

Recent Developments in Non-Equilibrium Statistical Physics

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Introduction

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

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

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

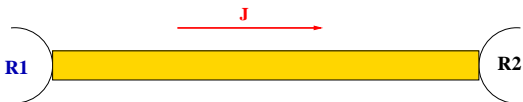
$$F = -kT \text{Log } Z$$

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 (Brownian Motion).

Systems far from equilibrium

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



- 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, thus breaking time-reversal invariance

EQUILIBRIUM

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).

FIRST PRINCIPLE

$$\Delta U = W + Q$$

THE ENERGY OF THE UNIVERSE IS CONSTANT.

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 (Clausius, Kelvin-Planck).

SECOND PRINCIPLE

A NEW physical concept (Clausius): **ENTROPY**.

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

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 \rightarrow water).

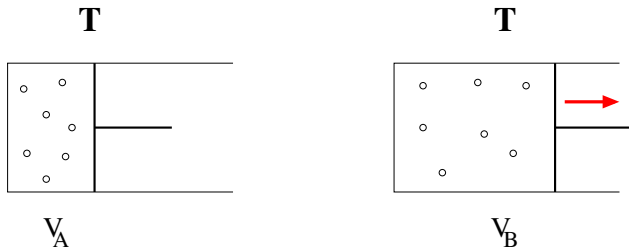
The two principles of thermodynamics can be embodied simultaneously by the **FREE ENERGY** F :

$$F = U - TS$$

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

Free energy: Maximal Work Theorem

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 its environment at fixed temperature T .



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

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

STATISTICAL MECHANICS



J. C. Maxwell



L. Boltzmann

The connection with thermodynamics is given by **Boltzmann's formula** or, equivalently

$$F = -kT \log Z$$

Close to Equilibrium: Linear Response

At **thermodynamic equilibrium** and **time-reversal invariance** is a key-property.

This implies that 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**.

For a small perturbation, these fluxes are proportional to the disturbance. The values of the susceptibilities can be calculated from equilibrium data: **Einstein Relation** (susceptibilities = fluctuations), **Onsager Relations** (Susceptibility Tensor is symmetric).

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.

A Surprise: The Jarzynski Identity

Remember the maximal work inequality:

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

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.

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

The Jarzynski Identity



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

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 was checked experimentally on single RNA folding/unfolding experiments (Bustamante et al.): it has experimental applications in biophysics and 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'.

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

Rare Events and Large Deviations

Let $\epsilon_1, \dots, \epsilon_N$ 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 $S_N/N \rightarrow p - q$ 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,

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

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.

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

Density Fluctuations

Consider a gas in a room, at thermal equilibrium. The probability of observing a density profile $\rho(x)$ takes the form:

$$\Pr\{\rho(x)\} \sim e^{-\beta V \mathcal{F}(\{\rho(x)\})}$$

What is $\mathcal{F}(\{\rho(x)\})$?

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What is $\mathcal{F}(\{\rho(x)\})$?

$$\mathcal{F}(\{\rho(x)\}) = \int_0^1 (f(\rho(x), T) - f(\bar{\rho}, T)) d^3x$$

Free Energy can be viewed as a Large Deviation Function.

Density Fluctuations

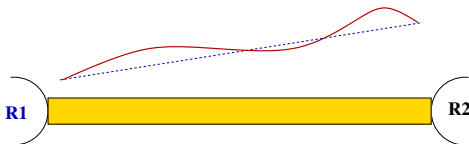
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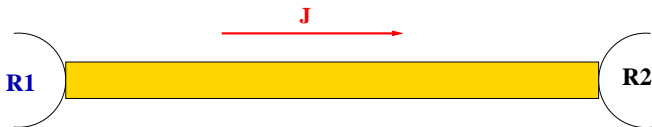
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Free Energy can be viewed as a Large Deviation Function.



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?

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 $\frac{Y_t}{t} \rightarrow J$

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).

The Gallavotti and Cohen Symmetry

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:

$$\Phi(j) - \Phi(-j) = \alpha j$$

Equivalently,

$$\frac{\text{Prob}(j)}{\text{Prob}(-j)} \sim e^{-\alpha j}$$

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).

The General Large Deviations Problem

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

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

Is there a Principle which gives this large deviation functional for systems out of equilibrium?

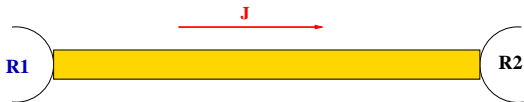
Why study Large Deviations?

- Equilibrium Thermodynamic potentials (Entropy, Free Energy) can be defined as large deviation functions.
- Large deviations are well defined far from equilibrium: they are **good candidates for being non-equilibrium potentials**.
- Large deviation functions obey remarkable identities, valid far from equilibrium (**Gallavotti-Cohen Fluctuation Theorem; Jarzynski and Crooks Relations**).
- These identities imply, in the vicinity of equilibrium, the fluctuation dissipation relation (Einstein), Onsager's relations and linear response theory (Kubo).

EXACT RESULTS FAR FROM EQUILIBRIUM

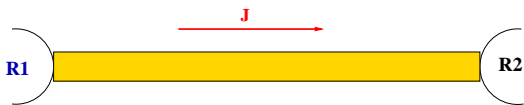
Study Non-Equilibrium via Model Solving

The fundamental non-equilibrium system

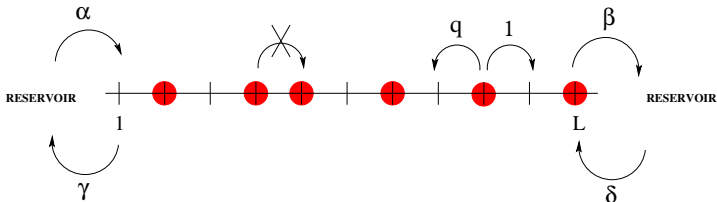


Study Non-Equilibrium via Model Solving

The fundamental non-equilibrium system



The asymmetric exclusion model with open boundaries (ASEP)



Thousands of articles devoted to this model in the last 20 years:
Paradigm for non-equilibrium behaviour

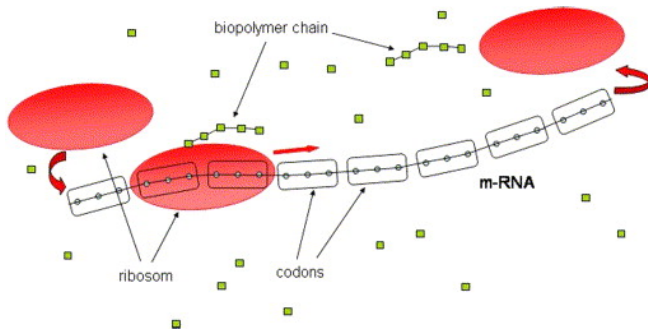
ORIGINS

- Interacting Brownian Processes (Spitzer, Harris, Liggett).
- Driven diffusive systems (Katz, Lebowitz and Spohn).
- Transport of Macromolecules through thin vessels.
Motion of RNA templates.
- Hopping conductivity in solid electrolytes.
- Directed Polymers in random media. Reptation models.
- Interface dynamics. KPZ equation

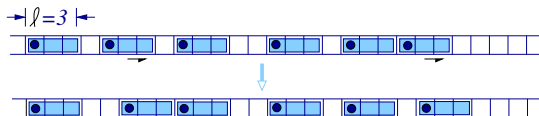
APPLICATIONS

- Traffic flow.
- Sequence matching.
- Brownian motors.

An Elementary Model for Protein Synthesis



C. T. MacDonald, J. H. Gibbs and A.C. Pipkin, Kinetics of biopolymerization on nucleic acid templates, *Biopolymers* (1968).



Large Deviations of the Density Profile in ASEP

The probability of observing an **atypical density profile in the steady state of the ASEP** was calculated starting from Matrix Ansatz for the exact microscopic solution (B. Derrida, J. Lebowitz E. Speer, 2002).

In the **symmetric case** $q = 0$:

$$\mathcal{F}(\{\rho(x)\}) = \int_0^1 dx \left(B(\rho(x), F(x)) + \log \frac{F'(x)}{\rho_2 - \rho_1} \right)$$

where $B(u, v) = (1 - u) \log \frac{1-u}{1-v} + u \log \frac{u}{v}$ and $F(x)$ satisfies

$$F (F'^2 + (1 - F)F'') = F'^2 \rho \quad \text{with} \quad F(0) = \rho_1 \text{ and } F(1) = \rho_2 .$$

This functional is non-local as soon as $\rho_1 \neq \rho_2$.

This functional is **NOT** identical to the one given by local equilibrium.

Note that in the case of equilibrium, for $\rho_1 = \rho_2 = \bar{\rho}$, we recover

$$\mathcal{F}(\{\rho(x)\}) = \int_0^1 dx \left\{ (1 - \rho(x)) \log \frac{1 - \rho(x)}{1 - \bar{\rho}} + \rho(x) \log \frac{\rho(x)}{\bar{\rho}} \right\}$$

Current Statistics

In the case $\alpha = \beta = 1$, a parametric representation of the cumulant generating function $E(\mu)$:

$$\mu = - \sum_{k=1}^{\infty} \frac{(2k)!}{k!} \frac{[2k(L+1)]!}{[k(L+1)]! [k(L+2)]!} \frac{B^k}{2k},$$

$$E = - \sum_{k=1}^{\infty} \frac{(2k)!}{k!} \frac{[2k(L+1)-2]!}{[k(L+1)-1]! [k(L+2)-1]!} \frac{B^k}{2k}.$$

First cumulants of the current

- **Mean Value** : $J = \frac{L+2}{2(2L+1)}$

- **Variance** : $\Delta = \frac{3}{2} \frac{(4L+1)! [L!(L+2)]^2}{[(2L+1)!]^3 (2L+3)!}$

- **Skewness** :

$$E_3 = 12 \frac{[(L+1)!]^2 [(L+2)!]^4}{(2L+1)! [(2L+2)!]^3} \left\{ 9 \frac{(L+1)!(L+2)!(4L+2)!(4L+4)!}{(2L+1)! [(2L+2)!]^2 [(2L+4)!]^2} - 20 \frac{(6L+4)!}{(3L+2)!(3L+6)!} \right\}$$

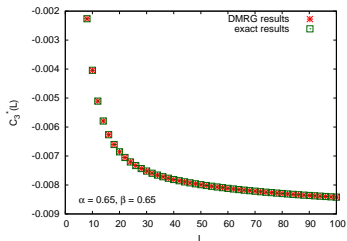
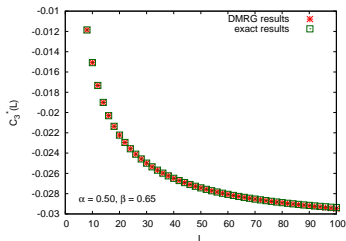
For large systems: $E_3 \rightarrow \frac{2187-1280\sqrt{3}}{10368} \pi \sim -0.0090978\dots$

Large Deviation Function of the Current

In the limit of large size systems, the following exact expression is found for the Large Deviation Function of the current:

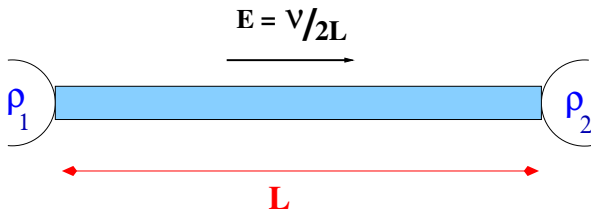
$$\Phi(j) = (1 - q) \left\{ \rho_a - r + r(1 - r) \ln \left(\frac{1 - \rho_a}{\rho_a} \frac{r}{1 - r} \right) \right\}$$

where the current j is parametrized as $j = (1 - q)r(1 - r)$.



SKEWNESS

The Hydrodynamic Limit: Diffusive case



Starting from the microscopic level, define local density $\rho(x, t)$ and current $j(x, t)$ with macroscopic space-time variables $x = i/L, t = s/L^2$ (diffusive scaling).

The typical evolution of the system is given by the hydrodynamic behaviour (Burgers-type equation):

$$\partial_t \rho = \nabla (D(\rho) \nabla \rho) - \nu \nabla \sigma(\rho) \quad \text{with} \quad D(\rho) = 1 \quad \text{and} \quad \sigma(\rho) = 2\rho(1 - \rho)$$

(Lebowitz, Spohn, Varadhan)

How can Fluctuations be taken into account?

Fluctuating Hydrodynamics

Consider Y_t the total number of particles transferred from the left reservoir to the right reservoir during time t .

- $\lim_{t \rightarrow \infty} \frac{\langle Y_t \rangle}{t} = D(\rho) \frac{\rho_1 - \rho_2}{L} + \sigma(\rho) \frac{\nu}{L}$ for $(\rho_1 - \rho_2)$ small
- $\lim_{t \rightarrow \infty} \frac{\langle Y_t^2 \rangle}{t} = \frac{\sigma(\rho)}{L}$ for $\rho_1 = \rho_2 = \rho$ and $\nu = 0$.

Then, the equation of motion is obtained as:

$$\partial_t \rho = -\partial_x j \quad \text{with} \quad j = -D(\rho) \nabla \rho + \nu \sigma(\rho) + \sqrt{\sigma(\rho)} \xi(x, t)$$

where $\xi(x, t)$ is a Gaussian white noise with variance

$$\langle \xi(x', t') \xi(x, t) \rangle = \frac{1}{L} \delta(x - x') \delta(t - t')$$

For the symmetric exclusion process, the 'phenomenological' coefficients are given by

$$D(\rho) = 1 \quad \text{and} \quad \sigma(\rho) = 2\rho(1 - \rho)$$

A General Principle for Large Deviations?

The probability to observe an **atypical** current $j(x, t)$ and the corresponding density profile $\rho(x, t)$ during a time $L^2 T$ (L being the size of the system) is given by

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

A general principle has been found (Jona-Lasinio et al.), to express this large deviation functional $\mathcal{I}(j, \rho)$ as an optimal path problem:

$$\mathcal{I}(j, \rho) = \min_{\rho, j} \left\{ \int_0^T dt \int_0^1 dx \frac{(j - v\sigma(\rho) + D(\rho)\nabla\rho)^2}{2\sigma(\rho)} \right\}$$

with the **constraint**: $\partial_t \rho = -\nabla \cdot j$

Knowing $\mathcal{I}(j, \rho)$, one could derive the large deviations of the current and of the density profile. For instance, $\Phi(j) = \min_{\rho} \{\mathcal{I}(j, \rho)\}$

However, at present, the available results for this variational theory are precisely the ones given by exact solutions of the ASEP.

Macroscopic Fluctuation Theory

Mathematically, one has to solve the corresponding Euler-Lagrange equations. The **Hamiltonian structure** is expressed by a pair of conjugate variables (p, q) .

After some transformations, one obtains a set of coupled PDE's (here, we take $\nu = 0$):

$$\begin{aligned}\partial_t q &= \partial_x [D(q) \partial_x q] - \partial_x [\sigma(q) \partial_x p] \\ \partial_t p &= -D(q) \partial_{xx} p - \frac{1}{2} \sigma'(q) (\partial_x p)^2\end{aligned}$$

where $q(x, t)$ is the density-field and $p(x, t)$ is a conjugate field.

The '**transport coefficients**' $D(q)(= 1)$ and $\sigma(q)(= 2q(1 - q))$ contain the information of the microscopic dynamics relevant at the macroscopic scale.

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- A general framework but the MFT equations are very difficult to solve in general. By using them one can in principle calculate large deviation functions **directly at the macroscopic level**.
- The analysis of this new set of 'hydrodynamic equations' has just begun!

Conclusions

Non-Equilibrium Statistical Physics has undergone remarkable developments in the last two decades and a unified framework is emerging.

Large deviation functions (LDF) appear as a generalization of the thermodynamic potentials for non-equilibrium systems. They satisfy remarkable identities (Gallavotti-Cohen, Jarzynski-Crooks) valid far from equilibrium.

The LDF's are very likely to play a key-role in the future of non-equilibrium statistical mechanics.

Current fluctuations are a signature of non-equilibrium behaviour. The exact results derived for the Exclusion Process can be used to calibrate the more general framework of fluctuating hydrodynamics (MFT), which is currently being developed.