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Information theoretic extended entropy for steady heat conduction in dense fluids

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Abstract. A phase space distribution for a far-from-equilibrium steady state in which thermodynamic temperature, T , and heat flux, J , are specified is calculated by maximising the information theoretic entropy. When this distribution is used to calculate free energy, F , the latter is obtained as a function of the distribution moduli which, in turn, are calculated from a consistency condition as functions of J and T . The coefficient of the $O(J^2)$ term in F can be expressed in terms of the radial distribution function, g_2 , and three-particle distribution, g_3 . A numerical estimate is made for a hard-sphere model of liquid Ar at 87 K and high density, using the Percus–Yevick solution for g_2 and the Kirkwood superposition for g_3 . The estimate confirms the conclusion of an earlier theory that non-linear effects at liquid density are negligible except, possibly, for unrealistically large J . Fluctuation theory is invoked to make an estimate of the negligibly small $O(J^4)$ term in F .

1. Introduction

By maximising the information theoretic entropy, one can derive a phase-space distribution $\rho(\Gamma)$ appropriate to non-equilibrium steady states (Levine and Tribus 1979, Zubarev 1974). This approach has been applied by Jou *et al* (1984) to the case where there is a steady heat flux, $J = \langle \hat{J} \rangle$, where $\hat{J}(\Gamma)$ is the heat flow expressed as a dynamical function of particle coordinates and momenta. The maximisation is effected subject to the subsidiary condition that $J = \int \rho \hat{J} d\Gamma$ in the steady state. In the present paper, we wish to extend this work to make numerical estimates of the first two J -dependent terms in the Helmholtz free energy. The free energy is a functional of ρ which in turn depends on J , allowing us to relate the $O(J^2)$ and $O(J^4)$ terms in F to the two- and three-particle distribution functions. The latter can be estimated from calculations found in the literature for dense hard-sphere fluids. The results can be compared with earlier calculations (Nettleton 1987a) based on extended non-equilibrium thermodynamics, where N , V , T and J are independent state variables. The Cattaneo–Vernotte equation for $\partial J / \partial t$, extended to include non-linear terms, was cast in Onsager–Casimir canonical form and the J -dependence of F was extracted by applying reciprocity and a model for the interaction between system and surroundings.

The system we consider is taken to be a macroscopically small cube of side l immersed in an infinite medium in which there is a steady heat flow. The entropy is defined by an integral over accessible phase space,

$$S = -\kappa \int \rho(\Gamma) \ln \rho(\Gamma) d\Gamma \quad (1)$$

which is maximised subject to the specification that total energy is E and the heat flow \mathbf{J} . Thus we solve the variational problem

$$\delta(\kappa^{-1}S - \beta E - \boldsymbol{\gamma} \cdot \mathbf{J}) = 0 \quad (2)$$

yielding

$$\rho = Z^{-1} \exp(-\beta \hat{H} - \boldsymbol{\gamma} \cdot \hat{\mathbf{J}}) \quad (3)$$

where β and $\boldsymbol{\gamma}$ are Lagrange multipliers and \hat{H} the classical Hamiltonian. The generalised partition function (Jou *et al* 1984) is

$$Z = \int \exp(-\beta \hat{H} - \boldsymbol{\gamma} \cdot \hat{\mathbf{J}}) d\Gamma. \quad (4)$$

The Lagrange multipliers are determined from the consistency conditions

$$E = \int \rho \hat{H} d\Gamma \quad (5a)$$

$$\mathbf{J} = Z^{-1} \int \hat{\mathbf{J}} \exp(-\beta \hat{H} - \boldsymbol{\gamma} \cdot \hat{\mathbf{J}}) d\Gamma. \quad (5b)$$

Equation (5a) gives $\beta \equiv 1/\kappa T$ as a function of $E \equiv U_0(N, V, \theta)$ and $\boldsymbol{\gamma}$, and this determines the thermodynamic temperature, T , as a function of $\boldsymbol{\gamma}$ and the local equilibrium temperature, θ (Jou *et al* 1984). U_0 is the equilibrium caloric equation of state. Equation (5b) determines the coefficients γ_0, γ_2 in an expansion for $\boldsymbol{\gamma}$:

$$\boldsymbol{\gamma} = \gamma_0(N, V, T)\mathbf{J} + \gamma_2 J^2 \mathbf{J} + \dots \quad (6)$$

Thus (5a) determines T as a function of θ and \mathbf{J} .

The linear terms in (6) have been shown (Jou *et al* 1984) to obey

$$\boldsymbol{\gamma} = \beta \boldsymbol{\Phi} = -\beta \partial F / \partial \mathbf{J} \quad (7)$$

where $\boldsymbol{\Phi}$ is the thermodynamic force conjugate to $\hat{\mathbf{J}}$ in the extended non-equilibrium thermodynamic formalism where

$$dF = -S dT - P dV - \boldsymbol{\Phi} \cdot d\mathbf{J}. \quad (8)$$

We shall show here that (6) and (7) hold when we include γ_2 . Thus if we expand

$$F = F_0(N, V, T) + \frac{1}{2}\nu_2 J^2 - \frac{1}{4}\nu_4 J^4 + \dots \quad (9)$$

then

$$\boldsymbol{\Phi} = \kappa T \boldsymbol{\gamma} = -\nu_2 \mathbf{J} + \nu_4 J^2 \mathbf{J} + \dots \quad (10)$$

and we can determine $\nu_2(N, V, T)$ and ν_4 , for comparison with earlier results (Nettleton 1987a), from the consistency condition (5b) which yields expressions for γ_0 and γ_2 .

In § 2 we shall write down the consistency conditions from (5b) which, in principle, determine γ_0 and γ_2 . γ_0 can be expressed in terms of the equilibrium pair and triplet distribution functions and is thus calculable when the latter have been estimated. In § 3, we shall summarise the derivation of (10), including its extension to include ν_4 . In § 4, we shall present an approximate method, based on the Einstein fluctuation distribution for fast variables, of estimating γ_2 and ν_4 when the five-particle equilibrium configuration-space distribution function is not known. The latter result, plus the expression from § 2 which relates ν_2 to the radial distribution function, will be used

in § 5 to estimate ν_2 and ν_4 for a hard-sphere model of liquid Ar at 87 K. These results will be compared to an earlier estimate (Nettleton 1987a) for this model which applied reciprocity to the kinetic equation for the approach of \mathbf{J} to the steady state (non-linear Cattaneo-Vernotte equation). Both estimates show that the ν_4 term in F and $O(J^2)$ contributions to P and to $T-\theta$ should be negligibly small under realisable conditions at liquid density. This result will be related in the discussion of § 6 to the kinematic conditions which should apply to the kinetic equation for \mathbf{J} . The results and conclusions of the paper will be summarised in § 6 and the effect of various approximations discussed.

2. Determination of γ

Expanding the integrand in (5b) in powers of γ and introducing (6), we obtain for the consistency conditions that (5b) should hold identically:

$$\mathbf{J} = -\gamma_0 Z_0^{-1} \int \mathbf{J} \cdot \hat{\mathbf{J}} \hat{\mathbf{J}} \exp(-\beta \hat{H}) d\Gamma \tag{11a}$$

$$0 = -\gamma_2 Z_0^{-1} \int J^2 \mathbf{J} \cdot \hat{\mathbf{J}} \hat{\mathbf{J}} \exp(-\beta \hat{H}) d\Gamma - \gamma_0^3 Z_0^{-1} \frac{1}{6} \int \hat{\mathbf{J}} (\mathbf{J} \cdot \hat{\mathbf{J}})^3 \exp(-\beta \hat{H}) d\Gamma + \gamma_0 Z_0^{-1} \int \hat{\mathbf{J}} \mathbf{J} \cdot \hat{\mathbf{J}} \exp(-\beta \hat{H}) d\Gamma \frac{1}{2} Z_0^{-1} \gamma_0^2 \int (\mathbf{J} \cdot \hat{\mathbf{J}})^2 \exp(-\beta \hat{H}) d\Gamma \tag{11b}$$

where Z_0 is the partition function of (4) evaluated with $\gamma = 0$. Using (11a) to simplify (11b), we find that the latter equation becomes

$$\gamma_0^4 (6Z_0)^{-1} \int (\mathbf{J} \cdot \hat{\mathbf{J}})^4 d\Gamma = \gamma_2 J^4 + \frac{1}{2} \gamma_0^2 J^4. \tag{12}$$

This equation can yield γ_2 provided we can extract an estimate of γ_0 from (11a) and, in addition, evaluate the integral.

To proceed further we introduce the expression for \mathbf{J} (Nettleton 1987a, Jou *et al* 1984)

$$l^3 \hat{\mathbf{J}} = \sum_i \left[\left((p_i^2/2m) - h + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right) \boldsymbol{\delta} + \frac{1}{2} \sum_{j \neq i} \mathbf{r}_{ij} \mathbf{F}_{ij} \right] \cdot (\mathbf{p}_i/m) \tag{13}$$

where ϕ is the pair potential, \mathbf{F}_{ij} is the force on particle i produced by the interaction with j , h is the enthalpy per particle and $\boldsymbol{\delta}$ is the unit tensor of rank two. On substituting (13) into the integral in (11a), we get

$$l^6 \int \hat{\mathbf{J}} \hat{\mathbf{J}} \exp(-\beta \hat{H}) d\Gamma = \frac{1}{3} \sum_i \int \exp(-\beta \hat{H}) d\Gamma (p_i^2/m^2) \left[\left((p_i^2/2m) - h + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right)^2 \boldsymbol{\delta} + \frac{1}{4} \sum_{j,k} \mathbf{r}_{ij} \mathbf{r}_{ik} \mathbf{F}_{ij} \cdot \mathbf{F}_{ik} + \left((p_i^2/2m) - h + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right) \sum_{k \neq i} \mathbf{r}_{ik} \mathbf{F}_{ik} \right]. \tag{14}$$

If we consider the middle term, we see on carrying out the momentum integration that it is proportional to $\langle p_i^2/2m \rangle = \frac{3}{2} \kappa T$. Terms in the integrand with $j = k$ will reduce

to $N(N-1)\rho^{(2)}(r)$ multiplying a function of r , where $\rho^{(2)}(r)$ is the probability amplitude, normalised to unity, for a particle at r , given that there is a particle at the origin. Terms with $j \neq k$ yield an integrand proportional to $N(N-1)(N-2)\rho^{(3)}$ multiplying a function of r_{12} and r_{13} , where $\rho^{(3)} d\mathbf{r}_2 d\mathbf{r}_3$ is the distribution, normalised to unity, for particles at r_2 and r_3 , given that there is a particle at the origin.

Similar considerations apply to the remaining terms in (14) and we find that (11a) reduces to

$$\begin{aligned}
 1 = & -(\kappa T \gamma_0 / m l^6) \left(\frac{1}{3} N(N-1) \int \rho^{(2)} d\mathbf{r}_{12} \left[\frac{1}{4} (\phi'_{12})^2 r_{12}^2 + (5\kappa T / 2 - h) \phi'_{12} r_{12} \right. \right. \\
 & + \frac{1}{2} \phi'_{12} \phi_{12} r_{12} + \frac{15}{2} \kappa T \phi_{12} + \frac{3}{4} \phi_{12}^2 \left. \right] + \frac{1}{6} N(N-1)(N-2) \\
 & \times \int \rho^{(3)} d\mathbf{r}_{12} d\mathbf{r}_{13} \left(\frac{1}{6} \phi'_{12} \phi'_{13} r_{12} r_{13} + \phi_{12} \phi'_{13} r_{13} + \frac{3}{2} \phi_{12} \phi_{13} \right) \\
 & \left. + N \kappa T \left(\frac{35}{4} \kappa T - 5h \right) \right). \tag{15}
 \end{aligned}$$

Equation (15) can be reduced further by introducing the radial distribution function

$$g_2(r) = n^{-1}(N-1)\rho^{(2)} \tag{16}$$

which is the form most often tabulated. Also we can use

$$g_3 = n^{-2}(N-1)(N-2)\rho^{(3)} = g_2(1, 2)g_2(1, 3)g_2(2, 3) \tag{17}$$

where the approximation is the Kirkwood superposition, useful at the high densities we shall consider in § 5 (Alder 1964). There we shall evaluate the integrals in (15) for the hard-sphere model. For that model, tabulations of $g_2(r)$ are available.

A reduction similar to the foregoing could be effected in (12). There, however, we should have to express the integral in terms of g_5 , for which reliable values are hard to obtain at high density. Accordingly, a different fluctuation theoretic approach to evaluation of the integrals in (11a) and (11b) will be developed in § 4. This permits us to use (11a) alone to estimate both ν_2 and ν_4 by evaluating the integral in two ways.

3. Relation between distribution modulus and extended free energy

To derive (7) as far as the lowest two orders in the J expansion of Φ , we substitute (3) into

$$F = \int \rho \hat{H} d\Gamma + \kappa T \int \rho \ln \rho d\Gamma. \tag{18}$$

The substitution, after simplification via (11a), gives

$$F = F_0(N, V, T) - \frac{1}{2} \gamma_0 \kappa T J^2 + \frac{1}{8} \gamma_0^2 \kappa T J^4 - \frac{1}{24} \gamma_0^4 Z_0^{-1} \int (\mathbf{J} \cdot \hat{\mathbf{J}})^4 \exp(-\beta \hat{H}) d\Gamma. \tag{19}$$

If we use (12) to eliminate the integral, (19) yields

$$F = F_0 - \frac{1}{2} \kappa T J^2 - \frac{1}{4} \gamma_2 \kappa T J^4 + O(J^6). \tag{20}$$

Comparison of (20) with (9) gives

$$\nu_4 = \kappa T \gamma_2 \tag{21a}$$

$$\nu_2 = -\kappa T \gamma_0 \tag{21b}$$

in agreement with (7). We can thus calculate ν_2 and ν_4 from (12) and (15) which determine γ_2 and γ_0 , respectively. However, because of the difficulties in evaluating the integral in (12), we shall use the method of § 4 to obtain ν_4 . Once we have ν_2 , we can estimate the coefficients P_2 and U_2 in the expansions:

$$P = P_0(N, V, T) + P_2 J^2 + O(J^4) \tag{22a}$$

$$U = U_0(N, V, T) + U_2 J^2 + O(J^4). \tag{22b}$$

Application of the integrability conditions yields (Nettleton 1987a) from (8):

$$P_2 = -\frac{1}{2} \partial \nu_2 / \partial V \tag{23a}$$

$$U_2 = \frac{1}{2} (\nu_2 - T \partial \nu_2 / \partial T). \tag{23b}$$

Equations (23a, b) will be used in § 5 to evaluate P_2 and U_2 for hard spheres. A comparison can then be made with an earlier estimate (Nettleton 1987a) obtained in a different way.

4. Approximate evaluation of ν_4

Since evaluation of the integral in (12) requires accurate knowledge of g_5 , we shall develop here an approximate estimate of ν_4 based on the application of fluctuation theory to the integral in (11a). If \mathbf{J} is taken to point in the z direction, (11a) becomes

$$1 = -\gamma_0 Z_0^{-1} \int \hat{J}_z^2 \exp(-\beta \hat{H}) d\Gamma = -\gamma_0 \int \rho(\mathbf{v}) v_z^2 d\mathbf{v} \tag{24}$$

where $\rho(\mathbf{v})$ is the probability amplitude for a fluctuation \mathbf{v} in the value of \mathbf{J} in a state where T is given and $\mathbf{J} = 0$. We shall make an estimate for $\rho(\mathbf{v})$ in terms of ν_2 and ν_4 by invoking fluctuation theory, neglecting ν_6 . On evaluation of the integral in (24) we obtain an expression for ν_4 in terms of ν_2 , and ν_2 is in turn obtainable from (15) and (21b). This procedure can be extended, since we could apply it to the integral in (12) yielding, together with (24), a pair of equations for evaluation of ν_4 and ν_6 , when the latter is not neglected. Alternatively, if we could evaluate g_5 , then a second evaluation of the integral in (12) using $\rho(\mathbf{v})$ would yield an equation relating ν_6 and ν_4 . These procedures are only approximate, but they yield orders of magnitude in agreement with an alternative approach (Nettleton 1987a).

To arrive at $\rho(\mathbf{v})$, we first observe that $\hat{\mathbf{J}}$ is a fast variable, so that fluctuations are reasonably assumed to occur in a time short compared with the time for appreciable heat exchange with the surroundings, i.e. the fluctuation is adiabatic when $\mathbf{J} = 0$. Under these circumstances, we should have

$$\rho(\mathbf{v}) = C \exp \Delta S(\mathbf{v}) / \kappa$$

where, since $U = U_0(N, V, \theta)$, with θ the local equilibrium temperature, we have

$$\Delta S(\mathbf{v}) = S(N, V, U, \mathbf{v}) - S_0(N, V, U) = S(N, V, \theta, \mathbf{v}) - S_0(N, V, \theta). \tag{25}$$

We can transform from θ to T by using

$$\theta - T = (C_v)^{-1} U_2 J^2 + O(J^4) \tag{26}$$

where C_v is the heat capacity at constant volume.

To calculate ΔS we assume the ansatz

$$\Phi(N, V, \theta, \mathbf{v}) = -\bar{\nu}_2(N, V, \theta)\mathbf{v} + \bar{\nu}_4(N, V, \theta)v^2\mathbf{v} \quad (27)$$

so that

$$T \partial S / \partial \mathbf{v} |_{U} = \Phi \quad (28a)$$

$$\begin{aligned} \partial S / \partial \mathbf{v} |_{U} &= (\theta - v^2 C_v^{-1} U_2)^{-1} (-\bar{\nu}_2 \mathbf{v} + \bar{\nu}_4 v^2 \mathbf{v} + \dots) \\ &= \theta^{-1} \{-\bar{\nu}_2 \mathbf{v} + v^2 \mathbf{v} [\bar{\nu}_4 - \bar{\nu}_2 (C_v \theta)^{-1} U_2] + \dots\}. \end{aligned} \quad (28b)$$

Integrating, we obtain

$$\Delta S = \theta^{-1} \{-\frac{1}{2} \bar{\nu}_2 v^2 + \frac{1}{4} v^4 [\bar{\nu}_4 - \bar{\nu}_2 (C_v \theta)^{-1} U_2] + \dots\}. \quad (29)$$

We now employ (26) to transform back from θ to T , yielding

$$\Delta S = T^{-1} (-\frac{1}{2} \nu_2 v^2 + \frac{1}{4} \tilde{\nu}_4 v^4 + \dots) \quad (30a)$$

$$\tilde{\nu}_4 \equiv \nu_4 - (C_v T)^{-1} (\nu_2 - T \partial \nu_2 / \partial T) (\nu_2 + T \partial \nu_2 / \partial T) \quad (30b)$$

$$\rho(\mathbf{v}) \approx C \exp[(\kappa T)^{-1} (-\frac{1}{2} \nu_2 v^2 + \frac{1}{4} \tilde{\nu}_4 v^4)] \quad (30c)$$

$$C = (\nu_2 / 2\pi\kappa T)^{3/2} [1 - \tilde{\nu}_4 (15/16\kappa T) (2\kappa T / \nu_2)^2] \quad (30d)$$

in the approximation which neglects higher powers of \mathbf{v} and $O(\tilde{\nu}_4^2)$.

When the distribution defined by (30c) and (30d) is introduced into (24), we find that the latter becomes

$$1 + \tilde{\nu}_4 (5\kappa T / \nu_2^2) + O(\tilde{\nu}_4^2) = -\nu_2 / \gamma_0 \kappa T. \quad (31)$$

This result and (21b) yield $\tilde{\nu}_4 = 0$ as the simplest solution. This implies that $\rho(\mathbf{v})$ is a Gaussian, as usually assumed. Setting $\tilde{\nu}_4 = 0$ in (30b), we obtain

$$\nu_4 = (C_v T)^{-1} (\nu_2 - T \partial \nu_2 / \partial T) (\nu_2 + T \partial \nu_2 / \partial T). \quad (32)$$

Equation (32) will be used in § 5 to estimate ν_4 / ν_2 in a dense hard-sphere fluid for comparison with an earlier estimate (Nettleton 1987a) based on the application of reciprocity to the kinetic relaxation rate equation for \mathbf{J} . In the current evaluation ν_2 is obtained by specialising (15) to a hard-sphere potential.

5. Numerical results for hard spheres

In this section, we shall evaluate ν_2 from (15) and ν_4 from (32) for a rigid-sphere model of liquid Ar at 87 K, with parameters listed in table 1. The effective hard-sphere diameter, σ , is chosen to fit viscosity measurements (Hirschfelder *et al* 1954). The density parameter $z = 1.68$ is not far below the gas-solid transition at $z = 1.866$, since we want the Kirkwood superposition approximation to hold, as well as the earlier results (Nettleton 1987a) with which the present estimates are to be compared. In the previous calculations we assumed a density high enough so that there should be negligible particle exchange with the surroundings during the relaxation time for \mathbf{J} . Also, we shall use the Percus-Yevick results for g_2 (Wertheim 1863, Thiele 1963) which works best at high density.

Table 1. Hard-sphere model of liquid Ar at 87 K. Atomic mass m , hard-sphere diameter σ , number density n , $\eta = (\pi/6)n\sigma^3$. Subscript '1' on coefficients, $-\nu_2$ of lowest term in Φ and ν_4 of next highest term, denote results of the present paper. Subscript '2' denotes computations from (46) and (47) derived in earlier work. Similar notation applies to P_2 , the coefficient of the $O(J^2)$ term in P . $(\nu_2)_2/(\nu_2)_1 = (T - \theta)_2/(T - \theta)_1$.

m	6.6331×10^{-26}	kg
σ	3.64×10^{-10}	m
$n\sigma^3$	0.800	
n	1.66×10^{28}	m^{-3}
z	1.68	
η	0.419	
$P_0/n\kappa T$	7.73	
$T\alpha_p^0$	0.286	
$(\nu_2 n/\beta^2 mV)_1$	1.10×10^{-2}	
$(\nu_2 n/\beta^2 mV)_2$	3.48×10^{-2}	
$(\nu_2)_2/(\nu_2)_1$	3.17	
$(P_2/P_0)_1$	-9.27×10^{-22}	$m^4 s^2 J^{-2}$
$(P_2/P_0)_2$	-2.19×10^{-20}	$m^4 s^2 J^{-2}$
$(\nu_4/\nu_2)_1$	-4.58×10^{-19}	$m^4 s^2 J^{-2}$
$(\nu_4/\nu_2)_2$	-9.96×10^{-19}	$m^4 s^2 J^{-2}$

To evaluate the integrals in (15), we invoke (17) and the well known results for a hard-sphere potential (McQuarrie 1976, p 280)

$$\int_0^\infty g_2(r)\phi'(r)r^3 dr = -\kappa T\sigma^3 g_2(\sigma^+) = -(3\kappa T/2\pi n)(P_0/n\kappa T - 1) \quad (33)$$

where P_0 is the equilibrium equation of state. The integrals proportional to ϕ_{12} and to no derivatives thereof vanish, since $\phi_{12} = 0$ for $r > \sigma$ and $g(r) \rightarrow 0$ exponentially for $r < \sigma$ as ϕ_{12} approaches its hard-sphere limit.

The integral proportional to $(\phi'_{12})^2$ requires more attention. Defining the direct correlation function

$$c(r) \equiv g(r) - y(r) \quad (34a)$$

$$y(r) \equiv g \exp(\beta\phi) \quad (34b)$$

we have

$$g(r)\phi'(r) = \beta^{-1}[y'(r)\exp(-\beta\phi) - g'(r)]. \quad (35)$$

This yields an expression for $\int g(r)(\phi')^2 r^4 dr$ as the sum of two integrals. These are

$$\int_0^\infty \exp(-\beta\phi)y'(r)\phi' r^4 dr = -\beta^{-1}\sigma^4 y'(\sigma^+) \quad (36a)$$

$$\int_0^\infty g'(r)\phi'(r)r^4 dr = g(r)\phi'(r)r^4|_0^\infty - \int_0^\infty g(r)[\phi''(r)r^4 + 4\phi'(r)r^3] dr \quad (36b)$$

where we start with a continuous potential and eventually take the hard-sphere limit. In this limit, $\phi'' \rightarrow 0$ everywhere, and all terms but the last in (36b) $\rightarrow 0$. Thus

$$\int_0^\infty g'(r)\phi'(r)r^4 dr = 4\beta^{-1}\sigma^3 g_2(\sigma^+) = -4\beta^{-1}\sigma^3 c(\sigma^-). \quad (37)$$

Here we have invoked the continuity of y at σ .

In (37) we shall employ the function $c(r)$ obtained (Wertheim 1963, Thiele 1963) from the solution of the Percus-Yevick equation for g_2 . This is (Gray and Gubbins 1984, p 345)

$$c(r) = c_0 + c_1(r/\sigma) + c_3(r/\sigma)^3 \quad (r < \sigma) \tag{38a}$$

$$c_0 \equiv -(1 + 2\eta)^2 / (1 - \eta)^4 \tag{38b}$$

$$c_1 \equiv 6\eta(1 + \frac{1}{2}\eta)^2 / (1 - \eta)^4 \tag{38c}$$

$$c_3 \equiv \frac{1}{2}\eta c_0 \tag{38d}$$

$$\eta \equiv (\pi/6)n\sigma^3. \tag{38e}$$

Using this approximate solution, we have

$$y'(\sigma^+) = -(9\eta/2\sigma)(1 - \eta^2)/(1 - \eta)^4 \tag{39a}$$

$$c(\sigma^-) = (-1 + \frac{3}{2}\eta - \frac{1}{2}\eta^3)/(1 - \eta)^4 \tag{39b}$$

which can be used in (36a) and (37), respectively.

If the Kirkwood superposition and (33) are applied to the integral involving $\rho^{(3)}$ in (15), the only non-vanishing term is proportional to

$$\int_{\pi/3}^{\pi} g_3(r_{13} = \sigma, r_{23} = \sigma, \cos \theta) \sin \theta \, d\theta = g_2(\sigma^+)^2 \int_{\pi/3}^{\pi} g_2(r_{23}) \sin \theta \, d\theta \tag{40}$$

where θ is the angle between r_{13} and r_{12} , and $r_{23}^2 = 2\sigma^2(1 - \cos \theta)$. Setting $x \equiv r_{23}/\sigma$, we find the integral is

$$\int_{\pi/3}^{\pi} g_2(r_{23}) \sin \theta \, d\theta = \int_1^2 g_2(x)x \, dx \equiv I_1. \tag{41}$$

I_1 is evaluated numerically from tabulated values of $g_2(x)$ (Throop and Bearman 1965). This yields an estimate of I_1 which is slightly too small, since $g_2(\sigma)$ in the Percus-Yevick solution is too low. We use the extended Simpson rule for the integration (Abramowitz and Stegun 1964, p 886).

Collecting the results in (33)-(41) for the various terms in (15) and setting $h = \frac{3}{2}T + P_0n^{-1}$, we find that the expression for ν_2 assumes the form:

$$-\nu_2^{-1} = \beta\gamma_0^{-1} = (n/mV\beta^2)\{2\eta[4 - (21\eta/2) + (13\eta^3/2)]/(1 - \eta)^4 - (2 + \frac{1}{2}I_1) \times [(P_0/n\kappa T - 1)^2 - \frac{35}{4} + 5(\frac{3}{2} + P_0/n\kappa T)]\}. \tag{42}$$

The equation of state P_0 has been obtained (Ree and Hoover 1964) by fitting a Padé approximant to computer results. This yields

$$P_0/n\kappa T = 1 + z\Phi_1/\Phi_2 \tag{43a}$$

$$z \equiv \frac{2}{3}\pi n\sigma^3 \tag{43b}$$

$$\Phi_1 \equiv 1 + 0.063\,507z + 0.017\,329z^2 \tag{43c}$$

$$\Phi_2 \equiv 1 - 0.561\,493z + 0.081\,313z^2. \tag{43d}$$

Equation (42) shows that ν_2 is proportional to T^{-2} , so that $-T \partial \nu_2 / \partial T = 2\nu_2$. If we use this in (23b) and (32), we find that

$$\nu_4 / \nu_2 = -(9/2 C_v T) \nu_2 \quad (44a)$$

$$(T - \theta) / \theta = -\nu_2 J^2 / N \kappa \theta. \quad (44b)$$

To evaluate P_2/P_0 using (23a) and (42), we must evaluate $\partial I_1 / \partial (n\sigma^3)$ numerically, which can be done since $g_2(x)$ in (41) is tabulated for a range of densities (Throop and Bearman 1965). We use five-point differentiation (Abramowitz and Stegun 1964, p 919) to find $\partial g_2 / \partial (n\sigma^2)$ and then integrate the derivative by the extended Simpson rule.

The numerical results for the hard-sphere model of liquid Ar at 87 K are listed in table 1. The density $n\sigma^2 = 0.8$ has been chosen in the range where the approximations work best. The ratios $(P_2/P_0)_1$, $(\nu_4/\nu_2)_1$ are calculated from (42) and (44a). For comparison we calculate the same ratios, $(P_2/P_0)_2$, etc, from the earlier work based on application of reciprocity. The latter gave (Nettleton 1987a, equations (4b), (24) and (26d))

$$(\nu_2)_2 = (\beta m V / P_0) [\frac{3}{2} + (P_0 / n \kappa T) T \alpha_p^0]^{-1} \quad (45)$$

where α_p^0 is the coefficient of volume expansion, calculable from (43a). Also, in a form specialised to the hard-sphere case, the earlier work gave

$$(\nu_4 / \nu_2)_2 = (\tilde{C}_p^0 + P_0 n^{-1} \alpha_p^0)^{-1} \{ (P_2 / P_0) (\tilde{C}_p^0 - 3 P_0 n^{-1} \alpha_p^0) - [(3 \nu_2 / N \theta) + \theta V (\alpha_p^0)^2 (2n)^{-1} \partial^2 \nu_2 / \partial V^2] \} \quad (46)$$

where $\tilde{C}_p^0 = 3\kappa/2$. Equation (45) shows that $(\nu_2)_2$ is proportional to T^{-2} like $(\nu_2)_1$ from (42). The values in table 1 show that (45) and (46) predict a negligibly small dependence of P and $(T - \theta) / \theta$ on J^2 as do (42) and (44a, b) for accessible values of J . However, the values from the earlier work (Nettleton 1987a), although of the same order of magnitude, are systematically higher than those based on (42). Further discussion of these results, including a kinematic reason for the smallness of ν_4 / ν_2 , will be given in § 6.

6. Discussion

Equations (45) and (46) were obtained in the earlier work (Nettleton 1987a) by arguing that, at liquid density, the effect of interactions between system and surroundings can be expressed in terms of the thermodynamic pressure, as in derivations of the virial equation of state relating P to g_2 . This holds, provided there is negligible diffusion across the boundaries during the short time required for J to approach its steady state value, given by the Fourier law. By contrast, in the present paper we have a method which can be applied at all densities provided we have accurate tables, e.g. from computer simulations, of g_2 and g_3 . This permits evaluation of the integrals in (15). Such an evaluation has been made here only at liquid density, where we can use the Kirkwood superposition for g_3 and the Percus-Yevick equation for g_2 , and where we can compare the numerical estimates of P_2/P_0 and ν_4/ν_2 with results obtained by the earlier high-density methods. In the gaseous region, non-linear transport can be approached via the Boltzmann equation and so methods like those developed here may not be needed.

In the liquid range, the present and earlier estimates of P_2/P_0 and $(T - \theta) / \theta$ both indicate that non-linear effects could not be seen unless $J \geq 10^{10} \text{ W m}^{-2}$ which is highly

unrealistic even for a computer simulation. A kinematic reason for this small effect can be found in an earlier study (Nettleton 1987b) which evaluates ν_2 and ν_4 by comparing the kinematic equation predicted for a flux such as \mathbf{J} according to extended non-equilibrium thermodynamics with a similar equation assumed to have been derived from a model. Equation (40a) of the latter work predicts that, if there is no state variable whose time derivative equals \mathbf{J} , then ν_4/ν_2 is proportional to the coefficient of the $O(J^4)$ term in the model equation for \mathbf{J} . This $O(J^4)$ term should be negligibly small in physically realisable states, since we want $\dot{\mathbf{J}} = -(1/\tau)\mathbf{J} + \dots$ to express the inertial effect that \mathbf{J} does not respond in times $\ll \tau$, while \mathbf{J} approaches the Fourier law in a time $\sim \tau$ if a constant ∇T is applied. τ is approximately the mean life of a hypersound phonon. Thus for a fast variable $\tilde{\eta}$, F should have an appreciable term $O(\tilde{\eta}^4)$ only when there is a state variable α such that $\tilde{\eta} = \dot{\alpha}$. Under these circumstances, the $O(\tilde{\eta}^4)$ term in F is not proportional to the $O(\tilde{\eta}^4)$ term in the model equation for $\tilde{\eta}$ and the latter could be zero without implying negligibility of the $O(\tilde{\eta}^4)$ contribution to F . Similar conditions apply to a diffusion flow where likewise the flux is not the time derivative of a state variable. Non-linear effects have been found in the latter case to be very small (Nettleton 1988).

While the orders of magnitude of the estimates based on (42) and (45a) on the one hand and (46) and (47) on the other are the same, the present work predicts values of ν_2 , P_2/P_0 and ν_4/ν_2 (table 1) which are systematically smaller than those based on the earlier work (Nettleton 1987a). If we ask whether this could stem from using the Percus-Yevick g_2 to calculate I_1 , we note that I_1 should be underestimated by a small amount, because the Percus-Yevick solution underestimates g_2 at $r = \sigma$. However, a larger I_1 in (42) should lead to a smaller ν_2 and accentuate $(\nu_2)_2/(\nu_2)_1$. The use of the Kirkwood superposition could have a more important effect. However, $\frac{1}{2}I_1 = 0.849$, and even if the I_1 term should be vanishingly small this could not change the estimate of ν_2 by a factor of three. The term proportional to η in (42) is small and would have to be grossly underestimated by the Percus-Yevick theory to appreciably change the estimate of ν_2 . The magnitude of $(\nu_2)_2/(\nu_2)_1$ in table 1 should therefore not be ascribed to the approximations used here. We conclude that $(\nu_2)_2$ may be an overestimate.

In addition to use of the Kirkwood and Percus-Yevick approximations in calculating ν_2 , we have made further assumptions in § 4 to estimate ν_4 . Since we have estimated $\tau \sim 10^{-11}$ s (Nettleton 1987a) we commonly assume that the dynamics of fast variable relaxation is the same as that in a closed system. This means the relaxation time should be short compared with the time for diffusion of appreciable energy across the boundaries. Thus the fluctuation probability distribution should be given by the Einstein function $\exp(\Delta S/\kappa)$ when $\mathbf{J} = 0$. Corrections (Nettleton 1984, 1985) will be proportional to a power of \mathbf{J} . The methods of § 4 are intended to provide an order-of-magnitude estimate when reliable results for g_s are not available. If g_s can be estimated, we can use (12) in place of the methods developed in § 4.

Agreement between the estimates of P_2/P_0 in table 1 is poorer than for the other functions calculated. In the present paper we have had to calculate $\partial I_1/\partial n$ by numerical differentiation, as well as to calculate $\partial P_0/\partial n$. At the same time, in the earlier work (Nettleton 1987a) it was necessary to estimate $\partial^2 \nu_2/\partial V^2$. Uncertainties in these estimates probably increase the error in both the present and the earlier calculations and account for poorer agreement.

An important consequence of the smallness of non-linear effects for reasonable magnitudes of \mathbf{J} is that, if we solve the non-linear Cattaneo-Vernotte equation in the steady state, we get an analytic expansion for \mathbf{J} in powers of ∇T , in contrast to the

viscoelastic case where pressure and internal energy can depend on the $\frac{2}{3}$ power of the shear rate when the latter is large (Hanley and Evans 1982, Nettleton 1987c).

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