Quantum Fluctuation Relations far from Equilibrium

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1. Thermodynamics and Linear Response.

2. Fluctuation Relations for Classical Systems

3. Nonequilibrium Fluctuation Relations for Quantum Dynamical Systems.

Joint Work with RAPHAËL CHETRITE (Lab. Jean Dieudonné, NICE).

THERMODYNAMICS

Aim and Scope of Thermodynamics

Thermodynamics describes the properties of matter at the macroscopic scale in terms of a limited number of macroscopic variables. It derives general relations between macroscopic observables, *regardless of the underlying atomic structure.*

Traditional thermodynamics deals only with equilibrium states: time never appears as an explicit variable.

Thermodynamics is the science of ENERGY CONVERSIONS:

- One must IDENTIFY correctly the various forms of energy involved in a problem to establish an exhaustive book-keeping (1st Principle).

- All forms of energy are NOT EQUIVALENT. Some conversions require *compensation fees* (Clausius).
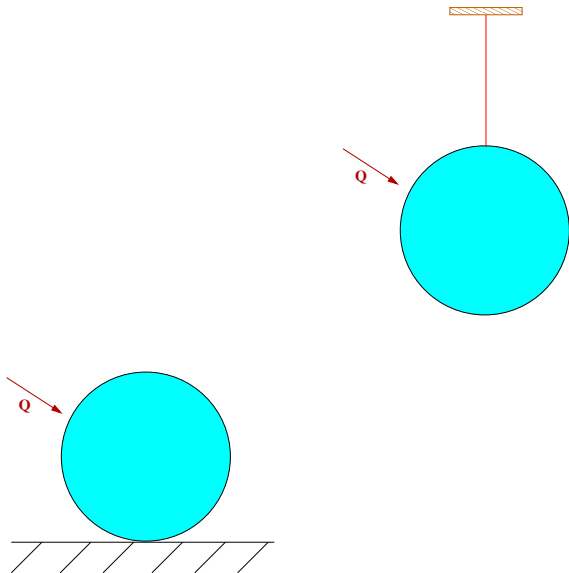
Lars Onsager (1903-1976)

'As in other kinds of bookeeping, the trickiest questions that arise in the application of thermodynamics deal with the proper identification and classification of the entries; the arithmetics is straightforward' (Onsager, 1967).

$$\Delta U = W + Q$$
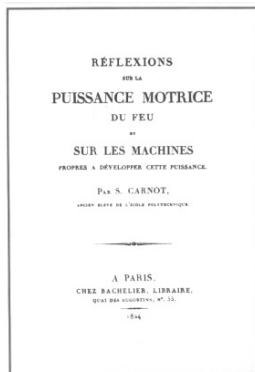
THE ENERGY OF THE UNIVERSE IS CONSERVED.

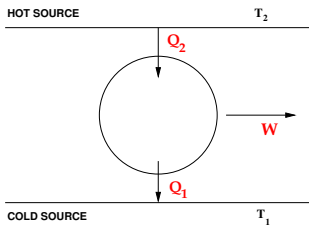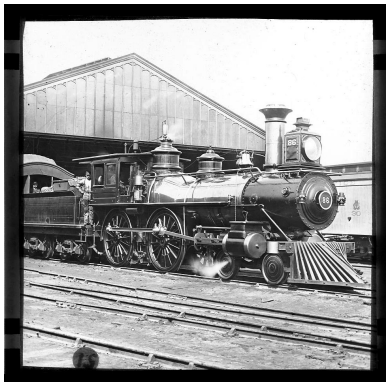# Which sphere is the hottest?

The Heat Engine

Clausius has defined a new concept in physics: THE ENTROPY.

$$S_2 - S_1 \geq \int_{1 \to 2} \frac{\partial Q}{T}$$

Clausius Inequality (1851)

THE ENTROPY OF THE UNIVERSE INCREASES.

The Mistress of the World and Her Shadow

The competition between energy and entropy lies at the heart of many daily-life phenomena (phase transitions).

A state function that embodies simultaneously both principles in many physical situations is **THE FREE ENERGY** F :

$$F = U - TS$$

Free Energy as Maximal available Work

Consider a system that evolves from a state A to a state B both at the temperature T equal to that of the environment. Suppose that the system exchanges heat only with the environment.

Then, the decrease of Free Energy represents the Maximum Available Work at the given temperature T that we can extract from the system:

$$\boxed{\langle \mathcal{W} \rangle \leq F_A - F_B = -\Delta F}$$

$$\mathbf{T} \qquad\qquad\qquad \mathbf{T}$$

$$V_A \qquad\qquad\qquad V_B$$
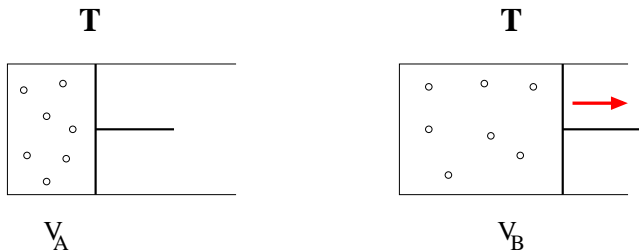
The work $\langle W \rangle$ *we perform* on the system is the *opposite* of the work $\mathcal{W}$ available *from* the system. Thus, we have

$$\boxed{\langle W \rangle \geq F_B - F_A = \Delta F}$$

- First Principle : $\Delta E = W + Q$
- Second Principle : $\int_{A \to B} \frac{\partial Q}{T} \leq S_B - S_A = \Delta S$. Therefore : $Q \leq T\Delta S$.

Thus

$$\Delta F = \Delta E - T\Delta S = W + Q - T\Delta S \leq W$$

Let us define the Dissipated Work as $W_{\mathrm{diss}} = W - \Delta F$. We then have

$$\frac{W_{\mathrm{diss}}}{T} = \Delta S + \left(\frac{-Q}{T}\right) \equiv \Delta S(\mathrm{universe}) \geq 0$$

Interpretation : W_{diss}/T represents the total entropy production by the process: this quantity must be non-negative.

FLUCTUATION RELATIONS

Jarzynski's Work Theorem

From classical thermodynamics, we have thus learnt that the work $\langle W \rangle$ that we perform on the system *must verify*

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There is a remarkable identity *underlying* this classical inequality:

$$\left\langle \mathrm{e}^{-\frac{W}{kT}} \right\rangle = \mathrm{e}^{-\frac{\Delta F}{kT}}$$

Jarzynski's Identity (1996)

The average is taken over an ensemble of non-equilibrium processes of duration T_f such that:

(i) At $t = 0$, the system starts in the equilibrium state A.

(ii) Between 0 and T_f, the operator acts on the system by changing a control parameter $\lambda(t)$ according to a fixed well-defined protocol

(iii) At T_f, the control parameter is fixed to a value λ_B. The system is *not at equilibrium*. During the whole process, the system remains in contact with a heat-bath at temperature T. Only after an infinite time, will the system reach the equilibrium state B.

1. Jarzynski's Work Theorem yields the Classical Inequality for the Maximum Work Available (by convexity).

2. However, this result implies that in order to have an equality, *there must be* individual trajectories that *do not obey* the Classical Inequality, i.e., for which

$$W < \Delta F$$

'Transient Violations of the Second Law'

3. Jarzynski's Identity allows to measure *Equilibrium* Free Energy differences by doing *Non-Equilibrium experiments* (single-molecule manipulations, cf F. Ritort).

4. There is a Fluctuation-type Relation underlying Jarzynski's Identity at the level of Work Probability Distributions:

$$\frac{\mathrm{P^F}(W)}{\mathrm{P^R}(-W)} = \mathrm{e}^{\frac{W - \Delta F}{kT}}$$

(Crooks, 1999)
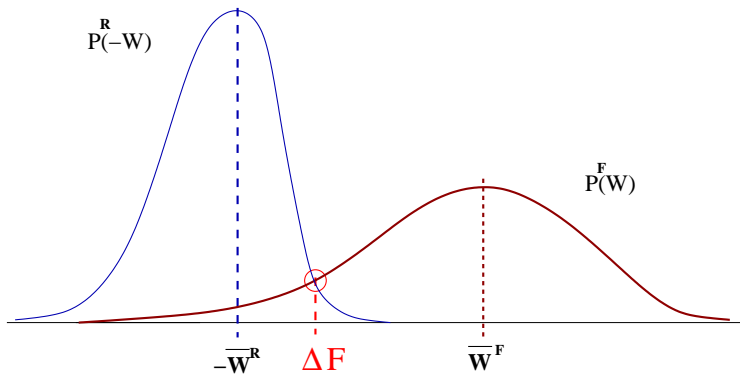
Crooks' Relation allows to quantify precisely the transient violations of the Second Law and to perform more precise measurements.

Framework: Classical Dynamical Systems

There exists a finer identity that implies Jarzynski's and Crooks' relations. Consider a system that evolves according to a given dynamics, that can be Deterministic (Hamiltonian; Coupled to a thermostat: Nosé-Hoover...) or Stochastic (Langevin; Markov...).
Typically, this evolution can be described as a first-order differential equation for the distribution function $\rho(z, t)$ at time t of the system amongst its microstates z:

$$\frac{\partial \rho}{\partial t} = \mathcal{L}.\rho$$

where the generator $\mathcal{L}$ depends on which type of evolution is considered.

- Hamiltonian case: z is a point in phase space and $\mathcal{L}$ is the Poisson Bracket $\mathcal{L}.\rho = -\{H, \rho\}$.

- Langevin equation: $\mathcal{L}$ is the Fokker-Planck operator (parabolic PDE: Brownian Motion $\rightarrow$ Heat Equation).

- Markov chain: $\mathcal{L}$ is a stochastic matrix and z is a configuration of the system.

Suppose that the dynamics of the system depends on a set of parameters λ that can be monitored by an external operator: i.e., the generator $\mathcal{L}_\lambda$ depends on λ. For a given and fixed value of λ, we assume that the Gibbs-Boltzmann distribution is stationary under the evolution, i.e.

$$\mathcal{L}_\lambda \cdot \frac{e^{-\beta H_\lambda(z)}}{Z_\lambda} = 0$$

Prepare the system at $t = 0$ in the Gibbs-Boltzmann state with H_0 and vary the external parameters λ according to a well-defined protocol $\lambda(t)$. *Note that the time-dependent Gibbs-Boltzmann distribution DOES NOT satisfy the fundamental evolution equation.*
However, we have

$$\langle \delta(z - z(t)) e^{-\beta W(t)} \rangle_{\mathrm{path}} = \frac{1}{Z_0} e^{-\beta H_{\lambda(t)}(z)}$$

where the 'Jarzynski Work' is defined as:

$$W(t) = \int_0^t \dot{\lambda}(\tau) \frac{\partial H_{\lambda(\tau)}(z(\tau))}{\partial \lambda} d\tau \,.$$

Consequences

- Work Relation by summing over z: $\langle e^{-\beta W(t)} \rangle_{\text{path}} = \frac{Z_{\lambda(t)}}{Z_0} = e^{-\beta \Delta F}$.

- For any observable $A(z)$:
  $$\langle A(z(t)) e^{-\beta W(t)} \rangle_{\text{path}} = e^{-\beta \Delta F} \langle A(z) \rangle_{\text{Equil. at } \lambda(t)}$$

- A Generalized Crook's identity that implies all the previous relations:
  Let $\mathcal{F}(z, \lambda)$ be an observable that depends on the whole path, then

  $$\langle F[c, \lambda] e^{-\beta W(t)} \rangle_{\text{path}} = \langle \tilde{F}[c, \lambda] \rangle_{\text{path}}^{R}$$

  where the tilde and the exponent R denote an average with respect to time-reversed paths. Here, a covariance property under time reversal (Generalized Detailed Balance) must be used.

- Kubo's fluctuation-dissipation relation: Apply the Jarzysnki identity to a family of Hamiltonians $H_0 - \lambda(t)O$ and take the functional derivative w.r.t. $\lambda(t)$ at $t = s$.

A Sketch of the Proof

Consider the joint probability distribution $P_t(z, W)$ for the system to be in the microstate z and to have 'accumulated' the work W at time t:

$$P_t(z, W) = \langle \delta(z - z(t))\delta(W - W(t)) \rangle_{\text{path}}$$

The marginal of $P_t(z, W)$ is $\rho(z, t)$ that satisfies the fundamental evolution equation with generator $\mathcal{L}$.
The Laplace transform of $P_t(z, W)$, $\hat{P}_t(z, \gamma) = \int dW P_t(z, W)e^{-\gamma\beta W}$, satisfies a dynamics similar to that of $\rho(z, t)$ but with a *γ-deformed generator $\mathcal{L}^\gamma$* :

$$\boxed{\frac{\partial \hat{P}_t}{\partial t} = \mathcal{L}^\gamma . \hat{P}_t}$$

The deformed generator is given by

$$\boxed{\mathcal{L}^\gamma = \mathcal{L} - \gamma\beta\dot{\lambda}\frac{\partial H_\lambda(z)}{\partial \lambda}}$$

Hence, weighing the correlators with $e^{-\gamma\beta W}$ leads to a γ-deformed dynamics.

The work identities result from algebraic properties of the operators $\mathcal{L}^\gamma$.
(1) The time-dependent Gibbs-Boltzmann distribution $e^{-\beta H_\lambda(z)}$ IS A
SOLUTION of the deformed evolution equation with $\gamma = 1$ for all times:

$$\frac{\partial e^{-\beta H_\lambda(z)}}{\partial t} = \mathcal{L}^\gamma . e^{-\beta H_\lambda(z)}$$

This is equivalent to

$$\hat{P}_t(z, \gamma = 1) = e^{-\beta H_\lambda(z)}$$

which is nothing but the generalized Jarzynski Relation.
(2) Using detailed balance, one can prove a similarity relation of the type:

$$(\mathcal{L}^\gamma)^\dagger \quad \simeq \quad \mathcal{L}^{1-\gamma}$$

This implies Crooks identity between the direct process and the
time-reversed dynamics.

The Kubo Formula

Consider a (classical) system at thermal equilibrium and governed by the time-independent Hamiltonian H_0. Suppose that this system is subject to a time-dependent perturbation $H_0 - \lambda(t)O$ from time s on.

Then the mean-value of a dynamic observable $A(t)$ at time $t > s$ over all path trajectories, $\langle A(t)\rangle_{\mathrm{path}}$, satisfies at first order in λ:

$$R_{eq}(t,s) = \frac{\delta\langle A(t)\rangle_{\mathrm{path}}}{\delta\lambda(s)} = \beta\frac{d}{ds}\langle O(s)A(t)\rangle_{eq}$$

where $\beta = 1/(kT)$ is the inverse temperature.
Note that the correlation function in the rhs is evaluated at equilibrium.

This relation (Kubo, 1966) is a fundamental tool in condensed matter physics: it allows, e.g., to extract linear response transport coefficients from an equilibrium situation.

THE QUANTUM CASE

CAVEATS

Major difficulties to define the quantities involved in the work identities:

- NO PATHS, NO TRAJECTORIES!
- NO WORK!

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Various attempts:
- Closed Quantum system: Define the work as the difference of the energies measured at time 0 and at the final time. Jarzynski's Identity follows from the unitarity of the evolution (Tasaki 2000; Kurchan 2001; Andrieux, Gaspard 2009).

- Open Quantum System: Embed it into a larger closed system, write Jarzynski's Identity for the global system and integrate out the environmental degrees of freedom (Campisi, Hanggi, Talkner 2009)

- Try to define a Quantum Work operator: Jarzynski's Identity fails.

- By multiple successive measurements, define an Effective Trajectory for the quantum system (S. Mukamel 2003-2008).

Density Matrix

A Quantum Statistical System is described via an operator, the Density Matrix ρ_t. A closed system prepared at temperature T has a canonical Density Matrix given by

$$\pi_0 = \frac{1}{Z} \sum_n e^{-\beta E_n} |\psi_n\rangle \langle \psi_n|$$

assuming that the Hamiltonian H_0 has a discrete set of eigenvalues E_n with normalized eigenvectors $|\psi_n\rangle$.

The Density Matrix of a closed system satisfies the Quantum Liouville equation:

$$\boxed{\frac{\partial \rho_t}{\partial t} = -\frac{i}{\hbar}[H_0, \rho_t] = \mathcal{L}.\rho_t}$$

The generator of the dynamics $\mathcal{L}$ is now a Super-Operator because it induces a mapping amongst density operators.

Lindblad Evolution

We consider a 'small' open system interacting with a large environment: there exists a Quantum Markov Equation, widely used in Quantum Optics, satisfied by the density matrix of the small system, the Lindblad Equation:

$$\frac{\partial \rho_t}{\partial t} = -\frac{i}{\hbar}[H_0, \rho_t] + \sum_{i=1}^{I} \left(A_i \rho_t A_i^\dagger - \frac{1}{2} A_i^\dagger A_i \rho_t - \frac{1}{2} \rho_t A_i^\dagger A_i \right)$$

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- The density matrix of a system driven by a Schrödinger-Langevin equation satisfies a Lindblad equation. Such an equation appears if you model a two-level system (spin $1/2$) in interaction with an infinite chain of harmonic oscillators.

- Abstract derivation: Under some general assumptions (Linearity, Trace Conservation, Strict Positivity + Markov) it is possible to prove that the Lindblad Equation is generic.

Strategy for deriving the Quantum Fluctuation Relation

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1. We do not define work or trajectories. We write the simplest deformation of the Lindblad Equation such that the time-dependent Gibbs-Boltzmann density matrix becomes an exact solution of the deformed evolution equation.

2. We add a parameter γ in order to define a one-parameter family of deformed Lindbladian superoperators $\mathcal{L}^\gamma$ that interpolate between the original Lindbladian and the fully deformed operator:

$$L_t(\gamma).\rho = (L_t - \gamma W_t).\rho$$

where the operator W_t, defined as

$$W_t = -(\pi_t)^{-1}\partial_t \pi_t,$$

will play in the quantum context a role analogous to Jarzynski's work.

3. We prove a key similarity relation between $(\mathcal{L}^\gamma)^\dagger$ and $\mathcal{L}^{1-\gamma}$. More precisely, we define a *conjugate Lindbladian* as

$$L^R_{T_f-t} = K\pi_t^{-1}L_t^\dagger \pi_t K$$

where K is the time-reversal operator. Then, the evolution (super)-operators associated with L_t and L_t^R satisfy

$$\pi_0 P_0^{T_f}(\gamma) = \left[\pi_{T_f} K P_0^{T_f,R}(1-\gamma)K\right]^\dagger$$

where $P_s^t(\gamma) = \overrightarrow{\exp}\left(\int_s^t du\, L_u(\gamma)\right)$ and $P_s^{t,R}(\gamma) = \overrightarrow{\exp}\left(\int_s^t du\, L_u^R(\gamma)\right)$.

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4. Applying this fundamental identity to two arbitrary observables A and B leads to

$$Tr\left(B^\dagger\pi_0 P_0^{T_f}(\gamma).A\right) = Tr\left((K.A^\dagger)\,\pi_0^R P_0^{T_f,R}(1-\gamma).(K.B)\right)$$

Writing this relation explicitly yields the Quantum Fluctuation Identity.

The Quantum Fluctuation Relation

Consider a quantum dynamical system $\mathcal{S}$, initially isolated, and prepared at time $t = 0$ in thermal equilibrium with a canonical density matrix π_0, which corresponds to a Hamiltonian H_0.

For $0 \leq t \leq T_f$, the Hamiltonian H_t that governs $\mathcal{S}$ becomes time dependent due to the change of some external control parameter(s). Besides, the system interacts with its environment.

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Let A and B be two arbitrary observables and $0 \leq \gamma \leq 1$. Then, the following Quantum Fluctuation Relation is satisfied:

$$\left\langle \left(\pi_0 B \pi_0^{-1} \right)^\dagger (0) \overrightarrow{\exp} \left(-\gamma \int_0^{T_f} du \, W_u \right) A(T_f) \right\rangle =$$

$$\left\langle \left(\pi_0^R \left(K.A \right) \left(\pi_0^R \right)^{-1} \right)^\dagger (0) \overrightarrow{\exp} \left(-(1-\gamma) \int_0^{T_f} du \, W_u^R \right) \left(K.B \right) (T_f) \right\rangle^R$$

Consequences

- Taking $A = B = 1$ and $\gamma = 1$, leads to the Quantum analog of J. E.

$$\left\langle \overrightarrow{\exp} \left(- \int_0^{T_f} du \, W_u \right) \right\rangle = 1$$

- For a closed system, the previous results of Kurchan et al. are recovered.
- For $\hbar = 0$, the classical identities are retrieved.
- By taking a first order derivative of the Quantum Fluctuation Identity, the Quantum Fluctuation-Dissipation Relation is obtained (This quantum analog of Kubo's relation is known as the Callen-Welton relation).

Conclusion

We have used a general mathematical framework to derive quantum analogs to the classical work relations. These relations stem from algebraic identities satisfied by the evolution operators. This provides us with an unified view on the work relations, whether applied to classical or quantum systems, to deterministic or stochastic models.

From technical point of view, the proof of the quantum work theorem requires an extension of the Feynman-Kac formula for Quantum Markov semi-groups.

The quantum fluctuation relations imply the Fluctuation-Dissipation Relation of Callen and Welton. They also imply higher order identities. They can in fact be viewed as *book-keeping devices or generating functions* for correlation identities at all-orders.

Beyond the present formal study:
(i) Consequences for simple solvable models?
(ii) Applications to experimental situations?