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Non equilibrium thermodynamic transformations

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1. *PRELIMINARIES*

Over the last ten years, in collaboration with L.Bertini, A. De Sole, D. Gabrielli and C. Landim we have formulated a theory, now known as Macroscopic Fluctuation Theory (MFT), based on the study of rare fluctuations.

This theory may be seen as an extension of Einstein equilibrium fluctuation theory to stationary nonequilibrium states combined with a dynamical point of view. The guide of lattice gas models has been crucial.

MFT is very powerful in studying concrete microscopic models but can be used also as a phenomenological theory. The input it requires are measurable transport coefficients. It leads to several new interesting predictions.

Einstein theory of equilibrium fluctuations

In Landau-Lifshitz book on statistical mechanics one finds the following formula for the probability of a fluctuation in a system in contact with an environment
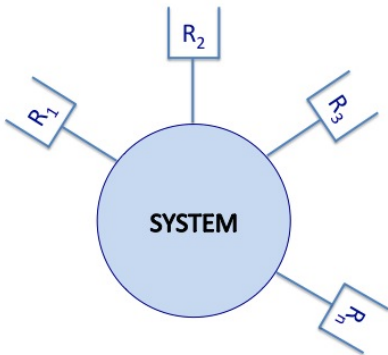
$$P \simeq e^{-\frac{R_{min}}{T_0}} \qquad (1)$$

where

$$R_{min} = \Delta E - T_0 \Delta S + P_0 \Delta V \qquad (2)$$

is the *minimal work* necessary to produce the fluctuation with a reversible transformation and $\Delta E, \Delta S, \Delta V$ are the corresponding variations of energy, entropy and volume. T_0, P_0 are the temperature and pressure of the environment.

Assumptions

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

2. *The macroscopic evolution is given by the continuity equation*

$$\partial_t \rho + \nabla \cdot j = 0 \tag{3}$$

together with the constitutive equation

$$j = J(t, \rho) = -D(\rho)\nabla\rho + \chi(\rho)\, E(t) \tag{4}$$

where the diffusion coefficient $D(\rho)$ and the mobility $\chi(\rho)$ are $d \times d$ positive matrices. The transport coefficients D and χ satisfy the local Einstein relation
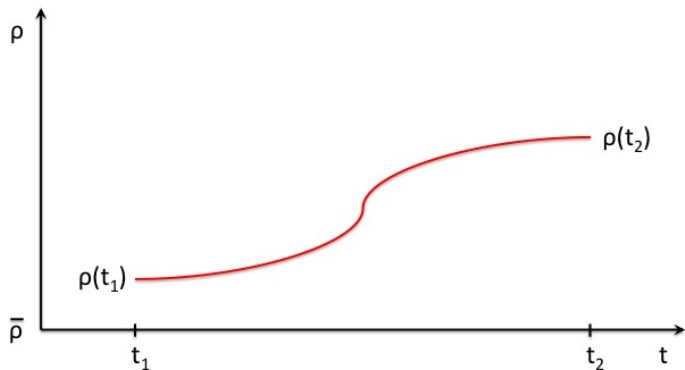
$$D(\rho) = \chi(\rho)\, f_0''(\rho) \tag{5}$$

where f_0 is the equilibrium specific free energy.

The equations (3)–(4) have to be supplemented by the appropriate boundary condition on $\partial\Lambda$ due to the interaction with the external reservoirs. If $\lambda(t, x)$, $x \in \partial\Lambda$ is the chemical potential of the external reservoirs, this boundary condition is

$$f_0'\big(\rho(t, x)\big) = \lambda(t, x) \qquad x \in \partial\Lambda. \tag{6}$$

Question: what is the probability of a macroscopic trajectory?

2. *RARE FLUCTUATIONS*

The large deviation formula for joint fluctuations of the density and current

$$\mathbb{P}\big(\rho(t), j(t) \ t \in [0, T]\big) \sim \exp\{-\epsilon^{-d}\mathcal{G}_{[0,T]}(\rho, j)\} \qquad (7)$$

Here $\mathbb{P}$ is the stationary probability measure,

$$\mathcal{G}_{[0,T]}(\rho, j) = \begin{cases} V(\rho(0)) + \mathcal{I}_{[0,T]}(j) & \text{if } \partial_t\rho + \nabla \cdot j = 0 \\ +\infty & \text{otherwise} \end{cases} \qquad (8)$$

where

$$\mathcal{I}_{[0,T]}(j) = \frac{1}{4}\int_0^T dt \, \langle [j - J(\rho)], \chi(\rho)^{-1}[j - J(\rho)]\rangle \qquad (9)$$

in which we recall that

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

Large deviations of the density

$$\mathbb{P}\big(\rho(t), \;\; t \in [0,T]\big) \sim \exp\{-\epsilon^{-d} \mathcal{A}_{[0,T]}(\rho)\} \tag{10}$$

Here $\mathbb{P}$ is the stationary probability measure,

$$\mathcal{A}_{[0,T]}(\rho) = V(\rho(0)) + I_{[0,T]}(\rho) \tag{11}$$

where

$$I_{[0,T]}(\rho) = \frac{1}{4} \int_{T_1}^{T_2} dt \left\langle \left[\partial_t \rho + \nabla \cdot J(\rho)\right] K(\rho)^{-1} \left[\partial_t \rho + \nabla \cdot J(\rho)\right] \right\rangle \tag{12}$$

The positive operator $K(\rho)$ is defined on functions $u : \Lambda \to R$ vanishing at the boundary $\partial \Lambda$ by $K(\rho)u = -\nabla \cdot \big(\chi(\rho)\nabla u\big)$. The scale factor ϵ is a ratio between typical microscopic and macroscopic lengths so that $\epsilon \to 0$ corresponds to the thermodynamic limit.

Time reversal

To the time reversed process corresponds the adjoint generator with respect to the stationary ensemble. Let us define the operator inverting the time of a trajectory $[\theta f](t) = f(-t)$ for f scalar and $[\theta j](t) = -j(-t)$ for the current. The stationary adjoint process, that we denote by $\mathbb{P}_{\mu^N}^{N,a}$, is the time reversal of $\mathbb{P}_{\mu^N}^N$, i.e. we have $\mathbb{P}_{\mu^N}^{N,a} = \mathbb{P}_{\mu^N}^N \circ \vartheta^{-1}$. Then

$$\mathbb{P}_{\mu^N}^N\Big(\rho, \ j \ \ t \in [-T,T]\Big)$$
$$= \mathbb{P}_{\mu^N}^{N,a}\Big(\vartheta\rho, \ \vartheta j \ \ t \in [-T,T]\Big) \tag{13}$$

At the level of large deviations this implies

$$\mathcal{G}_{[-T,T]}(\rho, j) = \mathcal{G}_{[-T,T]}^a(\vartheta\rho, \vartheta j) \tag{14}$$

where $\mathcal{G}_{[-T,T]}^a$ is the large deviation functional for the adjoint process.

The quasi-potential and the associated Hamilton-Jacobi equation

$$V(\rho) = \inf_{\substack{\rho \, : \, \rho(-\infty) = \bar{\rho} \\ \rho(0) = \rho}} I_{[-\infty,0]}(\rho) \tag{15}$$

By considering $I_{[0,T]}(\rho)$ as a Lagrangian we obtain that $V(\rho)$ satisfies the following Hamilton-Jacobi equation

$$\left\langle \nabla \frac{\delta V}{\delta \rho}, \chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right\rangle - \left\langle \frac{\delta V}{\delta \rho}, \nabla \cdot J(\rho) \right\rangle = 0 \tag{16}$$

corresponding to the Hamiltonian

$$\mathcal{H}(\rho, \pi) = \left\langle \nabla \pi \cdot \chi(\rho) \nabla \pi \right\rangle + \left\langle \nabla \pi \cdot J(\rho) \right\rangle \tag{17}$$

where π is the conjugate momentum.

The hydrodynamic equations in terms of V

$$\partial_t \rho = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) + \mathcal{A}(\rho) \qquad (18)$$

$$\partial_t \rho = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) - \mathcal{A}(\rho) \qquad (19)$$

The second equation is the hydrodynamics corresponding to the time reversed system. The Hamilton–Jacobi equation implies the orthogonality condition

$$\left\langle \frac{\delta V}{\delta \rho} \, , \, \mathcal{A}(\rho) \right\rangle = 0$$

Correspondingly there is an orthogonal decomposition of the current $J(\rho) = J_S(\rho) + J_A(\rho)$ with

$$J_S(\rho) = -\chi(\rho) \nabla \frac{\delta V}{\delta \rho}, \quad \left\langle J_S \chi^{-1} J_A \right\rangle = 0 \qquad (20)$$

As a simple illustration let us consider a charged particle in a viscous medium subjected to a magnetic field,

$$\dot{p} = \frac{e}{mc}\, p \wedge H - \frac{1}{\tau}\, p \ , \tag{21}$$

where p is the momentum, e the charge, H the magnetic field, m the mass, c the velocity of the light, and τ the relaxation time. The dissipative term p/τ is orthogonal to the Lorenz force $p \wedge H$.

We define time reversal as the transformation $p \mapsto -p$, $H \mapsto -H$. In this case the adjoint equation coincides with the time reversed dynamics, which is given by

$$\dot{p} = -\frac{e}{mc}\, p \wedge H - \frac{1}{\tau}\, p \tag{22}$$

In this example, $J_S(p) = p/\tau$ and $J_A(p) = -(e/mc)p \wedge H$.

Another simple example is the case of a system of independent particles, the corrisponding transport coefficients are $D(\rho) = I$ and $\chi(\rho) = \rho I$ where D_0, χ_0 are scalar and I denotes the identity matrix.

In the one dimensional case, with $\Lambda = (0, L)$, $\lambda(0) = \lambda_0$, $\lambda(L) = \lambda_1$ the stationary density profile is $\bar{\rho}(x) = \rho_0(1 - x/L) + \rho_1 x/L$ where ρ_0 and ρ_1 are the densities associated to λ_0 and λ_1. In this case

$$J_{\mathrm{S}}(\rho) = -\nabla\rho + \frac{\rho_1 - \rho_0}{L}\frac{\rho}{\bar{\rho}}$$

$$J_{\mathrm{A}}(\rho) = -\frac{\rho_1 - \rho_0}{L}\frac{\rho}{\bar{\rho}}$$

3. *THERMODYNAMIC TRANSFORMATIONS*

Energy balance

Fix $T > 0$, a density profile $\rho(x)$, an external field $E(t, x)$ and a chemical potential $\lambda(t, x)$, $0 \le t \le T$. 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

$$W_{[0,T]} = \int_0^T dt \left\{ -\int_{\partial\Lambda} d\sigma(x)\, \lambda(t,x)\, j(t,x) \cdot \hat{n}(x) + \int_\Lambda dx\, j(t,x) \cdot E(t,x) \right\},$$
(23)

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

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

$$(24)$$

where

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

From this equation the inequality follows

$$W_{[0,T]} \geq F(\rho(T)) - F(\rho(0)) \qquad (25)$$

which is the second law here derived dynamically.

For very slow transformations taking into account the orthogonal decomposition of the current $J(\rho) = J_S(\rho) + J_A(\rho)$ the second term in (24) can be written

$$\int_0^T dt \int_\Lambda dx \; j_S(t) \cdot \chi(u(t))^{-1} j_S(t) + \int_0^T dt \int_\Lambda dx \; j_A(t) \cdot \chi(u(t))^{-1} j_A(t)$$
(26)

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

$$\partial_t \rho = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) + \mathcal{A}(\rho)$$
(27)

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

Renormalized work

We define the renormalized work

$$W_{[0,T]}^{ren} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_\Lambda dx \, j_S(t) \cdot \chi(u(t))^{-1} j_S(t) \tag{28}$$

from which the stronger inequality follows

$$W_{[0,T]}^{ren} \geq F(\rho(T)) - F(\rho(0)) \tag{29}$$

Equality is obtained for quasi-static transformations. In fact in such a case the integral in (28) 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).

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

$$V_{\bar{\rho}_1}(\bar{\rho}_0) = \int_0^\infty dt \int_\Lambda dx \, j_S(t) \cdot \chi(u(t))^{-1} j_S(t)$$

$$= \lim_{T \to \infty} \left\{ W_{[0,T]} - \Delta F - \int_0^T dt \int_\Lambda dx \, j_A(t) \cdot \chi(u(t))^{-1} j_A(t) \right\} \quad (30)$$

$$= W^{ren} - \Delta F = W^{ren} - \min W^{ren} = W_{ex}$$

An alternative renormalization

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 $N \to \infty$. 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.

Analysis of the energy balance

L. Bertini, A. De Sole, D. Gabrielli, G. Jona-Lasinio , C. Landim, *paper in preparation*

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

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

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

$$\begin{cases} \partial_t \rho^\tau + \nabla \cdot J(t/\tau, \rho^\tau(t)) = 0, \\ j^\tau(t) = J(t/\tau, \rho^\tau(t)) \\ f'(\rho^\tau(t))\big|_{\partial\Lambda} = \lambda^\tau(t) \\ \rho^\tau(0) = \bar{\rho}(0) \end{cases} \quad (31)$$

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

$$\tau \int_0^1 ds \int_\Lambda dx \, j^\tau(\tau\, s) \cdot E(s) - \tau \int_0^1 ds \int_{\partial\Lambda} d\sigma \, \lambda(s) j^\tau(\tau\, s) \cdot \hat{n}$$

$$- \tau \int_0^1 ds \int_\Lambda dx J_A\big(s, \rho^\tau(\tau s)\big) \chi\big(\rho^\tau(\tau s)\big)^{-1} J_A\big(s, \rho^\tau(\tau s)\big)$$

$$= F\big(\rho^\tau(\tau)\big) - F\big(\bar{\rho}(0)\big)$$

$$+ \tau \int_0^1 ds \int_\Lambda dx J_S\big(s, \rho^\tau(\tau s)\big) \chi\big(\rho^\tau(\tau s)\big)^{-1} J_S\big(s, \rho^\tau(\tau s)\big)$$

$$(32)$$

We now expand in $1/\tau$

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

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

$$j^\tau(\tau s) = J(s, \bar{\rho}(s)) + \frac{1}{\tau} g(s) + O\left(\frac{1}{\tau^2}\right). \qquad (33)$$

$$J_S(s, \rho^\tau(\tau s)) = -\frac{1}{\tau} \chi(\bar{\rho}(s)) \nabla \left(C_s^{-1} \star r(s)\right) + O\left(\frac{1}{\tau^2}\right). \qquad (34)$$

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

r solves

$$
\begin{cases}
\partial_s \bar{\rho}(s) + \nabla \cdot g(s) = 0 \\
g(s) = -D(\bar{\rho}(s))\nabla r(s) \\
\qquad -r(s)\big[D'(\bar{\rho}(s))\nabla\bar{\rho}(s) + \chi'(\bar{\rho}(s))E(s)\big] \\
r(s,x) = 0, \ x \in \partial\Lambda
\end{cases}
\tag{35}
$$

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

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

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

For large finite τ a direct calculation shows that

$$W_{[0,\tau]}^{\text{ren}} = \Delta F + \frac{1}{\tau} B + O\left(\tfrac{1}{\tau^2}\right). \qquad (36)$$

where

$$B = \int_0^1 ds \int_\Lambda dx \, \chi(\bar{\rho}(s)) \left[C_s^{-1} \star r(s) \right]^2 > 0 \qquad (37)$$

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 but it has a strictly positive lower bound. For slow trasformation we can select the "best" protocol by minimizing B.

Dissipation

The infinitesimal version of the identity (24) gives the istantaneous energy balance which reads

$$\dot{W} = \int_{\Lambda} dx \left[f'(\rho)\dot{\rho} + j \cdot \chi(\rho)^{-1} j \right] \tag{38}$$

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

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

while the stationary profile is $\bar{\rho}(x) = \rho_0(1 - x/L) + \rho_1 x/L$. 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

$$S(\nu|\mu) = \int d\mu \, \frac{d\nu}{d\mu} \log \frac{d\nu}{d\mu} \cdot \qquad (39)$$

We discuss the case of stochastic lattice gases. If $\Lambda \subset R^d$ 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

$$\lim_{\epsilon \to 0} \epsilon^d \, S\big(\mu_{\Lambda_\epsilon}^{\lambda_0, E_0} | \mu_{\Lambda_\epsilon}^{\lambda_1, E_1}\big) = V_{\lambda_1, E_1}(\bar{\rho}_0), \qquad (40)$$

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

In view of the definition (39) of the relative entropy we have that

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

By the large deviation formula we then get

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

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

where $\rho_\epsilon(\eta)$ 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 (40) vanishes. On the other hand, by a direct computation, for $\beta_0 \neq \beta_1$, $\lim_\epsilon \epsilon S(\mu_\epsilon^{\beta_0}|\mu_\epsilon^{\beta_1}) > 0$.

However this example does not contradict (40) as we are comparing two ensembles in which we varied the temperature and not the magnetic field. In this example, the correct formulation of (40) 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.