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Macroscopic Fluctuation Theory 2: thermodynamic transformations

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Abstract

Thermodynamic transformations We consider the transformations of a macroscopic system from a stationary state to another state induced by varying parameters like boundary chemical potentials and/or external fields. We analyse the energy balance and observe that the work done on a system over an infinitely long time is infinite due to the energy spent to keep it out of equilibrium. Therefore the work has to be renormalized. In the macroscopic fluctuation theory this is done naturally by using the splitting of the current introduced in the previous lecture. A Clausius type inequality holds for the renormalized work. We then discuss transformations over a long but finite interval of time and expand in powers of the inverse of time. New relationships connecting the variation of the free energy to hydrodynamics are obtained. We finally discuss optimization problems concerning the protocols of a transformation in view of a minimal dissipation of energy.

Energy balance

Fix $T > 0$, a density profile $\rho(x)$, an external field $E(t, x)$ and a chemical potential $\lambda(t, x)$, $0 \leq t \leq T$. Let $\rho(t, x)$ the solution of hydrodynamics with initial condition $\rho(x)$ and $j(t, x)$ the corresponding current. The total energy involved in the process is

$$W_{[0,T]} = \int_0^T dt \left\{ - \int_{\partial\Lambda} d\sigma(x) \lambda(t, x) j(t, x) \cdot \hat{n}(x) + \int_{\Lambda} dx j(t, x) \cdot E(t, x) \right\}, \quad (1)$$

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. When $T = \infty$, we denote $W_{[0,T]}$ by W .

Using the Einstein relation and the divergence theorem $W_{[0,T]}$ can be written

$$W_{[0,T]} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_{\Lambda} dx j(t) \cdot \chi(\rho(t))^{-1} j(t) \quad (2)$$

where

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

From this equation the inequality follows

$$W_{[0,T]} \geq F(\rho(T)) - F(\rho(0)) \quad (3)$$

which is the second law here derived dynamically.

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 hydrodynamics with initial condition ρ_0 . Since $f'(\rho(t)) = \lambda(t)$ at the boundary, an application of the divergence theorem shows that (1) is equal to

$$\int_0^T dt \int_{\Lambda} dx \{ j(t) \cdot E(t) - \nabla \cdot [f'(\rho(t)) j(t)] \}.$$

Since $\nabla \cdot [f'(\rho(t)) j(t)] = f'(\rho(t)) \nabla \cdot j(t) - f''(\rho(t)) \nabla \rho(t) \cdot j(t)$, since by the continuity equation $-\nabla \cdot j(t) = \partial_t \rho$, and since by the Einstein relation $f''(\rho) = \chi(\rho)^{-1} D(\rho)$, the previous expression is equal to

$$\begin{aligned} & \int_0^T dt \frac{d}{dt} \int_{\Lambda} dx f(\rho(t)) \\ & + \int_0^T dt \int_{\Lambda} dx j(t) \cdot \chi(\rho(t))^{-1} j(t), \end{aligned}$$

because $j = -D(\rho) \nabla \rho(t) + \chi(\rho(t)) E(t)$.

Therefore our basic equation is

$$\begin{aligned} & \int_0^T dt \left\{ - \int_{\partial\Lambda} d\sigma(x) \lambda(t, x) j(t, x) \cdot \hat{n}(x) + \int_{\Lambda} dx j(t, x) \cdot E(t, x) \right\} \\ & = F(\rho(T)) - F(\rho(0)) \\ & + \int_0^T dt \int_{\Lambda} dx j(t) \cdot \chi(\rho(t))^{-1} j(t) , \end{aligned} \tag{4}$$

where F is the equilibrium free energy functional,

$$F(\rho) = \int_{\Lambda} dx f(\rho(x)) . \tag{5}$$

Renormalized work

L. Bertini, D. Gabrielli, G. Jona-Lasinio, C. Landim, (2012), *J. Stat. Phys.* **149**, 773 (2012); *Phys. Rev. Lett.* **110**, 020601 (2013).

Taking into account the orthogonal decomposition of the current $J(\rho) = J_S(\rho) + J_A(\rho)$ the dissipative term in (2) can be written

$$\int_0^T dt \int_{\Lambda} dx j_S(t) \cdot \chi(u(t))^{-1} j_S(t) + \int_0^T dt \int_{\Lambda} dx j_A(t) \cdot \chi(u(t))^{-1} j_A(t) \quad (6)$$

We identify the last term with the work necessary to keep the system out of equilibrium. This can be seen by writing the hydrodynamic equation in terms of V

$$\partial_t \rho = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) - \nabla J_A(\rho) \quad (7)$$

Consider a stationary state. Since $\frac{\delta V}{\delta \rho} = 0$ the stationary current coincides with J_A .

We define the renormalized work

$$W_{[0,T]}^{ren} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_{\Lambda} dx j_S(t) \cdot \chi(u(t))^{-1} j_S(t) \quad (8)$$

from which the stronger inequality follows

$$W_{[0,T]}^{ren} \geq F(\rho(T)) - F(\rho(0)) \quad (9)$$

Equality is obtained for quasi-static transformations. In fact in such a case the integral in (8) can be made as small as we want.

The idea of renormalized work was introduced in Y. Oono, M. Paniconi, Prog. Theor. Phys. Suppl. **130**, 29 (1998).

In equilibrium

$$W_{[0,T]}^{ren} = W_{[0,T]} \quad (10)$$

The quasi-potential as excess work

Consider the following transformation: at time $t = 0$ the system is in a stationary state $\bar{\rho}_0(x)$ corresponding to a chemical potential $\lambda_0(x)$ which suddenly changes to $\lambda_1(x)$. The system will relax to a new stationary state $\bar{\rho}_1(x)$ following hydrodynamics with new boundary conditions.

A simple computation shows that

$$\begin{aligned} V_{\bar{\rho}_1}(\bar{\rho}_0) &= \int_0^\infty dt \int_\Lambda dx j_S(t) \cdot \chi(\rho(t))^{-1} j_S(t) \\ &= \lim_{T \rightarrow \infty} \left\{ W_{[0,T]} - \Delta F - \int_0^T dt \int_\Lambda dx j_A(t) \cdot \chi(\rho(t))^{-1} j_A(t) \right\} \quad (11) \\ &= W^{ren} - \Delta F = W^{ren} - \min W^{ren} = W_{ex} \end{aligned}$$

An alternative renormalization

C. Maes, K. Netocny, arXiv:1206.3423

One may ask whether there exist alternative renormalizations of the total work. For instance, in a recent work, Maes and Netocny considered the topic of a renormalized Clausius inequality in the context of a single Brownian particle in a time dependent environment. To compare their approach to the present one, consider N independent diffusions in the thermodynamic limit $N \rightarrow \infty$. Each diffusion solves the Langevin equation $\dot{X} = E(t, X) + \sqrt{2} \dot{w}$, where E is a time dependent vector field and \dot{w} denotes white noise. The corresponding stationary measure with E frozen at time t is denoted by $\exp\{-v(t, x)\}$.

The scheme discussed here can be now applied. The transport coefficients are $D = 1$ and $\chi(\rho) = \rho$. We subtract the energy dissipated by $J_A(t, \rho) = \rho[E(t, x) + \nabla v(t, x)]$. The renormalization introduced in Maes and Netocny is instead obtained by introducing a potential field such that the corresponding stationary state has minimal entropy production. Namely, they write $E = f - \nabla U$ and subtract from the energy exchanged the space-time integral of $|J_t^\phi|^2/\rho$ where $J_t^\phi = \rho(f - \nabla\phi) - \nabla\rho$ and $\phi = \phi(t, x; \rho)$ is chosen so that $\nabla \cdot J_t^\phi = 0$. While the two renormalization schemes are different, both satisfy a Clausius inequality with $F(\rho) = \int dx \rho \log \rho$. Observe that in this case of independent particles our renormalization is local while the dependence of J_t^ϕ on ρ is nonlocal.

Comment

The splitting of the current appears interesting conceptually. However the two currents J_S and J_A , apart some special cases, are not easily accessible experimentally. In fact what is directly measurable is the total current which coincides with J_A in a stationary state while J_S represents the total current in a relaxation to an equilibrium state. In the general case their computation require the knowledge of the quasi-potential. A measurement of the quasi-potential via rare fluctuations is hopeless as very large times are involved. It can be either obtained from calculations by solving a variational principle or from simulations. Otherwise it can be approximately estimated from measurements of correlation functions in the stationary state. In fact V is the Legendre transform of the generating functional of density correlations in the stationary state.

Finite time thermodynamics

L. Bertini, A. De Sole, D. Gabrielli, G. Jona-Lasinio, C. Landim, arXiv:1404.6466

For simplicity we here restrict the discussion to one space dimension. Let $E(s)$ and $\lambda(s)$ with $s \in [0, 1]$ be a *protocol*. The slow transformation is then realized by

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

Let also $\rho^\tau(t)$ and $j^\tau(t)$, $0 \leq t \leq \tau$, be the solution to

$$\begin{cases} \partial_t \rho^\tau + \nabla \cdot J(t/\tau, \rho^\tau(t)) = 0, \\ j^\tau(t) = J(t/\tau, \rho^\tau(t)) \\ f'(\rho^\tau(t))|_{\partial\Lambda} = \lambda^\tau(t) \\ \rho^\tau(0) = \bar{\rho}(0) \end{cases} \quad (12)$$

where we recall that

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

and $\bar{\rho}(0)$ is the unique stationary solution of the hydrodynamics with external field $E(0)$ and chemical potential $\lambda(0)$.

Along the transformation (ρ^τ, j^τ) the energy balance can be written

$$\begin{aligned}
 & \tau \int_0^1 ds \int_{\Lambda} dx j^\tau(\tau s) \cdot E(s) - \tau \int_0^1 ds \int_{\partial\Lambda} d\sigma \lambda(s) j^\tau(\tau s) \cdot \hat{n} \\
 & - \tau \int_0^1 ds \int_{\Lambda} dx J_A(s, \rho^\tau(\tau s)) \chi(\rho^\tau(\tau s))^{-1} J_A(s, \rho^\tau(\tau s)) \\
 & = F(\rho^\tau(\tau)) - F(\bar{\rho}(0)) \\
 & + \tau \int_0^1 ds \int_{\Lambda} dx J_S(s, \rho^\tau(\tau s)) \chi(\rho^\tau(\tau s))^{-1} J_S(s, \rho^\tau(\tau s))
 \end{aligned} \tag{13}$$

We now expand in $1/\tau$

$$\rho^\tau(\tau s) = \bar{\rho}(s) + \frac{1}{\tau} r(s) + O\left(\frac{1}{\tau^2}\right), \quad s \in [0, 1]$$

where $\bar{\rho}(s)$ is the stationary solution to the hydrodynamic equation having external field $E(s)$ and chemical potential $\lambda(s)$.

$$j^\tau(\tau s) = J(s, \bar{\rho}(s)) + \frac{1}{\tau} g(s) + O\left(\frac{1}{\tau^2}\right). \quad (14)$$

$$J_S(s, \rho^\tau(\tau s)) = -\frac{1}{\tau} \chi(\bar{\rho}(s)) \nabla (C_s^{-1} \star r(s)) + O\left(\frac{1}{\tau^2}\right). \quad (15)$$

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

r solves

$$\begin{cases} \partial_s \bar{\rho}(s) + \nabla \cdot g(s) = 0 \\ g(s) = -D(\bar{\rho}(s)) \nabla r(s) \\ \quad -r(s) [D'(\bar{\rho}(s)) \nabla \bar{\rho}(s) + \chi'(\bar{\rho}(s)) E(s)] \\ r(s, x) = 0, x \in \partial\Lambda \end{cases} \quad (16)$$

which has the form of a Poisson equation for $r(s)$.

We obtain to order 0 in $1/\tau$

$$\begin{aligned} & F(\bar{\rho}(1)) - F(\bar{\rho}(0)) \\ &= \int_0^1 ds \int_{\Lambda} dx E(s) \cdot g(s) - \int_0^1 ds \int_{\partial\Lambda} d\sigma \lambda(s) g(s) \cdot n \\ & \quad - \int_0^1 ds \int_{\Lambda} dx r(s) \frac{\chi'(\bar{\rho}(s))}{\chi^2(\bar{\rho}(s))} J^2(s, \bar{\rho}(s)). \end{aligned}$$

Renormalized work to order $1/\tau$

For large finite τ a direct calculation shows that

$$W_{[0,\tau]}^{\text{ren}} = \Delta F + \frac{1}{\tau} B + O\left(\frac{1}{\tau^2}\right). \quad (17)$$

where

$$B = \int_0^1 ds \int_{\Lambda} dx \nabla(C_s^{-1}r(s)) \cdot \chi(\bar{\rho}(s)) \nabla(C_s^{-1}r(s)). \quad (18)$$

and

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

We observe that B depends on the protocol and it has a strictly positive lower bound. We can select the “best” protocol by minimizing B .

Optimization problems

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 $(\lambda(s), E(s))$, the excess (18) is a functional $B = B(\lambda, E)$ of the protocol $(\lambda(s), E(s))$, $s \in [0, 1]$. In (18) $r(s) = r_{\lambda(s), E(s)}(x)$ is obtained by solving the following Poisson equation:

$$\begin{cases} \partial_s \bar{\rho}(s) = \Delta(D(\bar{\rho}(s))r(s)) - \nabla(\chi'(\bar{\rho}(s))E(s)r(s)) \\ r(s, \pm 1) = 0. \end{cases} \quad (19)$$

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 (18) 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

$$\left\{ \begin{array}{l} \partial_s \bar{\rho}(s) + \frac{1}{2} \nabla(\chi(\bar{\rho}(s))) \nabla \bar{\pi}(s) = 0 \\ \partial_s \bar{\pi}(s) + \frac{1}{4} \chi'(\bar{\rho}(s)) (\nabla \bar{\pi}(s))^2 = 0 \\ \bar{\rho}(0) = \bar{\rho}_{\lambda_0, E_0}, \bar{\rho}(1) = \bar{\rho}_{\lambda_1, E_1}, \bar{\pi}(s, \pm 1) = 0, \end{array} \right. \quad (20)$$

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

$$E(s) = \frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} \nabla \bar{\rho}(s), \quad \lambda(s, \pm 1) = f'(\bar{\rho}(s, \pm 1)), \quad (21)$$

Equation (21) defines a transformation between and through equilibrium states, the corresponding minimal value of the excess functional is then given by

$$B_{\text{opt}} = \frac{1}{4} \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s)) (\nabla \pi(s))^2. \quad (22)$$

We emphasize that both the stationary equations (20) and the corresponding minimal excess B_{opt} in (22) 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.

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 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

$$\lambda(\pm 1) = f'(\bar{\rho}(\pm 1)), \quad E = \frac{1}{\chi(\bar{\rho})} (D(\bar{\rho})\nabla\bar{\rho} + \bar{J}). \quad (23)$$

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 $\rho : \Lambda \rightarrow R_+$, depending parametrically on $(\bar{\rho}, \bar{J})$. For $\bar{J} = 0$ it is the local functional (??),

$$V(\bar{\rho}, 0; \rho) = \int_{\Lambda} dx (f(\rho) - f(\bar{\rho}) - f'(\bar{\rho})(\rho - \bar{\rho})) . \quad (24)$$

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

$$\int_{\Lambda} dx \chi(\rho) \left(\nabla \frac{\delta V(\bar{\rho}, \bar{J}; \rho)}{\delta \rho} \right) \left(\nabla \left(\frac{\delta}{\delta \rho} (V(\bar{\rho}, \bar{J}; \rho) - V(\bar{\rho}, 0; \rho)) \right) + \frac{\bar{J}}{\chi(\bar{\rho})} \right) = 0 \quad (25)$$

where we used the Einstein relation.

In the present variables, the excess functional (18) becomes

$$B = \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s, x)) \left(\nabla_x \int_{\Lambda} dy \frac{\delta^2 V(\bar{\rho}(s), \bar{J}(s); \bar{\rho}(s))}{\delta \rho(x) \delta \rho(y)} r(s, y) \right)^2, \quad (26)$$

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

$$\begin{cases} \partial_s \bar{\rho}(s) = \nabla \left(\chi(\bar{\rho}(s)) \nabla \left(\frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} r(s) \right) - \frac{\chi'(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} r(s) \bar{J}(s) \right) \\ r(s, \pm 1) = 0. \end{cases} \quad (27)$$

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 (26) satisfies

$$\left. \frac{\delta B(\bar{\rho}, \bar{J})}{\delta \bar{J}(s)} \right|_{\bar{J}=0} = 0, \quad s \in [0, 1]. \quad (28)$$

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 $B(\bar{\rho}, 0)$.

Hamiltonian structure

For transformations between equilibrium states, in view of (28), 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 (26) can be rewritten as

$$B = \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s)) \left(\nabla \left(\frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s)) \right) \right)^2. \quad (29)$$

By introducing

$$\pi(s, x) = \pi(\bar{\rho}(s), \dot{\bar{\rho}}(s); x) = -2 \frac{D(\bar{\rho}(s, x))}{\chi(\bar{\rho}(s, x))} r_0(\bar{\rho}(s), \dot{\bar{\rho}}(s); x), \quad (30)$$

the excess functional B can be written as

$$B = \frac{1}{4} \int_0^1 ds \int_{\Lambda} dx \chi(\bar{\rho}(s)) (\nabla \pi(s))^2. \quad (31)$$

and equation (27) translates to the following equation for π :

$$\partial_s \bar{\rho}(s) + \frac{1}{2} \nabla \left(\chi(\bar{\rho}(s)) \nabla \pi(s) \right) = 0, \quad \pi(s, \pm 1) = 0. \quad (32)$$

In the form (31), the excess functional B can be interpreted as the action functional associated to the Lagrangian

$$L(\bar{\rho}, \dot{\rho}) = \frac{1}{4} \int_{\Lambda} dx \chi(\bar{\rho}(x)) (\nabla_x \pi(\bar{\rho}, \dot{\rho}; x))^2. \quad (33)$$

The corresponding Hamiltonian is

$$H(\bar{\rho}, \bar{\pi}) = \sup_{\dot{\rho}} \left\{ \int_{\Lambda} dx \bar{\pi} \dot{\rho} - L(\bar{\rho}, \dot{\rho}) \right\} = \frac{1}{4} \int_{\Lambda} dx \chi(\bar{\rho}) (\nabla_x \bar{\pi})^2. \quad (34)$$

A straightforward computation shows that (20) are the Hamiltonian equations for (34). Note that, apart for a factor $\frac{1}{4}$, (34) coincides with the Hamiltonian of the macroscopic fluctuation theory [?, Sec.IVB] in the degenerate case $D = 0$ and $E = 0$.

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 (31)-(32) 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 (32) for $\pi(s, x) = \pi(\bar{\rho}(s), \dot{\bar{\rho}}(s); x)$ becomes

$$\Delta\pi(s, x) = -2 \frac{\dot{\bar{\rho}}(s)}{\chi(\bar{\rho}(s))}, \quad \pi(s, \pm 1) = 0, \quad (35)$$

whose solution is

$$\pi(s, x) = \frac{\dot{\bar{\rho}}(s)}{\chi(\bar{\rho}(s))} (1 - x^2). \quad (36)$$

In view of (36), the functional B (31), restricted to homogeneous density protocols $\bar{\rho}(s)$ $s \in [0, 1]$, becomes

$$B = \frac{2}{3} \int_0^1 ds \frac{(\dot{\bar{\rho}}(s))^2}{\chi(\bar{\rho}(s))}. \quad (37)$$

Letting

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

we have

$$B = \frac{2}{3} \int_0^1 ds (\partial_s \Phi(\bar{\rho}(s)))^2. \quad (38)$$

Hence, the minimizer of this functional is obtained when

$$\partial_s \Phi(\bar{\rho}(s)) = \frac{\dot{\bar{\rho}}(s)}{\sqrt{\chi(\bar{\rho}(s))}} = \Phi(\bar{\rho}_1) - \Phi(\bar{\rho}_0). \quad (39)$$

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

$$B_{\text{opt}} = \frac{2}{3} \left[\Phi(\bar{\rho}_1) - \Phi(\bar{\rho}_0) \right]^2. \quad (40)$$

The protocol (39) corresponds to the one obtained by Sivak and Crooks in the context of Markov processes with finitely many degrees of freedom. However, the spatial structure of our setting allows to find better protocols. In other words, the protocol (39) is not a minimizer of the excess functional (31) without the constraint of transformations through homogeneous equilibrium states. Indeed, the function $\pi(t, x)$ in (36) does not solve Hamiltonian equation (20). 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.

Ideal gas

In the case $\chi(\rho) = \rho$, e.g., for ideal gases, the Hamilton equation (20) reads

$$\left\{ \begin{array}{l} \partial_s \bar{\rho}(s) + \frac{1}{2} \nabla(\bar{\rho}(s) \nabla \bar{\pi}(s)) = 0 \\ \partial_s \bar{\pi}(s) + \frac{1}{4} (\nabla \bar{\pi}(s))^2 = 0 \\ \bar{\rho}(0) = \bar{\rho}_{\lambda_0, E_0}, \quad \bar{\rho}(1) = \bar{\rho}_{\lambda_1, E_1}, \quad \bar{\pi}(s, \pm 1) = 0. \end{array} \right. \quad (41)$$

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:

$$\bar{\pi}(s, x) = \frac{1}{s} (1 - |x|)^2, \quad \bar{\rho}(s, x) = \frac{1}{s} \theta(|x| + s - 1) \bar{\rho}_1. \quad (42)$$

The corresponding minimal value of the excess functional is

$$B_{\text{opt}} = \frac{2}{3}\bar{\rho}_1. \quad (43)$$

This should be compared to the minimal value of B through homogeneous equilibria (40), which in this case is $\frac{8}{3}\bar{\rho}_1$, giving a flat reduction of 75%.

The interpretation of the solution (42) 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 .

Ginzburg-Landau

This model has a constant mobility $\chi(\rho) = c$. In this case equations (20) are linear and the solution is immediate

$$\begin{cases} \bar{\rho}(x, s) = \bar{\rho}_{\lambda_0, E_0} + s (\bar{\rho}_{\lambda_1, E_1} - \bar{\rho}_{\lambda_0, E_0}) , \\ \pi(s, x) = (\bar{\rho}_{\lambda_1, E_1} - \bar{\rho}_{\lambda_0, E_0}) (x^2 - 1) . \end{cases} \quad (44)$$

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

Dissipation

The infinitesimal version of the identity (2) gives the instantaneous energy balance which reads

$$\dot{W} = \int_{\Lambda} dx [f'(\rho)\dot{\rho} + j \cdot \chi(\rho)^{-1}j] \quad (45)$$

where \dot{W} is the power injected by the reservoirs and external field in the system. Accordingly, $f'(\rho)\dot{\rho}$ represents the rate of change of the free energy while $j \cdot \chi(\rho)^{-1}j$ is the dissipated power.

In general the dissipation is not minimal in the stationary state.

As a simple example let us consider the case of independent particles. the minimizer of the second term on the right with the prescribed boundary conditions $\rho(0) = \rho_0$, $\rho(L) = \rho_1$ is

$$\hat{\rho}(x) = [\sqrt{\rho_0}(1 - x/L) + \sqrt{\rho_1}x/L]^2$$

while the stationary profile is $\bar{\rho}(x) = \rho_0(1 - x/L) + \rho_1x/L$.

Observe that, in accordance with the Prigogine principle,

$$\bar{\rho} - \hat{\rho} = O([\rho_1 - \rho_0]/L)^2.$$

The quasi-potential as relative entropy

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

$$S(\nu|\mu) = \int d\mu \frac{d\nu}{d\mu} \log \frac{d\nu}{d\mu}. \quad (46)$$

We discuss the case of stochastic lattice gases. If $\Lambda \subset \mathbb{R}^d$ is the macroscopic volume and Λ_ϵ the corresponding subset of the lattice with spacing ϵ , the number of sites in Λ_ϵ is approximately $\epsilon^{-d}|\Lambda|$. Given (λ_0, E_0) and (λ_1, E_1) , we claim that

$$\lim_{\epsilon \rightarrow 0} \epsilon^d S(\mu_{\Lambda_\epsilon}^{\lambda_0, E_0} | \mu_{\Lambda_\epsilon}^{\lambda_1, E_1}) = V_{\lambda_1, E_1}(\bar{\rho}_0), \quad (47)$$

where $\bar{\rho}_0$ is the stationary profile corresponding to (λ_0, E_0) .

In view of the definition (46) of the relative entropy we have that

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

By the large deviation formula we then get

$$\begin{aligned} \epsilon^d S(\mu_{\Lambda_\epsilon}^{\lambda_0, E_0} | \mu_{\Lambda_\epsilon}^{\lambda_1, E_1}) &\approx \epsilon^d \beta \sum_{\eta} \mu_{\Lambda_\epsilon}^{\lambda_0, E_0}(\eta) [V_{\lambda_1, E_1}(\rho_\epsilon(\eta)) - V_{\lambda_0, E_0}(\rho_\epsilon(\eta))] \\ &\approx \beta [V_{\lambda_1, E_1}(\bar{\rho}_0) - V_{\lambda_0, E_0}(\bar{\rho}_0)] = \beta V_{\lambda_1, E_1}(\bar{\rho}_0), \end{aligned}$$

where $\rho_\epsilon(\eta)$ 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 $\mu_{\Lambda_\epsilon}^{\lambda_0, E_0}$.

False counterexamples

Let, for instance, μ_ϵ^β be the Gibbs measure for a one-dimensional Ising model at zero magnetic field and inverse temperatures β_0 and β_1 on a ring with ϵ^{-1} sites. The magnetization satisfies a large deviation formula and its typical value is zero for both ensembles so that the right hand side of (47) vanishes. On the other hand, by a direct computation, for $\beta_0 \neq \beta_1$, $\lim_{\epsilon \rightarrow \infty} \epsilon S(\mu_\epsilon^{\beta_0} | \mu_\epsilon^{\beta_1}) > 0$.

However this example does not contradict (47) as we are comparing two ensembles in which we varied the temperature and not the magnetic field. In this example, the correct formulation of (47) would have been in terms of the large deviation function for the energy, that is the extensive variable conjugated the the intensive parameter that has been changed.

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