

## Comment on “Probing the Equilibrium Dynamics of Colloidal Hard Spheres above the Mode-Coupling Glass Transition”

In the Letter [1], Brambilla *et al.* claimed to observe activated dynamics in colloidal hard spheres above the critical packing fraction  $\varphi_c$  of mode-coupling theory (MCT). By performing microscopic MCT calculations, we show that polydispersity in their system shifts  $\varphi_c$  above the value determined by van Meegen *et al.* for less polydisperse samples [2], and that the data agree with theory except for, possibly, the highest  $\varphi$ .

Brambilla *et al.* performed dynamic light scattering (DLS) on particles with average diameter  $\bar{d} = 210$  nm, and size polydispersity  $\sigma_{\text{pol}} \approx 12.2\%$  [3,4]. They purport to measure  $g_1 = w\Phi_q^s(t) + (1-w)\Phi_q(t)$  at wave vector  $q = 5.25/\bar{d}$ , where  $\Phi_q(t)$  [ $\Phi_q^s(t)$ ] are the coherent [incoherent] intermediate scattering functions, and  $w \approx 0.8$ .

It is generally expected, that the relaxation time  $\tau$  increases with packing fraction  $\varphi$ . However, several pairs of measured  $\tau$  violate this requirement; see inset (a). Based on this, we estimate an error in  $\varphi$  of about  $\pm 0.002$ .

Using MCT, we calculated the (in-) coherent correlators of (for simplicity) monodisperse hard spheres at  $qd = 5.25$  in Percus-Yevick approximation following Ref. [5]. The mixing parameter  $w = 0.53$  and the short-time diffusivity  $D_s = 0.59 \mu\text{m}^2/\text{s}$  were fixed by matching the amplitude of the final and the rate of the initial decay, respectively. The fits in Fig. 1 result from varying the packing fraction  $\varphi^{\text{mct}}$  as shown in inset (b). The correlators close to  $\varphi_c$  are described well [6], polydispersity shifts the glass transition upwards by 4% to  $\varphi_c = 0.595$  [2], and the relation

between experimental packing fraction  $\varphi$  and its fitted value in MCT is linear within the afore estimated error. The linearization predicts a power-law divergence of the relaxation time,  $\tau \propto (\varphi_c - \varphi)^{-2.46}$ , which is compatible with the measured relaxation times; see inset (c).

Brambilla *et al.* interpret the scatter of the data around the theoretical lines above  $\varphi = 0.585$  as indication of activated processes not contained in MCT. We find that the MCT fit only fails to explain the final decay at the highest density. We base this on the uncertainty in the packing fraction,  $\Delta\varphi = 0.002$ , estimated beforehand.

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- [5] W. Götze and T. Voigtmann, Phys. Rev. E **67**, 021502 (2003); G. Foffi *et al.*, Phys. Rev. Lett. **91**, 085701 (2003).
- [6] Base lines were estimated as shown. Correlators in Ref. [1], whose plateau height was not matched to short-time data and where crossings exist due to experimental uncertainties in the short-time matching, were neglected.

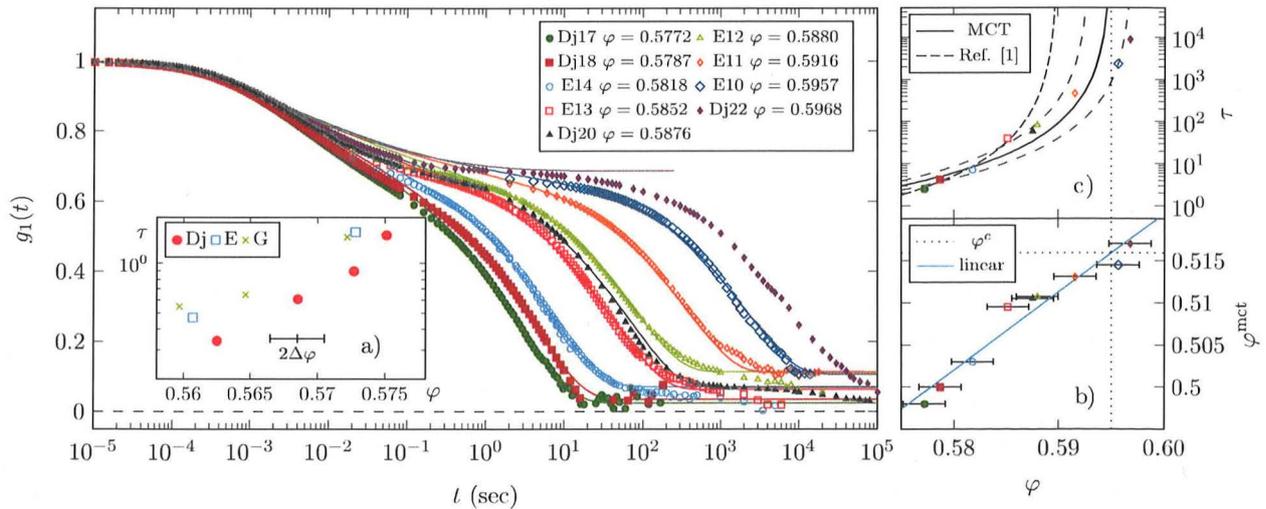


FIG. 1 (color online). Correlators from DLS [1] at packing fractions  $\varphi$  in two dilution series (abbr. Dj and E) and from MCT for fitted  $\varphi^{\text{mct}}$  given in inset (b). The fits lead to  $\varphi_c = 0.595$ , indicating that only Dj22 relaxes by activation not captured in MCT. The expected linear relation  $\varphi^{\text{mct}} - \varphi$  holds within errors, which are estimated as  $\pm \Delta\varphi = \pm 0.002$  from the nonmonotonous ordering of  $\tau - \varphi$  data (see inset a). The linear density relation gives a power-law divergence of  $\tau$  at  $\varphi_c$  (solid line in inset c), respectively, at  $\varphi_c \pm \Delta\varphi$  (dashed lines) accounting for the density uncertainty; the dot-dashed curve is reproduced from Ref. [1].