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Molecular Dynamics Study of Infinitely Thin Hard Rods: Scaling Behavior of Transport Properties

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A molecular dynamics study on a system of infinitely thin hard rods is reported. At low densities, rotational and translational diffusion is adequately described by the Enskog theory, but at high densities ($\rho^* \gg 1$) large deviations are observed. For $\rho^* >> 1$, the rotational diffusion constant (D_r) and the longitudinal translational diffusion constant ($D_\parallel$) are compared with scaling predictions. The molecular dynamics results confirm that $D_r \sim \rho^{*-2}$, and are consistent with a predicted divergence of $D_\parallel \sim \rho^{*1/2}$.

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A fluid consisting of infinitely thin hard rods ("hard lines") is remarkable in that all of its structural properties are those of an ideal gas, whereas all of its transport properties are nonideal and strongly dependent on density. The absence of structural correlations is a direct consequence of the fact that the hard-line system has zero excluded volume; at any density, all molecular positions and orientations are equally likely. Obviously, as the configurational part of the partition function equals $V^N/N!$, the pressure of a hard-line fluid must follow the ideal-gas law. In contrast, the dynamics of hard lines is very sensitive to the presence of other lines. In this Letter, we present results of molecular dynamics (MD) simulations on a system of hard lines, over a range of densities. We compare the results of these simulations with theoretical predictions for the density dependence of transport properties. Although we will briefly indicate the nature of the theories involved, we must refer the reader to a subsequent publication[1] for more details. Similarly, space does not permit us to elaborate on the computational method; Ref. 1 will contain a detailed discussion.

Theoretical predictions can be made about the dynamics of hard lines (in particular about translational and rotational diffusion), by using two very different approaches. The first is the well-known Enskog method for computing transport properties (we use the phrase "Enskog theory" in the sense explained by Chandler[2] and by O'Dell and Berne[3]). Because of the absence of structural correlations in the hard-line fluid, the following very simple expressions result for the self-diffusion constant D, and the angular momentum correlation time τ_J[1]:

$$D = (2.303\ldots)/\rho^* \tag{1}$$

and

$$\tau_J = (1.705\ldots)/\rho^*. \tag{2}$$

In the above equations, reduced units have been used: $\rho^* = \rho L^3$, where ρ is the number density

and L the length of the rod. We define L to be the unit of length, m (the mass of the rod) to be the unit of mass, and kT to be the unit of energy. The moment of inertia of the rod is chosen equal to $\frac{1}{12}$, which corresponds to a uniform mass distribution. The collision frequency in a hard-line fluid can be calculated *exactly*:

$$\Gamma = (1.23766\ldots)\rho^*. \tag{3}$$

At high densities Eq. (3) is still valid, but the Enskog expressions [Eqs. (1) and (2)] may fail. However, it is precisely at high densities ($\rho^* \gg 1$) that theoretical predictions can be made about rotational and translational diffusion, using scaling arguments similar to those presented by Doi and Edwards[4] (henceforth referred to as DE). These authors have developed a theory of Brownian dynamics of rodlike macromolecules in concentrated solutions. One of the predictions of the DE theory is that for thin inflexible rods, the following relation should hold between the rotational diffusion constant D_r, and the longitudinal translational diffusion constant $D_\parallel$ (i.e., along the rod axis):

$$D_r \sim D_\parallel/\rho^{*2}. \tag{4}$$

The basic idea behind this expression is that the reorientation of the rods is constrained by the presence of other rods. Only when one of the constraining rods diffuses away (typically, in a time $1/D_\parallel$) can the constrained molecule perform an angular jump of order $\theta \approx \rho^{*-1}$. Several attempts have been made to test the DE theory experimentally,[5] by using light scattering to study the rotational dynamics of long rodlike viruses. There are, however, some discrepancies between theory and experiment and it is not obvious, at present, whether these discrepancies are due to deficiencies in the DE theory, or to the fact that real viruses are not completely rigid, nor infinitely thin. MD simulations on a hard-line system should provide a more direct test of the DE theory. It should be noted, however, that the DE theory was derived for rods performing Brownian motion in a *viscous* fluid. For *smooth* hard lines, Eq. (4) has to be modified slightly,[1] and reads

$$D_r \sim 1/\rho^{*2}. \tag{4a}$$

The high-density behavior of $D_\parallel$ can be predicted by extending the scaling arguments used by Doi and Edwards. One arrives at a remarkable prediction, namely that $D_\parallel$ should *diverge* at high densities:

$$\lim_{\rho^* \to \infty} D_\parallel \sim \rho^{*1/2}. \tag{5}$$

The reason for this unexpected behavior is that, during a collision, only forces prependicular to the molecular axis act on a smooth hard line. As a simple approximation for the rate of change of the correlation function of the longitudinal velocity, $C_\parallel(t) \equiv \langle v_\parallel(0) v_\parallel(t)\rangle$, we may write

$$\dot{C}_\parallel(t) = -\gamma \langle \sin^2\theta(t)\rangle C_\parallel(t), \tag{6}$$

where $\theta(t)$ is the angle over which the rod has rotated since $t = 0$. The "friction constant" γ is proportional to the collision frequency, and hence to ρ^*. From Eq. (6) it follows that in the kinetic regime ($t < \Gamma^{-1}$), $C_\parallel(t) \sim \exp(-\gamma\langle\omega^2\rangle t^3/3)$, where $\langle\omega^2\rangle$ is the mean square rotation frequency of the rods. In the rotational diffusion regime ($\Gamma^{-1} \ll t \ll D_r^{-1}$), $C_\parallel(t)$ decays as $\exp(-2\gamma D_r t^2)$, and for $t \gg D_r^{-1}$, it should decay as $\exp(-2/3\gamma t)$. At high densities, the correlation function should become predominantly Gaussian, and hence $D_\parallel \approx (\pi/2\gamma D_r)^{1/2} \sim \rho^{*1/2}$.

The algorithm that we used to solve the equations of motion for the hard-line fluid is rather different from the conventional MD procedures for hard-core systems,[6] and will be described in Ref. 1. Suffice it to say that the method is exact, yet not prohibitively time consuming. Runs were done on a 100-particle system at densities $\rho^* = 1$, 2, 4, and 8, and on a 500-particle system for $\rho^* = 16$, 24, 32, and 48. Periodic boundary conditions were used. All runs were 20 000 collisions long. The estimated noise in the computed (single-particle) correlation functions is (1–2)%. At all densities studied autocorrelation functions (ACF's) of the molecular center-of-mass velocity $\langle \vec{v}(\tau) \cdot \vec{v}(\tau + t)\rangle$ {decomposed into components parallel $[C_\parallel(t)]$ and perpendicular $[C_\perp(t)]$ to the molecu-

TABLE I. Density dependence of computed collision frequency (Γ), longitudinal and transverse diffusion constants ($D_\parallel$ and $D_\perp$), and the decay times of the correlation functions of angular momentum (τ_J), $C_1(t)$ (τ_1), and $C_2(t)$ (τ_2).

ρ^*	Γ	$D_\parallel$	$D_\perp$	τ_J	τ_1	τ_2
1	1.24	2.59	2.30	1.69	0.12	0.49
2	2.44	1.37	1.05	0.93	0.14	0.30
4	4.89	0.82	0.51	0.44	0.21	0.22
6	7.24	0.60	0.36	0.31	0.25	0.17
8	9.99	0.53	0.25	0.20	0.30	0.18
16	19.8	0.50	0.11	0.088	0.51	0.23
24	30.2	0.49	0.073	0.058	0.73	0.36
32	40.0	0.50	0.049	0.039	0.93	0.36
48	61.5	0.76	0.021	0.021	1.54	0.56

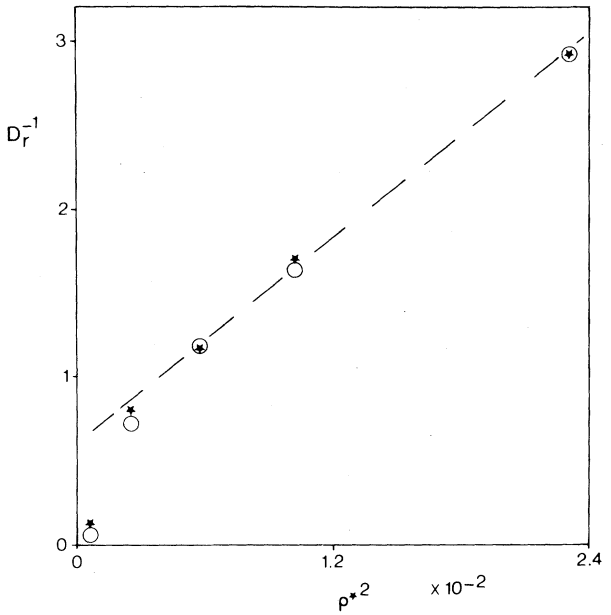

FIG. 1. Inverse rotational diffusion constant (D_r^{-1}) vs the square of the reduced density (ρ^{*2}). D_r was obtained with use of Eq. (7) on $C_1(t)$ (circles) and on $C_2(t)$ (stars). The dashed line is a best fit to the high-density points.

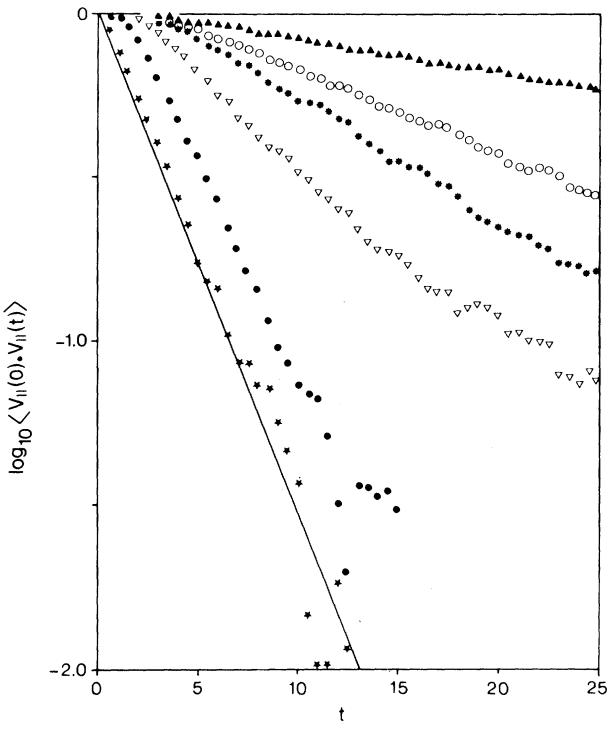

FIG. 2. $\ln C_{\parallel}(t)$ vs t. t is expressed in mean collision times. Stars, $\rho^*=1$; solid circles, $\rho^*=8$; open triangles, $\rho^*=16$; asterisks, $\rho^*=24$; open circles, $\rho^*=32$; solid triangles, $\rho^*=48$.

lar orientation} at time τ were computed, as well as the ACF's of the molecular angular momentum $[C_J(t) \equiv \langle \vec{J}(0)\cdot\vec{J}(t)\rangle]$. In addition, we computed the orientational correlation function $C_1(t) \equiv \langle P_1[\vec{u}(0)\cdot\vec{u}(t)]\rangle$ and $C_2(t) \equiv \langle P_2[\vec{u}(0)\cdot\vec{u}(t)]\rangle$, where $\vec{u}(t)$ is the molecular orientation at time t and P_l is the lth Legendre polynomial. All correlations were studied out to 25 collision times. Table I contains a summary of the transport properties obtained from the MD simulation. Tabulated are the collision frequency Γ, the diffusion constants $D_{\parallel}$ (see below) and $D_{\perp}$, the decay time τ_J $[\equiv \int_0^\infty C_J(t)\,dt/C_J(0)]$, and the orientational correlation times τ_1 and τ_2 $[\equiv \int_0^\infty C_l(t)\,dt,\ l=1,2]$.

At low densities ($\rho^*<8$), the velocity and angular momentum ACF's decay exponentially with a slope that agrees well with the Enskog predictions. At these densities, the orientational correlation functions closely follow the behavior predicted by a J-diffusion model (with a "correlation frequency" equal to $1/\tau_J^{\text{Enskog}}$).[1-3] At high densities, all correlation functions show marked deviations from the Enskog (or J-diffusion) predictions. With increasing density, the decay of $C_J(t)$ and $C_{\perp}(t)$ becomes faster than exponential, and for $\rho^*>30$ both ACF's develop a negative minimum after about six collision times ($6\tau_{BC}$). $C_1(t)$ and $C_2(t)$ decay exponentially at high ρ^*; from the slopes of these exponential correlation functions we determined the effective rotational diffusion constant D_r, using the relation

$$\frac{d}{dt}\ln C_l(t) = -l(l+1)D_r \quad (l=1,2). \tag{7}$$

Figure 1 shows a plot of D_r^{-1} vs ρ^{*2}. Clearly, at densities $\rho^*>8$, the (modified) Doi-Edwards prediction [Eq. (4a)] is in good agreement with the observed density dependence of D_r. Figure 2 shows the time dependence of $\ln[C_{\parallel}(t)]$. Several points should be noted. First of all, the initial slope of $\ln[C_{\parallel}(t)]$ is very flat; in fact, it follows the predicted t^3 dependence. One should also note the dramatic positive departures from the Enskog predictions; for $\rho^*>24$, $v_{\parallel}$ persists for much longer than $25\tau_{BC}$. The criteria formulated below Eq. (6) predict predominantly Gaussian behavior of $C_{\parallel}(t)$ for $\Gamma^{-1} \ll t \ll D_r^{-1}$. For densities $\rho^*=32$ and 48, $D_r^{-1} > 25\tau_{BC}$. At these densities one might, therefore, hope to observe Gaussian decay of $C_{\parallel}(t)$ in Fig. 2. Inspection of Fig. 2 suggests that the decay of $C_{\parallel}(t)$ is, in fact, simply exponential, but when $\ln[C_{\parallel}(t)]$ is plotted versus t^2, it is found that the high-density data are fitted

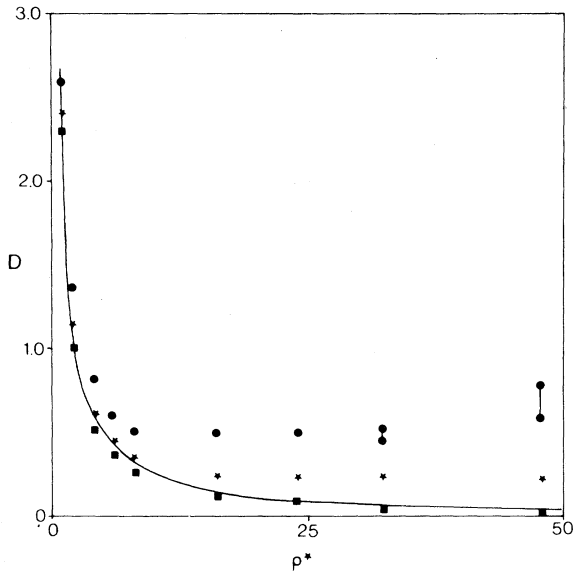

FIG. 3. $D_{\parallel}$ (circles), $D_{\perp}$ (squares), and $\mathrm{Tr}D = (2D_{\perp} + D_{\parallel})/3$ (stars) vs reduced density. For $\rho^* = 32$ and 48, two values for $D_{\parallel}$ are shown; the lower value is based on a Gaussian extrapolation, the higher one on an exponential extrapolation (see text). The solid curve is the Enskog prediction [Eq. (1)].

equally well by a Gaussian. On the basis of the present results we are unable to eliminate either possibility. The diffusion constants $D_{\parallel}$ and $D_{\perp}$ were obtained from the integrals of $C_{\parallel}(t)$ and $C_{\perp}(t)$. In order to perform the integral of $C_{\parallel}(t)$ for $\rho^* > 24$, we extrapolated $C_{\parallel}(t)$ for $t > 25\tau_{BC}$. Both Gaussian and exponential extrapolations were used. It is seen in Fig. 3 that, irrespective of the nature of the extrapolation, $D_{\parallel}$ increases with increasing ρ^* for $\rho > 24$. The corresponding Enskog predictions are shown for the sake of comparison. Figure 3 strongly suggests that $D_{\parallel}$ diverges as $\rho^* \to \infty$. On the basis of the present data we are, however, unable to confirm or reject the $\rho^{*1/2}$ dependence predicted by Eq. (5). As well as providing an unambiguous test of the limiting theories referred to in this Letter, the MD data should prove useful in the development and testing of any further unified theory of transport processes in fluids of strongly anisotropic molecules.

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