Effects of rotational anisotropy on the self-diffusion coefficient of a dilute fluid composed of infinitely thin hard needles

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Abstract

The self-diffusion coefficient of a dilute fluid composed of infinitely thin hard needles was studied by the molecular dynamics calculation together with the trajectory calculation over a wide range of the moment of inertia of the needle I. The self-diffusion coefficient at small moment of inertia agrees fairly well with the independent scattering approximation (ISA) that is equivalent to the first approximation of the Chapman–Enskog expansion. The deviation of the ISA, however, increases with the increase in the moment of inertia, and the deviation is almost saturated around $I = 1$ by 12% at a reduced density of $\rho = 0.01$. The increase of the deviation with the moment of inertia is ascribed to the rotational anisotropy in the translational motion; propeller-like motion in which the rotational axis is parallel to the translational velocity receives larger disturbance than Frisbee-like motion. The ISA works well at small moment of inertia, because the correlation of the rotational anisotropy is lost rapidly.

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1. Introduction

Transport properties of gases have been studied from the beginning of statistical physics [1, 2]. However, it is still a difficult task to evaluate the transport coefficients from the molecular characteristics especially due to the correlation among scattering processes. The correlation in a monatomic gas comes from the difference in the relaxation time of the molecular speed; faster molecules will have shorter relaxation time. Molecular fluids will have additional complicated correlations due to the internal degrees of freedom of the molecules. For example, we should consider the correlation between the collisions even

in a single scattering process; non-spherical particles will have two or more collisions in a single scattering, which is termed chattering collisions [3].

Relaxation of the molecular velocities accompanied by complicated correlations can be evaluated by the Boltzmann equation. Systematic expansion of the Boltzmann equation had been proposed to solve the correlations in scattering processes, such as the Chapman–Enskog expansion [2, 3]. The first approximation of the Chapman–Enskog expansion corresponds to the neglect of the correlation among the scattering processes that we will call the independent scattering approximation (ISA) or the independent collision approximation (ICA) in this paper. It is known that the ISA is a good approximation for the transport coefficients of monatomic gases; the ISA (or the ICA) gives rigorous results for the Maxwellian gas [1] and the deviation in the self-diffusion coefficient is only about 2% even for the hard-sphere gas [2].

The ISA, however, will not be so successful in molecular gases as in monatomic gases. An apparent difficulty is the correlation by the chattering collisions as referred to above; the ICA is no longer identical to the ISA in molecular gases. We showed that the chattering collisions bring about qualitatively different characteristics of the self-diffusion coefficient of the simplest model fluid composed of infinitely thin hard needles [4]. We will demonstrate in this paper the effect of another kind of correlation in the hard-needle gas due to the rotational anisotropy in the translational motion.

We carried out the molecular dynamics calculation with a number of hard needles and the trajectory calculation on the scattering of a pair of hard needles. The hard-needle fluid has a self-diffusion coefficient larger by more than 10% than that evaluated by the ISA at a large moment of inertia, though the chattering collisions rarely take place. The deviation from the ISA comes mainly from the effect of rotational anisotropy with respect to the translational motion; propeller-like motion, in which the rotational axis is parallel to the translational velocity, receives larger disturbance from the surrounding hard needles than Frisbee-like motion, in which the rotational axis is perpendicular to the translational velocity.

2. Model

Suppose a fluid is composed of infinitely thin hard needles. Equilibrium properties of the hard-needle fluid are identical to those of the ideal gas at any density, because the excluded volume is zero. The needle is assumed to be smooth, i.e. an impulse at a collision instant between two needles is perpendicular to both of the needles. For the sake of simplicity, we shall use the reduced units in which the length and the mass of the needle are unity. The temperature multiplied by the Boltzmann constant, k_BT, is also set equal to unity to avoid the evident temperature dependence; e.g. the collision frequency is proportional to $(k_BT)^{1/2}$ at constant density.

We consider a symmetrical needle in which the centre of mass coincides with the centre of the needle; the moment of inertia I around the centre of mass is $1/12$ for a homogeneous needle. If the distribution of mass is limited within the needle length, the moment of inertia cannot exceed $1/4$. We, however, will consider a moment of inertia greater than $1/4$ to demonstrate the effect of a large moment of inertia, while the mass distribution spreads out of the needle length [4].

When a needle B collides with a needle A at a relative translational velocity $\vec{v}_r$, the relative velocity between the contact points on A and B, $\vec{v}_{col}$, is given as

$$\vec{v}_{col} = \vec{v}_r + \beta(\vec{\omega}_B \times \vec{u}_B) - \alpha(\vec{\omega}_A \times \vec{u}_A) \tag{1}$$

where $\vec{\omega}$ and $\vec{u}$ represent the angular velocity and the unit vector along the needle, and α and β ($|\alpha| < 0.5$, $|\beta| < 0.5$) represent the collision points along $\vec{u}$ of needles A and B, respectively. The impulse at the collision instant on needle A, $\Delta\vec{P}$, is given as

$$\Delta\vec{P} = -\frac{\vec{v}_{\text{col}}^{\perp}}{1 + (\alpha^2 + \beta^2)/(2I)} \tag{2}$$

where the superscript $\perp$ denotes the component along the vector $\vec{u}_{\text{A}} \times \vec{u}_{\text{B}}$ that is perpendicular to the plane made by $\vec{u}_{\text{A}}$ and $\vec{u}_{\text{B}}$. The change in the angular velocity of needle A, $\Delta\vec{\omega}_{\text{A}}$, is expressed as

$$\Delta\vec{\omega}_{\text{A}} = \frac{\alpha}{I}(\vec{u}_{\text{A}} \times \Delta\vec{P}). \tag{3}$$

We will define the collision as an event in which an impulse happens between the needles, and the scattering as a whole process in which the separate needles encounter and go away. A scattering is not necessarily composed of one collision. When a scattering contains two or more collisions, the collisions are termed chattering collisions. The mean collision interval τ_{c} that is the inverse of the mean collision frequency is exactly evaluated by assuming the validity of the ergodicity as [5]

$$1/\tau_{\text{c}} = \tfrac{8}{3}\pi^{1/2}\rho I F_{3/2}(8I) \tag{4}$$

where the function $F_n(x)$ is defined as

$$F_n(x) = \int_0^{\pi/4}\left[\left(1 + \frac{1}{x\cos^2\phi}\right)^n - 1\right]\mathrm{d}\phi. \tag{5}$$

The function $F_n(x)$ will be proportional to x^{-n} at small x and converges on n/x at large x [4].

3. Independent scattering approximation (ISA) on the self-diffusion coefficient

The self-diffusion coefficient D is given by the velocity autocorrelation function as

$$D = \frac{1}{3}\int_0^\infty \langle\vec{v}(0)\cdot\vec{v}(t)\rangle\,\mathrm{d}t \tag{6}$$

where $\langle X\rangle$ represents the ensemble average of X, and $\vec{v}(t)$ is the translational velocity at the time t. When the velocity of the molecule is disturbed by impulsive random forces, the velocity autocorrelation function $C_v(t)$ will obey the exponential law as [6]

$$C_v(t) = \langle\vec{v}(0)\cdot\vec{v}(t)\rangle \tag{7}$$

$$= 3\exp(-t/\tau_v). \tag{8}$$

The relaxation time τ_v in equation (8), which is equal to the self-diffusion coefficient, is given by the initial slope of the velocity autocorrelation function as

$$1/D = -\tfrac{1}{3}\rho\langle\langle\vec{v}\cdot\Delta\vec{P}\rangle\rangle \tag{9}$$

where ρ and $\Delta\vec{P}$ denote the number density and the impulse at the scattering, respectively, and $\rho\langle\langle X\rangle\rangle$ represents the mean value of X for a single molecule scattered in the unit time; e.g. the scattering frequency of a single molecule is given by $\rho\langle\langle 1\rangle\rangle$. Since the incident molecules have the same statistical weight as the scattered molecules, equation (9) is expressed as [4]

$$1/D = \tfrac{2}{3}\rho\langle\langle(\Delta\vec{P})^2\rangle\rangle. \tag{10}$$

When a single scattering process is composed of many collisions, chattering collisions, the mean value $\rho\langle\langle X\rangle\rangle$ can be taken for each collision or for the whole scattering; we will call
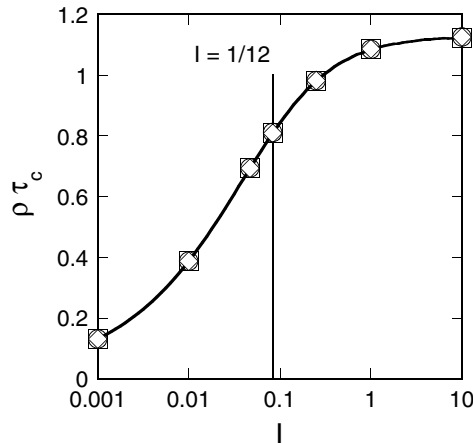
Figure 1. Mean collision interval τ_c in the molecular dynamics calculations at several densities $\rho = 0.01$ ($\bigcirc$), 0.1 ($\square$) and 1 ($\diamondsuit$). The solid line represents the analytical result in equation (4).

the former the independent collision approximation and the latter the independent scattering approximation in this paper. The square of the total impulse during a single scattering is composed of autocorrelation and correlation terms as

$$\langle\langle(\Delta \vec{P})^2\rangle\rangle = \sum_i \langle\langle(\Delta \vec{P}_i)^2\rangle\rangle + 2\sum_i \sum_{n>0} \langle\langle\Delta \vec{P}_i \cdot \Delta \vec{P}_{i+n}\rangle\rangle \tag{11}$$

where $\Delta \vec{P}_i$ represents the ith impulse in a scattering. The correlation terms on the right-hand-side of equation (11) are neglected in the ICA [4]. The self-diffusion coefficient by the ICA is given as [5]

$$1/D = \tfrac{16}{3}\sqrt{\pi}\rho I F_{1/2}(8I). \tag{12}$$

The ICA is identical to the ISA for monatomic gases in which no chattering collisions occur. However, a significant difference was found for the hard-needle gas [4]; the ISA shows an asymptotic behaviour at $I \to 0$ as $D \propto I^{-0.83}$, while the ICA gives $D \propto I^{-0.5}$. The correlation in a single scattering, which is evaluated in the ISA, reduces the total impulse in the scattering at small moment of inertia. The effect of the correlation between the scatterings neglected both in the ICA and the ISA will be shown by the molecular dynamics calculation in this paper.

4. Computational method

4.1. Molecular dynamics calculation

We carried out molecular dynamics calculation with a simple collision-to-collision method [7] over the moment of inertia $1 \times 10^{-3} \leqslant I \leqslant 10$ at low densities up to $\rho = 1$ under the microcanonical condition. All the needles move freely until a collision of a pair of needles happens, and then they move again after changing the velocities of the colliding pair. Mean collision intervals agreed fairly well with the analytical result equation (4) as shown in figure 1. The self-diffusion coefficient was evaluated by numerical integration of the velocity autocorrelation function as in equation (6). The velocity autocorrelation function at each run was evaluated with a time interval of $0.25\tau_c$. We used 500 needles in a cubic cell under

the periodic boundary condition. The needles were placed at random positions with random orientations in the cubic cell at the initial stage. The translational and angular velocities of the needles were given randomly according to the Maxwell–Boltzmann distribution. No equilibration procedure is needed because the infinitely thin hard needles have no correlations in the static structure. Each molecular dynamics calculation was performed up to 1×10^6 collisions. Several calculations with 250 needles or 1500 needles showed no deviation from the results of 500 needles within statistical error.

The self-diffusion coefficient can be divided into two components with respect to the orientation of the needle at the initial stage, $D_\parallel$ and $D_\perp$, defined as [5]

$$D_\parallel = \int_0^\infty \langle (\vec{v}(t) \cdot \vec{u}(0))(\vec{v}(0) \cdot \vec{u}(0)) \rangle \, \mathrm{d}t \tag{13}$$

$$D_\perp = \frac{1}{2} \int_0^\infty \langle \vec{v}(t) \cdot (\mathbf{1} - \vec{u}(0)^\mathrm{t}\vec{u}(0))\vec{v}(0) \rangle \, \mathrm{d}t \tag{14}$$

where $\vec{u}(0)^\mathrm{t}\vec{u}(0)$ is the dyadic. The self-diffusion coefficient is equal to the weighted average of $D_\parallel$ and $D_\perp$ as $D = (D_\parallel + 2D_\perp)/3$. The decomposition of the self-diffusion coefficient into the parallel (longitudinal) and the perpendicular (transverse) components is effective at high densities where the reorientation of molecules is highly restricted [5]; the parallel component of the hard-needle fluid increases at high densities with the increase in density, while the perpendicular component decreases to zero. However, the decomposition is also effective to elucidate the characteristics of the self-diffusion coefficient at low densities.

Integration of the velocity autocorrelation function was carried out numerically up to the time at which the velocity autocorrelation function vanishes in the statistical error of the molecular dynamics calculation for $I \geqslant 0.01$. The integral at $I < 0.01$ was evaluated by assuming the exponential decay of the velocity autocorrelation function at large t/τ_c, because the velocity autocorrelation function did not relax completely within the calculation time.

4.2. Trajectory calculation of the binary scattering

Necessary values in the ISA were evaluated by the trajectory calculation on the scattering of a pair of hard needles. We used two kinds of initial conditions on the translational velocity of the needles in evaluating $\langle (\vec{v} \cdot \Delta \vec{P}) \rangle$ etc; (i) two needles A and B move along the same axis in opposite directions and (ii) needle A running along an axis encounters the randomly moving needle B. The two initial conditions give the same results for randomly aligned needles. We can evaluate easily the effect of rotational anisotropy of needle A at the initial stage under condition (ii), while extra calculation is required for the determination of the initial position with the given impact parameter.

The procedures of the trajectory calculation under the above two initial conditions (i) and (ii) are the same. We generated a pair of thermally rotating needles of the angular velocities obeying the two-dimensional Maxwell–Boltzmann distribution. The pair of needles were placed at the distance unity with an impact parameter and translational velocities given according to the initial condition (i) or (ii), and then they ran on their trajectories according to the equation of motion. Integration over the collisions was carried out numerically for the translational velocity and the impact parameter; we used the constant interval 0.1 for the translational velocity up to 8 and the interval 0.05 for the impact parameter up to 1. The results were also reproduced by a fully Monte Carlo calculation for the generation of the translational velocities and the impact parameters with 1×10^6 trajectories. The collision frequency between randomly aligned needles evaluated by the trajectory calculation agreed fairly well with the analytical result in equation (4).
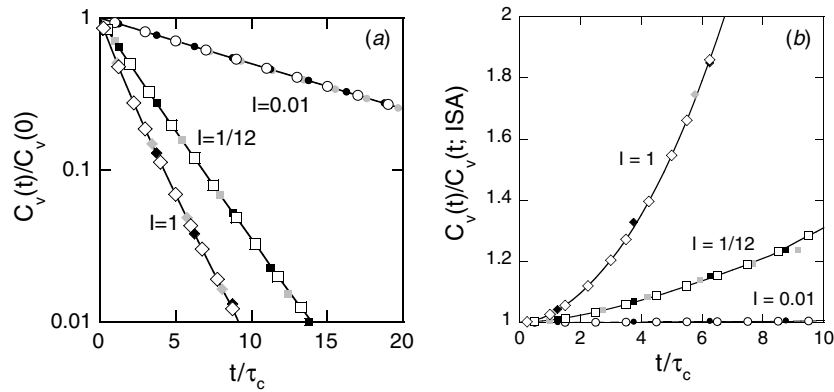
Figure 2. (*a*) Velocity autocorrelation functions $C_v(t)$ of the hard-needle fluid for several moments of inertia $I = 0.01$ (O), $1/12$ (□) and 1 (◇) at $\rho = 0.01$ with 500 needles. Grey and closed symbols represent the results with 250 needles and 1500 needles, respectively. (*b*) Deviation of the velocity autocorrelation function from the ISA.
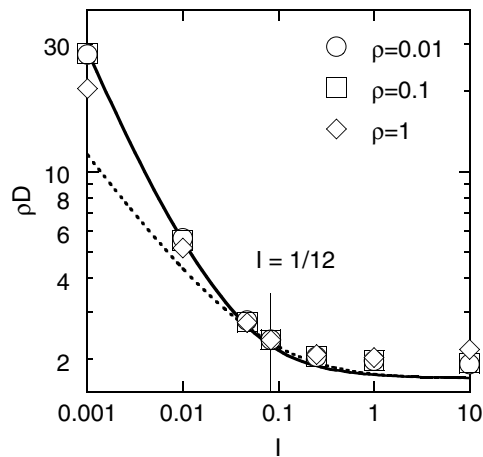

Figure 3. Self-diffusion coefficients of the hard-needle fluid obtained by the molecular dynamics calculation with 500 needles at several densities $\rho = 0.01$ (O), 0.1 (□) and 1 (◇). The dotted line and the solid line represent the self-diffusion coefficient by the ICA and the ISA, respectively [4].

5. Results and discussion

5.1. Velocity autocorrelation function and the self-diffusion coefficient

Figure 2 shows the calculated velocity autocorrelation functions at $\rho = 0.01$. The velocity autocorrelation function decreases almost exponentially and the relaxation time increases with the decrease in the moment of inertia. Although the ISA gives the correct slope at $t = 0$, the velocity autocorrelation function deviates from the value of the ISA by the correlation with successive scatterings. The larger the moment of inertia, the larger the deviation.

Dependence of the self-diffusion coefficients on the moment of inertia of the hard needle is shown in figure 3. We found no dependence on the number of needles in the molecular
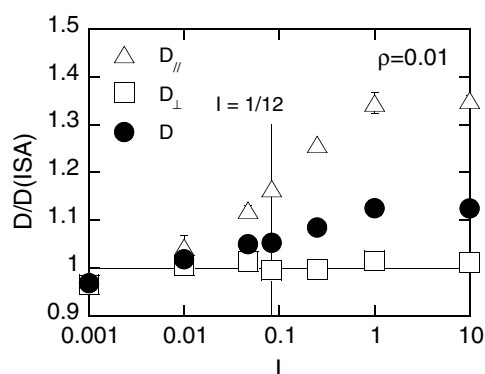
Figure 4. Parallel $D_{\parallel}$ ($\triangle$) and perpendicular $D_{\perp}$ ($\square$) components of the self-diffusion coefficient with respect to the initial orientation of the needle together with the resulted self-diffusion coefficient $D = (D_{\parallel} + 2D_{\perp})/3$ at $\rho = 0.01$.

dynamics calculation of the self-diffusion coefficient within the statistical error. The product of the number density and the self-diffusion coefficient ρD increases with the increase in density at large moment of inertia ($I > 0.05$), while ρD decreases at small moment of inertia. The density dependence can be ascribed to the effect of the ternary scattering that takes place before the binary scattering is completely finished: the mean time interval between the scatterings is of the order of unity around $\rho = 1$, which is comparable with the duration of the chattering collisions at small moment of inertia and the rotation of the needle at large moment of inertia. The value of ρD at $\rho = 0.01$ was not very different from the value at $\rho = 0.1$. The deviation in ρD at $\rho = 0.01$ from the limiting value at $\rho \to 0$ will be negligibly small in comparison with the statistical error of the calculation, because the effect of the ternary scattering is reduced in proportion to the density. We will use the value of ρD at $\rho = 0.01$ as the limiting value at $\rho \to 0$.

The ISA gives reasonable values for the self-diffusion coefficient at small moment of inertia as in monatomic gases. However, the deviation of the ISA increases with increasing moment of inertia as shown in figure 3. The ratio D/D(ISA) was almost saturated around $I = 1$ at 1.12. The deviation in the ratio 0.12 is much larger than that of the gas composed of hard spheres 0.02 [2], whereas the chattering collisions hardly occur at $I > 1$.

5.2. Effects of rotational anisotropy on the self-diffusion coefficient

The dependence of the parallel (longitudinal) $D_{\parallel}$ and the perpendicular (transverse) $D_{\perp}$ components of the self-diffusion coefficient on the moment of inertia is shown in figure 4. The perpendicular component agrees well with the ISA over the whole range of moment of inertia, while the deviation of the parallel component from the ISA increases with the increase in the moment of inertia. The deviation of the self-diffusion coefficient comes mainly from the parallel components. The difference in the parallel and the perpendicular components is attributed to the rotational anisotropy with respect to the translational motion. The parallel component $D_{\parallel}$ reflects the contribution from the needles of the rotational axis perpendicular to the translational velocity, whereas the needles that contribute to the perpendicular component $D_{\perp}$ have the rotational axis aligned isotropically to the translational velocity.
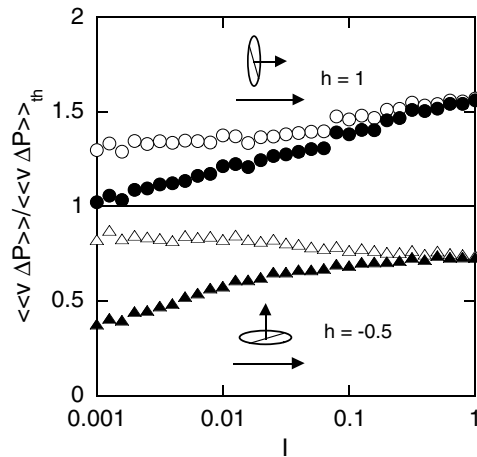
Figure 5. Difference in the disturbance on the initial velocity $\langle\langle \vec{v} \cdot \Delta \vec{P}\rangle\rangle$ with respect to the rotational anisotropy h at the initial stage; $h = 1$ (○) and $h = -0.5$ (△). Contribution of the initial collision is also depicted with closed symbols to elucidate the effects of the chattering collisions.

The rotational anisotropy in the translational motion can be evaluated by the Legendre polynomial of second order, h, as

$$h = P_2\left(\frac{\vec{j} \cdot \vec{v}}{|\vec{v}|}\right) \tag{15}$$

where $\vec{j}$ is the unit vector along the angular momentum $\vec{\omega}/|\vec{\omega}|$. We will pay attention to two extreme cases $h = 1$ and $h = -0.5$. When the angular momentum of the needle is parallel to the translational motion ($h = 1$) like that of a propeller, the needle will collide with other needles more frequently than for Frisbee-like motion ($h = -0.5$). The trajectory calculations show that the total collision cross section σ_{total} of the propeller-like motion ($h = 1$) is larger than the Frisbee-like motion ($h = -0.5$) with randomly aligned needles; $\sigma_{total} = 0.160\pi$ for $h = 1$ and 0.136π for $h = -0.5$ at $I = 1/12$.

The difference is more remarkable in the disturbance of the translational velocity $\langle\langle \vec{v} \cdot \Delta \vec{P}\rangle\rangle$ that is directly related to the self-diffusion coefficient; note that $\langle\langle \vec{v} \cdot \Delta \vec{P}\rangle\rangle$ with a fixed initial configuration cannot be simply expressed by $\langle\langle (\Delta \vec{P})^2\rangle\rangle$ as in equation (10). The ratio of $\langle\langle \vec{v} \cdot \Delta \vec{P}\rangle\rangle$ with a fixed h at the initial stage to that of the randomly aligned needle $\langle\langle \vec{v} \cdot \Delta \vec{P}\rangle\rangle_{th}$ is shown in figure 5. The propeller-like motion ($h = 1$) feels a larger disturbance than the Frisbee-like motion ($h = -0.5$). The difference between two initial configurations decreases with the decrease in the moment of inertia. The contribution from the initial collision in the scattering is also depicted in figure 5. The chattering collisions increase the disturbance of the translational velocity and play an important role in reducing the difference by the initial rotational anisotropy at small moment of inertia. However the effect of rotational anisotropy on the self-diffusion coefficient is not large at small moment of inertia, because the relaxation time of the rotational axis decreases with the decrease in the moment of inertia.

The correlation of the rotational axis before and after the scattering $\langle \vec{j}_{in} \cdot \vec{j}_{scat}\rangle$ is shown in figure 6. Rotational anisotropy is lost largely at small moment of inertia in a single scattering. The relaxation of the rotational anisotropy is accelerated further by the increase in the scattering cross section at small moment of inertia [4]; σ_{total} is 0.125π ($I = 1$) and 0.320π ($I = 0.001$) for randomly rotating needles. Rapid relaxation of the rotational anisotropy at a small moment
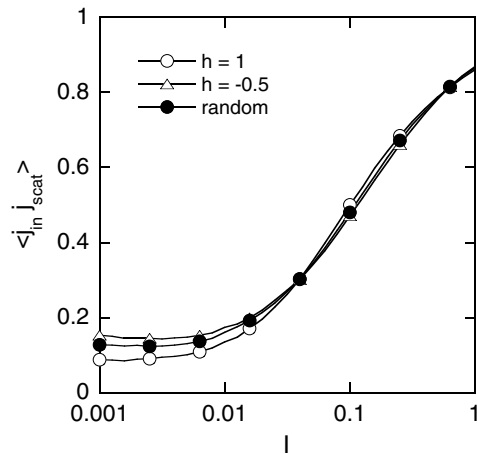
Figure 6. Correlation of the rotational axis of the needle $\vec{j} = \vec{\omega}/|\vec{\omega}|$ of the incident needle $\vec{j}_{in}$ with the scattered needle $\vec{j}_{scat}$. Rotational anisotropy of the needle is $h = 1$ (O) and $h = -0.5$ (△). The correlation for the randomly distributed needle is shown by ●.

of inertia can be deduced from the expression of the impulse at a collision instant in equation (2); the change in the angular velocity will be proportional to $I^{-1/2}$ at a small moment of inertia as shown in equation (3), because the impulse is proportional to $I^{1/2}$. Rapid relaxation of the rotational anisotropy at small moment of inertia is also apparent in the expression for the relaxation time of the autocorrelation function of the angular momentum, τ_ω, by the ICA [5] as

$$1/\tau_\omega = 4\sqrt{\pi}\rho I\left\{\tfrac{2}{3}F_{3/2}(8I) - 2F_{1/2}(8I)\right\}. \tag{16}$$

When the moment of inertia decreases, the relaxation time τ_ω will decrease in proportion to $I^{1/2}$ at $I \to 0$, though the relaxation time of the velocity autocorrelation τ_v diverges in proportion to $I^{-1/2}$ by the ICA.

A simple two-state model can demonstrate the mechanism of the acceleration of the self-diffusion in the hard-needle gas due to the correlation of rotational anisotropy. Suppose a molecule can have two conformations X and Y. The velocity autocorrelation functions of X and Y are relaxed by different rate constants k_v^X and k_v^Y, which are the reciprocal of the relaxation time τ_v in equation (8). At the same time, these two conformations can interchange with the rate constants k_{XY} and k_{YX} as

$$X \longrightarrow Y, \qquad k_{XY} \tag{17}$$

$$Y \longrightarrow X, \qquad k_{YX}. \tag{18}$$

If the interchange process is assumed to be independent of the relaxation of the velocity autocorrelation function, we will have two rate constants for the whole relaxation scheme as

$$k = p_+ + q_+ \pm \sqrt{q_+^2 + p_-^2 + 2p_- q_-} \tag{19}$$

where

$$p_+ = \left(k_v^X + k_v^Y\right)/2, \qquad p_- = \left(k_v^X - k_v^Y\right)/2,$$
$$q_+ = (k_{XY} + k_{YX})/2, \qquad q_- = (k_{XY} - k_{YX})/2. \tag{20}$$

When the interchange rates between X and Y are the same ($q_- = 0$) and they are much faster than the relaxation rates ($q_+ \gg p_+$), the slower relaxation rate constant k_s in equation (19) is given as

$$k_s = p_+ - \frac{p_-^2}{2q_+}. \tag{21}$$

The faster relaxation process with the rate constant, $2q_+$, will not play an important role in the whole relaxation process. The resulting relaxation time ($1/k_s$) corresponds to the self-diffusion coefficient of the whole system.

In the context of the two-state picture, the ISA corresponds to the approximation in which the interchange rate constant $2q_+$ is assumed to be infinitely large; the self-diffusion coefficient by the ISA is equal to the harmonic mean of the self-diffusion coefficients of two conformers X and Y ($1/p_+$). The ISA becomes a good approximation with decreasing correlation of the rotational anisotropy between scatterings by the increase in the interchange rate.

6. Conclusion

The self-diffusion coefficient of a dilute fluid composed of infinitely thin hard needles increases with the decrease in the moment of inertia of the needle. The ICA gives a simple picture of the change of the self-diffusion coefficient by the impulse and the cross section of a single molecular collision [4]. However, the ICA shows sizable deviation due to correlations between the collisions.

The internal degrees of freedom of the hard needle bring about two kinds of correlations between the collisions; one is the chattering collisions, that is the correlation in a single scattering, and the other is due to the rotational anisotropy in the translational motion between scatterings. The effect of the chattering collisions is important, when the needles rotate quickly and fickly at small moment of inertia. Although the ICA does not hold at small moment of inertia, the ISA works well because the correlation among the chattering collisions is taken into account in the ISA. The effect of rotational anisotropy is evident, when the relaxation of the molecular axis is slow at large moment of inertia. The ISA (or the ICA) underestimates the self-diffusion coefficient by more than 10% at $I > 1$, which is much larger than the deviation found for monatomic gases. A simple two-state picture is useful to describe the origin of the deviation of the self-diffusion coefficient due to the correlation in the rotational anisotropy.

It is well known that the internal degrees of freedom of the molecules lead to the bulk viscosity that is not found in monatomic gases [2, 3]. The correlation by the internal degrees of freedom can bring about large deviation of a usual transport coefficient from the ISA (or the ICA) also. We should be cautious about evaluating the deviation for the transport properties of molecular gases from the ISA that is identical to the first approximation in the Chapman–Enskog expansion.

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