Test of Stokes-Einstein Formula for a Tracer in a Large System by Molecular Dynamics Simulation

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In recent papers,[1,2] the friction and diffusion coefficients of a tracer in a Lennard-Jones (LJ) solvent (N=32,000) were evaluated by equilibrium molecular dynamics (MD) simulations in a micro-canonical 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. Positive deviation of the diffusion coefficient (D) of the tracer from a Stokes-Einstein behavior was observed and the plot of 1/D versus σ_2 showed a linear behavior. It was also observed that the friction coefficient ζ of the tracer varies linearly with σ_2 in accord with the prediction of the Stokes law but showed a smaller slope than the Stokes prediction. When the values of ratios (σ_2/σ_1) of sizes between the tracer and solvent molecules are higher than 5 approximately, the behavior of the friction and diffusion coefficients is well described by the Einstein relation,

$$D = kT/\zeta \qquad (1)$$

from which the tracer is considered as a Brownian particle, where k is the Boltzmann constant and T the absolute temperature.

When the tracers have a quasi-macroscopic size, the Stokes law can be derived from hydrodynamic arguments. It gives an expression of the friction coefficient

$$\zeta = C\pi\eta R_2, \qquad (2)$$

where R_2 is the radius of the diffusing particle and C is the hydrodynamic boundary condition which is 4 for 'slip' and 6 for 'stick'.[3]

Above two Eqs. (1) and (2) combines to give the Stokes-Einstein (SE) formula,

$$D = \frac{kT}{C\pi\eta R_2}. \qquad (3)$$

This relation has been verified experimentally in great detail[4] and is theoretically well understood.[5] If the size of the diffusing particle is not large compared with that of the solvent molecule, the Stokes-Einstein formula is not expected to remain valid.

The first attempt to determine the range of the size and mass values of the solute particles where the solute diffusion coefficient is well estimated from the SE formula was done by Ould-Kaddour and Levesque[6] carrying out a MD simulation. They found that positive deviations from the SE formula are observed as the size ratio or the mass ratio of the tracer to the solvent molecules is lowered, and that for equal masses of solvent and tracer molecules the crossover to the hydrodynamics regimes is found to occur when the size ratio is about 4.[6]

Later on, another MD simulations was performed by Willeke[7] to investigate the mass ratio dependence of the tracer self-diffusion coefficient as a function of density and length diameter ratio σ_2/σ_1. He concluded that for $\sigma_2/\sigma_1 > 1$ the SE prediction is not valid for mass ratios $1/16 \leq m_2/m_1 \leq 50$, and that for $\sigma_2/\sigma_1 > 2$ and for $m_2/m_1 < 1$ the SE regime is reached for smaller densities than for the same system but $m_2/m_1 > 1$. The test of SE formula for the size ratio or the mass ratio of the tracer was further discussed by Sokolovskii *et al*.[8] for hard sphere fluids, by Cappelezzo *et al*.[9] for Lennard-Jones (LJ) fluids, by Funazukuri *et al*.[10] for supercritical and liquid conditions, and by Harris[11] for LJ, molecular, and ionic liquids.

Three limiting procedures are involved in the definition of the friction coefficient: the long time limit (t→∞), the thermodynamic limit (N→∞), and the infinite mass limit (M→∞).[12] One can expect that the Langevin approximation is valid for a finite but sufficiently large mass of the tracer and for a large number of solvent particles. The resulting friction coefficient is zero in the infinite time limit (t→∞). The only route to have a non-zero value for the friction coefficient is by first taking M→∞. In the thermodynamic limit N→∞, the projected and unprojected force autocorrelation functions are the same[13-16] and Eq. (8) below can be used. Since MD simulations should be carried out at finite N, the study of the N dependence of the time dependent friction coefficient $\zeta(t)$ and the estimate of the friction coefficient from either the decay of the momentum or force autocorrelation functions is of interest.[13,17] The main purpose of this note is to study the validity of the SE relation by carrying out simple MD simulations of a tracer in a large number of LJ solvent molecules (N=320,000).

Molecular Dynamics Simulation Details. The LJ potential used in our MD simulations is a purely repulsive CWA (Chandler-Weeks-Andersen) potential[18]:

$$v^{CWA}(r)=\begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12}-\left(\dfrac{\sigma}{r}\right)^{6}+\dfrac{1}{4}\right], & r < r_c = 2^{1/6}\sigma \\ 0, & r \geq r_c \end{cases}, \quad (4)$$

We have chosen the LJ parameters for the solvent molecules as $\sigma = \sigma_1 = 0.2$ nm and $\varepsilon = 1.006$ kJ/mol. A preliminary MD simulation of NVE fixed microcanonical ensemble for N = 320,000 LJ particles with mass of m = 3.9948 g/mol was started in the cubic box of length L = 14.74 nm, of which the density is equal to 0.66338 g/cm^3. The corresponding reduced number density is $\rho^* = \rho\sigma_1^3 = (N/V)\sigma_1^3 = 0.8$ which is a typical value used for several MD simulation studies for transport coefficients of the LJ model fluid.[19] We have chosen the temperature of the system is chosen as 40.333 K for comparison with the mesoscopic solvent case[13] and $T^* = kT/\varepsilon = 1/3$.

A Lennard-Jones particle with various size (σ_2) and mass (M) is introduced at the center of the cubic simulation box after a full equilibration of the solvent-only system. The tracer and LJ solvent molecule interacts through the above CWA potential[18] with LJ parameters of $\sigma = (\sigma_1+\sigma_2)/2$ and the same ε. Two set of M and σ_2 are chosen. (1) M = m and $\sigma_2/\sigma_1 = 0.1, 0.5, 1, 2, 5$, and 10, and (2) M = ∞ and $\sigma_2/\sigma_1 = 0.1, 0.5, 1, 2, 5$, and 10. For size ratios higher than 1, in order to maintain a constant value of the pressure, the volume of the box was slightly increased by an amount that corresponds to the excess volume occupied by the tracer and so the length of the cubic simulation box for the system is redefined by $(N\sigma_1^3 + \sigma_2^3)/L^3 = 0.8$.

We have applied long range corrections to the energy, pressure, etc. due to the potential truncation by assuming that the pair distribution function was uniform beyond the cutoff distance.[20] The time integration for the equations of motion were solved using the velocity Verlet algorithm[21] with a time step of 0.2×10^{-14} second. The systems were fully equilibrated and the equilibrium properties were averaged over four blocks of 1,000,000 time steps of 10 different initial configurations. The configurations of LJ particles were stored every 5 time steps for further analysis.

Diffusion coefficient (D) and viscosity (η) are calculated from the mean square displacement and the stress auto-correlation function, respectively, by

$$D=\frac{1}{6}\lim_{t \to \infty}\frac{d\langle |r(t) - r(0)|^2\rangle}{dt} \quad (5)$$

and

$$\eta=\frac{V}{k_B T}\int_0^\infty dt \Sigma_i \langle p_{i\alpha\beta}(t) \cdot p_{i\alpha\beta}(0)\rangle, \quad (6)$$

where $p_{i\alpha\beta}$ is given by

$$p_{i\alpha\beta}=\frac{1}{v}m v_{i\alpha} \cdot v_{i\beta} + \Sigma_{j \neq i}r_{ij\alpha} \cdot f_{ij\beta} \quad (7)$$

with $\alpha\beta$ = xy, xz, and yz since $p_{i\alpha\beta} = p_{i\beta\alpha}$ for LJ system.

A time dependent friction coefficient $\zeta(t)$ is defined from the force autocorrelation function by[19]

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

and through the Laplace transforms of the projected and unprojected force autocorrelation functions,[14-16] in t space, the following relation is obtained

$$\zeta(t)=\zeta e^{-\zeta t/Nm}. \quad (9)$$

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

Results and Discussion

First we have calculated the viscosity from Eq. (6) for the solvent-only system of N = 320,000 Lennard-Jones (LJ) particles of mass m = 3.995 g/mol in the cubic simulation box of length L = 14.74 nm interacting through the CWA potential with LJ parameters $\sigma = 0.2$ nm and $\varepsilon = 1.00604$ kJ/mol at T = 40.33 K: $\eta = 2.62 \pm 0.01$ mP (10^{-4} kg/m·s). In the previous study[2] for the system of N = 32,000 with L = 6.84 nm, the obtained viscosity was $\eta = 2.53 \pm 0.01$ mP, and in the case of the mesoscopic solvent of N = 327,680,[13] $\eta = 4.70$ mP. According to the Stokes law [Eq. (2)] and the SE formula [Eq. (3)], the friction coefficient increases and the diffusion coefficient decreases with increasing the size of system since the viscosity increases with the size of system.

In order to estimate the diffusion coefficient of the tracer using Eq. (5), we have calculated the mean square displacement of the tracer in the systems of M = m and $\sigma_2/\sigma_1 = 0.1, 0.5, 1, 2, 5$, and 10. For the system of M = m and $\sigma_2 = \sigma_1 = 0.2$ nm, the diffusion coefficient of the tracer is estimated accurately since the statistics is very good with a solvent-only system of N = 320,001 molecules. The calculated diffusion coefficients of the tracer in this system is D = 2.53×10^{-5} cm^2/s compared with D = 2.43×10^{-5} cm^2/s for the system of N = 32,001. Both viscosity and diffusion coefficient of the solvent-only system are increased by increasing the number of solvent molecules. For the systems of $\sigma_2 \neq \sigma_1$ with M = m, the calculation of the diffusion coefficient of the tracer requires a long time simulation run since the statistics for one particle is very poor. The diffusion coefficients of the larger system (N = 320,000) are slightly larger than those of the smaller system (N = 32,000) as listed in Table 1. The effect of increasing the size of system on the result of diffusion coefficients conflicts with the prediction of the SE formula [Eq. (3)].

In the calculation of the friction coefficients of the tracer from Eq. (9), the mass of the tracer, M, becomes infinity, or the tracer is fixed in space using a holonomic constraint method.[22] The MD simulation by using an infinite mass violates the equation of motion since the tracer never moves with the force on it and the constraint method MD simulation returns the tracer back to its original position with zero velocity. The trajectories by both MD simulations are not the

same. It is found that the momentum of the whole system carried out by the infinite mass or by the constraint method MD simulations is not conserved, because 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.[12,17] A useful trick for this difficulty 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.

As discussed in the previous study,[2] there exist a total of 6 routes for the calculation of the friction coefficient of the tracer. The first two can be obtained directly from $\zeta(t)$ of Eq. (8), from the extrapolation of the exponential long time-decay of $\zeta(t)$ to $t = 0$ and from the decay rate of $\zeta(t)$, according to Eq. (9). We have found that the former may be determined correctly.[1,2,13] However, it is difficult to determine the latter from the decay rate of $\zeta(t)$, $-\zeta/Nm$, especially for very large N where the decay rate is close to zero. While the decay rates scale as $1/N$ for the smaller N values, the small value of the decay rate and relatively large statistical error makes it difficult to determine this scaling for very large values of N. The third is obtained from the decay rate, $-\zeta/Nm$, of the normalized momentum autocorrelation function, $C(t) = \langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle / \langle \mathbf{P}(0)^2 \rangle = e^{-\zeta t/Nm}$. However, this autocorrelation function of the tracer calculated from MD simulations was wrong (not shown).[2] One possible explanation for this is related to the well-known rounding error in calculation of velocity in the usual MD simulation or to the scaling of the decay rate in the thermodynamic limit ($N \rightarrow \infty$). The fourth and fifth are obtained from another time dependent friction coefficient, which is derived by the time of $C(t)$, according to Eq. (9). Again these friction coefficients turned out to be incorrect since $C(t)$ is wrong. The final friction coefficient is obtained from the decay rate, $-\zeta/Nm$, of another momentum autocorrelation function $c(t)$, which is derived by the time integration of $\zeta(t)$. Since $\zeta(t)$ calculated directly from Eq. (8) is correct, $c(t)$ may be also correct, but it is unable to estimate the friction coefficient form $c(t)$ due to the scaling of the decay rate in the thermodynamic limit ($N \rightarrow \infty$) again.

Therefore the only way to estimate the friction coefficient in the large N case is from the extrapolation of the exponential long time-decay of $\zeta(t)$ to $t = 0$ using Eq. (9). The friction coefficients of the tracer in the systems of $M = \infty$ and $\sigma_2/\sigma_1 = 0.1, 0.5, 1, 2, 5$, and 10 obtained from the momen-

tum-conserved MD simulation are listed in Table 1. The effect of increasing the size of system on the result of friction coefficients agrees with the prediction of the Stokes law [Eq. (2)] since the viscosity increases with the size of system.

We plot the friction coefficient of the tracer as a function of σ_2/σ_1 in Figure 1. It is seen that the friction coefficients of the tracer for both the larger (N = 320,000) and smaller (N = 32,000) systems vary linearly with σ_2/σ_1 in accord with the prediction of the Stokes law, Eq. (2). The slopes are different from each other: 0.153 and 0.138 kg/mol·ps, respectively. The hydrodynamic estimates of the friction $\zeta_h = C\pi\eta R_2$ versus σ_2/σ_1 with the slip boundary condition (C = 4) using the independently computed viscosities $\eta = 2.62 \times 10^{-4}$ kg/m·s and 2.53×10^{-4} kg/m·s of the solvent-only systems are also plotted in the same figure. The slopes are obtained from the Stokes law: 0.198 and 0.191 kg/mol·ps, respectively, for the larger and smaller systems. If the hydrodynamic boundary condition is chosen as C = 3.1 for the larger system or as C = 2.9 for the smaller system instead of 4, the two lines of the calculated friction coefficient and the Stokes law coincide with each other. Therefore the effect of
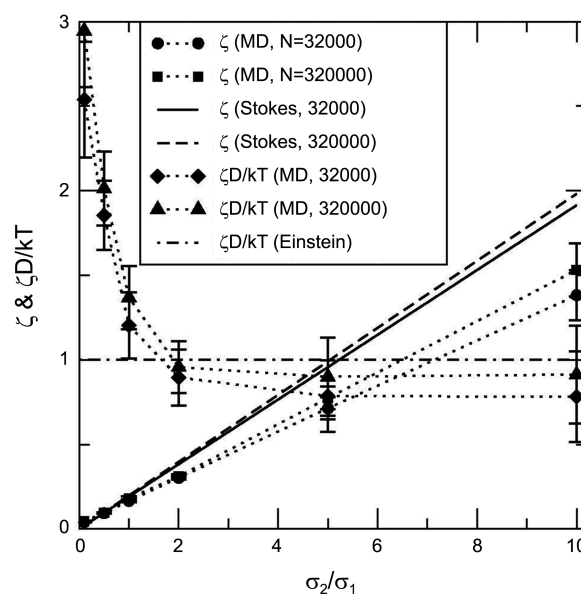

Figure 1. Friction coefficient, ζ (kg/mol·ps), of the tracer and $\zeta D/kT$ as a function of σ_2/σ_1. ● and ■: ζ obtained from MD simulations for N = 32,000 and 320,000, respectively. Solid and dashed lines : ζ by the Stokes law, Eq. (2). ◆ and ▲: $\zeta D/kT$ obtained from MD simulations for N = 32,000 and 320,000, respectively. Dot-dashed line : $\zeta D/kT = 1$ for the Einstein relation, Eq. (1).

Table 1. Comparison of diffusion D (10^{-5} cm²/s) and friction coefficients ζ (kg/mol·ps) of the tracer in the larger (N = 320,000) and the smaller (N = 32,000) systems. Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis

	σ_2/σ_1	0.1	0.5	1	2	5	10
D	N = 320,000	22.0(22)	6.99(58)	2.53(22)	1.03(16)	0.39(8)	0.20(5)
	N = 32,000	21.2(26)	6.74(60)	2.43(24)	0.99(15)	0.37(7)	0.19(4)
ζ	N = 320,000	0.045(2)	0.096(2)	0.181(11)	0.311(12)	0.774(67)	1.53(16)
	N = 32,000	0.040(1)	0.092(2)	0.166(10)	0.302(11)	0.713(64)	1.38(15)

increasing the size of system in the present work seems to give a better result to agree with the Stokes Law.

Finally, in Figure 1 we plot $\zeta D/kT$ as a function of σ_2/σ_1 for both the larger and the smaller systems. This value decreases initially as σ_2/σ_1 increases, and then levels off at σ_2/σ_1 independent values of 0.91 and 0.79, respectively. This leveling-off takes place for σ_2/σ_1 between 5 and 10. According to the Einstein relation, Eq. (1), however, the value of $\zeta D/kT$ is expected to be 1 for all σ_2/σ_1. Again the effect of increasing the size of system in the present work seems to give a better result to agree with the Einstein relation. If we choose the criterion that the solute can be considered as a Brownian particle as the diffusion coefficient of the solute obeys the Einstein relation between D and ζ the lower bound of the size ratio above which the motion of the solute is Brownian is determined as $\sigma_2/\sigma_1 \sim 5$ since the value of $\zeta D/kT$ above this size ratio is independent on σ_2/σ_1, even though it is not exactly 1 as expected by the Einstein relation. This result is in accord with the earlier work of Ould-Kaddour and Levesque that for $M/m = 1$, the crossover to the hydrodynamics regimes is found to occur when $\sigma_2/\sigma_1 \sim 4$.[6]

In summary, we have carried out micro-canonical molecular dynamics (MD) simulations of a Lennard-Jones tracer in a large solvent of similar molecules (N = 320,000). This work was motivated by determination of the diffusion (D) and friction (ζ) coefficients of the tracer in the thermodynamic limit (N$\rightarrow\infty$) and by test of the SE formula. The calculated viscosity (η) for the larger solvent-only system of N = 320,000 is slightly larger than that for the smaller system of N = 32,000 and D of the tracer is decreased according to the SE formula by increasing the number of solvent molecules. However, the obtained D of the tracer from MD simulations is slightly increased for all values of σ_2/σ_1. We found that the friction coefficients of the tracer for both the larger and smaller systems vary linearly with σ_2/σ_1 in accord with the prediction of the Stokes law. From the slopes of ζ *vs.* σ_2/σ_1, the estimated hydrodynamic boundary conditions are equal to C = 3.1 and 2.9, respectively, for the larger and smaller systems, compared with the Stokes law, C = 4. 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 0.91 and 0.79, respectively, compared with the prediction by the Einstein relation $\zeta D/kT = 1$ for all σ_2/σ_1. In order to confirm these results it is necessary to carry out an MD simulation for the system of N = 160,000 and this work is presently under study.

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