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Kinetic theory of dense fluids of rigid biaxial ellipsoids

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The transport equation for a one-particle distribution function *f* of a pure and dense fluid composed of hard biaxial ellipsoids has been derived by the Enskog method through a modification of the Taxman equation which describes the corresponding low-density fluid. The equation for *f* has been utilized in obtaining approximate equations of continuity, linear momentum, and energy of the dense fluid, and has then been solved through the Enskog infinite series expansion technique, and a second-order approximate formula for *f* has been achieved. Using this, results are derived for the hydrodynamic pressure, shear and bulk viscosity coefficients, and heat conductivity of the fluid. Fast exchange of energy between the translational and rotational motions is assumed throughout the calculation. The quantities ultimately appearing in the results, which cannot further be reduced analytically and require numerical evaluation, are the four-dimensional quadratures over the orientational coordinates of two interacting rigid ellipsoidal molecules. In the appropriate limit, all results reduce to those obtained by Enskog for a dense fluid of hard spheres, and a first-order modified Eucken-type formula for the dense fluid emerges.

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I. INTRODUCTION

The Boltzmann transport equation [1] of a low-density pure fluid composed of spherical molecules was derived by Boltzmann more than a century ago and is based on the assumptions that collisions between molecules are strictly binary and that successive collisions are uncorrelated (molecular chaos assumption). Enskog [1] had obtained normal solutions of the equation through an infinite series expansion method and derived fairly accurate expressions for the transport coefficients of hard-sphere (HS) fluids. Throughout their work both Boltzmann and Enskog neglected the internal energy of the molecule because the encounters between the molecules are elastic and therefore interconversion of internal and translational energies is not possible. Enskog [1(a),2–4] modified the HS Boltzmann equation in a way that extends its range of validity to considerably higher densities; this is now known as the Enskog equation. The Enskog theory retains the two basic assumptions used in the derivation of the Boltzmann equation and corrects for the finite size of the colliding particles in two important ways. First, account is taken of the fact that at high densities the collision frequency is modified by the excluded volume effect, and secondly instantaneous collisional or interactional transfer of translational energy as well as linear momentum is incorporated into the theory. Enskog solved his equation through the procedure that he had adopted in solving the Boltzmann equation. He obtained modified values for the viscosity and heat conductivity coefficients of the dense fluid and found that collisional transfer significantly changes the values of the coefficients from those of a low-density fluid. At moderate densities, the values of the coefficients agree very well with the results of Alder and co-workers [5(b),5(c)] obtained through molecular dynamics HS simulation. Enskog further suggested how the transport coefficient results can be applied in obtaining semiemperical formulas for the coefficients of real dense fluids.

Although both the Boltzmann and Enskog equations have an impressive list of very successful applications, their derivations are based on intuitive ideas of Boltzmann which do not depend in a rigorous manner on the laws of mechanics. However, the theoretical foundation of the Boltzmann equation was first laid out by Bogoliubov [6] and then by others [7]. The Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) equation was first derived from the Liouville equation, the generalized kinetic equation was then obtained from it by using the assumption of generalized molecular chaos [4], and finally the Boltzmann equation for a HS fluid was derived. Hollinger and Curtiss [8] and others [9] moved further and derived from the Liouville equation the Enskog equation or equations consistent with it and found that the Enskog equation is correct. Thus, the theoretical basis of the Boltzmann and Enskog equations was firmly established.

A semiclassical treatment of the first-order transport coefficients of a low-density fluid of molecules with internal energy, allowing for exchange of energy between the internal and translational degrees of freedom, has been given by Wang-Chang, Uhlenbeck and de Boer (WCUB) [10] and its classical counterpart has been studied independently by Taxman [11] and Curtiss [12]. In the classical method, both the translational and internal degrees of freedom are treated classically while in the semiclassical one the internal energy is considered quantum mechanically. Obviously, the encounters between the nonspherical molecules are inelastic and the transport equations of the one-particle distribution function *f* derived by the above mentioned workers are based upon a heuristically derived generalization of the Boltzmann equation. The WCUB, Curtiss, and Taxman equations have been given a common name as the generalized Boltzmann (GB) equation. The various formulas for the first-order transport coefficients of a low-density fluid of asymmetric molecules have been derived by solving the GB equation either by the

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Enskog method [10,11] or by a variational procedure [12]. Recently [13], a minor error has been detected and removed from the collisional integrals (CIs) of the coefficient formulas obtained through the Enskog technique. Curtiss and Dahler [14] have given a systematic statistical-mechanical derivation of the classical GB equation from the generalized Liouville equation by using the technique that Hollinger and Curtiss [8] had evolved in deriving the Enskog equation for a dense fluid of HS molecules. A generalized kinetic equation [15] for f and a generalized Langevin equation [16(b),16(c),16(f)] for time correlation functions (TCFs) of a dense fluid of polyatomic molecules have also recently been obtained from the Liouville equation, and the resulting equations have been solved to obtain formulas for the frequency-dependent transport co-efficients of a dense model fluid of hard uniaxial ellipsoids (spheroids). The results for the coefficients obtained through the solution of the generalized kinetic equation are very complicated. However, in the limit of hard spheres, the zero-frequency results yield the corresponding Enskog expressions for the coefficients.

The frequency-dependent formulas for the transport coefficients of the dense model fluid predicted through the TCF method and discussed in Refs. [16(b)–16(e)] are controversial and far from complete. The zero-frequency shear viscosity formula obtained through the method consists of the sum of two terms. One term is the same in Refs. [16(a)–16(f)], but the other term in Refs. [16(b)–16(e)] differs from that of Refs. [16(a)] and [16(f)], although the two different viscosity formulas given in Refs. [16(b)–16(e)] and in Ref. [16(a)] as well as in [16(f)] reduce in the HS limit to the corresponding Enskog formula [1(a)]. It is stated in Ref. [16(f)], of course, with a measure of justification that the formula given in Refs. [16(a)] and [16(f)] is far superior to that of Refs. [16(b)–16(e)]; however, the predicted values obtained through this superior formula do not agree even qualitatively with simulation results available for different densities. Furthermore, the frequency-dependent thermal conductivity expression in Refs. [16(b)–16(d)] for the fluid is inappropriate because its zero-frequency results for the dilute as well as for the dense model fluid fail to reduce in the appropriate limit to the HS Enskog formula [1(a)]. The TCF method has not yet been applied to obtaining an expression for the volume viscosity of a low-density model fluid and, therefore, it has not been possible through this method to predict a correct formula for the hydrostatic pressure of a dense fluid that is not in a steady state.

Different zero-frequency expressions for the thermal conductivity and volume viscosity of a low-density model fluid of hard uniaxial ellipsoids have been predicted [13] through an Enskog-type solution of the Taxman equation and, thereby, the controversy and drawbacks of the TCF method of calculations have been partially removed. Of course, the diffusion coefficient and shear viscosity derived in Ref. [13] for the low-density fluid do agree with those predicted through the TCF method [16].

The Mori-generalized Langevin techniques utilized in Refs. [15] and [16] have not so far focused attention on the study of transport phenomena in a dilute or dense model fluid composed of a pure or binary mixture of rigid biaxial ellipsoids. However, a modest beginning in this study through the Enskog-type technique has recently been made and the zero-frequency transport coefficient formulas for low-density model fluids have been predicted [18]. In the appropriate limit, the exact first-order formulas [16(a),16(b)] derived through the Enskog-type solution of the Taxman equation reduce to those [13] of a dilute fluid consisting of hard uniaxial ellipsoids.

The first objective of the present investigation is to develop an Enskog-type transport equation for a pure and dense model fluid consisting of rigid biaxial ellipsoids based on the Taxman or classical GB equation of the low-density fluid; this is described in Secs. II and III. There are two reasons behind choosing this model: First, this model and its simplified form, a hard uniaxial ellipsoidal fluid, are good reference [17] systems for the study of the thermodynamic and transport properties of nonlinear and linear polyatomic fluids. Over a range of eccentricities, these models form nematic and, in some cases, smectic liquid crystal phases and are currently being studied [13,18–22] by analytical and molecular dynamics simulation methods. The simulation studies suggest that the formation of a liquid crystal is, to a large extent, an anisotropic excluded volume effect. Secondly, the collision cross section for the inelastic collisions of the model molecules can be calculated exactly because the geometry of the molecules is now well understood [23,24], and thereby a complete analysis of collision problems can be performed.

The second purpose of this work is to derive formulas for the viscosity coefficients and heat conductivity of a dense fluid. In order to achieve this we first obtain in Sec. IV a normal solution of the modified Taxman equation, derived in Sec. III up to the second approximation, by the standard infinite series expansion technique of Enskog. During the course of the solution, we found a formula for the hydrostatic pressure and also three equations which are, respectively, the first approximations to the equations of continuity, linear momentum, and energy of the fluid. The pressure formula is valid provided the fluid is in a uniform steady state. The solution has been utilized in Sec. V for deriving results for the pressure tensor and thermal-flux vector that arise due to free motions of the molecules. Section VI deals with the collision transfer flux vectors, and in Sec. VII first-order approximate results for the transport co-efficients have been achieved, the outcome of the various fluxes generated from the motions of the molecules as well as from the instantaneous transfer across the distance separating the centers of two colliding molecules momentarily in contact and stationary.

It is shown in Sec. VIII that the results reduce in the limit of a HS to those of Enskog provided one neglects the contributions from the rotational energy of HS molecules. On the other hand, if one retains these contributions, a first-order modified Eucken formula emerges for the heat conductivity of a dense HS fluid. This formula is the outcome of the infinitely slow exchange (elastic collisions) between translational and rotational energies. Finally, Sec. IX presents numerical results for the shear viscosity of uniaxial ellipsoidal fluids using computationally convenient expressions given in the Appendix.

II. COLLISIONAL FREQUENCY

Consider a low-density pure fluid composed of hard biaxial ellipsoidal molecules each of mass m and principal mo-

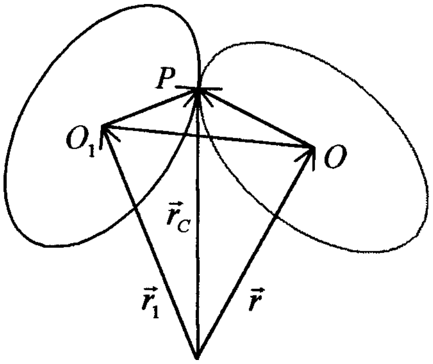

FIG. 1. Geometry of hard ellipsoid collision; O is the center of mass of the first molecule and O_1 that of the second one. $\overrightarrow{O_1P}=\vec{\rho}_1$ and $\overrightarrow{OP}=\vec{\rho}$.

ment of inertia tensor $\vec{I}$ with components I_ν $(\nu=1,2,3)$. The inelastic collisions of a pair of such molecules are described by their support functions h and h_1, the unweighted average $\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}$ of surface area element ζ_{ex} per unit solid angle $d\hat{k}$ on the volume excluded to the center of mass of the first molecule when the molecules are in contact at a fixed orientation, the unit outward surface normal $\hat{k}$ on the surface of the second molecule at the contact point, the translation-to-rotation-energy transfer function D, and the one-particle local distribution functions $f(\vec{c},\vec{\omega},\vec{r},t)$ and $f(\vec{c}_1,\vec{\omega}_1,\vec{r},t)$ of the first and second molecules at the vector position $\vec{r}$ and time t. The function f is defined in such a way that $f(\vec{c},\vec{\omega},\vec{r},t)d\vec{c}\,d\vec{\omega}$ is the number density of the first type of molecule having postcollisional linear and angular velocities $(\vec{c},\vec{\omega})$ in the velocity space element $d\vec{c}\,d\vec{\omega}$ and $f_1\equiv f(\vec{c}_1,\vec{\omega}_1,\vec{r},t)$ is similarly defined in the element $d\vec{c}_1\,d\vec{\omega}_1$. The definitions of h, h_1, D, and $\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}$ are given elsewhere [see Eqs. (1), (14), (42), and (A28) of Ref. [18(a)]].

For a fluid at ordinary pressure, the frequency of inelastic collision per unit volume is given [1(b)] under the assumption of molecular chaos, by

$$f(\vec{r})f_1(\vec{r})\hat{k}\cdot\vec{g}_{12}\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1\,d\vec{\omega}_1. \tag{1}$$

The relation between the postcollisional relative velocity $\vec{g}_{12}$ of the point of contact of the two colliding molecules and the corresponding relative velocity $\vec{v}_{12}$ of the center of mass O_1 of the second molecule with respect to O, that of the first one, is given by

$$\vec{g}_{12}=\vec{v}_{12}+\vec{\omega}_1\times\vec{\rho}_1-\vec{\omega}\times\vec{\rho}. \tag{2}$$

Here $\vec{v}_{12}=\vec{c}_1-\vec{c}$, and $\vec{\rho}_1$ and $\vec{\rho}$ are the vector positions of the second and first molecules at the point of contact measured, respectively, from O_1 and O, and are given by [24]

$$\vec{\rho}_\mu=[\hat{k}_\mu+\vec{\nabla}_{k_\mu}]h_\mu(y_\mu,z_\mu), \tag{3}$$

where $\mu=1,2$; $h_2\equiv h$, $\vec{\rho}_2\equiv\vec{\rho}$, and $\vec{\nabla}_{k_\mu}$ is the gradient operator with respect to $\hat{k}_\mu$. Also $\hat{k}_1\equiv\hat{k}=-\hat{k}_2$. The variables y_μ and z_μ are defined in Ref. [23].

Although we shall retain the molecular chaos assumption in the dense fluid, the frequency expression of Eq. (1) needs two modifications. First, because O (Fig. 1) is at $\vec{r}$, O_1 will be at $\vec{r}-\vec{d}_{12}(-\hat{k})$ and hence $f_1(\vec{r})$ should be replaced by $f_1(\vec{r}-\vec{d}_{12})$, where $\vec{d}_{12}(-\hat{k})=\vec{\rho}_1(\hat{k})-\vec{\rho}(-\hat{k})$. Secondly, the volume of the molecules in a dense fluid is not negligible as compared with the volume occupied by the fluid. As a consequence, the effective volume in which the center of any molecule can lie is reduced and thereby the frequency of collision is increased by a factor Y, the pair distribution function, which must be a function only of $\vec{r}_c(-\hat{k})=\vec{r}+\vec{\rho}(-\hat{k})$ where the biaxial molecules impinge, and not of the velocity of the point P (by the assumption of molecular chaos). Consequently, when a dense fluid is considered, the collision frequency per unit volume

$$\begin{aligned}&Y(\vec{r}_c(-\hat{k}))f(\vec{r})f_1(\vec{r}-\vec{d}_{12}(-\hat{k}))\\&\quad\times\hat{k}\cdot\vec{g}_{12}\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1\,d\vec{\omega}_1\end{aligned} \tag{4}$$

should be used instead of Eq. (1). It should be noted that in Eqs. (1) and (4) we have suppressed the translational and angular velocities and time dependence of f and f_1 for the sake of brevity.

III. MODIFIED TAXMAN EQUATION

A. Calculation of $(\partial f/\partial t)_{\mathrm{coll}}$

The Taxman [11] integro-differential equation for low-density fluid has the form

$$\frac{\partial f}{\partial t}+\vec{c}\cdot\frac{\partial f}{\partial\vec{r}}+\vec{F}\cdot\frac{\partial f}{\partial\vec{c}}=\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}}^{\mathrm{dilute}}, \tag{5}$$

where $\vec{F}$ represents an external acceleration acting only on the center of mass O of the molecule. We retain this form of the equation for a dense fluid. However, the expression for $(\partial f/\partial t)_{\mathrm{coll}}$, representing the rate of change due to collision in a dense fluid, is not the same as $(\partial f/\partial t)_{\mathrm{coll}}^{\mathrm{dilute}}$. We derive below the expression for $(\partial f/\partial t)_{\mathrm{coll}}$ and call the resulting equation the modified Taxman equation.

Consider the frequency per unit volume of an inverse collision whence $\hat{k}$ becomes $-\hat{k}$; hence it follows from Eq. (3) that $\vec{\rho}_\mu(-\hat{k})=-\vec{\rho}_\mu(\hat{k})$ and $\vec{d}_{12}(-\hat{k})=-\vec{d}_{12}(\hat{k})$. In such a collision, O_1 is at $\vec{r}+\vec{d}_{12}(\hat{k})$, while the molecules collide at $\vec{r}+\vec{\rho}(\hat{k})$. Hence from Eq. (4) the frequency of collision will be

$$\begin{aligned}&Y(\vec{r}_c(\hat{k}))f(\vec{c}\,',\vec{\omega}\,',\vec{r},t)f(\vec{c}_1',\vec{\omega}_1',\vec{r}-\vec{d}_{12}(\hat{k}),t)\hat{k}\cdot\vec{g}_{12}\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}\\&\quad\times d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1\,d\vec{\omega}_1\\&\equiv Y(\vec{r}_c(\hat{k}))f'(\vec{r})f_1'(\vec{r}-d_{12}(\hat{k}))\\&\quad\times\hat{k}\cdot\vec{g}_{12}\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1\,d\vec{\omega}_1.\end{aligned} \tag{6}$$

Consider an integral operator $\hat{O}_1$ which represents a four-dimensional integral over the orientational coordinates of a pair of molecules and is defined by

$$\hat{O}_1 w(\phi_1,\phi_2;z_1,z_2)=\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\int_0^1\int_0^1 d\phi_1 d\phi_2 dz_1 dz_2 \times\langle\zeta_{\text{ex}}\rangle_{\text{or}} w(\phi_1,\phi_2;z_1,z_2), \tag{7}$$

where w is any function of the orientational coordinates. It is now possible to write the form of the expression for $(\partial f/\partial t)_{\text{coll}}$ with the help of Eqs. (4), (6), and (7). We thus get

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}=2\chi(T)\hat{O}_1\int\int\int \hat{k}\cdot\vec{g}\,d\hat{k}\,d\vec{c}_1\,d\vec{\omega}_1 \times[Y(\vec{r}_c(\hat{k}))f'(\vec{r})f_1'(\vec{r}-\vec{d}_{12}(\hat{k})) - Y(\vec{r}_c(-\hat{k}))f(\vec{r})f_1(\vec{r}+\vec{d}_{12}(\hat{k}))] \tag{8}$$

and

$$\vec{g}=\frac{1}{2\chi(T)}\vec{g}_{12},\quad \chi(T)=\left(\frac{k_B T}{m}\right)^{1/2}. \tag{9}$$

B. Equation for $f^{(1)}$

If the fluid is uniform, Y, f_1, and f do not depend on $\vec{r}$ and $\vec{\rho}$ or $\vec{\rho}_1$, and Eq. (8) in this case takes the form

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}=2Y\chi(T)\hat{O}_1\int\int\int (f'f_1'-ff_1)\hat{k}\cdot\vec{g}\,d\hat{k}\,d\vec{c}_1\,d\vec{\omega}_1. \tag{10}$$

This expression differs from the corresponding expression [11] for the low-density fluid only by the factor Y and one can easily show [1(c)] that, in the uniform steady state, f has the generalized Maxwellian form

$$f^{(0)}=n\left(\frac{\sqrt{m}}{2\pi k_B T}\right)^3 (I_1 I_2 I_3)^{1/2}\exp\left(-\frac{1}{2k_B T}(mC^2+\overleftrightarrow{I}:\vec{\omega}\vec{\omega})\right) \tag{11}$$

such that the number density n, temperature T, mass velocity $\vec{c}_0$, and peculiar velocity $\vec{C}$ $(=\vec{c}-\vec{c}_0)$ are independent of $\vec{r}$ and t.

When the fluid is not in a uniform steady state, a first-order approximation $f^{(0)}$ to f is given by Eq. (11) where n, T, and $\vec{c}_0$ are now functions of $\vec{r}$ and t, and its second approximation $f^{(0)}+f^{(1)}$ is

$$f^{(0)}+f^{(1)}=f^{(0)}(1+\phi^{(1)}), \tag{12}$$

where $\phi^{(1)}$ is a linear function of the first derivatives of n, T, and $\vec{c}_0$. By substituting Eq. (12) into the left hand side of Eq. (5), neglecting all terms involving products of derivatives or derivatives of second order, and using the definition of $\vec{C}$, one finds that

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}=\frac{\partial f^{(0)}}{\partial t}+\vec{c}\cdot\frac{\partial f^{(0)}}{\partial\vec{r}}+\vec{F}\cdot\frac{\partial f^{(0)}}{\partial\vec{c}} \equiv f^{(0)}\left(\frac{D}{Dt}+\vec{c}\cdot\frac{\partial}{\partial\vec{r}}+\vec{F}\cdot\frac{\partial}{\partial\vec{C}}\right)\ln f^{(0)}, \tag{13}$$

where the ‘‘mobile’’ or ‘‘substantial’’ time-derivative operator [1(d)] D/Dt is defined as

$$\frac{D}{Dt}=\frac{\partial}{\partial t}+\vec{c}_0\cdot\frac{\partial}{\partial\vec{r}}. \tag{14}$$

If one substitutes the expression for $f^{(0)}$ from Eq. (11) corresponding to a nonuniform and unsteady state of the fluid into Eq. (13), one obtains

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}=f^{(0)}\left(\frac{1}{n}\frac{Dn}{Dt}+(\xi^2+\Omega^2-3)\frac{1}{T}\frac{DT}{Dt}+2\vec{\xi}\vec{\xi}:\vec{\nabla}\vec{c}_0\right) +f^{(0)}\vec{C}\cdot\left[\vec{\nabla}\ln(nk_BT)+(\xi^2+\Omega^2-4)\vec{\nabla}\ln T +\frac{m}{k_BT}\left(\frac{D\vec{c}_0}{Dt}-\vec{F}\right)\right], \tag{15}$$

where the dimensionless peculiar velocity $\vec{\xi}$ and the magnitude of the angular velocity $\vec{\Omega}$ of the first molecule are defined by

$$\vec{\xi}=\frac{1}{\sqrt{2}\chi(T)}\vec{C},\quad \Omega^2=\frac{1}{2k_BT}\overleftrightarrow{I}:\vec{\omega}\vec{\omega}. \tag{16}$$

IV. SOLUTION OF THE MODIFIED EQUATION

A. Second approximation to $(\partial f/\partial t)_{\text{coll}}$

An approximate form of Eq. (8) can easily be derived by Taylor-expanding Y, f, and f_1' in powers of $\vec{\rho}_\mu$, using Eqs. (3) and (9) together with the symmetry property of the operator $\hat{O}_1$, and retaining only the first derivatives. It is then given by

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}=J_1(\vec{r})+J_2(\vec{r})+J_3(\vec{r}), \tag{17}$$

where

$$J_1(\vec{r})=2\chi(T)Y(\vec{r})\hat{O}_1\int\int\int (f'f_1'-ff_1)\hat{k}\cdot\vec{g}\,d\hat{k}\,d\vec{c}_1 d\vec{\omega}_1, \tag{18}$$

$$J_2(\vec{r})=2\chi(T)Y(\vec{r})\hat{O}_2\int\int\int (f'\hat{k}\cdot\vec{\nabla}f_1'+f\hat{k}\cdot\vec{\nabla}f_1) \times\hat{k}\cdot\vec{v}\,d\hat{k}\,d\vec{c}_1 d\vec{\omega}_1, \tag{19}$$

and

$$J_3(\vec{r})=\chi(T)\vec{\nabla}Y(\vec{r})\cdot\left(\hat{O}_2\int\int\int \hat{k}(f'f_1'+ff_1) \times\hat{k}\cdot\vec{v}\,d\hat{k}\,d\vec{c}_1 d\vec{\omega}_1\right), \tag{20}$$

with

$$\hat{O}_2 w=\hat{O}_1 w(h+h_1). \tag{21}$$

The approximate form of $J_1(\vec{r})$ can be obtained by substituting Eq. (12) into Eq. (18), dropping the products $\phi^{(1)}\phi_1^{(1)}$ and $\phi'^{(1)}\phi_1'^{(1)}$ as before, and using

$$f^{(0)}f_1^{(0)}=f'^{(0)}f_1'^{(0)}. \tag{22}$$

Then one can see that

$$J_1(\vec{r})\simeq 2\chi(T)Y(\vec{r})\hat{O}_1\int\int\int \hat{k}\cdot\vec{g}\,d\hat{k}\,d\vec{c}_1 d\vec{\omega}_1 \times f^{(0)}f_1^{(0)}(\phi'^{(1)}+\phi_1'^{(1)}-\phi^{(1)}-\phi_1^{(1)}). \tag{23}$$

The expressions for $J_2(\vec{r})$ and $J_3(\vec{r})$ involve space derivatives; thus, in substituting Eq. (11) into Eqs. (19) and (20), one may drop the terms involving $\phi^{(1)}$ and $\phi_1'^{(1)}$, and replace f's by $f^{(0)}$'s. Then one finds with the help of Eq. (22) that

$$J_2(\vec{r})+J_3(\vec{r})\simeq 2\chi(T)Y(\vec{r})\hat{O}_2\int\int\int \hat{k}\cdot\vec{v}\,d\hat{k}\,d\vec{c}_1 d\vec{\omega}_1 \times f^{(0)}f_1^{(0)}\hat{k}\cdot\vec{\nabla}\ln(f_1'^{(0)}f_1^{(0)}Y). \tag{24}$$

After substituting the values of $f_1^{(0)}$ and $f_1'^{(0)}$ into $\vec{\nabla}\ln(f_1'^{(0)}f_1^{(0)}Y)$ of the above equation, we find that

$$\begin{aligned}J_2(\vec{r})+J_3(\vec{r})={}&2\chi(T)Y(\vec{r})\hat{O}_2\\&\times\int\int\int f^{(0)}f_1^{(0)}\hat{k}\cdot\vec{v}\,d\hat{k}\,d\vec{c}_1 d\vec{\omega}_1\\&\times\hat{k}\cdot\left[\vec{\nabla}\ln\left(\frac{n^2Y}{T^6}\right)+(\xi_1^2+\xi_1'^2+\Omega_1^2+\Omega_1'^2)\right.\\&\left.\times\vec{\nabla}\ln T+\frac{\sqrt{2}}{\chi}\vec{\nabla}\vec{c}_0(\vec{r},t)\cdot(\vec{\xi}_1+\vec{\xi}_1')\right],\end{aligned} \tag{25}$$

where $(\vec{\xi}',\vec{\Omega}')$ and $(\vec{\xi}_1',\vec{\Omega}_1')$ denote the precollisional dimensionless translational and angular velocities of the two molecules, such that [18,25]

$$\vec{\xi}'=\vec{\xi}+\frac{\sqrt{2}\hat{k}\hat{k}\cdot\vec{g}}{D^2},\quad \vec{\xi}_1'=\vec{\xi}_1-\frac{\sqrt{2}\hat{k}\hat{k}\cdot\vec{g}}{D^2}, \tag{26}$$

$$\vec{v}=\frac{1}{2\chi(T)}\vec{v}_{12}, \tag{27}$$

$$\vec{\Omega}_\mu=\vec{B}\cdot\vec{\omega}_\mu,\quad \vec{B}=\frac{1}{\sqrt{2k_BT}}(\sqrt{I_1}\hat{a}\hat{a}+\sqrt{I_2}\hat{b}\hat{b}+\sqrt{I_3}\hat{c}\hat{c}),$$

$$\vec{\Omega}_\mu'-\vec{\omega}_\mu=-2q_\mu\frac{\hat{k}\cdot\vec{g}}{D^2}, \tag{28}$$

and the expression for q_μ appears in Ref. [18(a)].

The $\vec{\xi}_1'$, $\xi_1'^2$, and $\Omega_1'^2$ of Eq. (25) can be expressed in terms of $\vec{\xi}_1$, ξ_1^2, Ω_1^2, $\hat{k}\cdot\vec{v}$, $\vec{q}_1$, and D^2 with the help of the approximate forms of Eqs. (26) and (28) when $\hat{k}\cdot\vec{g}$ there is approximated by $\hat{k}\cdot\vec{v}$. Integration performed with respect to $\hat{k}$ using the standard methods described in Ref. [1(a)] then give

$$\begin{aligned}J_2(\vec{r})+J_3(\vec{r})={}&\frac{4\pi}{3}\chi(T)Y(\vec{r})\hat{O}_2\\&\times\int\int f^{(0)}f_1^{(0)}d\vec{c}_1 d\vec{\omega}_1\vec{v}\cdot\vec{\nabla}\\&\times\ln\left(\frac{n^2Y}{T^6}\right)+2\xi_1^2\vec{v}-\frac{2\sqrt{2}}{5D^2}(2\vec{v}\vec{v}\cdot\vec{\xi}_1+v^2\vec{\xi}_1)\\&+\left(\frac{6v^2}{5D^4}+2\Omega_1^2\right)\vec{v}-3\left(\frac{\vec{a}_1\cdot\vec{\Omega}_1}{D^2}\right)v\vec{v}\\&+\frac{12a_1^2}{5D^4}v^2\vec{v}\cdot\vec{\nabla}\ln T+\frac{\sqrt{2}}{\chi(T)}\\&\times\left\{\left(2\vec{\xi}_1-\frac{2\sqrt{2}}{5D^2}\vec{v}\right)\vec{v}:\vec{\nabla}\vec{c}_0-\frac{\sqrt{2}v^2}{5D^4}\vec{\nabla}\cdot\vec{c}_0\right\}.\end{aligned} \tag{29}$$

It follows from Eqs. (11), (16), and (26)–(28) that

$$\vec{v}=\frac{1}{\sqrt{2}}(\vec{\xi}_1-\vec{\xi}),\quad f_1^{(0)}d\vec{c}_1 d\vec{\omega}_1=\frac{n}{\pi^3}\exp(-\xi_1^2-\Omega_1^2)d\vec{\xi}_1 d\vec{\Omega}_1. \tag{30}$$

By substituting Eq. (30) into Eq. (29), integrating with respect to $\vec{\xi}_1$ and $\vec{\Omega}_1$, and expressing a_1^2 in terms of D^2 since $D^2=1+a_1^2+a_2^2$, we get

$$\begin{aligned}J_2(\vec{r})+J_3(\vec{r})={}&-\frac{4\pi n}{3}\chi(T)Y(\vec{r})\hat{O}_2f^{(0)}\\&\times\left[\frac{1}{\sqrt{2}}\vec{\xi}\cdot\vec{\nabla}\ln(n^2YT)+\frac{\zeta_1}{\sqrt{2}}\vec{\xi}\cdot\vec{\nabla}\ln T\right.\\&\left.+\frac{1}{\chi}\left\{\zeta_2\vec{\nabla}\cdot\vec{c}_0+\frac{2}{5D^2}\vec{\xi}\vec{\xi}:\vec{\nabla}\vec{c}_0\right\}\right],\end{aligned} \tag{31}$$

where

$$\zeta_1=\frac{3\xi^2}{5D^2}-\frac{1}{2D^2}-1,\quad \zeta_2=\frac{\xi^2}{5D^2}+\frac{1}{2D^2}-1. \tag{32}$$

Now using Eqs. (23) and (31) in Eq. (17) we obtain the form for $(\partial f/\partial t)_{\rm coll}$.

B. Evaluation of $\phi^{(1)}$

The integro-differential equation satisfied by the function $\phi^{(1)}$ can be obtained by substituting the value of $(\partial f/\partial t)_{\rm coll}$ in Eq. (15) and using Eq. (9). We thus get

$$\begin{aligned}
&Y(\vec{r})\hat{O}_1\int\int\int f^{(0)}f_1^{(0)}(\phi^{(1)}+\phi_1^{(1)}-\phi'^{(1)}-\phi_1'^{(1)})\\
&\quad\times\hat{k}\cdot\vec{g}_{12}d\hat{k}\,d\vec{c}_1d\vec{\omega}_1\\
&=-f^{(0)}\left[\frac{1}{n}\frac{Dn}{Dt}+(\xi^2+\Omega^2-3)\frac{1}{T}\frac{DT}{Dt}\right]\\
&\quad-f^{(0)}\left[\sqrt{2}\chi(T)\vec{\xi}\cdot\left\{\chi^{-2}\left(\frac{D\vec{c}_0}{Dt}-\vec{F}\right)+\frac{1}{nk_BT}\vec{\nabla}p_0\right\}\right]\\
&\quad-f^{(0)}\left[\sqrt{2}\chi(T)\vec{\xi}\cdot\left\{(\xi^2+\Omega^2-4)+\frac{n}{3}Y(\vec{r})\hat{O}\zeta_1\right\}\right]\\
&\quad\times\vec{\nabla}\ln T-2\,f^{(0)}\left[\frac{n}{3}Y(\vec{r})\hat{O}\zeta_2\vec{\nabla}\cdot\vec{c}_0\right.\\
&\quad\left.+\left\{1+\frac{2n}{15}Y(\vec{r})\hat{O}\left(\frac{1}{D^2}\right)\right\}\vec{\xi}\vec{\xi}:\vec{\nabla}\vec{c}_0\right],
\end{aligned}\tag{33}$$

where

$$\hat{O}=2\pi\hat{O}_2,\quad p_0=nk_BT\left(1+\frac{n}{3}Y(\vec{r})\alpha\right)\tag{34}$$

and $\alpha=\hat{O}w$ with $w=1$.

If we multiply Eq. (33) by $\psi\,d\vec{c}\,d\vec{\omega}$, where any summational invariant ψ is not a function of $\vec{r}$, and then integrate with respect to $\vec{c}$ and $\vec{\omega}$, the left-hand side of the resulting equation vanishes by virtue of the transformation described in Ref. [1(e)]. Thus we have the result

$$\frac{Dn}{Dt}+\frac{1}{3}\left[3n+2n^2Y(\vec{r})\hat{O}\left(\frac{1}{D^2}-1\right)\right]\vec{\nabla}\cdot\vec{c}_0=0\tag{35}$$

when $\psi=1$,

$$\frac{D\vec{c}_0}{Dt}-\vec{F}+\frac{1}{\rho}\vec{\nabla}p_0+\frac{nk_BT}{3m}Y(\vec{r})\hat{O}\left(\frac{1}{D^2}-1\right)=0\tag{36}$$

when [1(f)] $\psi=m\vec{C}$, and

$$\frac{D}{Dt}\ln(nT)+\frac{1}{3}\left[\frac{n}{3}Y(\vec{r})\hat{O}\left(\frac{7}{D^2}-6\right)+4\right]\vec{\nabla}\cdot\vec{c}_0=0\tag{37}$$

when [18(a)] $\psi=1/2(mC^2+(\overleftrightarrow{I})^{-1}:\vec{L}\vec{L})$. Using Eqs. (34) and (35) in Eq. (37), we get

$$\frac{DT}{Dt}+\frac{p_0}{3nk_B}\vec{\nabla}\cdot\vec{c}_0+\frac{nT}{9}Y(\vec{r})\hat{O}\left(\frac{1}{D^2}-1\right)\vec{\nabla}\cdot\vec{c}_0=0,\tag{38}$$

where $\rho=mn$ and the angular momentum $\vec{L}=\overleftrightarrow{I}\cdot\vec{\omega}$.

Equations (35), (36), and (38) are the first approximations to the equations of continuity, linear momentum, and energy. These equations reduce to the corresponding equations [1(c),10] for a low-density fluid if the last terms of these equations are dropped together with that of p_0 in Eq. (34). On substituting the values of the mobile time derivatives of n, $\vec{c}_0$, and t from Eqs. (35)–(38) into Eq. (33), one obtains

$$\begin{aligned}
&J(\phi^{(1)})\equiv\hat{O}_1\int\int\int f^{(0)}f_1^{(0)}(\phi^{(1)}+\phi_1^{(1)}-\phi'^{(1)}-\phi_1'^{(1)})\\
&\quad\times\hat{k}\cdot\vec{g}_{12}d\hat{k}\,d\vec{c}_1d\vec{\omega}_1\\
&=-f^{(0)}Y^{-1}(\vec{r})\left[\left\{1+\frac{n}{5}Y(\vec{r})\hat{O}\left(\frac{1}{D^2}\right)\right\}\right.\\
&\quad\left.\times(\xi^2+\Omega^2-4)\right]\vec{C}\cdot\vec{\nabla}\ln T-2\,f^{(0)}Y^{-1}(\vec{r})\\
&\quad\times\left[1+\frac{2n}{15}Y(\vec{r})\hat{O}\left(\frac{1}{D^2}\right)\right]\vec{\xi}\overset{\circ}{\vec{\xi}}:\vec{\nabla}\cdot\vec{c}_0-\frac{1}{3}f^{(0)}Y^{-1}(\vec{r})\\
&\quad\times\left[\left\{1+\frac{n}{3}Y(\vec{r})\hat{O}\left(\frac{1}{D^2}\right)\right\}\right.\\
&\quad\left.\times(\xi^2-\Omega^2)\vec{\nabla}\cdot\vec{c}_0\right],
\end{aligned}\tag{39}$$

where the nondivergent tensor $\vec{\xi}\overset{\circ}{\vec{\xi}}$is defined by

$$\vec{\xi}\overset{\circ}{\vec{\xi}}=\vec{\xi}\vec{\xi}-\tfrac{1}{3}\,\overleftrightarrow{U},\tag{40}$$

with $\overleftrightarrow{U}$ a unit tensor of rank 2.

The counterpart of Eq. (39) for the low-density fluid, as given in Ref. [1(c)], can be written as

$$\begin{aligned}
J(\phi^{(1)})=-f^{(0)}&\left[(\xi^2+\Omega^2-4)\vec{C}\cdot\vec{\nabla}\ln T\right.\\
&\left.+2\vec{\xi}\overset{\circ}{\vec{\xi}}:\vec{\nabla}\cdot\vec{c}_0+\frac{1}{3}(\xi^2-\Omega^2)\vec{\nabla}\cdot\vec{c}_0\right],
\end{aligned}\tag{41}$$

whose solution has the form

$$\phi^{(1)}=-(\vec{A}_1+\vec{A}_2)\vec{\nabla}\ln T-2(\overleftrightarrow{B}:\vec{\nabla}\vec{c}_0+B\vec{\nabla}\cdot\vec{c}_0).\tag{42}$$

Here $\vec{A}_1$ and $\vec{A}_2$ correspond to the solutions of $(\xi^2-5/2)\vec{C}$ and $(\Omega^2-3/2)\vec{C}$ of Eq. (41) and their approximate forms as well as those of $\overleftrightarrow{B}$ and B are given in Ref. [1(c)].

The solution of Eq. (39) can at once be given in terms of $\vec{A}_1$, $\vec{A}_2$, $\overleftrightarrow{B}$, and B by just looking at the solution given in Eq. (42) and by comparing the terms containing $\vec{\nabla}\ln T$, $\vec{\nabla}\vec{c}_0$, and $\vec{\nabla}\cdot\vec{c}_0$ in Eqs. (39) and (41). This yields the solution of Eq. (39) as

$$\begin{aligned}
\phi^{(1)}=-Y^{-1}&\left[\left\{1+\frac{nY}{5}\hat{O}\left(\frac{1}{D^2}\right)\right\}\vec{A}_1+\vec{A}_2\right]\cdot\vec{\nabla}\ln T-2Y^{-1}\\
&\times\left[\left\{1+\frac{2nY}{15}\vec{O}\left(\frac{1}{D^2}\right)\right\}\overleftrightarrow{B}:\vec{\nabla}\vec{c}_0\right.\\
&\left.+\left\{1+\frac{nY}{3}\hat{O}\left(\frac{1}{D^2}\right)\right\}B\vec{\nabla}\cdot\vec{c}_0\right].
\end{aligned}\tag{43}$$

V. PRESSURE TENSOR AND THERMAL-FLUX VECTOR

The pressure tensor $\overleftrightarrow{P}^{(0)}$ and thermal-flux vector $\vec{q}^{(0)}$ of a pure low-density hard biaxial fluid are due only to the free motions of the molecules between collisions and their values correct up to the second approximation are given by [1(c)]

$$\overleftrightarrow{P}^{(0)}=\rho\overline{(\vec{C}\vec{C})^{(0)}}=nk_BT\overleftrightarrow{U}-2[\eta]_1\overset{\circ}{\overleftrightarrow{e}}-[\kappa]_1\overleftrightarrow{U}\vec{\nabla}\cdot\vec{c}_0 \tag{44}$$

and

$$\vec{q}^{(0)}=\frac{1}{2}[\rho\overline{(C^2\vec{C})^{(0)}}+n(\overleftrightarrow{I})^{-1}:\overline{\vec{L}\vec{L}}=-[\lambda]_1\vec{\nabla}T]. \tag{45}$$

Here

$$\overline{(\cdots)}\equiv\frac{1}{n}\int\int f^{(0)}(1+\phi^{(1)})(\cdots)d\vec{c}\,d\vec{\omega} \tag{46}$$

and $\overset{\circ}{\overleftrightarrow{e}}$ $(\equiv\overset{\circ}{\overline{\overline{\vec{\nabla}\vec{c}_0}}}$ is the rate-of-shear tensor. Also, $[\eta]_1$, $[\kappa]_1$, and $[\lambda]_1$ are the first approximate values of the shear and bulk viscosities and the thermal conductivity of the fluid. The expressions for these quantities have been derived in Ref. [18(a)], and specifically

$$\begin{aligned}[\lambda]_1&=\frac{k_B^2T}{2m}(5a_1+3a_2)\\&=\frac{3k_B^2T}{8m\Delta}[25a_{22}-10(N-3)a_{12}+(N-3)^2a_{11}],\end{aligned} \tag{47}$$

where the dynamically active degrees of freedom N in our problem are 6, and a_1 and a_2 are suitable constants of the equation

$$n(\vec{A}_1+\vec{A}_2)=a_1\left(\xi^2-\frac{5}{2}\right)\vec{C}+a_2\left(\Omega^2-\frac{3}{2}\right)\vec{C}. \tag{48}$$

The right side of the above equation contains the first approximations to $\vec{A}_1$ and $\vec{A}_2$, and the values of a_1 and a_2 turn out to be

$$a_1=\frac{3}{4\Delta}(5a_{22}-3a_{12}),\quad a_2=\frac{3}{4\Delta}(3a_{11}-5a_{12}), \tag{49}$$

with

$$\Delta=a_{11}a_{22}-a_{12}^2. \tag{50}$$

Recently, the collision integrals a_{11}, a_{12}, and a_{22} and thereby the quantity $[\lambda]_1$ have been evaluated by us [18(a)].

Now the kinetic contributions $\overleftrightarrow{P}_K$ and $\vec{q}_K$ to the pressure tensor $\overleftrightarrow{P}$ and heat-flux vector $\vec{q}$ of the dense fluid can be readily obtained from Eqs. (42)–(50). We thus get

$$\begin{aligned}\overleftrightarrow{P}_K=\rho\overline{(\vec{C}\vec{C})}=&\left[nk_BT-Y^{-1}\left\{1+\frac{nY}{3}\hat{O}\left(\frac{1}{D^2}\right)\right\}[\kappa]_1\vec{\nabla}\cdot\vec{c}_0\right]\\&\times\overleftrightarrow{U}-2Y^{-1}\left\{1+\frac{2nY}{15}\hat{O}\left(\frac{1}{D^2}\right)\right\}[\eta]_1\overset{\circ}{\overleftrightarrow{e}},\end{aligned} \tag{51}$$

$$\begin{aligned}\vec{q}_K&=\frac{1}{2}\rho\overline{(C^2\vec{C})}\\&=-\frac{k_B^2T}{2m}\left[5Y^{-1}\left\{1+\frac{nY}{5}\hat{O}\left(\frac{1}{D^2}\right)\right\}a_1+3Y^{-1}a_2\right]\vec{\nabla}T\\&=-\left[Y^{-1}[\lambda]_1+\frac{3nk_B^2T}{8m\Delta}\hat{O}\left(\frac{1}{D^2}\right)(5a_{22}-3a_{12})\right]\vec{\nabla}T.\end{aligned} \tag{52}$$

The quantities $\overleftrightarrow{P}_K$ and $\vec{q}_K$ are the parts of $\overleftrightarrow{P}$ and $\vec{q}$ that arise from the transport of linear momentum and energy by the motion of the molecules from one point to another. To these should be added the contributions arising from the transport of the momentum and energy by molecular collisions. These evaluations will be done up to the second approximation in subsequent sections.

VI. COLLISIONAL TRANSFER FLUX VECTOR

Let us consider the mechanism of transfer of a summational invariant ψ across an element of area dS at the point $\vec{r}_c$ (Fig. 1). A collision between the molecules on the opposite sides of dS transfers instantaneously only a part of ψ from one molecule to the other, such that a flow of ψ occurs, although neither of the molecules crosses through dS. As before, it is presumed that ψ is not a function of $\vec{r}_c$.

In a collision between the molecules, the first molecule with velocities $(\vec{c},\vec{\omega})$ lies on the positive side of dS, the second one with velocities $(\vec{c}_1,\vec{\omega}_1)$ on the negative side, and the unit vector $\hat{n}$ is the outward normal drawn on dS from the negative to the positive side. Since $\hat{k}$ is the unit vector at the point of contact P in the direction of motion of the second molecule, $\hat{k}\cdot\hat{n}$ is positive. If O (Fig. 1) lies in a cylinder of area element dS and length $\hat{k}\cdot\overrightarrow{OO_1}$ with generators parallel to $\hat{k}$, the volume of the cylinder is $(\hat{k}\cdot\hat{n})(\hat{k}\cdot\overrightarrow{OO_1})dS$. If O_1 of another molecule lies within this cylinder, a collision will occur. The positions of O and O_1 are $\vec{r}_c-\vec{\rho}(-\hat{k})$ and $\vec{r}_c-\vec{\rho}_1(\hat{k})$ while $\vec{r}_c$ gives the position of impact of the two molecules. Then by analogy with Eq. (4), the probable number of such collisions per unit time in which $(\vec{c},\vec{\omega})$, $(\vec{c}_1,\vec{\omega}_1)$, and $\hat{k}$ lie, respectively, in the ranges $(d\vec{c},d\vec{\omega})$, $(d\vec{c}_1,d\vec{\omega}_1)$, and $d\hat{k}$ is given by

$$\begin{aligned}&Y(\vec{r}_c)f(\vec{r}_c-\vec{\rho}(-\hat{k}))f_1(\vec{r}_c-\vec{\rho}_1(\hat{k}))(\hat{k}\cdot\hat{n})\\&\quad\times\hat{k}\cdot\overrightarrow{OO_1}\,dS\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}\times\hat{k}\cdot\vec{g}_{12}d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1d\vec{\omega}_1.\end{aligned}$$

In each such collision, a molecule on the positive side gains a quantity $\psi'-\psi$ of ψ from the molecule on the negative side, where ψ' is the precollisional value of ψ. Hence the total rate of transfer of ψ across dS by collision per unit area per unit time is

$$\hat{n}\cdot\vec{\psi}_{\mathrm{CT}}\equiv Y(\vec{r}_c)\hat{O}_1\int\int\int\int\int(\psi'-\psi)f(\vec{r}_c-\vec{\rho}(-\hat{k}))\times f_1(\vec{r}_c-\vec{\rho}_1(\hat{k}))\times\hat{k}\cdot\hat{n}(\hat{k}\cdot\overrightarrow{OO_1})\hat{k}\cdot\vec{g}_{12}\times d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1. \tag{53}$$

Here, integrations are over all values of the variables such that $\hat{k}\cdot\vec{g}$ and $\hat{k}\cdot\hat{n}$ are positive; and $\vec{\psi}_{\mathrm{CT}}$ may be defined as the collisional vector of flow of ψ.

The restriction on $\hat{k}\cdot\hat{n}$ is inconvenient and may be bypassed as follows. Let us change the variables $(\vec{c},\vec{\omega})$ in Eq. (53) to $(\vec{c}_1,\vec{\omega}_1)$. This is equivalent to exchanging the roles of the colliding molecules. Thus $\hat{k}$, $\vec{g}$, and $\psi'-\psi$ are changed, respectively, to $-\hat{k}$, $-\vec{g}$, and $\psi_1'-\psi_1=-(\psi'-\psi)$. With this interchange, $\hat{n}\cdot\vec{\psi}_{\mathrm{CT}}$ remains invariant but the integrations are now to be carried out over all the variables such that $\hat{k}\cdot\vec{g}_{12}$ is again positive but $\hat{k}\cdot\hat{n}$ is negative. It is then straightforward to show that

$$\hat{n}\cdot\vec{\psi}_{\mathrm{CT}}=\frac{1}{2}Y(\vec{r}_c)\hat{O}_1\int\int\int\int\int(\psi'-\psi)f_1(\vec{r}_c-\vec{\rho}(\hat{k}))\times f(\vec{r}_c-\vec{\rho}(-\hat{k}))\times\hat{k}\cdot\hat{n}(\hat{k}\cdot\overrightarrow{OO_1})\hat{k}\cdot\vec{g}_{12}d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1, \tag{54}$$

where the integrations are over all values of the variables such that $\hat{k}\cdot\vec{g}$ is positive.

As in Sec. IV, if we do the Taylor expansions of f and f_1, use the definitions of $\vec{g}_{12}$ and $\vec{\rho}_\mu$ from Eqs. (2) and (3), and retain only the first derivatives, we find that

$$\vec{\psi}_{\mathrm{CT}}=\frac{1}{2}Y(\vec{r}_c)\hat{O}_2\int\int\int\int\int(\psi'-\psi)ff_1\hat{k}(\hat{k}\cdot\vec{v}_{12})\times d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1+\frac{1}{2}Y(\vec{r}_c)\hat{O}_3\int\int\int\int\int(\psi'-\psi)f^{(0)}f_1^{(0)}\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)\hat{k}(\hat{k}\cdot\vec{v}_{12})d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1, \tag{55}$$

where

$$\hat{O}_3=\hat{O}_2(h)=\hat{O}_1(h+h_1)h. \tag{56}$$

VII. TRANSPORT COEFFICIENTS OF THE DENSE FLUID

A. Viscosities

The collisional transfer contribution $\overleftrightarrow{P}_{\mathrm{CT}}$ to the pressure tensor $\overleftrightarrow{P}$ may be derived from Eq. (55) by setting $\psi=m\vec{C}=m(\vec{c}-\vec{c}_0)$, where $\vec{c}_0$ is evaluated at the point $\vec{r}_c$ and does not vary with the position of the molecule. Then Eq. (55) becomes

$$\overleftrightarrow{P}_{\mathrm{CT}}=\frac{m}{2}Y(\vec{r}_c)\hat{O}_2\int\int\int\int\int(\vec{C}'-\vec{C})ff_1\hat{k}(\hat{k}\cdot\vec{v}_{12})\times d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1+\frac{m}{2}Y(\vec{r}_c)\hat{O}_3\int\int\int\int\int(\vec{C}'-\vec{C})f^{(0)}f_1^{(0)}\vec{\nabla}\times\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)\hat{k}(\hat{k}\cdot\vec{v}_{12})d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1, \tag{57}$$

The approximate form of $\vec{C}'-\vec{C}$ from Eqs. (9), (16), and (26) is

$$\vec{C}'-\vec{C}=\hat{k}(\hat{k}\cdot\vec{v}_{12})/D^2, \tag{58}$$

where $\hat{k}\cdot\vec{g}_{12}$ is approximated, as before to $\hat{k}\cdot\vec{v}_{12}$. By substituting Eq. (58) into Eq. (57) and then executing the $\hat{k}$ integrations by the standard technique [1(a)], one obtains

$$\overleftrightarrow{P}_{\mathrm{CT}}=\frac{\pi m}{15}Y(\vec{r}_c)\hat{O}_2\left(\frac{1}{D^2}\right)\int\int\int\int ff_1(2\vec{v}_{12}\vec{v}_{12}+v_{12}^2\overleftrightarrow{U})\times d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1+\frac{\pi m}{24}Y(\vec{r}_c)\hat{O}_3\times\left(\frac{1}{D^2}\right)\int\int\int\int f^{(0)}f_1^{(0)}d\vec{c}\,d\vec{\omega}\,d\vec{c}_1 d\vec{\omega}_1 v_{12}\times\left[\left\{\vec{v}_{12}\cdot\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)\right\}(\hat{v}_{12}\hat{v}_{12}+\overleftrightarrow{U})+\left\{\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)\right\}\vec{v}_{12}+\vec{v}_{12}\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)\right]. \tag{59}$$

Since the average value $\overline{\phi}$ of any function ϕ is defined by

$$n\overline{\phi}=\int\int f\phi\,d\vec{c}\,d\vec{\omega}=\int\int f_1\phi_1 d\vec{c}_1 d\vec{\omega}_1,$$

$\vec{v}_{12}=\vec{C}_1-\vec{C}$, and $\overline{\vec{C}_1}=\overline{\vec{C}}=0$, the value of the first term on the right-hand side of Eq. (59) becomes

$$\frac{2\pi mn^2}{15}Y(\vec{r}_c)\hat{O}_2\left(\frac{1}{D^2}\right)(2\overline{\vec{C}\vec{C}}+\overline{C^2}\overleftrightarrow{U}). \tag{60}$$

Further, one can see from Eq. (11) that

$$\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)=\frac{1}{2k_BT^2}[m(C^2-C_1^2)+\overleftrightarrow{I}:(\vec{\omega}\vec{\omega}-\vec{\omega}_1\vec{\omega}_1)]\vec{\nabla}T+\frac{m}{k_BT}\vec{\nabla}\vec{c}_0\cdot(\vec{C}-\vec{C}_1). \tag{61}$$

If Eq. (61) is substituted into the second integral of Eq. (59), the terms involving $\vec{\nabla}T$ identically vanish because each of these is an odd function of $\vec{C}$ or $\vec{C}_1$, and the second integral term of Eq. (59) becomes

$$-\frac{\pi m^2}{24k_BT}Y(\vec{r}_c)\hat{O}_3\left(\frac{1}{D^2}\right)\int\int\int\int f^{(0)}f_1^{(0)}d\vec{c}\,d\vec{\omega}\,d\vec{c}_1d\vec{\omega}_1$$
$$\times v_{12}[(\vec{\nabla}\vec{c}_0:\vec{v}_{12}\vec{v}_{12})(\hat{v}_{12}\hat{v}_{12}+\overleftrightarrow{U})+\{(\vec{\nabla}\vec{c}_0\cdot\vec{v}_{12})\vec{v}_{12}$$
$$+\vec{v}_{12}(\vec{\nabla}\vec{c}_0\cdot\vec{v}_{12})\}]. \tag{62}$$

The integrals of the above equation can readily be performed by changing the variables $\vec{c}$ and $\vec{c}_1$ to $\vec{G}_0$ and $\vec{v}_{12}$, where $\vec{G}_0=(\vec{C}+\vec{C}_1)/2$, and then Eq. (62) becomes

$$-\varpi_D\left[\frac{6}{5}\overset{\circ}{\overleftrightarrow{e}}+\overleftrightarrow{U}\overleftrightarrow{U}:\vec{\nabla}\vec{c}_0\right], \tag{63}$$

where

$$\varpi_D=\frac{8n^2}{9}(\pi mk_BT)^{1/2}Y(\vec{r}_c)\hat{O}_3\left(\frac{1}{D^2}\right). \tag{64}$$

The expression for $\overleftrightarrow{P}_{\mathrm{CT}}$ of Eq. (59) can be obtained by adding the contributions from Eqs. (60) and (63), and, if one adds to this sum the expression for $\overleftrightarrow{P}_K$ from Eq. (51), one gets the final expression for $\overleftrightarrow{P}$, which arises from the collisional transport of linear momentum as well as the transport of molecular motions. It is

$$\overleftrightarrow{P}=\overleftrightarrow{P}_K+\overleftrightarrow{P}_{\mathrm{CT}}$$
$$=\rho\left[1+\frac{4\pi n}{15}Y(\vec{r}_c)\hat{O}_2\left(\frac{1}{D^2}\right)\right]\overline{\vec{C}\vec{C}}$$
$$+\frac{2\pi\rho n}{15}Y(\vec{r}_c)\hat{O}_2\left(\frac{1}{D^2}\right)\overline{C^2}\overleftrightarrow{U}-\varpi_D[\tfrac{6}{5}\overset{\circ}{\overleftrightarrow{e}}+\overleftrightarrow{U}\overleftrightarrow{U}:\vec{\nabla}\vec{c}_0]. \tag{65}$$

On substituting in the above equation the values of $\overline{\rho\vec{C}\vec{C}}$ from Eq. (51), that of $\hat{O}$ from Eq. (34), and using the kinetic theory definition [1(g)] of temperature, it takes the form

$$\overleftrightarrow{P}=\Bigg(P_0-\Bigg\{\varpi_D+Y^{-1}\left[1+\frac{2n}{15}Y\hat{O}\left(\frac{1}{D^2}\right)\right]$$
$$\times\left[1+\frac{n}{3}Y\hat{O}\left(\frac{1}{D^2}\right)\right][\kappa]_1\Bigg\}\vec{\nabla}\cdot\vec{c}_0\Bigg)$$
$$\times\overleftrightarrow{U}-\left\{\frac{6}{5}\varpi_D+2Y^{-1}\left[1+\frac{2n}{15}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]^2[\eta]_1\right\}\overset{\circ}{\overleftrightarrow{e}}. \tag{66}$$

If the fluid is in a uniform and steady state, $\vec{\nabla}\cdot\vec{c}_0$ and $\overset{\circ}{\overleftrightarrow{e}}$ are zero and $\overleftrightarrow{P}$ reduces to the hydrostatic pressure P_0. For a fluid not in a uniform steady state, the hydrostatic pressure becomes

$$P_0-\varpi'\vec{\nabla}\cdot\vec{c}_0, \tag{67}$$

where

$$P_0=nk_8T\left[1+\frac{n}{3}Y(\vec{Y}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]$$

and

$$\varpi'=\varpi_D+Y^{-1}\left[1+\frac{2n}{15}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]$$
$$\times\left[1+\frac{n}{3}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right][\kappa]_1. \tag{68}$$

It follows from Eq. (35) that the extra term, i.e., $-\varpi'\vec{\nabla}\cdot\vec{c}_0$, of Eq. (67) differs from zero whenever the density of the fluid is varying; it represents a volume viscosity similar to that [1(c)] of a dilute fluid, and opposes expansion or contraction of the dense fluid. The deviation of $\overleftrightarrow{P}$ from its hydrostatic part is shown in the last two terms of Eq. (66) and can be equated to $-2\eta'\overset{\circ}{\overleftrightarrow{e}}$, where η' is the shear viscosity of the fluid. Thus

$$\eta'=Y^{-1}\left[1+\frac{2n}{15}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]^2[\eta]_1+\frac{3}{5}\varpi_D. \tag{69}$$

B. Thermal conductivity

The collisional transfer part $\vec{q}_{\mathrm{CT}}$ of the heat-flow vector $\vec{q}$ may be obtained by taking $\psi=(mC^2+\overleftrightarrow{I}:\vec{\omega}\vec{\omega})/2$, where $\vec{C}$ is still the velocity of a molecule relative to the mass velocity $\vec{c}_0$ of the fluid at the specific point $\vec{r}_c$. Then we have from Eq. (55)

$$\vec{q}_{\mathrm{CT}}=\vec{q}_{\mathrm{CT1}}+\vec{q}_{\mathrm{CT2}} \tag{70}$$

with

$$\vec{q}_{\mathrm{CT1}}=\frac{m}{4}Y(\vec{r}_c)\int\int\int\int\int d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1\,d\vec{\omega}_1\,\hat{O}_2$$
$$\times\{\vec{Q}ff_1(C'^2-C^2)\}$$
$$+\hat{O}_3\left\{\vec{Q}f^{(0)}f_1^{(0)}\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)(C'^2-C^2)\right\} \tag{71}$$

and

$$\vec{q}_{\mathrm{CT2}}=\frac{1}{4}Y(\vec{r}_c)\int\int\int\int\int d\hat{k}\,d\vec{c}\,d\vec{\omega}\,d\vec{c}_1\,d\vec{\omega}_1\hat{O}_2$$
$$\times\{\vec{Q}ff_1\overleftrightarrow{I}:(\vec{\omega}'\vec{\omega}'-\vec{\omega}\vec{\omega})\}$$
$$+\hat{O}_3\left\{\vec{Q}f^{(0)}f_1^{(0)}\vec{\nabla}\ln\left(\frac{f^{(0)}}{f_1^{(0)}}\right)\overleftrightarrow{I}:(\vec{\omega}'\vec{\omega}'-\vec{\omega}\vec{\omega})\right\}, \tag{72}$$

where $\vec{Q}=\hat{k}(\hat{k}\cdot\vec{v}_{12})$.

The integrations in $\vec{q}_{\mathrm{CT1}}$ can be performed in the same way as those in Sec. VII A, and the integrals in $\vec{q}_{\mathrm{CT2}}$ can be similarly executed by utilizing Eq. (28). On carrying out the integrations, $\vec{q}_{\mathrm{CT2}}$ turns out to be zero and so

$$\vec{q}_{\mathrm{CT}}=\vec{q}_{\mathrm{CT1}}=\frac{mn^2}{10}Y(\vec{\gamma}_c)\,\hat{O}\left(\frac{1}{D^2}\right)\overline{C^2\vec{C}}-\varpi_D(c_v)_{\mathrm{tr}}\vec{\nabla}T, \tag{73}$$

where the specific heat $(c_v)_{\mathrm{tr}}$ per unit mass due to the translational motion is $3k_B/2m$. To this $\vec{q}_{\mathrm{CT}}$ we must add $\vec{q}_K$ of

Eq. (52), which gives the rate of transport of molecular motions, and the total thermal-flux vector $\vec{q}$ is given by

$$\begin{aligned}\vec{q}=&\frac{\rho}{2}\left[1+\frac{n}{5}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]\overline{C^2\vec{C}}-\varpi_D(c_v)_{\rm tr}\vec{\nabla}T\\&-\left(\frac{k_B^2T}{2m}Y^{-1}\left[1+\frac{n}{5}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]\right.\\&\left.\times\left\{5\left[1+\frac{n}{5}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]a_1+3a_2\right\}\right)\\&\times\vec{\nabla}T-\varpi_D(c_v)_{\rm tr}\vec{\nabla}T\\\equiv&-[\lambda']_1\vec{\nabla}T.\end{aligned}\tag{74}$$

Thus at any temperature the first approximation $[\lambda']_1$ to the thermal conductivity λ' of the dense fluid is given in terms of that at ordinary densities $[\lambda]_1$ by the equation

$$\begin{aligned}[\lambda']_1=&\frac{k_B^2T}{2m}Y^{-1}\left[1+\frac{n}{5}Y(\vec{c}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]\\&\times\left\{5\left[1+\frac{n}{5}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]a_1+3a_2\right\}+\varpi_D(c_v)_{\rm tr}\\=&\left[1+\frac{n}{5}Y(\vec{r}_c)\hat{O}\left(\frac{1}{D^2}\right)\right]\left\{Y^{-1}[\lambda]_1+\frac{3nk_B^2T}{8m\Delta}\hat{O}\left(\frac{1}{D^2}\right)\right.\\&\left.\times(5a_{22}-3a_{12})\right\}+\varpi_D(c_v)_{\rm tr}.\end{aligned}\tag{75}$$

In Ref. [18(a)], the expressions for $[\eta]_1$ and $[\lambda]_1$ are given in terms of various collisional integrals over the four orientational coordinates of a pair of interacting hard biaxial molecules, and the numerical procedure for their evaluation is also given. Two extra collisional integrals $\hat{O}_3(1/D^2)$ and $\hat{O}(1/D^2)$ that appear in Eqs. (64), (69), and (75) are of the same type [see Eqs. (7), (34), and (56)] and can be similarly executed. An approximate formula for the contact pair distribution function $Y(\vec{r}_c)$ has been proposed by Song and Mason [26]. Therefore, ϖ', η' and $[\lambda']_1$ of Eqs. (68), (69) and (75) can be estimated numerically.

VIII. TRENDS AND LIMITING BEHAVIOR

The results in Eqs. (34) and (67) give, respectively, the values for the hydrostatic pressure p_0 of a dense hard biaxial fluid that is in a uniform steady state and the pressure $P_0-\overline{\omega'}\vec{\nabla}\cdot\vec{c}_0$ if the fluid is not in uniform steady state. First approximations η', ϖ', and $[\lambda']_1$ to the shear viscosity, bulk viscosity, and heat conductivity of the fluid are given, respectively, by Eqs. (69), (68), and (75).

For a pure fluid of hard spheres of diameter σ, we have $D=1$, $\langle s_{\rm ex}\rangle_\alpha=\sigma^2$, $\hat{O}(1)=2\pi\sigma^3$, $\hat{O}_3(1)=\sigma^4/4$, and the contact pair distribution function $Y(\vec{r}_c)=Y(\sigma)$. Hence for a pure and dense HS fluid P_0 reduces to the correct result $nk_BT[1+(2\pi/3)n\sigma^3Y(\sigma)]$, and $P_0-\varpi'\vec{\nabla}\cdot\vec{c}_0$ of Eq. (67) to the Enskog result [1(a),27]

$$nk_BT\left(1+\frac{2\pi}{3}n\sigma^3Y(\sigma)\right)-\frac{4}{9}(\pi mk_BT)^{1/2}n^2\sigma^4Y(\sigma)\vec{\nabla}\cdot\vec{c}_0.\tag{76}$$

Also, η' of Eq. (69) reduces to the corresponding Enskog HS result

$$\begin{aligned}\left(\frac{mk_BT}{\pi}\right)^{1/2}&\left[\frac{5}{16\sigma^2}Y^{-1}(\sigma)\left(1+\frac{4\pi n\sigma^3}{15}Y(\sigma)\right)^2\right.\\&\left.+\frac{4\pi}{15}n^2\sigma^4Y(\sigma)\right]\end{aligned}\tag{77}$$

because the value of $[\eta]_1$ given elsewhere [see Eqs. (53), (54), (59), and (62) of Ref. [18(a)]] becomes $(5/16\sigma^2)\sqrt{mk_BT/\pi}$. However, in the appropriate limit of a dense model fluid of uniaxial ellipsoids, this η' formula does not reduce completely to the corresponding formula [28] derived through the TCF method as given in Eq. (33) of Ref. [16(f)]. The first term of Eq. (69) does and the second one does not reduce, respectively, to the second and first terms of Ref. [16(f)]. We think that this difference between the shear viscosity formulas for the fluid derived through the TCF and our Enskog-type theory is the result of treating the collisional transfer effect differently in the two theories. This sort of discrepancy has also been seen in the viscosity results for a dense HS fluid derived through the Enskog [1(a)] and TCF [5(a)] techniques.

Discussion of the limiting behavior of $[\lambda']_1$ of Eq. (75) is interesting and requires some care. Chapman and Cowling [1] ignored the rotational kinetic energy of the molecule throughout their study of the kinetic theory of HS fluids and, therefore, in their work $N=3$, which takes into account only the translational motion of the molecules. For this case the first equation of (75) becomes

$$\frac{5k_B^2T}{2m}Y^{-1}(\sigma)\left(1+\frac{2\pi n\sigma^3}{5}Y(\sigma)\right)^2a_1+\varpi_D^{\rm (HS)}(c_v)_{\rm tr},\tag{78}$$

because it follows from Eq. (48) that a_2 does not figure in Eq. (75) for $N=3$ and from Eq. (76) $\varpi_D^{\rm (HS)}$ is equal to $(4/9)\sqrt{\pi mk_BT}n^2\sigma^4Y(\sigma)$. It can also be seen from Eqs. (53), (54), and (64)–(66) of Ref. [18(a)] that for a HS $a_{11}=8\sigma^2\sqrt{\pi k_BT/m}$, $a_{12}=0$, and $a_{22}=6\sigma^2\sqrt{\pi k_BT/m}$. Thus from Eqs. (49) and (50) $a_1=(15/32\sigma^2)\sqrt{m/\pi k_BT}$ and Eq. (78) reduces to the Enskog HS result

$$\frac{75k_B}{64\sigma^2}\left(\frac{k_BT}{\pi m}\right)^{1/2}Y^{-1}(\sigma)\left(1+\frac{2\pi n\sigma^3}{5}Y(\sigma)\right)^2+\varpi_D^{\rm (HS)}(c_v)_{\rm tr}.\tag{79}$$

However, for $N=6$, $[\lambda]_1$ of Eq. (47) is equal to $(3k_B^2T/8m)(25/a_{11}+9/a_{22})$ and finally reduces to $(111k_B/64\sigma^2)\sqrt{k_BT/\pi m}$ when the HS values of a_{11}, a_{12}, and a_{22} are utilized. With this HS value of $[\lambda]_1$, the second equation of (75) for $N=6$ becomes

TABLE I. Values of the shear viscosity for uniaxial (prolate) ellipsoidal fluids. KT, kinetic theory (calculations from our theory); MD, molecular dynamics (simulations by Allen *et al.* [16(f)]); TCF, time correlation function (theory of Allen *et al.* and calculations in Ref. [16(f)]). ‘‘Ours’’ implies calculations in this work using expressions as mentioned in the text.

c/a	n/n_{CP}	η' (KT) Ours	η_0' (MD) Ref. [18(f)]	η_0' (TCF) Ref. [18(f)]	η_0' Ours	$\eta_\infty^{\mathrm{sym}}$ (TCB) Ref. [18(f)]	$\eta_\infty^{\mathrm{sym}}$ Ours	C_1 Ours
2	0.3	0.3162	0.372(5)	0.3621	0.3534	0.1745	0.1657	0.1286
2	0.5	0.9204	1.15(6)	1.1431	1.1004	0.8456	0.8031	0.6231
2	0.7	3.1290	6.2(4)	4.0125	3.8433	3.3554	3.1865	2.4722
3	0.3	0.2833	0.40(1)	0.3885	0.3697	0.2341	0.2154	0.1290
3	0.5	0.8648	1.24(6)	1.3719	1.2815	1.1290	1.0387	0.6220
3	0.6	1.5672	2.7(3)	2.5664	2.3883	2.2247	2.0468	1.2257
5	0.2	0.1637	0.26(1)	0.2646	0.2393	0.1595	0.1341	0.0586
5	0.3	0.2963	0.47(3)	0.5915	0.5174	0.4665	0.3925	0.1714
5	0.4	0.5575	1.02(9)	1.2406	1.0691	1.0797	0.9083	0.3967
10	0.2	0.1957	0.8(1)	0.7019	0.4571	0.6294	0.3847	0.1232

$$\left(\frac{k_B^3 T}{\pi m}\right)^{1/2}\left(1+\frac{2\pi n\sigma^3}{5}Y(\sigma)\right)\left(\frac{111}{64\sigma^2}Y^{-1}(\sigma)+\frac{15\pi n\sigma}{32}\right)$$
$$+\varpi_D^{(\mathrm{HS})}(c_v)_{\mathrm{tr}}. \tag{80}$$

For a low-density HS fluid, one can drop those terms from Eqs. (79) and (80) that depend on n and take $Y(\sigma)$ to be unity, and then the equations reduce to the Eucken and modified Eucken formulas [1(c),18(a)] correct up to the first approximation. This reduction suggests that Eqs. (79) and (80) can be called the first-order Eucken and modified Eucken formulas for a dense HS fluid. In a separate communication, we shall redo the Chapman-Enskog transport theories of dilute as well as dense HS fluids by including the rotational energies of the molecules and directly derive the first-order modified Eucken formulas for dilute and dense fluids.

Equations (35)–(38) of continuity, linear momentum, and energy reduce to the corresponding equations of HS fluids with $N=6$ and $D=1$.

IX. NUMERICAL RESULTS AND DISCUSSION

We have computed the zero-frequency shear viscosity for fluids consisting of hard prolate spheroids taking $m=k_BT=1$ and expressing lengths in terms of l, where $l^3=8a^2c$ with a and c the semiminor and semimajor axes of a prolate molecule of mass m. In l units, we have $a=(1/2)(1+\epsilon_c)^{-1/6}$ and $c=(1/2)(1+\epsilon_c)^{1/3}$, where $\epsilon_c=(c/a)^2-1$ is the anisotropy parameter. Also, the close-packed density $n_{\mathrm{CP}}=1/(4\sqrt{2}a^2c)$ is now $\sqrt{2}$.

The values of η' obtained using Eq. (A8), which is an explicit and computationally convenient version of Eq. (69) obtained from our kinetic theory (KT), are presented in Table I for the axial ratios $c/a=2$, 3, 5, and 10 at various density ratios n/n_{CP}. The corresponding results obtained by Allen *et al.* [16(f)] using molecular dynamics (MD) simulations as well as TCF calculations are also shown for comparison. Our values of η' are consistently lower than those from the MD results of Allen *et al.* [16(f)]. The TCF results from Ref. [16(f)] are lower or higher than the corresponding MD values without any definite trend, but are in better agreement with the MD than with our results for η'. In order to analyze this irregular behavior, we have obtained in the Appendix [Eq. (A18)] a computationally convenient expression for Eq. (33) of Ref. [16(f)] and calculated the corresponding values shown as η_0' (ours) in Table I.

It can be seen from Eqs. (A8) and (A18) that both η' and η_0' consist of two parts, the first part having the same expression. However, the second parts, i.e., C_1 and $\eta_\infty^{\mathrm{sym}}$, of these two equations are different. The values of η_0' calculated by us are consistently lower than the TCF values of Ref. [16(f)] but the irregular behavior described above gets slightly smoothed out. The possible reasons for the difference between KT and TCF results have been expounded in the previous section, but it seems puzzling that the values of $\eta_\infty^{\mathrm{sym}}$ calculated by us using Eq. (A17) in conjunction with Eq. (A16) are at variance with those reported by Allen *et al.* although we have used their expression for $\eta_\infty^{\mathrm{sym}}$, albeit rewritten in an explicit form. One sees from Table I that for a given c/a and n/n_{CP} the numerical value for $(\eta'-C_1)$ is the same as that for $(\eta_0'-\eta_\infty^{\mathrm{sym}})$ calculated using TCF and reported in Ref. [16(f)] or calculated by us using Eqs. (A16) and (A17). Hence the disagreement between the values of the shear viscosity calculated by us and those reported in Ref. [16(f)] is solely due to the difference in the expressions for C_1 and $\eta_\infty^{\mathrm{sym}}$.

Formula (68) for the volume viscosity ϖ' of a dense fluid of hard biaxial ellipsoidal molecules is the sum of two terms: the first is the viscosity term arising due to the collisional transfer and the second is entirely due to fast exchange of energy between the rotational and translational motions. This exchange is very slow for nearly smooth molecules and, therefore, ϖ' will not contain the second term and there will be two different temperatures [1(c),3] characterizing the rotational and translational energies. The first-order expressions for the shear viscosity and heat conductivity of a dense fluid of nearly smooth hard biaxial molecules can be estimated from our work by approximating $v'=v$ and $\vec{\Omega}_\mu'=\vec{\Omega}_\mu$, but the transfer function $D\neq 1$. Under these approximations, the collisional integrals a_{11} and a_{12} of Eq. (47)

reduce to $a_{11}=5k_BT/2[\lambda]_1$ and $a_{12}=0$, and the equation becomes

$$\frac{3k_B^2T}{8m}\left(\frac{25}{a_{11}}+\frac{6}{a_{22}}\right). \tag{81}$$

The linear velocity and angular velocity parts of the collisional integral can easily be executed by the modified [13] Hoffman technique. The result will be different from ours used in this paper. The formula (81) may be called another modified Eucken formula for the heat conductivity because the values of a_{11} and a_{22} of Eq. (81) will be different from those [1(c)] of the original modified Eucken formula. We shall present a detailed analysis of this formula in a separate communication. The contribution of correlated multiple two-body interactions (chattering collisions) has not been incorporated in our work.

We have compared our numerical results for η' with the values of Allen *et al.* [16(f)] which in turn are the improvements over the values of their earlier calculations [16(c),16(e)]. We have not made any attempt at a comparison of the numerical values of $[\lambda']_1$ obtained using Eq. (75) with the corresponding molecular dynamics simulation results of Bereolos *et al.* [16(c)] as improvements of the latter are also required [13]. Our results in Eqs. (68) and (67) for ϖ' and the hydrostatic pressure $P_0-\varpi'\vec{\nabla}\cdot\vec{c}_0$ will await detailed testing until simulation studies of these quantities are carried out. The transport coefficient results of this work can be extended to derive semiclassical formulas for the coefficients of a real dense polyatomic fluid in the same way Enskog extended his results for a dense HS fluid to real monatomic fluids.

The results [15] for the first-order transport coefficients of a dense fluid of nearly smooth polyatomic molecules cannot be easily compared with ours because the exchange of energy between the translational and rotational degrees of freedom is fast in our work while it is slow in the problem of nearly smooth molecules.

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APPENDIX: SHEAR VISCOSITY OF UNIAXIAL ELLIPSOIDAL FLUIDS

Here, we obtain computationally convenient explicit expressions for the zero-frequency shear viscosity for prolate spheroids from our Eq. (69) as well as that from Eq. (33) of Ref. [16(f)]. All expressions are in units $m=k_BT=8a^2c=1$ as prescribed in Sec. IX.

First we consider η' from Eq. (69). With the help of Eqs. (7), (21), (34), (35), and (64), and denoting the support function h of the text by h_2, we can rewrite $\hat{O}(1/D^2)$ and ϖ_D of Eq. (69) in the forms

$$\begin{aligned}\hat{O}\left(\frac{1}{D^2}\right)&=2\pi\hat{O}_2\left(\frac{1}{D^2}\right)\\&=2\pi\hat{O}_1\left(\frac{h_1+h_2}{D^2}\right)\\&=\frac{1}{2\pi}\int_0^{2\pi}\int_0^{2\pi}\int_0^1\int_0^1 d\phi_1 d\phi_2 dz_1 dz_2\\&\quad\times\langle\zeta_{\rm ex}\rangle_{\rm or}\left(\frac{h_1+h_2}{D^2}\right)\end{aligned} \tag{A1}$$

and

$$\begin{aligned}\varpi_D&=\frac{5}{3}P\hat{O}_3\left(\frac{1}{D^2}\right)\\&=\frac{5}{3}P\hat{O}_2\left(\frac{h_2}{D^2}\right)=\frac{5}{3}P\hat{O}_1\left(\frac{h_2(h_1+h_2)}{D^2}\right)\\&=\frac{5P}{24\pi^2}\int_0^{2\pi}\int_0^{2\pi}\int_0^1\int_0^1 d\phi_1 d\phi_2 dz_1 dz_2\\&\quad\times\langle\zeta_{\rm ex}\rangle_{\rm or}\left(\frac{h_1+h_2}{D}\right)^2,\end{aligned} \tag{A2}$$

where $P=(8/15)\sqrt{\pi}n^2Y(\vec{r}_c)$ with $Y(\vec{r}_c)$ the contact pair distribution function. Furthermore, we have

$$h_\mu=\frac{H_\mu}{2}(1+\epsilon_c)^{-1/6},\quad H_\mu=(1+\epsilon_c z_\mu^2)^{1/2}, \tag{A3}$$

where $z_1=\hat{k}\cdot\hat{c}_1$ and $z_2=-\hat{k}\cdot\hat{c}_2$ with $\mu=1,2$. Also, $\hat{c}_\mu$ is the unit vector along the symmetry axis of the μth prolate spheroid.

From Eqs. (2), (14), and (A28) of Ref. [18(a)] together with the substitution $\epsilon_b=0$ therein, the orientationally averaged excluded volume surface element per unit solid angle for two colliding uniaxial ellipsoidal molecules turns out to be

$$\begin{aligned}\langle\zeta_{\rm ex}\rangle_{\rm or}&\equiv\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\zeta_{\rm ex}d\phi_1 d\phi_2\\&=\frac{1}{4}(1+\epsilon_c)^{2/3}\left(\frac{1}{H_1^4}+\frac{1}{H_2^4}\right)\\&\quad+\frac{(1+\epsilon_c)^{-1/3}}{8H_1H_2}\left[1+(1+\epsilon_c)\left(\frac{1}{H_1^2}+\frac{1}{H_2^2}\right)\right.\\&\quad\left.+\left(\frac{1+\epsilon_c}{H_1H_2}\right)^2\right],\end{aligned} \tag{A4}$$

since

$$\zeta_{\mathrm{ex}}=\frac{1}{4}(1+\epsilon_c)^{2/3}\left(\frac{1}{H_1}+\frac{1}{H_2}\right)\left(\frac{1}{H_1^3}+\frac{1}{H_2^3}\right)+\frac{1}{4H_1H_2}(1+\epsilon_c)^{-1/3}\times\left[1-(1+\epsilon_c)\left(\frac{1}{H_1^2}+\frac{1}{H_2^2}\right)+\left(\frac{1+\epsilon_c}{H_1H_2}\right)^2\right]\sin^2\phi_{12}, \tag{A5}$$

where ϕ_{12} is the angle between the projections of $\hat{c}_1$ and $\hat{c}_2$ in the plane perpendicular to $\hat{k}$.

The translation-to-rotation energy transfer function D is obtained from Eq. (42) of Ref. [18(a)] written as

$$D^2=1+\frac{5}{2}\left(\frac{\epsilon_c^2}{2+\epsilon_c}\right)\sum_{\mu=1}^{2}\frac{z_\mu^2(1-z_\mu^2)}{H_\mu^2}. \tag{A6}$$

The shear viscosity $[\eta]_1$ of Eq. (69) for low-density fluids of prolate spheroids is given in Eq. (68) of Ref. [18(a)] and reads as

$$[\eta]_1=\left(\frac{15}{16\sqrt{\pi}}\right)\left[\int_0^1\int_0^1 dz_1dz_2\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}\left(\frac{5}{D}-\frac{2}{D^3}\right)\right]^{-1}. \tag{A7}$$

By substitution of Eqs. (A1), (A2), and (A7) in Eq. (69), we finally obtain the expression for η' for a dense model fluid consisting of hard prolate spheroids as

$$\eta'=\frac{15A_1}{16\sqrt{\pi}}(1+B_1)^2+C_1 \tag{A8}$$

with

$$A_1=\left[Y(\vec{r}_c)\int_0^1\int_0^1 dz_1dz_2\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}\left(\frac{5}{D}-\frac{2}{D^3}\right)\right]^{-1}, \tag{A9}$$

$$B_1=\left(\frac{12n\pi}{15(1+\epsilon_c)^{1/6}}\right)Y(\vec{r}_c)\int_0^1\int_0^1 dz_1dz_2\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}\frac{H_1+H_2}{D^2}, \tag{A10}$$

and

$$C_1=\left(\frac{n^2\sqrt{\pi}}{15(1+\epsilon_c)^{1/3}}\right)Y(\vec{r}_c)\int_0^1\int_0^1 dz_1dz_2\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}\left(\frac{H_1+H_2}{D}\right)^2. \tag{A11}$$

Next, we consider the expression for the shear viscosity as given [28] in Eq. (33) of Ref. [16(f)]. This reads in our notation as

$$n_0'=\frac{n}{\nu_{22}}(1+q_\eta)^2+\eta_\infty^{\mathrm{sym}} \tag{A12}$$

with the form of q_η given in Eq. (29) of that reference. In the prescribed units, q_η reduces to B_1 of Eq. (A9) because $\hat{n}\cdot\vec{r}$ of [16(f)] is in our notation $\hat{k}\cdot\vec{r}=(H_1+H_2)/2(1+\epsilon_c)^{1/6}$. The definition of $\langle\cdots\rangle_c$ given in the Appendix of Ref. [16(f)] has also been utilized in the above reduction. The quantity ν_{22} of Eq. (A12) is defined in Eq. (26a) of Ref. [16(f)] in terms of the collision frequency Z; the expression for Z as mentioned in Ref. [16(c)] and derived in Ref. [18(c)] is

$$Z=4n\sqrt{\pi}Y(\vec{r}_c)\int_0^1\int_0^1 dz_1dz_2\langle\zeta_{\mathrm{ex}}\rangle_{\mathrm{or}}D, \tag{A13}$$

which helps in rewriting ν_{22} of Ref. [16(f)] in the form

$$\nu_{22}=\frac{16n\sqrt{\pi}}{15A_1}. \tag{A14}$$

The form of $\eta_\infty^{\mathrm{sym}}$ of Eq. (A12) is given in Eq. (20) of Ref. [16(f)] as

$$\eta_\infty^{\mathrm{sym}}=\left(\frac{nZ}{60\langle D\rangle_c}\right)\left\langle\frac{1}{D}[3r^2+(\hat{k}\cdot\vec{r})^2]\right\rangle_c. \tag{A15}$$

Our evaluation yields

$$3r^2+(\hat{k}\cdot\vec{r})^2=(H_1+H_2)^2(1+\epsilon_c)^{-1/3}+\tfrac{3}{4}(1+\epsilon_c)^{-1/3}\times\left[\epsilon_c^2\left\{\sum_{\mu=1}^{2}z_\mu^2(1-z_\mu^2)H_\mu^2)H_\mu^{-2}-\frac{2z_1z_2}{H_1H_2}\left(2+\cos\phi_{12}\prod_{\mu=1}^{2}(1-z_\mu^2)^{-1/2}\right)\right\}\right]. \tag{A16}$$

With the help of Eqs. (A13) and (A15), we get

$$\eta_\infty^{\mathrm{sym}}=\frac{n^2}{30\sqrt{\pi}}Y(\vec{r}_c)\int_0^1 dz_1\int_0^1 dz_2\int_0^{2\pi}d\phi_{12}\times\frac{S_{\mathrm{ex}}}{D}[3r^2+(\hat{k}\cdot\vec{r})^2]. \tag{A17}$$

As q_η has been shown to be equal to B_1 of Eq. (A10), we can write the final form of Eq. (A12) with the help of Eqs. (A14) and (A16) as

$$\eta_0'=\frac{15A_1}{16\sqrt{\pi}}(1+B_1)^2+\eta_\infty^{\mathrm{sym}}. \tag{A18}$$

It may be noted by looking at Eqs. (A8) and (A18) that the first term of η' is the same as that of η_0'. But the second terms, i.e., C_1 and $\eta_\infty^{\mathrm{sym}}$, are different, although both contain the factor n^2.

In our computations, we have used the corrected [29] Song and Mason [26] formula

$$Y(\vec{r}_c)=\frac{1-\gamma_1\eta_1+\gamma_2\eta_1^2}{1-\eta_1^3}, \tag{A19}$$

where $\eta_1=4\pi a^2cn/3=\pi n/6$ is the packing fraction,

$$\gamma_1=3-\frac{1+6\alpha+3\alpha^2}{1+3\alpha}, \tag{A20}$$

and

$$\gamma_2 = 3 - \frac{2 + 2.6352\alpha + 7\alpha^2}{1 + 3\alpha}, \tag{A21}$$

with $\alpha = RS/3V$. The expressions [29,30] for the average radius of curvature R, surface area S, and volume V for a prolate spheroid with $\eta_2 = \sqrt{\epsilon_c/(1+\epsilon_c)}$ are here given by

$$R = \frac{1}{4}(1+\epsilon_c)^{1/3}\left[1 + \frac{1-\eta_2^2}{2\eta_2}\ln\left(\frac{1+\eta_2}{1-\eta_2}\right)\right], \tag{A22}$$

$$S = \frac{\pi}{2}(1+\epsilon_c)^{-1/3}\left[1 + \frac{\sin^{-1}\eta_2}{\eta_2\sqrt{1-\eta_2^2}}\right], \tag{A23}$$

and $V = \pi/6$.

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[27] It is worth mentioning here that the formula (68) with $[\kappa]_1$ is valid only when $[\kappa]_1$ is small compared with the time scale of expansion of the fluid, but in the case of a dilute HS fluid $[\kappa]_1$ tends to infinity [18]. However, the reduction of Eq. (68) in the form of the second term of Eq. (76) has been possible because the counterpart [1(c),3] of formula (68) in the case of a dilute HS fluid does not possess the term containing viscosity $[\kappa]_1$.

[28] There is a misprint in Eq. (33) of Ref. [16(f)]: $1/m$ should be ρ, where ρ stands for the number density in that reference.

[29] The expression for γ_2 reported in Ref. [26] contains a misprint: The numerator in the second term should be $(2+2.6352\alpha+7\alpha^2)$ instead of $(1+2.6352\alpha+7\alpha^2)$ given in Ref. [26]. Equation (A21) here is the corrected version. The expression for γ_2 as quoted in Ref. [16(c)] is the same as that in Ref. [26] and hence Refs. [16(c)] and [16(f)] have possibly used the incorrect version in their computations.

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