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Response to "Rotational velocity autocorrelation function of interacting Brownian particles"

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In their paper, Cichocki and Felderhof re-analyse our numerical data for the angular velocity autocorrelation function (AVACF), $C_R(t)$, for colloidal hard spheres [1] in a concentrated suspension. They treat the normalized correlation function as a response function $\gamma_R(\tau)$, where $\tau = t/\tau_M$ and τ_M is the integral over all times of the normalized AVACF. For a single colloidal sphere, the Laplace transform of $\gamma_R(\tau)$ can be calculated analytically [2]. The denominator can be written in terms of the transform variable and the inverse of a polynomial involving the square root of the transform variable. In the time domain, the latter gives rise to the long time behaviour of the correlation function. Cichocki and Felderhof make the ad hoc approximation that, in a suspension, the Laplace transform of the AVACF takes a similar form. However, the inverse polynomial is replaced by the ratio of two polynomials whose coefficients are treated as adjustable parameters. They determine these parameters by fitting to our numerical data. At zero frequency their relaxation function is constructed to have a value of unity. In the time domain, this means that the integral over time of their fit is constrained to be equal to τ_M. Their fitting procedure therefore requires a value for τ_M as input. This value can nonetheless be calculated from the numerical data. Having carried out this procedure, Cichocki and Felderhof's fit appears rather poor at short times ($t < 20$), but adequately describes our data over the remainder of the time interval we studied. However, their method suggests that, at longer times than those simulated, the decay of the correlation function is somewhat different to that postulated by ourselves.

Before we address this substantive point, let us address the question of the integral of the normalized correlation function, τ_M. This, as Cichocki and Felderhof point out, is related to the rotational diffusion coefficient D_R. For this particular volume fraction (ϕ=0.2), we quoted a value of D_R=0.85D_R^0, with an upper limit of 4% for the numerical error. Here D_R^0 is the Debye–Einstein rotational diffusion coefficient, valid in the dilute

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limit. This corresponded to the value $\tau_M = 6.85$ in the lattice units defined in Ref. [1]. For their fit, Cichocki and Felderhof utilize the value $\tau_M = 7.235$, corresponding to $D_R = 0.88 D_R^0$. They arrive at this value by integrating the data from Fig. 5 of Ref. [1] and adding a small correction, based on their extrapolation, to account for the remainder of the integral. This discrepancy does not reflect an error in our analysis, just some subtlety. In the lattice Boltzmann method colloidal particles collide with solvent particles at discrete integer times. We cannot distinguish between the case where solvent/colloid particle collisions occur just after our time origin or just before. Both cases should of course carry equal weight so we average over the two. This is how we arrived at our value for τ_M. At long times, the difference between the correlation function calculated using the two time origins is insignificant compared to the statistical error. The data plotted in Fig. 5 of our article, being intended to illustrate the long-time behaviour of the correlation function, correspond to only the latter choice of time origin.

Turning to the comparison between Cichocki and Felderhof's fit and our interpretation of our data, there seem to be two notable points. Firstly, their fit seems very poor at short times ($t < 20$). Examining Fig. 3 of their paper, in this regime the fit appears to overestimate the correlation function by a factor of up to 50%. Because of the way the correlation function is plotted (multiplied by $t^{5/2}$) this seems rather unimportant. However, $C_R(t)$ has its maximum at $t = 0$ and over half the total integral of $C_R(t)$ comes from the range $t = 0$–20. Given that Cichocki and Felderhof's data substantially overestimate $C_R(t)$ in this region, and at no subsequent point appears to underestimate it, this is hard to reconcile with the fact that, by construction, their fit should have the same integral as the correlation function we calculated numerically.

Turning to longer times, Cichocki and Felderhof's fit, when extrapolated to times longer than those covered by the simulations, predicts an asymptotic decay of the form $C_R(t) \sim t^{-5/2}$. The same asymptotic "long-time tail" is found in the dilute limit. On this point our analyses coincide. However, their analysis suggests that the asymptotic decay adequately describes the data at shorter times than our analysis suggested and that the constant of proportionality (henceforth referred to as the tail coefficient) is greater than the value we estimated. If one assumes that at long times the suspension behaves as an "effective fluid", that is, as a Newtonian fluid with the viscosity of the suspension, the tail coefficient can be calculated analytically (by analogy with the single particle result). Although the theoretical analysis of Cichocki and Felderhof predicted a long-time tail in the velocity autocorrelation function independent of volume fraction [3,4], for the translational case the consensus of experimental [5], theoretical [6] and computer simulation [7] studies is that this is a sound hypothesis. Addressing first the time-scale on which the asymptotic decay is observed, effective fluid behaviour is only to be expected for long times compared to the time it takes hydrodynamic interactions between colloidal particles to propagate. For particles of radius a, it takes transverse momentum a time $\tau_\nu = a^2/\nu$, where ν is the kinematic viscosity of the solvent, to diffuse a distance the order of a particle radius. Since hydrodynamic interactions propagate by the diffusion of momentum between particles, one only expects effective fluid behaviour for

times $t/\tau_v \gg 1$. The data in our paper extend to times $t/\tau_v \sim 3$. Thus, whereas Cichocki and Felderhof state that in our analysis the asymptotic decay appears at "surprisingly long" times, we do not find it surprising. Indeed, a detailed analysis of the velocity autocorrelation function led to the same conclusion for the case of translational motion [7].

If we now consider the tail coefficient, then, on the basis of our extrapolation, we find an agreement with the analytic "effective fluid" value. It is clear, however, that this will depend on the functional form one assumes for the correlation function at times longer than those we studied. This point is emphasized by the fact that Cichocki and Felderhof's value is substantially greater than our own. It is thus true to say that our data are *consistent* with effective fluid behaviour but do not prove it. As Cichocki and Felderhof point out, this question can only be resolved by extending the time range covered by the simulations. However, whereas our data are consistent with effective fluid behaviour, Cichocki and Felderhof's fit is not. Making the effective fluid assumption, their value for the tail coefficient corresponds to a suspension viscosity $\eta(\phi)$ that is lower than the known value ($\eta(\phi)/\eta_0 = 1.64$ as opposed to $\eta(\phi)/\eta_0 = 1.81 \pm 0.02$ [8], where η_0 is the solvent viscosity). Cichocki and Felderhof state that, given the errors in the simulation, this is reasonable. We do not agree. The statistical errors in the simulation are very small by comparison. Thus, the only explanation would be a significant systematic error in the simulation data. There is no reason to believe that any such error exists. As pointed out in Ref. [1], at this volume fraction the value we obtained for the rotational diffusion coefficient is in agreement with theory, experiment and independent computer simulations. Furthermore, using the identical model one obtains, by independent means, an accurate value for the suspension viscosity [9]. Thus, the discrepancy cannot be ascribed to the model underestimating the suspension viscosity.

In summary, Cichocki and Felderhof's paper raises one substantive point; how well can their ad hoc approximation to the response function describe the AVACF in a concentrated suspension of hard spheres? For the time interval we studied numerically, the answer appears to be not very well at short times but adequate at intermediate times. For longer times it describes the response correctly only if the effective fluid picture is incorrect or if there is a systematic error in the simulation data. We have no reason to believe that either of these statements is correct.

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