Journal of Statistical Physics, Vol. 7, No. 2, 1973

On the Enskog-Thorne Theory for a Binary Mixture of Dissimilar Rigid Spheres

L. Barajas,[1] L. S. García-Colín,[1,2] and E. Piña[1,3]

Received July 17, 1972

Thorne's method for obtaining transport coefficients in a binary rigid-sphere mixture is reexamined. First, a close look is taken at the way in which the point where the Enskog functions χ_{ij} are evaluated is introduced. Second, the calculation of the fluxes in the system and the transport coefficients is given. Thorne's results are found to be correct and independent of the choice of the point where the transfer plane is located. This does not hold true for the diffusion flux. It is shown that a different diffusion force is obtained for each selection and that only those diffusional effects which are of first order in the density are consistent with irreversible thermodynamics.

KEY WORDS: Transport coefficients; rigid spheres; Thorne's theory; diffusion force; diffusional flux; comparison between kinetic theory and irreversible thermodynamics.

1. INTRODUCTION

The calculation of the transport properties for a system composed of a binary mixture of dissimilar spheres using the well-known Enskog approach(1) was done by H. H. Thorne approximately thirty five years ago. Although

---

[1] Instituto Mexicano del Petróleo, México 14, D. F., Mexico.

[2] Also at Facultad de Ciencias, Universidad de México, México 20, D. F., Mexico.

[3] Also at Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, Zacatenco, México 14, D. F., Mexico.

© 1973 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011.

his calculations were never published, the results have been reported in the literature(1) for a long time. On a first examination, the problem of a binary mixture looks so much like the one-component case that it would seem worthless to pursue any detailed calculation for its properties. Furthermore, many authors(2-11) have either used them or rederived them by other methods, apparently holding no doubt about their correctness. And even further, experimental work done mainly on hard-sphere-like mixtures, measuring essentially diffusion coefficients, has been compared with such expressions.(12) Thus, one more paper on this subject seems hardly justified. Yet we believe there to be some points, both essential and minor ones, which to our knowledge have not been adequately discussed in the literature. Due to the great importance that the Enskog–Thorne results have played in the kinetic theory of gases, we feel that clarification of such points will add to our understanding of these complicated phenomena.

Our paper is in essence of a pedagogical nature. New results are obtained but are not of a fundamental kind. However, we hope that the final results will be useful to those engaged in experimental work and/or in computing transport coefficients. This is not all at irrelevant, especially when in recent years(13-16) we have seen how suitable it is to use Enskog's theory to represent such properties for simple dense fluids at reasonably high densities and pressures. Hopefully, this will also be true for mixtures.

This work was motivated by the following considerations:

1. Although expressible in terms of a power series expansion in the density, Thorne's results for the transport coefficients are strictly only valid to first order. Indeed, the radial distribution function χ is only approximated to account for the common volume of two spheres. To include corrections which are of higher order, one would have to estimate volumes of pairs, triads, and so on of associated spheres. Furthermore, it has been shown recently by Sengers *et al.*(17,18) that for a one-component system and within the context of the generalized Boltzmann equation which includes the triple collision term,(19) Enskog's theory is only an approximation *to first order in the density*. This means that it would be hard to evaluate the importance of the higher virials for the transport coefficients when a general convergent kinetic theory of gases is still lacking.

2. In view of the preceding statement, one may wonder how valid are the comparisons which have been made between Thorne's results and experimental data. Indeed, one should not expect more than first density corrections to the formulas provided by the dilute hard-sphere mixture model. Furthermore, a comparison between the kinetic results with irreversible thermodynamics has, to our knowledge, not been carried out.

Thus, experimental quantities may very well not coincide with theoretical ones.

3. In a recent letter,⁽²⁰⁾ it was emphasized that the point at which Enskog's function χ_{ij} for a binary mixture is evaluated is related to the explicit values for the fluxes of molecular properties. Here, we show explicitly that as far as the transport of momentum and energy is concerned, such a point may be chosen anywhere along the line joining the centers of the colliding spheres, leaving their respective fluxes invariant. This is not the case for the mass flux, where there are as many forms for the diffusion force $\mathbf{d}_{ij}$ as possible choices, namely, an infinite number. All these vectors contain an additional term with respect to Thorne's original expression which is of higher order in the density, i.e., of order n^2. Furthermore, it is also shown that none of these vectors leads to results which are consistent with irreversible thermodynamics.⁽²¹⁾

4. Since the Choh–Uhlenbeck integral equation for multicomponent systems has been extensively discussed together with the explicit expressions for the transport coefficients,⁽²²⁾ one can compare how Thorne's results fit into this general scheme. This comparison has been dealt with independently and will be published elsewhere.⁽²³⁾

Features associated with the first three statements will be covered in this paper. Our purpose, again is to offer something useful to workers engaged mostly in the application of Thorne's results. Thus, we take as our starting point the generalization of Enskog's equation for a binary mixture⁽²⁴⁾ and proceed from there. This is summarized in Section 2. Section 3 contains an outline of their solution for the hydrodynamic regime using the Chapman–Enskog⁽²⁵⁾ approach. Since the method is a standard one, the algebraic details are minimized, including those involved in the derivation of the hydrodynamic equations. Section 4 contains a brief discussion of the solutions to the set of linear inhomogeneous integral equations for the perturbation functions ϕ_i using a "scaling" transformation which actually reduces them to the dilute gas case. Section 5 is devoted to the calculation of the fluxes of the molecular properties. The derivation of the transport coefficients is outlined in Section 6. Up to this point, the method is valid, in principle, to all orders in the density and to first order in the gradients of the system. Also, the explicit form for the diffusion force $\mathbf{d}_{ij}$ is a function of the point chosen to evaluate χ_{ij}. In Section 7, we analyze the content of these statements in the light of irreversible thermodynamics. In particular, we show that the diffusional effects arising from a Thorne–Enskog scheme are consistent with the phenomenological ones only to first order in the density.

2. KINETIC EQUATIONS

We consider a system composed of a binary mixture of rigid spheres with diameters σ_i and masses m_i, $i = 1, 2$, enclosed in a container of volume V with a number density n_i of species i.

In order to establish the kinetic equations for this system, we use Enskog's assumptions:

1. Only binary collisions between molecules are considered.
2. The molecular chaos assumption is made, i.e., the correlations between positions and velocities of two particles in μ-space are neglected.

Thus, in the absence of external forces, the kinetic equations for the single-particle distribution functions[1] f_i are given by(24)

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{r}} = \sum_{j=1}^{2} \iint [\chi_{ij}(\mathbf{r}_j + y_{ij}\mathbf{k}) f_j'(\mathbf{r}_i + \sigma_{ij}\mathbf{k}) f_i'(\mathbf{r}_i)$$
$$- \chi_{ij}(\mathbf{r}_i - y_{ij}\mathbf{k}) f_j(\mathbf{r}_i - \sigma_{ij}\mathbf{k}) f_i(\mathbf{r}_i)]\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j \quad (1)$$

where $\mathbf{v}_i$ and $\mathbf{v}_i'$ are the molecular velocities before and after the collision, respectively, and χ_{ij} is the generalization of Enskog's function which accounts for the shielding and the excluded volume in a collision between molecules of species i and j. This function is evaluated at an arbitrary point located between the centers of the colliding molecules (see Fig. 1). This arbitrariness

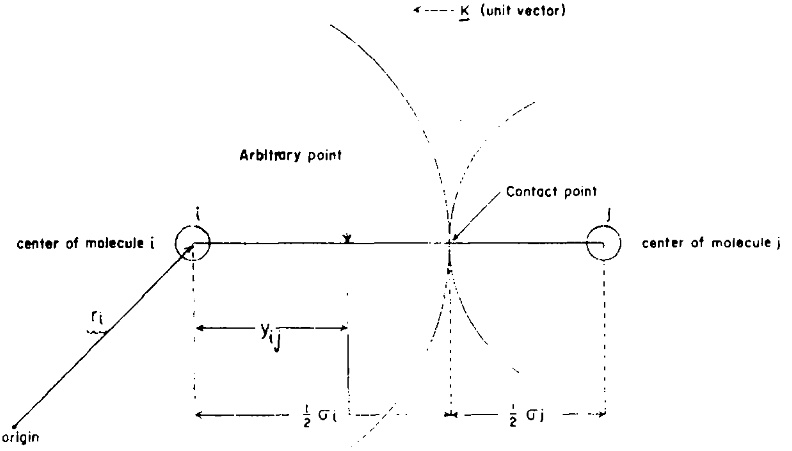

Fig. 1. An arbitrary point ($\mathbf{r}_i + y\mathbf{k}$), in the line joining the centers of molecules i and j is used to evaluate Enskog's function χ_{ij}.

---

[1] The following notation is being used: $f_i = f(\mathbf{r}_i, \mathbf{v}_i, t)$, where $\mathbf{r}_i$ is the position of a particle of species i.

will appear to be irrelevant in the calculation of all the fluxes related to the transfer of molecular properties, with the only exception being mass transfer, where a different diffusion force occurs for a particular selection of the point. Also, in Eq. (1), the quantities σ_{ij}, $\mathbf{k}$, and $\mathbf{g}_{ij}$ are defined by

$$\sigma_{ij} \equiv (\sigma_i + \sigma_j)/2 \tag{2a}$$

$$\mathbf{k} \equiv (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j| \tag{2b}$$

$$\mathbf{g}_{ji} \equiv \mathbf{v}_j - \mathbf{v}_i \tag{2c}$$

Since in Eq. (1), the function f_i, f_j, and χ_{ij} are evaluated at different points in configuration space, due to the fact that the colliding molecules are not point masses, a Taylor series expansion around the point $\mathbf{r}_i$ is performed. This expansion is justified on the basis that the assumption of local equilibrium is invoked. To first order in the spatial gradients, this yields the following result:[1]

$$[\partial f_i/\partial t]_{cj} = \sum_{k=1}^{3} \mathscr{L}_{ij}^{(k)} \tag{3}$$

where $[\partial f_i/\partial t]_{cj}$ stands for the rate of change of f_i due to collisions with molecules of species j. The $\mathscr{L}_{ij}^{(k)}$ terms of Eq. (3) are found to be

$$\mathscr{L}_{ij}^{(1)} \equiv \chi_{ij}(\mathbf{r}_i) \iint (f_i' f_j' - f_i f_j)\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j \tag{4}$$

$$\mathscr{L}_{ij}^{(2)} \equiv \chi_{ij}(\mathbf{r}_i) \iint \mathbf{k} \cdot (f_i' \nabla f_j' + f_i \nabla f_j)\, \sigma_{ij}^3 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j \tag{5}$$

$$\mathscr{L}_{ij}^{(3)} \equiv \iint \mathbf{k} \cdot \nabla \chi_{ij} (f_i' f_j' + f_i f_j)\, y_{ij} \sigma_{ij}^3 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j \tag{6}$$

where $\nabla = \partial/\partial\mathbf{r}$. Substitution of Eqs. (4)-(6) and (3) back into Eq. (1) yields

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{r}} = \sum_{j=1}^{2} \sum_{k=1}^{3} \mathscr{L}_{ij}^{(k)} \tag{7}$$

Equation (7) expresses the kinetic equations for f_i up to terms which are linear in the spatial gradients of the system.

3. HYDRODYNAMIC STAGE. HILBERT–ENSKOG METHOD

This section contains an outline of the standard Hilbert–Enskog method which is used to obtain the solution for the f_i satisfying Eq. (7) when the system is close to local equilibrium. In this stage, the so-called hydrodynamic stage, one assumes that the distribution functions can be expanded in a power series of a uniformity parameter ξ which is a measure of the spatial gradients in the system. Thus,

$$f_i = f_i^{(0)} + \xi f_i^{(1)} + \cdots \tag{8}$$

Substituting Eq. (8) into Eq. (7) and collecting terms of the equal powers in ξ, noticing that the left-hand side of (7) is already of first order in ξ, yields the following results.

(a) To zero order in ξ, we have that

$$\sum_{k=1}^{2} J(f_i^{(0)} f_k^{(0)}) = 0 \tag{9}$$

where

$$J(f_i f_j) = \iint (f_i f_j - f_i' f_j')\, \sigma_{ij}^2 (\mathbf{g}_{ij} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j \tag{10}$$

Equation (9) describes the uniform and stationary state of the mixture. The sufficient condition for these equations to be satisfied is that the $f_i^{(0)}$ be local Maxwellian distribution functions, namely

$$f_i^{(0)} = n_i (m_i / 2\pi k_B T)^{3/2} \exp(-m_i c_i^2 / 2k_B T) \tag{11}$$

but the necessary condition cannot be invoked due to the fact that no H-theorem has yet been proved for Eq. (1). Thus, one must assume that this solution is unique. Furthermore, the six arbitrary parameters which appear in Eqs. (11) are selected so that they correspond to the true local particle densities: n_i, $i = 1, 2$, the local hydrodynamic velocity $\mathbf{u}$, and the local temperature T. Therefore,

$$n_i = \int f_i^{(0)}\, d\mathbf{v}_i \tag{12}$$

$$\rho \mathbf{u} = \sum_{i=1}^{2} \int f_i^{(0)} m_i \mathbf{v}_i\, d\mathbf{v}_i \tag{13}$$

$$\tfrac{3}{2} n k_B T = \sum_{i=1}^{2} \int f_i^{(0)} \tfrac{1}{2} m_i c_i^2\, d\mathbf{v}_i \tag{14}$$

$\mathbf{c}_i = \mathbf{v}_i - \mathbf{u}$ is the thermal velocity, and k_B is Boltzmann's constant.

In order to obtain the hydrodynamic equations to this order in the gradients, one must first derive the transport equations to lowest order in the gradients. This is achieved by substitution of the first two terms in Eq. (8)

back into Eq. (7), keeping only those terms which are of first order in ξ. This gives the result$^{(1)}$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}}\right) f_i^{(0)} = -\sum_{j=1}^{2} \chi_{ij}[J(f_i^{(0)} f_j^{(1)}) + J(f_i^{(1)} f_j^{(0)})] - \sum_{j=1}^{2} \sum_{k \neq 1}^{3} \mathscr{J}_{ij}^{(k)}(f^{(0)}) \tag{15}$$

When these equations are multiplied by the collisional invariants $\psi_i = 1$, $m_i\mathbf{c}_i$, and $m_i c_i^2/2$, an integration is performed over the whole velocity space, and a summation is carried out over the species, the following results are obtained[5]:

(i) For $\psi = 1$, we get the equation of continuity

$$(Dn/Dt) + n\nabla \cdot \mathbf{u} = 0 \tag{16}$$

with $n = \sum_i n_i$.

(ii) For $\psi_i = m_i\mathbf{c}_i$, we get the equation of motion

$$(D\mathbf{u}/Dt) + (1/\rho)\nabla p_0 = 0 \tag{17}$$

where p_0 is the hydrostatic pressure defined as

$$p_0 = \sum_{i=1}^{2} \sum_{j=1}^{2} n_i k_B T(1 + b_{ij}\chi_{ij}) \tag{18}$$

with $\rho = \sum_i \rho_i = \sum_i m_i n_i$ and $b_{ij} = \frac{2}{3}\pi n_j \sigma_{ij}^3$

(iii) For $\psi_i = \frac{1}{2}m_i c_i^2$, we get the energy equation

$$\frac{1}{T}\frac{DT}{Dt} + \frac{2p_0}{3nk_B T}\nabla \cdot \mathbf{u} = 0 \tag{19}$$

where

$$D/Dt = (\partial/\partial t) + \mathbf{u} \cdot \nabla \tag{20}$$

Equations (16), (17), and (19) are the Euler equations for the mixture.

(b) To first order in ξ, the equations for $f_i^{(1)}$ are those defined by Eq. (15). In this case, the left-hand side, which is only a function of $f_i^{(0)}$, can be computed in a straightforward manner. Indeed, the streaming term $\mathscr{D}_i f_i^{(0)} = [(\partial/\partial t) + \mathbf{v}_i \cdot (\partial/\partial \mathbf{r})] f_i^{(0)}$ reduces to

$$\begin{aligned}\mathscr{D}_i f_i^{(0)} = {} & -3nk_B T[1 + (2p_0/3nk_B T)(\mathscr{C}_i^2 - \tfrac{3}{2})] + 2\mathscr{C}_i\mathscr{C}_i : \nabla\mathbf{u} \\ & + \mathbf{c}_i \cdot [\nabla \ln(n_i k_B T) + (\mathscr{C}_i^2 - \tfrac{5}{2})\nabla \ln T - (m_i/\rho k_B T)\nabla p_0]\end{aligned} \tag{21}$$

where $\mathscr{C}_i = (m_i/2k_B T)^{1/2}\mathbf{c}_i$.

---

[5] This procedure requires the previous evaluation of the integrals given by $\mathscr{J}_{ij}^{(k)}$, $k \neq 1$, with $f_i = f_i^{(0)}$, which is outlined in Appendix A.

Addition of this equation with the six terms arising from the remaining part of the inhomogeneous term of Eq. (15) leads to a set of integral equations for the $f_i^{(1)}$, namely

$$\sum_{j=1}^{2} \chi_{ij} \iint f_i^{(0)} f_j^{(0)} (\phi_i + \phi_j - \phi_i' - \phi_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j$$

$$= -f_i^{(0)} \{ K_i (\mathscr{C}_i^2 - \tfrac{5}{2})\, \mathbf{c}_i \cdot \nabla \ln T + (n/n_i)\, \mathbf{d}_{ij} \cdot \mathbf{c}_i$$

$$+ 2K_i' \{\mathscr{C}_i \mathscr{C}_i\}_s : \nabla \mathbf{u} + \tfrac{2}{3}(n_j/n)\, K_i'' (\mathscr{C}_i^2 - \tfrac{3}{2}) \nabla \cdot \mathbf{u} \} \tag{22}$$

where $f_i^{(1)} = f_i^{(0)} \phi_i$ and $\{S\}_s$ stands for the symmetric part of the tensor S. In Eq. (22), $\mathbf{d}_{ij}$ is the diffusion force defined by

$$\mathbf{d}_{ij} = \frac{\rho_i \rho_j}{\rho n k_B T} \left(\frac{1}{\rho_i} \nabla p_i - \frac{1}{\rho_j} \nabla p_j \right) + \frac{n_j}{n_i} b_{ji} \chi_{ij}$$

$$\times \left[\nabla \ln \left(\frac{n_j}{n_i} \right) + (M_{ij} - M_{ji}) \nabla \ln T + \frac{2y - \sigma_{ij}}{\sigma_{ij}} \nabla \ln \chi_{ij} \right] \tag{23}$$

where $p_i = n_i k_B T \sum_{j=1}^{2} (1 + b_{ij} \chi_{ij})$.

Here, the following notation has been introduced:

$$K_i = 1 + (12/5) \sum_{j=1}^{2} b_{ij} \chi_{ij} M_{ij} M_{ji} \tag{24}$$

$$K_i' = 1 + (4/5) \sum_{j=1}^{2} b_{ij} \chi_{ij} M_{ji} \tag{25}$$

$$K_i'' = 1 + 2 \sum_{j=1}^{2} b_{ij} \chi_{ij} M_{ji} - (p_0/n k_B T) \tag{26}$$

where $M_{ij} = m_i/(m_i + m_j) = m_i/m_0$ and $m_0 = \sum_{i=1}^{2} m_i$.

It is important to digress for a moment to emphasize the fact that there are as many forms for the diffusion force as choices of the point of evaluation of the χ_{ij} function. In particular, in Thorne's original calculation, his form for $\mathbf{d}_{ij}$ is compatible with the choice locating the point in the middle of the line joining the centers of the colliding molecules, i.e., $y_{ij} = \sigma_{ij}/2$. In this case, the last term in Eq. (23) vanishes. Two other choices have been suggested in the literature. The first one(20) suggests that χ_{ij} be evaluated at the contact point of the two molecules, i.e., $y_{ij} = \sigma_{ii}/2$, in which case the last term in Eq. 23 gives a contribution

$$[(\sigma_i - \sigma_j)/(\sigma_i + \sigma_j)] \nabla \ln \chi_{ij} \tag{27}$$

The second one[26] suggests that χ_{ij} is evaluated at the center of mass of the two colliding molecules, i.e., $y_{ij} = M_{ij}\sigma_{ij}$, and the contribution of such a term is

$$[(m_i - m_j)/(m_i + m_j)]\nabla \ln \chi_{ij} \tag{28}$$

As we shall see later, none of these choices is to be preferred with respect to the others.

The solution of the set of linear inhomogeneous integral equations for ϕ_i will be discussed in the following section.

4. SOLUTIONS TO THE LINEAR INHOMOGENEOUS INTEGRAL EQUATIONS FOR ϕ_i

In the previous section, we derived a set of linear inhomogeneous integral equations for the perturbation functions ϕ_i, $i = 1, 2$. In order to solve for these functions, we shall make use of the solutions of the analogous integral equations for the dilute mixture and then show that a simple transformation of variables will lead us to the solution of Eq. (22). In fact, if in these equations we set $K_i = K_i' = 1$, $\chi_{ii} = \chi_{ij} = 1$, and $K_i'' = 0$, we obtain the set of linear integral equations for the corresponding dilute mixture in the Boltzmann case. The solutions are well known to be of the form[1][6]

$$\tilde{\phi}_i = \tilde{\mathbf{A}}_i \cdot \nabla \ln T - n\tilde{\mathbf{D}}_i \cdot \tilde{\mathbf{d}}_{ij} - \tilde{\mathsf{B}}_i : \nabla \mathbf{u} \tag{29}$$

where $\tilde{\mathbf{A}}$, $\tilde{\mathbf{D}}$ and $\tilde{\mathsf{B}}$ satisfy the following integral equations:

$$\sum_{j=1}^{2} \iint f_i^{(0)} f_j^{(0)} (\tilde{\mathbf{A}}_i + \tilde{\mathbf{A}}_j - \tilde{\mathbf{A}}_i' - \tilde{\mathbf{A}}_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = f_i^{(0)} (\mathscr{C}_i^2 - \tfrac{5}{2})\, \mathbf{c}_i \tag{30}$$

$$\sum_{j=1}^{2} \iint f_i^{(0)} f_j^{(0)} (\tilde{\mathbf{D}}_i + \tilde{\mathbf{D}}_j - \tilde{\mathbf{D}}_i' - \tilde{\mathbf{D}}_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = (1/n_i) f_i^{(0)} \mathbf{c}_i \tag{31}$$

$$\sum_{j=1}^{2} \iint f_i^{(0)} f_j^{(0)} (\tilde{\mathsf{B}}_i + \tilde{\mathsf{B}}_j - \tilde{\mathsf{B}}_i' - \tilde{\mathsf{B}}_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = 2 f_i^{(0)} \{\mathscr{C}_i \mathscr{C}_i\}_s \tag{32}$$

In orders to solve for the functions ϕ_i satisfying Eq. (22), one assumes that they are of the form

$$\phi_i = -\mathbf{A}_i \cdot \nabla \ln T - n\mathbf{D}_i \cdot \mathbf{d}_{ij} - \mathsf{B}_i : \nabla \mathbf{u} - H_i \nabla \cdot \mathbf{u} \tag{33}$$

---

[6] The tilde stands for the dilute case.

By substitution of Eq. (33) back into Eq. (22), the following set of integral equations is obtained:

$$\sum_{j=1}^{2} \chi_{ij} \iint f_i^{(0)} f_j^{(0)} (\mathbf{A}_i + \mathbf{A}_j - \mathbf{A}_i' - \mathbf{A}_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = K_i f_i^{(0)} (\mathscr{C}_i^{\,2} - \tfrac{5}{2})\, \mathbf{c}_i \tag{34}$$

$$\sum_{j=1}^{2} \chi_{ij} \iint f_i^{(0)} f_j^{(0)} (\mathbf{D}_i + \mathbf{D}_j - \mathbf{D}_i' - \mathbf{D}_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = (1/n)\, f_i^{(0)} \mathbf{c}_i \tag{35}$$

$$\sum_{j=1}^{2} \chi_{ij} \iint f_i^{(0)} f_j^{(0)} (\mathsf{B}_i + \mathsf{B}_j - \mathsf{B}_i' - \mathsf{B}_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = 2K_i' f_i^{(0)} \{\mathscr{C}_i \mathscr{C}_i\}_s \tag{36}$$

$$\sum_{j=1}^{2} \chi_{ij} \iint f_i^{(0)} f_j^{(0)} (H_i + H_j - H_i' - H_j')\, \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = K_i'' f_i^{(0)} (\mathscr{C}_i^{\,2} - \tfrac{3}{2}) \tag{37}$$

with i standing for each species.

The solutions to Eqs. (34)–(36) are now obtained in a straightforward manner from Eqs. (30)–(32). Indeed, Eq. (34) can be reduced to the form of Eq. (30) through the following transformation:

$$\tilde{\mathbf{A}}_i \to \mathbf{A}_i, \qquad n_i \to n_i K_i, \qquad \sigma_{ij}^2 \to \chi_{ij}\sigma_{ij}^2 / K_i K_j \tag{38}$$

Also, Eq. (35) is reduced to the form of Eq. (31) if

$$\tilde{\mathbf{D}}_i \to \mathbf{D}_i, \qquad \sigma_{ij}^2 \to \chi_{ij}\sigma_{ij}^2 \tag{39}$$

and finally, Eq. (36) is reduced to the form of Eq. (32) if

$$\tilde{\mathsf{B}}_i \to \mathsf{B}_i, \qquad n_i \to n_i K_i', \qquad \sigma_{ij}^2 \to \chi_{ij}\sigma_{ij}^2 / K_i' K_j' \tag{40}$$

Equation (37), which gives the integral equations for the functions H_i which are the coefficients of $\nabla \cdot \mathbf{u}$, have to be dealt with in an independent manner. This is so because in the dilute mixture, the bulk viscosity, which arises precisely from the term containing $\nabla \cdot \mathbf{u}$, vanishes identically.

Since the solutions to the functions $\tilde{\mathbf{A}}$, $\tilde{\mathsf{B}}$, and $\tilde{\mathbf{D}}$ are already known for the Boltzmann mixture, one can easily write down the corresponding solutions for $\mathbf{A}$, $\mathbf{D}$, and B by simply applying the transformations given above. Their explicit form will be given at a later stage.

5. FLUXES OF MOLECULAR PROPERTIES

The flux of the various molecular properties, mass, momentum, and kinetic energy, can be calculated by direct derivation of the equations of change for such properties. This can be done by a standard procedure(2) which shall not be repeated here. The result is that the fluxes of molecular properties ψ_i ($=m_i$, $m_i\mathbf{c}_i$, and $m_i c_i^2/2$) is the sum of two contributions, the kinetic energy contribution and the one arising from the potential energy. The former contributions are given by

(i) Mass flux $$\mathbf{J}_i^{(k)} = \int f_i m_i \mathbf{c}_i \, d\mathbf{v}_i \tag{41}$$

(ii) Momentum flux $$\mathsf{P}^{(k)} = \sum_{i=1}^{2} \int f_i m_i \mathbf{c}_i\mathbf{c}_i \, d\mathbf{v}_i \tag{42}$$

(iii) Kinetic energy flux $$\mathbf{J}_e^{(k)} = \sum_{i=1}^{2} \int f_i \tfrac{1}{2} m_i c_i^2 \mathbf{c}_i \, d\mathbf{v}_i \tag{43}$$

The latter contributions, also called the collisional transfer contributions, are a bit more difficult to obtain. Here, we shall outline a generalization of Enskog's calculation for a single-component case to the binary mixture.

Let a plane be located at an arbitrary point with a vector **r** between the colliding molecules (Fig. 2). Then, the flux vector $\mathbf{\Psi}_{ij}$ of a molecular property ψ_i due to the collisions between molecules of species i and j is found to be[1,2]

$$\begin{aligned}\mathbf{\Psi}_{ij} = \tfrac{1}{2}\sigma_{ij}^3 \iiint (\psi_i' - \psi_i) f_i(\mathbf{r} + y_i\mathbf{k}) f_j(\mathbf{r} - y_j\mathbf{k})\, \chi_{ij}[\mathbf{r}] \\ \times (\mathbf{g}_{ji} \cdot \mathbf{k})\mathbf{k} \, d\mathbf{k} \, d\mathbf{c}_i \, d\mathbf{c}_j\end{aligned} \tag{44}$$

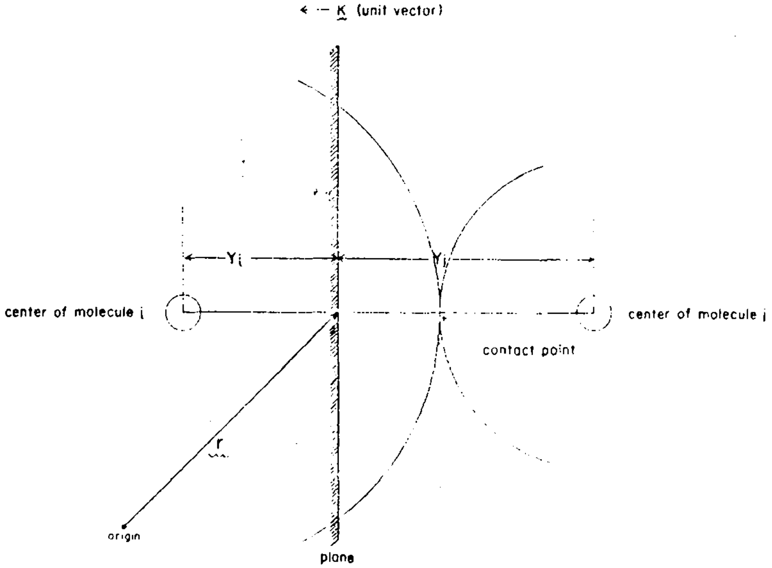

Fig. 2. An arbitrary point **r** between the colliding molecules is used to locate a transfer plane for molecular properties.

Expanding this expression in a Taylor series around $\mathbf{r}$, it reduces to the form

$$\begin{aligned}\Psi_{ij} = \tfrac{1}{2}\sigma_{ij}^3 \Big[\chi_{ij} \iiint (\psi_i' - \psi_i) f_i f_j (\mathbf{g}_{ji}\cdot\mathbf{k})\mathbf{k}\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j \\ + y_{ij}\chi_{ij} \iiint (\psi_i' - \psi_i) f_i f_j \mathbf{k}\cdot\nabla \ln f_i (\mathbf{g}_{ji}\cdot\mathbf{k})\mathbf{k}\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j \\ - y_{ji}\chi_{ij} \iiint (\psi_i' - \psi_i) f_i f_j \mathbf{k}\cdot\nabla \ln f_j (\mathbf{g}_{ji}\cdot\mathbf{k})\mathbf{k}\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j\Big]\end{aligned} \tag{45}$$

where all functions appearing in the right-hand side are now evaluated at the point $\mathbf{r}$. Thus, the collisional transfer contribution of any molecular property is independent of the point where the plane is chosen to lie.

The total contribution to the fluxes arising from collisional transfer is of the form

$$\Psi^{\phi} = \sum_{i,j} \psi_{ij}, \qquad i, j = 1, 2 \tag{46}$$

From symmetry arguments, one can see that $\psi_{ij} = \psi_{ji}$ and hence the evaluation of Eq. (46) is reduced to the calculation of ψ_{11} and ψ_{12}.

We consider now the collisional transport of the momentum of the molecules. When $\psi_i = m_i\mathbf{c}_i$ is substituted into Eq. (45) and the integrations are carried out (see Appendix B), one obtains

$$\begin{aligned}\mathsf{P}^{\phi} = \tfrac{4}{5} \sum_{i=1}^{2} \left(\sum_{j=1}^{2} M_{ji} b_{ij} \chi_{ij}\right) m_i \int f_i \mathbf{c}_i\mathbf{c}_i\, d\mathbf{c}_i \\ + \tfrac{2}{5} \sum_{i=1}^{2} \left(\sum_{j=1}^{2} M_{ji} b_{ij} \chi_{ij}\right) m_i \int f_i c_i^2\, d\mathbf{c}_i\, \mathbf{1} - [\tfrac{6}{5}\{\nabla\mathbf{u}\}_s + \nabla\cdot\mathbf{u}\mathbf{1}] \sum_{i=1}^{2}\sum_{j=1}^{2} \omega_{ij}\end{aligned} \tag{47}$$

since $\Psi^{\phi} = \mathsf{P}^{\phi}$. In Eq. (47), $\mathbf{1}$ is the unit tensor and

$$\omega_{ij} \equiv \tfrac{4}{9}(\pi k_B T)^{1/2} (2m_0 M_{ij} M_{ji})^{1/2} n_i n_j \sigma_{ij}^4 \tag{48}$$

In the case of the collisional transport of kinetic energy, we set $\psi_i = m_i c_i^2/2$. The evaluation of the corresponding integrals (see Appendix B) leads to the result that

$$\begin{aligned}\mathbf{J}_e^{\phi} = \tfrac{1}{2} \sum_{i=1}^{2} \left(\sum_{j=1}^{2} \tfrac{12}{5} M_{ij} M_{ji} b_{ij} \chi_{ij}\right) m_i \int f_i c_i^2 \mathbf{c}_i\, d\mathbf{c}_i \\ - \tfrac{4}{3}(2\pi k_B T) \sum_{i=1}^{2}\sum_{j=1}^{2} n_i n_j \chi_{ij} \sigma_{ij}^4 (M_{ij} M_{ji}/m_0)^{1/2}\, \nabla T\end{aligned} \tag{49}$$

Equations (47) and (49), when added to their respective kinetic contributions, give the complete expressions for the momentum and energy fluxes. These expressions, together with the explicit forms for f_i up to terms linear in the gradients, will be used in the following section to calculate the corresponding transport coefficients.

6. TRANSPORT COEFFICIENTS

In order to compute the transport coefficients for a mixture of dissimilar rigid spheres, we use the results obtained in the previous sections. Indeed, the fluxes for the system are given by Eqs. (41)-(43), (47), and (49), since there is no collisional transfer contribution to the mass flux, and also because

$$\mathbf{J}_e = \mathbf{J}_e^{(k)} + \mathbf{J}_e^{(\phi)} \tag{50}$$

$$\mathsf{P} = \mathsf{P}^{(k)} + \mathsf{P}^{(\phi)} \tag{51}$$

On the other hand, up to first order in the gradients, the single-particle distribution function for species i has the form

$$f_i = f_i^{(0)}(1 + \xi\phi_i + \cdots) \tag{52}$$

The procedure is now straightforward, so that we shall not repeat the details here.(1) Taking into account the modified form for the diffusion force $\mathbf{d}_{ij}$ given by Eq. (23), one finds that the diffusion coefficient D_{12} and the shear viscosity η are identical to the results obtained by Thorne.(1) The thermal diffusion ratio is given by

$$\begin{aligned} k_T = \tfrac{5}{2}\{&(n_1/n)\, m_1^{-1/2} K_1(a_{01}a_{-1\,-1} - a_{0\,-1}a_{1\,-1}) \\ &+ (n_2/n)\, m_2^{-1/2} K_2(a_{0\,-1}a_{11} - a_{01}a_{1\,-1})\}/(a_{11}a_{-1\,-1} - a_{1-1}^2) \end{aligned} \tag{53}$$

differing by a factor of χ_{12}^{-1} from Thorne's result.[7] Similarly, the thermal conductivity λ is simply k_B^{-1} times Thorne's value. Thus, all these results confirm their independence with respect to the point of evaluation of the function χ_{ij}.

The bulk viscosity is given by

$$\zeta = (\pi k_B T)^{1/2}[m_1^{1/2}n_1{}^2\chi_{11}\sigma_1{}^4 + 2(2m_0 M_{12} M_{21})^{1/2}\, n_1 n_2 \sigma_{12}^4 \chi_{12} + m_2^{1/2}n_2{}^2\chi_{22}\sigma_2{}^4] \tag{54}$$

showing that it is an effect at least of order n^2. This result is identical to that obtained by Tham and Gubbins.(5)

[7] All the quantities appearing in Eq. (53) have the same meaning as in Section 16.9 of Ref. 1.

Finally, we should like to emphasize that although these results are apparently correct to all orders in the density, this is not the case. In fact, a close comparison with irreversible thermodynamics will show that this is true only to first order in the density. This point will be discussed in the following section.

7. COMPARISON WITH IRREVERSIBLE THERMODYNAMICS

In view of the preceding results, we shall use Eq. (23) for the diffusion force in order to compare it with irreversible thermodynamics.

Boltzmann's equation corresponds in irreversible thermodynamics to the local validity of the perfect gas assumption. In this approximation, when the problem of mixtures is considered, one uses the same form for the diffusion flux from both the macroscopic and microscopic points of view, namely

$$\mathbf{c}_1 - \mathbf{c}_2 = -\frac{n^2}{n_1 n_2} D_{12} \left(\mathbf{d}_{12} + k_T \frac{1}{T} \frac{\partial T}{\partial \mathbf{r}}\right) \tag{55}$$

On the other hand, in the theory of moderately dense binary mixtures, one finds expressions for this flux which are formally identical to Eq. (55). However, in irreversible thermodynamics, the vector $\mathbf{d}_{12}$ is a function of those local thermodynamic variables which are consistent with the corresponding equation of state.[8] In kinetic theory, from Thorne's generalization of the Boltzmann equation for a dilute mixture, an expression for the diffusion flux is obtained which is of the same form as Eq. (55). Yet, the vector $\mathbf{d}_{12}$ has no obvious connection with irreversible thermodynamics. It is thus interesting to compare the two expressions for such a flux in order to find out the validity of the kinetic model proposed for the dense mixture.

This comparison will be carried out taking into account the fact that from the phenomenological point of view, $\mathbf{d}_{12}$ is determined up to a term proportional to the temperature gradient which may be included in the second term of Eq. (55). In fact, such a rearrangement of terms would correspond to a transformation between forces and fluxes where the diffusion flux is kept fixed, one force $\nabla T/T$ is fixed, and the force $\mathbf{d}_{12}$ and the coefficient k_T change.[9]

We recall that in irreversible thermodynamics, the vector[10] $\mathbf{d}_{12}^{(\mathrm{H})}$ is defined to be equal to$^{(2)}$

$$\mathbf{d}_{12}^{(\mathrm{H})} = \frac{\rho_1 \rho_2}{\rho n k_B T} \left(\frac{1}{m_1} \frac{\partial \mu_1}{\partial \mathbf{r}} - \frac{1}{m_2} \frac{\partial \mu_2}{\partial \mathbf{r}} + \frac{\bar{S}_1}{m_1} \frac{\partial T}{\partial \mathbf{r}} - \frac{\bar{S}_2}{m_2} \frac{\partial T}{\partial \mathbf{r}}\right) \tag{56}$$

---

[8] The equation of state for the ideal case corrected with higher-density terms.

[9] This calculation is outlined in Appendix C.

[10] The superscript *H* stands for Hirschfelder.

where μ_i and $\bar{S}_i$ are the chemical potential and partial entropy per particle of species i. These thermodynamic variables can be calculated from the equation of state given by Eq. (18), i.e., Thorne's equation of state. Since there are two corrections in orders in the density, we shall discuss them separately.

To first order in the density, Thorne's expression for $\mathbf{d}_{12}$, namely $\mathbf{d}_{12}^{(\mathrm{Th})}$, does not correspond to $\mathbf{d}_{12}^{(\mathrm{H})}$ but their difference is proportional to $\nabla T/T$. Consequently, the corresponding diffusion flux is compatible with the phenomenological equation (55) but by the above argument, the kinetic thermodiffusion coefficient $k_T^{(\mathrm{Th})}$ is not equal to the phenomenological one. They are related through the expression

$$k_T^{(\mathrm{H})} = k_T^{(\mathrm{Th})} + \frac{n_1 n_2}{n^2} \frac{2\pi}{3} \left(n_1 \sigma_1{}^3 - n_2 \sigma_2{}^3 + 2 \frac{m_2 n_2 - m_1 n_1}{m_1 + m_2} \sigma_{12}^3\right) \tag{57}$$

where $k_T^{(\mathrm{Th})}$ stands for the kinetic (Thorne) expression of k_T. Up to this order in the density, the point of evaluation of the function χ_{12} has no influence whatsoever on the results.

To second order in the density, the two expressions for k_T are different by other terms besides the one proportional to $\nabla T/T$. Consequently, the kinetic expression for the diffusion flux is inconsistent with the phenomenological one.

The difference between the two diffusion forces is given by

$$\begin{aligned} \mathbf{d}_{12}^{(\mathrm{H})} - \mathbf{d}_{12}^{(\mathrm{Th})} = {} & \frac{\pi^2}{18} \sigma_1 \sigma_2 \frac{\sigma_1 - \sigma_2}{2} \left(\sigma_1{}^3 \frac{\partial n_1}{\partial \mathbf{r}} + \sigma_2{}^3 \frac{\partial n_2}{\partial \mathbf{r}}\right) - \frac{\pi^2}{18} (2y_{12} - \sigma_1) \frac{n_1 n_2}{n} \sigma_{12} \\ & \times \left[(8\sigma_{12} - 3\sigma_1) \sigma_1{}^3 \frac{\partial n_1}{\partial \mathbf{r}} - (8\sigma_{12} - 3\sigma_2) \sigma_2{}^3 \frac{\partial n_2}{\partial \mathbf{r}}\right] \end{aligned} \tag{58}$$

where a term proportional to $\nabla T/T$ has not been taken into account. In Eq. (58), the point of evaluation of χ_{12} appears explicitly on the right-hand side and notice should be made of the fact that regardless of the point where it is evaluated, the right-hand side never vanishes.

These discrepancies, apparent ones to first order in the density, real ones to second order in the density, are important when comparison is made with experimental results. In order to emphasize this point, we have expressed our results in terms of those given by Landau and Lifshitz$^{(27)}$ and de Groot and Mazur$^{(28)}$ since they seem to be best fitted to express experimental data. In Refs. 27 and 28 the diffusion coefficient D is related to the coefficients D_{12} appearing in Eq. (55) through

$$D = D_{12}(n\rho_1\rho_2 m_1 m_2/\rho^3 k_B T)(\partial\mu_1/\partial c_1)_{p,T} \tag{59}$$

where c_1 is the mass concentration of species 1 and μ is the chemical potential of the mixture, $\mu = m_1^{-1}\mu_i - m_2^{-1}\mu_2$.

Also, their thermal diffusion ratio is not identical to $k_T^{(H)}$, but we have

$$(n^2/n_1n_2)\,D_{12}k_T^{(H)} = (\rho^2/\rho_1\rho_2)\,Dk_T \tag{60}$$

which thus relates $k_T^{(H)}$ with k_T through Eq. (57). Other quantities, such as the Soret and the Dufour coefficients, are also related to Eq. (60) and thus to the kinetic expression for $k_T^{(Th)}$, but these shall not be written here, since they are explicitly given in Ref. 22.

As a final remark, we would like to emphasize that the Thorne–Enskog scheme dealing with moderately dense mixtures for rigid spheres is not adequate if one goes to an order of approximation quadratic in the density. This holds true at least for the diffusional effects on the basis of irreversible thermodynamics. The clarification of this question will have to wait until the foundations of a kinetic theory of dense gases is laid.

APPENDIX A

Here, we outline the evaluation of the integrals $\mathscr{L}_{i \neq j}^{(k \neq 1)}(f^{(0)})$ by extending Enskog's method to a binary mixture.

(i) From Eq. (5),

$$\mathscr{L}_{ij}^{(2)} = \chi_{ij} \iint \mathbf{k} \cdot (f_i^{(0)}\,\nabla f_j^{(0)} + f_i^{(0)\prime}\,\nabla f_j^{(0)\prime})\,\sigma_{ij}^3 \mathbf{g}_{ji} \cdot \mathbf{k}\,d\mathbf{k}\,d\mathbf{c}_j \tag{A.1}$$

Owing to the form of $f_i^{(0)}, f_i^{(0)\prime} f_j^{(0)\prime} - f_i^{(0)} f_j^{(0)}$, Eq. (A.1) becomes

$$\mathscr{L}_{ij}^{(2)} = \iint f_i^{(0)} f_j^{(0)} \mathbf{k} \cdot \nabla \ln(f_j^{(0)\prime}/f_j^{(0)})\,\sigma_{ij}^3 \mathbf{g}_{ji} \cdot \mathbf{k}\,d\mathbf{k}\,d\mathbf{c}_j \tag{A.2}$$

Taking $\nabla \ln(f_j^{(0)\prime}/f_j^{(0)})$ from Eq. (11) and substituting into (A.2), we get

$$\begin{aligned}\mathscr{L}_{ij}^{(2)} = \chi_{ij} \iint f_i^{(0)} f_j^{(0)} \mathbf{k} \cdot [&\nabla \ln(n_j^2/T^3) + (m_j/2k_B T^2)(c_j'^2 + c_j^2)\,\nabla T \\ &+ (m_j/k_B T)(\mathbf{c}_j' + \mathbf{c}_j) \cdot \nabla \mathbf{u}]\,\sigma_{ij}^2 \mathbf{g}_{ji} \cdot \mathbf{k}\,d\mathbf{k}\,d\mathbf{c}_j \end{aligned}\tag{A.3}$$

Using techniques similar to the one used in Section 16.8 of Ref. 1 in order to integrate over $\mathbf{k}$, we obtain the following result:

$$\begin{aligned}\mathscr{L}_{ij}^{(2)} = \tfrac{2}{3}\pi\chi_{ij}\sigma_{ij}^3 f_i^{(0)} \int f_i^{(0)} \{&\mathbf{g}_{ji} \cdot \nabla \ln(n_j^2/T^3) \\ &+ (m_j/2k_B T^2)\,\nabla T \cdot [2c_j^2 \mathbf{g}_{ji} - \tfrac{4}{5}M_{ij}(2\mathbf{g}_{ji}(\mathbf{c}_j \cdot \mathbf{g}_{ji}) + g_{ji}^2 \mathbf{c}_j - 3M_{ij} g_{ji}^2 \mathbf{g}_{ji})] \\ &+ (2m_j/k_B T)[(\mathbf{c}_j \mathbf{g}_{ji} - \tfrac{2}{5}M_{ij}\mathbf{g}_{ji}\mathbf{g}_{ji}) : \nabla \mathbf{u} - \tfrac{1}{5}M_{ij} g_{ji}^2 \nabla \cdot \mathbf{u}]\}\,d\mathbf{c}_j \end{aligned}\tag{A.4}$$

Finally, integration over $\mathbf{c}_j$ yields

$$\begin{aligned}\mathscr{L}_{ij}^{(2)} = & - b_{ij}\chi_{ij}f_i^{(0)}\{[\nabla \ln(n_i n_j \chi_{ij} T) + \nabla \ln(n_j/n_i) \quad \nabla \ln(\chi_{ij}T) \\ & + M_{ij}(\tfrac{12}{5}M_{ji}\mathscr{C}_i^2 + 2M_{ij} - 4M_{ji})\nabla \ln T] \cdot \mathbf{c}_i \\ & + \tfrac{8}{5}M_{ji}\mathscr{C}_i\mathscr{C}_i : \nabla\mathbf{u} + \tfrac{4}{5}M_{ji}(\mathscr{C}_i^2 - \tfrac{5}{2})\nabla \cdot \mathbf{u}\}\end{aligned} \tag{A.5}$$

(ii) Evaluation of $\mathscr{L}_{ij}^{(3)}(f^{(0)})$. From Eq. (6),

$$\mathscr{L}_{ij}^{(3)} = \iint \mathbf{k} \cdot \nabla\chi_{ij}(f_i^{(0)}f_j^{(0)} + f_i^{(0)\prime}f_j^{(0)\prime})\, y_{ij}\sigma_{ij}^2(\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j \tag{A.6}$$

Integration of (A.6) over $\mathbf{k}$ gives

$$\mathscr{L}_{ij}^{(3)} = \tfrac{4}{3}\pi y_{ij}\sigma_{ij}^2 f_i^{(0)}\, \nabla\chi_{ij} \int f_j^{(0)}\mathbf{g}_{ji}\, d\mathbf{c}_j \tag{A.7}$$

Integration of (A.7) over $\mathbf{c}_j$ yields

$$\mathscr{L}_{ij}^{(3)} = -(2y_{ij}/\sigma_{ij})\, b_{ij}f_i^{(0)}\mathbf{c}_i \cdot \nabla\chi_{ij} \tag{A.8}$$

APPENDIX B

In this appendix, the collisional transfer of molecular properties due to collisions between dissimilar molecules is calculated.

(i) Collisional transfer of momentum. Only the first and the second integrals of Eq. (45) will be evaluated, because the evaluation method is the same for the remaining ones.

When $\psi_i = m_i\mathbf{c}_i$, the first integral of Eq. (45) becomes

$$\mathbf{I}_1 = m_i \iiint (\mathbf{c}_i' - \mathbf{c}_i) f_i f_j (\mathbf{g}_{ji} \cdot \mathbf{k})\mathbf{k}\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j \tag{B.1}$$

Integrating (B.1) over $\mathbf{k}$, taking into account that the velocities $\mathbf{c}_i$ and $\mathbf{c}_i'$ depend on the vector $\mathbf{k}$, and making use of Section 16.8 of Ref. 1, we obtain the following result:

$$\mathbf{I}_1 = (4\pi/15)\, m_i M_{ji} \iint f_i f_j (2\mathbf{g}_{ji}\mathbf{g}_{ji} + g_{ji}^2 \mathbf{1})\, d\mathbf{c}_i\, d\mathbf{c}_j \tag{B.2}$$

Substitution of $\mathbf{g}_{ji} = \mathbf{c}_j - \mathbf{c}_i$ in (B.2) and integration over $\mathbf{c}_i$ and $\mathbf{c}_j$ yields

$$\mathbf{I}_1 = 2n_i \sum_{j=1}^{2} m_j \int f_j \mathbf{c}_j\mathbf{c}_j\, d\mathbf{c}_j + n_i \mathbf{1} \sum_{j=1}^{2} m_j \int f_j c_j^2\, d\mathbf{c}_j \tag{B.3}$$

Substitution of $\boldsymbol{\psi}_i = m_i\mathbf{c}_i$ into the second integral of Eq. (45) yields the following expression:

$$\mathsf{I}_2 = m_i y_{ij} \iiint (\mathbf{c}_i' - \mathbf{c}_i) f_i^{(0)} f_j^{(0)} \mathbf{k} \cdot \nabla \ln f_i^{(0)} (\mathbf{g}_{ji} \cdot \mathbf{k})\mathbf{k}\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j \tag{B.4}$$

integration of (B.4) over $\mathbf{k}$ yields

$$\begin{aligned}\mathsf{I}_2 = {} & \tfrac{1}{6}\pi m_i M_{ji} y_{ij} \iint f_i^{(0)} f_j^{(0)} \{[(\mathbf{g}_{ji} \cdot \nabla \ln f_i^{(0)})(\mathbf{g}_{ji}\mathbf{g}_{ji} + g_{ji}^2 \mathsf{1})/g_{ji}] \\ & - g_{ji}[(\nabla \ln f_i^{(0)})\, \mathbf{g}_{ji} + \mathbf{g}_{ji} \nabla \ln f_i^{(0)}]\}\, d\mathbf{c}_i\, d\mathbf{c}_j\end{aligned} \tag{B.5}$$

In order to evaluate (B.5), a change of the variables of integration will be made from $\mathbf{c}_i$ and $\mathbf{c}_j$ to $\mathbf{g}_{ji}$, the relative velocity, and $\mathbf{G}_0 = \mathbf{G} - \mathbf{u}$, where $\mathbf{G}$ is the velocity of the center of mass and $\mathbf{u}$ is the hydrodynamic velocity. Thus

$$\mathbf{c}_i = \mathbf{G}_0 - M_{ji}\mathbf{g}_{ji} \tag{B.6}$$

and the Jacobian $|J|$ of the transformation is found to be equal to one. In terms of these new variables,

$$f_i^{(0)} f_j^{(0)} = n_i n_j [(m_i m_j)^{3/2}/(2\pi k_B T)^3] \exp[-m_0(G_0^2 + M_{ji} M_{ij} g_{ji}^2)/2k_B T] \tag{B.7}$$

and

$$\begin{aligned}\nabla \ln f_i^{(0)} = {} & \nabla \ln n_i + [(m_i/2k_B T)(G_0^2 + M_{ji}^2 g_{ji}^2 - 2M_{ji}\mathbf{G}_0 \cdot \mathbf{g}_{ji}) - \tfrac{3}{2}]\, \nabla \ln T \\ & + (m_i/k_B T)(\mathbf{G}_0 - M_{ji}\mathbf{g}_{ji}) \cdot \nabla\mathbf{u}\end{aligned} \tag{B.8}$$

Substituting (B.6)–(B.8) into (B.5) and taking into account that the terms arising from odd functions of $\mathbf{G}_0$ and $\mathbf{g}_{ji}$ vanish, the integral (B.5) becomes

$$\begin{aligned}\mathsf{I}_2 = {} & -\tfrac{1}{6}\pi y_i (m_i^2/k_B T) M_{ji}^2 \iint f_i^{(0)} f_j^{(0)} [(\nabla\mathbf{u} : \mathbf{g}_{ji}\mathbf{g}_{ji})(\mathbf{g}_{ji}\mathbf{g}_{ji} + g_{ji}^2 \mathsf{1})/g_{ji}]\, d\mathbf{G}_0\, d\mathbf{g}_{ji} \\ & - \tfrac{1}{6}\pi y_i (m_i^2/k_B T) M_{ji}^2 \iint f_i^{(0)} f_j^{(0)} \{g_{ji}[(\nabla\mathbf{u} \cdot \mathbf{g}_{ji})\mathbf{g}_{ji} + \mathbf{g}_{ji}(\nabla\mathbf{u} \cdot \mathbf{g}_{ji})]\}\, d\mathbf{G}_0\, d\mathbf{g}_{ji}\end{aligned} \tag{B.9}$$

Integration over $\mathbf{g}_{ji}$ and $\mathbf{G}_0$ yields the following results:

(a) First integral in (B.9):

$$\begin{aligned}& \iint f_i^{(0)} f_j^{(0)} [(\nabla\mathbf{u} : \mathbf{g}_{ji}\mathbf{g}_{ji})(\mathbf{g}_{ji}\mathbf{g}_{ji} + g_{ji}^2 \mathsf{1})/g_{ji}]\, d\mathbf{G}_0\, d\mathbf{g}_{ji} \\ & \quad = (4n_i n_j/\sqrt{\pi})(2k_B T m_0/m_i m_j)^{3/2}[(2/15)\{\nabla\mathbf{u}\}_s + (4/9)\nabla \cdot \mathbf{u}\mathsf{1}]\end{aligned} \tag{B.10}$$

(b) Second integral in (B.9):

$$\iint f_i^{(0)} f_j^{(0)} g_{ji} \{(\nabla \mathbf{u} \cdot \mathbf{g}_{ji})\mathbf{g}_{ji} + \mathbf{g}_{ji}(\nabla \mathbf{u} \cdot \mathbf{g}_{ji})\}\, d\mathbf{G}_0\, d\mathbf{g}_{ji}$$
$$= (4n_i n_j/\sqrt{\pi})(2k_B T m_0/m_i m_j)(\tfrac{2}{3}\{\nabla \mathbf{u}\}_s + \tfrac{2}{9}\nabla \cdot \mathbf{u}\mathbf{1}) \qquad \text{(B.11)}$$

Substituting (B.10) and (B.11) back into (B.9) and adding them to the result arising from the third integral in Eq. 45, which is readily evaluated, we get

$$-\tfrac{4}{9}(\pi k_B T)^{1/2}\, n_i n_j \chi_{ij} \sigma_{ij}^3 (2m_0 M_{ij} M_{ji})^{1/2} (y_{ij} + y_{ji})(\tfrac{6}{5}\{\nabla \mathbf{u}\}_s + \nabla \cdot \mathbf{u}\mathbf{1}) \qquad \text{(B.12)}$$

Since, from Fig. 2, $y_{ij} + y_{ji} = \sigma_{ij}$ for any choice of y_{ij}, then (B.12) becomes

$$-\omega_{ij}(\tfrac{6}{5}\{\nabla \mathbf{u}\}_s + \nabla \cdot \mathbf{u}\mathbf{1}) \qquad \text{(B.13)}$$

where $\omega_{ij} = \tfrac{4}{9}(\pi k_B T)^{1/2}\, n_i n_j \chi_{ij} \sigma_{ij}^4\, (2m_0 M_{ij} M_{ji})^{1/2}$.

Hence, the collisional flux of momentum due to collisions between dissimilar molecules is

$$\mathsf{p}_{ij}^{\phi} = \frac{2\pi}{15} \frac{\rho_i \rho_j}{m_0} \sigma_{ij}^3\, \chi_{ij} \left\{ \sum_{r=1}^{2} \frac{1}{n_r} \left(2\int f_r \mathbf{c}_r \mathbf{c}_r\, d\mathbf{c}_r + 1 \int f_r c_r^2\, d\mathbf{c}_r \right) \right\}$$
$$- \omega_{ij}[\tfrac{6}{5}\{\nabla \mathbf{u}\}_s + \nabla \cdot \mathbf{u}\mathbf{1}] \qquad \text{(B.14)}$$

(ii) Collisional transfer of kinetic energy. Substitution of $\psi_i = m_i c_i^2/2$ into Eq. (45) gives the potential contribution to the flux of kinetic energy due to collisions between dissimilar molecules. The method of evaluation for the resulting integrals is similar to that used in the case of the collisional transfer of momentum.

When $\psi_i = m_i c_i^2/2$, the first integral of Eq. (45) becomes

$$\mathbf{I}_3 = \tfrac{1}{4} m_i \sigma_{ij}^3 \chi_{ij} \iiint (c_i'^2 - c_i^2) f_i f_j \mathbf{k}(\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j \qquad \text{(B.15)}$$

Integration of (B.15) over **k** yields

$$\mathbf{I}_3 = (2\pi/15)\, \sigma_{ij}^3 m_i M_{ji} \iint f_i f_j [2\mathbf{g}_{ji}(\mathbf{g}_{ji} \cdot \mathbf{c}_i) + g_{ji}^2 \mathbf{c}_i + 3M_{ji} g_{ji}^2 \mathbf{g}_{ji}]\, d\mathbf{c}_i\, d\mathbf{c}_j \qquad \text{(B.16)}$$

Substituting $\mathbf{g}_{ji} = \mathbf{c}_i - \mathbf{c}_j$ into (B.16) and integrating over $\mathbf{c}_i$ and $\mathbf{c}_j$, taking into account that $\int f_i \mathbf{c}_i d\mathbf{c}_i = 0$, $\mathbf{I}_3$ becomes

$$\mathbf{I}_3 = \tfrac{3}{5} M_{ij} M_{ji} \chi_{ij} \sum_{i=1}^{2} b_{ij} m_i \int f_i c_i^2 \mathbf{c}_i\, d\mathbf{c}_i \qquad i \neq j \qquad \text{(B.17)}$$

Substitution of $\psi_i = m_i c_i^2/2$ into the second integral of (45) yields

$$\mathbf{I}_1 = \tfrac{1}{4}\sigma_{ij}^3 y_{ij}\chi_{ij}m_i \iiint (c_i'^2 - c_i^2) f_i^{(0)} f_j^{(0)} \mathbf{k} \cdot \nabla \ln f_i^{(0)} (\mathbf{g}_{ji} \cdot \mathbf{k})\mathbf{k}\, d\mathbf{k}\, d\mathbf{c}_i\, d\mathbf{c}_j \tag{B.18}$$

Integration of (B.18) over **k** yields

$$\mathbf{I}_4 = (\pi/12)\, \sigma_{ij}^3 y_{ij}\chi_{ij} m_i M_{ji} \iint f_i^{(0)} f_j^{(0)} \{[(\mathbf{c}_i \cdot \mathbf{g}_{ji})(\mathbf{g}_{ji}\mathbf{g}_{ji} + g_{ji}^2 \mathsf{1})/g_{ji}] \\ + g_{ji}(\mathbf{c}_i\mathbf{g}_{ji} + \mathbf{g}_{ji}\mathbf{c}_i) + M_{ji}(3g_{ji}\mathbf{g}_{ji}\mathbf{g}_{ji} + g_{ji}^3 \mathsf{1})\} \cdot \nabla \ln f_i^{(0)}\, d\mathbf{c}_i\, d\mathbf{c}_j \tag{B.19}$$

Making the change of variables (B.6), substituting (B.7) and (B.8) into (B.19), integrating the resulting expression over $\mathbf{g}_{ji}$ and $\mathbf{G}_0$, and adding the corresponding results from the third integral of Eq. (45) leads to the following expression:

$$-\tfrac{2}{3} n_i n_j (\pi k_B{}^3 T)^{1/2} (8 M_{ij} M_{ji}/m_0)\, \sigma_{ij}^4 \chi_{ij}\, \nabla T \tag{B.20}$$

where we have used $y_{ij} + y_{ji} = \sigma_{ij}$. Then the collisional transfer of kinetic energy due to collisions between dissimilar molecules is given by

$$[\mathbf{J}_e^{(\phi)}]_{ij} = \tfrac{3}{5} M_{ij} M_{ji} \chi_{ij} \sum_{i=1}^{2} b_{ij} m_i \int f_i c_i^2 \mathbf{c}_i\, d\mathbf{c}_i \\ - \tfrac{2}{3} n_i n_j (\pi k_B{}^3 T)^{1/2} (8 M_{ij} M_{ji}/m_0)\, \sigma_{ij}^4 \chi_{ij}\, \nabla T \tag{B.21}$$

APPENDIX C

In this appendix, we calculate the thermodynamic quantities appearing in the macroscopic diffusion vector (57). This macroscopic force is given by the equation[2]

$$\mathbf{d}_{12} = \frac{\rho_1 \rho_2}{\rho n k_B T} \left[\frac{1}{m_1} \frac{\partial \mu_1}{\partial \mathbf{r}} - \frac{1}{m_2} \frac{\partial \mu_2}{\partial \mathbf{r}} + \left(\frac{\bar{S}_1}{m_1} - \frac{\bar{S}_2}{m_2} \right) \frac{\partial T}{\partial \mathbf{r}} \right] \tag{C.1}$$

The chemical potential is obtained by standard methods: from Maxwell's relation,

$$(\partial \mu_1/\partial V)_{T, N_1, N_2} = -(\partial p/\partial N_1)_{T, V, N_2} \tag{C.2}$$

the right-hand side is calculated from the equation of state (18). We integrate Eq. (C.2) with respect to V, keeping constant the temperature and the numbers of particles. The integration constant is fixed by taking the dilute gas limit for a binary mixture, for which the chemical potentials are well known.

The partial entropies $\bar{S}_i$ per particle were similarly obtained.

In fact, when one works with the independent variables, temperature and densities of particles, instead of the pressure, temperature, and concentration, as is usual in phenomenological theory, it follows that the $\mathbf{d}_{12}$ vector takes the simplified form[29]

$$\mathbf{d}_{12} = \frac{\rho_1\rho_2}{\rho n k_{\mathrm{B}} T} \left\{ \frac{1}{m_1} \left(\frac{\partial \mu_1}{\partial \mathbf{r}}\right)_T - \frac{1}{m_2} \left(\frac{\partial \mu_2}{\partial \mathbf{r}}\right)_T \right.$$
$$\left. + \left[\frac{1}{m_1} \frac{(\partial p/\partial T)\,\partial p/\partial n_1}{\sum_j n_j\,\partial p/\partial n_j} - \frac{1}{m_2} \frac{(\partial p/\partial T)\,\partial p/\partial n_2}{\sum_j n_j\,\partial p/\partial n_j}\right] \frac{\partial T}{\partial \mathbf{r}} \right\} \tag{C.3}$$

where all these partial derivatives and gradients are calculated assuming n_1, n_2, and T to be the independent variables. The subscript T in the gradients of the chemical potentials means that these gradients are taken with variable number densities but at constant temperature.

The rest of the calculation is a purely algebraic exercise, with the result for the thermodynamic force

$$\mathbf{d}_{12} = \frac{\rho_1\rho_2}{\rho n} \left\{ \frac{1}{m_1} \left[\frac{1}{n_1} \nabla n_1 + \frac{4\pi}{3} \sigma_1{}^3 \nabla n_1 + \frac{4\pi}{3} \sigma_{12}^3 \nabla n_2 \right.\right.$$
$$+ \frac{5}{6} \pi^2 \sigma_1{}^6 n_1 \nabla n_1 + \frac{\pi^2 \sigma_1{}^3}{18} (\sigma_1{}^3 - 18\sigma_1 \sigma_{12}^2 + 32\sigma_{12}^3)(n_2 \nabla n_1 + n_1 \nabla n_2)$$
$$\left. + \frac{1}{18} \pi^2 \sigma_2{}^3 (\sigma_2{}^3 - 18\sigma_2 \sigma_{12}^2 + 32\sigma_{12}^3) n_2 \nabla n_2 \right]$$
$$- \frac{1}{m_2} \left[\frac{1}{n_2} \nabla n_2 + \frac{4\pi}{3} \sigma_2{}^3 \nabla n_2 + \frac{4\pi}{3} \sigma_{12}^3 \nabla n_1 \right.$$
$$+ \frac{5}{6} \pi^2 \sigma_2{}^6 n_2 \nabla n_2 + \frac{\pi^2 \sigma_2{}^3}{18} (\sigma_2{}^3 - 18\sigma_2 \sigma_{12}^2 + 32\sigma_{12}^3)(n_2 \nabla n_1 + n_1 \nabla n_2)$$
$$\left. + \frac{1}{18} \pi^2 \sigma_1{}^3 (\sigma_1{}^3 - 18\sigma_1 \sigma_{12}^2 + 32\sigma_{12}^3) n_1 \nabla n_1 \right]$$
$$\left. + \left[\frac{1}{m_1} \frac{(\partial p/\partial T)\,\partial p/\partial n_1}{\sum_j (\partial p/\partial n_j) n_j} - \frac{1}{m_2} \frac{(\partial p/\partial T)\,\partial p/\partial n_2}{\sum_j (\partial p/\partial n_j) n_j} \right] \nabla T \right\} \tag{C.4}$$

where up to terms of second order in density we have

$$\frac{(\partial p/\partial T)\,\partial p/\partial n_1}{\sum_j (\partial p/\partial n_j) n_j}$$
$$= k_{\mathrm{B}} \left\{ 1 + \frac{4\pi}{3} \sigma_1{}^3 n_1 + \frac{4\pi}{3} n_2 \sigma_{12}^3 \right.$$

$$
\begin{aligned}
&-\frac{1}{n}\left(\frac{2\pi}{3}\,{\sigma_1}^3{n_1}^2+\frac{4\pi}{3}\,\sigma_{12}^3 n_1 n_2+\frac{2\pi}{3}\,{\sigma_2}^3{n_2}^2\right)\\
&+\frac{5\pi^2}{6}\,{\sigma_1}^6{n_1}^2+\frac{\pi^2}{9}\,{\sigma_1}^3({\sigma_1}^3-18\sigma_1\sigma_{12}^2+32\sigma_{12}^3)\,n_1 n_2\\
&+\frac{\pi^2}{18}\,{\sigma_2}^3({\sigma_2}^3-18\sigma_2\sigma_{12}^2+32\sigma_{12}^3)\,{n_2}^2\\
&-\frac{2}{n}\left[\frac{5\pi^2}{18}\,{\sigma_1}^6{n_1}^3+\frac{1}{18}\,\pi^2{\sigma_1}^3({\sigma_1}^3-18\sigma_1\sigma_{12}^2+32\sigma_{12}^3)\,{n_1}^2 n_2\right.\\
&\left.+\frac{\pi^2}{18}\,{\sigma_2}^3({\sigma_2}^3-18\sigma_2\sigma_{12}^2+32\sigma_{12}^3)\,{n_2}^2 n_1+\frac{5\pi^2}{18}\,{\sigma_2}^6{n_2}^3\right]\\
&-\frac{2}{n}\left(\frac{2\pi}{3}\,{\sigma_1}^3 n_1+\frac{2\pi}{3}\,\sigma_{12}^3 n_2\right)\left(\frac{2\pi}{3}\,{\sigma_1}^3{n_1}^2+\frac{4\pi}{3}\,\sigma_{12}^3 n_1 n_2+\frac{2\pi}{3}\,{\sigma_2}^3{n_2}^2\right)\\
&+\frac{2}{n^2}\left(\frac{2\pi}{3}\,{\sigma_1}^3{n_1}^2+\frac{4\pi}{3}\,\sigma_{12}^3 n_1 n_2+\frac{2\pi}{3}\,{\sigma_2}^3{n_2}^2\right)^2\Bigg\} \qquad (\text{C.5})
\end{aligned}
$$

with a similar result for the other term obtained by interchanging 1 by 2.

These quantities have been ordered in ascending powers of the total density, to show their dependence up to quantities of second order in n. Equations (C.3) and (C.4) lead immediately to Eqs. (57) and (58) given in the text.

ACKNOWLEDGMENT

We would like to express our gratitude to Mr. J. A. Robles Domínguez for several helpful discussions of this work, and to Prof. H. Ted Davis for enlightening correspondence.

REFERENCES

1. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 2nd ed., Chapter 16, Cambridge Univ. Press, England, 1952.
2. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *The Molecular Theory of Gases and Liquids*, Wiley, New York, 1964.
3. I. L. McLaughlin and H. Ted Davis, *J. Chem. Phys.* **45**:2020 (1966).
4. D. E. Bennett III and C. F. Curtiss, *J. Chem. Phys.* **51**:2811 (1969).
5. M. K. Tham and K. E. Gubbins, *J. Chem. Phys.* **55**:268 (1971).
6. S. A. Rice, J. P. Boon, and H. T. Davis, in *Simple Dense Fluids*, H. L. Frisch and Z. W. Salsburg, eds., Academic, New York, 1968, p. 293.
7. J. H. Dymond and B. J. Alder, *J. Chem. Phys.* 52:923 (1970).
8. N. Jhunjhunwala, J. P. Boon, H. L. Frisch, and J. L. Lebowitz, *Physica* **41**:536 (1969).
9. E. McLaughlin, *J. Chem. Phys.* **50**:1254 (1969).
10. D. J. McConalogue and E. McLaughlin, *Mol. Phys.* **16**:501 (1969).
11. H. A. Al-Chalabi and E. McLaughlin, *Mol. Phys.* **19**:703 (1970).

12. Z. Balenovic, M. N. Myers, and J. Calvin Giddings, *J. Chem. Phys.* **52**:915 (1970), and literature cited therein.
13. E. McLaughlin, *Chem. Rev.* **64**:389 (1964).
14. J. V. Sengers, *J. Heat Mass Transfer* 8:1103 (1965).
15. S. K. Kim and J. Ross, *J. Chem. Phys.* **42**:263 (1965).
16. H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, *Physica* **60**:322 (1972).
17. J. V. Sengers, in *Kinetic Equations*, R. L. Liboff and N. Rostoker, eds., Gordon and Breach, New York, 1971, p. 137.
18. J. V. Sengers, M. H. Ernst, and D. T. Gillespie, *J. Chem. Phys.* **56**:5583 (1972).
19. E. G. D. Cohen, in *Lectures in Theoretical Physics*, Vol. IXC, W. E. Brittin, A. O. Barut, and M. Guenin, eds., Gordon and Breach, New York, 1967, p. 279.
20. L. S. García-Colín, L. Barajas, and E. Piña, *Phys. Letters* **37A**:395 (1971).
21. E. Piña, L. Barajas, and L. S. García-Colín, *Rev. Mex. Fís.* **21**: (1972).
22. E. G. D. Cohen, L. S. García-Colín, and M. H. Ernst, *Physica* **50**:177 (1970).
23. J. A. Robles-Domínguez and L. S. García-Colín, to be published.
24. J. A. Robles-Domínguez and E. Piña, *Rev. Mex. Fís.* **20**:171 (1971).
25. E. G. D. Cohen, in *Transport Phenomena in Fluids*, H. J. M. Hanley, ed., Dekker, New York, p. 119.
26. H. Ted Davis, private communication.
27. L. Landau and E. Lifshitz, *Fluid Mechanics*, Chapter 6, Addison-Wesley, Reading, Mass., 1959.
28. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, Chapter XI, North-Holland, Amsterdam, 1969.
29. E. Piña (to be published).