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On the Equivalence and Optimality of Transformations of Diffusive Systems

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Abstract
In this paper we introduce, inspired by Clausius and developing the ideas of [11], the concept of equivalence of transformations in non equilibrium theory of diffusive systems within the framework of macroscopic fluctuation theory. Besides providing a new proof of a formula derived in [3, 4], which is the basis of the equivalence, we show that equivalent quasistatic transformations can be distinguished in finite terms, by the renormalized work introduced in [1–4]. This allows us to tackle the problem of determining the optimal quasistatic transformation among the equivalent ones.

Keywords Diffusive systems · Quasistatic transformations

1 Introduction

In previous papers [3, 4] we have shown that for diffusive systems one can introduce a notion of renormalized work by subtracting the energy necessary to keep the system out of equilibrium. This interprets in a natural way, within the Macroscopic Fluctuation Theory (MFT), the concept of *house–keeping heat* formulated in [14]. In this way we have for the renormalized work a non–equilibrium Clausius type inequality. To a certain extent our approach is complementary to those of Hatano-Sasa [10] and Maes-Netocny [12].

The existence of entropy in classical equilibrium thermodynamics implies that the integral $\int \frac{\delta Q}{T}$ does not depend on the particular reversible quasi-static transformation joining two fixed initial and final states. For example in the simple case of an ideal gas we have the exact 1-form

$$dS = \frac{\delta Q}{T} = C_p \frac{dT}{T} - nR\frac{dp}{p}\,. \tag{1.1}$$

In his ninth memoir Clausius summarizes the two principles of thermodynamics as follows

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The whole mechanical theory of heat rests on two fundamental theorems, - that of equivalence of heat and work, and that of equivalence of transformations.

In particular all reversible transformations between fixed equilibrium states are equivalent in the sense of Clausius. In processes with dissipation it is important to have an optimality criterium. This was introduced in [4] in terms of the renormalized work. Practically the type of transformation in a process with dissipation may be dictated by experimental possibilities, the problem is then to find among all equivalent transformations, the best one. A solvable example was discussed in [4].

Previously [11] we pointed out that in the Macroscopic Fluctuation Theory of diffusive systems a formula containing only finite quantities obtained in [3, 4] implies the existence of an exact 1-form also in a dissipative context. This in turn implies an equivalence relationship of quasi–static transformations, possibly very different energetically: this point was not discussed in our previous papers and here we extend the discussion in [11]. The equivalence in the sense of Clausius [7] can be extended to stationary non equilibrium states of diffusive systems.

It may be surprising an equivalence relation in dissipative irreversible transformations which may differ in a quasi static limit by an infinite amount of dissipated energy. As we will show in the following two equivalent transformations can be distinguished in finite terms by the renormalized work which depends, in an asymptotic region in time [4], on the protocols of the transformations.

In the present paper, after recalling some basic facts of the MFT, we provide a different proof of the non–equilibrium equivalence relation and discuss a result on optimality of a transformation obtained in [4]. We then illustrate various aspects of this non–equilibrium equivalence with the help of examples.

Various definitions of renormalized work have been introduced for example by [10, 12]. What is of interest for us in the present context is the case of MFT. A comparison between [10] and [12] is made in this last work. The difference between our definition of the the renormalized work and that of [12] has been discussed in our paper [2]. We emphasize later that a solvable example discussed in [4] is a case of selecting the optimal transformation between two equivalent ones. Of course in concrete cases it may be difficult to solve the related variational principle analytically and we have to resort to numerical schemes.

2 Macroscopic Dynamics

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 $\lambda(t, x)$, $x \in \partial\Lambda$ and under the action of an external field $E(t, x)$, $x \in \Lambda$.

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

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

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 assumed to be $d \times d$ symmetric and positive definite matrices. This holds in the context of stochastic lattice gases [3]. We will consider in this paper just the cases where D and χ are multiple of the identity matrix, so that D, χ can be considered as scalars. Equation (2.2) relies on the local equilibrium hypothesis, small local gradients and linear response to the external field. We also assume that the time dependence of the external fields and chemical potentials is on a scale which is long with respect to the relaxation time. Otherwise we may expect that the hydrodynamic equations do not describe correctly the physics of the system.

The evolution of the density is thus given by the driven diffusive equation

$$\partial_t \rho(t) + \nabla \cdot \big(\chi(\rho)E(t)\big) = \nabla \cdot \big(D(\rho)\nabla\rho\big). \tag{2.3}$$

The transport coefficients D and χ satisfy the local Einstein relation

$$D(\rho) = \chi(\rho)\, f''(\rho), \tag{2.4}$$

where f is the equilibrium free energy per unit volume which we assume to depend on the local value $\rho(x)$.

Equations (2.1)–(2.2) have to be supplemented by the appropriate boundary conditions on $\partial\Lambda$ due to the interaction with the external reservoirs. If $\lambda(t, x)$, $x \in \partial\Lambda$, is the chemical potential of the external reservoirs, the boundary condition reads

$$f'\big(\rho(t, x)\big) = \lambda(t, x), \qquad x \in \partial\Lambda. \tag{2.5}$$

We observe that given any density profile $\rho(x, t)$ and any current $j(x, t)$, then there exists an external field $E(x, t)$ such that $j = J(\rho)$, this is given indeed by

$$E(t) = \frac{j(t) - D(\rho(t))\nabla\rho(t)}{\chi(\rho(t))}\,. \tag{2.6}$$

This fact implies that any pair $(\rho(x, t), j(x, t))$ related by the continuity equation can be realized as possible space time trajectory of the system for suitable external fields.

2.1 Equilibrium and Non Equilibrium States

We now introduce some terminology for non–equilibrium states.

2.1.1 Dynamical States

We call a *dynamical state of the system*, in the time window $[0, T]$, any pair $(\rho(t), j(t))_{t\in[0,T]}$, connected by the continuity equation (2.1), so that in the non equilibrium situation the state of the system is rather a trajectory.

There is a natural one to one correspondence between the pair $(\rho(t), j(t))_{t\in[0,T]}$ and the triple $\Big((\lambda(t), E(t))_{t\in[0,T]}, \rho(0)\Big)$ where the third element is the initial condition for the density.

Given the pair $(\rho(t),\, j(t))_{t\in[0,T]}$, the initial condition $\rho(0)$ is given and we obtain the pair $(\lambda(t),\, E(t))_{t\in[0,T]}$ by the equations (2.5) (2.6). Conversely given $(\lambda(t),\, E(t))_{t\in[0.T]}$ and $\rho(0)$, we obtain $(\rho(t),\, j(t))_{t\in[0,T]}$ solving the hydrodynamic equation that is summarized as

$$\begin{cases} \partial_t \rho(t) = \nabla\cdot\big(D(\rho)\nabla\rho\big) - \nabla\cdot\big(\chi(\rho)E(t)\big)\,, & x\in\Lambda\,,\\ f'\big(\rho(t,x)\big) = \lambda(t,x)\,, & x\in\partial\Lambda\,,\\ j(x,t) = -D(\rho(x,t))\nabla\rho(x,t) + \chi(\rho(x,t))\,E(x,t)\,, & x\in\Lambda\,, \end{cases} \tag{2.7}$$

adding the initial condition $\rho(0)$.

2.1.2 Stationary States

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),(2.5). The stationary density profile $\bar\rho$ is characterized by the vanishing of the divergence of the associated current, $\nabla\cdot J(\bar\rho) = 0$

$$\begin{cases} \nabla\cdot J(\bar\rho) = \nabla\cdot\big(-D(\bar\rho)\nabla\bar\rho + \chi(\bar\rho)\,E\big) = 0,\\ f'(\bar\rho(x)) = \lambda(x), \qquad x\in\partial\Lambda. \end{cases} \tag{2.8}$$

We will assume that the stationary solution is unique. The stationary states furthermore split into *equilibrium stationary states* and *non equilibrium stationary states*. As we will explain, the equilibrium states are characterized by the condition $\bar J = J(\bar\rho) = 0$. The following arguments are a reformulation of those in [5].

We examine the correspondence between variables (λ, E) and the stationary solution $(\bar\rho, \bar J) = (\bar\rho_{\lambda,E}, \bar J_{\lambda,E})$. As in the dynamical case, we have a one to one correspondence, that we now examine in some detail. Given a pair (λ, E) the (assumed) unique corresponding pair $(\bar\rho, \bar J)$ is obtained solving (2.8). Conversely, given a pair $(\bar\rho, \bar J)$ such that $\nabla\cdot\bar J = 0$, the values of the chemical potential at the boundary are obtained by the second relation in (2.8), while the external field E is obtained by a stationary version of equation (2.6)

$$E = \frac{\bar J - D(\bar\rho)\nabla\bar\rho}{\chi(\bar\rho)}\,. \tag{2.9}$$

In particular if we fix only the density stationary profile $\bar\rho$ we may have several corresponding variables (λ, E). A special situation is when the current itself vanishes, $J(\bar\rho) = 0$; if this is the case, which means that the boundary conditions and the external field balance each other, we say that the system is in a macroscopic equilibrium state; this can be viewed as a macroscopic counterpart to detailed balance [5].

We may have both homogeneous and non homogeneous equilibrium states. The homogeneous equilibrium states correspond to the case in which the external field vanishes and the chemical potential is constant in space, in this case also the stationary solution $\bar\rho$ is constant in space. We may have more general equilibrium states that are the inhomogeneous equilibrium states and 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 $U(x) = \lambda(x)$, $x\in\partial\Lambda$. We emphasize that if this second condition is not satisfied, the state is non equilibrium and the current $\bar J$ is not zero, even if the external field is of gradient type. This follows by the following argument.

We have an equilibrium state, in any dimension, when the stationary condition $\nabla\cdot J(\bar\rho) = 0$ is satisfied with $J(\bar\rho) = 0$. Using the form of the current given by the constitutive equation

(2.2), this corresponds to the condition

$$-D(\bar{\rho})\nabla\bar{\rho} + \chi(\bar{\rho})E = 0\,, \tag{2.10}$$

that by the local Einstein relation becomes

$$E = \chi^{-1}(\bar{\rho})D(\bar{\rho})\nabla\bar{\rho} = f''(\bar{\rho})\nabla\bar{\rho} = \nabla f'(\bar{\rho})\,. \tag{2.11}$$

This means that for equilibrium states the external field E has to be of gradient type $E = \nabla U$ and in particular we have that $U(x) = f'(\bar{\rho}(x)) + c$ for a constant c. By the boundary conditions that have to be satisfied in all cases, $f'(\bar{\rho}(x)) = \lambda(x)$ $x \in \partial\Lambda$, we have that $U(x) = \lambda(x) + c$ when $x \in \partial\Lambda$ and c is a suitable constant.

Conversely if we have $E(x) = \nabla U(x)$, the equation that characterizes the equilibrium states $J(\bar{\rho}) = 0$ becomes

$$-D(\bar{\rho}(x))\nabla\bar{\rho}(x) + \chi(\bar{\rho}(x))E(x) = 0\,, \qquad x \in \Lambda\,, \tag{2.12}$$

that, by the Einstein relation is equivalent to $\nabla U(x) = \nabla f'(\bar{\rho}(x))$ whose general solution is $f'(\bar{\rho}(x)) = U(x) + K$ for an arbitrary constant K. Imposing the boundary condition we obtain $\lambda(x) = U(x) + K$, $x \in \partial\Lambda$. When this is satisfied, for a given constant K^*, then the stationary density is given by $\bar{\rho}(x) = (f')^{-1}(U(x) + K^*)$. If instead there is not such a constant K^* then it is not possible to find a $\bar{\rho}$ satisfying (2.12) and the boundary conditions. This implies that the stationary current $\bar{J} \neq 0$ and the stationary state is a non equilibrium one.

If we fix the stationary density profile $\bar{\rho}$ and search for all the possible external fields that produce such a stationary profile, this class can be written as

$$E(x) = \nabla f'(\bar{\rho}(x)) + \chi^{-1}(\bar{\rho}(x))G(x) = E^*(x) + \chi^{-1}(\bar{\rho}(x))G(x)\,, \tag{2.13}$$

where $E^*(x)$ is defined by the last equality and G is an arbitrary divergence free field. Among all such external fields the only one for which (λ, E) is an equilibrium state is the one that corresponds to $G = 0$.

The stationary equation $\nabla \cdot J = 0$ with the associated boundary conditions play a role akin to the equation of state in equilibrium thermodynamics.

3 Transformations and Energy Balance

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

$$W_{[0,T]} = \int_0^T dt \left\{ \int_\Lambda dx\; j(t)\cdot E(t) - \int_{\partial\Lambda} d\sigma\; \lambda(t)\; j(t)\cdot\widehat{n} \right\}, \tag{3.1}$$

where $\widehat{n}$ 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 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

$$W_{[0,T]} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_\Lambda dx\ j(t) \cdot \chi(\rho(t))^{-1} j(t), \tag{3.2}$$

where F is the free energy functional of equilibrium thermodynamics,

$$F(\rho) = \int_\Lambda dx\ f(\rho(x)). \tag{3.3}$$

We emphasize that the functional $F(\rho)$ can be evaluated on any profile $\rho(x)$ and does not depend on the current. In particular can be evaluated on the stationary states $\bar{\rho}$ and the result is independent of the stationary current $\bar{J}$. The step from (3.1) to (3.2) uses the constitutive equation (2.2) and the Einstein relationship (2.4). It tells us that for the class of systems considered the change of the free energy ΔF is, as expected, the difference between the total work and the total dissipation. Notice that if the system is out of equilibrium for an infinite time both these quantities are infinite. The currents $j(t)$ must be evaluated on the solutions of the hydrodynamic equations.

From (3.2) follows the Clausius inequality

$$W_{[0,T]} \geq F(\rho(T)) - F(\rho(0)) \tag{3.4}$$

For quasi-static transformations between nonequilibrium stationary states, the Clausius inequality does not carry any significant information as discussed for example in [4].

3.1 Quasistatic Transformations

To analyze transformations over a long interval $[0, \tau]$ driven by slowly changing boundary conditions and external fields, it is convenient to rescale time and introduce the rescaled variable $s = t/\tau$. The *protocol* of a transformation is defined therefore 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 driving terms are assumed to be C^1 in the parameter $s \in [0, 1]$ and to satisfy the conditions

$$\begin{cases} \dot{E}(0) = \dot{E}(1) = 0\,, \\ \dot{\lambda}(0) = \dot{\lambda}(1) = 0\,. \end{cases} \tag{3.5}$$

This is a natural condition imagining that the drivings before and after the transformation are time independent.

A real transformation that takes place in the time window $[0, \tau]$ is the solution $(\rho^\tau(x,t), j^\tau(x,t))_{x\in\Lambda, t\in[0,\tau]}$ of the hydrodynamic equation

$$\begin{cases} \partial_t \rho^\tau(t) = \nabla \cdot \big(D(\rho^\tau)\nabla\rho^\tau\big) - \nabla \cdot \big(\chi(\rho^\tau)E^\tau(t)\big) & x \in \Lambda\,,\ t \in [0,\tau] \\ f'\big(\rho^\tau(t,x)\big) = \lambda^\tau(t,x), & x \in \partial\Lambda\,,\ t \in [0,\tau] \\ j^\tau(x,t) = -D(\rho^\tau(x,t))\nabla\rho^\tau(x,t) + \chi(\rho^\tau(x,t))\,E^\tau(x,t) & x \in \Lambda\,,\ t \in [0,\tau]\,, \end{cases} \tag{3.6}$$

where the external drivings $(E^\tau(x,t), \lambda^\tau(x,t))_{x\in\Lambda, t\in[0,\tau]}$ are defined by $E^\tau(x,t) := E(x, t/\tau)$, $\lambda^\tau(x,t) := \lambda(x, t/\tau)$.

Our analysis is based in the following asymptotic expansion for large τ

$$\begin{aligned} \rho^\tau(\tau s) &= \bar{\rho}(s) + \tfrac{1}{\tau}\, r(s) + o\big(\tfrac{1}{\tau}\big)\,, \\ j^\tau(\tau s) &= J(s, \bar{\rho}(s)) + \tfrac{1}{\tau}\, g(s) + o\big(\tfrac{1}{\tau}\big)\,, \end{aligned} \tag{3.7}$$

that is physically reasonable and in some cases can be verified to hold. .

It is easy to see that r, g obey the following equations

$$\begin{cases} \partial_s \bar{\rho}(s) + \nabla \cdot g(s) = 0 \\ g(s) = -\nabla\Big(D(\bar{\rho}(s))r(s)\Big) + r(s)\chi'(\bar{\rho}(s))E(s) \\ r(s,x) = 0, \ x \in \partial\Lambda \\ r(x,0) = r(x,1) = 0\,, \ x \in \Lambda\,, \end{cases} \tag{3.8}$$

which implies that r, g depend linearly on $\partial_s \bar{\rho}$ and are actually proportional to it. The equations on the last line follows by the conditions (3.5)

We now consider the identity (3.2), using also the definition (3.1), for the transformation $(\rho^\tau(x,t),\, j^\tau(x,t))_{x\in\Lambda, t\in[0,\tau]}$ and perform an expansion on the small parameter $1/\tau$ on both sides. We have equality among all the coefficients of the expansions on the two sides. The first non trivial relation, that corresponds to the zero order in $1/\tau$ is given by

$$\begin{aligned} F\big(\bar{\rho}(1)\big) - F\big(\bar{\rho}(0)\big) \ &= \int_0^1 ds \int_\Lambda dx\, E(s)\cdot g(s) - \int_0^1 ds \int_{\partial\Lambda} d\sigma\, \lambda(s) g(s)\cdot \widehat{n} \\ &+ \int_0^1 ds \int_\Lambda dx\, r(s) J(s,\bar{\rho}(s))\cdot (\chi^{-1})'\big(\bar{\rho}(s)\big) J(s,\bar{\rho}(s))\,. \end{aligned} \tag{3.9}$$

Equation (3.9) establishes a mathematical equivalence of quasi–static transformations for a class of dissipative systems. These transformations can be energetically very different as the energy necessary to keep the system out of equilibrium per unit of time can differ considerably. This relation gives the variation of equilibrium free energy in terms of an integration on quasistatic transformations with suitable variations (r, g) of density and current, the result is independent of the specific transformation. The first two terms of this formula represent a linearization of the total work along the transformation, while the third one is due to the variation of the mobility which in general will be a nonlinear function of the density. There is no corresponding term for the diffusion coefficient D since on the scale τ the relaxation of the system is instantaneous [4].

For a detailed derivation using a slow limit and an expansion we refer to [3, 4]. Here we give a direct proof.

Proof of equation (3.5) The left hand side of (3.9) can be written as $\int_0^1 ds \int_\Lambda dx \frac{\delta F}{\delta\bar{\rho}(s)} \partial_s \bar{\rho}(s) = \int_0^1 ds \int_\Lambda dx f'(\bar{\rho}(s)) \partial_s \bar{\rho}(s)$. To prove equality (3.9) it is enough therefore to verify

$$\begin{aligned} \int_\Lambda dx f'(\bar{\rho}(s))\partial_s\bar{\rho}(s) &= \int_\Lambda dx\, E(s)\cdot g(s) - \int_{\partial\Lambda} d\sigma\, \lambda(s) g(s)\cdot\widehat{n} \\ &+ \int_\Lambda dx\, r(s) J(s,\bar{\rho}(s))\cdot(\chi^{-1})'\big(\bar{\rho}(s)\big) J(s,\bar{\rho}(s))\,. \end{aligned}$$

Using the first equation in (3.8) an integration by parts and the boundary conditions of the hydrodynamics we get that the left hand side of the above equation is given by

$$-\int_{\partial\Lambda} d\sigma\, \lambda(s) g(s)\cdot\widehat{n} + \int_\Lambda dx f''(\bar{\rho}(s)) g\cdot\nabla\bar{\rho}(s)\,.$$

It remains therefore to show

$$\int_\Lambda dx \left[f''(\bar{\rho}(s))\nabla\bar{\rho}(s) - E\right]\cdot g = -\int_\Lambda dx\, r(s) J(s,\bar{\rho}(s))\cdot \frac{\chi'(\bar{\rho}(s))}{\chi^2(\bar{\rho}(s))} J(s,\bar{\rho}(s))\,.$$

We can now elaborate the left hand side as follows

$$\int_\Lambda dx \left[f''(\bar\rho(s))\nabla\bar\rho(s) - E\right]\cdot g = -\int_\Lambda dx \frac{J(\bar\rho(s))}{\chi(\bar\rho(s))}\cdot g$$
$$= \int_\Lambda dx \frac{J(\bar\rho(s))}{\chi(\bar\rho(s))}\cdot\Big(\nabla(D(\bar\rho(s))r(s)) - r(s)\chi'(\bar\rho(s))E(s)\Big)$$
$$= \int_\Lambda dx\Big[D(\bar\rho(s))r(s)\frac{\chi'(\bar\rho(s))\nabla\bar\rho(s)}{\chi^2(\bar\rho(s))}\cdot J(\bar\rho(s)) - r(s)\frac{\chi'(\bar\rho(s))E(s)}{\chi(\bar\rho(s))}\cdot J(\bar\rho(s))\Big]$$
$$= -\int_\Lambda dx\, r(s)J(s,\bar\rho(s))\cdot\frac{\chi'(\bar\rho(s))}{\chi^2(\bar\rho(s))}J(s,\bar\rho(s))\,.$$

In the first equality we used the Einstein relation, in the second equality the definition of g, in the third equality we did an integration by parts, used the fact that $r|_{\partial\Lambda} = 0$ and the fact that $\nabla\cdot J(\bar\rho(s)) = 0$, and finally in the last equality we used just the definition of $J(\bar\rho(s))$. This finishes the proof. □

We observe that equations (3.8) are invariant under the following time reversal transformations

$$\begin{cases}\bar\rho(s)\to\bar\rho(1-s)\\ r(s)\to -r(1-s)\\ g(s)\to -g(1-s)\end{cases} \tag{3.10}$$

and moreover the right hand side of formula (3.9) changes sign under the above transformations. This is an indication of the reversibility of quasistatic transformations.

3.2 States and free energy

A transformation corresponds to a path γ in the infinite dimensional space of the variables (E,λ) that completely identify the state. We recall that since $\bar\rho$ depends of the external drivings (E,λ), we have that $J(\bar\rho)$ and $F(\bar\rho)$ are functions of the variables (E,λ). With a small abuse of notation we call again $F(\lambda,E) := F(\bar\rho_{E,\lambda})$, the current and free energy written in terms of the external drivings (λ,E).

Given a curve γ on the space of states such that $(\lambda(0),E(0)) = \gamma(0)$ and $(\lambda(1),E(1)) = \gamma(1)$ we obtain a line integral of an exact 1–form

$$F(E(1),\lambda(1)) - F(E(0),\lambda(0)) = \int_\gamma \frac{\delta F}{\delta E}dE + \frac{\delta F}{\delta\lambda}d\lambda\,. \tag{3.11}$$

This formula corresponds to an integral version of the differential of the free energy F written as

$$dF = \int_\Lambda dx\frac{\delta F}{\delta E}(x)\delta E(x) + \int_{\partial\Lambda} d\sigma(x)\frac{\delta F}{\delta\lambda}(x)\delta\lambda(x)\,. \tag{3.12}$$

3.3 The Renormalized Work

3.3.1 Decomposition of the Current

In the framework of macroscopic fluctuation theory it is possible to define a thermodynamic functional V, called the quasi-potential, and coinciding with a large deviations rate functional of the stationary measure. It can be characterized as the maximal positive solution, vanishing

when $\rho = \bar\rho$, of the infinite dimensional Hamilton-Jacobi equation,

$$\int_\Lambda dx\, \nabla \frac{\delta V}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta V}{\delta \rho} - \int_\Lambda dx\, \frac{\delta V}{\delta \rho} \nabla \cdot J(\rho) = 0\,. \tag{3.13}$$

Using V it is possible to define the *symmetric current* J_S by

$$J_S(\rho) = -\chi(\rho) \nabla \frac{\delta V}{\delta \rho}. \tag{3.14}$$

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,

$$J_S(\bar\rho) \;=\; 0. \tag{3.15}$$

We rewrite the hydrodynamic current as

$$J(\rho) = J_S(\rho) + J_A(\rho), \tag{3.16}$$

which defines the *antisymmetric current* J_A.

In view of these definitions, the Hamilton Jacobi equation (3.13) becomes

$$\int_\Lambda dx\, J_S(\rho) \cdot \chi(\rho)^{-1} J_A(\rho) = 0\,, \tag{3.17}$$

that is an orthogonality condition with respect to the metric χ^{-1}.

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

$$V_{\lambda,E}(\rho) = \int_\Lambda dx \big(f(\rho) - f(\bar\rho) - f'(\bar\rho)(\rho - \bar\rho) \big)\,, \tag{3.18}$$

where $\bar\rho = \bar\rho_{\lambda,E}$ is the solution of (2.8).

3.3.2 Renormalized Work

In the case of a non equilibrium stationary state, we define a renormalized work subtracting the energy needed to maintain the system out of equilibrium. For time independent drivings, by the orthogonal decomposition (3.16) and (3.15), $J(\bar\rho) = J_{\rm A}(\bar\rho)$ is the macroscopic current in the stationary state. In view of the general formula for the total work (3.2), the amount of energy per unit time needed to maintain the system in the stationary profile $\bar\rho$ is

$$\int_\Lambda dx\, J_{\rm A}(\bar\rho) \cdot \chi(\bar\rho)^{-1} J_{\rm A}(\bar\rho). \tag{3.19}$$

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 $W^{\rm ren}_{[0,T]}$ done by the reservoirs and the external field in the time interval $[0, T]$ as

$$W^{\rm ren}_{[0,T]} = W_{[0,T]} - \int_0^T dt \int_\Lambda dx\, J_{\rm A}(t, \rho(t)) \cdot \chi(\rho(t))^{-1} J_{\rm A}(t, \rho(t)) \tag{3.20}$$

where $J_{\rm A}(t, \rho)$ 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 $J_{\rm A}(t)$ 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 (3.20) is natural within the macroscopic fluctuation theory and leads to a Clausius inequality. Indeed, in view of (3.2) and the orthogonality in (3.17) between the symmetric and the antisymmetric part of the current,

$$W^{\rm ren}_{[0,T]} = F(\rho(T)) - F(\rho_0) + \int_0^T dt \int_\Lambda dx\, J_{\rm S}(t,\rho(t)) \cdot \chi(\rho(t))^{-1} J_{\rm S}(t,\rho(t)) \\ \geq F(\rho(T)) - F(\rho_0)\,. \tag{3.21}$$

In the limit of slow transformations, the expansion in $1/\tau$ of the renormalized work is [3, 4]

$$W^{\rm ren}_{[0,\tau]} = \left[F(\rho^\tau(\tau)) - F(\rho^\tau(0))\right] + \frac{1}{\tau}\, B + O\left(\tfrac{1}{\tau^2}\right), \tag{3.22}$$

where the *excess* functional B is:

$$B = \int_0^1 ds \int_\Lambda dx\, \nabla\left(C_s^{-1} r(s)\right) \cdot \chi(\bar\rho(s)) \nabla\left(C_s^{-1} r(s)\right). \tag{3.23}$$

where $C_s^{-1}(x,y)$ is the inverse of the covariance in the stationary state associated to the external drivings $(\lambda(s), E(s))$.

By developing further for large τ

$$F(\bar\rho(1)) - F(\bar\rho(0)) + \frac{1}{\tau}[\partial_{\bar\rho(1)} F(\bar\rho(1)) r(\bar\rho(1)) - \partial_{\bar\rho(0)} F(\bar\rho(0)) r(\bar\rho(0))] + \frac{1}{\tau}\, B \tag{3.24}$$

taking into account that r depends linearly on $\partial_s \bar\rho$ and that the initial and final states are stationary, by (3.5), only the $\frac{1}{\tau}\, B$ survives which depends on the protocols and allows to distinguish equivalent transformations.

In [3, 4] we considered two cases of optimal transformations, one through homogeneous equilibrium states and the other through inhomogeneous equilibrium states. These transformations are clearly equivalent according to the definition of the present paper and are sharply distinguished by the value of B.

In [2] we have shown that in the limit of a quasi–static transformation we have $W^{\rm ren} = \Delta F$ where ΔF is the difference between the equilibrium free energies evaluated in the final and initial states of the transformation. From (3.11) we obtain for large τ the representations of the renormalized work

$$W^{ren} = \int_\gamma \frac{\delta F}{\delta E} dE + \frac{\delta F}{\delta \lambda} d\lambda\,. \tag{3.25}$$

4 Examples

To illustrate the different terms appearing in the above formula (3.9) we now concentrate on one dimensional examples with constant external field where everything can be made more explicit. Consider a one dimensional interval $\Lambda = [0, L]$. In this case we have that F is a functional depending on the two boundary values of the chemical potential λ_0 and λ_L and of the constant value of the external field E; there is also a dependence on the size L of the system that we do not write explicitly. Without loss of generality we assume $\lambda_0 \leq \lambda_L$. In formula (3.12) we have therefore to compute the derivatives $\frac{\partial F}{\partial E}$, $\frac{\partial F}{\partial \lambda_0}$ and $\frac{\partial F}{\partial \lambda_L}$ and formula (3.12) reads simply as

$$dF = \frac{\partial F}{\partial E} dE + \frac{\partial F}{\partial \lambda_0} d\lambda_0 + \frac{\partial F}{\partial \lambda_L} d\lambda_L\,. \tag{4.1}$$

The stationary condition (2.8) can be written as

$$\begin{cases} D(\bar{\rho})\partial_x \bar{\rho} = E\chi(\bar{\rho}) - c\,, \\ f'(\bar{\rho}(0)) = \lambda_0\,,\ f'(\bar{\rho}(L)) = \lambda_L \end{cases} \tag{4.2}$$

where c is a constant to be determined by the boundary conditions. Calling $\rho_0 := (f')^{-1}(\lambda_0)$ and $\rho_L := (f')^{-1}(\lambda_L)$ the constant c is determined by integrating both sides of the first equation in (4.2) obtaining

$$\int_{\rho_0}^{\rho_L} \frac{D(\rho)d\rho}{E\chi(\rho) - c} = L\,. \tag{4.3}$$

The constant c has the natural interpretation as the current observed in the stationary state, that by the constitutive equation (2.2) is $J(\bar{\rho}(x)) = c$, which we emphasize does not depend on x. If we define

$$G = G_{c,E,\rho_0}(\rho) := \int_{\rho_0}^{\rho} \frac{D(a)da}{E\chi(a) - c}\, d\,a\,, \tag{4.4}$$

condition (4.3) reads $G(\rho_L) = L$. Integrating by separation of variables the stationary condition (4.2), we get

$$\int_{\rho_0}^{\bar{\rho}(x)} \frac{D(\rho)d\rho}{E\chi(\rho) - c} = x \tag{4.5}$$

that is equivalent to $\bar{\rho}(x) = G^{-1}(x)$ and we deduce

$$F = \int_0^L f\Big(G^{-1}_{c,E,\rho_0}(x)\Big)dx\,, \tag{4.6}$$

where we recall that $c = c(E, \lambda)$ is determined by (4.3). This is a formula that can give explicitly the dependence of F on the different parameters.

4.1 Equilibrium States

Formula (4.6) can be made more explicit in the case of equilibrium states.

We consider first the homogeneous equilibrium states that correspond to the situation $\lambda_0 = \lambda_L = \lambda$ and $E = 0$. In this case the stationary profile is constant and given by $\bar{\rho} = \left(f'\right)^{-1}(\lambda)$. It is natural to define $\widehat{f} := f \circ \left(f'\right)^{-1}$ that is the density of free energy written in term of the chemical potential. The equilibrium free energy in the homogeneous case is therefore

$$F_{eq}(\lambda, \lambda) := F(0, \lambda, \lambda) = \int_0^L \widehat{f}(\lambda)dx = L\widehat{f}(\lambda)\,. \tag{4.7}$$

4.1.1 Inhomogeneous Equilibrium States

In the non homogeneous case, the equilibrium situation corresponds to the value $c = 0$ in (4.3). Using the Einstein relation in this case such condition becomes

$$\frac{1}{E}\int_{\rho_0}^{\rho_L} f'(\rho)d\rho = L$$

that fixes the value of the external field to $E_{eq} = E_{eq}(\lambda_0, \lambda_L) := \frac{\lambda_L - \lambda_0}{L}$. If we define $\bar{\lambda}(x) = f'(\bar{\rho}(x))$ we obtain by (4.5) $\bar{\lambda}(x) = \lambda_0 + \frac{x}{L}(\lambda_L - \lambda_0)$. By a change of variable we

obtain that the equilibrium free energy is given by

$$F_{eq}(\lambda_0,\lambda_L) := F(E_{eq},\lambda_0,\lambda_L) = \frac{L}{\lambda_L-\lambda_0}\int_{\lambda_0}^{\lambda_L}\widehat{f}(\lambda)d\lambda = \frac{L\left[\widehat{\mathcal{F}}(\lambda_L)-\widehat{\mathcal{F}}(\lambda_0)\right]}{\lambda_L-\lambda_0}\,, \quad (4.8)$$

where $\widehat{\mathcal{F}}(\lambda) = \int \widehat{f}(\lambda)d\lambda$.

Since the external field $E_{eq} = E_{eq}(\lambda_0,\lambda_L)$ is determined by the boundary values of the chemical potentials, in this case the differential (4.1) becomes

$$dF_{eq} = \frac{\partial F_{eq}}{\partial\lambda_0}d\lambda_0 + \frac{\partial F_{eq}}{\partial\lambda_L}d\lambda_L \quad (4.9)$$

and we have

$$\begin{cases} \frac{\partial F_{eq}}{\partial\lambda_0} = \frac{L\left[\widehat{\mathcal{F}}(\lambda_L)-\widehat{\mathcal{F}}(\lambda_0)-\widehat{f}(\lambda_0)(\lambda_L-\lambda_0)\right]}{(\lambda_L-\lambda_0)^2}\,, \\ \frac{\partial F_{eq}}{\partial\lambda_L} = \frac{L\left[\widehat{\mathcal{F}}(\lambda_0)-\widehat{\mathcal{F}}(\lambda_L)-\widehat{f}(\lambda_L)(\lambda_0-\lambda_L)\right]}{(\lambda_0-\lambda_L)^2}\,. \end{cases} \quad (4.10)$$

In the case of independent particles we have $f(x) = x\log x - x$ and by a direct computation we obtain $\widehat{\mathcal{F}}(x) = e^x(x-2)$ while in the case of exclusion process we have $f(x) = x\log x + (1-x)\log(1-x)$ and again by a direct computation we have $\widehat{\mathcal{F}}(x) = \mathrm{Li}_2(-e^x)+\log(e^x+1)$; where $\mathrm{Li}_2(z)$ is the polylogarithm of order 2 defined by $\mathrm{Li}_s(y) := \sum_{k=1}^{+\infty}\frac{y^k}{k^s}$.

We can also consider equilibrium states on which the external field is not constant and in dimension greater than one. This situation corresponds to the case when the external field $E(x) = \nabla U(x)$ with U a function such that $U(x) = \lambda(x)$ for $x \in \partial\Lambda$. In this case we have also that $\bar{\rho}(x) = \widehat{f}(U(x))$.

To have an equilibrium state of this type in the pair (E,λ) the external field and the chemical potential must be related one with the other and the equilibrium state can be parameterized naturally by the function U considering $F_{eq}(E,\lambda) = F_{eq}(U)$. We have

$$F_{eq}(U) = \int_\Lambda \widehat{f}(U(x))\,dx\,, \quad (4.11)$$

and therefore we get

$$dF_{eq} = \int_\Lambda \frac{\delta F_{eq}(U)}{\delta U(x)}\delta U(x)dx = \int_\Lambda \widehat{f}'(U(x))\delta U(x)dx\,. \quad (4.12)$$

4.2 Independent Particles

In the case of independent particles we have that $D(\rho) = 1$, $\chi(\rho) = \rho$ and $f(\rho) = \rho\log\rho - \rho$ and we discuss the general case considering also non equilibrium situations. We can then compute

$$G_{c,E}(\rho) = \frac{1}{E}\log\frac{|E\rho - c|}{|E\rho_0 - c|}\,, \quad (4.13)$$

from which we get that the constant c is given by

$$\widehat{J}(\lambda,\rho) = c = \frac{E(e^{\lambda_L} - e^{\lambda_0+EL})}{1-e^{EL}}\,. \quad (4.14)$$

From formula (4.5) we obtain

$$\bar{\rho}(x) = e^{\lambda_0+Ex} + \frac{e^{\lambda_L} - e^{\lambda_0+EL}}{1-e^{EL}}\left(1-e^{Ex}\right)\,, \quad (4.15)$$

that can be written as

$$\begin{cases} \bar{\rho}(x) = ae^{Ex} + b \\ a = \frac{e^{\lambda_0} - e^{\lambda_L}}{1 - e^{EL}}, \\ b = \frac{e^{\lambda_L} - e^{\lambda_0 + EL}}{1 - e^{EL}}. \end{cases} \tag{4.16}$$

We deduce therefore, with a change of variables, the form of the free energy

$$F(E, \lambda) = \int_1^{e^{EL}} dy \frac{(ay + b)(\log(ay + b) - 1)}{Ey}. \tag{4.17}$$

A more explicit form can be obtained using the fact that the primitive of the function appearing in the integral (4.17) is

$$\mathcal{G}_{a,b}(y) := \frac{\ln(ay + b)\left(b \ln\left(\frac{|a||y|}{|b|}\right) + ay + b\right) - b \ln(|y|) + b \operatorname{Li}_2\left(\frac{ay+b}{b}\right) - 2ay}{E}. \tag{4.18}$$

We have then

$$F(E, \lambda) = \mathcal{G}_{a,b}(e^{EL}) - \mathcal{G}_{a,b}(1), \tag{4.19}$$

where the constant a, b are defined in (4.16).

4.2.1 Formula (3.9) for $D = 1$ and $E = 0$

In this case we perform the computations solving equations (3.8). The Einstein relation gives $f'' = \chi^{-1}$, and the stationary solution is linear $\bar{\rho}_s(x) = \rho_0(s) + \frac{x}{L}(\rho_L(s) - \rho_0(s))$. The equation for r is given by

$$\begin{cases} \partial_s \bar{\rho}_s = \partial_x^2 r \\ r(s, 0) = r(s, L) = 0 \end{cases} \tag{4.20}$$

Since the left hand side of the first equation above is a first order polynomial in x then the solution is a third order polynomial in x

$$r(s, x) = R_3(s)x^3 + R_2(s)x^2 + R_1(s)x + R_0(s) \tag{4.21}$$

and by a direct inspection of the constraints we get

$$\begin{cases} R_3(s) = \frac{\dot{\rho}_L(s) - \dot{\rho}_0(s)}{6L} \\ R_2(s) = \frac{\dot{\rho}_0(s)}{2} \\ R_1(s) = -L\frac{\dot{\rho}_L(s) + 2\dot{\rho}_0(s)}{6} \\ R_0(s) = 0, \end{cases} \tag{4.22}$$

By using the arguments in section (4) we can obtain the form of the free energy in this case that is

$$F(\rho) = F(\rho_0, \rho_L) = \int_0^L f\left(\mathcal{D}^{-1}\left(\mathcal{D}(\rho_0) + \frac{\mathcal{D}(\rho_L) - \mathcal{D}(\rho_0)}{L}x\right)\right) dx, \tag{4.23}$$

where $\mathcal{D}(\alpha) := \int_0^\alpha D(y)dy$. In the case of a model with a constant diffusion, like independent particles or the exclusion process, formula (4.23) becomes

$$F(\rho) = F(\rho_0, \rho_L) = \int_0^L f\left(\rho_0 + \frac{\rho_L - \rho_0}{L}x\right) dx, \tag{4.24}$$

with $f(\alpha) = \alpha \log \alpha$ for independent particles and $f(\alpha) = \alpha \log \alpha + (1-\alpha)\log(1-\alpha)$ for the exclusion process.

In this case the identity (3.9) for quasistatic transformations can be verified with a direct computation of all the terms.

5 Concluding Remarks

In this paper we discussed the generalization of Clausius statement on the equivalence of quasi static transformations between two fixed initial and final equilibrium states to the stationary states of a class of dissipative systems, the diffusive systems, using a formula previously derived in [3, 4]. In this way the difference of equilibrium free energy F becomes an invariant under variations of the protocols in quasistatic transformations. We give here a direct proof.

Equivalent transformations can be distinguished in terms of the $1/\tau$ correction to the renormalized work introduced in [1–4], which confirms the reasonableness of our definitions.

It may be interesting to investigate if there is any connection with recent works, [6, 13, 15, 16] and references therein, who consider entropy as a Noether invariant.

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Declarations

Conflicts of interest The authors have no conflicts of interest. Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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