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# A Hamiltonian formulation for two hierarchies of thermodynamic evolution equations

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**Abstract.** Two hierarchies of thermodynamic evolution equations leading to continued-fraction expansions for generalized frequency- and wavevector-dependent transport coefficients are cast in Hamiltonian form. In the nonlinear regime, the Jacobi identity implies several requirements on the transport coefficients which had not been previously explored and which are beyond the scope of the thermodynamic restrictions coming from the second law.

## 1. Introduction

The methods of symplectic geometry have been increasingly used in many domains of physics, such as classical mechanics, geometrical optics, fluid mechanics and thermodynamics (Salmon 1988, Arnold and Givental 1990). Here we present an illustration of their use in two hierarchies of thermodynamic evolution equations which arise in the description of high-frequency phenomena in macroscopic systems.

When a macroscopic system is described on a timescale of the order of collision times, as required in ultrasound experiments in dilute gases and in neutron-scattering experiments in liquids, one must take into account not only the usual conserved variables, but a host of fast-relaxing non-conserved ones. At such high frequencies, the local equilibrium is never attained, and the fast variables must be considered as independent ones. The equations describing their evolution are of primary interest in these situations.

Of course, the detailed structure of such equations in real systems is very involved, but some relatively simple schemes have been proposed from several points of view. Some of them yield continued-fraction expansions for the corresponding generalized frequency- and wavevector-dependent transport coefficients. Indeed, from the fluctuation-dissipation theorem it is known that the generalized transport coefficients are proportional to the Fourier transform of the time-correlation function of the corresponding dissipative fluxes. For instance, one has for the generalized electrical conductivity  $\sigma_e(\omega)$  and for the generalized thermal conductivity  $\lambda(\omega)$  the expressions (Kubo 1957, Jou *et al* 1988)

$$\sigma_e(\omega) = (1/kT) \langle \delta J_x \delta J_x \rangle(\omega) \quad (1.1)$$

$$\lambda(\omega) = (1/kT^2) \langle \delta q_x \delta q_x \rangle(\omega) \quad (1.2)$$

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with  $\langle \dots \rangle$  standing for the equilibrium average,  $\delta J$  and  $\delta q$  being the fluctuations of the electric current and of the heat flux around their zero equilibrium value. Thus, the evolution equations describing the decay of the fluctuations of the fluxes around equilibrium are directly related to the generalized transport coefficients, consistent with the fluctuation-dissipation theorem.

Some relatively simple schemes of the evolution equations for the fluctuations yield continued-fraction expansions of the form (Mori 1965, Jou *et al* 1988)

$$\sigma_c(\omega) = \frac{\langle \delta J_x(0) \delta J_x(0) \rangle (kT)^{-1}}{1 + i\omega\tau_1 + \frac{a_1(k)}{1 + i\omega\tau_2 + \frac{a_2(k)}{1 + i\omega\tau_3 + \frac{a_3(k)}{1 + i\omega\tau_4 + \dots}}}} \quad (1.3)$$

with  $\delta J(0)$  the initial value of the fluctuation,  $\tau_i$  a set of suitable relaxation times and  $a_i(k)$  a set of coefficients which may be a function of the wavevector  $k$ .

The usual non-equilibrium thermodynamics, based on the local-equilibrium hypothesis, only gives information on the low-frequency limit of the transport coefficients, unless some internal variables are taken into account. However, other thermodynamic developments, such as the so-called extended irreversible thermodynamics (EIT) (Nettleton 1959, Casas-Vázquez *et al* 1984, Muller 1985, Jou *et al* 1988, García-Colín 1988), are able to cope with generalized transport coefficients and, in particular, with developments of the form of a continued fraction (Pérez-García and Jou 1985, 1986). The aim of EIT is to formulate a set of evolution equations for non-conserved variables, usually taken to be the common dissipative fluxes (heat flux, diffusion flux, electric flux, viscous pressure tensor, etc.) but extended to higher-order fluxes when it turns out to be necessary.

The aim of this paper is to provide a Hamiltonian formulation for the evolution of the fast variables leading to (1.3). There are several reasons that justify this aim. Conciseness and elegance is one of them: the whole set of equations is replaced by a single relation which, furthermore, throws a new light on the generating functional, which may be generally identified with a well defined physical quantity, such as entropy or Gibbs free energy (Grmela 1986, 1989). Besides this, the Hamiltonian formulation allows one to use of subtle and powerful mathematical techniques developed for general Hamiltonian systems (Holm *et al* 1985, Salmon 1988, Arnold and Givental 1990).

More important even is the fact that the Hamiltonian requirement yields a set of restrictions on the transport coefficients appearing in the reversible part of the evolution equations. Such restrictions are beyond the reach of non-equilibrium thermodynamics. To make it evident in a simple but very illustrative and important set of equations is the main result of this paper.

The equations of the standard version of EIT, involving only the heat flux and the viscous pressure tensor (Jou *et al* 1988), have been recently cast in Hamiltonian form by Grmela and Lebon (1990), to which we refer for explicit details. The present extension to hierarchies of equations has an interest on its own: it is more general, it has specific physical motivations, it may be written in a very compact form and it provides new information on nonlinear transport coefficients.

Sections 2 and 3 deal respectively with the homogeneous and the inhomogeneous situations. Section 2 is motivated by the well known Mori development of continued-

fraction expansions (Mori 1965) of the time-correlation functions based on projection-operator techniques. Section 3 comes from the higher-order moments developments of the non-equilibrium distribution function in kinetic theory of gases (Grad 1959, Waldmann 1967, Hess 1977, Eu 1981). The interest of both lines of research is a further motivation for the present attempt to write the corresponding equations in Hamiltonian form and to explore the Hamiltonian restriction in a nonlinear version. In section 4 we study explicitly the consequences of the Hamiltonian hypothesis on the nonlinear transport coefficients.

**2. The homogeneous problem**

Assume a solid electrical conductor subjected to an electric field  $\mathbf{E}$ . Let  $u$  be the specific internal energy per unit mass and  $\mathbf{J}$  the electric current density. The evolution equation for  $u$ , when the heat flux is disregarded, is

$$\rho \dot{u} = \mathbf{E} \cdot \mathbf{J}. \tag{2.1}$$

In standard non-equilibrium thermodynamics (De Groot and Mazur 1962), the entropy is assumed to be a function of the classical variables ( $u$ , in the present situation). In the simplest version of EIT, one assumes that the entropy  $s$  per unit mass depends also on the electric flux, i.e.  $s = s(u, \mathbf{J})$  (Jou *et al* 1988). More generally, one may assume (Jou and Ferrer 1989) that the entropy depends also on higher-order time derivatives of  $\mathbf{J}$ . To make them into independent quantities, we define (Mori 1965)

$$\begin{aligned} \mathbf{J}_1(t) &= \mathbf{J}(t) \\ \mathbf{J}_2(t) &= \dot{\mathbf{J}}_1(t) - (\dot{\mathbf{J}}_1(t), \mathbf{J}_1(0))\mathbf{J}_1(0) \\ \mathbf{J}_3(t) &= \dot{\mathbf{J}}_2(t) - (\dot{\mathbf{J}}_2(t), \mathbf{J}_2(0))\mathbf{J}_2(0) - (\dot{\mathbf{J}}_2(t), \mathbf{J}_1(0))\mathbf{J}_1(0) \end{aligned} \tag{2.2}$$

where  $(\mathbf{A}, \mathbf{B})$  is a 'scalar product' defined as

$$(\mathbf{A}, \mathbf{B}) = \int \hat{\mathbf{A}} \cdot \hat{\mathbf{B}} f_{eq} d\Gamma \tag{2.3}$$

with  $\hat{\mathbf{A}}$  and  $\hat{\mathbf{B}}$  the microscopic operators of  $\mathbf{A}$  and  $\mathbf{B}$ ,  $f_{eq}$  the equilibrium distribution function and  $d\Gamma$  the volume differential in the phase space. With this definition, the several  $\mathbf{J}_i(0)$  are uncorrelated with each other around equilibrium.

In EIT the generalized Gibbs equation is written as (Jou and Ferrer 1989)

$$ds = T^{-1} du - \sum_i v \alpha_i \mathbf{J}_i \cdot d\mathbf{J}_i \tag{2.4}$$

with  $v$  the specific volume per unit mass and  $\alpha_i$  parameters which may depend on  $\mathbf{J}_i \cdot \mathbf{J}_i$ , and whose physical meaning will be considered below. We will be interested in the evolution of fluctuations of  $\mathbf{J}_i$  around equilibrium in an isolated system ( $\mathbf{E} = 0$ ). In this case, the entropy production associated with the decay of the  $\mathbf{J}_i$  has the form

$$\sigma = -\sum_i \alpha_i \mathbf{J}_i \cdot \dot{\mathbf{J}}_i \tag{2.5}$$

where a dot denotes the material time derivative (we assume the system to be at rest here).

By following the usual methods of non-equilibrium thermodynamics we assume a linear relation between  $\dot{J}_i$  and the  $J_i$ . Since in this paper we are interested in the thermodynamic information about continued-fraction expansions, we assume a set of evolution equations for the  $J_i$  in the following tridiagonal form:

$$\begin{aligned} -\alpha_1 \dot{J}_1 &= \mathcal{U}'_1 J_1 + \mathcal{U}'_{12} J_2 \\ -\alpha_2 \dot{J}_2 &= \mathcal{U}'_{21} J_1 + \mathcal{U}'_2 J_2 + \mathcal{U}'_{23} J_3 \\ -\alpha_i \dot{J}_i &= \mathcal{U}'_{i,i-1} J_{i-1} + \mathcal{U}'_i J_i + \mathcal{U}'_{i,i+1} J_{i+1}. \end{aligned} \quad (2.6)$$

This set of equations directly leads to a continued-fraction expansion, as it is immediately seen in (2.7). Note that a more general set of equations could have been assumed, including more couplings in (2.6). However, since we are interested here in continued-fraction expansions and on an illustration of the restrictions coming from the Hamiltonian hypothesis, the set (2.6) is sufficient for our study.

In order to ensure that the entropy production is positive, the matrix of the phenomenological coefficients  $\mathcal{U}'_{ij}$  must be positive definite (this implies, amongst other requirements, that  $\mathcal{U}'_i \geq 0$ ). Furthermore, the Onsager-Casimir reciprocity relations imply  $\mathcal{U}'_{i,i-1} = -\mathcal{U}'_{-i,-i}$  because of the opposite time-reversal parity of  $J_i$  and  $J_{i-1}$ . Note that in the linear theory the coefficients  $\mathcal{U}'_{ij}$  do not depend on the fluxes  $J_k$ .

The set (2.6) yields for the Fourier transform of the time-correlation function of the fluctuations  $\delta J_i$

$$\langle \delta J_1 \delta J_1 \rangle(\omega) = \frac{\langle \delta J_1(0) \delta J_1(0) \rangle}{1 + i\omega\tau_1 + \frac{\mathcal{U}'_{12}\mathcal{U}'_{21}}{1 + i\omega\tau_2 + \frac{\mathcal{U}'_{23}\mathcal{U}'_{32}}{1 + i\omega\tau_3 + \dots}}} \quad (2.7)$$

which, according to the fluctuation-dissipation theorem (1.1) leads to a continued-fraction expansion for the generalized electrical conductivity  $\sigma_e(\omega)$ . Here, we have identified

$$\tau_i = \alpha_i / \mathcal{U}'_i \quad \mathcal{U}'_{i,i+1} = \mathcal{U}'_{i,i-1} / \mathcal{U}'_i. \quad (2.8)$$

One may also note that  $\alpha_i \geq 0$  because the entropy must be a maximum in equilibrium. In fact, the coefficients  $\alpha_i$  may be related to the second moments of the fluctuations of the corresponding  $J_i$  around equilibrium as

$$\langle \delta J_{i\alpha} \delta J_{i\beta} \rangle = (k_B / \alpha_i) \delta_{\alpha\beta} \quad (2.9)$$

where  $k_B$  is the Boltzmann constant.

To study the dynamics of the fluxes around a non-equilibrium steady state characterized by an electric field  $E$ , one may use as a potential the Legendre transform of  $s$  given by

$$\tilde{s}[E] = s(u, J_i) + \alpha_i v \sigma_e E \cdot J_1. \quad (2.10)$$

This potential satisfies

$$\partial \tilde{s} / \partial J_1 = -v \alpha_1 [J_1 - \sigma_e E] \quad \partial \tilde{s} / \partial J_i = -v \alpha_i J_i \quad (i \geq 2). \quad (2.11)$$

Following the same procedure as before, one finds for the corresponding evolution equations for the fluctuations around the steady-state value

$$\begin{aligned} -\alpha_1 \dot{J}_1 &= \mathcal{U}'_1 (J_1 - \sigma_e E) + \mathcal{U}'_{12} J_2 \\ -\alpha_2 \dot{J}_2 &= \mathcal{U}'_{21} (J_1 - \sigma_e E) + \mathcal{U}'_2 J_2 + \mathcal{U}'_{23} J_3 \\ -\alpha_i \dot{J}_i &= \mathcal{U}'_{i,i-1} J_{i-1} + \mathcal{U}'_i J_i + \mathcal{U}'_{i,i+1} J_{i+1} \end{aligned} \quad (2.12)$$

which give rise to a decay of the fluctuations of the same form as in the equilibrium situation.

We want now to write the hierarchy (2.6) of evolution equations in the form (Grmela 1986, 1989, Grmela and Lebon 1990)

$$dA/dt = \{A, G\} + [A, G] \tag{2.13}$$

with  $\{A, G\}$  a Poisson bracket,  $[A, G]$  a dissipative bracket and  $G$  a generating potential.

Let us first consider the reversible part, which is assumed to be Hamiltonian, i.e. to derive from a Poisson bracket formalism with a given generating functional. We use here as a Poisson bracket (Salmon 1988)

$$\{A, B\} = \sum_i \mu_i [(\partial A / \partial J_i)(\partial B / \partial J_{i+1}) - (\partial A / \partial J_{i+1})(\partial B / \partial J_i)]. \tag{2.14}$$

For the moment, we consider the  $\mu_i$  as constant parameters. It is easy to see that (2.14) is indeed a Poisson bracket because it satisfies (Salmon 1988, Arnold and Givental 1990)

$$\{A, B\} = -\{B, A\} \tag{2.15}$$

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0 \tag{2.16}$$

for every  $A, B, C$  function of the  $J_s$ . The second equality, the so-called Jacobi identity, will play a central role in section 4.

As the generating function  $G$  we take the Gibbs free energy

$$G = U - T\tilde{S} \tag{2.17}$$

which satisfies

$$\partial G / \partial J_1 = Tv\alpha_1 [J_1 - \sigma_e E] \quad \partial G / \partial J_i = Tv\alpha_i J_i \quad (i \geq 2). \tag{2.18}$$

It is easy to see that the hierarchies (2.6) and (2.12), without the dissipative part (corresponding to the diagonal terms in  $\mathcal{U}'_i$ ) follow from

$$dA/dt = \{A, G\} \tag{2.19}$$

provided one identifies

$$\mu_i = \mathcal{U}'_{i+1,i} (\alpha_{i+1} \alpha_i v)^{-1}. \tag{2.20}$$

The Onsager-Casimir antireciprocity comes now automatically from (2.19).

We now turn our attention to the irreversible part of (2.6) and (2.12). By following Grmela (1986, 1989), we define the dissipative bracket as

$$[A, G] = -\sum_i (\partial A / \partial J_i) (\partial \phi / \partial G_i) \tag{2.21}$$

with  $G_i$  standing for  $(\partial G / \partial J_i)$  and  $\phi$  a dissipative potential such that

$$\phi = \sum_i s_i (\partial \phi / \partial s_i) \tag{2.22}$$

$s_i$  being equal to  $(\partial s / \partial J_i)$ .

Note that when (2.6) is introduced into (2.5) and when one takes into account the antisymmetry of the  $\mathcal{U}'_{ij}$ , one obtains for the entropy production

$$\sigma = \rho \dot{s} = \sum_i \mathcal{U}'_i J_i \cdot J_i. \tag{2.23}$$

In the non-equilibrium steady state around an electric field  $\mathbf{E}$  we may use relation (2.23) but with the Legendre transform  $\tilde{s}$  of the entropy instead of  $s$  itself. This yields, according to (2.12),

$$\tilde{\sigma} = \sum_i \mathcal{U}'_i \mathbf{J}_i \cdot \mathbf{J}_i \quad (2.24)$$

with  $\tilde{\mathbf{J}}_1 = \mathbf{J}_1 - \sigma_e \mathbf{E}$  and  $\tilde{\mathbf{J}}_i = \mathbf{J}_i$  ( $i \geq 2$ ). Thus, we may write the potential  $\phi$  as

$$\tilde{\phi} = (T/2) \sum_i (\alpha_i / \tau_i) \tilde{\mathbf{J}}_i \cdot \tilde{\mathbf{J}}_i \quad (2.25)$$

When the prescriptions (2.14) and (2.21) are followed, (2.6) and (2.12) come directly from (2.13). Thus, the free energy of EIT acts as a generating function for the dynamics of those hierarchies.

It is also of interest to outline that this generating function is related to the fluctuations of the fluxes around a non-equilibrium steady state through

$$\text{Pr}(\delta u, \delta \mathbf{J}_i) \sim \exp(-(k_B T)^{-1} \Delta G) \quad (2.26)$$

where  $\Delta G$  is the change in the free energy associated with the fluctuation with respect to the steady state. Thus, (2.10) and (2.17) may be used to recast previous results on the fluctuations of the electric current around its steady-state value (Jou *et al* 1982), where the probability was directly related to the second differential of the non-equilibrium entropy instead of being related to the change in  $G$ .

### 3. The inhomogeneous problem

We deal here with an inhomogeneous situation. To be specific, we concentrate on the problem of heat transport in a rigid heat conductor. Other situations, such as diffusion or shear viscous pressure, could be studied in an analogous way.

The balance equation for the internal energy  $u$  is, for a rigid heat conductor,

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} \quad (3.1)$$

We have neglected the work related with volume variations because of the rigid character of the conductor. Whereas in standard non-equilibrium thermodynamics the entropy  $s$  would only depend on  $u$ , in the simplest form of EIT one assumes that it also depends on  $\mathbf{q}$  (Jou *et al* 1988). We take here a more general point of view and assume that  $s$  depends on the successive higher-order fluxes (Pérez-García and Jou 1986), i.e. we take as variables  $\mathbf{a}_1 = \mathbf{q}$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ , ... in which  $\mathbf{a}_n$ , a tensor of order  $n$ , is the flux of  $\mathbf{a}_{n-1}$ , a tensor of order  $n-1$ . The motivation to include the whole set of fluxes instead of only the heat flux is that all of them become 'slow' variables when  $\mathbf{q}$  becomes slow because their relaxation times are of the same order.

The generalized Gibbs equation now has the form (Pérez-García and Jou 1986)

$$ds = T^{-1} du - \sum_i v \alpha_i \mathbf{a}_i \cdot d\mathbf{a}_i \quad (3.2)$$

where a dot between the two tensors of order  $i$  stands for their complete contraction and  $v$  is the specific volume per unit mass. Furthermore, since we are now in an inhomogeneous situation, we need the entropy flux. We assume that it depends on all the fluxes  $\mathbf{a}_i$  as (Pérez-García and Jou 1986)

$$\mathbf{J}^s = T^{-1} \mathbf{q} - \sum_i \beta_i \mathbf{a}_{i+1} \cdot \mathbf{a}_i \quad (3.3)$$

Here, the dot means the contraction of  $\mathbf{a}_{i+1}$  and  $\mathbf{a}_i$  to give a vector.

The entropy production is given by

$$\begin{aligned} \rho \dot{s} + \nabla \cdot \mathbf{J}^s &= \mathbf{q} \cdot \nabla T^{-1} - \sum_i \mathbf{a}_i \cdot [\alpha_i d\mathbf{a}_i/dt + \beta_i \nabla \cdot (\mathbf{a}_{i+1}) + \nabla(\beta_{i-1} \mathbf{a}_{i-1})] \\ &= -\mathbf{q} \cdot [T^{-2} \nabla T + \alpha_1 d\mathbf{a}_1/dt + \beta_1 \nabla \cdot \mathbf{a}_2] \\ &\quad - \sum_i \mathbf{a}_i \cdot [\alpha_i d\mathbf{a}_i/dt + \beta_i \nabla \cdot (\mathbf{a}_{i+1}) + \nabla(\beta_{i-1} \mathbf{a}_{i-1})]. \end{aligned} \tag{3.4}$$

First, we will restrict our attention to the decay of the fluxes towards their zero value in a system in equilibrium ( $\nabla T = 0$ ). The simplest evolution equations for  $\mathbf{a}_i$  compatible with the positive character of the entropy production are

$$\alpha_i d\mathbf{a}_i/dt + \beta_i \nabla \cdot (\mathbf{a}_{i+1}) + \nabla(\beta_{i-1} \mathbf{a}_{i-1}) = -\mathcal{U}_i \mathbf{a}_i \tag{3.5}$$

with  $\mathcal{U}_i \geq 0$ . The definition of  $\mathbf{a}_{i+1}$  as the flux of  $\mathbf{a}_i$  implies  $\beta_i = \alpha_i$ . By identifying the relaxation time  $\tau_i$  of  $\mathbf{a}_i$  as  $\tau_i = \alpha_i/\mathcal{U}_i$ , one may write (3.5) as

$$d\mathbf{a}_i/dt + \nabla \cdot (\mathbf{a}_{i+1}) + (1/\alpha_i) \nabla(\alpha_{i-1} \mathbf{a}_{i-1}) = -(1/\tau_i) \mathbf{a}_i. \tag{3.6}$$

This hierarchy of equations leads to

$$\begin{aligned} \langle \delta q_x \delta q_x \rangle(\omega, k) &= \frac{\langle \delta q_x(0) \delta q_x(0) \rangle}{1 + i\omega\tau_1 + l_1^2 k^2} \\ &\quad \frac{1}{1 + i\omega\tau_2 + l_2^2 k^2} \\ &\quad \frac{1}{1 + i\omega\tau_3 + \dots} \end{aligned} \tag{3.7}$$

with  $\delta q(0)$  the initial value of the fluctuation and  $l_i^2 = (\alpha_i/\alpha_{i+1})\tau_i\tau_{i+1}$ . A hierarchy like (3.5) generalizes the Maxwell-Cattaneo equation obtained when  $l_i^2 = 0$  ( $i \geq 1$ ) and  $\tau_j = 0$  ( $j \geq 2$ ) and is useful for the analysis of thermal waves, a topic of experimental and theoretical interest (Jou *et al* 1988, Joseph and Preziosi 1989).

To study the evolution of the fluctuations of the  $\mathbf{a}_i$  around a non-equilibrium steady state characterized by a temperature gradient  $\nabla T$  one may use, in analogy to (2.11), the Legendre transform of  $\tilde{s}$

$$\tilde{s}[\nabla T] = s(u, \mathbf{a}_i) - v\alpha_1 \lambda \nabla T \cdot \mathbf{a}_1 \tag{3.8}$$

which yields

$$\partial \tilde{s} / \partial \mathbf{q} = -v\alpha_1 [\mathbf{q} + \lambda \nabla T] \quad \partial \tilde{s} / \partial \mathbf{a}_i = -v\alpha_i \mathbf{a}_i \quad (i \geq 2) \tag{3.9}$$

with  $\lambda$  the thermal conductivity. Thus, to describe the evolution equations for the fluctuations around a non-equilibrium steady state one may write the same evolution equations as in (3.5) but using  $\tilde{\mathbf{a}}_i$  defined as  $\tilde{\mathbf{a}}_1 = \mathbf{q} + \lambda \nabla T$ ,  $\tilde{\mathbf{a}}_i = \mathbf{a}_i$  ( $i \geq 2$ ), by analogy with what has been done in the preceding section.

We want now to write (3.6) in the form of (2.13). Since we are in an inhomogeneous situation, there appear some differences with respect to the previous section. Following Grmela (1989) and Grmela and Lebon (1990), we define the quantity

$$\{A, B\} = V^{-1} \int d\mathbf{r} \sum_i \mu_i [\nabla(\partial A / \partial \mathbf{a}_i) \cdot (\partial B / \partial \mathbf{a}_{i+1}) - \nabla(\partial B / \partial \mathbf{a}_i) \cdot (\partial A / \partial \mathbf{a}_{i+1})]. \tag{3.10}$$

Integration by parts yields

$$\{A, B\} = V^{-1} \int d\mathbf{r} \sum_i -[(\partial A / \partial \mathbf{a}_i) \cdot \nabla \cdot (\mu_i \partial B / \partial \mathbf{a}_{i+1}) + \mu_i (\partial A / \partial \mathbf{a}_{i+1}) \cdot \nabla(\partial B / \partial \mathbf{a}_i)] \tag{3.11}$$



which turns out to be a Poisson bracket when the  $\mu_i$  are constant. If they are not, the Jacobi identity (2.16) will imply that the  $\mu_i$  satisfy specific differential equations.

The bracket definition (3.11) and the use of the free energy  $G = \int d\mathbf{r}(u - T_0\bar{s})$ , with  $T_0$  a constant reference temperature, as the generating potential, yields the reversible part of (3.6), i.e. the left-hand side of (3.6), provided one identifies  $\mu_i = (T_0\alpha_{i+1})^{-1}$ . Note that  $\alpha_1 = \tau_1(\lambda T^2)^{-1}$ , with  $\tau_1$  the relaxation time of  $\mathbf{q}$ .

The dissipative part is formally identical to that of the previous section. Indeed, the entropy production obtained when (3.6) are introduced into (3.4) is

$$\sigma = \sum_i (\alpha_i / \tau_i) \mathbf{a}_i \cdot \mathbf{a}_i. \quad (3.12)$$

As in (2.21) we define the dissipative bracket as

$$[A, G] = -V^{-1} \int d\mathbf{r} \sum_i (\partial A / \partial \mathbf{a}_i) \cdot (\partial \phi / \partial \mathbf{G}_i) \quad (3.13)$$

with  $\mathbf{G}_i = (\partial G / \partial \mathbf{a}_i)$  and  $\phi$  a dissipative potential defined as in (2.22) and which now has the form

$$\phi = (T_0/2) \sum_i (\alpha_i / \tau_i) \mathbf{a}_i \cdot \mathbf{a}_i. \quad (3.14)$$

The definitions (3.10) and (3.13) of the Poisson bracket and the dissipative bracket and the use of the generalized free energy of EIT and the dissipative potential (3.14) allow one to write the hierarchy (3.6) of evolution equations in the compact form (2.13).

Note that the two kinds of hierarchies treated in sections 2 and 3 are not fundamentally different from each other. The term in the divergence of the flux  $\mathbf{a}_{i+1}$  in the evolution equation for  $\mathbf{a}_i$  may be considered as the part of  $d\mathbf{a}_i/dt$  orthogonal (in the statistical mechanical sense, i.e. according to the scalar product (2.3)) to the variables of lower orders, so that the general structure of section 2 could also cover the one in section 3. We have preferred to keep both presentations separated from each other for pedagogical reasons.

#### 4. The nonlinear regime: Hamiltonian versus thermodynamic restrictions

To write the dynamic equations of EIT in Hamiltonian form is much more than a formal exercise. To make the physical interest of such a reformulation evident, we must go to the nonlinear regime and *suppose that the transport coefficients are themselves functions of the dynamic variables*.

We concentrate our attention on the problem studied in section 2 (the other one, being inhomogeneous, leads to a much more complicated situation, though the basic ideas are of course the same). From the point of view of thermodynamics, the only pieces of information on the coefficients appearing in (2.6) are

$$\alpha_i(\mathbf{J}_j) \geq 0 \quad \mathcal{U}'_i(\mathbf{J}_j) \geq 0 \quad \mathcal{U}'_{i,i+1}(\mathbf{J}_j) = -\mathcal{U}'_{i+1,i}(\mathbf{J}_j). \quad (4.1)$$

Observe that now these coefficients are assumed to depend on the dynamic variables  $\mathbf{J}_j$ . With respect to the coefficients  $\mu_i$  identified in (2.20), nothing may be said from a thermodynamic point of view, since  $\mathcal{U}'_{i,i+1}$  may be positive or negative: thus, no particular restrictions arise on them.

In contrast, the Hamiltonian formulation is more stringent. This is so because of the requirements arising from the Jacobi identity (2.16). We will explore them in detail. To do that, it is useful to write the Poisson bracket in the form (Salmon 1988)

$$\{F, G\} = (\partial F / \partial J_i) J^{ij} (\partial G / \partial J_j) \tag{4.2}$$

where  $J^{ij}$  is an antisymmetric matrix given, in our case, by

$$J^{ij} = -J^{ji} = \mu_i \delta_{j,i+1}. \tag{4.3}$$

It is easily seen that indeed (4.2) and (4.3) are equivalent to the Poisson bracket (2.14). In terms of the elements of the matrix  $J^{ij}$ , the Jacobi identity (2.16) may be written as (Salmon 1988, p 230, Arnold and Givental 1990, p 32)

$$J^{im} (\partial J^{jk} / \partial J_m) + J^{jm} (\partial J^{ki} / \partial J_m) + J^{km} (\partial J^{ij} / \partial J_m) = 0. \tag{4.4}$$

Summation with respect to repeated indices is understood in (4.2) and (4.4). Given the special form of  $J^{ij}$  used in (4.3), (4.4) leads to the conditions (for  $j = i + 1, k = i + 2$ )

$$-\mu_i (\partial \mu_{i+2} / \partial J_i) + \mu_{i+1} (\partial \mu_{i+2} / \partial J_{i+2}) - \mu_{i+2} (\partial \mu_{i+1} / \partial J_{i+2}) + \mu_{i+3} (\partial \mu_{i+1} / \partial J_{i+4}) = 0. \tag{4.5}$$

To illustrate the restrictions (4.5) explicitly we assume, as a particular example, that the  $\mu_i$  are of the form

$$\mu_i = \mu_{i0} \exp \left( \sum_j a_{ij} J_j \cdot J_j \right). \tag{4.6}$$

When (4.6) are introduced into (4.5), and given the independent character of  $J_1, \dots, J_n \dots$  one finds the restrictions

$$a_{i+2,i} = 0 \quad a_{i+2,i+2} = a_{i+1,i+2} \quad a_{i+1,i+4} = 0. \tag{4.7}$$

In more explicit terms, one solution of (4.5) would be

$$\mu_i = \mu_{i0} \exp(a_i J_i \cdot J_i + a_{i+1} J_{i+1} \cdot J_{i+1}) \tag{4.8}$$

where the coefficients  $a_i$  do not depend on  $J_j$  but only on  $T$  and  $p$  (temperature and pressure of the system).

The restrictions (4.4) are valid for arbitrary  $i, j$  and  $k$ . The conditions (4.5) have been obtained for the special case  $j = i + 1, k = i + 2$ . One may obtain other restrictions on the  $\mu_i$  by considering different values of  $j$  and  $k$ . Due to (4.3), when  $j = k$ , (4.4) yields an identically vanishing expression. When  $j = i + 1$  and  $k = i + n$ , with  $n > 2$ , (4.4) and (4.3) yield

$$\mu_{i+n} (\partial \mu_i / \partial J_{i,n+1}) - \mu_{i+n-1} (\partial \mu_i / \partial J_{i+n-1}) = 0 \tag{4.9}$$

and for  $j = i + n, k = i + n + 1$  ( $n > 2$ )

$$\mu_i (\partial \mu_{i+n} / \partial J_{i+1}) - \mu_{i-1} (\partial \mu_{i+n} / \partial J_{i-1}) = 0. \tag{4.10}$$

If the form (4.6) for the  $\mu_i$  is used, (4.9) and (4.10) lead respectively to

$$a_{i,m} = 0 \quad (m > i + 2) \quad a_{m,i} = 0 \quad (m < i). \tag{4.11}$$

In synthesis, if the form (4.6) is adopted, then it follows that  $a_{i,j} = 0$  except when  $j = i$  or  $j = i + 1$ , i.e. the expression (4.8) is the only one allowed.

*The restrictions (4.5), (4.9) and (4.10) are clearly not obtainable from purely thermodynamic arguments, but arise in a very direct way in the Hamiltonian formalism. To our knowledge, these restrictions have never been mentioned in the literature on non-equilibrium thermodynamics.*

Let us finally mention that a Lagrangian formalism has been used by Nettleton (1986) to explore EIT in the nonlinear regime, but in another context different from the hierarchies studied in this paper and without using the conditions arising from the Jacobi identity.

### 5. Concluding remarks

Probably the most interesting result of the present paper concerns the *possibility of obtaining restrictions on the nonlinear transport coefficients* of the non-dissipative part of the constitutive equations for the evolution of the thermodynamic fluxes. Of course, whether the non-dissipative dynamics is really Hamiltonian or not should be decided experimentally. From a theoretical point of view, the hypothesis that the conservative part is Hamiltonian appears quite reasonable: the underlying microscopic dynamics is Hamiltonian and the hydrodynamics of the ideal fluid is also Hamiltonian (Salmon 1988). It seems normal to think that the conservative part of the evolution equations at the intermediate stages defined by taking more and more higher-order fluxes in the description should also be Hamiltonian.

The analysis in this paper shows a new argument to introduce the fluxes as independent variables into the entropy or into the Gibbs free energy. Several arguments have been examined at length by Jou *et al* (1988). Here, it can be seen that their introduction into the thermodynamic potentials allows one to use them as generating potentials, giving to the non-dissipative part of the evolution equations a Hamiltonian structure, *which would not have been achieved with the classical thermodynamic potentials*. This reinforces the physical convenience of their consideration as thermodynamic independent variables and, furthermore, it enlightens the role of the generalized potentials as generating functions of the dynamics of the fluxes (which are considered as 'fast' variables in the classical theory and as 'slow' variables in EIT, due to the difference of time-scale considered in both theories).

Another comment refers to the meaning of the positivity of the entropy production, which is taken as a postulate in EIT. Here, it is seen that the positive character of the generalized entropy production ensures that the generalized description including fast variables will decay to a local-equilibrium hydrodynamics in a short time. In fact, if we assume a (purely hypothetical) situation in which  $\tau_1 \gg \tau_2 \gg \dots$ , the positivity of the generalized entropy used in this paper would require that the description in terms of  $n$  variables would tend to the description in terms of  $n-1$  variables after a time  $\tau_{n-1} > t > \tau_n$ . In such a case, these hierarchical models offer a simple illustration of a many-level description of the system, ranging from the local-equilibrium one at long times to a completely kinetic description in terms of an infinite number of variables at very short times (in fact, for a system of  $N$  particles the microscopic description would require  $6N$  variables, which may be taken as infinite in the thermodynamic limit).

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