

DIPARTIMENTO DI FISICA



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On thermodynamic transformations

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0. *PRELIMINARIES*

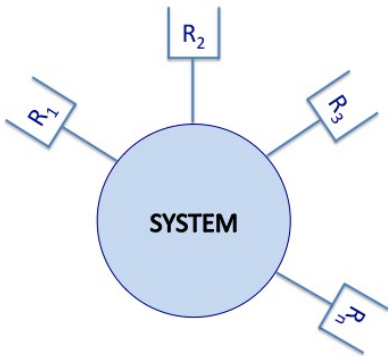
1. *FINITE TIME THERMODYNAMICS*

0. *PRELIMINARIES*

From Callen Thermodynamics

“A quasi-static process is thus defined in terms of a dense succession of equilibrium states. It is to be stressed that a quasi-static process therefore is an idealized concept, quite distinct from a real physical process, for a real process always involves nonequilibrium intermediate states having no representation in the thermodynamic configuration space. Furthermore, a quasistatic process, in contrast to a real process, does not involve considerations of rates, velocities or time. The quasi-static process simply is an ordered succession of equilibrium states, whereas a real process is a temporal succession of equilibrium and nonequilibrium states.”

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*

$$\partial_t \rho + \nabla \cdot j = 0 \quad (1)$$

together with the constitutive equation

$$j = J(t, \rho) = -D(\rho) \nabla \rho + \chi(\rho) E(t) \quad (2)$$

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

$$D(\rho) = \chi(\rho) f_0''(\rho) \quad (3)$$

where f_0 is the equilibrium specific free energy.

The equations (1)–(2) have to be supplemented by the appropriate boundary condition on $\partial\Omega$ due to the interaction with the external reservoirs. If $\lambda(t, x)$, $x \in \partial\Omega$ is the chemical potential of the external reservoirs, this boundary condition is

$$f'_0(\rho(t, x)) = \lambda(t, x) \quad x \in \partial\Omega. \quad (4)$$

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

$$W_{[0,T]} = \int_0^T dt \left\{ - \int_{\partial\Lambda} d\sigma(x) \lambda(t, x) j(t, x) \cdot \hat{n}(x) + \int_{\Lambda} dx j(t, x) \cdot E(t, x) \right\}, \quad (5)$$

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

$$W_{[0,T]} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_{\Lambda} dx j(t) \cdot \chi(\rho(t))^{-1} j(t) \quad (6)$$

where

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

From this equation the inequality follows

$$W_{[0,T]} \geq F(\rho(T)) - F(\rho(0)) \quad (7)$$

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 (5) 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

$$\begin{aligned} & \int_0^T dt \left\{ - \int_{\partial\Lambda} d\sigma(x) \lambda(t, x) j(t, x) \cdot \hat{n}(x) + \int_{\Lambda} dx j(t, x) \cdot E(t, x) \right\} \\ & = F(\rho(T)) - F(\rho(0)) \\ & + \int_0^T dt \int_{\Lambda} dx j(t) \cdot \chi(\rho(t))^{-1} j(t) , \end{aligned} \tag{8}$$

where F is the equilibrium free energy functional,

$$F(\rho) = \int_{\Lambda} dx f(\rho(x)) . \tag{9}$$

Splitting of the current

The current can be split into two parts with opposite transformation properties under time reversal

$$J(\rho) = J_S(\rho) + J_A(\rho), \quad (10)$$

where we define

$$J_S(\rho) = -\chi(\rho) \nabla \frac{\delta V}{\delta \rho}. \quad (11)$$

$V(\rho)$ is the large deviation functional of the stationary ensemble and is the minimal work necessary to create the fluctuation ρ .

$J_S(\rho)$ and $J_A(\rho)$ satisfy the orthogonality relationship

$$\int_{\Lambda} dx J_S(\rho) \cdot \chi(\rho)^{-1} J_A(\rho) = 0. \quad (12)$$

Charged particle in a magnetic field

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

$$\dot{p} = \frac{e}{mc} p \wedge H - \frac{1}{\tau} p, \quad (13)$$

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

$$\dot{p} = -\frac{e}{mc} p \wedge H - \frac{1}{\tau} p \quad (14)$$

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

Ideal gas

Another simple example is the case of a system of independent particles, the corresponding 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

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

$$J_A(\rho) = -\frac{\rho_1 - \rho_0}{L} \frac{\rho}{\bar{\rho}}$$

Circulation of a fluid in a ring

A more interesting example is provided by the circulation of a fluid in a ring. In absence of an external field we have an equilibrium state with constant density $\bar{\rho}$ and $J(\bar{\rho}) = 0$. If we switch on a constant weak driving field E tangent to the ring the system moves rigidly with a current $J(\bar{\rho}) = \chi(\bar{\rho})E$ and the same equilibrium $V(\rho)$. Time reversal corresponds to inverting the current, that is to changing E with $-E$. In this case $J_A(\rho) = \chi(\rho)E$.

A simple calculation shows that J_S and J_A are orthogonal.

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 (6) can be written

$$\int_0^T dt \int_{\Lambda} dx j_S(t) \cdot \chi(u(t))^{-1} j_S(t) + \int_0^T dt \int_{\Lambda} dx j_A(t) \cdot \chi(u(t))^{-1} j_A(t) \quad (15)$$

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

$$\partial_t \rho = \nabla \cdot \left(\chi(\rho) \nabla \frac{\delta V}{\delta \rho} \right) - \nabla J_A(\rho) \quad (16)$$

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

We define the renormalized work

$$W_{[0,T]}^{ren} = F(\rho(T)) - F(\rho(0)) + \int_0^T dt \int_{\Lambda} dx j_S(t) \cdot \chi(u(t))^{-1} j_S(t) \quad (17)$$

from which the stronger inequality follows

$$W_{[0,T]}^{ren} \geq F(\rho(T)) - F(\rho(0)) \quad (18)$$

Equality is obtained for quasi-static transformations. In fact in such a case the integral in (17) 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

$$W_{[0,T]}^{ren} = W_{[0,T]} \quad (19)$$

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

$$\begin{aligned} V_{\bar{\rho}_1}(\bar{\rho}_0) &= \int_0^\infty dt \int_\Lambda dx j_S(t) \cdot \chi(\rho(t))^{-1} j_S(t) \\ &= \lim_{T \rightarrow \infty} \left\{ W_{[0,T]} - \Delta F - \int_0^T dt \int_\Lambda dx j_A(t) \cdot \chi(\rho(t))^{-1} j_A(t) \right\} \quad (20) \\ &= W^{ren} - \Delta F = W^{ren} - \min W^{ren} = W_{ex} \end{aligned}$$

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.

1. *FINITE TIME THERMODYNAMICS*

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

$$\begin{cases} \partial_t \rho^\tau + \nabla \cdot J(t/\tau, \rho^\tau(t)) = 0, \\ j^\tau(t) = J(t/\tau, \rho^\tau(t)) \\ f'(\rho^\tau(t))|_{\partial\Lambda} = \lambda^\tau(t) \\ \rho^\tau(0) = \bar{\rho}(0) \end{cases} \quad (21)$$

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

$$\begin{aligned}
 & \tau \int_0^1 ds \int_{\Lambda} dx j^\tau(\tau s) \cdot E(s) - \tau \int_0^1 ds \int_{\partial\Lambda} d\sigma \lambda(s) j^\tau(\tau s) \cdot \hat{n} \\
 & - \tau \int_0^1 ds \int_{\Lambda} dx J_A(s, \rho^\tau(\tau s)) \chi(\rho^\tau(\tau s))^{-1} J_A(s, \rho^\tau(\tau s)) \\
 & = F(\rho^\tau(\tau)) - F(\bar{\rho}(0)) \\
 & + \tau \int_0^1 ds \int_{\Lambda} dx J_S(s, \rho^\tau(\tau s)) \chi(\rho^\tau(\tau s))^{-1} J_S(s, \rho^\tau(\tau s))
 \end{aligned} \tag{22}$$

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 $\lambda(s)$.

$$j^\tau(\tau s) = J(s, \bar{\rho}(s)) + \frac{1}{\tau} g(s) + O\left(\frac{1}{\tau^2}\right). \quad (23)$$

$$J_S(s, \rho^\tau(\tau s)) = -\frac{1}{\tau} \chi(\bar{\rho}(s)) \nabla (C_s^{-1} \star r(s)) + O\left(\frac{1}{\tau^2}\right). \quad (24)$$

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

r solves

$$\begin{cases} \partial_s \bar{\rho}(s) + \nabla \cdot g(s) = 0 \\ g(s) = -D(\bar{\rho}(s)) \nabla r(s) \\ \quad -r(s) [D'(\bar{\rho}(s)) \nabla \bar{\rho}(s) + \chi'(\bar{\rho}(s)) E(s)] \\ r(s, x) = 0, x \in \partial\Lambda \end{cases} \quad (25)$$

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

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

$$\begin{aligned} & F(\bar{\rho}(1)) - F(\bar{\rho}(0)) \\ &= \int_0^1 ds \int_{\Lambda} dx E(s) \cdot g(s) - \int_0^1 ds \int_{\partial\Lambda} d\sigma \lambda(s) g(s) \cdot n \\ & \quad - \int_0^1 ds \int_{\Lambda} dx r(s) \frac{\chi'(\bar{\rho}(s))}{\chi^2(\bar{\rho}(s))} J^2(s, \bar{\rho}(s)). \end{aligned} \quad (26)$$

Estimate of the energy dissipated by the J_S current to order $1/\tau$

We have to estimate

$$\int_0^\tau dt \int_\Lambda dx J_S(t/\tau, \rho^\tau(t)) \cdot \chi(\rho^\tau(t))^{-1} J_S(t/\tau, \rho^\tau(t)). \quad (27)$$

For large finite τ a direct calculation gives that it is of the order B/τ where

$$B = \int_0^1 ds \int_\Lambda dx \chi(\bar{\rho}(s)) [C_s^{-1} \star r(s)]^2 > 0 \quad (28)$$

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 compute the optimal protocol in the case of homogeneous equilibrium states. We thus assume that the external field vanishes and that the chemical potential does not depend on the space variable. The protocol is thus defined by a real function $\lambda(s)$, $s \in [0, 1]$. The associated stationary solution $\bar{\rho}(s)$ is also constant in space and solves $\lambda(s) = f'(\bar{\rho}(s))$.

The Poisson equation for r is solved by

$$r(s, x) = \frac{\partial_s \bar{\rho}(s)}{D(\bar{\rho}(s))} \int_{\Lambda} dy G_0(x, y) \quad (29)$$

where G_0 is the Green function of the Dirichlet Laplacian on Λ .

Since

$$\frac{\delta^2 V_{\lambda(s), E(s)}(\bar{\rho}(s))}{\delta \rho(x) \delta \rho(y)} = \frac{D(\bar{\rho}(s))}{\chi(\bar{\rho}(s))} \delta(x - y) \quad (30)$$

the term B is given by

$$B = \int_0^1 ds \frac{[\partial_s \bar{\rho}(s)]^2}{\chi(\bar{\rho}(s))} \int_{\Lambda} dx \left[\int_{\Lambda} dy G_0(x, y) \right]^2. \quad (31)$$

Observe that the dependence on space and time factorizes and that the result does not depend at all on the diffusion coefficient. It is now straightforward to minimize B with respect to $\bar{\rho}(s)$ with the constraints $\bar{\rho}(0) = \bar{\rho}_0$, $\bar{\rho}(1) = \bar{\rho}_1$. The minimizer is the unique function satisfying the constraints such that

$$\frac{\partial_s \bar{\rho}}{\sqrt{\chi(\bar{\rho})}} = \text{const.} \quad (32)$$

The optimal λ is then obtained by the relationship $\lambda = f'(\bar{\rho})$.

We next show that in the case of independent particles it is not convenient to pass through non-equilibrium states. For simplicity we restrict to the one dimensional case and we assume that the external field vanishes. We define a protocol in terms of the time dependence of the boundary values $\bar{\rho}_-(s) = \bar{\rho}(s, 0)$ and $\bar{\rho}_+(s) = \bar{\rho}(s, 1)$, $s \in [0, 1]$.

The functional B can be written as

$$B = \int_0^1 ds \int_{\Lambda} dx \frac{1}{4} x^2 (1-x)^2 \times \frac{\left\{ \dot{\bar{\rho}}_-(s) + \frac{1}{3}(1+x)[\dot{\bar{\rho}}_+(s) - \dot{\bar{\rho}}_-(s)] \right\}^2}{\bar{\rho}_-(s) + x[\bar{\rho}_+(s) - \bar{\rho}_-(s)]}$$

By writing the Euler-Lagrange equations, one can check that the protocol $\bar{\rho}_-(s) = \bar{\rho}_+(s) = \bar{\rho}(s)$ satisfying (32) is a stationary point for B .

Dissipation

The infinitesimal version of the identity (6) gives the instantaneous energy balance which reads

$$\dot{W} = \int_{\Lambda} dx [f'(\rho)\dot{\rho} + j \cdot \chi(\rho)^{-1}j] \quad (33)$$

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,

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

Final remarks

The previous discussion shows that a mathematical analysis of real slow transformations between stationary states is possible.

Transformations between equilibrium states is just a special case.

The consequences of the zeroth order equation (26) have to be analysed further.

The expansion provides an infinity of equations. They will involve derivatives of the free energy and their meaning has to be understood.

ANGELO!

IT HAS BEEN A LONG WAY

SINCE WE MET THE FIRST TIME

I WISH YOU MANY MANY MORE YEARS OF WORK

AND HOPE YOU WILL BE ABLE

TO SATISFY YOUR UNLIMITED CURIOSITY