Comment on "Viscosity and Structural Relaxation in Suspensions of Hard-Sphere Colloids"

Recently Segrè *et al.* [1] measured the basic Newtonian viscosity $\eta(\phi)$ as a function of the volume fraction ϕ of a suspension of neutral PMMA spheres in a *cis*-decalin solvent with viscosity η_0 over the entire fluid range. They obtain values for the relative viscosity $\eta_r(\phi) = \eta(\phi)/\eta_0$ which differ very significantly (up to 100%) from those found in the literature [2, 3].

Here we argue that this is due to their procedure to determine ϕ, which is at variance with established results from experiment [4], molecular dynamics computer simulations [5], and theory [6].

Segrè *et al.* determine the ϕ for all their measurements by normalizing all of them to one $\phi = \phi_F$, at which they observe their suspension freeze, setting *ad hoc* $\phi_F = 0.494$, the theoretical value for freezing of a pure hard sphere fluid. Leaving aside the question of the identity of a monodisperse hard-sphere colloidal suspension and a pure hard-sphere fluid and whether the PMMA particles used by Segrè *et al.* are really hard spheres [7], their suspensions exhibit a polydispersity $p \approx 0.05$, i.e., 5%. Experiments [4], molecular dynamics computer simulations [5], and density functional theory calculations [6] all show that the ϕ_F for colloidal suspensions is a sensitive function $\phi_F(p)$ of p, with $\phi_F(0) = 0.494$ at best a lower bound at freezing. In fact, $\phi_F(0.05)$ is significantly larger (5%–10%) than $\phi_F(0)$ [5, 6] and for $p \geq 0.08$ there is no freezing at all, at least up to $\phi = 0.60$ [4–6].

All this strongly suggests that Segrè *et al.*'s results for $\eta_r(\phi)$ must be reinterpreted using a value of ϕ_F which is about 5%–10% larger than $\phi_F(0) = 0.494$. In Fig. 1 we have done so using $\phi_F(0.05) = 0.53$. Then their $\eta_r(\phi)$ values agree very well with those of Van der Werff *et al.* [2] obtained for three different suspensions of silica spheres in cyclohexane, which can be considered benchmark measurements, since seven different experimental techniques were used to obtain ϕ [8]. They also agree then very well with the measurements on silica suspensions by Jones, Leary, and Boger [3], as well as with the $\eta_r(\phi)$ calculated theoretically for hard sphere colloids [9].

Obviously, independent *experimental* determinations of ϕ for the PMMA suspensions are needed before one can be confident that Segrè *et al.*'s renormalized $\eta_r(\phi)$ indeed agree with those obtained by Van der Werff *et al.* for their silica suspensions.

We acknowledge very helpful discussions with J. Mellema, J. K. G. Dhont, and especially C. G. de Kruif. E. G. D. C. acknowledges support by DOE Grant No. DE-FG02-88-ER13847 and R. V. by the Netherlands Foundation for Fundamental Research of Matter (FOM).

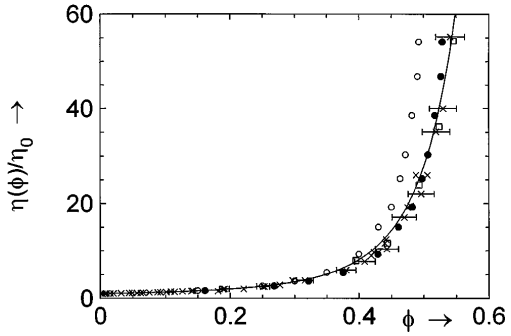

FIG. 1. $\eta_r(\phi) \equiv \eta(\phi)/\eta_0$ as a function of ϕ: Van der Werff *et al.* [2] (×) (with 4% experimental ϕ uncertainty); Jones *et al.* [3] (□); Segrè *et al.* [1] (○: with $\phi_F = 0.494$), (●; with $\phi_F = 0.53$); colloid theory [9] (—).

I. M. de Schepper,[1] E. G. D. Cohen,[2] and R. Verberg[1]
[1]IRI, Delft University of Technology
2629JB, Delft, The Netherlands
[2]The Rockefeller University
New York, New York 10021

Received 27 November 1995 [S0031-9007(96)00567-4]
PACS numbers: 82.70.Dd, 83.10.Pp

[1] P. N. Segrè, S. P. Meeker, P. N. Pusey, and W. C. K. Poon, Phys. Rev. Lett. **75**, 958 (1995).
[2] J. C. Van der Werff, C. G. de Kruif, C. Blom, and J. Mellema, Phys. Rev. A **39**, 795 (1989); J. C. Van der Werff and C. G. de Kruif, J. Rheol. **33**, 421 (1989).
[3] D. A. R. Jones, B. Leary, and D. V. Boger, J. Colloid Interface Sci. **147**, 479 (1991); **150**, 84 (1992).
[4] P. N. Pusey, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991), p. 803.
[5] I. Moriguchi, K. Kawasaki, and T. Kawakatsu, J. Phys. II (France) **3**, 1179 (1993).
[6] R. McRae and A. D. J. Haymet, J. Chem. Phys. **88**, 1114 (1988).
[7] W. J. Feith, J. Mewis, and T. A. Strivens, Powder Technol. **51**, 27 (1987).
[8] C. G. de Kruif, J. W. Jansen, and A. Vrij, in *Physics of Complex and Supermolecular Fluids*, edited by S. A. Safran and N. A. Clark (Wiley, New York, 1987), p. 315. We are not aware of any other experiments for which the values of ϕ have been tested so carefully.
[9] I. M. de Schepper, H. E. Smorenburg, and E. G. D. Cohen, Phys. Rev. Lett. **70**, 2178 (1993); E. G. D. Cohen and I. M. de Schepper, in *13th Symposium on Energy Engineering Sciences* (Argonne National Laboratory, Argonne, IL, 1995); E. G. D. Cohen and I. M. de Schepper, Phys. Rev. Lett. **75**, 2252 (1995).

 0031-9007/96/77(3)/584(1)$10.00