

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

In a recent Letter [1] and a subsequent more detailed account [2], Brambilla *et al.* report dynamic light scattering (DLS) measurements of the self-intermediate scattering function (ISF) of suspensions of particles with hard-sphere-like interactions. They claim, in apparent contradiction to previous studies on similar suspensions [3], that the sharp ergodic to nonergodic transition at a critical point ϕ_c , where according to the idealized mode-coupling theory (MCT) the α -relaxation time, τ_α , diverges algebraically, is avoided purportedly by a “new dynamical regime.” We question this interpretation and propose that the differences between the results of [1–3] can be explained by effects arising from differences in polydispersities of the particles used in the respective experiments, not considered by Brambilla *et al.*

The suspension in [3] has a polydispersity of 6%. It shows a first order transition and a glass transition (GT) at volume fractions $\phi_f = 0.494$ and $\phi_g = 0.57$, respectively, when referencing the observed equilibrium phase behavior to that of a one-component system of hard spheres. For $\phi < 0.57$, the ISFs of the colloidal “melt” phase decay to zero in the experimental time window. For $\phi > 0.57$, they do not, and any slow decays from the plateaux are, as stated, nonstationary: i.e., for $\phi > 0.57$, the suspension is not in equilibrium. Accordingly, $\phi_g = 0.57$ is identified as the location of the transition to non-ergodicity—the operational GT. Moreover, after fitting a power law to τ_α , the coincidence of ϕ_g and ϕ_c was found within experimental uncertainties. Unambiguous specification of τ_α is precluded for $\phi > \phi_c$ not, as suggested in [1,2], due to the intervention of crystallization, but because the final, slow decays of the ISFs depend on the waiting time. Widening the experimental time window would not alter these observations or inferences, a point ratified in recent work [4].

Brambilla *et al.* find, by fitting a power law to τ_α , a critical point at $\phi_c = 0.59$. They also find an operational GT at the higher value, $\phi_g \approx 0.6$. Between these two volume fractions, a new activated dynamical regime is exposed because, according to Brambilla *et al.*, τ_α deviates from the power law predicted by MCT. The polydispersity of the particles used by Brambilla *et al.* was nominally 10%. One effect of the larger polydispersity is to move the GT to a higher volume fraction. Indeed, previous DLS experiments [5] on binary mixtures of hard spheres and their analysis by MCT [6] show that increasing the polydispersity, by addition of a second component of smaller spheres while holding the total volume fraction fixed, effectively melts the putative glass.

The larger polydispersity may also, due to differential localization of the different species in the particle size distribution (PSD) [7], cause a deviation of τ_α from the algebraic divergence predicted by MCT for a one-component system. Here, we point out that the polydispersity estimated from cumulant analyses in [2] is not reliable. We can merely infer, since the first order transition is completely avoided, that the polydispersity is not likely to be less than 10% [8]. Moreover, detailed analyses of a variety of hard-sphere-like polymer particles, used in the experiments discussed here, show that the PSDs are always negatively skewed [9].

The ideal MCT does not contain any mechanism for ergodicity restoration of the (ideal) glass. But for $\phi_c < \phi < \phi_g$, the suspension of Brambilla *et al.* is still ergodic. So whatever the nature of the processes, observed in this range they are not excluded by MCT. We suggest that the anomalous volume fraction dependence of τ_α can be explained by MCT provided the (multi) components of the PSD are treated explicitly.

That nonstationary (aging) processes, i.e., processes that tend to restore ergodicity and round the sharp transition to an ideal glass, are present not only in molecular glass formers, but also in colloidal systems was first exposed in Ref. [3] and more recently in Ref. [10].

W. van Meegen

Department of Applied Physics,
Royal Melbourne Institute of Technology
Melbourne, Victoria 3000, Australia

Stephen R. Williams

Research School of Chemistry,
Australian National University
Canberra, ACT 0200, Australia

Received 11 May 2009; published 21 April 2010

DOI: 10.1103/PhysRevLett.104.169601

PACS numbers: 64.70.pv, 05.20.Jj

- [1] G. Brambilla *et al.*, *Phys. Rev. Lett.* **102**, 085703 (2009).
- [2] D. El Masri *et al.*, *J. Stat. Mech.* (2009) P07015.
- [3] W. van Meegen *et al.*, *Phys. Rev. E* **58**, 6073 (1998).
- [4] V. A. Martinez, G. Bryant, and W. van Meegen, *Phys. Rev. Lett.* **101**, 135702 (2008).
- [5] S. R. Williams and W. van Meegen, *Phys. Rev. E* **64**, 041502 (2001).
- [6] T. Voigtmann, *Phys. Rev. E* **68**, 051401 (2003).
- [7] J. Bosse and Y. Kaneko, *Phys. Rev. Lett.* **74**, 4023 (1995).
- [8] P. N. Pusey, *J. Phys. (Paris)* **48**, 709 (1987).
- [9] G. Bryant *et al.*, *Langmuir* **19**, 616 (2003).
- [10] W. van Meegen, V. A. Martinez, and G. Bryant, *Phys. Rev. Lett.* **102**, 168301 (2009).