Molecular hydrodynamics of the partially rough sphere fluid[a)]

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Molecular hydrodynamics is used to theoretically describe recent computer experiments on rough and partially rough sphere fluids. Agreement with the experimental translational and rotational diffusion coefficients may be obtained when the macroscopic boundary conditions of the hydrodynamics are made to depend on the microscopic boundary conditions of the collision dynamics. An attempt to extend the treatment to a self-consistent theory of the linear and angular velocity correlation functions (VCF and AVCF) fails, due to the unphysical short time behavior of the hydrodynamic VCF. The hydrodynamic AVCF appears to reproduce the structure due to changes in microscopic roughness, although quantitative agreement is not found at all densities. The long time behavior of the hydrodynamic AVCF is discussed.

I. INTRODUCTION

Hydrodynamics has been resurrected to explain various molecular relaxation processes in liquids ranging from translational diffusion coefficients to the full time dependence of the velocity autocorrelation functions—including long time tails. It is remarkable that hydrodynamic models can be applied with great accuracy to problems involving molecular motion. It is impossible to ignore the evidence for this—evidence that comes from several quarters.

Several years ago Alder *et al.*,[1] using computer experiments, have shown that the translational friction coefficient ζ_T of a sphere in a one component smooth hard sphere fluid is $\zeta_T = 4\pi\eta a$, where η is the shear viscosity and a is the radius of the sphere. This result is identical to Stokes' calculation of ζ_T for a sphere with slip boundary conditions in a continuum fluid. More recently, Levesque *et al.*[2] have shown that this hydrodynamic model with slip boundary conditions also describes their computer experiments on Lennard-Jones fluids.

The success of hydrodynamics does not stop with the determination of static friction constants. Several years ago Zwanzig and Bixon[3] calculated the normalized velocity correlation function

$$C_v(t) \equiv \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle v^2 \rangle \tag{1.1}$$

by solving the Navier–Stokes equation in the low Reynolds number limit for a particle executing nonuniform translatory motion in a compressible viscoelastic continuum fluid with boundary conditions intermediate between pure stick and pure slip boundary conditions. This model has the characteristic that at long times the correlation function $C_v(t)$ decays asymptotically as $t^{-3/2}$—a result in general agreement with the long time tails observed by Alder *et al.*[1] in their studies of the smooth hard sphere fluid. Recently, Levesque *et al.*[2] have shown that this hydrodynamic model gives very good agreement with their computer experiments on Lennard-Jones fluids only if two conditions are met. Slip boundary conditions must be used. More importantly, simple viscoelastic models do not suffice. Instead, it was necessary to determine the frequency dependence of the shear and bulk viscosity from computer experiments and to use these in the Zwanzig–Bixon theory.

It would appear from the foregoing that the details of the intermolecular potential are not important, except insofar as these details effect the value of the viscosity.

Given the success of molecular hydrodynamics when applied to translatory motions it is interesting to test its usefulness when applied to rotational motions. A variation principle has been used by Zwanzig and Hu[4] to calculate the rotational friction coefficient of a uniformly rotating slippery spheroid and have shown that this can differ from the friction coefficient of a sticky spheroid by as much as an order of magnitude or more. These calculations are in excellent agreement with rotational diffusion coefficients determined in recent depolarized light scattering experiments.[5] Thus, it would appear that simple hydrodynamic models give an accurate description of the rotational reorientations of structured molecules.

Several questions remain unanswered. Can molecular hydrodynamics simultaneously give correct translational and rotational correlation functions for the same system? How are the hydrodynamic boundary conditions related to the intermolecular potential? Why are small polyatomic molecules best described by hydrodynamic models with slip boundary conditions?

The simplest fluid that has translational and rotational degrees of freedom is the rough sphere fluid. In recent years we have extensively studied this fluid by computer experiment.[6] A collision between two rough spheres gives rise to a very strong interchange between translational and rotational energy. In grazing collisions between two smooth spheres there is no scattering, whereas in grazing collisions between two rough spheres there can be a large deflection angle. In kinetic theory rough spheres are the "roughest" possible objects with spherical symmetry. In this paper we show that despite their microscopic roughness these spheres are best described by a hydrodynamic model in which the boundary conditions are much closer to pure slip than pure stick boundary conditions.

Recently, we have generalized the rough sphere model

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TABLE I. Comparison of theory and experiment for the translational and rotational diffusion coefficients as a function of roughness.

λ	D_T(exp)	D_R(exp)	β	η_H	η_E	η_H/η_E	$\bar{\eta}$	$\eta_H/\bar{\eta}$	$D_{T,E}$	$D_T/D_{T,E}$	$D_{R,E}$	$D_R/D_{R,E}$
1.0	0.686	7.18	0.0175	0.113	0.0603	1.87	0.113	1.0	1.17	0.59	5.25	1.37
0.75	0.822	9.27	0.0135	0.0946	0.0559	1.69	0.101	0.94	1.24	0.67	7.00	1.32
0.5	0.903	13.3	0.00930	0.0867	0.0515	1.68	0.0884	0.98	1.32	0.69	10.5	1.26
0.25	1.04	26.1	0.00467	0.0759	0.0471	1.61	0.0760	0.99	1.40	0.74	21.0	1.24
0.1	1.12	58.1	0.00207	0.0702	0.0445	1.59	0.0686	1.03	1.46	0.77	52.5	1.11
0	1.25	∞	0	0.0637	0.0427	1.49	0.0637	1.0	1.50	0.83	∞	...

$$\eta_E(\lambda) = \lambda\eta_E(\text{rough}) + (1-\lambda)\eta_E(\text{smooth})$$

$$\bar{\eta}(\lambda) = \lambda\eta_H(\text{rough}) + (1-\lambda)\eta_H(\text{smooth})$$

The results of Table I are in the units $m = R = t_C = 1$ used in the molecular dynamics calculations, where m is the particle mass, R is the particle radius, and t_C is the mean collision time.

to cases intermediate between smooth and rough spheres.[7] In this generalization there is a natural parameter $0 \leq \lambda \leq 1$ that emerges, where $\lambda = 0$ corresponds to smooth spheres whereas $\lambda = 1$ corresponds to rough spheres. Pangali and Berne[8] have recently reported molecular dynamics calculations of the translational and rotational diffusion coefficients and time correlation functions in partially rough fluids.

Using molecular hydrodynamics we find these diffusion coefficients and correlation functions theoretically for spheres which are hydrodynamically partially slippery and compare these results with the molecular dynamics data.

An attempt to apply hydrodynamics to a self-consistent calculation of the linear and angular velocity correlation function fails, due to the unphysical initial decay of the hydrodynamic velocity correlation function. The hydrodynamic angular velocity function is compared with the molecular dynamics data with partial success.

II. GENERALIZED STOKES EINSTEIN RELATIONS

Using the rough domain model of partially rough spheres Pangali and Berne[8] have found the translational and rotational diffusion coefficients for different values of the roughness parameter λ from molecular dynamics. From hydrodynamics the diffusion coefficients may be calculated theoretically as a function of the degree of slip the fluid experiences tangential to the surface of the test particle. The hydrodynamic theory will now be compared with experiment, paying particular attention to the correspondence between the microscopic boundary conditions of the molecular dynamics experiment and the macroscopic boundary conditions of the hydrodynamics.

As discussed in previous work[9,12] the static friction coefficients for rotation and translation in a viscous fluid with arbitrary slip boundary conditions on the surface of the sphere may be found by a standard hydrodynamic calculation. Using the well-known Einstein relations the translational diffusion coefficient D_T and rotational diffusion coefficient D_R for a spherical test particle are found to be

$$D_T = \frac{kT}{6\pi\eta R}\left(\frac{1+3\eta/\beta}{1+2\eta/\beta}\right),$$

$$D_R = \frac{kT}{8\pi\eta R^3}\left(1+\frac{3\eta}{\beta}\right), \tag{2.1}$$

where T is the absolute temperature, k is Boltzmann's constant, η is the shear viscosity, and R is the radius of the test particle. β, the hydrodynamic slip coefficient, is defined by the boundary condition

$$F_\perp = (\beta/R)(v_\perp^{\text{fluid}} - v_\perp^{\text{particle}}) \tag{2.2}$$

relating the tangential component of the drag force exerted on the test particle by the fluid to the relative tangential velocity of the fluid with respect to the particle. The limits $\beta \to \infty$ and $\beta \to 0$ correspond to perfect stick and slip, respectively. Note that Eq. (2.2) is applied to both the translational and rotational problems.

Using the well-known Kubo relations for the translational and rotational diffusion coefficients

$$\begin{aligned} D_T &= \frac{1}{3}\int_0^\infty dt\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle, \\ D_R &= \frac{1}{3}\int_0^\infty dt\langle \omega(0)\cdot\omega(t)\rangle \end{aligned} \tag{2.3}$$

we have obtained D_T and D_R from the molecular dynamics data. These results are given in Table I. Note that no tail or $1/N$ corrections have been applied to the data.

Equations (2.1) were used to extract η and β from the experimental diffusion coefficients and these are reported in Table I as a function of the roughness parameter λ. While we have no theory of the slip coefficient β, Pangali and Berne[8] have found the Enskog shear viscosity for the rough domain model to be

$$\eta_E(\lambda) = \lambda\eta_E(\text{rough}) + (1-\lambda)\eta_E(\text{smooth}). \tag{2.4}$$

This result follows directly from the assumption of uncorrelated binary collisions in the Enskog theory. The Enskog results for rough and smooth spheres are well known[11] and Eq. (2.4) may be compared with the values η_H obtained from the hydrodynamic theory as done in Table I. For smooth spheres η/η_E has been found by Alder, Gass, and Wainwright[1] and our result for $\lambda = 1$ is in excellent agreement with theirs. Since the Enskog viscosity η_E deviates rather significantly from the true viscosity η at the density considered here, we have also compared the viscosity η_H, calculated from hydrodynamics, with

TABLE II. Analysis of diffusion coefficients for mixture.

	Test particles	Bath particles
D_T	0.299	0.737
D_R	0.341	5.58
η	0.104	0.104
β	0.051	0.023
	$M_{\text{test}} = 8M_{\text{bath}}$,	$R_{\text{test}} = 2R_{\text{bath}}$

The results of Table II are in the units $m_{\text{bath}} = R_{\text{bath}} = t_c = 1$ used in the molecular dynamics calculations, where m_{bath} is the bath particle mass, R_{bath} is the bath particle radius, and t_c here is the mean collision time between bath particles.

$$\bar{\eta}(\lambda) = \lambda\eta_H(\text{rough}) + (1-\lambda)\eta_H(\text{smooth}) \tag{2.5}$$

for intermediate values of λ. Table I shows excellent agreement in this case, supporting our argument that the translational and rotational diffusion coefficients in the partially rough sphere fluid are well described by a hydrodynamic theory with slip boundary conditions. This point could be further clarified by a nonequilibrium molecular dynamics calculation of the shear viscosity such as those recently done by Ashurst and Hoover[11] and Gosling *et al.*[13]

It is clear that the hydrodynamic slip boundary condition corresponds to perfect smoothness dynamically, as in this limit the angular velocity of the test particle is conserved and thus the rotational diffusion coefficient is infinite. It was, however, quite unexpected to find that a completely rough sphere is hydrodynamically very slippery (see Table I), with $\beta = 0.0175$. An explanation of this has been recently offered by Hynes, Kapral, and Weinberg.[14] They suggest that even a completely rough sphere will be surrounded by a hydrodynamic boundary layer and the presence of this boundary layer will make the particle hydrodynamically slippery.

It is now clear that neat fluids of hard spheres (rough and smooth) are hydrodynamically slippery ($\beta \ll \infty$). This raises the interesting question of when, if ever, stick boundary conditions are appropriate in molecular hydrodynamics. It is well known that the diffusion of macromolecules obeys Stokes' law with stick boundary conditions. This and other considerations led Pangali and Berne to perform molecular dynamics experiments on binary mixtures of large and small rough spheres. Their results for the translational and rotational diffusion coefficients of the large (test) and small (bath) particles are given in Table II, along with the values of η and β found from the data using Eqs. (2.1). We have used the bath particle viscosity to find the test particle slip coefficient, as suggested by Brownian motion theory. Note that the value of the slip parameter is about twice that of the bath particle, supporting the conjecture that stick hydrodynamics is approached in the Brownian motion limit of a very large test particle.[14]

We close our discussion of diffusion coefficients with a brief comparison of the molecular dynamics results with the Enskog theory. It is well known that the Enskog diffusion coefficients may be expressed in terms of the correlation times (usually referred to as the Enskog correlation times) found from the exact collision dynamics, making the Enskog assumption of uncorrelated binary collisions. Using the results of Berne and Montgomery[7] for the Enskog correlation times in a fluid of partially rough spheres we find

$$\begin{aligned} D_{T,E} &= \frac{kT}{m}\tau_{V,E}(\lambda) \\ &= \frac{kT}{m}\frac{\kappa+1}{(1+\lambda)\kappa+1}\frac{3}{2}t_c\,, \\ D_{R,E} &= \frac{kT}{I}\tau_{\omega,E}(\lambda) \\ &= \frac{kT}{I}\frac{\kappa+1}{\lambda}\frac{3}{2}t_c\,, \end{aligned} \tag{2.6}$$

where m is the mass, I is the moment of inertia, and t_c is the mean time between collisions. The loading parameter κ is given by $\kappa = I/mR^2$, where R is the particle radius.

Table I shows systematic deviations of the molecular dynamics results from the Enskog theory. $D_T/D_{T,E}$ decreases monotonically with increasing λ, whereas $D_R/D_{R,E}$ is monotonically increasing. That D/D_E changes with λ in both cases indicates that the deviations from the Enskog theory are not due entirely to the structure of the fluid at high densities, as all our models have the same structure at a given density.

These results indicate the hydrodynamics can successfully describe the diffusion coefficients observed in rough, partially rough, and smooth spheres when the hydrodynamic boundary conditions are appropriately chosen. The usual Stokes law results (pure stick) will be in poor agreement, especially for the rotational diffusion coefficient.

III. TIME CORRELATION FUNCTIONS

In this section we return to the question of how the hydrodynamic boundary conditions depend on the microscopic surface roughness. Encouraged by the success of the hydrodynamic theory of the diffusion coefficients we turn to a consideration of the linear and angular velocity correlation functions (VCF and AVCF, respectively). Theoretical calculation of the VCF and AVCF from hydrodynamics requires knowledge of the frequency dependent translational and rotational friction coefficients for the motion of a spherical test particle in a viscoelastic, compressible fluid with arbitrary slip boundary conditions. The rotational friction coefficient is taken from our own work.[9] For translational motion the result of Zwanzig and Bixon[15] is used here. In our reduced units of the hydrodynamic penetration time $(\rho_s R^2/\eta)$ the Laplace transform of the Zwanzig–Bixon friction coefficient is

$$\zeta_T(p) = \frac{4\pi}{3}\eta R x^2\left[(1+x)Q + 2(1+x)P\right],$$

$$
\begin{aligned}
Q &= (3/\Delta)[3+3x+x^2+x^2(1+x)/(2+\beta/\eta)]\,, \qquad (3.1)\\
P &= (3/\Delta)(3+3y+y^2)\,,\\
\Delta &= 2x^2(3+3y+y^2)+y^2(3+3x+x^2)\\
&\quad +3[x^2(1+x)(y^2+2y+2)]/(2+\beta/\eta_s)\,,\\
x &= \sqrt{p}\,, \qquad y = p\left[\left(\frac{\rho_s cR}{\eta_s}\right)^2 + p\left(\frac{4}{3}+\frac{\eta_v}{\eta}\right)\right]^{-1/2}.
\end{aligned}
$$

The Laplace transform of the rotational friction coefficient is

$$\zeta_R(p) = 8\pi\eta R^3\left[\frac{1+\sqrt{p}+\frac{1}{3}p}{1+\sqrt{p}+(3\eta/\beta)(1+\sqrt{p}+\frac{1}{3}p)}\right]. \qquad (3.2)$$

These results are valid for a test particle in a compressible, viscous fluid with arbitrary slip boundaries. Viscoelasticity may be introduced by substituting the desired frequency dependent visocisities into the above results.

The normalized VCF and AVCF, denoted $C_v(t)$ and $C_\omega(t)$, respectively, are found making the usual hydrodynamic approximation to their Laplace transforms

$$
\begin{aligned}
\tilde{C}_v(s) &= \int_0^\infty dt\, e^{st} C_V(t)\\
&= [s+\zeta_T(s)/m]^{-1}\,, \qquad (3.3)\\
\tilde{C}_\omega(s) &= [s+\zeta_R(s)/I]^{-1}.
\end{aligned}
$$

In these expressions m is the test particle mass, I is the test particle moment of inertia, and s is the Laplace variable in units of frequency. The dimensionless Laplace variable p used above is related to s by $p = \rho_s R^2 s/\eta$.

The analytical calculation of the Laplace inverses of the VCF and AVCF is made very difficult by the complex branch point structure of Eqs. (3.1) and (3.2). It is, however, possible to examine analytically the limiting cases when $t \to 0$ and $t \to \infty$. The latter case will be dealt with first as the result is independent of the slip, compressibility, and viscoelasticity. By standard techniques one finds

$$
\left.
\begin{aligned}
C_v(t) &\sim \frac{\rho}{9\sqrt{\pi}\,\rho_s}\left(\frac{R^2}{\nu t}\right)^{3/2}\\
C_\omega(t) &\sim \frac{\kappa\rho}{24\sqrt{\pi}\,\rho_s}\left(\frac{R^2}{\nu t}\right)^{5/2}
\end{aligned}
\right\} \text{ as } t \to \infty\,. \qquad (3.4)
$$

If one replaces ν by $\nu + D_T$, the above results are in agreement with the predictions of generalized hydrodynamics[16] and kinetic theory[17] for the long time tails. The translational diffusion coefficient does not appear in our result because we have used the hydrodynamic friction on a stationary test particle rather than a translationally diffusing one.

The decay of the partially rough sphere VCF and AVCF at very short times can be calculated from binary collision dynamics[7] and is given by

$$
\begin{aligned}
C_V(t) &= 1-\frac{2}{3}\left[\frac{(1+\lambda)\kappa+1}{\kappa+1}\right]\frac{t}{t_c}+O(t^2)\,,\\
C_\omega(t) &= 1-\frac{2}{3}\left(\frac{\lambda}{\kappa+1}\right)\frac{t}{t_c}+O(t^2)\,.
\end{aligned} \qquad (3.5)
$$

TABLE III. Initial decay of various hydrodynamic models of the VCF and AVCF.

Model	VCF	AVCF
	Incompressible fluid	
Viscous, stick ($\beta = \infty$)	$\left(\frac{2\epsilon}{2\epsilon+1}\right)\left(1-\frac{18}{2\epsilon+1}\,\frac{\sqrt{t^*}}{\pi}\right)$	$1-\frac{4}{\kappa\epsilon\sqrt{\pi}}\sqrt{t^*}$
Viscous, slip ($0 \le \beta \le \infty$)	$\left(\frac{2\epsilon}{2\epsilon+1}\right)\left[1-\frac{9}{2\epsilon+1}\left(2+\frac{\beta}{\eta}\right)t^*\right]$	$1-\frac{2\beta}{\kappa\epsilon\eta}t^*$
	Compressible fluid	
Viscous, stick ($\beta = \infty$)	$1-\frac{1}{\epsilon}\left(\frac{2a+\sqrt{a}}{a}\right)\frac{2}{\sqrt{\pi}}\sqrt{t^*}$	$1-\frac{4}{\kappa\epsilon\sqrt{\pi}}\sqrt{t^*}$
Viscous, slip ($0 \le \beta < \infty$)	$1-\frac{1}{\epsilon}\left(\frac{2}{\sqrt{\pi}}\right)\frac{\sqrt{t^*}}{\sqrt{a}}$	$1-\frac{2\beta}{\kappa\epsilon\eta}t^*$
Viscoelastic, stick (Maxwell)	$1-\frac{1}{\epsilon}\,\frac{\sigma+2}{\sqrt{\gamma}}t^*$	$1-\frac{2}{\kappa\epsilon\sqrt{\gamma}}t^*$
Viscoelastic, slip (Maxwell)	$1-\frac{1}{\epsilon}\left(\frac{\sigma}{\sqrt{\gamma}}+\frac{1}{\sqrt{\gamma}+\eta/\beta}\right)t^*$	$1-\frac{2}{\kappa\epsilon(\sqrt{\gamma}+\eta/\beta)}t^*$
Viscoelastic, stick (Dahler)	$1-\frac{1}{\epsilon}\,\frac{2}{\sqrt{\pi}}\left(\frac{2b+\sqrt{b}}{b}\right)\sqrt{t^*}$	$1-\frac{4}{\kappa\epsilon\sqrt{\pi}}\sqrt{\frac{\gamma_2}{\gamma_1}}\sqrt{t^*}$
Viscoelastic, slip (Dahler)	$1-\frac{1}{\epsilon}\,\frac{2}{\sqrt{\pi}}\,\frac{\sqrt{t^*}}{\sqrt{b}}$	$1-\frac{2\beta}{\kappa\epsilon\eta}t^*$

$$t^* = \frac{\eta t}{\rho_s R^2}, \quad \kappa = \frac{I}{mR^2}, \quad \epsilon = \frac{\rho}{\rho_s}$$

$$a = \left[\frac{4}{3}+\frac{\eta_v}{\eta}\right]^{-1}, \quad b = \left[\frac{\gamma_2}{\gamma_1}\left(\frac{4}{3}+\frac{\eta_v}{\eta}\,\frac{\gamma_1}{\gamma_2}\,\frac{\gamma_{2v}}{\gamma_{1v}}\right)\right]-1$$

$$\sigma = \left[\frac{4}{3}+\frac{\eta_v}{\eta}\,\frac{\gamma}{\gamma_v}+\gamma\left(\frac{\rho cR}{\eta}\right)^2\right]^{1/2}$$

Following the approach of our previous work the short time expansions of the hydrodynamic VCF and AVCF were calculated for different boundary conditions and viscoelastic models. These results are given in Table III where the dependence of the initial decay on the details of the hydrodynamic description is clearly shown.

For completeness Table III includes the results obtained for the VCF in an incompressible fluid (infinite sound speed). As noted previously compressibility effects are unimportant for a sphere rotating in its own volume. In contrast, the initial value of the normalized VCF in an incompressible fluid is not unity; this point has been noted previously and is discussed at some length by Zwanzig and Bixon.[18]

To properly treat the high frequency response of the fluid the frequency dependence of the viscosity must be adequately described. The simplest viscoelastic model is the single relaxation time approximation due to Maxwell

$$\eta(p) = \frac{\eta}{1+\gamma p}\,, \qquad \eta_v(p) = \frac{\eta_v}{1+\gamma_v p}\,, \qquad (3.6)$$

where η and η_v are the shear and bulk viscosities, respectively. This model has been successfully used by Zwanzig and Bixon[3] to account for the negative region found in the VCF of liquid argon at high density. Note that in this model the viscosity goes to zero as frequency goes to infinity, indicating that the fluid cannot respond to a shear at infinite frequency. However, this is not so for a hard fluid, due to the impulsive nature of the forces. Binary collisions of hard spheres occur instantaneously. Wainwright[19] has shown in this case that

$\eta(t)$ has a term proportional to $\delta(t)$, which gives a finite viscosity at infinite frequency. Using a generalized moment expansion, Theodosopulu and Dahler[9] have found the frequency dependent shear and bulk viscosities in a rough sphere fluid from kinetic theory. Their results are

$$\eta(p)=\eta\left(\frac{1+\gamma_2 p}{1+\gamma_1 p}\right), \qquad \eta_v(p)=\eta_v\left(\frac{1+\gamma_{2v} p}{1+\gamma_{1v} p}\right), \tag{3.7}$$

with microscopic expressions for η, η_v, γ_1, γ_2, γ_{1v}, and γ_{2v}. We have calculated the initial decay of the VCF and AVCF using both viscoelastic models discussed above (see Table III).

It is, of course, true that at times shorter than several mean collision times the decay of the VCF and AVCF may not be hydrodynamic; it is due to uncorrelated binary collisions. Nevertheless, we felt it might be worthwhile to see if the entire time dependence of the VCF and AVCF could be described by a hydrodynamic theory with suitable parameter choices. Note that this would eliminate the Theodosopulu and Dahler viscoelastic model, as it does not give the correct functional form for the initial decay of the VCF. Indeed, any viscoelastic model which approaches a constant value as frequency tends to infinity as required in hard systems will give a functionally incorrect initial decay for the VCF. Thus, a rather fundamental inconsistency appears in the theory if hydrodynamics is required to be correct at short times.

A slightly different point of view has been taken by Hynes, Kapral, and Weinberg.[20] They consider only the stick boundary condition ($\beta \to \infty$) to be purely hydrodynamic, in contrast to the slip condition which they consider to be due to microscopic effects. In support of this point of view they cite the extensive kinetic literature on the slip boundary condition. They also suggest that for a consideration of translational motion the boundary condition on the normal component of the velocity field

$$v_{\parallel}^{\text{fluid}} - v_{\parallel}^{\text{particle}} = 0 \tag{3.8}$$

at the surface of the test particle (macroscopic impenetrability) must be generalized to account for microscopic effects. Presumably, if this is appropriately done, the VCF so found will have a linear initial decay.

Some light is shed on this question by an examination of the Zwanzig–Bixon theory. In the limit of an incompressible fluid ($c \to \infty$) one finds a VCF which has linear initial decay with partial slip (see Table III), indicating that the unphysical decay of the full Zwanzig–Bixon VCF is due to the longitudinal component of the velocity field, which is likely more profoundly affected by the boundary condition of Eq. (3.8) than the transverse component.

IV. COMPARISON WITH MOLECULAR DYNAMICS

We now make a comparison of the hydrodynamic AVCF with the molecular dynamics results of O'Dell and Berne[6] for rough spheres and of Pangali and Berne[8] for partially rough spheres. The expressions for the Laplace transforms of the VCF and AVCF are inverted numerically using a fast Fourier transform computer program. Using Eq. (3.7) for the frequency dependent viscosity and taking the slip coefficient β to give the exact initial decay an *ab initio* calculation of the AVCF may be performed, as suggested previously.[9] For completely rough spheres ($\lambda = 1$) the results are shown in Figs. 1 and 2, along with the molecular dynamics results of O'Dell and Berne, for densities $\hat{\rho} = 0.1$, 0.333, and 0.625 (relative to closest packed). The agreement is seen to be quite good at the lowest density, but worsens considerably as density increases. Similar results for low densities have been reported by Hynes, Kapral, and Weinberg.[20]

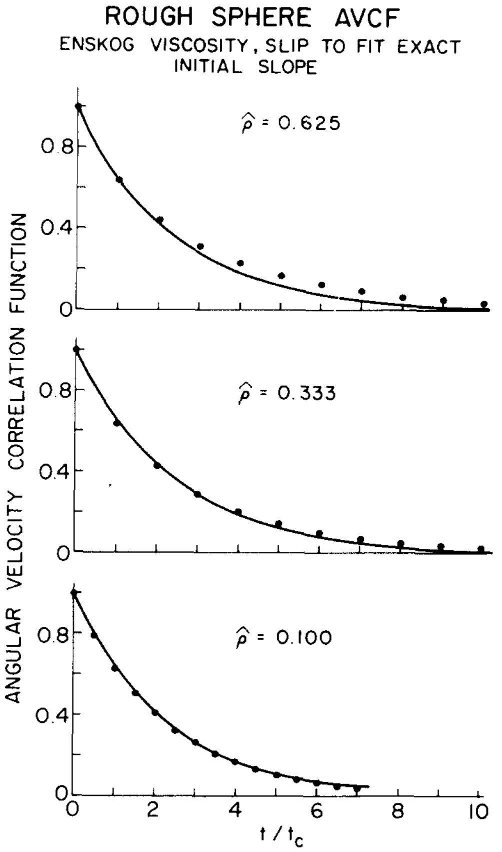

FIG. 1. Comparison of hydrodynamic theory and molecular dynamics for the rough sphere AVCF ($\lambda = 1$). The viscoelastic model of Eq. (3.7) and slip parameter β of Eq. (4.3) are used.

It is well known that Enskog transport coefficients have systematic errors at high densities.[1] We therefore made an exploration of the parameter space for the highest density case $\hat{\rho} = 0.625$ to check the dependence of our theory on the Enskog transport coefficients. Order of magnitude changes in the viscoelastic relaxation times produced no significant change in the agreement. A 50% decrease in the Enskog viscosity noticeably improved the agreement, whereas doubling the Enskog viscosity worsened agreement. This behavior seems anomalous to us as the Enskog viscosity in dense fluids of smooth spheres is known experimentally to be too small.[1] Our findings for the diffusion coefficients discussed above strongly suggest the same is true of the rough sphere fluid.

An examination of the AVCF on a logarithmic scale

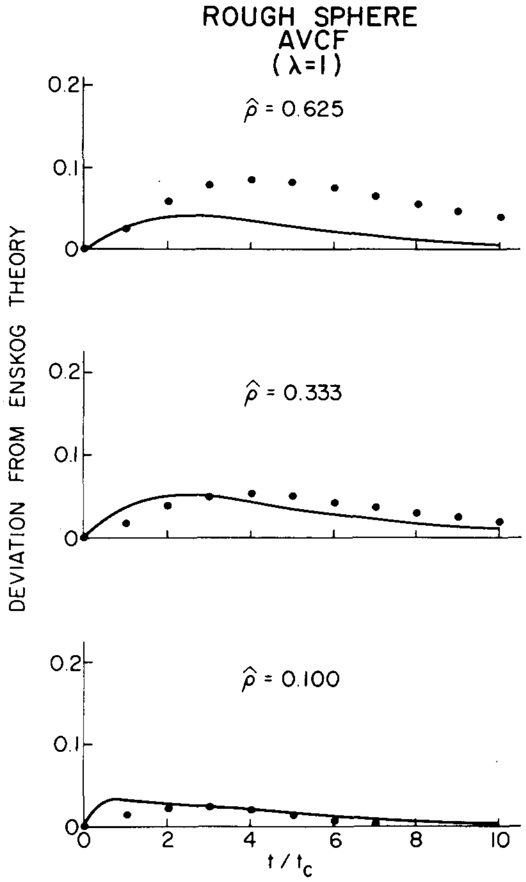

FIG. 2. The deviations of the hydrodynamic and molecular dynamics AVCF from the Enskog exponential are shown for rough spheres. The deviation plotted is defined as $C_\omega(t) - C_\omega^E(t)$, where the Enskog exponential $C_\omega^E(t)$ is defined by $C_\omega^E(t) = \exp - t/t_{\omega,E}$. $t_{\omega,E}$ is given in Eq. (2.6) of the text.

suggests that the functional form of the hydrodynamic theory is incorrect at high densities. The experimental data strongly suggest the short time behavior is given by a sum of two exponentials (see Fig. 3). Theoretically, such a result has been recently found by Yip[21] for the hard sphere VCF. The hydrodynamic theory, while showing deviations from exponential decay in Fig. 2, seems to have a dominant single exponential behavior at short times as shown in Fig. 3. One possibility is that a more general boundary condition than the slip condition of Eq. (2.2) is required at high densities. It is also possible that it is fundamentally incorrect to expect a hydrodynamic theory to be valid at short times.

To explore this latter possibility an attempt was made to fit the rough sphere AVCF at intermediate times (postinitial decay region) rather than the initial decay. In this calculation β and $C_\omega(0)$ were taken as adjustable parameters. Figure 4 shows that improved agreement can be obtained by this procedure.

It is of interest in connection with recent attempts[22] to observe the long time tail of the AVCF to determine at what times the hydrodynamic theory becomes asymptotic. Figure 5 shows $C_\omega(t)$ (calculated from parameters numerically optimized to fit the rough sphere AVCF at a density $\hat{\rho} = 0.333$) at long times plotted against $t^{-5/2}$. While a linear region is seen at relatively short times ($t \sim 10 t_c$), the correct asymptote of Eq. (3.4) is not approached until $t > 50 t_c$, as shown in the inset. This suggests that detection of the asymptotic region experimentally will be extremely difficult.

Pangali and Berne[8] have reported molecular dynamics results for partially rough (rough domain) spheres at a density of $\hat{\rho} = 0.625$. They have found that to a good approximation they scale on $t/\tau_\omega(\lambda)$, i.e., $C_\omega(\lambda, t) \cong C_\omega[t/\tau_\omega(\lambda)]$. Recall that

$$\frac{1}{\tau_\omega(\lambda)} = \frac{2\lambda}{3(\kappa+1)} \frac{1}{\tau_c}$$

$$= \lambda \frac{1}{\tau_\omega(\text{rough})} + (1 - \lambda \frac{1}{\tau_\omega(\text{smooth})} . \qquad (4.1)$$

We note that $1/\tau_\omega(\text{smooth}) = 0$ as angular velocity is conserved in completely smooth spheres. The hydrodynamic AVCF may be written as $C_\omega(\lambda, \beta, t) = C_\omega[\beta(\lambda),\ t/t_H(\lambda)]$. $t_H(\lambda)$ is the hydrodynamic penetration time $\rho_s R^2/\eta(\lambda)$ and depends on λ as

$$\frac{1}{t_H(\lambda)} = \lambda \frac{\eta(\text{smooth})}{\rho_s R^2} + (1 - \lambda) \frac{\eta(\text{rough})}{\rho_s R^2} . \qquad (4.2)$$

This has the same functional dependence on as λ as Eq. (4.1) above, but does not go to zero at $\lambda = 0$. It is, of

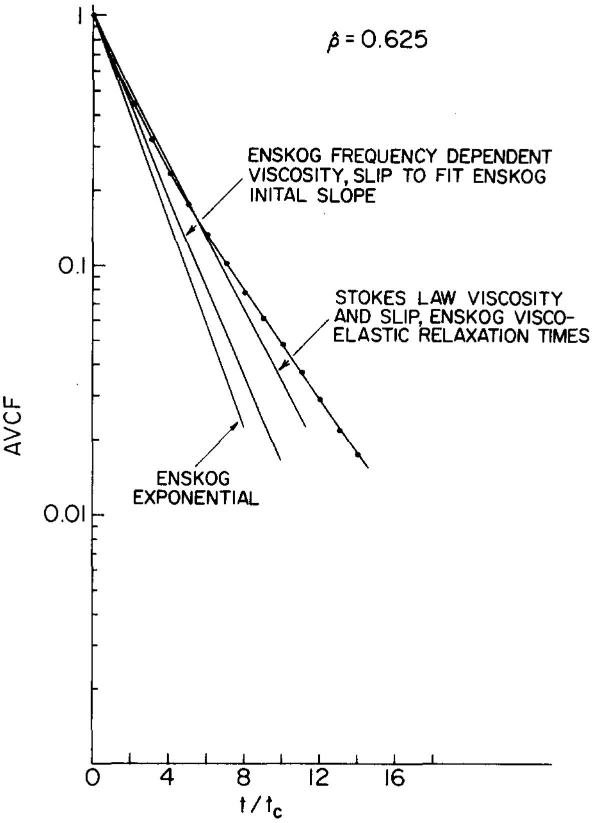

FIG. 3. A logarithmic plot of theory and experiment for the rough sphere AVCF. The molecular dynamics results are shown as data points connected by a smooth curve to emphasize the approximate separation of the data into two exponentials. Two hydrodynamic calculations are shown, one with the viscosity of Eq. (3.7) and the slip of Eq. (4.3) and the other using the Stokes law parameters given in Table I. The exact initial decay is given by the Enskog exponential.

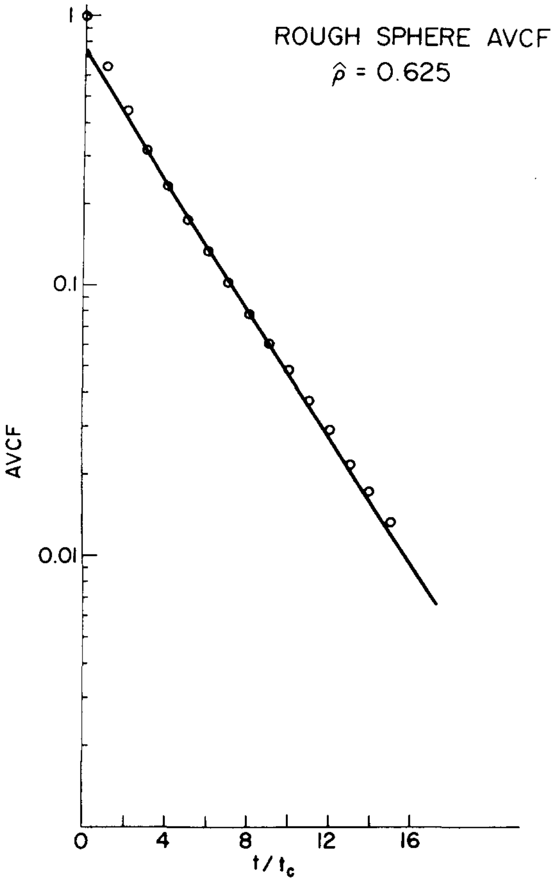

FIG. 4. A comparison of theory and experiment for the rough sphere AVCF when $C_\omega(0)$ and β are chosen to fit the post initial decay region.

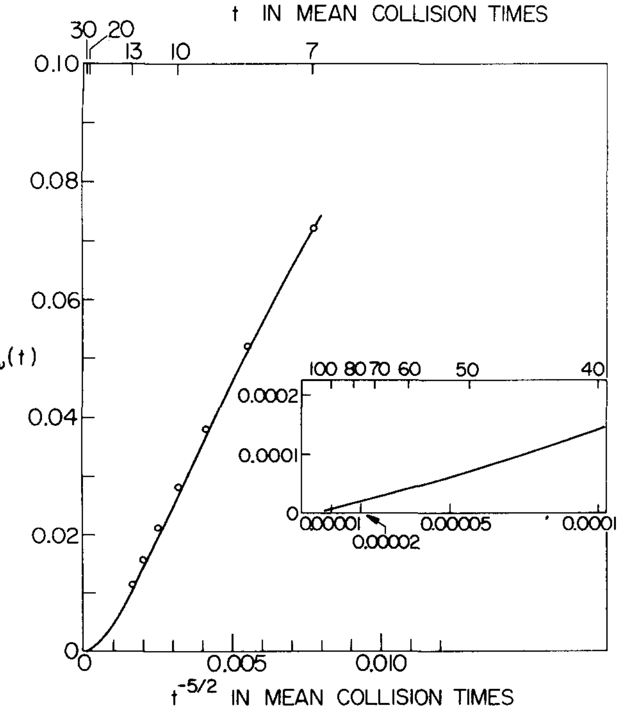

FIG. 5. The long time behavior of the hydrodynamic AVCF is shown. The theoretical AVCF was fit numerically to the experimental data (open circles) at a density $\hat{\rho}=0.333$ relative to closest packed. The inset shows the region in the vicinity of the origin where the true asymptotic behavior is observed.

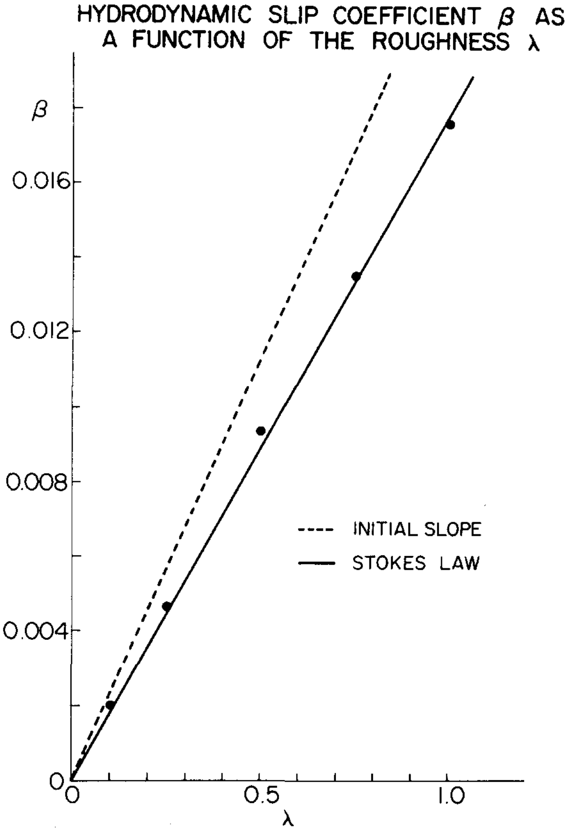

FIG. 6. The hydrodynamic slip coefficient β is shown as a function of the roughness parameter λ. The dashed line is taken from Eq. (4.3). The solid line is a fit to the data of Table I obtained from Stokes' law with slip. β is in the units $m=R=t_C=1$ used in the molecular dynamics calculations, where m is the particle mass, R is the particle radius, and t_C is the mean collision time. The density is 0.625 relative to closest packed.

course, necessary for $\beta(\lambda)$ to be zero to obtain the smooth sphere limit. If $\beta(\lambda)$ is chosen to give the exact initial decay of Eq. (3.5), we find in terms of $\tau_\omega(\lambda)$ given above

$$\beta=\frac{\kappa\rho_s R^2}{2}\frac{1}{\tau_\omega(\lambda)}$$
$$=\frac{\kappa\rho_s R^2}{3}\frac{\lambda}{\kappa+1}\frac{1}{\tau_c}\ . \tag{4.3}$$

This method of determining β is also used by Hynes, Kapral, and Weinberg[14,20] for completely rough spheres.

At fixed density β depends linearly on λ. Equation (4.3) above gives $\beta=0.0227\lambda$ for $\kappa=0.4$, $\hat{\rho}=0.625$, corresponding to the molecular dynamics experiment. The β values of Table II, determined from the experimental diffusion coefficients using Eq. (2.1), obey $\beta=0.0175\lambda$, in good agreement with Eq. (4.3). A plot of β as a function of λ is given in Fig. 6. We now compare the theoretical AVCF with the molecular dynamics results as a function of λ.

$\beta(\lambda)$ is taken from Eq. (4.3) to give the correct initial slope. Guided by Pangali and Berne,[8] the Enskog frequency dependent viscosity is taken to be

$$\eta(\lambda,p)=\eta(\lambda)\left[\frac{1+\gamma_2(\lambda)p}{1+\gamma_1(\lambda)p}\right], \tag{4.4}$$

$$\eta(\lambda) = \lambda\eta(\text{rough}) + (1-\lambda)\eta(\text{smooth}),$$
$$\gamma(\lambda) = \lambda\gamma(\text{rough}) + (1-\lambda)\gamma(\text{smooth}).$$

We note that although we have not proven $\gamma(\lambda)$ is given by Eq. (4.4), its exact functional form is of little numerical significance at the density $\hat{\rho} = 0.625$ considered here because γ(rough) and γ(smooth) are nearly equal. Figure 7 gives the deviations from the Enskog theory as a function of time for several values of λ.

There is, as mentioned before, a systematic disagreement between theory and experiment. Viewed on this scale the experimental data exhibits some structure due to changes in roughness (note, however, that we are speaking of differences that are comparable with statistical errors in the molecular dynamics data). A generally similar structure is exhibited by the theoretical curves, although there is not quantitative agreement. We suspect that better agreement would be found if molecular dynamics data were available at lower densities.

V. DISCUSSION

We have shown that the rotational and translational diffusion coefficients of partially rough spheres may be successfully described by a hydrodynamic theory with partial slip boundary conditions. It is found empirically that the slip parameter β of the hydrodynamic theory is linearly related to the roughness parameter λ of the collision dynamics. Equal size spheres, rough and smooth, are found to be hydrodynamically slippery, but it is suggested that a large Brownian particle in a fluid of smaller particles will approach hydrodynamic roughness.

We conclude that the effects of partial roughness can successfully be incorporated into a hydrodynamic description of angular velocity correlations. In particular, the linear relationship between β and λ found empirically from the diffusion coefficients emerges from the theory if β is determined from the initial slope of the hydrodynamic AVCF by requiring it to give the initial slope known from the collision dynamics. However, we have shown that the resulting theory does not quantitatively describe the AVCF at high densities, except at very long times. If a better description of short time effects as a function density is achieved, the methods of the present paper would probably successfully extend the resulting theory to partially rough fluids.

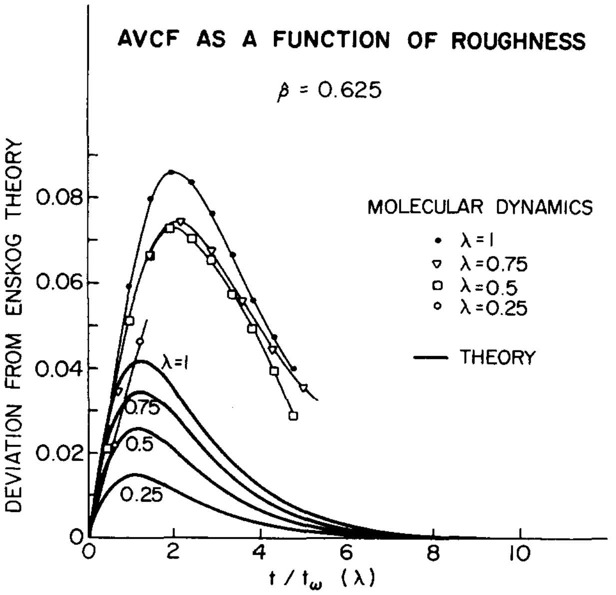

FIG. 7. The deviations of the hydrodynamic theory and molecular dynamics AVCF from the Enskog exponential are shown as a function of λ for partially rough spheres. The heavy curves give the theoretical result. The data points are connected by light curves for clarity.

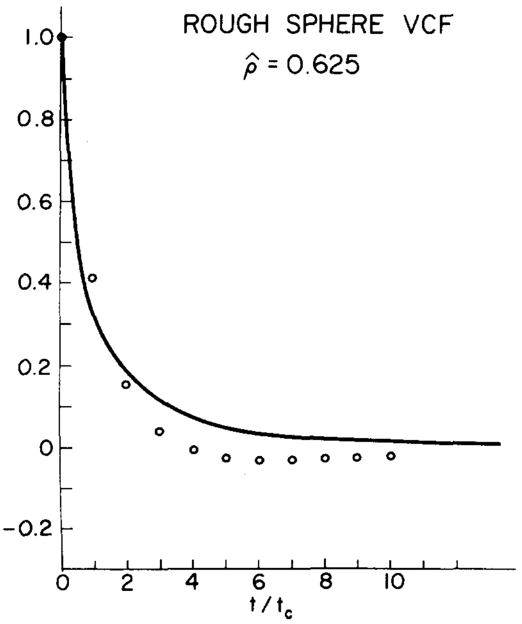

FIG. 8. A comparison of hydrodynamic theory and molecular dynamics for the rough sphere VCF. The viscosities of Eq. (3.7) are used and $\beta = 0$.

Molecular hydrodynamics is less successful at describing velocity correlations in hard particle fluids. Due to the unphysical initial decay of the Zwanzig–Bixon theory good agreement with the molecular dynamics VCF cannot be obtained at any density for any value of the slip parameter.

The VCF at high densities is well known to exhibit a negative region at intermediate times (commonly ascribed to rebounding collisions with the nearest neighbor shell). This structure is obtained by Zwanzig and Bixon[3] and by Levesque *et al.*[2] in their calculations on Lennard-Jones fluids, but not in our calculation of the rough sphere VCF at $\hat{\rho} = 0.625$ as shown in Fig. 8.

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