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A statistical-mechanical theory of self-diffusion in colloidal suspensions — application to colloidal glass transitions

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Abstract

A statistical-mechanical theory of self-diffusion in colloidal suspensions is presented. A renormalized linear Langevin equation is derived from a nonlinear Langevin equation by employing the Tokuyama–Mori projection operator method. The friction constant is thus shown to be renormalized by the many-body correlation effects due to not only the direct interactions between particles, but also due to the hydrodynamic interactions between particles. The equations for the mean-square displacement and the non-Gaussian parameter are then derived. The present theory is applied to colloidal glass transitions to discuss the crossover phenomena in the dynamics of a single particle from a short-time self-diffusion process to a long-time self-diffusion process via a β (caging) stage. The effects of the renormalized friction coefficient on self-diffusion are thus explored with the aid of the analyses of the experimental data and the simulation results by the mean-field theory proposed by the present author. It is thus shown that the relaxation time of the renormalized memory function is given by the β-relaxation time. It is also shown that the non-Gaussian parameter is very small, even near the glass transition, because of the existence of the short-time self-diffusion coefficient caused by the hydrodynamic interactions.

Keywords: Colloidal suspensions; Glass transition; Mean-square displacement; Projection operator method; Supercooled liquids

1. Introduction

The main purpose of the present paper is to formulate a statistical-mechanical theory of self-diffusion in colloidal suspensions and thus to study crossover phenomena from a short-time self-diffusion process with the short-time self-diffusion coefficient D_S^S to a long-time self-diffusion process with the long-time self-diffusion coefficient D_S^L, via a β (or caging) process near the colloidal glass transition. A well-known theory of this kind is the mode-coupling theory (MCT) [1], which was the origin of all later works on the colloidal glass transitions. The present theory is different from the MCT in the following way. First, the present theory is formulated based on the Tokuyama–Mori type projection operator method [2]. On the other hand, the MCT has been formulated based on the Mori type projection operator method [3]. As discussed in the previous paper [4], the dynamics of a single particle near the glass transition cannot be described by the Mori type approach. This is because it belongs to the intermediate time-scale phenomena, such as a random frequency modulation [5], an optical gain in semiconductor quantum-well lasers [6], an excitation

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relaxation in pigment–protein complexes [7], and an electron transfer in DNA [8], whose time scales of interest are much larger than the microscopic time t_m of thermal noise, but much smaller than the macroscopic time t_M of collective motion due to surrounding particles around a particle of interest. Hence, the non-Markov memory function is caused by the many-body correlation effects due to both direct and hydrodynamic interactions between particles, whose time scales are of order t_M. The Mori formula is not suitable for dealing with these kind of non-Markov processes. In fact, as shown in Figure 3 of Ref. [4], the discrepancy between the MCT solutions and the simulation results appears in β stage because of this reason, where the mean-square displacement $M_2(t)$ of the simulation results on the suspension of the Lennard–Jones binary colloids [9,10] is compared to the corresponding MCT solutions [9] at the same value of D_S^L/D_S^S. Here, the MCT solutions were calculated by using the static structure factors obtained from the simulations [9]. This comparison was done based on the universal feature that any experimental data and simulation results for $M_2(t)$ are all collapsed on a master curve at the same value of D_S^L/D_S^S [11,12]. The discrepancy becomes much larger as the system approaches the glass transition [13]. In the present paper, therefore, we use the Tokuyama–Mori type projection operator method to formulate a formal theory from first principles.

Secondly, the present theory deals with the renormalized friction coefficient caused by not only the direct interactions between particles but also by the hydrodynamic interactions between particles. On the other hand, the MCT takes into account only the direct interactions between particles. The hydrodynamic interactions, however, play an important role in the dynamics of a single particle for higher volume fractions. These are formally separated into two kinds of interactions, depending on the time scale [14,15]. The first are the short-time hydrodynamic interactions, which become important in a kinetic stage [K] from a Brownian relaxation time of order t_B to a mean-free time of order t_f and lead to the short-time self-diffusion coefficient D_S^S, where t_f $(=\ell^2/D_S^S)$ is the time required for a particle to diffuse over a distance ℓ in a cage, which is mostly formed by neighboring particles. Here, D_S^S depends only on the volume fraction ϕ. The second are the long-time hydrodynamic interactions which play an important role in a suspension–hydrodynamic stage [SH] for $t \geq t_f$. This leads to the long-time self-diffusion coefficient D_S^L together with the direct interactions. Hence D_S^L depends on ϕ and also on another control parameter λ, such as an inverse temperature. Without both kinds of hydrodynamic interactions, therefore, one cannot explain the experimental data consistently [16].

Although the importance of both hydrodynamic and direct interactions between particles have been recognized near the glass transition, there exist only a few theoretical approaches. The essential difficulties come from the following facts. The first difficulty is due to the fact that the hydrodynamic interactions have a long-range nature. Hence, one cannot truncate their interactions within a few–body interactions because they lead to divergent integrals [15]. The second is due to the fact that both many-body hydrodynamic and direct interactions become important near the glass transition. Hence, one cannot retain only these lowest-order terms. In order to study the colloidal suspension, the MCT has retained only the two–body direct interactions and has found the long-time self-diffusion coefficient D_S^L whose singular point $\phi_c \simeq 0.516$ is too small when compared to the value 0.556 predicted by the analysis of the experimental data [11]. On the other hand, Tokuyama–Oppenheim [14,15] have calculated the many-body hydrodynamic interactions and have obtained both coefficients D_S^S and D_S^L consistently, where $\phi_c = (4/3)^3/(7\ln 3 - 8\ln 2 + 2) \simeq 0.57184\cdots$. Since they have retained only the two–body direct interactions, however, the singular point ϕ_c is still different from the one predicted by the experiment. Thus, full accounts for both many-body hydrodynamic and direct interactions are indispensable to study the colloidal glass transitions. This has not been done by any previous authors yet. In the present paper, therefore, we do not calculate their explicit contributions to the memory function either. Instead, we first show that one can formally express the memory function in terms of those interactions and discuss how one can predict their effects on the dynamics of a single particle. In fact, we apply the present theory to the colloidal glass transitions and predict the asymptotic form of the memory function with the aid of analyses of the experimental data and the simulation results by the mean-field theory proposed recently by the present author [17, 18]. Thus, we show that the relaxation time of the memory function is given by the β-relaxation time t_β $(= \ell^2/D_S^L)$, over which a particle can escape the cage formed by the surrounding particles. We also show how the short-time hydrodynamic interactions weaken the magnitude of the non-Gaussian parameter drastically.

The paper is organized as follows. In Section 2, starting from the nonlinear Langevin equation with both hydrodynamic and direct interactions and employing the Tokuyama–Mori type projection operator method, we derive a renormalized linear Langevin equation for a particle i in a kinetic stage [K] on a time scale of t_B, where the memory function is renormalized by both hydrodynamic and direct interactions.