

## Response to “Comment on ‘The viscoelastic response of Brownian suspensions’” [J. Chem. Phys. 114, 3339 (2001)]

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In this comment, Felderhof highlights several interesting points raised by our computer simulation results for the viscoelastic response of a simple model colloidal suspension.<sup>1</sup> In the model, the particles making up the suspension are hard spheres diffusing independently while simultaneously undergoing direct collisions with each other. The complex many-body hydrodynamic interactions between the particles, that are present in a real suspension, are not explicitly included. Their effect only enters, in a simplified and indirect manner, if we interpret the diffusion coefficient, characterising the diffusive motion of the particles between collisions, as the short time diffusion coefficient. In such a way, the additional friction experienced by particles, due to the presence of their neighbors, is captured in an approximate fashion. Our central aim was to establish just how good this model is. Despite its simplicity, it forms the basis for theories which predict a viscoelastic response that is in remarkably good agreement with experiment.<sup>2,3</sup> This would suggest that the model is quite adequate, thus providing a convenient means for predicting, either theoretically or numerically, the long time properties of suspensions. However, in order to obtain analytic results for the simple model further simplifications are required. Our results showed that the reason these theories agree with experiment is because, having made these further approximations, they fail to describe the model itself. Thus the agreement between theories based on the model and experiment is fortuitous. The model itself is quite a poor representation of reality.

In our paper, we made a comparison with the mode-coupling theory of Verberg *et al.*<sup>3</sup> Their approach basically involves substituting a wave vector,  $k$ , and volume fraction,  $\phi$ , dependent “cage” diffusion coefficient,  $D_c(k, \phi)$ , into the two particle Smoluchowski equation, valid at low densities. The cage diffusion coefficient they approximate by analogy with the hard sphere fluid. The precise form is given in Eq. (13) of Ref. 3. Having done so, the result they obtain for the Brownian contribution to the viscosity,  $\eta_B$ , can be expressed as a Padé approximation,

$$\eta_B = \frac{k_B T}{3\pi D_0 \sigma} \left[ \frac{1.44\phi^2 g(\sigma)^3}{1 - 0.1241\phi + 10.46\phi^2} \right], \quad (1)$$

where  $g(\sigma)$  is the radial distribution at contact,  $\sigma$  is the particle diameter,  $T$  is the temperature, and  $k_B$  is Boltz-

mann’s constant. In order to compare this with our numerical simulations, we need to relate the Stokes–Einstein diffusion coefficient appearing in Eq. (1) to the diffusion coefficient characterizing the motion of the particles in our model system,  $D_{in}$ . In their paper,<sup>3</sup> Verberg *et al.* do not specifically interpret the diffusion coefficient appearing in the Smoluchowski equation as the short time diffusion coefficient until, in Sec. VI, they consider the high frequency viscoelastic response. In the basic equations, outlined in Sec. II of Ref. 3, the diffusion coefficient appearing is clearly the Stokes–Einstein value [Eq. (9)]. Thus, our interpretation of the theory is that  $D_{in} = D_0$  and on this basis we made our comparison. However, in order to construct a solution to the Smoluchowski equation valid at higher densities, Verberg *et al.* substitute their cage diffusion coefficient. For large wave vectors this is constructed to have a value  $D_0/g(\sigma)$ , coinciding with the approximation they later make for the short time diffusion coefficient. Thus if we matched the large wave vector diffusion coefficient to the the diffusion coefficient in the model we would have  $D_{in} = D_0/g(\sigma)$ . Substituting this in Eq. (1) gives a result of the form Felderhof suggests as appropriate. We did not make this interpretation because Verberg *et al.* stated that the cage diffusion process applies for times the order of the Péclet time scale. That is, the time scale on which particles collide with each other. It is meant to take into account the effect of these collisions hindering particle motion. On the other hand, our input diffusion coefficient,  $D_{in}$ , characterizes the motion of the particles on the much shorter Brownian time scale. This is well before there are any particle collisions and, we concluded, well before cage diffusion is relevant. We would agree that there is at least some scope for ambiguity in interpreting the mode-coupling theory. In the interests of brevity this point was not discussed in Ref. 1. Nonetheless, as Felderhof points out, if we use either result of the theory it fails at high volume fractions. With our interpretation, that  $D_{in} = D_0$ , the theory does give good results at low volume fraction.

Turning to the high frequency response calculated from the simulations, at low volume fractions we found agreement with the result derived by Cichocki and Felderhof.<sup>4</sup> This was the case in either the frequency domain or time domain. As we pointed out, this is surprising because even the lowest volume fraction studied in our simulation work does not cor-

respond to the limit of zero volume fraction considered by Cichocki and Felderhof. The radial distribution function at contact is significantly different from unity. Verberg *et al.*<sup>5</sup> argue that the Cichocki and Felderhof result should be multiplied by a factor of  $g(\sigma)$  and that this result is then exact. Our statement that no factor of  $g(\sigma)$  was required at low volume fractions was somewhat misleading. We should more accurately have stated that neglecting the factor of  $g(\sigma)$  gave a better approximation to the simulation results under these conditions. It was clear from the results at higher densities that it could not be concluded that the low density result simply applies at any volume fraction. Thus a correction is required but, as Felderhof points out, even at a volume fraction of 10% the required multiplying factor is not simply equal to the radial distribution function at contact. This contradicts the theory of Verberg *et al.* The origin of this dis-

crepancy is the subject of ongoing research. We conclude by concurring with Felderhof that, despite the simplicity of the model we studied, current theories for the viscoelastic response over the full range of volume fractions are seriously inadequate. More simulations and new theoretical insights are indeed required before we can claim a complete understanding of the dynamic processes giving rise to the observed viscoelastic response.

<sup>1</sup>C. P. Lowe and A. J. Masters, J. Chem. Phys. **111**, 8708 (1999).

<sup>2</sup>J. F. Brady, J. Chem. Phys. **99**, 567 (1993).

<sup>3</sup>R. Verberg, I. M. de Schepper, and E. G. D. Cohen, Phys. Rev. E **55**, 3143 (1997).

<sup>4</sup>B. Cichocki and B. U. Felderhof, Phys. Rev. A **43**, 5405 (1991).

<sup>5</sup>R. Verberg, I. M. de Schepper, M. J. Feigenbaum, and E. G. D. Cohen, J. Stat. Phys. **87**, 1037 (1997).