Microstructural theory and rheology in very concentrated Brownian suspensions

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A microstructural theory for concentrated Brownian colloidal suspensions is developed and applied to predict the macroscopic shear rheology, as well as active microrheology, of these mixtures. The discussion will focus on the shear-flow problem for hard spheres, but will outline the results for shear flow of suspensions of particles interacting through soft repulsive potentials, as well as active microrheology (where one particle is pulled through an otherwise quiescent bath). For the first time, a theory is available which applies for solid volume fractions up to $\phi = 0.5$, and for near equilibrium to hydrodynamically dominated conditions, i.e. over a very wide range of the Peclet number, $Pe = 6\pi\eta\dot{\gamma}a^3/kT$; here η is the fluid viscosity, $\dot{\gamma}$ is the shear rate, a is the particle radius, k is the Boltzmann constant and T is the absolute temperature.

The theory is based upon the Smoluchowski equation for the configuration of the dispersion, reduced to the pair level to describe the pair distribution function g(r). The novelty lies in de- veloping the pair Smoluchowski equation as an integro-differential equation, in which the integral aspect arises in order to capture the many-body nature of the problem. The integrals appear as coefficients which represent self-consistently two crucial aspects of the bath particles: first is the forcing of pairs toward contact by the bath, and second is the tendency for a third particle to be in the space intervening between the pair. The forcing toward contact results in the well-known flow-driven accumulation of pair probability at contact, while the fact that a particle may intervene propagates the correlation to large distances. These features are sufficient to capture the role of excluded volume in a hard-sphere suspension, showing not only correlation at contact but also long-range correlation in the form of a next-nearest neighbor ring. The results of the theory agree well with slight perturbations from equilibrium structure, and thus reproduce integral equation approaches in the limit of very small Pe, and agree with microstructure obtained by sampling from Accelerated Stokesian Dynamics simulation for $1 < Pe < 200$. It is shown that the inclusion of a shear-induced diffusion is essential to the theory for hard-sphere suspensions. Imposition of flow results in a progressively more anisotropic structure near contact of the pair as Pe increases, and the viscosity and normal stresses respond to the microstructural changes.The shear thinning and thickening of the suspension viscosity are qualitatively in agreement with simulation and experi- mental observations, with satisfactory quantitative agreement. Similar levels of agreement are seen for the normal stress differences.

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