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## Non-linear isotopic diffusion in dense fluids

R E Nettleton

Department of Physics, University of the Witwatersrand, Johannesburg, South Africa

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**Abstract.** A binary uncharged isotopic mixture at liquid density is described by the state variables  $M_1$  and  $M_2$ , the component masses, volume  $V$  and temperature  $T$ . To these, in an extended irreversible thermodynamic treatment, is added the diffusion flow  $J_d$ . In the framework of this approach, a kinetic equation relates  $J_d$  to the driving force,  $-\nabla_T(\mu_1 - \mu_2)$ , where the  $\mu_i$  are chemical potentials and  $T$  is kept constant in computing the gradient. To calculate the coefficient  $\gamma$  of this force, a microscopic model is adduced which expresses  $\gamma$  in terms of  $P_{xx}$ , the pressure tensor. Evaluation of  $\gamma$  and application of reciprocity permits the calculation of  $\Phi$ , the thermodynamic force associated with  $J_d$ . Once  $\Phi$  is known, integrability conditions for the Helmholtz function yield the  $O(J_d^2)$  terms in the pressure  $P$  and the  $\mu_i$ . From these results and an estimate from computer simulations of the relaxation time for  $J_d$ , we obtain  $D_2$  in the diffusion coefficient,  $D = D_0 + D_2 J_d^2$ . Estimates for a hard-sphere model representing a mixture of  $^{36}\text{Ar}$  and  $^{40}\text{Ar}$  predict that all the  $J_d^2$  terms in  $D$ ,  $P$ ,  $\mu_i$  are negligible unless  $|J_d| \geq 10^4 \text{ kg m}^{-2} \text{ s}^{-1}$  at liquid density.

### 1. Introduction

Early formulations (De Groot and Mazur 1962) of the non-equilibrium thermodynamics of diffusion in binary fluid mixtures, for states close to local equilibrium, chose the volume  $V$ , temperature  $T$  and the masses  $M_1$  and  $M_2$  of the two constituents as state variables. Such treatments for a non-uniform fluid set the flux  $J_1 = \rho_1(\mathbf{u}_1 - \mathbf{u})$  of one of the components, whose mass density is  $\rho_1$  and flow velocity  $\mathbf{u}_1$  in a mixture of mass velocity  $\mathbf{u}$ , proportional to the thermodynamic force  $-\nabla_T(\mu_1 - \mu_2)$ , where  $\mu_i$  is the Gibbs function per unit mass of  $i$ , and the gradient is calculated at constant  $T$ . With a view to obtaining new reciprocity relations useful in the calculation of liquid transport coefficients, the set of state variables was extended (Nettleton 1963) to include  $J_d \equiv J_1$  with conjugate flux  $\partial J_d / \partial t$  and linearised force  $\Phi$  which are associated with this new independent variable. In the present paper, we seek to extend this formalism still further by allowing  $\Phi$  and the phenomenological coefficients of the extended thermodynamic formalism to depend non-linearly on  $J_d$ . This permits us to investigate the dependence of transport coefficients on the square of the concentration gradient in steady states far from equilibrium.

A microscopic justification for this extension into the non-linear regime has been worked out (Nettleton 1985), based on application of the Zwanzig projection operator technique (Zwanzig 1960, 1961) to the classical Liouville equation. Under circumstances where  $\eta \equiv \langle iLA \rangle$ ,  $A$  being a dynamical function even in particle momenta and  $L$  the self-adjoint Liouville operator, one can define the conjugate flux  $\dot{\eta}$  and force  $-\partial F / \partial \eta$ , where  $F$  is the Helmholtz function, which are non-linear in  $\eta$ . The Onsager-Casimir reciprocity relations are preserved among the coefficients in the kinetic equation

for  $\eta$ . This result is relevant to the case of diffusion, since here we have

$$\mathbf{A}_D = V^{-1} \sum_{i \in \{1\}} m_i \mathbf{r}_i \quad (1a)$$

$$\mathbf{J}_d = \langle iL\mathbf{A}_D \rangle = V^{-1} \sum_{i \in \{1\}} \langle \mathbf{p}_i \rangle \quad (1b)$$

as the  $A$  and  $\eta$  variable, respectively, provided  $\mathbf{u} = 0$ , as is the case throughout the present paper. Here  $\mathbf{p}_i$  is the momentum of particle  $i$ , and the sum is over the particles of constituent 1.  $\mathbf{J}_d$  is thus an  $\eta$ -type variable, and there should exist an extended thermodynamic formalism with flux  $\mathbf{J}_d$  and force  $\Phi$  coupled by coefficients non-linear in  $\mathbf{J}_d$  and exhibiting Onsager symmetry.

If the phenomenological coefficients depend on  $\mathbf{J}_d$ , this should also be true of the steady-state diffusion coefficient. In § 3 we show that, in a steady state,

$$\mathbf{J}_d = -D\nabla c_1 \quad (2)$$

where  $c_1$  is the mole fraction of constituent 1.  $D$  should depend on the state variable  $\mathbf{J}_d$ , by symmetry, according to

$$D = D_0 + D_2 \mathbf{J}_d^2 + O(\mathbf{J}_d^4). \quad (3)$$

We want, using the reciprocity and integrability conditions derived in § 2, to find a way to estimate  $D_2/D_0$  in order to predict whether non-linear effects will be appreciable in situations realisable in experiment or computer simulation. Computers provide a way of studying steady states far from equilibrium, and interest in the non-linear contributions to transport coefficients has been stimulated by non-Newtonian effects in the viscosity of fluids subjected in computer studies (Holian and Evans 1983, Hanley and Evans 1982) to Couette flow at a high shear rate. The shear viscosity is found (Hanley and Evans 1982) to depend on the square root of the shear rate when the latter is large, and this raises the question whether similar non-analyticities can arise in other transport coefficients. The estimates in § 4 answer this question in the negative for the hard-sphere model.

We shall proceed in § 2 to develop the general extended thermodynamic formalism which adds  $\mathbf{J}_d$  to the set of state variables and associates with it a thermodynamic force  $\Phi$ . This implies a Gibbs equation from which we infer the integrability conditions used in calculating the  $\mathbf{J}_d$  dependence of the pressure and chemical potentials. By applying a Casimir anti-reciprocity relation to the kinetic equations, we obtain results useful in calculating  $D_2$  and the higher-order  $\mathbf{J}_d$  dependence of  $\Phi$ . To make numerical estimates, we need a microscopic molecular model for the driving terms in the kinetic equation for  $\mathbf{J}_d$ . This is discussed in § 3 where, for high densities and short times, it is argued that the force between a small fluid subvolume and its surroundings can be expressed in terms of the pressure. This picture is more appropriate to a mixture of isotopes than of different elements or compounds, and it is for this reason that the present discussion is limited to isotopic diffusion. The model makes possible numerical estimates, made in § 4, for an isotopic dense hard-sphere mixture. These estimates show that non-linear effects are negligible for realisable diffusion flows.

## 2. Gibbs equation, integrability and reciprocity conditions

The system to be considered is a macroscopically small subvolume  $V = l^3$ , of the order of a cubic micron, immersed in an infinite non-uniform dense fluid phase. There are

two isotopes, of masses  $M_i = m_i N_i$  ( $i = 1, 2$ ), where  $m_i$  is the atomic mass and  $N_i$  the number of atoms of component  $i$  in  $V$ . As an additional state variable, we specify the thermodynamic temperature  $T$ . In the spirit of extended non-equilibrium thermodynamics (Casas-Vázquez *et al* 1984), we add  $\mathbf{J}_d$  to the set of state variables, so that the entropy  $S = S(M_1, M_2, V, T, \mathbf{J}_d)$ . This implies the Gibbs equation and corresponding equation for the Helmholtz function,  $F$ :

$$T dS = dU + P dV - \mu_1 dM_1 - \mu_2 dM_2 + \Phi \cdot d\mathbf{J}_d \quad (4a)$$

$$dF = -P dV - S dT + \mu_1 dM_1 + \mu_2 dM_2 - \Phi \cdot d\mathbf{J}_d. \quad (4b)$$

The variables in (4a, b) were chosen to conform to earlier treatments (De Groot and Mazur 1962), and they are used in the present problem because they lead to a simple form for the force conjugate to  $\mathbf{J}_d$ . However, one could equally well use the particle numbers  $N_i$  and the partial Gibbs functions per particle instead of  $M_i$  and  $\mu_i$ , respectively. The volume  $V$  is used instead of  $P$  because the system has a fixed volume, and we want to extend the equilibrium equation of state, given for hard spheres in the form  $P_0(n, T)$ , by calculating an additive  $O(J_d^2)$  contribution. Equation (4b), with the present choice of variables, and its associated integrability conditions, provide a way of effecting this extension.

The integrability conditions for  $F$  are, from equation (4b),

$$\partial P / \partial \mathbf{J}_d = \partial \Phi / \partial V \quad (5a)$$

$$\partial \mu_i / \partial \mathbf{J}_d = -\partial \Phi / \partial M_i \quad (5b)$$

$$\partial S / \partial \mathbf{J}_d = \partial \Phi / \partial T. \quad (5c)$$

Equation (5a) can be used to calculate the thermodynamic pressure,  $P$ , provided we can calculate  $\Phi$  from the reciprocity relations to be developed below. Similarly, equation (5b) can be used to calculate the  $\mathbf{J}_d$  dependence of the chemical potentials, and this result is used in the calculation of  $D_2/D_0$ .

A further implication of equation (4a) is

$$T \partial S / \partial \mathbf{J}_d = \partial U / \partial \mathbf{J}_d + \Phi. \quad (6)$$

If we expand

$$U = U_0(N, V, T) + U_2 \mathbf{J}_d^2 + O(\mathbf{J}_d^4) \quad (7a)$$

$$\Phi = -\nu_2 \mathbf{J}_d + \nu_4 \mathbf{J}_d^2 \mathbf{J}_d + \dots \quad (7b)$$

Equations (5c), (6) and (7a, b) jointly imply that

$$2U_2 = \nu_2 - T \partial \nu_2 / \partial T \quad (8)$$

so that we can calculate  $U_2$  if we can find  $\nu_2$  with the aid of the reciprocity relations. Furthermore,

$$U \equiv U_0(N, V, \theta) \quad (9)$$

where  $\theta$  is the local equilibrium temperature defined by this equation. Then

$$C_v(T - \theta) = -U_2 \mathbf{J}_d^2 + O(\mathbf{J}_d^4). \quad (10)$$

We can use this result if we wish to predict the outcome of a computer experiment which uses  $\theta$  rather than  $T$  as the temperature variable. Equation (10) will also be used in § 4 to predict the magnitude of  $T - \theta$  for the hard-sphere model.

Using (4a) to compute  $dS/dt$ , we find

$$V^{-1} dS/dt = -\nabla \cdot \mathbf{J}_s + \sigma \quad (11a)$$

$$\mathbf{J}_s \equiv T^{-1}(\mathbf{J}_q - \mu_1 \mathbf{J}_1 - \mu_2 \mathbf{J}_2) \quad (11b)$$

$$T\sigma \equiv -\mathbf{J}' \cdot (T^{-1} \nabla T) + \mathbf{J}_d \cdot \nabla_T (\mu_2 - \mu_1) + V^{-1} \Phi \cdot \dot{\mathbf{J}}_d \quad (11c)$$

$$\mathbf{J}' \equiv \mathbf{J}_q - h_1 \mathbf{J}_1 - h_2 \mathbf{J}_2. \quad (11d)$$

Here  $\mathbf{J}_q$  is the total heat flux,  $h_i$  the partial enthalpies and  $\nabla_T$  the gradient calculated holding  $T$  constant and allowing  $M_1$  and  $M_2$  to vary.

Selecting the conjugate fluxes and forces from (11c), we construct the rate equation for  $\mathbf{J}_d$  in the form,

$$\dot{\mathbf{J}}_d = (L/V) \Phi - \gamma \nabla_T (\mu_1 - \mu_2) - \lambda T^{-1} \nabla T. \quad (12)$$

$L$ ,  $\gamma$  and  $\lambda$  are phenomenological coefficients which depend on  $\mathbf{J}_d$ . When equation (12) is substituted into equation (11c), the condition that  $\sigma$  be positive definite requires that

$$\mathbf{J}_d = -\gamma V^{-1} \Phi \quad (13)$$

i.e. an anti-reciprocal coupling between the phenomenological coefficients in (12) and (13).

If we substitute (7b) into the right-hand member of (13) and expand

$$\gamma = \gamma_0 + \gamma_2 \mathbf{J}_d^2 + O(\mathbf{J}_d^4) \quad (14)$$

the condition that the resulting equation be identically satisfied is

$$\nu_2 \gamma_0 V^{-1} = 1 \quad (15a)$$

$$\nu_2 \gamma_2 = \nu_4 \gamma_0. \quad (15b)$$

We shall invoke a model in § 3 to find  $\gamma_0$  and  $\gamma_2$ , and then we can use equations (15a, b) to calculate  $\nu_2$  and  $\nu_4$ . Reciprocity has thus given us  $\Phi$  provided we can determine  $\gamma$ .

If  $\lambda \neq 0$  in (12), a second application of anti-reciprocity requires that

$$\mathbf{J}' = -\lambda V^{-1} \Phi. \quad (16)$$

This should be at least approximately valid near a steady state, since coupling of  $\mathbf{J}_d$  and  $\mathbf{J}'$  will cause one flux to excite the other. We should note, however, that the choice of state variables implies an ensemble in which only  $\mathbf{J}_d$  is measured. If we wish to examine the coupling of  $\mathbf{J}_d$  and  $\mathbf{J}'$ , we should construct a formalism in which both are treated as relaxing state variables on the same footing as has been done in an earlier linear theory (Nettleton 1963). Predictions concerning  $\mathbf{J}'$  would then no longer be confined to the neighbourhood of a steady state. Equation (16) is therefore not advanced here as yielding a reliable prediction of the steady-state non-diffusive heat flow.

The evaluation of  $\lambda$  will be undertaken in § 3, where we shall calculate it in such a way that the driving terms in (12) are proportional to  $\nabla c_1$ , as predicted by a microscopic model to be developed in the same section. We shall also evaluate  $\gamma_0$  and  $\gamma_2$  by comparing the term proportional to  $\nabla c_1$  in (12) with the result obtained from the microscopic model.

**3. Model calculation of driving terms**

We proceed here to discuss the evaluation of  $\gamma$ , introduced in (12) and (14), and other quantities such as  $\nu_2, \nu_4, U_2$  and  $D_2$  calculable from  $\gamma_0$  and  $\gamma_2$ . First we observe that, if  $f$  is the solution of the classical Liouville equation,

$$J_d = \int f \dot{A}_D d\Gamma \quad \dot{A}_D \equiv iLA_D \tag{17}$$

where the integral is over phase space. The driving terms in equation (12) arise from the coupling of the fluid within  $V$  to the surroundings. This coupling adds a term

$$\phi = -\sum_j F_j \cdot \partial f / \partial p_j \tag{18}$$

to the Liouville equation, where the sum is over particles of the system, and  $F_j$  is the contribution to the force on particle  $j$  from interactions across the boundary separating the fluid from its surroundings. The reason for restricting the problem to an isotopic mixture now becomes apparent, since  $F_j$  under this restriction will depend on the position of  $j$  but not on which constituent it is to which the particle belongs—a very useful simplification. To calculate a kinetic equation such as (12), we multiply the Liouville equation by  $\dot{A}_D$  and integrate over  $\Gamma$  space. The result of applying this operation to the expression in (18) is to be compared with the driving terms in (12).

On multiplying (18) by  $\dot{A}_D$  and integrating, we get

$$\int \phi \dot{A}_D d\Gamma = V^{-1} \int \sum_{j \in [1]} F_j f d\Gamma. \tag{19}$$

This is a sum of contributions from the forces acting across the boundary on particles of component 1 whose  $x$  coordinates are close to  $\pm \frac{1}{2}l$ . We shall suppose that, at liquid densities, the fluid is approximately contained by the surrounding medium during the very short time (estimated for hard spheres in § 4) that  $J_d$  requires to relax to its steady-state value. The forces across the boundary can then be expressed in terms of the pressure  $P_{xx}$  at the boundary, so that (Nettleton 1984)

$$V \int \phi \dot{A}_D d\Gamma = \sum_{\delta=\pm} -\delta n_{1\delta} \int (P_{xx}/n_\delta) da = -P_{xx} l^2 (c_1^+ - c_1^-). \tag{20}$$

Equation (20) supposes that the force on particles of species 1 in a small volume element is  $c_1$  times the total force across the boundary on all particles in that element, since the force per particle is the same on particles of both species. The integral is over the bounding surfaces at  $x = \pm \frac{1}{2}l$ . We have defined  $n = n_1 + n_2$ , the sum of the number densities, and  $c_i = n_i/n$  ( $i = 1, 2$ ).  $P_{xx}$  is constant across the system and thus the same on both boundaries, but the condition of mechanical stability in the steady state,  $\partial P_{xx} / \partial x = 0$ . Putting  $c_1^+ - c_1^- = l \partial c_1 / \partial x$  and  $V = l^3$ , we get

$$\int \phi \dot{A}_D d\Gamma = -P_{xx} \partial c_1 / \partial x. \tag{21}$$

As  $J_d \rightarrow 0, P_{xx} \rightarrow P_0$ , the equilibrium equation of state. Particles moving with velocity  $J_d/m_1 n_1$  relative to  $u$  carry momentum  $J_d/n_1$ . Given that  $J_2 = -J_1 = -J_d$ , inclusion of the total contribution to the momentum flux from both  $J_1$  and  $J_2$  gives

$$P_{xx} = P_0 + J_{dx} J_{dx} (\rho_1^{-1} + \rho_2^{-1}) \tag{22}$$

where  $\rho_i \equiv m_i n_i$ .

To evaluate  $\gamma$  in equation (12), we must compare the coefficient of  $\nabla c_1$  in the latter equation with the result of combining (21) and (22). This requires evaluation of  $\mu_1 - \mu_2$ . The equilibrium functions  $\mu_{i0}$  can be found if we note that for isotopes whose total numbers are  $N_1$  and  $N_2$ , with  $N = N_1 + N_2$ , the Helmholtz function is

$$F = F_N - \kappa T \ln \left( \frac{N}{N_1} \right) \quad (23)$$

where  $F_N$  is the free energy of  $N$  identical particles of mass  $m$  satisfying

$$m^{3N/2} = m_1^{3N_1/2} m_2^{3N_2/2}.$$

Equation (23) implies that

$$P_0 = -\partial F_N / \partial V = P_0(n, T) \quad (24)$$

where  $P_0$  is the equilibrium equation of state of a single-component fluid, and

$$\mu_{i0} = m_i^{-1} \partial F_N / \partial N - \kappa T m_i^{-1} \ln(N/N_i) \quad (i = 1, 2). \quad (25)$$

The evaluation of the  $\mathbf{J}_d$ -dependent terms in  $\nabla_T(\mu_1 - \mu_2)$  entails calculating  $\partial \mu_{i0} / \partial n_k$  ( $i, k = 1, 2$ ). We can evaluate the  $n_i$  derivatives of the combination  $(m_1 \mu_{10} - m_2 \mu_{20})$  from equation (25). In addition, from the Gibbs–Duhem equation, we obtain

$$n_1 m_1 \partial \mu_{10} / \partial n_i + n_2 m_2 \partial \mu_{20} / \partial n_i = \partial P_0 / \partial n_i \quad (i = 1, 2). \quad (26)$$

These additional relations yield all the  $n_i$  derivatives of  $\mu_{k0}$  and finally lead to

$$\begin{aligned} \nabla_T(\mu_{10} - \mu_{20}) = & \nabla n_1 [(\kappa T \rho / n m_2 \rho_1) + n^{-1}(\partial P_0 / \partial n)(m_1^{-1} - m_2^{-1})] \\ & + \nabla n_2 [-(\kappa T \rho / n m_1 \rho_2) + n^{-1}(\partial P_0 / \partial n)(m_1^{-1} - m_2^{-1})]. \end{aligned} \quad (27)$$

The derivatives  $\nabla n_1$  and  $\nabla n_2$  in equation (27) are related by the mechanical equilibrium condition,  $\partial P_{xx} / \partial x = 0$ , which assumes the form

$$(\partial P_0 / \partial n)(\nabla n_1 + \nabla n_2) + (\partial P_0 / \partial T) \nabla T - \mathbf{J}_d^2 [(\rho_1 n_1)^{-1} \nabla n_1 + (\rho_2 n_2)^{-1} \nabla n_2] + O(\mathbf{J}_d^4) = 0. \quad (28)$$

This equation can be solved to derive a lengthy expression for  $\nabla n_2$  in terms of  $\nabla n_1$ ,  $\nabla T$  and  $\mathbf{J}_d^2$ , and permits us to express  $\nabla_T(\mu_{10} - \mu_{20})$  in terms of  $\nabla c_1$  and  $\nabla T$ . Putting this result into (12) and comparing the term in  $\nabla c_1$  with (21), we get

$$\gamma_0 = P_0 \rho_1 \rho_2 / (\kappa T \rho n). \quad (29)$$

To evaluate  $\gamma_2$ , we must compare the  $O(\mathbf{J}_d^2)$  terms in  $\gamma \nabla_T(\mu_1 - \mu_2)$  with the corresponding terms in  $P_{xx}$ . By using the integrability condition (5b) and then using equation (29) in equation (15a) to evaluate  $\nu_2$ , we get

$$\mu_i = \mu_{i0} + \mu_{i2} \mathbf{J}_d^2 + O(\mathbf{J}_d^4) \quad (30a)$$

$$\mu_{i2} = -(2m_i \gamma_0)^{-1} [P_0^{-1}(\partial P_0 / \partial n) + m_i(\rho_i^{-1} - \rho^{-1}) - n^{-1}] \quad (i = 1, 2). \quad (30b)$$

Equation (30b) can be used to evaluate the  $\mathbf{J}_d$  dependence of  $\nabla_T(\mu_{12} - \mu_{22})$ , and then this is used in turn to calculate the  $O(\mathbf{J}_d^2)$  terms in  $\gamma \nabla_T(\mu_1 - \mu_2)$ . Comparison with terms of the same order in  $\mathbf{J}_d$  in  $-P_{xx} \nabla c_1$  gives

$$\begin{aligned} \gamma_2 = & (n \kappa T)^{-1} + \gamma_0(\rho_1 n_1 - \rho_2 n_2)(n_1 n_2 \partial P_0 / \partial n)^{-1} [-2(n \rho_2 m_1)^{-1} \\ & + (n \rho \kappa T)^{-1} \partial P_0 / \partial n (m_1^{-1} - m_2^{-1})] \\ & - (2 \rho \kappa T)^{-1} (P_0^{-1} \partial P_0 / \partial n - n^{-1})(n_2 - n_1)(m_2 - m_1) \\ & - (\rho^2 \kappa T)^{-1} (n_1^{-1} \rho_2^2 + n_2^{-1} \rho_1^2). \end{aligned} \quad (31)$$

Equation (31), in conjunction with equation (15*b*), allows us to evaluate  $\nu_4/\nu_2$  and thus to estimate the relative importance of the  $O(J_d^4)$  terms in  $F$ . This will be done in § 4 for the hard-sphere model.

Having obtained  $\gamma_2$ , we proceed to consider other coefficients of interest which are calculable from it. First of all, we note that the circumstance that equation (28) contains a term in  $\nabla T$  means that  $\nabla_T(\mu_1 - \mu_2)$  also has a term linear in the temperature gradient, in addition to the term linear in  $\nabla c_1$ . Since such a term is absent from equation (21), it must cancel with  $-\lambda T^{-1}\nabla T$  in equation (12). The condition for this is

$$\lambda = \lambda_0 + \lambda_2 J_d^2 + O(J_d^4) \tag{32a}$$

$$\lambda_0 = (\gamma_0 T/n)(\partial P_0/\partial T)(m_1^{-1} - m_2^{-1}) \tag{32b}$$

$$\begin{aligned} \lambda_2 = T(\partial P_0/\partial T)(\partial P_0/\partial n)^{-1} \{ & (m_1^{-1} - m_2^{-1})[\frac{1}{2}(P_0^{-1} \partial P_0/\partial n - n^{-1})(n^{-1} + P_0^{-1} \partial P_0/\partial n + n_2^{-1}) \\ & - \frac{1}{2}(-P_0^{-2}(\partial P_0/\partial n)^2 + P_0^{-1} \partial^2 P_0/\partial n^2 + n^{-2}) + \gamma_2 n^{-1} \partial P_0/\partial n] \\ & - (\rho_1/\rho n_2 \rho_2) + (2\rho n \rho_1 \rho_2)^{-1}(\rho_2^2 - \rho_1^2)(1 + n P_0^{-1} \partial P_0/\partial n) \}. \end{aligned} \tag{32c}$$

Using  $\gamma_0$  from equation (29), we can employ this result in conjunction with equation (5*a*) to evaluate the  $O(J_d^2)$  contribution to  $P$ . We have

$$P = P_0(n, T) + P_2 J_d^2 + O(J_d^4) \tag{33a}$$

$$P_2 = -(2\gamma_0)^{-1}(1 + n P_0^{-1} \partial P_0/\partial n). \tag{33b}$$

Next, putting our result for  $\gamma_0$  into  $\nu_2 = V/\gamma_0$  from equation (15*a*), we get from equation (8)

$$U_2 = V(2\gamma_0)^{-1}(1 + T\gamma_0^{-1} \partial \gamma_0/\partial T). \tag{34}$$

With the aid of these results, we shall estimate  $P_2/P_0$  and  $U_2/U_0$  for the hard-sphere model in § 4.

As mentioned above, another quantity which we should like to estimate, in connection with possible steady-state computer simulations, is  $D_2/D_0$ . With such simulations in mind, we shall use  $\theta$  as the temperature variable rather than  $T$ . With this stipulation, expand

$$LV^{-1}\Phi = (a_0 + a_2 J_d^2)J_d + \dots \tag{35}$$

where  $a_0$  and  $a_2$  depend on  $n_1, n_2$  and  $\theta$ . In a previous work (Nettleton 1987*a*, cf (40*a*)), arguments were given, based on microscopic expressions for  $L$  obtained by projection operators, to the effect that

$$a_2 = -a_0 \nu_1/\nu_2 = -a_0 \gamma_2/\gamma_0. \tag{36}$$

The change of temperature variable from  $T$  to  $\theta$  modifies  $P_0$  in  $P_{xx}$ . Thus

$$P_0(n, T) = P_0(n, \theta) - (\partial P_0/\partial \theta)(U_2/C_v)J_d^2 + \dots \tag{37}$$

The steady-state form of equation (12) now has the form of equation (2), with

$$D_2(\theta)/D_0(\theta) = P_0^{-1}[\rho/(\rho_1 \rho_2) - (\partial P_2/\partial \theta)(U_2/C_v)] + \gamma_2/\gamma_0 \tag{38a}$$

$$D_0 = -P_0/a_0. \tag{38b}$$

$a_0 = -1/\tau_D$ , where  $\tau_D$  is the relaxation time for  $J_d$ . This will be estimated for hard spheres in § 4 by calculating  $D_0$  from the Enskog dense gas theory and using (38*b*).  $D_2/D_0$  will also be estimated for the hard-sphere mixture.



Finally, we can make an estimate of the thermal diffusion ratio,  $k_T$ . As remarked above, however, this may not be accurate because we should treat  $J_d$  and  $J'$  on the same footing to examine the coupling of heat flow and diffusion. With this reservation, we remark that

$$\nabla c_1 = -n^{-1} \nabla n_1 - (n_1/n^2) \nabla n. \quad (39)$$

From (28), we can express  $\nabla n$  in terms of  $\nabla T$ , neglecting  $O(J_d^2)$  as we do in calculating  $k_T$ . In this way, we obtain

$$J_d = -D_{12} \nabla \rho_1 - D_T T^{-1} n m_1 \nabla T \quad (40a)$$

$$k_T \equiv D_T / D_{12} = P_0 n_1 / (n^2 \partial P_0 / \partial n). \quad (40b)$$

Equation (40b) is evaluated for the hard-sphere model in § 4 and compared with the prediction of the Enskog theory.

#### 4. Numerical estimates for a hard-sphere isotopic mixture

The particular system for which we shall obtain numerical values for the expressions derived in the preceding section is a binary isotopic hard-sphere mixture with diameters of both constituents chosen to be  $\bar{\sigma} = 3.64 \times 10^{-10}$  m, appropriate for Ar (Hirschfelder *et al* 1954). The two isotopes have particle masses  $m_1$  and  $m_2$ , number densities  $n_1$  and  $n_2$ , and mass densities  $\rho_i = m_i n_i$  appropriate to  $^{36}\text{Ar}$  and  $^{40}\text{Ar}$ , listed in table 1. We shall take  $\theta = 87$  K, close to the gas-solid transition in Ar. The equation of state,

$$P_0 = (\kappa T x / b_0) [1 + (x \Phi_1(x) / \Phi_2(x))] \quad (41a)$$

$$\Phi_1(x) = 1 + 0.063\,507x + 0.017\,329x^2 \quad (41b)$$

$$\Phi_2(x) = 1 - 0.561\,439x + 0.081\,313x^2 \quad (41c)$$

$$x \equiv b_0 n = \frac{2}{3} \pi \bar{\sigma}^3 n \quad (41d)$$

has been obtained (Ree and Hoover 1964) by fitting a Padé approximant to computer simulations. We shall take  $x = 1.4$  and  $c_1 = 0.4$ . If there is to be a large  $J_d$ , then  $c_1$

**Table 1.** Numerical values calculated for binary hard-sphere isotopic mixture at  $\theta = 87$  K,  $x = 1.4$ , with particle masses and diameters appropriate to  $^{36}\text{Ar}$  and  $^{40}\text{Ar}$ . The subscript '0' denotes an equilibrium function and the subscript '2' the coefficient of the square of the diffusion flux in the pressure  $P$ , binary diffusion coefficient  $D$  and the coefficient  $\gamma$  of the driving force in (12).  $\nu_4/\nu_0$  is the ratio of the coefficient of the third-order to that of the first-order term in the force associated with the variable  $J_d$ .

$m_1$	$5.97 \times 10^{-26}$ kg	$\gamma_2$	$-5.91 \times 10^{-9}$ m <sup>4</sup> J <sup>-1</sup>
$m_2$	$6.63 \times 10^{-26}$ kg	$\nu_4/\nu_0$	$-5.49 \times 10^{-12}$ m <sup>6</sup> J <sup>-1</sup> kg <sup>-1</sup>
$n_1$	$5.54 \times 10^{27}$ m <sup>-3</sup>	$D_2/D_0$	$3.17 \times 10^{-11}$ m <sup>6</sup> J <sup>-1</sup> kg <sup>-1</sup>
$n_2$	$8.32 \times 10^{27}$ m <sup>-3</sup>	$D_0/D_E$	1.10
$P_0$	$8.67 \times 10^7$ Pa	$D_E$	$2.34 \times 10^{-6}$ kg m <sup>-1</sup> s <sup>-1</sup>
$P_2$	$-1.82 \times 10^{-3}$ m <sup>3</sup> kg <sup>-1</sup>	$\tau_D$	$2.97 \times 10^{-14}$ s
$\gamma_0$	$1.08 \times 10^3$ kg m <sup>-3</sup>	$k_T$	0.136
$(T - \theta) / \theta J_d^2$	$-1.86 \times 10^{-11}$ m <sup>4</sup> s <sup>2</sup> kg <sup>-2</sup>	$k_{TE}$	0.0227

must vary widely across a macroscopic system, and we shall place the mixture in  $V$  around the middle of the concentration range, i.e. in the middle of the diffusion cell.

Using these values of  $x$ ,  $\bar{\sigma}$  and  $\theta$  plus  $m_1$  and  $m_2$  from table 1 and  $C_v = \frac{3}{2}N\kappa$  in equation (10), we estimate

$$\theta J_d^2 / (T - \theta) = 3\gamma_0 n \kappa \theta = 5.38 \times 10^{10} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-2}. \quad (42)$$

Then  $(T - \theta)/\theta$  is appreciable only if  $|J_d| \geq 20 \times 10^3 \text{ kg m}^{-2} \text{ s}^{-1}$  which is a very large diffusion flow. Similarly, if we use equation (31) to compute  $\gamma_2$ , obtaining the value in table 1, we find  $|\gamma_2 J_d^2 / \gamma_0| \geq 0.01$  if  $|J_d| \geq 40 \times 10^3 \text{ kg m}^{-2} \text{ s}^{-1}$ . From (38a) we estimate  $D_2/D_0$ , and we find  $D_2 J_d^2 / D_0 \geq 0.01$  if  $|J_d| \geq 17 \times 10^3 \text{ kg m}^{-2} \text{ s}^{-1}$ . The same very large diffusion flux is therefore required for the observation of all non-linear effects we consider here, and so these effects, under realisable conditions, are expected to be negligible. The reason why the same threshold is obtained in each case is that  $U_2/U_0$ ,  $\gamma_2/\gamma_0$  and  $D_2/D_0$  are all proportional to  $(\gamma_0 n \kappa \theta)^{-1} = (\rho/\rho_1 \rho_2 P_0)$ .

Since, from equation (15b),  $\gamma_2/\gamma_0 = \nu_4/\nu_2$ , we can neglect the  $O(J_d^4)$  terms in  $F$  relative to those which are  $O(J_d^2)$ . A similar conclusion has been found to hold in the cases of a scalar structural variable (Nettleton 1987a) and of the heat flux (Nettleton 1987b), when the latter is treated as a relaxing state variable in a manner analogous to the treatment of  $J_d$  in the present paper. Thus, although  $\nu_4$  cannot be determined (Nettleton 1987a) by comparing a phenomenological equation such as equation (12) plus equations (7b), (14), (32a) and (35) with a derivation of an equation for  $\dot{J}_d$  from a model, it appears that higher-order terms  $O(J_d^2)$  or  $O(J_d^2)$  in  $\Phi$  or  $F$  can be neglected to a good approximation. We have been able to evaluate  $\nu_4$  in particular cases, as we do here.

While we can evaluate  $D_2/D_0$  from the results of § 3,  $D_0$  itself and, from equation (38b),  $a_0$  are obtainable only by computer simulations. Alder *et al* (1970) have determined the ratio  $D_0/D_E$  of the hard-sphere self-diffusion coefficient to the value obtained from the Enskog dense gas theory as a function of  $V/V_0$ ,  $V_0$  being the close-packed volume. When  $x = 1.4$ ,  $V/V_0 = 2.12$  which we use in conjunction with the curves of Alder *et al* (1970) to estimate  $D_0/D_E = 1.10$ . In turn,  $D_E \approx [D_0]_1/\chi$ , where  $[D_0]_1$  is the first approximation from the solution to the moderate-density Boltzmann equation (Chapman and Cowling 1939, p 168) and  $\chi$  the Enskog correction, given respectively by

$$[D_0]_1 = 3[8(2\pi)^{1/2}\bar{\sigma}^2]^{-1}(m_0 m_1 \kappa T/m_2)^{1/2} \quad (43a)$$

$$\chi = 1 + (5\pi/12)n\bar{\sigma}^3 \quad (43b)$$

with  $m_0 \equiv m_1 + m_2$ . In this way, we estimate  $D_E = 0.234 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$  and  $D_0 = 1.10 D_E = 0.258 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ . From equation (38b),

$$\tau_D = -a_0^{-1} = D_0/P_0 = 2.97 \times 10^{-14} \text{ s}. \quad (44)$$

This is smaller by  $\sim 10^{-4}$  than the relaxation time for the heat flux calculated at  $x = 1.7$ . Most of the heat is probably carried by hypersound rather than by self-diffusion. From a rough estimate (Nettleton 1987b) that the probability per unit time that a molecule is free to self-diffuse is  $\sim 10^9 \text{ s}^{-1}$ , only a very small fraction of particles can diffuse across the boundary in time  $\tau_D$ . This can be advanced to justify the expression in equation (20) of the forces across the boundary in terms of  $P_{xx}$ —appropriate when the fluid in  $V$  is contained to a good approximation by the surroundings.

If we use equation (40b) to calculate  $O(J_d^2)$ -independent terms in the thermal diffusion ratio,  $k_T$ , we obtain the value listed in table 1. For comparison, we may take the value  $k_{TE}$ , calculated from the Enskog dense gas theory (Chapman and Cowling 1939, p 293). The latter is  $k_{TE} = 0.0227$ , about one-sixth of the value from equation (40b). We should not expect these estimates to have better than order-of-magnitude agreement, since  $k_{TE}$  is obtained by applying the Enskog correction to the first approximation for the moderately dilute gas, and this approximation tends systematically to be too small, as seen from the computer simulations (Alder *et al* 1970). Also, as remarked above, the accurate treatment of the coupling of heat and diffusion flows requires a more general ensemble, with  $J'$  as an additional state variable. Therefore, equation (40b) is not expected to be highly accurate.

## 5. Summary and discussion

Since marked non-linear effects have been found (Holian and Evans 1983, Hanley and Evans 1982) in computer simulations of Lennard-Jones liquids subjected to very high rates of shear, including non-analytic dependence of pressure and viscosity on shear rate, the question arises whether similar non-analyticities can be found in other transport coefficients. For example, if  $D_2$  in equation (13) were large enough so that the  $O(J_d^2)$  term in  $D$  became dominant far from equilibrium, then in the steady state  $D$  might depend on some power of  $\nabla c_1$  other than the square. Alternatively, the diffusion coefficient might have a different constant value at high rates of flow from the value it assumes at low flow rates.

To elucidate this question, we need to calculate the  $O(J_d^2)$  dependence of  $\gamma$  in equation (12). This is done by comparing equation (12) with a microscopic model. The relaxation equation for  $\dot{J}_d$  should be obtainable by multiplying the classical Liouville equation by  $A_D$ , defined in equation (1), and integrating over  $\Gamma$  space. It has been shown (Nettleton 1985) that such an equation for  $\dot{J}_d$  can be cast in Onsager-Casimir canonical form, with  $J_d$  an extended state variable and  $\Phi = -\partial F/\partial J_d$  a thermodynamic force. The usual reciprocity and integrability conditions obtain, even when the phenomenological coefficients are non-linear in  $J_d$ . The driving terms in equation (12), proportional to  $\nabla c_1$  and  $\nabla T$ , must be calculated by adding to the Liouville equation contributions from interaction with the surroundings. Provided the fluid in  $V$  is contained by the surroundings during the short relaxation time  $\tau_D$  required for approach to the steady state, the force acting across the boundary can be expressed in terms of the pressure, as in applications of the virial theorem to a fluid confined to a box. This yields the driving term  $-P_{xx}\nabla c_1$  in equation (21) for comparison with the term  $-\nabla_T(\mu_1 - \mu_2)$  in equation (12), a comparison which permits us to evaluate  $\gamma$ .

To make this comparison and calculate  $\gamma_2$ , we need to evaluate the  $O(J_d^2)$  contributions to  $\mu_1$  and  $\mu_2$ . This is done by using the reciprocity relation (15a) to calculate the  $O(J_d)$  term in  $\Phi$  and the integrability condition (5b).  $\gamma_2$  is used in equation (36) which gives the  $O(J_d^2)$  dependence of  $L$  in equation (12). In equation (38a), with these results, we express  $D_2/D_0$  in terms of  $\gamma_2$ , permitting an estimate of non-linear effects in isotropic diffusion.

As seen from the numerical estimates for the hard-sphere model in table 1, to see an appreciable non-linear effect we should have to have  $|J_d| \geq 2 \times 10^4 \text{ kg m}^{-2} \text{ s}^{-1}$ , which would be very hard to achieve in an actual steady-state experiment. This conclusion is similar to one obtained earlier for heat conduction in a dense hard-sphere model

(Nettleton 1987b) where a flux of  $\sim 10^9 \text{ W m}^{-2}$  would be needed before non-linear effects could be seen. Such flows may be seen in shock waves, but the relevance there of the present analytic formalism is not established.

The best test of our predictions would be in molecular dynamics simulations. Existing results (Kincaid and Erpenbeck 1986) were made for a hard-sphere mixture with a mass ratio 10 to 1 and at much lower density. These predict that dependence of  $D$  on the concentration gradient is small, but there is no reliable determination of the precise magnitude and functional form of this dependence.

It should be emphasised that these conclusions regarding non-linear effects apply only at liquid densities and say nothing about, e.g., low-density plasmas. In the latter case, where heat is carried by electrons, non-linear effects in heat conduction have been found in solutions of the Boltzmann equation (Eu 1985a, b, c).

Furthermore, the particular ensemble chosen in the present paper, with  $M_1$ ,  $M_2$ ,  $V$ ,  $T$  and  $J_d$  as state variables, appears limited in its usefulness to the neighbourhood of a steady state. By an application of reciprocity, we predict equation (16), which we might expect to hold near a steady state because of the coupling of heat and diffusion flows. However, in a general non-equilibrium state,  $J'$  and  $J_d$  can relax independently and should both be used as state variables. In the ensemble used in the present treatment, the concentration and temperature may differ between system and surroundings, but no variables have been introduced to characterise their variation within the system. A theory which includes relaxation of the internal density gradient and couples it to components of the heat flux has been developed (Nettleton 1961) for the linear case in a one-component system. Introduction of  $\nabla n$  and  $\nabla c_1$  as internal state variables would add considerable complications not required for our present objective which is to estimate the order of magnitude of non-linear effects in the steady state.

Since the study of non-linear effects is frequently done on computers, we have pointed out that  $T - \theta = O(J_d^2)$ , where  $\theta$ , the local equilibrium temperature, is a natural choice for the temperature variable in a computer simulation. Since  $(T - \theta)/\theta$  is of the same order as other non-linear effects, the choice of  $T$  or  $\theta$  will not affect conclusions about the relative smallness of these effects.

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