Test of Stokes-Einstein Formula for a Tracer in a Mesoscopic Solvent by Molecular Dynamics Simulation

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In this work, the friction and diffusion coefficients of a tracer in a mesoscopic solvent are evaluated as a function of the tracer size by a hybrid molecular dynamics simulation where solute molecules evolve by Newton's equations of motion but the solvent evolves through the multi-particle collision dynamics. The friction coefficient is shown to scale linearly with the tracer size for larger tracers in accord with predictions of hydrodynamic theories. The diffusion coefficient of tracer is found to be inversely proportional to tracer size. The behavior of Stokes-Einstein formula is validated as a function of tracer size.

Key Words : Friction, Tracer, MD simulation, Mesoscopic solvent, Stoke-Einstein formula

Introduction

Recently, Kapral and co-worker have constructed a mesoscopic model for fluid dynamics.[1] In this model, fluid particles interact through multi-particle collision events which take place at discrete time intervals. Between such collision events the particles undergo free streaming motion. The dynamics conserves mass, momentum and energy and yields the exact hydrodynamic equations of motion for the conserved fields on long distance and time scales. One may consider the dynamics of solute molecules in this mesoscopic solvent and because the solvent is described at an effective particle level the solute and solvent molecules interact through intermolecular forces rather than through boundary conditions. This leads to a hybrid description of the dynamics where solute molecules evolve by Newton's equations of motion but the solvent evolves through the multi-particle mesoscale dynamics.[2,3]

Calculations of the diffusion and friction coefficients by molecular dynamics (MD) simulations are well-studied problems that have been addressed many times. 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.[4-6] The problems center around the definition of the friction coefficient in terms of the projected dynamics and its relation to the fixed-particle friction coefficient for a massive Brownian particle. The estimates of the friction coefficients have been shown to depend on the order in which the mass of the tracer 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 tracers, due to the importance of hydrodynamic contributions.

In recent papers,[7-9] the friction and diffusion coefficients of a tracer in a Lennard-Jones (LJ) solvent were evaluated by equilibrium molecular dynamics simulations in a microcanonical ensemble. The solvent molecules of diameter σ_1 interact with each other through a repulsive LJ force and the tracer of diameter σ_2 interacts with the solvent molecules through the same repulsive LJ force except a different LJ size or diameter parameter. These works were motivated by determination of the diffusion (D) and friction (ζ) coefficients of the tracer in the thermodynamic limit (N→∞) and by test of the Stokes-Einstein (SE) formula:

$$D = \frac{kT}{C\pi\eta\sigma} \qquad (1)$$

which is the combination of the Stokes' law:

$$\zeta = C\pi\eta\sigma \qquad (2)$$

and the Einstein relation:

$$D = \frac{kT}{\zeta}, \qquad (3)$$

where k is the Boltzmann constant, T the absolute temperature, σ the radius of the diffusing particle, and C the hydrodynamic boundary condition. They found that the behavior of the friction and diffusion coefficients is well described by the Einstein relation [Eq. (3)] when the values of σ_2/σ_1 are higher than 5 approximately, and the value of $\zeta D/kT$ decreases initially as σ_2/σ_1 increases, and then levels off at σ_2/σ_1 independent values of 0.79 (N = 32,000) and 0.91 (N = 320,000), respectively, compared with the prediction by the Einstein relation $\zeta D/kT = 1$ for all σ_2/σ_1.

The main purpose of this paper is to study the validity of the SE formula by carrying out simple MD simulations of a tracer in a mesoscopic solvent and compare with the result in a large number of LJ solvent molecules (N = 320,000).[9] The friction and diffusion coefficients of a tracer in a mesoscopic solvent were computed from the force and velocity autocorrelation functions,[10] but the systematic test for the validity of the SE formula was missed.

Multi-Particle Collision Dynamics and Simulation Details. The system comprises a tracer with mass M and phase space coordinates (**R**,**P**) interacting with a bath of N particles with mass m and phase space coordinates (**r**$_i$,**p**$_i$). The system Hamiltonian is

$$H = \frac{P^2}{2M} + \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + V(|R - r_i|) \right] \qquad (4)$$

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

$$V(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4} \right] & r < 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases} \qquad (5)$$

There are no intermolecular forces among the solvent molecules. Interactions among these particles are taken into account by mesoscopic multi-particle collision dynamics.[1] 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 multi-particle collision volumes.[11] At any time instant, a cell will contain a certain number of solvent molecules with velocities v_i'. Let V_ξ be the center of mass velocity of the particles in cell ξ. The post collision velocities of the particles in the cell are determined by rotating the particle velocities, relative to the center of mass velocity V_ξ, by the rotation operator $\hat{\omega}_\xi$, and then adding V_ξ to the result:

$$v_i = V_\xi + \hat{\omega}_\xi [v_i' - V_\xi] \qquad (6)$$

Such multi-particle collisions are carried out independently in each cell.

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

Newton's equations of motion were integrated using the velocity Verlet algorithm,[12] with a time step of $\Delta t = 0.006776$ ps. Multi-particle 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 $k_B T/\varepsilon = 1/3$. The results were obtained from ensembles of ten micro-canoni-cal MD trajectories of length ~100 ns. The statistical errors in the friction coefficients were determined from block averages over the ensemble members.

Results and Discussion

We have carried out a hybrid MD simulations for a tracer in a solvent of N mesoscopic particles for many different values of N and M/m. The tracer-solvent particle interaction parameters are $\sigma = 0.3$ nm and $\varepsilon = 1.00604$ kJ/mol. The mass of the solvent particle is m = 3.9948 g/mol. In particular, we investigated systems with N = 5120, 17280, 40960, 80000 and 327680 particles. The mass ratio M/m is taken to have the values M/m $\approx$ 100, 150, 250, 400 and 10^{90}. We also investigated the case where mass ratio is infinity or the tracer was fixed by a holonomic constraint.[13]

The normalized momentum auto-correlation function can be determined from the Langevin equation and decays exponentially in the following form:

$$C_p(t) = \frac{\langle P(t) \cdot P(0) \rangle}{\langle P(0)^2 \rangle} = \exp(-\zeta_1 t/Nm), \qquad (7)$$

where ζ_1 is the first friction constant.

A time dependent friction coefficient $\zeta_u(t)$ is defined from the force autocorrelation function by[14]

$$\zeta_u(t) = \frac{1}{3kT} \int_0^\infty dt \lim_{M \to \infty} \langle F(t) \cdot F(0) \rangle, \qquad (8)$$

and through the Laplace transforms of the projected and unprojected force autocorrelation functions,[15-17] in t space, the following relation is obtained

$$\zeta_u(t) = \zeta_2 \exp(-\zeta_3 t/Nm). \qquad (9)$$

The friction coefficient may then be estimated from the extrapolation (ζ_2) of the long time decay of the time dependent friction coefficient $\zeta_u(t)$ to t = 0 or from the decay rate (ζ_3) of $\zeta_u(t)$.

The friction coefficients of the tracer of $\sigma = 0.3$ nm as a function of N in the cases of M/m = 10^{90} and ∞ are listed in Table 1. The infinity mass of the tracer is involved with the momentum auto-correlation function, Eq. (7), and the time dependent friction coefficient, Eq. (8). It is found that the momentum of the whole system carried out by the infinite

Table 1. Friction coefficients (kg/mol·ps) of the tracer of $\sigma = 0.3$ nm as a function of N in the cases of M/m = 10^{90} and ∞. Uncertainties in the last reported digit(s) are given in parenthesis

	N	5120	17280	40960	80000	327680
ζ_1	10^{90}	0.702(22)	0.618(28)	0.615(23)	0.602(41)	0.603(20)
	∞	0.743(10)	0.793(15)	0.946(40)	1.172(115)	2.533(172)
ζ_2	10^{90}	0.661(14)	0.613(11)	0.606(11)	0.611(8)	0.605(6)
	∞	0.665(17)	0.614(6)	0.600(10)	0.609(25)	0.604(1)
ζ_3	10^{90}	0.678(34)	0.713(33)	0.869(221)	1.512(228)	48.85(173)
	∞	0.694(24)	0.657(30)	0.800(101)	1.160(470)	3.984(779)

mass or by the constraint method[13] MD simulations is not conserved since the momentum of the tracer is not well defined with zero velocity or infinite mass. In spite of this, the momentum of the fixed particle is defined as the negative of the total momentum of the solvent particles.[5,6] For this reason for $M = \infty$, it is difficult to determine the friction coefficient from the decay rates, ζ_1 and ζ_3, of $C_p(t)$ in Eq. (7) and $\zeta_u(t)$ in Eq. (8), especially for very large N. On the other hand, the extrapolation (ζ_2) of the long time decay of the time dependent friction coefficient $\zeta_u(t)$ to $t = 0$ is reliable for $M = \infty$.

A useful trick for the difficulty with $M = \infty$ is to put the mass of the tracer as 10^{90} g/mol, and then the momentum of the system is conserved: The magnitude of the mass of the tracer is on the order of 90 and its velocity is on the order of -90, but its momentum has a finite value and is equal to the negative of the total momentum of the solvent particles. The friction coefficients obtained for $M/m = 10^{90}$ are reliable except ζ_3 for very large N. The failure of ζ_3 for $M/m = 10^{90}$ comes from the difficulty in determining the slope for large N due to the small value of the slope and relatively large statistical error since the slopes scale as $1/N$.

As N increases more than ~30000 solvent particles, the friction coefficients, ζ_1 and ζ_2, reach an asymptotic value. MD simulations on systems with a smaller number of particles will yield poor estimates of the friction coefficient. Therefore the best friction coefficients of the tracer are ζ_1 and ζ_2 for $M/m = 10^{90}$ in a solvent of $N = 327680$ mesoscopic particles as listed in Table 2 as a function of σ.

The hydrodynamic estimate of the friction coefficient, ζ_h, is obtained through the Stoke's law, Eq. (2), from the computed viscosity of the mesoscopic solvent $\eta = 4.70 \times 10^{-4}$ kg/m·s[18] with $C = 4$ (the slip boundary condition), and listed in Table 2.
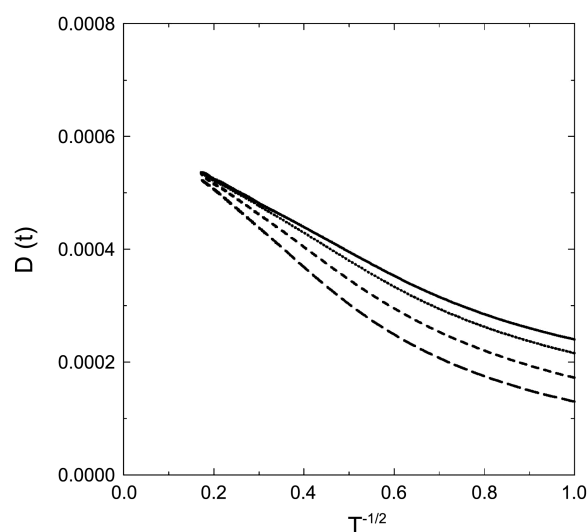
Diffusion coefficients (D) are determined from either the mean square displacement (MSD) of the tracer by

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d\langle |r(t) - r(0)|^2 \rangle}{dt} \qquad (10)$$

or the infinite time integral of the velocity autocorrelation (VAC) function by

$$D(t) = \frac{1}{3} \int_0^t d't \langle v(t') \cdot v(0) \rangle . \qquad (11)$$

The other estimation for diffusion constant comes from

Figure 1. The long time tail of the velocity autocorrelation function of the tracer of $\sigma = 0.3$ nm in a solvent of $N = 327680$ mesoscopic particles for $M/m = 100$ (solid line), 150 (dotted line), 250 (dashed line), and 400 (long-dashed line).

D(t) of Eq. (11) as function of $t^{-1/2}$.[2] Hydrodynamic contributions to the velocity autocorrelation function give rise to a $t^{3/2}$ long time tails[19] and consequently

$$D(t) \approx D - \alpha_0 \sqrt{t} . \qquad (12)$$

The diffusion coefficient can be obtained by extrapolating D(t) as $t^{-1/2} \to 0$. The results in Figure 1 are in accord with this functional form, indicating the presence of a hydrodynamic component in the velocity autocorrelation function.

The diffusion coefficients of the tracer of $\sigma = 0.3$ nm in a solvent of $N = 327680$ mesoscopic particles determined from the mean square displacement (MSD) of Eq. (10), the integral of the velocity autocorrelation function (VAC) of Eq. (11), and the long time tail analysis of Eq. (12) are listed in Table 3 for $M/m = 100, 150, 250$ and 400. Furthermore, D is nearly independent of mass for these parameter values within the statistical uncertainty.

In order to estimate the diffusion coefficient (D) of the tracer as a function of the size of the tracer, MD simulations for the tracers of $M/m = 100$ and $\sigma = 0.1, 0.5, 0.7, 0.9, 1.0, 1.5,$ and 2.0 nm ($\varepsilon = 1.00604$ kJ/mol) in a solvent of $N = 327680$ mesoscopic particles are further carried out. The results for D obtained from MSD are shown in Table 2.

Table 2. Friction coefficients (ζ_1, ζ_2, and ζ_h, kg/mol·ps) of the tracer for $M/m = 10^{90}$ and diffusion coefficients (D_{MD} and D_{SE}, 10^{-4} nm²/ps) of the tracer for $M/m = 100$ in a solvent of $N = 327680$ mesoscopic particles as a function of σ. Uncertainties in the last reported digit(s) are given in parenthesis

σ	0.1	0.3	0.5	0.7	0.9	1.0	1.5	2.0
ζ_1	0.133(3)	0.603(20)	1.20(5)	1.78(6)	2.40(9)	2.73(10)	4.21(12)	5.93(18)
ζ_2	0.134(2)	0.605(16)	1.16(4)	1.81(8)	2.44(11)	2.65(13)	4.32(15)	6.02(22)
ζ_h	0.356	1.067	1.778	2.490	3.201	3.557	5.335	7.113
D_{MD}	30.3(48)	6.12(38)	3.06(27)	2.04(20)	1.45(18)	1.20(10)	0.703(80)	0.479(80)
D_{SE}	9.429	3.143	1.886	1.347	1.048	0.9429	0.6286	0.4714

Table 3. Diffusion coefficients (D, 10^{-4} nm^2/ps) of the tracer of σ = 0.3 nm in a solvent of N = 327680 mesoscopic particles for M/m = 100, 150, 250 and 400, obtained from mean square displacement (MSD) of Eq. (10), velocity autocorrelation function (VAC) of Eq. (11), and the long time tail analysis of Eq. (12). Uncertainties in the last reported digit(s) are given in parenthesis
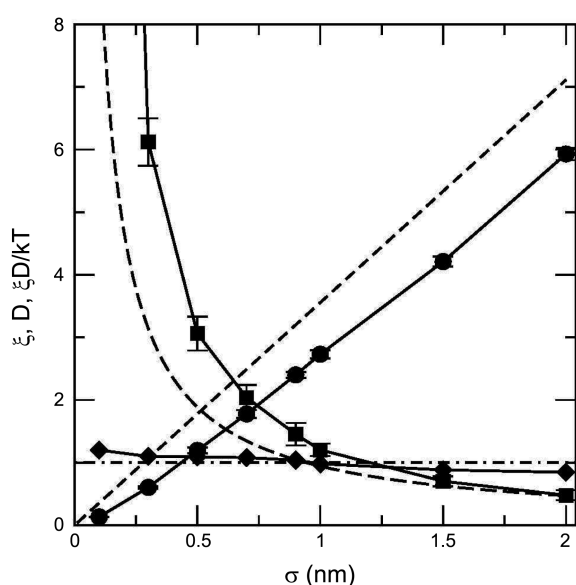
D	M/m = 100	M/m = 150	M/m = 250	M/m = 400
MSD	6.12(38)	6.15(27)	6.33(22)	6.24(21)
VAC	6.12(37)	6.19(27)	6.28(22)	6.23(29)
D(t)	6.12(32)	6.16(28)	6.31(26)	6.23(27)

Using the Stokes-Einstein relation, Eq. (1), another set of diffusion coefficient (D$_{SE}$) is obtained from the hydrodynamic estimate of the friction coefficient, ζ_h, and listed in Table 2.

Figure 2 shows the friction coefficient ζ_1 obtained from our hybrid MD simulations as a function of σ. One sees that the friction coefficient varies linearly with in accord with the prediction of the Stokes formula, Eq. (2). The hydrodynamic estimate of the friction *versus* with the slip boundary condition (C=4) using the independently computed viscosity η = 4.70×10^{-4} kg/m·s of the mesoscopic solvent is also plotted in the same figure. The slopes are different from each other: 0.315×10^{-2} and 0.591×10^{-2} kg/m·nm·s, respectively. If the hydrodynamic boundary condition is chosen as C = 2.1 instead of 4, the two lines coincide with each other.

The diffusion coefficients D$_{MD}$ obtained from our hybrid MD simulations and D$_{SE}$ from the prediction of the SE formula, Eq. (1), are also plotted in Figure 2. D$_{MD}$ is inversely proportional to s but the slope of 1/D$_{MD}$ *versus* σ is slightly different from that of 1/D$_{SE}$ (1.09×10^4 and 1.06×10^4 ps/nm^3). The ratio of D$_{MD}$/D$_{SE}$ approaches to 1 as σ increases as expected from hydrodynamic theories.

Finally we plot ζD/kT as a function of σ in Figure 2. The

values of ζ_{MD}D$_{MD}$/kT for all s are very close to 1, staring 1.2 at σ = 0.1 nm, decreasing slowly, and reaching at an asymptotic value of 0.85 at σ = 2 nm. That is, the prediction of the Einstein relation for the tracer in a mesoscopic solvent is almost valid for all the values of σ except σ = 0.1 nm. The primary reason for this is considered as that the mesoscopic solvent molecule has 0 size. This observation is remarkably different from the case of the tracer in a LJ solvent[8,9] which shows that the obtained value of ζD/kT is somewhat large (~2.5) at the size ratio between the tracer and solvent molecule (σ_2/σ_1) of 0.1, decreases initially as σ_2/σ_1 increases, and then levels off at σ_2/σ_1 = 5-10 independent values of 0.79 (N = 32,000) and 0.91 (N = 320,000), respectively, compared with the prediction by the Einstein relation ζD/kT = 1 for all σ_2/σ_1.

Conclusion

In this work we have presented a detailed investigation of the friction and diffusion behavior of a Lennard-Jones tracer in a mesoscopic solvent. This work was motivated by the determination of the lower bound of the tracer size above which the motion of the tracer is Brownian. The criterion chosen to locate these bounds is that the diffusion coefficient of the tracer obeys the Einstein relation between D and ζ. We found that ζ can be determined correctly from the long time exponential decay rate (ζ_1) of the momentum auto-correlation function C$_P$(t) or from the extrapolation (ζ_2) of the long time decay of the time dependent friction coefficient ζ_u(t) to t = 0. The friction coefficients of the tracer varies linearly with σ in accord with the prediction of the Stokes formula but shows a smaller slope than the Stokes prediction. Diffusion coefficients are obtained from three different routes and it is found that D is nearly independent of mass of the tracer within the statistical uncertainty. The behavior of 1/D$_{MD}$ *versus* σ is essentially linear for all the range of σ. The prediction from the Stokes-Einstein formula D$_{SE}$ slightly underestimates the diffusion coefficient of the tracer. The values of ζ_{MD}D$_{MD}$/kT for all σ are very close to 1, which indicates that the prediction of the Einstein relation for the tracer in a mesoscopic solvent is almost valid for all the values of σ except σ = 0.1 nm, from which the tracer is considered as a Brownian particle. However, this observation is remarkably different from the case of the tracer in a LJ solvent[8,9] which shows that the obtained value of ζD/kT then levels off at σ_2/σ_1 = 5-10 independent values of 0.79 and 0.91, respectively.

Figure 2. Friction coefficient ζ(kg/mol·ps), diffusion coefficient, D(10^{-5} cm^2/s), and D/kT. Filled circle ζ_1; dashed line ζ_h [Eq. (2)]; filled square D$_{MD}$; long-dashed line D$_{SE}$ [Eq. (1)]; filled diamond ζ_1D$_{MD}$/kT; and dot-dashed line ζD/kT = 1 [Eq. (3)].

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