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Non-equilibrium hydrodynamic fluctuations and a generalised entropy

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Abstract. We study the non-equilibrium corrections to the classical Landau–Lifshitz formulae for the fluctuations of the heat flux and of the viscous pressure. Our analysis is based both on a non-equilibrium entropy and on a microscopic model. The results are of the same order but not coincident.

1. Introduction

The description of non-equilibrium fluctuations in thermodynamic systems has deserved a great deal of attention for many years (Lax 1960). The analysis of hydrodynamic fluctuations near non-equilibrium steady states has received a great impulse in the last two years, with the theoretical prediction and experimental confirmation of some new features, mainly an asymmetry between the two Brillouin lines in the light-scattering spectrum in a fluid with a temperature or a velocity gradient, which has stimulated an intensive research in this field (Procaccia *et al* 1979, Ronis *et al* 1979, 1980, Tremblay *et al* 1981).

The purpose of this paper is to analyse some aspects of an extended thermodynamic formalism in connection with non-equilibrium hydrodynamic fluctuations. In previous papers (Jou *et al* 1980, Jou and Casas-Vázquez 1980) we have shown that starting from a generalised entropy that contains as supplementary variables the dissipative fluxes (Müller 1967, Lebon *et al* 1980) and from a generalised Einstein relation for the probability of fluctuations, we are directly led in equilibrium to a particular form of the fluctuation–dissipation theorem for the fluctuations of the heat flux and of the viscous pressure tensor. Our aim here is to analyse the non-equilibrium situation or, more specifically, to study the non-equilibrium corrections to the classical Landau–Lifshitz formulae for the fluctuations of dissipative fluxes in the presence of a temperature or a velocity gradient.

As is well known, purely phenomenological analyses of non-equilibrium fluctuations are problematic and generally inaccurate. However, since our entropy contains as independent variables some characteristic non-equilibrium parameters (the dissipative fluxes), it seems convenient to explore its ability to describe non-equilibrium fluctuations. With this in mind, we proceed also to the computation of the non-equilibrium corrections starting from a microscopic model based on a relaxational kinetic equation.

In § 2 we give a brief account of the extended thermodynamic theory and in § 3 we recall its application to equilibrium fluctuations to compute numerical values for the generalised equations of state. In §§ 4 and 5 we analyse heat fluctuations in a fluid with an imposed temperature gradient and viscous pressure fluctuations in the presence of a velocity gradient, respectively. In § 6 we calculate the corresponding corrections from a microscopic model, and in the concluding remarks we comment on the discrepancies between both results.

2. Extended irreversible thermodynamics

Our first aim is to formulate a thermodynamic framework able to describe the response of macroscopic systems to moderately high frequencies, i.e. for frequencies much lower than the inverse of the mean collision time between the particles of the system but high enough to produce some modifications to the results of the classical hydrodynamic theory. In the usual limit of very low frequency phenomena, the description of the system is based on its classical 'slow' conserved variables, such as the density, the linear momentum and the internal energy (Forster 1975). When the frequency of the perturbation becomes somewhat higher, comparable for instance to the relaxation times of the dissipative fluxes, we have to take account of these fluxes as new independent 'slow' variables, since in such short times they are no longer univocally determined by the spatial gradients of the classical hydrodynamic variables. Such an approach has been taken in some microscopic theories, as for instance in the thirteen-moments development of the kinetic theory of gases (Grad 1959) or dense fluids (Eu 1980) or in a memory-function analysis of generalised hydrodynamics of simple fluids (Akcasu and Daniels 1970). Our purpose in this section is to present a brief account of a thermodynamic formalism which includes as independent variables not only the classical ones but also the dissipative fluxes.

One of the central quantities in a thermodynamic theory is the entropy. In the classical theory of irreversible processes, one assumes that the entropy production is locally and instantaneously positive definite, which is in fact a statement stronger than the classical formulation of the second law, which is a global statement. From this requirement, one deduces some restrictions on the constitutive equations for the dissipative fluxes. In the usual linear theory, these restrictions imply the positive character of the thermal conductivity λ, the bulk viscosity ζ and the shear viscosity μ. Here, we look for more general constitutive equations for the dissipative fluxes. In order to obtain them from a thermodynamic point of view, we assume the existence of a generalised entropy s which is defined locally and which depends on the above mentioned set of variables,

$$s = s(u, v, \boldsymbol{q}, p^{\mathrm{v}}, \mathring{\boldsymbol{P}}^{\mathrm{v}}) \tag{1}$$

where u is the internal energy per unit mass, v the specific volume and $\boldsymbol{q}$, p^{v} and $\mathring{\boldsymbol{P}}^{\mathrm{v}}$ are the heat flux, the scalar viscous pressure and traceless viscous pressure, respectively. Assuming that (1) is differentiable enough, one can proceed in a way similar to the usual development of classical irreversible thermodynamics (De Groot and Mazur 1962) to obtain second-order constitutive equations for the evolution of the new independent variables, namely the dissipative fluxes, while the evolution of the classical variables is given by the well known balance equations of mass, linear momentum

and energy

$$\rho\dot{v} = \nabla\cdot\boldsymbol{v}, \tag{2}$$

$$\rho\dot{\boldsymbol{v}} = -\nabla\cdot\boldsymbol{P} + \rho\boldsymbol{F}, \tag{3}$$

$$\rho\dot{u} = -\nabla\cdot\boldsymbol{q} - \boldsymbol{P}:\boldsymbol{V}. \tag{4}$$

In these equations, ρ is the mass density, $\boldsymbol{F}$ the external body force per unit mass, $\boldsymbol{v}$ the baricentric velocity, $\boldsymbol{V}$ the symmetric part of the velocity gradient and $\boldsymbol{P}$ the pressure tensor, which is given by $\boldsymbol{P} = (p + p^{\mathrm{v}})\boldsymbol{U} + \mathring{\boldsymbol{P}}^{\mathrm{v}}$, with p the thermodynamic pressure and $\boldsymbol{U}$ the unit matrix, the colon between two tensors standing for their respective double contraction.

In the simplest linear approximation, the generalised constitutive equations for the evolution of the dissipative fluxes reduce to the well known Maxwell–Cattaneo relaxational equations (Lebon *et al* 1980). We do not develop the formalism in detail, because the reader may find longer accounts, for instance, in Lebon (1978), Jou *et al* (1979) and Lebon *et al* (1980). In the present approximation, the evolution equations of the dissipative fluxes are

$$\dot{\boldsymbol{q}} = -\tau_1^{-1}(\boldsymbol{q} + \lambda\nabla T), \tag{5}$$

$$\dot{p}^{\mathrm{v}} = -\tau_0^{-1}(p^{\mathrm{v}} + \zeta\nabla\cdot\boldsymbol{v}), \tag{6}$$

$$(\mathring{\boldsymbol{P}}^{\mathrm{v}})^{\cdot} = -\tau_2^{-1}(\mathring{\boldsymbol{P}}^{\mathrm{v}} + 2\mu\mathring{\boldsymbol{V}}). \tag{7}$$

Here, the τ's stand for the relaxation times of the respective fluxes. In the stationary limit, these equations reduce to the classical Fourier and Newton–Stokes equations. They can be justified from kinetic theory of gases in a relaxation-time approximation (Nonnenmacher 1980) or in the context of several different approximations (Carrassi 1978). Though very simple, they have been used for instance for the analysis of ultrasonic dispersion and absorption in monatomic gases (Carrassi and Morro 1972) and for the description of second sound in dielectric crystals at low temperatures, and they can be deduced from a Boltzmann equation for phonons (Guyer and Krumhansl 1966, Rogers 1971). It must be noted that more general equations may be obtained either from kinetic theory (Burnett equations) or from a thermodynamic formalism. Here, we take them as the simplest possible model able to describe in a direct way some features which are not covered by the classical non-equilibrium thermodynamics. In the case of a quiescent fluid, the Burnett equations reduce simply to (5)–(7), so that their use is provided with plausible physical meaning.

It has been shown on different occasions (Jou *et al* 1980, Jou and Casas-Vázquez 1980) that the generalised Gibbs equation compatible with the constitutive equations (5)–(7) is given by

$$\mathrm{d}s = \theta^{-1}\,\mathrm{d}u + \theta^{-1}\pi\,\mathrm{d}v - (\tau_1 v/\lambda T^2)\boldsymbol{q}\cdot\mathrm{d}\boldsymbol{q} - (\tau_0 v/\zeta T)p^{\mathrm{v}}\,\mathrm{d}p^{\mathrm{v}} - (\tau_2 v/2\mu T)\mathring{\boldsymbol{P}}^{\mathrm{v}}:\mathrm{d}\mathring{\boldsymbol{P}}^{\mathrm{v}} \tag{8}$$

where the equations of state for θ^{-1} and $\theta^{-1}\pi$, which are analogous to the classical equations of state of thermostatics, may be obtained up to order two in the dissipative fluxes from the generalised Maxwell relations corresponding to the equality of the second-order mixed derivatives of s. Indeed, from (8) we have

$$(\theta^{-1})_{\boldsymbol{q}} = -(\alpha_1)_u\boldsymbol{q}, \qquad (\theta^{-1})_p v = -(\alpha_0)_u p^{\mathrm{v}}, \qquad (\theta^{-1})_{\boldsymbol{P}^{\mathrm{v}}} = -(\alpha_2)_u\mathring{\boldsymbol{P}}^{\mathrm{v}}, \tag{9}$$

with $\alpha_1 \equiv \tau_1 v/\lambda T^2$, $\alpha_0 \equiv \tau_0 v/\zeta T$, $\alpha_2 \equiv \tau_2 v/2\mu T$, and where the subscripts stand for

partial derivatives, for instance, $(\theta^{-1})_q$ denotes $(\partial\theta^{-1}/\partial \boldsymbol{q})$. From (9) one can derive

$$\theta^{-1} = T^{-1}(u, v) - \tfrac{1}{2}[(\alpha_1)_u \boldsymbol{q}^2 + (\alpha_0)_u p^{\mathrm{v}2} + (\alpha_2)_u \mathring{\boldsymbol{P}}^{\mathrm{v}} : \mathring{\boldsymbol{P}}^{\mathrm{v}}] \tag{10}$$

and analogously, one can obtain

$$\theta^{-1}\pi = T^{-1}p(u, v) - \tfrac{1}{2}[(\alpha_1)_v \boldsymbol{q}^2 + (\alpha_0)_v p^{\mathrm{v}2} + (\alpha_2)_v \mathring{\boldsymbol{P}}^{\mathrm{v}} : \mathring{\boldsymbol{P}}^{\mathrm{v}}]. \tag{11}$$

In these expressions, T and p are the usual local-equilibrium absolute temperature and thermodynamic pressure respectively. The corresponding non-equilibrium contributions to the equation of state for θ were recently examined by Casas-Vázquez and Jou (1981) for a class of rigid heat conductors. While in general these corrections are small, they play a significant role in the analysis of non-equilibrium fluctuations. It may be seen from (8) that the relaxational terms of the generalised equations (5)–(7) modify the classical Gibbs equation in such a form that the local equilibrium is in fact not consistent with such generalised constitutive equations.

3. Equilibrium fluctuations and dissipative coefficients

As is well known, the equilibrium fluctuations of the thermodynamic fluxes are intimately connected with the dissipative coefficients, which are some of the central quantities of non-equilibrium thermodynamics. This connection has been stated in a rigorous mathematical form in the diverse formulations of the fluctuation–dissipation theorem (Balescu 1975) and it has inspired a great deal of research and development in statistical mechanics. As we have shown (Jou and Casas-Vázquez 1980), the non-equilibrium entropy defined in (8) leads in a very direct way to the fluctuation–dissipation theorem when the dynamics of the fluctuations of the fluxes is described by (5)–(7). This close connection of the generalised entropy with the fluctuation–dissipation theorem is a satisfactory feature not shared by other *a priori* formulations of non-equilibrium entropies as, for instance, in rational thermodynamics (Truesdell 1969).

The purpose of this section is to use the theory of fluctuations of the dissipative fluxes in equilibrium to evaluate the coefficients α_i of (10) and (11), or, in other words, to obtain microscopic values for the dissipative coefficients. In order to obtain some information on the fluctuations we assume, as in the classical theory (Callen 1960, chap 15), that the probability W of the fluctuations at constant temperature and pressure, and for fixed values of the temperature gradient and the velocity gradient, is given by

$$W \sim \exp[(1/2k)\delta^2 S] \tag{12}$$

where k is Boltzmann's constant. It is known (Callen 1960) that this approximate Gaussian distribution function, the so-called Einstein relation, predicts the second moments correctly, but it does not predict third and higher moments accurately. However, we are only interested in the second moments, so that we may restrict ourselves to the use of the simple Einstein formula (12). Of course, in our case S is the generalised entropy defined by (8), and not simply the classical equilibrium entropy.

The second differential of the generalised entropy as obtained from (8) is given by

$$\delta^2 s = \theta_u^{-1}(\delta u)^2 + 2\theta_v^{-1}\delta u\delta v + (\theta^{-1}\pi)_v(\delta v)^2 - \alpha_1\delta\boldsymbol{q}\cdot\delta\boldsymbol{q} - \alpha_0(\delta p^{\mathrm{v}})^2 - \alpha_2\delta\mathring{\boldsymbol{P}}^{\mathrm{v}}:\delta\mathring{\boldsymbol{P}}^{\mathrm{v}}$$
$$-2\boldsymbol{q}_0\alpha_{1u}\delta u\cdot\delta\boldsymbol{q} - 2\boldsymbol{q}_0\alpha_{1v}\delta v\cdot\delta\boldsymbol{q} - 2p_0^{\mathrm{v}}\alpha_{0u}\delta u\delta p^{\mathrm{v}} - 2p_0^{\mathrm{v}}\alpha_{0v}\delta v\delta p^{\mathrm{v}}$$
$$-2\mathring{\boldsymbol{P}}_0^{\mathrm{v}}\alpha_{2u}\delta u:\delta\mathring{\boldsymbol{P}}_{\mathrm{v}} - 2\mathring{\boldsymbol{P}}_0^{\mathrm{v}}\alpha_{2v}\delta v:\delta\mathring{\boldsymbol{P}}^{\mathrm{v}}. \tag{13}$$

In equilibrium, $\boldsymbol{q}_0 = 0$, $p_0^{\mathrm{v}} = 0$ and $\boldsymbol{P}_0^{\mathrm{v}} = 0$, so that this latter expression becomes very simplified. When it is introduced into (12) with M the mass of the system considered, we obtain for the probability of fluctuations

$$\Pr(\delta u, \delta v, \delta\boldsymbol{q}, \delta p^{\mathrm{v}}, \delta\mathring{\boldsymbol{P}}^{\mathrm{v}})$$
$$\sim\exp\{-(M/2k)[T_u^{-1}(\delta u)^2 + 2T_v^{-1}\delta v\delta u$$
$$+(T^{-1}p)_v(\delta v)^2 - \alpha_1\delta\boldsymbol{q}\cdot\delta\boldsymbol{q} - \alpha_0(\delta p^{\mathrm{v}})^2 - \alpha_2\delta\mathring{\boldsymbol{P}}^{\mathrm{v}}:\delta\mathring{\boldsymbol{P}}^{\mathrm{v}}]\}. \tag{14}$$

Note that while M is fixed, the volume of the system $V = Mv$ may fluctuate, so that this expression may be applied to compressible systems. The corresponding second moments of the fluctuations are respectively

$$\langle\delta u\delta u\rangle = -(k/M)(\partial T^{-1}/\partial u)_{pT^{-1}}^{-1}, \tag{15}$$

$$\langle\delta v\delta v\rangle = -(k/M)(\partial T^{-1}p/\partial v)_T^{-1}, \tag{16}$$

$$\langle\delta u\delta v\rangle = -(k/M)(\partial T^{-1}/\partial v)_{pT^{-1}}^{-1}, \tag{17}$$

which are just the classical results (Callen 1960) and

$$\langle\delta q_i\delta q_j\rangle = k\lambda T^2\tau_1^{-1}V^{-1}\delta_{ij}, \tag{18}$$

$$\langle\delta p^{\mathrm{v}}\delta p^{\mathrm{v}}\rangle = k\zeta T\tau_0^{-1}V^{-1}, \tag{19}$$

$$\langle\delta\mathring{P}_{ij}^{\mathrm{v}}\delta\mathring{P}_{kl}^{\mathrm{v}}\rangle = k\mu T\tau_2^{-1}V^{-1}\Delta_{ijkl}, \tag{20}$$

where we have denoted $\Delta_{ijkl} = \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}$. These expressions relate the dissipative coefficients λ, ζ and μ with the fluctuations of the fluxes. As is usual, they may be regarded in two alternative ways: (a) the dissipative coefficients determine the fluctuations, and (b) the fluctuations determine the dissipative coefficients. This latter point of view has been exploited in the Green–Kubo formulae for the dissipative coefficients (Balescu 1975) which have received wide attention in the last twenty years. Note that (18)–(20) coincide with the Green–Kubo formulae when the evolution of the fluctuations of the fluxes is described by the relaxational equations (5)–(7).

Up to now, our results have been purely macroscopic. Now, we proceed to calculate λ and μ (or α_1 and α_2) from a microscopic interpretation of (18) and (20) for a simple gas. The bulk coefficient ζ is known to vanish for a simple monatomic gas. Equations (18) and (20) may be written as

$$\lambda = \tau_1 V(kT^2)^{-1}\langle\delta q_1\delta q_1\rangle, \tag{21}$$

$$\mu = \tau_2 V(kT)^{-1}\langle\delta\mathring{P}_{12}^{\mathrm{v}}\delta\mathring{P}_{12}^{\mathrm{v}}\rangle. \tag{22}$$

The fluctuations of the fluxes may be calculated from a microscopic point of view. The microscopic operators of the dissipative fluxes in a fluid of rigid spheres of mass m and relative velocity $\boldsymbol{v} = \boldsymbol{c} - \boldsymbol{u}$ with respect to the mean velocity of the system, $\boldsymbol{u}$, are (Résibois and De Leener 1977, p 305)

$$q_1 = \tfrac{1}{2}mv^2v_1 - hv_1, \tag{23}$$

$$\mathring{P}^{\mathrm{v}}_{12} = mv_1v_2, \tag{24}$$

where $h = \frac{5}{2}kT$ is the enthalpy per particle. The fluctuations of macroscopic variables from their steady-state values may be related to the fluctuations of the distribution function $f(\boldsymbol{r}, \boldsymbol{v}, t)$ (Lax 1960, § 12). For a macroscopic variable A with a microscopic operator $A(\boldsymbol{v})$, whose steady-state value is given by

$$A_0(\boldsymbol{r}, t) = \int A(\boldsymbol{v}) f(\boldsymbol{r}, \boldsymbol{v}, t)\, \mathrm{d}\boldsymbol{v}, \tag{25}$$

the fluctuations $\delta A \equiv A - A_0$ satisfy

$$\langle \delta A(t) \delta A(0) \rangle = \iint A(\boldsymbol{v}) A(\boldsymbol{v}') \langle \delta f(\boldsymbol{v}, t) \delta f(\boldsymbol{v}', 0) \rangle\, \mathrm{d}\boldsymbol{v}\, \mathrm{d}\boldsymbol{v}'. \tag{26}$$

In the case of Boltzmann statistics it has been shown (Lax 1960) that

$$\langle \delta f(\boldsymbol{v}) \delta f(\boldsymbol{v}') \rangle = V^{-1} f_{\mathrm{st}}(\boldsymbol{v}) \delta(\boldsymbol{v} - \boldsymbol{v}') \tag{27}$$

with $f_{\mathrm{st}}(\boldsymbol{v})$ the distribution function corresponding to the steady state, either in equilibrium or not. In equilibrium we have

$$f_{\mathrm{st}} = n(m/2\pi kT)^{3/2} \exp(-m\boldsymbol{v}^2/2kT) \tag{28}$$

with $n = N/V$. Therefore we obtain

$$\langle \delta q_1 \delta q_1 \rangle = (4\pi/3) n V^{-1} (m/2\pi kT)^{3/2} \int_0^\infty v^4 (\tfrac{1}{2}mv^2 - h)^2 \exp(-mv^2/2kT)\, \mathrm{d}v, \tag{29}$$

$$\langle \delta \mathring{P}^{\mathrm{v}}_{12} \delta \mathring{P}^{\mathrm{v}}_{12} \rangle = (4\pi/15) n V^{-1} m^2 (m/2\pi kT)^{3/2} \int_0^\infty v^6 \exp(-mv^2/2kT)\, \mathrm{d}v, \tag{30}$$

where we have taken into account that $\langle \delta q_1 \delta q_1 \rangle = \frac{1}{3}\langle \delta \boldsymbol{q} \cdot \delta \boldsymbol{q} \rangle$ and that $\int F(v) v_1^2 v_2^2\, \mathrm{d}\boldsymbol{v} = \frac{1}{15} \int F(v) v^4\, \mathrm{d}\boldsymbol{v}$. The integrals in (29) and (30) are easily performed and we get finally

$$\lambda = \tfrac{5}{2} k^2 T n m^{-1} \tau_1, \tag{31}$$

$$\mu = kTn\tau_2. \tag{32}$$

These expressions provide microscopic values for λ and μ in terms of the relaxation times τ_1 and τ_2. It is seen that these relaxation times are not at all academic quantities but, on the contrary, if they are assumed to vanish, the dissipative coefficients also vanish. They are, therefore, central quantities in the theory of non-equilibrium and it seems worthwhile to build a thermodynamic framework giving them an adequate account. Though the theoretical computation of τ_1 and τ_2 is very difficult, we note that the relations (31) and (32) are enough to establish microscopic expressions for the coefficients τ_1/λ and τ_2/μ appearing in the equations of state of (8).

We may compare these results with those of kinetic theory, based on a simplified relaxational model of the Boltzmann equation. In this approximation, it is assumed that the evolution of the distribution function is given by

$$\partial f/\partial t + \boldsymbol{v} \cdot \partial f/\partial \boldsymbol{r} + \boldsymbol{a} \cdot \partial f/\partial \boldsymbol{v} = -\tau^{-1}(f - f_0) \tag{33}$$

where f_0 is a local-equilibrium Maxwell–Boltzmann distribution function and τ is a relaxation time characteristic of the period required for equilibration. From (33), and through a standard development (Wannier 1966, Balescu 1975, Résibois and De

Leener 1977), we obtain

$$\lambda = \tfrac{5}{2}k^2 Tnm^{-1}\tau, \qquad \mu = nkT\tau. \tag{34}$$

By comparing (31) and (32) with (34), we have $\tau_1 = \tau_2 = \tau$, so that the fluctuation–dissipation formulae (21) and (22) recover the results of the relaxational kinetic equation (34) as a particular case, with the advantage of being valid at arbitrary densities.

In fact, (31) and (32) are more general than (34). Indeed, let us consider the ratio $m\lambda/\mu c_v$, with c_v the specific heat per particle at constant volume $c_v = \frac{3}{2}kT$. In this case, we have from (31) and (32)

$$m\lambda/\mu c_v = \tfrac{5}{3}(\tau_1\tau_2). \tag{35}$$

While the value of this ratio in the kinetic relaxational model is $\frac{5}{3}$, a more detailed analysis of the solutions of the Boltzmann equation in the Chapman–Enskog development shows that $m\lambda/\mu c_v = \frac{5}{2}$, independently of the interaction potential. This result is confirmed experimentally and it indicates that $\tau_1 = \frac{3}{2}\tau_2 = \frac{3}{2}\tau$. This result is also obtained from the solutions of the Boltzmann equation in the thirteen-moments approximation (Grad 1959). Of course, our macroscopic results are not so detailed, but they are compatible with these results, while it would be difficult to recover them from a simple two-relaxation-times generalisation of equation (33).

4. Non-equilibrium heat fluctuations with a temperature gradient

In the last three years, there has been a renewed interest in the description of hydrodynamic fluctuations near non-equilibrium steady states (Procaccia *et al* 1979, Ronis *et al* 1979, 1980, Tremblay *et al* 1981, Keizer 1976, 1978, Graham 1974, Onuki and Kawasaki 1979). Here, we consider the purely statistical problem of the non-equilibrium Langevin noise which is added to the linearised equations for the fluctuations. It is generally assumed that this Langevin force, due to the fluctuations of the dissipative fluxes, is described by the same correlation function as in equilibrium, with local values of temperature and of transport coefficients. Indeed, it is argued that the corresponding random forces, due to the fluctuating heat flux and viscous pressure, have such short correlation times that they do not have time enough to 'know' whether the system is in equilibrium or not (Swift and Hohenberg 1977, Ronis *et al* 1980, Tremblay *et al* 1981), so that they are adequately characterised by a local-equilibrium average. Starting from this prescription for the noise, one can obtain from the dynamical stochastic equations the corresponding non-equilibrium corrections to the classical formulae for the hydrodynamic fluctuations, due to the spatial variation of the thermodynamic variables.

Our purpose is to explore the consequences of the preceding analysis in non-equilibrium fluctuations, in order to provide an expression for the non-equilibrium hydrodynamic Langevin noise. Indeed, since in our approach the relaxation time of the fluctuations does not vanish, they have some time to know that the system is not in equilibrium, and therefore there arise some non-equilibrium corrections to the stochastic noise.

Our analysis is based on the hypothesis that, at least very near from equilibrium, the probability of the fluctuations is still given by (12). Since our generalised entropy contains as independent variables the dissipative fluxes, one may expect that this

dependence may give some information on the effects of a non-vanishing mean heat flux on the hydrodynamic fluctuations. Of course, our results, based on this simple hypothesis, are not rigorous. Our aim here is precisely to test their degree of accuracy.

In this section, we specialise our analysis to the problem of heat fluctuations in a fluid with an externally imposed temperature gradient in the x direction. In this case, the general expression (13) for the second differential of the entropy reduces to

$$\delta^2 s = \theta_u^{-1}(\delta u)^2 + 2\theta_v^{-1}\delta u\delta v + (\theta^{-1}\pi)(\delta v)^2 - \alpha_1\delta q\cdot\delta q - 2q_0\alpha_{1u}\delta u\delta q - 2q_0\alpha_{1v}\delta v\delta q \quad (36)$$

where q_0 is given by the classical Fourier law $q_0 = -\lambda T_{0x}$, with the subscript x standing for the partial derivative with respect to x.

Introducing this expression into the generalised Einstein formula (12), we obtain a multivariant distribution function for the probability of fluctuations of u, v and q. Taking into account that for a Gaussian probability distribution function of the form

$$W \sim \exp(-\tfrac{1}{2}E_{jk}\delta x_j\delta x_k) \quad (37)$$

the second moments are given by $\langle\delta x_i\delta x_j\rangle = E_{ij}^{-1}$, we get, by leaving aside the results for the classical variables,

$$\langle\delta q\delta q\rangle = (kE/M\alpha_1)\{\Delta - \tfrac{1}{2}q_0^2[T_u^{-1}\alpha_{1vv} + (T^{-1}p)_v\alpha_{1uu} - 2T_v^{-1}\alpha_{1uv}]\}, \quad (38)$$

$$\langle\delta u\delta q\rangle = -(kE/M\alpha_1)q_0\{T_v^{-1}\alpha_{1v} - (T^{-1}p)_v\alpha_{1u}], \quad (39)$$

$$\langle\delta v\delta q\rangle = -(kE/M\alpha_1)q_0(T_v^{-1}\alpha_{1u} - T_u^{-1}\alpha_{1v}), \quad (40)$$

where

$$\Delta = T_u^{-1}(T^{-1}p)_v - (T_v^{-1})^2, \quad (41)$$

E stands for $\{\Delta[1+q_0^2(A/\Delta)]\}^{-1}$ and A is given by

$$A = T_u^{-1}[\alpha_1^{-1}(\alpha_{1v})^2 - \tfrac{1}{2}\alpha_{1vv}] + (T^{-1}p)_v[\alpha_1^{-1}(\alpha_{1u})^2 - \tfrac{1}{2}\alpha_{1uu}] - 2T_v^{-1}(\alpha_1^{-1}\alpha_{1u}\alpha_{1v} - \tfrac{1}{2}\alpha_{1uv}). \quad (42)$$

These expressions reduce to the equilibrium ones when $q_0 = 0$, and they show the corrections arising from a non-vanishing heat flux. We note that in non-equilibrium, the correlations between quantities of different time-reversal parity do not vanish, as for instance $\langle\delta u\delta q\rangle$ and $\langle\delta v\delta q\rangle$. This indicates a breaking of the time-reversal symmetry in non-equilibrium as noted in a similar context but from a statistical basis by Ronis *et al* (1979). The equation (38) for the fluctuations of the heat flux contains non-equilibrium corrections to the classical Landau–Lifshitz formulae (Landau and Lifshitz 1971).

In order to get a clearer insight into these equations, we assume that the temperature gradient is very small, so that the denominator can be expanded up to second order in q_0. Also, we specialise our results to the case of an ideal monatomic gas. For such a gas

$$(T^{-1}p)_v = -p(Tv)^{-1}, \qquad T_v^{-1} = 0, \qquad T_u^{-1} = -(c_vT^2)^{-1}, \quad (43)$$

with $c_v = \frac{3}{2}(kT/m)$. Furthermore, from (31) we know that α_1 is given by $\alpha_1 = \frac{2}{5}(k^2T^3n^2)^{-1}$, so that

$$\alpha_{1u} = -\tfrac{4}{5}m(n^2T^4k^3)^{-1}, \qquad \alpha_{1v} = \tfrac{4}{5}m(nk^2T^3)^{-1}. \quad (44)$$

When (43) and (44) are introduced into (38)–(40), and up to second order in q_0, they

become highly simplified and reduce to

$$\langle \delta q \delta q \rangle = k\lambda T^2 \tau_1^{-1} V^{-1}[1 + (25\pi/8) l^2 (\nabla \ln T)_0^2], \tag{45}$$

$$\langle \delta u \delta q \rangle = -3kTM^{-1}\lambda (\nabla T)_0, \tag{46}$$

$$\langle \delta v \delta q \rangle = 2v\lambda (\nabla T)_0, \tag{47}$$

which show the numerical values of the non-equilibrium corrections in this simple case, l being the mean-free-path defined as $l = \tau_1 \bar{v}$, with $\bar{v}$ the mean velocity given by the usual expression $\bar{v} = (8kT/\pi m)^{1/2}$. Since in this case the velocity is zero, the Burnett equations reduce to the Maxwell–Cattaneo equations and our simple analysis is meaningful.

5. Non-equilibrium viscous pressure fluctuations with a velocity gradient

Another typical problem in non-equilibrium hydrodynamics is the plane Couette flow. In this case, the fluid is placed between two infinite parallel planes in the xz directions. One of them is at rest while the other one is moving at a constant velocity u in the x direction. In this simple situation, the only variables of interest are u, v and P_{12}^{v}. Some problems related with the fluctuations of a fluid in this situation have been analysed by Onuki and Kawasaki (1979) in a series of papers, mainly in the proximity of a critical point.

As in the previous section, we assume that the fluid is far from the critical point, and we look for the non-equilibrium corrections in the correlation formula for the stochastic noise due to the fluctuations of the viscous pressure tensor. As above, we assume that near to equilibrium, the probability of the fluctuations is given by (12) with the corresponding simplified expression of the generalised entropy, with $P_{120}^{\mathrm{v}} = -\mu(\partial u/\partial y)_0$ according to the classical Newton law. Now, we obtain for the second moments of the fluctuations of the fluxes

$$\langle \delta P_{12}^{\mathrm{v}} \delta P_{12}^{\mathrm{v}} \rangle = (kE'/M\alpha_2)[\Delta - \tfrac{1}{2} P_{120}^{\mathrm{v}2} (T_u^{-1}\alpha_{2vv} + T_v^{-1}\alpha_{2uu} - 2T_v^{-1}\alpha_{2uv})], \tag{48}$$

$$\langle \delta u \delta P_{12}^{\mathrm{v}} \rangle = -(kE'/M\alpha_2) P_{120}^{\mathrm{v}} [T_v^{-1}\alpha_{2v} - (T^{-1}p)_v \alpha_{2u}], \tag{49}$$

$$\langle \delta v \delta P_{12}^{\mathrm{v}} \rangle = -(kE'/M\alpha_2) P_{120}^{\mathrm{v}} (T_v^{-1}\alpha_{2u} - T_u^{-1}\alpha_{2v}), \tag{50}$$

with Δ and A' given by the corresponding expressions (41) and (42) with α_1 substituted by α_2, and with E' standing for $\{\Delta[1 + 2P_{120}^{\mathrm{v}2}(A'/\Delta)]\}^{-1}$.

As in the preceding case, the non-equilibrium situation induces a breaking of the time-reversal symmetry, as is seen in the non-vanishing correlations (49) and (50), and a correction to the Landau–Lifshitz expression, as is evident in (48). In order to have some numerical estimates, we assume now small values of the velocity gradient and an ideal monatomic gas. In this case, taking into account (32), we have $\alpha_2 = \tau_2 v/2\mu T = (2mn^2kT^2)^{-1}$. Introducing this result and (43) into (48)–(50), we get

$$\langle \delta \mathring{P}_{12}^{\mathrm{v}} \delta \mathring{P}_{12}^{\mathrm{v}} \rangle = \mu k T \tau_2^{-1} V^{-1} [1 + \tfrac{20}{3} \tau_2^2 (\partial u/\partial y)_0^2], \tag{51}$$

$$\langle \delta u \delta \mathring{P}_{12}^{\mathrm{v}} \rangle = -2kTM^{-1}\mu (\partial u_1/\partial y)_0, \tag{52}$$

$$\langle \delta v \delta \mathring{P}_{12}^{\mathrm{v}} \rangle = 2v\mu (\partial u_1/\partial y)_0, \tag{53}$$

which are analogous to (45)–(47) in the present physical situation.

6. Non-equilibrium fluctuations from a microscopic model

In order to have an insight into the signification of (45)–(47) and (51)–(53), and to be able to test their accuracy, we proceed to evaluate the non-equilibrium second moments of the fluctuations of the heat flux and of the viscous pressure from a simple kinetic model. To obtain an expression for the non-equilibrium distribution function needed in (27), we start from the kinetic relaxational equation (33). If the external forces (and hence $\boldsymbol{a}$) are assumed to vanish, this equation may be written as

$$f=[1+\tau(\partial/\partial t+\boldsymbol{c}\cdot\nabla)]^{-1}f_{\mathrm{eq}} \tag{54}$$

with f_{eq} given by (28), and a perturbative solution of it may be obtained by developing formally the operator of the right-hand side of (54) in series of τ (Nonnenmacher 1980). Up to second order in τ and in a stationary situation, the non-equilibrium distribution function f_{st} is given by

$$f_{\mathrm{st}}=f_{\mathrm{eq}}-\tau\boldsymbol{v}\cdot\nabla f_{\mathrm{eq}}+(\tau\boldsymbol{v}\cdot\nabla)(\tau\boldsymbol{v}\cdot\nabla)f_{\mathrm{eq}}. \tag{55}$$

Let us assume at first that a temperature gradient in the x direction is imposed on a gas at rest, uniform in pressure. In this case, the first- and second-order contributions to f_{st} are respectively

$$f^{(1)}=-\tau v_1[(mv^2/2kT^2)-5/2T]f_{\mathrm{eq}}(\partial T/\partial x), \tag{56}$$

$$f^{(2)}=\tau^2v_1^2[(mv^2/2kT^2)^2+(35/4T^2)-\tfrac{7}{2}(mv^2/kT^3)]f_{\mathrm{eq}}(\partial T/\partial x)^2. \tag{57}$$

Introducing these expressions and the corresponding microscopic operator (23) into (26), and having in mind that in equilibrium $\langle\delta q_1\delta q_1\rangle=\frac{5}{2}k^3T^3n/mV$, we have finally

$$\langle\delta q_1\delta q_1\rangle_{\mathrm{ne}}=\langle\delta q_1\delta q_1\rangle_{\mathrm{eq}}[1+8.925\pi l^2(\nabla\ln T)^2] \tag{58}$$

where we have used the mean-free path l. Analogously, when (57) and the microscopic operator (24) of the viscous pressure are introduced into (26), and having in mind that in equilibrium $\langle\delta\mathring{P}^{\mathrm{v}}_{12}\delta\mathring{P}^{\mathrm{v}}_{12}\rangle=k^2T^2n/V$, one may find

$$\langle\delta\mathring{P}^{\mathrm{v}}_{12}\delta\mathring{P}^{\mathrm{v}}_{12}\rangle_{\mathrm{ne}}=\langle\delta\mathring{P}^{\mathrm{v}}_{12}\delta\mathring{P}^{\mathrm{v}}_{12}\rangle_{\mathrm{eq}}[1+0.750\pi l^2(\nabla\ln T)^2]. \tag{59}$$

Let us now assume that a velocity gradient is imposed on a gas at constant pressure and temperature. The flow is in the x direction. In this case, the first- and second-order contributions to the non-equilibrium distribution function take the respective forms

$$f^{(1)}=-\tau v_1v_2(m/kT)f_{\mathrm{eq}}(\partial u_1/\partial y), \tag{60}$$

$$f^{(2)}=\tau^2v_1^2v_2^2(m/kT)^2f_{\mathrm{eq}}(\partial u_1/\partial y)^2. \tag{61}$$

Introducing these expressions and the microscopic operators (23) and (24) into (26), one is led to

$$\langle\delta q_2\delta q_2\rangle_{\mathrm{ne}}=\langle\delta q_2\delta q_2\rangle_{\mathrm{eq}}[1+10.200\tau_2^2(\partial u_1/\partial y)^2], \tag{62}$$

$$\langle\delta\mathring{P}^{\mathrm{v}}_{12}\delta\mathring{P}^{\mathrm{v}}_{12}\rangle_{\mathrm{ne}}=\langle\delta\mathring{P}^{\mathrm{v}}_{12}\delta\mathring{P}^{\mathrm{v}}_{12}\rangle_{\mathrm{eq}}[1+9\tau_2^2(\partial u_1/\partial y)^2]. \tag{63}$$

By combining the expression of the internal energy, the operators (23) and (24) of the fluxes and the first-order contributions to the non-equilibrium distribution function (56) and (60), one gets

$$\langle\delta u\delta q_1\rangle_{\mathrm{ne}}=-4.75kTM^{-1}\lambda(\partial T/\partial x)_0, \tag{64}$$

$$\langle \delta u \delta \mathring{P}^{\mathrm{v}}_{12} \rangle_{\mathrm{ne}} = -3.50 kTM^{-1} \mu (\partial u_1/\partial y)_0. \tag{65}$$

To make some of these expressions more familiar to the reader, recall that the dynamics of the fluctuations is described by (5)–(7), so that in the Fourier space we have

$$\langle \delta q_i(\omega) \delta q_j(\omega') \rangle = \langle \delta q_i \delta q_j \rangle \frac{2\tau_1}{1+(\omega\tau_1)^2} \delta_{ij} \delta(\omega+\omega'), \tag{66}$$

$$\langle \delta P^{\mathrm{v}}_{ij}(\omega) \delta P^{\mathrm{v}}_{kl}(\omega') \rangle = \langle \delta P^{\mathrm{v}}_{ij} \delta P^{\mathrm{v}}_{kl} \rangle \frac{2\tau_2}{1+(\omega\tau_2)^2} \Delta_{ijkl} \delta(\omega+\omega'). \tag{67}$$

In the low-frequency limit and per unit volume, (58) and (59) may be written in the more usual form

$$\langle \delta q_1 \delta q_1 \rangle_{\mathrm{ne}} = 2k\lambda T^2 [1 + 8.925 \pi l^2 (\nabla \ln T)^2], \tag{68}$$

$$\langle \delta \mathring{P}^{\mathrm{v}}_{12} \delta \mathring{P}^{\mathrm{v}}_{12} \rangle_{\mathrm{ne}} = 2k\mu T [1 + 0.750 \pi l^2 (\nabla \ln T)^2], \tag{69}$$

and in the case of a velocity gradient, (62) and (63) lead to

$$\langle \delta q_2 \delta q_2 \rangle_{\mathrm{ne}} = 2k\lambda T^2 [1 + 10.200 \tau_2^2 (\partial u_1/\partial y)^2], \tag{70}$$

$$\langle \delta \mathring{P}^{\mathrm{v}}_{12} \delta \mathring{P}^{\mathrm{v}}_{12} \rangle_{\mathrm{ne}} = 2k\mu T [1 + 9 \tau_2^2 (\partial u_1/\partial y)^2]. \tag{71}$$

We note that the non-equilibrium corrections to the Landau–Lifshitz formulae are very small, since the relaxation times are usually very short, and therefore the use of the classical expressions for the hydrodynamic Langevin noise is rather justified in common situations. Other features typical of non-equilibrium arise from the local variation of the temperature and hence of the physical parameters involved in these expressions. These corrections influence the correlation function of the density and are therefore, in principle, observable. They have been analysed in detail (Tremblay *et al* 1981, Ronis *et al* 1980, Van der Zaan and Mazur 1980) and are of a different origin from those studied here.

7. Concluding remarks

Comparison of macroscopic expressions (45) and (46), (51) and (52) with their respective microscopic counterparts (58) and (64), (63) and (65) shows a discrepancy which may be analysed in some detail. On the one hand, the microscopic values are not necessarily the exact real values of the fluctuations. Remember, for instance, that the kinetic equation (33) leads to a ratio $m\lambda/\mu c_v$ which is related to the experimental ratio by a factor $\frac{3}{2}$, which can be obtained by more refined microscopic models. In particular, this leads to the identification $\tau_2 \equiv \tau$ and $\tau_1 \equiv \frac{3}{2}\tau$, a factor which, if taken into account in (45) and (46), changes the respective factors $25\pi/8$ and 3 to 7.031π and 4.5, which are closer to the microscopic values 8.925π of (58) and 4.75 of (64). This fact mitigates somewhat the disagreement between the microscopic and the macroscopic results. On the other hand, it is known that the classical entropy is related to the probability of fluctuations through the Einstein relation in equilibrium, but not out of equilibrium. We have seen here that our entropy, in spite of containing as variables some typical non-equilibrium parameters, is related to the fluctuations of the dissipative fluxes only in equilibrium, while in non-equilibrium it gives corrections of the right order of magnitude, but quantitatively inaccurate.

This result, though not surprising, is not immediate. Indeed, if one defines a non-equilibrium entropy for Boltzmann statistics as

$$\rho s = -k \int f(\ln f - 1)\, \mathrm{d}\boldsymbol{v}, \tag{72}$$

the non-equilibrium fluctuations of the distribution function are well described by the second differential of the entropy through the Einstein relation (Lax 1960). This is seen if one takes $f = f_{\mathrm{st}} + \delta f$ and retains only the second-order contribution of δf to (72). In this way, one obtains

$$\Pr(\delta f) \sim \exp[-(v/2)(\delta f)^2/f_{\mathrm{st}}] \tag{73}$$

which leads to the correct result (27). Since we are dealing with Boltzmann statistics, one could ask therefore whether the integrated entropy (72) does describe non-equilibrium fluctuations at a macroscopic level.

Note at this point that the entropy (8) does indeed correspond to (72). We restrict our attention to the case of a heat flux, because the extension to the viscous pressure is straightforward. When (8) is integrated we get

$$\rho s = \rho s_0 - (\tau/2\lambda T^2) q^2. \tag{74}$$

On the other hand, the first- and second-order contributions of (72) to the entropy are given by (De Groot and Mazur 1962, p 182)

$$\rho s_1 = -k \int f_{\mathrm{eq}} \phi_1 \ln f_{\mathrm{eq}}\, \mathrm{d}\boldsymbol{v} = 0, \tag{75}$$

$$\rho s_2 = -\tfrac{1}{2} k \int f_{\mathrm{eq}} \phi_1^2\, \mathrm{d}\boldsymbol{v}, \tag{76}$$

where ϕ_1 is defined by $f_1 \equiv f_{\mathrm{eq}} \phi_1$. From (56) and from the microscopic operator (23) it is seen that

$$\phi_1 = -(\tau/kT^2) q_z(\boldsymbol{v})(\partial T/\partial z) \tag{77}$$

which, when introduced into (76), leads to

$$\rho s_2 = -(\tau/2T^2)(\partial T/\partial z)^2 \left((\tau/kT^2) \int q_z^2 f_{\mathrm{eq}}\, \mathrm{d}\boldsymbol{v} \right) \tag{78}$$

which, in view of the results of § 3, is precisely $\rho s_2 = -(\tau/2\lambda T^2) q^2$, in accordance with (74). The coincidence of (74) with the microscopic integration of (72) can also be shown from more elaborate models, such as the thirteen-moments one (Grad 1959). Therefore, though (72) describes the fluctuations of the distribution function, it does not describe accurately the fluctuations of the macroscopic variables.

One could argue that the disagreement is due to the very simple form of (5)–(7) as compared with the more complicated Burnett equations. However, in both situations studied here and in these simple geometries, the Burnett equations reduce essentially to (5)–(7). One could also ask for the influence of the fourth-order terms ρs_4 on the second derivative of ρs, and hence on the fluctuations. Of course they may modify the result presented here, but they must be omitted because they are not compatible with (5)–(7), and hence they are beyond the present scope of our simple phenomenological model.

Though the present analysis of the fluctuations is not sufficiently accurate at this stage, it reproduces some qualitative features of non-equilibrium fluctuations which are not covered by the classical theory, as seen in our recent study of heat fluctuations in rigid heat conductors (Jou *et al* 1982). The study of the fluctuations leads to quantitative conclusions from the non-equilibrium equations of state, and therefore it may be a method to compare the relative merits of non-equilibrium entropies with respect to the problem of fluctuations. In fact, some recent approaches to thermodynamics of non-equilibrium steady states have started from this problem (Keizer 1976, 1978): from the second moments of the fluctuations obtained from microscopic theories (kinetic models, master equations) one constructs an entropy through the Einstein relation (12). Here, on the contrary, we have a non-equilibrium thermodynamic potential and we have looked for its consequences in non-equilibrium fluctuations.

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