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Statistical-mechanical theory of nonlinear density fluctuations near the glass transition

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HIGHLIGHTS

- A new time-convolutionless equation is derived for the density fluctuations.
- A new equation is found for the Debye–Waller factor.
- The critical temperature is expected to be much lower than that of ideal MCT.
- The non-Gaussian parameter is shown to be zero at an initial time.

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ABSTRACT

The Tokuyama–Mori type projection-operator method is employed to study the dynamics of nonlinear density fluctuations near the glass transition. A linear non-Markov time-convolutionless equation for the scattering function $F_\alpha(q,t)$ is first derived from the Newton equation with the memory function $\psi_\alpha(\boldsymbol{q},t)$, where $\alpha = c$ for the coherent–intermediate scattering function and s for the self–intermediate scattering function. In order to calculate $\psi_\alpha(\boldsymbol{q},t)$, the Mori type projection-operator method is then used and a linear non-Markov time-convolution equation for $\psi_\alpha(\boldsymbol{q},t)$ is derived with the memory function $\varphi_\alpha(q,t)$. In order to calculate $\varphi_\alpha(\boldsymbol{q},t)$, the same binary approximation as that used in the mode-coupling theory (MCT) is also employed and hence $\varphi_\alpha(\boldsymbol{q},t)$ is shown to be identical with that obtained by MCT. Thus, the coupled equations are finally derived to calculate the scattering functions, which are quite different from the so-called ideal MCT equation. The most important difference between the present theory and MCT appears in the Debye–Waller factor $f_\alpha(q)$. In MCT it is given by $f_\alpha(q) = \Gamma_\alpha(q)/(\Gamma_\alpha(q)+1)$, where $\Gamma_\alpha(q)$ is the long-time limit of the memory function $\varphi_\alpha(\boldsymbol{q},t)$. On the other hand, in the present theory it is given by $f_\alpha(q) = \exp[-1/\Gamma_\alpha(q)]$. Thus, it is expected that the critical temperature T_c of the present theory would be much lower than that of MCT. The other differences are also discussed.

1. Introduction

The main purpose of the present paper is to formulate a general scheme for deriving basic equations for density fluctuations near the glass transition, and thus to clarify the role of nonlinear density fluctuations in supercooled liquids from first principles. A well-known example of this kind is the mode-coupling theory (MCT) equation [1,2]. A rigorous formulation has been established to predict a critical temperature T_c, below which the MCT solutions reduce to non-zero values even in the long-time limit [3]. In fact, the MCT equations have been solved numerically for various systems [4–12] to confirm this prediction. As long as the system is in equilibrium, this situation is exactly the same as that in critical phenomena,

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except that the crossover from an equilibrium state to a nonequilibrium state occurs at the glass transition temperature T_g, which should be higher than T_c. Thus, MCT has been applied for wide varieties of glass-forming liquids to understand the mechanism of the glass transition [13–27].

Although MCT was the origin of all later studies on the glass transition, we still find a few unsatisfactory points. First, the critical temperature T_c of MCT is close to the melting temperature T_m, which is much higher than T_g. As a result, the peak height of the non-Gaussian parameter $\alpha_2(t)$ [28] is always much smaller than 1 since the system is in a liquid state. This is a first problem (i). Secondly, the initial value of $\alpha_2(t)$ is not zero but $\alpha_2(t=0) = -2/3$. This is a second problem (ii). Thirdly, the MCT solutions do not satisfy such a universality in dynamics that all the dynamics in different systems coincide with each other if the values of their self-diffusion coefficients are identical [29]. In fact, the MCT solutions have been shown not to agree with the simulation results in the cage region [30,11]. This is a third problem (iii). In the previous paper [31,32], therefore, we have proposed the alternative MCT (AMCT) equations to solve those problems. As is shown in Section 2, the problems (i) and (iii) are partially solved. In the present paper, therefore, we propose a theoretical approach completely different from the previous ones and show how one could avoid the above three problems safely within the MCT binary approximation [3].

Our approach is mainly based on the fact that the self–intermediate scattering function $F_s(q,t)$ is well-known to be described by the following cumulant expansion form [33]:

$$\begin{aligned} F_s(q,t) &= \exp\left[-q^2\int_0^t \Psi(q,s)\mathrm{d}s\right] \\ &= \exp\left[-\frac{q^2}{6}M_2(t) + \frac{q^4}{2}\left(\frac{M_2(t)}{6}\right)^2\alpha_2(t) + \cdots\right] \end{aligned} \tag{1}$$

with the non-Gaussian parameter [28]

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

where $M_{2n}(t) = \langle|\boldsymbol{X}_j(t) - \boldsymbol{X}_j(0)|^{2n}\rangle$, $\boldsymbol{X}_j(t)$ being a position vector of a particle j at time t. By taking the time derivative of Eq. (1), one can then find

$$\frac{\partial}{\partial t}F_s(q,t) = -q^2\Psi(q,t)F_s(q,t). \tag{3}$$

This equation is different from the so-called MCT equation. In fact, the MCT equations for the scattering functions $F_\alpha(q,t)$ are given by

$$\frac{\partial^2}{\partial t^2}F_\alpha(q,t) = -\frac{q^2v_{th}^2}{S_\alpha(q)}F_\alpha(q,t) - \int_0^t \varphi_\alpha(\boldsymbol{q},t-s)\frac{\partial}{\partial s}F_\alpha(q,s)\mathrm{d}s, \tag{4}$$

where $\varphi_\alpha(\boldsymbol{q},t)$ is the memory function, v_{th} the thermal velocity, and $S_\alpha(q) = F_\alpha(q,0)$. Here $\alpha = c$ stands for the coherent–intermediate scattering function and s for the self–intermediate scattering function, where $S_s(q) = 1$. Then, MCT [3] shows that an ergodic to nonergodic transition occurs at a critical temperature T_c, below which the long-time solution reduces to a non-zero value $f_\alpha(q)$. For $T \le T_c$, one can thus find the so-called Debye–Waller factor $f_\alpha(q)$ as

$$f_\alpha(q) = \lim_{t\to\infty}\frac{F_\alpha(q,t)}{S_\alpha(q)} = \frac{\Gamma_\alpha(q)}{\Gamma_\alpha(q)+1} \tag{5}$$

with the long-time limit of the memory function

$$\Gamma_\alpha(q) = \lim_{z\to 0}\frac{z\varphi_\alpha[\boldsymbol{q},z]}{q^2v_{th}^2}S_\alpha(q), \tag{6}$$

where $\varphi_\alpha[\boldsymbol{q},z]$ is a Laplace transform of $\varphi_\alpha(\boldsymbol{q},t)$. One of the most important results in the present paper is to predict that the critical temperature T_c would be much lower than that of MCT. In fact, the present theory leads to the coupled equations

$$\frac{\partial}{\partial t}F_\alpha(q,t) = -q^2\int_0^t \psi_\alpha(\boldsymbol{q},s)\mathrm{d}sF_\alpha(q,t), \tag{7}$$

$$\frac{\partial}{\partial t}\psi_\alpha(\boldsymbol{q},t) = -\int_0^t \varphi_\alpha(\boldsymbol{q},s)\psi_\alpha(\boldsymbol{q},t-s)\mathrm{d}s, \tag{8}$$

where the memory function $\varphi_\alpha(\boldsymbol{q},t)$ coincides with that of MCT within the MCT binary approximation. Similarly to Eq. (5), by using Eqs. (7) and (8), one can then find for $T \le T_c$

$$f_\alpha(q) = \exp\left[-\frac{1}{\Gamma_\alpha(q)}\right]. \tag{9}$$