Thermodynamic Transformations of Nonequilibrium States

**Lorenzo Bertini · Davide Gabrielli ·
Giovanni Jona-Lasinio · Claudio Landim**

Abstract We consider a macroscopic system in contact with boundary reservoirs and/or under the action of an external field. We discuss the case in which the external forcing depends explicitly on time and drives the system from a nonequilibrium state to another one. In this case the amount of energy dissipated along the transformation becomes infinite when an unbounded time window is considered. Following the general proposal by Oono and Paniconi and using results of the macroscopic fluctuation theory, we give a natural definition of a renormalized work. We then discuss its thermodynamic relevance by showing that it satisfies a Clausius inequality and that quasi static transformations minimize the renormalized work. In addition, we connect the renormalized work to the quasi potential describing the fluctuations in the stationary nonequilibrium ensemble. The latter result provides a characterization of the quasi potential that does not involve rare fluctuations.

L. Bertini
Dipartimento di Matematica, Università di Roma 'La Sapienza', P.le Aldo Moro 2, 00185 Rome, Italy
e-mail: bertini@mat.uniroma1.it

D. Gabrielli
Dipartimento di Matematica, Università dell'Aquila, 67100 Coppito, AQ, Italy
e-mail: gabriell@univaq.it

G. Jona-Lasinio (✉)
Dipartimento di Fisica and INFN, Università di Roma La Sapienza, P.le A. Moro 2, 00185 Rome, Italy
e-mail: gianni.jona@roma1.infn.it

C. Landim
IMPA, Estrada Dona Castorina 110, J. Botanico, 22460 Rio de Janeiro, Brazil
e-mail: landim@impa.br

C. Landim
CNRS UMR 6085, Université de Rouen, Avenue de l'Université, BP 12, Technopôle du Madrillet,
76801 Saint-Étienne-du-Rouvray, France

1 Introduction

The basic paradigm of equilibrium statistical mechanics states that in order to obtain the typical value of macroscopic observables and their fluctuations we do not have to solve any equation of motion and the calculations can be performed by using the Gibbs distribution. 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, mass, . . .) through the system whose macroscopic behavior is encoded in transport coefficients like the diffusion coefficient, the conductivity or the mobility. In this case we cannot bypass an analysis of the dynamical properties of the system. Indeed, the Gibbs distribution has to be replaced by the invariant distribution for the microscopic dynamics. The calculation of this distribution, even for very simple models, is a most challenging task. On the other hand, we are mainly interested in the macroscopic behavior of "few" observables and this question may be answered without the complete microscopic knowledge of the stationary ensemble.

A main goal that we want to reach for nonequilibrium stationary states is therefore to construct analogues of thermodynamic potentials from which we can extract the typical macroscopic behavior of the system as well as the asymptotic probability of fluctuations. As it has been shown in [6], this program can be implemented without the explicit knowledge of the stationary ensemble and requires as input the macroscopic dynamical behavior of systems which can be characterized by the transport coefficients. This theory, now known as *macroscopic fluctuation theory*, is based on an extension of Einstein equilibrium fluctuation theory to stationary nonequilibrium states combined with a dynamical point of view. It has been very powerful in studying concrete microscopic models but can be used also as a phenomenological theory. It has led to several new interesting predictions [1, 8, 9, 11, 12, 14].

In this paper we develop a theory of thermodynamic transformations for nonequilibrium stationary states. We thus consider an open system in contact with boundary reservoirs and/or under the action of an external field and we analyze the situation in which the reservoirs and field vary with time driving the system from a state to another one. In the case in which the initial and final states are equilibrium states, according to the standard thermodynamic theory, the transformation is *reversible* if the energy exchanged between the system and the environment is minimal. A thermodynamic principle asserts that reversible transformations are accomplished by a sequence of equilibrium states and are well approximated by *quasi static transformations* in which the variations of the environment are very slow. By an explicit construction of quasi static transformations, we show that this principle can be derived from the assumption that during the transformation the system is a *local equilibrium* state so that the macroscopic evolution can be described by hydrodynamic equations. Consider now the situation in which either the initial or the final state is a nonequilibrium state which supports a non vanishing current. To maintain such states one needs to dissipate a positive amount of energy per unit of time. If we consider a transformation between nonequilibrium stationary states, the energy dissipated along such transformation will necessarily include the contribution needed to maintain such states which is infinite when an unbounded time window is considered. Following the general proposal in [24], we thus define a *renormalized work* performed by a given transformation that is obtained by subtracting from the total energy exchanged the energy needed to maintain the (nonequilibrium) stationary state. We prove that the renormalized work satisfies a Clausius inequality which states that it is larger then the variation of the equilibrium free energy functional evaluated at the corresponding nonequilibrium profiles. As a particular case, we recover the equilibrium Clausius inequality. We finally show that also for nonequilibrium states quasi static transformations are optimal, in the sense that they minimize the renormalized work.

The second main topic that we here discuss is the connection between the energy exchanged in a thermodynamic transformation and the asymptotic probability of fluctuations in the stationary ensemble. In the context of equilibrium statistical mechanics, the Boltzmann-Einstein theory, see e.g. [23, Eq. (112.2)], states that the probability of a fluctuation for a system in contact with an environment at temperature T_{env}, pressure p_{env}, and chemical potential λ_{env}, is given by

$$P \asymp \exp\left\{-\frac{R}{\kappa T_{env}}\right\} \qquad (1.1)$$

where κ is the Boltzmann constant and

$$R = \Delta U - T_{env}\Delta S + p_{env}\Delta V - \lambda_{env}\Delta N \qquad (1.2)$$

in which ΔU, ΔS, ΔV, and ΔN are the variations of energy, entropy, volume, and number of particles of the system. The quantity R coincides with the variation of the *availability*, see [25, Chap. 7], and it has the interpretation of maximal useful work that can be extracted from a system in a given environment (e.g. a boiler of hot water in a colder environment). Equivalently, R is the minimal work to produce the given fluctuation. In the context of equilibrium states we identify R with the *quasi potential* introduced in the macroscopic fluctuation theory. Furthermore, we show that R is the *excess work* (with respect to a quasi static transformation) associated to the transformation given by the relaxation path described by the hydrodynamic equations which brings the system from the state associated with the fluctuation to one in equilibrium with the environment.

For nonequilibrium stationary states the formula (1.2) cannot be used. By taking a dynamical point of view we can however properly define R as the excess work with respect to the minimal renormalized work mentioned before, so that the fluctuation formula (1.1) still holds. Furthermore, we show that the same expression can be used to compare two different nonequilibrium stationary states. More precisely, the relative entropy of the stationary ensembles associated to two boundary driven stochastic lattice gases with different boundary reservoirs can be expressed in terms of R.

The theory of thermodynamic transformations here developed is presented without any reference to the underlying microscopic dynamics. On the other hand, the transformations here considered have well defined microscopic counterparts. In particular, for stochastic lattice gases it is possible to give a microscopic definition of the work exchanged between the system and the environment. This is a fluctuating variable whose typical behavior in the hydrodynamic scaling limit agrees with the macroscopic description. The statistics of the fluctuations can be derived from the fluctuations of the empirical current [8] but will not be discussed in this paper.

Outline   In Sect. 2 we formulate the basic assumptions for the thermodynamic description of driven diffusive systems. These assumptions are based on the notion of local equilibrium and the validity of the local Einstein relation.

In Sect. 3 we discuss the case of equilibrium states and show how the Clausius inequality can be deduced from the previous assumptions. In addition, we connect the *availability* of classical thermodynamic with the relative entropy between Gibbs states.

In Sect. 4 we analyze the case of nonequilibrium states and their transformations. We thus introduce the *renormalized work* performed along a given transformation and connect it to the quasi potential of the macroscopic fluctuation theory. We also show that the relative entropy between two different nonequilibrium states can be expressed in terms of the quasi potential.

In Sect. 5 we consider a system with a general time dependent forcing. We introduce the corresponding time dependent quasi potential which takes into account the fact that the system has a finite relaxation time and provides a fluctuation formula for each fixed time. We then connect also the time dependent quasi potential to a properly defined renormalized work.

In Sects. 6 and 7 we exemplify the theory discussed above by considering respectively the case of stochastic lattice gases, giving also a microscopic definition of work, and Langevin dynamics.

2 Basic Assumptions

We introduce in this section the thermodynamic description of 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, and under the action of an external field E. We denote by $\Lambda \subset \mathbb{R}^d$ the bounded region occupied by the system, by x the macroscopic space coordinates and by t the macroscopic time. With respect to our previous work [6–11], we consider the case in which λ and E can depend explicitly on the time t.

The macroscopic dynamics is given by the hydrodynamic equation for the density which satisfies the following general assumption, based on the notion of local equilibrium. It will be convenient to use a different notation for space-time density paths and space dependent density profiles. In the sequel we denote by $u = u(t, x)$ space-time dependent paths and by $\rho = \rho(x)$ time independent profiles.

1. The macroscopic state is completely described by the local density $u(t, x)$ and the associated current $j(t, x)$.
2. The macroscopic evolution is given by the continuity equation together with the constitutive equation which express the current in function of the density. Namely,

$$\begin{cases} \partial_t u(t) + \nabla \cdot j(t) = 0, \\ j(t) = J\big(t, u(t)\big), \end{cases} \tag{2.1}$$

where we omit the explicit dependence on the space variable $x \in \Lambda$. For driven diffusive systems the constitutive equation takes the form

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

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

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

where f is the equilibrium free energy per unit of volume.
4. Equations (2.1)–(2.2) have to be supplemented by the appropriate boundary condition on $\partial\Lambda$ due to the interaction with the external reservoirs. If $\lambda(t, x)$, $x \in \partial\Lambda$, is the chemical potential of the external reservoirs, this boundary condition reads

$$f'\big(u(t, x)\big) = \lambda(t, x), \quad x \in \partial\Lambda. \tag{2.4}$$

In the case of stochastic microscopic models with time independent driving, the above macroscopic description is derived in the diffusive scaling limit [6, 8, 14, 20, 27]. As we discuss later, the extension to time dependent driving is straightforward.

Given time-independent chemical potential $\lambda(x)$ and external field $E(x)$, we drop the dependence on t from $J(t, \rho)$ and denote by $\bar{\rho}_{\lambda, E}$ the stationary solution of (2.1)–(2.4),

$$\begin{cases} \nabla \cdot J(\bar{\rho}) = \nabla \cdot (-D(\bar{\rho})\nabla\bar{\rho} + \chi(\bar{\rho})E) = 0, & x \in \Lambda, \\ f'(\bar{\rho}(x)) = \lambda(x), & x \in \partial\Lambda. \end{cases} \quad (2.5)$$

Observe that if the field E is gradient, $E = \nabla U$, and if it is possible to choose the arbitrary constant in the definition of U such that $U(x) = \lambda(x)$, $x \in \partial\Lambda$, then the stationary solution satisfies $f'(\bar{\rho}_{\lambda, E}(x)) = U(x)$ and the stationary current vanishes, $J(\bar{\rho}_{\lambda, E}) = 0$. Conversely, given any profile $\bar{\rho}(x)$ it is possible to choose $\lambda(x)$ and $E(x)$ so that $\bar{\rho}$ solves (2.5) and moreover $J(\bar{\rho}) = 0$. It is indeed enough to set $\lambda(x) = f'(\bar{\rho}(x))$, $x \in \partial\Lambda$, and $E(x) = \nabla f'(\bar{\rho}(x))$, $x \in \Lambda$. According to the point of view introduced in [10], we refer to this case as (inhomogeneous) equilibrium states.

Given time-dependent chemical potential $\lambda(t, x)$ and external field $E(t, x)$, for $t \geq 0$ the profile $\bar{\rho}_{\lambda(t), E(t)}$ is the solution of (2.5) with λ and E "frozen" at the time t. By using such profile, it is possible to reduce the equations with time-dependent boundary conditions (2.4) to the case of time independent boundary conditions. Indeed, by writing $u(t) = \bar{\rho}_{\lambda(t), E(t)} + v(t)$ we deduce that v solves

$$\partial_t v = \nabla \cdot \left[D(\bar{\rho}_{\lambda(t), E(t)} + v)\nabla(\bar{\rho}_{\lambda(t), E(t)} + v) - \chi(\bar{\rho}_{\lambda(t), E(t)} + v)E \right] - \partial_t \bar{\rho}_{\lambda(t), E(t)}$$

with boundary conditions $v(t, x) = 0$ for $x \in \partial\Lambda$.

Energy Balance   The energy exchanged between the system and the external reservoirs and fields in the time interval $[0, T]$ is given by

$$\int_0^T dt \left\{ -\int_{\partial\Lambda} d\sigma(x)\,\lambda(t, x)\,j(t, x) \cdot \hat{n}(x) + \int_\Lambda dx\,j(t, x) \cdot E(t, x) \right\}, \quad (2.6)$$

where $\hat{n}$ is the outer normal to $\partial\Lambda$ and $d\sigma$ is the surface measure on $\partial\Lambda$. The first term on the right hand side is the energy provided by the reservoirs while the second is the energy provided by the external field.

Fix time dependent paths $\lambda(t, x)$ of the chemical potential and $E(t, x)$ of the driving field. Given a density profile ρ, let $u(t, x)$, $j(t, x)$, $t \geq 0$, $x \in \Lambda$, be the solution of (2.1)–(2.4) with initial condition ρ. We then denote by $W_{[0, T]} = W_{[0, T]}(\lambda, E, \rho)$, the energy exchanged between the system and the external driving, dropping the subscript when $T = +\infty$. We claim that

$$W_{[0, T]} \geq F\big(u(T)\big) - F(\rho), \quad (2.7)$$

where F is the equilibrium free energy functional,

$$F(\rho) = \int_\Lambda dx\,f\big(\rho(x)\big). \quad (2.8)$$

Indeed, by using the boundary condition (2.4) and by the divergence theorem in (2.6) (from now on we drop from the notation the dependence on x)

$$\begin{aligned} W_{[0, T]} &= \int_0^T dt \left\{ -\int_{\partial\Lambda} d\sigma\,f'\big(u(t)\big)j(t) \cdot \hat{n} + \int_\Lambda dx\,j(t) \cdot E(t) \right\} \\ &= \int_0^T dt \int_\Lambda dx \left\{ -\nabla \cdot \big[f'\big(u(t)\big)j(t) \big] + j(t) \cdot E(t) \right\} \end{aligned}$$

$$= \int_0^T dt \int_\Lambda dx \left[-f'\big(u(t)\big) \nabla \cdot j(t) - f''\big(u(t)\big) \nabla u(t) \cdot j(t) + j(t) \cdot E(t) \right]$$

$$= \int_0^T dt \, \frac{d}{dt} \int_\Lambda dx \, f\big(u(t)\big) + \int_0^T dt \int_\Lambda dx \, j(t) \cdot \chi\big(u(t)\big)^{-1} j(t), \tag{2.9}$$

where we used the continuity equation (2.1), the Einstein relation (2.3), and the constitutive equation (2.2). Since the first term is a total derivative and the second one is positive, the inequality (2.7) follows.

This argument provides a dynamic derivation of the second law of thermodynamics as expressed by the Clausius inequality (2.7). The key ingredients have been the assumption of local equilibrium together with the local Einstein relationship (2.3).

3 Equilibrium States

We examine in this section the case of equilibrium states and their transformations.

Reversible and Quasi Static Transformations We consider first the simpler case of spatially homogeneous equilibrium states. Such states are characterized by a vanishing external field E and by a chemical potential λ constant in space and time. In this case the stationary solution $\bar{\rho}_{\lambda,0}$ of the hydrodynamic equations (2.1)–(2.4) is the constant ρ satisfying $f'(\rho) = \lambda$. Hereafter, we denote $\bar{\rho}_{\lambda,0}$ simply by $\bar{\rho}_\lambda$.

Fix two constant chemical potentials λ_0, λ_1. Consider a system initially in the state $\bar{\rho}_0 = \bar{\rho}_{\lambda_0}$ which is driven to a new state $\bar{\rho}_1 = \bar{\rho}_{\lambda_1}$ by changing the chemical potential in time in a way that $\lambda(t) = \lambda_0$ for $t \leq 0$ and $\lambda(t) = \lambda_1$ for $t \geq T$; here T is some fixed positive time. This transformation from $\bar{\rho}_0$ to $\bar{\rho}_1$ is called *reversible* if the energy exchanged with the reservoirs is minimal. A basic thermodynamic principle asserts that reversible transformation are accomplished by a sequence of equilibrium states and are well approximated by *quasi static* transformations, transformations in which the variation of the chemical potential is very slow so that the density profile at time $u(t)$ is very close to the stationary profile $\bar{\rho}_{\lambda(t)}$. We show that this principle can be derived from the general assumptions of Sect. 2.

Let $u(t,x)$, $j(t,x)$, $t \geq 0$, $x \in \Lambda$, be the solution of (2.1)–(2.4) with initial condition $\bar{\rho}_0$. Since the chemical potential is equal to λ_1 for $t \geq T$, it holds $u(t) \to \bar{\rho}_1$ as $t \to +\infty$. Moreover, as $\bar{\rho}_1$ is an equilibrium state, the current $j(t)$ relaxes to $J(\bar{\rho}_1) = 0$. Observe that, since the system has a finite relaxation time, the convergence is exponentially fast. We deduce that the last integral in (2.9) is finite as $T \to \infty$ and

$$W = \int_0^\infty dt \, \frac{d}{dt} \int_\Lambda dx \, f\big(u(t)\big) + \int_0^\infty dt \int_\Lambda dx \, j(t) \cdot \chi\big(u(t)\big)^{-1} j(t)$$

$$\geq |\Lambda| \big[f(\bar{\rho}_1) - f(\bar{\rho}_0) \big]. \tag{3.1}$$

Note that we did not assume any regularity of the chemical potential in time so that it can be also discontinuous.

It remains to show that in the quasi static limit equality in (3.1) is achieved. That is the thermodynamic relation

$$W = \Delta F \tag{3.2}$$

holds, where $\Delta F = |\Lambda| [f(\bar{\rho}_1) - f(\bar{\rho}_0)]$ is the variation of the free energy. If this is case, by running the transformation backward in time, we can return to the original state exchanging the energy $-\Delta F$. For this reason the transformations for which (3.1) becomes equality are

called reversible. Since for any fixed transformation the inequality in (3.1) is strict because the second term on the right hand side of the first line in (3.1) cannot be identically zero, reversible transformations cannot be achieved exactly. We can however exhibit a sequence of transformations for which the second term on the right hand side of the first line in (3.1) term can be made arbitrarily small. This sequence of transformations is what we call quasi static transformations. Fix a smooth function $\lambda(t)$ such that $\lambda(0) = \lambda_0$ and $\lambda(t) = \lambda_1$ for $t \geq T$. Given $\delta > 0$ we set $\lambda_\delta(t) = \lambda(\delta t)$. Since $E = 0$, the second term on the right hand side of (3.1) is given by

$$\int_0^\infty dt \int_\Lambda dx \, \nabla f'\big(u_\delta(t)\big) \cdot \chi\big(u_\delta(t)\big) \nabla f'\big(u_\delta(t)\big),$$

where u_δ is the solution to (2.1)–(2.4) with initial condition $\bar\rho_0$ and boundary conditions $\lambda_\delta(t)$. Recall that $\bar\rho_{\lambda_\delta(t)}$ is the equilibrium state associated to the constant chemical potential $\lambda_\delta(t)$ (with t frozen). Since $\nabla f'(\bar\rho_{\lambda_\delta(t)}) = 0$, we can rewrite the previous integral as

$$\int_0^\infty dt \int_\Lambda dx \, \nabla\big[f'\big(u_\delta(t)\big) - f'(\bar\rho_{\lambda_\delta(t)})\big] \cdot \chi\big(u_\delta(t)\big) \nabla\big[f'\big(u_\delta(t)\big) - f'(\bar\rho_{\lambda_\delta(t)})\big].$$

The difference between the solution of the hydrodynamic equation $u_\delta(t)$ and the stationary profile $\bar\rho_{\lambda_\delta(t)}$ is of order δ uniformly in time, and so is the difference $f'(u_\delta(t)) - f'(\bar\rho_{\lambda_\delta(t)})$. As the integration over time essentially extends over an interval of length δ^{-1}, the previous expression vanishes for $\delta \to 0$. This implies that equality in (3.1) is achieved in the limit $\delta \to 0$. Note that in the previous argument we did not use any special property of the path $\lambda(t)$ besides its smoothness in time. The trajectory $\lambda(t)$ from λ_0 to λ_1 can be otherwise arbitrary.

We now discuss the case of spatially inhomogeneous equilibrium states. According to the point of view introduced in [10], in absence of external magnetic fields, such states $\bar\rho = \bar\rho(x)$ are characterized by the vanishing of the associated current, $J(\bar\rho) = 0$. An example is provided by a sedimentation equilibrium in gravitational and centrifugal fields.

Consider a density profile ρ, a time dependent chemical potential $\lambda(t, x)$ and a time dependent external field $E(t, x)$. We assume that $\lambda(t, x)$, $E(t, x)$ converge to $\lambda_1(x)$, $E_1(x)$ as $t \to +\infty$ fast enough, e.g. exponentially fast. Let $\bar\rho_1 = \bar\rho_{\lambda_1, E_1}$ be the stationary state associated to the chemical potential λ_1 and the external field E_1. We also assume that $\bar\rho_1$ is an equilibrium state, that is the current $J(\bar\rho_1)$ vanishes.

Let $u(t, x)$, $j(t, x)$, $t \geq 0$, $x \in \Lambda$, be the solution of (2.1)–(2.4) with initial condition ρ. Since $\bar\rho_1$ is an equilibrium state, the current $j(t)$ relaxes as $t \to +\infty$, to $J(\bar\rho_1) = 0$. The argument presented for homogeneous equilibrium applies also to the present setting and yields

$$W(\lambda, E, \rho) \geq F(\bar\rho_1) - F(\rho), \tag{3.3}$$

where F is the equilibrium free energy defined in (2.8).

It remains to introduce quasi static transformations in this more general context and show that equality in (3.3) is achieved. Let $\lambda_0(x) = \lambda(0, x)$, $E_0(x) = E(0, x)$. Assume that the initial profile ρ is the stationary profile associated to λ_0, E_0, $\rho = \bar\rho_{\lambda_0, E_0} = \bar\rho_0$, and that $\bar\rho_0$, is an equilibrium state, $J(\bar\rho_0) = 0$. Fix $T > 0$ and choose smooth functions $(\lambda(t), E(t))$, such that $(\lambda(0), E(0)) = (\lambda_0, E_0)$, $(\lambda(t), E(t)) = (\lambda_1, E_1)$, $t \geq T$, and $J(\bar\rho_{\lambda(t), E(t)}) = 0$ for $t \geq 0$. Such transformations always exist but are not unique. We may, for instance, first choose a smooth path $\bar\rho(t)$, such that $\bar\rho(0) = \bar\rho_0$ and $\bar\rho(t) = \bar\rho_1$ for $t \geq T$. Then choose $\lambda(t) = f'(\bar\rho(t))$ and $E(t) = \nabla f'(\bar\rho(t))$. In view of the discussion below (2.5), we then have $\bar\rho_{\lambda(t), E(t)} = \bar\rho(t)$.

For $\delta > 0$, let $(\lambda_\delta(t), E_\delta(t)) = (\lambda(\delta t), E(\delta t))$. Let $u_\delta(t)$ be the solution of (2.1)–(2.4) with initial condition $\bar\rho_0$, boundary condition $\lambda_\delta(t)$ and external field $E_\delta(t)$. At this point we can repeat the argument for homogeneous equilibrium states and show that equality in (3.3) is achieved in the quasi static limit $\delta \to 0$.

Excess Work   Consider a transformation $(\lambda(t), E(t))$, $t \geq 0$, and an initial density profile ρ. We assume that as $t \to +\infty$ it holds $(\lambda(t), E(t)) \to (\lambda_1, E_1)$ fast enough where (λ_1, E_1) defines the equilibrium state $\bar\rho_1 = \bar\rho_{\lambda_1, E_1}$, i.e. $J(\bar\rho_1) = 0$. We then introduce the *excess work* $W_{\mathrm{ex}} = W_{\mathrm{ex}}(\lambda, E, \rho)$ as the difference between the energy exchanged between the system and the external driving and the work involved in a reversible transformation from ρ to $\bar\rho_1$, namely

$$W_{\mathrm{ex}} = W(\lambda, E, \rho) - \min W = \int_0^\infty dt \int_\Lambda dx\, j(t) \cdot \chi\big(u(t)\big)^{-1} j(t), \qquad (3.4)$$

where we used (3.1) as well as the fact that the minimum of W is given by the right hand side of (3.2). Observe that W_{ex} is a positive functional of the transformation $(\lambda(t), E(t))$ and the initial condition ρ. Of course, by taking a sequence of quasi static transformations W_{ex} can be made arbitrarily small. Below we shall compute W_{ex} for specific transformations and illustrate its thermodynamic relevance.

Relaxation Path and Availability   Consider an equilibrium system in the state $\bar\rho_0$, characterized by a chemical potential λ_0 and an external field E_0. This system is put in contact with reservoirs at constant chemical potential λ_1 and an external field E_1, different from the chemical potential λ_0 and the external field E_0 associated to $\bar\rho_0$. For $t > 0$ the system thus evolves according to the hydrodynamic equation (2.1)–(2.4) with initial condition $\bar\rho_0$, external field E_1, and boundary condition λ_1. Such a transformation can be realized by considering first a smooth transition from λ_0 to λ_1 and then taking the limit in which it becomes a step function. When $t \to +\infty$ the system relaxes to the equilibrium state $\bar\rho_1$. In view of (3.4) and the constitutive equation (2.2), the excess work along such a path is given by

$$W_{\mathrm{ex}}(\lambda_1, E_1, \bar\rho_0) = -\int_0^\infty dt \int_\Lambda dx\, \big[\nabla f'\big(u(t)\big) - E_1\big] \cdot J\big(u(t)\big).$$

Since $J(\bar\rho_1) = 0$, $\nabla f'(\bar\rho_1) = E_1$, and we may replace E_1 by $\nabla f'(\bar\rho_1)$ in the previous equation. As $u(t)$ and $\bar\rho_1$ satisfy the same boundary conditions, after an integration by parts the previous expression becomes

$$W_{\mathrm{ex}}(\lambda_1, E_1, \bar\rho_0) = \int_0^\infty dt \int_\Lambda dx \big[f'\big(u(t)\big) - f'(\bar\rho_1)\big]\nabla \cdot J\big(u(t)\big)$$
$$= -\int_0^\infty dt \int_\Lambda dx \big[f'\big(u(t)\big) - f'(\bar\rho_1)\big]\partial_t u(t).$$

We have therefore shown that

$$W_{\mathrm{ex}}(\lambda_1, E_1, \bar\rho_0) = \int_\Lambda dx \big[f(\bar\rho_0) - f(\bar\rho_1) - f'(\bar\rho_1)(\bar\rho_0 - \bar\rho_1)\big]. \qquad (3.5)$$

Observe that the excess work W_{ex} is not the difference of a thermodynamic potential between the states $\bar\rho_0$ and $\bar\rho_1$. In the case of spatially homogeneous equilibria with vanishing external field, (3.5) becomes

$$W_{\mathrm{ex}}[\lambda_1, 0, \bar\rho_0] = |\Lambda|\big[f(\bar\rho_0) - f(\bar\rho_1) - \lambda_1(\bar\rho_0 - \bar\rho_1)\big]. \qquad (3.6)$$

To connect this computation with classical thermodynamics, we briefly recall the notion of *availability*, see e.g., [25, Chap. 7]. Since the temperature of the system is the same of the environment, the availability per unit of volume is defined by $a = f(\bar\rho_0) - \lambda_1 \bar\rho_0$. The function a, which depends on the state of the system $\bar\rho_0$ and the environment λ_1, can be used to compute the maximal useful work that can be extracted from the system in the given environment. More precisely, recalling that $f'(\bar\rho_1) = \lambda_1$,

$$-\Delta a = f(\bar\rho_0) - f(\bar\rho_1) - \lambda_1(\bar\rho_0 - \bar\rho_1) \geq 0 \tag{3.7}$$

is the maximal useful work per unit of volume that can be extracted from the system in the given environment, see [25, Chap. 7] or [23, § 20]. The inequality in (3.7) is due to the convexity of f and expresses the thermodynamic stability. We have thus concluded that, along the relaxation path specified above the excess work W_{ex} is equal to the maximal useful work that can be extracted from the system.

Fluctuations and Quasi Potential   The Einstein theory of thermodynamic fluctuations, see e.g. [23, Eq. (112.2)], establishes a precise connection between the excess work computed along the transformation described before and the probability of observing a fluctuation. Denote by $\mu^{\lambda,E}$ the statistical ensemble of an equilibrium (not necessarily spatially homogeneous) system in contact with reservoirs at chemical potential λ and with an external field E. The probability of observing a fluctuation ρ of the density in the macroscopic volume Λ can be expressed as

$$\mu^{\lambda,E}(\rho_\varepsilon \approx \rho) \asymp \exp\{-\varepsilon^{-d}\beta V_{\lambda,E}(\rho)\}, \tag{3.8}$$

where $\beta = 1/\kappa T$ (here T is the temperature), $\varepsilon \ll 1$ is the (a-dimensional) scaling factor, i.e. the ratio between the microscopic length scale (say the typical intermolecular distance) and the macroscopic one, and ρ_ε is the *empirical density* namely, $\rho_\varepsilon(x)$ is the average number of particles is a macroscopically small volume around x. The symbol $\asymp$ denotes logarithmic equivalence as $\varepsilon \to 0$ and

$$V_{\lambda,E}(\rho) = W_{ex}(\lambda, E, \rho). \tag{3.9}$$

In the right hand side of (3.9) the chemical potential λ and the external field E are constant in time so that W_{ex} is given by (3.5).

Referring to [7, 10] for more details, we briefly present the connection of the functional $V_{\lambda,E}$ to a control problem. Instead of computing the asymptotic probability of observing a given fluctuation, we take an active viewpoint looking at the most convenient way to produce such fluctuation. Consider at time $t = -\infty$ an equilibrium system in the state $\bar\rho_1$ in contact with reservoirs whose chemical potential is λ_1 and an external field E_1. We drive the system in the time interval $(-\infty, 0]$ to the new state ρ, attained at time $t = 0$ by superimposing a field $e(t)$ to the original external field E_1. We introduce the associated cost functional I as

$$I(u, j) = \frac{1}{4} \int_{-\infty}^{0} dt \int_{\Lambda} dx\, e(t) \cdot \chi(u(t)) e(t) \tag{3.10}$$

where the path $(u(t), j(t))$, $t \in (-\infty, 0]$ satisfies (2.1)–(2.4) with fixed chemical potential λ_1 and external field $E_1 + e(t)$. Observe that there is a one-to-one correspondence between the path $(u(t), j(t))$ and the driving field $e(t)$. We can thus consider, as in (3.10), the functional I to be defined on the set of space-time paths $(u(t), j(t))$.

As discussed below (2.5), the arbitrary density profile ρ can be regarded as an equilibrium state associated to some chemical potential and some external field. As shown in [7, 10]

$$V_{\lambda_1, E_1}(\rho) = W_{ex}(\lambda_1, E_1, \rho) = \min I(u, j), \tag{3.11}$$

where the minimum is carried over all driving $e(t)$ such that $u(0) = \rho$. Observe that in this argument (λ_1, E_1) is the state at time $t = -\infty$ while ρ is the density profile at time $t = 0$.

As shown in [10], the optimal trajectory $(u(t), j(t))$ for the variational problem on the right hand side of (3.11) is the time reversal of the relaxation trajectory defined as follows. It is the solution to the hydrodynamic equations (2.1)–(2.4) where the chemical potential and the external field are respectively equal to λ_1 and E_1, while the initial condition, at $t = 0$, is ρ. In particular it relaxes toward $\bar{\rho}_1$. A simple computation indeed shows that if we evaluate the functional I along the time reversal of such trajectory we indeed get the excess work $W_{\mathrm{ex}}(\lambda_1, E_1, \rho)$ that has been computed in before. Such a time reversal symmetry is a peculiar feature of equilibrium states.

As discussed in [6, 8], the functional $I(u, j)$ describes the probability of space-time fluctuations of the density and current and, by solving the variational problem on the right hand side of (3.11), the probability of static fluctuations (3.8) is recovered. In the concrete models of stochastic lattice gases, these statements can be rigorously proven.

Relative Entropy   We conclude this section establishing the connection between the functional $V_{\lambda, E}$ with the Gibbs states of equilibrium statistical mechanics. For simplicity of notation we consider the case of lattice gases without external field and constant chemical potential, i.e. the case of homogeneous equilibrium states. Let Λ_ℓ be the cube of side length ℓ in $\mathbb{Z}^d$ and, for $\lambda \in \mathbb{R}$, let μ_ℓ^λ be the grand-canonical Gibbs measure on Λ_ℓ with chemical potential λ,

$$\mu_\ell^\lambda(\eta) = \frac{1}{Z_\ell(\lambda)} \exp\left\{ -\beta H_\ell(\eta) + \beta\lambda \sum_{x \in \Lambda_\ell} \eta(x) \right\}, \tag{3.12}$$

where $\beta = 1/\kappa T$, $\eta(x)$, $x \in \Lambda_\ell$, are the occupation variables, $H_\ell(\eta)$ is the energy of the configuration η, and $Z_\ell(\lambda)$ is the grand-canonical partition function. The pressure p is given by

$$p(\lambda) = \frac{1}{\beta} \lim_{\ell \to \infty} \frac{1}{\ell^d} \log Z_\ell(\lambda), \tag{3.13}$$

and the free energy per unit of volume f, the function which appears in (2.3), is obtained as the Legendre transform of p,

$$f(\rho) = \sup_\lambda \{ \rho\lambda - p(\lambda) \}.$$

The *relative entropy* $S(\nu|\mu)$ of the probability ν with respect to μ is defined by

$$S(\nu|\mu) = \int d\mu \, \frac{d\nu}{d\mu} \log \frac{d\nu}{d\mu}. \tag{3.14}$$

Fix two chemical potentials λ_0 and λ_1. We claim that

$$\lim_{\ell \to \infty} \frac{1}{\ell^d} S\big(\mu_\ell^{\lambda_0} | \mu_\ell^{\lambda_1}\big) = \beta\big[f(\bar{\rho}_0) - f(\bar{\rho}_1) - \lambda_1(\bar{\rho}_0 - \bar{\rho}_1) \big], \tag{3.15}$$

where $\bar{\rho}_0$ and $\bar{\rho}_1$ are the densities associated to λ_0 and λ_1. In view of (3.6)–(3.9) this implies that in the thermodynamic limit $\ell \to \infty$ the relative entropy per unit of volume is proportional to the function $V_{\lambda_1,0}(\bar{\rho}_0)$ per unit volume. To prove (3.15), observe that in view of (3.14) and the Gibbsian form (3.12),

$$\frac{1}{\ell^d} S\big(\mu_\ell^{\lambda_0} | \mu_\ell^{\lambda_1}\big) = \frac{1}{\ell^d} \log \frac{Z_\ell(\lambda_1)}{Z_\ell(\lambda_0)} + \beta(\lambda_0 - \lambda_1) \sum_\eta \mu_\ell^{\lambda_0}(\eta) \frac{1}{\ell^d} \sum_{x \in \Lambda_\ell} \eta(x)$$

By definition of the pressure, the first term converges to $\beta[p(\lambda_1) - p(\lambda_0)]$, while the second one converges to $\beta(\lambda_0 - \lambda_1)\bar{\rho}_0$. The identity (3.15) then follows by Legendre duality.

The above interpretations of the functional $V_{\lambda,E}$, hereafter referred to as the *quasi potential*, reveal the connections between the static and dynamical properties of equilibrium systems. These connections are the starting point for a macroscopic description of nonequilibrium systems.

4 Nonequilibrium States

Nonequilibrium states are characterized by the presence of a non vanishing current in the stationary density profile. Therefore, to maintain such states one needs to dissipate a positive amount of energy per unit of time. If we consider a transformation between nonequilibrium stationary states, the energy dissipated along such transformation will necessarily include the contribution needed to maintain such states. The arguments of the previous section have therefore to be modified in order to take into account this amount of energy. This issue, first raised in [24], has been more recently considered e.g. in [4, 13, 19, 21, 22].

The appropriate definition of thermodynamic functionals for nonequilibrium systems is a central but difficult topic. Our starting point is the fluctuation formula (3.8), which, provided we replace $\mu^{\lambda,E}$ with the appropriate ensemble, makes good sense also in nonequilibrium so that the notion of the quasi potential can be defined also for nonequilibrium states. This has been the basis of our previous work on the subject [6, 9]. We recall however that even for equilibrium systems the quasi potential is not really a function of the state but expresses a property of the system in a given environment, see (3.5). In this section we show that—even for nonequilibrium states—the quasi potential is connected to the excess work and to the specific relative entropy between two states. We first recall some relevant results from [6, 7].

Quasi Potential Fix time independent chemical potential $\lambda = \lambda(x)$, $x \in \partial\Lambda$, external field $E = E(x)$, $x \in \Lambda$, and recall that $\bar{\rho}_{\lambda,E}$, the solution of (2.5), is the stationary solution of the hydrodynamic equation. We assume that λ, E define a nonequilibrium state in the sense that $J(\bar{\rho}_{\lambda,E}) \neq 0$. The statistical ensemble associated to such state is still denoted by $\mu^{\lambda,E}$. Then, as shown in [6], the fluctuation formula (3.8) holds where the quasi potential $V_{\lambda,E}$ solves the same variational problem as in equilibrium states. Namely,

$$V_{\lambda,E}(\rho) = \min I(u, j) \tag{4.1}$$

where I is the action functional defined in (3.10) and the minimum is carried out over all paths such that $u(-\infty) = \bar{\rho}_{\lambda,E}$ and $u(0) = \rho$.

In nonequilibrium there is no simple formula for the quasi potential but it can be characterized [6–8] as the maximal solution of the stationary Hamilton-Jacobi equation

$$\int_\Lambda dx \, \nabla \frac{\delta V_{\lambda,E}(\rho)}{\delta\rho} \cdot \chi(\rho) \nabla \frac{\delta V_{\lambda,E}(\rho)}{\delta\rho} - \int_\Lambda dx \, \frac{\delta V_{\lambda,E}(\rho)}{\delta\rho} \nabla \cdot J(\rho) = 0. \tag{4.2}$$

where $\delta V_{\lambda,E}/\delta\rho$ vanishes at the boundary $\partial\Lambda$ and ρ satisfies the boundary condition $f'(\rho(x)) = \lambda(x)$, $x \in \partial\Lambda$. The current $J(\rho)$ in (2.2) may therefore be decomposed as

$$J(\rho) = J_S(\rho) + J_A(\rho), \tag{4.3}$$

where

$$J_S(\rho) = -\chi(\rho)\nabla\frac{\delta V_{\lambda,E}(\rho)}{\delta\rho} \tag{4.4}$$

and $J_A(\rho) = J(\rho) - J_S(\rho)$. In view of the stationary Hamilton-Jacobi equation (4.2), the decomposition (4.3) is orthogonal in the sense that for each ρ

$$\int_\Lambda dx \, J_S(\rho) \cdot \chi(\rho)^{-1} J_A(\rho) = 0. \tag{4.5}$$

We shall refer to $J_S(\rho)$ as the *symmetric* current and to $J_A(\rho)$ as the *antisymmetric* current. This terminology refers to symmetric and antisymmetric part of the underlying Markovian microscopic dynamics [6–8]. More precisely, the generator of the evolution can be decomposed into a symmetric and an antisymmetric part which are respectively even and odd under time reversal. The current $J_S(\rho)$ is due to symmetric part and is responsible for the relaxation, while $J_A(\rho)$ to the antisymmetric part; we refer to Sect. 6.1 in which we discuss this decomposition for the zero range model. We finally emphasize that the decomposition (4.3) depends not trivially on λ, E.

Since the quasi potential $V_{\lambda,E}$ is minimal in the stationary profile, we deduce that $J_S(\bar\rho_{\lambda,E}) = 0$; namely, the stationary current is purely antisymmetric. In particular, $J_A(\bar\rho_{\lambda,E})$ is the typical current in the stationary nonequilibrium ensemble associated to (λ, E) and it is therefore experimentally accessible. In view of the general formula (2.9) for the total work, the amount of energy per unit of time needed to maintain the system in the stationary profile $\bar\rho_{\lambda,E}$ is

$$\int_\Lambda dx \, J_A(\bar\rho_{\lambda,E}) \cdot \chi(\bar\rho_{\lambda,E})^{-1} J_A(\bar\rho_{\lambda,E}). \tag{4.6}$$

Renormalized Work   In view of the previous paragraph, by interpreting the ideas in [24], it is natural to define in a nonequilibrium setting the renormalized work as the total work minus the work needed to maintain the stationary profile. Fix, therefore, $T > 0$, a density profile ρ, and space-time dependent chemical potentials $\lambda(t) = \lambda(t, x)$ and external field $E(t) = E(t, x)$, $0 \le t \le T$, $x \in \Lambda$. Let $u(t) = u(t, x)$, $j(t) = j(t, x)$, $t \ge 0$, $x \in \Lambda$, be the solution of (2.1)–(2.4) with initial condition ρ. Recalling (4.6), we thus define the renormalized work $W^{\mathrm{ren}}_{[0,T]} = W^{\mathrm{ren}}_{[0,T]}(\lambda, E, \rho)$ performed by the reservoirs and the external field in the time interval $[0, T]$ as

$$W^{\mathrm{ren}}_{[0,T]} = W_{[0,T]} - \int_0^T dt \int_\Lambda dx \, J_A\big(t, u(t)\big) \cdot \chi\big(u(t)\big)^{-1} J_A\big(t, u(t)\big). \tag{4.7}$$

In this formula $W_{[0,T]} = W_{[0,T]}(\lambda, E, \rho)$ is given in (2.6),

$$J(t, \rho) = J_S(t, \rho) + J_A(t, \rho), \qquad J_S(t, \rho) = -\chi(\rho)\nabla \frac{\delta V_{\lambda(t),E(t)}(\rho)}{\delta\rho}$$

in which $J(t, \rho)$ is given by (2.2) and $V_{\lambda(t),E(t)}$ is the quasi potential relative to the state $\lambda(t), E(t)$ with frozen t. Observe that the definition of the renormalized work involves the antisymmetric current $J_A(t)$ computed not at density profile $\bar\rho_{\lambda(t),E(t)}$ but at the solution $u(t)$ of the time dependent hydrodynamic equation. Therefore the second term on the right hand side of (4.7) is not directly measurable but requires first the computation of the quasi potential. The thermodynamic relevance of the above definition will be clear in the sequel. In contrast with the terminology in [24], we used the term *renormalized work* for the functional in (4.7) in order to reserve the term *excess work* to the extra work with respect to the minimal one.

Since the symmetric and the antisymmetric part of the current are orthogonal, repeating the computation performed in (2.9), we get that

$$W^{\mathrm{ren}}_{[0,T]}(\lambda, E, \rho) = F\big(u(T)\big) - F(\rho) + \int_0^T dt \int_\Lambda dx \, J_S\big(t, u(t)\big) \cdot \chi\big(u(t)\big)^{-1} J_S\big(t, u(t)\big).$$

We observe that for nonequilibrium states the quasi potential is generically a non local functional in view of the long range correlations [9, 14]. Therefore the symmetric current J_S above is generically non local and thus the renormalized work is also non local, compare with [22].

Consider a density profile ρ and a space-time dependent chemical potential $\lambda(t)$ and external field $E(t)$. Assume hereafter that $\lambda(t)$, $E(t)$ converge to λ_1, E_1 as $t \to +\infty$ fast enough, e.g. exponentially fast. Let $\bar{\rho}_1 = \bar{\rho}_{\lambda_1, E_1}$ be the stationary profile associated to the chemical potential λ_1, E_1, and $(u(t), j(t))$, $t \geq 0$, be the solution of (2.1)–(2.4) with initial condition ρ. Since $u(T)$ converges to $\bar{\rho}_1$, the symmetric part of the current, $J_S(u(T))$, relaxes as $T \to +\infty$ to $J_S(\bar{\rho}_1) = 0$ fast enough. In particular, the last integral in the previous formula is convergent as $T \to +\infty$ and we get

$$W^{\mathrm{ren}}(\lambda, E, \rho) = F(\bar{\rho}_1) - F(\rho)$$
$$+ \int_0^\infty dt \int_\Lambda dx\, J_S\big(t, u(t)\big) \cdot \chi\big(u(t)\big)^{-1} J_S\big(t, u(t)\big) \qquad (4.8)$$

where F is the equilibrium free energy functional, see (2.8). In particular,

$$W^{\mathrm{ren}}(\lambda, E, \rho) \geq F(\bar{\rho}_1) - F(\rho). \qquad (4.9)$$

As follows immediately from (4.7), $W^{\mathrm{ren}}_{[0,T]}(\lambda, E, \rho) \leq W_{[0,T]}(\lambda, E, \rho)$ and therefore (4.9) is stronger than the general inequality (2.7). Indeed, (4.9) states that the Clausius inequality holds for the renormalized work, see [22].

Quasi Static Transformations   As for equilibrium states, we show that, given two nonequilibrium states, there exists a sequence of transformations from the first to the second for which the second term on the right hand of (4.8) can be made arbitrarily small.

Let $(\lambda_0, E_0) = (\lambda(0), E(0))$ and assume that the initial profile ρ is the stationary profile associated to λ_0, E_0, i.e. $\rho = \bar{\rho}_{\lambda_0, E_0}$. Fix $T > 0$ and choose smooth function $\lambda(t)$, $E(t)$, $0 \leq t \leq T$, such that $(\lambda(0), E(0)) = (\lambda_0, E_0)$, $(\lambda(T), E(T)) = (\lambda_1, E_1)$. For $\delta > 0$, let $(\lambda_\delta(t), E_\delta(t)) = (\lambda(\delta t), E(\delta t))$, and $(u_\delta(t), j_\delta(t))$ be the solution of (2.1)–(2.4) with initial condition $\bar{\rho}_0 = \bar{\rho}_{\lambda_0, E_0}$, external field $E_\delta(t)$, and boundary condition $\lambda_\delta(t)$. The second term on the right hand side of (4.8) is given by

$$\int_0^\infty dt \int_\Lambda dx\, J_S\big(t, u_\delta(t)\big) \cdot \chi\big(u_\delta(t)\big)^{-1} J_S\big(t, u_\delta(t)\big).$$

For each fixed t, let $\bar{\rho}_\delta(t) = \bar{\rho}_{\lambda_\delta(t), E_\delta(t)}$ be the stationary profile associated to the driving $\lambda_\delta(t)$, $E_\delta(t)$ with frozen t. Since $J_S(t, \bar{\rho}_\delta(t)) = 0$, we can rewrite the previous integral as

$$\int_0^\infty dt \int_\Lambda dx\, \big[J_S\big(t, u_\delta(t)\big) - J_S\big(t, \bar{\rho}_\delta(t)\big)\big] \cdot \chi\big(u_\delta(t)\big)^{-1} \big[J_S\big(t, u_\delta(t)\big) - J_S\big(t, \bar{\rho}_\delta(t)\big)\big].$$

The difference between the solution of the hydrodynamic equation $u_\delta(t)$ and the stationary profile $\bar{\rho}_\delta(t)$ is of order δ uniformly in time, and so is the difference $J_S(t, u_\delta(t)) - J_S(t, \bar{\rho}_\delta(t))$. As the integration over time essentially extends over an interval of length δ^{-1}, the previous expression vanishes for $\delta \to 0$. This implies that equality in (4.9) is achieved in the limit $\delta \to 0$. In this argument we did not use any special property of the path $(\lambda(t), E(t))$ besides its smoothness in time, the trajectory $(\lambda(t), E(t))$ from (λ_0, E_0) to (λ_1, E_1) can be otherwise arbitrary.

Quasi static transformations thus minimize asymptotically the renormalized work and in the limit $\delta \to 0$ we obtain the nonequilibrium version of the thermodynamic relation (3.2), that is

$$W^{\mathrm{ren}} = \Delta F, \qquad (4.10)$$

where ΔF represents the variation of the equilibrium free energy functional, $\Delta F = F(\bar\rho_1) - F(\bar\rho_0)$. It is remarkable that the Clausius inequality and the optimality of quasi static transformations, basic laws of equilibrium thermodynamics, admit exactly the same formulation, after the subtraction performed in (4.7), for nonequilibrium states. Of course, (4.10) contains as a particular case the equilibrium situations in which the subtracted term vanishes.

Excess Work Consider space-time dependent chemical potential and external field $(\lambda(t), E(t))$, $t \geq 0$, such that $(\lambda(t), E(t))$ converges to (λ_1, E_1) as $t \to +\infty$ and an initial density profile ρ. We denote by $\bar\rho_1 = \bar\rho_{\lambda_1, E_1}$ the stationary profile associated to (λ_1, E_1).

We introduce the *excess work* $W_{\mathrm{ex}} = W_{\mathrm{ex}}(\lambda, E, \rho)$ as the difference between the renormalized energy $W^{\mathrm{ren}}[\lambda, E, \rho]$ exchanged between the system and the driving, and the minimal renormalized energy involved in a quasi static transformation from ρ to $\bar\rho_1$. Namely,

$$W_{\mathrm{ex}}(\lambda, E, \rho) = W^{\mathrm{ren}}(\lambda, E, \rho) - \min W^{\mathrm{ren}}(\lambda', E', \rho)$$

$$= \int_0^\infty dt \int_\Lambda dx \, J_{\mathrm{S}}(t, u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{S}}(t, u(t)) \tag{4.11}$$

where we used (4.8) and the minimum is take on all the paths (λ', E') such that $(\lambda'(+\infty), E'(+\infty)) = (\lambda_1, E_1)$. In the case of transformations which are realized by a sequence of equilibrium states, for each time t the current $J(t)$ is purely symmetric and the above definition coincides with (3.4).

Relaxation Path: Excess Work and Quasi Potential Consider at time $t = 0$ a stationary nonequilibrium profile $\bar\rho_0$ corresponding to some driving (λ_0, E_0). This system is put in contact with new reservoirs at chemical potential λ_1 and a new external field E_1. For $t > 0$ the system evolves according to the hydrodynamic equation (2.1)–(2.4) with initial condition $\bar\rho_0$, time independent boundary condition λ_1 and external field E_1. In particular, as $t \to \infty$ the system relaxes to $\bar\rho_1$. Along such a path, in view of the orthogonality relation (4.5), the excess work is given by

$$W_{\mathrm{ex}}(\lambda_1, E_1, \bar\rho_0) = \int_0^\infty dt \int_\Lambda dx \, J(u(t)) \cdot \chi(u(t))^{-1} J_{\mathrm{S}}(u(t))$$

where J_{S} is computed by using the quasi potential V_{λ_1, E_1}.

By definition (4.4) of the symmetric part of the current and by an integration by parts, the previous expression is equal to

$$\int_0^\infty dt \int_\Lambda dx \, \nabla \cdot J(u(t)) \frac{\delta V_{\lambda_1, E_1}(u(t))}{\delta \rho} = -\int_0^\infty dt \int_\Lambda dx \, \partial_t u(t) \frac{\delta V_{\lambda_1, E_1}(u(t))}{\delta \rho}.$$

We have therefore shown that

$$W_{\mathrm{ex}}(\lambda_1, E_1, \bar\rho_0) = V_{\lambda_1, E_1}(\bar\rho_0) - V_{\lambda_1, E_1}(\bar\rho_1) = V_{\lambda_1, E_1}(\bar\rho_0) \tag{4.12}$$

which extends to nonequilibrium states the relation (3.5) between the excess work and the quasi potential.

Time Dependent Transformations Instead of the transformations examined in the previous subsection, where the external driving is constant in time, we consider a transformation with smooth space-time dependent chemical potential and external field. We thus consider a path $(\lambda(t), E(t))$, $t \geq 0$, such that $(\lambda(t), E(t)) \to (\lambda_1, E_1)$ as $t \to +\infty$ fast enough. We denote by $\bar\rho_1 = \bar\rho_{\lambda_1, E_1}$ the stationary profile corresponding to (λ_1, E_1) and let $(u(t), j(t))$, $t \geq 0$ be

the solution to the hydrodynamic equation (2.1)–(2.4) with initial condition $u(0) = \rho$. Here ρ is an arbitrary density profile.

In this case, the computations which led to (4.12) give that the excess of work is equal to

$$
\begin{aligned}
W_{\text{ex}}(\lambda, E, \rho) &= -\int_0^\infty dt \int_\Lambda dx \, \frac{\delta V_{\lambda(t), E(t)}(u(t))}{\delta \rho} \partial_t u(t) \\
&= -\int_0^\infty dt \, \frac{d}{dt} V_{\lambda(t), E(t)}(u(t)) + \int_0^\infty dt \, (\partial_t V_{\lambda(t), E(t)})(u(t)). \\
&= V_{\lambda(0), E(0)}(\rho) + \int_0^\infty dt \, (\partial_t V_{\lambda(t), E(t)})(u(t))
\end{aligned}
$$

where we used that $u(t) \to \bar\rho_1$ as $t \to +\infty$ fast enough and $V_{\lambda_1, E_1}(\bar\rho_1) = 0$.

In particular, when we start from the stationary density profile associated to $(\lambda(0), E(0))$, i.e. $\rho = \bar\rho_0 = \bar\rho_{\lambda(0), E(0)}$, we conclude

$$
W_{\text{ex}}(\lambda, E, \bar\rho_0) = \int_0^\infty dt \, (\partial_t V_{\lambda(t), E(t)})(u(t)) \geq 0. \tag{4.13}
$$

Note that the right hand side is not a total derivative and, in particular, the excess work depends on the path of the driving $(\lambda(t), E(t))$. From the previous formula we deduce that excess work can be computed in terms of the time derivatives of the driving forces. The inequality in (4.13), which follows from (4.11), is a restatement of the Clausius inequality (4.9).

Quasi Potential and Specific Relative Entropy The relationship (3.15) between the relative entropy and the quasi potential extends, exactly with the same formulation, to nonequilibrium states. We discuss only the case of stochastic lattice gases. Recall that $\Lambda \subset \mathbb{R}^d$ is the macroscopic volume, and denote by Λ_ε the corresponding subset of the lattice with spacing ε, so that the number of sites in Λ_ε is approximately $\varepsilon^{-d}|\Lambda|$. Given the chemical potential λ of the boundary reservoirs and the external field E, let $\mu_{\Lambda_\varepsilon}^{\lambda, E}$ be the stationary measure of a driven stochastic lattice gas.

Given (λ_0, E_0) and (λ_1, E_1), we claim that

$$
\lim_{\varepsilon \to 0} \varepsilon^d \, S\big(\mu_{\Lambda_\varepsilon}^{\lambda_0, E_0} | \mu_{\Lambda_\varepsilon}^{\lambda_1, E_1}\big) = \beta V_{\lambda_1, E_1}(\bar\rho_0), \tag{4.14}
$$

where $\beta = 1/\kappa T$, the relative entropy S has been defined in (3.14), and $\bar\rho_0$ is the stationary profile corresponding to (λ_0, E_0).

We refer to Sect. 6.2 for a detailed derivation of (4.14) under the assumptions that the stationary measures satisfy a strong form of local equilibrium (that holds e.g. for the boundary driven symmetric simple exclusion process). We next present a simple heuristic argument leading to (4.14). In view of the definition (3.14) of the relative entropy we have that

$$
\varepsilon^d \, S\big(\mu_{\Lambda_\varepsilon}^{\lambda_0, E_0} | \mu_{\Lambda_\varepsilon}^{\lambda_1, E_1}\big) = \varepsilon^d \sum_\eta \mu_{\Lambda_\varepsilon}^{\lambda_0, E_0}(\eta) \log \frac{\mu_{\Lambda_\varepsilon}^{\lambda_0, E_0}(\eta)}{\mu_{\Lambda_\varepsilon}^{\lambda_1, E_1}(\eta)}.
$$

By the large deviation formula (3.8), we then get

$$
\varepsilon^d \, S\big(\mu_{\Lambda_\varepsilon}^{\lambda_0, E_0} | \mu_{\Lambda_\varepsilon}^{\lambda_1, E_1}\big) \approx \varepsilon^d \beta \sum_\eta \mu_{\Lambda_\varepsilon}^{\lambda_0, E_0}(\eta) \big[V_{\lambda_1, E_1}(\rho_\varepsilon(\eta)) - V_{\lambda_0, E_0}(\rho_\varepsilon(\eta)) \big]
$$

$$
\approx \beta \big[V_{\lambda_1, E_1}(\bar\rho_0) - V_{\lambda_0, E_0}(\bar\rho_0) \big] = \beta V_{\lambda_1, E_1}(\bar\rho_0),
$$

where $\rho_\varepsilon(\eta)$ denotes the density profile associated to the microscopic configuration η. In the final step we used the law of large numbers for the microscopic density profile under the probability $\mu_{\Lambda_\varepsilon}^{\lambda_0, E_0}$.

Actually, the above argument is somewhat misleading. The identity (4.14) is not a consequence only of the large deviation formula (3.8). It is in fact not difficult to construct counterexamples to such a general statement. Let, for instance, μ_ε^β be the Gibbs measure for a one-dimensional Ising model at zero magnetic field and inverse temperature β on a ring with ε^{-1} sites. The magnetization satisfy the large deviation formula (3.8) and its typical value is zero for both ensembles so that the right hand side of (4.14) vanishes. On the other hand, by a direct computation, for $\beta_0 \neq \beta_1$, $\lim_\varepsilon \varepsilon S(\mu_\varepsilon^{\beta_0} | \mu_\varepsilon^{\beta_1}) > 0$. Observe that this example does not contradict (4.14) as we are comparing two ensembles in which we varied the temperature and not the magnetic field. In this example, the correct formulation of (4.14) would have been in terms of the large deviation function for the energy, that is the extensive variable conjugated the intensive parameter that has been changed.

5 Time Dependent Quasi Potential

In the previous section we have considered the case in which the external driving changes over time scales that are comparable to or longer than the typical relaxation times of the system. The renormalized work has thus been defined by considering the values of the chemical potential and the external field frozen at a given time, see (4.7). In this section we consider a different approach, suited for faster transformations, in which we take into account the fact that the system has a finite relaxation time. We here define the renormalized work by using a time dependent quasi potential which, at a given time, depends on the previous history.

Throughout all this section we fix a space-time dependent chemical potential $\lambda(t)$ and an external field $E(t)$, where now $-\infty < t < +\infty$. We assume that $(\lambda(t), E(t))$ converges (fast enough) to (λ_0, E_0) and (λ_1, E_1) as $t \to -\infty$ and $t \to +\infty$, respectively. We denote by $\bar\rho_0$ and $\bar\rho_1$ the stationary profiles corresponding to (λ_0, E_0) and (λ_1, E_1), i.e. $\bar\rho_i = \bar\rho_{\lambda_i, E_i}$, $i = 0, 1$.

For $T_- < T_+$, denote by $I_{[T_-, T_+]}$ the action functional on the set of paths $(u(t), j(t))$, $t \in [T_-, T_+]$, defined as in (3.10)

$$I_{[T_-, T_+]}(u, j) = \frac{1}{4} \int_{T_-}^{T_+} dt \int_\Lambda dx \left[j(t) - J(t, u(t)) \right] \cdot \chi(u(t))^{-1} \left[j(t) - J(t, u(t)) \right],$$

where $(u(t), j(t))$ satisfy the continuity equation $\partial_t u + \nabla \cdot j = 0$ and $J(t, \rho)$ is given in (2.2). In particular, if $(u(t), j(t))$ is a solution of the hydrodynamic equation (2.1) then $I_{[T_-, T_+]}(u, j) = 0$.

For two density profiles ρ_-, ρ_+, denote by $V_{\lambda, E}(T_-, \rho_-; T_+, \rho_+)$ the minimal action in the transition from ρ_- to ρ_+ in the time interval $[T_-, T_+]$:

$$V_{\lambda, E}(T_-, \rho_-; T_+, \rho_+) = \inf\{I_{[T_-, T_+]}(u, j), u(T_-) = \rho_-, u(T_+) = \rho_+\}. \tag{5.1}$$

By a calculus of variations, similar to the one performed in classical mechanics, $V_{\lambda, E}(T_-, \rho_-; t, \rho)$, as a function of $t \in (T_-, T_+)$ and ρ, solves the time dependent Hamilton-Jacobi equation

$$\partial_t V_{\lambda, E} + \int_\Lambda dx \, \nabla \frac{\delta V_{\lambda, E}}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta V_{\lambda, E}}{\delta \rho} - \int_\Lambda dx \frac{\delta V_{\lambda, E}}{\delta \rho} \nabla \cdot J(t, \rho) = 0, \tag{5.2}$$

where $\delta V_{\lambda, E} / \delta \rho = \delta V_{\lambda, E}(T_-, \rho_-; t, \rho) / \delta \rho$ vanishes at the boundary $\partial \Lambda$ and ρ satisfies the boundary condition $f'(\rho(x)) = \lambda(t, x)$, $x \in \partial \Lambda$.

Let

$$V_{\lambda,E}(\rho_-;t,\rho) = \lim_{T_-\to-\infty} V_{\lambda,E}(T_-,\rho_-;t,\rho).$$

By taking the limit $T_-\to-\infty$ the dependence on the initial condition ρ_- disappears so that

$$V_{\lambda,E}(\rho_-;t,\rho) = V_{\lambda,E}(t,\rho) = \inf\Big\{I_{(-\infty,t]}(u,j),\, u(t)=\rho,\, \lim_{s\to-\infty} u(s)=\bar\rho_0\Big\}. \quad (5.3)$$

In fact, when $T_-\to-\infty$ the optimal path for the variational problem on the right hand side of (5.1) first essentially relaxes to $\bar\rho_0$ according to the hydrodynamic equation (since $(\lambda(s),E(s))\to(\lambda_0,E_0)$ as $s\to-\infty$) and then follows the optimal path for the right hand side of (5.3). Observe that $V_{\lambda,E}(t,\rho)$ is obtained by solving a time dependent variational problem while the functional $V_{\lambda(t),E(t)}(\rho)$ used in Sect. 4 is obtained by solving a time independent variational problem with the chemical potential and the external field frozen at time t. We remark that if ρ coincides with the solution of (2.1) at time t then $V_{\lambda,E}(t,\rho)=0$.

Note that $V_{\lambda,E}(t,\rho)$ provides a large deviation formula analogous to (3.8) in the case of time dependent chemical potentials and external fields,

$$\mathbb{P}^{\lambda,E}\big[u_\varepsilon(t)\approx\rho\big] \asymp \exp\big\{-\varepsilon^{-d}\beta V_{\lambda,E}(t,\rho)\big\}, \quad (5.4)$$

where $\mathbb{P}^{\lambda,E}$ is the ensemble (defined on space-time paths) corresponding to the time dependent chemical potential and external field, ε is the scaling parameter, and $u_\varepsilon(t)$ is the empirical density at time t. The asymptotics (5.4) can be derived as follows. If we look at the large deviations probability for a space-time path $(u(s),j(s))$, $-\infty<s\le t$ of the empirical density and current we get

$$\mathbb{P}^{\lambda,E}\big((u_\varepsilon(s),j_\varepsilon(s))\approx(u(s),j(s)),s\in(-\infty,t]\big) \asymp \exp\big\{-\varepsilon^{-d}\beta I_{(-\infty,t]}(u,j)\big\}. \quad (5.5)$$

This formula has been derived in [6, 8] when the chemical potential and external field do not depend on time. The argument can be extended to the present setting. By minimizing with respect to the path $(u(s),j(s))$, $-\infty<s\le t$, with the constraint $u(t)=\rho$ we deduce (5.4).

We observe that the functional $V_{\lambda,E}(t,\rho)$ still solves the time dependent Hamilton-Jacobi equation (5.2). Moreover, by taking the limit $t\to\pm\infty$ we recover the time independent quasi potentials associated to the chemical potentials and external fields (λ_0,E_0), (λ_1,E_1), namely

$$\lim_{t\to-\infty} V_{\lambda,E}(t,\rho) = V_{\lambda_0,E_0}(\rho), \qquad \lim_{t\to+\infty} V_{\lambda,E}(t,\rho) = V_{\lambda_1,E_1}(\rho).$$

Renormalized Work   Let $V_{\lambda,E}(t,\rho)$ be the time dependent quasi potential defined in (5.3) in which we emphasize that $V_{\lambda,E}(t,\rho)$ depends on the whole path $(\lambda(s),E(s))$ for $-\infty<s\le t$. In analogy with (4.3) we decompose the current as

$$J(t,\rho) = J_1(t,\rho) + J_2(t,\rho), \quad (5.6)$$

where

$$J_1(t,\rho) = -\chi(\rho)\nabla\frac{\delta V_{\lambda,E}(t,\rho)}{\delta\rho}, \quad (5.7)$$

and, recalling (2.2), $J_2(t,\rho)$ is defined via (5.6) by difference. Observe that the definition of $J_1(t,\rho)$ differs from the symmetric current $J_S(t,\rho)$ introduced in (4.4). In fact in definition (4.4) we introduced the "thermodynamic force" $\delta V_{\lambda(t),E(t)}(\rho)/\delta\rho$ by considering the quasi potential with the chemical potential and external field frozen at time t while in (5.7) we used the time dependent quasi potential, i.e. we considered the time dependent thermodynamic force $\delta V_{\lambda,E}(t,\rho)/\delta\rho$. The difference among these two definition is the following. The

symmetric current $J_S(t, \rho)$ in (4.4) takes into account only the values of the driving λ, E at the time t and not the actual state of the system, in particular it is independent of the values $\lambda(s)$, $E(s)$ for $s < t$. On the other hand the current $J_1(t, \rho)$ in (5.7) depends on the actual state of the system and reflects the fact that the system has a strictly positive relaxation time. Since $V(t, \rho)$ is minimal when ρ coincides with the solution of the hydrodynamic equation (2.1) at time t we get that in this case $J_1(t, \rho) = 0$ or equivalently $J(t, \rho) = J_2(t, \rho)$. In the quasi static limit, i.e. for transformations λ, E which vary very slowly, the definitions (4.4) and (5.7) coincide.

In contrast with (4.5), the decomposition (5.6) is not orthogonal and the time dependent Hamilton-Jacobi equation (5.2) implies

$$\int_\Lambda dx \, J_1(t, \rho) \cdot \chi(\rho)^{-1} J_2(t, \rho) = \int_\Lambda dx \, \frac{\delta V_{\lambda, E}(t, \rho)}{\delta \rho} \nabla \cdot J_2(t, \rho) = \partial_t V_{\lambda, E}(t, \rho). \quad (5.8)$$

Fix a time window $[t, T]$ and let $(u(s), j(s))$, $t \leq s \leq T$, be the solution of (2.1)–(2.4) with initial condition $u(t) = \rho$. Here ρ is an arbitrary density profile (not necessarily the solution of the hydrodynamic equation at time t). We now define the renormalized work $\widehat{W}^{\text{ren}}_{[t, T]}(\lambda, E, \rho)$ in the time interval $[t, T]$ as

$$\widehat{W}^{\text{ren}}_{[t, T]}(\lambda, E, \rho) = W_{[t, T]}(\lambda, E, \rho)$$
$$- \int_t^T ds \int_\Lambda dx \, J_2(s, u(s)) \cdot \chi(u(s))^{-1} J_2(s, u(s))$$
$$- 2 \int_t^T ds \, \partial_s V_{\lambda, E}(s, u(s)), \quad (5.9)$$

where $W_{[t, T]}(\lambda, E, \rho)$ is given in (2.6) and last term above takes into account the energy exchanged due to the variation of the external driving in time. By taking the limit $T \to +\infty$ and using (2.9) together with (5.8) we deduce

$$\widehat{W}^{\text{ren}}_{[t, +\infty)}(\lambda, E, \rho) = F(\bar\rho_1) - F(\rho)$$
$$+ \int_t^\infty ds \int_\Lambda dx \, J_1(s, u(s)) \cdot \chi(u(s))^{-1} J_1(s, u(s)). \quad (5.10)$$

In particular, the renormalized work $\widehat{W}^{\text{ren}}_{[t, +\infty)}(\lambda, E, \rho)$ satisfies the Clausius inequality

$$\widehat{W}^{\text{ren}}_{[t, \infty)}(\lambda, E, \rho) \geq F(\bar\rho_1) - F(\rho) = \Delta F \quad (5.11)$$

where we recall that ρ is the initial datum at time t and $\bar\rho_1 = u(+\infty)$. As we discuss below, definition (5.9) also yields the identity between the associated excess work and the time dependent quasi potential $V(t, \rho)$.

Quasi Static Transformations   The arguments of the previous sections concerning quasi static transformations can be easily modified to the present setting. Recall that $\widehat{W}^{\text{ren}}_{[t, +\infty)}(\lambda, E, \rho)$ involves the current $J_1(s, \rho)$, for $t < s < +\infty$, as defined in (5.7), which depends on the path $(\lambda(s), E(s))$ for $-\infty < s \leq t$. As the right hand side of (5.10) depends also on $u(s)$ for $s > t$ which is determined by $(\lambda(s), E(s))$ for $t \leq s < +\infty$, we conclude that $\widehat{W}^{\text{ren}}_{[t, \infty)}(\lambda, E, \rho)$ depends on the whole path $(\lambda(s), E(s))$ for $-\infty < s < +\infty$. In particular, a relevant statement of optimality of quasi static transformation in the Clausius inequality (5.11) needs to include the condition that the driving (λ, E) is not changed in the time interval $(-\infty, t)$.

As before we denote by ρ, which is an arbitrary density profile, the initial datum of the density at time t. Given such time t and the density profile ρ, we claim that there exists a

sequence of smooth paths $(\lambda_\delta(s), E_\delta(s))$, $-\infty < s < +\infty$, $\delta > 0$ such that: (i) the history before time t is not changed, i.e. $(\lambda_\delta(s), E_\delta(s)) = (\lambda(s), E(s))$ for $-\infty < s < t$; (ii) at time $t + \delta$ the stationary profile associated to $(\lambda_\delta, E_\delta)$ is ρ, i.e. $\bar{\rho}_{\lambda_\delta(t+\delta), E_\delta(t+\delta)} = \rho$; (iii) the asymptotic state at time $s = +\infty$ is unchanged, i.e. $(\lambda_\delta(+\infty), E_\delta(+\infty)) = (\lambda_1, E_1)$; (iv) in the quasi static limit $\delta \to 0$ equality in (5.11) is achieved, i.e.

$$\lim_{\delta \to 0} \widehat{W}_{[t,\infty)}^{\text{ren}}(\lambda_\delta, E_\delta, \rho) = F(\bar{\rho}_1) - F(\rho) = \Delta F.$$

The sequence $(\lambda_\delta(s), E_\delta(s))$, $-\infty < s < +\infty$, $\delta > 0$, can be constructed as in the previous sections and we omit the details.

Excess Work　As before, given the time window $[t, +\infty)$ we let $(u(s), j(s))$, $s \in [t, +\infty)$, be the solution of (2.1)–(2.4) with initial condition $u(t) = \rho$, where ρ is an arbitrary density profile. We then define the excess work along this path by

$$\widehat{W}_{[t,+\infty)}^{\text{ex}}(\lambda, E, \rho) = \widehat{W}_{[t,+\infty)}^{\text{ren}}(\lambda, E, \rho) - \left[F(\bar{\rho}_1) - F(\rho)\right]$$
$$= \int_t^\infty ds \int_\Lambda dx \, J_1(s, u(s)) \cdot \chi(u(s))^{-1} J_1(s, u(s)). \quad (5.12)$$

We claim that

$$\widehat{W}_{[t,+\infty)}^{\text{ex}}(\lambda, E, \rho) = V_{\lambda,E}(t, \rho) - V_{\lambda,E}(+\infty, \bar{\rho}_1) = V_{\lambda,E}(t, \rho) \quad (5.13)$$

where $V_{\lambda,E}(t, \rho)$ is the time dependent quasi potential. Observe that *a priori* the excess work $\widehat{W}_{[t,+\infty)}^{\text{ex}}(\lambda, E, \rho)$, as it involves the time integral of the current $J_1(s, u(s))$ on the time window $[t, +\infty)$, should depend on the whole path $(\lambda(s), E(s))$, $-\infty < s < +\infty$. However, the quasi potential $V_{\lambda,E}(t, \rho)$ on the right hand side of (5.13) depends only on the path $(\lambda(s), E(s))$ for $-\infty < s \le t$. Observe that if ρ coincides with the solution of the hydrodynamic equation (2.1) on the time interval $(-\infty, t)$ evaluated at time t then we get $\widehat{W}_{[t,+\infty)}^{\text{ex}}(\lambda, E, \rho) = 0$ as it is apparent from the right hand side of (5.12).

To prove (5.13) we write $J_1(t, u(t))$ as $J(t, u(t)) - J_2(t, u(t))$. By using (5.7) and (5.8) we deduce

$$\widehat{W}_{[t,+\infty)}^{\text{ex}}(\lambda, E, \rho) = \int_t^\infty ds \int_\Lambda dx \, J_1(s, u(s)) \cdot \chi(u(s))^{-1} J_1(s, u(s))$$
$$= \int_t^\infty ds \int_\Lambda dx \, \frac{\delta V_{\lambda,E}(s, u(s))}{\delta \rho} \nabla \cdot J(s, u(s)) - \int_t^\infty ds \, \partial_s V_{\lambda,E}(s, u(s)).$$

Since $\nabla \cdot J(s, u(s)) = -\partial_s u(s)$, we get

$$\widehat{W}_{[t,+\infty)}^{\text{ex}}(\lambda, E, \rho) = -\int_t^\infty ds \, \frac{d}{ds} V_{\lambda,E}(s, u(s)) = V_{\lambda,E}(t, \rho),$$

where we used that $V_{\lambda,E}(+\infty, u(+\infty)) = V_{\lambda_1, E_1}(\bar{\rho}_1) = 0$.

6 Stochastic Lattice Gases

As basic microscopic model we consider a stochastic lattice gas in a bounded domain with time dependent external field and boundary conditions. In the sequel we first exemplify the previous discussion in a simple nonequilibrium model, the so-called zero range process, in which the computations can be performed explicitly. We refer the reader e.g. to [9] for a more general setting. We then conclude this section by proving the relationship (4.14) between the relative entropy and the quasi potential under the assumption that the stationary ensemble satisfies a strong form of local equilibrium.

6.1 Time Dependent Zero Range Process

Fix $\Lambda \subset \mathbb{R}^d$ and, given $\varepsilon > 0$, let $\Lambda_\varepsilon = (\varepsilon^{-1}\Lambda) \cap \mathbb{Z}^d$ its discrete approximation. The microscopic configuration is given by the collection of occupation variables η_i, $i \in \Lambda_\varepsilon$ so that η_i is the number of particles at the site i. The dynamics can be informally described as follows. At each site, independently from the others, particles wait exponential times, whose parameter depends only on the number of particles at that site, and then jumps to a nearest neighboring site according to some transition probability of a random walk on Λ_ε. Superimposed to this bulk dynamics, to model the effect of the reservoirs, we have creation and annihilation of particles, according to some birth and death process, at the boundary of Λ_ε.

Microscopic Dynamics   To define formally the microscopic dynamics, recall that a continuous time Markov chain $\eta(\tau)$ on some state space Ω can be described in term of its time dependent infinitesimal *generator* L_τ defined as follows. Let $f : \Omega \to \mathbb{R}$ be an observable, then

$$\mathbb{E}\big(f\big(\eta(\tau + h)\big)|\eta(\tau)\big) = (L_\tau f)\big(\eta(\tau)\big)h + o(h) \tag{6.1}$$

where $\mathbb{E}(|)$ is the conditional expectation, so that the *expected* infinitesimal increment of $f(\eta(\tau))$ is $(L_\tau f)(\eta(\tau))\, d\tau$. The transition probability of the Markov process $\eta(\tau)$ is then given by the kernel of the semigroup generated by L_τ.

For the zero range process with time depend external field $E = E(t, x)$ and chemical potential $\lambda = \lambda(t, x)$ (where t and x are the macroscopic time and space variables), the generator L_τ is given by

$$L_\tau = L_{\tau,0} + L_{\tau,1}$$

where $L_{\tau,0}$ describes the bulk dynamics and $L_{\tau,1}$ the boundary dynamics; they are given by

$$L_{\tau,0} f(\eta) = \sum_{\substack{i,j \in \Lambda_\varepsilon \\ |i-j|=1}} g(\eta_i)\, e^{(1/2)\varepsilon E(\varepsilon^2\tau, \varepsilon(i+j)/2)\cdot(j-i)}\big[f\big(\eta^{i,j}\big) - f(\eta)\big]$$

$$L_{\tau,1} f(\eta) = \sum_{\substack{i \in \Lambda_\varepsilon, j \notin \Lambda_\varepsilon \\ |i-j|=1}} \Big\{ g(\eta_i)\, e^{(1/2)\varepsilon E(\varepsilon^2\tau, \varepsilon(i+j)/2)\cdot(j-i)}\big[f\big(\eta^{i,-}\big) - f(\eta)\big] \tag{6.2}$$
$$+ e^{\lambda(\varepsilon^2\tau, \varepsilon j)+(1/2)\varepsilon E(\varepsilon^2 t, \varepsilon(i+j)/2)\cdot(i-j)}\big[f\big(\eta^{i,+}\big) - f(\eta)\big]\Big\}$$

in which

$$\eta_k^{i,j} = \begin{cases} \eta_k & \text{if } k \neq i, j \\ \eta_k - 1 & \text{if } k = i \\ \eta_k + 1 & \text{if } k = j \end{cases} \tag{6.3}$$

is the configuration obtained from η when a particle jumps from i to j, and

$$\eta_k^{i,\pm} = \begin{cases} \eta_k & \text{if } k \neq i \\ \eta_k \pm 1 & \text{if } k = i \end{cases} \tag{6.4}$$

is the configuration where we added (respectively subtracted) one particle at i.

The function g describes the jump rate. More precisely, if at some site there are $k \geq 1$ particles, each one independently waits an exponential time with parameter proportional to $g(k)/k$ and then jumps to one of the neighboring sites with a transition probability which depends on the external field E. We also set $g(0) = 0$ so that no jumps occur when the site is empty. In the special case $g(k) = k$ the dynamics introduced above represents the evolution of the occupation numbers η_i for not interacting random walks in the space-time

dependent external field E on Λ_ε with the appropriate boundary conditions depending on λ. For simplicity of notation, we did not introduced the dependence on the temperature in the model.

Denoting by $\mu_\varepsilon(\tau, \cdot)$ the distribution of the occupation variables η_i, $i \in \Lambda_\varepsilon$ at time τ, then it satisfies

$$\sum_\eta \mu_\varepsilon(\tau_1, \eta) p_{\tau_1, \tau_2}(\eta, \eta') = \mu_\varepsilon(\tau_2, \eta'), \quad \tau_1 \le \tau_2, \tag{6.5}$$

where $p_{\tau_1, \tau_2}(\eta, \eta')$ is the transition probability associated to the generator L_τ, i.e., the kernel of the operator

$$P_{\tau_1, \tau_2} = \mathcal{T} \exp\left\{ \int_{\tau_1}^{\tau_2} d\tau \, L_\tau \right\} \tag{6.6}$$

where $\mathcal{T}$ denotes the time ordering.

Invariant Measure We consider here the case in which the driving (λ, E) does not depend on time, so that the semigroup P_{τ_1, τ_2} in (6.6) depends only on $\tau_2 - \tau_1$ and is given by $P_{\tau_2 - \tau_1} = \exp\{(\tau_2 - \tau_1)L\}$ where L is the time independent generator. In this case we next discuss the invariant measure of the microscopic dynamics.

Since the Markov chain is irreducible (it is possible to go with positive probability from any configuration to any other), under very general hypotheses on the function $g(k)$ there exists a unique invariant measure. This is the time independent probability μ_ε on the configuration state which solves (6.5). It is remarkable that such invariant measure can be constructed explicitly and it is product, see [16] for the one dimensional case.

Fix a time independent chemical potential λ and external field E. Let $\phi_\varepsilon(i)$, $i \in \Lambda_\varepsilon$, be the solution of the equations

$$\begin{cases} \sum_{j \sim i} [\phi_\varepsilon(j) \, e^{(1/2)\varepsilon E(\varepsilon(i+j)/2)\cdot(i-j)} - \phi_\varepsilon(i) \, e^{(1/2)\varepsilon E(\varepsilon(i+j)/2)\cdot(j-i)}] = 0, & i \in \Lambda_\varepsilon \\ \phi_\varepsilon(i) = \exp\{\lambda(\varepsilon i)\}, & i \notin \Lambda_\varepsilon \end{cases} \tag{6.7}$$

where the sum runs over the nearest neighbors of i. The invariant measure μ_ε is the product measure $\mu_\varepsilon = \prod_{i \in \Lambda_\varepsilon} \mu_{\varepsilon, i}$ obtained by taking the product of the marginal distributions

$$\mu_{\varepsilon, i}(\eta_i = k) = \frac{1}{Z(\phi_\varepsilon(i))} \frac{\phi_\varepsilon(i)^k}{g(1) \cdots g(k)} \tag{6.8}$$

where

$$Z(\varphi) = 1 + \sum_{k=1}^{\infty} \frac{\varphi^k}{g(1) \cdots g(k)} \tag{6.9}$$

is the normalization constant. The fact that μ_ε is the invariant measure can be verified by showing that $\sum_\eta \mu_\varepsilon(\eta) L f(\eta) = 0$ for any observable f.

Consider now an homogeneous equilibrium state which is obtained by choosing $E = 0$ and λ constant. In this case $\phi_\varepsilon = \exp\{\lambda\}$ so that the invariant measure is Gibbs with Hamiltonian

$$H_\varepsilon(\eta) = \sum_{i \in \Lambda_\varepsilon} \sum_{k=1}^{\eta_i} \log g(k)$$

where, comparing with (3.12), we understand that $\beta = 1$. In particular, in the stationary ensemble there is no interaction among particles on different sites.

The computation of the pressure, see (3.13), can be done explicitly and by Legendre duality one obtains that the specific free energy is given by

$$f(\rho) = \rho \log \Phi(\rho) - \log Z(\Phi(\rho)) \tag{6.10}$$

where $\Phi : \mathbb{R}_+ \to \mathbb{R}_+$ is the inverse of the strictly increasing function $R(\varphi) = \varphi Z'(\varphi)/Z(\varphi)$.

Hydrodynamic Limit   For $x \in \Lambda$, $t \geq 0$, we introduce the *empirical density* as

$$u_\varepsilon(t, x) = \varepsilon^d \sum_{i \in \Lambda_\varepsilon} \eta_i(\varepsilon^{-2}t) \, \delta(x - \varepsilon i) \tag{6.11}$$

where δ denotes the Dirac function. Given $B \subset \Lambda$ let $B_\varepsilon = \varepsilon^{-1} B \cap \mathbb{Z}^d$. Then

$$\int_B dx \, u_\varepsilon(t, x) = \varepsilon^d \sum_{i \in B_\varepsilon} \eta_i(\varepsilon^{-2}t)$$

is the total mass in the volume B at the macroscopic time t.

It is not difficult to extend the standard arguments of hydrodynamic limits, see e.g. [6] for a heuristic derivation and [20, 27] for a rigorous analysis, to the present time dependent setting. The formal statement is that in the scaling limit $\varepsilon \to 0$ a law of large numbers for the empirical density holds. More precisely, if at time $t = 0$ the empirical density converges to some profile ρ (i.e. $u_\varepsilon(0, x) \to \rho(x)$, $x \in \Lambda$) then at time t the empirical density $u_\varepsilon(t)$ converges to the solution $u(t)$ of the hydrodynamic equation

$$\begin{cases} \partial_t u + \nabla \cdot (\Phi(u)E(t)) = \Delta \Phi(u), & (t, x) \in \mathbb{R}_+ \times \Lambda \\ \Phi(u(t, x)) = \exp\{\lambda(t, x)\}, & (t, x) \in \mathbb{R}_+ \times \partial \Lambda \\ u(0, x) = \rho(x), & x \in \Lambda \end{cases} \tag{6.12}$$

where Δ is the Laplacian and the function $\Phi : \mathbb{R}_+ \to \mathbb{R}_+$ has been introduced above. In particular, by comparing (6.12) with (2.1)–(2.2) for the zero range process the diffusion coefficient is $D = \Phi'$ and the mobility is $\chi = \Phi$. As follows from (6.10) the local Einstein relation (2.3) holds. Finally, since $f'(\rho) = \log \Phi(\rho)$ (also this follows from (6.10)) the boundary conditions above agree with (2.4).

The fluctuation formula (5.5) with the functional I given by (3.10) is discussed in [6, 8] for time-independent driving. The arguments can be extended to the present time-dependent setting.

Microscopic Work   We next present the microscopic definition of the work done by external field and the boundary reservoirs. To this aim, we first recall the definition of the *empirical current*, see e.g., [8]. Fix a path $\eta(\tau)$ of the microscopic configuration. Given an oriented bond (i, j), let $\mathcal{N}_{i,j}(\tau)$ be the number of particles that jumped from i to j in the time interval $[0, \tau]$. Here we adopt the convention that $\mathcal{N}_{i,j}(\tau)$ is the number of particles created at j due to the reservoir at i if $i \notin \Lambda_\varepsilon$, $j \in \Lambda_\varepsilon$, and that $\mathcal{N}_{i,j}(\tau)$ is the number of particles that left the system at i by jumping to j if $i \in \Lambda_\varepsilon$, $j \notin \Lambda_\varepsilon$. The difference $\mathcal{J}_{i,j}(\tau) = \mathcal{N}_{i,j}(\tau) - \mathcal{N}_{j,i}(\tau)$ is the net number of particles flown across the bond (i, j) in the time interval $[0, \tau]$. The instantaneous current across (i, j), denoted by $J_{i,j}$, is defined as $J_{i,j} = d\mathcal{J}_{i,j}/d\tau$. Of course, $J_{i,j}$ is a sum of δ-functions localized at the jump times with weight $+1$, respectively -1, if a particle jumped from i to j, respectively from j to i.

Let now $(\lambda(\cdot), E(\cdot))$ be a path of the external driving and denote by $\eta(\tau)$ the corresponding microscopic trajectory. The natural microscopic definition of the work exchanged between the system and the external driving in the time interval $[0, \tau]$ is

$$\mathcal{W}_{[0,\tau]} = - \sum_{i \in \Lambda_\varepsilon,\, j \notin \Lambda_\varepsilon} \int_0^\tau d\tau'\, \lambda\big(\varepsilon^2\tau', \varepsilon j\big) J_{i,j}(\tau')$$

$$+ \frac{1}{2} \sum_{(i,j)} \int_0^\tau d\tau'\, \varepsilon E\left(\varepsilon^2\tau', \varepsilon\frac{i+j}{2}\right) \cdot (j-i) J_{i,j}(\tau') \tag{6.13}$$

where the second sum is carried out over all bonds intersecting Λ_ε. We emphasize that the above definition is given in terms of microscopic quantities, indeed the dependence on the scaling parameter ε is due to the fact that we have considered the external field of order ε, see (6.2), and the drivings as functions of the macroscopic variables.

We now consider the scaling limit of the microscopic work. We thus set $\tau = \varepsilon^{-2}T$ and assume that the initial configuration of particles corresponds to a density profile ρ. In view of the law of large numbers for the empirical current, see e.g., [8], as $\varepsilon \to 0$

$$\varepsilon^d \mathcal{W}_{[0,\varepsilon^{-2}T]} \longrightarrow W_{[0,T]} \tag{6.14}$$

where the right hand side is the macroscopic work defined in (2.9). The fluctuations properties of $\mathcal{W}$ as $\varepsilon \to 0$ can be derived from those of the empirical current [8].

Quasi Potential We discuss first the case of time-independent driving. Since for the zero range process the invariant measure is product, the fluctuation formula (3.8) can be proven directly. By straightforward computations, see [6] for the case $E = 0$, we get that the quasi potential $V_{\lambda,E}$ is given by

$$V_{\lambda,E}(\rho) = \int_\Lambda dx \left[\rho \log \frac{\Phi(\rho)}{\bar{\phi}} - \log \frac{Z(\Phi(\rho))}{Z(\bar{\phi})} \right] \tag{6.15}$$

where $\bar{\phi} = \Phi(\bar{\rho}_{\lambda,E})$ in which $\bar{\rho}_{\lambda,E}$ is the stationary solution of (6.12). It is also simple to check that the function ϕ_ε which solves (6.7) converges to $\bar{\phi}$ in the scaling limit $\varepsilon \to 0$. In terms of the macroscopic fluctuation theory, a couple of integration by parts show that the right hand side of (6.15) is a stationary solution of the Hamilton-Jacobi equation (5.2) and this provides an alternative proof of the fluctuation formula (3.8).

By using the explicit formula (6.8) for the invariant measure together with the convergence of ϕ_ε to $\bar{\phi}$ computations analogous the ones presented in the Gibbsian setting show that the relationship (4.14) between the limiting relative entropy and the quasi potential holds.

Since in this case the quasi potential has an explicit expression the decomposition (4.3) of the current $J(\rho)$ is

$$J_S(\rho) = -\Phi(\rho)\big[\nabla \log \Phi(\rho) - \nabla \log \bar{\phi}\big]$$

$$J_A(\rho) = \Phi(\rho)[E - \nabla \log \bar{\phi}] \tag{6.16}$$

where we recall that $\bar{\phi} = \Phi(\bar{\rho}_{\lambda,E})$. In particular, the dependence on (λ, E) in J_S appears only through the stationary solution $\bar{\rho}_{\lambda,E}$. This is a special feature of the zero range process.

According to the discussion in Sect. 4, the power needed to maintain the zero range process in a nonequilibrium stationary state is

$$\int_\Lambda dx\, \bar{\phi}[E - \nabla \log \bar{\phi}]^2.$$

Time Dependent Quasi Potential The time dependent Hamilton-Jacobi equation (5.2) has not a simple solution in general. However, when $\Phi(\rho) = \rho$, that corresponds to the case of independent random walks, it holds

$$V_{\lambda,E}(t,\rho) = \int_\Lambda dx \left[\rho \left(\log \frac{\rho}{\psi(t)} - 1 \right) + \psi(t) \right] \tag{6.17}$$

where $\psi(t) = \psi(t,x)$ is obtained as the value at time t of the solution to

$$\begin{cases} \partial_s \psi + \nabla \cdot \left(\psi \, E(s) \right) = \Delta \psi, & (s,x) \in (-\infty, t) \times \Lambda \\ \psi(s,x) = \exp\{\lambda(s,x)\}, & (s,x) \in (-\infty, t) \times \partial\Lambda \\ \lim_{s \to -\infty} \psi(s) = \bar{\rho}_0 \end{cases} \tag{6.18}$$

where $\bar{\rho}_0$ is the density profile at time $-\infty$. From the above expression is apparent that $V_{\lambda,E}(t,\cdot)$ depends on the path $(\lambda(s), E(s))$ for $s \in (-\infty, t]$. On the other hand the quasi potential $V_{\lambda(t),E(t)}$ with the values of λ, E frozen at time t is obtained by replacing $\psi(t)$ in (6.17) with the solution of $\nabla \cdot (\psi E(t)) = \Delta \psi$ with the boundary condition $\psi(x) = \exp\{\lambda(t,x)\}$, $x \in \partial\Lambda$. That is by replacing ψ with $\bar{\rho}_{\lambda(t),E(t)}$. The proof of the representation (6.17) amounts to straightforward computations and it is omitted.

6.2 Relative Entropy Between Nonequilibrium Stationary States

We next give some mathematical details on the relationship (4.14) which expresses the relative entropy between two nonequilibrium states in terms of the quasi potential. We first present a general argument which shows, without any further assumption, that an inequality is always satisfied. We then show that equality holds if the stationary ensembles satisfies a strong form of local equilibrium. As proven in [5] this condition holds for the boundary driven symmetric simple exclusion process. We also remark that for this model the validity of (4.14) has been already proven (with a different motivation) in [3, 15] in the particular case in which the reference ensemble is an equilibrium state.

Recall the definition (3.14) of the relative entropy $S(\nu|\mu)$ of the probability ν with respect to μ. Consider two sequences of probabilities ν_n and μ_n on some space E. We assume that μ_n satisfies the large deviation formula

$$\mu_n(\mathcal{O}_x) \asymp \exp\{-n V(x)\} \tag{6.19}$$

where $\mathcal{O}_x$ is a small neighborhood of x and the *rate function* V is a function on E. We also assume that ν_n satisfies the law of large numbers

$$\nu_n(\mathcal{O}_{\bar{x}}^c) \longrightarrow 0$$

where $\bar{x} \in E$ and $\mathcal{O}_{\bar{x}}^c$ denotes the complementary set of $\mathcal{O}_{\bar{x}}$. We then claim that the inequality

$$\varliminf_{n \to +\infty} \frac{1}{n} S(\nu_n|\mu_n) \geq V(\bar{x}) \tag{6.20}$$

holds. Indeed, recall the variational representation of the relative entropy, see e.g. [20, Appendix A1]

$$S(\nu_n|\mu_n) = \sup_f \left\{ \int d\nu_n \, f - \log \int d\mu_n \, e^f \right\}$$

where the supremum is carried out over the functions f on E. By choosing f equal to nV we get

$$\frac{1}{n} S(\nu_n|\mu_n) \geq \int d\nu_n \, V - \frac{1}{n} \log \int d\mu_n \, e^{nV}. \tag{6.21}$$

Recall the Laplace-Varadhan theorem, see e.g. [17, Theorem 4.3.1], which states that—under the assumption (6.19)—for each function ϕ on E it holds

$$\lim_{n\to\infty} \frac{1}{n} \log \int d\mu_n\, e^{n\phi} = \sup_{x\in E}\{\phi(x) - V(x)\}.$$

In view of the law of large numbers for ν_n, the inequality (6.20) now follows from (6.21).

Consider a stochastic lattice gas in the domain $\Lambda_\varepsilon = (\varepsilon^{-1}\Lambda) \cap \mathbb{Z}^d$. Assume for simplicity that the external field E vanishes. Given a time independent chemical potential $\lambda(x)$ we denote by μ_ε^λ the associated stationary ensemble. Observe that μ_ε^λ is a probability on $\mathbb{N}^{\Lambda_\varepsilon}$. As for the zero range process, we denote by $\eta_i = 0, 1, \ldots$ the number of particles at the site $i \in \Lambda_\varepsilon$.

Given $\delta > 0$, we decompose the domain Λ_ε into small boxes $B_1, B_2, \ldots$ of size $\delta\varepsilon^{-1}$ and denote by $\mathbf{N} = (N_1, N_2, \ldots)$ the number of particles in each box. We let $\nu_\varepsilon^\lambda(\mathbf{N})$ the probability of having N_1 particles in the box B_1, N_2 particles in the box B_2, and so on. Namely,

$$\nu_\varepsilon^\lambda(\mathbf{N}) = \mu_\varepsilon^\lambda\bigg(\sum_{i\in B_1}\eta_i = N_1, \sum_{i\in B_2}\eta_i = N_2, \ldots\bigg).$$

We also introduce the *conditional ensemble*, denoted by $\mu_\varepsilon^\lambda(\cdot|\mathbf{N})$, as the probability μ_ε^λ conditioned to have N_1 particles in the box B_1, N_2 particles in the box B_2, and so on.

For a box $B \subset \mathbb{Z}^d$, $n \geq 0$, denote by $\mu_{B,n}^{\mathrm{can}}$ the equilibrium canonical measure on B with n particles, that is

$$\mu_{B,n}^{\mathrm{can}}(\eta) \propto \exp\{-\beta H_B(\eta)\}$$

where $H_B(\eta)$ is the energy of a configuration η with n particles in B.

We shall assume that the conditional ensemble $\mu_\varepsilon^\lambda(\cdot|\mathbf{N})$ is close to the product of the canonical ensembles:

$$\mu_\varepsilon^\lambda(\eta|\mathbf{N}) \approx \prod_\ell \mu_{B_\ell, N_\ell}^{\mathrm{can}}(\eta)$$

in the sense that

$$\varepsilon^d \log \frac{\mu_\varepsilon^\lambda(\eta|\mathbf{N})}{\prod_\ell \mu_{B_\ell, N_\ell}^{\mathrm{can}}(\eta)} \to 0 \tag{6.22}$$

uniformly over η as we let first $\varepsilon \to 0$ and then $\delta \to 0$. As proven in [5], this condition is satisfied for the boundary driven one-dimensional symmetric simple exclusion process.

We prove the equality (4.14) under the previous assumption. Fix two chemical potentials λ_0, λ_1. By definition of the relative entropy (3.14),

$$\varepsilon^d S\big(\mu_\varepsilon^{\lambda_0}|\mu_\varepsilon^{\lambda_1}\big) = \varepsilon^d \sum_\eta \mu_\varepsilon^{\lambda_0}(\eta) \log \mu_\varepsilon^{\lambda_0}(\eta) - \varepsilon^d \sum_\eta \mu_\varepsilon^{\lambda_0}(\eta) \log \mu_\varepsilon^{\lambda_1}(\eta).$$

Rewrite the expressions inside the logarithms as $\mu_\varepsilon^{\lambda_i}(\eta|\mathbf{N})\nu_\varepsilon^{\lambda_i}(\mathbf{N})$. By (6.22), the contribution to the sum of the term $\log\{\mu_\varepsilon^{\lambda_0}(\eta|\mathbf{N})/\mu_\varepsilon^{\lambda_1}(\eta|\mathbf{N})\}$ vanishes as $\varepsilon \to 0$ and then $\delta \to 0$. It remains to estimate the limit

$$\varepsilon^d \sum_{\mathbf{N}} \nu_\varepsilon^{\lambda_0}(\mathbf{N}) \log \nu_\varepsilon^{\lambda_0}(\mathbf{N}) - \varepsilon^d \sum_{\mathbf{N}} \nu_\varepsilon^{\lambda_0}(\mathbf{N}) \log \nu_\varepsilon^{\lambda_1}(\mathbf{N})$$

in view of the law of large numbers, we expect $\nu_\varepsilon^{\lambda_0}$ to concentrate on the density profile $\bar\rho_0$, while $\log \nu_\varepsilon^{\lambda_i}(\mathbf{N})$ converges to $-\beta V_{\lambda_i}(\bar\rho_0)$. This statement concludes the proof of (4.14). For boundary driven symmetric simple exclusion processes, by adapting the arguments in [5], also the last step can be justified rigorously.

7 Langevin Dynamics

We next illustrate the general thermodynamic theory in the simpler context of Langevin dynamics which is nowadays very popular, see e.g. [26] for a recent review. In the Smoluchowski approximation, the motion of a particle in a viscous d-dimensional medium is described by the Langevin equation

$$\gamma \dot{X}_t = -\nabla U(X_t) + q E(t, X_t) + \sqrt{\frac{2\gamma}{\beta}}\, \dot{W}_t, \tag{7.1}$$

where U is the reference potential, $\beta = 1/\kappa T$, γ is the friction coefficient, q is the charge, $E(t, x)$ is an applied field, e.g. an electric field, and W_t is a d-dimensional Brownian motion. We discuss the zero temperature limit $\beta \to \infty$ which is analogous to the thermodynamic limit for stochastic lattice gases.

In the limit $\beta \to \infty$ the Smoluchowski equation becomes the deterministic equation

$$\gamma \dot{x}_t = -\nabla U(x_t) + q E(t, x_t). \tag{7.2}$$

Fix an initial state $\bar{x}_0$, a path $E(t, \cdot)$, $0 \le t \le T$, and denote by x_t the solution of (7.2) with initial condition $\bar{x}_0$. The work done by the applied field E in the time interval $[0, T]$, denoted by $W_{[0,T]}(\bar{x}_0, E)$, is given by

$$W_{[0,T]}(\bar{x}_0, E) = q \int_0^T dt\, E(t, x_t) \cdot \dot{x}_t. \tag{7.3}$$

Excess Work and Quasi Potential   Assume that E is a time independent gradient, $E = -\nabla \Phi$, which corresponds to the case of equilibrium states. Given a time independent potential Φ, denote by $\bar{x}_\Phi$ the minimum point of $U + q\Phi$, assumed to be unique and a global attractor for the flow (7.2). Fix two time independent potentials Φ_0, Φ_1. Consider a particle initially at the position $\bar{x}_0 = \bar{x}_{\Phi_0}$ which is driven to a new position $\bar{x}_1 = \bar{x}_{\Phi_1}$ by changing the potential in time in a way that $\Phi(t) = \Phi_0$ for $t \le 0$ and $\Phi(t) = \Phi_1$ for $t \ge T$, where T is some fixed positive time. Let $x(t)$, $t \ge 0$, be the solution of (7.2) with initial condition $\bar{x}_0$. Since the potential is equal to Φ_1 for $t \ge T$, it holds $x(t) \to \bar{x}_1$ as $t \to +\infty$. Moreover, as $\bar{x}_1$ is an equilibrium state, $x(t), \dot{x}(t)$ relax exponentially fast to $\bar{x}_1, 0$, respectively. The integral in (7.3) is thus convergent for $T \to \infty$ and we deduce

$$\begin{aligned} W(\bar{x}_0, E) = W_{[0,\infty)}(\bar{x}_0, E) &= \int_0^\infty dt\, \left[\gamma \dot{x}_t + \nabla U(x_t)\right] \cdot \dot{x}_t \\ &= U(\bar{x}_1) - U(\bar{x}_0) + \gamma \int_0^\infty dt\, |\dot{x}_t|^2 \\ &\ge \Delta U, \end{aligned} \tag{7.4}$$

which expresses the Clausius inequality in this setting. By arguing as in Sect. 3, we can show that in the quasi static limit, obtained by letting $\Phi(t)$ change in time very slowly, the equality $W(\bar{x}_0, E) = U(\bar{x}_1) - U(\bar{x}_0)$ holds.

Define the *excess work*, $W_{\text{ex}}(\bar{x}_0, E)$, as the difference between the work performed by the applied field and the work involved in a quasi static transformation from $\bar{x}_0$ to $\bar{x}_1$, namely

$$W_{\text{ex}} = W(\bar{x}_0, E) - \min W = \gamma \int_0^\infty dt\, |\dot{x}_t|^2.$$

Consider the equilibrium point $\bar{x}_0$ associated to a potential Φ_0 and the path $\gamma \dot{x}_t = -\nabla U(x_t) - q\nabla \Phi_1(x_t)$, for some $\Phi_1 \ne \Phi_0$, with initial condition $\bar{x}_0$. The excess work along such a path is given by

$$W_{\text{ex}}(\bar{x}_0, -\nabla\Phi_1) = -\int_0^\infty dt \left[\nabla U(x_t) + q\nabla\Phi_1(x_t)\right] \cdot \dot{x}_t$$
$$= (U + q\Phi_1)(\bar{x}_0) - (U + q\Phi_1)(\bar{x}_1).$$

The right hand side of the previous equation represents the quasi-potential corresponding to the final equilibrium state evaluated at the initial state $\bar{x}_0$. More precisely, denote by $\mathbb{P}_{\bar{x}}^\beta$, $\bar{x} \in \mathbb{R}^d$, the distribution of the process X_t which solves (7.1) starting from $\bar{x}$. One is interested in the asymptotic behavior of X_t as $\beta \to \infty$. Fix a time interval $[T_-, T_+]$ and a trajectory $x:[T_-, T_+] \to \mathbb{R}^d$. It is well known [18] that

$$\mathbb{P}_{\bar{x}}^\beta[X_t \approx x_t, T_- \le t \le T_+] \asymp \exp\{-\beta I_{[T_-, T_+]}(x|\bar{x})\},$$

where

$$I_{[T_-, T_+]}(x|\bar{x}) = \frac{1}{4\gamma} \int_{T_-}^{T_+} dt \left|\gamma\dot{x}_t + \nabla U(x_t) - qE(t, x_t)\right|^2$$

if $x(0) = \bar{x}$ and $I_{[T_-, T_+]}(x|\bar{x}) = +\infty$, otherwise.

Fix a time independent field E and denote by $V_E : \mathbb{R}^d \to \mathbb{R}_+$ the quasi potential defined by

$$V_E(\bar{x}) = \inf I_{(-\infty, 0]}(x|\bar{x}_0),$$

where the infimum is carried over all paths $x(t)$ such that $x(0) = \bar{x}$, $\lim_{t\to-\infty} x(t) = \bar{x}_0$ in which $\bar{x}_0$ belongs to the global attractor. When E is gradient, $E = -\nabla\Phi$, it is well known that $V_\Phi = U + q\Phi$ up to an additive constant that is fixed by requiring $V_\Phi(\bar{x}_\Phi) = 0$. In this case, the quasi potential coincides with the excess work as computed above. The corrections to the above result when a finite time window is considered has been recently analyzed in [2].

Denote by $\mu_{\beta,E}$ the stationary distribution for the Langevin dynamics (7.1). When $E = -\nabla\Phi$, it is well known that the distribution $\mu_{\beta,E}$ is proportional to $\exp\{-\beta(U + q\Phi)\}$ and one can show that the relative entropy, as defined in (3.14), satisfies

$$\lim_{\beta\to\infty} \frac{1}{\beta} S(\mu_{\beta,\Phi_0}|\mu_{\beta,\Phi_1}) = V_{\Phi_1}(\bar{x}_0).$$

We turn to the nonequilibrium case, i.e. when E is not a gradient field. Assume that Eq. (7.2) has a unique global attractor, e.g. an equilibrium point or a periodic orbit. When E is not a gradient there are no simple expression for the quasi potential, but it can be characterized as a solution of the stationary Hamilton-Jacobi equation

$$|\nabla V_E|^2 + \nabla V_E \cdot [-\nabla U + qE] = 0.$$

Decompose the vector field $-\nabla U + qE$ as the sum of two orthogonal pieces, J_S and J_A, where

$$J_S = -\nabla V_E, \qquad J_A = -\nabla U + qE + \nabla V_E,$$

so that $-\nabla U + qE = J_S + J_A$. It follows from the Hamilton-Jacobi equation that J_S, J_A are pointwise orthogonal, $J_S(x) \cdot J_A(x) = 0$ for all $x \in \mathbb{R}^d$.

Recall the expression (7.4) for the work done by the applied time dependent field $E(t)$ in the time interval $[0, T]$ and define the renormalized work, denoted by $W_{[0,T]}^{\text{ren}}$, as

$$W_{[0,T]}^{\text{ren}}(\bar{x}_0, E) = W_{[0,T]}(\bar{x}_0, E) - \frac{1}{\gamma}\int_0^T dt \left|J_A(t, x(t))\right|^2$$
$$= U(x(T)) - U(x(0)) + \frac{1}{\gamma}\int_0^T dt \left|J_S(t, x(t))\right|^2 \qquad (7.5)$$

where, as in (4.7), we compute the quasi potential $V_{E(t)}$ with t frozen and denoted by $J_S(t)$, $J_A(t)$ the corresponding decomposition of the applied field. The validity of the Clausius inequality for the renormalized work follows immediately from (7.5). Moreover, by arguing as in Sect. 4, it is simple to check that equality is achieved in the quasi static limit.

Define the *excess* work as the difference between the renormalized work and the one involved in a quasi static transformation:

$$W_{ex}(\bar{x}_0, E) = \frac{1}{\gamma} \int_0^\infty dt \, |J_S(t, x(t))|^2.$$

Fix a point $\bar{x}$ and an external field E_1 constant in time. Consider the path $\gamma \dot{x}_t = -\nabla U(x_t) + q E_1(x_t)$ with initial condition $\bar{x}$. Computing the excess work along this path we get

$$W_{ex}(\bar{x}, E_1) = V_{E_1}(\bar{x}).$$

To illustrate the previous definitions, consider the Langevin equation (7.1) in two dimensions with $U(x) = (\lambda/4)|x|^4$ and

$$E(t, x) = \alpha(t)x + A_0 \frac{x^\perp}{|x|},$$

where $A_0 > 0$, $\lambda > 0$, $\alpha(t)$ is a positive function, and for $x = (x_1, x_2)$ we set $x^\perp = (-x_2, x_1)$.

Assume that α does not depend on t and let r_α be the minimum of $U(r) - (q/2)\alpha r^2$, $r_\alpha = \sqrt{q\alpha/\lambda}$. The deterministic flow defined by (7.2) has then the limit cycle $x(t) = r_\alpha(\cos(\omega t), \sin(\omega t))$, where $\omega = A_0 q/\gamma r_\alpha$. The quasi potential is given by $V_\alpha(x) = U(x) - (q/2)\alpha|x|^2 - (q^2\alpha^2/2\lambda)$ so that $J_S(x) = -\nabla U(x) + q\alpha x$, $J_A(x) = q A_0(x^\perp/|x|)$. The power dissipated along the periodic orbit is $\gamma r_\alpha^2 \omega^2$ so the energy dissipated in an infinite time window is infinite.

Fix $\alpha_0 \neq \alpha_1$ and consider a function $\alpha(t)$ such that $\alpha(0) = \alpha_0$, $\alpha(t) = \alpha_1$, $t \geq T$. Let $x(t)$ be the solution of (7.2) with initial condition $\bar{x}$. The renormalized work and the excess work along such path are given by

$$W^{ren}(\bar{x}, E) = U(\bar{x}_1) - U(\bar{x}) + \frac{1}{\gamma} \int_0^\infty dt \, |\nabla U(x(t)) - q\alpha(t)x(t)|^2,$$

$$W_{ex}(\bar{x}, E) = \frac{1}{\gamma} \int_0^\infty dt \, |\nabla U(x(t)) - q\alpha(t)x(t)|^2,$$

where $\bar{x}_1$ is a point in the limit cycle corresponding to α_1. If the initial condition $\bar{x}$ belongs to the limit cycle corresponding to α_0, the previous integral is equal to

$$\int_0^\infty dt \, (\partial_t V_{\alpha(t)})(x(t)) = \frac{q^2}{4\lambda}(\alpha_1^2 - \alpha_0^2) - \frac{q}{2} \int_0^\infty dt \, \dot{\alpha}(t)|x(t)|^2 \geq 0.$$

What we have done is very close to the well known paper by Hatano and Sasa [19]. The main difference is that we are considering the limit of small noise in order to relate the quasi potential to the work involved in the transformations. In particular, our W^{ren} is not a random variable. There is also a difference in terminology as we call W^{ren} what they would call W^{ex}, while we reserved this notation for a quantity which is more closely related to the quasi potential.

Time Dependent Quasi Potential   To illustrate the time dependent quasi potential, consider the time dependent Langevin equation with linear drift

$$\dot{X}_t = B(t) X_t + E(t) + \sqrt{\frac{2}{\beta}}\, \dot{W}_t$$

where $E(t) \in \mathbb{R}^n$ and $B(t)$ is an $n \times n$ time dependent matrix. As X_t is a Gaussian process, its distribution can be computed explicitly for any $\beta > 0$. In particular, the covariance and the mean of its distribution at time t can be recovered from the expression of the time dependent quasi potential given below.

As $\beta \to \infty$ the evolution of X_t in the time interval $[T_1, T_2]$ satisfies a large deviations principle with rate function

$$I_{[T_1, T_2]}(x) = \frac{1}{4} \int_{T_1}^{T_2} dt \, \left| \dot{x}(t) - B(t)\, x(t) - E(t) \right|^2.$$

The associated time dependent Hamilton-Jacobi equation is

$$\partial_t V(t, x) + \left| \nabla V(t, x) \right|^2 + \nabla V(t, x) \cdot \left[B(t)\, x + E(t) \right] = 0. \qquad (7.6)$$

Assume that $E(t), B(t)$ are such that $(E(t), B(t)) \to (E_0, B_0)$, as $t \to -\infty$, $(E(t), B(t)) \to (E_1, B_1)$ as $t \to \infty$, respectively, and that the eigenvalues of B_0, B_1 have strictly negative real part. Let $m_0 = -B_0^{-1} E_0$ and S_0 be the symmetric $n \times n$ matrix such that $S_0^2 = -(S_0 B_0 + B_0^T S_0)/2$. Let $S(t), m(t)$ be the solution of

$$\begin{cases} \dot{S} = -2S^2 - [SB + B^T S], \\ \dot{m} = Bm + E, \end{cases}$$

with boundary conditions $S(-\infty) = S_0, m(-\infty) = m_0$. Then

$$V(t, x) = \frac{1}{2} \left[x - m(t) \right] \cdot S(t) \left[x - m(t) \right]$$

is the solution of the time dependent Hamilton-Jacobi equation. As $t \to \infty$, $(S(t), m(t))$ converge to (S_1, m_1), where $S_1^2 = -(S_1 B_1 + B_1^T S_1)/2$ and $m_1 = -B_1^{-1} E_1$. If B_1 is normal, i.e. $B_1 B_1^T = B_1^T B_1$, then $S_1 = -(1/2)(B_1 + B_1^T)$.

In the one dimensional case, with $B = -(1/\theta), \theta > 0$, we get

$$m(t) = \int_{-\infty}^{t} ds \exp\left\{ -\frac{t - s}{\theta} \right\} E(s), \qquad S(t) = \frac{1}{\theta}.$$

In particular, $m(t) \to \theta E_0$, as $t \to -\infty$, $m(t) \to \theta E_1$, as $t \to \infty$. When $\theta \ll 1$, that is when the system relaxes very fast, the time dependent quasi potential at time t becomes the quasi potential computed with time frozen at t, $V(t, \cdot) \approx V_{E(t)}(\cdot)$.

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