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Towards a Nonequilibrium Thermodynamics: A Self-Contained Macroscopic Description of Driven Diffusive Systems

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Abstract In this paper we present a self-contained macroscopic description of diffusive systems interacting with boundary reservoirs and under the action of external fields. The approach is based on simple postulates which are suggested by a wide class of microscopic stochastic models where they are satisfied. The description however does not refer in any way to an underlying microscopic dynamics: the only input required are transport coefficients as functions of thermodynamic variables, which are experimentally accessible. The basic postulates are local equilibrium which allows a hydrodynamic description of the evolution, the Einstein relation among the transport coefficients, and a variational principle defining the out of equilibrium free energy. Associated to the variational principle there is a Hamilton-Jacobi equation satisfied by the free energy, very useful for concrete calculations. Correlations over a macroscopic scale are, in our scheme, a generic property of nonequi-

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librium states. Correlation functions of any order can be calculated from the free energy functional which is generically a non local functional of thermodynamic variables. Special attention is given to the notion of equilibrium state from the standpoint of nonequilibrium.

Keywords Nonequilibrium processes · Stationary states · Long range correlations

1 Introduction

The main purpose of the present paper is to describe a "physical theory" for a certain class of thermodynamic systems out of equilibrium, which is founded on and supported by the analysis of a large family of stochastic microscopic models. Out of equilibrium the variety of phenomena one can conceive makes it difficult to define general classes of phenomena for which a unified study is possible. Furthermore the details of the microscopic dynamics play a far greater role than in equilibrium. Since the first attempts to construct a non equilibrium thermodynamics, a guiding idea has been that of *local equilibrium*, which means that locally on the macroscopic scale it is possible to define thermodynamic variables like density, temperature, chemical potentials... which vary smoothly on the same scale. Microscopically this implies that the system reaches local equilibrium in a time which is short compared to the times typical of macroscopic evolutions, as described for example by *hydrodynamic equations*. There are important cases however where local equilibrium apparently fails like aging phenomena in disordered systems due to insufficient ergodicity. These will not be considered in this paper. Also the case in which magnetic fields play a role is not covered by our analysis.

The simplest nonequilibrium states one can imagine are *stationary states* of systems in contact with different reservoirs and/or under the action of external (electric) fields. In such cases, contrary to equilibrium, there are currents (electrical, heat, matter of various chemical constitutions ...) through the system whose macroscopic behavior is encoded in transport coefficients like the diffusion coefficient, the conductivity or the mobility.

The ideal would be to approach the study of these states starting from a microscopic dynamics of molecules interacting with realistic forces and evolving with Newtonian dynamics. This is beyond the reach of present day mathematical tools and much simpler models have to be adopted in the reasonable hope that some essential features are adequately captured. In the last decades stochastic models of interacting particle systems have provided a very useful laboratory for studying properties of stationary nonequilibrium states. From the study of these models has emerged a macroscopic theory for nonequilibrium diffusive systems which can be used as a phenomenological theory.

A basic issue is the definition of nonequilibrium thermodynamic functions. For stochastic lattice gases a natural solution to this problem has been given via a theory of dynamic large deviations (deviations from hydrodynamic trajectories) and an associated variational principle leading to a definition of the free energy in terms of transport coefficients.

One of the main differences between equilibrium and nonequilibrium systems, is that out of equilibrium the free energy is, in general, a non local functional thus implying the existence of correlations at the macroscopic scale. These correlations have been observed experimentally [11] and appear to be a generic consequence of our variational principle which can be reformulated as a time independent Hamilton-Jacobi equation for the free energy. This is a functional derivative equation whose independent arguments are the local thermodynamic variables and which requires as input the transport coefficients. The presence of long range correlations for out of equilibrium states had been derived within kinetic theory, see [11] and reference therein, as well as within fluctuating hydrodynamics, see e.g. [27].

We believe that the theory we propose is a substantial improvement with respect to the theory developed long ago by Onsager [23, 24] and then by Onsager-Machlup [25] which applies to states close to equilibrium, namely for linear evolution equations, and does not really include the effect of nontrivial boundary reservoirs. In principle, the theory we suggest should be applicable to real systems, i.e. with nonlinear evolution equations and arbitrary boundary conditions, where the diffusion is the dominant dynamical mechanism. We emphasize however that we assume a linear response with respect to the external applied field. Of course, the Onsager theory is recovered as first order approximation.

The basic principle of the theory here proposed is a variational principle for the nonequilibrium thermodynamic functionals. This principle has the following content. Take the stationary state as the reference state and consider a trajectory leading the system to a new state. This trajectory can be realized by imposing a suitable additional external field (in addition to the one already acting on the system). Then compute the work done by this extra field and minimize it over all possible trajectories leading to the new state. This minimal work is identified with the variation of the free energy between the reference and the final state. As well known in thermodynamics, in the case of equilibrium states this definition agrees with the standard one.

Our treatment is based on an approach developed by the authors in the analysis of fluctuations in stochastic lattice gases [1–7]. For recent overviews on nonequilibrium phenomena see also [13, 18, 22] and [26] for a different approach which includes a discussion on long range correlations.

The outline of the paper is the following.

In Sect. 2 we introduce the basic principles for a self-contained macroscopic description of driven diffusive systems out of equilibrium. These systems are described by local thermodynamic variables which evolve according to (nonlinear) diffusion equations with boundary conditions and/or external fields which force the system out of equilibrium. We emphasize that such evolution equations have the structure of conservation laws. The possibility of such description is of course based on the assumption of local equilibrium. We then formulate mathematically the above mentioned variational principle for the nonequilibrium free energy and characterize the optimal trajectory. As we already remarked, our approach gives the usual equilibrium free energy when we consider an equilibrium state. In this connection, we remark that the optimal trajectory provides a dynamical alternative to the usual prescription of equilibrium thermodynamics to calculate the free energy variation via a quasi static transformation.

In Sect. 3 we discuss the notion of *equilibrium* from the standpoint of *nonequilibrium* under the assumptions formulated is Sect. 2. In particular we introduce the notion of macroscopic reversibility and discuss its relationship, actually equivalence, to thermodynamic equilibrium. An important outcome of our analysis is that the correct definition of equilibrium, for the driven diffusive systems here considered, is the vanishing of the currents. Nonetheless, in presence of external (electric) fields and boundary reservoirs an equilibrium state can be highly inhomogeneous. An example of such a situation is provided by sedimentation equilibrium in gravitational and centrifugal fields. In spite of this, the free energy is a local function of the state variables and coincides locally with the equilibrium free energy in absence of external fields and boundary driving. In particular there are no macroscopic correlations.

In Sect. 4 we derive from the Hamilton-Jacobi equation the generic existence of long range correlations in nonequilibrium states and we discuss the conditions on the transport coefficients for their appearance in the two point correlation function. We also establish a simple criterion to determine whether density fluctuations are positively or negatively correlated. Finally, from the Hamilton-Jacobi equation, by expanding around the stationary state, we derive a recursive equation for the correlation functions of any order.

In Appendix we discuss a specific example, the *ABC model* [10, 14] which does not satisfy all the assumptions formulated in Sect. 2. In fact the ABC model has the peculiarity to be a reversible system with a nonlocal free energy. We show nonetheless that this free energy can be easily derived from the Hamilton-Jacobi equation. This model has been brought to our attention by D. Mukamel and J.L. Lebowitz.

2 Macroscopic Systems out of Equilibrium

We here introduce the thermodynamic description for out of equilibrium driven diffusive systems which are characterized by conservation laws. For simplicity of notation, we restrict to the case of a single conservation law, e.g. the conservation of the mass. The system is in contact with boundary reservoirs, characterized by their chemical potential λ_0, and under the action of an external field E. We denote by $\Lambda \subset \mathbb{R}^d$ the region occupied by the system, by x the macroscopic space coordinates and by t the time. We next state our basic axioms and their main implications.

1. *The macroscopic state is completely described by the local density* $\rho = \rho(t,x)$ *and the associated current* $j = j(t,x)$.
2. *The macroscopic evolution is given by the continuity equation*

$$\partial_t \rho + \nabla \cdot j = 0 \tag{2.1}$$

together with the constitutive equation

$$j = J(\rho) = -D(\rho)\nabla\rho + \chi(\rho)E \tag{2.2}$$

where the diffusion coefficient $D(\rho)$ *and the* mobility $\chi(\rho)$ *are* $d \times d$ *positive matrices. The transport coefficients* D *and* χ *satisfy the local Einstein relation*

$$D(\rho) = \chi(\rho) f_0''(\rho) \tag{2.3}$$

where f_0 *is the equilibrium free energy of the homogeneous system. The equations* (2.1)–(2.2) *have to be supplemented by the appropriate boundary conditions on* $\partial\Lambda$ *due to the interaction with the external reservoirs. Recalling that* $\lambda_0(x)$, $x \in \partial\Lambda$, *is the chemical potential of the external reservoirs, these boundary conditions are*

$$f_0'\big(\rho(x)\big) = \lambda_0(x), \qquad x \in \partial\Lambda \tag{2.4}$$

We denote by $\bar\rho = \bar\rho(x)$, $x \in \Lambda$, *the stationary solution, assumed to be unique, of* (2.1), (2.2), *and* (2.4).

In postulating the constitutive equation (2.2) we assumed a linear response with respect to the external field E and the thermodynamic forces. On the other hand the transport coefficients D and χ are allowed to depend on the density ρ. In the case the system has more than one component, say n, the diffusion coefficient D and the mobility become $nd \times nd$ matrices. Moreover, in view of Onsager reciprocity, the matrix χ is symmetric both in the space and in the component indices while D is symmetric only in the space indices. In such a case the local Einstein relation (2.3) is $D = \chi R$ where $R_{ij} = \partial_{\rho_i} \partial_{\rho_j} f_0$ does not depend on the space indices. In the context of stochastic lattice gases, (2.1) and (2.2) describe the evolution of the empirical density in the diffusive scaling limit, see e.g. [6, 19, 28]; the validity of the local Einstein relationship (2.3) can be deduced from the local detailed balance of the underlying microscopic dynamics, see e.g. [28]. However, as we will see later, (2.3) it is also a consequence of the locality of the free energy and our third postulate once equilibrium is characterized within our theory.

To state the third postulate, we need some preliminaries. Consider a time dependent variation $F = F(t,x)$ of the external field so that the total applied field is $E + F$. The local current then becomes $j = J^F(\rho) = J(\rho) + \chi(\rho)F$. Given a time interval $[T_1, T_2]$, we compute the energy necessary to create the extra current $J^F - J$ and drive the system along the corresponding trajectory:

$$L_{[T_1,T_2]}(F) = \int_{T_1}^{T_2} dt \big\langle \big[J^F(\rho^F) - J(\rho^F)\big] \cdot F \big\rangle = \int_{T_1}^{T_2} dt \big\langle F \cdot \chi(\rho^F) F \big\rangle \tag{2.5}$$

where $\cdot$ is the scalar product in $\mathbb{R}^d$, $\langle \cdot \rangle$ is the integration over Λ, and ρ^F is the solution of the continuity equation with current $j = J^F(\rho)$.

We define a *cost functional* on the set of space time trajectories as follows. Given a trajectory $\hat\rho = \hat\rho(t,x)$, $t \in [T_1, T_2]$, $x \in \Lambda$, we set

$$I_{[T_1,T_2]}(\hat\rho) = \frac{1}{4} \inf_{F:\rho^F = \hat\rho} L_{[T_1,T_2]}(F) \tag{2.6}$$

namely we minimize over the variations F of the applied field which produce the trajectory $\hat\rho$. The introduction of this functional in the context of fluid dynamics equations appears to be new. The functional I (with the factor 1/4) has a precise statistical interpretation within the context of stochastic lattice gases: it gives the asymptotics, as the number of degrees of freedom diverges, of the probability of observing a space time fluctuation of the empirical density [1, 2, 5, 19, 20]. Note indeed that if $\hat\rho$ solves the hydrodynamic equation (2.1), (2.2), (2.4) its cost vanishes. We shall explain below the choice of the factor 1/4 in (2.6).

We next show that the optimal F in (2.6) is given by $F = \nabla \Pi$ where $\Pi : [T_1, T_2] \times \Lambda \to \mathbb{R}$ is the unique solution to the Poisson equation

$$-\nabla \cdot \big[\chi(\hat\rho) \nabla \Pi\big] = \partial_t \hat\rho + \nabla \cdot J(\hat\rho)$$

which vanishes at the boundary of Λ for any $t \in [T_1, T_2]$. Indeed, by writing $F = \nabla \Pi + \tilde F$ for each $t \in [T_1, T_2]$ we have the orthogonal decomposition

$$\big\langle F \cdot \chi(\hat\rho) F \big\rangle = \big\langle \nabla \Pi \cdot \chi(\hat\rho) \nabla \Pi \big\rangle + \big\langle \tilde F \cdot \chi(\hat\rho) \tilde F \big\rangle$$

where we used that $\partial_t \hat\rho + \nabla \cdot J^F(\hat\rho) = 0$. The above equation clearly shows that $\tilde F = 0$ is the optimal choice. Hence

$$I_{[T_1,T_2]}(\hat\rho) = \frac{1}{4} \int_{T_1}^{T_2} dt \Big\langle \big[\partial_t \hat\rho + \nabla \cdot J(\hat\rho)\big] K(\hat\rho)^{-1} \big[\partial_t \hat\rho + \nabla \cdot J(\hat\rho)\big] \Big\rangle \tag{2.7}$$

where the positive operator $K(\hat\rho)$ is defined on functions $u : \Lambda \to \mathbb{R}$ vanishing at the boundary $\partial\Lambda$ by $K(\hat\rho)u = -\nabla \cdot (\chi(\hat\rho) \nabla u)$.

Our third postulate then characterizes the free energy $\mathcal{F}(\rho)$ of the system with a density profile $\rho = \rho(x)$, $x \in \Lambda$, as the minimal cost to reach, starting from the stationary profile $\bar{\rho}$, the density profile ρ, in an infinitely long time interval.

3. *The nonequilibrium free energy of the system is*

$$\mathcal{F}(\rho) = \inf_{\substack{\hat{\rho}:\hat{\rho}(-\infty)=\bar{\rho}\\ \hat{\rho}(0)=\rho}} I_{[-\infty,0]}(\hat{\rho}) \tag{2.8}$$

As we shall see later, this is in fact proportional to the total work done by the optimal external field F along the optimal time evolution to reach the density profile ρ. The functional $\mathcal{F}$ has a precise statistical interpretation within the context of (non equilibrium) stationary states of stochastic lattice gases: it gives the asymptotics, as the number of degrees of freedom diverges, of the probability of observing a static fluctuation of the empirical density [1, 2, 5]. In this sense the functional $\mathcal{F}$ is the correct extension of the equilibrium free energy to non equilibrium thermodynamics.

As shown in [1, 2] the functional $\mathcal{F}$ is the maximal solution of the infinite dimensional Hamilton-Jacobi equation

$$\Big\langle \nabla \frac{\delta \mathcal{F}}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} \Big\rangle - \Big\langle \frac{\delta \mathcal{F}}{\delta \rho} \nabla \cdot J(\rho) \Big\rangle = 0 \tag{2.9}$$

where, for ρ that satisfies (2.4), $\delta \mathcal{F}/\delta \rho$ vanishes at the boundary of Λ. At the macroscopic level this condition reflects the fact that we consider variations of the density that do not change the boundary values. In the context of stochastic lattice gases, the boundary condition (2.4) is realized by superimposing to the bulk dynamics suitable birth and death processes at the boundary; the probability of deviations of the empirical density at the boundary is then shown to be super-exponentially small in the scaling limit [2]. Note however that in the stationary state the density is not fixed at the boundary, i.e. $\mathcal{F}(\rho) < \infty$ even if the profile $\rho = \rho(x)$ does not satisfy the boundary condition (2.4).

The arbitrary additive constant on the maximal solution of (2.9) is determined by the condition $\mathcal{F}(\bar{\rho}) = 0$. By maximal solution we mean that any solution to (2.9) (satisfying $F(\bar{\rho}) = 0$) is a lower bound for $\mathcal{F}$, as defined in (2.8). This bound is sharp. Indeed, by considering the functional in (2.7) as an action functional in variables $\hat{\rho}$ and $\partial_t \hat{\rho}$ and performing a Legendre transform, the associated Hamiltonian is

$$\mathcal{H}(\rho, \Pi) = \Big\langle \nabla \Pi \cdot \chi(\rho) \nabla \Pi \Big\rangle + \Big\langle \nabla \Pi \cdot J(\rho) \Big\rangle \tag{2.10}$$

where the *momentum* Π vanishes at the boundary of Λ. By noticing that the stationary solution of the hydrodynamic equation corresponds to the equilibrium point $(\bar{\rho}, 0)$ of the system with Hamiltonian $\mathcal{H}$ and $\mathcal{H}(\bar{\rho}, 0) = 0$, the equation (2.9) is the Hamilton-Jacobi equation $\mathcal{H}(\rho, \delta \mathcal{F}/\delta \rho) = 0$.

The optimal trajectory ρ^* for the variational problem (2.8) is characterized as follows. Let

$$J^*(\rho) = -2\chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} - J(\rho) \tag{2.11}$$

then ρ^* is the time reversal of the solution to

$$\partial_t \rho + \nabla \cdot J^*(\rho) = \partial_t \rho + \nabla \cdot \Big\{ D(\rho) \nabla \rho - \chi(\rho) \Big[E + 2\nabla \frac{\delta \mathcal{F}}{\delta \rho} \Big] \Big\} = 0 \tag{2.12}$$

with the boundary condition (2.4). We refer to [1, 2, 5] for the microscopic interpretation of J^* in terms of the time reversed dynamics. In particular, the optimal external field F forcing the system on the time evolution $\rho^*(t)$ is so that $J^F(\rho) = -J^*(\rho)$, namely

$$F = 2\nabla \frac{\delta \mathcal{F}}{\delta \rho} \tag{2.13}$$

This characterization of ρ^* is obtained as follows. Let $\mathcal{F}$ be the maximal solution of the Hamilton-Jacobi equation and J^* as in (2.11). Fix a time interval $[T_1, T_2]$ and a path $\hat{\rho}(t)$, $t \in [T_1, T_2]$. We claim that

$$\begin{aligned} I_{[T_1,T_2]}(\hat{\rho}) &= \mathcal{F}\big(\hat{\rho}(T_2)\big) - \mathcal{F}\big(\hat{\rho}(T_1)\big) \\ &\quad + \frac{1}{4}\int_{T_1}^{T_2} dt \Big\langle \big[\partial_t \hat{\rho} - \nabla \cdot J^*(\hat{\rho})\big] K(\hat{\rho})^{-1} \big[\partial_t \hat{\rho} - \nabla \cdot J^*(\hat{\rho})\big] \Big\rangle \end{aligned} \tag{2.14}$$

as can be shown by a direct computation using (2.7), the Hamilton-Jacobi equation (2.9) and the definition (2.11) of J^*. From the identity (2.14) we immediately deduce that the optimal path for the variational problem (2.8) is the time reversal of the solution to (2.12).

The classical thermodynamic setting considers only spatially homogeneous system in which ρ does not depend on x. In this case the variation of the free energy between $\bar{\rho}$ and ρ is the minimal work required to drive the system from $\bar{\rho}$ to ρ, which is realized by a *quasi static* transformation, see e.g. [21]. For an equilibrium inhomogeneous density profile ρ, by a quasi static transformation we understand the following: pick a macroscopic point x and consider a macroscopically small volume around x, perform quasi static transformation from $\bar{\rho}(x)$ to $\rho(x)$, repeat independently for all x and sum the results. Of course, if the system is in contact with a reservoir also the contribution describing the interaction with the reservoir has to be included.

We next show that according to definition (2.8), the free energy $\mathcal{F}(\rho)$ is proportional to the work done by the optimal external field F on the system along the optimal trajectory ρ^*. We emphasize that this is not a quasi static transformation in the above sense, but it is the solution of the hydrodynamic equation perturbed by the optimal external field. As we shall discuss later, the definition (2.8) of the free energy (with the factor $1/4$ in (2.6)) agrees with the thermodynamic one for equilibrium states, but in general, due to presence of long range correlations, the variation obtained along a quasi static transformation as defined above gives a different result.

Indeed, since ρ^* is the time reversal of the solution to (2.12), using (2.13) we deduce

$$\begin{aligned} \mathcal{F}(\rho) - \mathcal{F}(\bar{\rho}) &= \int_{-\infty}^{0} dt \Big\langle \frac{\delta \mathcal{F}}{\delta \rho}, \partial_t \rho^* \Big\rangle \\ &= \int_{-\infty}^{0} dt \Big\langle \frac{\delta \mathcal{F}}{\delta \rho}, \nabla \cdot J^*(\rho^*) \Big\rangle = \frac{1}{2}\int_{-\infty}^{0} dt \Big\langle (-J^*(\rho^*)) \cdot F \Big\rangle \end{aligned}$$

Namely, the variation $\mathcal{F}(\rho) - \mathcal{F}(\bar{\rho})$ is proportional the work done by the external field F along the optimal trajectory ρ^*. The factor $1/2$ above is connected to our definition of the transport coefficients and the associated Einstein relation (2.3).

As shown in the next section, equilibrium states are characterized by $J = J^*$. In this case the optimal path for the variational problem (2.8) is the time reversal of the solution to the original hydrodynamic equation (2.1)–(2.2). In [2] we called such a symmetry property the Onsager-Machlup time reversal symmetry.

3 Characterizations of Equilibrium States

We define the system to be in *equilibrium* if and only if the current in the stationary profile $\bar{\rho}$ vanishes, i.e. $J(\bar{\rho}) = 0$. A particular case is that of a *homogeneous equilibrium state*, obtained by setting the external field $E = 0$ and choosing a constant chemical potential at the boundary, i.e. $\lambda_0(x) = \bar{\lambda}$. Let $\bar{\rho} =$ const. be the equilibrium density, i.e. $\bar{\rho}$ solves $\bar{\lambda} = f_0'(\bar{\rho})$. It is then readily seen that the functional $\mathcal{F}$ defined in (2.8) is given by

$$\mathcal{F}(\rho) = \int_\Lambda dx \big\{ f_0\big(\rho(x)\big) - f_0(\bar{\rho}) - \bar{\lambda}\big[\rho(x) - \bar{\rho}\big]\big\} \tag{3.1}$$

in which the first difference is the variation of the free energy f_0 while the second term is due to the interaction with the reservoirs. The variational definition (2.8) of the functional $\mathcal{F}$ gives, when applied to equilibrium states, the variation of the equilibrium free energy (3.1). This shows that the choice of the factor $1/4$ in (2.6) is appropriate.

We next show that also for a non homogeneous equilibrium, characterized by a non constant stationary profile $\bar{\rho}(x)$ such that $J(\bar{\rho}) = 0$ the free energy functional $\mathcal{F}$ can be explicitly computed. Let

$$f(\rho, x) = \int_{\bar{\rho}(x)}^{\rho} dr \int_{\bar{\rho}(x)}^{r} dr' f_0''(r') = f_0(\rho) - f_0(\bar{\rho}(x)) - f_0'\big(\bar{\rho}(x)\big)\big[\rho - \bar{\rho}(x)\big]$$

we claim that the maximal solution of the Hamilton-Jacobi equation is

$$\mathcal{F}(\rho) = \int_\Lambda dx f\big(\rho(x), x\big) \tag{3.2}$$

Indeed

$$\frac{\delta \mathcal{F}}{\delta \rho(x)} = f_0'(\rho(x)) - f_0'(\bar{\rho}(x)) \tag{3.3}$$

so that, by an integration by parts,

$$\begin{aligned} &\Big\langle \nabla\big[f_0'(\rho) - f_0'(\bar{\rho})\big] \cdot \chi(\rho) \nabla\big[f_0'(\rho) - f_0'(\bar{\rho})\big]\Big\rangle \\ &\quad + \Big\langle \big[f_0'(\rho) - f_0'(\bar{\rho})\big] \nabla \cdot \Big[D(\rho)\nabla\rho - \chi(\rho)E\Big]\Big\rangle \\ &= \Big\langle \nabla\big[f_0'(\rho) - f_0'(\bar{\rho})\big] \cdot \chi(\rho)\Big[\nabla f_0'(\bar{\rho}) - E\Big]\Big\rangle = 0 \end{aligned}$$

where we used (2.3) and $\nabla f_0'(\bar{\rho}) - E = -\chi(\bar{\rho})^{-1} J(\bar{\rho}) = 0$. Therefore the functional $\mathcal{F}$ in (3.2) satisfies the Hamilton-Jacobi equation (2.9). To show it is the maximal solution, recalling (2.7), simple computations show that

$$\begin{aligned} I_{[T_1,T_2]}(\hat{\rho}) &= \mathcal{F}\big(\hat{\rho}(T_2)\big) - \mathcal{F}\big(\hat{\rho}(T_1)\big) \\ &\quad + \frac{1}{4}\int_{T_1}^{T_2} dt \Big\langle \big[\partial_t \hat{\rho} - \nabla \cdot J(\hat{\rho})\big] K(\hat{\rho})^{-1} \big[\partial_t \hat{\rho} - \nabla \cdot J(\hat{\rho})\big]\Big\rangle \end{aligned} \tag{3.4}$$

which clearly implies the maximality of $\mathcal{F}$.

We emphasize that the above argument depends crucially on the structure (2.2) of the current and on validity of the local Einstein relation (2.3). In Appendix we discuss the example of the ABC model [10, 14] in which these conditions are not met and the free energy is not a local functional even if $J(\bar\rho)=0$. Another example is given by the anisotropic zero-range process [9, 29] for which—as discussed in [29]—the local Einstein relation is violated.

We next show that the condition $J(\bar\rho)=0$ is equivalent to either one of the following statements.

- There exists a function $\lambda:\Lambda\to\mathbb{R}$ such that

$$E(x)=\nabla\lambda(x),\quad x\in\Lambda,\qquad \lambda(x)=\lambda_0(x),\quad x\in\partial\Lambda \tag{3.5}$$

- The system is *macroscopically reversible* in the sense that for each profile ρ we have $J^*(\rho)=J(\rho)$.

We emphasize that the notion of macroscopic reversibility does not imply that an underlying microscopic model satisfies the detailed balance condition. Indeed, as it has been shown by explicit examples [15–17], there are non reversible microscopic models which are macroscopically reversible.

We start by showing that $J(\bar\rho)=0$ if and only if (3.5) holds. From the local Einstein relation (2.3) and $J(\bar\rho)=0$ we deduce

$$E(x)=f_0''\big(\bar\rho(x)\big)\nabla\bar\rho(x)=\nabla f_0'(\bar\rho(x))$$

hence (3.5). Conversely, let the external field E be such that (3.5) holds. Since f_0'' is positive the function f_0' is invertible and we can define $\bar\rho(x)=(f_0')^{-1}(\lambda(x))$. The profile $\bar\rho$ satisfies (2.4) as well as $J(\bar\rho)=0$, consequently also $\nabla\cdot J(\bar\rho)=0$ so that it is the unique stationary profile.

We next show that $J(\bar\rho)=0$ if and only if $J(\rho)=J^*(\rho)$. By evaluating the Hamilton-Jacobi equation for $\rho=\bar\rho$ we deduce $\nabla[\delta\mathcal{F}(\bar\rho)/\delta\rho]=0$. From (2.11) we then get $J(\bar\rho)=0$. To show the converse implication, note that if $J(\bar\rho)=0$ then $\mathcal{F}$ is given by (3.2). We deduce

$$\chi(\rho)\nabla\frac{\delta\mathcal{F}}{\delta\rho}=D(\rho)\nabla\rho-\chi(\rho)E=-J(\rho)$$

hence, recalling (2.2) and (2.11), $J(\rho)=J^*(\rho)$.

We also note that macroscopic reversibility $J(\rho)=J^*(\rho)$ implies the invariance of the Hamiltonian $\mathcal{H}$ in (2.10) under the time reversal symmetry, see [2], $(\rho,\Pi)\mapsto(\rho,\delta\mathcal{F}/\delta\rho-\Pi)$, where $\mathcal{F}$ is the maximal solution of the Hamilton-Jacobi equation (2.9). As remarked before, macroscopic reversibility implies the Onsager-Machlup time reversal symmetry, on the other hand we shall give at the end of this section an example of a nonequilibrium system for which such a symmetry holds. Hence macroscopic reversibility is a stronger condition.

So far we have assumed the local Einstein relation and we have shown that—for equilibrium systems—it implies (3.2). Conversely, we now show that macroscopic reversibility and (3.2) imply the local Einstein relation (2.3). By writing explicitly $J(\rho)=J^*(\rho)$ we obtain

$$-\big[\chi(\rho)R(\rho)-D(\rho)\big]\nabla\rho+\chi(\rho)\big[R(\bar\rho)-\chi^{-1}(\bar\rho)D(\bar\rho)\big]\nabla\bar\rho=0 \tag{3.6}$$

where R is the second derivative of f_0 in the case of one-component systems while $R_{ij}=\partial_{\rho_i}\partial_{\rho_j}f_0$ for multi-component systems. In (3.6) we used, besides (3.2), $J(\bar\rho)=0$ to eliminate E. Note that $J(\bar\rho)=0$ follows from the Hamilton-Jacobi equation and $J(\rho)=J^*(\rho)$ without further assumptions. Since ρ and $\nabla\rho$ are arbitrary the local Einstein relation $D=\chi R$ follows from (3.6).

We have defined the macroscopic reversibility as the identity between the currents $J(\rho)$ and $J^*(\rho)$. We emphasize that this is not equivalent to the identity between $\nabla \cdot J(\rho)$ and $\nabla \cdot J^*(\rho)$. Indeed, we next give an example of a non reversible system, i.e. with $J(\bar\rho) \neq 0$, such that the optimal trajectory for the variational problem (2.8) is the time reversal of the solution to the hydrodynamic equation (2.1),(2.2), and (2.4).

Let $\Lambda = [0,1]$, $D(\rho) = \chi(\rho) = 1$, $\lambda_0(0) = \lambda_0(1) = \bar\lambda$, and a constant external field $E \neq 0$. In this case hydrodynamic evolution of the density is given by the heat equation independently of the field E. The stationary profile is $\bar\rho = \bar\lambda$, the associated current is $J(\bar\rho) = E \neq 0$. By a computation analogous to the one leading to (3.4), we easily get that

$$\mathcal{F}(\rho) = \frac{1}{2}\int_0^1 dx \big[\rho(x) - \bar\rho\big]^2$$

and the optimal trajectory for the variational problem (2.8) is the time reversal of the solution to the heat equation. On the other hand $J(\rho) = -\nabla\rho + E$ while $J^*(\rho) = -\nabla\rho - E$.

We remark that, even if the free energy $\mathcal{F}$ is a non local functional, the equality $J(\rho) = J^*(\rho)$ implies that the thermodynamic force $\nabla\delta\mathcal{F}/\delta\rho$ is local. Moreover, the Hamilton-Jacobi equation reduces to the statement

$$J(\rho) = -\chi(\rho)\nabla\frac{\delta\mathcal{F}}{\delta\rho}(\rho) \tag{3.7}$$

This identity, viewed as a special case of (2.11), represents the general form—for reversible systems—of the relationship between currents and thermodynamic forces. It holds both when the free energy is local and nonlocal. For reversible systems it is therefore enough to integrate (3.7) to compute the free energy. An example of such a situation with a nonlocal free energy, illustrated in Appendix, is provided by the ABC model on a ring with equal densities [10, 14].

4 Correlation Functions

In classical equilibrium thermodynamics the second derivatives of the thermodynamic potentials like the free energy are response coefficients like the compressibility. In a statistical mechanics framework they are identified with the Fourier transform evaluated at zero of correlation functions of the underlying Gibbs measure. Analogous interpretation is given to the higher order derivatives.

As we defined the (nonequilibrium) free energy as a functional on the set of density profiles, we can obtain the (nonequilibrium) density correlations functions of arbitrary order in terms of the functional derivatives of $\mathcal{F}$. In general the functional $\mathcal{F}$ cannot be written in a closed form, but—by a suitable perturbation theory on the Hamilton-Jacobi equation (2.9)—we can derive such correlations functions. In this section we first discuss the two-point correlation and establish a criterion to decide whether the density fluctuations are positively or negatively correlated. Then, we deduce a recursive equation for the correlation function of any order.

We remark that we are concerned only with *macroscopic correlations* which are a generic feature of nonequilibrium models. Microscopic correlations which decay as a summable power law disappear at the macroscopic level.

We introduce the *pressure* functional as the Legendre transform of free energy $\mathcal{F}$

$$\mathcal{G}(h) = \sup_\rho \big\{\langle h\rho\rangle - \mathcal{F}(\rho)\big\}$$

By Legendre duality we have the change of variable formulae $h = \frac{\delta \mathcal{F}}{\delta \rho}$, $\rho = \frac{\delta \mathcal{G}}{\delta h}$, so that the Hamilton-Jacobi equation (2.9) can then be rewritten in terms of $\mathcal{G}$ as

$$\left\langle \nabla h \cdot \chi\left(\frac{\delta \mathcal{G}}{\delta h}\right) \nabla h \right\rangle - \left\langle \nabla h \cdot D\left(\frac{\delta \mathcal{G}}{\delta h}\right) \nabla \frac{\delta \mathcal{G}}{\delta h} - \chi\left(\frac{\delta \mathcal{G}}{\delta h}\right) E \right\rangle = 0 \tag{4.1}$$

where h vanishes at the boundary of Λ. As for equilibrium systems, $\mathcal{G}$ is the generating functional of the correlation functions. In particular by defining

$$C(x, y) = \frac{\delta^2 \mathcal{G}(h)}{\delta h(x) \delta h(y)}\bigg|_{h=0}$$

we have, since $\mathcal{F}$ has a minimum at $\bar{\rho}$,

$$\mathcal{G}(h) = \langle h, \bar{\rho} \rangle + \frac{1}{2} \langle h, Ch \rangle + o(h^2)$$

or equivalently

$$\mathcal{F}(\rho) = \frac{1}{2} \langle (\rho - \bar{\rho}), C^{-1}(\rho - \bar{\rho}) \rangle + o((\rho - \bar{\rho})^2)$$

By expanding the Hamilton-Jacobi equation (4.1) to the second order in h, and using that $\delta \mathcal{G} / \delta h(x) = \bar{\rho}(x) + Ch(x) + o(h^2)$, we get the following equation for C

$$\left\langle \nabla h \cdot \left[\chi(\bar{\rho}) \nabla h - \nabla(D(\bar{\rho}) Ch) + \chi'(\bar{\rho})(Ch) E \right] \right\rangle = 0 \tag{4.2}$$

We now make the change of variable

$$C(x, y) = C_{\mathrm{eq}}(x) \delta(x - y) + B(x, y)$$

where $C_{\mathrm{eq}}(x)$ is the equilibrium covariance. By using (2.3) we deduce that

$$C_{\mathrm{eq}}(x) = D^{-1}(\bar{\rho}(x)) \chi(\bar{\rho}(x))$$

Equation (4.2) for the correlation function then gives the following equation for B

$$\mathcal{L}^{\dagger} B(x, y) = \alpha(x) \delta(x - y) \tag{4.3}$$

where $\mathcal{L}^{\dagger}$ is the formal adjoint of the elliptic operator $\mathcal{L} = L_x + L_y$ given by, using the usual convention that repeated indices are summed,

$$L_x = D_{ij}(\bar{\rho}(x)) \partial_{x_i} \partial_{x_j} + \chi'_{ij}(\bar{\rho}(x)) E_j(x) \partial_{x_i} \tag{4.4}$$

and

$$\alpha(x) = \partial_{x_i} \left[\chi'_{ij}\big(\bar{\rho}(x)\big) D^{-1}_{jk}\big(\bar{\rho}(x)\big) \bar{J}_k(x) \right]$$

where we recall $\bar{J} = J(\bar{\rho}) = -D(\bar{\rho}(x)) \nabla \bar{\rho}(x) + \chi(\bar{\rho}(x)) E(x)$ is the macroscopic current in the stationary profile.

In agreement with the discussion in Sect. 3, for equilibrium systems $\bar{J} = 0$ so that we have $\alpha = 0$, hence $B = 0$, namely there are no long range correlations and $C(x, y) = C_{\mathrm{eq}}(x) \delta(x - y)$. Moreover, since $\mathcal{L}$ is an elliptic operator (i.e. it has a negative kernel), the sign of B is determined by the sign of α: if $\alpha(x) \geq 0, \forall x$, then $B(x, y) \leq 0, \forall x, y$, while if $\alpha(x) \le 0, \forall x$, then $B(x,y) \ge 0, \forall x, y$. For example, consider the following special case. The system is one-dimensional, $d = 1$, the diffusion coefficient is constant, i.e. $D(\rho) = D_0$, the mobility $\chi(\rho)$ is a quadratic function of ρ, and there is no external field, $E = 0$. Then

$$B(x,y) = -\frac{1}{2D_0}\chi''(\nabla\bar{\rho})^2\Delta^{-1}(x,y) \tag{4.5}$$

where $\Delta^{-1}(x,y)$ is the Green function of the Dirichlet Laplacian. Two remarkable models, the symmetric exclusion process, where $\chi(\rho) = \rho(1-\rho)$, and the KMP process, where $\chi(\rho) = \rho^2$, meet the above conditions. Then (4.5) shows that their correlations have opposite signs.

We next derive, using the Hamilton-Jacobi equation (4.1), a recursive formula for the n-point correlation function $C_n(x_1, \dots, x_n)$. This is defined in terms of the pressure functional $\mathcal{G}$ as

$$C_n(x_1, \dots, x_n) = \frac{\delta^n \mathcal{G}}{\delta h(x_1)\cdots\delta h(x_n)}\Big|_{h=0} \tag{4.6}$$

so that $C_1(x) = \bar{\rho}(x)$ and C_2 is the two-point correlation function discussed above. Note that for equilibrium systems the free energy is given by (3.2), hence we have no long range correlations and the n-point correlation function is

$$C_{n,\mathrm{eq}}(x_1, \dots, x_n) = c_n(\bar{\rho}(x_1))\delta(x_1 - x_2)\cdots\delta(x_1 - x_n) \tag{4.7}$$

where $c_n(\bar{\rho}) = \frac{d^n}{dx^n}(f_0')^{-1}(x)|_{x=f_0'(\bar{\rho})}$.

By expanding the functional derivative of $\mathcal{G}$ we get

$$\frac{\delta\mathcal{G}(h)}{\delta h(x_1)} = \bar{\rho}(x_1) + \sum_{n\ge 1}\frac{1}{n!}\mathcal{G}_n(h; x_1) \tag{4.8}$$

where

$$\mathcal{G}_n(h; x_1) = \int_\Lambda dx_2\cdots dx_{n+1} h(x_2)\cdots h(x_{n+1}) C_{n+1}(x_1, x_2, \dots, x_{n+1}) \tag{4.9}$$

If we consider the terms of order h^{n+1} in the Hamilton-Jacobi equation (4.1) we get, using (4.8) and after some algebraic manipulations,

$$\begin{aligned}
\Bigg\langle \nabla h \cdot \Bigg[&\sum_{\substack{i_1, i_2, \dots \ge 0\\ \sum_k k i_k = n-1}} \frac{1}{i_1!(1!)^{i_1} i_2!(2!)^{i_2}\cdots}\chi^{(\sum_k i_k)}(\bar{\rho})(\mathcal{G}_1)^{i_1}(\mathcal{G}_2)^{i_2}\cdots\nabla h \\
&- \sum_{\substack{i_1, i_2, \dots \ge 0\\ \sum_k k i_k = n}} \frac{1}{i_1!(1!)^{i_1} i_2!(2!)^{i_2}\cdots}\nabla\Big(D^{(\sum_k i_k - 1)}(\bar{\rho})(\mathcal{G}_1)^{i_1}(\mathcal{G}_2)^{i_2}\cdots\Big) \\
&+ \sum_{\substack{i_1, i_2, \dots \ge 0\\ \sum_k k i_k = n}} \frac{1}{i_1!(1!)^{i_1} i_2!(2!)^{i_2}\cdots}\chi^{(\sum_k i_k)}(\bar{\rho})(\mathcal{G}_1)^{i_1}(\mathcal{G}_2)^{i_2}\cdots E\Bigg]\Bigg\rangle = 0
\end{aligned}$$

where, for f given by either χ or D, the notation $f^{(k)}$ stands for the k-th derivative of f.

Since the above identity holds for every function h vanishing at the boundary of Λ, we get from it a recursive formula for the n-point correlation functions which generalizes (4.3).

We start by introducing some notation. For $n \geq 1$, we let $\mathcal{L}_{n+1}^{\dagger}$ be the formal adjoint of the operator $\mathcal{L}_{n+1} = \sum_{k=1}^{n+1} L_{x_k}$, where L_x is defined in (4.4). Given functions f and g in $n+1$ and $m+1$ variables respectively, their 1st shuffle product $f \#_1 g$ is, by definition, the following function in $m+n+1$ variables

$$\begin{aligned} & f \#_1 g(x_1, \ldots, x_{m+n+1}) \\ & \quad = \frac{1}{(m+n)!} \sum_{\pi} f(x_1, x_{\pi_2}, \ldots, x_{\pi_{n+1}}) g(x_1, x_{\pi_{n+2}}, \ldots, x_{\pi_{m+n+1}}) \end{aligned}$$

where the sum is over all permutations of the indices $\{2, 3, \ldots, m+n+1\}$. Clearly $\#_1$ is a commutative associative product, and $f \#_1 g$ is symmetric in the variables $x_2, \ldots, x_{m+n+2}$. Furthermore, given a function f in n variables, we denote by f^{sym} its symmetrization, namely

$$f^{sym}(x_1, \ldots, x_n) = \frac{1}{n!} \sum_{\pi \in S_n} f(x_{\pi_1}, \ldots, x_{\pi_n})$$

Given a sequence $\vec{\imath} = (i_1, i_2, i_3, \ldots)$ of non negative integers with only finitely many non zero entries, we also denote

$$\begin{aligned} \Sigma(\vec{\imath}) &= i_1 + i_2 + \cdots = \sum_k i_k \\ N(\vec{\imath}) &= i_1 + 2i_2 + \cdots = \sum_k k i_k \\ K(\vec{\imath}) &= i_1!(1!)^{i_1} i_2!(2!)^{i_2} \cdots = \prod_k i_k!(k!)^{i_k} \end{aligned}$$

Finally, for $\vec{\imath}$ with $N(\vec{\imath}) = n$, we let

$$C_{\vec{\imath}}(x_1, \ldots, x_{n+1}) = \big(C_2^{\#_1 i_1} \#_1 C_3^{\#_1 i_2} \#_1 \cdots\big)(x_1, x_2, \ldots, x_{n+1})$$

Then the recursive equation satisfied by the $n+1$-point correlation function reads

$$\begin{aligned} & \frac{1}{(n+1)!} \mathcal{L}_{n+1}^{\dagger} C_{n+1}(x_1, x_2, \ldots, x_{n+1}) \\ & \quad = \Bigg\{ \sum_{\substack{\vec{\imath} \\ N(\vec{\imath})=n-1}} \frac{1}{K(\vec{\imath})} \nabla_{x_1} \cdot \Big(\chi^{(\Sigma(\vec{\imath}))}(\bar{\rho}(x_1)) C_{\vec{\imath}}(x_1, \ldots, x_n) \nabla_{x_1} \delta(x_1 - x_{n+1}) \Big) \\ & \qquad - \sum_{\substack{\vec{\imath} \\ N(\vec{\imath})=n, i_n=0}} \frac{1}{K(\vec{\imath})} \nabla_{x_1} \cdot \nabla_{x_1} \Big(D^{(\Sigma(\vec{\imath})-1)}(\bar{\rho}(x_1)) C_{\vec{\imath}}(x_1, \ldots, x_{n+1}) \Big) \\ & \qquad + \sum_{\substack{\vec{\imath} \\ N(\vec{\imath})=n, i_n=0}} \frac{1}{K(\vec{\imath})} \nabla_{x_1} \cdot \Big(\chi^{(\Sigma(\vec{\imath}))}(\bar{\rho}(x_1)) C_{\vec{\imath}}(x_1, \ldots, x_{n+1}) E(x_1) \Big) \Bigg\}^{sym} \end{aligned} \tag{4.10}$$

It is easy to check that, for $n = 1$, equation (4.10) reduces to (4.3). Moreover, in the case of equilibrium states the solution to (4.10) is (4.7). We refer to [2, §4.5] for the application to the boundary driven simple exclusion process.

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Appendix: The ABC Model

We here consider—both from a microscopic and macroscopic point of view—a model with two conservation laws. Given an integer $N \geq 1$ let $\mathbb{Z}_N = \{1, \dots, N\}$ be the discrete ring with N sites so that $N + 1 \equiv 1$. The microscopic space state is given by $\Omega_N = \{A, B, C\}^{\mathbb{Z}_N}$ so that at each site $x \in \mathbb{Z}_N$ the occupation variable, denoted by η_x, take values in the set $\{A, B, C\}$; one may think that A, B stand for two different species of particles and C for an empty site. Note that this state space takes into account an exclusion condition: at each site there is at most one species of particles.

We first consider a weakly asymmetric dynamics that fits in the framework discussed in Sect. 2 that is defined by choosing the following transition rates. If the occupation variables across the bond $\{x, x+1\}$ are (ξ, ζ), they are exchanged to (ζ, ξ) with rate $c^E_{x,x+1} = \exp\{(E_\xi - E_\zeta)/(2N)\}$ for fixed constant external fields E_A, E_B, E_C. This choice satisfies the so-called *local detailed balance* condition that, in general, requires the weakly asymmetric rates $c^E_{x,x+1}$ to satisfy

$$c^E_{x,x+1}(\eta^{x,x+1}) = c^E_{x,x+1}(\eta) \exp\Big\{\nabla_{x,x+1}\Big[H(\eta) - \frac{1}{N}\sum_x \big(E_A x \mathbb{1}_A(\eta_x) + E_B x \mathbb{1}_B(\eta_x) + E_C x \mathbb{1}_C(\eta_x)\big)\Big]\Big\} \tag{A.1}$$

where $\eta^{x,x+1}$ is the configuration obtained from η by exchanging the occupation variables in x and $x+1$, $\nabla_{x,x+1} f(\eta) = f(\eta^{x,x+1}) - f(\eta)$, and $H(\eta)$ is the energy of the configuration η, which is constant in this model.

Following [12, 19, 20], the hydrodynamic equations for the densities of A and B particles are given by

$$\partial_t \begin{pmatrix} \rho_A \\ \rho_B \end{pmatrix} = \Delta \begin{pmatrix} \rho_A \\ \rho_B \end{pmatrix} - \nabla \cdot \begin{pmatrix} \rho_A(1-\rho_A) & -\rho_A\rho_B \\ -\rho_A\rho_B & \rho_B(1-\rho_B) \end{pmatrix} \begin{pmatrix} E_A - E_C \\ E_B - E_C \end{pmatrix} \tag{A.2}$$

of course the density of C particles is then $\rho_C = 1 - \rho_A - \rho_B$.

The functional $I_{[T_1,T_2]}$ in (2.7) with $D = \mathbb{1}$ and mobility

$$\chi(\rho_A, \rho_B) = \begin{pmatrix} \rho_A(1-\rho_A) & -\rho_A\rho_B \\ -\rho_A\rho_B & \rho_B(1-\rho_B) \end{pmatrix} \tag{A.3}$$

is the dynamical large functional associated to this model. The free energy is the maximal solution of the Hamilton-Jacobi equation (2.9) which can be easily computed. Namely,

$$\mathcal{F}^0_{m_A,m_B}(\rho_A, \rho_B) = \int dx \Big[\rho_A \log\frac{\rho_A}{m_A} + \rho_B \log\frac{\rho_B}{m_B} + (1-\rho_A-\rho_B)\log\frac{1-\rho_A-\rho_B}{1-m_A-m_B}\Big] \tag{A.4}$$

where $\int dx \rho_A = m_A$ and $\int dx \rho_B = m_B$. If E_A, E_B and E_C are not all equal, this model is a nonequilibrium model nevertheless, in view of the periodic boundary conditions, its free energy is independent of the external field; see [6, §3.4].

We next discuss a different choice of the weakly asymmetric perturbation which, as we shall see, does not fit in the scheme discussed in Sect. 2. This choice is the one referred to in the literature [10, 14] as the *ABC model*. The transition rates are the following. If the occupation variables across the bond $\{x, x+1\}$ are (ξ, ζ), they are exchanged to (ζ, ξ) with rate $\exp\{V(\xi, \eta)/N\}$ where $V(A,B) = V(B,C) = V(C,A) = -\beta/2$ and $V(B,A) = V(C,B) = V(A,C) = \beta/2$ for some $\beta > 0$. Therefore the A-particles prefer to jump to the left of the B-particles but to the right of the C-particles while the B-particles prefer to jump to the left of the C-particles, i.e. the preferred sequence is ABC and its cyclic permutations. These rates do not satisfy the local detailed balance (A.1).

Again by the methods developed in [12, 19, 20], the hydrodynamic equations are

$$\partial_t \begin{pmatrix} \rho_A \\ \rho_B \end{pmatrix} + \nabla \cdot \begin{pmatrix} J_A(\rho_A, \rho_B) \\ J_B(\rho_A, \rho_B) \end{pmatrix} = 0 \tag{A.5}$$

where

$$J(\rho_A, \rho_B) = \begin{pmatrix} J_A(\rho_A, \rho_B) \\ J_B(\rho_A, \rho_B) \end{pmatrix} = \begin{pmatrix} -\nabla \rho_A + \beta \rho_A (1 - 2\rho_B - \rho_A) \\ -\nabla \rho_B + \beta \rho_B (2\rho_A + \rho_B - 1) \end{pmatrix} \tag{A.6}$$

The asymmetric term in the hydrodynamic equation (A.5) is not of the form $\nabla \cdot (\chi(\rho) E)$ as in (2.1)–(2.3). Hence the results obtained in Sect. 3 do not apply.

The appropriate cost functional is however still given by (2.7) with J as in (A.6) and χ as in (A.3). The solution of the Hamilton-Jacobi equation (2.9) then gives the free energy. In the case of equal densities $\int dx \rho_A = \int dx \rho_B = 1/3$, a straightforward computation shows that for any positive β the solution is given by the functional

$$\begin{aligned} \mathcal{F}^{\beta}_{\frac{1}{3},\frac{1}{3}}(\rho_A, \rho_B) = \mathcal{F}^{0}_{\frac{1}{3},\frac{1}{3}}(\rho_A, \rho_B) + \beta \int_0^1 dx \int_0^1 dy y \Big\{ &\rho_A(x) \rho_B(x+y) \\ &+ \rho_B(x)[1 - \rho_A(x+y) - \rho_B(x+y)] \\ &+ [1 - \rho_A(x) - \rho_B(x)] \rho_A(x+y) \Big\} + \varkappa \end{aligned} \tag{A.7}$$

where $\mathcal{F}^{0}_{\frac{1}{3},\frac{1}{3}}$ is the functional in (A.4) with $m_A = m_B = 1/3$ and $\varkappa$ is the appropriate normalization constant. This result has been already obtained in [10] by direct computations from the invariant measure. Indeed, in this case, the ABC model is *microscopically* reversible and the invariant measure can be computed explicitly. From a macroscopic point of view, the reversibility of the model is expressed as the identity, which holds in the case of equal densities, $J(\rho) = J^*(\rho)$. Hence, as discussed at the end of Sect. 3, the free energy (A.7) can also be macroscopically derived by integrating (3.7).

We mention the recent preprint [8], of which we became aware after the completion of this work, in which the nonequilibrium free energy of the ABC model is also computed from the variational principle (2.8).

References

1. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Fluctuations in stationary non equilibrium states of irreversible processes. Phys. Rev. Lett. **87**, 040601 (2001)

2. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Macroscopic fluctuation theory for stationary non equilibrium state. J. Stat. Phys. **107**, 635–675 (2002)
3. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Minimum dissipation principle in stationary non equilibrium states. J. Stat. Phys. **116**, 831–841 (2004)
4. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Current fluctuations in stochastic lattice gases. Phys. Rev. Lett. **94**, 030601 (2005)
5. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Non equilibrium current fluctuations in stochastic lattice gases. J. Stat. Phys. **123**, 237–276 (2006)
6. Bertini, L., De Sole, A., Gabrielli, D., Jona-Lasinio, G., Landim, C.: Stochastic interacting particle systems out of equilibrium. J. Stat. Mech. P07014 (2007)
7. Bertini, L., Gabrielli, D., Lebowitz, J.L.: Large deviations for a stochastic model of heat flow. J. Stat. Phys. **121**, 843–885 (2005)
8. Bodineau, T., Derrida, B., Lecompte, V., van Wijland, F.: Long range correlations and phase transition in non-equilibrium diffusive systems. Preprint (2008). arXiv:0807.2394
9. Cheng, Z., Garrido, P.L., Lebowitz, J.L., Vallés, J.L.: Long range correlations in stationary nonequilibrium systems with conservative anisotropic dynamics. Europhys. Lett. **6**, 507–513 (1991)
10. Clincy, M., Derrida, B., Evans, M.R.: Phase transition in the ABC model. Phys. Rev. E **67**, 066115 (2003)
11. Dorfman, J.R., Kirkpatrick, T.R., Sengers, J.V.: Generic long-range correlations in molecular fluids. Annu. Rev. Phys. Chem. **45**, 213–239 (1994)
12. De Masi, A., Presutti, E., Scacciatelli, E.: The weakly asymmetric simple exclusion process. Ann. Inst. Henri Poincaré Probab. **25**, 1–38 (1989)
13. Derrida, B.: Non-equilibrium steady states: fluctuations and large deviations of the density and of the current. J. Stat. Mech. P07023 (2007)
14. Evans, M.R., Kafri, Y., Koduvely, H.M., Mukamel, D.: Phase separation in one-dimensional driven diffusive systems: local dynamics leading to long-range Hamiltonians. Phys. Rev. E **58**, 2764–2778 (1998)
15. Gabrielli, D., Jona-Lasinio, G., Landim, C.: Onsager reciprocity relations without microscopic reversibility. Phys. Rev. Lett. **77**, 1202–1205 (1996)
16. Lebowitz, J.L., Spohn, H.: Comment on "Onsager reciprocity relations without microscopic reversibility" and Reply. Phys. Rev. Lett. **78**, 394–395 (1996)
17. Gabrielli, D., Jona-Lasinio, G., Landim, C.: Onsager symmetry from microscopic TP invariance. J. Stat. Phys. **96**, 639–652 (1999)
18. Harris, R.J., Schütz, G.M.: Fluctuation theorems for stochastic dynamics. Preprint (2007). cond-mat/0702553
19. Kipnis, C., Landim, C.: Scaling Limits of Interacting Particle Systems. Springer, Berlin (1999)
20. Kipnis, C., Olla, S., Varadhan, S.R.S.: Hydrodynamics and large deviations for simple exclusion processes. Commun. Pure Appl. Math. **42**, 115–137 (1989)
21. Landau, L., Lifshitz, E.: Physique Statistique. MIR, Moscow (1967)
22. Maes, C., Netocny, K., Shergelashvili, B.: A Selection of Nonequilibrium Issues. Lecture Notes from the 5th Prague Summer School on Mathematical Statistical Mechanics (2006). math-ph/0701047
23. Onsager, L.: Reciprocal relations in irreversible processes. I. Phys. Rev. **37**, 405–426 (1931)
24. Onsager, L.: Reciprocal relations in irreversible processes. II. Phys. Rev. **38**, 2265–2279 (1931)
25. Onsager, L., Machlup, S.: Fluctuations and irreversible processes. Phys. Rev. **91**, 1505–1512 (1953). Phys. Rev. **91**, 1512–1515 (1953)
26. Sewell, G.L.: Quantum macrostatistical theory of nonequilibrium steady states. Rev. Math. Phys. **17**, 977–1020 (2005)
27. Spohn, H.: Long range correlations for stochastic lattice gases in a nonequilibrium steady state. J. Phys. A **16**, 4275–4291 (1983)
28. Spohn, H.: Large Scale Dynamics of Interacting Particles. Springer, Berlin (1991)
29. van Beijeren, H.: Long-range spatial correlations in a simple diffusion model. J. Stat. Phys. **60**, 845–849 (1990)