Introduction to Nonequilibrium Processes

Annecy, April 20-24, 2015

Outline of the lectures

1. Review of statistical physics: Equilibrium versus Non-equilibrium. Dynamics, Detailed Balance and Time-reversal.

2. Out of Equilibrium: Large Deviations, Generalized Detailed Balance and the Gallavotti-Cohen theorem.

3. Work Identities: the Jarzynski and Crooks identities.

4. The Asymmetric Exclusion Process: Exact Results

5. A unifying framework: the Macroscopic Fluctuation Theory.

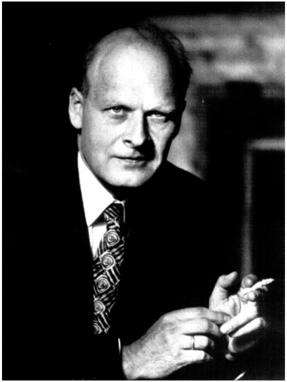
THERMODYNAMICS

THERMODYNAMICS is the science of ENERGY CONVERSIONS:

- IDENTIFY correctly the various forms of energy involved in a process and WRITE a balance (First Principle).
- Different type of energies are NOT necessarily EQUIVALENT. Converting energy from one form to another involves a *compensation fee* called the ENTROPY (Second Principle, Clausius).

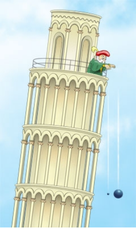
Classical thermodynamics deals only with equilibrium states that do not change with time: time plays no role as a thermodynamic variable.

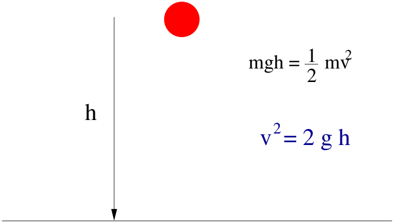
Lars Onsager (1903-1976)



‘As in other kinds of book-keeping, 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).

Kinetic and Potential energies





$$mgh = \frac{1}{2} mv^2$$

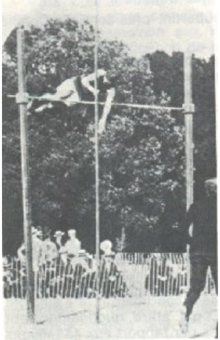
$$v^2 = 2\ g\ h$$

$h = 20\text{m}$ $v = 20\ \text{m/s} = 72\ \text{km/h}$

The work that can be extracted from an object in free fall is equal to the decrease in potential energy:

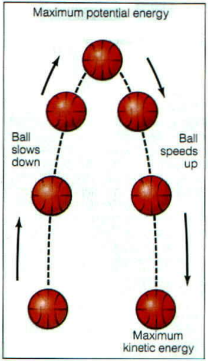
$$\boxed{\mathcal{W} = E_{\text{initial}} - E_{\text{final}} = -\Delta E = mgh}$$

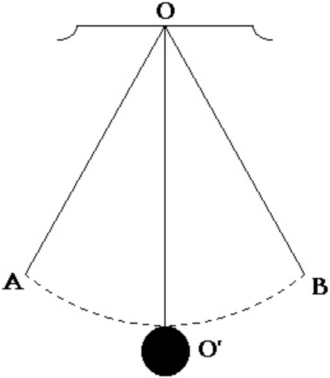
What maximal height can be reached by a vault-jumper?



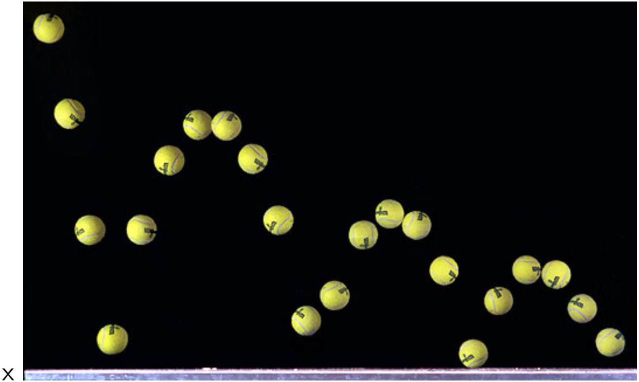
Conversion of Mechanical Energy

Figure 16–12 *As a basketball player throws the ball in the air, various energy conversions take place. What are these conversions?*





Where is the energy?

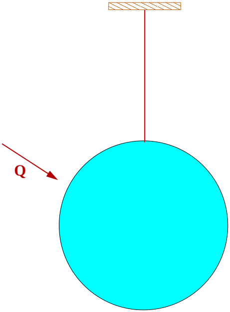


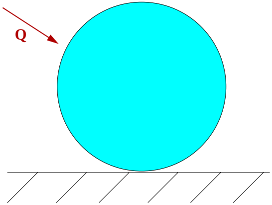
FIRST PRINCIPE

$$\boxed{\Delta U = W + Q}$$

THE ENERGY OF THE UNIVERSE IS CONSTANT.

Which Sphere is hotter?





Reversibility

Non-dissipative mechanical processes are time reversible: A movie of the oscillations of a pendulum can be projected forward and backward in time.

The periodic motion of a metronome allows us to decompose time into regular intervals but the arrow of time is lost!

IRREVERSIBILITY

Whenever dissipation and heat exchanges are involved, time reversibility seems to be lost
SOME EVENTS ARE ALLOWED BY NATURE BUT NOT THE OTHERS!

A criterion for separating allowed processes from impossible one is required.

IMPOSSIBLE PROCESSES

No process is possible whose *sole* result is the transfer of heat from a cooler body to a hotter body (Clausius).

No process is possible whose *sole* result is the absorption of heat from a reservoir and the conversion of this heat into work (Kelvin-Planck).

SADI CARNOT (1796-1832)

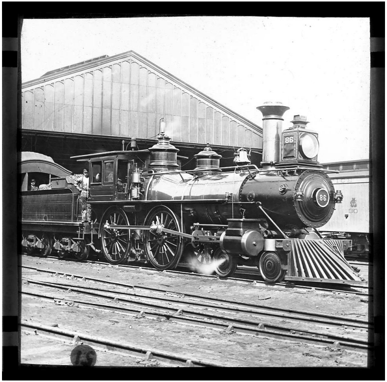
RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.

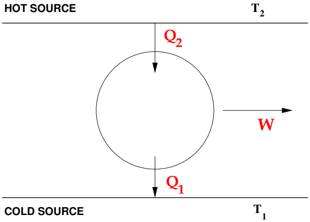
PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, Nº. 55.

1824

THE STEAM-ENGINE





HOT SOURCE T_2

Q_2

W

Q_1

COLD SOURCE T_1

$$\boxed{\eta_{max} = 1 - \frac{T_1}{T_2}}$$

SECOND PRINCIPLE

A NEW physical concept (Clausius): ENTROPY.

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

Clausius Inequality (1851)

THE ENTROPY OF THE UNIVERSE INCREASES.

The Mistress of the World and Her Shadow

- A system wants to **minimize its energy**.
- A system wants to **maximize its entropy**.

This competition between energy and entropy is at the heart of most of everyday physical phenomena (such as phase transitions: ice → water).

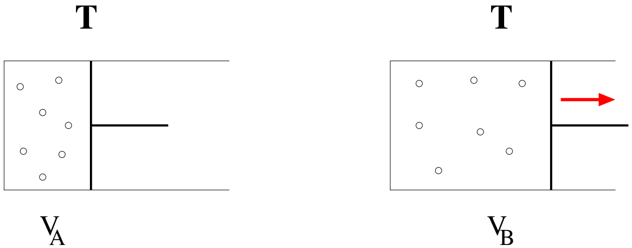
The two principles of thermodynamics can be embodied simultaneously by the **FREE ENERGY** F **:**

$$\boxed{F = U - TS}$$

The decrease of free energy represents the maximal work that one can extract from a system.

Free energy: A physical example

Consider a gas enclosed in a chamber with a moving piston. We suppose that the gas evolves from state A to B and that it can exchange heat only with it environment at fixed temperature T.



Because of irreversibility, the Work, $\mathcal{W}_{useful}$, that one can extract from this system is at most equal to to the decrease of free energy:

$$\boxed{\mathcal{W}_{useful} \leq F_{\text{initial}} - F_{\text{final}} = -\Delta F}$$

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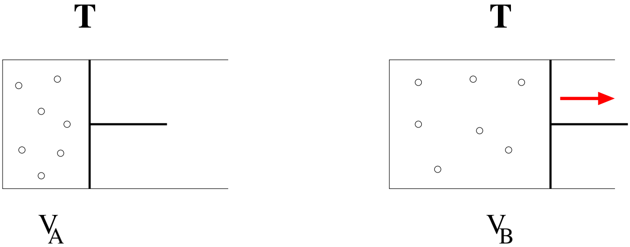

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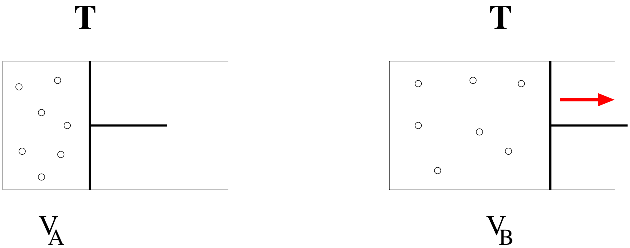

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RECALL GALILEO: $\mathcal{W}_{useful} = E_{\mathrm{initial}} - E_{\mathrm{final}} = -\Delta E$

Proof of the Maximal Work Theorem

- First Principle : $\Delta E = W + Q$
  (Recall that $\mathcal{W}_{useful}$ is equal to $-W$)
- Second Principle : $\int_{A\to B} \frac{\partial Q}{T} \leq S_B - S_A = \Delta S$.
  Thus: $Q \leq T\Delta S$.

Therefore

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

Let $W_{\rm diss} = W - \Delta F$, be the dissipated work. We have

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

Interpretation:

$W_{\rm diss}/T$ represents the total entropy production by the process: this entropy production must be positive (or zero).

EQUILIBRIUM STATISTICAL MECHANICS

MOLECULAR THEORY OF HEAT

L. Boltzmann

J. C. Maxwell

THE BOLTZMANN FORMULA

$$\boxed{S = k \log \Omega}$$

$$k = \frac{R}{\mathcal{N}}$$

The canonical Law

The statistical mechanics of a system at thermal equilibrium is encoded in the Boltzmann-Gibbs canonical law:

$$P_{\mathrm{eq}}(\mathcal{C}) = \frac{\mathrm{e}^{-E(\mathcal{C})/kT}}{Z}$$

the Partition Function Z being related to the Thermodynamic Free Energy F:

$$F = -kTLog\, Z$$

This provides us with a well-defined prescription to analyze systems *at equilibrium*:
(i) Observables are mean values w.r.t. the canonical measure.
(ii) Statistical Mechanics predicts fluctuations (typically Gaussian) that are out of reach of Classical Thermodynamics.

Thermal Equilibrium: a dynamical state

Equilibrium is a dynamical concept. At the molecular scale things constantly change and a system keeps on evolving through various microscopic configurations:

Thermodynamic observables are nothing but average values of fluctuating, probabilistic, microscopic quantities.


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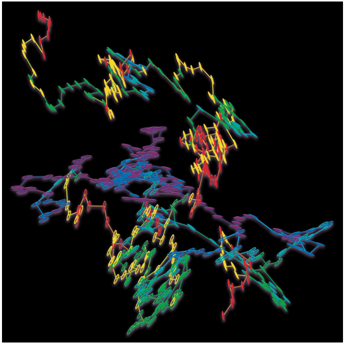
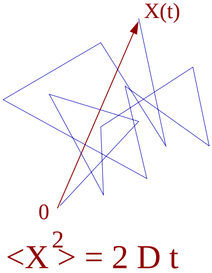


Robert Brown (1773-1858)

Physics of Brownian Motion

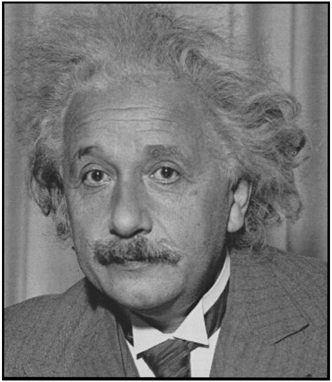
The Brownian Particle is restlessly shaken by water molecules. Its dynamics resembles that of a drunken-walker.

Suppose that the piece of pollen has a speed v. Then it experiences a friction force $-\gamma v$ with $\gamma = 6\pi\eta a$, η being the viscosity of water (Stokes).



The Brownian Particle diffuses around its initial position according to a Gaussian Law: $\langle X^2(t) \rangle = 2Dt$

The Einstein Formula



$$\boxed{D = \frac{RT}{6\pi\eta a\mathcal{N}}}$$

R: Perfect Gas Constant

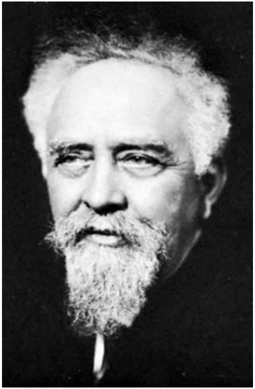
T: Temperature

η : viscosity of water

a: diameter of the pollen

$\mathcal{N}$: Avogadro Number

‘I weighted the Hydrogen Atom’



Jean Perrin (1870-1942)

$\eta \sim 10^{-3} \quad a \sim 10^{-7} \quad R \sim 8.3$

$D \simeq 1\,\mu m^2/s$

Mass of the Hydrogen Atom:

$$1.6\,10^{-24}\mathrm{g}$$

Fluctuation-Dissipation Relation

Suppose that the Brownian Particle is subject to a small force f_{ext}. Balancing with the viscous force $-(6\pi\eta a)v$, we obtain the limiting speed

$$v_\infty = \sigma f_{\mathrm{ext}} \quad \text{with } \sigma = \frac{1}{6\pi\eta a}$$

The response coefficient σ is called a susceptibility.

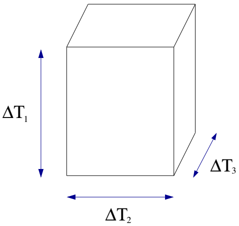
The Einstein Relation can be rewritten as;

$$\sigma = \frac{D}{kT}$$

Susceptibility (Linear Response) ≡ Fluctuations at Equilibrium

(Kubo Formula)

Onsager's Reciprocity Relations (1931)



$$J_i = -\sum_{k=1}^{3} L_{ik} \frac{\partial T}{\partial x_k}$$

(Fourier Law)

The Conductivity Tensor **L** remains symmetric even though the crystal does not display any special symmetry

$$\boxed{L_{ik} = L_{ki}}$$

Crucial for Thermoelectric Effects.

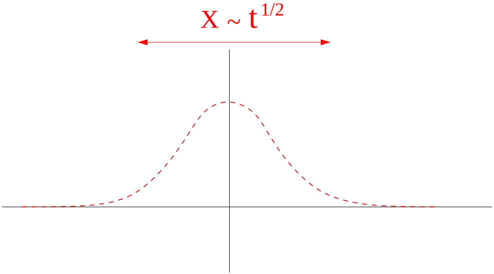
Linear Response Theory

The fact that the dynamics converges towards **thermodynamic equilibrium** and **time-reversal invariance** (detailed-balance) are the key-properties behind Einstein and Onsager's Relations.

Thermodynamic equilibrium is characterized by the fact that the average values of all the **fluxes exchanged** between the system and its environment (matter, charge, energy, spin...) **identically vanish**.

Brownian Fluctuations show that Equilibrium is a dynamical concept.

UNIVERSALITY



La courbe de Gauss

Universality of Statistical Properties explains the existence of emergent phenomena that describe collective behaviour at macroscopic scale.

UNIVERSAL MODELS

Many collective phenomena do not depend upon details at the microscopic scale (phase transitions, hydrodynamic equations...).

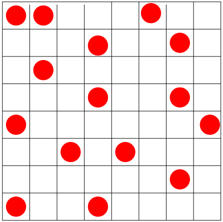
A *sound* model, even if it is over-simplified at the microscopic scale can provide us with the *correct physics* at macroscopic scales. A sound model has to be

(i) *Rich enough* to capture the physics.

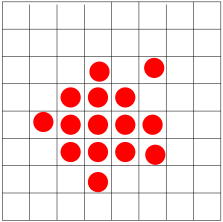
(ii) *Simple enough* to be analyzable or computable.

'Make everything as simple as possible, but not simpler' (Einstein).

The Ising Model of Phase Transitions



Haute Temperature

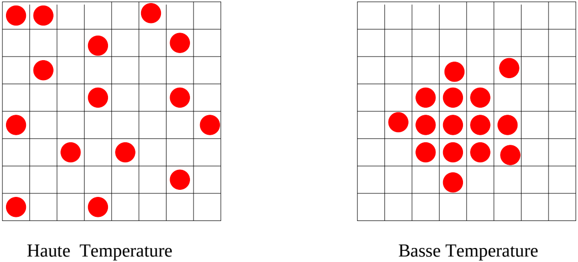


Basse Temperature

SCORE of a configuration = number of particles without neighbour

$$\boxed{\text{Likelihood of a configuration} = \left(\frac{1}{2}\right)^{\beta * \text{SCORE}}}$$

The Ising Model of Phase Transitions



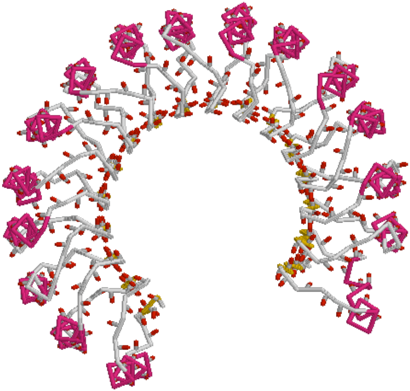
SCORE of a configuration = number of particles without neighbour

$$\boxed{\text{Likelihood of a configuration} = \left(\frac{1}{2}\right)^{\beta * \text{SCORE}}}$$

- At High Temperature, $\beta \to 0$, all configurations equiprobable: gas.
- At Low Temperature, $\beta \to \infty$ clustering occurs: condensed phase.

A phase transition occurs at a Critical Temperature β_c.

Model of a Protein



Pierre-Gilles de Gennes (1932-2007)

DYNAMICS

Probabilistic Approach to Microscopic Dynamics

A convenient manner to model the dynamics of a complex system:

- Enumerate the Micro-states $\{\mathcal{C}_1, \mathcal{C}_2 \ldots\}$
- Transition Rates from $\mathcal{C}$ to $\mathcal{C}'$ between t and $t + dt$ do not depend on the previous history of the system (short time correlations are neglected: Markovian hypothesis).

$$\boxed{\mathcal{C} \to \mathcal{C}' \quad \textit{with probability} \;\; M(\mathcal{C}', \mathcal{C})dt}$$

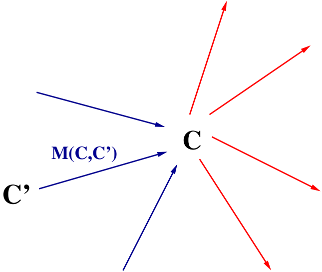
Evolution of $P_t(\mathcal{C})$, probability of being in the micro-state $\mathcal{C}$ at time t:

$$\boxed{\frac{d}{dt} P_t(\mathcal{C}) = \sum_{\mathcal{C}' \neq \mathcal{C}} M(\mathcal{C}, \mathcal{C}') P_t(\mathcal{C}') - \left\{ \sum_{\mathcal{C}' \neq \mathcal{C}} M(\mathcal{C}', \mathcal{C}) \right\} P_t(\mathcal{C})}$$

MASTER EQUATION

The Markov Operator M

The Master equation can be interpreted as a balance equation in a *network* between the configurations:



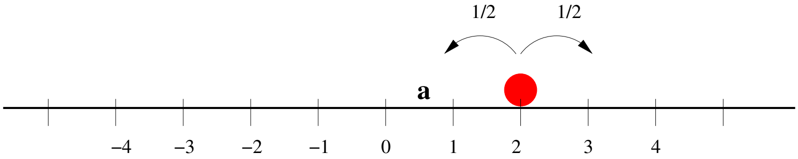
The Master Equation can be written in a matrix form:

$$\boxed{\frac{d\mathbf{P_t}}{dt} = \mathbf{M}.\mathbf{P_t}}$$

where the diagonal term is defined as: $M(\mathcal{C},\mathcal{C}) = -\sum_{\mathcal{C}'\neq\mathcal{C}} M(\mathcal{C}',\mathcal{C})$

Simple Examples

Discrete Random Walk:

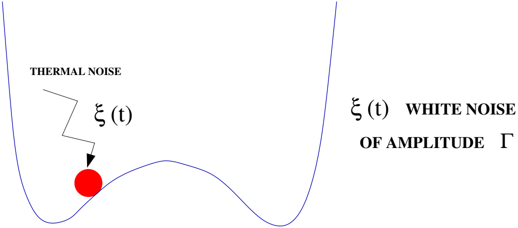


$$\frac{d\,P(n)}{dt} = 1/2[P(n+1) + P(n-1) - 2\,P(n)]$$

$$M = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & & & \\ 0 & 1 & -2 & 1 & 0 & & \\ 0 & 0 & 1 & -2 & 1 & 0 & \\ & 0 & 0 & 1 & -2 & 1 & \ddots \\ & & \ddots & \ddots & \ddots & \ddots & \ddots \end{pmatrix}$$

Stochastic Dynamics

A particle subject to a random force



$$\boxed{m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} - \nabla\mathcal{U}(x) + \xi(t)}$$

Stochastic Dynamics

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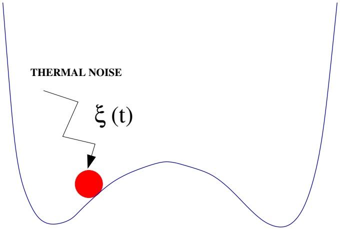

ξ (t) **WHITE NOISE OF AMPLITUDE** Γ

$$\boxed{m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} - \nabla\mathcal{U}(x) + \xi(t)}$$

$P_t(x,v)$, the probability of being at x with velocity v, satisfies the Fokker-Planck Equation

$$\boxed{\frac{dP_t}{dt} = -\frac{\partial}{\partial x}\left\{vP_t\right\} + \frac{\partial}{\partial v}\left\{\frac{\gamma v+\nabla U}{m}P_t\right\} + \frac{\Gamma}{m^2}\frac{\partial^2 P_t}{\partial v^2} = \mathcal{L}_{FP}.P_t}$$

Connecting to Thermodynamics

1. Discrete Markov Equation:

Impose that the stationary state is given by the Boltzmann-Gibbs canonical law:

$$P_{\mathrm{eq}}(\mathcal{C}) = \frac{\mathrm{e}^{-E(\mathcal{C})/kT}}{Z}$$

This condition implies that

$$\boxed{\sum_{\mathcal{C}' \neq \mathcal{C}} M(\mathcal{C}, \mathcal{C}')\mathrm{e}^{-E(\mathcal{C}')/kT} = \mathrm{e}^{-E(\mathcal{C})/kT} \left\{\sum_{\mathcal{C}' \neq \mathcal{C}} M(\mathcal{C}', \mathcal{C})\right\}}$$

This is a set of *global constraints* on the rates: Global Balance.

Connecting to Thermodynamics II

2. Stochastic Differential Equation:

One imposes that the canonical Boltzmann-Gibbs Law is the stationary solution of the Fokker-Planck equation:

$$P_{\mathrm{eq}}(x, v) = \frac{1}{Z}\mathrm{e}^{-\frac{1/2mv^2+\mathcal{U}(x)}{kT}}$$

This *fixes* the noise-amplitude Γ as a function of temperature

$$\boxed{\Gamma = \gamma kT}$$

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Special case: Free Brownian Motion ($\mathcal{U} = 0$):

$$m \frac{dv}{dt} = -\gamma v + \xi(t) \rightarrow \quad \frac{dP_t}{dt} = \frac{\gamma}{m} \frac{\partial}{\partial v}(v P_t) + \frac{\gamma k T}{m^2} \frac{\partial^2 P_t}{\partial v^2}$$

$$\boxed{\langle x^2 \rangle = 2Dt \qquad \text{with} \qquad D = \frac{kT}{\gamma} \quad \text{where} \quad \gamma = 6\pi\eta a}$$

PAUL LANGEVIN (1872-1946)

Time-reversal Invariance and Detailed Balance

The master equation can be written in the following manner:

$$\frac{d}{dt} P_t(\mathcal{C}) = \sum_{\mathcal{C}'} \{ M(\mathcal{C},\mathcal{C}')\, P_t(\mathcal{C}') - M(\mathcal{C}',\mathcal{C})\, P_t(\mathcal{C}) \} = \sum_{\mathcal{C}'} J_t(\mathcal{C},\mathcal{C}')$$

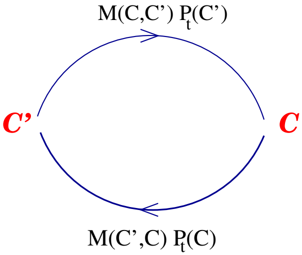
At equilibrium, the microscopic dynamics of the system is time-reversible. This symmetry property implies that all *local* currents vanish (Onsager)

$$\boxed{M(\mathcal{C},\mathcal{C}')P_{\rm eq}(\mathcal{C}') = M(\mathcal{C}',\mathcal{C})P_{\rm eq}(\mathcal{C})}$$

DETAILED BALANCE

Detailed Balance and Vanishing Currents

Detailed balance is a **strong property** that goes beyond the laws of classical thermodynamics.



The net local current $J_t(\mathcal{C}, \mathcal{C}')$ from $\mathcal{C}$ to $\mathcal{C}'$ vanishes at thermodynamic equilibrium.

Detailed Balance as Hermiticity

Rewrite detailed balance as

$$P_{\rm eq}(\mathcal{C})^{-1/2}M(\mathcal{C},\mathcal{C}')P_{\rm eq}(\mathcal{C}')^{1/2} = P_{\rm eq}(\mathcal{C}')^{-1/2}M(\mathcal{C}',\mathcal{C})P_{\rm eq}(\mathcal{C})^{1/2}$$

Using the diagonal matrix

$$Q = \begin{pmatrix} \ddots & & \\ & P_{\rm eq}(\mathcal{C})^{1/2} & \\ & & \ddots \end{pmatrix},$$

we observe that detailed balance implies that the operator $\mathcal{W} = Q^{-1}MQ$ is symmetric:

$$\boxed{\mathcal{W} = \mathcal{W}^\dagger}$$

When detailed balance is satisfied, the spectrum of the Markov matrix is real: the system relaxes to its stationary state without oscillating.

Physical Interpretation of Detailed Balance

We are now going to prove the relation between Detailed Balance and Time-Reversal.

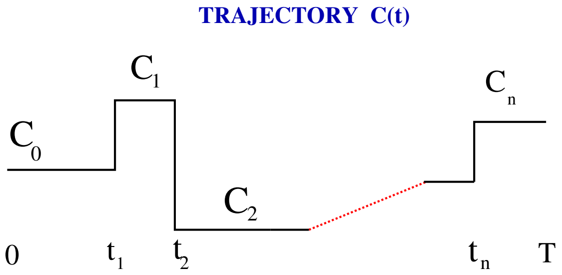
The main idea is to construct a measure on time-trajectories of the system.

- Probability of remaining in $\mathcal{C}$ during a time interval τ:

$$\lim_{dt \to 0} (1 + M(\mathcal{C}, \mathcal{C}) dt)^{\frac{\tau}{dt}} = \mathrm{e}^{M(\mathcal{C},\mathcal{C})\tau}$$

- Probability of going from $\mathcal{C}$ to $\mathcal{C}'$ during dt: $M(\mathcal{C}', \mathcal{C}) dt$

Weight of a Trajectory

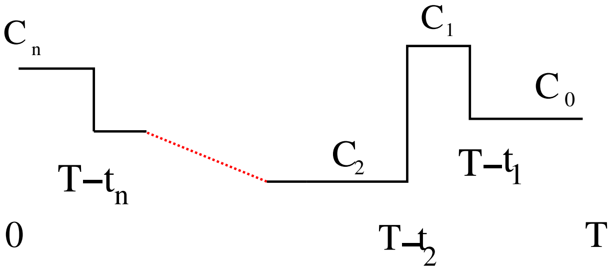


Probability $\mathrm{Pr}\{\mathcal{C}(t)\}$ of observing a trajectory $\mathcal{C}(t)$:

$$\mathrm{Pr}\{\mathcal{C}(t)\} = \mathrm{e}^{M(\mathcal{C}_n,\mathcal{C}_n)(T-t_n)}\, M(\mathcal{C}_n,\mathcal{C}_{n-1})dt_n\, \mathrm{e}^{M(\mathcal{C}_{n-1},\mathcal{C}_{n-1})(t_n-t_{n-1})} \dots$$
$$M(\mathcal{C}_2,\mathcal{C}_1)dt_2\, \mathrm{e}^{M(\mathcal{C}_1,\mathcal{C}_1)(t_2-t_1)}\, M(\mathcal{C}_1,\mathcal{C}_0)dt_1\, \mathrm{e}^{M(\mathcal{C}_0,\mathcal{C}_0)t_1} P_{\mathrm{eq}}(\mathcal{C}_0)$$

Weight of the reversed Trajectory

TIME–REVERSED TRAJECTORY C(T–t)



$$\mathrm{Pr}\{\hat{\mathcal{C}}(t)\} = \mathrm{e}^{M(\mathcal{C}_0,\mathcal{C}_0)t_1} \; M(\mathcal{C}_0,\mathcal{C}_1)dt_1 \; \mathrm{e}^{M(\mathcal{C}_1,\mathcal{C}_1)(t_2-t_1)} \ldots$$

$$\mathrm{e}^{M(\mathcal{C}_{n-1},\mathcal{C}_{n-1})(t_n-t_{n-1})} \; M(\mathcal{C}_{n-1},\mathcal{C}_n)dt_n \; \mathrm{e}^{M(\mathcal{C}_n,\mathcal{C}_n)(T-t_n)} \; P_{\mathrm{eq}}(\mathcal{C}_n)$$

Detailed Balance and Time Reversal

Ratio of the forward-backward Probabilities:

$$\frac{\Pr\{\mathcal{C}(t)\}}{\Pr\{\hat{\mathcal{C}}(t)\}} = \frac{M(\mathcal{C}_n, \mathcal{C}_{n-1}) M(\mathcal{C}_{n-1}, \mathcal{C}_{n-2}) \ldots M(\mathcal{C}_1, \mathcal{C}_0)\, P_{\mathrm{eq}}(\mathcal{C}_0)}{M(\mathcal{C}_0, \mathcal{C}_1)\, M(\mathcal{C}_1, \mathcal{C}_2)\, \ldots \qquad M(\mathcal{C}_{n-1}, \mathcal{C}_n)\, P_{\mathrm{eq}}(\mathcal{C}_n)}$$

Use recursively the *detailed balance condition:*

$$M(\mathcal{C}_1, \mathcal{C}_0) P_{\mathrm{eq}}(\mathcal{C}_0) = P_{\mathrm{eq}}(\mathcal{C}_1) M(\mathcal{C}_0, \mathcal{C}_1)$$

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$$M(\mathcal{C}_1, \mathcal{C}_0) P_{\mathrm{eq}}(\mathcal{C}_0) = P_{\mathrm{eq}}(\mathcal{C}_1) M(\mathcal{C}_0, \mathcal{C}_1)$$

$$\frac{\mathrm{Pr}\{\mathcal{C}(t)\}}{\mathrm{Pr}\{\hat{\mathcal{C}}(t)\}} = 1$$

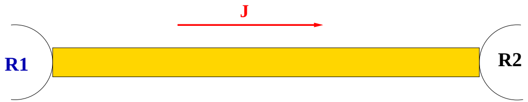
Detailed balance implies that the dynamics is time reversible. The converse property is true.

OUT OF EQUILIBRIUM

In Nature, many systems are far from thermodynamic equilibrium and keep on exchanging matter, energy, information with their surroundings. There is no general conceptual framework to study such systems.

Systems far from equilibrium

Consider a Stationary Driven System in contact with reservoirs at different potentials: no microscopic theory is yet available.



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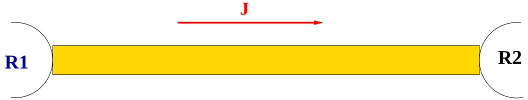


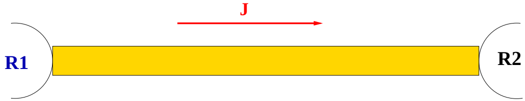
- What are the relevant macroscopic parameters?
- Which functions describe the state of a system?
- Do Universal Laws exist? Can one define Universality Classes?
- Can one postulate a general form for the microscopic measure?
- What do the fluctuations look like ('non-gaussianity')?

In the steady state, a non-vanishing macroscopic current J flows.

What can we say about the properties of this current from the point of view of Statistical Physics?

A Paradigm

The fundamental non-equilibrium system



A Paradigm

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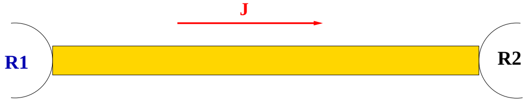
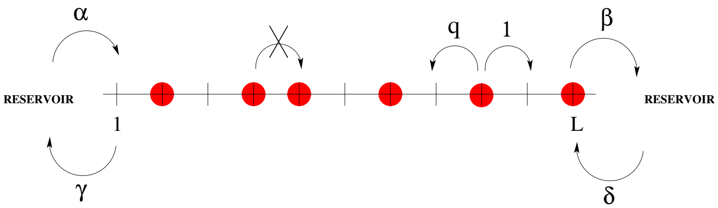


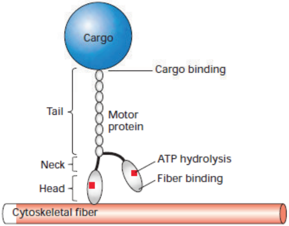
A paradigm: The asymmetric exclusion model with open boundaries (ASEP)



Thousands of articles devoted to this model in the last 20 years.

Biophysical processes are out-of-equilibrium

Living matter is dominated by Brownian fluctuations:



Could the energetics of molecular motors provides us with a new conceptual scheme that would play the role of Carnot's engine and molecular systems out of equilibrium?

Rare Events and Large Deviations

Let $\epsilon_1, \ldots, \epsilon_N$ be N independent binary variables, $\epsilon_k = \pm 1$, with probability p (resp. $q = 1 - p$). Their sum is denoted by $S_N = \sum_1^N \epsilon_k$.

- The Law of Large Numbers implies that $S_N/N \to p - q$ a.s.
- The Central Limit Theorem implies that $[S_N - N(p - q)]/\sqrt{N}$ converges towards a Gaussian Law.

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- The Law of Large Numbers implies that $S_N/N \to p - q$ a.s.
- The Central Limit Theorem implies that $[S_N - N(p-q)]/\sqrt{N}$ converges towards a Gaussian Law.

One can show that for $-1 < r < 1$, in the large N limit,

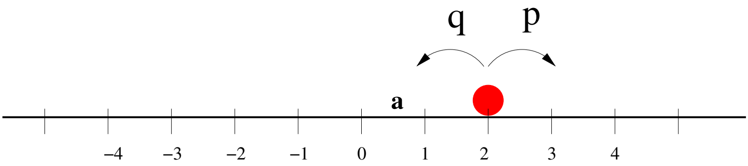
$$\mathrm{Proba}\left(\frac{S_N}{N} = r\right) \sim \mathrm{e}^{-N\,\Phi(r)}$$

where the positive function $\Phi(r)$ vanishes for $r = (p - q)$.

The function $\Phi(r)$ is a Large Deviation Function: it encodes the probability of rare events (*use Stirling's Formula*)

$$\Phi(r) = \frac{1+r}{2} \ln\left(\frac{1+r}{2p}\right) + \frac{1-r}{2} \ln\left(\frac{1-r}{2q}\right)$$

Large Deviations of an asymmetric walk



$$\frac{d\,P(n)}{dt} = q\,P(n+1) + p\,P(n-1) - (p+q)\,P(n)$$

The asymmetric walker has an average speed given by $p - q$. If X_t is its position at time t we have

$$\frac{X_t}{t} \to p - q \quad (a.s.)$$

We can again define a large deviation function as

$$\mathrm{Proba}\left(\frac{X_t}{t} = v\right) \sim \mathrm{e}^{-t\,G(v)}$$

This function can be calculated explicitly. It is given by:

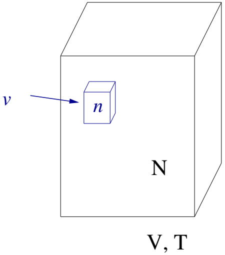
$$G(v) = q + \frac{v}{2} \log \frac{q}{p} - \sqrt{v^2 + 4pq} - |v| \log \frac{2\sqrt{pq}}{|v| + \sqrt{v^2 + 4pq}}$$

Note that

- $G(v)$ is a positive function that vanishes at $v = p - q$.
- $G(v)$ is convex.
- $G(v) - G(-v) = v \log \frac{q}{p}$.
- In the large time limit, the previous identity means that:

$$\frac{\mathrm{Proba}\left(\frac{X_t}{t} = v\right)}{\mathrm{Proba}\left(\frac{X_t}{t} = -v\right)} = \mathrm{e}^{t\, v \log \frac{p}{q}}$$

Local density fluctuations in a gas at thermal equilibrium



Mean Density $\rho_0 = \frac{N}{V}$

In a volume v s. t. $1 \ll v \ll V$
$\left\langle \frac{n}{v} \right\rangle = \rho_0$

The local density varies around ρ_0 . Typical fluctuations scale as $\sqrt{v/V}$.

The probability of observing large fluctuations is given by

$$\mathrm{Proba}\left(\frac{n}{v} = \rho\right) \sim \mathrm{e}^{-v\,\Phi(\rho)} \text{ with } \Phi(\rho_0) = 0$$

Large Deviations of the Density fluctuations

How can we calculate the Large Deviation Function $\Phi(\rho)$ using elementary statistical mechanics?

We must count the fraction of the configurations of the gas that have $n = \rho v$ particles in the small volume v and $N - n$ particles in the rest of the volume $V - v$.

Suppose that the interactions of the gas molecules are local. Then, neglecting surface effects, this number is given by

$$\mathrm{Proba}\left(\frac{n}{v} = \rho\right) \simeq \frac{Z(v, n, T)Z(V - v, N - n, T)}{Z(V, N, T)}$$

Use that, by definition,

$$Z(v, n, T) = \mathrm{e}^{-v\beta f(\rho, T)}$$

where $\beta = 1/k_B T$ is the inverse temperature and $f(\rho, T)$ is the free energy per unit volume and perform an expansion for $1 \ll v \ll V$.

The Large Deviation Function for density fluctuations is given by

$$\Phi(\rho) = \beta\left(f(\rho, T) - f(\rho_0, T) - (\rho - \rho_0)\frac{\partial f}{\partial \rho_0}\right)$$

We can ask the more general question of the large deviation of a density profile: cover the large box with $K = V/v$ small boxes and calculate the probability of having a density ρ_1 in the first box, ρ_2 in the second box ...

$$\mathrm{Proba}\left(\rho_1, \rho_2, \ldots \rho_K\right) \simeq \mathrm{e}^{-V\,\mathcal{F}(\rho_1, \rho_2, \ldots \rho_K)}$$

A reasoning similar to the one above allows us to show that

$$\mathrm{Proba}\left(\rho_1, \rho_2, \ldots \rho_K\right) \sim \frac{\prod_k Z(n_k, v, T)}{Z(V, N, T)}$$

Taking the infinite volume limit, we obtain

$$\mathcal{F}(\rho_1, \rho_2, \ldots \rho_K) = \frac{\beta}{K}\sum_{k=1}^{K}\left(f(\rho_i, T) - f(\rho_0, T)\right)$$

The Free Energy as a L. D. F.

If we let the number K of boxes go to infinity, then the question we are asking is the probability of observing a given density profile $\rho(x)$ in the big volume V. The large deviation function $\mathcal{F}$ becomes a functional of the density profile:

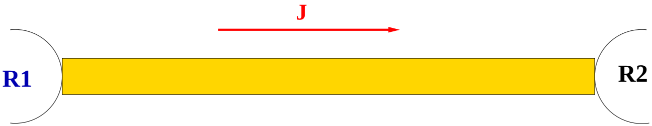
$$\mathcal{F}[\rho(x)] = \beta \int dx \, (f(\rho(x), T) - f(\rho_0, T))$$

$f = -\log Z(\rho, T)$ being, as above, the *free energy per unit volume*.

The Free Energy of Thermodynamics can be viewed as a Large Deviation Function

Conversely, large deviation functions *may* play the role of potentials in non-equilibrium statistical mechanics. Indeed, they can be defined for very general processes, even far from equilibrium.

Large Deviations of the Total Current



Let Y_t be the total charge transported through the system (total current) between time 0 and time t.

In the stationary state: a non-vanishing mean-current $\frac{Y_t}{t} \to J$

The fluctuations of Y_t obey a Large Deviation Principle:

$$P\left(\frac{Y_t}{t} = j\right) \sim e^{-t\Phi(j)}$$

$\Phi(j)$ being the *large deviation function* of the total current.

Note that $\Phi(j)$ is positive, vanishes at $j = J$ and is convex (in general).

Cumulant generating function

Equivalently, we can consider the moment-generating function defined as the average value $\left\langle \mathrm{e}^{\mu Y_t} \right\rangle$. Expanding with respect of μ, we get

$$\log \left\langle \mathrm{e}^{\mu Y_t} \right\rangle = \sum_k \frac{\mu^k}{k!} \langle\langle Y^k \rangle\rangle_c$$

where $\langle\langle Y^k \rangle\rangle_c$ is the k-th cumulant of Y_t.

In many problems, one can show that in the long time limit, we have

$$\left\langle \mathrm{e}^{\mu Y_t} \right\rangle \simeq \mathrm{e}^{E(\mu) t} \qquad \text{when} \quad t \to \infty$$

The function $E(\mu)$ is the cumulant generating function.

Hence, all cumulants of Y_t grow linearly with time and their values are given by the successive derivatives of $E(\mu)$.

Legendre Transform

The cumulant generating function $E(\mu)$ and the large deviation function $\Phi(j)$ are related by Legendre transform:

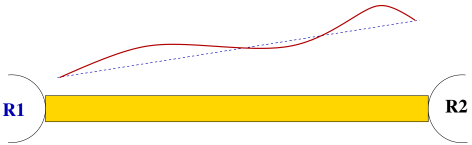
$$\boxed{E(\mu) = \max_j \left(\mu j - \Phi(j)\right)}$$

Indeed, using saddle-point,

$$\left\langle \mathrm{e}^{\gamma Y_t} \right\rangle = \int \mathrm{Pr}(Y_t) \mathrm{e}^{\gamma Y_t} dY_t = t \int \mathrm{Pr}\left(\frac{Y_t}{t} = j \right) \mathrm{e}^{\gamma t j} dj \sim \int \mathrm{e}^{\gamma t j - t\Phi(j)}$$

A natural question is to calculate the large deviation function or the cumulant generating function of the current.

Large Deviations of a Non-Equilibrium profile



What is the probability of observing an atypical density profile in the steady state? What does the functional $\mathcal{F}(\{\rho(x)\})$ look like for such a non-equilibrium system? Recall that in the equilibrium case, this functional is the free energy.

More generally, the probability to observe an atypical current $j(x,t)$ and the corresponding density profile $\rho(x,t)$ during $0 \leq s \leq L^2\, T$ (L being the size of the system) is given by

$$\mathrm{Pr}\{j(x,t), \rho(x,t)\} \sim \mathrm{e}^{-L\,\mathcal{I}(j,\rho)}$$

Can one calculate this large deviation functional for systems out of equilibrium?

A Symmetry of the Large Deviation Function

Large deviation functions obey remarkable identities that remain valid far from equilibrium: *The Fluctuation Theorem of Gallavotti and Cohen.*

Large deviation functions obey a symmetry that remains valid far from equilibrium:

$$\boxed{\Phi(r) - \Phi(-r) = Ar}$$

The coefficient A is a constant, e.g. $A = \ln q/p$ in the example of the walker above.

This Fluctuation Theorem of Gallavotti and Cohen is deep and general: it reflects covariance properties under time-reversal.

In the vicinity of equilibrium the Fluctuation Theorem yields the fluctuation-dissipation relation (Einstein), Onsager's relations and linear response theory (Kubo).

Generalized Detailed Balance

Is there a 'natural way' of breaking detailed balance? What happens to detailed balance for a system connected to reservoirs?

Equilibrium Case:
A system is a thermal equilibrium with a reservoir at T satisfies the detailed balance with respect to the Boltzmann weights:

$$M(\mathcal{C}',\mathcal{C})\mathrm{e}^{-\beta E(\mathcal{C})} = M(\mathcal{C},\mathcal{C}')\ \mathrm{e}^{-\beta E(\mathcal{C}')}$$

Equivalently, defining $\Delta E = E(\mathcal{C}') - E(\mathcal{C})$,

$$M_{+\Delta E}(\mathcal{C} \to \mathcal{C}') = M_{-\Delta E}(\mathcal{C}' \to \mathcal{C})\ \mathrm{e}^{-\beta \Delta E}$$

where we have added an index to keep track of the exchanges of energy.

Non-Equilibrium Case:
Consider a system S in contact with two reservoirs R_1 and R_2 at T_1 and T_2. Suppose that during an elementary step of the process, the system can exchange energy (or matter...) ΔE_1 with the first reservoir and ΔE_2 with the second one.

Detailed balance can be generalized as follows:

$$\boxed{M_{\Delta E_1,\Delta E_2}(\mathcal{C} \to \mathcal{C}') = M_{-\Delta E_1,-\Delta E_2}(\mathcal{C}' \to \mathcal{C})\, \mathrm{e}^{-\frac{\Delta E_1}{kT_1} - \frac{\Delta E_2}{kT_2}}}$$

with $\Delta E_i = E_i(\mathcal{C}') - E_i(\mathcal{C})\,.$

Detailed balance can be generalized as follows:

$$\boxed{M_{\Delta E_1,\Delta E_2}(\mathcal{C}\to\mathcal{C}') = M_{-\Delta E_1,-\Delta E_2}(\mathcal{C}'\to\mathcal{C})\,\mathrm{e}^{-\frac{\Delta E_1}{kT_1}-\frac{\Delta E_2}{kT_2}}}$$

with $\Delta E_i = E_i(\mathcal{C}') - E_i(\mathcal{C})\,.$

The global system $S + R_1 + R_2$ is isolated: $E_1 + E_2 + E(\mathcal{C})$ is conserved by the dynamics. The system has to satisfy detailed balance with respect to the microcanonical measure:

$$\mathrm{e}^{-\frac{S_1(E_1)+S(E_2)}{k}}\; M(\{\mathcal{C}, E_1, E_2\}\to\{\mathcal{C}', E_1', E_2'\})$$
$$= M(\{\mathcal{C}', E_1', E_2'\}\to\{\mathcal{C}, E_1, E_2\})\,\mathrm{e}^{-\frac{S_1(E_1')+S(E_2')}{k}}$$

Expanding the phase space volumes for $\Delta E_i/E_i \ll 1$ gives the previous relation.

Generalized Detailed Balance

Consider that during an elementary transition between t and $t + dt$, the total charge (or energy, or entropy...) transfered from the surroundings, denoted by Y_t, is incremented by y

$$\boxed{\mathcal{C} \to \mathcal{C}' \text{ and } \quad Y_t \to Y_t + y \quad \text{ with probability } M_y(\mathcal{C}', \mathcal{C})dt}$$

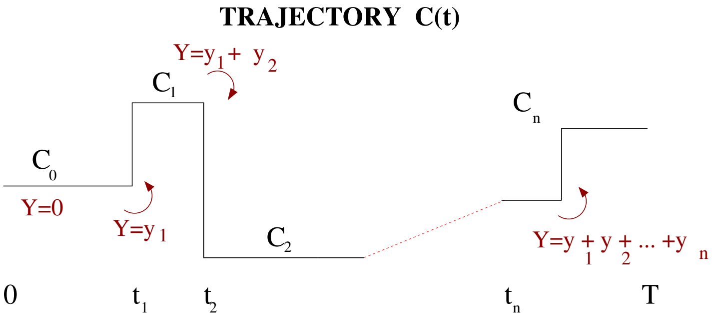
By *time reversal*, the increment y changes its sign:
$\mathcal{C}' \to \mathcal{C}$ and $\quad Y_t \to Y_t - y$
Suppose that there exists a constant γ_0 such that transition rates satisfy

$$\boxed{M_{+y}(\mathcal{C}', \mathcal{C}) = M_{-y}(\mathcal{C}, \mathcal{C}')\, \mathrm{e}^{\gamma_0 y}}$$

GENERALIZED DETAILED BALANCE

True, under general assumption, for a system in contact with reservoirs: a consequence of detailed balance for the system+reservoirs

Generalized Detailed Balance and Time Reversal



$$\frac{\Pr\{\mathcal{C}(t)\}}{\Pr\{\hat{\mathcal{C}}(t)\}} = e^{\gamma_0 Y\{\mathcal{C}(t)\}} \quad \frac{P_{\rm stat}(\mathcal{C}_0)}{P_{\rm stat}(\mathcal{C}_n)}$$

where $Y\{\mathcal{C}(t)\} = y_1 + y_2 + \ldots y_n$ is total charge transfered when the system follows the trajectory $\mathcal{C}(t)$ between 0 and t.

By time-reversal, we have

$$Y\{\hat{\mathcal{C}}(t)\} = -Y\{\mathcal{C}(t)\}$$

It is now useful to define the auxiliary quantity:

$$Z\{\mathcal{C}(t)\} = Y\{\mathcal{C}(t)\} + \frac{1}{\gamma_0} \log \frac{P_{\mathrm{stat}}(\mathcal{C}_0)}{P_{\mathrm{stat}}(\mathcal{C}_n)}$$

The quantity $Z\{\mathcal{C}(t)\}$ is again odd w.r.t. time-reversal and it satisfies

$$\frac{\mathrm{Pr}\{\mathcal{C}(t)\}}{\mathrm{Pr}\{\hat{\mathcal{C}}(t)\}} = \mathrm{e}^{\gamma_0 Z\{\mathcal{C}(t)\}}$$

or, equivalently,

$$\mathrm{e}^{(\gamma-\gamma_0)Z\{\mathcal{C}(t)\}}\mathrm{Pr}\{\mathcal{C}(t)\} = \mathrm{e}^{\gamma Z\{\mathcal{C}(t)\}}\mathrm{Pr}\{\hat{\mathcal{C}}(t)\} = \mathrm{e}^{-\gamma Z\{\hat{\mathcal{C}}(t)\}}\mathrm{Pr}\{\hat{\mathcal{C}}(t)\}$$

It is now useful to define the auxiliary quantity:

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or, equivalently,

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Summing over all possible histories between time 0 and t

$$\sum_{\{\mathcal{C}(t)\}} \mathrm{e}^{(\gamma-\gamma_0)Z}\ \mathrm{Pr}\{\mathcal{C}(t)\} = \sum_{\{\hat{\mathcal{C}}(t)\}} \mathrm{e}^{-\gamma Z\{\hat{\mathcal{C}}(t)\}}\ \mathrm{Pr}\{\hat{\mathcal{C}}(t)\}$$

i.e.,

$$\left\langle \mathrm{e}^{(\gamma-\gamma_0)Z_t} \right\rangle = \left\langle \mathrm{e}^{-\gamma Z_t} \right\rangle$$

The Gallavotti-Cohen Theorem

The quantities Z_t and Y_t grow with time, linearly in general. Their difference remains, generically, bounded. This implies that, in the long time limit, Z_t and Y_t have the same statistical behaviour:

$$\left\langle \mathrm{e}^{(\gamma-\gamma_0)Y_t} \right\rangle \simeq \left\langle \mathrm{e}^{-\gamma Y_t} \right\rangle \quad \text{when } t \to \infty$$

Using $\left\langle \mathrm{e}^{\gamma Y_t} \right\rangle \simeq \mathrm{e}^{\mathcal{E}(\gamma)t}$, we find

$$\mathcal{E}(\gamma - \gamma_0) = \mathcal{E}(-\gamma)$$

A Legendre transform yields the Gallavotti-Cohen Fluctuation Theorem:

$$\boxed{\Phi(j) = \Phi(-j) - \gamma_0 j}$$

From the definition of the Large Deviation Function this implies

$$\frac{\mathrm{Pr}\left(\frac{Y_t}{t} = j\right)}{\mathrm{Pr}\left(\frac{Y_t}{t} = -j\right)} \simeq \mathrm{e}^{\gamma_0 j t}$$

This relation is true **far from equilibrium**. *It has been proved rigorously in various contexts (chaotic systems, Markov/Langevin dynamics...).*

The multi-variable case

Suppose we observe multiples exchanges of various quantities between different reservoirs. A statement of generalized detailed balance in this context is

$$\boxed{M_{y_1,y_2,\ldots y_k}(\mathcal{C} \to \mathcal{C}') = M_{-y_1,-y_2,\ldots -y_k}(\mathcal{C}' \to \mathcal{C})\, \mathrm{e}^{\gamma_1 y_1 + \ldots \gamma_k y_k}}$$

One would obtain for the cumulant generating function

$$\mathcal{E}(\mu_1 - \gamma_1, \ldots, \mu_k - \gamma_k) = \mathcal{E}(-\gamma_1, \ldots, -\gamma_k)$$

Or equivalently, for the large deviation function,

$$\boxed{\Phi(j_1, \ldots, j_k) = \Phi(-j_1, \ldots, -j_k) - \textstyle\sum_{i=1}^{k} \gamma_i j_i}$$

FT for entropy production

In many original works, the authors studied the LDF of the entropy production σ. Starting from the entropy flow given by

$$\frac{d_e S}{dt} = -\frac{1}{2}\sum_{\mathcal{C},\mathcal{C}'} J_t(\mathcal{C},\mathcal{C}') \log \frac{M(\mathcal{C}',\mathcal{C})}{M(\mathcal{C},\mathcal{C}')}$$

one defines an entropy transfer for each jump given by

$$\delta\sigma = \log \frac{M(\mathcal{C}',\mathcal{C})}{M(\mathcal{C},\mathcal{C}')}$$

For this quantity, the generalized detailed balance property is *tautologically true*, by taking $\gamma_0 = 1$

$$M_{\delta\sigma}(\mathcal{C}',\mathcal{C}) = M_{-\delta\sigma}(\mathcal{C},\mathcal{C}')\mathrm{e}^{\gamma_0\delta\sigma}$$

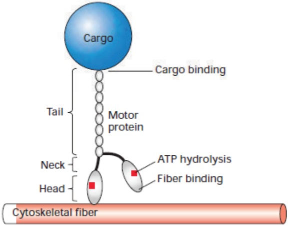
The FT is thus given by

$$\boxed{\mathcal{E}(\gamma-1) = \mathcal{E}(-\gamma) \quad i.e. \quad \Phi(\sigma) - \Phi(-\sigma) = -\sigma}$$

Illustration on Brownian Motors

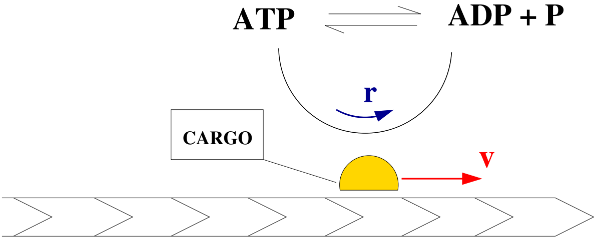
Molecular Motors move by using the ratchet effect:

rectification of Brownian motion relying on an external energy source, (ATP hydrolysis) that enables the motor to undergo transitions between different states.

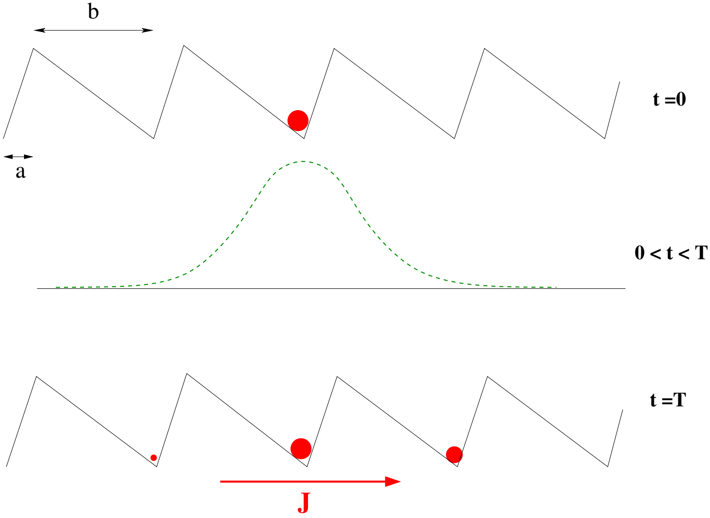


Basic Description of a Molecular Motor

Such a process is possible only by using an energy source, provided by ATP hydrolysis: this coupling between chemical and mechanical currents is characteristic of a non-equilibrium process.
The motor performs dynamical transitions between microscopic states that break detailed balance and allow for a directed motion.



The Ratchet Model



How can one analyze the energetics of such a system?

2-States Motor

Statistics of the displacement and the ATP consumption as functions of the external mechanical and chemical loads?

Velocity of the motor(mechanical current): $v(f_{\mathrm{ext}}, \Delta\mu)$

ATP consumption rate (chemical current): $r(f_{\mathrm{ext}}, \Delta\mu)$

Energetics of the motor

- At thermodynamic equilibrium: $f_{\mathrm{ext}} = 0$ and $\Delta\mu = 0$ and the two currents v and r vanish. The position of the motor and the number of ATP molecules consumed exhibit Gaussian fluctuations, characterized by two diffusion constants D_1 and D_2.

- Near equilibrium: for small values of f_{ext} and $\Delta\mu$, linear response theory holds and we have

$$\begin{aligned} v &= L_{11} f_{\mathrm{ext}} + L_{12}\Delta\mu \\ r &= L_{21} f_{\mathrm{ext}} + L_{22}\Delta\mu \end{aligned}$$

Einstein Relations: $L_{11} = D_1$ and $L_{22} = D_2$.
Onsager Reciprocity Relation: $L_{12} = L_{21}$.

- What Happens Far from Equilibrium? Can we quantify deviations from these relations? How is linear response theory broken?

Large Deviations

Far from Equilibrium:

Now v and r are non-linear functions of the external loads f_{ext} and $\Delta\mu$.

Let X_t be the total displacement of the motor and Q_t the total number of ATP molecules consumed between 0 and t.

The long-time statistical properties of X_t and Q_t can be embodied in the cumulant generating function $\mathcal{E}(\gamma, \lambda)$ and one can show that in the long-time limit

$$\left\langle \mathrm{e}^{\gamma X_t + \lambda Q_t} \right\rangle \simeq \mathrm{e}^{\mathcal{E}(\gamma,\lambda) t}$$

In particular, we have

$$v = \frac{\partial \mathcal{E}}{\partial \gamma}(0,0) \text{ and } r = \frac{\partial \mathcal{E}}{\partial \lambda}(0,0)$$

$\mathcal{E}(\gamma, \lambda)$ is the Legendre transform of the LDF $\mathcal{G}(v_1, r_1)$

$$\mathrm{Prob}\left(\frac{X_t}{t} = v_1, \frac{Q_t}{t} = r_1 \right) \simeq \mathrm{e}^{-t\mathcal{G}(v_1, r_1)}$$

$\mathcal{G}$ vanishes for the mean values of the mechanical and chemical currents.

Gallavotti-Cohen Relation

The function $\mathcal{E}(\gamma, \lambda)$ satisfies the *Gallavotti-Cohen relation:*

$$\boxed{\mathcal{E}(\gamma, \lambda) = \mathcal{E}(-\gamma - f_{\mathrm{ext}}, -\lambda - \Delta\mu)}$$

This identity results from constraints satisfied a priori by the switching rates in the model (Generalized Detailed Balance).

The Gallavotti-Cohen symmetry implies in particular:

$$v = -\frac{\partial \mathcal{E}}{\partial \gamma}(-f_{\mathrm{ext}}, -\Delta\mu) \quad \text{and} \quad r = \frac{\partial \mathcal{E}}{\partial \lambda}(-f_{\mathrm{ext}}, -\Delta\mu)$$

These relations are valid arbitrarily far from equilibrium.

Near equilibrium,the FT yields Einstein and Onsager's Relations.
Developing for small values of f_{ext} and $\Delta\mu$:

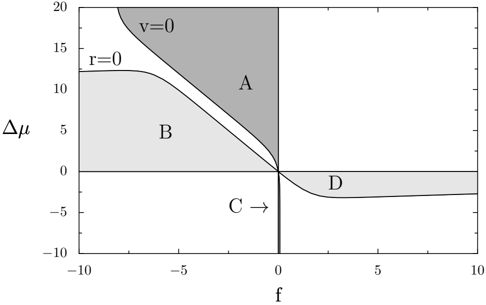
$$\begin{aligned} v &= \left.\frac{\partial^2 \mathcal{E}}{\partial\gamma^2}\right|_{(0,0)} f_{\mathrm{ext}} + \left.\frac{\partial^2 \mathcal{E}}{\partial\gamma\partial\lambda}\right|_{(0,0)} \Delta\mu \\ r &= \left.\frac{\partial^2 \mathcal{E}}{\partial\lambda\partial\gamma}\right|_{(0,0)} f_{\mathrm{ext}} + \left.\frac{\partial^2 \mathcal{E}}{\partial\lambda^2}\right|_{(0,0)} \Delta\mu \end{aligned}$$

By identifying the linear-response coefficients, we obtain

$$\begin{aligned} L_{11} &= \left.\frac{\partial^2 \mathcal{E}}{\partial\gamma^2}\right|_{(0,0)} = \frac{\langle X_t^2\rangle - \langle X_t\rangle^2}{t} = D_1 \\ L_{12} &= \left.\frac{\partial^2 \mathcal{E}}{\partial\gamma\partial\lambda}\right|_{(0,0)} = \left.\frac{\partial^2 \mathcal{E}}{\partial\lambda\partial\gamma}\right|_{(0,0)} = L_{21} \\ L_{22} &= \left.\frac{\partial^2 \mathcal{E}}{\partial\lambda^2}\right|_{(0,0)} = \frac{\langle Q_t^2\rangle - \langle Q_t\rangle^2}{t} = D_2 \end{aligned}$$

Phase-Diagram of the motor

Modes of operation of the molecular motor



Regions A and C ($f_{\mathrm{ext}}\, v < 0, r\, \Delta\mu > 0$): Chemical energy → Mechanical Work

Regions B and D ($f_{\mathrm{ext}}\, v > 0, r\, \Delta\mu < 0$): Mechanical Work → Chemical energy

WORK IDENTITIES

Another major breakthrough: the Work Theorem

Remember the maximal work inequality:

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

We put brackets to emphasize that we consider the average work:
Statistical Physics has taught us that physical observables fluctuate.

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It was found very recently that there exists a remarkable equality that *underlies* this classical inequality.

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

The Jarzynski Identity

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

Jarzynski's Work Theorem (1997)

Consequences

1. Jarzynski's identity mathematically implies the good old maximal work inequality.

2. But, in order to have an EQUALITY, there must exist some occurrences in which

$$W > -\Delta F$$

There must be instances in which the classical inequality which results from the Entropy Principle is 'violated'.

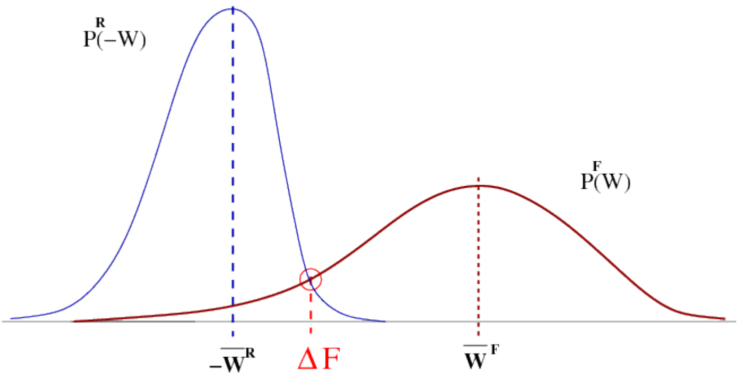
3. Jarzynski's identity can be used to calculate chemical free energies of biopolymer configurations: it has experimental applications in biophysics or at the nanoscale.

4. The relation of Crooks: a refinement Jarzynski's identity that allows us to quantify precisely the 'transient violations of the second principle'.

$$\frac{\mathrm{P}^{\mathrm{F}}(W)}{\mathrm{P}^{\mathrm{R}}(-W)} = \mathrm{e}^{\frac{W-\Delta F}{kT}} \qquad \text{(Crooks,1999)}$$

Graphical representation of the Crooks'relation

Crooks' Relation allows us to quantify precisely the 'transient violations' of the Second Principle and can be checked experimentally.



Vérification Expérimentale de l'identité de Crooks

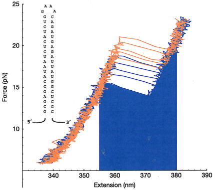


Figure 1 | **Force–extension curves.** The stochasticity of the unfolding and refolding process is characterized by a distribution of unfolding or refolding work trajectories. Five unfolding (orange) and refolding (blue) force–extension curves for the RNA hairpin are shown (loading rate of 7.5 pN s^{-1}). The blue area under the curve represents the work returned to the machine as the molecule switches from the unfolded to the folded state. The RNA sequence is shown as an inset.

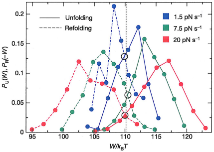


Figure 2 | **Test of the CFT using an RNA hairpin.** Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines). We plot negative work, $P_R(-W)$, for refolding. Statistics: 130 pulls and three molecules ($r = 1.5\,\mathrm{pN\,s^{-1}}$), 380 pulls and four molecules ($r = 7.5\,\mathrm{pN\,s^{-1}}$), 700 pulls and three molecules ($r = 20.0\,\mathrm{pN\,s^{-1}}$), for a total of ten separate experiments. Good reproducibility was obtained among molecules (see Supplementary Fig. S2). Work values were binned into about ten equally spaced intervals. Unfolding and refolding distributions at different speeds show a common crossing around $\Delta G = 110.3\,k_BT$.