Thermodynamic transformations of nonequilibrium states

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1. **INTRODUCTION**
Why is the theory of irreversible processes so much more difficult than the theory of equilibrium phenomena?

In equilibrium we do not have to solve any equation of motion and the Gibbs distribution provides the basis for the calculation of macroscopic quantities and their fluctuations. In nonequilibrium we cannot bypass the dynamics even in the study of stationary states which we may consider as the simplest beyond equilibrium.

The calculation of the nonequilibrium distribution is very difficult. Out of equilibrium therefore the basic object to define analogs of entropy or thermodynamic potentials which we need to construct a natural extension of thermodynamics, that is the stationary distribution, is not immediately available.
To obtain information on the behavior of macroscopic quantities we do not need however a complete knowledge of the stationary ensemble.

In the approach developed 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 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 has been 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

\[ P \approx e^{-\frac{R_{\text{min}}}{T_0}} \]  

(1)

where

\[ R_{\text{min}} = \Delta E - T_0\Delta S + P_0\Delta V \]  

(2)

is the \textit{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.
2. BASIC THEORY
Typical setting
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

$$\partial_t \rho + \nabla \cdot j = 0$$

(3)

(together with the constitutive equation

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

(4)

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

$$D(\rho) = \chi(\rho) f''_0(\rho)$$

(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

\[
f'_0(\rho(t, x)) = \lambda(t, x) \quad x \in \partial \Lambda. \tag{6}
\]
Given time-dependent chemical potential $\lambda(t, x)$ and external field $E(t, x)$, for $t \geq 0$ the profile $\bar{\rho}_{\lambda(t), E(t)}$ is the solution of

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

(7)

with $\lambda$ and $E$ “frozen” at the time $t$. By using such profile, it is possible to reduce the equations with time-dependent boundary conditions (6) to the case of time independent boundary conditions. Indeed, by writing $u(t) = \bar{\rho}_{\lambda(t), E(t)} + v(t)$ we deduce that $v$ solves

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

$$- \partial_t \bar{\rho}_{\lambda(t), E(t)}$$

with boundary conditions $v(t, x) = 0$ for $x \in \partial \Lambda$. 
Question: what is the probability of a macroscopic trajectory?
Large deviations of the density

\[ \mathbb{P}(\rho(t), \ t \in [0, T]) \sim \exp\{-\epsilon^{-d} A_{[0,T]}(\rho)\} \] (8)

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

\[ A_{[0,T]}(\rho) = V(\rho(0)) + I_{[0,T]}(\rho) \] (9)

where

\[ I_{[0,T]}(\rho) = \frac{1}{4} \int_{T_1}^{T_2} dt \left\langle \left[ \partial_t \rho + \nabla \cdot J(\rho) \right] K(\rho)^{-1} \left[ \partial_t \rho + \nabla \cdot J(\rho) \right] \right\rangle \] (10)

The positive operator \( K(\rho) \) is defined on functions \( u : \Lambda \rightarrow R \) vanishing at the boundary \( \partial \Lambda \) by \( K(\rho)u = -\nabla \cdot \left( \chi(\rho) \nabla u \right) \). The scale factor \( \epsilon \) is a ratio between typical microscopic and macroscopic lengths so that \( \epsilon \rightarrow 0 \) corresponds to the thermodynamic limit.
The quasi-potential and the associated Hamilton-Jacobi equation

\[ V(\rho) = \inf_{\rho: \rho(-\infty)=\bar{\rho}, \rho(0)=\rho} I_{[-\infty,0]}(\rho) \] (11)

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

\[ \langle \nabla \frac{\delta V}{\delta \rho}, \chi(\rho) \nabla \frac{\delta V}{\delta \rho} \rangle - \langle \frac{\delta V}{\delta \rho}, \nabla \cdot J(\rho) \rangle = 0 \] (12)

corresponding to the Hamiltonian

\[ \mathcal{H}(\rho, \pi) = \langle \nabla \pi \cdot \chi(\rho) \nabla \pi \rangle + \langle \nabla \pi \cdot J(\rho) \rangle \] (13)

where \( \pi \) is the conjugate momentum. From the H-J it follows that \( V(\rho) \) is a Lyapunov function for the macroscopic evolution.
The macroscopic evolution equations in terms of $V$

\[ \partial_t \rho = \nabla \cdot \left( \chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) + A(\rho) \quad (14) \]

\[ \partial_t \rho = \nabla \cdot \left( \chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) - A(\rho) \quad (15) \]

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

\[ \langle \frac{\delta V}{\delta \rho}, A(\rho) \rangle = 0 \]

The above decompositions remind of the electrical conduction in presence of a magnetic field. Correspondingly there is an orthogonal decomposition of the current $J(\rho) = J_S(\rho) + J_A(\rho)$ with

\[ J_S(\rho) = -\chi(\rho) \nabla \frac{\delta V}{\delta \rho}, \quad \langle J_S \chi^{-1} J_A \rangle = 0 \quad (16) \]
The identification of the minimizing trajectory

Consider a trajectory connecting the density profiles $\rho_{t_1}$ and $\rho_{t_2}$ and its time reversal. Denoting $I^a$ the large deviation functional for the time-reversed dynamics we have

$$V(\rho_{t_1}) + I_{[t_1,t_2]}(\rho) = V(\rho_{t_2}) + I^a_{[-t_2,-t_1]}(\theta \rho)$$  \hspace{1cm} (17)

By taking $\rho_{t_1} = \bar{\rho}$, which implies $V(\rho_{t_1}) = 0$, $\rho_{t_2} = \rho$, the inf over all possible trajectories and time intervals we obtain the variational expression of $V$ with the minimizer defined by

$$I^a_{[-\infty,0]}(\theta \rho) = 0$$  \hspace{1cm} (18)

that is $\theta \rho$ must be a solution of the adjoint hydrodynamics.
An example


\[ dx_t = f(x_t)dt + \epsilon dw_t, \quad f(x) = (x - x^3 - axy^2, -(1 + x^2)y) \]
2. THERMODYNAMIC TRANSFORMATIONS
**Energy balance**

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

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

(19)

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

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

where

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

From this equation the inequality follows

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

which is the second law here derived dynamically.
Taking into account the orthogonal decomposition of the current $J(\rho) = J_S(\rho) + J_A(\rho)$ the second term in (27) can be written

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

(22)

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 $V$

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

(23)

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

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

(24)

from which the stronger inequality follows

\[ W^{ren}_{[0,T]} \geq F(\rho(T)) - F(\rho(0)) \]  

(25)

Equality is obtained for quasi-static transformations. In fact in such a case the integral in (24) can be made as small as we want.
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

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

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

\[
= W^{ren} - \Delta F = W^{ren} - \min W^{ren} = W_{ex}
\]
Consider a different renormalization, e.g.

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

\[- \int_0^T dt \int_\Lambda dx \, j(\bar{\rho}) \cdot \chi(\bar{\rho})^{-1} j(\bar{\rho}) \]

Its time derivative is zero in the stationary state. However the right hand side does not have a definite sign during the time evolution because, except for special cases, dissipation is not minimal in stationary states. Therefore it cannot be the derivative of a Lyapunov function.

**QUESTION**: is it possible to find a local functional which is a Lyapunov function for the evolution? Remember that \( V(\rho) \) is a Lyapunov function but is generically non-local.
Smooth time-dependent transformations

We consider a path \((\lambda(t), E(t))\), \(t \geq 0\), such that \((\lambda(t), E(t)) \to (\lambda_1, E_1)\) as \(t \to +\infty\). We denote by \(\bar{\rho}_1 = \bar{\rho}_{\lambda_1,E_1}\) the stationary profile corresponding to \((\lambda_1, E_1)\) and let \((u(t), j(t))\), \(t \geq 0\) be the solution to the hydrodynamic equation with initial condition \(u(0) = \rho\). Here \(\rho\) is an arbitrary density profile.

A direct computation gives that the excess of work is equal to

\[
W_{\text{ex}}(\lambda, E, \rho) = - \int_{0}^{\infty} dt \int_{\Lambda} dx \frac{\delta V_{\lambda(t),E(t)}(u(t))}{\delta \rho} \partial_t u(t)
\]

\[
= - \int_{0}^{\infty} dt \frac{d}{dt} V_{\lambda(t),E(t)}(u(t)) + \int_{0}^{\infty} dt \left( \partial_t V_{\lambda(t),E(t)} \right) (u(t)) .
\]

\[
= V_{\lambda(0),E(0)}(\rho) + \int_{0}^{\infty} dt \left( \partial_t V_{\lambda(t),E(t)} \right) (u(t))
\]

where we used that \(u(t) \to \bar{\rho}_1\) as \(t \to +\infty\) and \(V_{\lambda_1,E_1}(\bar{\rho}_1) = 0\).
The quasi-potential as relative entropy

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

$$S(\nu|\mu) = \int d\mu \frac{d\nu}{d\mu} \log \frac{d\nu}{d\mu}. \quad (27)$$

We discuss the case of stochastic lattice gases. If $\Lambda \subset \mathbb{R}^d$ is the macroscopic volume and $\Lambda_\epsilon$ the corresponding subset of the lattice with spacing $\epsilon$, the number of sites in $\Lambda_\epsilon$ is approximately $\epsilon^{-d}|\Lambda|$. Given $(\lambda_0, E_0)$ and $(\lambda_1, E_1)$, we claim that

$$\lim_{\epsilon \to 0} \epsilon^d S(\mu_{\Lambda_\epsilon}^{\lambda_0, E_0}|\mu_{\Lambda_\epsilon}^{\lambda_1, E_1}) = V_{\lambda_1, E_1}(\bar{\rho}_0), \quad (28)$$

where $\bar{\rho}_0$ is the stationary profile corresponding to $(\lambda_0, E_0)$.
In view of the definition (27) of the relative entropy we have that

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

By the large deviation formula we then get

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

\[ \approx \beta \left[ V_{\lambda_1,E_1}(\bar{\rho}_0) - V_{\lambda_0,E_0}(\bar{\rho}_0) \right] = \beta V_{\lambda_1,E_1}(\bar{\rho}_0), \]

where \( \rho_\epsilon(\eta) \) denotes the density profile associated to the microscopic configuration \( \eta \). In the final step we used the law of large numbers for the microscopic density profile under the probability \( \mu_{\Lambda_\epsilon}^{\lambda_0,E_0} \).
Actually, the above argument is incomplete. The identity is not a consequence only of the large deviation formula. It is in fact not difficult to construct counterexamples to such a general statement. Nevertheless, if the stationary ensemble $\mu_{\Lambda, \epsilon}^{\lambda_0, E_0}$ satisfies a strong form of local equilibrium (that holds e.g. for the boundary driven symmetric simple exclusion process) then (28) holds.
Consider a stochastic lattice gas in the domain $\Lambda_\epsilon = (\epsilon^{-1}\Lambda) \cap \mathbb{Z}^d$. Assume for simplicity that the external field $E$ vanishes. Given a time independent chemical potential $\lambda(x)$ we denote by $\mu_\epsilon^\lambda$ the associated stationary ensemble. Observe that $\mu_\epsilon^\lambda$ is a probability on $\mathcal{N}_{\Lambda_\epsilon}$. As for the zero range process, we denote by $\eta_i = 0, 1, \ldots$ the number of particles at the site $i \in \Lambda_\epsilon$.

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

$$
\nu_\epsilon^\lambda(N) = \mu_\epsilon^\lambda\left( \sum_{i \in B_1} \eta_i = N_1, \sum_{i \in B_2} \eta_i = N_2, \ldots \right).
$$

We also introduce the *conditional ensemble*, denoted by $\mu_\epsilon^\lambda(\cdot|N)$, as the probability $\mu_\epsilon^\lambda$ conditioned to have $N_1$ particles in the box $B_1$, $N_2$ particles in the box $B_2$, and so on.
For a box $B \subset \mathbb{Z}^d$, $n \geq 0$, denote by $\mu_{B,n}^{\text{can}}$ the equilibrium canonical measure on $B$ with $n$ particles, that is

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

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

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

$$\mu_\epsilon^\lambda(\eta|N) \approx \prod_\ell \mu_{B_\ell,N_\ell}^{\text{can}}(\eta) .$$

in the sense that

$$\epsilon^d \log \frac{\mu_\epsilon^\lambda(\eta|N)}{\prod_\ell \mu_{B_\ell,N_\ell}^{\text{can}}(\eta)} \to 0 \quad (29)$$

uniformly over $\eta$ as we let first $\epsilon \to 0$ and then $\delta \to 0$. As proven by Bernardin and Landim, this condition is satisfied for the boundary driven one-dimensional symmetric simple exclusion process.
Time dependent quasi potential

In the case of transformations fast on the macroscopic scale we have to take into account the fact that the system has a finite relaxation time. For this purpose we introduce a time dependent quasi potential

\[ V_{\lambda,E}(t, \rho) = \inf \left\{ I_{(-\infty,t]}(u,j) , u(t) = \rho , \lim_{s \to -\infty} u(s) = \bar{\rho}_0 \right\}. \] (30)

which solves the time dependent Hamilton-Jacobi equation

\[ \partial_t V_{\lambda,E} + \int_{\Lambda} dx \nabla \frac{\delta V_{\lambda,E}}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta V_{\lambda,E}}{\delta \rho} - \int_{\Lambda} dx \frac{\delta V_{\lambda,E}}{\delta \rho} \nabla \cdot J(t, \rho) = 0, \] \hspace{1cm} (31)

where \( \rho \) satisfies the boundary condition \( f'(\rho(x)) = \lambda(t, x), \) \( x \in \partial \Lambda. \)
We decompose the current

\[ J(t, \rho) = J_1(t, \rho) + J_2(t, \rho), \]  

(32)

where

\[ J_1(t, \rho) = -\chi(\rho) \nabla \frac{\delta V_{\lambda,E}(t, \rho)}{\delta \rho}, \]  

(33)

and \( J_2(t, \rho) \) is defined by difference. The decomposition (32) is not orthogonal and the time dependent Hamilton-Jacobi equation (31) implies

\[
\int_{\Lambda} dx \ J_1(t, \rho) \cdot \chi(\rho)^{-1} J_2(t, \rho) = \int_{\Lambda} dx \ \frac{\delta V_{\lambda,E}(t, \rho)}{\delta \rho} \nabla \cdot J_2(t, \rho)
\]

\[ = \partial_t V_{\lambda,E}(t, \rho). \]  

(34)
The definitions of renormalized and excess work natural in this case are

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

(35)

The renormalized work \(\hat{W}_{[t,\infty]}^{\text{ren}}(\lambda, E, \rho)\) satisfies the Clausius inequality

\[
\hat{W}_{[t,\infty]}^{\text{ren}}(\lambda, E, \rho) \geq F(\bar{\rho}_1) - F(\rho) = \Delta F
\]

(36)

where we recall that \(\rho\) is the initial datum at time \(t\) and \(\bar{\rho}_1 = u(+\infty)\).

\[
\hat{W}_{[t,\infty]}^{\text{ex}}(\lambda, E, \rho) = \int_t^\infty ds \int_\Lambda dx J_1(s, u(s)) \cdot \chi(u(s))^{-1} J_1(s, u(s))
\]

\[
= - \int_t^\infty ds \frac{d}{ds} V_{\lambda,E}(s, u(s)) = V_{\lambda,E}(t, \rho),
\]
Langevin dynamics

In the Smoluchowski approximation, the motion of a particle in a viscous $d$-dimensional medium is described by the Langevin equation

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

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

$$
\gamma \dot{x}_t = -\nabla U(x_t) + q E(t, x_t).
$$
To illustrate the previous definitions, consider the Langevin equation (37) in two dimensions with $U(x) = (\lambda/4)|x|^4$ and

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

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

Assume that $\alpha$ does not depend on $t$ and let $r_\alpha$ be the minimum of $U(r) - (q/2)\alpha r^2$, $r_\alpha = \sqrt{q\alpha/\lambda}$. The attractor of (38) is given by the periodic orbit $x(t) = r_\alpha (\cos(\omega t), \sin(\omega t))$, where $\omega = A_0 q/\gamma r_\alpha$. The quasi potential is given by $V_\alpha(x) = U(x) - (q/2)\alpha |x|^2 - (q^2\alpha^2/2\lambda)$ so that $J_S(x) = -\nabla U(x) + q\alpha x$, $J_A(x) = q A_0 (x^\perp/|x|)$. The power dissipated along the periodic orbit is $\gamma r_\alpha^2 \omega^2$ so the energy dissipated in an infinite time window is infinite.
Fix $\alpha_0 \neq \alpha_1$ and consider a function $\alpha(t)$ such that $\alpha(0) = \alpha_0$, $\alpha(t) = \alpha_1$, $t \geq T$. Let $x(t)$ be the solution of (38) with initial condition $\bar{x}$. The renormalized work and the excess work along such path are given by

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

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

where $\bar{x}_1$ is a point in the limit cycle corresponding to $\alpha_1$. If the initial condition $\bar{x}$ belongs to the limit cycle corresponding to $\alpha_0$, the previous integral is equal to

$$\int_0^\infty dt \left( \partial_t V_{\alpha(t)} \right)(x(t)) = \frac{q^2}{4\lambda} (\alpha_1^2 - \alpha_0^2) - \frac{q}{2} \int_0^\infty dt \dot{\alpha}(t) |x(t)|^2 \geq 0.$$
What we have done is very close to a well known paper by T. Hatano, S. Sasa, Phys. Rev. Lett. 86, 3463 (2001). The main difference is that we are considering the limit of small noise in order to relate the quasi potential to the work involved in the transformations. In particular, our $W^{\text{ren}}$ is not a random variable. There is also a difference in terminology as we call $W^{\text{ren}}$ what they would call $W^{\text{ex}}$, while we reserved this notation for a quantity which is more closely related to the quasi potential.
To illustrate the time dependent quasi potential, consider the time dependent Langevin equation with linear drift

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

where \( E(t) \in \mathbb{R}^n \) and \( B(t) \) is a \( n \times n \) time dependent matrix. As \( X_t \) is a Gaussian process, its distribution can be computed explicitly for any \( \beta > 0 \). The associated time dependent Hamilton-Jacobi equation is

\[ \partial_t V(t, x) + |\nabla V(t, x)|^2 + \nabla V(t, x) \cdot [B(t)x + E(t)] = 0. \] (39)
Assume that $E(t), B(t)$ are such that $(E(t), B(t)) \to (E_0, B_0)$, as $t \to -\infty$, $(E(t), B(t)) \to (E_1, B_1)$ as $t \to \infty$, respectively, and that the eigenvalues of $B_0, B_1$ have strictly negative real part. Let $m_0 = -B_0^{-1}E_0$ and $S_0$ be the symmetric $n \times n$ matrix such that $S_0^2 = -(S_0B_0 + B_0^TS_0)/2$. Let $S(t), m(t)$ be the solution of

\[
\begin{align*}
\dot{S} &= -2S^2 - [SB + B^TS], \\
\dot{m} &= Bm + E,
\end{align*}
\]

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

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

is the solution of the time dependent Hamilton-Jacobi equation.

As $t \to \infty$, $(S(t), m(t))$ converge to $(S_1, m_1)$, where $S_1^2 = -(S_1B_1 + B_1^TS_1)/2$ and $m_1 = -B_1^{-1}E_1$. If $B_1$ is normal, i.e. $B_1B_1^T = B_1^TB_1$, then $S_1 = -(1/2)(B_1 + B_1^T)$. 
In the one dimensional case, with $B = -(1/\theta)$, $\theta > 0$, we get

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

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

- We have extended the macroscopic fluctuation theory to time dependent boundary conditions and external fields in order to describe thermodynamic transformations between stationary nonequilibrium states.

- We have shown that, as in equilibrium, quasi static transformations are optimal.

- We have defined a renormalized work which satisfies a Clausius inequality.

- We have established connections between the large deviation functional and the work involved in the transformations.