PHYSICAL REVIEW E **67**, 062403 (2003)

Test of mean-field equations for two types of hard-sphere systems by a Brownian-dynamics simulation and a molecular-dynamics simulation

Michio Tokuyama,[1] Hiroyuki Yamazaki,[2] and Yayoi Terada[2]
[1]*Institute of Fluid Science, Tohoku University, Sendai 980-8577, Japan*
[2]*Department of Mechanical Engineering, Tohoku University, Sendai 980-8579, Japan*

(Received 26 February 2003; published 25 June 2003)

A mean-field nonlinear equation for the mean-square displacement, recently proposed by one of the present authors [M. Tokuyama, Phys. Rev. E **62**, R5915 (2000); Physica A **289**, 57 (2001)], for concentrated, equilibrium suspensions of hard spheres is extended to describe equilibrium atomic systems of hard spheres. The validity of two types of mean-field equations is investigated by two kinds of computer simulations; a Brownian-dynamics simulation on suspensions of hard spheres and a molecular-dynamics simulation on atomic systems of hard spheres. A good agreement between the mean-field equations and simulations is then shown for different volume fractions. The two types of model systems of hard spheres are thus shown to be identical to each other on the study of the liquid-solid transition. However, analyses suggest that a new interaction is indispensable to understand the mechanism for the liquid-glass transition in both systems.

DOI: 10.1103/PhysRevE.67.062403 PACS number(s): 82.70.Dd, 05.40.−a, 51.10.+y

There has been considerable interest in the dynamics of colloidal suspensions of hard spheres since the discovery of the colloidal glass transition [1–3]. However, our understanding of the mechanism for the glass transition in colloidal systems as well as in atomic systems is still incomplete. In this Brief Report, we propose two types of mean-field equations, the first type for colloidal suspensions of hard spheres and the second type for atomic systems of hard spheres. Then, we investigate their validity by performing two kinds of computer simulations, a Brownian-dynamics (BD) simulation on the suspensions and a molecular-dynamics (MD) simulation on the atomic systems. Thus, we show that the mean-field results are in good agreement with simulation results for different volume fractions. Hence, we expect that both the equations could be useful tools to describe the dynamical behavior of hard spheres near the glass transition.

Recently, Tokuyama [4,5] has proposed the following nonlinear equation for the particle mean-square displacement $M_2(t)$, to describe the equilibrium suspensions of colloidal hard spheres near the colloidal glass transition:

$$\frac{d}{dt}M_2(t)=2dD_S^L(\phi)+2d[D_S^S(\phi)-D_S^L(\phi)]e^{-\lambda M_2(t)} \tag{1}$$

with the long-time self-diffusion coefficient

$$D_S^L(\phi)=\frac{D_S^S(\phi)(1-9\phi/32)}{1+(\phi D_S^S/\phi_g^{TO}D_0)(1-\phi/\phi_g^{TO})^{-2}}, \tag{2}$$

where ϕ is the particle volume fraction of hard spheres, d the spatial dimensionality, and $D_S^S(\phi)$ the short-time self-diffusion coefficient given by Eq. (11) of Ref. [6]. Here $\lambda(\phi)$ is a free parameter to be determined, where $\lambda^{-d/2}$ is related to the free volume of a particle and ϕ_g^{TO} represents a theoretical colloidal glass transition volume fraction given by $\phi_g^{TO}=(4/3)^3/(7\ln 3-8\ln 2+2)\simeq 0.571\,84\ldots$ [6,7]. D_0 $(=k_BT/6\pi\eta a)$ is the free diffusion coefficient of the sphere, where η is a viscosity of the fluid. We note here that the singular term in Eq. (2) results from the many-body correlation effects due to the long-range hydrodynamic interactions between spheres, and factor $9\phi/32$ indicates the coupling effects between the direct interactions and the short-range hydrodynamic interactions [6,7].

Equation (1) can be solved to give a formal solution

$$M_2(t)=\frac{1}{\lambda}\ln\left[1+\frac{t_\beta}{t_C}\{e^{t/t_\beta}-1\}\right], \tag{3}$$

where $t_\beta=1/(2d\lambda D_S^L)$ denotes the β-relaxation time, around which the many-body interactions between particles becomes important, and $t_C=1/(2d\lambda D_S^S)$ is the short time for a colloid to diffuse over a distance of order $\lambda^{-1/2}$. This solution suggests three different time scales; t_C, t_β, and a long time $t_L(=a^2/D_S^L)$, where $t_C\ll t_\beta\ll t_L$ and a is the average particle radius. In fact, one can find the following asymptotic forms:

$$M_2(t)\simeq\begin{cases}2dD_S^S t & \text{for } t\ll t_C\ll t_\beta\\ 2dD_S^L t & \text{for } t_\beta\ll t_L\leq t.\end{cases} \tag{4}$$

Thus, Eq. (1) describes the dynamics of a crossover from the short-time self-diffusion process characterized by D_S^S to the long-time self-diffusion process characterized by D_S^L. Equation (3) has been used to analyze the recent experimental data for equilibrium colloidal suspensions near the colloidal glass transition and has been shown to describe those data very well for a wide range of volume fractions from a liquid state to a glass state by adjusting λ (see Fig. 1) [4,5]. Thus, parameter λ has been found to approximately obey [5]

$$\lambda(\phi)a^2=\frac{d_0\phi}{\phi_g^{TO}(\phi_g^{TO}-\phi)}-d_1\phi+d_2\phi^2, \tag{5}$$

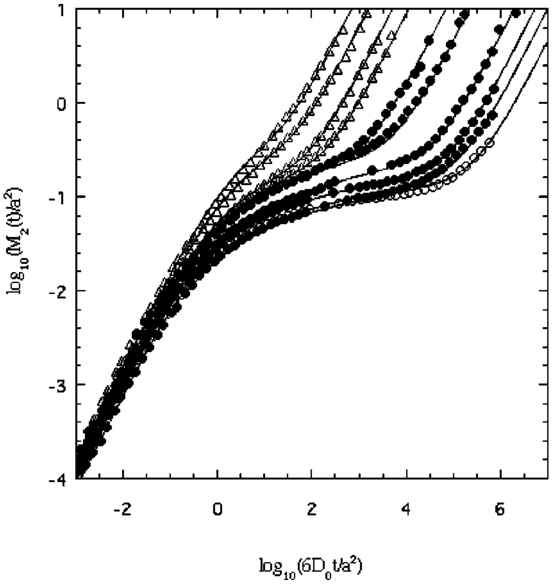

FIG. 1. A log-log plot of the mean-square displacement $M_2(t)$ vs time. The solid line indicates the theoretical results from Ref. [5]. The symbols indicate the experimental data from Ref. [8]: △ for a liquid state, ● for a supercooled state, and ○ for a glass state.

for $0.4 \leq \phi < \phi_g^{TO}$, where $d_0 = 0.032$, $d_1 = 57.514$, and $d_2 = 194.574$. In order to describe the equilibrium atomic systems of hard spheres, we also propose the following nonlinear equation for $M_2(t)$:

$$\frac{d}{dt}M_2(t) = 2dD_S^L(\phi) + 2d\left[\frac{v_0^2}{d}t - D_S^L(\phi)\right]e^{-\lambda M_2(t)}, \quad (6)$$

where D_S^L is the long-time self-diffusion coefficient for atomic systems to be determined. Here $v_0 = \sqrt{dk_BT/m}$ denotes the average velocity of an atom, where T and m are the temperature and the average particle mass, respectively. In Eq. (6), the short-time self-diffusion coefficient D_S^S is replaced by term $(v_0^2/d)t$. This is reasonable because in atomic systems the short-time process is governed by the ballistic motion, leading to $M_2(t) \simeq (v_0t)^2$, while in suspensions it is governed by the short-time diffusion process. Equation (6) can be solved to give

$$M_2(t) = \frac{1}{\lambda}\ln\left[1 + 2\left(\frac{t_\beta}{t_A}\right)^2\{e^{t/t_\beta} - (1 + t/t_\beta)\}\right], \quad (7)$$

where $t_A = 1/(v_0\lambda^{1/2})$ is the short time for an atom to move over a distance of order $\lambda^{-1/2}$. Similar to the colloidal suspensions, there are three different time scales t_A, t_β, and t_L, where $t_A \ll t_\beta \ll t_L$. In fact, one can find the following asymptotic forms:

$$M_2(t) \simeq \begin{cases} (v_0t)^2 & \text{for } t \ll t_A \ll t_\beta, \\ 2dD_S^L t & \text{for } t_\beta \ll t_L \leq t. \end{cases} \quad (8)$$

Thus, Eq. (6) describes the dynamics of a crossover from the ballistic motion characterized by v_0 to the long-time self-diffusion process characterized by D_S^L. In order to test the two types of mean-field equations given by Eqs. (1) and (6), we perform two kinds of computer simulations, BD and MD. In both simulations we consider N different hard spheres with radius a_i and mass m_i $(i = 1, \ldots, N)$ in a cubic box of length L at a constant temperature T, where N is chosen to be 10 976 here. We also simulate two cases separately, a monodisperse case where spheres are all identical, that is, $a_i = a$ and $m_i = m$, and a polydisperse case where the distribution of radii obeys a Gaussian distribution with standard deviation σ divided by a, and mass m_i proportional to a_i^3. The volume fraction ϕ is then given by $\phi = (4\pi a^3 N/3L^3)(1 + 3\sigma^2)$. In the suspensions, the spheres are suspended in an equilibrium fluid. For simplicity, however, we neglect the hydrodynamic interactions between spheres, leading to $D_S^S = D_0$. Hence there are two interactions, the direct interactions between spheres leading to binary collisions, and the interactions between spheres and fluid particles leading to a Brownian motion. On a time scale of order t_D, the position vector $\boldsymbol{X}_i(t)$ of ith sphere then obeys the Langevin-like equation

$$\frac{d}{dt}\boldsymbol{X}_i(t) = \frac{1}{\gamma_i}\sum_{j \neq i}\boldsymbol{F}_{ij}(t) + \boldsymbol{R}_i(t), \quad (9)$$

where $\boldsymbol{F}_{ij}$ indicates the force between spheres i and j, and $\gamma_i (= 6\pi\eta a_i)$ is the friction coefficient. We assume elastic binary collisions between particles. Here $\boldsymbol{R}_i(t)$ is the reduced Gaussian random force with zero mean, and satisfies $\langle \boldsymbol{R}_i(t)\boldsymbol{R}_j(t')\rangle = 2D_{0i}\delta(t - t')\delta_{i,j}\mathbf{1}$, where the brackets denote the average over an equilibrium ensemble and $D_{0i} = k_BT/\gamma_i$. We then employ the forward Euler difference scheme to integrate Eq. (9) with time step $10^{-3}t_D$ under periodic boundary and appropriate initial conditions. On the other hand, in the atomic systems, the spheres obey the Newton equations with forces $\boldsymbol{F}_{ij}(t)$. We then solve them under periodic boundary and appropriate initial conditions, together with the momentum and the energy conservation laws. In BD, space is scaled with the particle average radius a, time is scaled with the structural relaxation time given by $t_D = a^2/D_0$, and diffusion coefficients D_S^S and D_S^L are scaled by D_0. In MD, space is scaled with the particle average radius a, time is scaled with time a/v_0, and the diffusion coefficient D_S^L is scaled by $d_0 (= av_0)$. The mean-square displacement $M_2(t)$ is given by

$$M_2(t) = \frac{1}{N}\sum_{i=1}^{N}\langle[\boldsymbol{X}_i(t) - \boldsymbol{X}_i(0)]^2\rangle. \quad (10)$$

In both simulations, we start from a random configuration obtained by using the Jodrey-Tory algorithm [9] and wait for a long enough time to reach a final state where the mean-square displacement grows linearly in time and the radial distribution function does not change. Then, we use this final state as an initial state and repeat the same simulation procedures to obtain the numerical results in an equilibrium liquid state. Thus, the mean-square displacements obtained by both simulations are compared with the mean-field results given by Eqs. (3) and (7) which are calculated by using the

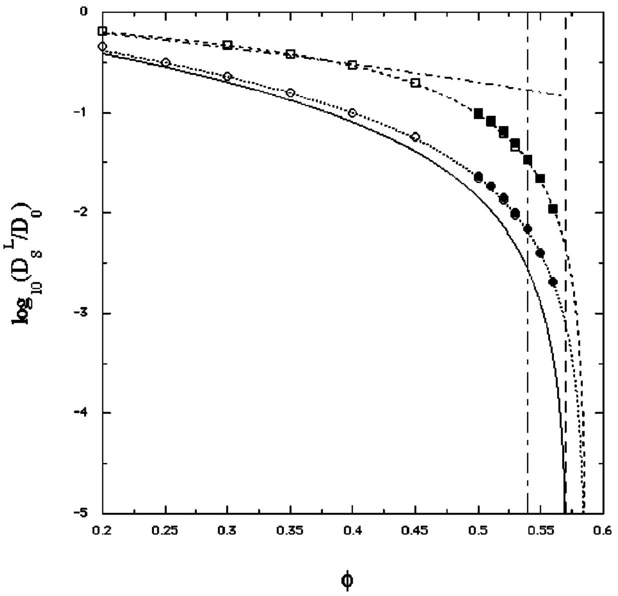

FIG. 2. A log plot of the long-time self-diffusion coefficient D_S^L vs ϕ. The open symbols indicate the simulation results in a monodisperse case: the squares for $D_S^{L(C)}$ and the circles for $D_S^{L(A)}$. The filled symbols indicate the simulation results for a polydisperse case. The solid and dot-dashed lines are the theoretical results for D_S^L and for D_S^S, respectively. The dashed and dotted lines indicate diffusion coefficients $D_S^{L(C)}$ and $D_S^{L(A)}$ given by Eqs. (11) and (12), respectively. The dot–long-dashed and the long-dashed lines denote $\phi_m(0)$ and $\phi_m(0.06)$, respectively.

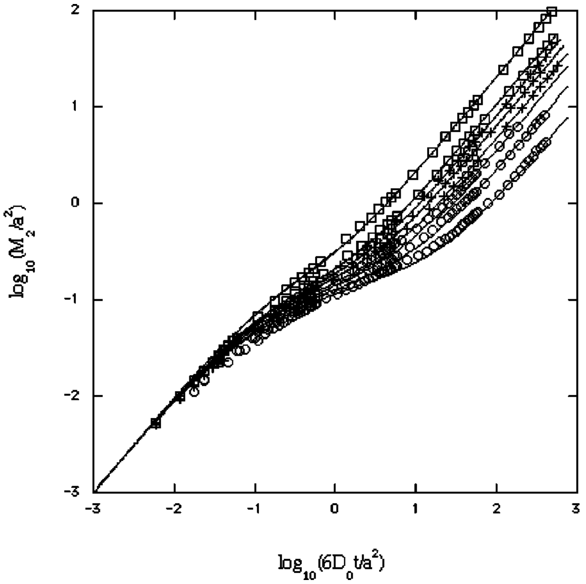

FIG. 3. A log-log plot of the mean-square displacement $M_2(t)$ for BD vs time, for different volume fractions (from left to right) 0.45, 0.50, 0.51, 0.52, 0.53, 0.54, 0.55, and 0.56. The solid line indicates the mean-field results obtained by Eq. (3). The symbols indicate the BD results: the open square is for a monodisperse equilibrium fluid state, the cross is for a monodisperse metastable fluid state, and the open circle is for a polydisperse metastable fluid state.

simulation data for scaled diffusion coefficients and by adjusting λ to fit with the simulation results.

Depending on the values of the volume fraction, there are three phase regions; a fluid region for $0<\phi<\phi_f(\sigma)$, a metastable region for $\phi_f(\sigma)\leqslant\phi<\phi_m(\sigma)$, and a crystal region for $\phi_m(\sigma)\leqslant\phi$, where $\phi_f(\sigma)$ and $\phi_m(\sigma)$ are the so-called freezing and melting volume fractions, respectively. Our simulations show that $\phi_f(0.0)\simeq0.51$, $\phi_f(0.06)\simeq0.53$, $\phi_m(0.0)\simeq0.54$, and $\phi_m(0.06)\simeq0.57$. We note here that this kind of a first-order fluid-solid transition and the existence of a metastable branch in the hard-sphere systems are the same as those discussed already by a number of computer simulations [10–17] since the pioneering work of Alder and Wainwright [18]. Both in an equilibrium fluid state and in a metastable fluid state, the long-time self-diffusion coefficient $D_S^{L(p)}$ can be obtained as $D_S^{L(p)}(\phi)/d_p=\lim_{t\to\infty}M_2(t)/(2dt)$, where $p=A$ for the atomic systems, $p=C$ for the suspensions, $d_A=d_0$, and $d_C=D_0$. In Fig. 2 we plot the coefficients $D_S^{L(p)}(\phi)/d_p$ versus ϕ. For comparison, the theoretical results D_S^L given by Eq. (2) and D_S^S given by Eq. (11) of Ref. [6], are also shown. As discussed in the previous paper [19], the coefficients $D_S^{L(p)}$ are well described by the following functions:

$$D_S^{L(C)}(\phi)/D_0=[D_S^{L(A)}(\phi)/d_0]/[D_S^S(\phi)/D_0], \tag{11}$$

$$\frac{D_S^{L(A)}(\phi)}{d_0}=\frac{D_S^S(\phi)/D_0}{1+[\phi D_S^S(\phi)/\phi_c D_0][1-\phi/\phi_c(\sigma)]^{-2}}, \tag{12}$$

where the singular point $\phi_c(\sigma)$ is given by $\phi_c(0.06)\simeq0.586$ and $D_S^S(\phi)$ is given by Eq. (11) of Ref. [6]. For higher volume fractions, both coefficients become singular as $D_S^{L(p)}(\phi)/d_p\simeq(1-\phi/\phi_c)^2$. Both coefficients show the same singular behavior as that of Eq. (2), except that the singular point ϕ_g^{TO} is now replaced by ϕ_c. This is because the long-time behavior is considered not to depend on the details of interactions [19], where the singular terms of Eqs. (11) and (12) result from the long-time correlations due to the many-body collision interactions, while the singular term of Eq. (2) results from the long-time correlations due to the long-range hydrodynamic interactions. We note here that the diffusion coefficients for a polydisperse case are slightly larger than those for a monodisperse case at higher volume fractions.

In Fig. 3 we show a log-log plot of $M_2(t)$ in the suspensions, together with the mean-field results obtained by Eq. (3), for different volume fractions. In Fig. 4 we also show a log-log plot of $M_2(t)$ in the atomic systems, together with the mean-field results obtained by Eq. (7), for different volume fractions. In both cases, parameter $\lambda(\phi)$ is obtained by fitting the theoretical values given by Eqs. (3) and (7) to the simulation results and is found to be approximated by the same equation as Eq. (5), except that the singular point is now replaced by ϕ_c. In any fluid state, the mean-field results are thus shown to agree with the simulation results well. It is also shown that the long-time behavior of the equilibrium physical quantities, in both the hard-sphere systems, such as the mean-square displacement, the diffusion coefficient, and the radial distribution function, is exactly identical to each other, although their short-time behavior is different.

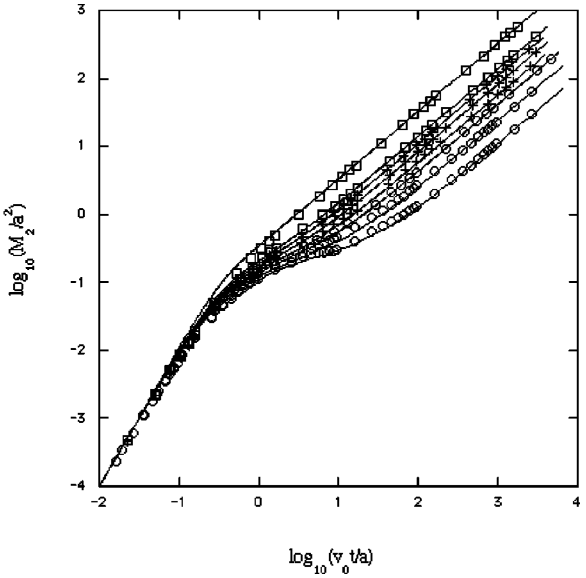

FIG. 4. A log-log plot of the mean-square displacement $M_2(t)$ for MD vs time, for different volume fractions (from left to right) 0.45, 0.50, 0.51, 0.52, 0.53, 0.54, 0.55, and 0.56. The solid line indicates the mean-field results obtained by Eq. (6). The details are the same as in Fig. 3.

In this paper we have tested the validity of two types of mean-field equations through comparison with two kinds of computer simulations. One is the mean-field equation (1) for colloidal suspensions tested by BD and the other is the mean-field equation (6) for atomic systems tested by MD. We have performed those simulations for different volume fractions in two cases, a monodisperse case and a polydisperse case. Thus, we have shown that the mean-field results agree with the simulation results very well, where the free parameter λ obeys the same equation as Eq. (5), except that ϕ_g^{TO} is now replaced by ϕ_c. Since Eq. (1) has been successfully used to analyze the recent experiments near the glass transition [5], therefore, Eq. (6) may also be expected to be a useful tool to analyze the experiments in glass-forming materials near the glass transition. Finally, we should refer to model systems to study the liquid-glass transition. If the short-time hydrodynamic interactions are considered self-consistent, the colloidal suspensions of hard spheres can serve as valuable models for the study of the atomic systems of hard spheres on the liquid-solid transition [see Eq. (11)]. Both simulations show that there exists a liquid-solid transition but not a liquid-glass transition even for a polydisperse case. Hence both systems may still lack an important interaction to understand the mechanism for the liquid-glass transition. In the suspensions, it is considered to be a long-time hydrodynamic interaction between particles as discussed in Refs. [6,7]. In the atomic systems a new interaction is also considered to be indispensable to undergo the glass transition. This will be discussed elsewhere.

This work was partially supported by Grants-in-aid for Science Research No. 14540348 from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Numerical computations for this work were performed on the ORIGIN 2000 machine at the Institute of Fluid Science, Tohoku University.

---

[1] P.N. Pusey and W. van Megen, Nature (London) **320**, 340 (1986).
[2] M. Medina-Noyola, Faraday Discuss. R. Soc. Chem. **83**, 21 (1987).
[3] E.R. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield, and D.A. Weitz, Science **287**, 627 (2000).
[4] M. Tokuyama, Phys. Rev. E **62**, R5915 (2000).
[5] M. Tokuyama, Physica A **289**, 57 (2001).
[6] M. Tokuyama and I. Oppenheim, Phys. Rev. E **50**, R16 (1994).
[7] M. Tokuyama and I. Oppenheim, Physica A **216**, 85 (1995).
[8] W. van Megen *et al.*, Phys. Rev. E **58**, 6073 (1998).
[9] W.S. Jodrey and E.M. Tory, Phys. Rev. A **32**, 2347 (1985).
[10] W.W. Wood and J.D. Jacobson, J. Chem. Phys. **27**, 1207 (1957).
[11] W.G. Hoover and F.H. Ree, J. Chem. Phys. **49**, 3609 (1968).
[12] B. Cichocki and K. Hinsen, Physica A **187**, 133 (1992).
[13] R.J. Speedy, J. Chem. Phys. **100**, 6684 (1994).
[14] M.D. Rintoul and S. Torquato, Phys. Rev. Lett. **77**, 4198 (1996).
[15] See-Eng Phan *et al.*, J. Chem. Phys. **108**, 9789 (1998).
[16] B. Doliwa and A. Heuer, Phys. Rev. E **61**, 6898 (2000).
[17] D.R. Foss and J.F. Brady, J. Rheol. **44**, 629 (2000).
[18] B.J. Alder and T.E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).
[19] M. Tokuyama and Y. Yamazaki, Physica A (to be published).