

INTRODUCTION

There is no theory so far of irreversible processes that is of the same generality as equilibrium statistical mechanics and presumably it cannot exist. While in equilibrium the Gibbs distribution provides all the information and no equation of motion has to be solved, the dynamics plays the major role in non equilibrium. The theory illustrated below refers to stationary states not restricted to being close to equilibrium and for a wide class of models it can be shown to be exact. In this case one begins to see the appearance of some general principles.

In equilibrium statistical mechanics there is a well defined relationship, established by Boltzmann, between the probability of a state and its entropy. This fact was exploited by Einstein to study thermodynamic fluctuations. When we are out of equilibrium, for example in a stationary state of a system in contact with two reservoirs, it is not completely clear how to define thermodynamic quantities like the entropy or the free energy. One possibility is to use fluctuation theory to define their non equilibrium analogs. In fact in this way extensive quantities can be obtained although not necessarily simply additive due to the presence of long range correlations which seem to be a rather generic feature of non equilibrium. This possibility has been pursued in recent years leading to a considerable number of interesting results. One can recognize two main lines:

1. exact calculations in simplified models. This is well exemplified by the work of Derrida, Lebowitz and Speer (2002).

2. a general treatment of a class of continuous time Markov chains for which the simplified models provide examples. This is the point of view developed by Bertini, De Sole, Gabrielli, Jona-Lasinio, Landim (2002, 2004).

Both approaches have been very effective and of course give the same results when a comparison is possible. The second approach seems to encompass a wide class of systems and has the advantage of leading to equations which apply to very different situations. This is the point of view we shall adopt in the following. The question whether there are alternative more natural ways of defining non equilibrium entropies or free energies is for the moment open.

BOLTZMANN-EINSTEIN FORMULA

The Boltzmann–Einstein theory of equilibrium thermodynamic fluctuations, as described for example in the book *Physique Statistique* by Landau-Lifshitz, states that the probability of a fluctuation from equilibrium in a macroscopic region of fixed volume V is proportional to $\exp\{V\Delta S/k\}$ where ΔS is the variation of entropy density in the region calculated along a reversible transformation creating the fluctuation and k is the Boltzmann constant.

This formula was derived by Einstein simply by inverting the Boltzmann relationship between entropy and probability. He considered this relationship as a phenomenological definition of the probability of a state.

Einstein theory refers to fluctuations from an equilibrium state, that is from a stationary state of a system isolated or in contact with reservoirs characterized by the same chemical potentials so that there is no flow of heat, electricity, chemical substances, etc. across the system. When in contact with reservoirs ΔS is the variation of the total entropy (system + reservoirs) which for fluctuations of constant volume and temperature is equal to $-\Delta F/T$, that is minus the variation of the free energy of the system divided by the temperature. In the following we shall refer to $\Delta F/T$, our main object of study, as the entropy and use the letter S for it but no confusion should arise.

The important question we address is then: what happens if the system is stationary but not in equilibrium, that is flows of physical quantities are present due to external fields and/or different chemical potentials at the boundaries? To start with it is not always clear whether a closed macroscopic dynamical description is possible. If the system admits such a description of the kind provided by hydrodynamic equations, a fact which can be rigorously established in simplified models, a reasonable goal is to find an explicit connection between time independent thermodynamic quantities like the entropy and dynamical macroscopic properties like transport coefficients. As we shall see the study of large fluctuations provides such a connection. It leads in fact to a dynamical theory of the entropy which is shown to satisfy a Hamilton-Jacobi equation (HJE) in infinitely many variables requiring as input the transport coefficients. Its solution is straightforward in the case of homogeneous equilibrium states and highly non trivial in stationary non equilibrium states (SNS). In the first case we recover a well known relationship widely used in the physical

and physico-chemical literature. There are several one-dimensional models, where the HJE reduces to a non linear ordinary differential equation which, even if it cannot be solved explicitly, leads to the important conclusion that the non equilibrium entropy is a non local functional of the thermodynamic variables. This implies that correlations over macroscopic scales are present. The existence of long range correlations is probably a generic feature of SNS and more generally of situations where the dynamics is not time reversal invariant. As a consequence if we divide a system into two subsystems the entropy is not necessarily simply additive.

The first step towards the definition of a non equilibrium entropy is the study of fluctuations in macroscopic evolutions described by hydrodynamic equations. In a dynamical setting a typical question one may ask is the following: what is the most probable trajectory followed by the system in the spontaneous emergence of a fluctuation or in its relaxation to an equilibrium or a stationary state? To answer this question one first derives a generalized Boltzmann-Einstein formula from which the most probable trajectory can be calculated by solving a variational principle. The entropy is related to the logarithm of the probability of such a trajectory and satisfies the HJE associated to the variational principle.

For states near equilibrium an answer to this type of questions was given by Onsager and Machlup in 1953. The Onsager-Machlup theory gives the following result under the assumption of time reversibility of the microscopic dynamics. In the situation of a linear hydrodynamic equation and small fluctuations, that is, close to equilibrium, the most probable creation and relaxation trajectories of a fluctuation are one the time reversal of the other. This conclusion holds also in nonlinear hydrodynamic regimes and without the assumption of small fluctuations. This follows from the study of concrete models. In SNS on the other hand time reversal invariance is broken and the creation and relaxation trajectories of a fluctuation are not one the time reversal of the other.

In the following we shall refer to boundary driven stationary non equilibrium states, e.g. a thermodynamic system in contact with reservoirs characterized by different temperatures and chemical potentials, but there is no difficulty in including an external field acting in the bulk.

MICROSCOPIC AND MACROSCOPIC DYNAMICS

We consider many-body systems in the limit of infinitely many degrees of freedom. The basic general assumptions of the theory is Markovian evolution. Microscopically we assume that the evolution is described by a Markov process X_τ which represents the state of the

system at time τ . This hypothesis probably is not so restrictive because also the dynamics of Hamiltonian systems interacting with thermostats finally is reduced to the analysis of a Markov process. Several examples are discussed in the literature. To be more precise X_τ represents the set of variables necessary to specify the state of the microscopic constituents interacting among themselves and with the reservoirs. The SNS is described by a stationary, i.e. invariant with respect to time shifts, probability distribution P_{st} over the trajectories of X_τ .

Macroscopically the usual interpretation of markovian evolution is that the time derivatives of thermodynamic variables $\dot{\rho}_i$ at a given instant of time depend only on the ρ_i 's and the affinities (thermodynamic forces) $\frac{\partial S}{\partial \rho_i}$ at the same instant of time. Our next assumption can then be formulated as follows: the system admits a macroscopic description in terms of density fields which are the local thermodynamic variables. For simplicity of notation we assume that there is only one thermodynamic variable ρ e.g. the density. The evolution of the field $\rho = \rho(t, u)$ where t and u are the macroscopic time and space coordinates (see below), is given by a diffusion type hydrodynamic equation of the form

$$\begin{aligned} \partial_t \rho &= \frac{1}{2} \nabla \cdot (D(\rho) \nabla \rho) \\ &= \frac{1}{2} \sum_{1 \leq i, j \leq d} \partial_{u_i} (D_{i,j}(\rho) \partial_{u_j} \rho) \\ &= \mathcal{D}(\rho) \end{aligned} \quad (1)$$

The interaction with the reservoirs appears as boundary conditions to be imposed on solutions of (1). We assume that there exists a unique stationary solution $\bar{\rho}$ of (1), i.e. a profile $\bar{\rho}(u)$, which satisfies the appropriate boundary conditions and such that $\mathcal{D}(\bar{\rho}) = 0$. This holds if the diffusion matrix $D_{i,j}(\rho)$ in (1) is strictly elliptic, namely there exists a constant $c > 0$ such that $D(\rho) \geq c$ (in matrix sense).

These equations derive from the underlying microscopic dynamics through an appropriate scaling limit in which the microscopic time and space coordinates τ, x are rescaled as follows: $t = \tau/N^2$, $u = x/N$ where N represents the linear size of the system. For lattice systems N is an integer. The hydrodynamic equation (1) represents a law of large numbers with respect to the probability measure P_{st} conditioned on an initial state X_0 . The initial conditions for (1) are determined by X_0 . Of course many microscopic configurations give rise to the same value of $\rho(0, u)$. In general $\rho = \rho(t, u)$ is an appropriate limit of a local observable $\rho_N(X_\tau)$ as the number N of degrees of freedom diverges.

The hypothesis of Markovian evolution is also the basis of the 1931 Onsager's theory of irreversible processes near equilibrium. Onsager however did not rely on any microscopic model and assumed near equilibrium linear hydrodynamic equations or regression equations as he

called them. His equations, ignoring space dependence, were of the form

$$\dot{\rho}_i = - \sum_j D_{ij} \rho_j \quad (2)$$

The diffusion matrix D is related to Onsager transport matrix χ and the entropy by the relationship

$$D = \chi s \quad (3)$$

where the elements of s are $\frac{\partial^2 S}{\partial \rho_i \partial \rho_j}$. The matrix χ is defined by the relationship between flows and affinities

$$\dot{\rho}_i = - \sum_j \chi_{ij} \frac{\partial S}{\partial \rho_j} \quad (4)$$

The indices ij here label different thermodynamic variables. The matrix χ is symmetric, a property known as Onsager reciprocity. Equations (2) and (3) follow by developing the entropy near an equilibrium state, that is by taking as an approximation a quadratic expression. The minus sign in equation (4) is due to our convention in which the entropy has the same sign as the free energy.

Equation (3) permits to reconstruct the entropy from the knowledge of the coefficients D and χ and has been widely used especially in physical chemistry. In SNS equation (3) is replaced by a Hamilton-Jacobi type equation for the entropy.

DYNAMICAL BOLTZMANN-EINSTEIN FORMULA

The basic assumption is that the stationary ensemble P_{st} admits a principle of large deviations describing the fluctuations of the thermodynamic variables appearing in the hydrodynamic equation. This means the following. The probability that for large N the evolution of the random variable ρ_N deviates from the solution of the hydrodynamic equation and is close to some trajectory $\hat{\rho}(t)$, is exponentially small and of the form

$$\begin{aligned} P_{st}(\rho_N(X_{N^2t}) \sim \hat{\rho}(t), t \in [t_1, t_2]) \\ \approx e^{-N^d [S(\hat{\rho}(t_1)) + J_{[t_1, t_2]}(\hat{\rho})]} \\ = e^{-N^d I_{[t_1, t_2]}(\hat{\rho})} \end{aligned} \quad (5)$$

where d is the dimensionality of the system, $J(\hat{\rho})$ is a functional which vanishes if $\hat{\rho}(t)$ is a solution of (1) and $S(\hat{\rho}(t_1))$ is the entropy cost to produce the initial density profile $\hat{\rho}(t_1)$. We normalize S so that $S(\bar{\rho}) = 0$. Therefore $J(\hat{\rho})$ represents the extra cost necessary to follow the trajectory $\hat{\rho}(t)$. Finally $\rho_N(X_{N^2t}) \sim \hat{\rho}(t)$ means closeness in some metric and \approx denotes logarithmic equivalence as $N \rightarrow \infty$. Equation (5) is the dynamical generalization of

the Boltzmann-Einstein formula. Experience with many models justifies this assumption.

To understand how (5) leads to a dynamical theory of the entropy we discuss its properties under time reversal. Let us denote by θ the time inversion operator defined by $\theta X_\tau = X_{-\tau}$. The probability measure P_{st}^* describing the evolution of the time reversed process X_τ^* is given by the composition of P_{st} and θ^{-1} that is

$$\begin{aligned} P_{st}^*(X_\tau^* = \phi_\tau, \tau \in [\tau_1, \tau_2]) \\ = P_{st}(X_\tau = \phi_{-\tau}, \tau \in [-\tau_2, -\tau_1]) \end{aligned} \quad (6)$$

Let L be the generator of the microscopic dynamics. We remind that L induces the evolution of observables (functions on the state space) according to the equation $\partial_\tau E_{X_0}[f(X_\tau)] = E_{X_0}[(Lf)(X_\tau)]$, where E_{X_0} stands for the expectation with respect to P_{st} conditioned on the initial state X_0 .

The time reversed dynamics, that is the dynamics which inverts the direction of the fluxes through the system, e.g. heat flows under this dynamics from lower to higher temperatures, is generated by the adjoint L^* of L with respect to the invariant measure μ

$$E^\mu[fLg] = E^\mu[(L^*f)g] \quad (7)$$

The measure μ , which is the same for both processes, is a distribution over the configurations of the system and formally satisfies $\mu L = 0$. The expectation with respect to μ is denoted by E^μ and f, g are observables. We note that the probability P_{st} , and therefore P_{st}^* , depends on the invariant measure μ . The finite dimensional distributions of P_{st} are in fact given by

$$\begin{aligned} P_{st}(X_{\tau_1} = \phi_{\tau_1}, \dots, X_{\tau_n} = \phi_{\tau_n}) \\ = \mu(\phi_{\tau_1}) p_{\tau_2 - \tau_1}(\phi_{\tau_1} \rightarrow \phi_{\tau_2}) \cdots p_{\tau_n - \tau_{n-1}}(\phi_{\tau_{n-1}} \rightarrow \phi_{\tau_n}) \end{aligned} \quad (8)$$

where $p_\tau(\phi_1 \rightarrow \phi_2)$ is the transition probability. According to (6) the finite dimensional distributions of P_{st}^* are

$$\begin{aligned} P_{st}^*(X_{\tau_1}^* = \phi_{\tau_1}, \dots, X_{\tau_n}^* = \phi_{\tau_n}) \\ = \mu(\phi_{\tau_1}) p_{\tau_2 - \tau_1}^*(\phi_{\tau_1} \rightarrow \phi_{\tau_2}) \cdots p_{\tau_n - \tau_{n-1}}^*(\phi_{\tau_{n-1}} \rightarrow \phi_{\tau_n}) \\ = \mu(\phi_{\tau_n}) p_{\tau_n - \tau_{n-1}}(\phi_{\tau_n} \rightarrow \phi_{\tau_{n-1}}) \cdots p_{\tau_2 - \tau_1}(\phi_{\tau_2} \rightarrow \phi_{\tau_1}) \end{aligned} \quad (9)$$

in particular the transition probabilities $p_\tau(\phi_1 \rightarrow \phi_2)$ and $p_\tau^*(\phi_1 \rightarrow \phi_2)$ are related by

$$\mu(\phi_1) p_\tau(\phi_1 \rightarrow \phi_2) = \mu(\phi_2) p_\tau^*(\phi_2 \rightarrow \phi_1) \quad (10)$$

This relationship reduces to the well known detailed balance condition if $p_\tau(\phi_1 \rightarrow \phi_2) = p_\tau^*(\phi_1 \rightarrow \phi_2)$.

We require that also the evolution generated by L^* admit a hydrodynamic description, that we call the adjoint hydrodynamics, which, however, is not necessarily of the same form as (1). In fact we shall consider models in which the adjoint hydrodynamics is non local in space.

In order to avoid confusion we emphasize that what is usually called an equilibrium state for a reversible dynamics, as distinguished from a SNS, corresponds to the special case $L^* = L$, i.e. the detailed balance principle holds. In such a case P_{st} is invariant under time reversal and the two hydrodynamics coincide.

We now derive a first consequence of our assumptions, that is the relationship between the functionals I and I^* associated to the dynamics L and L^* by (5). From equation (6) it follows that

$$I_{[t_1, t_2]}^*(\hat{\rho}) = I_{[-t_2, -t_1]}(\theta\hat{\rho}) \quad (11)$$

with obvious notations. More explicitly this equation reads

$$S(\hat{\rho}(t_1)) + J_{[t_1, t_2]}^*(\hat{\rho}) = S(\hat{\rho}(t_2)) + J_{[-t_2, -t_1]}(\theta\hat{\rho}) \quad (12)$$

where $\hat{\rho}(t_1), \hat{\rho}(t_2)$ are the initial and final points of the trajectory and $S(\hat{\rho}(t_i))$ the entropies associated with the creation of the fluctuations $\hat{\rho}(t_i)$ starting from the SNS. The functional J^* vanishes on the solutions of the adjoint hydrodynamics. To compute J^* it is necessary to know the entropy S .

We consider now the following physical situation. The system is macroscopically in the stationary state $\bar{\rho}$ at $t = -\infty$ but at $t = 0$ we find it in the state ρ . We want to determine the most probable trajectory followed in the spontaneous creation of this fluctuation. According to (5) this trajectory is the one that minimizes J among all trajectories $\hat{\rho}(t)$ connecting $\bar{\rho}$ to ρ in the time interval $[-\infty, 0]$. From (12), recalling that $S(\bar{\rho}) = 0$, we have that

$$J_{[-\infty, 0]}(\hat{\rho}) = S(\rho) + J_{[0, \infty]}^*(\theta\hat{\rho}) \quad (13)$$

The right hand side is minimal if $J_{[0, \infty]}^*(\theta\hat{\rho}) = 0$ that is if $\theta\hat{\rho}$ is a solution of the adjoint hydrodynamics. The existence of such a relaxation solution is due to the fact that the stationary solution $\bar{\rho}$ is attractive also for the adjoint hydrodynamics. We have therefore the following consequences

“In a SNS the spontaneous emergence of a macroscopic fluctuation takes place most likely following a trajectory which is the time reversal of the relaxation path according to the adjoint hydrodynamics”

This implies that the entropy is related to J by

$$S(\rho) = \inf_{\hat{\rho}} J_{[-\infty, 0]}(\hat{\rho}) \quad (14)$$

where the minimum is taken over all trajectories $\hat{\rho}(t)$ connecting $\bar{\rho}$ to ρ .

We note that the reversibility of the microscopic process X_τ , which we call microscopic reversibility, is not needed in order to deduce the Onsager–Machlup result (i.e. that the trajectory which creates the fluctuation is the time reversal of the relaxation trajectory). In fact

Onsager–Machlup holds if and only if the hydrodynamics coincides with the adjoint hydrodynamic, which we call macroscopic reversibility. Indeed it is possible to construct microscopic non reversible models, $L \neq L^*$, in which the hydrodynamics and the adjoint hydrodynamics coincide.

Spontaneous fluctuations, including Onsager–Machlup time-reversal symmetry, have been observed in stochastically perturbed reversible electronic devices. In non reversible systems an asymmetry between the emergence and the relaxation of fluctuations has been observed. The above discussion provides the explanation.

THE HAMILTON–JACOBI EQUATION AND ITS CONSEQUENCES

We assume that the functional J has a density (which plays the role of a Lagrangian), i.e.

$$J_{[t_1, t_2]}(\hat{\rho}) = \int_{t_1}^{t_2} dt \mathcal{L}(\hat{\rho}(t), \partial_t \hat{\rho}(t)) \quad (15)$$

Let us introduce the Hamiltonian $\mathcal{H}(\rho, H)$ as the Legendre transform of $\mathcal{L}(\rho, \partial_t \rho)$, i.e.

$$\mathcal{H}(\rho, H) = \sup_{\xi} \{ \langle \xi, H \rangle - \mathcal{L}(\rho, \xi) \} \quad (16)$$

where $\langle \cdot, \cdot \rangle$ denotes integration with respect to the macroscopic space coordinates u .

Noting that $\mathcal{H}(\bar{\rho}, 0) = 0$, the Hamilton–Jacobi equation associated to (14) is

$$\mathcal{H}\left(\rho, \frac{\delta S}{\delta \rho}\right) = 0 \quad (17)$$

This is an equation for the functional derivative $C(\rho) = \delta S / \delta \rho$ but not all the solutions of the equation $\mathcal{H}(\rho, C(\rho)) = 0$ are the derivative of some functional. Of course only those which are the derivative of a functional are relevant for us.

We now specify the Hamilton–Jacobi equation (17) for boundary driven lattice gases. For models with purely diffusive hydrodynamics (1) we expect a quadratic large deviation functional of the form

$$J_{[t_1, t_2]}(\hat{\rho}) = \frac{1}{2} \int_{t_1}^{t_2} dt \left\langle \nabla^{-1}(\partial_t \hat{\rho} - \mathcal{D}(\rho)), \chi(\hat{\rho})^{-1} \nabla^{-1}(\partial_t \hat{\rho} - \mathcal{D}(\rho)) \right\rangle \quad (18)$$

where $\mathcal{D}(\rho)$ is the right hand side of the hydrodynamic equation (1) and by $\nabla^{-1}f$ we mean a vector field whose divergence equals f . The form (18), which can be derived for several models is expected to be very general: the functional $J(\hat{\rho})$ measures how much $\hat{\rho}$ differs from a

solution of the hydrodynamics (1). The matrix $\chi(\rho)$ has the same role in our more general context, as the Onsager matrix in (4). This form of J is also typical for diffusion processes described by finite dimensional Langevin equations (Freidlin-Wentzell theory).

In this case the Lagrangian \mathcal{L} is quadratic in $\partial_t \hat{\rho}(t)$ and the associated Hamiltonian is given by

$$\mathcal{H}(\rho, H) = \frac{1}{2} \langle \nabla H, \chi(\rho) \nabla H \rangle + \langle H, \mathcal{D}(\rho) \rangle \quad (19)$$

so that the Hamilton–Jacobi equation (17) takes the form

$$\frac{1}{2} \left\langle \nabla \frac{\delta S}{\delta \rho}, \chi(\rho) \nabla \frac{\delta S}{\delta \rho} \right\rangle + \left\langle \frac{\delta S}{\delta \rho}, \mathcal{D}(\rho) \right\rangle = 0. \quad (20)$$

As well known in mechanics, the Hamilton–Jacobi equation has many solutions and we must give a criterion to select the correct one. The criterion which the correct solution has to satisfy is that it must be a Lyapunov function with respect to the unique stationary state.

It is a simple calculation to show that equation (3) follows from HJE if we look for a solution which is a local function of ρ . This is the right choice in equilibrium where correlations over macroscopic distances are not expected if the microscopic forces are short range.

Out of equilibrium it has been shown by direct calculation that for a special model, the symmetric simple exclusion, the entropy is a non local function of the thermodynamic variables, that is space correlations extend to macroscopic distances. This result can be derived in a simple way from HJE as we will discuss later.

Lattice gases which do not conserve the number of particles do not give rise in general to a purely diffusive hydrodynamics but rather to a reaction diffusion equation. In these case the large deviation functional will not have the quadratic form (18) and also the HJE will not be quadratic. An example in which particles can be created and destroyed, is the so called *Kawasaki-Glauber* dynamics. In this case HJE has exponential nonlinearities.

Non equilibrium fluctuation dissipation relation

We now derive a twofold generalization of the celebrated fluctuation dissipation relationship: it is valid in non equilibrium states and in non linear regimes.

Such a relationship will hold provided the rate function J^* of the time reversed process is of the form (18) with \mathcal{D} replaced by \mathcal{D}^* , the adjoint hydrodynamics,

$$\partial_t \rho = \mathcal{D}^*(\rho) \quad (21)$$

with the same boundary conditions as (1).

If J^* has the form

$$J_{[t_1, t_2]}^*(\hat{\rho}) = \frac{1}{2} \int_{t_1}^{t_2} dt \left\langle (\nabla^{-1} (\partial_t \hat{\rho} - \mathcal{D}^*(\hat{\rho})), \chi(\hat{\rho})^{-1} \nabla^{-1} (\partial_t \hat{\rho} - \mathcal{D}^*(\hat{\rho}))) \right\rangle \quad (22)$$

by taking the variation of equation (12), we get

$$\mathcal{D}(\rho) + \mathcal{D}^*(\rho) = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta S}{\delta \rho} \right) \quad (23)$$

This relation can be verified explicitly for the non-equilibrium zero range process which we discuss later and holds for several other models. It is also easy to check that the linearization of (23) around the stationary profile $\bar{\rho}$ yields a fluctuation dissipation relationship which reduces to the usual one in equilibrium.

The fluctuation dissipation relation (23) can be used to obtain the adjoint hydrodynamics from $\mathcal{D}(\rho)$ and $\delta S/\delta \rho$; the first is usually known and the second can be calculated from the Hamilton–Jacobi equation.

H Theorem

We show that the functional S is decreasing along the solutions of both the hydrodynamic equation (1) and the adjoint hydrodynamics

$$\partial_t \rho = \mathcal{D}^*(\rho) = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta S}{\delta \rho} \right) - \mathcal{D}(\rho) \quad (24)$$

Let $\rho(t)$ be a solution of (1) or (24), by using the Hamilton–Jacobi equation (20), we get

$$\begin{aligned} \frac{d}{dt} S(\rho(t)) &= \left\langle \frac{\delta S}{\delta \rho}(\rho(t)), \partial_t \rho(t) \right\rangle = \\ &= -\frac{1}{2} \left\langle \nabla \frac{\delta S}{\delta \rho}(\rho(t)), \chi(\rho(t)) \nabla \frac{\delta S}{\delta \rho}(\rho(t)) \right\rangle \leq 0 \end{aligned} \quad (25)$$

In particular we have that $\frac{d}{dt} S(\rho(t)) = 0$ if and only if $\frac{\delta S}{\delta \rho}(\rho(t)) = 0$.

We remark that the right hand side of (25) vanishes in the stationary state, that is there is no internal entropy production due to the evolution. On the other hand there is a steady entropy production due to the differences in the chemical potentials of the reservoirs. This will not be discussed in this article.

Decomposition of hydrodynamics

There is a structural property of hydrodynamics which follows from the HJE. The hydrodynamic equation can be decomposed as the sum of a gradient vector field and

a vector field \mathcal{A} orthogonal to it in the metric induced by the operator K^{-1} where $Kf = -\nabla \cdot (\chi(\rho)\nabla f)$, namely

$$\mathcal{D}(\rho) = \frac{1}{2}\nabla \cdot \left(\chi(\rho)\nabla \frac{\delta S}{\delta \rho} \right) + \mathcal{A}(\rho) \quad (26)$$

with

$$\left\langle K \frac{\delta S}{\delta \rho}, K^{-1} \mathcal{A}(\rho) \right\rangle = \left\langle \frac{\delta S}{\delta \rho}, \mathcal{A}(\rho) \right\rangle = 0$$

Similarly, using the fluctuation dissipation relationship (23), for the adjoint hydrodynamics we have

$$\mathcal{D}^*(\rho) = \frac{1}{2}\nabla \cdot \left(\chi(\rho)\nabla \frac{\delta S}{\delta \rho} \right) - \mathcal{A}(\rho) \quad (27)$$

Since \mathcal{A} is orthogonal to $\delta S/\delta \rho$, it does not contribute to the entropy production. The vector field \mathcal{A} is odd under time reversal: it behaves under time reversal like the Lorentz force, that is a magnetic term.

Both terms of the decomposition vanish in the stationary state that is when $\rho = \bar{\rho}$. Whereas in equilibrium the hydrodynamics is the gradient flow of the entropy S , the term $\mathcal{A}(\rho)$ is characteristic of non equilibrium states. Note that, for small fluctuations $\rho \approx \bar{\rho}$, small differences in the chemical potentials at the boundaries, $\mathcal{A}(\rho)$ becomes a second order quantity and Onsager theory is a consistent approximation.

Equation (26) is interesting because it separates the dissipative part of the hydrodynamic evolution associated to the thermodynamic force $\frac{\delta S}{\delta \rho}$ and provides therefore an important physical information. Notice that the thermodynamic force $\frac{\delta S}{\delta \rho}$ appears linearly in the hydrodynamic equation even when this is non linear in the macroscopic variables.

In general, the two terms of the decomposition (26) are non local in space even if \mathcal{D} is a local function of ρ . This is the case for the simple exclusion process discussed later. Furthermore while the form of the hydrodynamic equation does not depend explicitly on the chemical potentials, $\frac{\delta S}{\delta \rho}$ and \mathcal{A} do.

To understand how the decomposition (26) arises microscopically let us consider a stochastic lattice gas. Let L be its Markov generator; we can write it as follows

$$L = \frac{1}{2}(L + L^*) + \frac{1}{2}(L - L^*) \quad (28)$$

where L^* is the adjoint of L with respect to the invariant measure, namely the generator of the time reversed microscopic dynamics. The term $L - L^*$ behaves like a Liouville operator i.e. is antihermitian and, in the scaling limit, produces the term \mathcal{A} in the hydrodynamic equation. This can be verified explicitly in the boundary driven zero-range model introduced in the next section.

Since the adjoint generator can be written as $L^* = (L + L^*)/2 - (L - L^*)/2$, the adjoint hydrodynamics

must be of the form (27). In particular if the microscopic generator is self-adjoint, we get $\mathcal{A} = 0$ and thus $\mathcal{D}(\rho) = \mathcal{D}^*(\rho)$. On the other hand, it may happen that microscopic non reversible processes, namely for which $L \neq L^*$, can produce macroscopic reversible hydrodynamics if $L - L^*$ does not contribute to the hydrodynamic limit.

The decompositions (26) and (27) remind of the electrical conduction in presence of a magnetic field. Consider the motion of electrons in a conductor: a simple model is given by the effective equation

$$\dot{\mathbf{p}} = -e \left(\mathbf{E} + \frac{1}{mc} \mathbf{p} \wedge \mathbf{H} \right) - \frac{1}{\tau} \mathbf{p} \quad (29)$$

where \mathbf{p} is the momentum, e the electron charge, \mathbf{E} the electric field, \mathbf{H} the magnetic field, m the mass, c the velocity of the light, and τ the relaxation time. The dissipative term \mathbf{p}/τ is orthogonal to the Lorentz force $\mathbf{p} \wedge \mathbf{H}$. We define time reversal as the transformation $\mathbf{p} \mapsto -\mathbf{p}$, $\mathbf{H} \mapsto -\mathbf{H}$. The adjoint evolution is given by

$$\dot{\mathbf{p}} = e \left(\mathbf{E} + \frac{1}{mc} \mathbf{p} \wedge \mathbf{H} \right) - \frac{1}{\tau} \mathbf{p} \quad (30)$$

where the signs of the dissipation and the electromagnetic force transform in analogy to (26) and (27).

Let us consider in particular the Hall effect where we have conduction along a rectangular plate immersed in a perpendicular magnetic field H with a potential difference across the longer side. The magnetic field determines a potential difference across the other side of the plate. In our setting on the contrary it is the difference in chemical potentials at the boundaries that introduces in the equations a *magnetic-like* term. There is therefore a kind of equivalence between certain externally applied fields and driving the system at the boundaries.

Minimum dissipation principle

In 1931 Onsager formulated, within his near equilibrium theory, a variational principle which shows that the hydrodynamic evolution minimizes at each instant of time a quadratic functional of $\dot{\rho}$. He called this the *minimum dissipation principle*. We now show that the decomposition of the previous subsection leads to a natural exact generalization of this principle. We want to construct a functional of the variables ρ and $\dot{\rho}$ such that the Euler equation associated to the vanishing of the first variation under arbitrary changes of $\dot{\rho}$ is the hydrodynamic equation (1). We define the *dissipation function*

$$F(\rho, \dot{\rho}) = \left\langle (\dot{\rho} - \mathcal{A}(\rho)), K^{-1}(\dot{\rho} - \mathcal{A}(\rho)) \right\rangle \quad (31)$$

and the functional

$$\begin{aligned} \Phi(\rho, \dot{\rho}) &= \dot{S}(\rho) + F(\rho, \dot{\rho}) = \\ &\left\langle \frac{\delta S}{\delta \rho}, \dot{\rho} \right\rangle + \left\langle (\dot{\rho} - \mathcal{A}(\rho)), K^{-1}(\dot{\rho} - \mathcal{A}(\rho)) \right\rangle \end{aligned} \quad (32)$$

which generalize the corresponding Onsager's 1931 definitions. The operator K has been defined in the previous subsection.

It is easy to verify that

$$\delta_{\dot{\rho}} \Phi = 0 \quad (33)$$

is equivalent to the hydrodynamic equation (1). Furthermore, a simple calculation gives

$$F|_{\dot{\rho}=\mathcal{D}(\rho)} = \frac{1}{4} \left\langle \nabla \frac{\delta S}{\delta \rho}, \chi(\rho) \nabla \frac{\delta S}{\delta \rho} \right\rangle \quad (34)$$

that is $2F$ on the hydrodynamic trajectories equals the entropy production rate as in Onsager's near equilibrium approximation.

The dissipation function for the adjoint hydrodynamics is obtained by changing the sign of \mathcal{A} in (31).

Entropy and optimal control

There is an interesting interpretation of the entropy as a minimal cost to produce a fluctuation by externally acting on the system. The idea is to show that there exists a cost function which on the optimal control trajectory coincides with the entropy difference with respect to the stationary state.

We add an external perturbation v to the hydrodynamic equation

$$\partial_t \rho = \frac{1}{2} \nabla \cdot (D(\rho) \nabla \rho) + v = \mathcal{D}(\rho) + v \quad (35)$$

We want to choose v so as to drive, with minimal cost, the system from its stationary state $\bar{\rho}$ to an arbitrary state ρ . A simple cost function is

$$\frac{1}{2} \int_{t_1}^{t_2} ds \langle v(s), K^{-1}(\rho(s))v(s) \rangle \quad (36)$$

where $\rho(s)$ is the solution of (35) and we recall that $K(\rho)f = -\nabla \cdot (\chi(\rho) \nabla f)$. More precisely, given $\rho(t_1) = \bar{\rho}$ we want to drive the system to $\rho(t_2) = \rho$ by an external field v which minimizes (36). This is a standard problem in control theory. Let

$$\mathcal{V}(\rho) = \inf \frac{1}{2} \int_{t_1}^{t_2} ds \langle v(s), K^{-1}(\rho(s))v(s) \rangle \quad (37)$$

where the infimum is taken with respect to all fields v which drive the system to ρ in an arbitrary time interval

$[t_1, t_2]$. The optimal field v can be obtained by solving the Bellman equation which reads

$$\min_v \left\{ \frac{1}{2} \langle v, K^{-1}(\rho)v \rangle - \left\langle \mathcal{D}(\rho) + v, \frac{\delta \mathcal{V}}{\delta \rho} \right\rangle \right\} = 0 \quad (38)$$

It is easy to express the optimal v in terms of \mathcal{V} ; we get

$$v = K \frac{\delta \mathcal{V}}{\delta \rho} \quad (39)$$

Hence (38) now becomes

$$\frac{1}{2} \left\langle \frac{\delta \mathcal{V}}{\delta \rho}, K(\rho) \frac{\delta \mathcal{V}}{\delta \rho} \right\rangle + \left\langle \mathcal{D}(\rho), \frac{\delta \mathcal{V}}{\delta \rho} \right\rangle = 0 \quad (40)$$

By identifying the cost functional $\mathcal{V}(\rho)$ with $S(\rho)$, equation (40) coincides with the Hamilton–Jacobi equation (20).

By inserting the optimal v (39) in (35) and identifying \mathcal{V} with S , we get that the optimal trajectory $\rho(t)$ solves the time reversed adjoint hydrodynamics, namely

$$\partial_t \rho = -\mathcal{D}^*(\rho) \quad (41)$$

The trajectory of the spontaneous emergence of a fluctuation coincides therefore with the trajectory of minimal cost for the optimal control. The optimal field v does not depend on the non dissipative part \mathcal{A} of the hydrodynamics.

MODELS

The general theory will be now illustrated by briefly describing models where it has been successfully applied. We consider examples of different nature in order to emphasize the generality and flexibility of the point of view developed in the previous paragraphs.

We have chosen three examples in which the theory is used in different ways. The first one, the zero range process, can be solved in a simple way so that the theory can be verified in detail. In the second one, the symmetric simple exclusion, we derive from the HJE a non linear ordinary differential equation first obtained by Derrida, Lebowitz and Speer through a direct rather complex calculation. This equation implies the non locality of the entropy in the SNS of this model. The third model, the Kawasaki-Glauber dynamics, provides the illustration of two aspects. Non locality of the entropy, that is long range correlations, can appear in isolated equilibrium states if the microscopic dynamics is not time reversal invariant. This means that long range correlations as a signature of time reversal violation is not restricted to SNS. The second aspect to be underlined is the effectiveness of the HJE in a more complex case: in fact in this model the number of particles is not conserved which leads to a very complicated structure of the HJE.

As a general comment we emphasize that dynamics microscopically different but leading to the same macroscopic description, in particular the same hydrodynamics and large deviation functional, are indistinguishable for the theory which is purely macroscopic.

Zero range

We consider the so called zero-range process which models a nonlinear diffusion of a lattice gas. The model is described by a positive integer variable $\eta_\tau(x)$ representing the number of particles at site x and time τ of a finite lattice which for simplicity we assume one-dimensional. The particles jump with rates $g(\eta(x))$ to one of the nearest-neighbor sites $x+1, x-1$ with probability $1/2$. The function $g(k)$ is non decreasing and $g(0) = 0$. We assume that our system interacts with two reservoirs of particles in positions N and $-N$ with rates p_+ and p_- respectively. This model can be solved exactly and the previous theory can be checked in full detail.

Let us introduce the macroscopic coordinates, time $t = \tau/N^2$ and space $u = x/N$. To describe the macroscopic dynamics we introduce the empirical density

$$\rho_N(t, u) = \frac{1}{N} \sum_{x=-N}^N \eta_{N^2 t}(x) \delta(u - x/N) \quad (42)$$

where $\delta(u - x/N)$ is the Dirac δ . One can prove that in the limit $N \rightarrow \infty$ the empirical density (42) tends in probability to a continuous function $\rho_t(u)$ which satisfies the following hydrodynamic equation

$$\partial_t \rho = \frac{1}{2} \Delta \phi(\rho) = \mathcal{D}(\rho) \quad (43)$$

where $\phi(\rho)$ can be explicitly defined in terms of the rates $g(\eta)$. The boundary conditions for (43) are $\phi(\rho(t, \pm 1)) = p_\pm$.

The adjoint hydrodynamics is

$$\partial_t \rho = \frac{1}{2} \Delta \phi(\rho) - \alpha \nabla \left\{ \frac{\phi(\rho)}{\lambda(u)} \right\} = \mathcal{D}^*(\rho) \quad (44)$$

with $\lambda(u) = \frac{p_+ - p_-}{2} u + \frac{p_+ + p_-}{2}$ and $\alpha = \frac{p_+ - p_-}{2}$. The boundary conditions for (44) are the same as for (43). The second term on the right hand side of (44) is proportional to the difference of the chemical potentials and produces an inversion of the particle flux. The action functionals $J(\hat{\rho})$ and $J^*(\hat{\rho})$ for this model have been computed and have the form (18) and (22) respectively with $\chi(\rho) = \phi(\rho)$. The entropy $S(\rho)$ can be easily computed directly from the expression of the invariant measure which is of product type and is known explicitly

$$S(\rho) = \int_{-1}^1 du \left[\rho(u) \log \frac{\phi(\rho(u))}{\lambda(u)} - \log \frac{Z(\phi(\rho(u)))}{Z(\lambda(u))} \right] \quad (45)$$

where $Z(\phi) = 1 + \sum_{k=1}^{\infty} \frac{\phi^k}{g(1) \cdots g(k)}$. It is easy to verify that it solves the HJE. Due to the special zero range character of the interaction in this model there are no long range correlations in non equilibrium states.

Simple exclusion

The simple exclusion process is a model of a lattice gas with an exclusion principle: a particle can move to a neighboring site, with rate $1/2$ for each side, only if this is empty. We consider again a one dimensional case and we denote by $\eta_x(\tau) \in \{0, 1\}$ the number of particles at the site x at (microscopic) time τ . The system is in contact with particle reservoirs at the boundaries $\pm N$ where a particle is created with rates p_\pm if the boundary site is empty and is destroyed with rates $1 - p_\pm$ if it is occupied. In contrast to the zero range model the invariant measure carries long range correlations making the entropy non local.

The hydrodynamic equation for the simple exclusion process can be derived as for the zero range process; in fact it is easier in this case because a simple computation leads directly to a closed equation for the empirical density which is defined as in (42) except that the variable η now takes only the values 0 or 1. We find that the limiting density evolves according to the linear heat equation

$$\partial_t \rho(t, u) = \frac{1}{2} \Delta \rho(t, u) = \mathcal{D}(\rho) \quad (46)$$

with boundary conditions $\rho(t, \pm 1) = \frac{p_\pm}{1+p_\pm} = \rho_\pm$. In this case the density of particles ρ takes values in $[0, 1]$. We use the HJE to calculate the entropy. For this model we have $\chi(\rho) = \rho(1 - \rho)$. We show that the solution of the HJE for $S(\rho)$ (which is a functional derivative equation) can be reduced to the solution of an ordinary differential equation.

The Hamilton-Jacobi equation for the simple exclusion process is

$$\left\langle \nabla \frac{\delta S}{\delta \rho}, \rho(1 - \rho) \nabla \frac{\delta S}{\delta \rho} \right\rangle + \left\langle \frac{\delta S}{\delta \rho}, \Delta \rho \right\rangle = 0 \quad (47)$$

We look for a solution of the form

$$\frac{\delta S}{\delta \rho(u)} = \log \frac{\rho(u)}{1 - \rho(u)} - \phi(u; \rho) \quad (48)$$

for some functional $\phi(u; \rho)$ to be determined satisfying the boundary conditions $\phi(\pm 1) = \log \frac{\rho_\pm}{1 - \rho_\pm}$ in the space variable. The first term on the right hand side is the derivative of the equilibrium entropy, that is for boundary conditions $\rho_- = \rho_+$.

Inserting (48) into (47), we get (note that $\rho -$

$e^\phi/(1+e^\phi)$ vanishes at the boundary)

$$\begin{aligned}
0 &= -\left\langle \nabla \left(\log \frac{\rho}{1-\rho} - \phi \right), \rho(1-\rho) \nabla \phi \right\rangle \\
&= -\langle \nabla \rho, \nabla \phi \rangle + \langle \rho(1-\rho), (\nabla \phi)^2 \rangle \\
&= -\left\langle \nabla \left(\rho - \frac{e^\phi}{1+e^\phi} \right), \nabla \phi \right\rangle \\
&\quad - \left\langle \left(\rho - \frac{e^\phi}{1+e^\phi} \right) \left(\rho - \frac{1}{1+e^\phi} \right), (\nabla \phi)^2 \right\rangle \\
&= \left\langle \left(\rho - \frac{e^\phi}{1+e^\phi} \right), \left(\Delta \phi + \frac{(\nabla \phi)^2}{1+e^\phi} - \rho(\nabla \phi)^2 \right) \right\rangle
\end{aligned}$$

We obtain a non trivial solution of the Hamilton–Jacobi if we solve the following ordinary differential equation, corresponding to the vanishing of the right side of the scalar product, which relates the functional $\phi(u) = \phi(u; \rho)$ to ρ

$$\begin{cases} \frac{\Delta \phi(u)}{[\nabla \phi(u)]^2} + \frac{1}{1+e^{\phi(u)}} = \rho(u) & u \in (-1, 1) \\ \phi(\pm 1) = \log \frac{\rho_\pm}{1-\rho_\pm} \end{cases} \quad (49)$$

It is clear that ϕ is a non local functional of ρ . A computation shows that the derivative of the functional

$$\begin{aligned}
S(\rho) &= \int du \left\{ \rho \log \rho + (1-\rho) \log(1-\rho) \right. \\
&\quad \left. + (1-\rho)\phi - \log(1+e^\phi) + \log \frac{\nabla \phi}{\nabla \bar{\rho}} \right\}
\end{aligned}$$

is given by (48) when $\phi(u; \rho)$ solves (49).

Kawasaki-Glauber dynamics

The model consists of particles on a lattice evolving according to two basic dynamical processes:

- i) a particle can move to a neighbouring site if this is empty as in the simple exclusion.
- ii) a particle can disappear in an occupied site or be created if this is empty, the rate depending on the nearby configuration.

The first process is conservative while the second is not.

As before the object of our study is the empirical density (42). It is possible to show that as N goes to infinity $\rho(t, u)$ is a solution of

$$\partial_t \rho = \frac{1}{2} \Delta \rho + B(\rho) - D(\rho) \quad (50)$$

with

$$B(\rho) = E_{\nu_\rho}(c(\eta)(1-\eta(0))) \quad (51)$$

$$D(\rho) = E_{\nu_\rho}(c(\eta)\eta(0)) \quad (52)$$

where ν_ρ is the Bernoulli product distribution with parameter ρ . Typically $B(\rho)$ and $D(\rho)$ are polynomials in ρ . For this model we consider equilibrium states so that we can take periodic boundary conditions. An equilibrium state corresponds to a density $\bar{\rho}$ which is the solution of the equation $B(\rho) = D(\rho)$ and gives a minimum of the potential $V(\rho) = \int^\rho [D(\rho') - B(\rho')] d\rho'$. We admit potentials with several minima. The Hamiltonian associated to the large deviation functional for this model is not quadratic

$$\begin{aligned}
\mathcal{H}(\rho, H) &= \int du \left\{ \frac{1}{2} H \Delta \rho + \frac{1}{2} (\nabla H)^2 \rho(1-\rho) \right. \\
&\quad \left. - B(\rho)(1 - \exp H) - D(\rho)(1 - \exp -H) \right\} \quad (53)
\end{aligned}$$

where H has the role of the conjugate momentum. The Hamilton-Jacobi equation

$$\mathcal{H}(\rho, \frac{\delta S}{\delta \rho}) = 0 \quad (54)$$

is therefore very complicated but can be solved by successive approximations using as an expansion parameter $\rho - \bar{\rho}$ where $\bar{\rho}$ is a solution of $B(\rho) = D(\rho)$ that is a stationary solution of hydrodynamics. For $\rho = \bar{\rho}$ we have $\frac{\delta S}{\delta \rho} = 0$. We are looking for an approximate solution of (54) of the form

$$S(\rho) = \frac{1}{2} \int du \int dv (\rho(u) - \bar{\rho}) k(u, v) (\rho(v) - \bar{\rho}) + o(\rho - \bar{\rho})^2 \quad (55)$$

The kernel $k(u, v)$ is the inverse of the density correlation function $c(u, v)$.

$$\int c(u, y) k(y, v) dy = \delta(u - v) \quad (56)$$

By inserting (55) in (54) one can show that $k(u, v)$ satisfies the following equation

$$\begin{aligned}
\frac{1}{2} \bar{\rho}(1-\bar{\rho}) \Delta_u k(u, v) - b_0 k(u, v) - \frac{1}{2} \Delta_u \delta(u-v) \\
+ (d_1 - b_1) \delta(u-v) = 0 \quad (57)
\end{aligned}$$

where

$$b_1 = B'(\rho)|_{\rho=\bar{\rho}}, \quad d_1 = D'(\rho)|_{\rho=\bar{\rho}}$$

and

$$b_0 = B(\bar{\rho}) = D(\bar{\rho}) = d_0 \quad (58)$$

If the entropy is a local functional of the density, $k(u, v)$ must be of the form $k(u, v) = f(\bar{\rho}) \delta(u-v)$ which inserted in (57) gives

$$f(\bar{\rho}) = [\bar{\rho}(1-\bar{\rho})]^{-1} \quad (59)$$

and

$$b_0[\bar{\rho}(1 - \bar{\rho})]^{-1} - (d_1 - b_1) = 0. \quad (60)$$

Therefore if b_0, b_1, d_1 do not satisfy the last equation the entropy cannot be a local functional of the density. It can be shown that in this case time reversal invariance is violated and the adjoint hydrodynamics is different from (50). This calculation supports the conjecture that macroscopic correlations are a generic feature of equilibrium states of non reversible lattice gases.

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