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# Inelastic-collision-frequency theory of transport in low-density fluids

G. S. Singh
*Department of Physics, University of Roorkee, Roorkee 247 667, India*

B. Kumar
*Department of Physics, University of Ranchi, Ranchi 834 008, India*

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A formula for the average inelastic collision rate $N_{11}$ per unit volume of a hard biaxial ellipsoidal molecule has been derived in terms of a product of the average speed $\overline{c}$ of the molecule, the number density $n$ of a pure and dilute fluid of the molecules, and a multidimensional collisional integral (MCI). The formula has been utilized in obtaining approximate expressions for the transport coefficients of the fluid in terms of $\overline{c}$, $n$, and the MCI. The expression for the ratio of $N_{11}$ and the relaxation rate is also obtained. [S1063-651X(99)01502-0]

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## I. INTRODUCTION

Boltzmann has very satisfactorily shown that a pure and dilute fluid composed of spherically symmetric molecules has a Maxwellian linear velocity distribution function in a uniform steady state, called the Maxwellian state. If the fluid consisting of smooth spheres is at rest in such a state, the distribution function can be used in obtaining the average frequency $N_{11}$ per unit volume corresponding to elastic collisions of any one hard-sphere (HS) molecule with the identical molecules. When the fluid departs slightly from the Maxwellian state, the function still gives the first approximation to the actual velocity distribution. Hence the function together with the expression for $N_{11}$ has been utilized in obtaining the transport coefficients of the fluid. Another set of approximate expressions for these coefficients has also been derived by Enskog from the normal solution of the classical Boltzmann equation. It is amazing that the only difference in the transport coefficients obtained through the nonrigorous collision frequency theory and the rigorous Enskog transport theory was the presence of numerical factors of order unity. All of these results are systematically and beautifully presented in the treatise [1] of Chapman and Cowling as well as in the books by Ferziger and Karper [2] and Rigby *et al.* [3].

It has also been explored [4] that the uniaxial and biaxial rigid ellipsoidal molecules are fairly good reference models for the description of the thermodynamic and transport properties of the liquid-crystal-forming liquids. Recently, the first-order approximate formulas [5,6] for the transport coefficients of such model fluids have been derived rigorously from the normal solution of the modified [7] generalized [8,9] Boltzmann equation. The generalized velocity distribution function of the fluid in the Maxwellian state is also well known. It is tempting to derive the $N_{11}$ expression of a smooth hard biaxial molecule undergoing inelastic collisions with its neighbors in the pure fluid.

The primary purpose of this Brief Report is to address such an endeavor by considering only the binary collisions and ignoring the chattering collisions that may occur between the pairs of colliding molecules. In Sec. II the expression has been obtained in terms of the product of a four-dimensional orientational integral, the average speed of a molecule, and the number density of the fluid. The corresponding $N_{11}$ formula for the dense fluid has also been presented and its utility is described in estimating the contact pair distribution function of the fluid, which cannot be calculated from the Boltzmann equation. Section III estimates the transport coefficients of the fluid, when it marginally deviates from the Maxwellian state, by using the form of the velocity distribution function and the expression for $N_{11}$. We find that these results also differ from the rigorous ones derived by us [5,6] only in the numerical factors that vary with the semiaxes of the molecules. Section IV derives an expression for $\tau^*$, which is the ratio of the collision and relaxation [1] rates. It is a useful quantity and in the past has frequently been utilized [8,10] in the $\tau^*$ expansion of the heat conductivity of a low-density pure fluid composed of polyatomic molecules.

## II. FREQUENCY OF COLLISIONS

When a pure and low-density fluid of hard biaxial molecules is at rest and is in the Maxwellian state the average inelastic collision rate $N_{11}$ per unit volume undergone by each molecule is given by

$$N_{11}=\frac{1}{n}\int\int\int\int\int\int f_1 f_2 g_{21}\wp \, d\wp \, d\varepsilon \, d\vec{c}_1 d\vec{c}_2 d\vec{\omega}_1 d\vec{\omega}_2 . \tag{1}$$

Here $n$ is the number density of the fluid consisting of identical molecules of mass $m$, $\wp$ is the impact parameter having azimuthal angle $\varepsilon$, $f_\mu \equiv f_\mu(\vec{c}_\mu , \vec{\omega}_\mu)$ is the Maxwellian distribution function with postcollisional linear and angular velocities $\vec{c}_\mu$ and $\vec{\omega}_\mu$ of the $\mu$th ($\mu = 1,2$) molecule, and $g_{21}$ is the magnitude of the postcollisional velocity of the point of contact on molecule 2 relative to the velocity of the point of contact on molecule 1. Specifically, $\vec{g}_{21} = \vec{c}_{21} + \vec{\omega}_2 \times \vec{\rho}_2 - \vec{\omega}_1 \times \vec{\rho}_1$, where $\vec{c}_{21} = \vec{c}_2 - \vec{c}_1$ and $\vec{\rho}_\mu$ is the vector joining the center of the $\mu$th molecule to the point of contact.

By adopting the technical analysis of Ref. [1], it is possible to rewrite Eq. (1) in an analytically convenient form

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$$N_{11}=\left(\frac{4n^2k_BT}{m\pi^9}\right)^{1/2}\times\int_0^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty\int_0^{2\pi}\int_0^{2\pi}\int_0^1\int_0^1\exp\{-[(\hat{k}\cdot\vec{v})^2+\Omega_1^2+\Omega_2^2]\}\hat{k}\cdot\vec{g}\langle s_{\mathrm{ex}}\rangle_\alpha d(\hat{k}\cdot\vec{v})d\vec{\Omega}_1 d\vec{\Omega}_2 d\phi_1 d\phi_2 dz_1 dz_2, \quad (2)$$

where $s_{\mathrm{ex}}$ is the surface element per unit solid angle on the excluded volume of the two colliding molecules, $\hat{k}=\hat{k}_2=-\hat{k}_1$ is a unit vector normal to the surface of molecule 2 at the point of contact,

$$\vec{g}=\frac{1}{2}\left(\frac{m}{k_BT}\right)^{1/2}\vec{g}_{21}, \quad (3)$$

$$\hat{k}\cdot\vec{g}=\hat{k}\cdot\vec{v}+\vec{\Omega}_1\cdot\vec{q}_1+\vec{\Omega}_2\cdot\vec{q}_2, \quad (4)$$

$$\vec{v}=\left(\frac{m}{4k_BT}\right)^{1/2}\vec{c}_{21}, \quad (5)$$

$$\vec{\Omega}_\mu=\overleftrightarrow{A}\cdot\vec{M}_\mu, \quad (6)$$

$$\overleftrightarrow{A}=(\det\overleftrightarrow{I})^{1/6}[I_a^{-1/2}\hat{a}\hat{a}+I_b^{-1/2}\hat{b}\hat{b}+I_c^{-1/2}\hat{c}\hat{c}], \quad (7)$$

$$\vec{M}_\mu=[2(\det\overleftrightarrow{I})^{1/3}k_BT]^{-1/2}\vec{L}_\mu, \quad (8)$$

and

$$\vec{q}_\mu=\sqrt{\frac{m}{2}}(\det\overleftrightarrow{I})^{-1/6}\overleftrightarrow{A}\cdot(\vec{\rho}_\mu\times\hat{k}_\mu). \quad (9)$$

The angular momentum $\vec{L}_\mu$ and the principal moment of inertia tensor $\overleftrightarrow{I}$ of the $\mu$ molecule are defined by

$$\vec{L}_\mu=\overleftrightarrow{I}\cdot\vec{\omega}_\mu \quad (10)$$

and

$$\overleftrightarrow{I}=I_a\hat{a}\hat{a}+I_b\hat{b}\hat{b}+I_c\hat{c}\hat{c}, \quad (11)$$

where $I_a$, $I_b$, and $I_c$ are the components of $\overleftrightarrow{I}$ along the axes $\hat{a}$, $\hat{b}$, and $\hat{c}$ and are given by

$$I_a=\frac{m}{5}(b^2+c^2), \quad I_b=\frac{m}{5}(a^2+c^2), \quad I_c=\frac{m}{5}(a^2+b^2), \quad (12)$$

with

$$\det\overleftrightarrow{I}=I_aI_bI_c. \quad (13)$$

The form of $\langle s_{\mathrm{ex}}\rangle_\alpha$ is given by

$$\langle s_{\mathrm{ex}}\rangle_\alpha=\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}d\alpha_1 d\alpha_2 s_{\mathrm{ex}}=a^2(1+\epsilon_b)(1+\epsilon_c)\left(\frac{1}{F_1^2}+\frac{1}{F_2^2}\right)+u_1u_2, \quad (14)$$

with $a<b<c$ the semiaxes along the principal axes coordinate system $(\hat{a}_\mu,\hat{b}_\mu,\hat{c}_\mu)$ of the $\mu$th ellipsoidal molecule having anisotropy parameters $\epsilon_b$ and $\epsilon_c$,

$$\epsilon_b=(b/a)^2-1, \quad \epsilon_c=(c/a)^2-1. \quad (15)$$

In addition,

$$F_\mu=1+\epsilon_b y_\mu^2+\epsilon_c z_\mu^2 \quad (16)$$

and

$$u_\mu(y_\mu,z_\mu)=\frac{a}{\sqrt{2F_\mu^3}}[(1+\epsilon_c)+(1+\epsilon_b)F_\mu+\epsilon_b(\epsilon_c-\epsilon_b)y_\mu^2]. \quad (17)$$

The variables of integrations are given by $y_\mu=\hat{k}\cdot\hat{b}_\mu=\sin\theta_\mu\sin\phi_\mu=(1-z_\mu^2)^{1/2}\sin\phi_\mu$ and $z_\mu=\hat{k}\cdot\hat{c}_\mu=\cos\theta_\mu$, where $\theta_\mu$ ($\phi_\mu$) is the polar (azimuthal) angle of $\hat{k}$ with respect to $(\hat{a}_\mu,\hat{b}_\mu,\hat{c}_\mu)$, $\alpha_\mu$ is one of the Euler angles $(\alpha_\mu,\beta_\mu,\gamma_\mu)$ through which the orthogonal coordinate system $(\hat{k}_x,\hat{k}_y,\hat{k}_z=\hat{k})$ can be rotated such that the latter system coincides with the former and $\alpha=\alpha_2-\alpha_1$.

The linear and angular velocity parts of Eq. (2) can be analytically executed using the modified [6] Hoffman [11] procedure and the final result for $N_{11}$ becomes

$$N_{11}=\frac{n\overline{c}}{2\sqrt{2}\pi}\langle D\rangle_{\mathrm{or}}, \quad (18)$$

where $\langle\,\rangle_{\mathrm{or}}$ represents the integrals over the orientational coordinates of a pair of colliding molecules and requires numerical computation [5]. It is given by

$$\langle\cdots\rangle_{\mathrm{or}}=\int_0^{2\pi}\int_0^{2\pi}\int_0^1\int_0^1 d\phi_1 d\phi_2 dz_1 dz_2(\cdots)\langle s_{\mathrm{ex}}\rangle_\alpha. \quad (19)$$

Further, $D$ represents the rotation-to-translation energy transfer function [6,11] whose value is

$$D=(1+q_1^2+q_2^2)^{1/2} \quad (20)$$

and the expression for the average speed $\overline{c}$ of a molecule is given by

$$\overline{c}=\frac{1}{n}\int\int fc d\vec{c}\, d\vec{\omega}=\left(\frac{8k_BT}{\pi m}\right)^{1/2}. \quad (21)$$

For HS molecules of diameter $\sigma$, it can be seen from Eqs. (14)–(17), (9), (20), and (19) that $\epsilon_b=\epsilon_c=0$, $\langle s_{\mathrm{ex}}\rangle_\alpha=\sigma^2$, $q_\mu=0$, $D=1$, and

$$\langle D^j\rangle_{\mathrm{or}}=4\pi^2\sigma^2, \quad (22)$$

where $j$ is any number. Hence, in the appropriate limit, the $N_{11}$ formula reduces to the corresponding HS value

$$N_{11}^{\mathrm{HS}}=\sqrt{2}n\pi\overline{c}\sigma^2. \quad (23)$$

For a dense fluid of hard ellipsoids, Eq. (18) takes a slightly different form (see p. 301 of Ref. [1])

$$N_{11}=\frac{n\bar{c}}{2\sqrt{2}\pi}Y_c\langle D\rangle_{\rm or}. \tag{24}$$

Here $Y_c$ is the contact pair distribution function that can be numerically estimated by using Eq. (24) and measuring $N_{11}$ through molecular dynamics simulations. The accurate values of $Y_c$ obtained by this procedure can be compared with the results calculated through the approximate analytical expression proposed by Song and Mason [12]. The calculation requires as input the formulas for mean radius of curvature *R*, surface area *S*, and volume *V* of an ellipsoid, which are now [13] known.

### III. TRANSPORT COEFFICIENTS

The expression for the mean free path $\Lambda$ of the biaxial fluid follows from Eq. (18):

$$\Lambda=\frac{\bar{c}}{N_{11}}=\frac{2\sqrt{2}\pi}{n\langle D\rangle_{\rm or}}. \tag{25}$$

From the collision frequency theory, the appropriate formulas [1] for the shear viscosity $\eta$, thermal conductivity $\lambda$, and self-diffusion coefficient $D_{11}$ of the low-density biaxial fluid, corresponding to six dynamically active degrees of freedom of a molecule, can be obtained in terms of $\bar{c}$ and $\Lambda$ by using Eq. (25). We thus get

$$\eta=\frac{1}{2}mn\bar{c}u_\eta\Lambda=\frac{\sqrt{2}\pi u_\eta m\bar{c}}{\langle D\rangle_{\rm or}}, \tag{26}$$

$$\lambda=\frac{1}{2}mn\bar{c}c_v u_\lambda\Lambda=\chi_1\eta c_v, \tag{27}$$

and

$$D_{11}=\frac{1}{2}\bar{c}u_D\Lambda=\chi_2\frac{\eta}{nm}, \tag{28}$$

with $\chi_1=u_\lambda/u_\eta$, $\chi_2=u_D/u_\eta$, and $c_v=3k_B/m$ as the specific heat per unit mass of the fluid at constant volume.

The defect of the mean free path formulas is that they depend on the undetermined factors $u_\eta$, $u_\lambda$, and $u_D$ that arise if allowances are made for the persistence (see Chap. 6 of Ref. [1]) of velocities, energies, and concentrations of particles after a collision. In effect, the factors modify the free path to $u_\eta\Lambda$, $u_\lambda\Lambda$, and $u_D\Lambda$, which are present, respectively, in Eqs. (26)–(28). However, the first-order approximate values of the factors can be estimated by comparing the above three equations with the first-order approximate forms of $\eta$, $\lambda$, and $D_{11}$, which have recently been obtained [5] from a systematic analysis of the Boltzmann-Enskog equation. The values are given by

$$u_\eta=\frac{15\pi\langle D\rangle_{\rm or}}{16\langle 5D^{-1}-2D^{-3}\rangle_{\rm or}}, \tag{29}$$

$$u_D=\frac{3\pi\langle D\rangle_{\rm or}}{8\langle D^{-1}\rangle_{\rm or}}, \tag{30}$$

and

$$u_\lambda=\frac{3\pi\langle D\rangle_{\rm or}(9a_{11}-30a_{12}+25a_{22})}{16mc_v(a_{11}a_{22}-a_{12}^2)}, \tag{31}$$

with

$$a_{11}=\left\langle\frac{15}{D}-\frac{11}{D^3}\right\rangle_{\rm or}, \tag{32}$$

$$a_{12}=5\left\langle\frac{1}{D^3}-\frac{1}{D}\right\rangle_{\rm or}, \tag{33}$$

and

$$a_{22}=\left\langle\frac{47}{4D}-\frac{31}{2D^3}+\frac{27}{4D^5}+\frac{12q_1^2q_2^2}{D^3}\left(1-\frac{9}{4D^2}\right)\right\rangle_{\rm or}. \tag{34}$$

It seems pertinent to mention that the correct value of the flux of molecules across a unit area of the plane $z=0$ from the negative to the positive side or vice versa is $n\bar{c}/4$ (see pp. 71 and 97 of Ref. [1]). We have used this value in the derivation of the formulas for $\eta$, $\lambda$, and $D_{11}$. However, some authors (see, for example, Ref. [14]) inadvertently assume that the flux is equal to $n\bar{c}/6$, which would obviously replace the factor 1/2 by 1/3 in Eqs. (26)–(28).

The coefficients of $a_{11}$ and $a_{12}$ in the expression for $u_\lambda$ are given, in general, by $(N-3)^2$ and $10(N-3)$, respectively, with *N* the dynamically active degrees of freedom of a molecule. The coefficients appearing in Eq. (31) correspond to $N=6$ for a rigid biaxial molecule. It can be seen from Eqs. (22) and (29)–(31) that in the HS limit $u_\eta=5\pi/16$ and $u_D=3\pi/8$. Also, $u_\lambda=37\pi/16$ if $N=6$ and $u_\lambda=25\pi/32$ if $N=3$.

### IV. CONCLUDING REMARKS

The expressions for $N_{11}$ in Eqs. (18) and (24) are the main results of this work. We have used Eq. (18) in the preceding section and here we present one more application of it. The reciprocal of $N_{11}$ of Eq. (18) is the average time $\tau_{\rm coll}$ between two consecutive inelastic collisions and is given by

$$\tau_{\rm coll}=\frac{2\sqrt{2}\pi}{n\bar{c}\langle D\rangle_{\rm or}}. \tag{35}$$

The first approximation of the relaxation time for the transition of translational energy into rotational energy and vice versa is given by [1]

$$\tau=\frac{N-3}{4nd}. \tag{36}$$

In our work $N=6$ and *d* is given by [5]

$$d=\frac{\bar{c}}{2\sqrt{2}\pi}\left\langle\frac{1}{D}-\frac{1}{D^3}\right\rangle_{\rm or}. \tag{37}$$

Hence

$$\tau^*\equiv\frac{\tau_{\rm coll}}{\tau}=\frac{4\langle D^{-1}-D^{-3}\rangle_{\rm or}}{3\langle D\rangle_{\rm or}}. \tag{38}$$

The quantity $\tau^*$, which vanishes in the hard-sphere limit, has been fruitfully utilized in the past in the expansion [8,10] of a low-density pure quantal fluid whose molecules possess internal energy.

In summary, we find that the present semiquantitative analysis is interesting mainly as a supplement to our more careful previous [5] analysis.

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