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Time-convolutionless mode-coupling theory near the glass transition—A recursion formula and its asymptotic solutions

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HIGHLIGHTS

- Time-convolutionless mode coupling theory is analyzed mathematically and numerically.
- An ergodic to non-ergodic transition at a critical point is found.
- The same two-step relaxation process as that discussed in MCT is obtained.
- A recursion formula is solved for simulations numerically within a simplified model.

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ABSTRACT

The time-convolutionless mode-coupling theory (TMCT) equation for the intermediate scattering function $f_\alpha(q, t)$ derived recently by the present author is analyzed mathematically and numerically, where $\alpha = c$ stands for a collective case and $\alpha = s$ for a self case. All the mathematical formulations discussed by Götze for the MCT equation are then shown to be directly applicable to the TMCT equation. Firstly, it is shown that similarly to MCT, there exists an ergodic to non-ergodic transition at a critical point, above which the long-time solution $f_\alpha(q, t = \infty)$, that is, the so-called Debye–Waller factor $f_\alpha(q)$, reduces to a non-zero value. The critical point is then shown to be definitely different from that of MCT. Secondly, it is also shown that there is a two-step relaxation process in a β stage near the critical point, which is described by the same two different power-law decays as those obtained in MCT. In order to discuss the asymptotic solutions, the TMCT equation is then transformed into a recursion formula for a cumulant function $K_\alpha(\boldsymbol{q}, t)(= -\ln[f_\alpha(q, t)])$. By employing the same simplified model as that proposed by MCT, the simplified asymptotic recursion formula is then numerically solved for different temperatures under the initial conditions obtained from the simulations. Thus, it is discussed how the TMCT equation can describe the simulation results within the simplified model.

1. 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 ideal MCT equations for the intermediate scattering function $f_\alpha(q, t)$ 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 numerical solutions show an ergodic to non-ergodic transition at a critical temperature T_c (or a critical volume fraction ϕ_c), T_c (or ϕ_c) is always much higher (or

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lower) than the so-called thermodynamic glass transition temperature T_g (or the glass transition volume fraction ϕ_g). Thus, the critical point exists in a region away from the glass transition.

In order to overcome the above problem, we have recently proposed the time-convolutionless MCT (TMCT) equations for $f_\alpha(q,t)$ [17] by employing the Tokuyama–Mori projection operator method [18]. This method was originally proposed to calculate the cumulant functions from first principles, which are obtained by using the cumulant expansion method proposed by Kubo [19]. The reason why one should use the time-convolutionless equation for $f_\alpha(q,t)$ is mainly due to the following fact. Let us consider the self-intermediate scattering function $f_s(q,t)$ given by $f_s(q,t) = \langle \exp[i\boldsymbol{q}\cdot\{\boldsymbol{X}_j(t) - \boldsymbol{X}_j(0)\}]\rangle$, where $\boldsymbol{X}_j(t)$ is the position vector of a particle j at time t and the brackets the average over an equilibrium ensemble. By employing the Kubo cumulant expansion method, one can then transform it into an exponential form as

$$f_s(q,t) = \exp[-K_s(q,t)] \tag{1}$$

with the cumulant function

$$K_s(q,t) = \frac{q^2}{6}M_2(t) - \frac{q^4}{2}\left(\frac{M_2(t)}{6}\right)^2 \alpha_2(t) + \cdots, \tag{2}$$

where the non-Gaussian parameter $\alpha_2(t)$ [20] is given by

$$\alpha_2(t) = \frac{3M_4(t)}{5M_2(t)^2} - 1, \tag{3}$$

and $M_n(t)$ the mean-nth displacement given by $M_n(t) = \langle|\boldsymbol{X}_j(t) - \boldsymbol{X}_j(0)|^n\rangle$. By taking the time derivative of Eq. (1), one can find the time-convolutionless equation for $f_s(q,t)$ as

$$\frac{\partial}{\partial t}f_s(q,t) = -q^2 D_s(q,t) f_s(q,t) \tag{4}$$

with the time-dependent self-diffusion coefficient $D_s(q,t)(= q^{-2}\mathrm{d}K_s(q,t)/\mathrm{d}t)$. Thus, it turns out that the cumulant expansion method leads to the time-convolutionless equation. In order to calculate $\alpha_2(t)$ from a first principle, therefore, the memory function of the starting equation for $f_s(q,t)$ should be convolutionless in time. In the previous paper [17], we have thus proposed the time-convolutionless mode-coupling (TMCT) equation for $f_\alpha(q,t)$.

In the present paper, we first review the TMCT equation briefly. In order to show how one can directly apply the same mathematical formulations as those discussed by Götze [2] in the MCT equations to the TMCT equations, we introduce the cumulant function $K_\alpha(q,t)$ by $K_\alpha(\boldsymbol{q},t) = -\ln[f_\alpha(q,t)]$. Then, we derive the second-order differential equation for $K_\alpha(q,t)$

$$\frac{\partial^2 K_\alpha(q,t)}{\partial t^2} = \frac{q^2 v_{th}^2}{S_\alpha(q)} - \gamma_\alpha \frac{\partial K_\alpha(q,t)}{\partial t} - \int_0^t \Delta\varphi_\alpha(\boldsymbol{q}, t-\tau)\frac{\partial K_\alpha(q,\tau)}{\partial \tau}\mathrm{d}\tau \tag{5}$$

with the ideal MCT nonlinear memory function $\Delta\varphi_\alpha(\boldsymbol{q},t)$, where v_{th} is an average thermal velocity, $S_\alpha(q)$ a static structure factor, and γ_α a damping constant. On the other hand, the ideal MCT equation for $f_\alpha(q,t)$ is given by

$$\frac{\partial^2 f_\alpha(q,t)}{\partial t^2} = -\frac{q^2 v_{th}^2}{S_\alpha(q)} f_\alpha(q,t) - \gamma_\alpha \frac{\partial f_\alpha(q,t)}{\partial t} - \int_0^t \Delta\varphi_\alpha(\boldsymbol{q}, t-\tau)\frac{\partial f_\alpha(q,\tau)}{\partial \tau}\mathrm{d}\tau. \tag{6}$$

Since Eq. (5) has exactly the same form as that of Eq. (6), except the first term, we show that similarly to MCT, there also exists the ergodic to non-ergodic transition at a critical point, above which the long-time non-zero solution, that is, the so-called Debye–Waller factor $f_\alpha(q)$, exists. We also show that there is a two-step relaxation process in a β stage near the critical point, which is described by the same two different power-law decays as those obtained in MCT.

In order to investigate the long-time asymptotic solution of $K_\alpha(q,t)$, it is convenient to use the same simplification on the nonlinear memory function as that discussed in MCT [1]. By fixing q at a first-peak position q_m of the static structure factor $S(q)$, we then show from Eq. (5) that the Debye–Waller factor $f_\alpha(q_m)$ satisfies a simple relation

$$f_\alpha = \exp[-K_\alpha], \quad K_\alpha = \frac{1}{\kappa_\alpha f_c f_\alpha}, \tag{7}$$

where κ_α is a coupling parameter of the long-time memory function discussed in the MCT simplified model. Eq. (7) has two non-zero real solutions only when $\kappa_c \geq 2e$. Hence the critical Debye–Waller factor f_c^c is given by $f_c^c = \mathrm{e}^{-K_c^c}$ at $\kappa_c = 2e(\simeq 5.437)$, where $K_c^c = 1/2$. On the other hand, from Eq. (6) MCT gives the following well-known relation:

$$f_\alpha = \frac{\kappa_\alpha f_c f_\alpha}{1 + \kappa_\alpha f_c f_\alpha}. \tag{8}$$

Eq. (8) has two non-zero real solutions only when $\kappa_c \geq 4$. Hence $f_c^c = 1/2$ at $\kappa_c = 4$. Here we should note that since the critical value $2e$ is larger than 4, the critical temperature T_c is expected to be lower than that obtained by MCT.

Next, we transform the second-order differential equation for $K_\alpha(q,t)$ into a simple recursion formula. Then, we solve it asymptotically within the simplified model under the initial conditions obtained from the simulations. Thus, we show