

Two-particle friction in a mesoscopic solvent

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The effects of hydrodynamic interactions on the friction tensors for two particles in solution are studied. The particles have linear dimensions on nanometer scales and are either simple spherical particles interacting with the solvent through repulsive Lennard-Jones forces or are composite cluster particles whose atomic components interact with the solvent through repulsive Lennard-Jones forces. The solvent dynamics is modeled at a mesoscopic level through multiparticle collisions that conserve mass, momentum, and energy. The dependence of the two-particle relative friction tensors on the interparticle separation indicates the importance of hydrodynamic interactions for these nanoparticles. © 2005 American Institute of Physics. [DOI: 10.1063/1.1924505]

I. INTRODUCTION

Particle dynamics in solution is modified by interaction with the hydrodynamic modes of the solvent. Disturbances in the fluid created by the solute molecules are transmitted to other parts of the fluid through solvent collective modes, such as the solvent velocity field, and this gives rise to a long-range hydrodynamic coupling among the solute molecules. As a result, the motions of particles are coupled by hydrodynamic interactions even though they may be separated by distances greater than the range of direct intermolecular forces.¹ Hydrodynamic interactions play an important role in many processes. The frictional properties of polymer molecules in solution and the dynamics of structural changes such as polymer collapse are strongly influenced by hydrodynamic interactions among the monomers comprising the polymer chain.² Hydrodynamic interactions govern the frictional properties of colloidal suspensions and the full treatment of such interactions for concentrated colloidal suspensions is a challenging task.³

The simplest context in which such hydrodynamic interactions can be investigated is for two particles fixed in a solution at a distance R_{12} and this is the case we study in this paper. In particular, we examine how the friction depends on the separation between the two particles. Studies of hydrodynamic effects on the two-particle friction are difficult to carry out by full molecular dynamics because of the need to simulate large systems for long times in order to be able to capture the coupling through hydrodynamic fields. To circumvent this difficulty, we model the solvent at a mesoscale level that satisfies the microscopic conservation laws and is therefore able to yield the correct hydrodynamic coupling among the solute molecules.^{4,5}

The outline of the paper is as follows. In Sec. II we specify the system being investigated and also sketch the

multiparticle collision dynamics that is used to model the solvent motions. The friction coefficients that are of interest in this study are defined in Sec. III. In this section we also present the results of simulations of the friction for two smooth spherical Brownian particles interacting with the solvent molecules through repulsive Lennard-Jones forces. In Sec. IV we consider the more complex situation where the two Brownian particles are clusters of Lennard-Jones particles and describe the new features that arise because of the composite nature of the particles. The conclusions of the paper are given in Sec. V.

II. DYNAMICS OF TWO BROWNIAN PARTICLES

We study a system with two Brownian particles with particle masses m_B in a solvent or bath of N_s particles with particle masses m ($m_B \gg m$). The solvent particles are labelled $1, \dots, N_s$ and have position and velocity coordinates $(\mathbf{r}, \mathbf{v}) = \{\mathbf{r}_i, \mathbf{v}_i | i = 1, \dots, N_s\}$. Similarly, for the two Brownian particles we define $(\mathbf{R}, \mathbf{V}) = \{\mathbf{R}_\alpha, \mathbf{V}_\alpha | \alpha = 1, 2\}$. The general form of the Hamiltonian for such a system is

$$\begin{aligned}
 H(\mathbf{R}, \mathbf{V}, \mathbf{r}, \mathbf{v}) &= \frac{m_B}{2} V^2 + V_{BB}(\mathbf{R}) \\
 &+ \frac{m}{2} v^2 + V_{ss}(\mathbf{r}) + \sum_{\alpha=1}^2 V_{Bs}(\mathbf{R}_\alpha, \mathbf{r}) \\
 &= H_B(\mathbf{R}, \mathbf{V}) + H_0(\mathbf{r}, \mathbf{v}; \mathbf{R}).
 \end{aligned}
 \tag{1}$$

In this equation we have defined the Hamiltonian H_B for the pair of Brownian particles in the absence of solvent and the Hamiltonian H_0 for the solvent in the potential field of the fixed positions of the B particles. The solvent particle-solvent particle potential energy is V_{ss} , the interaction energy between a Brownian particle and the solvent particles is V_{Bs} , and V_{BB} is the interaction energy between the two Brownian particles.

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Our calculations of the two-particle friction are carried out in a mesoscopic solvent rather than in a full molecular solvent. We adopt the multiparticle collision (random rotation) model for the solvent dynamics.^{4,6,7} In this model the intermolecular forces among the solvent molecules are set to zero ($V_{ss}=0$) and replaced by multiparticle collisions at discrete time intervals τ which are carried out in the following way: the simulation box is partitioned into n^3 cells (multiparticle collision volumes) labeled by ξ and at each time interval τ rotation operators $\hat{\omega}_\xi$, chosen at random from a set of rotation operators, are assigned to each cell. In the simulations described in this paper we use rotations by $\pm\pi/2$ about a randomly chosen axis. We have employed random shifting of the grid used to define the multiparticle collision volumes.⁸

At any time instant, a cell will contain a certain number of solvent molecules with velocities $\mathbf{v}_i'$. Let $\mathbf{V}_\xi$ be the center-of-mass velocity of the particles in cell ξ . The postcollision velocities of the particles in the cell are determined by rotating the particle velocities, relative to the center-of-mass velocity $\mathbf{V}_\xi$, by the rotation operator $\hat{\omega}_\xi$, and then adding $\mathbf{V}_\xi$ to the result:

$$\mathbf{v}_i = \mathbf{V}_\xi + \hat{\omega}_\xi[\mathbf{v}_i' - \mathbf{V}_\xi]. \quad (2)$$

Such multiparticle collisions are carried out independently in each cell. Between multiparticle collisions the system evolves by Newton's equations of motion that follow from the Hamiltonian in Eq. (1) with V_{ss} set to zero. This mesoscopic dynamics satisfies the mass, momentum, and energy conservation laws. Thus, the dynamics is microcanonical, preserves phase-space volumes, and will generate the correct hydrodynamic coupling between the two Brownian particles on long distance and time scales.⁴⁻⁶

Simulation details

We have carried out molecular-dynamics (MD) simulations for two Brownian particles in a solvent of N_s mesoscopic particles. Our primary interest is in the situation where the two Brownian particles are fixed at a given distance or are massive so that their motion occurs on a long time scale. We suppose that $V_{BB}=0$ so that the only interactions between the particles are through the solvent. This allows us to isolate solvent coupling effects without having to account for contributions to the friction arising from direct intermolecular forces between the Brownian particles.

The Brownian particle-solvent particle interactions, V_{Bs} , are repulsive Lennard-Jones (LJ) interactions with parameters: $\sigma=0.3, 0.7$ and 1.0 nm, and $\epsilon=1.006\,04$ kJ/mol. The repulsive LJ potential is the same as that used in our study of the friction of a single Brownian particle.⁹ Since the solvent particles are treated as point particles σ is proportional to the radius of the Brownian particle. The masses of the solvent particles are $m=3.9948$ g/mol. The distances between two Brownian particles are chosen to lie between $R_{12}=0.7$ and 2.5 nm for $\sigma=0.3$ nm, $R_{12}=1.5$ and 2.7 nm for $\sigma=0.7$ nm, and $R_{12}=2.3$ and 4.0 nm for $\sigma=1.0$ nm. The particle pair is oriented along the z axis with Brownian particle centers at $-R_{12}/2$ and $R_{12}/2$.

The simulations were carried out in a cubic box of volume $V=L^3$ with periodic boundary conditions. If the volume of the Brownian particle is $V_B=\frac{4}{3}\pi\sigma^3$, V_0 is defined as the volume of the system occupied by solvent molecules, $V_0=V-2V_B$. The multiparticle collision cell volume is given by $V_\xi=V/n^3=(L/n)^3=\ell^3$. We have taken $n=32$. For $\sigma=1.0$ nm, the simulation box was changed to a rectangular shape where the length along z was doubled and the number of solvent molecules was doubled. The values of L and N_s were chosen to fix the number density of solvent particles at $\rho_s=N_s/V_0=2035.42$ nm⁻³ or an average of 10 particles per collision cell so that there are either 327 680 or 655 360 solvent molecules in the simulation box.

Newton's equations of motion were integrated using the velocity Verlet algorithm¹⁰ with a time step of $\Delta t=0.003\,388$ ps. Multiparticle solvent collisions were carried out in cells with linear dimension $\ell=L/n=0.17$ nm every 100 molecular-dynamics time steps so that $\tau=100\Delta t=0.3388$ ps. The temperature, determined from the average kinetic energy, was taken to be $T=40.33$ K so that the reduced temperature $k_B T/\epsilon=1/3$. The results were obtained from ensembles of ten microcanonical MD trajectories of length approximately 68 ns. The statistical errors in the friction coefficients were determined from block averages over the ensemble members.

III. TWO-PARTICLE FRICTION

Our focus is on the calculation of the fixed-particle friction tensor for two Brownian particles.¹¹ The friction tensor can be obtained from the time integral of the force autocorrelation function as

$$\zeta^{\alpha\beta}(\mathbf{R}_{12}) = \beta \int_0^\infty dt \langle \mathbf{f}_\alpha(0) \mathbf{f}_\beta(t) \rangle_0, \quad (3)$$

where $\mathbf{f}_\alpha(t)$ is the random force,

$$\mathbf{f}_\alpha(t) = e^{iL_0 t}(\mathbf{F}_\alpha - \langle \mathbf{F}_\alpha \rangle) \equiv e^{iL_0 t} \mathbf{f}_\alpha(0), \quad (4)$$

and $\mathbf{F}_\alpha$ is the force on Brownian particle α . The Liouvillian $iL_0 \cdot = \{H_0, \cdot\}$, where $\{\cdot, \cdot\}$ is the Poisson bracket, describes the evolution governed by the bath Hamiltonian H_0 , again with V_{ss} set to zero and its effect modeled by multiparticle collisions. Here the angular brackets signify an average over a canonical equilibrium distribution of the bath particles with the two Brownian particles fixed at positions $\mathbf{R}_1$ and $\mathbf{R}_2$, $\langle \cdots \rangle_0 = Z_0^{-1} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H_0} \cdots$, where Z_0 is the partition function. Isotropy yields the relations, $\zeta_{zz}^{11} = \zeta_{zz}^{22}$, $\zeta_{xx}^{11} = \zeta_{xx}^{22} = \zeta_{yy}^{22}$, $\zeta_{zz}^{12} = \zeta_{zz}^{21}$, and $\zeta_{xx}^{12} = \zeta_{xx}^{21} = \zeta_{yy}^{21}$.

Figure 1 shows the MD simulation results for the two-particle friction coefficients for two LJ particles with $\sigma=0.7$ nm as a function of the interparticle separation, R_{12} . (A set of calculations was carried out for $\sigma=0.3$ and 1.0 nm showing similar trends.) The friction coefficients were obtained from the extrapolation of the time-dependent friction to $t=0$ as discussed in our earlier investigation of the friction coefficient for a single Brownian particle.⁹

A number of different friction tensors can be defined for this two-Brownian particle problem since the friction tensor in Eq. (3) is labeled by particle indices and spatial compo-

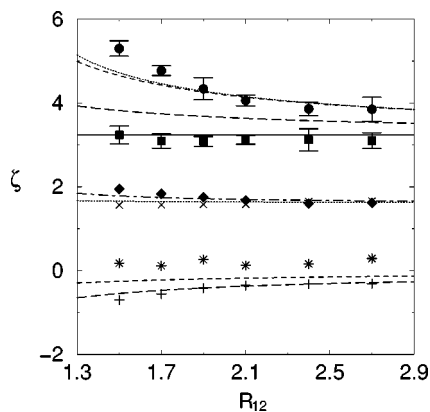


FIG. 1. Friction coefficients (kg/mol ps) for $\sigma=0.7$ nm as function of R_{12} (nm). $\bullet$: $\zeta_{zz}^{(-)}$, $\blacksquare$: $\zeta_{xx}^{(-)}$, $\blacklozenge$: ζ_{zz}^{11} , $\times$: ζ_{xx}^{11} , $*$: ζ_{zz}^{12} , and $+$: ζ_{xx}^{12} , respectively. The solid line indicates twice the single particle friction, $2 \cdot \zeta_0 = 3.242$ kg/mol ps, and the other lines from top are the analytic results for ζ_{zz}^{11} , ζ_{xx}^{11} , ζ_{zz}^{12} , ζ_{xx}^{12} , and ζ_{zz}^{12} , respectively. The uppermost dotted line is the more accurate analytical result (see text).

nents. In view of the symmetry properties noted above, we plot the $\zeta_{zz}^{\alpha\beta}(R_{12})$ and $\zeta_{xx}^{\alpha\beta}(R_{12})$ components of the friction tensor. In this figure we also plot the relative friction defined by

$$\zeta^{(-)}(\mathbf{R}_{12}) = \beta \int_0^\infty dt \langle \mathbf{f}_{12}(0) \mathbf{f}_{12}(t) \rangle_0$$

$$= 2[\zeta^{11}(\mathbf{R}_{12}) - \zeta^{12}(\mathbf{R}_{12})], \quad (5)$$

where $\mathbf{f}_{12}(t)$ is defined by

$$\mathbf{f}_{12} = \mathbf{F}_1 - \mathbf{F}_2. \quad (6)$$

The components of the friction normal to the intermolecular axis, ζ_{xx}^{11} and ζ_{xx}^{12} , are seen to be almost independent of R_{12} while the components parallel to this axis, ζ_{zz}^{11} and ζ_{zz}^{12} , increase as the particle separation decreases. This trend is seen even more clearly in the relative friction where $\zeta_{xx}^{(-)}$ is nearly independent of R_{12} and equal to its asymptotic value of twice the single-particle friction coefficient. The parallel component, $\zeta_{zz}^{(-)}$, increases strongly as R_{12} decreases.

If the Brownian particles were macroscopic in size, the solvent could be treated as a viscous continuum, and the particles would couple to the continuum solvent through slip boundary conditions in view of the central forces that act between the Brownian and solvent particles. The single-particle friction would then be given by Stokes law, $\zeta^S = 4\pi\eta\sigma$, where η is the solvent viscosity. The two-particle friction could be calculated by solving the Navier–Stokes equations in the presence of the two fixed particles. This is a well-known problem that has been extensively studied and exact solutions have been constructed for steady incompressible flows.^{12,13} More tractable expressions obtained using the method of reflections have also been constructed for the distance dependence of the friction and mobility tensors.^{14,15}

The Brownian particles in our study are not macroscopically large so that even the single-particle friction has important microscopic contributions and cannot be simply described in terms of the Stokes law form.⁹ In our simulations, the interactions of the Brownian particles with the solvent

molecules are through repulsive LJ intermolecular forces rather than through boundary conditions as is usual in hydrodynamic treatments of the friction. It is also important to realize that the mesoscopic solvent is a compressible fluid, while most hydrodynamic treatments of the friction assume an incompressible fluid. For these reasons it is very difficult to construct simple models for our two-particle friction data and the present simulations probably represent the most accurate description of the dependence of the friction on the interparticle separation for this system. For these reasons we have chosen to contrast our simulation results with the predictions of a very simple hydrodynamic model simply to gauge the rough magnitudes of hydrodynamic effects.

If we assume that hydrodynamic interactions between the particles are given by Oseen interactions, the two-particle friction tensor takes the form,¹⁶

$$\zeta(\mathbf{R}_{12}) = \zeta_0[\mathbf{I} + \zeta_0 \mathbf{T}(\mathbf{R}_{12})]^{-1}, \quad (7)$$

where ζ_0 is the one-particle friction coefficient and $\mathbf{T}(\mathbf{R}_{12})$ is the Oseen tensor,

$$\mathbf{T}_{\alpha\beta}(\mathbf{R}_{12}) = (1 - \delta_{\alpha\beta}) \frac{1}{8\pi\eta R_{12}} (1 + \hat{\mathbf{R}}_{12} \hat{\mathbf{R}}_{12}). \quad (8)$$

Here $\hat{\mathbf{R}}_{12}$ is a unit vector along the interparticle (z) axis. Taking the inverse of the matrix in Eq. (7) we find,¹¹

$$\zeta_{zz}^{11} = \frac{\zeta_0}{1 - [2h(R_{12})]^2}, \quad \zeta_{xx}^{11} = \frac{\zeta_0}{1 - [h(R_{12})]^2}, \quad (9)$$

$$\zeta_{zz}^{12} = \frac{-2\zeta_0 h(R_{12})}{1 - [2h(R_{12})]^2}, \quad \zeta_{xx}^{12} = \frac{-\zeta_0 h(R_{12})}{1 - [h(R_{12})]^2}, \quad (10)$$

where $h(R_{12}) = \zeta_0 / 8\pi\eta R_{12}$.

For comparison, in Fig. 1 we also plot these expressions for the friction tensor components. There are deviations at small separations as might be expected since the simple hydrodynamic approximations will be poorest at these distances. Our simulations show that ζ_{xx}^{12} varies much more weakly with internuclear separation than the predictions of the simple hydrodynamic model.

Much more detailed theoretical treatments of the distance dependence of the friction tensors have been carried out. In particular, Jones and Schmitz¹⁷ have presented a series of solutions for the mobility (from which the friction can be computed) as a power series in the ratio of the particle size to the distance between the particles that provide a better description of the friction at small separations. The upper dotted line in Fig. 1 shows that while the theory predicts that the friction should increase more strongly at small separations than the simple point particle approximation, the result still lies below the simulation results.

IV. TWO-CLUSTER FRICTION

The two-particle friction calculations discussed in the previous section pertain to a somewhat ideal situation since the two particles interact with the solvent through central repulsive LJ forces. In most instances of solute molecule Brownian motion in solution one is concerned with the motions of large molecules or other aggregates of atomic

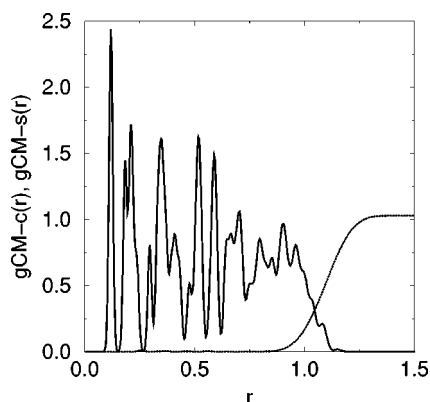


FIG. 2. Radial distribution functions $g_{CM-c}(r)$ (solid line) and $g_{CM-s}(r)$ (dotted line) vs $r(\text{nm})$ for $M=155$.

groups. In such situations the solvent molecules will interact primarily with the atomic surface sites and macroscopically one will have stick boundary conditions. To investigate the issues that come into play when two composite particles interact through the solvent by hydrodynamic forces, we study the two-particle friction for clusters of particles.

Specifically, the M particles comprising of a cluster interact through LJ forces with $\epsilon_{cc}=1.006$ kJ/mol and $\sigma_{cc}=0.34$ nm. The masses of the cluster particles are $m_c=39.948$ g/mol. The individual particles in the cluster interact with the solvent molecules through repulsive LJ forces with $\epsilon_{cs}=1.006$ kJ/mol and $\sigma_{cs}=0.221$ nm. The position of the center of mass of a cluster is denoted by $\mathbf{R}_\alpha$ where α labels the cluster. The LJ forces that bind the cluster particles together are sufficiently strong that no evaporation of the clusters is observed on the long time scale of our simulations. The number of solvent molecules per cell is $N_s/V_0=10$, the same as that for two LJ particles in the previous section.

We first compute the friction of a single cluster in order to be able to assess the importance of hydrodynamic interactions when two clusters interact through the solvent. The structure and some aspects of the diffusional motion of single LJ clusters in the mesoscopic solvent were studied earlier.¹⁸ The numbers of LJ atoms in a cluster were chosen to be $M=25, 50, 100$, and 155 . The structure of the cluster can be determined from an examination of the radial distribution functions for cluster and solvent molecules relative to the center of mass (c.m.) of the cluster which are defined as

$$g_{\text{c.m.}-\nu}(r) = \frac{1}{4\pi r^2 \rho_\nu} \left\langle \sum_i^{N_\nu} \delta(|\mathbf{r}_i - \mathbf{R}_1| - r) \right\rangle, \quad (11)$$

where $\nu=c$ or s labels a cluster or solvent molecule, $\mathbf{R}_1$ is the center of mass of the cluster, and ρ_ν is the number density of cluster or solvent molecules. Figure 2 shows these radial distribution functions for a cluster with $M=155$ particles. The highly structured cluster particle radial distribution function with sharp peaks indicates that the cluster is solidlike. The solvent molecule distribution function shows that solvent molecules do not penetrate deeply into the cluster so that most cluster-solvent interactions are with the surface cluster particles. The radius of the cluster r_c can be estimated

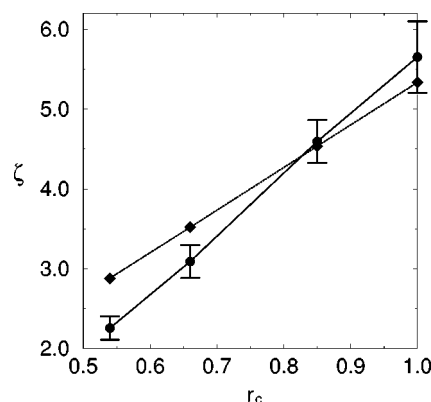


FIG. 3. The friction coefficients (kg/mol ps) ζ_c (●) and $\zeta^S=6\pi\eta r_c$ (◆) as function of radius of cluster, r_c .

from the radial distribution functions and was found to be $r_c \approx 1.0$ nm. For clusters with $M=25, 50$, and 100 we find $r_c \approx 0.54, 0.66$, and 0.85 nm, respectively.

The friction coefficient for cluster is defined in terms of the autocorrelation function of the force on the center of mass of the cluster,

$$\zeta_c = \beta \int_0^\infty dt \langle \mathbf{f}_1^c(0) \mathbf{f}_1^c(t) \rangle_0, \quad (12)$$

where $\mathbf{f}_1^c = \mathbf{F}_1^c - \langle \mathbf{F}_1^c \rangle$ with $\mathbf{F}_1^c$ the total force on the cluster center of mass, $\mathbf{F}_1^c = M^{-1} \sum_{i=1}^M \mathbf{F}_i$ where $\mathbf{F}_i$ is the force on cluster particle i . Notice that this expression for the friction includes contributions from cluster particle-cluster particle interactions as well as cluster particle-solvent particle interactions.

In our calculations of the friction, the center of mass of the cluster was fixed by a holonomic constraint.¹⁹ Figure 3 plots the friction coefficients, obtained from the extrapolation of the time-dependent friction to $t=0$, versus the cluster radius r_c . We see that the friction increases linearly with r_c , indicative of a significant hydrodynamic component to the friction for these nanometer scale composite particles. If the clusters were macroscopic objects in an incompressible fluid one would expect Stokes law to hold with stick boundary conditions. In the figure we plot $\zeta^S=6\pi\eta r_c$ for comparison. The slope of the cluster simulation data is larger than that predicted by Stokes law, presumably due to the fact that macroscopic theory is not fully applicable to these mesoscale particles and there are internal contributions to the friction.

The diffusion coefficient of the cluster was also computed from both the mean-square displacement and center-of-mass velocity autocorrelation function for the moving clusters. The results are shown in Fig. 4 as a function of the number M of cluster particles. As expected, the diffusion coefficient falls rapidly as the number of particles in the cluster increases. We also plot estimates of the cluster diffusion coefficient using the Stokes-Einstein relation with the friction coefficient approximated by its simulation value when the center of mass of the cluster is fixed and the Stokes value of the friction for stick boundary conditions. While these estimates show a similar dependence on M , especially that

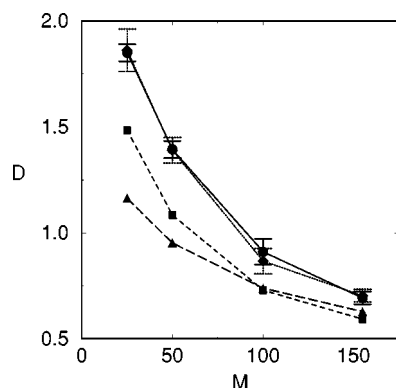


FIG. 4. Diffusion coefficients ($10^{-4} \text{ nm}^2/\text{ps}$) of moving clusters as function of number of cluster particles, M , obtained from mean-square displacement ($\bullet$), velocity autocorrelation functions ($\blacklozenge$), and $D=k_B T/\zeta$ with ζ_c ($\blacksquare$) and with ζ^S ($\blacktriangle$).

obtained using the simulation value of ζ_c , there are quantitative differences likely due to the use of the fixed-particle friction.

Having characterized the frictional properties of a single cluster, we turn to the study of the two-cluster friction coefficient. Specifically, we consider two clusters, each with $M=25$ particles, separated by distances ranging from $R_{12}=0.15$ to 0.27 nm between their centers of mass. The cluster separation was held fixed by a holonomic constraint. Again the particles within each cluster interact through LJ forces and with the solvent through repulsive LJ forces. There are no direct interactions between the particles in different clusters. An example of a two-cluster configuration in the mesoscopic solvent is shown in Fig. 5. We see that the clusters are not spherical and various cluster configurations contribute to the value of the two-cluster friction.

The cluster relative friction coefficients, $\zeta_c^{(-)}(R_{12})$, were computed using the analog of Eq. (5) and the results are shown in Fig. 6 as function of the intercluster separation, R_{12} . As for the two LJ particle case, the component of the relative friction along the cluster internuclear axis [$\zeta_{c,zz}^{(-)}$] exhibits a strong variation with decreasing internuclear separation. The normal component of the friction [$\zeta_{c,xx}^{(-)}$] is almost independent of R_{12} and is closely approximated by twice the single cluster friction coefficient. For comparison, we also plot on this graph the hydrodynamic approximation to the relative friction determined from Eqs. (9) and (10) with $\zeta_{c,0}$ given by the simulation result for the single cluster friction. In this approximation the hydrodynamic interactions are treated assuming that the clusters are structureless objects. This simple Oseen hydrodynamic approximation predicts a

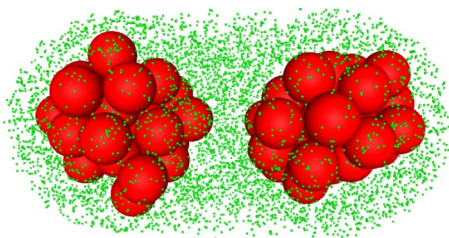


FIG. 5. Instantaneous configuration of two clusters with $M=25$ particles and separated by $R_{12}=1.5 \text{ nm}$ in the mesoscopic solvent.

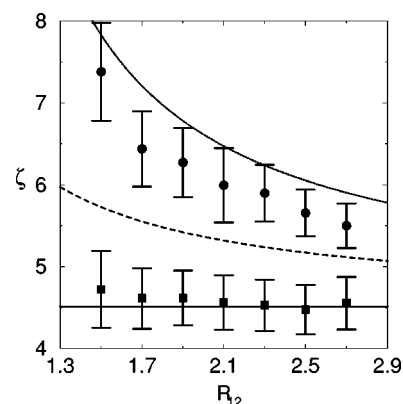


FIG. 6. Friction coefficients (kg/mol ps) for $M=25$ as function of $R_{12} \text{ (nm)}$. $\bullet$: $\zeta_{c,zz}^{(-)}$ and $\blacksquare$: $\zeta_{c,xx}^{(-)}$, respectively. The solid line indicates $2 \cdot \zeta_{c,0} = 4.516 \text{ kg/mol ps}$, and the other lines from top are the hydrodynamic results for $\zeta_{c,zz}^{(-)}$ and $\zeta_{c,xx}^{(-)}$, respectively.

much stronger variation with R_{12} , especially for the normal component of the relative friction. Most of this difference can be ascribed to differences in $\zeta_{c,xx}^{12}(R_{12})$. We have also examined the solvent particle distribution in the vicinity of the clusters, in particular, for small inter-cluster separations. Even at the smallest internuclear separation in our study, the solvent particles lie between the clusters, although the solvent density is reduced. Consequently, a decrease in the friction due to a strong particle depletion effect does not seem to play an important role. This is evident in the simulation data which show a rising relative friction coefficient even at the shortest distances.

V. CONCLUSION

The computation of the friction coefficient is a demanding task for molecular-dynamics simulation. Large system sizes and long simulation times are needed to accurately estimate the friction. The determination of the two-particle friction tensors is even more challenging. The use of the mesoscopic multiparticle collision model for the solvent dynamics has allowed us to carry out extensive simulations of the effects of hydrodynamic interactions on the friction tensors for nanoscale LJ and composite cluster particles. Since the particles have nanometer dimensions they lie in the intermediate size range where a pure hydrodynamic treatment is not fully applicable and yet solvent collective effects are sufficiently large that hydrodynamic contributions are likely to play an important role. Our simulations bear out these considerations. We find clear signatures for the importance of hydrodynamic effects. Hydrodynamic effects manifest themselves in the magnitudes of the single-molecule friction coefficients. The dependence of the two-particle friction on the interparticle separation is clear evidence for the influence of hydrodynamic interactions on this transport property. Simple hydrodynamic models cannot quantitatively describe the simulation results.

The mesoscopic multiparticle collision dynamics conserves mass momentum and energy and as a result can capture correctly the hydrodynamic interactions among solute species. In this connection, the model has proved useful in studies of polymer^{20–23} and colloid^{24,25} dynamics where such

hydrodynamic interactions are important and yet are difficult to model by other techniques such as Brownian dynamics. In Brownian dynamics the spatially dependent friction tensors must be supplied as input. Analogous considerations apply to diffusion-influenced reactions where the long-range diffusion coupling influences reaction rates.²⁶ The present calculations have shown that the hydrodynamic interactions among small solute species can be described in such simulations and thus provide a basis for studies of more complex molecular systems in solution.

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