Transport tensors in perfectly aligned low-density fluids: Self-diffusion and thermal conductivity

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The modified Taxman equation for the kinetic theory of low-density fluids composed of rigid aspherical molecules possessing internal degrees of freedom is generalized to obtain the transport tensors in a fluid of aligned molecules. The theory takes care of the shape of the particles exactly but the solution has been obtained only for the case of perfectly aligned hard spheroids within the framework of the first Sonine polynomial approximation. The expressions for the thermal-conductivity components have been obtained for the first time whereas the self-diffusion components obtained here turn out to be exactly the same as those derived by Kumar and Masters [Mol. Phys. **81**, 491 (1994)] through the solution of the Lorentz-Boltzmann equation. All our expressions yield correct results in the hard-sphere limit.

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I. INTRODUCTION

The hard uniaxial-ellipsoidal molecules serve as the most commonly employed model for the study of structural, static, and dynamic properties of the fluids that undergo isotropic-nematic phase transition. The degree of orientation in such model fluids is characterized by the Maier-Saupe [1] order parameter $S=\frac{1}{2}\langle 3(\hat{c}\cdot\hat{n})-1\rangle$, where $\hat{c}$ is a unit vector along the molecular symmetry axis, $\hat{n}$ is the director in the nematic phase, and the angular bracket represents averaging with single-particle orientational distribution function. The value of S lies in the range $0\leqslant S\leqslant 1$; the isotropic phase of the fluid is described by $S=0$ whereas $S=1$ defines perfect alignment of spheroidal nematogens. The self-diffusion coefficient tensor $\overleftrightarrow{D}_s$ and shear-viscosity tensor $\overleftrightarrow{\eta}$ in $S>0$ phase have been calculated by various theoretical as well as simulation methods but the thermal-conductivity tensor $\overleftrightarrow{\lambda}$ has been studied so far only by the latter approach. The simulations have yielded results [2,3] for the components D_{zz} and λ_{zz} of $\overleftrightarrow{D}_s$ and $\overleftrightarrow{\lambda}$ parallel to the director as well as the transverse components $D_{xx}=D_{yy}$ and $\lambda_{xx}=\lambda_{yy}$.

The affine transformation (AT) and the modified affine transformation (MAT) theories developed by Hess and coworkers [4] give predictions for D_{xx} as well as D_{zz}, respectively, for perfectly and partially aligned fluids of hard spheroids. These quantities have also been obtained in Ref. [5] through the solution of the modified version of the Lorentz-Boltzmann (LB) kinetic equation [6]. In LB theory the calculation has been carried out only to the first Sonine-polynomial approximation but the shape dependence of the friction and the mobility tensors has been treated exactly. On comparing the numerical values with the uncorrelated time-correlation function (TCF) theory of Tang and Evans [7], it has been concluded in Ref. [5] that the approximations made in [7] in treating the shape dependence of the friction tensor are judicious and their predictions of components of $\overleftrightarrow{D}_s$ differ at most by 4% from the corresponding exact LB theory results. However, it was found in [5] that AT theory values for the diffusion components differ from the LB kinetic theory predictions by up to 40% and the genesis for this can be traced back to the mathematical fact that the affine transformation maps a hard spheroid onto a hard sphere (HS) with the same volume but with a different surface area. Since the expressions for the transport-coefficient tensors involve various integrations over the surface element of the excluded volume, the volume-conserving transformation cannot be expected to relate simply the transport results for the spheroids and hard spheres. Furthermore, the aligned spheroids have angular velocities that affect the dynamics of collision but the corresponding contributions do not appear in the affine-transformed smooth HS fluids. Nevertheless, the affine-transformed approaches provide some reasonable results too and the deficiencies as well as the qualities of AT and MAT theories have been thoroughly discussed in Ref. [5].

The AT and MAT have also been applied to predict the viscosities, respectively, of perfectly [8] and partially [9] aligned hard spheroids and compared with the corresponding nonequilibrium molecular dynamics (NEMD) simulations [10] and the experimental data [11]. The viscosities have recently been calculated [12] by the TCF method also and the results have been found to track the experimental data [13] and the NEMD simulations [3] as well as the predictions of MAT [9]. However, the AT, MAT or TCF theory has not focused attention so far on the calculation of $\overleftrightarrow{\lambda}$ in $S>0$ phase and the LB theory has not been applied for the predictions of the viscosities or the thermal conductivity corresponding to any value of the parameter S, i.e., either in the isotropic or the nematic phase.

The ordinary diffusions (self as well as mutual), thermal diffusion, viscosities (shear as well as bulk), and thermal conductivity of fluids composed of uniaxial or biaxial ellipsoids have been studied [14–18] in isotropic phase through the modified [14] Taxman (MT) kinetic approach [19]. The historical perspective leading to the modified version [14] of the Taxman equation has recently been summarized by us [20] wherein we have extended the MT theory to discuss the kinetic theory of dense fluids composed of rigid biaxial molecules. The formulas for the shear viscosity of fluids of pure spheroids derived through the low-density MT as well as the

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uncorrelated TCF [21,22] theories are found to be identical but the thermal conductivity expressions are different due to the approximation made in the TCF approach, as expounded in Ref. [14]. Moreover, result for the bulk viscosity has been obtained through the MT theory but not through the TCF method. Also, it is somewhat surprising that the above two theories, although based on uncorrelated collisions, are successful in describing the physics even at liquid densities. Because of all these successes of the MT theory and out of pragmatism, we feel encouraged to generalize the theory for the nematics and to find out explicit expressions for $\overleftrightarrow{D}_s$ and $\overleftrightarrow{\lambda}$ in a perfectly aligned nematic environment.

Section II considers the generalization of the MT theory for application in the nematic phase. Section III derives expressions for the components of $\overleftrightarrow{D}_s$ of a pure fluid of perfectly aligned hard spheroids and the results turn out to be exactly the same as obtained in Ref. [5] by the application of the LB kinetic theory. This perfect agreement between the results obtained from the two independent approaches clearly indicates that the generalized Taxman theory is the right choice for the derivation of the expressions for other transport tensors as well. Hence Sec. IV is devoted to obtaining formulas for the components of $\overleftrightarrow{\lambda}$ of the perfectly aligned nematogens. Finally, Sec. V provides the concluding remarks wherein it is shown that $\overleftrightarrow{D}_s$ result reduces in the limit of low-density HS fluid to the Enskog self-diffusion coefficient formula [23]. Similarly, the $\overleftrightarrow{\lambda}$ result retrieves, in the limiting case, respectively, the Enskog thermal conductivity or the modified Eucken formula [23] for the HS fluids provided one neglects or retains the contributions from the rotational energy of HS molecules. This section also outlines the scope as well as necessity for our low-density theory in the study of transport phenomena for the spheroidal-nematic liquid crystals.

II. GENERALIZED TAXMAN THEORY

Consider any hard convex-body low-density pure fluid in which each molecule of mass m has translational as well as rotational degrees of freedom and, thereby, possesses principal moment of inertia tensor $\overleftrightarrow{I}$. Consider that a tagged molecule, designated as 1, undergoes binary collision with any other molecule designated as 2. The μth molecule ($\mu = 1, 2$) has at space-time point $(\vec{r},t)$ postcollisional peculiar velocity [23] $\vec{V}_\mu$, angular velocity $\vec{\omega}_\mu$, and their precollisional counterparts as $\vec{V}'_\mu$ and $\vec{\omega}'_\mu$. The transport properties of the fluid can be calculated from the knowledge of the single-particle distribution function that in turn is obtained from the solution of an appropriate integro-differential kinetic equation. The collision term in such an equation is conveniently described in terms of the unit surface-normal $\hat{k}\equiv\hat{k}_2=-\hat{k}_1$ at the point of contact, i.e., the point where a pair of hard convex molecules are momentarily in contact during collision, and the postcollisional relative velocity

$$\vec{g}_{21}=\sum_{\mu=1}^{2}(-1)^{\mu}[\vec{V}_\mu+\vec{\omega}_\mu\times\vec{\rho}_\mu] \tag{1}$$

with $\vec{\rho}_\mu$ as the vector joining particle's mass-center to this point. We now define the dimensionless quantities [18,24]

$$\vec{v}=\frac{1}{\sqrt{2}}(\vec{v}_2-\vec{v}_1)=\left(\frac{m}{4k_BT}\right)^{1/2}(\vec{V}_2-\vec{V}_1),$$

$$\vec{g}=\left(\frac{m}{4k_BT}\right)^{1/2}\vec{g}_{21} \tag{2}$$

and

$$\vec{\Omega}_\mu=\left(\frac{1}{2k_BT}\right)^{1/2}\left(\frac{\hat{a}\hat{a}}{\sqrt{I_a}}+\frac{\hat{b}\hat{b}}{\sqrt{I_b}}+\frac{\hat{c}\hat{c}}{\sqrt{I_c}}\right)^{1/2}\cdot\overleftrightarrow{I}\cdot\vec{\omega}_\mu, \tag{3}$$

where (I_a, I_b, I_c) are the components of $\overleftrightarrow{I}$ along the principal axes $(\hat{a},\hat{b},\hat{c})$, and $T=T(\vec{r},t)$ is the local temperature.

The solution of the MT equation provides information regarding single-particle distribution function $\phi_\mu(\vec{v}_\mu,\vec{\Omega}_\mu,\vec{r},t)$ in $S=0$ phase. However, the nematic phase of the spheroidal fluid can be described in terms of a function $F_\mu(\xi_\mu,\vec{r},t)$ that incorporates orientational order with ξ_μ representing a set of variables $(\vec{v}_\mu,\vec{\Omega}_\mu,\hat{c}_\mu,\hat{n})$. We consider the ansatz that

$$F_\mu(\xi_\mu,\vec{r},t)=4\pi f(\hat{c}_\mu\cdot\hat{n})\phi_\mu(\vec{v}_\mu,\vec{\Omega}_\mu,\vec{r},t), \tag{4}$$

with $f(\hat{c}_\mu\cdot\hat{n})$ taken as equilibrium value of the normalized single-particle orientational distribution function, satisfies the equation

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\frac{\partial}{\partial\vec{r}}+\vec{a}_1\cdot\frac{\partial}{\partial\vec{v}_1}\right)F_1(\xi_1,\vec{r},t)$$
$$=\left(\frac{k_BT}{4\pi^2m}\right)^{1/2}\int\int\int\int\int(F'_2F'_1-F_2F_1)$$
$$\times\hat{k}\cdot\vec{g}\zeta_{\text{ex}}(\hat{k},\hat{c}_1,\hat{c}_2)d\hat{k}\,d\vec{v}_2\,d\vec{\Omega}_2\,d\hat{c}_2. \tag{5}$$

Here $\vec{a}_1$ is the acceleration of the particle and $\zeta_{\text{ex}}(\hat{k},\hat{c}_1,\hat{c}_2)$ is the excluded-volume surface element per unit solid angle at the point of contact. Also, $F'_\mu\equiv F'_\mu(\vec{v}'_\mu,\vec{\Omega}'_\mu,\hat{c}_\mu,\hat{n},\vec{r},t)$ is the precollisional counterpart of F_μ.

In a real nematic, interparticle interaction alone is responsible for creating orientational order. However, if we consider that a hypothetical external potential $V_{\text{ext}}(\hat{c}_\mu\cdot\hat{n})$ given by

$$V_{\text{ext}}(\hat{c}_\mu\cdot\hat{n})=-\frac{\alpha}{\beta}\left[\frac{3}{2}(\hat{c}_\mu\cdot\hat{n})^2-\frac{1}{2}\right], \tag{6}$$

with $\beta=1/k_BT$ and $0\leqslant\alpha<\infty$, creates such an order, one can approximate $f(\hat{c}_\mu\cdot\hat{n})$ for uniaxial ellipsoidal nematogens as [1,5]

$$f(\hat{c}_\mu\cdot\hat{n})=\frac{\exp[-\beta V_{\text{ext}}(\hat{c}_\mu\cdot\hat{n})]}{\int\exp[-\beta V_{\text{ext}}(\hat{c}_\mu\cdot\hat{n})]d\hat{c}_\mu}. \tag{7}$$

It is now straightforward to see that Eq. (5) is a generalization of the MT equation since the former reduces to the latter one in the isotropic phase when $\alpha=0$ provided the former is further averaged over $\hat{c}_1$. Moreover, by adopting the method for the evaluation of ϕ_μ by successive approximations, as in the isotropic case [23], F_μ can be determined to any degree of accuracy. The first and second approximations to F_μ for spheroidal fluids are given by $F_\mu^{(0)}$ and $F_\mu^{(0)} + F_\mu^{(1)}$, where

$$F_\mu^{(0)}(\xi_\mu,\vec{r},t)=4\pi f(\hat{c}_\mu\cdot\hat{n})\phi_\mu^{(0)}(v_\mu,\Omega_\mu,\vec{r},t) \tag{8}$$

with [25]

$$\phi_\mu^{(0)}(v_\mu,\Omega_\mu,\vec{r},t)=\pi^{-5/2}n(\vec{r},t)\exp[-(v_\mu^2+\Omega_\mu^2)] \tag{9}$$

and $n(\vec{r},t)$ as the number density of a pure fluid at the point $(\vec{r},t)$. The form for $F_\mu^{(1)}$ depends on the consideration of any particular transport process and we will consider the appropriate forms in Secs. III and IV.

Also, for spheroids, one has [5,7]

$$\zeta_{\rm ex}(\hat{k},\hat{c}_1,\hat{c}_2)=a^6\left[\frac{a^2\epsilon_c^2}{h_1^3h_2^3}[\hat{k}\cdot(\hat{c}_1\times\hat{c}_2)]^2 +(1+\epsilon_c)\left(\frac{1}{h_1}+\frac{1}{h_2}\right)\left(\frac{1}{h_1^3}+\frac{1}{h_2^3}\right)\right], \tag{10}$$

where

$$h_\mu=a(1+\epsilon_c z_\mu^2)^{1/2}, \tag{11}$$

is the support function for μth spheroid with $z_1=-\hat{k}\cdot\hat{c}_1$ and $z_2=\hat{k}\cdot\hat{c}_2$. The anisotropy parameter ϵ_c is defined as $\epsilon_c=(c/a)^2-1$ with "c" and "a" as the semiaxes, respectively, parallel and perpendicular to the symmetry axis.

We consider now onwards the perfectly aligned limit, i.e., the situation when $\hat{c}_1=\hat{c}_2=\hat{n}$, and so there is no possibility of occurrence of the chattering collisions [26], which is a process wherein a pair of hard convex molecules collide two or more times without any intervening collisions with other molecules.

III. SELF-DIFFUSION TENSOR

To determine $\overleftrightarrow{D}_s$, we imagine that the given pure fluid is a binary mixture in which the spheroids belonging to two different sets are of the same mass and obey the same law of interaction at collision so that they are mechanically similar [23]. The definition of $\overleftrightarrow{D}_s$ refers to a state of the fluid in which no external force other than the aligning torque acts on the particles, and the pressure and temperature of the fluid are uniform so that the total number density $n=n_1(\vec{r},t)+n_2(\vec{r},t)$ is independent of $(\vec{r},t)$. The self-diffusion tensor is now defined through the equation

$$\overline{\vec{V}}_2-\overline{\vec{V}}_1=\overleftrightarrow{D}_s\cdot(\vec{\nabla}\ln n_1-\vec{\nabla}\ln n_2)=\frac{n}{n_1n_2}\overleftrightarrow{D}_s\cdot\vec{\nabla}n_1, \tag{12}$$

which is a generalized form of the Fick's law for any anisotropic fluid and where $\overline{\vec{V}}_\mu$ refers to the average peculiar velocity of any one particle of the set μ. The expression for $\overleftrightarrow{D}_s$ can be obtained if we can find an alternative form for $(\overline{\vec{V}}_2-\overline{\vec{V}}_1)$. In order to achieve this, we follow the approach adopted in Ref. [23] for isotropic fluids and get

$$\overline{\vec{V}}_\mu=\left(\frac{2k_BT}{mn_\mu^2}\right)^{1/2}\int\int\int F_\mu^{(1)}(\xi_\mu,\vec{r},t)\vec{v}_\mu\, d\vec{v}_\mu\, d\vec{\Omega}_\mu\, d\hat{c}_\mu \tag{13}$$

with

$$F_\mu^{(1)}=-\frac{1}{n}f(\hat{c}_\mu\cdot\hat{n})\phi_\mu^{(0)}(v_\mu,\Omega_\mu,\vec{r},t)\vec{A}_\mu\cdot\vec{\nabla}n_1(\vec{r},t), \tag{14}$$

where $\vec{A}_\mu\equiv\vec{A}_\mu(\vec{v}_\mu,\vec{\Omega}_\mu,\hat{c}_\mu;\hat{n})$ is a postcollisional vector function that is to be determined. It may also be recalled that the average of $\vec{V}_\mu$ with respect to $F_\mu^{(0)}$ is zero.

We combine Eqs. (13) and (14) to get an expression for $\overline{\vec{V}}_2-\overline{\vec{V}}_1$, and compare the resulting equation with Eq. (12). We thus obtain

$$\overleftrightarrow{D}_s=\frac{n_1n_2}{n^2}\left(\frac{2k_BT}{m}\right)^{1/2}\sum_{\mu=1}^{2}\frac{(-1)^{\mu+1}}{n_\mu} \times\int\int\int f(\hat{c}_\mu\cdot\hat{n})\phi_\mu\vec{A}_\mu\vec{v}_\mu\, d\vec{v}_\mu\, d\vec{\Omega}_\mu\, d\hat{c}_\mu . \tag{15}$$

The unknown function $\vec{A}_\mu$ satisfies the equation

$$\vec{J}_\mu(\vec{A}_\mu)=\frac{(-1)^{\mu+1}}{4\pi x_\mu}F_\mu^{(0)}\vec{V}_\mu, \tag{16}$$

and we write the first Sonine-polynomial approximation in the form

$$\vec{A}_\mu=\frac{(-1)^{\mu+1}}{x_\mu}\overleftrightarrow{\gamma}_0\cdot\vec{V}_\mu, \tag{17}$$

where $x_\mu=n_\mu/n$ and $\overleftrightarrow{\gamma}_0$ is a constant diagonal tensor. In an isotropic fluid environment, the components of $\overleftrightarrow{\gamma}_0$ are equal, i.e., γ_0, so that $\overleftrightarrow{\gamma}_0\cdot\vec{V}_\mu=\gamma_0\vec{V}_\mu$. Also, the collisional integral $\vec{J}_\mu(\vec{A})$ has the form

$$\vec{J}_\mu(\vec{A})=\frac{1}{8\pi^2}\left(\frac{k_BT}{m}\right)^{1/2} \times\int\int\int\int F_\mu^{(0)}F_\nu^{(0)}(\vec{A}_\mu+\vec{A}_\nu-\vec{A}'_\mu-\vec{A}'_\nu) \times\hat{k}\cdot\vec{g}\zeta_{\rm ex}(\hat{k})d\hat{k}\, d\vec{v}_\nu\, d\vec{\Omega}_\nu\, d\hat{c}_\nu, \tag{18}$$

where $\vec{A}'_\mu$ (or $\vec{A}'_\nu$) is the precollisional value of $\vec{A}_\mu$ (or $\vec{A}_\nu$) with μ or $\nu=1,2$ and $\mu\neq\nu$. Insertion of Eqs. (17) and (7) into Eq. (15) and the use of Eq. (9) yields the first approximation for $\vec{D}_s$ in the form

$$[\vec{\vec{D}}_s]_1=\left(\frac{k_BT}{m}\right)\vec{\vec{\gamma}}_0 \tag{19}$$

since $\int\int(\hat{c}_\nu\cdot\hat{n})d\hat{c}_\nu=1$.

To find the value of $\vec{\vec{\gamma}}_0$, we now combine Eq. (16) with Eqs. (4) and (9) to get

$$\sum_{\mu=1}^{2}\frac{(-1)^{\mu+1}}{x_\mu}\int\int\int \vec{J}_\mu(\vec{A}_\mu)\vec{v}_\mu\, d\vec{v}_\mu\, d\vec{\Omega}_\mu\, d\hat{c}_\mu$$
$$=\left(\frac{k_BT}{2m}\right)^{1/2}\frac{n^3}{n_1n_2}\vec{\vec{U}}, \tag{20}$$

where $\vec{\vec{U}}$ is the unit tensor. We further combine Eqs. (4), and (9), (17), and (18) with (20). We then use the form

$$\zeta_{\rm ex}(\hat{k})=\frac{4a^4c^2}{h^4} \tag{21}$$

obtained from Eq. (10) writing $z_2=-z_1\equiv z$ and $h_1=h_2\equiv h(z)=a(1+\epsilon_c z^2)^{1/2}$ in case of a pair of perfectly aligned identical spheroids, which is of our concern here, together with the symmetry relation (3.54.3) of Ref. [23], whence we find

$$\vec{\vec{\gamma}}_0\cdot\int\int\int\int\left[\sum_{\mu=1}^{2}\sum_{\nu=1}^{2}\frac{(-1)^{\mu+\nu}}{x_\mu x_\nu}(\vec{v}_\mu-\vec{v}'_\mu)(\vec{v}_\nu-\vec{v}'_\nu)\right]$$
$$\times\phi_1^{(0)}\phi_2^{(0)}\hat{k}\cdot\vec{g}\,\zeta_{\rm ex}(\hat{k})d\hat{k}\, d\vec{v}_1\, d\vec{v}_2\, d\vec{\Omega}_1\, d\vec{\Omega}_2$$
$$=\frac{n^3}{2n_1n_2}\left(\frac{m}{k_BT}\right)^{1/2}\vec{\vec{U}}. \tag{22}$$

We now transform the velocity variables $\vec{v}_\mu$ and $\vec{v}'_\mu$ of a pair of molecules to $\vec{G}$, $\vec{v}$, and $\vec{v}'$, where $\vec{G}=m\,\vec{G}_0/k_BT$ is the dimensionless variable corresponding to the center-of-mass velocity $\vec{G}_0$ of the pair, $\vec{v}_\mu=[\vec{G}+(-1)^\mu\vec{v}]/\sqrt{2}$ and $\vec{v}'_\mu=[G+(-1)^\mu\vec{v}']/\sqrt{2}$. We then perform the integration over $\vec{G}$ and thus find that Eq. (22) takes the form

$$\vec{\vec{\gamma}}_0\cdot\int\int\int\int \exp[-(v^2+\Omega_1^2+\Omega_2^2)]$$
$$\times(\vec{v}-\vec{v}')(\vec{v}-\vec{v}')\hat{k}\cdot\vec{g}\,\zeta_{\rm ex}(\hat{k})d\hat{k}\, d\vec{v}\, d\vec{\Omega}_1\, d\vec{\Omega}_2$$
$$=\left(\frac{m\pi^7}{n^2k_BT}\right)^{1/2}\vec{\vec{U}}. \tag{23}$$

The quantity $(\vec{v}-\vec{v}')$ appearing in the above equation is related to $\hat{k}\cdot\vec{g}$ and is given [14,15] by

$$\vec{v}-\vec{v}'=2\hat{k}\frac{\hat{k}\cdot\vec{g}}{\varphi^2}, \tag{24}$$

where φ is the rotation-to-translation energy transfer function having the form

$$\varphi=(1+d_1^2+d_2^2)^{1/2} \tag{25}$$

with

$$\vec{d}_\mu=\left(\frac{m}{2I}\right)^{1/2}(\vec{\rho}_\mu\times\hat{k}_\mu)=\left(\frac{ma^4\epsilon_c^2}{2I}\right)^{1/2}(1-z_\mu^2)^{1/2}\frac{z_\mu}{h_\mu}. \tag{26}$$

Here I is the moment of inertia of an elongated-spheroid perpendicular to its symmetry axis and for a pair of perfectly aligned identical spheroids, Eq. (25) can be written as

$$\varphi^2=1+2d^2=1-\left(\frac{m}{Ih^2}\right)(h^2-c^2)(h^2-a^2), \tag{27}$$

where $d\equiv d_1=d_2$.

The velocity and angular velocity integrations in Eq. (23) can be performed by the Hoffman-like technique [14,24] after insertion of Eq. (24) into it and the result is

$$\vec{\vec{\gamma}}_0\cdot\int\frac{\hat{k}\hat{k}}{\varphi}\zeta_{\rm ex}(\hat{k})d\hat{k}=\frac{1}{2n}\left(\frac{\pi m}{k_BT}\right)^{1/2}\vec{\vec{U}}. \tag{28}$$

We now express $\hat{k}$ in terms of its components along $\hat{c}\equiv\hat{c}_1=\hat{c}_2$ and perpendicular to it (i.e., along $\hat{c}_{\perp 1}$ and $\hat{c}_{\perp 2}$) obtaining

$$\hat{k}=\hat{c}(\hat{k}\cdot\hat{c})+(\vec{\vec{U}}-\hat{c}\hat{c})\cdot\hat{k}$$
$$=\hat{c}z+(\hat{c}_{\perp 1}\cos\phi+\hat{c}_{\perp 2}\sin\phi)(1-z^2)^{1/2}, \tag{29}$$

where ϕ is the azimuthal angle of $\hat{k}$ with respect to $\hat{c}$.

Inserting $\zeta_{\rm ex}(\hat{k})$ from Eq. (21) and $\hat{k}$ from Eq. (29) into Eq. (28), using $d\hat{k}=-dz\,d\phi$ and then performing the ϕ-integration, one finally obtains

$$\vec{\vec{\gamma}}_0\cdot\int_0^1\frac{1}{\varphi h^4}[2\hat{c}\hat{c}z^2+(\vec{\vec{U}}-\hat{c}\hat{c})(1-z^2)]dz$$
$$=\frac{1}{16na^4c^2}\left(\frac{m}{\pi k_BT}\right)^{1/2}\vec{\vec{U}}. \tag{30}$$

The terms containing $\hat{c}\hat{c}\cdot\vec{\vec{\gamma}}_0$ and $(\vec{\vec{U}}-\hat{c}\hat{c})\cdot\vec{\vec{\gamma}}_0$ can be readily separated from the above equation. When they are substituted in Eq. (19), we finally obtain first-order results for the parallel and perpendicular components of $[\vec{\vec{D}}_s]_1$ as

$$D_{zz}=\frac{1}{32na^4c^2}\left(\frac{k_BT}{\pi m}\right)^{1/2}\left[\int_0^1\frac{z^2\,dz}{\varphi(z)h^4}\right]^{-1} \tag{31}$$

and

$$D_{xx}=\frac{1}{16na^4c^2}\left(\frac{k_BT}{\pi m}\right)^{1/2}\left[\int_0^1\frac{(1-z^2)}{\varphi(z)h^4}dz\right]^{-1}. \tag{32}$$

Hence, the anisotropy of diffusion defined [4,5] by the ratio $R_D=(D_{zz}-D_{xx})/(D_{zz}+2D_{xx})$ has the form

$$R_D=\left[\int_0^1\frac{(1-3z^2)}{\varphi(z)h^4}dz\right]\left[\int_0^1\frac{(1+3z^2)}{\varphi(z)h^4}dz\right]^{-1}. \tag{33}$$

The results in Eqs. (31) and (32) are identical with those derived in Ref. [5] through the LB kinetic equation. This testifies that the application of the generalized MT theory for the study of transport phenomena in the perfectly aligned model nematics is fully justified. Hence, our approach can be extended to study other transport coefficients and we now set out to apply our generalized theory toward the study of the thermal-conductivity tensor for the fluids comprising perfectly aligned hard prolates.

IV. THERMAL CONDUCTIVITY TENSOR

We follow the approach adopted in Ref. [16] to solve the MT equation whence the thermal flux vector $\vec{q}$ is obtained in the generalized form

$$\begin{aligned}\vec{q}&=-\int\int\int f_2(\hat{c}_2\cdot\hat{n})\phi_2(v_2,\Omega_2,\vec{r},t)\\&\quad\times\vec{C}\cdot\vec{\nabla}\ln T(\vec{r},t)E\vec{V}_2\,d\vec{v}_2\,d\vec{\Omega}_2\,d\hat{c}_2\\&=-\left(\frac{2k_B^3T}{m}\right)^{1/2}(\vec{\nabla}T)\cdot\int\int\int f_2\phi_2\vec{C}\vec{v}_2(v_2^2+\Omega_2^2)\\&\quad\times d\vec{v}_2\,d\vec{\Omega}_2\,d\hat{c}_2,\end{aligned} \tag{34}$$

where $\vec{C}=\vec{C}(\vec{v}_2,\vec{\Omega}_2,\hat{c}_2;\hat{n})$ is a postcollisional vector function which is to be evaluated and we have substituted for the thermal energy, $E=k_BT(v_2^2+\Omega_2^2)$. On the other hand, the thermal conductivity tensor $\overleftrightarrow{\lambda}$ is defined through the generalized Fourier's law

$$\vec{q}=-\overleftrightarrow{\lambda}\cdot\vec{\nabla}T \tag{35}$$

and, hence, we have

$$\overleftrightarrow{\lambda}=\left(\frac{2k_B^3T}{m}\right)^{1/2}\int\int\int f_2\phi_2^{(0)}\vec{C}\vec{v}_2(v_2^2+\Omega_2^2)d\vec{v}_2\,d\vec{\Omega}_2\,d\hat{c}_2 \tag{36}$$

in the first approximation.

As a first Sonine-polynomial approximation to $\vec{C}$, we adopt the form [27]

$$\vec{C}=\frac{1}{n}[\overleftrightarrow{\gamma}_1\cdot\vec{V}_2(v_2^2-\tfrac{5}{2})+\overleftrightarrow{\gamma}_2\cdot\vec{V}_2(\Omega_2^2-1)], \tag{37}$$

which is a generalization of the corresponding expression of Ref. [16]. Here, $\overleftrightarrow{\gamma}_1$ and $\overleftrightarrow{\gamma}_2$ are constant diagonal tensors and are to be determined. In isotropic fluid phase of the spheroids, we have $\overleftrightarrow{\gamma}_j=\gamma_j\overleftrightarrow{U}$ so that $\overleftrightarrow{\gamma}_j\cdot\vec{V}_j=\gamma_j\vec{V}_j$. We substitute Eq. (37) into Eq. (36), use $\int f_2 d\hat{c}_2=1$ as $\vec{C}$ is now not a function of $\hat{c}_2$, and perform the velocity and angular velocity integrations to obtain the first approximation of $\overleftrightarrow{\lambda}$ as

$$[\overleftrightarrow{\lambda}]_1=\frac{k_B^2T}{2m}(5\overleftrightarrow{\gamma}_1+2\overleftrightarrow{\gamma}_2). \tag{38}$$

To determine $\overleftrightarrow{\gamma}_1$ and $\overleftrightarrow{\gamma}_2$, we note that $\vec{C}$ satisfies [16,23] the equation

$$\vec{J}_2(\vec{C})=\frac{1}{4\pi}F_2^{(0)}(v_2^2+\Omega_2^2-\tfrac{7}{2})\vec{V}_2, \tag{39}$$

where the form of the collision integral $\vec{J}_2(\vec{C})$ follows from Eq. (18) by just replacing $\vec{A}$ by $\vec{C}$. We then substitute $\vec{C}$ from Eq. (37) in the equation so obtained, multiply it, respectively, by $(v_2^2-\frac{5}{2})\vec{V}_2$ and $(\Omega_2^2-1)\vec{V}_2$, and integrate the right-hand sides of the resulting two equations over $\vec{v}_2$, $\vec{\Omega}_2$, and $\hat{c}_2$. We thus obtain

$$\sum_{i=1}^{2}\overleftrightarrow{\gamma}_i\cdot\overleftrightarrow{\Gamma}_{ij}=\frac{7-2j}{2(j+1)}\overleftrightarrow{U}, \tag{40}$$

with $j=1,2$ and where

$$\overleftrightarrow{\Gamma}_{11}=[(v_2^2-\tfrac{5}{2})\vec{v}_2,(v_2^2-\tfrac{5}{2})\vec{v}_2], \tag{41}$$

$$\overleftrightarrow{\Gamma}_{12}=[(v_2^2-\tfrac{5}{2})\vec{v}_2,(\Omega_2^2-1)\vec{v}_2], \tag{42}$$

$$\overleftrightarrow{\Gamma}_{21}=[(\Omega_2^2-1)\vec{v}_2,(v_2^2-\tfrac{5}{2})\vec{v}_2], \tag{43}$$

$$\overleftrightarrow{\Gamma}_{22}=[(\Omega_2^2-1)\vec{v}_2,(\Omega_2^2-1)\vec{v}_2]. \tag{44}$$

are the so-called square bracket integral (SBI) tensors $[\vec{\chi},\vec{\psi}]$ defined as the generalization of the corresponding SBI's of Ref. [16]:

$$\begin{aligned}[\vec{\chi},\vec{\psi}]&\equiv\frac{1}{n^2}\int\int\int\vec{\chi}\vec{J}(\vec{\psi})d\vec{v}_2\,d\vec{\Omega}_2\,d\hat{c}_2\\&=\frac{1}{(4\pi n)^2}\left(\frac{k_BT}{4m}\right)^{1/2}\int\int\int\int\int\int\int F_1^{(0)}F_2^{(0)}\\&\quad\times(\vec{\chi}_2+\vec{\chi}_1-\vec{\chi}_2'-\vec{\chi}_1')(\vec{\psi}_2+\vec{\psi}_1-\vec{\psi}_2'-\vec{\psi}_1')\\&\quad\times\hat{k}\cdot\vec{g}\zeta_{\rm ex}(\hat{k})d\hat{k}\,d\vec{v}_1\,d\vec{v}_2\,d\vec{\Omega}_1\,d\vec{\Omega}_2\,d\hat{c}_1\,d\hat{c}_2.\end{aligned} \tag{45}$$

We also have $\overleftrightarrow{\Gamma}_{21}=\overleftrightarrow{\Gamma}_{12}$.

The velocities $\vec{v}_\mu$ and $\vec{v}_\mu'$ in the SBI tensors are replaced by $\vec{G}$, $\vec{v}$, and $\vec{v}\,'$, and the integrations with respect to $\vec{G}$ are performed, whence the final results have the form

$$\overleftrightarrow{\Gamma}_{ij}=(-1)^{i+j}\overleftrightarrow{\Lambda}+\overleftrightarrow{\Pi}_{ij}, \tag{46}$$

where

$$\overleftrightarrow{\Lambda}=\overleftrightarrow{U}\hat{O}\{(v^2-v'^2)^2\}, \tag{47}$$

$$\overleftrightarrow{\Pi}_{11}=4\hat{O}\{v^2\vec{v}\vec{v}+v'^2\vec{v}'\vec{v}'+(v^2-v'^2)(\vec{v}\vec{v}-\vec{v}'\vec{v}')-\vec{v}\cdot\vec{v}'(\vec{v}\vec{v}'+\vec{v}'\vec{v})\}, \tag{48}$$

$$\overleftrightarrow{\Pi}_{12}=2\hat{O}\{(v'^2-v^2)(\vec{v}\vec{v}-\vec{v}'\vec{v}')\} \tag{49}$$

and

$$\overleftrightarrow{\Pi}_{22}=2\hat{O}\{(\Omega_2^2-\Omega_1^2)^2\vec{v}\vec{v}+(\Omega_2'^2-\Omega_1'^2)^2\vec{v}'\vec{v}'-(\Omega_2^2-\Omega_1^2)\times(\Omega_2'^2-\Omega_1'^2)(\vec{v}\vec{v}'+\vec{v}'\vec{v})\}, \tag{50}$$

and we have defined an integral operator as

$$\hat{O}\{\cdots\}=\frac{1}{8\pi^3}\left(\frac{k_BT}{\pi m}\right)^{1/2}\int\int\int\int\{\cdots\}\exp[-(v^2+\Omega_1^2+\Omega_2^2)]\hat{k}\cdot\vec{g}\,\zeta_{\rm ex}(\hat{k})d\vec{v}\,d\vec{\Omega}_1\,d\vec{\Omega}_2\,d\hat{k}. \tag{51}$$

By using

$$\vec{\Omega}'_\mu-\vec{\Omega}_\mu=-2\vec{d}_\mu\frac{\hat{k}\cdot\vec{g}}{\varphi^2}, \tag{52}$$

together with the relation given in Eq. (24), the velocity and angular velocity integrations appearing in Eqs. (47)–(50) can be performed by the standard Hoffman-like [14,24] method. We then use Eq. (29) and do ϕ-integration whence the results are obtained finally as

$$\overleftrightarrow{\Lambda}=2\kappa\overleftrightarrow{U}\int_0^1\left(\frac{1}{\varphi}-\frac{1}{\varphi^3}\right)\zeta_{\rm ex}(z)dz, \tag{53}$$

$$\overleftrightarrow{\Pi}_{11}=2\kappa\overleftrightarrow{U}\int_0^1\frac{1}{\varphi}\zeta_{\rm ex}(z)dz+\kappa\int_0^1\left(\frac{9}{\varphi}-\frac{8}{\varphi^3}\right)\times\{[2\hat{c}\hat{c}z^2+(\overleftrightarrow{U}-\hat{c}\hat{c})(1-z^2)]\zeta_{\rm ex}(z)\}dz, \tag{54}$$

$$\overleftrightarrow{\Pi}_{12}=-2\kappa\int_0^1\left(\frac{1}{\varphi}-\frac{1}{\varphi^3}\right)\times\{[2\hat{c}\hat{c}z^2+(\overleftrightarrow{U}-\hat{c}\hat{c})(1-z^2)]\zeta_{\rm ex}(z)\}dz \tag{55}$$

and

$$\overleftrightarrow{\Pi}_{22}=4\kappa\overleftrightarrow{U}\int_0^1\frac{d^2}{\varphi}\zeta_{\rm ex}(z)dz+8\kappa\int_0^1\left[\left(\frac{1}{2\varphi}-\frac{2d^2}{\varphi^3}\right)\hat{c}\hat{c}z^2+\left(\frac{1}{4\varphi}-\frac{3d^2}{2\varphi^3}\right)(\overleftrightarrow{U}-\hat{c}\hat{c})(1-z^2)\right]\zeta_{\rm ex}(z)dz, \tag{56}$$

where $\kappa=(\pi k_BT/m)^{1/2}$.

The components of $(\overleftrightarrow{\Gamma}_{11},\overleftrightarrow{\Gamma}_{12},\overleftrightarrow{\Gamma}_{22})$ parallel and perpendicular to the symmetry axis of a perfectly aligned hard spheroid readily follow from Eq. (46) together with Eqs. (27) and (53)–(56). We thus have

$$\Gamma_{11}^{zz}=2\kappa\int_0^1\left[\left(\frac{2}{\varphi}-\frac{1}{\varphi^3}\right)+z^2\left(\frac{9}{\varphi}-\frac{8}{\varphi^3}\right)\right]\zeta_{\rm ex}(z)dz, \tag{57}$$

$$\Gamma_{11}^{xx}=\kappa\int_0^1\left[\left(\frac{13}{\varphi}-\frac{10}{\varphi^3}\right)-z^2\left(\frac{9}{\varphi}-\frac{8}{\varphi^3}\right)\right]\zeta_{\rm ex}(z)dz, \tag{58}$$

$$\Gamma_{12}^{zz}=-2\kappa\int_0^1\left(\frac{1}{\varphi}-\frac{1}{\varphi^3}\right)(1+2z^2)\zeta_{\rm ex}(z)dz, \tag{59}$$

$$\Gamma_{12}^{xx}=-2\kappa\int_0^1\left(\frac{1}{\varphi}-\frac{1}{\varphi^3}\right)(2-z^2)\zeta_{\rm ex}(z)dz, \tag{60}$$

$$\Gamma_{22}^{zz}=2\kappa\int_0^1\left[\left(\varphi-\frac{1}{\varphi^3}\right)-2z^2\left(\frac{1}{\varphi}-\frac{2}{\varphi^3}\right)\right]\zeta_{\rm ex}(z)dz, \tag{61}$$

and

$$\Gamma_{22}^{xx}=2\kappa\int_0^1\left[\left(\varphi-\frac{1}{\varphi^3}\right)-(1-z^2)\left(\frac{2}{\varphi}-\frac{3}{\varphi^3}\right)\right]\zeta_{\rm ex}(z)dz. \tag{62}$$

Now writing Eq. (40) in the component forms and solving the simultaneous equations so obtained, we get

$$\gamma_j^{tt}=\frac{1}{\Delta^{tt}}[2\Gamma_{11}^{tt}\delta_{j,2}+5\Gamma_{22}^{tt}\delta_{j,1}-(3j-1)\Gamma_{12}^{tt}], \tag{63}$$

where $j=1$ or 2, $\Delta^{tt}=4[\Gamma_{11}^{tt}\Gamma_{22}^{tt}-(\Gamma_{12}^{tt})^2]$, δ_{ji} is the Kronecker delta function, and the symbol *tt* stands for *zz* or *xx*. Furthermore, considering the component forms of Eq. (38) and using Eqs. (63) in conjugation with Eqs. (57)–(62), we finally obtain the formulas for the components of $[\overleftrightarrow{\lambda}]_1$ as

$$\lambda_{zz}=\left(\frac{\pi k_BT}{m}\right)^{3/2}\frac{k_B}{\pi\Delta^{zz}}\int_0^1\left[\left(25\varphi+\frac{28}{\varphi}-\frac{49}{\varphi^3}\right)+2z^2\left(\frac{13}{\varphi}+\frac{14}{\varphi^3}\right)\right]\zeta_{\rm ex}(z)dz \tag{64}$$

and

$$\lambda_{xx}=\left(\frac{\pi k_BT}{m}\right)^{3/2}\frac{k_B}{\pi\Delta^{xx}}\int_0^1\left[\left(25\varphi+\frac{16}{\varphi}-\frac{10}{\varphi^3}\right)+3z^2\left(\frac{4}{\varphi}-\frac{13}{\varphi^3}\right)\right]\zeta_{\rm ex}(z)dz. \tag{65}$$

Hence, the anisotropy of the thermal conductivity characterized by the ratio $R_\lambda=(\lambda_{zz}-\lambda_{xx})/(\lambda_{zz}+2\lambda_{xx})$ can also be calculated.

V. CONCLUDING REMARKS

The consideration of an ansatz has helped us in generalizing the modified Taxman equation to a form that is suitable to deal with transport tensors in systems with the nematic order. The theory has been applied, by adopting the Chapman-Enskog (CE)-like method [23], to obtain explicit expressions for the self-diffusion and thermal conductivity tensors for low-density fluids composed of perfectly aligned hard spheroidal molecules. The components D_{zz} and D_{xx} have been found to be exactly of the same form as those obtained in Ref. [5] through the solution of the modified Lorentz-Boltzmann equation. Hence, we have applied the generalized theory to obtain the explicit formulas for λ_{zz} and λ_{xx} that had not earlier been obtained through any approach. The validity of our procedure can further be checked by taking recourse to the limiting-isotropic phase. Since, we have considered here the perfectly aligned nematics, we cannot go to the limiting spheroidal-isotropic phase. However, the HS limit, when $\overleftrightarrow{\gamma}_0=\gamma_0\overleftrightarrow{U}$ and also $h=c=a$, $\zeta_{\rm ex}=4a^2$, and $\varphi=1$, can be looked into.

It is straightforward to see from Eqs. (31) and (32) that for a HS molecule of diameter σ, one gets

$$D_s^{(HS)}=D_{zz}^{(HS)}=D_{xx}^{(HS)}=\frac{3}{8n\sigma^2}\left(\frac{k_BT}{\pi m}\right)^{1/2} \tag{66}$$

up to the first approximation that is the same as the Enskog formula [23]. However, in view of [25] and [27], it is not possible to see straightway the HS-limiting behavior from Eqs. (64) and (65); these equations have been derived for the hard, elongated, spheroidal molecules with five degrees of freedom—three translational and two rotational. We first take care of the remarks in [25] and [27] and hence introduce the appropriate changes in Eq. (37). We then follow the subsequent procedure, of course, in a trivial manner and ultimately get

$$\lambda^{(HS)}=\lambda_{zz}^{(HS)}=\lambda_{xx}^{(HS)}=\frac{75k_B}{64\sigma^2}\left(\frac{k_BT}{\pi m}\right)^{1/2} \tag{67}$$

for a nonrotating sphere and

$$\lambda^{(HS)}=\lambda_{zz}^{(HS)}=\lambda_{xx}^{(HS)}=\frac{111k_B}{64\sigma^2}\left(\frac{k_BT}{\pi m}\right)^{1/2} \tag{68}$$

for a rotating sphere, which are respectively the Eucken and the modified Eucken thermal conductivity formulas [23] for the low-density HS fluids, correct up to the first approximation.

It may well be possible to extend the theory developed here for the general situation when partial alignment is there in the low-density fluids and also for the discussion of the viscosities of the aligned molecules. Also, one may like to generalize out theory [20] for the dense fluids for the study of the transport phenomena in the nematic environment. However, it seems pertinent to point out that the MT equation considers only binary collisions and so, ordinarily, is not applicable to dense fluids of nematogens. But in the case of rigid spheroids the collisions are instantaneous and so probability of multiple encounters is negligible [28] provided one ignores the chattering collisions. One can use this fact to graft a dense, hard, spheroid transport theory on the generalized MT equation. It is worth recalling that Enskog had developed a theory for a dense isotropic fluid of hard spheres [23] and we have generalized it for the isotropic fluids of biaxial ellipsoids [20]. This work requires further generalization in order to have a new generalized MT equation that would be applicable in the liquid-crystalline phase composed of spheroidal nematogens. The CE method of solution of the MT equation adopted in the isotropic phase would be applicable here also and Eq. (29) has to be utilized in the execution of the difficult $\hat{k}$ integrations appearing therein. Nevertheless, the CE method would require some basic improvements in predicting the Miesowicz viscosities η_1, η_2, and η_3 [8,9,12], and the Helfrich viscosity η_{12} [12,29] of the nematics because the antisymmetric part of the pressure tensor is not included in the CE method whereas this part contributes to η_1 and η_2 although not to η_3 and η_{12} [9,30].

The equilibrium velocity distribution function is anisotropic in the AT technique [30] and hence the kinetic contribution to the friction tensor of the nematics cannot be calculated using the kinetic theory approach of the isotropic fluid of spheroids. However, the sum of both kinetic and potential contributions are measured in an experiment, and NEMD calculations [8] predict that the kinetic contributions to η_1 and η_3 for the perfectly aligned soft or Lennard-Jones prolate spheroids cannot be disregarded. Based on these results, one may conclude that the kinetic contribution to $\overleftrightarrow{\lambda}$ should not be ignored because both viscosity and thermal conductivity are collective phenomena. More importantly, the development of the CE method for the calculation of this tensor at the Enskog level of approximation requires the kinetic contribution as an important input and the method cannot work without it. It should also be noted that, so far, AT or MAT theory has not predicted even the potential contribution, which is within its ambit, to the thermal conductivity of spheroids.

By neglecting the memory term from the exact Mori transport equation for the velocity autocorrelation function and by making approximations, as in [7], that the pair distribution function (PDF) of the nematics is isotropic on the contact surface and the same contact PDF can be utilized in the isotropic and nematic environments, we have obtained [31] in a very simple way the forms for the components of $\overleftrightarrow{D}_s$ for spheroidal fluids at the Enskog level of approximation. The results so derived reduce to Eqs. (31) and (32) if the PDF is approximated to unity. However, the results in Eqs. (64) and (65) for the thermal conductivity components cannot be derived through the Mori method, the reason [14] being that the result for the thermal conductivity even for an isotropic dilute fluid of spheroids obtained through a Mori-generalized Langevin method [21] is approximate.

Summarizing, the thermal conductivity has not yet been determined either by any theory or by simulations, even at low-density of aligned spheroidal molecules, and the liquid-crystalline phase requires evaluation of the so-called kinetic, potential, and cross contributions. The AT, MAT, or TCF theory has its own limitations, at least till now, and hence, ours is a modest approach along proper direction; our low-density results will be required as a leading term in extending the present theory at the Enskog level.

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