Towards a nonequilibrium thermodynamics: a self-contained macroscopic description of driven diffusive systems

L. Bertini[1] A. De Sole[2] D. Gabrielli[3] G. Jona–Lasinio[4] C. Landim[5]

1 Dipartimento di Matematica, Università di Roma La Sapienza
P.le A. Moro 2, 00185 Roma, Italy
E–mail: lorenzo@carpenter.mat.uniroma1.it

2 Dipartimento di Matematica, Università di Roma La Sapienza, Roma, Italy
Mathematics Department, Harvard University, Cambridge MA, USA
E–mail: desole@math.harvard.edu

3 Dipartimento di Matematica, Università dell'Aquila
67100 Coppito, L'Aquila, Italy
E–mail: gabriell@univaq.it

4 Dipartimento di Fisica and INFN, Università di Roma La Sapienza
P.le A. Moro 2, 00185 Roma, Italy
E–mail: gianni.jona@roma1.infn.it

5 IMPA, Estrada Dona Castorina 110, J. Botanico, 22460 Rio de Janeiro, Brazil
CNRS UPRES–A 6085, Université de Rouen, 76128 Mont–Saint–Aignan Cedex, France
E–mail: landim@impa.br

Vienna, June 2-6, 2008

We present a self-contained macroscopic description of diffusive systems interacting with boundary reservoirs and under the action of external fields. The approach is based on simple postulates which are suggested by a wide class of microscopic stochastic models where they are satisfied. The description however does not refer in any way to an underlying microscopic dynamics: the only input required are transport coefficients as functions of thermodynamic variables, which are experimentally accessible. The basic postulates are local equilibrium which allows a hydrodynamic description of the evolution and a variational principle defining the out of equilibrium free energy. Associated to the variational principle there is a Hamilton-Jacobi equation satisfied by the free energy, very useful for concrete calculations. Correlations over a macroscopic scale are, in our scheme, a generic property of nonequilibrium states. Correlation functions of any order can be calculated from the free energy functional which is generically a non local functional of thermodynamic variables. Special attention is given to the notion of equilibrium state from the standpoint of nonequilibrium.

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*

$$\partial_t \rho + \nabla \cdot j = 0 \tag{2.1}$$

together with the constitutive equation

$$j = J(\rho) = -D(\rho)\nabla\rho + \chi(\rho)E \tag{2.2}$$

The transport coefficients D and χ satisfy the local Einstein relation

$$2\,D(\rho) = \chi(\rho)\, f_0''(\rho) \tag{2.3}$$

where f_0 is the equilibrium free energy of the homogeneous system.

$$f_0'\big(\rho(x)\big) = \lambda_0(x) \qquad\qquad x \in \partial\Lambda \tag{2.4}$$

We denote by $\bar\rho = \bar\rho(x)$, $x \in \Lambda$, the stationary solution, assumed to be unique, of (2.1)–(2.4).

To state the third postulate, we need some preliminaries. Consider a time dependent variation $F = F(t,x)$ of the external field so that the total applied field is $E+F$. The current then becomes $j = J^F(\rho) = J(\rho) + \chi(\rho)F$.

Given a time interval $[0,T]$, we then introduce the total power dissipated by the extra current

$$L_{[0,T]}(F) = \frac{1}{2}\int_0^T dt\, \big\langle \big[J^F(\rho^F) - J(\rho^F)\big] \cdot F \big\rangle = \frac{1}{2}\int_0^T dt\, \big\langle F \cdot \chi(\rho^F) F \big\rangle \quad (2.5)$$

where $\langle \cdot \rangle$ denotes the integration over Λ and ρ^F is the solution of the continuity equation with current $j = J^F(\rho)$.

The argument behind (2.5) is the following. Fix a point (t,x) and let $\rho(t,x)$ be the local density. A local variation dF of the external field induces the variation of current $dj = \chi\big(\rho(t,x)\big)dF$. The infinitesimal power dissipated locally is therefore $F \cdot dj = F \cdot \chi\big(\rho(t,x)\big)dF$. By integrating firstly over dF, keeping the value of $\rho(t,x)$ constant and then over dx and dt we get (2.5).

We define a *cost functional* on the set of space time trajectories as follows. Given a trajectory $\hat\rho = \hat\rho(t,x)$ we set

$$I_{[0,T]}(\hat\rho) = \inf_{F\,:\,\rho^F=\hat\rho} L_{[0,T]}(F) \tag{2.6}$$

namely we minimize over all the variation of the applied field F which produce the trajectory $\hat\rho$. If $\hat\rho$ solves the hydrodynamic equation (2.1)–(2.4) its cost vanishes. In view of (2.5), a computation shows that

$$I_{[0,T]}(\hat\rho) = \frac{1}{2}\int_0^T dt\,\Big\langle \big[\partial_t\hat\rho + \nabla\cdot J(\hat\rho)\big]\, K(\hat\rho)^{-1}\big[\partial_t\hat\rho + \nabla\cdot J(\hat\rho)\big]\Big\rangle \tag{2.7}$$

where the positive operator $K(\hat\rho)$ is defined on functions $u:\Lambda\to\mathbb{R}$ vanishing at the boundary $\partial\Lambda$ by $K(\hat\rho)u = -\nabla\cdot\big(\chi(\hat\rho)\nabla u\big)$.

Our third postulate is then stated as follows.

3. *The nonequilibrium free energy of the system is*

$$\mathcal{F}(\rho) = \inf_{\substack{\hat\rho\,:\,\hat\rho(0)=\bar\rho\\ \hat\rho(+\infty)=\rho}} I_{[0,\infty]}(\hat\rho) \tag{2.8}$$

the functional $\mathcal{F}$ is the maximal solution of the infinite dimensional Hamilton-Jacobi equation

$$\frac{1}{2}\Big\langle \nabla \frac{\delta \mathcal{F}}{\delta \rho} \cdot \chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} \Big\rangle - \Big\langle \frac{\delta \mathcal{F}}{\delta \rho}\, \nabla \cdot J(\rho) \Big\rangle = 0 \tag{2.9}$$

where, for ρ that satisfies (2.4), $\delta\mathcal{F}/\delta\rho$ vanishes at the boundary of Λ. The arbitrary additive constant on such solution is determined by the condition $\mathcal{F}(\bar{\rho}) = 0$. Indeed, by considering the functional in (2.7) as an action functional in variables $\hat{\rho}$ and $\partial_t \hat{\rho}$ and performing a Legendre transform, the associated Hamiltonian is

$$\mathcal{H}(\rho, \Pi) = \frac{1}{2}\Big\langle \nabla \Pi \cdot \chi(\rho) \nabla \Pi \Big\rangle + \Big\langle \nabla \Pi \cdot J(\rho) \Big\rangle \tag{2.10}$$

The optimal trajectory ρ^* for the variational problem (2.8) is characterized as follows. Let

$$J^*(\rho) = -\chi(\rho) \nabla \frac{\delta \mathcal{F}}{\delta \rho} - J(\rho) \tag{2.11}$$

then ρ^* is the time reversal of the solution to

$$\partial_t \rho + \nabla \cdot J^*(\rho) = \partial_t \rho - \nabla \cdot \Big\{ D(\rho) \nabla \rho - \chi(\rho) \Big[E + \nabla \frac{\delta \mathcal{F}}{\delta \rho} \Big] \Big\} = 0 \tag{2.12}$$

with the boundary condition (2.4).

The previous claim is proven as follows. Let $\mathcal{F}$ be the maximal solution of the Hamilton-Jacobi equation and J^* as defined in (2.11). Fix a time interval $[0, T]$ and a path $\hat{\rho}(t)$, $t \in [0, T]$. We claim that

$$I_{[0,T]}(\hat{\rho}) = \mathcal{F}\big(\rho(T)\big) - \mathcal{F}\big(\rho(0)\big) + \frac{1}{2}\int_0^T dt\, \Big\langle \big[\partial_t \hat{\rho} - \nabla \cdot J^*(\hat{\rho})\big]\, K(\hat{\rho})^{-1} \big[\partial_t \hat{\rho} - \nabla \cdot J^*(\hat{\rho})\big] \Big\rangle \tag{2.13}$$

as can be shown by a direct computation using (2.7), the Hamilton-Jacobi equation (2.9) and the definition (2.11) of J^*. From the identity (2.13) we immediately deduce that the optimal path for the variational problem (2.8) is the time reversal of the solution to (2.12).

Since the optimal trajectory is the time reversal of the solution to (2.12), the applied field is

$$F = -\nabla \frac{\delta \mathcal{F}}{\delta \rho}$$

On the other hand, by (2.11) and the Hamilton-Jacobi equation (2.9),

$$\Big\langle \frac{\delta F}{\delta \rho}\, \partial_t \hat{\rho} \Big\rangle = -\Big\langle J(\hat{\rho}) \cdot \chi(\hat{\rho}) \nabla \frac{\delta \mathcal{F}}{\delta \rho} \Big\rangle = \big\langle J(\hat{\rho}) \cdot F \big\rangle$$

which is the power given to system by the applied field F. Hence

$$\mathcal{F}(\rho) - \mathcal{F}(\bar{\rho}) = \int_0^\infty dt\, \Big\langle \frac{\delta \mathcal{F}}{\delta \rho}\, \partial_t \hat{\rho} \Big\rangle = \int_0^\infty dt\, \big\langle J(\hat{\rho}) \cdot F \big\rangle$$

is the total work done by the external field.

Characterization of equilibrium systems

We define the system to be in *equilibrium* if and only if the current in the stationary profile $\bar{\rho}$ vanishes, i.e. $J(\bar{\rho}) = 0$. A particular case is that of a *homogeneous equilibrium state*, obtained by setting the external field $E = 0$ and chosing a constant chemical potential potential at the boundary, i.e. $\lambda_0(x) = \bar{\lambda}$. Let $\bar{\rho} = \text{const.}$ be the equilibrium density, i.e. $\bar{\rho}$ solves $\bar{\lambda} = f_0'(\bar{\rho})$. It is then readily seen that the functional $\mathcal{F}$ defined in (2.8) is given by

$$\mathcal{F}(\rho) = \int_\Lambda dx \, \left\{ f_0\big(\rho(x)\big) - f_0(\bar{\rho}) - f_0'(\bar{\rho}) \big[\rho(x) - \bar{\rho}\big] \right\}$$

in which the first difference is the variation of the free energy f_0 while the second term is due the interaction with the reservoirs.

We next show that also for a non homogenous equilibrium, characterized by a non constant stationary profile $\bar{\rho}(x)$ such that $J(\bar{\rho}) = 0$ the free energy functional $\mathcal{F}$ can be explicitly computed. Let

$$f(\rho, x) = \int_{\bar{\rho}(x)}^{\rho} dr \int_{\bar{\rho}(x)}^{r} ds \; f_0''(s) = f_0(\rho) - f_0(\bar{\rho}(x)) - f_0'\big(\bar{\rho}(x)\big) \left[\rho - \bar{\rho}(x)\right]$$

we claim that the maximal solution of the Hamilton-Jacobi equation (2.9) is

$$\mathcal{F}(\rho) = \int_\Lambda dx \; f\big(\rho(x), x\big) \tag{3.1}$$

Indeed from the previous expression we get

$$\frac{\delta \mathcal{F}}{\delta \rho(x)} = f_0'(\rho(x)) - f_0'(\bar\rho(x))$$

so that, by an integration by parts,

$$\begin{aligned}
&\frac{1}{2}\Big\langle \nabla\big[f_0'(\rho) - f_0'(\bar\rho)\big] \cdot \chi(\rho)\nabla\big[f_0'(\rho) - f_0'(\bar\rho)\big]\Big\rangle \\
&\qquad + \Big\langle \big[f_0'(\rho) - f_0'(\bar\rho)\big]\nabla\cdot\Big[D(\rho)\nabla\rho - \chi(\rho)E\Big]\Big\rangle \\
&= \frac{1}{2}\Big\langle \nabla\big[f_0'(\rho) - f_0'(\bar\rho)\big] \cdot \chi(\rho)\Big[\nabla f_0'(\bar\rho) - 2E\Big]\Big\rangle = 0
\end{aligned}$$

where we used (2.3) and $(1/2)\nabla f_0'(\bar\rho) - E = \chi(\bar\rho)^{-1} J(\bar\rho) = 0$.

In remains to show that $\mathcal{F}$, as defined in (3.1), is the maximal solution to the Hamilton-Jacobi equation (2.9). Recalling (2.7), simple computations show that

$$\begin{aligned}
I_{[0,T]}(\hat\rho) &= \mathcal{F}\big(\hat\rho(T)\big) - \mathcal{F}\big(\hat\rho(0)\big) \\
&\quad + \frac{1}{2}\int_0^T dt\,\Big\langle \big[\partial_t\hat\rho - \nabla\cdot J(\hat\rho)\big]\,K(\hat\rho)^{-1}\big[\partial_t\hat\rho - \nabla\cdot J(\hat\rho)\big]\Big\rangle
\end{aligned} \tag{3.2}$$

which clearly implies the maximality of $\mathcal{F}$.

the condition $J(\bar\rho) = 0$ is equivalent to either one of the following statements.

- There exists a function $\lambda : \Lambda \to \mathbb{R}$ such that

$$2\,E(x) = \nabla\lambda(x)\,, \quad x \in \Lambda \qquad\qquad \lambda(x) = \lambda_0(x)\,, \quad x \in \partial\Lambda \tag{3.3}$$

- The system is *macroscpically reversible* in the sense that for each profile ρ we have $J^*(\rho) = J(\rho)$.

We emphasize that the notion of macroscopic reversibility does not imply that an underlying microscopic model satisfies the detailed balance condition.

We also note that macroscopic reversibility $J(\rho) = J^*(\rho)$ implies the invariance of the Hamiltonian $\mathcal{H}$ in (2.10) under the time reversal symmetry, $(\rho, \Pi) \mapsto \big(\rho, \delta\mathcal{F}/\delta\rho - \Pi\big)$, where $\mathcal{F}$ is the maximal solution of the Hamilton-Jacobi equation (2.9).

So far we have assumed the Einstein relation and we have shown that -for equilibrium systems- it implies (3.1). Conversely, we now show that macroscopic reversibility and (3.1) implies the Einstein relation (2.3). By writing explicitely $J(\rho) = J^*(\rho)$ we obtain

$$-\big[\chi(\rho)R(\rho) - 2D(\rho)\big]\nabla\rho + \chi(\rho)\big[R(\bar\rho) - 2\chi^{-1}(\bar\rho)D(\bar\rho)\big]\nabla\bar\rho = 0 \tag{3.4}$$

where R is the second derivative of f_0 in the case of one-component systems while $R_{ij} = \partial_{\rho_i}\partial_{\rho_j} f_0$ for multi-component systems. In (3.4) we used, besides (3.1), $J(\bar\rho) = 0$ to eliminate E. Note that $J(\bar\rho) = 0$ follows from the Hamilton-Jacobi equation and $J(\rho) = J^*(\rho)$ without further assumptions. Since $\nabla\rho$ and $\nabla\bar\rho$ are arbitrary the Einstein relation $2D = \chi R$ follows from (3.4).

We have defined the macroscopic reversibility as the identity between the currents $J(\rho)$ and $J^*(\rho)$. We emphasize that this is not equivalent to the identity between $\nabla \cdot J(\rho)$ and $\nabla \cdot J^*(\rho)$. Indeed, we next show that there exists a non reversible system, i.e. satisfying $J(\bar{\rho}) \neq 0$, such that the optimal trajectory for the variational problem (2.8) is the time reversal of the solution to the hydrodynamic equation (2.1)–(2.5).

Let $\Lambda = [0,1]$, $D(\rho) = \chi(\rho) = 1$, $\lambda_0(0) = \lambda_0(1) = \bar{\lambda}$, and a constant external field $E \neq 0$. In this case hydrodynamic evolution of the density is given by the heat equation independently of the field E. The stationary profile is $\bar{\rho} = \bar{\lambda}$, the associated current is $J(\bar{\rho}) = E \neq 0$. By a computation analogous to the one leading to (3.2), we easily get that

$$\mathcal{F}(\rho) = \int_0^1 dx \left[\rho(x) - \bar{\rho}\right]^2$$

and the optimal trajectory for the variational problem (2.8) is the time reversal of the solution to the heat equation. On the other hand $J(\rho) = -\nabla \rho + E$ while $J^*(\rho) = -\nabla \rho - E$

Perturbation theory and correlation functions

We introduce the *pressure* functional as the Legendre transform of free energy $\mathcal{F}$

$$\mathcal{G}(h) = \sup_{\rho} \big\{ \langle h\rho \rangle - \mathcal{F}(\rho) \big\}$$

By Legendre duality, the Hamilton-Jacobi equation (2.9) can then be rewritten in terms of $\mathcal{G}$ as

$$\frac{1}{2}\Big\langle \nabla h \cdot \chi\Big(\frac{\delta \mathcal{G}}{\delta h}\Big) \nabla h \Big\rangle - \Big\langle \nabla h \cdot D\Big(\frac{\delta \mathcal{G}}{\delta h}\Big) \nabla \frac{\delta \mathcal{G}}{\delta h} + \chi\Big(\frac{\delta \mathcal{G}}{\delta h}\Big) E \Big\rangle = 0 \tag{4.1}$$

where h vanishes at the boundary of Λ.

The functional $\mathcal{G}$ is the generating functional of the correlation functions; in particular by defining

$$C(x,y) = \frac{\delta^2}{\delta h(x) \delta h(y)} \mathcal{G}(h)$$

we have, since $\mathcal{F}$ has a minimum at $\bar{\rho}$,

$$\mathcal{G}(h) = \langle h, \bar{\rho} \rangle + \frac{1}{2} \langle h, Ch \rangle + o(h^2)$$

or equivalently

$$\mathcal{F}(\rho) = \frac{1}{2} \langle (\rho - \bar{\rho}), C^{-1}(\rho - \bar{\rho}) \rangle + o((\rho - \bar{\rho})^2)$$

By expanding the Hamilton-Jacobi equation (4.1) to the second order in h, and we using that $\delta\mathcal{G}/\delta h(x) = \bar{\rho}(x) + Ch(x) + o(h^2)$, we get the following equation for C

$$\left\langle \nabla h \cdot \left[\frac{1}{2}\chi(\bar{\rho})\nabla h - \nabla(D(\bar{\rho})Ch) + \chi'(\bar{\rho})(Ch)E\right]\right\rangle = 0 \qquad (4.2)$$

We now make the change of variable

$$C(x,y) = C_{eq}(x)\delta(x-y) + B(x,y)$$

where $C_{eq}(x)$ is the equilibrium covariance, given by $C_{eq}(x) = (1/2)D^{-1}(\bar{\rho}(x))\chi(\bar{\rho}(x))$. Equation (4.2) for the correlation function then gives the following equation for B

$$\mathcal{L}^{\dagger}B(x,y) = \alpha(x)\delta(x-y) \qquad (4.3)$$

where $\mathcal{L}^{\dagger}$ is the formal adjoint of the elliptic operator $\mathcal{L} = L_x + L_y$, where

$$L_x = D_{ij}(\bar{\rho}(x))\partial_{x_i}\partial_{x_j} + \chi'_{ij}(\bar{\rho}(x))E_j(x)\partial_{x_i}$$

and

$$\alpha(x) = \partial_{x_i}\left[\chi'_{ij}\left(\bar{\rho}(x)\right) D^{-1}_{jk}\left(\bar{\rho}(x)\right)\bar{J}_k(x)\right]$$

where we racall $\bar{J} = J(\bar{\rho}) = -D(\bar{\rho}(x))\nabla\bar{\rho}(x) + \chi(\bar{\rho}(x))E(x)$ is the macroscopic current in the stationary profile.