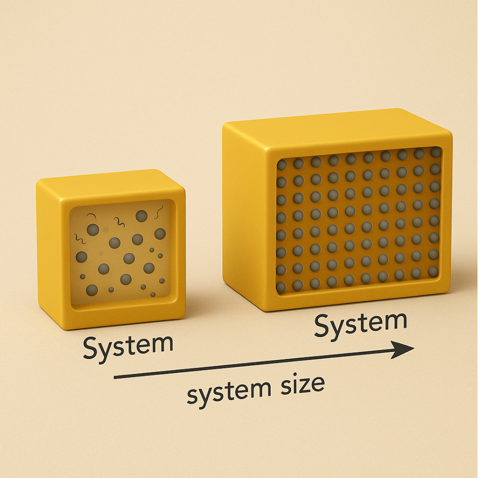
The laws of thermodynamics

- **Equilibrium states**. There exists particular states that, macroscopically, are characterized completely by the internal energy, the volume and the mole numbers of the chemical components.
- **Entropy**. There exists a function of the extensive parameters defined by all equilibrium states and having the following property: The values assumed by these parameters are those that maximize the entropy.
- **Properties of the entropy**. The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and it is a monotonically increasing function of the energy.
- **Absolute zero**. The entropy of any system vanishes at zero temperature.

The thermodynamic limit

When the number of degrees of freedom goes to infinity and fluctuations vanish. In this limit, thermodynamic variables are not stochastic.

What happens when fluctuations come into play?



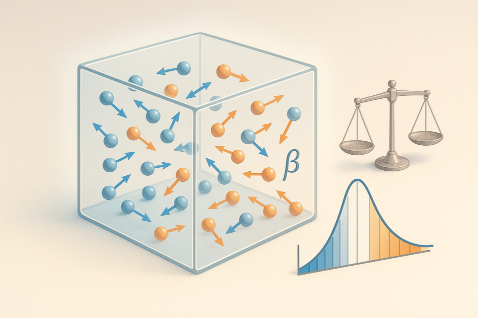
The role of fluctuations

Equilibrium statistical mechanics

At equilibrium, we can employ the rules of statistical mechanics to describe the fluctuating quantities. For instance, the particles in a rarefied and weakly interacting gas follow the Maxwell-Boltzmann velocity distribution

$$f(v) = \frac{4}{\sqrt{\pi}} \alpha_{m,T}^{3/2} v^2 e^{-\alpha_{m,T} v^2}$$

What happens *out-of-equilibrium*?



Assumptions

In the following, we will rely on two fundamental assumptions:

1. The initial state of the system is a thermal state

$$\rho = \frac{1}{Z} e^{-\beta H}$$

   $\beta = 1/T$ is the inverse temperature, Z is the partition function while H is the Hamiltonian. We can also consider other thermal equilibrium states, like the microcanonical of the gran-canonical.

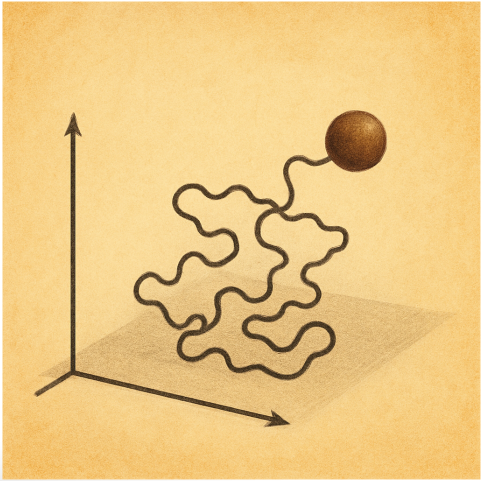
2. The microscopic dynamics is reversible.

Bit of history — Einstein

The linear response of a system in thermal equilibrium, driven out of equilibrium by an external force F, is determined by the fluctuation properties at equilibrium [a]

$$\mu = \beta D = \frac{v_d}{F} D$$

D is the diffusion constant and v_d is the drift velocity.



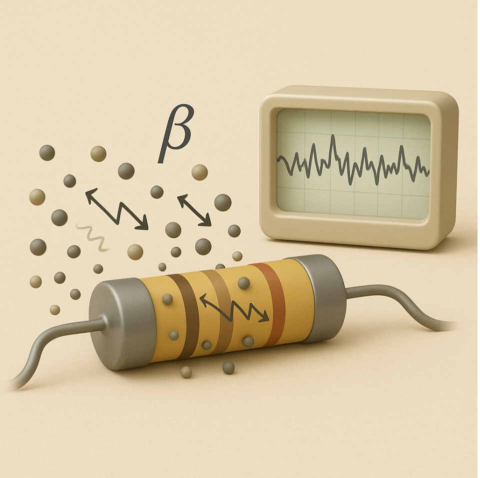
[a] A. Einstein, Ann. Phys. **322**, 549 (1905).

Bit of history — Johnson–Nyquist

Due to the thermal agitation of electrons in a conductor at equilibrium, electrical thermal noise appears. Its mean square fulfils [a]

$$\langle V^2 \rangle = \frac{4R\Delta\nu}{\beta}$$

R is the resistance while $\Delta\nu$ is the bandwidth.



[a] J. Johnson, Phys. Rev. **32**, 97 (1928).
H. Nyquist, Phys. Rev. **32**, 110 (1928).

Linear response theory

Fluctuation-dissipation theorem
Provides a fundamental connection between the response of a physical system to external perturbations and the internal fluctuations that occur in thermal equilibrium.

System described by

$$H(t) = H_0 - h(t)A$$

System is initially in thermal equilibrium

$$\rho_0 = e^{-\beta H_0}/Z$$

What is the linear response of another observable B due to the perturbation?

Linear response theory

In the interaction picture, the time evolution of the density operator $\rho(t)$ is

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}[H_I(t), \rho(t)]$$

We solve this to first order in $h(t)$

$$\rho(t) = \rho_0 + \delta\rho(t), \quad \text{with } \delta\rho(t) = \frac{i}{\hbar}\int_{-\infty}^{t} dt' h(t')[\rho_0, A(t')]$$

Then the expectation value of B becomes

$$\langle B(t)\rangle = \text{Tr}[\rho(t)B(t)] = \langle B(t)\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{t} dt' h(t')\langle[B(t), A(t')]\rangle_0$$

Linear response theory

The **response function** is defined as

$$\chi_{BA}(t-t') = \frac{i}{\hbar}\theta(t-t')\langle[B(t), A(t')]\rangle_0$$

such that the linear response of B to a perturbation through A is characterized by

$$\delta\langle B(t)\rangle = \int_{-\infty}^{\infty} dt'\, \chi_{BA}(t-t')h(t')$$

The equilibrium (symmetrized) correlation function is defined as

$$C_{BA}(t) = \frac{1}{2}\langle\{B(t), A(0)\}\rangle_0 = \frac{1}{2}\left(\langle B(t)A(0)\rangle_0 + \langle A(0)B(t)\rangle_0\right)$$

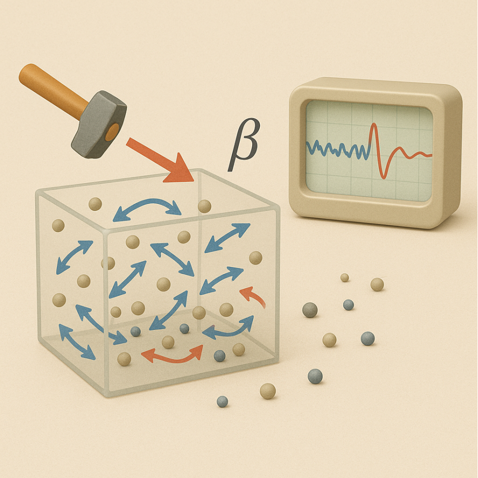
The corresponding power spectral density is then

$$S_{BA}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} C_{BA}(t)$$

Green-Kubo theorem

The Kubo fluctuation-dissipation theorem then relates the imaginary part of the response function to the spectral density as [a]

$$\mathrm{Im}[\chi_{BA}(\omega)] = \frac{1}{2\hbar}\left(1 - e^{-\beta\hbar\omega}\right) S_{BA}(\omega)$$



[a] M. S. Green, J. Chem. Phys. **22**, 398 (1954). R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).

Crooks theorem — Beyond linear response

Setup

- Classical system with phase space coordinates x.
- Evolution during a time interval $t \in [0, \tau]$ is governed by $H(x, \lambda_t)$, with λ_t begin a time-dependent parameter.
- The system is initially prepared in thermal equilibrium at inverse temperature β under the parameter value λ_0

$$p_0(x) = \frac{1}{Z_0} e^{-\beta H(x,\lambda_0)}, \quad Z_0 = \int \mathrm{d}x \, e^{-\beta H(x,\lambda_0)}.$$

- Its dynamics are assumed to be Markovian and microscopically reversible.

Crooks theorem

Two protocols

- The **forward process**: The system evolves forward in time under $\lambda_F(t)$ from λ_0 to λ_τ.
- The **reverse process**: Defined by the time-reversed protocol $\lambda_R(t) = \lambda_F(\tau - t)$, starting from equilibrium at λ_τ.
- A trajectory is denoted by $\Gamma = \{x(t)\}_{0 \leq t \leq \tau}$. The probability of observing Γ in the forward process is denoted as $P_F[\Gamma]$, and $\tilde{\Gamma} = \{\tilde{x}(t) = x(\tau - t)\}$ has probability $P_R[\tilde{\Gamma}]$ in the reverse process.

Crooks theorem

The work $W[\Gamma]$ performed along a single trajectory in the forward protocol is defined as

$$W[\Gamma] = \int_0^\tau dt\, \dot{\lambda}_F(t) \frac{\partial H(x(t), \lambda)}{\partial \lambda}\Big|_{\lambda=\lambda_F(t)}$$

Let $\Delta E = H(x_\tau, \lambda_\tau) - H(x_0, \lambda_0)$ denote the total energy change. Then, the heat transferred to the environment is simply

$$Q[\Gamma] = W[\Gamma] - \Delta E$$

We now assume that the dynamics satisfy a *local detailed balance* condition

$$\frac{P_F[\Gamma]}{P_R[\tilde{\Gamma}]} = \frac{p_0(x_0)}{p_\tau(x_\tau)} e^{-\beta Q[\Gamma]}.$$

Crooks theorem

Using $Q = W - (H(x_\tau, \lambda_\tau) - H(x_0, \lambda_0))$ and the Boltzmann weights

$$\frac{p_0(x_0)}{p_\tau(x_\tau)} = \frac{Z_\tau}{Z_0} e^{-\beta[H(x_0,\lambda_0)-H(x_\tau,\lambda_\tau)]},$$

we obtain

$$\frac{P_F[\Gamma]}{P_R[\tilde{\Gamma}]} = \frac{Z_\tau}{Z_0} e^{-\beta W[\Gamma]} = e^{-\beta(W[\Gamma]-\Delta F)},$$

Where

$$\Delta F = F(\lambda_\tau) - F(\lambda_0) = -\beta^{-1} \ln(Z_\tau / Z_0)$$

is the equilibrium free energy difference.

Crooks theorem

The rules of statistical mechanics tell us that the work probability density in the forward process is given by

$$P_F(W) = \int \mathcal{D}\Gamma\, P_F[\Gamma]\, \delta(W - W[\Gamma])$$

Similarly, in the reverse process

$$P_R(-W) = \int \mathcal{D}\Gamma\, P_R[\tilde{\Gamma}]\, \delta(W + W[\Gamma])$$

This can be rewritten by using the trajectory probability ratio as

$$P_R(-W) = \int \mathcal{D}\Gamma\, P_F[\Gamma]\, e^{-\beta(W[\Gamma]-\Delta F)} \delta(-W + W[\Gamma]) = e^{\beta(W+\Delta F)} P_F(-W).$$

Crooks theorem

Therefore, we obtain

$$\frac{P_F(W)}{P_R(-W)} = e^{\beta(W-\Delta F)} = e^{\sigma}$$

Crooks fluctuation theorem

Rigorously quantifies irreversibility in terms of measurable fluctuations of work. While trajectories violating the second law are possible, they are exponentially suppressed.

Jarzynski relation

Jarzynski equality can be derived from this theorem by means of the normalization of the probability density. Multiplying both sides by $P_R(-W)e^{-\beta W}$ and integrating, we obtain

$$\int \mathrm{d}W\, P_F(W)e^{-\beta W} = e^{-\beta \Delta F} \int \mathrm{d}W\, P_R(-W) = e^{-\beta \Delta F}$$

which gives us Jarzynski equality

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

Using the convexity of the exponential function, we get the second law of thermodynamics

$$\beta(\langle W \rangle - \Delta F) = \langle \sigma \rangle \geq 0$$

Quantum fluctuations

Crooks theorem

Setup

- Quantum system evolving under $H(t) = H(\lambda_t)$ over a time interval $[0, \tau]$.
- he system is initially in equilibrium at inverse temperature β

$$\rho_0 = \frac{1}{Z_0} e^{-\beta H_0}.$$

- Evolution is unitary.
- What is the work done on the system?

Crooks theorem

Two-point measurement scheme

- At $t = 0$ we perform an energy measurement

$$p_n^0 = \frac{e^{-\beta\epsilon_n^0}}{Z_0} \qquad Z_0 = \text{Tr}e^{-\beta H_0}$$

- Evolve the system under $U = \mathcal{T}\exp\left(-\frac{i}{\hbar}\int_0^\tau H(t)\mathrm{d}t\right)$.
- At $t = \tau$, another energy measurement

$$p_{m|n}^\tau = \text{Tr}\left[\Pi_m^\tau U \Pi_n^0 U^\dagger\right],$$

- The joint probability of obtaining ϵ_n^0 and ϵ_m^τ is then given by

$$p_{m,n} = p_n^0 p_{m|n}^\tau.$$

Crooks theorem

The quantum stochastic work

$$W_{m,n} = \epsilon_m^\tau - \epsilon_n^0.$$

Forward and backward protocols

- Forward: The joint work probability is

$$p^F_{m,n} = \text{Tr}\left[\Pi_m^\tau U \Pi_n^0 \rho_0 \Pi_n^0 U^\dagger\right] = \frac{e^{-\beta\epsilon_n^0}}{Z_0} |\langle\epsilon_m^\tau|U|\epsilon_n^0\rangle|^2.$$

- Backwards: $\tilde{\lambda}_t = \lambda(\tau - t) \Rightarrow \tilde{U} = \Theta U^\dagger \Theta^{-1}$ and $\rho_\tau = e^{-\beta H_\tau}/Z_\tau$. This results in

$$p^R_{n,m} = \text{Tr}\left[\Pi_n^0 \tilde{U} \Pi_m^\tau \rho_\tau \Pi_m^\tau \tilde{U}^\dagger\right] = \frac{e^{-\beta\epsilon_m^\tau}}{Z_\tau} |\langle\epsilon_m^\tau|U|\epsilon_n^0\rangle|^2.$$

Crooks theorem

From this we get

$$\frac{p^F_{m,n}}{p^R_{n,m}} = \frac{\frac{e^{-\beta\epsilon^0_n}}{Z_0}|\langle\epsilon^\tau_m|U|\epsilon^0_n\rangle|^2}{\frac{e^{-\beta\epsilon^\tau_m}}{Z_\tau}|\langle\epsilon^\tau_m|U|\epsilon^0_n\rangle|^2} = \frac{Z_\tau}{Z_0}e^{\beta(\epsilon^\tau_m-\epsilon^0_n)} = e^{\beta(W_{m,n}-\Delta F)}.$$

Work distributions

- Forward

$$p^F(W) = \sum_{m,n} p^F_{m,n}\delta(W - W_{m,n})$$

- Backwards

$$p^R(-W) = \sum p^R_{n,m}\delta(-W + W_{m,n}).$$

Crooks theorem

Crooks theorem

$$\frac{p^F(W)}{p^R(-W)} = e^{\beta(W-\Delta F)}$$

Jarzynski equality

$$\left\langle e^{-\beta W} \right\rangle = \int \mathrm{d}W \, p^F(W) e^{-\beta W} = e^{-\beta \Delta F} \int \mathrm{d}W \, p^R(-W) = e^{-\beta \Delta F}$$

That is all, Folks!

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