Comparison of mode-coupling theory with molecular dynamics simulations from a unified point of view

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We study the tagged-particle dynamics by solving equations of the mode-coupling theory (MCT). The numerical solutions are compared with results obtained by the molecular dynamics (MD) simulations from a unified point of view proposed by Tokuyama [Phys. Rev. E **80**, 031503 (2009)]. We propose a way of comparison in which the reduced long-time self-diffusion coefficient is used to characterize states of the system. The comparison reveals that the tagged-particle dynamics calculated from MCT qualitatively deviates from that obtained by MD. Our results suggest that the deviation originates from the starting equation of MCT.

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I. INTRODUCTION

Glass transition is an unsolved problem in condensed matter physics [1–3]. As systems approach glass transition, their dynamic properties such as the diffusion coefficient and viscosity change drastically, showing slow dynamics, while the static properties hardly do. Slow dynamics is thought to originate from the cooperative motion [4–7]. In fact, the critical phenomenon in which cooperative motion plays an significant role shows the critical slowing down near the critical point [8]. One of the theories for explaining the critical phenomenon is the mode-coupling theory (MCT) [9]. This theory explicitly considers nonlinear effects to explain the dynamics near the critical point. In the 1980s, MCT was first applied to the study of supercooled liquids [10,11] to derive the equation of motion for relaxation functions such as the intermediate scattering function. Nowadays, MCT is the most well-known theory for studying the dynamics of supercooled liquids. It predicts the nonergodic transition from the ergodic state to the nonergodic state in which the relaxation function converges to nonzero value even in the long-time limit.

The MCT equations have been solved numerically for several models [12–20], and hence have been widely used to explain results of experiments and simulations [21,22]. Nevertheless, some challenges remain. A problem is that MCT solutions do not agree with the simulation results in the cage region as discussed in the previous study [23]. Another problem is that MCT underestimates control parameters such as the inverse temperature and the volume fraction. Although it is unclear whether the nonergodic transition can be regarded as the ideal glass transition or not, the nonergodic transition always occurs at a higher temperature than the glass transition temperature [14].

The comparison of MCT solutions with molecular dynamics (MD) results is a strategy to reveal where problems of MCT are. One should not compare them at the same temperature because the underestimation of the control parameters makes their states different even at the same temperature. We need a unified point of view to compare MCT solutions with MD results in the same state. Our approach in comparing MCT with MD is based on the mean-field theory (MFT) [24], which predicts the dynamics of a tagged particle. MFT suggests that the long-time self-diffusion coefficient D_S^L can determine the state of the system [25]. This means that the dynamics in the different systems coincides with each other if the value of D_S^L is the same. Thus, MCT solutions can be compared consistently with the simulation results at the same D_S^L.

In this paper, we compare the numerical solutions of MCT equations with the MD results for Kob-Andersen binary mixtures [26] to study the tagged-particle dynamics. Kob, Nauroth, and Sciortino have already studied the same model by solving the MCT equations numerically [13–16]. However, our comparison is done based on Ref. [25]. In addition, we offer a method of comparison in which the reduced long-time self-diffusion coefficient D^r is used to scale out the ballistic motion.

II. MODEL

We consider a three-dimensional system of volume V. The system consists of two kinds of particles, A and B, where the ratio of the number of particle is given by N_A:$N_B = 4$:1. Here the radius of A is larger than that of B, but their masses m are the same. The control parameter is given by the inverse temperature $1/T$. The number density $\rho = N/V$ is fixed, where N denotes the total number of particles: $N = N_A + N_B$. The interaction among particles is represented by the binary Lennard-Jones potential

$$u_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right], \tag{1}$$

where $\{\alpha,\beta\} \in \{A,B\}$. We employ the Kob-Andersen model [26]: $\varepsilon_{AB}/\varepsilon_{AA} = 1.5$, $\varepsilon_{BB}/\varepsilon_{AA} = 0.50$, $\sigma_{AB}/\sigma_{AA} = 0.80$, $\sigma_{BB}/\sigma_{AA} = 0.88$, and $\rho = 1.20{\sigma_{AA}}^{-3}$.

MCT predicts the dynamics of supercooled liquids with some approximations [22,27] and can treat not only coherent dynamics but also incoherent (tagged-particle) dynamics [14,28–30]. We focus on the tagged-particle dynamics such as the self-intermediate scattering function

$$F_s^{(\alpha)}(q,t) = \frac{1}{N_\alpha}\sum_i^{(\alpha)} \langle \exp\{i\boldsymbol{q}\cdot[\boldsymbol{X}_i(t) - \boldsymbol{X}_i(0)]\}\rangle, \tag{2}$$

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where N_α denotes the number of particle α, the summation with (α) the sum up only for particle α, and $\boldsymbol{X}_i(t)$ the position vector of ith particle at time t. $F_s^{(\alpha)}(q,t)$ can be expanded in powers of q as

$$F_s^{(\alpha)}(q,t) = 1 - \frac{q^2}{6} M_2^{(\alpha)}(t) + \frac{q^4}{120} M_4^{(\alpha)}(t) + \mathcal{O}(q^6), \tag{3}$$

where $M_n^{(\alpha)}(t)$ is defined as

$$M_n^{(\alpha)}(t) = \frac{1}{N_\alpha} \sum_i^{(\alpha)} \langle |\boldsymbol{X}_i(t) - \boldsymbol{X}_i(0)|^n \rangle. \tag{4}$$

$M_2^{(\alpha)}(t)$ is the mean-square displacement, and $M_4^{(\alpha)}(t)$ is the mean quartic displacement.

To obtain the tagged-particle dynamics numerically, the intermediate scattering function $F^{(\alpha\beta)}(q,t)$ is first solved, in which the partial static structure factor $S^{(\alpha\beta)}(q) = F^{(\alpha\beta)}(q,0)$ is required as the initial condition. We prepare $S^{(\alpha\beta)}(q)$ from MD simulations [31] in which the total number of particle is $N = 10\,976$. We calculate the partial radial distribution function $g^{(\alpha\beta)}(r)$ in MD simulations, and then obtain $S^{(\alpha\beta)}(q)$ as the Fourier transform of $g^{(\alpha\beta)}(r)$. Note that $S^{(\alpha\beta)}(q)$ is averaged out at least 100 times. Since the simulation box is finite ($V^{1/3} = 20.89\sigma_{\mathrm{AA}}$), $S^{(\alpha\beta)}(q)$ in the small wave number region is not meaningful. Our data are extrapolated with the quadratic function to approximate them. The convolution integral is calculated using the algorithm proposed by Fuchs *et al.* [12]. The integral step of the wave number is $\Delta q = 0.25/\sigma_{\mathrm{AA}}$. Note that $\Delta q V^{1/3} < 2\pi$. The upper limit of the integral is $q_{\max}$. To carry out the double integral with regard to the wave number correctly, we should set $q_{\max}$ as the direct correlation function $c_2(q) \simeq 0$ for $q > q_{\max}$. We set $q_{\max} = 60/\sigma_{\mathrm{AA}}$, which is large enough to hold the above condition at each temperature. The time step Δt doubles every 256 calculation steps, and the initial time step is $\Delta t = 10^{-5}$.

In this paper the length is scaled by σ_{AA}, the temperature by $\varepsilon_{\mathrm{AA}}/k_B$ with the Boltzmann constant k_B, the time by $\tau_{\mathrm{LJ}} = \sigma_{\mathrm{AA}}\sqrt{m/48\varepsilon_{\mathrm{AA}}}$, and the diffusion coefficient by $d_0 = \sigma_{\mathrm{AA}}\sqrt{\varepsilon_{\mathrm{AA}}/m}$.

III. RESULT AND DISCUSSION

According to MFT, one can distinguish liquid, supercooled liquid, and glass by using D_S^L: Supercooled liquid is in the range $-2.6 \geqslant \log_{10} D_S^L \geqslant -5.1$ and glass in $-5.1 \geqslant \log_{10} D_S^L$ [24,25]. Universality among different glass-forming systems can be discussed by using MFT. We, however, apply MFT as a unified viewpoint to compare MCT solutions with MD results because of the overestimated temperature in MCT. Instead of the long-time self-diffusion coefficient D_S^L, we offer a reduced long-time self-diffusion coefficient $D^r = D_S^L/\sqrt{T}$ to scale out the ballistic motion. The comparison at the same D^r is different from that at the same D_S^L. Nevertheless, the difference is quantitatively minor because states are categorized by $\log_{10} D_S^L$, rather than D_S^L. The reduced long-time self-diffusion coefficient D^r of particle A is shown in Fig. 1. Since particle A is dominant in the Kob-Andersen model, we focus only on the dynamics of particle A in what follows. Note that, as T approaches the singular temperature $T_{\mathrm{MCT}} \approx 0.922$, D_S^L rapidly decreases and decays to zero. The value of T_{MCT} is consistent with that reported by Nauroth *et al.* [14,15].

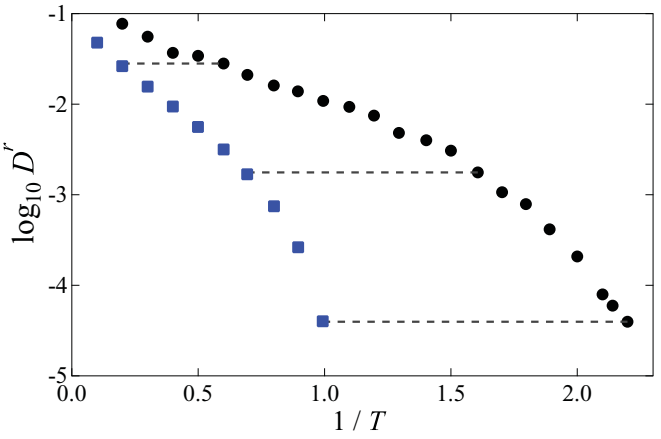

FIG. 1. (Color online) The reduced long-time self-diffusion coefficient $D^r = D_S^L/\sqrt{T}$ as a function of inverse temperature. The blue square indicates the MCT solution of particle A and the black circle the MD result of particle A. The broken lines represent $\log_{10} D_1^r = -1.55$, $\log_{10} D_2^r = -2.75$, and $\log_{10} D_3^r = -4.40$ from top to bottom.

We select three pairs of temperatures for MCT and MD as shown in Fig. 1. The temperatures are (T in MCT, T in MD) = (5.00, 1.67), (1.43, 0.625), and (1.00, 0.455). The first state ($\log_{10} D_1^r = -1.55$) is a liquid, the second one ($\log_{10} D_2^r = -2.75$) a weak supercooled liquid, and the third one ($\log_{10} D_3^r = -4.40$) a strong supercooled liquid. Figure 2 shows the comparison of $M_2(t)$ of particle A between MD and MCT at the same D^r. This plot style emphasizes the qualitative difference between MCT solutions and MD results in the intermediate time regime. In Fig. 2, $M_2(t)$ calculated by the MCT overshoots the highest-temperature couples (D_1^r). On the other hand, MCT results do not approach MD results in the lower temperature couples (D_2^r and D_3^r). These differences

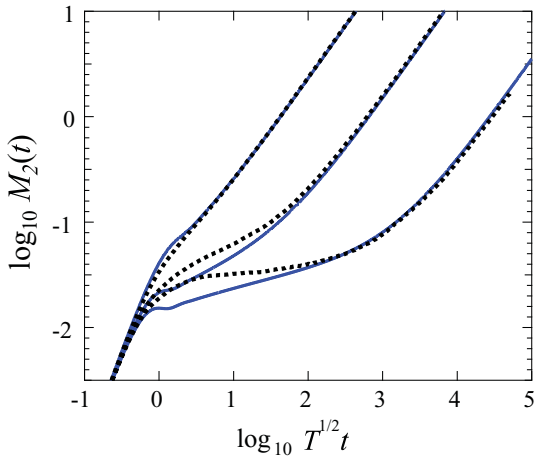

FIG. 2. (Color online) The mean-square displacement of particle A as a function of T-compensated time for the three pairs of T: (T in MCT, T in MD) = (5.00, 1.67) at D_1^r, (1.43, 0.625) at D_2^r, and (1.00, 0.455) at D_3^r (from left to right). The blue solid line represents the MCT solution and the black broken one the MD result averaged over 15 results.

indicate that, although T of MCT is larger than that of MD, the mean-free path ($\sim\sqrt{M_2}$ in the intermediate regime) calculated by MCT is shorter than that by MD. In addition, a small dent appears in the MCT solution, which is absent in the MD results. The dent can intrinsically exist in the MCT equation as explained next. In MCT, $M_2^{(\alpha)}(t)$ satisfies

$$\ddot{M}_2^{(\alpha)}(t) + \int_0^t ds K_0^{(\alpha)}(t-s)\dot{M}_2^{(\alpha)}(s) = \frac{6k_BT}{m}, \tag{5}$$

where $K_0^{(\alpha)}(t)$ denotes the self-term of the approximative memory function at $q \to 0$, represented as

$$K_0^{(\alpha)}(t) = \frac{k_BTV}{6\pi^2 m N_\alpha}\int_0^\infty dk k^4 F_s^{(\alpha)}(k,t) \times \sum_{\gamma,\epsilon}^{\mathrm{A,B}} c_2^{(\alpha\gamma)}(k)F^{(\gamma\epsilon)}(k,t)c_2^{(\epsilon\alpha)}(k), \tag{6}$$

where $F^{(\alpha\beta)}(q,t)$ denotes the partial intermediate scattering function and $c_2^{(\alpha\beta)}(q) := \delta_{\alpha\beta} - [\mathsf{S}^{-1}(q)]^{(\alpha\beta)}$. Ballistic motion dominates in the short time regime, and hence we can approximate the memory term to be constant:

$$K_c^{(\alpha)} := \lim_{t\to 0} K_0^{(\alpha)}(t) = \frac{k_BTV}{6\pi^2 m N_\alpha}\int_0^\infty dk k^4 \{S^{(\alpha\alpha)}(k) + [\mathsf{S}^{-1}(k)]^{(\alpha\alpha)} - 2\}. \tag{7}$$

Substituting the above expression for $K_0^{(\alpha)}(t)$, one can analytically express $M_2^{(\alpha)}(t)$ in the regime as

$$M_2^{(\alpha)}(t) = \frac{6k_BT}{mK_c^{(\alpha)}}\left[1 - \cos\left(\sqrt{K_c^{(\alpha)}}t\right)\right]. \tag{8}$$

Thus, it is expected that the small dent originates from this oscillating term whose frequency is $\sqrt{K_c^{(\alpha)}}$.

The origin of the oscillation is not due to the MCT approximations but due to the starting equation which is a convolution-type generalized Langevin equation [32]. The convolution-type equation seems to be compatibility with systems that have a distinct time scale such as single-particle Brownian motion (e.g., Ref. [33]). In contrast, it can be stated that supercooled liquids or glasses do not have clearly distinct time scale, but rather a scale-influenced (hierarchical) structure [34,35]. Tokuyama has proposed the alternative MCT [35]. The starting equation is the convolutionless-type equation [36] that is compatibility with multiscaled systems (e.g., Refs. [37–39]). The equation of motion in the alternative MCT is described by

$$\ddot{M}_2^{(\alpha)}(t) + \int_0^t ds K_0^{(\alpha)}(s)\dot{M}_2^{(\alpha)}(t) - \frac{6k_BT}{m}\left[1 + \int_0^t dss K_0^{(\alpha)}(s)\right] = 0. \tag{9}$$

Note that the approximated memory term $K_0^{(\alpha)}(t)$ of the alternative MCT is exactly the same as that of the conventional MCT [34,35]. The formal solution under $K_0^{(\alpha)}(t) \simeq K_c^{(\alpha)}(>0)$ is obtained as

$$\dot{M}_2^{(\alpha)}(t) = \int_0^t ds \left(1 + \frac{K_c^{(\alpha)}}{2}s^2\right) e^{-K_c^{(\alpha)}(t^2-s^2)/2}. \tag{10}$$

It is clear that $\dot{M}_2^{(\alpha)}(t) > 0$ for $t \geqslant s \geqslant 0$. Therefore, $M_2^{(\alpha)}(t)$ is monotonic and has no oscillation in the alternative MCT. It actually does not show a dent in numerical calculations [40]. Our results imply that the starting equation should be selected carefully in response to the dynamics.

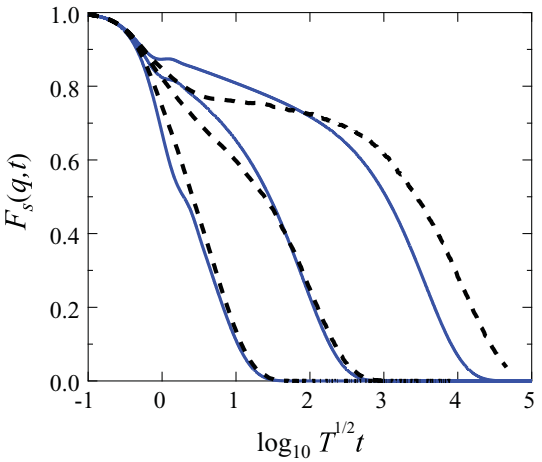

FIG. 3. (Color online) The self-intermediate-scattering function of particle A as a function of T-compensated time for the three pairs of T: (T in MCT, T in MD) = (5.00, 1.67) at D_1^r, (1.43, 0.625) at D_2^r, and (1.00, 0.455) at D_3^r (from left to right). The blue solid line represents the MCT solution and the black broken one the MD result averaged over 15 results.

Figure 3 shows the comparison of $F_s(q,t)$ of particle A between MD and MCT at the same D^r. Note that we employ $q = 7.25{\sigma_{\mathrm{AA}}}^{-1}$ corresponding to the first peak of $S(q)$. As expressed in Eq. (3), the higher terms of q cannot be neglected in $q\sigma_{\mathrm{AA}} > 1$. Thus, the long-time behavior of MCT deviates from that of MD even at the same D^r. On the other hand, in the intermediate time scale, the dynamics is qualitatively different between MCT and MD, as well as $M_2(t)$.

IV. SUMMARY

We have numerically solved the equations of MCT for Kob-Andersen binary mixtures to study the tagged-particle dynamics. We have proposed a method of comparison: The comparison between MCT and MD has been done from a unified point of view by using the reduced long-time self-diffusion coefficient D^r. The qualitative comparison at the same reduced long-time self-diffusion coefficient has shown that the tagged-particle dynamics calculated from the MCT equations deviates from that obtained by the MD simulations in the intermediate time regime. There exists an oscillation in MCT solutions. We have briefly mentioned an alternative starting equation. The alternative MCT is constructed by the same framework as the conventional MCT; however, the starting equations differ from each other. We have shown that the alternative MCT can avoid oscillation in the intermediate time scale. It implies that the origin of the oscillation is due to the starting equation, namely, the convolution-type generalized

Langevin equation. The numerical analysis of the alternative MCT will be discussed elsewhere.

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