Comment on "Scaling of Transient Hydrodynamic Interactions in Concentrated Suspensions"

In a recent experiment, Zhu *et al.* [1] deduced for the first time the velocity autocorrelation function $R(t,\phi)$ of a (tagged) Brownian particle with radius a in a suspension of identical particles for volume fractions $0.02 < \phi < 0.3$ on the short (viscous) time scale $t_\nu^0 = a^2/\nu_0$, where ν_0/ρ is the kinematic viscosity of the pure solvent with mass density ρ and viscosity η_0. For all ϕ and $0.1 t_\nu^0 < t < 100 t_0^\nu$, they fitted $R(t,\phi) = C(\phi) R_H(t/t_\nu(\phi))$ (1) with $C(\phi)$ and $t_\nu(\phi)$ as adjustable parameters and used Hinch's $R_H(t/t_\nu)$ [1] for a single Brownian particle in a fluid with $t_\nu = a^2/\nu$ [1]. Zhu *et al.* noted that $\eta_s^{\mathrm{eff}}(\phi) = \rho a^2/t_\nu(\phi)$ is a short time effective viscosity for suspensions when the nontagged particles do not move, while the self-diffusion coefficient $D_s(\phi) \equiv \int_0^\infty dt\, R(t,\phi) = C(\phi) D_s^E(\phi)$, where $1 \le C(\phi) \le 1.2$ and $D_s^E(\phi)$, rather than $D_s(\phi)$, obeys Einstein's relation $D_s^E(\phi) = k_B T/6\pi\eta_s^{\mathrm{eff}}(\phi) a$. Moreover, they wonder why (1) holds down to $t \approx t_\nu^0/2$, where $R(t,\phi)$ should be independent of ϕ, since the vorticity associated with the tagged particle motion cannot have diffused far enough to be disrupted by the neighbors.

We propose that these two apparent contradictions can be resolved by considering, on the appropriate small time scale $t/t_\nu^0 < 1$, (instantaneous) thermodynamic forces arising from the canonical distribution of the Brownian particles, as expressed by the hard sphere radial distribution function at contact $\chi(\phi) = (1 - \phi/2)(1 - \phi)^{-3}$, in the Carnahan-Starling approximation [2]. Then $D_s^E(\phi) = D_0/\chi(\phi)$ with $\chi(\phi) = 1 - 2.5\phi + O(\phi^2)$, instead of Batchelor's $D_s(\phi) \cong D_0(1 - 1.83\phi)$ [2] (2) as Zhu *et al.* find, and $\eta_s^{\mathrm{eff}}(\phi) = \eta_0\chi(\phi)$ for $0 < \phi < 0.6$ within experimental accuracy (cf. Fig. 1). However, (2) is derived from the correlated hydrodynamic motion of *two* Brownian particles for times $t \gg t_\nu^0$, when the surrounding particles can no longer be considered fixed. If a fit of $R(t,0)$ is made with $C(\phi) \equiv 1$ and only for $t \ll 100 t_\nu^0$, Einstein's relation for $D_s(\phi) \equiv D_s^E(\phi)$ and $\eta_s^{\mathrm{eff}}(\phi)$ is found [3]. Therefore, Zhu *et al.*'s experiment suggests the relevance of the thermodynamic force

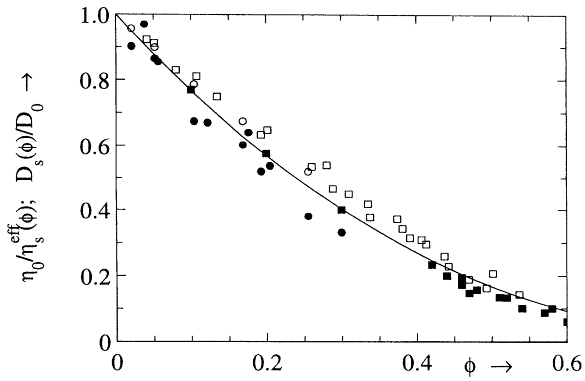

FIG. 1. Experiments $\eta_0/\eta_s^{\mathrm{eff}}(\phi)$: (•) Zhu *et al.* [1]; (□) Van der Werff *et al.* (Ref. [17] in [1]). $D_s(\phi)/D_0 \equiv D_s^E(\phi)/D_0$: (○) Zhu *et al.* [1]: (□) Van Megen *et al.* (Ref. [11] in [1]). Theory: $1/\chi(\phi)$, solid line.

$\chi(\phi)$ and of Einstein's relation, whenever the background fluid is passive and the nontagged particles are effectively trapped, i.e., also for very concentrated suspensions $0.4 < \phi < 0.6$, as is indeed confirmed in Fig. 1.

E. G. D. Cohen[1] and I. M. de Schepper[2]
[1]The Rockefeller University
New York, New York 10021

[2]Interuniversitair Reactor Instituut, Technical University
2629 JB Delft, The Netherlands

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