Generalized Stokes-Einstein Relations and Viscoelasticity

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The prediction of transport coefficients of colloidal suspensions from microscopic models is a major theoretical challenge. Properties of particular technological relevance are the suspension shear viscosity η and the frequency-dependent elastic storage and viscous loss moduli $G'(\omega)$ and $G''(\omega)$. The latter two quantities describe the viscoelastic response of the suspension to a weak oscillatory shear flow of frequency ω. We have derived a self-consistent mode coupling theory (MCT) for the linear viscoelasticity of concentrated colloidal mixtures [1,2]. This theory accounts not only for the direct particle interactions, but also for the far-field part of the solvent mediated hydrodynamic interaction (HI). It accounts further for polydispersity and mixing effects, and leads naturally to a diverging viscosity at a glass transition point. Mixing effects are particularly interesting, since experiments show that mixing of particles of different sizes and interactions can alter the rheological behaviour dramatically.

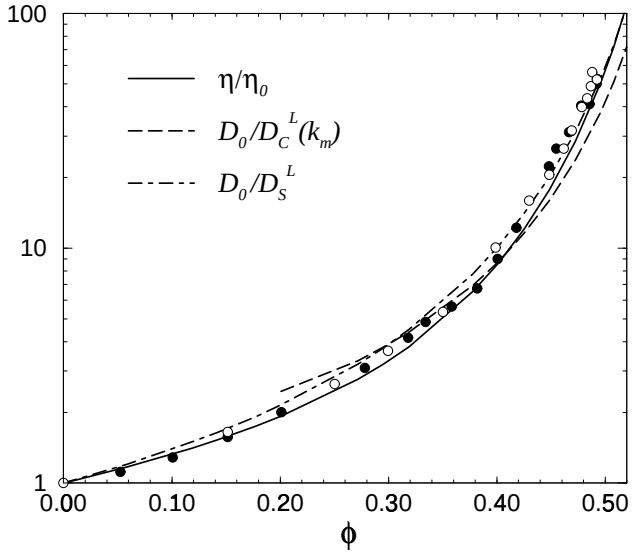

Figure 1: Experimental normalized zero-shear limiting viscosity η/η_0 ($\circ$) and reciprocal long-time collective diffusion coefficient $D_0/D_C^L(k_m)$ ($\bullet$) for hard sphere suspensions as functions of volume fraction ϕ [6]. The lines are the corresponding density-scaled MCT predictions as labelled.

Combined with our recent work on the MCT of tracer-diffusion [3] and cooperative diffusion [4] of colloidal mixtures we have obtained a unified description of linear viscoelasticity and diffusion mechanisms. Our MCT has been worked out so far for charge-stabilized particles where HI is well approximated by the leading order far-field forms. For these systems, the MCT has led to some unexpected predictions like the hydrodynamic enhancement of long-time diffusion [5]. For hard sphere suspensions where near-field HI prevails, we have used a short-time scaling method which allows for a quantitative comparison of the MCT predictions with experimental data [2].

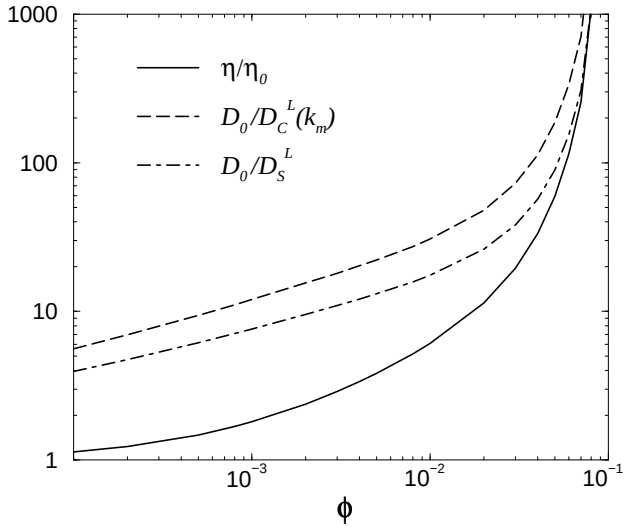

Figure 2: MCT results for the long-time transport coefficients of charge-stabilized suspensions with surface charge number $Z = 500$ and diameter $\sigma = 100$ nm as functions of ϕ. The Hansen-Verlet criterion reveals that above $\phi \approx 2.4 \cdot 10^{-3}$ the suspension is in an under-cooled liquid state. The MCT glass transition occurs here at $\phi \approx 0.1$.

Moreover, the ϕ-dependence of the long-time transport coefficients is rescaled with respect to the glass transition concentration.

In Fig. 1 we compare the short-time and density rescaled MCT results for the normalized viscosity η/η_0 and for the reciprocal normalized long-time collective diffusion coefficient $D_0/D_C^L(k_m)$ with experimental hard sphere results [6]. $D_C^L(k_m)$ is measured at a wave number k_m corresponding to the peak position of the static structure factor. As seen, there is good agreement between the MCT predictions and the experimental data. The experimental generalized Stokes-Einstein relation (GSE) between η/η_0 and $D_C^L(k_m)$ is well reproduced by the scaled MCT. Our MCT predicts that the viscosity of hard sphere suspensions obeys nearly quantitative GSE relations with both $D_C^L(k_m)$ and the long-time self-diffusion coefficient D_S^L. The MCT further predicts that both GSE relations are violated in case of highly charged particle suspensions. This is seen from Fig. 2, which shows MCT results for the long-time transport coefficients of highly charged particles. Another appealing feature of the (scaled) MCT is that it relates the static Hansen-Verlet criterion to the dynamic freezing criterion proposed by Löwen et al. [7]: in MCT, $D_S^L/D_0 \approx 0.1$ for volume fractions ϕ where $S(k_m) \approx 2.85$. We have further investigated on another empirical GSE relation found by Mason and Weitz [8], which relates $G^{'}(\omega)$ and $G^{''}(\omega)$ to the particle mean square displacement. According to our MCT, this GSE works fairly well for concentrated hard sphere suspensions, but strong deviations are found for charge-stabilized suspensions [9]. In [9] we propose an improved frequency-dependent GSE which should be approximately valid also for charge-stabilized dispersions. This paper includes further a thorough discussion of short-time GSEs, and the relation between the Maxwell relaxation time of shear stress and long-time self-diffusion. Experiments concerned with the proposed violation of the long-time and frequency-dependent GSE relations in charge-stabilized colloids at low salinity have not been performed so far.

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