

Segrè *et al.* Reply: de Schepper, Cohen, and Verberg [1] do not question the main result of our Letter [2], that the inverse rate of structural relaxation of a colloidal suspension shows the same dependence on concentration as its low-shear-rate viscosity. They do, however, raise valid questions concerning the volume fractions of the suspensions.

It is perhaps surprising that one of the main experimental difficulties in colloid physics is the accurate determination of volume fraction. Weight fractions c , in terms of dry weight of the colloidal particles per unit weight of liquid, can be measured precisely. Conversion of weight fraction to volume fraction ϕ requires knowledge of the particles' density. Frequently this is uncertain. For example, the particles may be somewhat porous and have a different effective density from the bulk material. In the case of sterically stabilized particles, the polymer coating is usually solvated to an unknown degree, affecting the density of the composite particle. Two main methods have been used to circumvent this difficulty. One popular method [3–8] is to measure a property, usually the viscosity, of dilute suspensions as a function of weight fraction; comparison with theoretical predictions for the volume-fraction dependence of the property then allows conversion of weight to volume fractions. The other, used by us [2], is to exploit the freezing transition as a high-concentration “marker.”

Einstein's result for the viscosity η of a suspension, $\eta = \eta_0(1 + 2.5\phi + \dots)$, where η_0 is the viscosity of the liquid, can be written $\eta = \eta_0(1 + 2.5qc + \dots)$; measurements of η as a function of weight fraction c , fitted by this expression, yield the inverse particle density q from which the volume fraction $\phi = qc$ can be calculated. There are two related problems associated with this method. First, the quadratic term in ϕ must be considered, $\eta = \eta_0(1 + 2.5\phi + 5.9\phi^2 + \dots)$ [9]. If actual data are fitted by the linear expression (omitting the quadratic term), as was done in [3–8], it is not difficult to show that q , and therefore ϕ , is overestimated by the factor $1 + 2.36\phi_{\max}$, where ϕ_{\max} is the largest volume fraction at which measurements are made. Thus a systematic overestimate of 7% is made even if ϕ_{\max} is as small as 0.03. Second, for $\phi_{\max} < 0.05$, say, where $\eta/\eta_0 < 1.14$, there is inevitably a significant random error in the derived ϕ , even with very precise measurements of η and c . We conclude that in [3–8] ϕ was probably overestimated by several percent.

de Schepper *et al.* rightly point out that, in associating the observed freezing volume fraction ϕ_F of our samples with the hard-sphere computer value 0.494, we neglected possible effects of the polydispersity, $\sim 5\%$, of the particles. Here the situation is somewhat confused. Two calculations [10, 11], based on density functional theory, give different predictions and do not reproduce exactly the computer results for a monodisperse system. The com-

puter simulations of [12] were for soft spheres which froze at $\phi \sim 0.38$ and are therefore not directly relevant. Nevertheless, the existing evidence does suggest that the effect of 5% polydispersity is to increase ϕ_F by maybe 3%, so that the volume fractions we quoted may be underestimated by this amount.

As Fig. 1 of [1] shows, our data are not inconsistent with earlier work if the volume fractions ϕ are scaled relative to each other by a few percent, as suggested by the arguments above. However, some uncertainty in the actual value of ϕ remains. Furthermore, none of the studies have considered possible effects of sample polydispersity on viscosity at a well-defined volume fraction. Nevertheless, it seems likely that the relative low-shear-rate viscosity $\eta_r = \eta/\eta_0$ of an ideal suspension of monodisperse hard spheres at $\phi = 0.494$ is greater than the ~ 20 of [3] but somewhat smaller than our ~ 50 [2].

Finally we point out that the theory of de Schepper, Smorenburg, and Cohen [13], which predicts $\eta_r(0.494) \sim 20$, neglects hydrodynamic interactions and therefore almost certainly underestimates viscosity.

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