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Abstract. We obtain, from a thermodynamic basis, evolution equations for the kinetic and the potential contributions to the viscous pressure tensor for a real gas. The macroscopic predictions of the theory, previously checked from kinetic theory for ideal gases up to first order in the density, are also confirmed for real gases, up to second order in the density.

1. Introduction

Extended irreversible thermodynamics is a phenomenological approach to a meso-scopic description of thermodynamic systems (Casas-Vázquez *et al* 1984, Müller 1985). Such a mesoscopic description includes the dissipative fluxes (viscous pressure tensor, heat flux) in the set of basic independent variables, besides the usual conserved variables (mass, energy and momentum). It explores the thermodynamic consequences of the dynamics of the dissipative fluxes and it is not based on the local-equilibrium hypothesis. In this way, it constitutes a generalisation of the classical local-equilibrium irreversible thermodynamics and allows us to have a clearer insight on the limits of validity of the latter theory.

As a phenomenological theory, extended thermodynamics is not restricted to a particular system, but is rather general. Its present limitations come from the use of simple equations for the evolution of the fluxes, as the Maxwell-Cattaneo equations or some generalisations of them, but not from the specific system it is applied to. In this way, it has been used in connection with solid systems, as rigid heat and electrical conductors or dielectric solids, as well as with fluid systems, as gases, simple liquids and viscoelastic liquids. However, the comparison of the macroscopic results with microscopic theories has been done rather extensively in the case of ideal gases (Müller 1967, Lebon 1978, Jou *et al* 1979, Jou and Careta 1982, Nonnenmacher 1980, García-Colín and López de Haro 1982, García-Colín and Fuentes-Martínez 1982, Eu 1979, 1980, 1981) but it is almost lacking for other systems, with the exception of some formal general attempts (Eu 1981) or very specific models (Nettleton 1959).

Our purpose in this paper is to carry out such a comparison in the case of dilute but non-ideal gases, by taking into account the interaction amongst the molecules. Such an analysis is not a trivial extension of the existing developments, but it contributes with some new facts. Indeed, the traceless part of the viscous pressure tensor, for instance, no longer has a purely kinetic origin, but it includes the contribution of the interaction forces. In this way, it is no longer a single physical entity, but the sum of two independent quantities, each one with its own evolution equation. This requires the reformulation of the macroscopic theory in a more general way.

The layout of the paper is as follows. In § 2, we generalise the macroscopic theory. In § 3 we obtain an explicit microscopic expression for the entropy and for the evolution equations of the fluxes, and we compare them with the results of the macroscopic theory. In § 4, we deal with the fluctuations of the viscous pressure tensor and arrive at similar conclusions.

2. Macroscopic theory

A simple fluid is described in the classical theory of irreversible thermodynamics by means of five local variables: mass density ρ, internal energy per unit mass e and velocity u. These variables are related to the conservation equations of mass, momentum and energy, which are

$$\dot{\rho} = -\rho \nabla \cdot u \tag{2.1}$$

$$\rho \dot{u} = -\nabla \cdot P + \rho F \tag{2.2}$$

$$\rho \dot{e} = -\nabla \cdot q - P : V. \tag{2.3}$$

Here, q is the heat flux, V the symmetric part of the velocity gradient, F the external force per unit mass and P the pressure tensor, which can be decomposed as

$$P = (p + p^{v}) U + \overset{\circ}{P}{}^{v} \tag{2.4}$$

with p the thermodynamic pressure, p^{v} the bulk viscous pressure, P^{v} the traceless viscous pressure tensor, which is assumed to be symmetric, and U the identity tensor.

In the classical theory, q, p^{v} and $\overset{\circ}{P}{}^{v}$ are expressed in terms of ρ, e, u and their spatial gradients by means of the so-called constitutive laws of Fourier and Newton-Stokes, respectively. In extended thermodynamics, one considers q, p^{v} and $\overset{\circ}{P}{}^{v}$ as independent variables in their own right, and one looks for their evolution equations.

Usually, one considers $\overset{\circ}{P}{}^{v}$ as a single physical entity: in the case of a dilute non-interacting gas, $\overset{\circ}{P}{}^{v}$ is due to the kinetic exchange of momentum, whereas for a dense fluid it is mainly due to the interaction between the molecules. There is a regime, however, where both factors—kinetic and potential—have contributions of the same order. This is the case of a real, interacting gas in a moderately dilute regime. Therefore, $\overset{\circ}{P}{}^{v}$ must not be considered in this case as a single quantity—kinetic or potential—but as the sum of two quantities: $\overset{\circ}{P}{}^{vc}$, the kinetic part, plus $\overset{\circ}{P}{}^{vp}$, the potential part. Since both of them are independent, they will follow their own temporal evolution, described by the respective differential equations.

In this paper we will neglect the effect of the heat flux and we will focus our attention on the viscous effects. In this way we assume the existence of a generalised entropy per unit mass s, which will depend on ρ, e, $\overset{\circ}{P}{}^{vc}$, $\overset{\circ}{P}{}^{vp}$ and p^{v}. We do not write any index in the case of bulk viscous pressure p^{v}, because it is due exclusively to the interaction forces, p^{v} being zero in the case of a non-interacting gas.

The generalised Gibbs equation for the entropy will then have the form (Jou *et al* 1979, Casas-Vázquez *et al* 1984)

$$ds = T^{-1} de - T^{-1}\rho^{-2}p \, d\rho - (T\rho)^{-1}\boldsymbol{\alpha}_c : dP^{vc} - (T\rho)^{-1}\boldsymbol{\alpha}_p : dP^{vp} - (T\rho)^{-1}\alpha \, dp^{v}. \tag{2.5}$$

Here, the tensors $\boldsymbol{\alpha}_c$ and $\boldsymbol{\alpha}_p$ and the scalar α will be written, up to first order in the

fluxes, as

$$\boldsymbol{\alpha}_c = \alpha_{cc}\mathring{\boldsymbol{P}}^{vc} + \alpha_{cp}\mathring{\boldsymbol{P}}^{vp}$$

$$\boldsymbol{\alpha}_p = \alpha_{pc}\mathring{\boldsymbol{P}}^{vc} + \alpha_{pp}\mathring{\boldsymbol{P}}^{vp} \tag{2.6}$$

$$\alpha = \alpha_0 p^v$$

where the newly introduced α are functions of e and ρ.

In order to obtain the thermodynamic restrictions on the evolution equations for $\mathring{\boldsymbol{P}}^{vc}$, $\mathring{\boldsymbol{P}}^{vp}$ and p^v, we must find the entropy production σ from the balance equation for the entropy, which has the general form

$$\rho\dot{s} + \nabla \cdot \boldsymbol{J}_s = \sigma. \tag{2.7}$$

Since we are neglecting the heat flux, which is the only vector we have at hand, we will assume that $\boldsymbol{J}_s$, the non-convective part of the entropy flux, is zero. We have then, by taking into account (2.5), (2.6), (2.1), (2.2) and (2.4)

$$\sigma = -T^{-1}p^v(\nabla \cdot \boldsymbol{u} + \alpha_0 \dot{p}^v) - T^{-1}\mathring{\boldsymbol{P}}^{vc}:[\mathring{\boldsymbol{V}} + \alpha_{cc}(\mathring{\boldsymbol{P}}^{vc})^{\cdot} + \alpha_{pc}(\mathring{\boldsymbol{P}}^{vp})^{\cdot}]$$
$$- T^{-1}\mathring{\boldsymbol{P}}^{vp}:[\mathring{\boldsymbol{V}} + \alpha_{cp}(\mathring{\boldsymbol{P}}^{vc})^{\cdot} + \alpha_{pp}(\mathring{\boldsymbol{P}}^{vp})^{\cdot}]. \tag{2.8}$$

Now we want to obtain expressions for $(\mathring{\boldsymbol{P}}^{vc})^{\cdot}$, $(\mathring{\boldsymbol{P}}^{vp})^{\cdot}$ and P^v in terms of the basic variables and their spatial gradients. The simplest assumption compatible with the positive definite character of (2.8), taking advantage of the bilinear form of (2.9), is that

$$\mathring{\boldsymbol{V}} + \alpha_{cc}(\mathring{\boldsymbol{P}}^{vc})^{\cdot} + \alpha_{pc}(\mathring{\boldsymbol{P}}^{vp})^{\cdot} = -u_{cc}\mathring{\boldsymbol{P}}^{vc} - u_{pc}\mathring{\boldsymbol{P}}^{vp} \tag{2.9}$$

$$\mathring{\boldsymbol{V}} + \alpha_{cp}(\mathring{\boldsymbol{P}}^{vc})^{\cdot} + \alpha_{pp}(\mathring{\boldsymbol{P}}^{vp})^{\cdot} = -u_{cp}\mathring{\boldsymbol{P}}^{vc} - u_{pp}\mathring{\boldsymbol{P}}^{vp} \tag{2.10}$$

$$\nabla \cdot \boldsymbol{u} + \alpha_0 \dot{p}^v = -u_0 p^v \tag{2.11}$$

where the u are phenomenological coefficients satisfying the conditions $u_0 \geqslant 0$, $u_{cc} \geqslant 0$, $u_{pp} \geqslant 0$ and $u_{cc}u_{pp} \gg u_{cp}u_{pc}$. In fact, we will not need such general but cumbersome equations, but the much simpler form obtained when $\alpha_{cp} = \alpha_{pc} = u_{pc} = u_{cp} = 0$ will be sufficient for our purposes. In doing so, we may write (2.9)–(2.11) in the form

$$(\mathring{\boldsymbol{P}}^{vc})^{\cdot} = -(1/\tau_c)(\mathring{\boldsymbol{P}}^{vc} + 2\eta_c\mathring{\boldsymbol{V}}) \tag{2.12}$$

$$(\mathring{\boldsymbol{P}}^{vp})^{\cdot} = -(1/\tau_p)(\mathring{\boldsymbol{P}}^{vp} + 2\eta_p\mathring{\boldsymbol{V}}) \tag{2.13}$$

$$\mathring{\boldsymbol{P}}^v = -(1/\tau_0)(p^v + \eta_v\nabla \cdot \boldsymbol{u}) \tag{2.14}$$

where τ_c, τ_p and τ_0 are the respective relaxation times associated with $\mathring{\boldsymbol{P}}^{vc}$, $\mathring{\boldsymbol{P}}^{vp}$ and p^v, η_c and η_p are the kinetic and potential shear viscosities and η_v is the bulk viscosity. These coefficients are related to α_{cc}, α_{pp}, u_{cc}, u_{pp} and u_0 through

$$u_{cc} = (2\eta_c)^{-1} \qquad u_{pp} = (2\eta_p)^{-1} \qquad u_0 = \eta_v^{-1}$$
$$\alpha_{cc} = \tau_c(2\eta_c)^{-1} \qquad \alpha_{pp} = \tau_p(2\eta_p)^{-1} \qquad \alpha_0 = \tau_0\eta_v^{-1} \tag{2.15}$$

as may be seen by straightforward comparison.

In this way, the generalised Gibbs equation (2.5) becomes

$$\mathrm{d}s = T^{-1}\,\mathrm{d}e - T^{-1}\rho^{-2}p\,\mathrm{d}\rho - \frac{\tau_c}{2\eta_c T\rho}\mathring{\boldsymbol{P}}^{vc}:\mathrm{d}\mathring{\boldsymbol{P}}^{vc} - \frac{\tau_p}{2\eta_p T\rho}\mathring{\boldsymbol{P}}^{vp}:\mathrm{d}\mathring{\boldsymbol{P}}^{vp}$$

$$- \frac{\tau_0}{\eta_v T\rho}p^v\,\mathrm{d}p^v. \tag{2.16}$$

A look at the evolution equations (2.12)–(2.14) and the generalised Gibbs equation (2.16) shows the thermodynamic consequences of the appearance of the fluxes $\mathring{\boldsymbol{P}}^{vc}$,

$\mathring{\boldsymbol{P}}^{vp}$ and p^v as independent variables, transforming the whole thermodynamic formalism. Note that in the limit of vanishing relaxation times, we recover the local-equilibrium version of irreversible thermodynamics. Furthermore, if one considers $\tau_c = \tau_p$, the viscous pressure tensor behaves as a whole, and (2.9) and (2.10) and (2.16) reduce to the evolution equations and Gibbs equation used up to now in irreversible extended thermodynamics.

Let us point out finally that the thermodynamics of real gases has also been studied by Kremer (1985) in the context of Müller's version of extended thermodynamics (Müller 1985, Liu and Müller 1983). In this version, no explicit interpretation is given of the new terms appearing in the entropy differential, but one tries to obtain a relation between α_{cc}, α_{pp} and the equilibrium equations of state by purely thermodynamic methods. Such relations turn out to be rather complicated in the real gas case, whereas the present version is more suitable for a comparison with kinetic theory.

3. Microscopic theory

So far, we have arrived at an explicit expression for the generalised entropy. Its validity is restricted to the validity of the evolution equations of the form (2.12)–(2.14) or, in fact, to a somewhat larger domain which is not the subject of the present analysis (Jou *et al* 1982). Our purpose in this section is to check the macroscopic predictions from a microscopic point of view, as has been previously done in the case of ideal gases.

In the latter situation, the one-particle distribution function f_1 is sufficient for a microscopic description of the system. This is no longer the case with interacting particles, where the two-, three-, four-, ..., particle distribution functions $f_2, f_3, f_4, \ldots,$ are in principle needed. Starting from the Liouville equation, it is possible to obtain evolution equations for the reduced distribution functions, the well known BBGKY hierarchy. The complexity of the description, however, increases rapidly with the number of reduced distribution functions being used. Here we shall limit ourselves to a description based on the one- and two-particle distribution functions. This is enough even for the description of liquids (Green 1960, Rice and Gray 1965). However, the restriction to the use of f_1 and f_2 limits our analysis of the entropy to second-order terms in the density.

The microscopic definition of the entropy in terms of the reduced distribution functions is, up to second order (Green 1969),

$$S = -k\left(\int f_1(1) \ln f_1(1) \, d\Gamma_1 + (\tfrac{1}{2}) \int f_2(1,2) \ln \frac{f_2(1,2)}{f_1(1)f_1(2)} \, d\Gamma_2 \right) \qquad (3.1)$$

with $d\Gamma_n$ the volume differential in the phase space of n particles, i.e. $d\Gamma_n = dr_1 \ldots dr_n \, dv_1 \ldots dv_n$, r_i and v_i being the position and velocity respectively, of the ith particle.

The pressure tensor can also be written in terms of the distribution functions f_1 and f_2 (Green 1960, Rice and Gray 1965). We have for the kinetic and potential parts

$$\boldsymbol{P}^c = m \int \boldsymbol{cc}f_1 \, d\boldsymbol{c}$$

$$\boldsymbol{P}^p = -(n^2/2) \int \phi'(R) R^{-1} \boldsymbol{RR}g_2 \, d\boldsymbol{R} \qquad (3.2)$$

where $g_2(R)$ is the pair correlation function, defined as (Green 1960)

$$n^2 g_2(R) = \int f_2 \, d\boldsymbol{v}_1 \, d\boldsymbol{v}_2. \tag{3.3}$$

Here, $\boldsymbol{R} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ is the relative position between molecules, $\boldsymbol{c} = \boldsymbol{v} - \boldsymbol{u}$ is the relative velocity of the particles with respect to the mean velocity, ϕ is the interaction potential between molecules, a tilde indicates a derivative with respect to R and n is the particle number density. From now on, we omit the subscripts for f_1 and g_2.

In equilibrium, (3.2) leads to the following expression for the thermodynamic pressure (defined as one third of the trace of $\boldsymbol{P} = \boldsymbol{P}^c + \boldsymbol{P}^p$):

$$p = nkT - (n^2/6) \int \phi' R g_0(R) \, dR$$

with $g_0(R)$ the equilibrium pair correlation function.

To obtain an explicit expression for the entropy, which will be needed below, we write (3.1) in terms of f and g, by assuming that $f_2(1, 2) = f_1(1) f_1(2) g_2(1, 2)$. This is exactly true in equilibrium, and out of equilibrium it is valid up to first order in the shear rate in the limit of rigid sphere fluids (vanishing soft forces) or in the Fokker-Planck approximation (vanishing rigid core)(Rice and Gray 1965, pp 346, 387-90). In such a case, one has

$$s = -k \left(\int f \ln f \, d\boldsymbol{v} + (n^2/2) \int g \ln g \, d\boldsymbol{R} \right). \tag{3.4}$$

This expression is not as general as (3.1), but it is enough for our purposes to examine from a microscopic point of view the relation between the evolution equations for $\mathring{\boldsymbol{P}}^{vc}$ and $\mathring{\boldsymbol{P}}^{vp}$ (2.12)-(2.14) with the entropy (2.16) obtained in the previous section. Keep in mind that neither (2.12)-(2.14) nor (2.16) are general for all fluids, but that our statement is that relaxational evolution equations such as (2.12)-(2.14) are consistent not with the local-equilibrium entropy but with the generalised entropy (2.16), in their domain of validity.

The evolution equations for f and g are of the form (Green 1960, Rice and Gray 1965)

$$\partial f/\partial t + \boldsymbol{v} \cdot \nabla f = \mathscr{C}(f) \tag{3.5}$$

$$\partial g/\partial t + \boldsymbol{R} \cdot \nabla \boldsymbol{u} \cdot \nabla_R g = \mathscr{D}(g) \tag{3.6}$$

where ∇_R stands for the gradients with respect to the relative position R between two molecules. We do not need the specific form of the operators on the right-hand sides of (3.5) and (3.6). It is enough to know that for the equilibrium distribution functions f_0 and g_0, which are of the form

$$f_0 \sim \exp\left(\frac{mc^2}{2kT}\right) \qquad g_0 \sim \exp\left(-\frac{w(R)}{kT}\right) \tag{3.7}$$

they satisfy $\mathscr{C}(f_0) = \mathscr{D}(g_0) = 0$.

We will write the solutions of (3.5) and (3.6) in a moment expansion with respect to the velocity c and to the relative position R, following the ideas of Grad (1958) and Hess (1980, 1982, 1983). In this way we assume that

$$f = f_0 [1 + \alpha(c) c \mathring{c} : \mathring{\boldsymbol{A}}(\boldsymbol{r}, t)] \tag{3.8}$$

$$g = g_0 [1 + \beta_1(R) \boldsymbol{R} \mathring{\boldsymbol{R}} : \mathring{\boldsymbol{B}}(\boldsymbol{r}, t) + \beta_2(R) R^2 b(\boldsymbol{r}, t)]. \tag{3.9}$$

Here $\overset{\circ}{A}$ and $\overset{\circ}{B}$ are traceless symmetric tensors and we have limited the expansion to only one term. Note that the expansion of f is limited to the traceless term $c\overset{\circ}{c}$, due to the restriction imposed by the kinetic definition of the temperature, namely $\int fc^2 \, dc = \int f_0 c^2 \, dc$, which implies that the bulk viscosity vanishes in an ideal gas. This restriction does not concern g, so that we have included in (3.9) the separate contributions of the traceless tensor $R\overset{\circ}{R}$ and its trace R^2.

The coefficients $\overset{\circ}{A}$, $\overset{\circ}{B}$ and b are related to the viscous pressure by means of relations (3.3) and (3.4), so that we have

$$\overset{\circ}{P}{}^{vc} = \frac{2m}{15} \int \alpha(c)c^4 \, dc \, \overset{\circ}{A} \tag{3.10}$$

$$\overset{\circ}{P}{}^{vp} = -\frac{n^2}{15} \int \beta_1(R)\phi' R^3 g_0 \, dR \, \overset{\circ}{B} \tag{3.11}$$

$$p^v = -\frac{n^2}{6} \int \beta_2(R)\phi' R^3 g_0 \, dR \, b. \tag{3.12}$$

From (3.8) and (3.9) it is easy to obtain an expression for the non-equilibrium entropy. Assuming that the terms in A, B and b are small, one may expand (3.2) up to second order to obtain

$$s = s_0 - (k/2) \int f_0 \psi_f^2 \, dc - k(n^2/4) \int g_0 \psi_g^2 \, dR \tag{3.13}$$

where s_0 is the equilibrium entropy, and ψ_f and ψ_g stand for the small non-equilibrium terms in (3.8) and (3.9), namely $f = f_0(1 + \psi_f)$ and $g = g_0(1 + \psi_g)$.

Therefore the explicit expression for the entropy in terms of $\overset{\circ}{P}{}^{vc}$, $\overset{\circ}{P}{}^{vp}$ and p^v will be

$$s = s_0 - (2T)^{-1} \alpha_{cc} \overset{\circ}{P}{}^{vc} : \overset{\circ}{P}{}^{vc} - (2T)^{-1} \alpha_{pp} \overset{\circ}{P}{}^{vp} : \overset{\circ}{P}{}^{vp} - (2T)^{-1} \alpha p^{v2} \tag{3.14}$$

with

$$\alpha_{cc} = \frac{15 \, kT}{2m^2} \int f_0 \alpha^2 c^4 \, dc \left(\int f_0 \alpha c^4 \, dc \right)^{-2} \tag{3.15}$$

$$\alpha_{pp} = \frac{15 \, kT}{n^2} \int g_0 \beta_1^2 R^4 \, dR \left(\int g_0 \phi' \beta_1 R^3 \, dR \right)^{-2} \tag{3.16}$$

$$\alpha_0 = \frac{18 \, kT}{n^2} \int g_0 \beta_2^2 R^4 \, dR \left(\int g_0 \phi' \beta_2 R^3 \, dR \right)^{-2}. \tag{3.17}$$

Now we compare equations (3.15)-(3.17) with the macroscopic predictions of (2.15). In order to do this, we must obtain the evolution equations (2.12)-(2.14) for the fluxes in the linear approximation. With this in mind, we introduce (3.8) and (3.9) into (3.5) and (3.6), respectively, and project the results on the functions $\alpha(c)c\overset{\circ}{c}$, $\beta_1(R)R\overset{\circ}{R}$ and $\beta_2(R)R^2$, respectively. We obtain in this way

$$\frac{2}{15} \int f_0 \alpha^2 c^4 \, dc \frac{\partial \overset{\circ}{A}}{\partial t} + \frac{2}{15} \frac{m}{kT} \int f_0 \alpha c^4 \, dc \, \overset{\circ}{V} = -\frac{1}{\tau_c} \overset{\circ}{A} + \text{NL} \tag{3.18}$$

$$\frac{2}{15} \int g_0 \beta_1^2 R^4 \, dR \frac{\partial \overset{\circ}{B}}{\partial t} - \frac{2}{15} \int g_0 \beta_1 \frac{w'}{kT} R^3 \, dR \, \overset{\circ}{V} = -\frac{1}{\tau_p} \overset{\circ}{B} + \text{NL} \tag{3.19}$$

$$\int g_0 \beta_2^2 R^4 \, dR \frac{\partial b}{\partial t} - \frac{1}{3} \int g_0 \beta_2 \frac{w'}{kT} R^3 \, dR (\nabla \cdot \boldsymbol{u}) = -\frac{1}{\tau_0} b + \text{NL} \tag{3.20}$$

where NL stands for non-linear terms, which are not the concern of this work, and

where the relaxation times are related to the operators $\mathscr{C}$ and $\mathscr{D}$ of (3.5) and (3.6) by

$$-\frac{1}{\tau_c} = \int f_0 \alpha c_i c_j \mathscr{C}(\alpha c_i c_j) \, \mathrm{d}\mathbf{c}$$

$$-\frac{1}{\tau_p} = \int g_0 \beta_1 R_i R_j \mathscr{D}(\beta_1 R_i R_j) \, \mathrm{d}\mathbf{R}$$

$$-\frac{1}{\tau_0} = \int g_0 \beta_2 R^2 \mathscr{D}(\beta_2 R^2) \, \mathrm{d}\mathbf{R}.$$

We do not need the explicit expressions for the relaxation times. The ratios τ/η may be directly obtained from the quotient between the terms in the time derivative of the viscous pressure and the terms in velocity gradients, as can be seen in (2.12)–(2.14). We therefore obtain from (3.18)–(3.20), taking into account (3.10)–(3.12),

$$\frac{\tau_c}{2\eta_c} = \frac{15 \, kT}{m^2} \int f_0 \alpha^2 c^4 \, \mathrm{d}\mathbf{c} \left(\int f_0 \alpha c^4 \, \mathrm{d}\mathbf{c} \right)^{-2} \tag{3.21}$$

$$\frac{\tau_p}{2\eta_p} = \frac{15 \, kT}{n^2} \int g_0 \beta_1^2 R^4 \, \mathrm{d}\mathbf{R} \left(\int g_0 \phi' \beta_1 R^3 \, \mathrm{d}\mathbf{R} \int g_0 w' \beta_1 R^3 \, \mathrm{d}\mathbf{R} \right)^{-1} \tag{3.22}$$

$$\frac{\tau_0}{\eta_v} = \frac{18 \, kT}{n^2} \int g_0 \beta_2^2 R^4 \, \mathrm{d}\mathbf{R} \left(\int g_0 \phi' \beta_2 R^3 \, \mathrm{d}\mathbf{R} \int g_0 w' \beta^2 R^3 \, \mathrm{d}\mathbf{R} \right)^{-1}. \tag{3.23}$$

When comparing (3.21) with (3.15), one sees that the thermodynamic prediction $\alpha_{cc} = \tau_c/2\eta_c$ is always satisfied. Comparison of (3.22) with (3.16) and (3.23) with (3.17) is not so direct. In fact, the equality between these expressions implies a restriction upon the functions appearing in the integrals. An easy way to satisfy the restriction is to put $w' = \phi'$; this is indeed the case up to first order in the density. The equilibrium pair correlation function may be written as (Green 1960)

$$g = \exp(-w/kT) = \exp(-\phi/kT)\left(1 + \sum_i a_i n^i\right)$$

so that, up to first order in the density, w (the effective potential) does coincide with ϕ (the interaction potential).

Since the viscous pressure due to the interaction terms is by itself of order n^2, as is seen in (3.4), we conclude that the thermodynamic prediction for the entropy is confirmed not only for the ideal gas terms (order n), but also in the order n^2 corresponding to the real gas. However, no definite conclusion can be reached up to the order n^3, though in this order w no longer coincides with ϕ, the entropy contributions coming from f_3, the three-particle distribution function, have been neglected in (3.2) from the outset.

It is worth mentioning that the evolution equations for the fluxes can be obtained in a more general way (Kirkwood *et al* 1949, Hess 1983). If we multiply both sides of (3.5) by $mc\mathring{c}$ and, on the other hand, we multiply (3.6) by $-(n^2/2)(\phi'/R)R\mathring{R}$ and by $-(n^2/6)\phi'R$ and integrate, we find in the linear approximation

$$\frac{\partial \mathring{\mathbf{P}}^{vc}}{\partial t} + \frac{2m^2}{15 \, kT} \int c^4 f_0 \, \mathrm{d}\mathbf{c} \, \mathring{\mathbf{V}} = m \int c\mathring{c} \mathscr{C}(f) \, \mathrm{d}\mathbf{c} \tag{3.24}$$

$$\frac{\partial \mathring{\mathbf{P}}^{vp}}{\partial t} + \frac{n^2}{15} \int (4R\phi' + R^2\phi'') g_0 \, \mathrm{d}\mathbf{R} \, \mathring{\mathbf{V}} = -\tfrac{1}{2} n^2 \int \frac{\phi'}{R} R\mathring{R} D(g) \, \mathrm{d}\mathbf{R} \tag{3.25}$$

$$\frac{\partial p^v}{\partial t} + \frac{n^2}{18} \int (4R\phi' + R^2\phi'') g_0 \, \mathrm{d}\mathbf{R} (\nabla \cdot \mathbf{u}) = -\tfrac{1}{2} n^2 \int \phi' R \mathscr{D}(g) \, \mathrm{d}\mathbf{R} \tag{3.26}$$

where the right-hand sides can be written as in (3.18)–(3.20) if (3.8) and (3.9) are introduced into the integrals.

Comparing the above equations with (2.12)–(2.14), one obtains

$$\frac{\tau_c}{2\eta_c} = \left(\frac{2m^2}{15\,kT} \int c^4 f_0 \, \mathrm{d}c\right)^{-1} = (2nKT)^{-1} \tag{3.27}$$

$$\frac{\tau_p}{2\eta_p} = \left(\frac{n^2}{15} \int (4R\phi' + R^2\phi'')g_0 \, \mathrm{d}R\right)^{-1} \tag{3.28}$$

$$\frac{\tau_0}{\eta_v} = \left(\frac{n^2}{18} \int (4R\phi' + R^2\phi'')g_0 \, \mathrm{d}R\right)^{-1} \tag{3.29}$$

which should in turn be equivalent to (3.15)–(3.17). This requirement places conditions on the functions $\alpha(c)$, $\beta_1(R)$ and $\beta_2(R)$. It is easy to see that (3.15) coincides with (3.27) if $\alpha(c) = $ constant, for instance. In (3.16) and (3.17) we put $\beta_1 \sim \beta_2 \sim (\phi'/R)$ and the integrals become of the form $I = \int \phi'^2 R^2 g_0 \, \mathrm{d}R$. If, furthermore, $w' \simeq \phi'$, then $g_0' = -(w'/kT)g_0 \simeq -(\phi'/kT)g_0$, and we get $I = -kT \int \phi' R^2 g_0' \, \mathrm{d}R$. Now we integrate by parts:

$$I = \int \frac{g_0}{R^2}(\phi' R^4)' \, \mathrm{d}R = KT \int (4R\phi' + R^2\phi'')g_0 \, \mathrm{d}R$$

which shows the equivalence with (3.35) and (3.36), assuming that ϕ' goes to zero faster than R^{-4}.

Summing up, we have the following sufficient conditions on the form of the distribution functions (3.8) and (3.9): (i) $\alpha(c) = $ constant, (ii) $\beta_1(R) \sim \phi'/R$, (iii) $\beta_2(R) \sim \phi'/R$, and also the condition $w' \simeq \phi'$. In the domain of validity of these conditions, the macroscopic results are supported by the microscopic ones. This is the case up to order n^2, as we will confirm from fluctuation theory.

4. Fluctuation theory

In this section we will show that fluctuation theory also places restrictions on the comparison of macroscopic theory and kinetic theory, which are the kind of restrictions we have found in the previous section.

We may use the generalised entropy (2.16) to calculate the fluctuations of dissipative fluxes (Jou and Careta 1982, Casas-Vázquez and Jou 1984), in combination with the Einstein formula for the probability of fluctuations, namely

$$Pr \sim \exp(\delta^2 S/2k). \tag{4.1}$$

This procedure leads to the following expressions for the second moments of the fluctuations of the fluxes:

$$\langle \delta \mathring{P}_{12}^{vc} \delta \mathring{P}_{12}^{vc}\rangle = \frac{kT\eta_c}{V\tau_c} \tag{4.2}$$

$$\langle \delta \mathring{P}_{12}^{vp} \delta \mathring{P}_{12}^{vp}\rangle = \frac{kT\eta_p}{V\tau_p} \tag{4.3}$$

$$\langle \delta p^v \delta p^v\rangle = \frac{kT\eta_v}{V\tau_0} \tag{4.4}$$

where the angular brackets stand for the equilibrium average of the fluctuations.

The second moments of the fluctuations, i.e. the left-hand-side of (4.2)–(4.4), may also be evaluated from kinetic theory. Indeed, from (3.2) and (3.3) one has

$$\langle \delta \mathring{P}^{vc}_{12} \delta \mathring{P}^{vc}_{12} \rangle = m^2 \int d\boldsymbol{c} \int d\boldsymbol{c}' \ c_1 c_2 c_1' c_2' \langle \delta f cc \rangle \delta f cc' \rangle \rangle \tag{4.5}$$

$$\langle \delta \mathring{P}^{vp}_{12} \delta \mathring{P}^{vp}_{12} \rangle = \frac{n^4}{4} \int d\boldsymbol{R} \int d\tilde{\boldsymbol{R}} \frac{\phi'(R)}{R} R_1 R_2 \frac{\phi'(\tilde{R})}{\tilde{R}} \tilde{R}_1 \tilde{R}_2 \langle \delta g(\boldsymbol{R}) \delta g(\tilde{\boldsymbol{R}}) \rangle \tag{4.6}$$

$$\langle \delta p^v \delta p^v \rangle = \frac{n^4}{36} \int d\tilde{\boldsymbol{R}} \ \phi'(R) \phi'(\tilde{R}) R \tilde{R} \langle \delta g(\boldsymbol{R}) \delta g(\tilde{\boldsymbol{R}}) \rangle \tag{4.7}$$

where δf and δg stand for the fluctuations of f and g with respect to their equilibrium values.

We may obtain the second moments of the fluctuations of f and g by applying the Einstein formula (4.1) to the entropy (3.2) expressed in terms of f and g. We obtain

$$\langle \delta f(\boldsymbol{c}) \delta f(\boldsymbol{c}') \rangle = \delta(\boldsymbol{c} - \boldsymbol{c}') f_0(c) / V \tag{4.8}$$

$$\langle \delta g(\boldsymbol{R}) \delta g(\boldsymbol{R}') \rangle = \delta(\boldsymbol{R} - \boldsymbol{R}') \frac{2}{n^2} \frac{g_0(R)}{V} \tag{4.9}$$

$\delta(\boldsymbol{c} - \boldsymbol{c}')$ and $\delta(\boldsymbol{R} - \boldsymbol{R}')$ being the respective Dirac deltas.

These are now introduced into (4.5)–(4.7); then

$$\langle \delta \mathring{P}^{vc}_{12} \delta \mathring{P}^{vc}_{12} \rangle = \frac{m^2}{15 V} \int c^4 f_0 \, dc \tag{4.10}$$

$$\langle \delta \mathring{P}^{vp}_{12} \delta \mathring{P}^{vp}_{12} \rangle = \frac{n^2}{30 V} \int \phi'^2 R^2 g_0 \, d\boldsymbol{R} \tag{4.11}$$

$$\langle \delta p^v \delta p^v \rangle = (n^2 / 18 V) \int \phi'^2 R^2 g_0 \, d\boldsymbol{R}. \tag{4.12}$$

Finally, taking into account (4.2)–(4.4), we obtain

$$\frac{\tau_c}{2\eta_c} = \frac{15 \ kT}{2 \ m^2} \left(\int c^4 f_0 \, dc^1 \right)^{-1} = (2n \ kT)^{-1} \tag{4.13}$$

$$\frac{\tau_p}{2\eta_p} = \frac{15 \ kT}{n^2} \left(\int \phi'^2 R^2 g_0 \, d\boldsymbol{R} \right)^{-1} \tag{4.14}$$

$$\frac{\tau_0}{\eta_v} = \frac{18 \ kT}{n^2} \left(\int \phi'^2 R^2 g_0 \, d\boldsymbol{R} \right)^{-1}. \tag{4.15}$$

Now we compare (4.13)–(4.15) with (3.24)–(3.26). Both sets of relations will coincide if (i) $\alpha(c) = $ constant, (ii) $\beta_1 \sim \beta_2 \sim \phi'/R$, (iii) $\phi \simeq w$. Therefore the comparison with fluctuation theory is more restrictive than that with the entropy results, and confirms the results obtained in the previous section.

We may further examine the requirements $\alpha = $ constant, $\beta_1 \sim \beta_2 \sim \phi'/R$ from another point of view. These correspond to the non-equilibrium distribution functions (3.8) and (3.9) of the form

$$f = f_0 \left[1 + \left(\frac{m}{15} \int c^4 f_0 \, dc \right)^{-1} c\mathring{c} : \mathring{P}^{vc} \right] \tag{4.16}$$

$$g = g_0 \left[1 - \left(\frac{n^2}{15} \int \phi'^2 R^2 g_0 \, d\boldsymbol{R} \right)^{-1} \frac{\phi'}{R} R\mathring{R} : \mathring{P}^{vp} - \left(\frac{n^2}{6} \int \phi'^2 R^2 g_0 \, d\boldsymbol{R} \right)^{-1} \phi' R p^v \right]. \tag{4.17}$$

These distribution functions are precisely those which would be obtained by maximum entropy arguments (Levine and Tribus 1979). Indeed, with these arguments one has for the distribution functions f and g, maximising the entropy (3.2) under conditions of fixed density, energy, momentum and viscous pressures $\mathring{\boldsymbol{P}}^{vc}$, $\mathring{\boldsymbol{P}}^{vp}$ and p^v,

$$f = f_0 \exp[-mc\mathring{c} : \boldsymbol{a}_c] \tag{4.18}$$

$$g = g_0 \exp[-\tfrac{1}{2}n^2(\phi'/R)\boldsymbol{R}\mathring{\boldsymbol{R}} : \boldsymbol{a}_p - \tfrac{1}{6}n^2\phi'Ra_0] \tag{4.19}$$

with $\boldsymbol{a}_c$, $\boldsymbol{a}_p$ and a_0 being Lagrange multipliers. In the exponent of (4.18) and (4.19) there appear the microscopic operators corresponding to the fixed quantities $\mathring{\boldsymbol{P}}^{vc}$, $\mathring{\boldsymbol{P}}^{vp}$ and p^v. Expanding these exponentials up to the linear terms in the multipliers and evaluating them with the help of (3.2) and (3.3), we regain (4.16) and (4.17). Therefore the conditions to be satisfied by the functions $\alpha(c)$, $\beta_1(R)$ and $\beta_2(R)$ are those corresponding to the maximum entropy formalism. In this case, the predictions of extended thermodynamics are confirmed by microscopic theory.

5. Conclusions

We have been able to show in this paper that the predictions of extended irreversible thermodynamics, are verified by a microscopic theory up to second order in the density in the case of a real gas. To this end, the viscous pressure tensor was considered as a sum of two terms corresponding to the kinetic and potential parts of a molecular picture of the gas, each term being characterised by its own contribution to the transport coefficient and its own relaxation time. In this way we showed that extended thermodynamics may incorporate microscopic information about the system it describes and it is able to reach definite predictions which may be checked from microscopic theories. This formalism is seen to be flexible enough to be applied in different circumstances.

The physical motivation for the decomposition of the traceless part of the viscous pressure tensor has here been a microscopic one. One could ask whether it is possible to reach such a conclusion from a purely macroscopic basis. The model adopted in § 2 of this paper leads, for the damping coefficient of ultrasound (Balescu 1975), to

$$\Gamma(\omega) = \frac{1}{2\rho} \left[\frac{4}{3} \left(\frac{\eta_c}{1+\omega^2\tau_c^2} + \frac{\eta_p}{1+\omega^2\tau_p^2} \right) + \frac{\eta_v}{1+\omega^2\tau_0^2} \right] \tag{5.1}$$

which for low frequencies reduces to the classical value (neglecting heat conduction effects).

In principle, comparison of (5.1) with experimental results could indicate whether or not the assumption $\tau_c = \tau_p$ of usual extended thermodynamics is adequate. However, it would probably be difficult to reach such a conclusion from a purely experimental basis, since in liquids $\eta_c \ll \eta_p$ and in rarefied gases $\eta_c \gg \eta_p$, so that in many cases the assumption of the traceless viscous pressure tensor being a single quantity would be sufficiently satisfactory.

Recall, finally, that we have not stated that all real fluids satisfy extended irreversible thermodynamics, but only those fluids whose constitutive equations for the evolutions of the viscous pressure are of the relaxational form (2.12)–(2.14). In this case, the connection between these equations and a generalised entropy of the form (2.16) is confirmed, up to second order in the density, from a microscopic point of view.

Acknowledgments

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