

## Rheology and Dynamics of Colloidal Suspensions

A. J. Banchio, J. Bergenholtz,\* and G. Nägele

*Faculty of Physics, University of Konstanz, P.O. Box 5560, D-78457 Konstanz, Germany*

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Predictions from a recently developed mode coupling theory (MCT) are compared with experimental results for hard-sphere suspensions. A simple scaling of the MCT results leads to good agreement with the data. The scaled MCT predicts that for hard-sphere suspensions the zero-shear limiting viscosity obeys a generalized Stokes-Einstein (GSE) relation with both the long-time self-diffusion coefficient and the long-time collective diffusion coefficient measured at the peak of the structure factor. MCT suggests that the same GSE relations do not hold for salt-free charge-stabilized suspensions. [S0031-9007(99)08526-9]

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The prediction of transport properties of concentrated colloidal suspensions has been the goal of numerous theoretical investigations [1–9]. Properties of particular interest are the zero-shear rate limiting shear viscosity and long-time collective and self-diffusion coefficients. Many attempts have been made to connect experimentally the rheological and diffusional transport behavior of concentrated colloidal suspensions [10]. The underlying idea is that both processes reflect relaxation by diffusion in response to a structural deformation caused by an applied flow or by the diffusing particles themselves. These studies, leading to generalizations of the Stokes-Einstein relation, have yielded empirical formulas in which a diffusion coefficient qualitatively correlates with a rheological property. Segre *et al.* [11] used new experimental dynamic light scattering techniques to identify a generalized Stokes-Einstein (GSE) relation which holds quantitatively for hard-sphere suspensions for particle concentrations up to the freezing transition. Their results show that the zero-shear limiting viscosity  $\eta$  of the suspension obeys a GSE relation with the long-time collective diffusion coefficient  $D_C^L(q_m)$  measured at a wave number  $q_m$ , corresponding to the peak position of the static structure factor  $S(q)$ . This GSE relation reads [11]

$$\eta/\eta_0 = D_0/D_C^L(q_m), \quad (1)$$

where  $\eta_0$  is the solvent shear viscosity and  $D_0$  is the Stokes-Einstein diffusion coefficient.

Replacing  $D_C^L(q_m)$  in Eq. (1) by  $D_S^L$ , the long-time self-diffusion coefficient, results in another GSE relation that has been widely explored for a variety of systems, such as hard-sphere suspensions [12–15], surfactant systems [16], and protein suspensions [17]. While this GSE relation works reasonably well for these systems, experiments show that it does not hold for charge-stabilized suspensions [18].

In this Letter, we explore the predictions of a recently developed mode coupling theory (MCT) for colloidal suspensions [7–9]. We establish the MCT as a viable predictive theory for both diffusion and linear viscoelasticity by making quantitative comparisons with experi-

mental data. We find that scaling the MCT predictions for the colloidal transport properties with respect to the liquid-glass transition concentration and, in addition, with their corresponding short-time counterparts leads to agreement with experimental data. We examine also the MCT predictions with regard to the GSE relations for hard-sphere and salt-free charge-stabilized suspensions.

The MCT used differs in several respects from that used by others [6,19–21]; most importantly, it employs a self-consistent determination of the dynamic structure factor, which in this work obeys a generalized diffusion equation [7–9]. As a result, the theory predicts an ideal glass transition where long-time diffusion ceases and  $\eta$  diverges [22–26]. Hence, within MCT  $\eta$  diverges not at random close packing, but at the glass transition point. This feature is particularly important as recent experimental studies suggest that this is the case for hard-sphere suspensions [27,28]. The theory predicts also vanishing long-time self-diffusion coefficients and diverging viscosities for charge-stabilized systems without resorting to mapping the electrostatic repulsion onto that of hard spheres.

In previous articles, we developed a MCT for collective [9] and tracer diffusion [8] and linear viscoelasticity [7] of concentrated colloidal mixtures. The starting point for the MCT is the exact memory equation for the dynamic structure factor  $S(q, t)$  [29–32]:

$$\begin{aligned} \frac{\partial}{\partial t} S(q, t) = & -q^2 D_{\text{eff}}(q) S(q, t) \\ & - \int_0^t dt' M^{\text{irr}}(q, t - t') \frac{\partial}{\partial t'} S(q, t'), \end{aligned} \quad (2)$$

where  $D_{\text{eff}}(q)$  is an effective short-time collective diffusion coefficient. The self-intermediate scattering function  $G(q, t)$  satisfies a similar memory equation [8]. MCT provides an expression for the irreducible memory function  $M^{\text{irr}}(q, t)$  in Eq. (2), leading to a closed set of equations which can be solved self-consistently for  $S(q, t)$  [23,24,31–33].

In a previous paper [7], we linked the zero-shear limiting linear viscoelastic behavior to  $S(q, t)$ . This provides a

route to calculating  $\eta$  from the self-consistent MCT solution for  $S(q, t)$ . Although the theory provides opportunity for inclusion of leading order hydrodynamic interactions and is applicable to colloidal mixtures [7,9], the present results have been obtained for monodisperse suspensions under neglect of hydrodynamic interactions (HI). With these simplifications, the viscosity is given by [7]

$$\eta^{\text{MCT}} = \eta_0 + \frac{k_B T}{60\pi^2} \int_0^\infty dt \int_0^\infty dk k^4 \times \left[ \frac{S(k, t)}{S(k)} \frac{d}{dk} \ln S(k) \right]^2, \quad (3)$$

Similar results have been obtained by Geszti [34] and de Schepper *et al.* [5,6]. The result in [5,6] can be obtained from Eq. (3) by substituting an exponential form for  $S(q, t)$  with a  $q$ -dependent decay rate. Unlike these authors, we require that  $S(q, t)$  must satisfy Eq. (2) and the MCT expression for  $M^{\text{irr}}(q, t)$  self-consistently, giving rise to a glass transition [22–24].

The  $q$ -dependent long-time collective diffusion coefficient and the long-time self-diffusion coefficient are also calculated from  $S(q, t)$ , according to

$$D_C^{L, \text{MCT}}(q) = -q^{-2} \lim_{t \rightarrow \infty} \frac{d}{dt} \ln S(q, t), \quad (4)$$

$$D_S^{L, \text{MCT}} = - \lim_{t \rightarrow \infty} \lim_{q \rightarrow 0} q^{-2} \frac{d}{dt} \ln G(q, t). \quad (5)$$

As seen from these expressions, there is no evident reason to expect that a universal GSE relation exists between  $\eta$  and either  $D_S^L$  or  $D_C^L(q_m)$ .

In Fig. 1 we compare the MCT predictions for  $D_S^L$  of hard-sphere suspensions as a function of particle volume fraction  $\phi$  with Brownian Dynamics (BD) simulation data [35,36]. The MCT glass transition occurs at  $\phi = 0.525$  [23,24,37], where  $D_S^L$  vanishes. The caging of particles is overestimated in MCT, leading to a glass transition concentration which is too low compared to experiments [23–25,37,38]. While the idealized MCT does not predict an exact glass transition concentration, it reproduces the special features of the colloidal hard-sphere glass transition scenario [24,25,38]. Therefore, we follow Götze and co-workers [23–25,32] and scale the concentration dependence as  $D_S^L[\phi(\phi_g/0.525)]$ . We determine  $\phi_g$  such that the MCT result for  $D_S^L$  reproduces the BD simulation data at high concentrations. This procedure yields  $\phi_g = 0.62$ , which is somewhat larger than the experimental finding of 0.58 for hard spheres [38]. A similar fit of the MCT prediction for  $D_S^L$  of atomic hard spheres to MD simulation data results in  $\phi_g = 0.60$  [37].

As seen in Fig. 1, this scaling of the  $\phi$  dependence can be used to obtain agreement between the MCT and BD  $D_S^L$  for  $\phi > 0.4$ . The exact dilute limiting behavior is also shown in Fig. 1, illustrating that MCT does not reproduce the correct dilute limit. For such low concentrations, the calculation of both long- and short-time suspension properties can be accomplished by Batchelor's relaxation approach and extensions thereof [39].

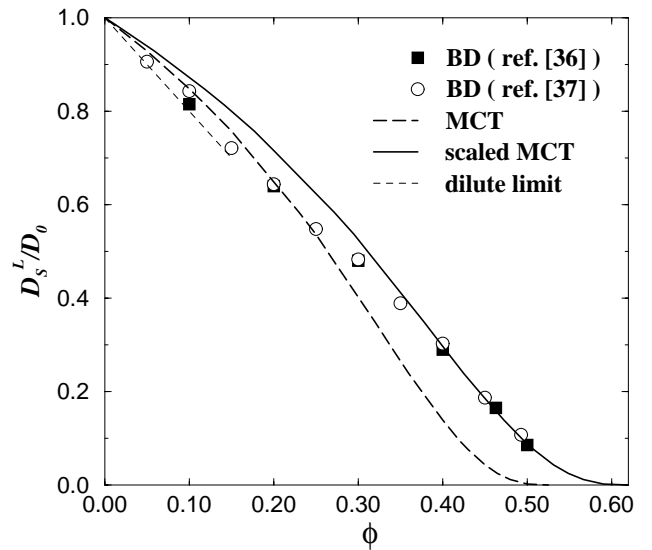


FIG. 1. Normalized long-time self-diffusion coefficient as a function of volume fraction  $\phi$ , showing BD simulation data for hard-sphere suspensions (without HI) [35,36] and the MCT results with and without scaling of  $\phi$ . Also shown is the exact dilute limit:  $D_S^L/D_0 = 1 - \alpha\phi$ , with  $\alpha = 2$  without HI. For comparison, MCT leads to  $\alpha = 4/3$ .

In comparing the MCT results for  $\eta/\eta_0$  and  $D_0/D_C^L(q_m)$ , we find that  $\eta/\eta_0$  is about a factor of 2 smaller at high  $\phi$ . However, in our MCT calculation we include many-body excluded volume effects but do not account for HI. The formulation of the MCT with far-field HI included, which compares well with data for dilute charge-stabilized suspensions [31], will not suffice for hard-sphere suspensions due to the neglect of near-field HI and the assumption of pairwise additive HI. Therefore, we attempt to account for HI by identifying a scaling procedure similar to those proposed by Medina-Noyola [40] and Brady [14,15]. They suggest that  $D_S^L$  can be factored into a hydrodynamic part, given by the short-time self-diffusion coefficient  $D_S^S$ , and a structural part, calculated without HI. They give different justifications for the factorization, and, while Brady also considers  $\eta$  [14], neither of them address collective diffusion.

We find that the MCT long-time coefficients, with the  $\phi$  dependence adjusted as described above, can be brought into accord with the experimental data through scaling with their corresponding short-time counterparts:  $\eta \approx \eta'_\infty \eta^{\text{MCT}}/\eta_0$ ,  $D_C^L(q_m) \approx H(q_m) D_C^{L, \text{MCT}}(q_m)$ , and  $D_S^L \approx D_S^S D_S^{L, \text{MCT}}/D_0$ , where  $\eta'_\infty$  is the high-frequency shear viscosity, and  $H(q_m)$  is the hydrodynamic function [1,3].  $H(q_m)$  arises from the ratio of the effective short-time collective diffusion coefficient with HI,  $D_{\text{eff}}(q) = D_0 H(q)/S(q)$ , to that without,  $D_0/S(q)$ ; the latter is used in the MCT solution.

The above scaling procedure is empirical and does not reproduce the correct dilute limits of the long-time transport coefficients, but corrects the neglect of the HI in the short-time contributions. Moreover, it assumes that

the memory contribution to the dynamics is determined by structural effects and not HI. The scaled expression for  $D_C^L(q_m)$  with  $q_m$  replaced by  $q$  reduces to that for  $D_S^L$  when  $q \rightarrow \infty$ . The latter is the scaling expression proposed in Refs. [14,15,40].

To make quantitative comparisons with experimental data, we have used the semiempirical hard-sphere formulas for  $\eta_\infty$  and  $D_S^L$  given in [4].  $H(q_m)$  is well represented by the form  $H(q_m) = 1 - 1.35\phi$ , which reproduces both the computer simulation results and the experimental data of Segre *et al.* [41] up to the freezing transition, and conforms also unexpectedly to the exact numerical value in the dilute limit.

In Fig. 2 we compare the scaled MCT results for  $\eta/\eta_0$  and  $D_0/D_C^L(q_m)$  with the experimental hard-sphere results in [11]. The experimental GSE relation between  $\eta/\eta_0$  and  $D_0/D_C^L(q_m)$  is well reproduced by the scaled MCT, although  $\eta/\eta_0$  lies slightly above the result for  $D_0/D_C^L(q_m)$ . The scaling is, however, sensitive to the  $\phi$  dependence of the short-time coefficients, so we accept small discrepancies. We also note that the hard-sphere  $\eta/\eta_0$  data measured by Phan *et al.* [42] agree with those in [11] shown in Fig. 2, whereas the data of de Kruif *et al.* [43] lie below—presumably due to a higher particle size polydispersity.

In Fig. 2 we also display the scaled MCT result for  $D_S^L$ . There is near quantitative agreement between  $D_0/D_S^L$  and  $\eta/\eta_0$ , both obtained from the scaled MCT. Close agreement between these two quantities was indeed observed experimentally by Imhof *et al.* [18], while Segre *et al.* found differences at high  $\phi$ . According to our scaled MCT for hard-sphere suspensions,  $\eta$  obeys GSE relations with both  $D_C^L(q_m)$  and  $D_S^L$ .

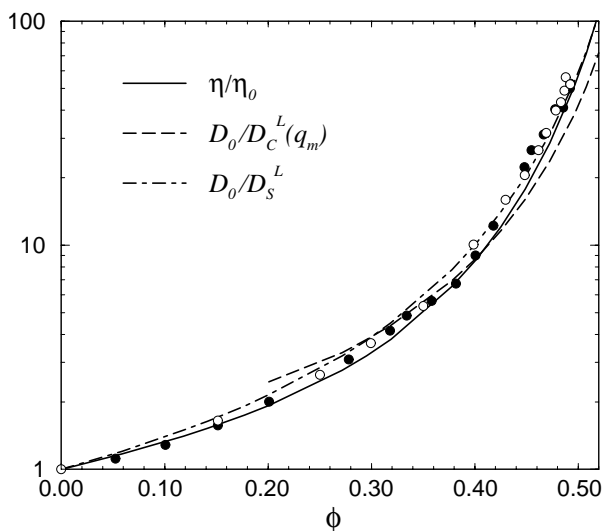


FIG. 2. Normalized zero-shear limiting viscosity ( $\circ$ ) and reciprocal long-time collective diffusion coefficient at wave vector  $q_m$  ( $\bullet$ ) for hard-sphere suspensions as functions of volume fraction from experiments of Segre *et al.* [11]. The lines are the corresponding scaled MCT predictions as labeled.

The GSE relation found experimentally and the MCT results in Fig. 2 lead to the question of whether Eq. (1) holds independent of the form of the interaction potential. To answer this question, we have solved the MCT for salt-free charge-stabilized suspensions, modeled by the repulsive screened Coulomb part of the Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction potential [3]. Also for systems with long-range repulsive interactions MCT predicts the presence of a glass transition, which is supported by experiments [44]. We have selected a deionized charge-stabilized system with particle diameter  $\sigma = 100$  nm, Bjerrum length  $L_B = 7.14$  Å, and effective surface charge  $Z = 500e$ . Here, the MCT glass transition occurs at  $\phi \approx 0.10$  when the rescaled mean spherical approximation is used for  $S(q)$ . This value is much lower than that measured experimentally ( $\phi_g \approx 0.2$ ) due to the high surface charge chosen.

Figure 3 shows the MCT results for  $\eta/\eta_0$ ,  $D_0/D_C^L(q_m)$ , and  $D_0/D_S^L$  as functions of  $\phi$ . These results are shown without scaling of either the  $\phi$  dependence or using the short-time coefficients. The  $\phi$  scaling is not employed because an experimental reference point for  $\phi_g$  is not known for systems with such high surface charge. The short-time scaling is not used because the short-time coefficients vary little as  $\phi$  increases from 0 to 0.10; for example, for  $\phi = 0.10$ , we find  $\eta_\infty/\eta_0 = 1.28$ ,  $D_S^L/D_0 = 0.87$ , and  $H(q_m) = 1.58$  using pairwise additive HI. For these highly charged particles  $H(q_m)$  is well approximated by  $H(q_m) \approx 1 + 1.5\phi^{0.4}$ ; the fractional  $\phi$  dependence is typical for short-time properties of salt-free charge-stabilized suspensions [45]. Although the application of the scaling with these short-time coefficients shifts the

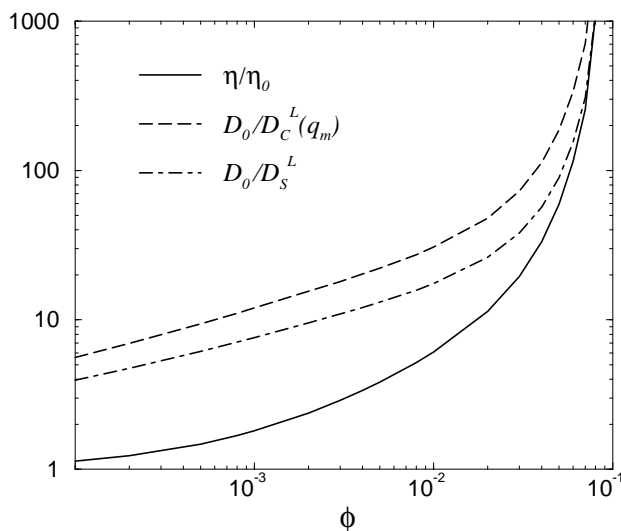


FIG. 3. MCT results for the long-time transport coefficients of model charge-stabilized suspensions with  $Z = 500$  and  $\sigma = 100$  nm as functions of volume fraction. The Hansen-Verlet criterion [ $S(q_m) \approx 2.85$ ] reveals that above  $\phi \approx 2.4 \cdot 10^{-3}$  the suspension is in an undercooled liquid state;  $D_S^L/D_0 \approx 0.1$  for this  $\phi$ , in agreement with the dynamic freezing criterion of Löwen *et al.* [46].

MCT results for  $D_0/D_C^L(q_m)$  to smaller values, it does not lead to a GSE relation with  $\eta$ . Also the GSE relation between  $\eta$  and  $D_S^L$ , which holds within the scaled MCT for hard spheres, is violated for these salt-free highly charged particle systems. Similar observations have been made in [18].

While these results do not provide conclusive evidence for a violation of the GSE relations for charge-stabilized suspensions, taken together with the experimental observations, it is unlikely that the GSE relations are universal for concentrated or highly correlated colloidal suspensions. Thus, the near equality of  $\eta/\eta_0$  and the reciprocal long-time diffusion coefficients for hard-sphere suspensions is likely fortuitous. For hard-sphere suspensions, the proposed scaling provides an empirical means by which the MCT can be used to predict quantitatively the dynamical and linear viscoelastic suspension properties.

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\*Author to whom correspondence should be addressed.

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