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Understanding non-equilibrium: some recent advances and a challenge for the future

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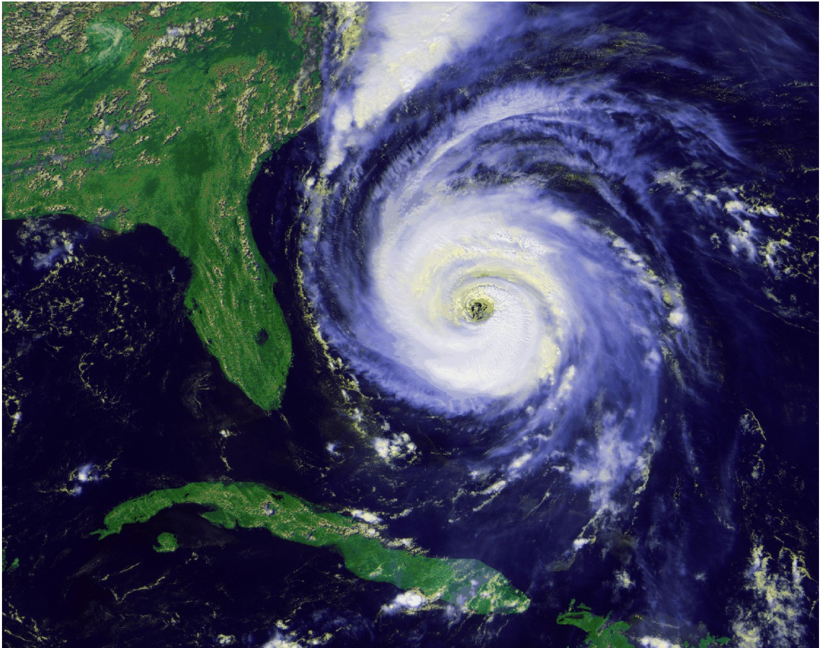
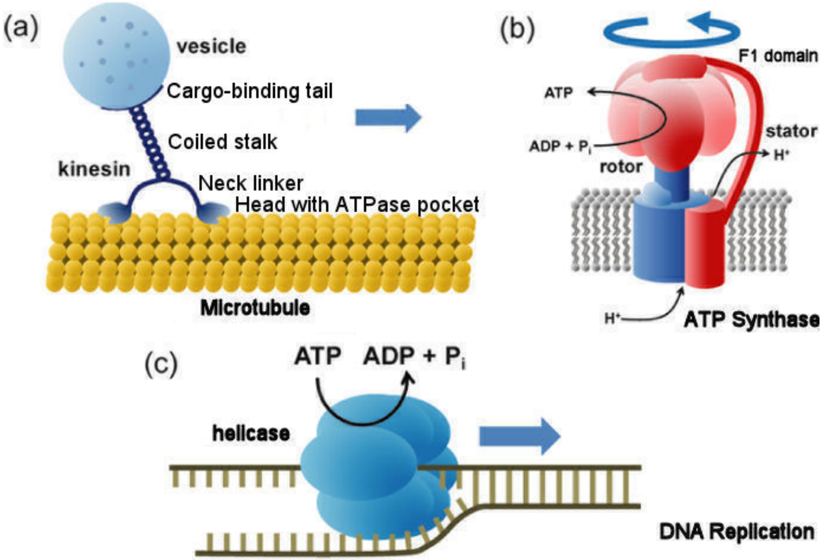
Far from equilibrium behavior is ubiquitous. Indeed most of the processes that characterize energy flow occur far from equilibrium. These range from very large systems, such as weather patterns or ocean currents that remain far from equilibrium owing to an influx of energy, to biological structures. Away-from-equilibrium processes occur on time scales ranging from nanoseconds to millennia. Despite the pervasiveness of non-equilibrium systems and processes, most of our current understanding of physical and biological systems is based on equilibrium concepts.

Hurricane



Andromeda galaxy

Molecular motors



Tectonics

Explosion

The concepts of equilibrium and non-equilibrium belong to mechanics and thermodynamics. Here we are mainly interested in the thermodynamic point of view. Even when we deal with microscopic systems as in biological matter or nanostructures in advanced technology, the number of atoms or molecules involved is so large that thermodynamics and a statistical point of view provide the appropriate approach.

Classical thermodynamics deals with states of a system, possibly in contact with an environment, where no flow of energy is present. These states either do not change in time (equilibrium) or change very slowly so that they can be described by a sequence of equilibrium states. This is the notion of quasi static or reversible transformation. However, as emphasized in a well known textbook on thermodynamics, to define in a precise way this notion we need to go beyond equilibrium

Callen

“A quasi-static process is thus defined in terms of a dense succession of equilibrium states. It is to be stressed that a quasi-static process therefore is an idealized concept, quite distinct from a real physical process, for a real process always involves nonequilibrium intermediate states having no representation in the thermodynamic configuration space. Furthermore, a quasistatic process, in contrast to a real process, does not involve considerations of rates, velocities or time. The quasi-static process simply is an ordered succession of equilibrium states, whereas a real process is a temporal succession of equilibrium and non-equilibrium states.”

In spite of the inadequacy in clarifying its own foundations, classical thermodynamics has been very successful. Its principles were formulated in the XIXth century at the time of the first industrial revolution and provided the basis for conceiving and producing the necessary engines and machines. The first principle, recognizing that heat is a form of energy, states that

1. *in a transformation of a system the variation of its energy is equal to the sum of the mechanical work and the heat exchanged.*

Several formulations have been given for the second principle and we choose the one which is convenient for the ensuing discussion even though more abstract.

2. *There is a quantity called entropy which in a transformation of an isolated system (universe) can either remain constant or increase. An equilibrium state is therefore a state of maximum entropy.*

There is also a third principle which is of a more special character but will not be relevant in the following.

Entropy is a somewhat mysterious concept and when reading the original papers of its inventor, Robert Clausius, the first reaction is "How did he think of it?". Actually entropy was introduced by Clausius as a quantitative characterisation of the equivalence of two transformations, i.e. transformations which can be substituted one to the other as they produce exactly the same effects.

Statistical interpretation of entropy

The microscopic meaning of entropy was discovered by Boltzmann. He realized that the entropy is related in a simple way to the probability of a macroscopic state

$$S = k \ln W + const. \tag{1}$$

A macroscopic state is characterized by few parameters like energy, density, temperature, pressure, etc. and many different microscopic atomic configurations are compatible with them. The probability of a macroscopic state is proportional to the number of the microscopic configurations compatible with these parameters. The more microscopic states correspond to the macroscopic parameters, the higher is the probability.

Shannon entropy

There is also a similar definition of entropy in information theory which measures the content of information of a message

$$h = -\sum_k p_k \ln p_k \tag{2}$$

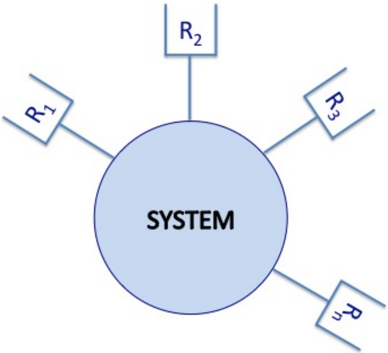
where p_k is for example the probability distribution of characters or words. A story says that such a terminology was suggested to Shannon, the inventor of the theory, by the famous mathematician John Von Neumann with the comment

> *"You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, no one really knows what entropy really is, so in a debate you will always have the advantage."*

Stationary states

For systems out of equilibrium it does not exist yet a macroscopic description of a scope comparable with equilibrium thermodynamics. In non-equilibrium one has to cope with a variety of phenomena much greater than in equilibrium. From a conceptual point of view the non-equilibrium situations closest to equilibrium are the stationary non-equilibrium states which describe a steady flow through some system. Simple examples are the heat flow in an iron rod whose endpoints are thermostated at different temperatures or the stationary flow of electrical current in a given potential difference. For such states the fluctuations exhibit novel and rich features with respect to the equilibrium situation. For example, as experimentally observed, the space correlations of the density extend to macroscopic distances, which means that the fluctuations of the density in different points of the system are not independent.

Typical setting for a stationary state



The first important question is to what extent can we formulate a thermodynamics for these states based on general principles. The first difficulty encountered for such a program is that there is no obvious definition of basic thermodynamic concepts as free energy or entropy in states far from equilibrium. In the examples above energy flows through the bar or the wire and there is dissipation of heat in the environment, which is usually called production of entropy. In other words it is not easy to define entropy for the bar or the wire but it is natural to define entropy production in terms of the increase of the entropy of the environment which is supposed approximately in equilibrium.

The leitmotiv has been the study of fluctuations within a variety of approaches and physical models. Fluctuations of thermodynamic variables in equilibrium due to the atomic structure of matter is an old subject to which Einstein devoted a series of basic papers showing the strict connection between fluctuations and thermodynamic functions like free energy and entropy.

Near equilibrium an expansion solves the problem

$$S(\rho_1, \rho_2, ..., \rho_n) = \bar{S} + \frac{1}{2} \sum_{i,k} \frac{\partial^n S}{\partial \rho_i \partial \rho_k} (\rho_i - \bar{\rho}_i)(\rho_k - \bar{\rho}_k) + ... \quad (3)$$

Einstein's interpretation of Boltzmann

Annalen der Physik **33**, *1275 (1910)*

"Boltzmann principle can be expressed by the equation

$$S = \frac{R}{N} \ln W + const. \tag{4}$$

where S is the entropy, R the gas constant, N Avogadro's number, W is customarily designated as the "probability" of the state with which the entropy value is associated. W is commonly equated with the number of possible ways (complexions) in which the state considered can conceivably be realized. In order to be able to calculate W one needs a complete theory of the system under considoeration....... Considered from a phenomenological point of view equation (4) *appears devoid of content."*

"However Boltzmann's principle does acquire some content independent of any elementary theory if one assumes and generalizes from molecular kinetics the proposition that the irreversibility of physical processes is only apparent.
For let a state of a system be determined in the phenomenological sense by the viariables $\lambda_1, ..., \lambda_k$ *that are observable in principle.*
To each state Z *there corresponds a combination of values of these variables. If the system is externally closed then the energy - and in general no other function of the [microscopic] variables - is constant."*

"Let us think of all the states of the system that are compatible with the energy value, and denote them by $Z_1 \ldots Z_i$. If the irreversibility of the process is not one of principle, in the course of time, the system will pass through these states again and again. On this assumption one can speak of the probability of individual states in the following sense: suppose we observe the system for an immensely long time θ and deternine the fraction τ_1 during which the system is in the state Z_1; then τ_1/θ represents the probability of the state Z_1. The same holds for the probability of the other states"

"It follows from (4) that

$$W = const \cdot e^{\frac{N}{R}S} \tag{5}$$

The order of magnitude of the constant is determined by taking into account that for the state of maximum entropy (entropy S_0) W is of the order of magnitude one, so that we then have, with order of magnitude accuracy,

$$W = e^{\frac{N}{R}(S-S_0)} \tag{6}$$

From this we can conclude that the probability dW that the quantities $\lambda_1, ..., \lambda_k$ lie between λ_1 and $\lambda_1 + d\lambda_1$, ..., λ_k and $\lambda_k + d\lambda_k$ is given, in order of magnitude, by the equation

$$dW = e^{\frac{N}{R}(S-S_0)} d\lambda_1 ....d\lambda_k \tag{7}$$

."

Unpublished manuscript of a conference given by Einstein on November 2, 1910 at the Zürich Physical Society

Seminaire Poincaré, 1 (2005) 213. French translation by B. Duplantier

> *"La signification principale de la formule de Boltzmann ne réside cependant pas, à mon avis, en ce qu'on puisse grace à elle calculer l'entropie en présence d'une representation moléculaire connue. La manière la plus importante de l'utiliser consiste bien plus en ce qu'à l'inverse, à partir de la function entropie déterminée empiriquement, on puisse déterminer la probabilité statistique des états individuels à l'aide de la formule de Boltzmann. On acquiert ainsi une possibilité de jauger de combien devie le comportement du système par rapport au comportement requis par la thermodynamique."*

Exemple. Particule en suspension dans un fluide, et qui est un peu plus lourde que le fluide qu'elle deplace

"Une telle particule devrait, d'après la thermodynamique, couler au fond du récipient et y rester. D'après la formule de Boltzmann cependant, une probabilité W va $\hat{e}$tre associée a chaque hauteur z au dessus du fond...... Soient μ la masse de la particule, μ_0 celle du fluide deplacé par elle. ..... De la formule de Boltzmann s'ensuit

$$W = const \quad e^{-\frac{N}{RT}(\mu-\mu_0)gz} \tag{8}$$

Cette relation a été testée, et s'est trouvée confirmée, par Perrin."

La loi du mouvement brownien

“La loi du mouvement brownien peut $\hat{e}$tre deduite très facilement de cette relation .... à cause de sa densité plus grande la particule tombe d'après la loi de Stokes de $D = \frac{g(\mu - \mu_0)}{6\pi\eta P}\tau$ dans le temps τ, ou η représente le coefficient de viscosité du fluide et P le rayon de la particule. ..... Une particule qui, à l'orée du temps τ se trouve à la hauteur z, est à l'issue de ce temps τ á la hauteur $z - D + \Delta = z'$ [Δ déplacement brownien]. Comme la loi de distribution d'une particule ne doit pas dépendre du temps, la valeur moyenne de z^2 doit $\hat{e}$tre égale à celle de z'^2, donc $\overline{(z - D + \Delta)^2} = \overline{z^2}$, ou encore, pour τ assez petit pour pouvoir négliger D^2, et $\overline{z\Delta} = \overline{z\Delta} = \overline{D\Delta} = 0$

$$\overline{\Delta^2} = 2\overline{z}D = \frac{RT}{N}\frac{1}{3\pi\eta P}\tau \tag{9}$$

”

Non isolated systems out of equilibrium

The main idea of a recently developed study of non–equilibrium stationary states known under the name of Macroscopic Fluctuation Theory is to start with the analysis of large macroscopic fluctuations in such states. This means searching for extensions of formulas like (6).

To discuss this problem we need to analyze the meaning of the difference $S - S_0$ in (6). In an isolated system energy is conserved so that, if the volume remains constant, $S - S_0 = -\frac{F - F_0}{T}$ where F is the Helmholtz free energy. The quantity $F_0 - F$ represents the minimal work to bring the equilibrium state to the state corresponding to F at constant temperature and volume.

The concept of minimal work is meaningful also in non–equilibrium and can be taken as a generalization of the free energy.

The difference with respect to an isolated system, or one in equilibrium with its environment, is that currents are flowing through the system. Currents are empirically related to spacial gradients of the thermodynamic variables and to external fields. The relationship is typically expressed by diffusion coefficients and conductivities and it is reasonable to expect that the minimal work to create a fluctuation can be calculated in terms of these quantities. In fact it can be shown that the calculation of the minimal work can be reduced to the solution of a variational principle if we restrict sufficiently the class of system considered. We shall concentrate on purely diffusive systems.

Hydrodynamics of diffusive systems

The macroscopic dynamics of diffusive systems is described by hydrodynamic equations provided by conservation laws and constitutive equations, that is equations expressing the current in terms of the thermodynamic variables. More precisely on the basis of a local equilibrium assumption, at the macroscopic level the system is completely described by a local multicomponent density $\rho(t,x)$ and the corresponding local currents $j(t,x)$. Their evolution is given by the continuity equation and the constitutive equation which expresses the current as a function of the density. Namely,

$$\begin{cases} \partial_t \rho(t) + \nabla \cdot j(t) = 0 \\ j(t) = J(\rho(t)) \end{cases} \tag{10}$$

where we omit the explicit dependence on the space variable x.

Constitutive equations

For diffusive systems the constitutive equation takes the form

$$J(\rho) = -D(\rho)\nabla\rho + \chi(\rho)\, E \tag{11}$$

where the *diffusion coefficient* $D(\rho)$ and the *mobility* $\chi(\rho)$ are $d \times d$ symmetric and positive definite matrices, E is an external field. These equations must be supplemented with boundary conditions expressing the interaction with the reservoirs. The diffusive regime is revealed in (11) by the absence of inertial terms. Equations (10) and (11) are macroscopic dynamical phenomenological laws of wide applicability. The input they require are the transport coefficients D, χ which are measurable quantities. Systems for which the current at time t can be expressed in terms of thermodynamic variables at the same time, as in (11), are called Markovian independently of whether the microscopic dynamics is Markovian or not.

Minimal work

We now sketch how for these systems the calculation of the minimal work to create a fluctuation can be reduced to the solution of a macroscopic variational principle, so that a detailed microscopic theory is not necessary. An important remark. The theory of stationary states includes as a particular case equilibrium and the usual thermodynamic free energy can be recovered via a dynamical calculation. This follows from the fact that in local equilibrium, which is necessary for the validity of the phenomenological equations, there is a relationship between the transport coefficients and the equilibrium free energy usually called Einstein relation. This is given by $D(\rho) = \chi(\rho) f''(\rho)$ where $f''(\rho)$ is the second derivative of the equilibrium free energy.

Consider a system in a stationary state characterized by a time independent solution $\bar{\rho}$ of the hydrodynamic equations and suppose that, due to a fluctuation, a value of the density ρ_0 is attained which is also the initial point of an arbitrary trajectory $\rho(t)$. Let in addition $j(t) - J(\rho(t))$ be a fluctuation of the current with respect to the value prescribed by the constitutive equation. The current j and the density ρ must always be connected by the continuity equation $\partial_t \rho(t) + \nabla \cdot j(t) = 0$.

The cost of this fluctuation will consist of two terms: the cost necessary to create the initial condition and the cost necessary to follow the trajectory $(j(t), \rho(t))$.

We shall denote the first term by $V(\rho_0)$ and in non–equilibrium will represent the analog of $S_0 - S$. It turns out that the second term is proportional to the energy dissipated by the extra current $j(t) - J(\rho(t))$

$$\mathcal{I}_{[T_0,T_1]}(\rho, j) = \frac{1}{4}\int_{T_0}^{T_1} dt \int_{\Lambda} dx \, [j - J(\rho)] \cdot \chi(\rho)^{-1} [j - J(\rho)] \quad (12)$$

For a simple interpretation of this formula think of an electric circuit. In this case χ^{-1} is the resistance and the double integral in (12) is the energy dissipated by $j(t) - J(\rho(t)$ according to Ohm's law. The factor $1/4$ is fixed by the gaussian nature of the stochasticity responsible for the fluctuations and by the consistency with equilibrium.

Using the Markovian hypothesis we can now write the probability of the joint fluctuations of density and current in a stationary state

$$\begin{aligned} P\big((\rho_\epsilon(t), j_\epsilon(t)) \approx (\rho(t), j(t))\,,\, t \in [T_0, T_1]\,\big) \\ \asymp \exp\big\{ -\epsilon^{-d}\, R_{[T_0,T_1]}(\rho, j)\big\} \end{aligned} \tag{13}$$

where

$$R_{[T_0,T_1]}(\rho, j) = V(\rho(T_0)) + \mathcal{I}_{[T_0,T_1]}(\rho, j) \tag{14}$$

Let us explain the meaning of the various symbols. The parameter ϵ is a dimensionless scaling factor, i.e. the ratio between the microscopic length scale (typical intermolecular distance) and the macroscopic one. The factor ϵ^{-d} is of the order of the number of particles in a macroscopic volume. The role of Avogadro's number in (6) is played here by ϵ^{-d}. With $\rho_\epsilon(t), j_\epsilon(t)$ we denote the empirical density and current corresponding to a coarse graining over a small macroscopic volume. Clearly these quantities depend on ϵ.

It is not difficult to see that the functional $V(\rho)$ is related to $\mathcal{I}_{[T_0,T_1]}(\rho, j)$ by projection

$$V(\rho) = \inf_{\substack{\rho(t),j(t):\\ \nabla\cdot j=-\partial_t\rho \\ \rho(-\infty)=\bar{\rho},\rho(0)=\rho}} \mathcal{I}_{[-\infty,0]}(\rho, j) \tag{15}$$

where $\bar{\rho}$ is the stationary solution.

A functional differential equation for V

$$\int_\Lambda dx\, \nabla \frac{\delta V}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta V}{\delta \rho} - \int_\Lambda dx\, \frac{\delta V}{\delta \rho} \nabla \cdot J(\rho) = 0\,. \tag{16}$$

This is the Hamilton-Jacobi equation associated to the variational principle (15). V is the maximal positive solution to (16) which vanishes when $\rho = \bar{\rho}$.

An example of calculation of $V(\rho)$: the boundary driven simple exclusion process

We consider the variational problem defining $V(\rho)$ for the one-dimensional simple exclusion process. In this case the associated Hamilton-Jacobi equation

$$\int_\Lambda \left(\nabla \frac{\delta V}{\delta \rho} \rho(1-\rho) \nabla \frac{\delta V}{\delta \rho} + \frac{\delta V}{\delta \rho} \Delta \rho \right) dx = 0 \qquad (17)$$

can be reduced to the a non-linear ordinary differential equation..

We obtain a solution of the Hamilton-Jacobi if we solve the following ordinary differential equation which relates the functional $\phi(x) = \phi(x;\rho)$ to ρ

$$\begin{cases} \dfrac{\Delta\phi(x)}{[\nabla\phi(x)]^2} + \dfrac{1}{1+e^{\phi(x)}} = \rho(x) \quad x \in (-1,1)\,, \\ \\ \phi(\pm 1) = \log \rho(\pm 1)/[1-\rho(\pm 1)]\,. \end{cases} \tag{18}$$

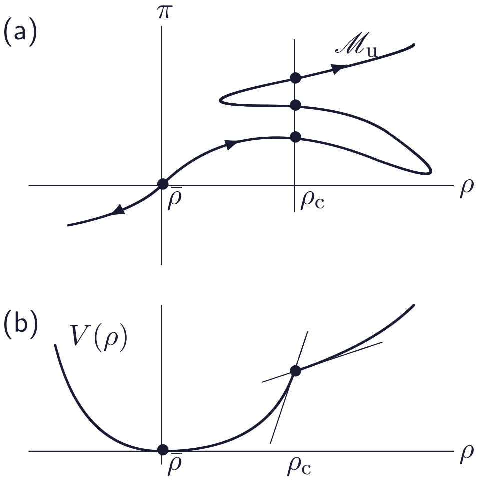
This equation admits a unique monotone solution which is the relevant one for the quasi-potential. A computation shows taht the functional

$$V(\rho) = F(\rho) + \int_\Lambda dx \left\{ (1-\rho)\phi + \log\left[\frac{\nabla\phi}{\nabla\bar{\rho}\,(1+e^{\phi})}\right]\right\} \tag{19}$$

satisfies the Hamilton-Jacobi equation when $\phi(x;\rho)$ solves (18).

Lagrangian phase transitions: singularities of $V(\rho)$

The quasi-potential $V(\rho)$ of the weakly asymmetric simple exclusion process is non-differentiable for large values of the external field if $\rho_0 < \rho_1$. This shows that there are phase transitions possible in non-equilibrium but not in equilibrium.


(a)
π
$\mathscr{M}_{\mathrm{u}}$
$\bar{\rho}$
ρ_{c}
ρ
(b)
$V(\rho)$
$\bar{\rho}$
ρ_{c}
ρ

Thermodynamics of currents: the $\Phi(J)$ functional

Currents involve time in their definition so it is natural to consider space-time thermodynamics. The *cost functional* to produce a current trajectory $j(t,x)$ is

$$\mathcal{I}_{[0,T]}(j) \; = \; \frac{1}{4}\int_0^T dt \left\langle [j - J(\rho)], \chi(\rho)^{-1}[j - J(\rho)] \right\rangle \tag{20}$$

in which we recall that

$$J(\rho) = -D(\rho)\nabla\rho + \chi(\rho)E \; .$$

where $\rho = \rho(t,u)$ is obtained by solving the continuity equation $\partial_t\rho + \nabla \cdot j = 0$.

Let $J(x)$ be the time average of $j(t,x)$ that we assume divergence free, i.e.

$$J(x) = \frac{1}{T}\int_0^T j(x,t)dt \tag{21}$$

and define

$$\Phi(J) = \lim_{T\to\infty} \inf_j \frac{1}{T}\,\mathcal{I}_{[0,T]}(j)\ , \tag{22}$$

where the infimum is carried over all paths $j = j(t,u)$ having time average J.
This functional is convex and satisfies a Gallavotti-Cohen type relationship

$$\Phi(J) - \Phi(-J) = \Phi(J) - \Phi^a(J) = -\langle J, E\rangle + \int_{\partial\Lambda} d\Sigma\,\lambda_0\,J\cdot\hat{n} \tag{23}$$

Note that the right hand side of (23) is the power produced by the external field and the boundary reservoirs. Entropy production can be simply derived from $\Phi(J)$).

Dynamical phase transitions: singularities of $\Phi(J)$

We consider the case when the matrices $D(\rho)$ and $\chi(\rho)$ are multiple of the identity, i.e., $D(\rho)_{i,j} = D(\rho)\delta_{i,j}$, $\chi(\rho)_{i,j} = \chi(\rho)\delta_{i,j}$, $i, j = 1, \dots, d$. We denote derivatives with a superscript. Let us first consider the case with no external field, i.e. $E = 0$. If

$$D(\rho)\chi''(\rho) \leq D'(\rho)\chi'(\rho) \quad \text{for any } \rho \tag{24}$$

this is a sufficient stability condition for not having a phase transition. However it has been recently shown by Akkermans and Shpielberg that is also necessary even in presence of an external field. Moreover if

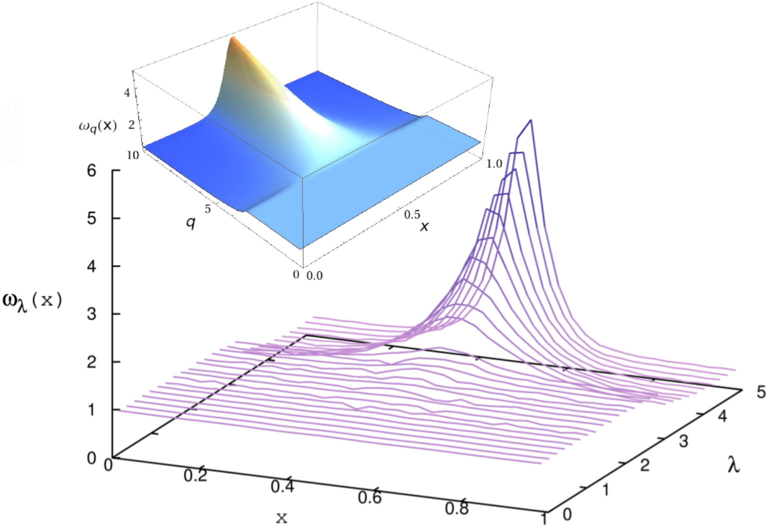
$$D(\rho)\chi''(\rho) = D'(\rho)\chi'(\rho) \quad \text{for any } \rho \tag{25}$$

then we have stability for any external field E.

Condition ((24)) is satisfied e.g. for the symmetric simple exclusion process, where $D = 1$ and $\chi(\rho) = \rho(1-\rho)$, $\rho \in [0,1]$. Condition ((25)) is satisfied either if D is proportional to χ' or χ is constant and D arbitrary. Examples are the zero range model, where $D(\rho) = \Psi'(\rho)$ and $\chi(\rho) = \Psi(\rho)$ for some strictly increasing function $\Psi : R_+ \to R_+$, and the non interacting Ginzburg–Landau model, where $D(\rho)$, $\rho \in R$, is an arbitrary strictly positive function and $\chi(\rho)$ is constant.

Numerical simulation

P. I. Hurtado, P.L. Garrido, Phys. Rev. Lett. **107**, *180601 (2011)*



Universality properties in higher dimensions

Akkermans, Bodineau, Derrida, Shpielberg

Consider a domain Λ in dimension $d > 1$ and assume that there are two external reservoirs, at densities ρ_A and ρ_B, in the regions $A, B \subset \Lambda$. The authors show that

$$\Phi^\sharp(s) = \mathrm{Cap}_\Lambda\big(A, B\big)\,\Phi_1^\sharp(s) \tag{26}$$

where $\Phi_1^\sharp$ is the Legendre transform of $\Phi_1(J)$ computed for a one-dimensional system on the interval $(0, 1)$ with boundary densities ρ_A, ρ_B. $\mathrm{Cap}_\Lambda\big(A, B\big)$ is the capacity, that depends only on the geometry, of a condenser formed by A and B in Λ. From (26) it follows in particular that the ratio between any pair of cumulants is the same as in one dimension.

Concluding remarks and outlook

- The MFT provides a unified treatment of the thermodynamics of driven diffusive systems and their fluctuations. Its formulation has required an adroit balancing of thermodynamic and statistical mechanics arguments. The outcome is a purely macroscopic theory which can be used as a phenomenological description requiring as input only the transport coefficients which are measurable. New variational principles are naturally formulated within the MFT.

- As the Boltzmann-Einstein formula, the MFT provides an interface between thermodynamics and the underlying microscopic world. It can thus be used in different ways. At the level of thermodynamics it introduces, for non-equilibrium states, the quasi-potential $V(\rho)$ as the analog of the free energy. Furthermore $\Phi(J)$ describes for the first time the thermodynamics of currents. With respect to Onsager theory, this is a further step in the formulation of a non-equilibrium thermodynamics for stationary states.

- Most challenging potential applications of the Macroscopic Fluctuation Theory may lie in biology. Indeed, many of the processes in living beings can be described as diffusive systems in stationary or quasi stationary states depending on the time scales considered.

Te Macroscopic Fluctuation Theory was developed over the last fifteen years with the contribution of many people. The following is a review with an extended bibliography

L. Bertini, A. De Sole, D. Gabrielli, G. Jona-Lasinio, C. Landim, Rev. Mod. Phys., 87, 593636 (2015), arXiv:1404.6466.