PHYSICAL REVIEW E **68**, 021203 (2003)

System size dependence of the diffusion coefficient in a simple liquid

M. Fushiki*

RICS, National Institute of Advanced Industrial Science and Technology (AIST), Central 2,1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

(Received 25 March 2003; published 29 August 2003)

An equation to estimate the system size dependence of the self-diffusion coefficient of a tagged particle moving in a simple fluid is given using linear-response theory and linearized hydrodynamics. Estimates made by the equation are compared with the results of the molecular dynamics simulation for a hard-sphere fluid at two densities, $\rho\sigma^3 \approx 0.88$ and 0.47, where σ is the hard-sphere diameter. Good agreement between theory and simulation is obtained at the higher density. At the lower density, the agreement becomes poorer, but it is improved by taking into account the diffusion effect of the tagged particle. The equation gives the same diffusion coefficient for the infinite system as that obtained by taking into account the long-time tail contribution of the velocity autocorrelation function [B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. **53**, 3813 (1970)]. When the tagged particle has a larger mass than the fluid particles, the equation presented here gives the better estimates. It is confirmed by the molecular dynamics calculation.

DOI: 10.1103/PhysRevE.68.021203 PACS number(s): 66.10.Cb, 02.70.Ns, 47.15.Gf

I. INTRODUCTION

The self-diffusion coefficient D, one of the fundamental transport coefficients in a simple liquid, has been studied by experiment and molecular level simulation for many years [1–3]. We should note, however, that D as obtained by simulations is always affected by the finiteness of the simulation box, and the correction for it is not negligible (about 10% in the case of a 500-particle dense hard-sphere fluid) [2]. Although this correction has been argued in connection with the long-time behavior of the velocity autocorrelation function [2,3], the argument is not applicable for D of a heavy particle moving in a fluid of lighter particles [4]. In this paper, we present an equation to estimate the system size dependence of D. It can be utilized even for the diffusion of a heavy particle.

Let us first consider a fluid consisting of one solute particle labeled 1 and $N-1$ solvent particles labeled $2 \sim N$ placed in a cubic simulation box, and impose periodic boundary conditions. The solute particle may have different size, mass, etc., from the solvent particles. When a constant force F_z in the z direction is applied to the solute particle, after a time the system reaches a steady state in which the solute particle has a constant drift velocity

$$U_{drift,N} = v_{1,z} - v_z^{fluid} \tag{1}$$

measured relative to the mean velocity of the surrounding fluid,

$$v_z^{fluid} = \frac{1}{N-1} \sum_{i=2}^{N} v_{i,z}, \tag{2}$$

where $v_{i,z}$ is the z component of the ith particle velocity. We see from linear-response theory [5,6] that the ratio $U_{drift,N}/F_z$ for a sufficiently small F_z gives the diffusion coefficient for the N-particle fluid,

$$\frac{D_N}{kT} = \frac{m_f}{m_1 + m_f} \frac{U_{drift,N}}{F_z}, \tag{3}$$

where $m_f = (N-1)m$ is the mass of the surrounding fluid, and m_1 and m are mass of the solute and solvent particles, respectively. The diffusion coefficient in Eq. (3) can be written as

$$D_N = \int_0^{\infty} \rho_D(t;N)\, dt, \tag{4}$$

with the velocity autocorrelation function (VAF)

$$\rho_D(t;N) = \langle v_{1,z}(t) v_{1,z}(0) \rangle, \tag{5}$$

where $\langle \, \rangle$ denotes an equilibrium ensemble average [see Appendix A for the derivation of Eq. (3)]. When we take the laboratory frame as a reference and look at the fluid in the steady state at the hydrodynamic scale, we will see that velocity field $\mathbf{v}^{(lab)}(r)$ is created around the solute particle. The mean velocity of the surrounding fluid defined by Eq. (2) can be approximately written with the z component of $\mathbf{v}^{(lab)}(r)$,

$$v_z^{fluid} \simeq \int v_z^{(lab)}(\mathbf{r})\, d\mathbf{r}/L^3, \tag{6}$$

where L is the simulation box length. Since F_z in Eq. (3) should be small enough to ensure linear response, $\mathbf{v}^{(lab)}(\mathbf{r})$ is likely to obey linearized hydrodynamics, i.e., the so-called Stokes equation. Since the solution of the Stokes equation for a sufficiently large simulation box decays as $1/r$ far from the solute particle [7–9], by putting the solution into Eq. (6) we find that v_{fluid}^z is inversely proportional to L. Using this fact together with Eqs. (1) and (3), we have

$$D_N = D_\infty - \frac{\alpha}{L}, \tag{7}$$

*Electronic address: m.fushiki@aist.go.jp

 ©2003 The American Physical Society

where D_∞ is the diffusion coefficient for the infinite system and α is a constant which is independent of the system size. Since the solute particle and its images form a cubic lattice, the constant α can be evaluated using the hydrodynamic calculation for a cubic lattice of spherical particles.

We will show the results of the hydrodynamic calculation in Sec. II and compare them with those obtained by the equilibrium molecular dynamics (MD) simulations for a hard-sphere fluid in Sec. III.

II. STOKES EQUATION FOR A CUBIC LATTICE OF SPHERES

In this section we will solve the Stokes equation for a cubic lattice of spheres by using the vorticity. F_z and $U_{drift,N}$ in Eq. (3) can be written with the azimuthal component of the vorticity.

When we change the frame of reference for measuring the velocity field from the laboratory frame to one that is moving with the solute particle, we have a hydrodynamic problem of a steady flow along the z direction through a cubic lattice of spherical particles from the positive to negative of the z axis. When the fluid is incompressible and has a uniform viscosity η, the steady state velocity field $\mathbf{v}(\mathbf{r})$ is obtained by solving the Stokes equations

$$\nabla p = \eta \Delta \mathbf{v} \tag{8}$$

and

$$\mathrm{div}\mathbf{v} = 0, \tag{9}$$

where $p = p(\mathbf{r})$ is the local pressure at $\mathbf{r}$. We consider one of the spherical particles located at the center of a unit cell Ω_0. When we take the spherical coordinate system centered at the particle, we can expand each component of $\mathbf{v} = (v_r, v_\theta, v_\phi)$ in Ω_0 with the spherical harmonics and their derivatives [7,8]. If L is much larger than the radius a of the spherical particle, only the lowest-order terms in each of the expansions

$$v_r(r,\theta) = f_r(r)\cos\theta, \tag{10}$$

$$v_\theta(r,\theta) = f_\theta(r)\sin\theta, \tag{11}$$

and

$$v_\phi(r,\theta) = 0 \tag{12}$$

give a set of good approximate solutions.

Substituting these approximate solutions, Eqs. (10)–(12) into Eq. (9) and calculating div$\mathbf{v}$ in the spherical coordinate system lead to

$$\frac{df_r(r)}{dr} + 2\frac{f_r(r) + f_\theta(r)}{r} = 0. \tag{13}$$

On the other hand, the substitution of Eqs. (10)–(12) into the expression of the vorticity $\boldsymbol{\omega} = \nabla \times \mathbf{v}$ in the spherical coordinate system leads to $\omega_r = \omega_\theta = 0$ and $\omega_\phi(r,\theta) = f_\omega(r)\sin\theta$, where

$$f_\omega(r) = \frac{df_\theta(r)}{dr} + \frac{f_r(r) + f_\theta(r)}{r}. \tag{14}$$

When we take the rotation of Eq. (8), we have the Laplace equation for $\boldsymbol{\omega}$,

$$\triangle \boldsymbol{\omega} = \nabla \cdot \boldsymbol{\omega} - \nabla \times (\nabla \times \boldsymbol{\omega}) = -\nabla \times (\nabla \times \boldsymbol{\omega}) = 0. \tag{15}$$

Substituting $\boldsymbol{\omega} = (0,0,\omega_\phi)$ into Eq. (15), we obtain the ordinary differential equation for $f_\omega(r)$,

$$\frac{d^2 f_\omega(r)}{dr^2} + \frac{2}{r}\frac{df_\omega(r)}{dr} - 2\frac{f_\omega(r)}{r^2} = 0. \tag{16}$$

The solution of Eq. (16) is

$$f_\omega(r) = \frac{A}{r^2} + Br \tag{17}$$

with two constants A and B, where the ratio between A and B is determined by the boundary conditions at the four side planes $\Gamma_i, i = 1, \ldots, 4$, of the unit cell Ω_0. Since each Γ_i is the plane of mirror symmetry [10] and the vorticity is an axial vector, vorticity components parallel to Γ_i vanish on Γ_i. By approximating the boundary of Ω_0 with the Wigner-Seitz sphere of radius $r_0 = (3/4\pi)^{1/3}L$ [11], and remembering that the vorticity has only one nonzero component $\omega_\phi(r,\theta) = f_\omega(r)\sin\theta$, the boundary conditions for the vorticity components at Γ_i lead to

$$f_\omega(r_0) = 0. \tag{18}$$

Equation (18) gives the ratio between A and B and the final form is

$$f_\omega(r) = A/r^2[1 - (r/r_0)^3]. \tag{19}$$

Equations (13) and (19) are the basic relations in our hydrodynamic calculation, and F_z and $U_{drift,N}$ can be written in simple forms using these relations. To evaluate F_z, we first note that the constant A in Eq. (19) is related to the force F_{fluid} exerted on a spherical particle by the fluid (see Appendix B for the derivation),

$$F_{fluid} = -4\pi\eta A. \tag{20}$$

When we look at the equation of motion for the solute particle in the finite fluid, we see that

$$F_{fluid} = -\frac{m_f}{m_1 + m_f}F_z \tag{21}$$

(see Appendix B for the derivation). By combining Eqs. (20) and (21) we have

$$F_z = \left(1 + \frac{m_1}{m_f}\right)4\pi\eta A. \tag{22}$$

On the other hand, substituting Eq. (6) into Eq. (1), $U_{drift,N}$ is written as

$$U_{drift,N} = -\int v_z(r) d\mathbf{r} / V_{out}, \tag{23}$$

where

$$v_z(r) = v_r(r,\theta)\cos\theta - v_\theta(r,\theta)\sin\theta \tag{24}$$

is the z component of the velocity field defined in the frame moving with the solute particle and $V_{out} = L^3 - 4\pi a^3/3$. By putting Eqs. (10) and (11) into Eq. (24) and performing the angular integration in Eq. (23), we obtain

$$U_{drift,N} = -\frac{\int_a^{r_0} f_z(r) r^2 dr}{r_0^3 - a^3}, \tag{25}$$

$$f_z(r) = f_r(r) - 2 f_\theta(r), \tag{26}$$

where we have approximated the unit cell with the Wigner-Seitz sphere introduced above Eq. (18). By differentiating Eq. (26) with respect to r and calculating $df_r(r)/dr$ and $df_\theta(r)/dr$ in the resulting equation using Eqs. (13) and (14), we have a differential equation for $f_z(r)$:

$$\frac{df_z(r)}{dr} = -2 f_\omega(r). \tag{27}$$

When we put Eq. (19) into Eq. (27) and integrate it, we have

$$f_z(r) = f_z(r_1) + \frac{2A}{r}\left[1 + \frac{1}{2}(r/r_0)^3\right] - \frac{2A}{r_1}\left[1 + \frac{1}{2}(r_1/r_0)^3\right], \tag{28}$$

where $r_1(\simeq a)$ is a reference distance and $f_z(r_1)$ is the boundary value. Substituting Eq. (28) into Eq. (25) and performing the integration, we have

$$U_{drift,N} = -\frac{1}{3}\left[f_z(r_1) - \frac{2A}{r_1}\right] - \frac{1.2A}{a}\frac{a}{r_0} + O\left[\left(\frac{a}{r_0}\right)^3\right]. \tag{29}$$

Substituting Eqs. (22) and (29) into the right hand side of Eq. (3) and omitting higher-order terms than a/r_0, we have

$$\frac{D_N}{D_{slip}} = \frac{D_\infty}{D_{slip}} - \frac{1.2a}{r_0}, \tag{30}$$

where $D_{slip} = kT/4\pi\eta a$ is the diffusion coefficient obtained with the hydrodynamic slip boundary condition [1]. Since $r_0 = (3/4\pi)^{1/3} L$, Eq. (30) is equivalent to Eq. (7) with coefficient $\alpha = 1.2(4\pi/3)^{1/3}/4\pi\eta$. We note that the slope -1.2 of Eq. (30) was obtained by approximating the cubic cell with a sphere. This value is slightly different from that obtained by the expansion of the Ewald sum with a/r_0, -1.173 [12,13].

III. COMPARISON WITH SIMULATION RESULTS

We have examined the asymptotic equation (30) by a series of equilibrium MD simulations for identical hard spheres of $N = 16$–$16\,384$ at two volumes, $V = 1.6V_0$ and $3V_0$, where $V_0 = N\sigma^3/\sqrt{2}$ is the close-packed volume and σ is the diameter of a hard sphere [14]. Each simulation was carried out during a $1.6\times 10^5 \tau_E$ time period for equilibration and a $10^6\tau_E$–$4\times 10^6 \tau_E$ time period for taking an ensemble average, where $\tau_E = \sqrt{m/(\pi kT)}/[4\rho\sigma^2 g(\sigma)]$ is the Enskog collision time with the mean fluid density $\rho = N/V$ and the radial distribution function at the contact distance, $g(\sigma)$. From the result of each MD simulation, the diffusion coefficient was calculated using Eq. (4). Since the velocity autocorrelation function for identical particles is written as

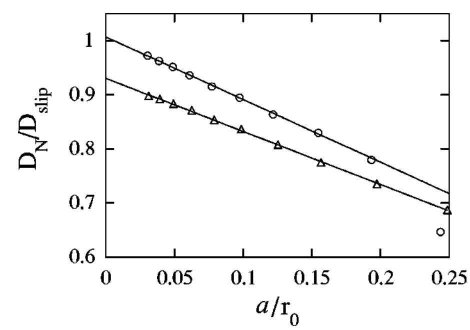

FIG. 1. Diffusion coefficient for a hard-sphere fluid as a function of system size $r_0 = (3V/4\pi)^{1/3}$. Circles and triangles are MD results at $V/V_0 = 1.6$ and 3, respectively. Straight lines are the least squares fits of the MD results. The standard deviations of the MD results are less than the sizes of the symbols.

$$\rho_D(t;N) = \frac{1}{3N}\sum_{i=1}^{N}\langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle, \tag{31}$$

putting Eq. (31) into Eq. (4) and performing the time integration, we have [3]

$$D_N = \lim_{t\to\infty} D(t;N), \tag{32}$$

where

$$D(t;N) = \frac{1}{6N}\sum_{i=1}^{N}\langle[\mathbf{r}_i(t) - \mathbf{r}_i(0)]\cdot[\mathbf{v}_i(t) + \mathbf{v}_i(0)]\rangle. \tag{33}$$

In the numerical calculation $\lim_{t\to\infty}$ on the right-hand side of Eq. (32) is replaced with the plateau value of $D(t;N)$.

We note that the viscosity η appears in the asymptotic equation, Eq. (30), through $D_{slip} = kT/4\pi\eta a$. We took η values at $V/V_0 = 1.6$ and 3 as $1.5\eta_E$ [15] and $1.02\eta_E$ [2] from the previous MD results for the hard-sphere fluids, where $\eta_E = (5\pi/24)\rho\sigma\sqrt{mkT/\pi}(1/y + 0.8 + 0.761y)$ is the Enskog estimate [16,17] with the configurational part of the pressure $y = PV/NkT - 1 = (2\pi/3)\rho\sigma^3 g(\sigma)$ [18]. After evaluating η in this way, we plotted the MD results of D_N at the two densities as functions of a/r_0 in Fig. 1. Except for the result of the smallest N at $V/V_0 = 1.6$, all the MD results at each density seem to sit on a line, so we determined the line by the least squares fit of the MD data. The slopes and y intercepts are in Table I. The table shows that the slope at the higher density is in fairly good agreement with the hydrodynamic estimate, -1.2, but at the lower density the fitted

TABLE I. Slope and y intercepts, D_∞/D_{slip}, of the least squares fitted line in Fig. 1.

V/V_0	Slope	D_∞/D_{slip}
1.6	-1.158 ± 0.008	1.0072 ± 0.0007
3.0	-0.981 ± 0.005	0.9305 ± 0.0004

value of the slope becomes 20% smaller in absolute value than the hydrodynamic estimate. This disagreement at lower density can be attributed to diffusion of the solute particle. Substituting Eq. (29) into Eq. (3), we see that the slope of Eq. (30) is proportional to the ratio A/F_z, and with the aid of Eq. (22) the ratio A/F_z is evaluated as $A/F_z=(1-1/N)/4\pi\eta\approx1/4\pi\eta$ for a fluid consisting of identical particles. However, due to the diffusion of the solute particle that acts as a mediator of the momentum from the outside to the fluid, A/F_z becomes smaller than that determined by Eq. (22). A similar diffusion effect of the solute particle has been considered by Alder and Wainwright in the argument of the long-time behavior of the VAF [19,20]. By adopting their argument, we multiply the correction factor

$$\chi=\frac{\nu}{\nu+D_E} \tag{34}$$

to the slope of Eq. (30), where $\nu=\eta/(\rho m)$ is the kinematic viscosity of the fluid and $D_E=3kT\tau_E/(2m)$ is the Enskog estimate of the diffusion coefficient [21]. When we put the η values presented above into Eq. (34), we have the corrected slopes $-1.2\chi=-1.19$ and -1.00 for $V/V_0=1.6$ and 3, respectively. Each of the corrected slopes agree with that tabulated in Table I within a few percent [22].

Thus we found that the MD results of the diffusion coefficient in the large N region can be estimated by Eq. (30) with the corrected slope -1.2χ. Using this fact, we can estimate D_∞ with a few to several MD simulations for finite systems. For instance, after fitting the MD results of D_N at the three smallest N values in $V/V_0=1.6$ using a quadratic function of a/r_0, we can determine D_∞ with the condition that the asymptotic line is tangent to the quadratic function. In this way we obtain $D_\infty=1.02$, which is in a fairly good agreement with the value in Table I.

Another method of estimating D_∞ may be worth mentioning. This method is based on the long time behavior of the VAF that was referred to in deriving Eq. (34). More than three decades ago, Alder and Wainwright found a long-time tail in the VAF of a hard-disk or hard-sphere fluid [19,23],

$$\rho_D(t;N)\sim\alpha t^{-d/2}, \tag{35}$$

where d is the space dimension of the fluid. For $d=3$ the coefficient α is evaluated as [2,24–26]

$$\alpha=\frac{2kT}{3\rho m_1}\left(\frac{4\pi\nu}{\chi}\right)^{-3/2} \tag{36}$$

with χ defined in Eq. (34). In a MD simulation with periodically aligned cells, the long-time tail is interfered by the

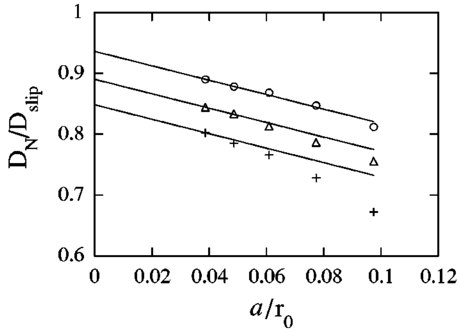

FIG. 2. Diffusion coefficient for a hard-sphere fluid at $V/V_0=1.6$ as a function of system size. Circles, triangles, and crosses are MD results for $m_1/m=4$,10, and 25, respectively. Each straight line is the asymptotic line passing through D_N/D_{slip} of $a/r_0\simeq0.039$. The standard deviations of the MD results are about same as the sizes of the symbols.

acoustic wave propagating across the periodic cells and disappears around time t_c [3,19,27,28]. Using this fact, D_∞ is estimated as [2,3]

$$D_\infty=\int_0^{t_c}\rho_D(t;N)dt+\alpha\int_{t_c}^{\infty}t^{-3/2}dt\simeq D_N+\frac{2\alpha}{t_c^{1/2}}. \tag{37}$$

By applying Eq. (37) to the MD results for $N=108$ and 500, Alder *et al.* obtained $D_\infty/D_{slip}=0.98$ and 0.927 for $V/V_0=1.6$ and 3.0, respectively [2,29]. Erpenbeck and Wood later analyzed their own results for $N=4000$ hard-sphere fluids [28] and obtained an improved value $D_\infty/D_{slip}=1.007$ for $V/V_0=1.6$ [3,17]. Our estimates shown in Table I are in agreements with these values within a few percent. However, we should note that, due to the $1/m_1$ factor in Eq. (36), α in Eq. (37) becomes insignificant for a heavy solute particle. Thus Eq. (37) implies that D_N for a heavy solute particle converges with a finite N. On the other hand, since Eq. (30) does not contain m_1, this implies that the difference between D_N and D_∞ remains in the same order of magnitude irrespective of the solute mass. In order to see the mass effect, we have performed the MD simulations for hard-sphere fluid at $V=1.6V_0$ with mass ratios $m_1/m=4$, 10, and 25 [30]. The results of D_N together with the line of Eq. (30) are shown in Fig. 2. The figure shows that D_N has similar system size dependence as that for the identical particles. No mass dependence was obtained and D_N can be described by the asymptotic equation (30). From the y intercepts of the straight lines, we obtained $D_\infty/D_{slip}=0.94$, 0.89, and 0.85 for $m_1/m=4$, 10, and 25, respectively. We note that the computation of D_N for the heavy solute particle is time consuming because the sampling over N particles in Eq. (33) no longer holds. Thus our method of extrapolating D_N at small N to D_∞ is very relevant in these cases.

ACKNOWLEDGMENTS

The calculations in this study were performed on an IBM RS/6000 SP at Tsukuba Advanced Computing Center (TACC) in National Institute of Advanced Industrial Science and

Technology (AIST). We thank T. Ooshida, B. Hafskjold, and T. Ikeshoji for useful comments.

APPENDIX A: LINEAR-RESPONSE THEORY

In this appendix we will derive Eq. (3) using linear-response theory. The derivation is analogous to that for a fluid consisting of identical particles [31–33]. We first note that the situation of a constant external force F_z applying to the solute particle for $t>0$ is handled by adding a perturbation term $H_{ext}(t)=-z_1F_z\theta(t)$ to the system Hamiltonian, where $\theta(t)$ is the Heaviside step function. Then linear-response theory tells us that the nonequilibrium ensemble average of a dynamical variable Q for $t>0$ is related to the time integral of the equilibrium ensemble average [5,6],

$$\langle Q(t)\rangle_{ne}=\frac{F_z}{kT}\int_0^t\langle Q(t')v_{1,z}(0)\rangle dt', \tag{A1}$$

where $\langle\ \rangle_{ne}$ denotes the nonequilibrium ensemble average. When we choose $Q(t)=v_{1,z}(t)-v_z^{fluid}(t)\equiv v_z^{rel}(t)$, we have from Eq. (A1),

$$\begin{aligned}\langle v_z^{rel}(t)\rangle_{ne}&=\frac{F_z}{kT}\int_0^t\langle v_z^{rel}(t)v_{1,z}(0)\rangle dt'\\&=\frac{F_z}{kT}\left(1+\frac{m_1}{m_f}\right)\int_0^t\langle v_{1,z}(t')v_{1,z}(0)\rangle dt'.\end{aligned} \tag{A2}$$

To derive the last equation we have used the fact that total momentum is zero. By taking $t\to\infty$ of Eq. (A2) and noting $\lim_{t\to\infty}v_z^{rel}(t)=U_{drift}$, we obtain Eq. (3).

APPENDIX B: DRAG FORCE

According to hydrodynamics, the force exerted on a spherical particle by a fluid, F_{fluid}, is written as the surface integral of the stress as [9]

$$F_{fluid}=\int\{[-p(r)+\sigma_{rr}]\cos\theta-\sigma_{r\theta}\sin\theta\}dS, \tag{B1}$$

where $\sigma_{rr}=2\eta\partial v_r/\partial r$ and $\sigma_{r\theta}=\eta(\partial v_\theta/\partial r-v_\theta/r-1/r\partial v_r/\partial\theta)$ are respectively the $r-r$ and $r-\theta$ components of the shear stress and integration is done at a spherical surface of radius $r\geqslant a$. By performing the angular integral in Eq. (B1) and using Eqs. (13) and (14), we get

$$F_{fluid}=-\frac{4\pi}{3}\eta r^2[f_p(r)+2\eta f_\omega(r)], \tag{B2}$$

where $f_p(r)$ is the coefficient for $\cos\theta$ in the spherical harmonic expansion of the pressure. When we write Eq. (8) as

$$\nabla p=-\eta\nabla\times\boldsymbol{\omega} \tag{B3}$$

with the aid of Eq. (9), we see that the θ component of Eq. (B3) leads to

$$f_p(r)=-\eta\left[r\frac{df_\omega}{dr}+f_\omega(r)\right]. \tag{B4}$$

By putting Eq. (B4) into Eq. (B2), we get

$$F_{fluid}=\frac{4\pi}{3}\eta r^2\left[r\frac{df_\omega}{dr}-f_\omega(r)\right]. \tag{B5}$$

When we put Eq. (19) into Eq. (B5), we obtain Eq. (20) in the text.

To relate F_{fluid} with F_z, we note the z component of the equation of motion for the solute particle in the laboratory frame of reference,

$$m_1\dot{v}_{1,z}=F_z+F_{fluid}, \tag{B6}$$

for the total momentum balance condition,

$$m_1\dot{v}_{1,z}+m_f\dot{v}_z^{fluid}=F_z, \tag{B7}$$

and for the steady state condition,

$$\dot{U}_{drift,N}=\dot{v}_{1,z}-\dot{v}_z^{fluid}=0. \tag{B8}$$

By eliminating $\dot{v}_{1,z}$ and $\dot{v}_z^{fluid}$ from Eqs. (B6)–(B8), we have Eq. (21) in the text.

[1] R. Castillo, C. Garza, and S. Ramos, J. Phys. Chem. **98**, 4188 (1993), and references therein.
[2] B.J. Alder, D.M. Gass, and T.E. Wainwright, J. Chem. Phys. **53**, 3813 (1970).
[3] J.J. Erpenbeck and W.W. Wood, Phys. Rev. A **43**, 4254 (1991).
[4] We will discuss this point in more detail at the end of Sec. III.
[5] D.A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), pp. 507–509.
[6] J.P. Hansen and O.R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, Amsterdam, 1986), pp. 230–236; 240–247.
[7] H. Lamb, *Hydrodynamics*, 6th ed. (Cambridge University Press, Cambridge, 1975), pp. 594–604.
[8] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Prentice-Hall, London, 1965), Chaps. 3 and 4.
[9] L.D. Landau and E.M. Lifshitz, *Fluid Mechanics*, 2nd ed. (Pergamon, London, 1987), pp. 58-67.
[10] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, 3rd ed., Part 1 (Pergamon, London, 1980), pp. 411–412.
[11] H. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).
[12] H. Hashimoto, J. Fluid Mech. **5**, 317 (1959).
[13] O. Emersleben, Phys. Z. **36**, 73 (1923); **36**, 97 (1923).
[14] These volumes are those used by previous authors. See Refs. [2,3] for example.
[15] J.J. Erpenbeck and W.W. Wood, J. Stat. Phys. **24**, 455 (1981).
[16] J.P. Hansen and O.R. McDonald, *Theory of Simple Liquids*

(Ref. [6]), p. 269.

[17] We should note that, for the Enskog estimates of the transport coefficients, Erpenbeck and Wood used slightly different definitions from those presented in this paper. See Eq. (18) in Ref. [3].

[18] We evaluated y with the Carnahan-Starling equation of state, N.F. Carnahan and K.E. Starling, J. Chem. Phys. **51**, 635 (1969); see also J.P. Hansen and O.R. McDonald, *Theory of Simple Liquids* (Ref. [6]), pp. 95 and 123.

[19] B.J. Alder and T.E. Wainwright, Phys. Rev. A **1**, 18 (1970).

[20] The precise form of the VAF in the long time region will be shown in Eqs. (35) and (36).

[21] In the process of calculating α in Eq. (36), some authors have used D_∞ for D_E in Eq. (34) [3,25,26,28]. We used D_E in this work because the substitution of D_∞ in Eq. (34) gives $-1.2\chi = 0.94$ at the lower density. This produces poorer agreement with the value in Table I than using D_E.

[22] The differences left can be attributed to the approximation of the cubic unit cell with the Wigner-Seitz sphere. When we take the Ewald sum mentioned at the end of Sec. II, we have the slope -1.17χ. This decreases the difference at each density to less than 1%.

[23] B.J. Alder and T.E. Wainwright, J. Phys. Soc. Jpn. **26**, 267 (1969).

[24] J.R. Dorfman and E.G.D. Cohen, Phys. Rev. Lett. **25**, 1257 (1970); Phys. Rev. A **6**, 776 (1972); **12**, 292 (1975).

[25] M.H. Ernst, E.H. Hauge, and J.M.J. Van Leeuwen, Phys. Rev. Lett. **25**, 1254 (1970); Phys. Rev. A **4**, 2055 (1971); J. Stat. Phys. **15**, 7 (1976); **15**, 23 (1976).

[26] A concise explanation is given in J.P. Hansen and O.R. McDonald, *Theory of Simple Liquids* (Ref. [6]), pp. 296–302.

[27] J.J. Erpenbeck and W.W. Wood, Phys. Rev. A **26**, 1648 (1982).

[28] J.J. Erpenbeck and W.W. Wood, Phys. Rev. A **32**, 412 (1985).

[29] To evaluate D_∞, the authors assumed a $1/N$ dependence in addition to the existence of the long-time tail.

[30] To increase the statistical accuracy, we have used 64 different MD trajectories. Each trajectory starts from a different set of initial particles' velocities sampled from the Maxwell-Boltzmann distribution, and has a similar time length as those for the identical particles.

[31] D.J. Evans, W.G. Hoover, B.H. Failor, B. Moran, and A.J.C. Ladd, Phys. Rev. A **28**, 1016 (1983).

[32] D.J. Evans and G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic Press, London, 1990), pp. 128–132.

[33] G.V. Paolini, G. Ciccotti, and H. van Beijeren, Phys. Rev. A **42**, 5912 (1990).