

Quantitative analysis of the Clausius inequality

Lorenzo Bertini¹, Alberto De Sole¹, Davide Gabrielli²,
Giovanni Jona-Lasinio³ and Claudio Landim^{4,5}

¹ Dipartimento di Matematica, Università di Roma 'La Sapienza' P.Le Aldo Moro 2, 00185 Roma, Italy

² DISIM, Università dell'Aquila, Via Vetoio, Loc. Coppito 67100 L'Aquila, Italy

³ Dipartimento di Fisica and INFN, Università di Roma La Sapienza, P.Le A. Moro 2, 00185 Roma, Italy

⁴ IMPA, Estrada Dona Castorina 110, J Botânico, 22460 Rio de Janeiro, Brazil

⁵ CNRS UMR 6085, Université de Rouen, Avenue de l'Université, BP.12, Technopôle du Madrillet, F76801 Saint-Étienne-du-Rouvray, France

E-mail: bertini@mat.uniroma1.it, desole@mat.uniroma1.it, gabriell@univaq.it, gianni.jona@roma1.infn.it and landim@impa.br

Received 18 June 2015

Accepted for publication 17 September 2015

Published 21 October 2015



Online at stacks.iop.org/JSTAT/2015/P10018

[doi:10.1088/1742-5468/2015/10/P10018](https://doi.org/10.1088/1742-5468/2015/10/P10018)

Abstract. In the context of driven diffusive systems, for thermodynamic transformations over a large but finite time window, we derive an expansion of the energy balance. In particular, we characterize the transformations which minimize the energy dissipation and describe the optimal correction to the quasi-static limit. Surprisingly, in the case of transformations between homogeneous equilibrium states of an ideal gas, the optimal transformation is a sequence of inhomogeneous equilibrium states.

Keywords: driven diffusive systems (theory), transport processes/heat transfer (theory), stationary states

Contents

1. Introduction	2
2. The Clausius inequality and its nonequilibrium counterparts	4
2.1. Hydrodynamical description	4
2.2. The Clausius inequality	6
2.3. Renormalized work	7
3. Finite time thermodynamics	8
3.1. Slow transformations	8
3.2. Quantitative analysis of the Clausius inequality	10
4. Optimal transformations between equilibrium states	11
4.1. Remark on boundary conditions	11
4.2. Change of variables	12
4.3. Hamiltonian structure	13
5. Explicit minimizers	14
5.1. Optimal transformations through homogeneous equilibria	14
5.2. Ideal gas	15
5.3. Ginzburg–Landau	16
6. Conclusions	16
Acknowledgments	17
Appendix A. Analysis of the excess functional	17
A.1. Preliminary computations	17
A.2. Proof of (4.11)	18
References	19

1. Introduction

As discussed in thermodynamic textbooks, in a transformation between equilibrium states a system necessarily goes through deviations from equilibrium which are small if the transformation is quasi-static. As clearly stated in Callen [5],

‘A quasi-static process is thus defined in terms of a dense succession of equilibrium states. It is to be stressed that a quasi-static process therefore is an idealized concept, quite distinct from a real physical process, for a real process always involves nonequilibrium intermediate states having no representation in the thermodynamic configuration space. Furthermore, a quasi-static process, in contrast

to a real process, does not involve considerations of rates, velocities or time. The quasi-static process simply is an ordered succession of equilibrium states, whereas a real process is a temporal succession of equilibrium and nonequilibrium states’.

Our aim is to develop the analysis, started in [2, 3], of real transformations for driven diffusive systems, both in equilibrium and nonequilibrium. As emphasized in the previous quotation this analysis will necessarily involve dynamical considerations that are outside the scope of classical thermodynamics.

The dynamic evolution of driven diffusive systems is described by the continuity equation together with the constitutive equation that expresses the local current as a function of the density and the driving field. The interaction with boundary reservoirs specifies the appropriate boundary conditions. A (real) transformation is thus defined by a choice of time-dependent driving field and chemical potentials of the reservoirs. Within this scheme, a dynamical derivation of the Clausius inequality $W \geq \Delta F$ for isothermal transformations has been obtained in [2, 3]. Here W is the work done in the transformation and ΔF is the variation of the free energy. Moreover, we have shown that the Clausius inequality becomes an equality, i.e. $W = \Delta F$ in the limit of very slow transformations, that is in the quasi-static limit.

Since real transformations last a finite time, the quasi-static limit cannot be achieved. A meaningful issue is thus to describe the corrections to the quasi-static limit for transformations over a large but finite time window τ . To describe the evolution of the system it is convenient to rescale time by introducing the dimensionless variable $s = t/\tau$ where t is the original time variable. We then expand the evolution and the energy balance in powers of $1/\tau$ and compute the first order corrections.

Consider now transformations through equilibrium states namely those for which the stationary current, corresponding to the given external drivings at time s , vanishes. In the absence of an external field, transformations through equilibrium states are those in which the chemical potentials, while varying in time, are the same on each point of the boundary. For transformations through equilibrium states we show that, up to order $1/\tau^2$, $W = \Delta F + (1/\tau) B$ where B is a positive functional of the transformation, that is of the time dependent external drivings. For real but slow transformations we can thus optimize the dissipated energy by minimizing the functional B . Not surprisingly, we prove that for transformations between equilibrium states (namely such that the initial and final states are equilibrium states), the functional B is minimized by transformations through equilibrium states.

In the case of an ideal gas, the minimizer of B can be computed explicitly. Somehow surprisingly, for transformation between homogeneous equilibrium states (characterized by the absence of external field), the optimal transformation is a sequence of inhomogeneous equilibrium states. In other words, it is profitable to switch on an external field. In the context of Langevin dynamics, finite time refinements to the second law of thermodynamics have been discussed in [1], see also [11] for the case of jump Markov processes.

For transformations between nonequilibrium states, the Clausius inequality $W \geq \Delta F$ does not carry any significant information. In fact, the energy dissipated along such transformations will necessarily include the contribution needed to maintain the non-equilibrium stationary states, which is infinite in an unbounded time window. It is

however possible to formulate a meaningful version of the Clausius inequality for nonequilibrium states by introducing a *renormalized work* W^{ren} that is defined by subtracting from the total work W the energy needed to maintain the nonequilibrium state. Within the setting of the macroscopic fluctuation theory [4], a definition of renormalized work has been proposed in [2, 3] following the point of view in [12] further developed in [6–8]. The analysis of real thermodynamic transformations carried out in this paper and outlined above includes transformations between nonequilibrium states provided the work is replaced by the renormalized work.

We draw the reader's attention to the very recent paper [10]. This paper analyzes, in the context of Markov chains with finitely many degrees of freedom, problems similar to the ones discussed here. In particular, the authors introduce an optimization problem for the finite time correction to the Clausius inequality, with motivations similar to ours.

2. The Clausius inequality and its nonequilibrium counterparts

In this section we review the dynamical approach to thermodynamic transformations introduced in [2, 3] and developed in [4].

2.1. Hydrodynamical description

We introduce the hydrodynamic description of out of equilibrium driven diffusive systems which are characterized by conservation laws. We restrict to the case of a single conservation law, e.g. the conservation of the mass.

We denote by $\Lambda \subset \mathbb{R}^d$ the bounded region occupied by the system, by $\partial\Lambda$ the boundary of Λ , by x the macroscopic space coordinates and by t the macroscopic time. The system is in contact with boundary reservoirs, characterized by their chemical potential $\lambda(t, x)$, and under the action of an external field $E(t, x)$.

At the macroscopic level the system is completely described by the local density $\rho(t, x)$ and the local density current $j(t, x)$. Their evolution is given by the continuity equation together with the constitutive equation which expresses the current as a function of the density. Namely,

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

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

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

where the *diffusion coefficient* $D(\rho)$ and the *mobility* $\chi(\rho)$ are assumed to be $d \times d$ symmetric and positive definite matrices. This holds in the context of stochastic lattice gases [14]. Equation (2.2) relies on the diffusive approximation and on the linear response to the external field. The evolution of the density is thus given by the driven diffusive equation

$$\partial_t \rho(t) + \nabla \cdot (\chi(\rho)E(t)) = \nabla \cdot (D(\rho)\nabla\rho). \quad (2.3)$$

The transport coefficients D and χ satisfy the local Einstein relation

$$D(\rho) = \chi(\rho) f''(\rho), \quad (2.4)$$

where f is the equilibrium free energy per unit volume.

Equations (2.1) and (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, the boundary condition reads

$$f'(\rho(t, x)) = \lambda(t, x), \quad x \in \partial\Lambda. \quad (2.5)$$

If the chemical potential and external field do not depend on time, we denote by $\bar{\rho} = \bar{\rho}_{\lambda, E}$ the stationary solution of (2.3) and (2.5),

$$\begin{cases} \nabla \cdot J(\bar{\rho}) = \nabla \cdot (-D(\bar{\rho})\nabla\bar{\rho} + \chi(\bar{\rho})E) = 0, \\ f'(\bar{\rho}(x)) = \lambda(x), \quad x \in \partial\Lambda. \end{cases} \quad (2.6)$$

We will assume that this stationary solution is unique. The stationary density profile $\bar{\rho}$ is characterized by the vanishing of the divergence of the associated current, $\nabla \cdot J(\bar{\rho}) = 0$. A special situation is when the current itself vanishes, $J(\bar{\rho}) = 0$; if this is the case we say that the system is in an equilibrium state; this can be viewed as a macroscopic counterpart to detailed balance. Conversely given a density profile $\bar{\rho}$ there is not a unique pair (λ, E) such that $\bar{\rho} = \bar{\rho}_{\lambda, E}$. Indeed λ is uniquely determined by the second equation in (2.6) while the external field can be chosen in the form

$$E = \chi^{-1}(\bar{\rho})(G + D(\bar{\rho})\nabla\bar{\rho}), \quad (2.7)$$

where G is an arbitrary divergence free vector field. We note that for equilibrium states there is a one-to-one correspondence between the pair (λ, E) and the stationary solution of (2.6), that is defined by choosing $G = 0$ in (2.7).

Homogeneous equilibrium states correspond to the case in which the external field vanishes and the chemical potential is constant. The stationary solution is then constant and satisfies $f'(\bar{\rho}_{\lambda, 0}) = \lambda$. Inhomogeneous equilibrium states correspond to the case in which the external field is gradient, $E = -\nabla U$, and it is possible to choose the arbitrary constant in the definition of U such that $U(x) = -\lambda(x)$, $x \in \partial\Lambda$. By the Einstein relation (2.4), the stationary solution satisfies $-f'(\bar{\rho}_{\lambda, E}(x)) = U(x)$ and the stationary current vanishes, $J(\bar{\rho}_{\lambda, E}) = 0$. Examples of inhomogeneous equilibrium states in the presence of an external field are provided by a still atmosphere in the gravitational field or by sedimentation in a centrifuge.

In this framework it is possible to define a thermodynamic functional V , called the quasi-potential, generalizing the free energy for systems out of equilibrium. It can be characterized as the maximal positive solution, vanishing when $\rho = \bar{\rho}$, of the Hamilton–Jacobi equation,

$$\int_{\Lambda} dx \nabla \frac{\delta V}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta V}{\delta \rho} - \int_{\Lambda} dx \frac{\delta V}{\delta \rho} \nabla \cdot J(\rho) = 0. \quad (2.8)$$

We now define the *symmetric current* J_S by

$$J_S(\rho) = -\chi(\rho)\nabla\frac{\delta V}{\delta\rho}. \quad (2.9)$$

Since the stationary density $\bar{\rho}$ is a minimum for V , then $(\delta V/\delta\rho)(\bar{\rho}) = 0$. The symmetric current thus vanishes at the stationary profile,

$$J_S(\bar{\rho}) = 0. \quad (2.10)$$

We rewrite the hydrodynamic current as

$$J(\rho) = J_S(\rho) + J_A(\rho), \quad (2.11)$$

which defines the *antisymmetric current* J_A .

In view of these definitions, equation (2.8) becomes

$$\int_{\Lambda} dx J_S(\rho) \cdot \chi(\rho)^{-1} J_A(\rho) = 0. \quad (2.12)$$

In the case of an equilibrium state the quasi-potential $V = V_{\lambda,E}(\rho)$ is the local functional

$$V_{\lambda,E}(\rho) = \int_{\Lambda} dx (f(\rho) - f(\bar{\rho}) - f'(\bar{\rho})(\rho - \bar{\rho})), \quad (2.13)$$

where $\bar{\rho} = \bar{\rho}_{\lambda,E}$ is the solution of (2.6).

2.2. The Clausius inequality

The second law of thermodynamics can be expressed as follows. Consider a system in an equilibrium state in thermal contact with an environment at a given temperature. The system then undergoes an isothermal transformation to a final state. The Clausius inequality states

$$W \geq \Delta F, \quad (2.14)$$

where W is the mechanical work done on the system and ΔF is the difference of the free energy between the final and the initial state. If equality holds the transformation is said to be reversible. It can be implemented by performing very slow variations so that the system goes through a sequence of equilibrium states.

We review the dynamical derivation of the Clausius inequality in [2, 3]. Consider a system in a time dependent environment, that is, E and λ depend on time. The work done by the environment on the system in the time interval $[0, T]$ is

$$W_{[0,T]} = \int_0^T dt \left\{ \int_{\Lambda} dx j(t) \cdot E(t) - \int_{\partial\Lambda} d\sigma \lambda(t) j(t) \cdot \hat{n} \right\}, \quad (2.15)$$

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 external field while the second is the energy provided by the reservoirs.

Fix time dependent paths $\lambda(t)$ of the chemical potential and $E(t)$ of the driving field. Given a density profile ρ_0 , let $\rho(t)$, $j(t)$, $t \geq 0$, be the solution of (2.1)–(2.5) with initial condition ρ_0 . By using the Einstein relation (2.4) and the boundary condition $f'(\rho(t)) = \lambda(t)$, an application of the divergence theorem yields

$$W_{[0, T]} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_{\Lambda} dx j(t) \cdot \chi(\rho(t))^{-1} j(t), \quad (2.16)$$

where F is the equilibrium free energy functional,

$$F(\rho) = \int_{\Lambda} dx f(\rho(x)). \quad (2.17)$$

Equation (2.16) is not simply a rewriting of (2.15), as it depends on a physical principle, the local Einstein relationship.

Since the second term on the right hand side of (2.16) is positive, we deduce the Clausius inequality (2.14) with $\Delta F = F(\rho_1) - F(\rho_0)$ for arbitrary density profiles $\rho_0 = \rho(0)$, $\rho_1 = \rho(T)$. Note that this derivation holds both for equilibrium and nonequilibrium systems.

2.3. Renormalized work

The idea to define a renormalized work is to subtract the energy needed to maintain the system out of equilibrium. For time independent drivings, by the orthogonal decomposition (2.11) and (2.10), $J(\bar{\rho}) = J_A(\bar{\rho})$ is the macroscopic current in the stationary state. In view of the general formula for the total work (2.16), the amount of energy per unit time needed to maintain the system in the stationary profile $\bar{\rho}$ is

$$\int_{\Lambda} dx J_A(\bar{\rho}) \cdot \chi(\bar{\rho})^{-1} J_A(\bar{\rho}). \quad (2.18)$$

Fix now $T > 0$, a density profile ρ_0 , and space-time dependent chemical potentials $\lambda(t)$ and external field $E(t)$, $t \in [0, T]$. Let $(\rho(t), j(t))$ be the corresponding solution of (2.1)–(2.5) with initial condition ρ_0 . We define the renormalized work $W_{[0, T]}^{\text{ren}}$ done by the reservoirs and the external field in the time interval $[0, T]$ as

$$W_{[0, T]}^{\text{ren}} = W_{[0, T]} - \int_0^T dt \int_{\Lambda} dx J_A(t, \rho(t)) \cdot \chi(\rho(t))^{-1} J_A(t, \rho(t)) \quad (2.19)$$

where $J_A(t, \rho)$ is the antisymmetric current for the system with the time independent external driving obtained by freezing the time dependent chemical potential λ and external field E at time 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 $\rho(t)$ of the time dependent hydrodynamic equation.

The definition (2.19) is natural within the macroscopic fluctuation theory and leads to a Clausius inequality. Indeed, in view of (2.16) and the orthogonality in (2.12) between the symmetric and the antisymmetric part of the current,

$$\begin{aligned} W_{[0, T]}^{\text{ren}} &= F(\rho(T)) - F(\rho_0) + \int_0^T dt \int_{\Lambda} dx J_S(t, \rho(t)) \cdot \chi(\rho(t))^{-1} J_S(t, \rho(t)) \\ &\geq F(\rho(T)) - F(\rho_0). \end{aligned} \quad (2.20)$$

In the context of Langevin dynamics, a different definition of renormalized work has been proposed in [9], see [3] for a comparison.

We obtain next a macroscopic version of the well known Hatano–Sasa inequality [6]. Consider the dissipation due to the symmetric current

$$\int_0^T dt \int_{\Lambda} dx J_S(t, \rho(t)) \cdot \chi(\rho(t))^{-1} J_S(t, \rho(t)) = - \int_0^T dt \int_{\Lambda} dx \nabla \frac{\delta V_t}{\delta \rho} \cdot J_S(t, \rho(t)) \geq 0,$$

where V_t is the quasi-potential corresponding to the driving $\alpha = (\lambda(t), E(t))$ at frozen time t . Integrating by parts and using the orthogonality between J_S and J_A we obtain

$$\int_0^T dt \int_{\Lambda} dx \dot{\alpha} \cdot \frac{\delta V_t}{\delta \alpha} \geq V_T(\rho(T)) - V_0(\rho(0)) \quad (2.21)$$

If the initial state is the stationary profile for $(\lambda(0), E(0))$, then the right hand side is $V_T(\rho(T)) \geq 0$.

3. Finite time thermodynamics

In this section we develop an approach to thermodynamic transformations which takes into account the fact that any real transformation lasts for a finite time. We consider transformations over an interval of time $[0, \tau]$ and we discuss their asymptotic properties for large τ . In particular, for slow transformation, we shall obtain the correction of order $\frac{1}{\tau}$ to the equality $W = \Delta F$ which holds in the quasi-static limit. We finally discuss which transformations minimize such a correction.

3.1. Slow transformations

To analyze transformations over the interval $[0, \tau]$ it is convenient to introduce the dimensionless variable $s = t/\tau$. A *protocol* is defined by a choice of the external drivings $E(s, x)$, $x \in \Lambda$, and $\lambda(s, x)$, $x \in \partial\Lambda$, $s \in [0, 1]$. The transformation is then realized by

$$\begin{cases} E^\tau(t) = E(t/\tau), \\ \lambda^\tau(t) = \lambda(t/\tau), \end{cases} t \in [0, \tau]. \quad (3.1)$$

The asymptotics in which we are interested is for τ large compared to the typical relaxation time of the system, corresponding to slow transformations. Let $\rho^\tau(t)$ and $j^\tau(t)$, $0 \leq t \leq \tau$, be the solution to the hydrodynamic equations (2.1), (2.2) and (2.5) with the slow external field E^τ and chemical potential λ^τ , that is

$$\begin{cases} \partial_t \rho^\tau + \nabla \cdot J(t/\tau, \rho^\tau(t)) = 0, \\ j^\tau(t) = J(t/\tau, \rho^\tau(t)) \\ f'(\rho^\tau(t))|_{\partial\Lambda} = \lambda^\tau(t) \end{cases} \quad (3.2)$$

where we recall that $J(t, \rho) = -D(\rho)\nabla\rho + \chi(\rho)E(t)$.

For $s \in [0, 1]$, let $\bar{\rho}(s)$ be the unique stationary solution of the hydrodynamics with external field $E(s)$ and chemical potential $\lambda(s)$. When τ is large the solution (ρ^τ, j^τ) has an expansion of the type

$$\begin{aligned}\rho^\tau(\tau s) &= \bar{\rho}(s) + \frac{1}{\tau} r(s) + o\left(\frac{1}{\tau}\right), \\ j^\tau(\tau s) &= J(s, \bar{\rho}(s)) + \frac{1}{\tau} g(s) + o\left(\frac{1}{\tau}\right).\end{aligned}\quad (3.3)$$

By (3.2) we get the corresponding linear evolution equations for the first order correction (r, g) ,

$$\begin{cases} \partial_s \bar{\rho}(s) + \nabla \cdot g(s) = 0 \\ g(s) = -\nabla \cdot (D(\bar{\rho}(s))r(s)) + r(s)\chi'(\bar{\rho}(s))E(s) \\ r(s, x) = 0, \quad x \in \partial\Lambda \end{cases}\quad (3.4)$$

where we use the notation that, for a matrix $A = (a_{ij}(x))_{i,j=1}^n$, $\nabla \cdot A$ is the vector with i th coordinate $\sum_j \partial_{x_j} a_{ij}(x)$. Note that the system (3.4) has the form of a Poisson equation for $r(s)$.

Recalling the definition (2.15) of the work, by evaluating the energy balance (2.16) along the transformation (ρ^τ, j^τ) , we obtain

$$\begin{aligned}F(\rho^\tau(\tau)) - F(\rho^\tau(0)) &= \tau \int_0^1 ds \int_\Lambda dx j^\tau(\tau s) \cdot E(s) \\ &\quad - \tau \int_0^1 ds \int_{\partial\Lambda} d\sigma \lambda(s) j^\tau(\tau s) \cdot \hat{n} - \tau \int_0^1 ds \int_\Lambda dx j^\tau(\tau s) \cdot \chi(\rho^\tau(\tau s))^{-1} j^\tau(\tau s).\end{aligned}\quad (3.5)$$

In this equation $\rho^\tau(0)$ and $\rho^\tau(\tau)$ are the initial condition for the hydrodynamic equation (3.2) with the external drivings given in (3.1) and the corresponding value of the density at time τ . Due to the finite relaxation time of the system, $\rho^\tau(0)$ and $\rho^\tau(\tau)$ are not the stationary density profiles associated with the drivings $(\lambda(0), E(0))$ and $(\lambda(1), E(1))$. At order $1/\tau$, the difference between $\rho^\tau(0)$ and $\bar{\rho}(0)$ is obtained by solving the equation (3.4) for $s = 0$ (here $\partial_s \bar{\rho}(s)$ plays the role of a given source). The analogous statement holds for the difference between $\rho^\tau(\tau)$ and $\bar{\rho}(1)$. Observe that in this formulation the value of the density at time 0 and τ can be exchanged so that a slow transformation from the final to the initial state can be obtained by time reversal of the protocol.

We can analyze the equation (3.5) at the different orders in $1/\tau$, obtaining an identity for each order. Direct computations yield that at order τ the right hand side of (3.5) vanishes.

At order τ^0 we get the first non trivial relationship,

$$\begin{aligned}F(\bar{\rho}(1)) - F(\bar{\rho}(0)) &= \int_0^1 ds \int_\Lambda dx E(s) \cdot g(s) - \int_0^1 ds \int_{\partial\Lambda} d\sigma \lambda(s) g(s) \cdot \hat{n} \\ &\quad + \int_0^1 ds \int_\Lambda dx r(s) J(s, \bar{\rho}(s)) \cdot (\chi^{-1})'(\bar{\rho}(s)) J(s, \bar{\rho}(s)),\end{aligned}\quad (3.6)$$

where we used that $\rho^\tau(0) = \bar{\rho}(0) + O(1/\tau)$ and $\rho^\tau(\tau) = \bar{\rho}(1) + O(1/\tau)$. The above relation connects the variation of the free energy to the first order corrections to the

solutions of the hydrodynamic equations. We observe that, if we consider transformations between two equilibrium states, the last term in the right hand side of (3.6) vanishes when the intermediate states are also of equilibrium so that $J(s, \bar{\rho}(s)) = 0$. However the transformation can go through nonequilibrium intermediate states.

3.2. Quantitative analysis of the Clausius inequality

Consider the equation (2.20) which expresses the energy balance in the time interval $[0, \tau]$. Recall that the last term vanishes in the quasi-static limit. We now compute its asymptotics when τ is large and for a slow transformation given, as in (3.1), in terms of a protocol $(\lambda(s), E(s))$, $s \in [0, 1]$.

Rewrite equation (2.20) for a slow transformation,

$$\begin{aligned} W_{[0,\tau]}^{\text{ren}} - [F(\rho^\tau(\tau)) - F(\rho^\tau(0))] \\ = \int_0^\tau dt \int_\Lambda dx J_S(t/\tau, \rho^\tau(t)) \cdot \chi(\rho^\tau(t))^{-1} J_S(t/\tau, \rho^\tau(t)). \end{aligned} \quad (3.7)$$

Recalling (2.9), the symmetric part of the current is

$$J_S(s, \rho) = -\chi(\rho) \nabla \frac{\delta V_{\lambda(s), E(s)}(\rho)}{\delta \rho} \quad (3.8)$$

where $V_{\lambda(s), E(s)}$ is the quasi-potential associated with $(\lambda(s), E(s))$ (we regard s here as a fixed parameter). In view of (3.3), the symmetric current has the expansion

$$J_S(s, \rho^\tau(\tau s)) = -\frac{1}{\tau} \chi(\bar{\rho}(s)) \nabla (C_s^{-1} r(s)) + O\left(\frac{1}{\tau^2}\right). \quad (3.9)$$

where C_s^{-1} is the linear operator with integral kernel

$$C_s^{-1}(x, y) = \frac{\delta^2 V_{\lambda(s), E(s)}(\bar{\rho}(s))}{\delta \rho(x) \delta \rho(y)}. \quad (3.10)$$

Hence,

$$W_{[0,\tau]}^{\text{ren}} - [F(\rho^\tau(\tau)) - F(\rho^\tau(0))] = \frac{1}{\tau} B + O\left(\frac{1}{\tau^2}\right), \quad (3.11)$$

where the *excess* functional B is:

$$B = \int_0^1 ds \int_\Lambda dx \nabla (C_s^{-1} r(s)) \cdot \chi(\bar{\rho}(s)) \nabla (C_s^{-1} r(s)). \quad (3.12)$$

For a transformation between and through equilibrium states, $W_{[0,\tau]}^{\text{ren}}$ coincides with the total work $W_{[0,\tau]}$. Hence, the inequality $B \geq 0$ is a restatement of the second principle of thermodynamics and (3.11) expresses a quantitative version of the Clausius inequality. Note that, in the limit $\tau \rightarrow \infty$, all protocols realize the equality $W = \Delta F$. On the other hand, for finite time τ , this identity cannot be achieved and we can select an optimal protocol by minimizing B .

4. Optimal transformations between equilibrium states

We consider, for simplicity, a system in one space dimension, in the domain $\Lambda = [-1, 1]$, with diffusion coefficient $D(\rho)$ and mobility $\chi(\rho)$. Since $\bar{\rho}(s)$ is determined by $(\lambda(s), E(s))$ through (2.6), the excess (3.12) is a functional $B = B(\lambda, E)$ of the protocol $(\lambda(s), E(s))$, $s \in [0, 1]$. In (3.12) $r(s) = r_{\lambda(s), E(s)}(x)$ is obtained by solving the following Poisson equation, derived from (3.4):

$$\begin{cases} \partial_s \bar{\rho}(s) = \Delta(D(\bar{\rho}(s))r(s)) - \nabla(\chi'(\bar{\rho}(s))E(s)r(s)) \\ r(s, \pm 1) = 0. \end{cases} \quad (4.1)$$

Given an initial state (λ_0, E_0) and a final state (λ_1, E_1) , we want to minimize the excess $B(\lambda, E)$ in (3.12) as a functional of the protocol, with the constraints $(\lambda(0), E(0)) = (\lambda_0, E_0)$ and $(\lambda(1), E(1)) = (\lambda_1, E_1)$.

This problem is already relevant when the initial and final states (λ_0, E_0) and (λ_1, E_1) are equilibrium states. It appears reasonable that, in this case, an optimal protocol will pass through equilibrium states $(\lambda(s), E(s))$ at every time s . We will show that this is indeed the case. Moreover, an optimal protocol can be obtained as follows. Solve the system of partial differential equations

$$\begin{cases} \partial_s \bar{\rho}(s) + \frac{1}{2} \nabla(\chi(\bar{\rho}(s))\nabla\bar{\pi}(s)) = 0 \\ \partial_s \bar{\pi}(s) + \frac{1}{4} \chi'(\bar{\rho}(s))(\nabla\bar{\pi}(s))^2 = 0 \\ \bar{\rho}(0) = \bar{\rho}_{\lambda_0, E_0}, \quad \bar{\rho}(1) = \bar{\rho}_{\lambda_1, E_1}, \quad \bar{\pi}(s, \pm 1) = 0, \end{cases} \quad (4.2)$$

in the unknown $\bar{\rho}(s) = \bar{\rho}(s, x)$, $\bar{\pi}(s) = \bar{\pi}(s, x)$, $(s, x) \in [0, 1] \times \Lambda$. Set

$$E(s) = \frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} \nabla \bar{\rho}(s), \quad \lambda(s, \pm 1) = f'(\bar{\rho}(s, \pm 1)), \quad (4.3)$$

which corresponds to the choice $G = 0$ in (2.7). Equation (4.3) defines a transformation between and through equilibrium states, the corresponding minimal value of the excess functional is then given by

$$B_{\text{opt}} = \frac{1}{4} \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s)) (\nabla \bar{\pi}(s))^2. \quad (4.4)$$

We emphasize that both the stationary equation (4.2) and the corresponding minimal excess B_{opt} in (4.4) do not depend on the diffusion coefficient D . In fact, in the rescaled time $s = \frac{t}{\tau}$, and in the asymptotics $\tau \rightarrow \infty$, the system relaxes instantaneously, and therefore the value of D becomes irrelevant.

4.1. Remark on boundary conditions

Note that in the minimization of B we have not fixed the value of $r(s)$ at $s = 0$ or 1 , which corresponds, in terms of the unscaled time variable t , to fix the values of the initial and final density profiles $\rho^\tau(0)$ and $\rho^\tau(\tau)$ only at the order 1, and not at the

order $\frac{1}{\tau}$. On the other hand, we claim that optimizing B with the added constraints $r(0) = r(1) = 0$ the infimum does not change. Indeed, we can consider a sequence of protocols that are constant in time in the time intervals $[0, \varepsilon]$ and $[1 - \varepsilon, 1]$, and close to the optimal protocol for $s \in [\varepsilon, 1 - \varepsilon]$. In the limit $\varepsilon \rightarrow 0$ the corresponding value of B approaches B_{opt} . As a consequence, we deduce that, for all protocols $(\lambda(s), E(s))$,

$$W_{[0, \tau]}^{\text{ren}} - (F(\bar{\rho}_1) - F(\bar{\rho}_0)) \geq \frac{1}{\tau} B_{\text{opt}} + O\left(\frac{1}{\tau^2}\right), \quad (4.5)$$

provided that, up to order $1/\tau^2$ $\rho^\tau(0) = \bar{\rho}_0$ and $\rho^\tau(\tau) = \bar{\rho}_1$. Equality in (4.5) can be achieved by the limiting procedure described above.

4.2. Change of variables

It will be convenient to perform a change of variables in the space of states. Given a state (λ, E) , we associate to it the pair density-current $(\bar{\rho}, \bar{J})$, where $\bar{\rho} = \bar{\rho}_{\lambda, E}$ is the stationary density profile defined by equation (2.6), and $\bar{J} = -D(\bar{\rho})\nabla\bar{\rho} + \chi(\bar{\rho})E$ is the corresponding stationary current. The correspondence $(\lambda, E) \mapsto (\bar{\rho}, \bar{J})$ is one-to-one and the inverse map $(\bar{\rho}, \bar{J}) \mapsto (\lambda, E)$ is given by

$$\lambda(\pm 1) = f'(\bar{\rho}(\pm 1)), \quad E = \frac{1}{\chi(\bar{\rho})}(D(\bar{\rho})\nabla\bar{\rho} + \bar{J}). \quad (4.6)$$

Observe that, since we are in one space dimension, \bar{J} is constant in x . Under this change of variables, equilibrium states (λ, E) correspond to elements $(\bar{\rho}, 0)$ with vanishing current.

In the new variables, the quasi-potential $V = V(\bar{\rho}, \bar{J}; \rho)$ becomes a functional on the set of density profiles $\rho : \Lambda \rightarrow \mathbb{R}_+$, depending parametrically on $(\bar{\rho}, \bar{J})$. For $\bar{J} = 0$ it is the local functional (2.13),

$$V(\bar{\rho}, 0; \rho) = \int_{\Lambda} dx (f(\rho) - f(\bar{\rho}) - f'(\bar{\rho})(\rho - \bar{\rho})). \quad (4.7)$$

While for arbitrary current $\bar{J} \in \mathbb{R}$, the quasi-potential solves the Hamilton–Jacobi equation (2.8), that in the present variables reads

$$\int_{\Lambda} dx \chi(\rho) \left(\nabla \frac{\delta V(\bar{\rho}, \bar{J}; \rho)}{\delta \rho} \right) \left(\nabla \left(\frac{\delta}{\delta \rho} (V(\bar{\rho}, \bar{J}; \rho) - V(\bar{\rho}, 0; \rho)) \right) + \frac{\bar{J}}{\chi(\bar{\rho})} \right) = 0, \quad (4.8)$$

where we used the Einstein relation (2.4).

In the present variables, the excess functional (3.12) becomes

$$B = \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s, x)) \left(\nabla_x \int_{\Lambda} dy \frac{\delta^2 V(\bar{\rho}(s), \bar{J}(s); \bar{\rho}(s))}{\delta \rho(x) \delta \rho(y)} r(s, y) \right)^2, \quad (4.9)$$

where $r(s) = r(\bar{\rho}(s), \partial_s \bar{\rho}(s), \bar{J}(s); x)$ solves

$$\begin{cases} \partial_s \bar{\rho}(s) = \nabla \left(\chi(\bar{\rho}(s)) \nabla \left(\frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} r(s) \right) - \frac{\chi'(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} r(s) \bar{J}(s) \right) \\ r(s, \pm 1) = 0. \end{cases} \quad (4.10)$$

If the initial and final states are in equilibrium, then an optimal protocol consists of a family of equilibrium states $(\bar{\rho}(s), 0)$, $s \in [0, 1]$. This will be shown by proving that the excess functional B in (4.9) satisfies

$$\left. \frac{\delta B(\bar{\rho}, \bar{J})}{\delta \bar{J}(s)} \right|_{\bar{J}=0} = 0, \quad s \in [0, 1]. \quad (4.11)$$

Indeed, this condition guarantees that stationary paths $(\bar{\rho}(s), \bar{J}(s))$, $s \in [0, 1]$, of the excess functional $B(\bar{\rho}, \bar{J})$ can be obtained as $(\bar{\rho}(s), 0)$, $s \in [0, 1]$, where $\bar{\rho}(s)$ is a stationary path for the functional $B(\bar{\rho}, 0)$. The proof of (4.11) is detailed in appendix A.

4.3. Hamiltonian structure

For transformations between equilibrium states, in view of (4.11), we can restrict the functional B to transformations through equilibrium states $(\bar{\rho}(s), 0)$, $s \in [0, 1]$. Under this assumption, the excess functional B (4.9) can be rewritten as

$$B = \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s)) \left(\nabla \left(\frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s)) \right) \right)^2, \quad (4.12)$$

where r_0 is the first order correction to ρ for equilibrium states, see (A.10). By introducing

$$\pi(s, x) = \pi(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) = -2 \frac{D(\bar{\rho}(s, x))}{\chi(\bar{\rho}(s, x))} r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x), \quad (4.13)$$

the excess functional B can be written as

$$B = \frac{1}{4} \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s)) (\nabla \pi(s))^2. \quad (4.14)$$

and equation (4.10) translates to the following equation for π :

$$\partial_s \bar{\rho}(s) + \frac{1}{2} \nabla (\chi(\bar{\rho}(s)) \nabla \pi(s)) = 0, \quad \pi(s, \pm 1) = 0. \quad (4.15)$$

In the form (4.14), the excess functional B can be interpreted as the action functional associated with the Lagrangian

$$\mathcal{L}(\bar{\rho}, \dot{\bar{\rho}}) = \frac{1}{4} \int_{\Lambda} dx \chi(\bar{\rho}(x)) (\nabla_x \pi(\bar{\rho}, \dot{\bar{\rho}}; x))^2. \quad (4.16)$$

The corresponding Hamiltonian is

$$\mathcal{H}(\bar{\rho}, \bar{\pi}) = \sup_{\dot{\bar{\rho}}} \left\{ \int_{\Lambda} dx \bar{\pi} \dot{\bar{\rho}} - \mathcal{L}(\bar{\rho}, \dot{\bar{\rho}}) \right\} = \frac{1}{4} \int_{\Lambda} dx \chi(\bar{\rho}) (\nabla_x \bar{\pi})^2. \quad (4.17)$$

A straightforward computation shows that (4.2) are the Hamiltonian equations for (4.17). Note that, apart from a factor $\frac{1}{4}$, (4.17) coincides with the Hamiltonian of the macroscopic fluctuation theory [4, section IV.B] in the degenerate case $D = 0$ and $E = 0$.

5. Explicit minimizers

5.1. Optimal transformations through homogeneous equilibria

We start by discussing how the excess functional B can be minimized if we restrict it to transformations through homogeneous equilibrium states. Namely, we consider B in (4.14) and (4.15) as a functional on paths $\bar{\rho}(s)$, $s \in [0, 1]$, constant in x (which corresponds to having zero external field: $E(s) = 0$).

Within this setting equation (4.15) for $\pi(s, x) = \pi(\bar{\rho}(s), \dot{\bar{\rho}}(s); x)$ becomes

$$\Delta\pi(s, x) = -2\frac{\dot{\bar{\rho}}(s)}{\chi(\bar{\rho}(s))}, \quad \pi(s, \pm 1) = 0, \quad (5.1)$$

whose solution is

$$\pi(s, x) = \frac{\dot{\bar{\rho}}(s)}{\chi(\bar{\rho}(s))}(1 - x^2). \quad (5.2)$$

In view of (5.2), the functional B (4.14), restricted to homogeneous density protocols $\bar{\rho}(s)$ $s \in [0, 1]$, becomes

$$B = \frac{2}{3} \int_0^1 ds \frac{(\dot{\bar{\rho}}(s))^2}{\chi(\bar{\rho}(s))}. \quad (5.3)$$

Letting

$$\Phi(\rho) = \int^\rho d\alpha \frac{1}{\sqrt{\chi(\alpha)}},$$

we have

$$B = \frac{2}{3} \int_0^1 ds (\partial_s \Phi(\bar{\rho}(s)))^2. \quad (5.4)$$

Hence, the minimizer of this functional is obtained when

$$\partial_s \Phi(\bar{\rho}(s)) = \frac{\dot{\bar{\rho}}(s)}{\sqrt{\chi(\bar{\rho}(s))}} = \Phi(\bar{\rho}_1) - \Phi(\bar{\rho}_0). \quad (5.5)$$

Thus the minimal excess (minimizing among the homogeneous protocols) is:

$$B_{\text{opt}} = \frac{2}{3} [\Phi(\bar{\rho}_1) - \Phi(\bar{\rho}_0)]^2. \quad (5.6)$$

The protocol (5.5) corresponds to the one obtained in [13, equation (18)] in the context of Markov processes with finitely many degrees of freedom. However, the spatial structure of our setting allows one to find better protocols. In other words, the protocol (5.5) is not a minimizer of the excess functional (4.14) without the constraint of transformations through homogeneous equilibrium states. Indeed, the function $\pi(t, x)$ in (5.2) does not solve Hamiltonian equation (4.2). In fact we get

$$\partial_s \pi(s, x) + \frac{1}{4} \chi'(\bar{\rho}(s)) (\nabla \pi(s, x))^2 = \frac{1}{2} \chi'(\bar{\rho}(s)) \left(\frac{\dot{\bar{\rho}}(s)}{\chi(\bar{\rho}(s))} \right)^2 (3x^2 - 1),$$

which does not vanish unless χ is constant (as in the so-called Ginzburg–Landau model). This means, in particular, that the optimal protocol will not be a sequence of homogeneous equilibrium states. In the case of ideal gases the actual minimizer will be found next.

5.2. Ideal gas

In the case $\chi(\rho) = \rho$, e.g. for ideal gases, the Hamilton equation (4.2) reads

$$\begin{cases} \partial_s \bar{\rho}(s) + \frac{1}{2} \nabla(\bar{\rho}(s)) \nabla \bar{\pi}(s) = 0 \\ \partial_s \bar{\pi}(s) + \frac{1}{4} (\nabla \bar{\pi}(s))^2 = 0 \\ \bar{\rho}(0) = \bar{\rho}_{\lambda_0, E_0}, \quad \bar{\rho}(1) = \bar{\rho}_{\lambda_1, E_1}, \quad \bar{\pi}(s, \pm 1) = 0. \end{cases} \quad (5.7)$$

In particular, the second equation is decoupled and it admits solutions with separated variables. In the case $\bar{\rho}(0) = 0$ and $\bar{\rho}(1) = \bar{\rho}_1$, as can be checked by direct computations, the solution is as follows:

$$\bar{\pi}(s, x) = \frac{1}{s} (1 - |x|)^2, \quad \bar{\rho}(s, x) = \frac{1}{s} \theta(|x| + s - 1) \bar{\rho}_1. \quad (5.8)$$

The corresponding minimal value of the excess functional is

$$B_{\text{opt}} = \frac{2}{3} \bar{\rho}_1. \quad (5.9)$$

This should be compared to the minimal value of B through homogeneous equilibria (5.6), which in this case is $\frac{8}{3} \bar{\rho}_1$, giving a flat reduction of 75%.

The interpretation of the solution (5.8) is the following. At time $s = 0^+$ inject the required total mass $2\bar{\rho}_1$ at the endpoints of the domain, giving a positive contribution to the functional B . Then switch on the field $E = D(\bar{\rho}) \frac{\nabla \bar{\rho}}{\bar{\rho}}$, which is concentrated at the points $x = \pm(1 - s)$, so that the density profile $\bar{\rho}$ remains a step function at all times. Observe that the field E is opposite to the current, so the work done by the field is negative, and thus it gives a negative contribution to the excess functional B .

5.3. Ginzburg–Landau

This model has a constant mobility $\chi(\rho) = c$. In this case equations (4.2) are linear and the solution is immediate

$$\begin{cases} \bar{\rho}(x, s) = \bar{\rho}_{\lambda_0, E_0} + s(\bar{\rho}_{\lambda_1, E_1} - \bar{\rho}_{\lambda_0, E_0}), \\ \pi(s, x) = (\bar{\rho}_{\lambda_1, E_1} - \bar{\rho}_{\lambda_0, E_0})(x^2 - 1). \end{cases} \quad (5.10)$$

In particular, the optimal protocol is a sequence of homogeneous equilibrium states.

6. Conclusions

We have reviewed, in the context of driven diffusive systems, the macroscopic fluctuation theory approach to non-equilibrium stationary states [4]. In particular, we discussed the notion of renormalized work for which it is possible to prove a meaningful version of the Clausius inequality for transformation between non-equilibrium states. In the quasi-static limit this inequality becomes an equality.

The main purpose of the present paper has been a quantitative discussion of the energy balance for real transformations, that is transformations lasting over a large but finite time window. By rescaling the time variable we have obtained a relationship between the variation of the equilibrium free energy evaluated at the stationary density profiles and the first order correction to the hydrodynamic equation, see equation (3.6). We then introduced the excess functional B (see equations (3.11) and (3.12)) which accounts for the excess of the renormalized work with respect to the variation of free energy. Finally, we have analyzed the minimization of B . It is remarkable that, for transformations between homogeneous equilibrium states the optimal protocol for B is not a sequence of homogeneous equilibrium states. This is due to the fact that in the framework of driven diffusive systems the spatial structure plays a nontrivial role and the system has a finite relaxation time. This result can be compared with the optimal protocol derived in [13] in the context of Markov processes with finitely many degrees of freedom. The optimal protocol for B has been explicitly computed in the case of an ideal gas in one space dimension, and it exhibits peculiar features. We also mention that, from a mathematical point of view, the optimization problem of B can be recast as a suitable optimal mass transportation problem.

For real transformations between equilibrium states, the optimality criterion based on the minimization of the functional B in (3.12) appears a natural choice. On the other hand, for transformations between stationary non-equilibrium states, B only accounts for the excess of the renormalized work with respect to the variation of free energy. Therefore, a selection criterion based on the minimization of B in this case is meaningful when the subtracted counter-term $\int_0^T dt \int_{\Lambda} dx J_A(t, \rho(t)) \cdot \chi(\rho(t))^{-1} J_A(t, \rho(t))$ in (2.19) can be disregarded. This makes sense when the energy needed to maintain the stationary states is supplied by free unlimited sources, e.g. the solar energy.

Acknowledgments

We thank S Ruffo for useful discussions, the Galileo Galilei Institute for Theoretical Physics for the stimulating atmosphere during the 2014 Workshop ‘Advances in Nonequilibrium Statistical Mechanics’, and INFN for financial support.

Appendix A. Analysis of the excess functional

A.1. Preliminary computations

When the quasi-potential is local, i.e. it is as in (4.7), then the operator C^{-1} in (3.10) is diagonal, and, in particular, it is given by

$$C_{\text{eq}}^{-1}(\bar{\rho}; x, y) := C^{-1}(\bar{\rho}, 0; x, y) = \frac{\delta^2 V}{\delta \rho(x) \delta \rho(y)}(\bar{\rho}, 0; \bar{\rho}) = \frac{D(\bar{\rho}(x))}{\chi(\bar{\rho}(x))} \delta(x - y). \quad (\text{A.1})$$

The quasi-potential $V = V(\bar{\rho}, \bar{J}; \rho)$ has a minimum (equal to 0) in $\rho = \bar{\rho}$, hence it has the general form:

$$V(\bar{\rho}, \bar{J}; \rho) = \frac{1}{2} \int_{\Lambda} dx \int_{\Lambda} dy C^{-1}(\bar{\rho}, \bar{J}; x, y) (\rho(x) - \bar{\rho}(x)) (\rho(y) - \bar{\rho}(y)) + o(\rho - \bar{\rho})^2, \quad (\text{A.2})$$

where $C(\bar{\rho}, \bar{J}; x, y)$ is the limiting covariance of density correlations. By setting

$$\Gamma(\bar{\rho}; x, y) = \left(\frac{\partial}{\partial \bar{J}} \frac{\delta^2}{\delta \rho(x) \delta \rho(y)} V(\bar{\rho}, \bar{J}; \rho) \right) \Big|_{\rho=\bar{\rho}, \bar{J}=0} \quad (\text{A.3})$$

the kernel C^{-1} in (A.2) satisfies

$$C^{-1}(\bar{\rho}, \bar{J}; x, y) = \frac{D(\bar{\rho}(x))}{\chi(\bar{\rho}(x))} \delta(x - y) + \bar{J} \Gamma(\bar{\rho}; x, y) + o(\bar{J}). \quad (\text{A.4})$$

In order to prove (4.11) we need to find an equation for $\Gamma(\bar{\rho}; x, y)$. From (A.2) and (A.4), we get

$$\frac{\delta V(\bar{\rho}, \bar{J}; \rho)}{\delta \rho(x)} = \frac{D(\bar{\rho}(x))}{\chi(\bar{\rho}(x))} (\rho(x) - \bar{\rho}(x)) + \bar{J} \int_{\Lambda} dy \Gamma(\bar{\rho}; x, y) (\rho(y) - \bar{\rho}(y)) + \dots \quad (\text{A.5})$$

We use equation (A.5) to expand the Hamilton–Jacobi equation (4.8) at order 2 in $(\rho - \bar{\rho})$ and at order 1 in \bar{J} . We get, after some simple algebraic manipulation and an integration by parts:

$$\begin{aligned} & \int_{\Lambda} dx \int_{\Lambda} dy (\rho(x) - \bar{\rho}(x)) (\rho(y) - \bar{\rho}(y)) \frac{D(\bar{\rho}(x))}{\chi(\bar{\rho}(x))} \nabla_x (\chi(\bar{\rho}(x))) \nabla_x \Gamma(\bar{\rho}; x, y) \\ &= \int_{\Lambda} dx (\rho(x) - \bar{\rho}(x)) \frac{\chi'(\bar{\rho}(x))}{\chi(\bar{\rho}(x))} \nabla_x \left(\frac{D(\bar{\rho}(x))}{\chi(\bar{\rho}(x))} (\rho(x) - \bar{\rho}(x)) \right) \end{aligned} \quad (\text{A.6})$$

Since $\rho(x) - \bar{\rho}(x)$ is arbitrary, we conclude that $\Gamma(\bar{\rho}; x, y)$ (which is symmetric with respect to the exchange of x and y) satisfies

$$\begin{aligned} (L_x(\bar{\rho}) + L_y(\bar{\rho}))\Gamma(\bar{\rho}; x, y) &= -(R_x(\bar{\rho}) + R_y(\bar{\rho}))\delta(x - y), \\ \Gamma(\bar{\rho}; x, y)|_{\partial(\Lambda \times \Lambda)} &= 0, \end{aligned} \quad (\text{A.7})$$

where $L(\bar{\rho})$ and $R(\bar{\rho})$ are the differential operators defined by

$$L(\bar{\rho})\psi = \frac{D(\bar{\rho})}{\chi(\bar{\rho})}\nabla(\chi(\bar{\rho})\nabla\psi), \quad R(\bar{\rho})\psi = \frac{D(\bar{\rho})}{\chi(\bar{\rho})}\nabla\left(\frac{\chi'(\bar{\rho})}{\chi(\bar{\rho})}\psi\right). \quad (\text{A.8})$$

Equation (A.7) is the desired equation for $\Gamma(\bar{\rho}; x, y)$.

Recall that, given $s \in [0, 1]$, the function $r(s) : \Lambda \rightarrow \mathbb{R}$ defined by (4.10), depending on the variable $x \in \Lambda$, is a functional of $\bar{\rho}(s) : \Lambda \rightarrow \mathbb{R}_+$, $\partial_s \bar{\rho}(s) : \Lambda \rightarrow \mathbb{R}$, and $\bar{J}(s) \in \mathbb{R}$. Namely, we should denote $r = r(\bar{\rho}, \dot{\bar{\rho}}, \bar{J}; x)$, and it is defined by the equation:

$$\nabla\left(\chi(\bar{\rho})\nabla\left(\frac{D(\bar{\rho})}{\chi(\bar{\rho})}r\right)\right) - \bar{J}\nabla\left(\frac{\chi'(\bar{\rho})}{\chi(\bar{\rho})}r\right) = \dot{\bar{\rho}}, \quad r(\pm 1) = 0. \quad (\text{A.9})$$

In the following we shall denote

$$r_0(\bar{\rho}, \dot{\bar{\rho}}; x) := r(\bar{\rho}, \dot{\bar{\rho}}, 0; x). \quad (\text{A.10})$$

We also introduce the new function

$$\gamma(\bar{\rho}, \dot{\bar{\rho}}; x) := \left. \frac{\partial r(\bar{\rho}, \dot{\bar{\rho}}, \bar{J}; x)}{\partial \bar{J}} \right|_{\bar{J}=0}. \quad (\text{A.11})$$

In order to prove (4.11) we need to find an equation for $\gamma(\bar{\rho}, \dot{\bar{\rho}}; x)$.

If we take the derivative of both sides of (A.9) with respect to \bar{J} and we let $\bar{J} = 0$, we get, after multiplying both sides by $\frac{D(\bar{\rho})}{\chi(\bar{\rho})}$,

$$L(\bar{\rho})\left(\frac{D(\bar{\rho})}{\chi(\bar{\rho})}\gamma(\bar{\rho}, \dot{\bar{\rho}})\right) = R(\bar{\rho})r_0(\bar{\rho}, \dot{\bar{\rho}}), \quad \gamma(\pm 1) = 0, \quad (\text{A.12})$$

where $L(\bar{\rho})$ and $R(\bar{\rho})$ are the differential operators (A.8). Equation (A.12) is the desired equation for γ .

A.2. Proof of (4.11)

By the definition (4.9) of the excess functional B and equations (A.1), (A.3), (A.10) and (A.11), we have

$$\begin{aligned} \left. \frac{\delta B(\bar{\rho}, \bar{J})}{\delta \bar{J}(s)} \right|_{\bar{J}=0} &= 2 \int_{\Lambda} dx \chi(\bar{\rho}(s, x)) \left(\nabla_x \left(\frac{D(\bar{\rho}(s, x))}{\chi(\bar{\rho}(s, x))} r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) \right) \right. \\ &\quad \left. \times \left(\int_{\Lambda} dy \nabla_x \Gamma(\bar{\rho}(s); x, y) r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); y) + \nabla_x \left(\frac{D(\bar{\rho}(s, x))}{\chi(\bar{\rho}(s, x))} \gamma(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) \right) \right) \right). \end{aligned} \quad (\text{A.13})$$

Integrating by parts and recalling the definition (A.8) of the differential operator $L(\bar{\rho})$, we can rewrite the right hand side of (A.13), divided by -2 , as

$$\int_{\Lambda} dx \int_{\Lambda} dy r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); y) L_x(\bar{\rho}) \Gamma(\bar{\rho}; x, y) + \int_{\Lambda} dx r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) L_x(\bar{\rho}) \left(\frac{D(\bar{\rho}(s, x))}{\chi(\rho(s, x))} \gamma(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) \right). \quad (\text{A.14})$$

Using equation (A.7), we get

$$\int_{\Lambda} dx \int_{\Lambda} dy r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); y) L_x(\bar{\rho}) \Gamma(\bar{\rho}; x, y) = - \int_{\Lambda} dx r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) R_x(\bar{\rho}) r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x). \quad (\text{A.15})$$

Moreover, using equation (A.12), we get

$$\int_{\Lambda} dx r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) L_x(\bar{\rho}) \left(\frac{D(\bar{\rho}(s, x))}{\chi(\rho(s, x))} \gamma(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) \right) = \int_{\Lambda} dx r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) R_x(\bar{\rho}) r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x). \quad (\text{A.16})$$

Combining (A.14)–(A.16), we get (4.11).

References

- [1] Aurell E, Gawedzki K, Mejía-Monasterio C, Mohayae R and Muratore-Ginanneschi P 2012 Refined second law of thermodynamics for fast random processes *J. Stat. Phys.* **147** 487–505
- [2] Bertini L, Gabrielli D, Jona-Lasinio G and Landim C 2012 Thermodynamic transformations of nonequilibrium states *J. Stat. Phys.* **149** 773–802
- [3] Bertini L, Gabrielli D, Jona-Lasinio G and Landim C 2013 Clausius inequality and optimality of quasistatic transformations for nonequilibrium stationary states *Phys. Rev. Lett.* **110** 020601
- [4] Bertini L, De Sole A, Gabrielli D, Jona-Lasinio G and Landim C 2015 Macroscopic fluctuation theory *Rev. Mod. Phys.* **87** 593–636
- [5] Callen H 1985 *Thermodynamics and an Introduction to Thermostatistics* 2nd edn (New York: Wiley)
- [6] Hatano T and Sasa S 2001 Steady-state thermodynamics of Langevin systems *Phys. Rev. Lett.* **86** 3463
- [7] Komatsu T and Nakagawa N 2008 Expression for the stationary distribution in nonequilibrium steady states *Phys. Rev. Lett.* **100** 030601
- [8] Komatsu T, Nakagawa N, Sasa S and Tasaki H 2011 Entropy and nonlinear nonequilibrium thermodynamic relation for heat conducting steady states *J. Stat. Phys.* **142** 127–53
- [9] Maes C and Netočný K 2014 A nonequilibrium extension of the Clausius heat theorem *J. Stat. Phys.* **154** 188–203
- [10] Mandal D and Jarzynski C 2015 Analysis of slow transitions between nonequilibrium steady states arXiv:1507.06269
- [11] Muratore-Ginanneschi P, Mejía-Monasterio C and Peliti L 2013 Heat release by controlled continuous-time Markov jump processes *J. Stat. Phys.* **150** 181–203
- [12] Oono Y and Paniconi M 1998 Steady state thermodynamics *Dynamic Organization of Fluctuations—Molecular Machines, Powder Flows and Fluid Turbulence—Proc. 12th Nishinomiya Yukawa Memorial Symp. (Progress of Theoretical Physics Supplements vol 130)* pp 29–44
- [13] Sivak D and Crooks G 2012 Thermodynamic metrics and optimal paths *Phys. Rev. Lett.* **108** 190602
- [14] Spohn H 1991 *Large Scale Dynamics of Interacting Particles* (Heidelberg: Springer)