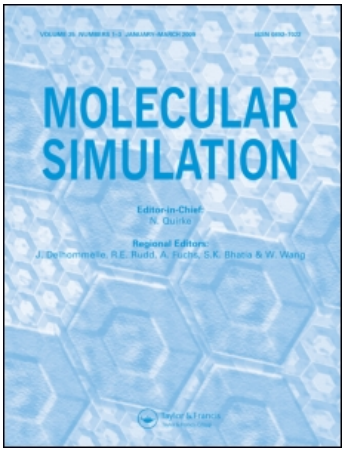

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Shear Viscosity of a Fluid Composed of Infinitely-Thin Hard Needles

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SHEAR VISCOSITY OF A FLUID COMPOSED OF INFINITELY-THIN HARD NEEDLES

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The shear viscosity of an ideal gas composed of infinitely-thin hard needles was studied by the molecular dynamics simulation. The shear viscosity of the hard-needle fluid increases linearly with increasing density at high densities, though it is almost constant at low densities. No anomaly of the shear viscosity is detected around the density at which the self diffusion coefficient has the minimum. The Stokes–Einstein relation does not hold in the hard-needle fluid.

Keywords: Shear viscosity; hard-needle fluid; molecular dynamics; self diffusion coefficient

1. INTRODUCTION

Ideal gases are often assumed to be composed of non-interacting molecules, and those transport properties have scarcely been discussed. However we can construct an ideal gas which has finite relaxation time. The simplest and non-trivial model of the ideal gas is the fluid composed of infinitely-thin hard needles. The hard-needle fluid behaves as an ideal gas, because the excluded volume is zero [1]. Static correlations, such as the density–density correlation, are diminished in the hard-needle fluid. The transparent static structure of the hard-needle fluid enables us to get insight into the purely dynamical characteristics of fluids, which are often hidden behind the complicated static structures.

It has been shown that the self diffusion coefficient of the hard-needle fluid has a minimum with increasing the density, because the transltional

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diffusion along the needle axis is facilitated by the hindrance of the rotational diffusion at high densities [1, 2]. The diffusion coefficient of the solute molecule is often correlated to the shear viscosity of the solvent [3]. If the correlation holds in the hard-needle fluid, the minimum of the self diffusion coefficient will be accompanied with a maximum of the shear viscosity. We tried to detect anomaly in the shear viscosity that corresponds to the minimum of the self diffusion coefficient by the molecular dynamics (MD) simulation in equilibrium. However, no anomaly in the shear viscosity was found.

2. MOLECULAR DYNAMICS SIMULATION

2.1. Model

Suppose an infinitely-thin homogeneous and smooth hard needle which has unit length and unit mass. Its moment of inertia is 1/12, and the impact at the collision is perpendicular to the needle axis. Since the length of the system is reduced by the needle length, the increase in the needle length is equivalent to the increase in the number density ρ. The time evolution of the hard-needle fluid is governed by the kinetic energy, *i.e.*, the unit of the time can be reduced by the square root of the temperature. We reduce the time by $1/\sqrt{(k_B T)}$ where k_B is the Boltzmann constant and T is the absolute temperature. We set $k_B T = 1$ to avoid the evident temperature dependence, because the self diffusion coefficient and the shear viscosity depends on the temperature with a factor $\sqrt{(k_B T)}$.

Since the hard-needle fluid is an ideal gas, its radial distribution function is exactly equal to unity for arbitrary distance and density. This enables us to calculate precisely the collision frequency of a needle as $1/\tau_c = 1.238\rho$, where τ_c is the mean collision interval [1].

2.2. Calculation of the Collision Instance

Since the collision of two needles is an instantaneous event, it is difficult to apply the usual step-by-step algorithm, in which the molecules are moved simultaneously by a short time interval in each step, to the hard-needle fluid [1]. The present MD calculation of the hard-needle fluid is also based on the collision-by-collision algorithm, in which the time is proceeded to the next collision instance in the system. We, however, implemented partly a step-by-step algorithm for the calculation of the collision instance that is the key for an efficient collision-by-collision algorithm.

When two needles A and B collide, the needle axes of A and B are in the same plane as

$$\boldsymbol{r}_A(t) + \alpha_A \boldsymbol{u}_A(t) = \boldsymbol{r}_B(t) + \alpha_B \boldsymbol{u}_B(t), \tag{1}$$

where $\boldsymbol{r}$ is the positional vector of the center of the needle, and $\boldsymbol{u}$ is the unit vector parallel to the needle axis. Since the contact position is on both the needles, the parameters α_A and α_B in Eq. (1) should satisfy the condition as

$$|\alpha_A| < 0.5, \quad |\alpha_B| < 0.5. \tag{2}$$

The in-plane condition can be expressed by using the function $F(t)$ [1]:

$$F(t) = (\boldsymbol{r}_A(t) - \boldsymbol{r}_B(t)) \cdot (\boldsymbol{u}_A(t) \wedge \boldsymbol{u}_B(t)) = 0. \tag{3}$$

The function $F(t)$ oscillates in a complicated way due to the term $\boldsymbol{u}_A(t) \wedge \boldsymbol{u}_B(t)$, because the needles rotate with different angular velocities ω_A and ω_B. Although we can limit the range of the collision time by several criterions [1], Eq. (3) has often more than five roots that are burried in the complex oscillation of $F(t)$ in the limited region. The usual Newton–Raphson (NR) method does not work without an efficient choice in the initial conditions. We applied a step-by-step method for the determination of the initial time for the NR method. The time step was set at $0.5\pi/(|\omega_A| + |\omega_B|)$ that is one quarter of the period in the most frequent component of $F(t)$. This step-by-step approach was successful. A typical run took about 96 s for 1000 collision of 500 hard needles at $\rho = 50$ on a personal computer (Pentium 166 MHz), which is about twice faster than the previous MD calculation on CIBER 170–750 [1].

2.3. Conditions of Molecular Dynamics Simulation

We used 500 needles (partly 1000 needles) contained in a cubic cell under a periodic boundary condition. The range of the simulated number density is from 0.5 to 60, and each simulation was performed up to 3×10^5 collisions (for self diffusion coefficient) or 5×10^6 collisions (for shear viscosity).

3. RESULTS AND DISCUSSION

3.1. Validity of the Simulation

We confirmed the validity of our molecular dynamics simulation by calculating the collision frequency and the radial distribution function. The

collision frequency agreed well with the rigorous value 1.238ρ within 0.5%. The center–center and end–end radial distribution functions of the needles were unity within statistical error at any distance.

3.2. Self Diffusion Coefficient

Translational velocity autocorrelation function, $C_v(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$, are shown in Figure 1 at several densities. The time is normalized by the collision frequency. The Enskog theory, which assumes no correlation between successive collisions, predicts that the $C_v(t)$ is an exponential function and that the self diffusion coefficient is $2.303\rho^{-1}$ [1]. If the Enskog theory is valid, each $C_v(t)$ coincides with the line ' Enskog' in the figure.

However a slow component gradually grows up as the density increases. Frenkel *et al.*, have shown that the slow component is due to the translational motion along the needle axis, and that the self diffusion coefficient will diverge with increasing the density due to the slow component. This slow component makes difficult the direct numerical integration of the translational autocorrelation function. We thus fitted our data to a double-exponential function for each curve to evaluate the self diffusion coefficient. All $C_v(t)$ curves are fitted by this function very well

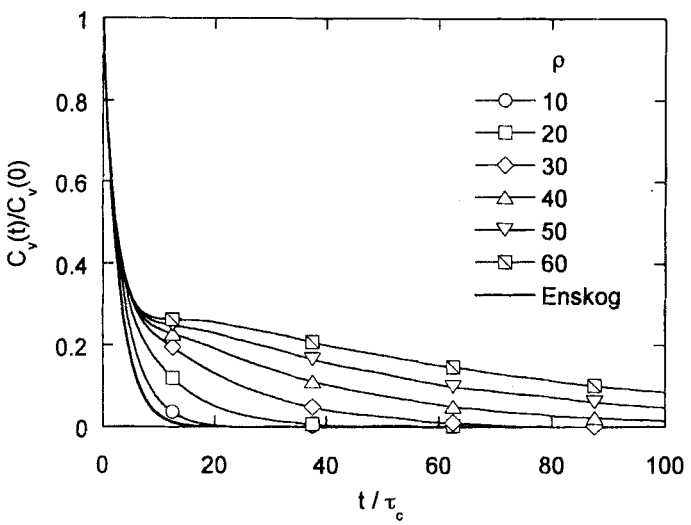

FIGURE 1 Translational velocity autocorrelation function of the hard-needle fluid at several densities. The time is normalized by the mean collision interval τ_c. If the Enskog theory is valid, all the lines are the same as the line 'Enskog' (= $\exp(-0.351\, t/\tau_c)$).

except for around $t/\tau_c \sim 10$. Square sum of the difference between the data and the fitting curve was 0.027 for 500 data points at the density $\rho = 60$.

The self diffusion coefficient shown in Figure 2 are in good agreement with the literature values [1, 2] and the minimum of the self diffusion coefficient is reproduced.

3.3. Shear Viscosity

Shear viscosity η of the fluid composed of hard bodies can be divided into three parts as the kinetic part η_k, the potential part η_p, and the cross part η_c, which are given as follows [5]:

$$\eta_k = \lim_{t\to\infty} \eta_k(t) = \lim_{t\to\infty} \frac{1}{2Vt} \left\langle \left[\sum_{\text{coll}} \sum_i v_{iz} \cdot v_{ix} \cdot \Delta t_c \right]^2 \right\rangle, \tag{4}$$

$$\eta_p = \lim_{t\to\infty} \eta_p(t) = \lim_{t\to\infty} \frac{1}{2Vt} \left\langle \left[\sum_{\text{coll}} \Delta v_{iz} \cdot (r_{ix} - r_{jx}) \right]^2 \right\rangle, \tag{5}$$

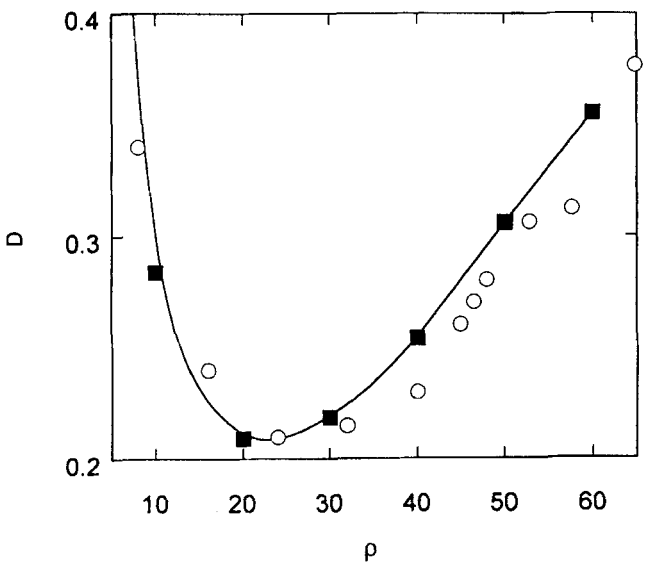

FIGURE 2 Density dependence of the self diffusion coefficient of the hard-needle fluid at several densities. This work (■) agrees well with the literature values (○). ($\rho \leq 24$ [1], $\rho \geq 32$ [2]).

$$\eta_c = \lim_{t\to\infty} \eta_c(t) = \lim_{t\to\infty} \frac{1}{2Vt} \left\langle \left[\sum_{\text{coll}} \sum_i v_{iz} \cdot v_{ix} \cdot \Delta t_c \right] \cdot \left[\sum_{\text{coll}} \Delta v_{iz} \cdot (r_{ix} - r_{jx}) \right] \right\rangle, \tag{6}$$

where r_{ix} is the x-component in the Cartesian coordinate of the center of mass of the i-th needle. v_{iz} is the translational velocity along the z-axis of the i-th needle, and Δv_{iz} is the change of v_{iz} at a collision. The symbol Σ_{coll} stands for the summation over all collisions in time t, and Δt_c is the time interval between two successive collisions. V is the volume of the cell. Although $\eta_k(t)$ and $\eta_c(t)$ are diminished at $t = 0$, $\eta_p(0)$ has non-zero value that is proportional to square of the density.

Figure 3 shows three components $\eta_k(t)$, $\eta_p(t)$, and $\eta_c(t)$ at densities $\rho = 10$ and 30. Computed $\eta_p(0)$ are 1.23 ($\rho = 10$) and 11.2 ($\rho = 30$). Square root of their ratio, 3.02, is alomst the same with the ratio of the density. On the other hand, $\eta_p(t)$ after a long time is not proportional to ρ^2, *e.g.*, η_p are 0.5 ($\rho = 10$) and 6.1 ($\rho = 30$). The kinetic part η_k increases gradually with the increase in the density, 1.8 ($\rho = 10$) and 2.9 ($\rho = 30$). The cross part η_c is small enough to be ignored at densities studied.

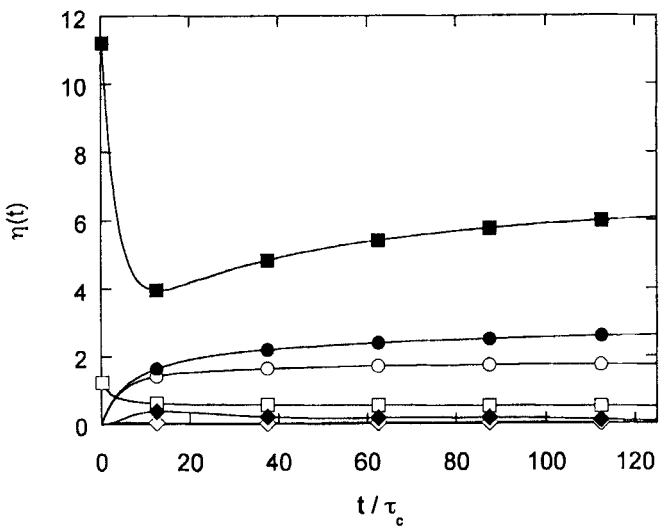

FIGURE 3 Time dependence of the three components of the shear viscosity of the hard-needle fluid. The kinetic part $\eta_k(t)$ (○, $\rho = 10$; ●, $\rho = 30$), the potential part $\eta_p(t)$ (□, $\rho = 10$; ■, $\rho = 30$), and the cross part $\eta_c(t)$ (◇, $\rho = 10$; ◆, $\rho = 30$). $\eta_p(0)$ is proportional to ρ^2. The time is normalized by the mean collison interval τ_c.

Density dependence of the shear viscosity is shown in Figure 4. No anormaly was found around the density $\rho = 30$ where the self diffusion coefficient has the minimum. The shear viscosity is almost constant as expected from the kinetic theory of gases at low densities ($\rho \leq 10$), however increases almost in proportion to the density at high densities ($\rho \geq 10$). At the highest density $\rho = 50$ in Figure 4, we simulated a larger system composed of 1000 needles to examine the system size effect. However the effect of the system size was not found.

The density dependence in Figure 4 is smaller than the square of the density proposed by the Enskog theory and the cubic proposed by Doi and Edwards [6], while the simulation results contained a large ambiguity due to the statistical error and the difficulty in the evaluation of the long time behavior of $\eta(t)$ (see Fig. 3). The Enskog theory overestimates the density dependence because of the neglect of the correlation among the collisions as shown in the decrease of $\eta_p(t)$ with time in Figure 3. Although the theory by Doi and Edwards may be valid in the system immersed in a continuum solvent, it will not hold for the present system, in which the rod-like molecules move in the vacuum. The evaluation of the hydrodynamic interaction in the hard-needle fluid will be helpful to have an insight into the validity of the theory by Doi and Edwards at higher densities (say $\rho = 200$) where the MD simulation of the shear viscosity becomes impractical due to the long relaxation time.

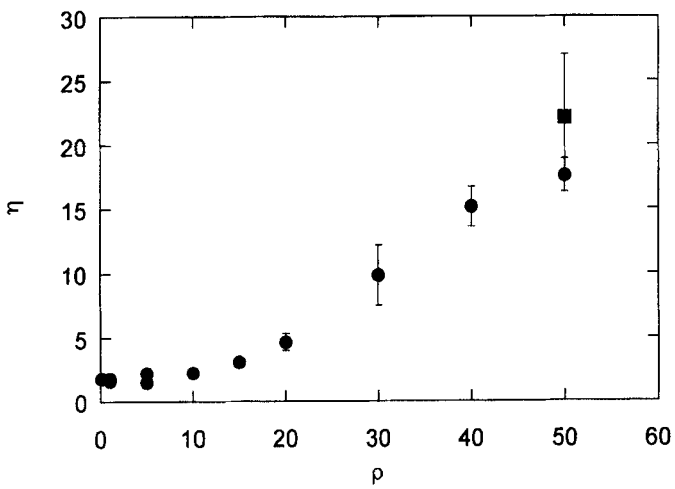

FIGURE 4 Density dependence of the shear viscosity of the hard-needle fluid. Calculated with 500 needles (●) and 1000 needles (■).

The relation between the shear viscosity and the self diffusion coefficient is demonstrated in Figure 5. The Stokes–Einstein relation, in which the diffusion coefficient is inversely proportional to the shear viscosity, is often assumed for the diffusion in liquids. The self diffusion coefficient, however, can change for the constant shear viscosity at low densities as is well known for all the fluids [3]. The hard-needle fluid shows another limitation of the Stokes–Einstein relation, *i.e.*, the self diffusion coefficient can increase with the increase in the shear viscosity at high densities.

The hydrodynamic picture on the self diffusion, which leads to the Stokes–Einstein relation, assumes that the friction acting on the molecule is proportional to the shear viscosity of the surrounding medium, which corresponds to the transport coefficient of the momentum. The picture will be effective at high densities, because the momentum transport by mass transfer is not important at high densities. However, it will not be the case for the system that has multi-modes in motion as the hard-needle fluid. The hard needle has two different translational modes; parallel and perpendicular motions to the needle axis. The parallel mode is predominant in the self diffusion at high densities by the hindrance of the perpendicular motion

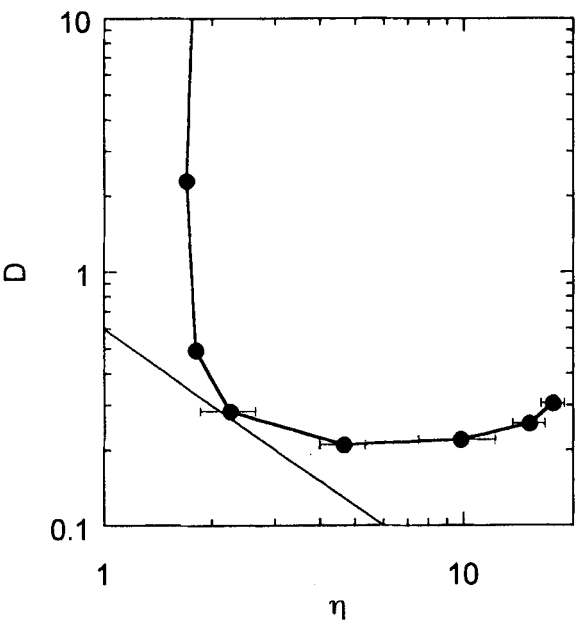

FIGURE 5 Relation between the self diffusion coefficient and the shear viscosity of the hard-needle fluid. The straight line shows the slope -1.

[1]. On the other hand, the shear viscosity may be governed by the perpendicular mode, because the parallel component of the momemtum does not change at the collision instance.

The present MD simulations has shown that the Stokes–Einstein relation does not hold for the hard-needle fluid. The invalidity of the Stokes–Einstein relation at high densities will be attributed to the difference in the dominant translational mode for the self diffusion coefficient (parallel mode) and the shear viscosity (perpendicular mode). The contribution of each mode to the shear viscosity is under study now.

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