

Brownian dynamics of suspensions of rodlike particles

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A molecular colloidal fluid of moderately nonspherical axisymmetric molecules interacting via a two-site Yukawa potential is studied by the Brownian dynamics simulation method. The long-time translational self-diffusion coefficient and the rotational self-diffusion coefficient are calculated, at several concentrations and for different anisotropies of the one-particle diffusion tensor. The influence of the one-particle diffusion tensor on the dynamical properties is studied. It is shown that the rotational motion of the tracer molecule can be well described up to high volume fractions over a considerable time interval by the rotational diffusion equation with a state dependent rotational diffusion coefficient.

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I. INTRODUCTION

There are many inorganic and polymeric colloidal dispersions that consist of rigid and compact *nonspherical* particles, such as rodlike macromolecules. The macroparticles interact through both interparticle colloidal forces and hydrodynamic forces mediated via the continuum fluid. The macroparticles also receive fluctuating Brownian forces which arise from the apparently random thermal motion of the fluid. In colloidal dispersions, in general, one is faced with a dauntingly large spread of important time scales that are well separated [1,2]. As a result, the dynamical behavior of a colloidal dispersion is usually simplified in terms of a model consisting of large and massive macroparticles or "Brownian" particles in a *continuum* fluid medium.

Compared with colloids composed of spherical particles, the modeling of anisotropic colloid particles is less well developed because of the complex interplay between the different anisotropic interactions present in these molecular suspensions. The intermolecular potential and hydrodynamic interactions between nonspherical colloidal particles are considerably more complex than between spherical ones. In the case of rodlike particles, for example, the potential interaction depends on the relative orientations of the axes of the rods and on the distance between their centers of mass. There is no well-established functional form for such an interaction. For hydrodynamic interactions, the situation is even worse. Only very recently has this difficult aspect of suspensions of nonspherical rigid particles been treated in a systematic way by means of Stokesian dynamics [3], which still ignores Brownian forces. An alternative route is the bead model approach [4,5]. The idea behind this method is that each object (e.g., rodlike particle) is modeled by a set of beads. The hydrodynamic interactions between these objects is calculated as a superposition of those of the beads (e.g., sphere) interactions. This approach is suitable for macromolecules or chain objects where bead-

shaped subunits can easily be defined. Another advantage of this approach, identifying the object as a collection of beads joined together, is the flexibility of the object that can be taken into account. For a system of rigid compact objects, the bead method seems to be less appropriate and less efficient, because to get a good representation of some convex shapes, like an ellipsoid or rod, you would need many beads.

In the present report, we consider a model of interacting linear rigid particles (colloidal molecules). It is assumed that the particles interact via a site-site Yukawa potential and the solvent is treated through a one-particle diffusion matrix. Thus, the model accounts for anisotropic interparticle interactions and anisotropic friction but ignores many-body hydrodynamic interactions. It is a sufficiently simple model to start our investigations, as we consider it to include some of the main features of suspensions of short rodlike particles. In particular, it is a reasonable model for a system in which the range of the interparticle potential is much greater than that of the solvent mediated hydrodynamic interactions. This is the case in, for example, suspensions of charged rodlike particles. Recently, those systems have attracted considerable attention. They have been studied by scattering experiments [6,7] and various theoretical techniques [8–12].

Most of the numerical and theoretical studies to date have been concentrated on structural properties and/or properties of highly anisotropic rodlike particles. Few real materials, however, consist of distinctly nonspherical particles (e.g., very slender rods) and the need exists, clearly, for investigations of suspensions of elongated particles with moderate aspect ratios. For such particles, there is still little known about their dynamical behavior at a molecular level, for example, the role of the one-particle diffusion tensor on transport properties of the suspension. Recently, for example, Felderhof and Jones [13] have shown that in a colloidal suspension of spheres, in the absence of hydrodynamic interactions, the short-time decay of the rotational correlation function is

governed by one-particle translational and rotational diffusion coefficients.

In this report, we focus on tracer translational and rotational diffusivities of moderately nonspherical interacting colloidal molecules. Both properties are of a great practical interest and are amenable to a range of experimental techniques, e.g., the dynamic light and neutron scattering, photon correlation spectroscopy, fluorescence recovery after photobleaching [14]. In particular, we study how the diffusivities depend on the one-particle diffusion matrix, the nature of the interparticle forces and on the density of the colloidal molecules. Similar studies on the translational diffusivity have been undertaken, recently by Löwen and Szamel for a fluid of the Yukawa-type representing spherical colloidal suspensions [15]. As the dynamical properties of molecule suspensions are hardly amenable to any analytical treatment, Brownian dynamics computer simulations are *de facto* the only efficient approach to study these systems [16,17].

The algorithm for Brownian dynamic simulation is presented in Sec. II together with a description of the model and computational details. The simulation results for the diffusion coefficients are given in Sec. III, and summarized in Sec. IV.

II. BROWNIAN DYNAMICS SIMULATIONS

A. The model

We consider a system of N rigid linear molecules suspended in an incompressible fluid of viscosity, η_0 , and using site-site direct (nonhydrodynamic) interactions. For linear molecules the orientation is naturally defined by a unit vector \mathbf{e} along the molecular axis. The positions of the sites are given in terms of their distances along this axis from the center of mass. Thus, the interaction energy between two rigid linear molecules is a sum of pairwise additive contributions from distinct sites a in molecule i and b in molecule j ,

$$V(\mathbf{r}_{ij}, \mathbf{e}_i, \mathbf{e}_j) = \sum_a \sum_b u(r_{ab}), \quad (1)$$

where $r_{ab} = |\mathbf{r}_{ia} - \mathbf{r}_{jb}|$ is the site-site distance. In our model the molecular sites are equally spaced and the separation distance, L , is a variable parameter of the model. The site-site potential is modeled by a Yukawa potential,

$$u(r) = U_0 \exp[-\lambda(r-1)]/r, \quad (2)$$

where U_0 sets the energy scale and λ is the screening parameter characterizing the steepness and range of the potential. The Yukawa potential, being the electrostatic part of the Derjaguin-Landau-Verweg-Overbeek potential, is considered to give a good description of the interaction of a dilute charge-stabilized spherical colloidal suspension [1,18]. It has been used recently as a site-site potential to model interactions between charged rodlike particles [7,11,12].

As many-body hydrodynamic interactions are neglected in our model the hydrodynamic interaction of the molecule with the solvent is represented by a one-particle diffusion tensor. For a nonspherical particle the diffusion

tensor is a symmetric 6×6 matrix in position-orientation space, which can be partitioned into 3×3 submatrices: translational \mathbf{D}^t , rotational \mathbf{D}^r , and coupling \mathbf{D}^c . The number of nonzero components of the diffusion tensor is determined by the symmetry of the particle [19]. For rodlike molecule, the diffusion tensor contains four nonzero components (two translational, $D_{\perp}^t, D_{\parallel}^t$, and two rotational $D_{\perp}^r, D_{\parallel}^r$, coefficients), the diffusion submatrices are of the form [20]

$$\mathbf{D}^* = \begin{pmatrix} D_{\perp}^* & 0 & 0 \\ 0 & D_{\perp}^* & 0 \\ 0 & 0 & D_{\parallel}^* \end{pmatrix}, \quad (3)$$

where $*$ denotes t or r , and \mathbf{D}^c is here a zero matrix (no coupling occurs between translational and rotational motion for this kind of the molecular symmetry). The subscripts \parallel and \perp denote parallel and perpendicular to the molecular axis, respectively. In our model, the rotational diffusion around the symmetry axis, D_{\parallel}^r , can be safely ignored. (For linear molecules the torque is perpendicular to the molecular axis all the time.) The D_{\perp}^r coefficient will subsequently be denoted as D_0^R .

The effective hydrodynamic anisotropy of a rodlike particle can be characterized by the following factor,

$$\chi = \frac{D_{\parallel}^t - D_{\perp}^t}{D_{\parallel}^t + D_{\perp}^t}, \quad (4)$$

which changes from -1 ($D_{\parallel}^t = 0$, no diffusivity parallel to the rod axis) to $+1$ ($D_{\perp}^t = 0$, no diffusivity normal to the rod axis) and is zero when $D_{\parallel}^t = D_{\perp}^t$ (isotropic diffusivity). The one-particle diffusion tensor is available only for a few molecular models, e.g., ellipsoids with the stick hydrodynamic boundary conditions [21,22]. In general, values of the diffusion coefficients depend markedly on the size and shape of the molecule, solvent properties [23,24], and the hydrodynamic boundary conditions used in their evaluation [25–27]. As a result the dynamical properties of the suspension are strongly model dependent [27] and a systematic study of their dependence on the one-particle diffusion tensor is desirable. To explore this dependence, we shall use several different values of D_0^R and χ .

In order to study a system of particles that can rotate in time, the diffusion tensor in Eq. (3) has to be transformed from the molecular-fixed frame to the laboratory-fixed frame. This transformation leads to the following form for the translational diffusion tensor \mathbf{D}^T in the laboratory-fixed frame:

$$D_{\alpha\beta}^T = D_{\perp}^t \delta_{\alpha\beta} + e_{\alpha} e_{\beta} (D_{\parallel}^t - D_{\perp}^t), \quad (5)$$

where e_{α} is the α component of the unit vector \mathbf{e} and $\delta_{\alpha\beta}$ is the Kronecker δ . As the molecule rotates, the tensor \mathbf{D}^T changes in time. This means that the translational motion of the rodlike particle, therefore, depends on its orientation, which is a result of different diffusivities in the directions parallel and normal to the rod axis. The expression in Eq. (5) can be rearranged into a form that

has a part of the tensor that is independent of molecular orientations:

$$D_{\alpha\beta}^T = D_I \delta_{\alpha\beta} + D_A (e_\alpha e_\beta - 1/3 \delta_{\alpha\beta}), \quad (6)$$

where $D_A \equiv (D_{\parallel}^t - D_{\perp}^t)$ is the anisotropic component of the translational diffusion coefficient and $D_I \equiv (D_{\parallel}^t + 2D_{\perp}^t)/3$ is the isotropic translational diffusion coefficient.

If the orientations of the molecule are randomly distributed (which is the case in an isotropic fluid) the average value of the D^T tensor is

$$\langle D_{\alpha\beta}^T \rangle = D_I \delta_{\alpha\beta}, \quad (7)$$

and its correlation functions can be expressed in the following way:

$$\begin{aligned} \langle D_{\alpha\beta}^T(0) D_{\gamma\delta}^T(t) \rangle \\ = D_I^2 \delta_{\alpha\beta} \delta_{\gamma\delta} + \frac{D_A^2}{15} \langle P_2(\mathbf{e}(0) \cdot \mathbf{e}(t)) \rangle \\ \times [\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} - \frac{2}{3} \delta_{\alpha\beta} \delta_{\gamma\delta}], \end{aligned} \quad (8)$$

where $P_2(x)$ is the second-order Legendre polynomial. Although the derivation of Eq. (8) is the same as, for example, the molecular polarizability tensor [28], we think the use of this expression is different in the context of colloidal systems.

B. The algorithm

An algorithm for simulating the Brownian motion of an assembly of interacting spherical particles was proposed by Ermak and McCammon [16]. Dickinson extended the algorithm to a form that incorporates rotation of the particles explicitly in the equations of motion [20,29]. The algorithm updates the displacements and orientations in time steps of, Δt , and for our system it can be written as follows:

$$\Delta r_{i\alpha} = \frac{\Delta t}{k_B T} \sum_{\beta} D_{i\alpha\beta}^T F_{i\beta} + \delta r_{i\alpha}, \quad (9)$$

$$\Delta \varphi_{i\alpha} = \frac{\Delta t}{k_B T} D_0^R \tau_{i\alpha} + \delta \varphi_{i\alpha}, \quad (10)$$

where $i=1, \dots, N$ labels the molecules and α, β indicates the Cartesian coordinates (x, y, z or $1, 2, 3$). $F_{i\alpha}$ and $\tau_{i,\alpha}$ are the net force and torque, respectively, acting in the α direction on particle, i . The temperature is denoted by T and k_B is the Boltzmann constant. $\delta \varphi_{i\alpha}$ is a random orientational displacement which is sampled from a Gaussian distribution of zero mean and variance,

$$\langle \delta \varphi_{\alpha}^2 \rangle = 2D_0^R \Delta t, \quad (11)$$

where D_0^R is the rotational diffusion coefficient in the limit of infinite dilution. Similarly, $\delta r_{i\alpha}$ denotes a random displacement of the molecular center of mass. In this case, however, the Cartesian components of the displacement vector $\delta \mathbf{r}$, for a given molecule, are correlated in accordance with the D^T tensor. These have to be sampled from a multivariate Gaussian distribution with zero mean

and the variance-covariance matrix given by

$$\langle \delta r_{i\alpha} \delta r_{i\beta} \rangle = 2D_{i\alpha\beta}^T \Delta t, \quad (12)$$

which can be obtained from a set of three Gaussian random numbers, X_α , according to the following procedure [29],

$$\delta r_{i\alpha} = \sum_{\beta=1}^{\alpha} \sigma_{\alpha\beta} X_{\beta} \quad (13)$$

$$\sigma_{\alpha\alpha} = \left[D_{\alpha\alpha}^T - \sum_{\gamma=1}^{\alpha-1} \sigma_{\alpha\gamma}^2 \right]^{1/2} \quad (14)$$

$$\sigma_{\alpha\beta} = \frac{1}{\sigma_{\beta\beta}} \left[D_{\alpha\beta}^T - \sum_{\gamma=1}^{\beta-1} \sigma_{\alpha\gamma} \sigma_{\beta\gamma} \right] \quad (\alpha > \beta) \quad (15)$$

$$\langle X_{\alpha} \rangle = 0, \quad \langle X_{\alpha} X_{\beta} \rangle = 2\delta_{\alpha\beta} \Delta t, \quad (16)$$

where $\alpha, \beta, \gamma=1, 2, 3$ and the molecular index i has been omitted.

All quantities quoted here are in dimensionless units, using σ , σ^2/D_0 and U_0/σ as the characteristic values for length, time and forces, respectively. Temperature is in k_B/U_0 and all the translational diffusion coefficients are in $D_0 = k_B T / 6\pi\sigma\eta_0$, where η_0 is the solvent viscosity.

In the Dickinson *et al.* [29] algorithm the rotational displacements, $\Delta \varphi_{i\alpha}$, are angular rotations of the particle i about the laboratory-fixed x , y , and z axes. The time evolution of the unit vector \mathbf{e} is obtained by using the Cartesian rotational transformation matrices

$$\mathbf{e}(t + \Delta t) = A_x A_y A_z \mathbf{e}(t), \quad (17)$$

where

$$A_x = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\Delta \varphi_x) & -\sin(\Delta \varphi_x) \\ 0 & \sin(\Delta \varphi_x) & \cos(\Delta \varphi_x) \end{bmatrix}, \quad (18)$$

$$A_y = \begin{bmatrix} \cos(\Delta \varphi_y) & 0 & \sin(\Delta \varphi_y) \\ 0 & 1 & 0 \\ -\sin(\Delta \varphi_y) & 0 & \cos(\Delta \varphi_y) \end{bmatrix}, \quad (19)$$

$$A_z = \begin{bmatrix} \cos(\Delta \varphi_z) & -\sin(\Delta \varphi_z) & 0 \\ \sin(\Delta \varphi_z) & \cos(\Delta \varphi_z) & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (20)$$

are the rotation matrices corresponding to a rotation of $\Delta \varphi_x$ about the x axis, $\Delta \varphi_y$ about the y axis, and $\Delta \varphi_z$ about the z axis, respectively. As the matrices are not commutable a small error is introduced into the algorithm, but for small rotational displacements it appears to be statistically irrelevant [30].

C. Simulation details

The calculations were performed for a system of moderately nonspherical particles with $L=0.5$, interacting via a two-site Yukawa potential of the form given in Eq. (2). The system consisted of $N=125$ molecules in a

periodic boundary condition and the basic simulation cell was a cube of volume V . Particle trajectories were generated according to the algorithm of Eqs. (9)–(12). In order to reduce further the ordering error, the transformation of Eq. (17) was made by choosing at random (for each molecule at each time step) one from the six possible sequences of the rotation matrices: $A_x A_y A_z, A_x A_z A_y, \dots$. During the simulations the center of mass of the system was fixed.

The screening parameter in the interaction potential was $\lambda=8$ and the reduced temperature was $T=1$, i.e., the values chose for the spherical particles in Ref. [15]. As the potential is strongly repulsive a sufficiently small time step had to be used. The actual value of Δt in our simulations was 5×10^{-5} [we have checked, for some state points, that values from the range $(1-8) \times 10^{-5}$ did not change calculated properties].

The simulations were performed for several values of χ and D_0^R and for a range of particle reduced densities $\rho=N/V$ or packing fraction $\phi=v\rho$ [$v=\pi(1+\frac{3}{2}L)/6$ is the volume of the spheroid approximating the size of the Yukawa molecule]. For each χ and D_0^R the simulations were started at low density ($\rho=0.05$) and after a long equilibration run of 10^5 time steps the production simulation of $10^6 \Delta t$ (i.e., a period of $50 \sigma^2/D_0$) was made. Next, the system was gradually increased to a higher density, equilibrated for $0.5 \times 10^5 \Delta t$ and then the basic run of $10^6 \Delta t$ was performed from which the averages were calculated. This procedure was repeated until $\rho=0.5$. Long, well-equilibrated, simulations were necessary, particularly at low densities, to obtain sufficiently good statistics in order to determine the dynamical properties. Equations (7) and (8) were used as an additional cross check of correctness of the program. [In Eq. (8) calculations were performed for two correlation functions $\langle D_{11}^T(0)D_{11}^T(t) \rangle$ and $\langle D_{12}^T(0)D_{12}^T(t) \rangle$].

III. RESULTS AND DISCUSSION

First, we consider the rotational motion of the rodlike particles. Rotational motion of rodlike particles can be conveniently characterized using the single-particle orientational time-correlation functions,

$$C_l(t) = \langle P_l(\mathbf{e}(t) \cdot \mathbf{e}(0)) \rangle, \quad (21)$$

where $P_l(x)$ is the l th Legendre polynomial. These functions are used, for example, to describe light scattering from tracer particles [28]. In very dilute solutions the rotational motion is a diffusive process, so that the Debye rotational diffusion equation is applicable, and which leads to an exponentially decaying correlation function,

$$C_l(t) = \exp[-l(l+1)D_0^R t]. \quad (22)$$

In a solution of interacting Brownian particles one expects that the hydrodynamic and potential interactions will modify this purely exponential decay. We have studied the first two orientational correlation functions reexpressed from Eq. (22) as

$$p_1(t) = -\frac{1}{2} \ln \langle P_1(t) \rangle / D_0^R, \quad (23)$$

$$p_2(t) = -\frac{1}{6} \ln \langle P_2(t) \rangle / D_0^R. \quad (24)$$

The typical time behavior of these functions is plotted in Fig. 1. This figure shows that initially, both functions, increase linearly with time and are practically indistinguishable. Thus, orientational motion over a considerable time interval can be well described by the rotational diffusion equation (for all studied state points this time interval exceeded 0.3). However, at longer times the functions deviate from this analytic form and display a complicated nonlinear behavior. At these relatively long-times statistical uncertainty is large and it is difficult to make any quantitative conclusions. Nevertheless, reorientational motion over a considerable time interval can be described well by the rotational diffusion equation. However, the slope of the functions in the linear regime is less than unity, which indicates that a modified rotational diffusion coefficient, D_r^R must be employed in Eq. (22). The range of the linear region depends on D_0^R and it becomes larger as D_0^R becomes smaller (e.g., for $D_0^R=1$ the linear region is almost two times larger than for $D_0^R=5$). Such behavior clearly indicates that the diffusive character of rotation is mainly determined by the forces exerted by the solvent.

Figure 2 shows also that for an initial, very short but observable time interval ($t < 0.01$), a decrease of the slope occurs from 1 to D_r^R/D_0^R . Thus, our calculations confirm the observation made by Bitsanis, Davis, and Tirrell [31] that initially the particles rotate as in a dilute solution, i.e., there exists an initial period of unhindered rotation (for typically 0.25 rad).

The coefficients, D_r^R , calculated from the slope of the p_1 over the time interval 0.02–0.32, are given in Table I and are displayed graphically in Fig. 3. At low densities, the coefficients, D_r^R , decrease linearly with increasing density and there is weak dependence on the one-particle diffusion matrix. As density increases the concentration

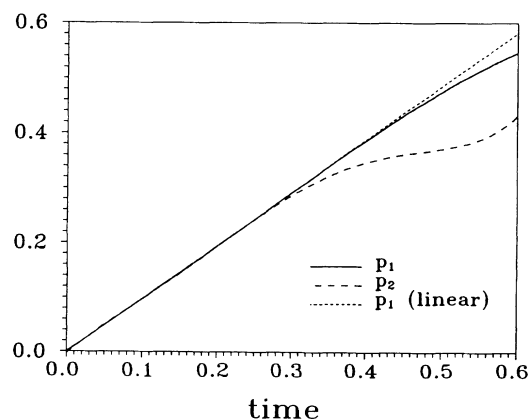


FIG. 1. The time evolution of the rotational correlation functions [Eqs. (23) and (24)] for a suspension of two-site Yukawa rodlike molecules at different densities. The broken straight line is a linear fit to the p_1 function over the time interval (0.02–0.32). The results are for $\rho=0.4$, $D_0^R=3$, $\chi=\frac{2}{3}$.

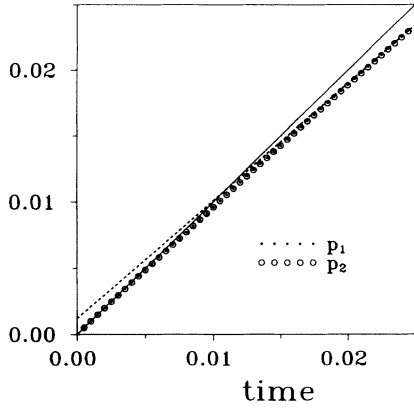


FIG. 2. The rotational correlation functions (see Fig. 1) at short times. The broken and solid lines are $D_r^R t + 0.001$ and $D_0^R t$, respectively.

dependence of D_r^R/D_0^R becomes stronger and the dependence on (χ, D_0^R) becomes rather more pronounced. A weak concentration dependence of the rotational diffusion coefficient, at low densities, has been predicted by Jones [32] and recently demonstrated experimentally in a suspension of spherical particles possessing an intrinsic optical anisotropy [33]. Our data show, to our knowledge, for the first time, the dependence of D_r^R on the one-particle diffusion matrix in a suspension of molecules.

To derive some insights into the dynamics of translational motion, the long-time self-diffusion coefficient, D_L , was evaluated from the rate of change of the mean square displacement, $W(t) = \langle [\mathbf{R}(t) - \mathbf{R}(0)]^2 \rangle / 6$, of the center of mass of the tagged particle,

$$D_L = \lim_{t \rightarrow \infty} \frac{dW(t)}{dt}. \quad (25)$$

The D_L coefficients are given in Table I. At infinite dilution D_L tends to D_I , as expected in the absence of many-body hydrodynamics. At finite concentration the diffusion process is slowed down by the interaction of the tagged molecule with the other molecules and the ratio D_L/D_I is less than unity. (The ratio D_L/D_I is an informative way of presenting D_L , as it goes to unity at infinite dilution and reduces to the ratio D_L/D_0 as the molecule tends to a sphere.)

As seen in Fig. 4, the density dependence of D_L/D_I on the one-particle diffusion matrix is greater than in the case of D_r^R . The density dependence for various χ , D_0^R can be quite different even at very low concentrations (e.g., for densities 0.05 and 0.1). For a given value of D_0^R , the ratio D_L/D_I is a decreasing function of χ with the maximum occurring at $\chi=0$ (i.e., the relative translational diffusivity is most efficient for the isotropic case).

Interparticle potential interactions can have a significant influence on the tracer diffusivity. Recently, it has been demonstrated that the self-diffusion coefficient of colloidal suspensions of spheres increases as the interaction becomes softer [15,34]. In our system, the interparticle interaction becomes harder as the distance between the two interaction sites is reduced. Thus, one ex-

pects that D_L/D_I will decrease with increase in molecular anisotropy. Results in Fig. 4 plotting D_L/D_I against density confirm this prediction. In the figure, the results (crosses) for the limiting (extreme) case $L=0$ (i.e., when the two interaction sites coincide) are presented. At all concentrations they are below the results for the ap-

TABLE I. The long-time translational self-diffusion coefficients and rotational diffusion coefficients at different densities and for different diffusion anisotropies. The errors for D_r^R/D_0^R and D_L/D_I are estimated to be less than 0.003 and 0.005, respectively. Results are for two-site Yukawa system with $\lambda=8$, $L=0.5$, at $T=1$. $\phi = \nu\rho$ is a packing fraction where $\nu = (\pi/6)(1 + \frac{3}{2}L)$ is the volume of a spheroid approximating the size of the Yukawa molecule.

ρ	ϕ	D_{\perp}^I	D_{\parallel}^I	χ	D_0^R	D_r^R/D_0^R	D_L/D_I
0.05	0.0458	1	1	0	1	1.001	0.89
0.05	0.0458	1	2	$\frac{1}{3}$	1	1.000	0.88
0.05	0.0458	1	3	$\frac{1}{2}$	1	1.001	0.87
0.05	0.0458	1	5	$\frac{2}{3}$	1	0.999	0.845
0.05	0.0458	1	5	$\frac{2}{3}$	3	1.000	0.86
0.05	0.0458	1	5	$\frac{2}{3}$	5	0.999	0.87
0.10	0.0916	1	1	0	1	0.993	0.80
0.10	0.0916	1	2	$\frac{1}{3}$	1	0.995	0.785
0.10	0.0916	1	3	$\frac{1}{2}$	1	0.995	0.77
0.10	0.0916	1	5	$\frac{2}{3}$	1	0.997	0.73
0.10	0.0916	1	5	$\frac{2}{3}$	3	0.996	0.765
0.10	0.0916	1	5	$\frac{2}{3}$	5	0.994	0.77
0.20	0.1833	1	1	0	1	0.986	0.63
0.20	0.1833	1	2	$\frac{1}{3}$	1	0.990	0.62
0.20	0.1833	1	3	$\frac{1}{2}$	1	0.992	0.60
0.20	0.1833	1	5	$\frac{2}{3}$	1	0.993	0.55
0.20	0.1833	1	5	$\frac{2}{3}$	3	0.982	0.58
0.20	0.1833	1	5	$\frac{2}{3}$	5	0.970	0.59
0.30	0.2749	1	1	0	1	0.972	0.50
0.30	0.2749	1	2	$\frac{1}{3}$	1	0.982	0.48
0.30	0.2749	1	3	$\frac{1}{2}$	1	0.984	0.465
0.30	0.2749	1	5	$\frac{2}{3}$	1	0.989	0.41
0.30	0.2749	1	5	$\frac{2}{3}$	3	0.962	0.44
0.30	0.2749	1	5	$\frac{2}{3}$	5	0.949	0.45
0.40	0.3665	1	1	0	1	0.950	0.37
0.40	0.3665	1	2	$\frac{1}{3}$	1	0.967	0.36
0.40	0.3665	1	3	$\frac{1}{2}$	1	0.970	0.34
0.40	0.3665	1	5	$\frac{2}{3}$	1	0.982	0.29
0.40	0.3665	1	5	$\frac{2}{3}$	3	0.924	0.32
0.40	0.3665	1	5	$\frac{2}{3}$	5	0.900	0.33
0.50	0.4581	1	1	0	1	0.915	0.26
0.50	0.4581	1	2	$\frac{1}{3}$	1	0.925	0.255
0.50	0.4581	1	3	$\frac{1}{2}$	1	0.930	0.24
0.50	0.4581	1	5	$\frac{2}{3}$	1	0.945	0.19
0.50	0.4581	1	5	$\frac{2}{3}$	3	0.876	0.21
0.50	0.4581	1	5	$\frac{2}{3}$	5	0.830	0.23

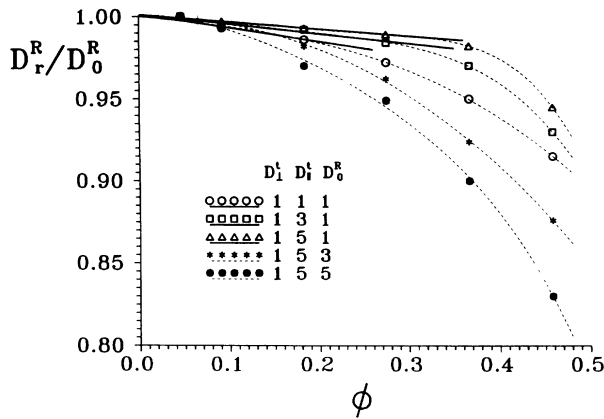


FIG. 3. The rotational diffusivity against concentration for different one-particle diffusion coefficients. (The lines are to guide the eye.)

appropriate Yukawa molecules ($\chi=0, D_0^R=1$). It is interesting to note (see Fig. 4) that D_L of the suspension of the Yukawa spheres is larger, at all concentrations. Thus, the D_L of one- and two-site Yukawa spheres form upper and lower bounds, respectively, for the two-site Yukawa molecule D_L/D_I .

IV. CONCLUSIONS

We have studied a two-site Yukawa molecular system obeying Brownian dynamics, which can be considered as an approximation to a charged rodlike particle suspension. A feature of our work is that the anisotropic solvent friction is explicitly built into the model. In the present work, we have concentrated on moderately anisotropic molecules. The self-diffusion translational and rotational coefficients have been calculated for a range of densities. As has been shown, both properties display considerable density and molecular anisotropy dependence. Apart from a very short initial time, the rotational motion can be described well, for a considerable time

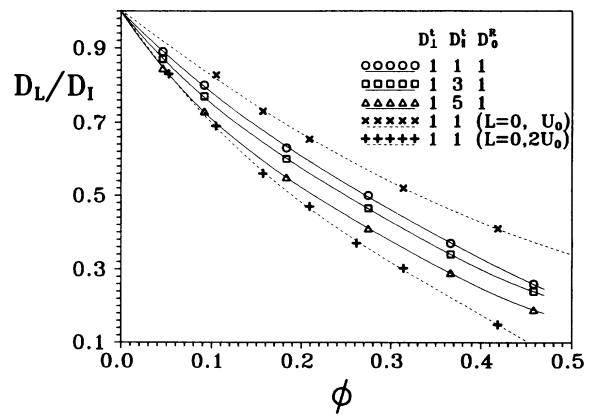


FIG. 4. Density dependence of the long-time translational self-diffusion coefficients for different one-particle diffusion coefficients. +, × [34] are results for suspensions of the Yukawa spheres. (The lines are to guide the eye.)

interval, by the rotational diffusion equation with a state dependent rotational diffusion coefficient. It has been demonstrated how the anisotropy in the solvent-particle interaction, in the form of one-particle diffusion matrix, does influence both the rotational and translational diffusion properties. This indicates that it should be taken into account in any rigorous model of the dynamics of nonspherical particle dispersions.

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