Recursion formulas for nonlinear density fluctuations near the glass transition

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The time-convolutionless mode-coupling (TMCT) equation for the intermediate scattering function \( f_α(q,t) \) derived recently by the present author is transformed into a simple nonlinear recursion formula for a generating function \( Ω_α(q,t) = -\ln[f_α(q,t)]/q^2 \), where \( α = c \) stands for a collective case and \( α = s \) for a self case. By employing the same simplification on the nonlinear memory function as that proposed by the mode-coupling theory (MCT), the simplified asymptotic recursion formula is then derived and is numerically analyzed for different temperatures under the initial conditions obtained from the simulation. In a liquid state the numerical results are shown to recover the simulation results well. Although they can describe the simulation results well in the \( β \)-relaxation stage even for lower temperatures, they do not agree with those in the so-called \( α \)-relaxation stage because of the simplified model. The coupling parameter \( λ^{(α)} \) dependence of the Debye-Waller factor \( f_α \) is also discussed. The critical point is found as \( λ^{(c)}_c = 3 \times 10^{-3} \) and \( f_α = 1/2 \). Then, the critical temperature \( T_c \) is shown to be definitely lower than that predicted by MCT. Thus, it is emphasized that the present theory can improve the high \( T_c \) problem appeared in MCT.

The time evolution of the memory function and that of the diffusion coefficient are also investigated within asymptotic formulas.

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I. INTRODUCTION

The principal purpose of the present paper is to formulate a statistical-mechanical theory of understanding the dynamics of supercooled liquids from first principles. Well-known example of this kind is the so-called mode-coupling theory (MCT) proposed by Bengtzelius, Götze, and Sjölander [1], [2], and independently by Leutheusser [3]. The MCT equations for the intermediate scattering function \( f_α(q,t) \) have been formally derived by employing the Mori projection-operator method [4] and solved numerically for various glass-forming systems [5–16]. Although the MCT solutions show an ergodic to non-ergodic transition at a critical temperature \( T_c \), \( T_c \) is always much higher than the glass transition temperature \( T_γ \).

In order to overcome the high \( T_c \) problem, we have recently proposed the time-convolutionless MCT (TMCT) equations for \( f_α(q,t) \) [17] by employing the Tokuyama-Mori projection operator method [18]. In the present paper, we first transform them into a simple recursion formula for a generating function \( Ω_α(q,t) \), where \( Ω_α(q,t) = -\ln[f_α(q,t)]/q^2 \). Then, we make the same simplification on the nonlinear memory function as that discussed in MCT [1]. Thus, by fixing \( q \) at a peak position \( q_m \) of the static structure factor \( S(q) \), we first show that the Debye-Waller factor \( f_α \), which is a non-zero solution of \( f_α(q_m,t) \) at long times, satisfies a simple relation

\[
f_α = \exp \left[ -\frac{1}{κ^{(α)} f_α f_α} \right], \tag{1}
\]

where \( κ^{(α)} \) is a coupling parameter of the long-time memory function discussed in the MCT simplified model. Equation (1) has a non-zero real solution only when \( κ^{(α)} \geq 2e \). On the other hand, MCT gives the following simple relation:

\[
f_α = \frac{κ^{(α)} f_α f_α}{1 + κ^{(α)} f_α f_α}. \tag{2}
\]

Equation (2) has a non-zero real solution only when \( κ^{(c)} \geq 4 \). Since the critical value \( κ^{(c)}_c = 2e \) is larger than 4, the critical temperature \( T_c \) is expected to be lower than that obtained by MCT. In fact, this is checked by investigating the numerical solutions of the recursion formula. In the present paper, this is done as follow. By taking into account the time difference between the \( α \)-relaxation process and the \( β \)-relaxation process, we first derive the asymptotic recursion formula

\[
Ω_α(t) = \frac{γ_α t - 1 + e^{-γ_α t}}{γ_α 1 + q_α^2 κ^{(α)} t^2} \tag{3}
\]

where \( γ_α = v_{th}/(γ_α S(q_m)) \) and \( γ_α \) are positive constants, \( v_{th} \) being an average thermal velocity. Since \( Ω_α(t) \approx D_α t \) for a long time, the long-time diffusion coefficient \( D_α \) is also found as

\[
D_α = \frac{g_α}{1 + q_α^2 g_α κ^{(α)} t^2} \tag{4}
\]

Since Eq. (3) is a closed equation for \( Ω_α(t) \), it can be solved numerically by an iteration under the initial conditions obtained from the molecular-dynamics simulations. Although such an iteration procedure works well for higher temperatures, a large number of iterations must be done for lower temperatures. Therefore, we calculate the nonlinear memory terms in Eqs. (3) and (4) simply by using the asymptotic analytic function for \( f_α(q_m,t) \) which is obtained from the simulation results by fitting at each temperature. By fixing the value of \( D_α \) from the simulations, one can then calculate the value of \( κ^{(α)} \) from Eq. (4) at each temperature. In order to check whether this procedure is valid or not, we solve Eq. (3) independently by an iteration at a given value of \( κ^{(α)} \) and show that the iteration results are consistent with the numerical results for higher temperatures. By using the temperature dependence of \( κ^{(c)}_c \), we then show that the critical temperature \( T_c \) corresponding to \( κ^{(c)}_c \) is close to a glass transition
temperature $T_g$, which is predicted by the mean-field analyses \cite{19,20}. Thus, we emphasize that the present theory can improve at least the high $T_g$ problem appeared in MCT. At a given value of $k^{\infty}$, one can solve Eq. (3) numerically in the same manner as that done in Eq. (4). Then, we show that the numerical results for $f_\alpha(q_m,t)$ coincide with the simulation results well in a liquid state. Although they can describe the simulation results well in the $\beta$-relaxation stage even for lower temperatures, they do not agree with those in the so-called $\alpha$-relaxation stage. In fact, the stretched exponent $\beta$ for the numerical results is given by $\beta \approx 1.00$, while $\beta \approx 0.76$ for the simulations. This difference must be inherent to the simplified model. In order to check whether the $\alpha$ process obtained by the simulations is recovered or not, therefore, one has to solve the original recursion formula by using the static structure factor obtained from the simulation.

We begin in Section 2 by reviewing the time-convolutionless MCT equations. We then transform them into a simple recursion formula. In Section 3, we introduce the same simplified approach as that discussed by Bengtzelius et al. [1] and discuss the Debye-Waller factor. In Section 4, we analyze the asymptotic recursion formula numerically at different temperatures under the initial conditions obtained from the molecular-dynamics simulations on the Stillinger-Weber binary mixtures. We then discuss the critical temperature and compare the numerical results with the simulation results. We conclude in Section 5 with a summary.

II. BASIC EQUATIONS

We consider the three-dimensional equilibrium glass-forming system, which consists of $N$ particles with mass $m$ and diameter $\sigma$ in the total volume $V$ at temperature $T$. Near the glass transition, the slowly-varying variables are then given by the collective density fluctuation $\rho_\alpha(q,t) = N^{-1/2} \sum_{j=1}^{N} \rho_j(q,t) - N\delta_{q,0}$ and the self density fluctuation $\rho_j(q,t) = e^{iq \cdot X_j(t)}$, where $X_j(t)$ denotes the position vector of the $j$th particle at time $t$. We now define the intermediate scattering function by $F_\alpha(q,t) = \langle \rho_\alpha(q,t) \rho_\alpha(q,0) \rangle$, where $\alpha = c$ stands for a collective case, $\alpha = s$ for a self case, and $q = |q|$. Here $F_c(q,0) = S_c(q) = S(q)$ and $F_s(q,0) = S_s(q) = 1$, where $S(q)$ is a static structure factor. The TMCT equations are then given by \cite{17}

\[ \frac{\partial}{\partial t} F_\alpha(q,t) = -q^2 \int_0^\infty \psi_\alpha(q,s) d s F_\alpha(q,t) \] (5)

\[ \frac{\partial}{\partial t} \psi_\alpha(q,t) = -\gamma_\alpha \psi_\alpha(q,t) - \int_0^\infty \Delta \varphi_\alpha(q,s) \psi_\alpha(q,t-s) d s \] (6)

with the nonlinear memory function

\[ \Delta \varphi_\alpha(q,t) = \frac{\gamma_\alpha^2}{2^\nu_\alpha \rho} \int \frac{d k}{(2\pi)^3} \nu_\alpha(q,k)^2 F_\alpha(|q-k|,t), \] (7)

where $\gamma_\alpha$ is a positive constant. Here $\nu_\alpha(q,k)$ is the vertex amplitude given by

\[ \nu_\alpha(q,k) = \hat{q} \cdot k c(k) + n_c \hat{q} \cdot (q-k) c(|q-k|), \] (8)

where $c(k) = 1 - 1/S(k)$, $n_c = 1$, $n_s = 0$, $\rho = N/V$, $\nu_{th} = (k_b T/m)^{1/2}$, and $\hat{q} = q/q$. Here we note that the nonlinear memory function $\Delta \varphi_\alpha(q,t)$ has the same form as that obtained by the ideal MCT \cite{1,2}.

In order to show whether the same analyses as those proposed by MCT \cite{1,2} can be directly applicable to TMCT or not, it is convenient to introduce the generating function $K_\alpha(q,t)$ by

\[ K_\alpha(q,t) = -\ln[f_\alpha(q,t)] = -\ln[F_\alpha(q,t)/S_\alpha(q)]. \] (9)

From Eqs. (5) and (6), one can then derive the following equation for $K_\alpha(q,t)$:

\[ \frac{\partial^2 K_\alpha(q,t)}{\partial t^2} = \frac{q^2 \nu_{th}^2}{S_\alpha(q)} \frac{\partial^2 K_\alpha(q,t)}{\partial q^2} - \gamma_\alpha \frac{\partial K_\alpha(q,t)}{\partial t} - \int_0^\infty \Delta \varphi_\alpha(q,t-\tau) \frac{\partial K_\alpha(q,\tau)}{\partial \tau} d \tau, \] (10)

where the initial conditions are given by $K_\alpha(q,t = 0) = dK_\alpha(q,t)/dt|_{t=0} = 0$. On the other hand, the ideal MCT equation is given by \cite{1}

\[ \frac{\partial^2 F_c(q,t)}{\partial t^2} = \frac{q^2 \nu_{th}^2}{S_c(q)} F_c(q,t) - \gamma_\alpha \frac{\partial F_c(q,t)}{\partial t} - \int_0^\infty \Delta \varphi_c(q,t-\tau) \frac{\partial F_c(q,\tau)}{\partial \tau} d \tau, \]

Since Eq. (10) has exactly the same form as that of Eq. (11), except the first term, all the analyses proposed by MCT turn out to be applicable to TMCT, except that $F_c(q,t)$ is now replaced by $K_\alpha(q,t)$. We briefly discuss this next.

A. Debye-Waller factor

We first discuss the so-called Debye-Waller factor, which is a non-zero solution of $F_c(q,t)$ at long times. The most important prediction of MCT is the ergodic to non-ergodic transition at a critical temperature $T_c$, below which the long-time solutions reduce to non-zero values. As shown in the previous paper \cite{17}, this prediction also holds for TMCT. In fact, the non-zero solution $f_c(q,t)$ of Eq. (5) at $t \to \infty$ is given by

\[ f_c(q) = \lim_{t \to \infty} F_c(q,t)/S_c(q) = \exp[-1/F_c(q)] \] (12)

with the long-time limit of the memory function

\[ f_c(q) = \frac{\gamma_\alpha)^2}{2^\nu_\alpha \rho} \int d k V^{(2)}_\alpha(q,k,|q-k|) f_c(k)f_c(|q-k|), \]

where the vertex $V^{(2)}_\alpha$ is given by

\[ V^{(2)}_\alpha(q,k,|q-k|) = S_c(q)S_c(k)S_c(q-k)\nu_\alpha(q,k)^2/(pq)^2. \] (14)

On the other hand, the MCT equation (11) leads to

\[ f_c(q) = \frac{\gamma_\alpha)^2}{2^\nu_\alpha \rho} \frac{e^{\gamma_\alpha q^2 (q-k)^2/(pq)^2}}{1 + \gamma_\alpha q^2 (q-k)^2/(pq)^2}. \] (15)

The solution of Eq. (12) is compared with that of Eq. (15) later based on a simplified model proposed by MCT.
B. A two-step relaxation

We next discuss the asymptotic behavior of \( f_{c}(q,t) \) in each time stage. As demonstrated in Refs. [21], MCT shows that \( f_{c}(q,t) \) obeys a characteristic two-step relaxation process at the so-called \( \beta \)-relaxation stage [\( \beta \)] near the critical point. By introducing the Laplace transform \( f_{c}(q,z) = \mathcal{L}[f_{c}(q,t)] = \int_{0}^{\infty} e^{-zt} f_{c}(q,t) dt \), the long-time dynamics is then determined from Eq. (111) as

\[
\frac{z f_{c}(q,z)}{1 - z f_{c}(q,z)} = z \mathcal{L}[f_{c}(q,t) \hat{f}_{c}(q,t)](z). \tag{17}
\]

Following MCT [2], one can split \( f_{c}(q,t) \) into the trivial asymptotic part and the a non-trivial part \( G \):

\[
f_{c}(q,t) = f_{c}^{0}(q) + h_{t} G(t), \quad z f_{c}(q,z) = f_{c}^{0}(q) + z h_{t} G[z] \tag{18}
\]

with \( h_{t} = (1 - f_{c}^{0})^{2}e_{\sigma}^{2}, \) where \( f_{c}^{0}(q) \) is the critical Debye-Waller factor at the critical point, and \( e_{\sigma} \) is an appropriately normalized right eigenvector of the stability matrix \( C_{\sigma} = (\partial f_{\sigma}/\partial f_{c}(k))(1 - f_{c}^{0}(k))^{2} \) at the critical point. From Eqs. (17) and (13), one can then find near the critical point

\[
\sigma + \lambda (z \mathcal{L}[G(t)]^{2})[z] - z G[z]^{2} = 0, \tag{19}
\]

where \( \sigma \) is a separation parameter given by \( \sigma = C(q)/C - 1 \) or \( C(q)/C_{\beta} - 1 \), \( C \) being a positive constant to be determined. Here \( \lambda \) is the so-called exponent parameter given by [2]

\[
\lambda = \frac{1}{2} \sum_{q,k,p} \tilde{e}_{\sigma}^{*} y^{(2)}(q,k,p) h_{t} h_{p}, \tag{20}
\]

where \( \tilde{e}_{\sigma}^{*} \) is a left eigenvector defined by \( \sum \tilde{e}_{\sigma}^{*} e_{\sigma}^{2} = 1. \) As shown in Ref. [2], use of Eq. (19) leads to two different power-law decays for \( G(t) \) near the critical point; the so-called critical decay at a fast \( \beta \) stage

\[
G(t) = |\sigma|^{1/2}(t_{\sigma}/t)^{\alpha}, \tag{21}
\]

and the so-called von Schweidler decay at a slow \( \beta \) stage

\[
G(t) = -(t/t_{\sigma})^{b}, \tag{22}
\]

where \( t_{0} \) is a microscopic time, \( t_{\sigma} = t_{0}/|\sigma|^{2/3} \), and \( t_{\sigma} = t_{0} B^{-1/3} \left| \sigma \right|^{2(a+b)+2/3} B \) being a positive constant to be determined. Here the time exponents \( a \) and \( b \) are determined by the exponent parameter \( \lambda \) through the relation

\[
\frac{\Gamma[1 - a]^{2}}{\Gamma[1 - 2a]} = \frac{\Gamma[1 + b]^{2}}{\Gamma[1 + 2b]} = \lambda, \tag{23}
\]

\( \Gamma[x] \) being the gamma function. As a simple example, \( \lambda \) is calculated by using the Percus-Yevick structure factor \( S(q) \). In fact, one finds \( \lambda = 0.735 \), leading to \( a = 0.312 \) and \( b = 0.583 \) [22]. On the other hand, in TMCT use of Eqs. (9) and (10) leads to

\[
\frac{1}{z K_{c}(q,z)} = z \mathcal{L}[f_{c}(q,t), f_{c}(t)][z]. \tag{24}
\]

From Eq. (9) and (18), one can find, up to lowest order in \( h_{t} \),

\[
K_{c}(q,t) = K_{c}^{*}(q) - h_{t} G(t) / f_{c}(q), \quad z K_{c}(q,z) = K_{c}^{*}(q) - z h_{t} G[z] / f_{c}^{0}(q), \tag{25}
\]

where \( K_{c}^{*}(q) = -\ln [f_{c}^{0}(q)]. \) One can then directly apply the same formulation as that employed by MCT to Eq. (24) near the critical point. In fact, from Eqs. (24) and (25), one can obtain Eq. (19) under the condition \( f_{c}^{0} = e^{-K_{c}^{*}} \approx 1 - K_{c}^{*} \). Hence \( G(t) \) also obeys Eqs. (21) and (22). Thus, from Eqs. (5) and (25) one can find the same two different power-law decays for \( f_{c}(q,t) \) as those of MCT, up to lowest order. Since \( \lambda \) is defined at the critical point, \( \lambda \) of TMCT must have the same value as that of MCT. This can be easily checked within a simplified model. Since \( \lambda \) of MCT is calculated for the Percus-Yevick model, one can use its value for TMCT to check this. Thus, the same value of \( \lambda \) is shown to hold for both theories [23]. Finally, at the so-called \( \alpha \)-relaxation stage after the \( \beta \) stage, \( f_{c}(q,t) \) is also shown to obey the Kohrausch-Williams-Watts (KWW) function

\[
f_{c}(q,t) = f_{c}^{0}(q) \exp \left[-(t/\tau_{c})^{\beta}\right] \tag{26}
\]

with a stretched exponent \( \beta \) and an \( \alpha \)-relaxation time \( \tau_{c} \).

III. RECURSIVE FORMULAS

In order to find the asymptotic solutions of the TMCT equations (5) and (6), we now transform them into a recursion formula. Introducing a new function \( \Omega_{s}(q,t) \) by \( \Omega_{s}(q,t) = K_{s}(q,t)/q^{2} \), from Eq. (5), one can find

\[
\Omega_{s}(q,t) = \int_{0}^{\infty} ds \int_{0}^{\infty} d\tau \psi_{s}(q,\tau) = \int_{0}^{\infty} (t-s) \psi_{s}(q,s) ds. \tag{27}
\]

Here we note that the expansion of \( \Omega_{s}(q,t) \) in powers of \( q \) exactly gives a cumulant expansion [18] [24]. We also introduce the time-dependent diffusion coefficient by

\[
D_{s}(q,t) = \frac{d}{dt} \Omega_{s}(q,t) = \int_{0}^{t} \psi_{s}(q,s) ds. \tag{28}
\]

In order to solve Eq. (6) formally, it is convenient to introduce the Laplace transform of \( \psi_{s}(q,t) \) by \( \psi_{s}[q,z] = \int_{0}^{\infty} \psi_{s}(q,t)e^{-zt} dt \). Then, use of Eq. (6) leads to

\[
\psi_{s}[q,z] = \frac{\psi_{s}(q,0)}{z + \gamma_{s}} - \frac{\Delta \psi_{s}[q,z]}{z + \gamma_{s}} \psi_{s}[q,z], \tag{29}
\]

where \( \psi_{s}(q,0) = v_{th}^{2}/\Sigma_{s}(q) \). Since \( \Omega_{s}[q,z] = D_{s}[q,z]/z \) is the inverse Laplace transform of Eq. (29), it thus leads to the recursion formulas

\[
\Omega_{s}(q,t) = \Omega_{s}^{(0)}(q,t) - \int_{0}^{t} M_{s}(q,s) \Omega_{s}(q,t-s) ds, \tag{30}
\]

\[
D_{s}(q,t) = D_{s}^{(0)}(q,t) - \int_{0}^{t} M_{s}(q,s) D_{s}(q,t-s) ds, \tag{31}
\]

\[
\psi_{s}(q,t) = \psi_{s}^{(0)}(q,t) - \int_{0}^{t} \psi_{s}(q,s) M_{s}(q,t-s) ds \tag{32}
\]
with the nonlinear memory term

\[ M_\alpha(q, s) = e^{-\gamma_\alpha s} \int_0^\tau e^{\gamma_\alpha \tau} \Delta \varphi_\alpha(q, \tau) d\tau, \quad (33) \]

where \( D^{(0)}_\alpha(q, t) = d\Omega^{(0)}_\alpha(q, t)/dt, \psi^{(0)}_\alpha(q, t) = d\Omega^{(0)}_\alpha(q, t)/dt, \)
and

\[ \Omega^{(0)}_\alpha(q, t) = \psi^{2}_\alpha \left( \gamma_\alpha t - 1 + e^{-\gamma_\alpha t} \right) / \left( S_\alpha(q) \gamma_\alpha^2 \right). \quad (34) \]

Since Eq. (30) is a closed nonlinear equation for \( \varphi_\alpha(q, t) \), one has to solve it first, and then inserts its solution into Eqs. (31) and (32) to obtain \( D_\alpha(q, t) \) and \( \psi_\alpha(q, t) \), respectively.

IV. A SIMPLIFIED MODEL

Equation (30) can be solved only numerically because it contains the static structure factor \( S(k) \) in the memory function \( \Delta \varphi_\alpha(q, t) \). In the present section, therefore, we just employ the same simplified approach as that discussed by Bengtzelius et al [11]. In fact, the dominant contribution in \( \Delta \varphi_\alpha(q, t) \) is considered to result from the first peak at \( q_m \) in \( S(q) \). Hence one can simplify \( S(q) \) as

\[ S(q) = 1 + A\delta(q - q_m), \quad (35) \]

where \( A \) is a positive constant to be determined. Then, one can write Eq. (13) as

\[ \Gamma_\alpha(q_m) = k^{(c)} f_\alpha(q_m) g_\alpha(q_m), \quad (36) \]

with the coupling parameter

\[ k^{(c)} = q_m^{2-n_\alpha} A^{1+n_\alpha} S_\alpha(q_m)/[(6 + 2n_\alpha)n^2 \rho]. \quad (37) \]

Since we consider \( q = q_m \), in the following we simply ignore \( q_m \) dependence, except in case of necessity.

A. Debye-Waller factor

We first discuss the Debye-Waller factor. Use of Eq. (12) then leads to

\[ f_\alpha = \exp \left[ -1/k^{(c)} p \right]. \quad (38) \]

We now discuss the numerical solutions of Eq. (38). For \( k^{(c)} < k^{(c)} \), there exists only one real solution \( f_\alpha = 0 \), where \( k^{(c)} \) is a critical point. On the other hand, for \( k^{(c)} > k^{(c)} \), there exist a non-zero real solution \( f_\alpha \neq 0 \). In fact, putting \( f_\alpha = e^{-K^{(c)}}, \) from Eq. (38), one can find

\[ k^{(c)} = e^{2K^{(c)}}, \quad \text{or} \quad \frac{dK^{(c)}}{dK^{(c)}} = \frac{k^{(c)}}{k^{(c)}(2K^{(c)} - 1)} \quad (39) \]

\[ k^{(c)} = e^{K^{(c)} + K^{(c)}}, \quad \text{or} \quad \frac{dK^{(c)}}{dK^{(c)}} = \frac{k^{(c)}}{k^{(c)}(K^{(c)} - 1)} \quad (40) \]

Then, Eq. (39) has a non-zero real solution only for \( k^{(c)} > 2e \). Hence we find the critical value \( k^{(c)} = 2e(\approx 5.43656) \), which leads to \( K^{(c)} = 1/2 \) and \( f_\alpha^{(c)}(k^{(c)}) = e^{-1/2}(\approx 0.60653) \). Similarly, Eq. (40) has a non-zero real solution only for \( k^{(c)} > e^{K^{(c)}} \). This leads to \( k^{(c)} = e^{K^{(c)} + 1}, K^{(c)} = 1, \) and \( f_\alpha^{(c)}(k^{(c)}) = e^{-1} \). In Fig. 1 the solution \( f_\alpha^{(c)} \) is plotted versus \( k^{(c)} \). For comparison, the MCT result is also shown in Fig. 1 which is given from Eq. (15) as

\[ f_\alpha^{(c)} = 1/2 + (1/4 - 1/k^{(c)})^{1/2}, \quad (41) \]

where \( k^{(c)} = 4 \) and \( f_\alpha^{(c)}(k^{(c)}) = 1/2 \). Thus, the critical point \( k^{(c)} \) of the present theory is shown to be larger than that of MCT. As is shown later, this suggests that the critical temperature \( T_c \) is definitely lower than that of MCT. The similar results are also found for the self case.

B. Asymptotic recursion formulas

We first discuss the nonlinear memory function based on the simplified model. Similarly to Eq. (36), use of Eqs. (7) and (35) leads to

\[ \Delta \varphi_\alpha(t) \approx B_\alpha f_\alpha(t) f_\alpha(t). \quad (42) \]

with the dynamic coupling parameter

\[ B_\alpha = q_m^2 \gamma_\alpha^2 k^{(c)} S_\alpha(q_m). \quad (43) \]

As is shown in the next section, the unknown parameter \( k^{(c)} \) is determined so that the diffusion coefficient \( D \) coincides with
the simulation result at each temperature. Thus, one can find the temperature dependence of $\kappa^{(c)}$ and predict the critical temperature $T_c$ corresponding to the critical point $\kappa^{(c)}$.

In order to solve Eq. (30) in a simple manner such as an iteration, we now derive the asymptotic recursion formulas from Eqs. (30,32) by using a kind of Markov approximation in time. As discussed in Ref. (17), $\Omega_{\alpha}(q,t)$ is a slowly-varying function in time whose time scale is of order $\tau_{\alpha}$, while $\psi_{\alpha}(q,t)$ is a rapidly-varying function in time whose time scale is of order $1/\gamma_{\alpha}$, where $\tau_{\alpha}$ is the so-called $\alpha$-relaxation time. On the other hand, the time scale of the memory term $M_{\alpha}(q,s)$ is of order $\tau_{\beta}$, where $\tau_{\alpha}$ is a $\beta$-relaxation time over which the caging is over. Here $1/\gamma_{\alpha} \ll \tau_{\alpha} \ll \tau_{\beta}$. For a long time of interest, therefore, one can first expand $\Omega_{\alpha}(q_{mt},t-s)$ in powers of $s/t$ as $\Omega_{\alpha}(t-s) \approx \Omega_{\alpha}(t) + O(s/t)$. From Eq. (30), one then finds

$$\Omega_{\alpha}(t) \approx \Omega_{\alpha}^{(0)}(t) - \int_0^t M_{\alpha}(s) \Omega_{\alpha}(t) \frac{d\Omega_{\alpha}(t)}{1 + \Sigma_{\alpha}(t)}.$$  (44)

with the renormalized memory function

$$\Sigma_{\alpha}(t) = \int_0^t M_{\alpha}(s) ds = \frac{1}{\gamma_{\alpha}} \int_0^t \left( 1 - e^{-\gamma_{\alpha}(t-s)} \right) \Delta \psi_{\alpha}(s) ds.$$  (45)

By using the relation $D_{\alpha}(t) = d\Omega_{\alpha}(t)/dt$, from Eq. (44), one can also obtain

$$D_{\alpha}(t) \approx \frac{D_{\alpha}^{(0)}(t)}{1 + \Sigma_{\alpha}(t)} - \frac{M_{\alpha}(t)\Omega_{\alpha}^{(0)}(t)}{(1 + \Sigma_{\alpha}(t))^2}.$$  (46)

For a long time, Eqs. (44) then reduces to

$$\Omega_{\alpha}(t) \approx D_{\alpha} t.$$  (47)

with the diffusion coefficient

$$D_{\alpha} = D_{\alpha}(q_{mt},t = \infty) = \frac{v_m^2/k_{B}(q_{mt})}{\gamma_{\alpha} + B_{\alpha} \int_0^\infty f_\alpha(s)f_\alpha(s)ds}.$$  (48)

For a short time, those equations also reduce to $\Omega_{\alpha}(t) \approx v_m^2 t^2/(2S_{\alpha}(q_{mt})) + O(t^2)$ and $D_{\alpha}(t) \approx v_m^2 t/(S_{\alpha}(q_{mt}) + O(t^2))$. Finally, we discuss the asymptotic equation for $\psi_{\alpha}(t)$. Since the time scale of $\psi_{\alpha}(t)$ is of order $1/\gamma_{\alpha}$, one can expand $\Omega_{\alpha}(t-s)$ in powers of $s/t$ as $M_{\alpha}(t-s) \approx M_{\alpha}(t) + O(s/t)$. From Eq. (32), one then finds

$$\psi_{\alpha}(t) \approx \psi_{\alpha}^{(0)}(t) - M_{\alpha}(t) \int_0^t \psi_{\alpha}(s) ds$$

$$= \psi_{\alpha}^{(0)}(t) \left[ 1 - M_{\alpha}(t)e^{-\gamma_{\alpha}t}\int_0^t ds e^{-\gamma_{\alpha}s}\Sigma_{\alpha}(s) \right].$$  (49)

Once the memory term $M_{\alpha}(t)$ is calculated by an appropriate manner, one can thus obtain $\Omega_{\alpha}(t)$, $D_{\alpha}(t)$, and $\psi_{\alpha}(t)$ approximately.

V. NUMERICAL CALCULATIONS OF ASYMPTOTIC RECURSION EQUATIONS

In the following, we discuss the collective case only for simplicity. Equation (44) is a closed nonlinear equation for $\Omega_{\alpha}(t)$. Once $\Omega_{\alpha}(t)$ is found, therefore, $f_{\alpha}(t)$, $D_{\alpha}(t)$, and $\psi_{\alpha}(t)$ are obtained from Eqs. (9), (40) and (49), respectively. The simplest way to solve Eq. (44) numerically is just to take an iterative procedure under the initial conditions given by the simulation results. Then, the values of unknown parameters $\gamma_{\alpha}$ and $\kappa^{(c)}$ are fixed at each temperature. Although this procedure works well for higher temperatures, a large number of iterations are required to obtain the numerical results at lower temperatures. Hence we take a different approach to calculate Eqs. (44), (40), and (49) here. This approach is checked by solving Eq. (44) by an iterative procedure independently and is verified to be consistent with the iterative approach for higher temperatures.

A. Molecular-dynamics simulations

As a typical example of simulations, we here take the extensive molecular-dynamic simulations on binary mixtures $A_{26}B_{20}$ with the Stillinger-Weber potential (25).

$$U_{\alpha\beta}(r) = \begin{cases} 
\epsilon_{\alpha\beta}(r)\left(\frac{r}{\sigma_{\alpha\beta}}\right)^{12} - 1 \exp\left[\frac{\left(\frac{r}{\sigma_{\alpha\beta}}\right)^{\frac{1}{2}}}{\sigma_{\alpha\beta}}\right] \quad & \text{for } \frac{r}{\sigma_{\alpha\beta}} < R_c, \\
0 \quad & \text{for } \frac{r}{\sigma_{\alpha\beta}} > R_c,
\end{cases}$$  (50)

where $\alpha, \beta \in \{A, B\}$. Here the parameters $\epsilon_{\alpha\beta}$, $\sigma_{\alpha\beta}$, and $R_c$ are given by $\sigma_{AA} = 1.0\sigma$, $\sigma_{AB} = 8.8\sigma$, $\sigma_{BB} = 13.2\sigma$, $\epsilon_{BB} = 0.88\epsilon$, $\epsilon_{AB} = 4.4\epsilon$, and $R_c = 1.652$ where $\sigma$ and $\epsilon$ are length and energy units, respectively. The system contains $N = 10976$ particles, which is composed of $N_A = 8780$ particles of type A with mass $m$ and $N_B = 2196$ particles of type B with mass $m$. Length, time, and temperature are scaled by $\sigma$, $\tau_0(= \sigma/v_0)$, and $\epsilon/k_B$, respectively, where $v_0 = (\epsilon/m)^{1/2}$. The simulations have been performed in a cubic box of length $20.89\sigma$ with periodic boundary conditions under the so-called NVT method, where the number density is $1.2\sigma^{-3}$ (26). By using the simulation results, one can calculate the intermediate scattering function $F_{\alpha}(q,t)$ simply as

$$F_{\alpha}(q,t) = \frac{1}{N} \sum_{j=1}^{N} e^{iq(\mathbf{X}_j(t)-\mathbf{X}_j(0))},$$

$$F_{\alpha}(q,t) = \frac{1}{N} \sum_{j=1}^{N} \sum_{j=1}^{N} e^{iq(\mathbf{X}_j(t)-\mathbf{X}_j(0))},$$  (51)

where $\mathbf{X}_j(t)$ is a position vector of $j$th particle and $N = N_A + N_B$. Here $S(q) = F_{\alpha}(q,t) = 0$. The diffusion coefficient $D_{\alpha}$ is then obtained from the relation $D_{\alpha} = \lim_{t \to \infty} \Delta \psi_{\alpha}(t) = \ln[f_{\alpha}(q,t)]$. The detailed analyses are done for the simulation results. Thus, all the simulation results for $f_{\alpha}(q,t)$ are shown to be described well by the following summation of multiple decays:

$$f_{\alpha}(q,t) = \sum_{j=1}^{6} a_j e^{-b_j\Omega_{\alpha}^{(c)}(q_{mt})},$$  (52)

where $a_j$ and $b_j$ are constants to be determined and $\sum_{j=1}^{6} a_j = 1$. In Fig. (2), the simulation results for $f_{\alpha}(q,t)$ are plotted versus time together with the fitting results obtained by Eq. (52). The same fittings also hold for $f_{\beta}(q,t)$. In Fig. (3) the diffusion...
FIG. 2: (Color online) A plot of \( f_\alpha(q, t) \) versus \( \log_{10}(t/\tau_0) \) for different temperatures. The symbols (●) indicate the simulation results from Ref. [26] at \( qr_\tau = 7.25 \). \( T = 5.0, 2.5, 1.667, 1.25, 1.0, 0.833, 0.714, 0.625, 0.556 \), and 0.5 from left to right. The solid lines indicate the fitting results obtained by Eq. (52) at \( \gamma , \tau_0 = 6 \).

Coefficient \( D_\alpha \) is plotted versus \( 1/T \). Similarly to the master curve for the self-diffusion coefficient discussed in Ref. [19, 20], the simulation results are then shown to obey the following singular function well:

\[
D_\alpha(T) = d_0^{(\alpha)} (1 - x)^{10/3}/x \exp[62.1^{13/3}(1 - x)^{10/3}],
\]

(53)

where \( x = T_f^{(\alpha)}/T \) and \( d_0^{(\alpha)} \) is a positive constant to be determined, \( T_f^{(\alpha)} \) being a fictive singular temperature. The mean-field theory [19, 20] predicts that the glass transition temperature \( T_g \) is given by the temperature, below which the simulation results start to deviate from the master curve for \( D_\alpha \). This temperature is corresponding to the so-called thermodynamic glass transition temperature, which is given by a crossover point in the enthalpy-temperature line. Thus, we find \( T_g \approx 0.557 (1/T_g = 1.7948) \) at \( D_\alpha/\sigma v_0 \approx 10^{-5} \), which coincides with the singular temperature of \( D_\alpha \).

Depending on \( T \), there exist three characteristic regions; an equilibrium liquid region [L] for \( T > T_v \), an equilibrium supercooled region [S] for \( T_v \geq T > T_g \), and a non-equilibrium glass region [G] for \( T_g \geq T \), where \( T_v \) is a supercooled point. Here the mean-field theory predicts that \( T_g \) is given by the temperature at \( D_\alpha/\sigma v_0 \approx 10^{-3} \), which coincides with the peak position of the specific heat. Thus, we find \( T_g \approx 0.730 (1/T_g = 1.3692) \). In a supercooled state, there exist the following four characteristic time stages. The first is the early stage for \( t \leq t_0 \). After this stage, the particle behaves as if it is trapped in a cage which is mostly formed by neighboring particles. This second stage is a so-called \( \beta \)-relaxation stage for \( t_0 \ll t \ll t_v \), which consists of two stages; a fast \( \beta \)-relaxation stage for \( t_0 \ll t \ll t_v \) and a slow \( \beta \)-relaxation stage for \( t_v \ll t \ll t_u \). After this stage, the scattering function \( f_\alpha(q, t) \) is well approximated by the Kohlrausch-Williams-Watts (KWW) function given by Eq. (26). This is an \( \alpha \)-relaxation stage for \( \tau_\alpha \ll t \ll \tau_L \), where \( \tau_L (= 1/\gamma_0 D_\alpha) \) is a long diffusion time. The last is a late stage for \( t \gg \tau_L \), where \( f_\alpha(q, t) \) obeys an exponential decay \( \exp[-q^2 D_\alpha(T)t] \).

B. Critical temperature

We first discuss a critical temperature \( T_c \) corresponding to the critical coupling parameter \( \kappa_c^{(\alpha)} (= 2\gamma_\alpha) \). We here use the simulation results to fix the values of unknown parameters \( \gamma_\alpha \) and \( S(q_\alpha) \) for different temperatures.

| state | [G]         | [S]         | [L]         |
|-------|-------------|-------------|-------------|
| \( T \) | 0.5 | 0.556 | 0.625 | 0.714 | 0.833 | 1.0 | 1.25 | 1.667 | 2.0 | 2.5 | 5.0 |
| \( \kappa_c \) | 7.994 | 6.993 | 5.008 | 4.568 | 3.739 | 2.919 | 2.270 | 1.813 | 1.498 | 1.279 | 0.849 |
| \( A \) | 7.018 | 6.624 | 5.606 | 5.482 | 5.037 | 4.515 | 4.088 | 3.772 | 3.490 | 3.308 | 2.856 |
| \( S(q_\alpha) \) | 2.121 | 2.083 | 2.047 | 1.987 | 1.926 | 1.871 | 1.776 | 1.666 | 1.607 | 1.524 | 1.361 |
and $B_c$. In fact, the parameter $\gamma_c$ is fixed so that the short-time behavior coincides with the simulation results. Thus, $\gamma_c \tau_0 \approx 6$ is found for all temperatures. The coupling parameter $B_c$ is obtained by Eq. (43) as

$$B_c = \left( \frac{v_0^2}{D_s S(q)} - \gamma_c \right) / \int_0^\infty f_c(s)^2 ds. \quad (54)$$

In order to calculate the memory terms in Eqs. (44) and (54) numerically, we use the asymptotic analytic function given by Eq. (52). This approach is reasonable because it must be one of numerical solutions since the simulation results for $f_c(t)$ are well described by it numerically. Then, $B_c$ is calculated from Eq. (54) at each temperature and the numerical results for $f_c(t)$ are obtained from Eq. (44) at a given value of $B_c$. In order to check whether this approach is valid or not, we next solve Eq. (44) independently by an iteration at each given value of $B_c$. The iteration procedure is as follow. In the 0th iteration, the renormalized memory function $\Sigma_c(t)$ is just neglected. In the 1st iteration, the generating function $\Omega_c(s)$ contained in $\Sigma_c(t)$ is replaced by $\Omega_c^{(0)}(s)$, leading to a single integral over time $s$, in the 2nd iteration, $\Omega_c(s')$ in $\Sigma_c(s)$ is replaced by $\Omega_c^{(0)}(s')$, leading to double integrals over times $s$ and $s'$, and vice versa. As the number of iterations increases at a given value of $B_c$, the diffusion coefficient $D_c$ decreases to reach the simulation result. As is shown in Fig. 4 in a liquid state [L] the iteration results for $f_c(t)$ exactly reduce to the numerical results and the simulation results within several iterations. In a supercooled state [S], however, a large number of iterations are still required to describe the numerical results. Although the numerical results do not agree with the simulation results in the $\alpha$ stage, as is discussed later, this is just because the simplified model is used. Thus, the value of $\kappa^{(c)}$ obtained from Eq. (54) by using Eq. (52) is confirmed to be reasonable and is listed in Table I. In Fig. 5 $\kappa^{(c)}$ is plotted versus inverse temperature $1/T$ together with the corresponding value for $A$ obtained by Eq. (53). Those values predict that the critical temperature $T_c$ exists around $T_r \approx 0.557$. Here we should note that the critical temperature predicted by MCT at $\kappa^{(c)} = 4.0$ is expected to be $T_c \approx 0.791$, which is higher than $T_r$. Thus, it is shown that the present theory can improve the high $T_c$ problem appeared in MCT.

### C. Numerical results

Similarly to the calculation of $B_c$, one can use Eq. (52) safely to calculate the memory term $\Sigma_c(t)$ in Eq. (44) since the numerical results exactly coincide with the iteration results for higher temperatures. In Fig. (6) the numerical results for $f_c(t)$ are then plotted versus time for different temperatures. In a liquid state [L] for $T > T_c$, the numerical results agree with the simulation results well within error. In a supercooled state

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**FIG. 4:** (Color online) A plot of $f_c(q, t)$ versus $\log_{10}(t/\tau_0)$ for $T = 1.25$ and 0.714. The solid lines indicate the numerical results and the dotted lines the 0th, 1st, 2nd, 3rd, and 4th iteration results from left to right, where $B_c = 84.002$ for $T = 1.25$ and 87.244 for $T = 0.714$. The symbols (●) indicate the simulation results.

**FIG. 5:** (Color online) A plot of $\kappa^{(c)}$ and $A$ versus $1/T$. The symbols (●) indicate the results for $\kappa^{(c)}$ and (□) for $A$. The horizontal solid line indicates the critical value $\kappa^{(c)} = 2\epsilon(\approx 5.43656)$ and the horizontal dashed line $\kappa^{(c)} = 4$ obtained by MCT. The vertical dotted line indicates the glass transition temperature $T_g = 0.557 (1/T_g = 1.7948)$ and the vertical dashed line the supercooled temperature $T_s = 0.730 (1/T_s = 1.3692)$. 

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$T_g < T \leq T_s$, however, they do not agree with the simulation results in the $\alpha$ stage. In fact, the stretched exponent of the numerical results is given by $\beta \approx 1.00$, while $\beta \approx 0.76$ for the simulation results. This is mainly because the simplified model is used. In order to find a reasonable value of $\beta$, therefore, the original recursion formula given by Eq. (30) must be solved by using the static structure factor $S(q)$ obtained from the simulation. In a glass state $[G]$ for $T \leq T_g$, the disagreement becomes more clear not only in the $\alpha$ stage but also in the slow $\beta$ stage. The disagreement in the slow $\beta$ stage for lower temperatures is mainly due to the fact that the simulation time is not long enough to obtain the final results. Here we should mention that the numerical results seem to decay to zero even in $[G]$, although the long-time non-zero solutions will be expected. This is just caused because of the approximation made to obtain Eq. (44). Similarly to the calculation of $\Omega_c(t)$, $D_c(t)$ and $\psi_c(t)$ are also calculated numerically from Eq. (46) and (49), respectively. In Figs. 7 and 8 the numerical results for $D_c(t)$ and $\psi_c(t)$ are shown versus time at $T = 1.25$ and $0.714$, respectively. The numerical results for $D_c(t)$ do not agree with the simulation results in the $\alpha$ stage in $[S]$. For comparison, the 4th iteration results are also shown. A large number of iterations are still required to obtain the final results at $T = 0.714$, while a few more iterations are enough to obtain the simulation results at $T = 1.25$. On the other hand, the numerical results for $\psi_c(t)$ agree with the simulation results well within error. This is because its time scale is much smaller.
than \( \tau_\beta \) and the effect of the nonlinear memory function on it is small. As is shown in Fig. 8, therefore, the iteration results independently obtained from Eq. (49) also coincide with the numerical results exactly after the 2nd iteration even in [S].

VI. SUMMARY

In the present paper, we have first transformed the TMCT equations given by Eqs. (5) and (6) into the recursion formula given by Eq. (30). Then, we have made the same simplification on the nonlinear memory function as that employed by MCT. By using the time difference between the \( \alpha \)-relaxation time \( \tau_\alpha \) and the \( \beta \)-relaxation time \( \tau_\beta \), we have then derived the asymptotic recursion formula given by Eq. (44). We have used the simulation results as initial conditions to fix the values of unknown parameters \( \gamma_c \) and \( k^{(c)} \). In order to calculate the memory term \( \Sigma_c(t) \) numerically, we have used the asymptotic fitting function given by Eq. (52). This procedure has been confirmed to be reasonable by solving Eq. (44) by the iterative procedure independently. We have then found the temperature dependence of \( k^{(c)} \) from Eq. (48). Thus, we have shown that the critical temperature \( T_c \) corresponding to the critical value \( k^{(c)} \) is consistent with the glass transition temperature \( T_g \) predicted by the mean-field theory for \( D_\alpha \) and is definitely lower than that obtained by MCT. Hence we have emphasized that TMCT can improve at least the high \( T_c \) problem appeared in MCT. Next, we have also analyzed Eq. (44) numerically at each temperature. In a liquid state [L] we have shown that the numerical results agree with the simulation results well within error. In a supercooled state [S], however, we have shown that they do not agree with those in the \( \alpha \) stage, although they can describe those in the \( \beta \) stage well. In fact, the stretched exponent \( \beta \) is given by \( \beta \approx 1.00 \) for the numerical results, while \( \beta \approx 0.76 \) for the simulation results. This non-stretched exponent is considered to be just inherent to the simplified model. Finally, we should mention that the MCT nonlinear memory function \( \Delta \varphi_\alpha(q, t) \) given by Eq. (7) is expected to work well on TMCT and will give very good agreement with simulations if the original recursion formula given by Eq. (44) is solved by using the static structure factor obtained from the simulation. This is now in progress and will be discussed elsewhere.

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