Nonlinear Rheology and Flow-Induced Structure in a Concentrated Spherical Silica Suspension

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In hard-sphere suspensions of solid particles, the stress has the Brownian (thermodynamic) and hydrodynamic components σ_B and σ_H, the former reflecting the anisotropy of the particle distribution while the latter being determined by the hydrodynamic interaction between the particles. These two components exhibit nonlinearities under steady shear flow with different mechanisms. The nonlinearity of σ_B results from the particle distribution insensitive to the shear rate, while σ_H becomes nonlinear due to flow-induced clustering of the particles. These structural origins of the nonlinearities were confirmed from flow-SANS experiments.

Keywords: hard-sphere suspension/ Brownian stress/ hydrodynamic stress/ shear-thinning/ shear-thickening/ small angle neutron scattering

Hard-sphere suspensions of solid particles having no long-ranged potentials provide a rich field in current rheological research. At equilibrium, the particles have a liquid-like, isotropic spatial distribution. On application of strain/flow, this distribution is distorted and the particles exhibit stresses having Brownian and hydrodynamic components σ_B and σ_H [1]. Under small strain/slow shear flow, the particle distribution is only slightly distorted to exhibit the linear viscoelasticity, i.e., increases of σ_B and σ_H in proportion to the strain (γ) and/or shear rate ($\dot{\gamma}$). Large strains/fast flow considerably distort the particle distribution thereby inducing nonlinearities of σ_B and σ_H.

Recently, we investigated nonlinear rheological behavior of a concentrated hard-sphere suspension of monodisperse silica particles in an ethylene glycol/glycerol mixture (2.27/1 wt/wt) [2]. The particle radius was 40 nm, and the particle concentration was 50 wt%. For large step strains γ, the nonlinear relaxation modulus $G(t,\gamma)$ of this suspension exhibited strong damping and obeyed the time-strain separability at long times. This damping, seen under absence of flow and not attributable to changes in the hydrodynamic σ_H, was related to the nonlinearity of the Brownian σ_B. Under flow, the same suspension showed thinning and thickening of the viscosity $\eta(\dot{\gamma})$ at low and high $\dot{\gamma}$.

Structural origins of these thinning and thickening were examined through a rheological approach that uti-

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Scope of research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.

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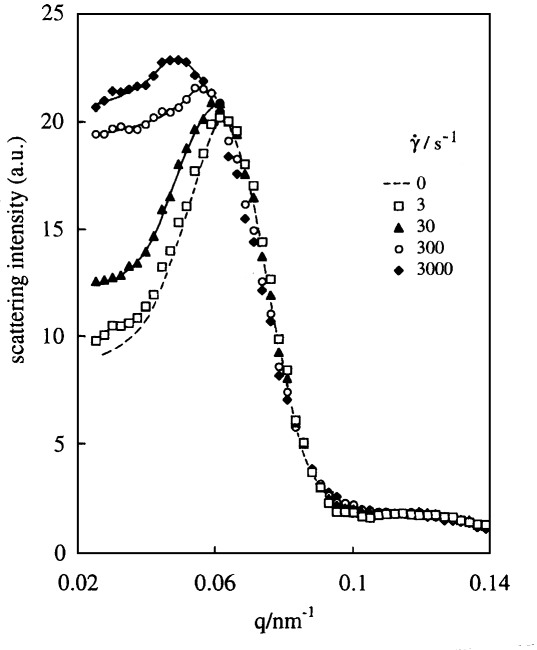

Figure 1. Scattering profile of the silica suspension at 25 ˚C detected along the velocity direction in the velocity-vorticity plane.

lized a BKZ-type constitutive equation incorporating the G(t,γ) data [2]. This equation successfully described the $\eta(\dot{\gamma})$ data in the thinning regime. Thus the thinning of $\eta(\dot{\gamma})$ and damping of G(t,γ) were commonly attributed to the nonlinearity of σ_B due to γ- and $\dot{\gamma}$-insensitive particle distribution under moderately large strain/flow [2].

In contrast, the BKZ equation failed in describing the $\eta(\dot{\gamma})$ data in the thickening regime [2]. From this result, the thickening was related to the nonlinearity of σ_H not incorporated in the equation. This nonlinearity was attributed to dynamic clustering of the particles under the flow faster than the Brownian motion of the particles.

Neutron scattering experiments were carried out for the suspension under flow to test the above structural arguments for the thinning/thickening behavior [3]. The experiments were conducted with the 30 m SANS machine on the NG3 beam line at the National Institute of Standards and Technology (NIST) at Gaithersburg, Maryland, USA, with a generous help by Prof. N. Balsara at Polytechnic University and Dr. B. Hammouda at NIST. Figure 1 shows the scattering profile at 25 ˚C detected along the velocity axis in the velocity-vorticity plane (radial view). The corresponding $\eta(\dot{\gamma})$ data are shown in Figure 2.

As seen in Figure 1, the suspension in the quiescent state ($\dot{\gamma}$ = 0 s^{-1}) exhibits a peak at the scattering vector q ≅ 0.06 nm^{-1}. This peak corresponds to the liquid-like, nearest neighbor order of the particles in this state. (This

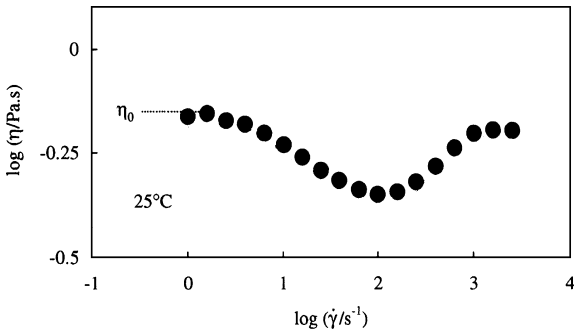

Figure 2. Steady state viscosity of the silica suspension at 25˚C. (The data were obtained in the Couette geometry.)

scattering profile was isotropic). In the shear-thinning regime ($\dot{\gamma}$ < 100 s^{-1}; Figure 2), the scattering profile is distorted from this quiescent profile only a little. Small, corresponding changes were observed in the vorticity as well as shear gradient directions. Thus the particle distribution is rather insensitive to the flow in this regime, lending support to the thinning mechanism explained earlier.

In contrast, in the thickening regime ($\dot{\gamma}$ > 100 s^{-1}; Figure 2), the scattering profile in the velocity direction is largely distorted. Specifically, the peak shifts to a lower q side and increases its intensity, indicating that large clusters of the particles are formed under the flow in this regime. Changes in the profiles detected in the other directions suggested that the clusters of anisotropic shape were formed. (A detailed analysis of this cluster structure was described in [4].) The quiescent profile was recovered in all directions on cessation of the flow, demonstrating the dynamic (non-permanent) nature of the clusters. All these results are in harmony with the thickening mechanism deduced from our rheological approach [2].

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