Corrections to maximum entropy formalism for steady heat conduction

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Abstract. Corrections to the maximum entropy formalism for heat conduction in a dense fluid can be made to ensure that the heat flux, J, is calculated in a mass-centre-fixed frame and to take into account the density gradient ∇n which builds up in a steady state. The first correction effects only $O(J^6)$ in the free energy, F. The second correction yields $O([\nabla n]^2)$ in F which, in $P = -\partial F/\partial V$ for a hard-sphere model, dominates the $O(J^2)$ term, calculated in earlier work, in a steady state. The maximum entropy formalism, when applied to an experimental problem, must maximise the entropy functional subject to all conditions implicit in that problem if quantiative predictions are to be made.

1. Introduction

In a previous work (Nettleton 1988) the formalism developed by Jou *et al* (1984) was applied to calculate the dependence of the free energy and pressure of a dense fluid on the square of the heat flux, which is a state variable in the framework of extended non-equilibrium thermodynamics. The method determines a phase-space distribution, $\rho(x)$, which maximises the information-theoretic entropy

$$S = -\kappa \int \rho \ln \rho \, dx \tag{1}$$

subject to the condition that the internal energy E and heat flux J, calculated from $\rho(x)$, have specified values. In the case of dense hard spheres, the $O(J^2)$ terms in the thermodynamic functions were found to be negligibly small for a reasonable rate of heat flow, in agreement with an earlier work (Nettleton 1987) which calculated the same terms by applying reciprocity, in the context of extended non-equilibrium thermo-dynamics, to a kinetic equation for $\partial J/\partial t$ derived from the Liouville equation. Nevertheless, systematic differences between the two treatments were observed. Specifically, the $O(J^2)$ term in the pressure calculated from the maximum entropy formalism was two orders of magnitude smaller than the same term calculated via reciprocity. This discrepancy may be related to the fact that the approach utilising reciprocity applied a mechanical stability condition neglected in the more recent work (Nettleton 1988). We shall proceed here to show that if thermodynamic potentials for a particular physical situation are to be derived by maximising S given by equation (1), then the subsidiary conditions must include all the information implicit in the experiment to be analysed, including mechanical stability when one is dealing with a steady state.

There are two items of physical information which have been omitted in earlier applications (Jou *et al* 1984, Nettleton 1988) of the maximum entropy formalism to heat conduction. The first of these is that the calculation must be done in a frame in which the mass centre is fixed. Thus if $\hat{P}$ is the total momentum, we have

$$\int \rho\hat{P}\,\mathrm{d}x = 0 \tag{2}$$

as an additional condition to be applied in maximising the information-theoretic S. Application of a large temperature gradient causes the centre of mass initially to move, and we wish to determine the lowest order in the J dependence of F which is affected if we calculate all quantities in a centre-of-mass-fixed frame. The second item of information we must include in maximising S is the presence of a density gradient in the steady state. For such a state to exist, the pressure must be uniform across the system, and so a density gradient builds up until, in hard spheres where P_0 is proportional to T,

$$\nabla n = -P_0 n\beta_t T^{-1}\nabla T \qquad \beta_t \equiv n^{-1}(\partial n/\partial P)_T \tag{3}$$

where $P_0(n, t)$ is the equilibrium equation of state. Given that a density gradient is present, we conclude that if $\hat{A}$ is an operator whose average value is $\partial n/\partial x$, assuming ∇n is in the x direction, we get

$$\alpha \equiv \partial n/\partial x = \int \rho\hat{A}\,\mathrm{d}x \tag{4}$$

as an additional subsidiary condition to be applied in maximising S.

The addition of the state variable α implies that F, and the pressure $P = -\partial F/\partial V$, will have contributions $O(\alpha^2)$ in addition to the $O(J^2)$ terms previously considered (Jou *et al* 1984, Nettleton 1988). In a steady state, since $\nabla T = -J/\lambda$, where λ is the thermal conductivity, equation (3) yields

$$\alpha = P_0 n\beta_t(\lambda T)^{-1}J_x \tag{5}$$

and so F and P will have two terms proportional to J^2 whose relative magnitudes we can compare for the case of dense hard spheres. While both contributions remain unobservably small, the $O(\alpha^2)$ terms in P dominate the $O(J^2)$ terms. This points up the fact that the density gradient is a state variable whose relaxation toward a steady state is coupled to the heat flow (Nettleton 1961), and an information-theoretic approach to states far from equilibrium must take it, and any other information pertinent to a particular experiment, into account.

In the following section, we shall examine the maximisation of S, given by equation (1), subject to condition (2) among others. This serves to establish very generally that condition (2) does not affect the computation of the first two terms in the J dependence of F and functions such as pressure P derivable from it. In section 3, we discuss the model and define the operator $\hat{A}$ in equation (4). By maximising the information-theoretic S subject to (4), we relate the $O(\alpha^2)$ term in F to the equilibrium correlation $\langle\hat{A}\hat{A}\rangle_0$. The latter can be evaluated in terms of the equilibrium radial distribution function, $g(r)$, and numerical details for dense hard spheres are worked out in section 4, based on the Percus-Yevick equation for $g(r)$. There we compare the relative magnitudes in the steady state of the $O(\alpha^2)$ and $O(J^2)$ terms in P and conclude that the density gradient must be taken into account in applying information theory to steady heat conduction. In section 5, these results will be summarised along with our general conclusions.

2. Fixed centre-of-mass condition

In this section, we examine the maximisation of the functional (1) subject to the conditions

$$E = \int \rho \hat{H} \, dx \tag{6a}$$

$$J = \int \rho \hat{J} \, dx \tag{6b}$$

$$0 = \int \rho \hat{P} \, dx. \tag{6c}$$

The system is taken to be a cube of side $l = 10^{-6}$ m immersed in a continuous liquid phase, as in earlier work (Nettleton 1987, 1988). This system is macroscopically small but large enough to associate with it a thermodynamic temperature T which varies from one cubic cell to another, producing the macroscopic temperature gradient. The heat flux operator, $\hat{J}$, and total momentum, $\hat{P}$, are given by

$$l^3 \hat{J} \equiv \sum_i [\{(p_i^2/2m) - h + \tfrac{1}{2} \sum_{j \neq i} \phi_{ij}\} \delta + \tfrac{1}{2} \sum_{j \neq i} r_{ij} F_{ij}] \cdot (p_i/m) \tag{7a}$$

$$\hat{P} \equiv \sum_i p_i \tag{7b}$$

where h is the enthalpy per particle, ϕ the pair potential, and the sums are over the N particles in the system. F_{ij} is the force on the particle at r_i arising from its interaction with the particle j at r_j, with $r_{ij} \equiv r_j - r_i$ and δ is the Kronecker delta.

The solution of the variational problem of maximising (1) subject to ($6a$–c) is:

$$\rho = Z^{-1} \exp(-\beta \hat{H} - \gamma \cdot \hat{J} - \nu \cdot \hat{P}) \tag{8}$$

where Z normalises ρ to unity, and β, γ, and ν are Lagrange multipliers. Jou *et al* (1984) have shown that $\beta = (\kappa T)^{-1}$, where T is the thermodynamic temperature. If we substitute (8) back into (1) and calculate $F = E - TS$, using ($6a$), we find the thermodynamic force

$$\Phi = -\partial F/\partial J = \beta^{-1} \gamma. \tag{9}$$

Φ and ν can be found in the form of expansions in powers of J from the consistency conditions ($6b, c$) written in the form:

$$J = Z^{-1} \int \hat{J} \exp(-\beta \hat{H} - \beta \Phi \cdot \hat{J} - \nu \cdot \hat{P}) \, dx \tag{10a}$$

$$0 = Z^{-1} \int \hat{P} \exp(-\beta \hat{H} - \beta \Phi \cdot \hat{J} - \nu \cdot \hat{P}) \, dx. \tag{10b}$$

We can put

$$\nu = \mu_1 \Phi + \mu_3 \Phi^2 \Phi + O(\Phi^5) \tag{11}$$

in ($10b$) and solve for μ_1, μ_3 by equating to zero the coefficient of each power of Φ. Substitution of the result into ($10a$) permits us to obtain, in a similar fashion, an expansion of Φ in powers of J. The maximum entropy formalism thus provides a way of using the consistency conditions to calculate the forces in extended thermodynamics as expansions in powers of the corresponding state variable. Equation (9) ensures that the result is consistent with the Gibbs equation.

When we expand ($10b$) in powers of $\boldsymbol{\Phi}$ and ν, we can utilise, with zero subscript denoting an equilibrium canonical average,

$$\langle (\boldsymbol{\nu} \cdot \hat{\boldsymbol{P}})^2 \rangle_0 = \nu^2 Nm\kappa T \tag{12a}$$

$$\langle \boldsymbol{\Phi} \cdot \boldsymbol{J}\boldsymbol{\nu} \cdot \hat{\boldsymbol{P}} \rangle_0 = n\kappa T\boldsymbol{\Phi} \cdot \boldsymbol{\nu}\left(\tfrac{3}{2}\kappa T - h + \tfrac{1}{2}\int \phi(r)ng(r)\,\mathrm{d}r + (P_0/n)\right)$$

$$= 0. \tag{12b}$$

The last result follows from the definition of h. Equation ($10b$) reduces to:

$$Nm\nu\kappa T + \tfrac{1}{6}\langle \hat{\boldsymbol{P}}(\boldsymbol{\Phi} \cdot \hat{\boldsymbol{J}})^3 \rangle_0 \beta^3 = 0 \tag{13}$$

so that $\nu = \mathrm{O}(\Phi^3)$.

Taking into account ($12b$), we see that ν contributes to ($12a$) terms of order higher than three in $\boldsymbol{\Phi}$. Therefore, it will not affect the calculation of $\boldsymbol{\Phi}$ to terms $\mathrm{O}(J^2 J)$ or F to $\mathrm{O}(J^4)$. The earlier calculations of these terms (Jou *et al* 1984, Nettleton 1988) are not changed, although condition ($10b$) may affect the calculation of terms of still higher order. The latter, however, are expected to be very small, which is true of the $\mathrm{O}(J^2 J)$ terms already estimated.

3. Dependence of free energy on the density gradient

When a fluid is divided up into macroscopically small cells having each a volume of $1\ \mu\mathrm{m}^3$ and the 'system' is taken to be one of these cells, there are two density gradients relevant to such a description. In defining one of these gradients, we introduce a continuous function $\bar{n}(r)$ which agrees at the centre of each cell with the mean density Nl^{-3} in the cell. This is similar to the introduction of a continuously varying thermodynamic temperature $T(r)$. The functions $\bar{n}(r)$ and $T(r)$ characterise phenomena having wavelengths much greater than l. Alternatively $\nu(r_1) = N \int \rho \, \mathrm{d}r_2 \ldots \mathrm{d}r_N$ is a local density which varies from place to place in the interior of a cell. The average value of $\nabla_r \nu(r)$, taken over the volume l^3, is a density gradient which describes the internal state of the fluid and which need not equal $\nabla \bar{n}$.

So long as we are concerned only with the description of phenomena whose associated wavelengths are much greater than l, we need not distinguish between the macroscopic and average microscopic ∇n. We shall suppose that ∇n is in the x direction and that $\alpha \equiv \partial n/\partial x$ is an internal state variable which appears in F and the thermodynamic potentials. Under these circumstances, we have Gibbs equation, equivalent to

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V - X\,\mathrm{d}\alpha - \boldsymbol{\Phi} \cdot \mathrm{d}\boldsymbol{J}. \tag{14}$$

X, in first approximation, is proportional to α, and we can calculate it much as we can calculate $\boldsymbol{\Phi}$ from ($6b$). Once we have X, we can find the $\mathrm{O}(\alpha^2)$ term in F from $\partial F/\partial \alpha = -X$, as demonstrated in earlier work (Nettleton 1961) based on (14) and a kinetic equation linking $\dot{\alpha}$ to the heat flux. The latter work set up the general extended thermodyanamics incorporating the density gradient as a relaxing state variable.

To apply the maximum entropy formalism to the calculation of X, we require an $\hat{A}$ consistent with (4). To set up such an operator, observe that the Fourier k transform of the local density is:

$$\hat{n}(k) = \sum_i \exp(\mathrm{i}k \cdot r_i). \tag{15}$$

The average of the density gradient operator taken over a cell of volume l^3 is

$$\hat{A} = l^{-1}[\hat{n}(x = \tfrac{1}{2}l) - \hat{n}(x = -\tfrac{1}{2}l)]$$

$$= l^{-1}(2\pi)^{-3} \int \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i)[\exp(-ik_x l/2) - \exp(ik_x l/2)] \, d\mathbf{k}. \tag{16}$$

In calculating the integral in (16), we shall introduce the stipulation that, in the x direction, we are interested only in wavelengths greater than l. Structural variations of smaller wavelength are associated with very short-wavelength hypersound which governs the kinetics of structural relaxation. It produces local expansions of diameter having the order of the intermolecular separation which permit self-diffusion and molecular rearrangement. In the y and z direction, there is no macroscopic structural variation, and so there is no physical reason to restrict k_y and k_z in (16). Accordingly, the domain of the k integration in (16) is:

$$\frac{-2\pi}{l} \leq k_x \leq \frac{2\pi}{l} \qquad \frac{-\pi}{\sigma} \leq k_y \leq \frac{\pi}{\sigma} \qquad \frac{-\pi}{\sigma} \leq k_z \leq \frac{\pi}{\sigma}. \tag{17}$$

σ is the effective hard-core diameter, anticipating the application to hard spheres in the next section. There should be no structural wavelengths less than 2σ, the smallest intermolecular separation. Equation (17) is a sufficient condition for F and X to be extensive, i.e. proportional to l^3.

By analogy with (8), we write down the expression for ρ, given by maximising S, in the form

$$\rho = Z^{-1} \exp[-\beta(\hat{H} + X\hat{A})]. \tag{18}$$

Drawing on the result of section 2 which carries over to the situation considered here, we have not introduced $\hat{P}$. Inserting this result into (4) and expanding in powers of X, we have

$$\alpha = -\beta Z_0^{-1} \int \exp(-\beta\hat{H})\hat{A}\hat{A}X \, dx + O(X^3). \tag{19}$$

Thus

$$X = -\kappa T\alpha/\langle\hat{A}\hat{A}\rangle_0 + O(\alpha^3) = -\partial F/\partial\alpha \tag{20a}$$

$$F = \tfrac{1}{2}(\kappa T/\langle\hat{A}\hat{A}\rangle_0)\alpha^2 + O(\alpha^4) \tag{20b}$$

where subscript zero denotes an equilibrium canonical average.

Using (16), we can write

$$\langle\hat{A}\hat{A}\rangle_0 = [l^2(2\pi)^6 Z_0]^{-1} \int \exp(-\beta\hat{H}) \, dx \, d\mathbf{k} \, d\mathbf{k}'$$

$$\times [\exp(\tfrac{1}{2}ik_x l) - \exp(-\tfrac{1}{2}ik_x l)]$$

$$\times [\exp(\tfrac{1}{2}ik_x' l) - \exp(-\tfrac{1}{2}ik_x' l)] \sum_i \exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}_i] \sum_j \exp[i\mathbf{k}' \cdot (\mathbf{r}_j - \mathbf{r}_i)]$$

$$\tag{21}$$

where the limits on $\mathbf{k}$ and $\mathbf{k}'$ are given in (17).

To simplify (21), consider separately the N terms in which $i = j$ and the $N(N-1)$ terms where $i \neq j$. Typically, we can set $i = 1, j = 2$. Equation (21) becomes

$$\langle \hat{A}\hat{A} \rangle_0 = -[l^2(2\pi)^6]^{-1} \int \mathrm{d}\mathbf{k}\, \mathrm{d}\mathbf{k}' \sin(\tfrac{1}{2}k_x l) \sin(\tfrac{1}{2}k'_x l)$$

$$\times \prod_{i=1}^{3} \{2 \sin[\tfrac{1}{2}(k_i + k'_i)l](k_i + k'_i)^{-1}\}\left[n + n^2 \int g(r) \exp(\mathrm{i}\mathbf{k}' \cdot \mathbf{r})\,\mathrm{d}\mathbf{r} \right] \qquad (22)$$

where $g(r)$ is the radial distribution function. In the first term in the square bracket, we have two factors, equal to

$$\int_{-\pi/\sigma}^{\pi/\sigma} \int_{-\pi/\sigma}^{\pi/\sigma} 2(k_i + k'_i)^{-1} [\sin(k_i + k'_i)l/2]\, \mathrm{d}k_i\, \mathrm{d}k'_i$$

$$\simeq \frac{8\pi}{\sigma} \int_0^{2\pi/\sigma} \bar{k}^{-1} \sin(\bar{k}l)\, \mathrm{d}\bar{k} \simeq 4\pi^2/\sigma \qquad i = 2, 3. \qquad (23)$$

We have introduced new coordinates, $\bar{k} \equiv k + k'$ and $\bar{k}' \equiv k - k'$ and have extended the range of integration to infinity because σ is small. The third factor in the first term is

$$\int_{-2\pi/l}^{2\pi/l} \int_{-2\pi/l}^{2\pi/l} \mathrm{d}k_x\, \mathrm{d}k'_x \sin(\tfrac{1}{2}k_x l) \sin(\tfrac{1}{2}k'_x l)[2/(k_x + k'_x)] \sin[\tfrac{1}{2}(k_x + k'_x)l]$$

$$= -4\pi l^{-1} \mathrm{Si}(4\pi) - 2l^{-1} \mathrm{Cin}(4\pi) \qquad (24)$$

which is achieved by introducing the same change of integration variable as in (23). The function Cin is defined by Abramowitz and Stegun (1964, p 231).

When we examine the term in (22) involving $g(r)$, we find the integrals corresponding to (23) have the form:

$$2 \int_{-\pi/\sigma}^{\pi/\sigma} \int_{-\pi/\sigma}^{\pi/\sigma} \mathrm{d}k_y\, \mathrm{d}k'_y (k_y + k'_y)^{-1} \sin[\tfrac{1}{2}(k_y + k'_y)l] \exp(\mathrm{i}k'_y r_y)$$

$$= 2 \int_{-2\pi/\sigma}^{2\pi/\sigma} \bar{k}^{-1} \sin(\tfrac{1}{2}\bar{k}l) \int_{\bar{k}-\pi/\sigma}^{\bar{k}+\pi/\sigma} \exp(\mathrm{i}k'_y r_y)\, \mathrm{d}k'_y\, \mathrm{d}\bar{k}$$

$$= 4 \int_{-2\pi/\sigma}^{2\pi/\sigma} \bar{k}^{-1} \sin(\tfrac{1}{2}\bar{k}l) r_y^{-1} \exp(\mathrm{i}\bar{k}r_y) \sin(\pi r_y/\sigma)\, \mathrm{d}\bar{k} \simeq 4\pi^2 \delta(r_y). \qquad (25)$$

Equation (25) holds as well for the z component of the $\mathbf{k}$ integration. We have let $\sigma \to 0$ as is done above where this leads to a finite result. A consequence of this is that the $\mathbf{r}$ integration in (22) reduces to an integral over r_x. The remaining integration over k_x and k'_x is the same as in (23) and (24), since the factor $\exp(\mathrm{i}k'_x r_x)$ can be set equal to unity, except for a very small shape-dependent correction.

The final result is:

$$\langle \hat{A}\hat{A} \rangle_0 = 4(l^3 \pi^2)^{-1}[\mathrm{Si}(4\pi) + \tfrac{1}{2} \mathrm{Cin}(4\pi)]\left(n\sigma^{-2} + 2n^2 \int_0^\infty \{g(r) - 1\}\, \mathrm{d}r \right). \qquad (26)$$

Since the system is immersed in an infinite fluid, the appropriate $g(r)$ corresponds to an infinite system. The r integration has been extended to infinity, since the integral converges for $k' \neq 0$, and this extension eschews finite-size effects which are artifacts of the cellular coarse graining. The approximate numerical evaluation of the integral in (26) will be discussed in section 4, using an exact solution to the hard-sphere Percus–Yevick equation for $g(r)$. There we shall compare the magnitudes in the steady state of the $\mathrm{O}(\alpha^2)$ and $\mathrm{O}(J^2)$ terms in P.

4. Numerical estimates for dense hard spheres

Since our objective is to compare the $O(\alpha^2)$ term in P calculated here with the $O(J^2)$ term obtained previously (Nettleton 1988), in a steady state where α and J_x are proportional, we choose the same model as before. This is a hard sphere fluid with $n\sigma^3 = 0.8$. $\sigma = 3.64 \times 10^{-10}$ m is an effective sphere diameter for Ar (Hirschfelder *et al* 1954, p 545) and $T = 87$ K is in the liquid density range for Ar at the pressure indicated in table 1. The density is below, but near, the gas–solid point for hard spheres, since in the approach (Nettleton 1987) which utilised reciprocity to evaluate the $O(J^2)$ contribution to F, it was necessary for the liquid to be dense enough to be contained within the system boundary during one relaxation time for J. That was a sufficient condition for interaction across the boundary to be proportional to P. The macroscopically small system for which we calculate F is a cube of side $l = 10^{-6}$ m containing $N = 1.66 \times 10^{10}$ spheres. For the equation of state $P_0(n, T)$, we use the expression obtained by Ree and Hoover (1964) by fitting a Padé approximant to computer results.

Table 1. Number density n at temperature T for hard spheres of diameter σ in cell of side l at pressure P_0. β_1 is the isothermal compressibility, λ the thermal conductivity, c_i ($i = 1, 2, 3$) and the parameters in equations (27c–f). $\bar{P}_2^{(n)}$ denotes the coefficient of α^2 in P, while $\bar{P}_2^{(n,J)} = \bar{P}_2^{(n)}(P_0 n \beta_1 / \lambda T)^2$ is the coefficient of J^2 which results when equation (5) is substituted for α in $\bar{P}_2^{(n)}\alpha^2$. $\bar{P}_2^{(J)}/P_0$ is the ratio to P_0 of the coefficient of J^2 in P obtained by applying the maximum entropy formalism and treating J as the only relaxing state variable. $\frac{1}{2}\nu_2^{(n)}$ is the coefficient of α^2 in F.

T	8.7	K
$n\sigma^3$	0.8	
σ	$3.64 \cdot 10^{-10}$	m
l	$1.00 \cdot 10^{-6}$	m
P_0	$1.54 \cdot 10^8$	Pa
β_1	$1.86 \cdot 10^{-9}$	Pa^{-1}
λ	$9.60 \cdot 10^{-3}$	$J\,s^{-1}\,m^{-1}\,K^{-1}$
c_0	-29.6	
c_1	32.2	
c_3	-6.20	
η	0.419	
$\langle \hat{A}\hat{A} \rangle$	$1.51 \cdot 10^{65}$	m^{-8}
$\bar{P}_2^{(n)}$	$6.44 \cdot 10^{-69}$	$J\,m^5$
$\bar{P}_2^{(n,J)}$	$2.08 \cdot 10^{-11}$	$m\,s^2 J^{-1}$
$\bar{P}_2^{(n,J)}/P_0$	$1.35 \cdot 10^{-19}$	$s^2\,m^4\,J^{-2}$
$\bar{P}_2^{(J)}/P_0$	$-9.27 \cdot 10^{-22}$	$s^2\,m^4\,J^{-2}$
$\nu_2^{(n)}$	$7.93 \cdot 10^{-87}$	$J\,m^8$

In the case of hard spheres, the Percus–Yevick approximate equation for $g(r)$ (McQuarrie 1976, p 276) has proved successful at liquid densities (Gray and Gubbins 1984, p 345), and we have utilised (Nettleton 1987, 1988) the exact solution thereto discussed by Wertheim (1963) and Thiele (1963). We propose to use this solution here to evaluate $\int [g(r) - 1] \, dr$. We cannot use the tabulated values of $g(r)$ given, for example, by Throop and Bearman (1965) because the table is truncated and does not extend to sufficiently large r. Instead, we start with the Fourier k transform of the Ornstein–Zernike equation

$$h(k) = c(k)/[1 - nc(k)] \tag{27}$$

where $h(r) \equiv g(r) - 1$, and $c(r)$ is the direct correlation function for which the Wertheim–Thiele solution gives an analytic expression (Gray and Gubbins 1984, p 345)

$$c(r) = c_0 + c_1(r/\sigma) + c_3(r/\sigma)^3 \qquad r < \sigma \tag{27a}$$

$$c(r) = 0 \qquad\qquad\qquad\qquad\qquad r > \sigma \tag{27b}$$

$$c_0 \equiv -(1 + 2\eta)^2/(1 - \eta)^4 \tag{27c}$$

$$c_1 \equiv 6\eta(1 + \tfrac{1}{2}\eta)^2/(1 - \eta)^4 \tag{27d}$$

$$c_3 \equiv \tfrac{1}{2}\eta c_0 \tag{27e}$$

$$\eta \equiv (\pi/6)n\sigma^3. \tag{27f}$$

From $(27a\text{-}e)$ $c(k)$ is readily calculated.

The result for $c(k)$ can be used in (27) which in turn can be introduced into

$$h(r) = \tfrac{1}{2}\pi^{-2} \int_0^x h(k) k r^{-1} \sin(kr)\,\mathrm{d}k. \tag{28}$$

From (28), we conclude that

$$\int_0^x h(r)\,\mathrm{d}r = (4\pi)^{-1} \int_0^x h(k)k\,\mathrm{d}k. \tag{29}$$

With $z \equiv \sigma k$, and

$$\phi(z) \equiv z^{-3}\{c_0(\sin z - z \cos z) + c_1 z^{-1}[2(z \sin z + \cos z - 1) - z^2 \cos z]$$
$$+ c_3 z^{-3}[\cos z(12z^2 - z^4 - 24) + \sin z(4z^3 - 24z) + 24]\} \tag{30}$$

we have

$$\int_0^x h(k)k\,\mathrm{d}k = 4\pi\sigma \int_0^x \mathrm{d}z\, \phi(z)[1 - 4\pi n\sigma^3 \phi(z)]^{-1}. \tag{31}$$

We thus express the integral of $h(r)$ in a form whose integrand is a well defined analytic function, rather than a truncated table, although, unfortunately, the integrand in (31) decays very slowly with increasing z. The integral is estimated here by using 48-point Gaussian quadrature in the range $0 \le z \le 100$ and by approximating the integral over the range $100 \le z \le \infty$ through keeping only the dominant term, $-\mathrm{Ci}(100)$. The resulting value of $\langle \hat{A}\hat{A} \rangle_0$ and the coefficient

$$\nu_2^{(n)} \equiv \kappa T/\langle \hat{A}\hat{A} \rangle_0 \tag{32}$$

are listed in table 1 for the values of n, σ, T, c_i, and η listed there.

If we write

$$P = P_0(n, T) + \bar{P}_2^{(n)}\alpha^2 \tag{33}$$

then from (26) and (32) we have

$$\bar{P}_2^{(n)} = -\tfrac{1}{2}(\partial/\partial V)\nu_2^{(n)}$$

$$= \tfrac{1}{2}\kappa T(\langle \hat{A}\hat{A} \rangle_0)^{-2} V^{-1}\left[-\hat{A}\hat{A}_0 - 4V^{-1}\left(n\sigma^{-2} + 4n^2 \right.\right.$$

$$\left.\left. \times \int_0^x h(r)\,\mathrm{d}r - 2n^3 \int_0^x \frac{\partial g(r)}{\partial n}\,\mathrm{d}r \right) \right]. \tag{34}$$

The only term whose calculation has not been discussed is the integral of $\partial g(r)/\partial n$. This has the form

$$\int_0^x \frac{\partial g}{\partial n} \, \mathrm{d}r = n^{-1}\sigma \int_0^x z \, \mathrm{d}z[(\tilde{\phi}(z) + 4\pi n\sigma^3\phi^2)(1 - 4\pi n\sigma^3\phi)^{-2}] \tag{35a}$$

$$\tilde{\phi}(z) \equiv n\partial\phi(z)/\partial n. \tag{35b}$$

$\tilde{\phi}$ can be calculated by finding the n-derivatives of $(27c-e)$. The z integration is then approximated as in (31) by 48-point Gaussian quadrature for the range $0 \le z \le 100$ and by $\sigma(\partial/\partial n)(c_0 + c_1 + c_3)\mathrm{Ci}(100)$ for the contribution from the range $z > 100$.

On inspecting the results in table 1, we see that, in a steady state with α proportional to J_x, the ratio $\bar{P}_2\alpha^2/P_0J^2 \equiv \bar{P}_2^{(n,J)}/P_0$ has the opposite sign and is two orders of magnitude larger than the corresponding ratio $\bar{P}_2^{(J)}/P_0$ of the coefficient of J^2 to P_0, calculated without taking α into account. This does not change the conclusion (Nettleton 1987, 1988) that in a computer simulation of hard spheres subject to a large temperature gradient we are unlikely to see contributions $O(|\nabla T|^2)$ in P and the thermal conductivity λ. It shows, however, that care must be taken when using the maximum entropy formalism to include all relevant information among the subsidiary conditions applied in maximising the information-theoretic S. Otherwise, quantitative predictions cannot be made.

4. Summary and discussion

Given a set of internal state variables, N, V, T, J, α, the maximum entropy formalism (Jaynes 1957a, b) is designed to make the best estimate of S consistent with the prescription that these variables have specified values, given e.g. by (4) and (6b). To maximise (1) subject to these specifications, one introduces Lagrange multipliers which were shown by Jou *et al* (1984) to be proportional to the thermodynamic forces. Such a proportionality assures consistency between the information-theoretic S and the Gibbs equation. The result is the non-equilibrium phase-space distribution (18).

In earlier treatments (Jou *et al* 1984, Nettleton 1988) the maximum entropy formalism was applied to heat conduction, with J the only non-equilibrium state variable. We observe here, however, that under a large temperature gradient the mass centre of the fluid will move until a density gradient builds up, satisfying the mechanical equilibrium condition $\nabla P = 0$. Therefore in the steady state an additional condition must be adduced in maximising S, namely that ∇n have the value calculated from this condition. An additional possible correction was considered, namely that J must be calculated in a frame in which the mass centre is at rest, but this condition does not affect terms in F out to $O(J^4)$.

The circumstance that ∇n appears in our treatment of the steady state reflects the fact that, in the neighbourhood of a steady state far from equilibrium, ∇n and J are both relaxing state variables obeying coupled equations of motion (Nettleton 1961). In an extended non-equilibrium thermodyanmic treatment (Nettleton 1987) with J as the only relaxing variable, ∇n was set proportional to ∇T and both were held constant, which may be valid very near a steady state, but not in general. If $\partial n/\partial x \equiv \alpha$ is a state variable, then $F = F_0 + \frac{1}{2}\nu_2^{(n)}\alpha^2 + \ldots$, and $X = -\partial F/\partial\alpha = -\nu_2^{(n)}\alpha$ is a thermodynamic force. We can calculate $\nu_2^{(n)}$ from the consistency condition (19), as is done in section 3, with numerical evaluation in section 4 for a hard-sphere model of liquid Ar at 87 K.

This permits a comparison of the relative magnitudes of the $O(\alpha^2)$ and $O(J^2)$ contributions to thermodynamic functions such as P. These terms are unobservably small in realisable steady states, but the $O(\alpha^2)$ contribution to P actually dominates.

We see from this result that the maximum entropy formalism offers a deceptive simplicity. One must take care in any problem to maximise the functional in (1) subject to all the conditions implicit in the experimental situation one seeks to analyse. Both the theory which applies reciprocity to a kinetic equation for J treated as the only relaxing variable (Nettleton 1987) and the maximum entropy result for the same case (Nettleton 1988) yield results for $\bar{P}_2$ differing in sign and magnitude from those obtained in the present paper. They serve only to make a qualitative prediction that nonlinear effects are expected to be small in liquids at high density.

We do not find any α^2 term in the internal energy, E, unlike the situation with regard to J where E has a contribution $O(J^2)$. To see this, calculate

$$\partial E / \partial \alpha = T \partial S / \partial \alpha - X = T \partial X / \partial T - X. \tag{36}$$

Since $\langle \hat{A}\hat{A} \rangle_0$ depends only on n, X is proportional to T, and $\partial E / \partial \alpha$ vanishes. Also, since $E = N(3/2)\kappa\theta$ for hard spheres, where θ is the local equilibrium temperature, we conclude that $T - \theta$ does not have an $O(\alpha^2)$ contribution. We have not attempted to calculate $O(\alpha^2)$ in X, despite the fact that $O(J^3)$ was considered previously (Nettleton 1988). In principle, these higher terms can be extracted from (19). The result involves the distribution function g_4 which must be known accurately, since there is a near cancellation of contributions of opposite sign. We were able previously (Nettleton 1988) to estimate $O(J^4)$ contributions to F by invoking fluctuation theory, but this is hard to justify here because ∇n is not a fast variable. This raises questions about the use of a generalised Einstein fluctuation distribution in attempting to calculate correlations such as $\langle \hat{A}\hat{A}\hat{A} \rangle_0$.

The $O(\alpha^2)$ term in F has applications beyond the field of heat transport. It can be used (Cahn and Hilliard 1958) in determining the density profile across a liquid-vapour interface. The results of section 3 can be carried over to this case, with the minimum $k = \pi/\delta$, for δ the intermolecular separation, and $g(r)$ calculated numerically for a soft potential. Such a result can be compared with earlier work (Nettleton 1961) which calculated the $O(\alpha^2)$ in F by applying reciprocity to the kinetic equations linking $\dot{\alpha}$ to the relaxation equations for the hypersound and self-diffusion components of J.

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