Microstructure of Colloidal Gels

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Introduction

Suspensions of colloidal particles exhibit a diverse range of rheological properties, varying from simple viscous fluids to highly elastic pastes and gels. This is one of the key reasons for their widespread technological utility in consumer and food products and ceramics that involve the flow and processing of concentrated suspensions and gels. In all these applications, it is critical to have good control over the rheological properties (elastic modulus and yield stress) of the gelled suspension. In order to fine-tune the viscoelastic properties of these suspensions, it is important to first find a tool that can predict measurable properties. Once this has been established, it is possible to fine-tune the variables to achieve the desired properties that are suited for the particular application.

The approach that has been used until now to predict the viscoelastic properties of gels has been microstructure-based. A fractal model is used for the gels to describe the microstructure and to calculate the resulting elastic modulus. However, this theory is valid only for the dilute colloid concentrations where fractal arguments can be applied. No one has yet tested this theory in the dense concentration regime, which is of importance to the industry.

Ultrasmall-angle x-ray scattering (USAXS) [1, 2] gives us the opportunity to directly look at the microstructures of the gels without perturbing them. Useful information like the fractal dimension, osmotic compressibility, and average spacing between particles in the gel can be gathered from scattering experiments. These data are necessary for developing theories to predict the macroscopic properties.

In this work, we report on USAXS studies of the structure of gelled suspensions of model colloid-polymer mixtures. The colloid suspensions gel when a polymer of sufficient concentration is added to them. Our aim in measuring the structure is twofold: (1) to test the validity of the fractal-based approach for predicting moduli in dense suspensions and (2) to relate the observed microstructure to macroscopic flow properties.

Methods and Materials

The system used in this work consists of 90-nm-diameter silica particles coated with octadecanol (1- to 2-nm hairs) and suspended in decalin. In the absence of added polymer, the particles behave as hard spheres (no interactions except volume exclusion). The polymer used is polystyrene (18,700 g/mol), and the size ratio of the polymer to the colloid (R_g/R) is 0.078. The polymer concentration (nondimensionalized by the overlap concentration c_p^*) is varied from just enough to cause the colloidal suspension to gel ($c_p/c_p^* = 0.15$) to a value that can make a strong gel ($c_p/c_p^* = 0.6$). The resulting microstructure of the gels was determined by using side-bounce USAXS (SBUSAXS) at UNI-CAT beamline 33-ID at the APS.

Results and Discussion

Figure 1 illustrates the measured structure factor S(q) of the colloidal gels from SBUSAXS. Two interesting facts are revealed in the figure: (1) strong upturns at low q's and (2) the location of the first peak in S(q). This location is a measure of the average spacing between the colloidal particles in solution. As the colloid concentration is increased (as ϕ increases), one would expect that the particles would, on average, get closer and hence that the peak would shift to higher q's. A constant value for the location of the peak suggests that the structure is frozen in the gel, especially around the first cage of the particles. This is a signature of gelation [1, 2].

Figure 2 is a plot of the data in Fig. 1 that can be used to analyze the huge upturns at low q's. The extracted

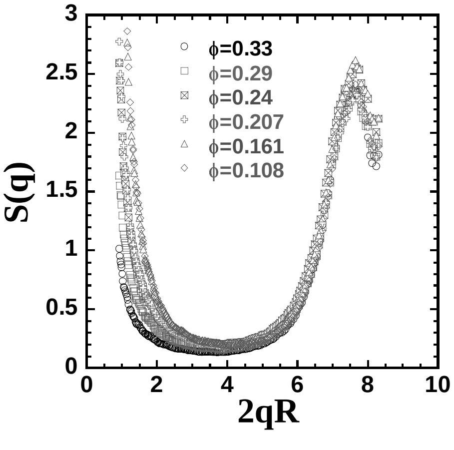

FIG. 1. Structure factor S(q) as a function of the nondimensionalized wave vector 2qR for colloid polymer suspensions (colloid volume fraction ϕ), with R_g/R = 0.078 and c_p/c_p^* = 0.6 (strong gel). The experimental points are for different colloid volume fractions ϕ.

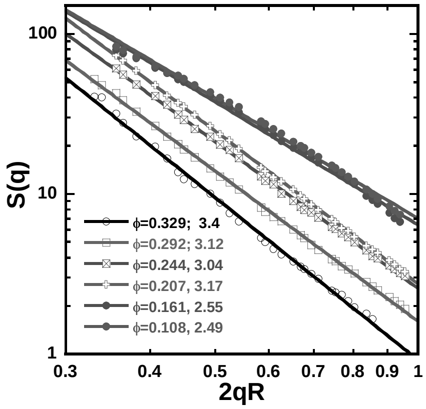

FIG. 2. Analysis of the low-angle data given in Fig. 1. The experimental points represent different colloid volume fractions (ϕ). The solid lines are curve fits to the data $[S(q) = (2qR)^x]$ to extract the fractal dimension x. The values of x are given next to the volume fraction ϕ.

fractal exponents have values greater than 3 at volume fractions of 0.2 and higher. A fractal dimension of 3 suggests a dense cluster, and it is unphysical to have numbers greater than 3. This implies that the microstructure of the colloidal gels is not fractal and that the use of standard fractal models to predict flow properties is no longer good.

In order to explain the huge upturns at low q's, we invoke the Debye-Bueche analysis that is normally applied to scattering from a homogenous solid with randomly distributed voids. In this instance, we treat the upturns as scattering from clusters of particles with randomly distributed voids. A schematic of the colloidal gel that we extract from this analysis is given in Fig. 3.

The above schematic of the colloidal gel plays an important role when theoretical predictions are compared with experimental results. (We have recently developed a theory [3] in which the viscoelastic properties of colloidal gels can be predicted.) Theoretical calculations do not take cluster formation into account; hence, the predicted elastic moduli are higher than experimentally measured values. However, when the above picture of the microstructure of gels is taken into account in the theory, excellent agreement is obtained with measured values [3]. Thus, the scattering experiments have played an important role in determining the microstructure, which is crucial when trying to compare experiments to theory.

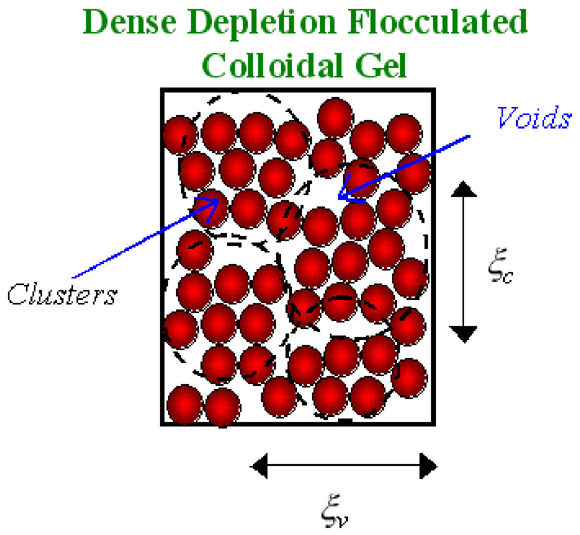

FIG. 3. Schematic illustration of interpenetrating, polydisperse, dense, percolated clusters of an average size ξ_c. The surrounding voids or heterogeneities are characterized by a correlation length ξ_v of ~10 to 16 R.

Acknowledgments

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