



# A crucial role of long-range hydrodynamic interactions near the colloidal glass transition based on time-convolutionless mode-coupling theory

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## HIGHLIGHTS

- Time-convolutionless mode-coupling theory is applied for colloidal suspensions.
- Nonlinear memory function consists of mechanical interactions and hydrodynamic interactions.
- Importance of long-range hydrodynamic interactions is emphasized.
- Theoretical prediction for a critical point is qualitatively consistent with that obtained from experimental data.

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## ABSTRACT

The time-convolutionless mode-coupling theory (TMCT) recently proposed for molecular systems is employed to derive a TMCT equation for the collective-intermediate scattering function in suspensions of hard-sphere colloids from the nonlinear Langevin equations with the hydrodynamic interactions between colloids. The nonlinear memory function contained in the TMCT equation consists of two types of interactions between colloids; a mechanical interaction and a hydrodynamic interaction. It is predicted from the TMCT equation how the hydrodynamic interactions can affect the ergodic to non-ergodic transition at a critical point. Then, such a hydrodynamic effect is tested by the experimental data for suspensions of hard-sphere colloids with size polydispersities. Thus, it is emphasized that the long-range hydrodynamic interactions are indispensable to explain the polydispersity dependence of the experimental critical points which is quite different from that of simulations where only the mechanical interactions are taken into.

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## 1. Introduction

A large number of fundamental works on suspensions of colloids have been performed experimentally [1–18] and theoretically [19–43]. Understanding their dynamics is one of important problems in soft matter science not only from an academic point of view as in fundamental colloidal physics but also from a practical point of view as in chemical engineering and biology. In most cases, however, the important effect of hydrodynamic interactions between colloids on their dynamics near the glass transition is not fully recognized yet.

In this paper, we apply the time-convolutionless mode-coupling theory (TMCT) [44–47] for suspension of hard-sphere colloids and derive the TMCT equation for the collective-intermediate scattering function, where the nonlinear memory

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function contains two different terms resulted from mechanical interactions and hydrodynamic interactions. We then show how the critical point (or kinetic glass transition point) is determined by two different interactions. In order to check the important role of the hydrodynamic interactions, we discuss the critical volume fraction  $\phi_c(\sigma)$  for the suspension of polydisperse colloids, where  $\sigma$  is a size polydispersity. Then, the present theory predicts the following three cases for  $\phi_c$ :

$$\begin{cases} \text{(i)} & \phi_c(\sigma) = \phi_h(\sigma) < \phi_c^{(m)}(\sigma), \quad \text{for } 0 \leq \sigma < \sigma_0, \\ \text{(ii)} & \phi_c(\sigma) = \phi_h(\sigma) = \phi_c^{(m)}(\sigma), \quad \text{for } \sigma = \sigma_0, \\ \text{(iii)} & \phi_c(\sigma) = \phi_h(\sigma) > \phi_c^{(m)}(\sigma), \quad \text{for } \sigma > \sigma_0. \end{cases} \quad (1)$$

where  $\sigma_0$  is a constant to be determined. Here  $\phi_c^{(m)}(\sigma)$  is a critical volume fraction obtained only from the mechanical interactions and is found from all the simulations, while  $\phi_h(\sigma)$  is a critical volume fraction obtained from the correlation effect due to the long-range hydrodynamic interactions among colloids and is given by

$$\phi_h(\sigma) = \phi_h(0)(1 + 3\sigma^2) \quad (2)$$

with the hydrodynamic critical point at  $\sigma = 0$  [20,21]

$$\phi_h(0) = (4/3)^3 / (7 \ln 3 - 8 \ln 2 + 2) \simeq 0.571847 \dots, \quad (3)$$

where in order to obtain Eq. (2), the Gaussian distribution was assumed for particle radius [1]. In case (i), the mechanical interactions are enhanced by the hydrodynamic interactions, leading to  $\phi_c(\sigma) < \phi_c^{(m)}(\sigma)$ . In case (ii), both interactions are equally important, leading to  $\phi_c(\sigma) = \phi_c^{(m)}(\sigma) = \phi_h(\sigma)$ . In case (iii), the mechanical interactions are reduced by the hydrodynamic interactions, leading to  $\phi_c(\sigma) > \phi_c^{(m)}(\sigma)$ . In cases (i) and (iii), the hydrodynamic correlation effects dominate the system, leading to  $\phi_c(\sigma) = \phi_h(\sigma)$ . Here we note that only in case (ii) the simulation results can describe the experimental data. Since the TMCT equation with the hydrodynamic memory function cannot be solved analytically nor numerically at the present moment, we just demonstrate from a phenomenological point of view based on the theoretical prediction how one can qualitatively explain the three cases consistently. In order to check the existence of those three cases, therefore, we investigate not only the polydispersity dependence of the critical point obtained from the experiments for suspensions of polydisperse hard-sphere colloids [4,5,7–11] but also that of the simulations [28–36]. Then, we show on a schematic representation of the phase diagram in volume fraction-polydispersity plane that the polydispersity dependence of the experimental critical point  $\phi_c(\sigma)$  coincides with Eq. (2) within error and is quite different from that of the simulations given by  $\phi_c^{(m)}(\sigma)$ . Thus, we emphasize that the hydrodynamic interactions are indispensable to explain the experimental results for the suspensions of polydisperse hard-sphere colloids.

We begin in Section 2 by briefly explaining the theoretical background of TMCT. Then, we derive the TMCT equation for colloidal suspensions, starting from the nonlinear Markov Langevin equations with the friction coefficient resulted from the long-range hydrodynamic interactions between colloids. In Section 3, we investigate the nonlinear memory function in TMCT equation, which contains two different correlation effects; one due to the mechanical interactions and the other due to the hydrodynamic interactions. In Section 4, we discuss the ergodic to non-ergodic transition at a critical point and derive a nonlinear equation to find a Debye–Waller factor. In Section 5, we propose an asymptotic form of the friction coefficient to obtain three cases qualitatively. In Section 6, we investigate the critical volume fractions obtained from the experiments and the simulations for the suspensions of polydisperse hard-sphere colloids. Thus, we show the phase diagram in volume fraction-polydispersity plane and discuss how the hydrodynamic interactions are indispensable to explain such a phase diagram qualitatively. We conclude in Section 7 with a summary.

## 2. TMCT for colloidal suspensions

In this section, we show how to apply the same TMCT formulation [44] as that employed in the molecular systems for colloidal suspensions. We consider the three-dimensional system which contains  $N$  spherical colloids with mass  $m_i$  and radius  $a_i$  of particle  $i$  suspended in an equilibrium fluid with a viscosity  $\eta$  in the total volume  $V$  at temperature  $T$ . Before we go into the details, we briefly review the theoretical background.

### 2.1. Theoretical background of TMCT

In this subsection, we briefly summarize the macroscopic equations in the suspensions which are derived from first principles by using a new formulation based on TMCT [44–47]. The outline of TMCT is as follows. As is shown in Fig. 1, the basic equations discussed in the present paper can be classified into four stages, [N], [L], [K], and [H], depending on a space–time scale. In a microscopic stage [N], the position  $\mathbf{X}_j(t)$  and the momentum  $\mathbf{P}_j(t)$  of  $j$ th particle at time  $t$  are described by the Newton (or Heisenberg) equations. In a Langevin stage [L], a nonlinear Langevin equation for the momentum  $\mathbf{P}_j(t)$  is derived from the Newton equations. In a kinetic stage [K], the relevant variables are given by the current densities and the number densities. Linear non-Markov Langevin type equations for the current densities are derived from the Langevin equation by using the Mori projection-operator method [48] (see a dashed arrow (M) in Fig. 1), where the memory terms are convolution in time and are written in terms of correlation function of the fluctuating forces. Linear non-Markov stochastic

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