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Friction and diffusion of a Brownian particle in a mesoscopic solvent

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The friction and diffusion coefficients of a massive Brownian particle in a mesoscopic solvent are computed from the force and the velocity autocorrelation functions. The mesoscopic solvent is described in terms of free streaming of the solvent molecules, interrupted at discrete time intervals by multiparticle collisions that conserve mass, momentum, and energy. The Brownian particle interacts with the solvent molecules through repulsive Lennard-Jones forces. The decays of the force and velocity autocorrelation functions are analyzed in the microcanonical ensemble as a function of the number N of solvent molecules and Brownian particle mass and diameter. The simulations are carried out for large system sizes and long times to assess the N dependence of the friction coefficient. The decay rates of these correlations are confirmed to vary as N^{-1} in accord with earlier predictions. Hydrodynamic effects on the velocity autocorrelation function and diffusion coefficient are studied as a function of Brownian particle mass and diameter. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1815291]

I. INTRODUCTION

The friction and diffusion coefficients are two of the basic transport properties that can be used to characterize the dynamics of solute molecules in solution. Both of these coefficients play a central role in problems ranging from the rates of chemical reactions in the condensed phase to the description of polymer dynamics in solution. The force and velocity autocorrelation functions from which these transport coefficients may be determined present interesting features. The calculation of the diffusion coefficient from the velocity autocorrelation must account for the power law decay of this quantity at long times due to the coupling of the solute molecule motion to the hydrodynamic fields of the solvent.[1] The computation of the friction from the time integral of the force autocorrelation function must deal with the plateau value problem since the infinite time integral of this correlation function is zero.[2]

These are well-studied problems that have been addressed many times, and calculations of these quantities by molecular dynamics (MD) simulation are now common. Nevertheless, the computation of the friction coefficient from MD simulations involves a number of subtle issues for finite-size systems as discussed in several recent papers.[3,4] The problems center around the definition of the friction coefficient in terms of projected dynamics and its relation to the fixed-particle friction coefficient for a massive Brownian particle. The estimates of the friction coefficient have been shown to depend on the order in which the mass of the Brownian particle and the solvent particle number N are taken to infinity. For finite-size systems one must investigate how large N must be to obtain a reliable estimate of the friction; this typically requires very large MD simulations. Similarly, the estimate of the diffusion coefficient from the velocity autocorrelation function requires large scale simulations, especially for large Brownian particles, due to the importance of hydrodynamic contributions.

The purpose of this paper is twofold: First, we investigate the issues discussed above by carrying out very large scale simulations involving up to millions of solvent molecules for long times. Second, we use these calculations to demonstrate the utility of a hybrid molecular dynamics-mesoscopic multiparticle collision model[5–7] for studying solute motion when coupling to hydrodynamic modes of the solvent is important. The use of the mesoscopic model permits us to efficiently carry out the large scale simulations of solvent motion.

The outline of the paper is as follows: In Sec. II we summarize the issues related to the computation of the friction and diffusion coefficients for Brownian particles in finite-size systems. The hybrid mesoscopic model is sketched in Sec. III along with the specification of the specific system under investigation. The results of the simulations are described in Sec. IV and the conclusions of the paper are given in Sec. V.

II. FORCE AND MOMENTUM AUTOCORRELATION FUNCTIONS

The generalized Langevin equation for the momentum **P** of a Brownian particle (B particle) with mass M in a bath of N solvent molecules with mass m has the form[8]

$$\frac{d\mathbf{P}(t)}{dt} = -\int_0^t dt' \; k(t')\mathbf{P}(t-t') + \mathbf{F}^+(t), \tag{1}$$

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where $\mathbf{F}^{+}(t)$ a random force whose time evolution is determined by evolution where the momentum of the B particle is projected out (the plus superscript denotes this projected evolution) and the memory kernel $k(t)$ is given by the random force autocorrelation function,

$$k(t)=\langle \mathbf{F}^{+}(t)\cdot\mathbf{F}\rangle/\langle P^2\rangle, \tag{2}$$

where the angular brackets denote a suitable equilibrium average. It is convenient to define a time dependent friction coefficient as the finite time integral of the projected force autocorrelation function as

$$\zeta(t)=\frac{1}{3k_BT}\int_0^t dt'\langle \mathbf{F}^{+}(t')\cdot\mathbf{F}\rangle, \tag{3}$$

where T is the temperature and k_B is Boltzmann's constant. The friction coefficient is then the infinite time value of the quantity, $\zeta=\lim_{t\to\infty}\zeta(t)$. Making a Markovian approximation the generalized Langevin equation reduces the Langevin equation,[9]

$$\frac{d\mathbf{P}(t)}{dt}=-\frac{\zeta}{\mu}\mathbf{P}(t)+\mathbf{F}^{+}(t), \tag{4}$$

where $\mu=\langle P^2\rangle/3k_BT$. In the canonical ensemble $\langle P^2\rangle=3k_BTM$ and $\mu=M$. In the limit of a massive Brownian particle $(M\gg m)$ and bath relaxation that is rapid compared to the characteristic decay time of the B particle momentum, Mazur and Oppenheim[10] demonstrated that one may derive the Langevin equation from the microscopic equations of motion using projection operator methods and discussed the conditions under which such a reduction is valid. The conditions under which the Stokes law formula can be used for the friction have also been determined.[11]

The momentum autocorrelation function can be determined from the Langevin equation and decays exponentially as

$$C_P(t)=\langle \mathbf{P}(t)\cdot\mathbf{P}\rangle\langle P^2\rangle^{-1}=e^{-\zeta t/\mu}. \tag{5}$$

Since the diffusion coefficient is the infinite time integral of the velocity autocorrelation function we have the Einstein relation, $D=k_BT/\zeta$. The friction coefficient can be determined from the long time decay of the momentum autocorrelation function or the time integral of the projected force autocorrelation function.

Transport properties are typically determined in molecular dynamics simulations in the microcanonical ensemble and some subtle issues are encountered when determining the friction coefficient from such simulations. These issues have been discussed by Español and Zúñiga.[3] Briefly, they are as follows: The friction coefficient is estimated in MD simulations by computing the time integral of the force autocorrelation function using ordinary dynamics, since it is in general very difficult to carry out projected evolution. The Laplace transforms of the projected and unprojected force autocorrelation functions are related by the formula[2]

$$\langle \hat{\mathbf{F}}(z)\cdot\mathbf{F}\rangle=\frac{z\langle \hat{\mathbf{F}}^{+}(z)\cdot\mathbf{F}\rangle}{z+\langle \hat{\mathbf{F}}^{+}(z)\cdot\mathbf{F}\rangle/\langle P^2\rangle}. \tag{6}$$

Since $\lim_{z\to 0}\langle \hat{\mathbf{F}}^{+}(z)\cdot\mathbf{F}\rangle=3k_BT\zeta$, $\lim_{z\to 0}\langle \hat{\mathbf{F}}(z)\cdot\mathbf{F}\rangle=\int_0^\infty dt\langle \mathbf{F}(t)\cdot\mathbf{F}\rangle=0$. This is the well-known plateau value problem: the friction must be estimated from the integral of the short time decay of the unprojected force autocorrelation function since its infinite time integral is zero.[2] In analogy with Eq. (3) we can define a time dependent friction $\zeta_u(t)$ in terms of the unprojected force autocorrelation function,

$$\zeta_u(t)=\frac{1}{3k_BT}\int_0^t dt'\langle \mathbf{F}(t')\cdot\mathbf{F}\rangle. \tag{7}$$

Its Laplace transform is $\hat{\zeta}_u(z)=\langle \hat{\mathbf{F}}(z)\cdot\mathbf{F}\rangle/(z3k_BT)$; thus, from Eq. (6) we have

$$\hat{\zeta}_u(z)=\frac{\zeta(z)}{z+\zeta(z)/\mu}, \tag{8}$$

whose small z form is $\hat{\zeta}_u(z)\approx\zeta/(z+\zeta/\mu)$, or, in t space,

$$\zeta_u(t)\approx\zeta e^{-\zeta t/\mu}. \tag{9}$$

The friction coefficient may then be estimated from the extrapolation of the long time decay of $\zeta_u(t)$ to $t=0$, or from the decay rates of the momentum atuocorrelation function or $\zeta_u(t)$.

In the microcanonical ensemble $\langle P^2\rangle=3k_BT\mu=3k_BTMNm/(M+Nm)$.[3] If the limit $M\to\infty$ is first taken in the calculation of the force autocorrelation function, then $\mu=Nm$ and, as can be seen from Eq. (6), in the thermodynamic limit the projected and unprojected force autocorrelations are the same. Since MD simulations are carried out at finite N, the study of the N (and M) dependence of $\zeta_u(t)$ and the estimate of the friction coefficient from either the decay of the momentum or force correlation functions is of interest. This has prompted the MD simulations of the momentum and force autocorrelation functions as a function of N in Refs. 3 and 4 to explore this question.

III. MULTIPARTICLE COLLISION DYNAMICS

The system we study comprises a B particle with mass M and phase space coordinates $(\mathbf{R},\mathbf{P})$ interacting with a bath of N particles with mass m and phase space coordinates $(\mathbf{r}_i,\mathbf{p}_i)$. The system Hamiltonian is

$$\mathsf{H}=\frac{P^2}{2M}+\sum_{i=1}^{N}\left[\frac{p_i^2}{2m}+V(|\mathbf{R}-\mathbf{r}_i|)\right], \tag{10}$$

where the interaction between the B particle and a solvent particle is repulsive and is given by a truncated Lennard-Jones potential,

$$V(r)=\begin{cases}4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}+\frac{1}{4}\right], & r<2^{1/6}\sigma\\ 0, & r>2^{1/6}\sigma.\end{cases} \tag{11}$$

There are no intermolecular forces among the solvent molecules. Interactions among these particles are taken into account by mesoscopic multiparticle collision dynamics.[5] Multi-particle collisions among the solvent molecules are carried out at discrete time intervals τ. To carry out such collisions, the simulation box is partitioned into n^3 cells labeled by ξ and at each time interval τ rotation operators $\hat{\omega}_\xi$, chosen at random from 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.[12]

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:

$$\mathbf{v}_i = \mathbf{V}_\xi + \hat{\omega}_\xi[\mathbf{v}_i' - \mathbf{V}_\xi]. \tag{12}$$

Such multiparticle collisions are carried out independently in each cell. Between multiparticle collisions solvent molecules undergo free streaming motion. The multiparticle collisions and free streaming steps constitute the mesoscopic solvent dynamics.

This mesoscopic dynamics conserves mass, momentum, and energy. Phase space volumes are preserved. The equilibrium distribution is microcanonical and one may show that the single particle velocity distribution evolves to a Maxwell-Boltzmann distribution. On long distance and time scales the conserved fields satisfy the hydrodynamic equations with transport properties determined by discrete-time analogs of the Green-Kubo formulas.[5–7]

When a B particle is present in solution we use the hybrid MD-multiparticle collision model.[6,7] In the hybrid model, between multiparticle solvent collisions which take place at time intervals τ, instead of free streaming, the system evolves by Newton's equations of motion that follow from the Hamiltonian in Eq. (10). This hybrid model satisfies the conservation laws. Consequently, although the solvent dynamics is described at a mesoscopic level, the dynamics is microcanonical, preserves phase space volumes and will generate the correct coupling between the B particle motion and the solvent hydrodynamic fields on long distance and time scales. Because of the simplicity of the mesoscopic solvent dynamics, we can investigate the B particle motion on long time scales for systems containing many solvent molecules. The mesoscopic multiparticle collision model has been used previously to study hydrodynamic flows,[12] cluster dynamics,[13] polymer dynamics,[14] phase segregation, colloidal suspensions[15] and complex fluids,[16] and diffusion-influenced reaction dynamics.[17]

IV. SIMULATION RESULTS

A. Simulation details

We have carried out MD simulations for a B particle in a solvent of N mesoscopic particles for many different values of N and M/m. In particular, we investigated systems with $N = 5120$, 17 280, 40 960, 80 000, and 327 680 particles. The mass ratio M/m was taken to have the values $M/m \approx 5N$, $10N$, $20N$, and $200N$. We also investigated the case where mass ratio is infinity and the B particle was fixed by a holonomic constraint.[18]

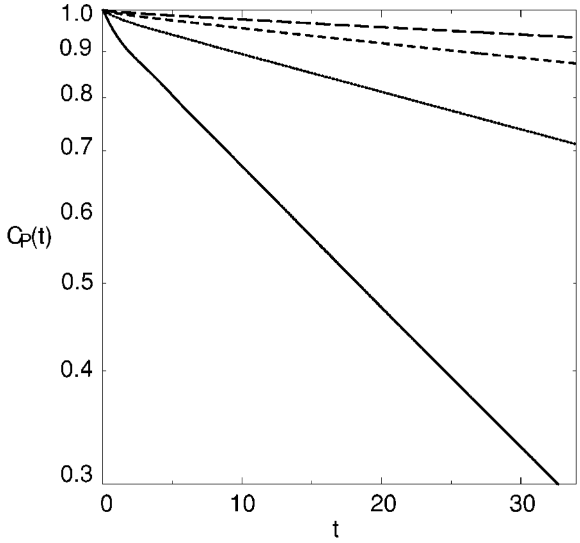

FIG. 1. Semilogarithmic plot of normalized momentum autocorrelation function as function of time (picoseconds) for $M/m \approx 20N$. Solid line, $N = 5120$; dotted, $N = 17\,280$; dashed, $N = 40\,960$; and long-dashed, $N = 80\,000$.

The B particle–solvent particle interaction parameters are $\sigma = 0.3$ nm and $\epsilon = 1.006\,04$ kJ/mol. The masses of the solvent particles are $m = 3.9948$ g/mol. In a subsequent section on size effects, results are presented as a function of σ.

The simulations were carried out in a cubic box of volume $V = L^3$ with periodic boundary conditions. If the volume of the B particle is $V_B = 4/3\pi\sigma^3$, V_0 is defined as the volume of the system occupied by solvent molecules, $V_0 = V - V_B$. The multiparticle collision cell volume is given by $V_\xi = V/n^3 = (L/n)^3 = \ell^3$. The values of L and N were chosen to fix the number density of solvent particles at $\rho_s = N/V_0 = 2035.42\ \mathrm{nm}^{-3}$ or an average of ten particles per collision cell.

Newton's equations of motion were integrated using the velocity Verlet algorithm,[19] with a time step of $\Delta t = 0.006\,776$ ps. Multiparticle solvent collisions were carried out in cells with linear dimension ℓ every 50 molecular dynamics time steps so that $\tau = 50\Delta t = 0.3388$ ps. The temperature, determined from the average kinetic energy, was taken to be $T = 40.33$ K so that the reduced temperature $k_BT/\epsilon = 1/3$. The results were obtained from ensembles of ten microcanonical MD trajectories of length ≈ 68 ns. The statistical errors in the friction coefficients were determined from block averages over the ensemble members.

B. N dependence of the friction for massive Brownian particles

From Eq. (5), for long times the momentum autocorrelation function decays exponentially with a decay constant ζ/μ. Here we study the decay of this correlation function for very massive B particles whose mass M is greater than that of the sum of all the solvent particle masses, $M \gg mN$. If we let $q = M/(mN)$, then the reduced mass takes the form $\mu = mNq/(q+1)$; hence, for fixed q, the momentum decay rate should vary as $1/N$. This is borne out by the data in Fig. 1 which plots the normalized momentum autocorrelation

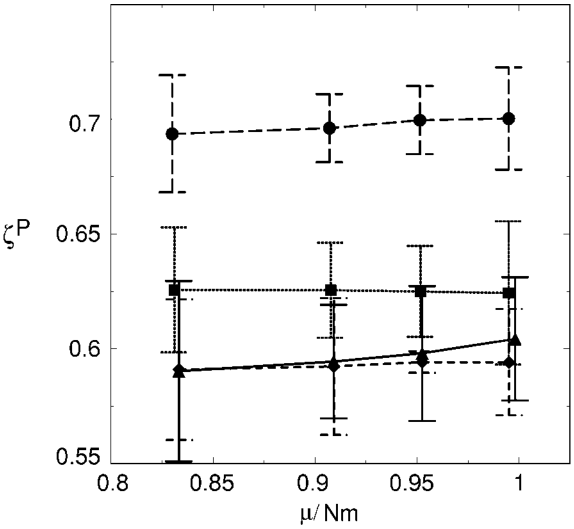

FIG. 2. The friction coefficient ζ^P (kg/mol ps) as function of $\mu/(Nm)$. Circles, $N=5120$; squares, $N=17\,280$; diamonds, $N=40\,960$; and triangles, $N=80\,000$.

function $C_P(t)$ versus t for $q\approx 20$ and different values of N on a semilogarithmic scale. Linear decay is observed for long times with decreasing slopes as N increases.

The friction coefficients extracted from such simulation data are summarized in Fig. 2 which shows ζ^P (we denote the value of ζ obtained from the decay of the momentum correlation function by ζ^P) versus $\mu/(mN)=q/(q+1)$ for various values of q and N. For fixed N, ζ^P is independent of $\mu/(mN)$ (within the statistical error) and tends to a limiting value for sufficiently large N. The value of the friction coefficient for $\mu/(mN)=1$ corresponds to a very massive B particle ($M\gg mN$). Systems with more than $\approx 30\,000$ solvent particles are required to reach this asymptotic regime. Molecular dynamics simulations on systems with a smaller number of particles will yield poor estimates of the friction coefficient. These findings are consistent with earlier MD simulation studies of this problem by Ould-Kaddour and Levesque.[4]

The friction coefficient can also be determined from $\zeta_u(t)$, either by measuring the slope of the decay of this quantity or from the extrapolation of its long time decay to $t=0$. The semilogarithmic plots of this quantity in Fig. 3 for various values of N show the expected linear decay at long times. In this figure we also show the extrapolation of the long time linear decay to $t=0$ which has been used to obtain ζ^F, the estimate of ζ from this extrapolation of the integral of the force autocorrelation function.

For long times the finite time integral of the unprojected force autocorrelation function can be related to the time derivative of the normalized momentum autocorrelation function by $\zeta_u(t)=-\mu dC_P(t)/dt$. As a check on the consistency of the simulation data, in Fig. 3 we have plotted both $\zeta_u(t)$ obtained from the simulation of the force autocorrelation function and and the numerical time derivative of the momentum autocorrelation function. As required, these two estimates are well within the statistical errors and the different curves are difficult to distinguish in the figure.

We have found that it is difficult to determine the friction coefficient from the slope of $\zeta_u(t)$, especially for very large N where the slope is close to zero. While the slopes scale as $1/N$ for the smaller N values in our study, the small value of the slope and relatively large statistical error makes it difficult to determine this scaling for very large values of N. However, ζ may be determined accurately from the extrapolation of the long time behavior of $\zeta_u(t)$ to $t=0$, as shown in Fig. 3. The friction coefficients obtained in this way are plotted in Fig. 4 versus $\mu/(mN)$ for various values of N. One again sees that for sufficiently large N the friction coefficient determined in this way is independent of $\mu/(mN)$. The value of the friction coefficient for $\mu/(mN)=1$ corresponds to an

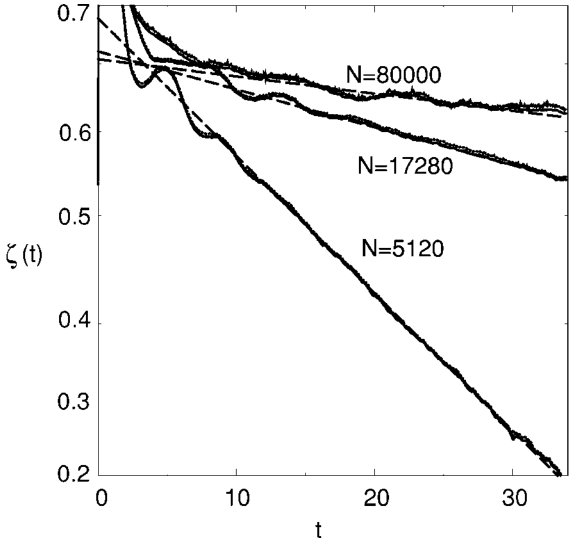

FIG. 3. Semilogarithmic plot of time dependent friction coefficient (kg/mol ps), Eq. (3), (solid lines) and time derivative of normalized momentum autocorrelation function, Eq. (5), (dotted lines) as function of time (picoseconds) for $M/m\approx 20N$ for three values of N. The straight lines show the extrapolation of the exponential long time-decay to $t=0$ used to determine the value of ζ^F.

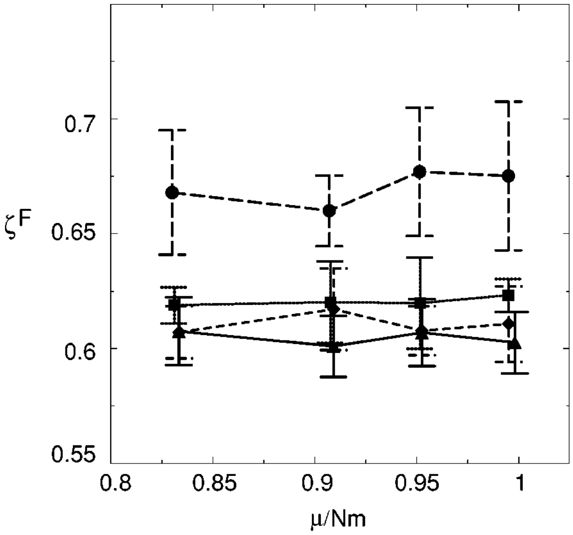

FIG. 4. Plot of the friction coefficient ζ^F (kg/mol ps) as function of $\mu/(Nm)$. Circles, $N=5120$; squares, $N=17\,280$; diamonds, $N=40\,960$; and triangles, $N=80\,000$.

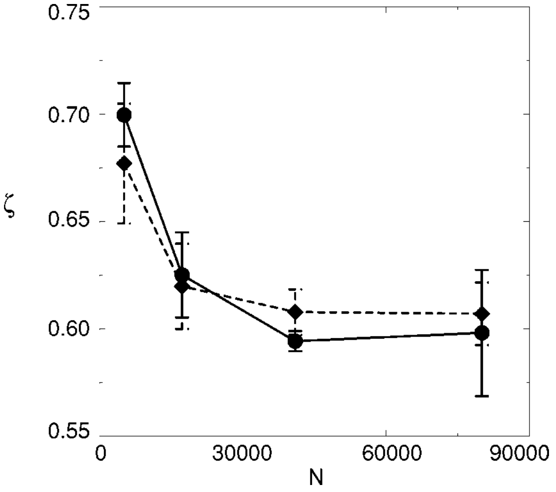

FIG. 5. Friction coefficient (kg/mol ps) as function of N for $M/m \approx 20N$. Circles, ζ^P and diamonds, ζ^F.

infinitely massive B particle whose position was fixed by a holonomic constraint.[18]

Another representation of the friction coefficient data is shown in Fig. 5 where both the ζ^P and ζ^F estimates are plotted versus N for $M/m \approx 20N$. The figure shows that both estimates of ζ are in agreement and converge to approximately the same asymptotic value for $N > 30\,000$.

C. Diffusion coefficient and velocity autocorrelation function

The diffusion coefficient may be determined from either the mean square displacement of the B particle or the infinite time integral of the velocity autocorrelation function. In our simulations, the diffusion coefficients determined by both of these methods are in accord. Figure 6 shows

$$D(t) = \frac{1}{3}\int_0^t dt' \langle \mathbf{V}(t') \cdot \mathbf{V} \rangle, \tag{13}$$

the running integral of velocity autocorrelation function as function of time for a solvent with $N = 327\,680$ particles and for mass ratios of B particle to solvent particle masses of $M/m = 100$, 150, 250, and 400. One can see the slow approach of $D(t)$ to its asymptotic value D, the diffusion coefficient. Furthermore, D is nearly independent of mass for these parameter values within the statistical uncertainty. The diffusion coefficients (in units of 10^{-4} nm^2/ps) determined from the mean-square displacement (MSD) and integral of the velocity autocorrelation function (VAC) are, for instance: $D(\text{MSD}) = 6.12 \pm 0.38$, $D(\text{VAC}) = 6.12 \pm 0.37$ for $M/m = 100$ and $D(\text{MSD}) = 6.24 \pm 0.21$, $D(\text{VAC}) = 6.23 \pm 0.29$ for $M/m = 400$. Using the friction data obtained earlier and the Einstein relation the estimate of the diffusion coefficient for this parameter value is $D = k_B T/\zeta = 5.55 \pm 0.20 \times 10^{-4}$ nm^2/ps.

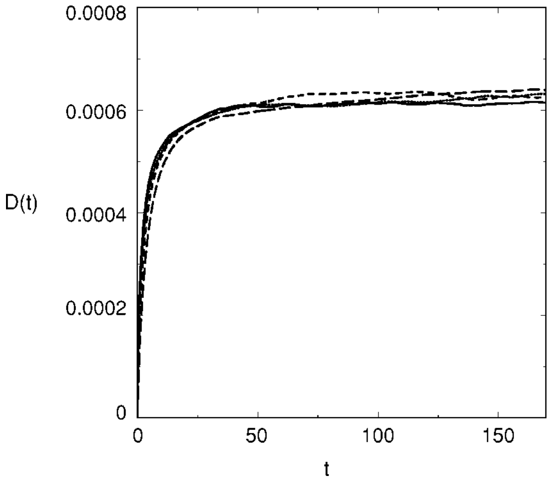

FIG. 6. Running integral of velocity autocorrelation function, $D(t)$ (nm^2/ps) as function of time (picoseconds) for $N = 327\,680$. Solid line, $M/m = 100$; dotted line, $M/m = 150$; dashed line, $M/m = 250$; and long-dashed line, $M/m = 400$.

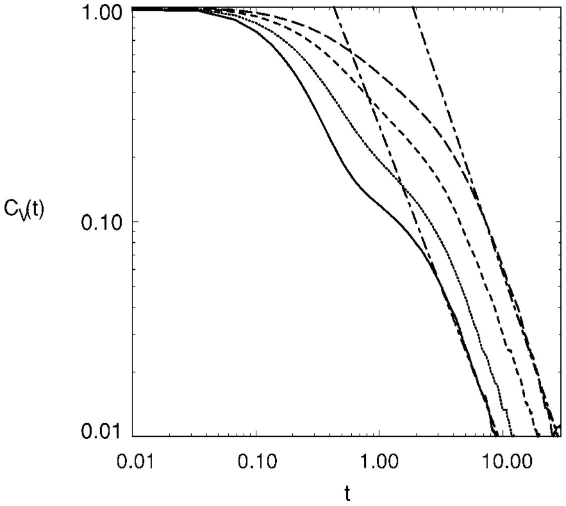

FIG. 7. A log-log plot of velocity autocorrelation function, $C_V(t)$ as function of time (picoseconds) for $N = 327\,680$. Solid line, $M/m = 100$; dotted line, $M/m = 150$; dashed line, $M/m = 250$; and long-dashed line, $M/m = 400$. The straight-line fits at long times were used to determine the long-time power law decay. The slopes extracted from such fits are -1.50 for $M/m = 100$ and -1.61 for $M/m = 400$.

Figure 7 shows a log-log plot of the normalized velocity autocorrelation function, $C_V(t) = \langle \mathbf{V}(t) \cdot \mathbf{V} \rangle / \langle V^2 \rangle$, as function of time for the same values of the mass ratio as in Fig. 6. At long times one observes power law decay. The fits to this long-time decay shown in the figure yield slopes consistent with the expected $t^{-3/2}$ power law decay of the velocity autocorrelation function that arises from the coupling of the B particle velocity to the hydrodynamic modes of the solvent.[1]

D. Size dependence of the friction coefficient

The friction coefficient of a large B particle is strongly influenced by hydrodynamic effects. The importance of hydrodynamic effects is reflected in the Stokes formula, $\zeta = c\pi\eta a$, where $c = 4$ or 6 for slip or stick boundary conditions, respectively. The characteristic size of the B particle is a and η is the solvent viscosity. We have calculated the friction coefficient for a system with $N = 327\,680$ solvent molecules as function of σ, which determines the effective size of the B particle. All other system parameters were the

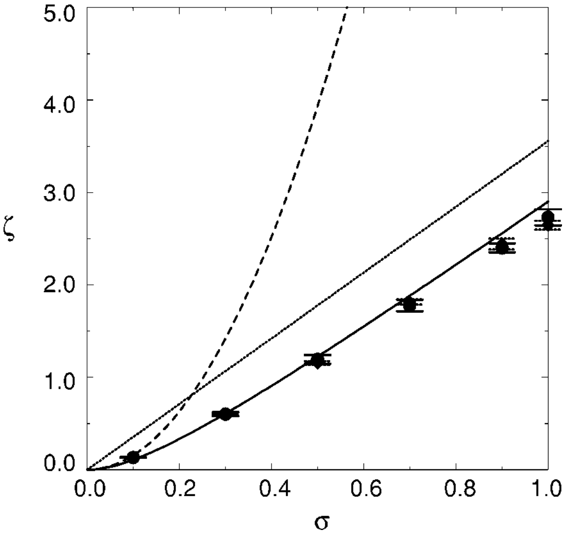

FIG. 8. Friction coefficient as function of σ. Circles, ζ^P; diamonds, ζ^F; dotted line, ζ_h; dashed line, ζ_m; and solid line, ζ.

same as those introduced earlier. As σ increased, the box size was varied in order to maintain a constant density of the mesoscopic solvent. We have used a large system size for these studies since Ould-Kaddour and Levesque[4] have demonstrated that the system size needed to obtain converged friction results increases with the size of the B particle. A MD study of the velocity autocorrelation function and diffusion coefficient for large, massive B particles was recently carried out to investigate the influence of hydrodynamic contributions.[20]

Figure 8 shows the friction coefficient as function of σ. For large σ one sees that the friction coefficient varies linearly with σ in accord with the prediction of the Stokes formula.

One may analyze the size dependence of the friction coefficient in more detail. For the central force interactions between the solvent and B particle used in this study, only the component of the force along the line of centers joining the center of the B particle to a solvent particle contributes. Consequently, slip boundary conditions will result on macroscopic scales. We have independently computed the viscosity of the mesoscopic solvent[12,21] to be $\eta = 4.70 \times 10^{-4}$ kg/m s. In Fig. 8 we plot the hydrodynamic estimate of the friction $\zeta_h = 4\pi\eta\sigma$ versus σ. One can see that it lies close to the simulation value for large σ but overestimates the friction for small σ. When σ is small one expects microscopic contributions to dominate the friction coefficient. A rough estimate of the microscopic friction can be obtained using a hard sphere binary collision model with the collision diameter chosen to be σ: $\zeta_m = 8/3\rho\sigma^2(2\pi m k_B T)^{1/2}$. The plot of ζ_m versus σ in Fig. 8 shows close correspondence with the simulation data at small σ but the variation of ζ_m with σ^2 leads to a strong increase that deviates from the simulation data for large σ. An estimate[22] of the friction that accounts for both microscopic and hydrodynamic contributions to the friction is $\zeta^{-1} = \zeta_m^{-1} + \zeta_h^{-1}$ and this estimate is also plotted in the figure. It interpolates between the two limiting forms and is close accord with the simulation data.

V. CONCLUSION

The large-scale simulations of both the momentum and force autocorrelation functions in the microcanonical ensemble confirm the predicted dependence[3,4] of the decay rates of these correlation functions on the number N of solvent particles in the system. The friction coefficient can be determined accurately from either the decay rate of the of momentum autocorrelation function or the extrapolation of the long time decay of the force autocorrelation function to $t=0$, provided N is sufficiently large, typically $N > 30\,000$ in our simulations. The strong N dependence of the friction for smaller N leads to poor estimates of this quantity. The long-time $t^{-3/2}$ power law decay of the velocity autocorrelation function is also found in the simulations and the diffusion and friction coefficients reflect the corresponding contributions from hydrodynamic effects on the B particle transport properties. In particular, the friction coefficient is shown to scale linearly with size for large B particles in accord with predictions of hydrodynamic theories.

It was possible to carry out large-scale simulations to obtain the results reported in this paper because of the use of the mesoscopic multi-particle collision description of the solvent dynamics. This mesoscopic dynamics satisfies the exact conservation laws and preserves phase space volumes like full molecular dynamics. As a result, the important effects arising from coupling of the B particle motion to hydrodynamic solvent modes is properly taken into account. The simulation results presented above serve to confirm the utility of such mesoscopic models for the investigations of solute molecular dynamics.

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