

System-Size Dependence of Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations with Periodic Boundary Conditions

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We study the system-size dependence of translational diffusion coefficients and viscosities in molecular dynamics simulations under periodic boundary conditions. Simulations of water under ambient conditions and a Lennard-Jones (LJ) fluid show that the diffusion coefficients increase strongly as the system size increases. We test a simple analytic correction for the system-size effects that is based on hydrodynamic arguments. This correction scales as $N^{-1/3}$, where N is the number of particles. For a cubic simulation box of length L , the diffusion coefficient corrected for system-size effects is $D_0 = D_{\text{PBC}} + 2.837297k_{\text{B}}T/(6\pi\eta L)$, where D_{PBC} is the diffusion coefficient calculated in the simulation, k_{B} the Boltzmann constant, T the absolute temperature, and η the shear viscosity of the solvent. For water, LJ fluids, and hard-sphere fluids, this correction quantitatively accounts for the system-size dependence of the calculated self-diffusion coefficients. In contrast to diffusion coefficients, the shear viscosities of water and the LJ fluid show no significant system-size dependences.

I. Introduction

Long-range interactions can lead to significant dependences on the system size in computer simulations of condensed matter under periodic boundary conditions.¹ Effects from the Coulombic $1/r$ interactions have been particularly well-characterized (see, e.g., ref 2). Hydrodynamics can also lead to effective long-range interactions, as witnessed, for instance, by the $1/r$ decay of the Oseen tensor.^{3,4} Such hydrodynamic interactions can indeed cause significant finite-size effects, as shown by Dünweg and Kremer^{5,6} for the diffusion coefficients of polymers. For the diffusion of small single-stranded ribonucleic acid molecules (RNA) in water, we recently observed that the calculated diffusion coefficients deviate from the extrapolated infinite-system limit by factors of 2–3 for typical system sizes.⁷ Here, we show that, even for relatively small molecules such as water, the apparent self-diffusion coefficients depend significantly on system size. For a system of ~ 2000 water molecules in a periodically replicated cubic simulation cell, we find the diffusion coefficient to be underestimated by $\sim 10\%$. Correcting for such systematic errors is particularly important in comparisons of simulations to experiment,^{7,8} and if transport properties are used to assess and fit interaction potentials.

We use a simple hydrodynamic model to obtain an analytic expression for the system-size dependence of the diffusion coefficient. The same expression was obtained previously by Dünweg and Kremer,⁶ using a closely related derivation. The correction is analogous to that developed earlier for electrostatic self-interactions in ion-solvation free energies.^{2,9–15} The hydrodynamic correction builds on earlier work by Hasimoto on the viscous flow past lattices of spheres¹⁶ and by Beenakker¹⁷ on an Ewald summation¹⁸ of the Rotne–Prager hydrodynamic mobility tensor.¹⁹ A related hydrodynamic correction for finite-size effects was discussed by Fushiki,²⁰ who imposed spherical

symmetry by applying the hydrodynamic boundary conditions on the Wigner–Seitz sphere, rather than the simulation cell.²¹ To avoid possible confusion, we emphasize at the outset that the hydrodynamic correction developed here is *not* concerned with so-called hydrodynamic long-time tails in, e.g., the particle velocity autocorrelation function.^{22–24}

The paper is outlined as follows. We first derive the Oseen tensors^{3,4} for finite periodic and infinite nonperiodic systems. From their difference, we estimate a hydrodynamic self-interaction. Following the Kirkwood–Riseman theory of polymer diffusion,^{4,25} we relate the periodicity-induced hydrodynamic self-interaction to the effect of periodic boundary conditions on diffusion coefficients. This results in an analytic correction formula for diffusion coefficients that we test for water at ambient conditions, a Lennard-Jones (LJ) fluid at high temperature and density, and a hard-sphere fluid. We also calculate the viscosity of water and of the LJ fluid as a function of system size.

II. Theory

Diffusion Coefficient. To derive an analytic correction for system-size effects on the diffusion coefficient, we use a simple hydrodynamic model of a particle surrounded by a solvent of viscosity η in a periodically replicated simulation box. The diffusion of this particle will be affected by hydrodynamic interactions not only with the solvent in the immediate surrounding, but also with the periodic images of the particle itself and the solvent. In an infinite nonperiodic system, hydrodynamic interactions between particles can be approximated by the Oseen tensor.³ Here, we use an Oseen tensor modified for periodic boundary conditions. From the difference between the Oseen tensor in the finite periodic and infinite nonperiodic systems, we will estimate the hydrodynamic self-interactions induced specifically by the periodic boundary conditions. The Kirkwood–Riseman theory of polymer diffusion^{4,25} will then give us an estimate of the system-size correction to the diffusion coefficient. Our derivation is closely related to that of Dünweg

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and Kremer,⁶ which is built on an approximate Fourier representation of the pair diffusion tensor.²⁶

To construct the Oseen tensor for a finite periodic system, we adapt a derivation for an infinite nonperiodic system³ that was given by Stockmayer²⁷ and attributed to R. Zwanzig. Consider an incompressible fluid perturbed by a point force acting at the center of a periodically replicated cell of volume V . The perturbation of the velocity field $\mathbf{v}(\mathbf{r})$ caused by the point force is assumed to satisfy the Stokes equation (i.e., the linearized Navier–Stokes equation for an incompressible fluid),²⁸

$$\eta \nabla^2 \mathbf{v}(\mathbf{r}) = \nabla p(\mathbf{r}) - \left[\delta(\mathbf{r}) - \frac{1}{V} \right] \mathbf{F} \quad (1)$$

where p is the pressure, $\nabla = \partial/\partial \mathbf{r}$, and $[\delta(\mathbf{r}) - 1/V]\mathbf{F}$ is the point-force perturbation, with $\delta(\mathbf{r})$ as the δ function. The $1/V$ term ensures that the net force on the cell is zero, such that Newton's third law is satisfied. For an incompressible fluid with $\nabla \cdot \mathbf{v} = 0$, taking the divergence of eq 1 leads to

$$\nabla^2 p - \mathbf{F} \cdot \nabla \left[\delta(\mathbf{r}) - \frac{1}{V} \right] = 0 \quad (2)$$

We transform these equations into Fourier space, such that $\hat{\mathbf{v}}_{\mathbf{k}} \equiv \int_V \mathbf{v}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}$ and $\mathbf{v}(\mathbf{r}) \equiv V^{-1} \sum_{\mathbf{k}} \hat{\mathbf{v}}_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{r})$. The integral extends over the simulation cell V , and $\mathbf{k}$ is a vector of the reciprocal lattice of simulation cells. For a cubic lattice of length L , those vectors are given by $\mathbf{k} = 2\pi L^{-1}(l_x, l_y, l_z)$, where l_x , l_y , and l_z are integers.

In Fourier space, eq 1 becomes

$$\eta k^2 \hat{\mathbf{v}}_{\mathbf{k}} = i\mathbf{k} \hat{p}_{\mathbf{k}} + (1 - \delta_{\mathbf{k}}) \mathbf{F} \quad (3)$$

where $\delta_{\mathbf{k}} = 1$ for $\mathbf{k} = 0$ and $\delta_{\mathbf{k}} = 0$ otherwise. For eq 2, we obtain

$$k^2 \hat{p}_{\mathbf{k}} = i(1 - \delta_{\mathbf{k}}) \mathbf{k} \cdot \mathbf{F} \quad (4)$$

Combination of eqs 3 and 4 results in

$$\hat{\mathbf{v}}_{\mathbf{k}} = \frac{1 - \delta_{\mathbf{k}}}{\eta k^2} \left(\mathbf{1} - \frac{\mathbf{k}\mathbf{k}}{k^2} \right) \cdot \mathbf{F} \quad (5)$$

with $\mathbf{1}$ being the 3×3 unity matrix. The Oseen mobility tensor for a periodic system, which is defined by the relation

$$\mathbf{v}(\mathbf{r}) = \mathbf{T}_{\text{PBC}}(\mathbf{r}) \cdot \mathbf{F} \quad (6)$$

is then given by

$$\mathbf{T}_{\text{PBC}}(\mathbf{r}) = \sum_{\mathbf{k} \neq 0} \frac{\exp(-i\mathbf{k} \cdot \mathbf{r})}{\eta k^2 V} \left(\mathbf{1} - \frac{\mathbf{k}\mathbf{k}}{k^2} \right) \quad (7)$$

where the sum extends over the reciprocal lattice vectors, excluding $\mathbf{k} = 0$. In an infinite nonperiodic system, the Oseen tensor is given by²⁷

$$\mathbf{T}_0(\mathbf{r}) = \frac{1}{8\pi\eta r} \left(\mathbf{1} + \frac{\mathbf{r}\mathbf{r}}{r^2} \right) \quad (8)$$

To connect the Oseen mobility tensors $\mathbf{T}_0(\mathbf{r})$ and $\mathbf{T}_{\text{PBC}}(\mathbf{r})$ to particle diffusion coefficients, we adapt the Kirkwood–Riseman theory of polymer diffusion.^{4,25} In the infinite nonperiodic system, the particle mobility tensor is given by $(k_B T)^{-1} D_0 \mathbf{1}$, where D_0 is the diffusion coefficient of the particle in an infinite system, k_B the Boltzmann constant, and T the absolute

temperature. In the finite periodic system, we correct the mobility for hydrodynamic self-interactions. The resulting correction is given by the difference of the hydrodynamic self-interactions in the finite periodic and infinite nonperiodic systems, $\mathbf{T}_{\text{PBC}} - \mathbf{T}_0$. The diffusion tensor modified for periodicity, $\mathbf{D}_{\text{PBC}}$, is then given by

$$\mathbf{D}_{\text{PBC}} = D_0 \mathbf{1} + k_B T \lim_{r \rightarrow 0} [\mathbf{T}_{\text{PBC}}(\mathbf{r}) - \mathbf{T}_0(\mathbf{r})] \quad (9)$$

This result is formally equivalent to eq 33 of Dünweg and Kremer.⁶ We note that eq 9 is also obtained if we use the Oseen–Burgers approximation^{29,30} to estimate the difference in the diffusion coefficients of a small sphere (radius $|\mathbf{r}| \rightarrow 0$) in a finite periodic and an infinite nonperiodic system.

From eq 9, we obtain the apparent scalar diffusion coefficient D_{PBC} by taking the trace:

$$D_{\text{PBC}} = \frac{1}{3} \text{Tr}(\mathbf{D}_{\text{PBC}}) = D_0 + \frac{k_B T}{6\pi\eta} \lim_{r \rightarrow 0} \left[\sum_{\mathbf{k} \neq 0} \frac{4\pi \exp(-i\mathbf{k} \cdot \mathbf{r})}{k^2 V} - \frac{1}{|\mathbf{r}|} \right] \quad (10)$$

In the lattice sum, we recognize the Ewald potential of electrostatics.^{31–33} In particular, the limit of the term in square brackets is identical to the self-interaction of a point charge in a Wigner lattice:³⁴

$$D_{\text{PBC}} = D_0 + \frac{k_B T}{6\pi\eta} \left[-\frac{2\alpha}{\pi^{1/2}} + \sum_{\mathbf{n} \neq 0} \frac{\text{erfc}(\alpha n)}{n} + \sum_{\mathbf{k} \neq 0} \frac{4\pi e^{-k^2/4\alpha^2}}{k^2 V} - \frac{\pi}{V\alpha^2} \right] \quad (11)$$

where the first sum is over the lattice vectors $\mathbf{n}$ (excluding the origin), and α is an arbitrary convergence factor ($\alpha > 0$). For a cubic simulation cell of length L , the lattice vectors are $\mathbf{n} = L(l_x, l_y, l_z)$, where l_x , l_y , and l_z are integers. This results in

$$D_{\text{PBC}} = D_0 - \frac{k_B T \xi}{6\pi\eta L} \quad (12)$$

with $\xi \approx 2.837297$.^{10,16,34,35} The same expression was obtained previously by Dünweg and Kremer.⁶ For noncubic unit cells, the Ewald summation can be performed numerically, and values for the constant ξ have been given, for instance, by Hasimoto.¹⁶ Interestingly, note that, as in electrostatics,¹⁰ the dominant contribution to the correction ξ comes from the compensating background in the minimum-image cell (2.38 versus 2.837 for the complete cubic lattice sum). The “ $-\mathbf{F}/V$ ” background force density in eq 1, which reflects the requirement of zero net force (i.e., momentum conservation, analogous to charge neutrality in electrostatics), is thus essential and accounts for much of the system-size dependence of diffusion coefficients.

Equation 12 will be particularly useful to correct the observed diffusion coefficients of solutes at “infinite” dilution in a well-characterized solvent of known viscosity η . To obtain D_0 , one simply adds $k_B T \xi / (6\pi\eta L)$ to the calculated apparent diffusion coefficient D_{PBC} . If the viscosity is not known, apparent diffusion coefficients D_{PBC} should be calculated for different system sizes. D_0 can then be estimated from the y intercept of a linear fit of D_{PBC} , with respect to $1/L$, which corresponds to an extrapolation to infinite system size.

Alternatively, one can also obtain an approximate estimate of the system-size correction by using the Stokes–Einstein relation for the diffusion coefficient with either stick or slip boundary conditions:²⁴

$$D_0 \approx \begin{cases} \frac{k_B T}{6\pi\eta R} & (\text{stick}) \\ \frac{k_B T}{4\pi\eta R} & (\text{slip}) \end{cases} \quad (13)$$

where R is the hydrodynamic radius of the particle. Equations 12 and 13 can be solved self-consistently to give

$$D_0 \approx D_{\text{PBC}} \times \begin{cases} \left(1 - \frac{\xi R}{L}\right)^{-1} & (\text{stick}) \\ \left(1 - \frac{2\xi R}{3L}\right)^{-1} & (\text{slip}) \end{cases} \quad (14)$$

Equation 14 is an approximate correction formula for diffusion coefficients that does not require the solvent viscosity η as input. Instead, it requires an estimate of the hydrodynamic radius R and the choice of stick or slip boundary conditions.

We note that the result for the difference in the trace of the periodic and nonperiodic Oseen tensors (eqs 7 and 8) is already contained in eq 4.8 of the work of Hasimoto.¹⁶ Moreover, Hasimoto’s solution of the Stokes equation under periodic boundary conditions provides additional correction terms to eq 12 that are dependent on the particle size. From Hasimoto’s eq 5.25, we obtain the next order of the system-size correction, in terms of the radius R of a spherical particle in a cubic simulation cell:

$$D_{\text{PBC}} = D_0 - \frac{k_B T}{6\pi\eta L} \left(\xi - \frac{4\pi R^2}{3L^2} \right) \quad (15)$$

For all $R < L/2$, the particle-size-dependent R^2/L^3 term reduces the system-size correction of eq 12 by a relatively small amount.

Hasimoto¹⁶ also explicitly comments on the need to include a compensating background in the Stokes equation (here, $1/V$ in eq 1), which, in the case of flow past a lattice of spheres, results from the mean pressure gradient over a cell. This eliminates the divergence problem noted by Burgers.¹⁶ We note further that Beenakker’s¹⁷ Ewald summation of the Rotne–Prager tensor¹⁹ also leads to eq 12, with the trace of the correction to the Oseen tensor being zero. Beenakker’s analysis did not explicitly consider the $1/V$ background term that results from Newton’s third law, which is, however, implicitly added to the otherwise divergent lattice sums when Ewald summation is used.^{10,18,33}

Finally, we note that the derivation of the hydrodynamic self-interaction is largely analogous to that of ionic self-interactions in electrostatics.^{2,9–15} Corresponding to the $1/V$ correction in the source term of eq 1, the divergence of the electrostatic lattice sum for a Wigner crystal is removed by a neutralizing background charge (see, e.g., refs 31–33). Just as in electrostatics, the lattice sums in eqs 7 and 10 are only conditionally convergent and should be evaluated using summation over spherical shells,³⁴ which corresponds to Ewald summation. This leads to eq 11.

Viscosity. The preceding analysis implicitly assumes that the shear viscosity η of the fluid is independent of system size. One might expect that the apparent viscosity of a system simulated with periodic boundary conditions also suffers from system-size effects, because of the Stokes–Einstein relation (eq

TABLE 1: Simulation Results for TIP3P Water under Ambient Conditions ($T = 298$ K, $\rho = 33.00$ nm⁻³)^a

number of water molecules, N	shear viscosity, η [10 ⁻⁴ kg m ⁻¹ s ⁻¹]	pressure, p [bar]	Diffusion Coefficient [10 ⁻⁵ cm ² /s]	
			D_{PBC}^b	D_0^c
128	3.00(09)	-26.0(1.5)	4.884(32)	6.16(7)
256	3.06(04)	-2.9(2.5)	5.123(27)	6.14(6)
512	3.14(09)	3.5(1.3)	5.315(14)	6.12(4)
1024	3.15(07)	10.8(1.0)	5.466(11)	6.11(3)
2048	3.06(10)	9.3(0.8)	5.590(13)	6.10(3)

^a The numbers in parentheses indicate the statistical errors of the last digits (one standard deviation of the mean estimated from block averages). ^b Diffusion coefficient obtained from the simulations through eq 17. ^c Diffusion coefficients corrected for system-size dependences, using eq 12. For the corrections, we used a constant shear viscosity of $\eta = (3.08 \pm 0.1) \times 10^{-4}$ kg m⁻¹ s⁻¹.

13). However, no significant system-size dependence was observed in computer simulations of LJ fluids.^{6,36} To explore the system-size dependence, we calculate the shear viscosity η , using the Green–Kubo relation:¹

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \delta P_{xy}(t) \delta P_{xy}(0) \rangle dt \quad (16)$$

where the integrand is the autocorrelation function of $\delta P_{xy}(t)$, which is the deviation of an off-diagonal element of the instantaneous pressure tensor from the average (zero in an infinitely long run). By symmetry, equivalent expressions are obtained if we replace δP_{xy} in eq 16 with other off-diagonal elements, and with differences between diagonal elements such as $\delta P_{xx} - \delta P_{yy}$. The latter follows from a rotation of the laboratory reference frame.³⁶ One of the difficulties in using eq 16 results from possible long-time tails in the correlation functions.^{22–24}

III. Simulations of Water

To test the system-size correction in eq 12, we calculate the self-diffusion coefficients D_{PBC} of TIP3P water³⁷ in cubic simulation cells with $N = 128, 256, 512, 1024$, and 2048 water molecules. In the simulations, we use the Sander module of AMBER 6.0 (University of California at San Francisco) with particle-mesh Ewald summation for the long-range electrostatic interactions.^{38,39} The equations of motion are integrated with a time step of 0.002 ps. A temperature of 298 K is maintained with the Berendsen thermostat,⁴⁰ using a relaxation time of 1 ps. The constant particle density of 33.00 nm⁻³ gives near-ambient pressures. The production time of the simulations is 20 ns ($N \leq 512$), 15 ns ($N = 1024$), and 10 ns ($N = 2048$). Simulation results are listed in Table 1.

Self-diffusion coefficients were calculated from the slope of the mean-square displacement averaged over the trajectories of individual particles,

$$D_{\text{PBC}} = \lim_{t \rightarrow \infty} \frac{\partial \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{\partial t} \frac{1}{6} \quad (17)$$

where $\mathbf{r}(t)$ denotes particle trajectories that are continuous in Cartesian space. After a brief initial period (~ 1 ps for water under ambient conditions), the mean-square displacement grows linearly with time within statistical uncertainties (Figure 1), and a straight-line fit gives us an estimate of the diffusion coefficient.

Figure 2 shows the apparent diffusion coefficients of water from the simulations, as a function of the inverse box size ($1/L$

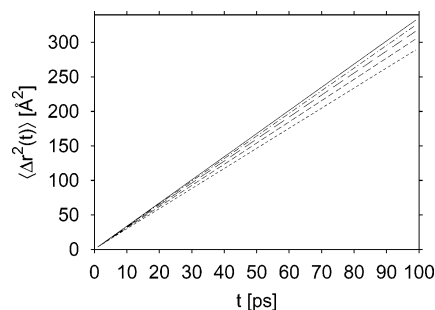


Figure 1. Mean-square displacement of TIP3P water as a function of time t . The lines are for $N = 128, 256, 512, 1024$, and 2048 water molecules (bottom to top).

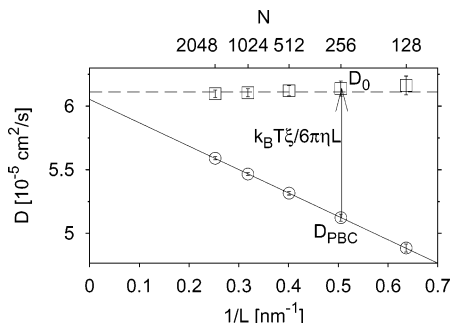


Figure 2. Diffusion coefficient of TIP3P water as a function of the inverse box length $1/L$ (bottom scale) for $N = 128$ – 2048 water molecules (top scale). Circles show uncorrected results (D_{PBC}) from simulations, with error bars estimated from block averages. Squares show the diffusion coefficients (D_0) corrected for finite-size effects with eq 12, as indicated by the arrow for $N = 256$. The solid line is a straight-line fit of the uncorrected diffusion coefficients D_{PBC} to $1/L$. The dashed line is a fit of the corrected diffusion coefficients D_0 to a constant.

L). As indicated by the different slopes of the mean-square displacement in Figure 1 and predicted by the hydrodynamic theory, we find that the diffusion coefficient D_{PBC} depends linearly on $1/L$. A straight-line fit extrapolates to a diffusion coefficient $D_0 = 6.05 \times 10^{-5} \text{ cm}^2/\text{s}$ for an infinite system of TIP3P water at 298 K and ambient pressure. If we apply eq 12 to correct the observed diffusion coefficients with a viscosity of $\eta = (3.08 \pm 0.1) \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ (as calculated below), the resulting diffusion coefficients are independent of system size, within one estimated standard deviation of the error. However, the average value of $D_0 = 6.11 \times 10^{-5} \text{ cm}^2/\text{s}$ is slightly larger than that obtained from a straight-line fit ($\sim 0.06 \times 10^{-5} \text{ cm}^2/\text{s}$).

The small overcorrection of eq 12 is within the estimated statistical errors. It may be caused, for instance, by contributions from long-range electrostatic interactions, as would follow from a simple argument. For charged and dipolar fluids, a finite periodic system is expected to be less polarized overall than an infinite nonperiodic system, because of the periodic boundary conditions imposed on the polarization. The instantaneous polarization effectively “traps” individual dipolar or charged particles near their respective positions, thus reducing their mobility.⁴¹ Following this argument, we expect that the smaller overall polarization in a finite periodic system, compared to an infinite system, would increase the apparent mobility. In turn, this relative mobility increase would result in a smaller correction factor for the system-size dependence of D_{PBC} than that expected from hydrodynamics alone. This is consistent with the results shown here for water, which is a polar molecule. Consistent with this electrostatic explanation, we earlier found an even larger effect for the diffusion of charged particles.⁷ For

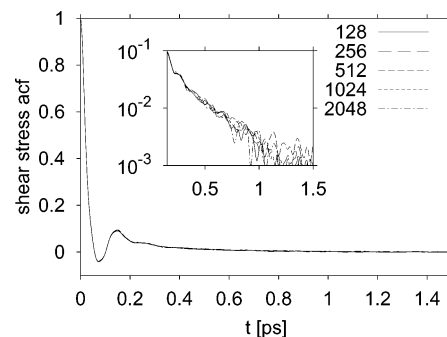


Figure 3. Normalized shear-stress autocorrelation function in the integrand of eq 16. Results are shown for $N = 128$ – 2048 TIP3P water molecules. The inset shows the autocorrelation function on a logarithmic scale.

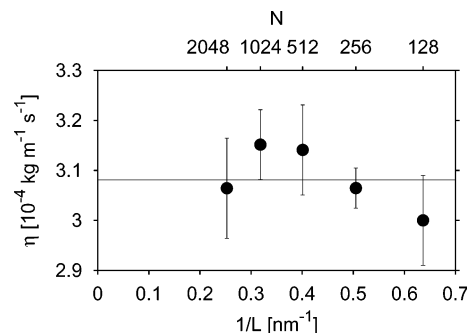


Figure 4. Shear viscosity (η) of TIP3P water as a function of the inverse box length $1/L$ (bottom scale) for $N = 128$ – 2048 water molecules (top scale).

potassium ions (with a single charge) and a small RNA (with two charges) in water, scaling the correction factor of eq 12 by 0.88 and 0.76, respectively, accounted more accurately for the observed system-size dependences. However, the magnitude of “dielectric friction” effects is still a matter of debate.⁴³

We also calculated the shear viscosity of TIP3P water under ambient conditions, as a function of system size. Figure 3 shows the normalized shear-stress autocorrelation function entering eq 16 for the simulations with $N = 128$ – 2048 water molecules. We do not see any significant system-size dependences in the autocorrelation functions, which is consistent with an essentially system-size independent bulk pressure (see Table 1 and ref 42). Moreover, within the accuracy of the data, the correlation functions seem to decay exponentially at times of $t \gtrsim 0.3$ ps. With the assumption of exponential decays, we evaluate the integral in eq 16 by summation up to $t = 0.4$ ps, followed by integration of the exponential fit at longer times. From that, we obtain the viscosities shown in Figure 4 as a function of $1/L$. Based on the results shown in Figures 3 and 4, we conclude that there is no strong system-size dependence in the viscosity data, and that the value of the viscosity of TIP3P water at 298 K and a density of 33.00 nm^{-3} is $(3.08 \pm 0.1) \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$. Essentially system-size independent viscosities of water were also obtained by Hess,⁴⁴ and our viscosity value agrees well with that for a slightly modified TIP3P water model, as calculated by Feller et al.⁴⁵ at 293 K using an Einstein relation. In particular, the ratio of experimental and TIP3P viscosities is ~ 2.9 in both cases.

IV. Lennard-Jones and Hard-Sphere Fluids

In this section, we study diffusion in Lennard-Jones (LJ) and hard-sphere fluids to eliminate the possible influence of long-range electrostatic interactions. Specifically, we have tested the

TABLE 2: Simulation Results for the Lennard-Jones (LJ) Fluid at a Reduced Density of $\rho\sigma^3 = 0.7$

particle number, N	average temperature in constant-energy simulations, $k_B T$ [ε]	shear viscosity, η [$\sigma^2(m\epsilon)^{-1/2}$]	Diffusion Coefficient [$\sigma(\epsilon/m)^{1/2}$]	
			D_{PBC}^b	D_0^c
8	2.749	2.248(700)	0.1873(13)	0.3276(23)
27	2.754	1.305(016)	0.2250(09)	0.3185(16)
64	2.746	1.301(011)	0.2486(06)	0.3187(11)
125	2.749	1.322(008)	0.2615(10)	0.3176(14)
216	2.749	1.309(013)	0.2729(07)	0.3196(10)
512	2.744	1.315(008)	0.2804(08)	0.3155(10)
1000	2.753	1.311(011)	0.2899(13)	0.3180(15)

^a The numbers in parentheses indicate the statistical errors of the last digits (one standard deviation of the mean estimated from block averages). ^b Diffusion coefficient obtained from the simulations through eq 17. ^c Diffusion coefficients corrected for system-size dependences, using eq 12. For the corrections, we used a constant shear viscosity of $\eta = (1.31 \pm 0.01) \sigma^2(m\epsilon)^{-1/2}$.

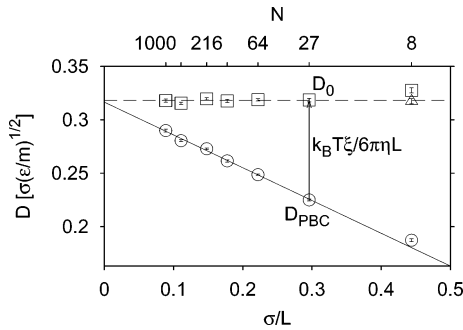


Figure 5. System-size dependence of the self-diffusion coefficient of a Lennard-Jones (LJ) fluid (in units of $\sigma(\epsilon/m)^{1/2}$) at a reduced temperature of $k_B T/\epsilon = 2.75$ and a reduced density of $\rho\sigma^3 = 0.7$. Error bars correspond to one standard deviation estimated from block averages. Circles show uncorrected results (D_{PBC}) from simulations, whereas squares show the diffusion coefficients (D_0) corrected for finite-size effects with eq 12, as indicated by the arrow for $N = 27$. The solid line is a straight-line fit of the uncorrected diffusion coefficients D_{PBC} to $1/L$ (for $N \geq 27$), whereas the dashed line is a fit of the corrected diffusion coefficients D_0 to a constant ($N \geq 27$). The triangle shows the $N = 8$ diffusion coefficient corrected with eq 15.

system-size correction for the diffusion coefficient of a LJ fluid at a reduced temperature of $k_B T/\epsilon = 2.75$ and a reduced density of $\rho\sigma^3 = 0.7$, where ϵ and σ are the well depth and intersection with the zero-axis of the LJ potential, respectively. The simulations were performed with the velocity Verlet algorithm¹ at constant energy and volume, with a time step of 0.001 in reduced units of time ($\sigma(m/\epsilon)^{1/2}$), except for $N = 512$ and 1000, where we used a time step of 0.005. The parameter m represents the particle mass. Results are summarized in Table 2. In the simulations, we use the full LJ potential, shifted to zero at a cutoff distance of $L/2$. In an earlier study by Holian and Evans,³⁶ a LJ fluid at the same temperature and density was studied, but with a potential truncated smoothly at $\sim 1.74\sigma$.

Figure 5 shows the resulting diffusion coefficients as a function of $1/L$. For $N \geq 27$ particles, the diffusion coefficient scales as $1/L$, as predicted by the hydrodynamic theory. This $1/L$ scaling was also observed for hard spheres.²⁰ If we use the viscosity of $(1.31 \pm 0.02) \sigma^2(m\epsilon)^{-1/2}$ obtained from the data in Figure 6 and Table 2, the diffusion coefficients corrected with eq 12 are independent of system size and are fully consistent with the value obtained by extrapolating a linear fit of D_{PBC} (with variable slope and intercept) to infinite system size ($1/L \rightarrow 0$). Even for a very small system of $N = 8$ particles, the deviation of the corrected diffusion coefficient from the average

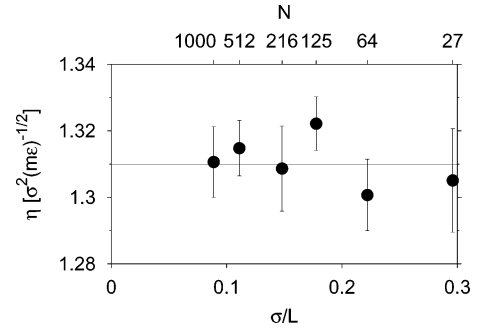


Figure 6. System-size dependence of the shear viscosity η of a LJ fluid at a reduced temperature of $k_B T/\epsilon = 2.75$ and a reduced density of $\rho\sigma^3 = 0.7$.

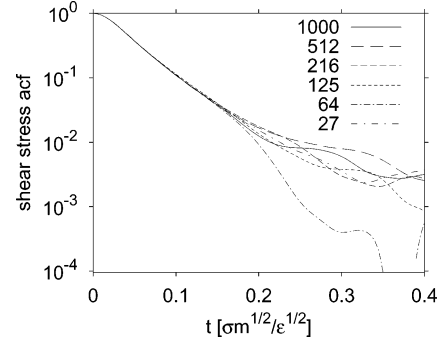


Figure 7. Normalized shear-stress autocorrelation function of a LJ fluid at a reduced temperature of $k_B T/\epsilon = 2.75$ and a reduced density of $\rho\sigma^3 = 0.7$. Results are shown for different numbers of particles between $N = 27$ and $N = 1000$.

of larger system sizes ($N \geq 27$) is less than two estimated standard deviations of the statistical error. For the smallest systems, a slight overestimate of the diffusion coefficients after correction with eq 12 is expected from the particle-size-dependent term in eq 15. If we assume $R = \sigma/2$ for the R^2 term in eq 15, the $N = 8$ result is consistent with the corrected diffusion coefficients for larger system sizes (see Figure 5). This agreement is likely fortuitous, considering the small system size. However, we do note that similar agreement down to the smallest system sizes was obtained for system-size corrections of electrostatic solvation effects.^{9,10,14,33} Dünweg and Kremer⁶ also studied the system-size dependence of the self-diffusion coefficient of a fluid with purely repulsive truncated LJ interactions at a higher density and lower temperature. They found more scatter in the plot of D_{PBC} versus $1/L$, and a slope that is in good agreement with eq 12.

As for water, we also examined the system-size dependence of the shear viscosity η . Figure 6 shows the viscosity of the LJ fluid as a function of $1/L$. We do not find any significant system-size dependence in the viscosity values for $N \geq 27$. A similar conclusion was reached previously by Holian and Evans³⁶ for the truncated LJ fluid, and by Dünweg and Kremer⁶ for a LJ fluid at a lower temperature. The viscosity results in Figure 6 and Table 2 were obtained by assuming an exponential decay of the stress autocorrelation functions beyond a time of $0.2 \sigma(m/\epsilon)^{1/2}$ (see Figure 7). We also fitted the long-time tails to an algebraic $t^{-1.5}$ decay. That increased the viscosity from ~ 1.31 to $\sim 1.4 \sigma^2(m\epsilon)^{-1/2}$. A possible weak dependence on system size was masked by the substantially larger statistical errors of the viscosities obtained with corrections for algebraic long-time tails.

Finally, we have reanalyzed simulation data of Sigurgeirsson and Heyes for hard-sphere fluids.⁴⁶ Figure 8 shows the dependence of the diffusion coefficient D_{PBC} on the inverse box length $1/L$ at a packing fraction of $\zeta = 0.35$, corresponding to

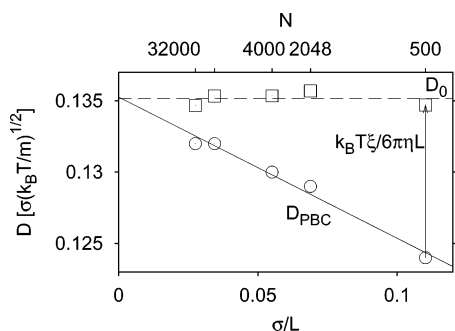


Figure 8. System-size dependence of the self-diffusion coefficient of a hard-sphere fluid at a packing fraction of $\xi = 0.35$ corresponding to a particle density of $\rho\sigma^3 \approx 0.66845$. Circles show uncorrected simulation results (D_{PBC}) from ref 46. Squares show the diffusion coefficients (D_0) corrected for finite-size effects with eq 12, as indicated by the vertical arrow. The solid line is a straight-line fit of the uncorrected diffusion coefficients D_{PBC} to $1/L$, whereas the dashed line is the average of the corrected diffusion coefficients D_0 .

a particle density of $\rho\sigma^3 = 6\xi/\pi \approx 0.66845$. At that density, Sigurgeirsson and Heyes⁴⁶ estimated a shear viscosity of $\eta = 1.136\sigma^{-2}(mk_{\text{B}}T)^{1/2}$. With that viscosity, the correction in eq 12 essentially removes the system-size dependence of the calculated diffusion coefficients taken from Table 1 of ref 46. In particular, a linear two-parameter fit of D_{PBC} to $1/L$ (as had already been used by Sigurgeirsson and Heyes⁴⁶ to extrapolate to infinite system size) is consistent with the average D_0 after correction with eq 12. Consistent with our results for water and the LJ fluid, the calculated shear viscosities of the hard-sphere fluid⁴⁶ do not seem to depend strongly on system size.

V. Conclusions

We have tested a simple analytic correction for the significant ($1/L$) system-size dependence of self-diffusion coefficients from simulations with periodic boundary conditions. The correction formula was derived previously by Dünweg and Kremer.⁶ Here, we derive it by adapting the Kirkwood–Riseman theory of polymer diffusion^{4,25} to estimate the hydrodynamic self-interaction from the differences in the Oseen tensors for finite periodic^{16,17} and nonperiodic infinite systems.³ We have applied the correction formula to the diffusion coefficients of water, as well as Lennard–Jones (LJ) and hard-sphere fluids, and observed not only the predicted $1/L$ scaling but quantitative accuracy of the predicted system-size dependence. We have also shown, using computer simulations, that the shear viscosity, unlike the diffusion coefficient, does not suffer from large finite-size effects for the systems studied. However, possible system-size dependences in the viscosity that result from hydrodynamic long-time tails in the shear–stress autocorrelation function may not have been resolved, because of statistical uncertainties.

For the self-diffusion coefficients of water, a LJ fluid, and a hard-sphere fluid, we show that the analytic correction term (eq 12) removes system-size dependences within statistical uncertainties. However, for polar and, particularly, charged particles in a polar or ionic medium, electrostatic effects could result in smaller correction terms, as observed for ions and RNA diffusing in water.⁷ In those cases, the correction terms were inversely proportional to the box length, but needed to be reduced by constant scaling factors to account for the system-size dependence of the calculated diffusion coefficients (D_{PBC}). We present arguments for an electrostatic origin of these deviations. System-size corrections will be useful when results from different simulations are compared.^{47,48} More importantly, the corrections

are essential in comparisons between simulations and experiments,^{7,8} and, in particular, in force-field parametrizations that use measured diffusion coefficients as reference values.^{49,50}

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