Accuracy of Enskog theory for rotational versus translational motion: A molecular-dynamics study

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Molecular-dynamics simulations of fluids composed of hard ellipsoids yield translational diffusional coefficients that deviate from the predictions of kinetic theory in the same way, but to a greater degree than, those of hard spheres. Surprisingly, however, the rotational diffusion coefficients are closely predicted by Enskog theory for all but the highest densities. However, for both motions, even at zero density, there are small deviations from kinetic theory, presumably due to chattering recollisions. Though the phase diagram is approximately symmetric between prolate and oblate ellipsoids of the same asymmetry, the dynamical properties are not. No existing theory explains these observations.

The utility of the hard-core fluid as a model for both the structural and dynamical properties of real fluids is well established.[1] Molecular-dynamics (MD) and theoretical studies of hard spheres have been extensively pursued,[1-3] but only recently, thanks to advances in computer technology and the development of efficient overlap criteria, has the simulation of the dynamical properties of anisotropic hard-core fluids become feasible.[4,5] These studies are desirable because most liquids are, in fact, composed of anisotropic molecules, and though one might expect the translational properties of spherical and anisotropic molecules to be rather similar, the latter exhibit rotational behavior not found in spherical molecules. The motivation for studying hard ellipsoids for the purpose of modeling fluids of anisotropic molecules is similar to that for studying hard spheres to model fluids composed of spherical molecules: A reduction in the number of parameters that allows one to focus on the geometric effects, which are thought to dominate molecular dynamics in condensed phases. Of course there is no unique choice for the shape of the hard-core particle used to represent the molecular fluid: The ellipsoid is a simple and convenient choice for which overlap criteria have been developed.

The observed deviations of the transitional diffusion constant of the hard-sphere fluid from the Enskog values has prompted many theoretical studies.[2,3] Physically, the deviations are thought of as arising from two competing effects. At medium densities momentum feedback (also known as the hydrodynamic shear mode or vortex flow[6]), which enhances the forward motion, is dominant, while at higher densities caging or correlated backscattering is responsible for retarding the motion of the tagged particle.

In this Rapid Communication we present the results of extensive MD simulations for both the rotational D_R and translational D_T diffusion constants of the hard-ellipsoidal fluid. The variation of the translational diffusion constant relative to the Enskog prediction D_T^E is qualitatively similar for both hard spheres and hard ellipsoids; even at low densities appreciable deviations from the result predicted by the Enskog kinetic theory are observed, the deviations increasing with increasing asphericity (see Fig. 1). But our most striking result is that except for a small deviation, which persists even in the zero-density limit, the computed rotational diffusion constant is in almost quantitative agreement with the Enskog theory D_R^E up to densities of about $\rho^* = 0.5$. [$\rho^* = \rho/\rho_0$ is the density relative to closest packing (see below for a definition of this quantity).] This suggests that correlated recollisions have a much weaker effect for rotational than for translational phenomena (see Fig. 2).

The fact that in the zero-density limit $D_T/D_T^E < 1$ and $D_R/D_R^E > 1$ is interesting and probably arises from chattering; indeed such deviations are predicted by an extended Enskog theory.[7] Chattering is favored for particles with a large asphericity and a low moment of inertia (i.e., when the mass is concentrated near the molecular center). Such molecules rotate more rapidly than they translate and can therefore collide more than once before moving apart. In accord with these ideas, note that the zero-density limits of D_T/D_T^E and D_R/D_R^E deviate most
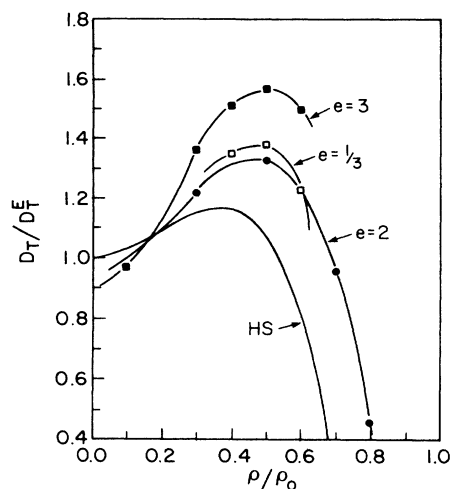
FIG. 1. Ratio of the hard-ellipsoid translational diffusion constant calculated by MD simulation ($N = 125$) D_T to the Enskog kinetic theory value D_T^E as a function of density relative to the density of closest packing. Hard-sphere results (for $N = 108$) (Ref. 2) are shown fitted by a smooth curve. Filled squares represent $e = 3$, filled circles represent $e = 2$, and open squares represent $e = \frac{1}{3}$ (oblate). The solid lines are drawn as a guide for the eye only.

markedly from 1 for the $e = 3$ ellipsoid fluid (see Figs. 1 and 2).

At densities above $\rho^* = 0.5$ both D_R/D_R^E and D_T/D_T^E falloff precipitously with increasing density even though there is no associated phase transition. [For $e = 2$ there is no stable nematic phase and the fluid-solid transition occurs at around $\rho^* = 0.85$, while for $e = 3$ the isotropic phase becomes less stable than the nematic at $\rho^* = 0.65$
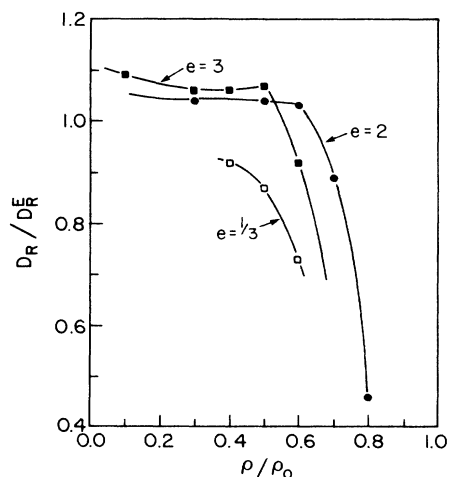

FIG. 2. Ratio of the hard-ellipsoid rotational diffusion constant calculated by MD simulation ($N = 125$) D_R to the Enskog kinetic theory value D_R^E as a function of density relative to the density of closest packing. Filled squares represent $e = 3$, filled circles represent $e = 2$, and open squares represent $e = \frac{1}{3}$ (oblate). The solid lines are drawn as a guide for the eye only.

(Ref. 8); we do not exceed these densities.]

Still another surprising property revealed by our simulations is that though the hard-ellipsoidal phase diagram is remarkably symmetric under the transformation between prolate and oblate ellipsoids of the same asymmetry,[8] our results indicate that this transformation symmetry does not extend to the dynamical properties.

At moderate ρ, one might attribute the greater increase of D_T/D_T^E for greater asphericity to the fact that caging, which causes the high-density decrease in this ratio, may, as indicated by kinetic theory,[9] be less effective for anisometric than for spherical molecules. However, it is not obvious why at intermediate densities where D_T/D_T^E is significantly enhanced, D_R should remain close to its Enskog value. It should be noted that very large positive deviations from kinetic theory have been found in systems of extremely prolate molecules (needles), where both caging and momentum feedback are effectively eliminated by topological constraints.[10] Although we do not yet have quantitative explanations for any of these newly observed phenomena, we believe that our results will be useful in the development of an understanding of the molecular motions in liquids.

For completeness we now present some technical details of the molecular dynamics simulations. Each hard ellipsoid of revolution has a $D_{\infty h}$ axis of length $2a$ and two perpendicular axes of length $2b$. In all but one simulation the mass of each ellipsoid is assumed to be evenly distributed throughout the body and the moment of inertia is evaluated accordingly (see below). Since we assume that the ellipsoids are smooth, there is no mechanism for the transfer of angular momentum to or from the $D_{\infty h}$ axis; accordingly this component is set to zero. A detailed description of the simulation algorithm will be presented elsewhere;[11] here we give a brief summary. Between collisions the particles translate and rotate freely. At the moment of contact of two ellipsoidal surfaces the collision dynamics are implemented on the basis of conservation of energy and of linear and angular momentum. The temperature is fixed at $k_B T = 1$, where k_B is Boltzmann's constant. Our unit of length is $l = (8ab^2)^{1/3}$, and densities are expressed relative to the density of closest packing $\rho^* = \rho/\rho_0$, here $\rho_0 = \sqrt{2}/l^3$. All of the simulations were performed in the conventional microcanonical ensemble in a truncated octahedral cell with periodic boundary conditions. Two system sizes were used: The majority of runs were for $N = 125$, although two checks of size dependence were made with $N = 512$. The translational and rotational diffusion constants were obtained by integrating the appropriate time-correlation functions:

$$D_T = \frac{1}{3} \int_0^\infty \langle v(t) \cdot v(0) \rangle dt ,$$

$$D_R = \frac{1}{2} \int_0^\infty \langle \omega(t) \cdot \omega(0) \rangle dt ,$$

where v and ω are the linear and angular velocities, respectively, and angular brackets denote an equilibrium ensemble average. As a check, the translational diffusion constant was also evaluated from the Einstein relation for the mean-squared displacement at long times $\langle \Delta r(t)^2 \rangle = 6 D_T t$. The length of each simulation was around

0.75×10^6 collisions, and all of this information was used in evaluating the transport coefficients (see Table I).

Enskog values for the transport coefficients are usually expressed[12] as averages of geometric functions for a contact pair of ellipsoids, and these averages were also obtained from the simulation. The details of these calculations will be reported elsewhere. Here we simply note that values precise enough for our purposes were obtained by averaging over a few hundred thousand collisions.

As a check on the correct functioning of the analysis programs a simulation for the almost spherical case $a/b \equiv e = 1.1$ at $\rho^* = 0.5$ ($N = 125$) was performed. Our value of $D_T/D_T^E = 1.05$ compares favorably with the hard-sphere value $D_T/D_T^E = 1.06$ ($N = 108$).[2]

In order to investigate the effect of mass distribution on the diffusion constants we performed one simulation for $e = 3$ at $\rho^* = 0.5$ with a moment of inertia four times larger than usual. Physically this corresponds to concentrating the mass equally at the two-ellipsoid foci and would be a reasonable choice for a diatomic molecule. The ratio of the translational diffusion constant to its Enskog value is virtually unchanged by this substitution, while the simulated rotational diffusion constant is even closer to the Enskog value.

From the two larger system ($N = 512$) simulations we observe, in accord with the hard sphere results, that the translational diffusion constant is quite sensitive to system size. A larger system favors the hydrodynamic shear mode and hence further increases D_T/D_T^E. Note that in the figures we display results for $N = 125$, we have not attempted to extrapolate to the infinite system. For comparison, in the transitional case we show results obtained with $N = 108$ hard spheres.[2] The rotational diffusion constants are much less sensitive to system size.

TABLE I. Translational D_T and rotational D_R diffusion constants relative to the Enskog kinetic theory predictions for the hard-ellipsoid fluid. e is the axial ratio and ρ is the density expressed relative to the close-packed density $\rho_0 = \sqrt{2}/l^3$. All results are for $N = 125$ except for those marked with footnote b.

e	ρ/ρ_0	D_T/D_T^E	D_R/D_R^E
3	0.1	0.97	1.09
3	0.3	1.36	1.06
3	0.4	1.51	1.06
3	0.5	1.57	1.07
3[a]	0.5	1.55	1.00
3	0.6	1.50	0.92
3[b]	0.6	1.65	0.89
2	0.3	1.22	1.04
2	0.5	1.33	1.04
2	0.6	1.23	1.03
2[b]	0.6	1.32	1.01
2	0.7	0.96	0.89
2	0.8	0.46	0.46
$\frac{1}{3}$	0.4	1.35	0.92
$\frac{1}{3}$	0.5	1.38	0.87
$\frac{1}{3}$	0.6	1.23	0.73

[a]Increased moment of inertia (see text).
[b]Results for $N = 512$.

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