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# On a non-equilibrium partition function for heat conduction

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**Abstract.** We provide a physical interpretation for the Lagrange multipliers associated with heat conduction in an information-theoretical description of non-equilibrium systems. Such an identification is based on the generalised Gibbs equation of extended irreversible thermodynamics.

## 1. Introduction

The statistical description of non-equilibrium steady states is one of the central aims of non-equilibrium statistical mechanics. Information theory has been applied to such a problem (Levine and Tribus 1979) in order to define non-equilibrium ensembles similar to the Gibbsian ensembles used in equilibrium statistical mechanics (Zubarev 1974). Such ensembles could be clarifying in some aspects of the definition of nonequilibrium entropies or in the analysis of statistical aspects of non-equilibrium fluctuations near steady states, which are open problems in non-equilibrium thermodynamics.

Assume a system of  $N$  particles with fixed mean energy  $U$  and mean heat flux  $Q$ . For the description of this system, and in analogy with equilibrium statistical mechanics, the information-theoretical approach leads to a partition function of the form

$$Z = (h^{3N} N!)^{-1} \int d\Gamma \exp(-\beta H - \gamma \cdot J) \quad (1.1)$$

where  $h$  is Planck's constant,  $d\Gamma$  is the volume differential in the phase space of the system,  $H$  is the Hamiltonian and  $J$  the microscopic heat flux operator, and  $\beta$  and  $\gamma$  are Lagrange multipliers. The latter ones are determined by the conditions imposed by the information we have on the system, which are expressed by the equations

$$U = \langle H \rangle = -\partial \ln Z / \partial \beta \quad \text{and} \quad Q = \langle J \rangle = -\partial \ln Z / \partial \gamma. \quad (1.2)$$

The information-theoretical formulation has been applied to an ideal gas transporting energy but not mass, by Corbet and Morowitz (1972), Corbet (1974) and Nisbet and Gurney (1974). Furthermore, heat flow in a linear harmonic chain has been analysed on this basis by Miller and Larson (1979). However, these works, based on specific microscopic models, provide a computation but not a physical interpretation for  $\gamma$ . Such an interpretation is the main aim of this paper. Indeed, it would be desirable to have such a physical interpretation for  $\gamma$  in some general conditions without any recourse to microscopic calculations. In this way, all Lagrange multipliers appearing in (1.1) would be treated on the same footing and could be assigned a macroscopic

meaning. The problem here has been the lack of a generalised Gibbs equation applicable to this situation.

Our purpose is not only to translate into non-equilibrium the symmetry with which Lagrange multipliers are considered in equilibrium grand canonical ensemble, but it has also a practical point of view. Without a physical interpretation of the Lagrange multipliers, information theory does not lead to any expressions for dissipative coefficients. In contrast, an identification of such multipliers increases the potentiality of information theory with the possibility of computing dissipative coefficients, provided the relaxation times of the corresponding fluxes are known.

In § 2, we present our identification of the Lagrange multipliers of the generalised partition function. In § 3 we compare our identification with other alternative procedures for identifying the multipliers. In § 4 we apply this formalism to the computation of non-equilibrium equations of state and the pair-correlation function.

## 2. Identification of Lagrange multipliers

The identification of the Lagrange multipliers in (1.1) is carried out by comparison with the macroscopic expression for the generalised Gibbs equation usual in extended irreversible thermodynamics (Nettleton 1960, Müller 1967, Lebon 1978, Casas-Vázquez *et al* 1984). Such a theory includes the dissipative fluxes amongst the set of independent thermodynamic variables and, therefore, it considers a generalised entropy which depends on both classical variables and dissipative fluxes. In our case we consider  $U$  and  $Q$  as independent variables and the corresponding Gibbs equation takes the form (Casas-Vázquez and Jou 1981)

$$dS = T^{-1} dU - (\tau/\lambda T^2 V) Q \cdot dQ. \quad (2.1)$$

Here  $\lambda$  is the thermal conductivity,  $V$  the volume and  $\tau$  the relaxation time of the heat flux, as given by the Maxwell–Cattaneo equation

$$\tau \dot{Q} + Q = -\lambda \nabla \nabla T. \quad (2.2)$$

In fact,  $T$  is not strictly the local-equilibrium absolute temperature, but has some second-order corrections in  $Q^2$ , which are of the form (Casas-Vázquez and Jou 1981)

$$T^{-1} = T_{\text{eq}}^{-1} - \frac{1}{2} [\partial(\tau/\lambda T^2 V)/\partial U] Q^2 \quad (2.3)$$

where  $T_{\text{eq}}$  is the local-equilibrium absolute temperature. We omit here these corrections for a greater transparency of the development.

We may work in analogy with equilibrium statistical mechanics. When the mean energy  $U$  and the mean number of particles  $N$  are specified, the most probable distribution function is of the form

$$f \sim \exp(-\beta H - \alpha N') \quad (2.4)$$

with  $N'$  the microscopic particle-number operator, and  $\beta$  and  $\alpha$  Lagrange multipliers. This is the grand canonical distribution function. The Gibbs equation is in this case the classical one

$$dS = T^{-1} dU - \mu T^{-1} dN \quad (2.5)$$

with  $\mu$  the chemical potential. Through a standard procedure, one arrives at the

following identification of the Lagrange multipliers

$$\beta = 1/kT \quad \text{and} \quad \alpha = -\mu/kT. \quad (2.6)$$

In our case, the most probable distribution function is, according to information theory and corresponding to (1.1),

$$f \sim \exp(-\beta H - \gamma \cdot J) \quad (2.7)$$

while instead of (2.5) we have the generalised Gibbs equation (2.1). A parallel procedure leads to

$$\beta = 1/kT \quad \text{and} \quad \gamma = -\tau Q/k\lambda T^2 V. \quad (2.8)$$

While the process leading from (2.5) to (2.6) is classical and well known, the one leading to (2.8) is conceptually more problematic, because it deals with the newer and still open problems of non-equilibrium thermodynamic potentials.

In equilibrium statistical mechanics, the second derivatives of  $\ln Z$  are linked to the fluctuations of  $U$  and  $N$ . A similar situation is found in our development, where we obtain

$$\begin{aligned} \langle \delta U^2 \rangle &= \partial^2 \ln Z / \partial \beta^2 = kT^2 C \\ \langle \delta Q^2 \rangle &= \partial^2 \ln Z / \partial \gamma^2 = k\lambda T^2 V / \tau \end{aligned} \quad (2.9)$$

where  $C$  is the thermal capacity of the system. The first expression is the classical one while the second is a particular form of the fluctuation-dissipation theorem.

In this section we have provided an interpretation of the Lagrange multipliers  $\beta$  and  $\gamma$  in a way independent of any microscopic model. This identification is limited to a local description of systems not too far from equilibrium and satisfying Maxwell-Cattaneo laws. This loss of generality as compared with the equilibrium situation is not at all surprising, since dynamics offers a much greater diversity than just equilibrium and it is more involved to deal with.

### 3. Comparison with some previous results

The aim of this section is to compare our formalism with previous works in order to provide more elements of plausibility for the present results. Since the identification (2.8) is independent of any microscopic models, we shall be able to compare with previously known results in kinetic theory of gases and in information-theoretical approaches to heat flux in harmonic chains. These results confirm our identification, and provide an alternative method to obtain it, at least in the domain of validity of the generalised Gibbs equation.

It is usually convenient to start the analysis of non-equilibrium phenomena in dilute gases from the relaxation-time approximation to the Boltzmann equation for the one-particle distribution function  $f(\mathbf{r}, \mathbf{v}, t)$  per unit volume in the absence of external forces

$$(\partial/\partial t + \mathbf{v} \cdot \nabla)f = -\tau^{-1}(f - f_{\text{eq}}) \quad (3.1)$$

where  $\tau$  is the relaxation of time of  $f$  and  $f_{\text{eq}}$  is the local-equilibrium distribution. One gets for the non-equilibrium distribution function in the steady state, up to first order in  $\tau$ ,

$$f = f_{\text{eq}}[1 + (\tau/kT^2\lambda)\mathbf{q}(\mathbf{v}) \cdot \mathbf{q}_0]. \quad (3.2)$$

Here,  $\mathbf{q}(\mathbf{v}) = \frac{1}{2}(m\mathbf{v}^2 - 5kT)\mathbf{v}$  is the heat-flux microscopic operator for one particle, whereas  $\mathbf{q}_0 = -\lambda\nabla T$  is the steady mean heat flux as given by Fourier's law. It may be seen that (3.2) is a special case of (2.7) because for a dilute gas both the Hamiltonian and the total heat flux are merely additive quantities and therefore the total distribution function is the product of the distribution functions of the particles. If the mean heat flux  $\mathbf{q}_0$  is small in such a way that  $\exp(-\boldsymbol{\gamma} \cdot \mathbf{q}) \approx 1 - \boldsymbol{\gamma} \cdot \mathbf{q}$ , we recover (3.2) from (2.7).

Note that this provides an alternative procedure of identifying  $\boldsymbol{\gamma}$ , by developing the exponential up to first order in  $\boldsymbol{\gamma}$  and comparing with the kinetic expression (3.2). This leads of course to the same results. The difference between both procedures is that ours starts from the generalised Gibbs equation and arrives at (3.2) as a consequence. In the alternative method, (3.2) would be the starting point and the generalised Gibbs equation a derived result. This duality of possibilities is also known in equilibrium statistical mechanics, where the multipliers  $\beta$  and  $\alpha$  can be identified both from the Gibbs equation or from the thermodynamic expressions for ideal gases. The first procedure seems to us more elegant than the second one.

As an illustration of the practical advantage of our interpretation over previous formulations of this problem, we may compare our development with that of Nisbet and Gurney (1974). These authors have obtained for the Lagrange multiplier  $\boldsymbol{\gamma}$  in the case of a dilute gas  $\boldsymbol{\gamma} = -(2m/5\rho k^3 T^3)\mathbf{Q}$ , where  $\rho$  is the particle number density. This is as far as a computation of  $\boldsymbol{\gamma}$  may lead. However, if we dispose of our interpretation (2.8) for  $\boldsymbol{\gamma}$  we may identify  $(\tau/k\lambda T^2) = (2m/5\rho k^3 T^3)$ , since we are working per unit volume. As a consequence we obtain for the thermal conductivity  $\lambda = \frac{5}{2}(k^2 T/m)\rho\tau$ , in accordance to the results of kinetic theory. Without the physical interpretation of  $\boldsymbol{\gamma}$  this result would not be obtainable.

Furthermore, we compare our results with those of Miller and Larson (1979) for heat flow in a closed linear harmonic chain of  $N$  oscillators. This chain is isotopic to  $\frac{1}{2}N$  two-dimensional oscillators. In such a case, Miller and Larson obtain for  $\beta$  and  $\boldsymbol{\gamma}$

$$\beta = (1/\varepsilon)(1+x^2)(1-x^2)^{-1} \quad \text{and} \quad \boldsymbol{\gamma} = -N\beta 2\mathbf{x}(1+x^2)^{-1} \quad (3.3)$$

with  $\varepsilon$  the average energy per particle  $\varepsilon = E/N$  and  $\mathbf{x}$  the relative heat flux  $\mathbf{x} = \mathbf{Q}/\varepsilon$ . Here, mass, time and energy are suitably normalised so that phonon velocity is taken as unity. Since there is no interaction between modes, there are no collisions between phonons so that both  $\tau$  and  $\lambda$  diverge. However, we may obtain a value for the ratio  $\tau/\lambda$  from the well known expression (two dimensions)  $\lambda = \frac{1}{2}c^2 C\tau$ . In this case  $c$  (phonon velocity) is unity and  $C$  (specific heat per unit length) is equal to  $k$  (Boltzmann's constant), so that  $\tau/\lambda = 2/k$ . Neglecting second-order terms, this result agrees with (2.8). Note that if an anharmonic term is included in the Miller-Larson formalism, their analysis becomes very involved. However, to a first approximation, our model predicts that the final result will be the same, with the only difference of both  $\tau$  and  $\lambda$  being finite in this case.

#### 4. Non-equilibrium equations of state and pair-correlation function

The partition function (1.1) may be used to compute non-equilibrium equations of state for the generalised entropy and pressure. Here, we analyse briefly the latter equation, which provides a basis for some of our previous work (Jou and Pérez-García 1983). In particular, one may use the perturbative methods of the theory of non-ideal

equilibrium systems (McQuarrie 1976) by considering the dissipative part  $-\boldsymbol{\gamma} \cdot \mathbf{J}$  as a perturbation to the equilibrium Hamiltonian. In this way, one may develop

$$Z = Z(\text{eq}) \langle \exp(-\boldsymbol{\gamma} \cdot \mathbf{J}) \rangle \approx Z(\text{eq}) [1 - \langle \boldsymbol{\gamma} \cdot \mathbf{J} \rangle + \frac{1}{2} \boldsymbol{\gamma}^2 \langle \mathbf{J}^2 \rangle]. \tag{4.1}$$

Here  $\langle \rangle$  means the equilibrium average, so that  $\langle \boldsymbol{\gamma} \cdot \mathbf{J} \rangle = 0$  and  $\langle \mathbf{J}^2 \rangle = k\lambda T^2 V / \tau$ , according to (2.9). Furthermore,  $Z(\text{eq})$  stands for the equilibrium partition function.

In this way, we obtain a second-order development for the partition function  $Z(\beta, \boldsymbol{\gamma})$ . From here, one could define a generalised free energy  $F(\beta, \boldsymbol{\gamma})$  as  $F = -\beta^{-1} \ln Z$ . However, in order to compare with our previous work it is preferable to have  $\mathbf{Q}$  instead of  $\boldsymbol{\gamma}$  as independent variable. As in classical thermodynamics, such a change of variables is suitably carried out by means of a Legendre transformation (Callen 1960) of the form  $F'(\beta, \mathbf{Q}) = F(\beta, \boldsymbol{\gamma}) + \boldsymbol{\gamma} \cdot \mathbf{Q}$ , which leads to

$$F'(\beta, \mathbf{Q}) = F_{\text{eq}}(\beta) + \frac{1}{2} (\tau / \lambda TV) \mathbf{Q}^2. \tag{4.2}$$

The latter expression for the free energy may be used to obtain the equation of state for the pressure, defined as  $p = -(\partial F' / \partial V)_{T, \mathbf{Q}}$ . We are led to

$$p = p_{\text{eq}} + \frac{1}{2} kT [\partial (\tau / k\lambda T^2 V) \mathbf{Q}^2 / \partial V] \tag{4.3}$$

where  $p_{\text{eq}}$  is the local-equilibrium pressure. An equation of this kind has been used (Jou and Pérez-García 1983) with a Van der Waals expression for  $p_{\text{eq}}$  as an illustration to evaluate the modifications on the crucial point of a fluid in the presence of a heat flux.

A physical explanation of these non-equilibrium modifications of the equations of state is the distortion produced in the pair-correlation function by the presence of a heat flux. As a consequence, the analysis of such a function is of interest from both the theoretical and the experimental points of view. The distortion induced by a shear has been studied by Hess (1980), Hess and Hanley (1982) and Evan and Watts (1980), either from molecular dynamics or from the Smoluchowsky equation. Here we take a different approach, based on the partition function (1.1), to illustrate a possible field of application of the present formalism.

As in equilibrium statistical mechanics, we define the pair-correlation function  $g(r)$  as

$$g(r) = V^2 N! [N^2 (N-2)! Z]^{-1} \int \exp(-\beta H - \boldsymbol{\gamma} \cdot \mathbf{J}) d\mathbf{r}_3 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N. \tag{4.4}$$

In the classical expression the dissipative term is lacking because  $\boldsymbol{\gamma} = \mathbf{0}$ .

The microscopic operator for  $\mathbf{J}$  is in general (Resibois and De Leener 1977)

$$\mathbf{J} = \sum_{i=1}^N \{ (\frac{1}{2} m \mathbf{v}_i^2 + \frac{1}{2} \varphi(r_{ij}) - h') \mathbf{v}_i - \mathbf{v}_i \cdot [\frac{1}{2} \partial \varphi(r_{ij}) / \partial \mathbf{r}_{ij}] \mathbf{r}_{ij} \} \tag{4.5}$$

where  $h'$  is the enthalpy per unit volume and  $\varphi(r_{ij})$  is the interaction potential between particles  $i$  and  $j$ . According to (4.4) one gets, up to second order in  $\mathbf{Q}$ ,

$$g(r, \boldsymbol{\gamma}) = g_{\text{eq}}(r) [1 - k\lambda T^2 V \tau^{-1} \boldsymbol{\gamma}^2] + (V/N)^2 (3kT/m) A \boldsymbol{\gamma}^2 \tag{4.6}$$

with  $A = (\frac{1}{4} [\varphi^2 - 2\boldsymbol{\varphi} \mathbf{r} \cdot \partial \varphi / \partial \mathbf{r} + 2r^2 (\partial \varphi / \partial r)^2]) (\int \exp(-\beta \varphi) d\mathbf{r})^{-1}$ . In the work of Evans and Watts, based on molecular dynamics, the development of the pair-correlation function in terms of the shear rate is non-analytic. In this case, the relaxation time  $\tau$  would be a non-analytic function of  $Q^2$  (Pérez-García and Jou 1982, 1983), but we do not deal with this case here.

### 5. Concluding remarks

The present ideas being macroscopic, and therefore rather general, may be applied not only to heat conduction but also to other kinds of dissipative processes. In the case of viscous and heat conducting fluids, the generalised Gibbs equation reads as (Jou and Casas-Vázquez 1980)

$$dS = dS_{\text{eq}} - (\tau_1/\lambda T^2 V) \mathbf{Q} \cdot d\mathbf{Q} - (\tau_2/2\eta TV) \mathbf{P}^v \cdot d\mathbf{P}^v \quad (5.1)$$

where  $S_{\text{eq}}$  stands for the classical local-equilibrium entropy,  $\lambda$  and  $\eta$  are thermal conductivity and shear viscosity, respectively,  $\mathbf{P}^v$  is the viscous pressure tensor and  $\tau_1$  and  $\tau_2$  are the respective relaxation times of  $\mathbf{Q}$  and  $\mathbf{P}^v$ . Neglecting here heat conduction, which has been studied in the preceding sections, it is seen that a partition function analogous to (1.1) may be obtained with the replacement of  $\mathbf{J}$  by  $\mathbf{\Pi}$ , the microscopic operator for the viscous pressure tensor, and of  $-(\tau_1 \mathbf{Q}/\lambda T^2 V)$  by  $-(\tau_2 \mathbf{P}^v/2\eta TV)$ . One is led in this way to

$$Z = (h^{3N} N!)^{-1} \int d\Gamma \exp[-\beta H + (\tau_2/2k\eta TV) \mathbf{P}^v \cdot \mathbf{\Pi}]. \quad (5.2)$$

In dealing with electrical conductors, the corresponding generalised Gibbs equation is (Jou and Llebot 1980)

$$dS = dS_{\text{eq}} - (\tau/\sigma TV) \mathbf{I} \cdot d\mathbf{I} \quad (5.3)$$

where  $\mathbf{I}$  is the electric current integrated over the volume  $V$ ,  $\sigma$  the electrical conductivity and  $\tau$  the relaxation time of  $\mathbf{I}$ . We have in this case

$$Z = (h^{3N} N!)^{-1} \int d\Gamma \exp[-\beta H + (\tau/k\sigma TV) \mathbf{I} \cdot \mathbf{J}_e] \quad (5.4)$$

Our treatment is limited to systems described by linear constitutive equations of the Maxwell–Cattaneo kind. Therefore, it is not possible to carry out an indiscriminate higher-order development of the distribution function, which is only valid up to second order in the fluxes, because this is the limit of validity of the starting Gibbs equation. Though the importance of these limitations, this model has the advantage of giving a general macroscopic interpretation of the Lagrange multipliers appearing in information theory and it strongly underlines the interconnection between the macroscopic generalised entropy and the microscopic developments based on information theory.

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