Comment on "Glass Transition in Colloidal Hard Spheres: Mode-Coupling Theory Analysis"

van Megen and Underwood (VMU) [1,2] have used their dynamic light scattering data on hard colloidal spheres to test the validity of the simple mode-coupling theory (MCT). We question the validity of the test. In Fig. 3 of Ref. [1], VMU depict the characteristic time τ_β of what is interpreted as the β relaxation as a function of the particle volume fraction ϕ. A striking feature is that for ϕ larger than the glass transition value ϕ_g, their τ_β increases with decreasing ϕ, reaching a maximum at ϕ_g. When combined with the values determined from the analysis for ϕ less than ϕ_g, the plot of τ_β versus ϕ gives rise to a sharp cusp at ϕ_g. Since cusplike features are the most characteristic property of critical phenomena, the cusp reported by VMU has been proposed as strong supporting evidence for the applicability of the simple MCT. We see no evidence that τ_β in the glass increases with decreasing ϕ for $\phi > \phi_g$. We address this point.

The relaxation data $f(t,q,\phi)$ gathered by VMU for $\phi > \phi_g$ reach asymptotic values $f(\infty,q,\phi)$. Following their approach, we introduce a function $F(t,q,\phi) = f(t,q,\phi) - f_c(q)$, where $f_c(q) = f(\infty,q,\phi_g)$, and a function $C(\phi-\phi_c,q) = F(\infty,q,\phi)/h(q)$, where $\phi_c = \phi_g$ and $h(q)$ is a function calculated for hard spheres. Although f_c and ϕ_c should be experimentally determined, VMU treat them both as adjustable parameters and from considerations of only the asymptotes they adjust $f_c(q)$ and ϕ_c so that $C(\phi-\phi_c,q)$ is as nearly independent of q as possible.

To study the time dependence, one can define

$$K(t,q,\phi) = F(t,q,\phi)/h(q)C(\phi-\phi_c) - 1 .$$

This function is very flat and featureless over many orders of magnitude, from the longest times studied down to ill-defined cutoffs at which it begins to rise appreciably and to exhibit both q and ϕ dependence (see Fig. 5 of Ref. [1] and Fig. 8 of Ref. [2]). VMU are only interested in this flattish segment above the cutoffs, and so the resulting truncated $K(t,q,\phi)_{\text{trunc}}$ is *by construction* independent of q. VMU assume this truncated function to be of the form $K(t/\tau_\beta)_{\text{trunc}}$ where τ_β is a function of $\phi-\phi_c$, and the τ_β so determined, when plotted versus $\phi-\phi_c$, yields the lower part of the critical cusp discussed above. ϕ_c, $f_c(q)$ at each q, and a lower cutoff time at each ϕ all enter as adjustable parameters, a large number to fit flat and featureless segments of relaxation curves.

To illustrate the hazards of the VMU analysis, we have plotted in Fig. 1 two arbitrary stretched exponentials with the same relaxation time and the same stretching parameter, but with different asymptotes. We then scale them so that the asymptotes are identical and we scale the time so as to optimize overlapping of the two curves over times beyond some not quite well-defined lower cutoff time. [Think of these as $F(t,q,\phi)$'s with the same q, but different ϕ's; asymptote scaling corresponds to adjusting $F(t,q,\phi)/C(\phi-\phi_c)$ and time scaling corresponds to letting $t \to t/\tau_\beta$.] In this example, where we have explicitly introduced a relaxation time τ_β that is independent of ϕ, we obtain an apparent τ_β that decreases as ϕ increases, the result reported by VMU. [The actual procedure used by VMU scales the flat part of the MCT hard sphere calculations to the flat part of the experimental $K(t,q,\phi)$ curves, with arbitrary short time cutoffs; this is essentially equivalent to what we have outlined.]

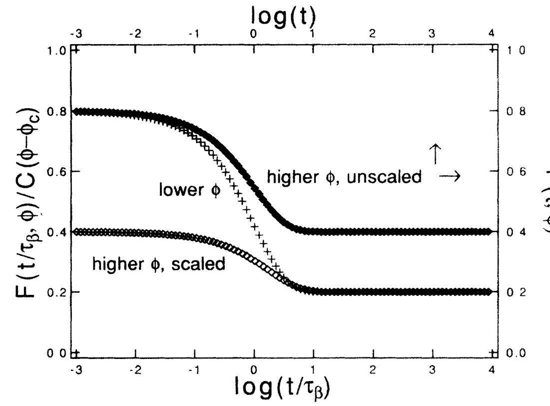

FIG. 1. Two relaxation functions, $F(t,\phi) = A\exp[-(t)^{0.8}] + (0.8-A)$, versus $\log(t)$ with (♦) $A=0.4$ (higher ϕ, deeper in glass) and (+) $A=0.6$. Also same functions scaled, $F(t/\tau_\beta,\phi)/C(\phi-\phi_c)$, versus $\log(t/\tau_\beta)$ with (◇) $C=2$ and $\tau_\beta=0.59$ for the first (higher ϕ), and (+) $C=1$ and $\tau_\beta=1$ for the second.

In conclusion, we believe that there are no grounds for assuming that the truncated $K(t,\phi)_{\text{trunc}}$, i.e., the featureless long time tail of a "fast" process, can be used to determine τ_β, for assuming that for $\phi > \phi_g$ the time τ_β increases with increasing ϕ, and more specifically that τ_β varies as $(\phi-\phi_g)^{-a}$.

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Xiao-Chen Zeng and Daniel Kivelson
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

Gilles Tarjus
Laboratoire de Physique Theorique des Liquides
Universite Pierre et Marie Curie
4, Place Jussieu
75252 Paris Cedex 05, France

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[2] W. van Megen and S. M. Underwood, Phys. Rev. E **47**, 248 (1993).

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