

### Comment on "Universal Self-Diffusion and Subdiffusion in Colloids at Freezing"

In a recent Letter [1] a mode coupling calculation of the longtime self-diffusion coefficient  $D_L$  of colloidal liquids at freezing was presented. We show that approximations used in [1] are not justified and correct the calculation. We show that the findings of [1] are qualitatively explained by asymptotic scaling laws of mode coupling theory (MCT) and numerically discuss crossover behaviors.

(1) In a system of interacting Brownian particles, the total force on all particles vanishes [2]. Therefore, the second Eq. (6) of [1] has to be replaced by

$$\frac{C_c(k, z)}{S(k)} = \left[ z + \frac{ik^2 S^{-1}(k)}{1 + k^2 \Sigma_c(k, z)} \right]^{-1},$$

where  $\Sigma_c(k, z) \rightarrow \Sigma_c(0, z)$  is finite for  $k \rightarrow 0$  [2]. Equation (6) in [1] does not properly describe the hydrodynamic limit and, therefore, diffusion processes.

(2) The assumption that the collective-density correlator  $C_c$  is determined by the same damping rate  $\Sigma$  as the self-density correlation  $C_s$  is not compatible with the standard expression for  $\Sigma_c$  of MCT [3]. Fully self-consistent solutions of the MCT equations for  $C_c$  (and  $C_s$ ) have been calculated [3,4] and compared to experimental data on colloidal hard spheres for densities between freezing and random close packing [5]. Agreement within errors of (10–20)% was reported [5].

(3) The standard result, see, e.g., Ref. [3] quoted in [4], for the interaction vertex  $v$  determining  $\Sigma$  differs from vertex (5) in [1] and does not permit the simplification of the wave vector integrals in (4) which is used in [1].

The factorization approximation underlying the MCT is definitive but uncontrolled. As discussed, e.g., in the review [3], the results are determined by  $S(k)$  and can thus be tested quantitatively. The MCT equations have been solved self-consistently, e.g., [3,4] and the findings discussed in [1] can be obtained from these results.

Figure 1 shows the  $D_L/D_0$  of Brownian hard spheres with diameter  $d$  versus the packing fraction  $\varphi = \pi/6nd^3$

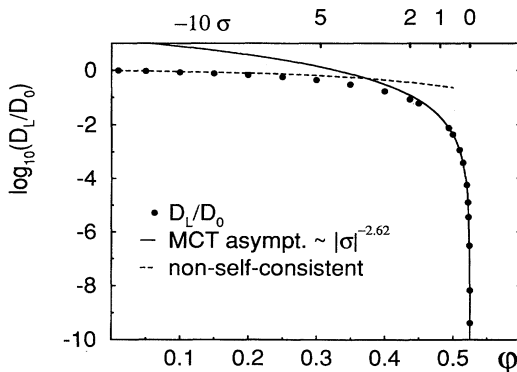


FIG. 1. Self-diffusion coefficients  $D_L/D_0$ .

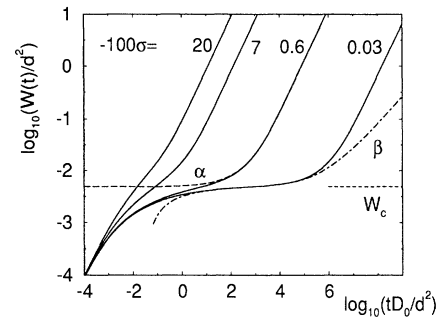


FIG. 2. Mean square displacements.

obtained from the corrected equations.  $D_L$  vanishes at a density  $\varphi_c \approx 0.525$ .  $\varphi_c$  is identified with the glass transition which, in a colloidal suspension of hard spheres, is observed at  $\varphi_c^{\text{expt}} \approx 0.58$  [5]. In the experiment, the assumption to neglect the cut-off mechanisms mentioned in [1] is found to hold well [5]. Since the singularity at  $\varphi_c$  dominates  $D_L(\varphi)$ , one has to use the separation  $\sigma \equiv C(\varphi - \varphi_c)/\varphi_c$  as parameter. Taking  $\sigma(\varphi_F = 0.494) \approx -0.20$  from [5], we find  $D_L/D_0 \approx 0.085$ . With the predicted  $\alpha$ -scale universality [3] and Refs. [4–6], one estimates  $D_L/D_{\text{short}}^{\text{self}} \approx 0.074$  at  $\varphi_F$ . In Fig. 2 the mean square displacements  $W(t)$  show subdiffusive behavior at intermediate times as predicted by the MCT [3]. For  $\sigma \rightarrow 0$ , the trend of  $W$  to arrest  $W_c \approx 0.005d^2$  [4] and the asymptotic  $\alpha$ - and  $\beta$ -scaling laws of the MCT [3] appear more clearly. They are included in Fig. 2 with  $t_0 \approx 2.2 \times 10^{-3}d^2/D_0$  ( $t_0 \approx 2.5 \times 10^{-3}d^2/D_S^S$  from [4–6]).

The asymptotic laws of the MCT [3,4] remain useful for separations as large as  $\varphi_c - \varphi_F$  [5]. The findings in [1] can be understood from these asymptotes.

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- [1] A. V. Indrani and S. Ramaswamy, Phys. Rev. Lett. **73**, 360 (1994).
- [2] B. Cichocki and W. Hess, Physica (Amsterdam) **141A**, 475 (1987).
- [3] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992), and references cited therein.
- [4] M. Fuchs *et al.*, Phys. Rev. A **45**, 898 (1992).
- [5] W. van Meegen and S. M. Underwood, Phys. Rev. E **49**, 4206 (1994), and references cited therein.
- [6] W. van Meegen and S. M. Underwood, J. Chem. Phys. **91**, 552 (1989).