Viscoelasticity of Depletion-Induced Gels in Emulsion−Polymer Systems

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Using rheometry and light scattering, we have studied the viscoelasticity of gels formed by the kinetically arrested phase separation in an emulsion−polymer mixture; to prevent the gels from collapsing under their own weight, we have used an isopycnic solvent. At constant osmotic pressure (set by the polymer concentration) and droplet volume fractions ϕ well above the gelation transition, we find the elastic modulus to increase roughly linearly with ϕ, indicating an entropic elasticity based on the cluster packing.

Introduction

When nonadsorbing polymer is added to a suspension of colloidal particles, an attractive interaction is induced between the latter, which, if strong enough, can trigger a phase separation into particle rich and poor phases.[1−3] This depletion force is entropic in nature: if two particles are separated by a distance smaller than the size of a polymer molecule, the volume inaccessible to the latter results in an imbalance of the osmotic pressure which leads to an effective attraction between the particles. Depletion forces not only arise in polymer−colloid mixtures but also in binary colloidal mixtures such as emulsions consisting of droplets of two different sizes,[4] as well as in colloid−surfactant systems.[5] Their ubiquity has attracted considerable attention in recent years, partly because of their importance in the food and paint industries, but also because of their fundamental role for the stability of complex fluids and biological systems.[6]

Depletion-induced phase separation in a polymer−emulsion mixture leads, at high concentrations of both components, to very complex structures: strong attraction between the droplets causes a rapid growth of very large clusters. Accordingly, their rearrangement is slowed tremendously, preventing the formation of two well-separated, homogeneous phases. The resulting structure is a gel of interconnected droplet clusters spanning the whole sample volume, as shown in Figure 1. The high connectivity of the clusters shares many features in
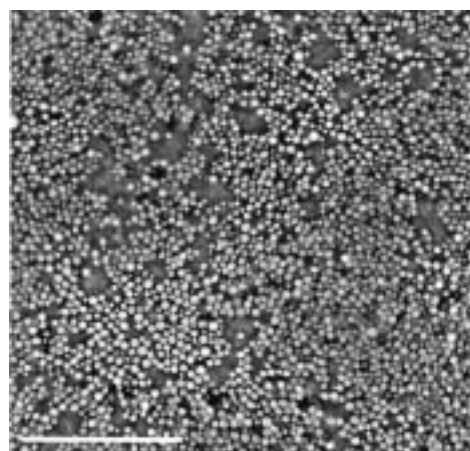

Figure 1. Optical micrograph of a gel formed by depletion flocculation of emulsion droplets by nonadsorbing poly(ethylene oxide) (M_w = 900 000 g/mol) at a concentration c_p = 4 mg/mL. The droplet diameter is 2.1 μm, and the volume fraction is 0.35. Note that the clusters are connected by a relatively small number of bonds, giving rise to large voids between them. The scale bar represents 50 μm.

common with other complex materials such as foams and sponges, and we therefore expect these gels to exhibit not only a significantly increased viscosity but also some characteristic elastic behavior reflecting the large scale cluster connectivity.[7,8]

Experiments have shown that depletion-induced gels are, due to their relatively small cohesive energies, rather fragile and prone to collapse under their own weight. We have thus performed all our experiments in an isopycnic solvent, thereby also avoiding irreversible changes to the gel structure due to shearing. Also, we have used emulsions with rather narrow size distributions, thereby excluding phase separation by mutual depletion attraction, as well as eliminating coarsening due to different Laplace pressures.

To characterize the viscoelastic properties of our emulsion−polymer gels, we used both mechanical and optical techniques which probe different length scales in our system. Mechanical measurements with a rheometer are

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sensitive to bulk properties; the finite torque resolution, however, precludes the investigation of weak gels, and the accessible frequency range is limited by instrumental inertia. On the other hand, the local dynamics of a single emulsion droplet in a gel can be probed with light scattering, thus providing a tool complementary to rheometry that allows one to study weaker gels and a larger range of frequencies.

Experimental Methods and Materials

Oil-in-water emulsions were made of silicon oil, sodium dodecyl sulfate as a surfactant, and water. The density of the oil we used was 1.049 g/mL at $T = 20$ °C. Using the fractionated crystallization technique,[9] we selected droplets with mean diameters $2a = 2.2$, 1.7, and 1.2 μm, with a polydispersity of roughly 10% for the first two and 20% for the third. The density of the droplets was then matched by the addition of deuterium oxide. Under these conditions, neither sedimentation nor creaming was observed, even after several weeks. As a polymer we used poly-(ethylene oxide) of molecular weight $M_w = 900\,000$, which does not adsorb at the surfactant-coated droplets. We note that the highest polymer concentration we used ($c_p = 4$ mg/mL) is still below the overlap concentration. To attain the desired volume fraction ϕ of droplets, we centrifuged the samples before density matching and measured ϕ by weighing small amounts before and after evaporation of the water phase. We note that the attraction induced by the polymer does not cause any droplet coagulation, and the droplets redisperse homogeneously throughout the sample upon dilution of the gel. Moreover, the Laplace pressure $2\sigma/a = 2 \times 10^5$ dyn/cm² (for $2a = 1.1$ μm and a surface tension for the oil–water interface $\sigma = 9.8$ dyn/cm²) is much larger than the osmotic pressure applied by the polymer in the bulk $\Pi_p \sim 110$ dyn/cm² (for $c_p = 4$ mg/mL), which we calculated for an ideal solution of polymers with a radius of gyration $R_g = 47$ nm. Therefore, we may treat the droplets as spherical, with contact facets of very small area.

All mechanical measurements were performed with a controlled-strain rheometer in a double wall Couette cell at $T = 20$ °C. Special care was taken to avoid evaporation which leads to the formation of a dense skin at the air–water interface. To destroy any structure formed during the loading of the rheometer, we subjected the samples to a large strain $\gamma > 10$ prior to each experiment. After this presheating process, the modulus at fixed frequency (usually 10 rad/s) was monitored using an oscillatory excitation with a small strain amplitude $\gamma = 10^{-4}$, until the modulus had reached a constant, time-independent value; this typically occurred within 1 h after the presheating. The limits of linear response were probed by increasing the strain amplitude γ at fixed frequency. Frequency-dependent storage and loss moduli $G'(\omega)$ and $G''(\omega)$ were then measured with a strain amplitude that did not exceed the maximal strain measured in the variable-strain experiment. Repeated frequency sweeps with small strain amplitudes resulted in reproducible, time-independent values for $G'(\omega)$ and $G''(\omega)$, provided the presheating had been applied after loading of the sample and a buoyancy-matched solvent had been used. In contrast, samples that were not buoyancy-matched showed an increase in the observed moduli with time, even at very small strain amplitudes.

As a complement to the mechanical experiments, we also determined the complex modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$, from droplet mean-square displacements $\langle \Delta r^2(t) \rangle$ measured with diffusing-wave spectroscopy (DWS),[10] using a generalization of the Stokes–Einstein relation to finite frequencies.[11] This generalization is based on the description of the dynamics of a droplet by means of a generalized Langevin equation and the identification of the memory function that describes the response as the relaxation modulus of the surrounding medium, $G(t)$. Solution of the Langevin equation through a Laplace transform yields a

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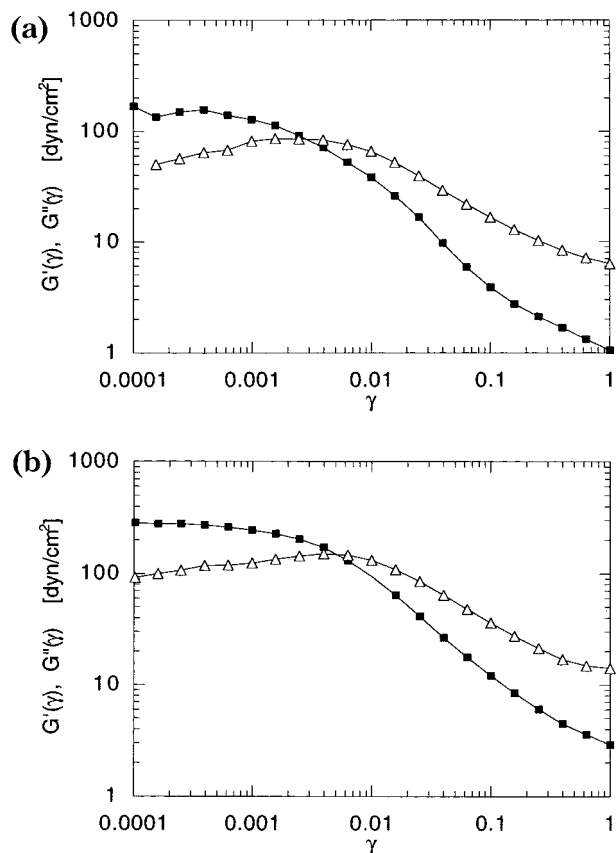(11) Mason, T. G.; Weitz, D. A. *Phys. Rev. Lett.* **1995**, *74*, 1250.

relationship between the Laplace transform of the relaxation modulus, $\tilde{G}(s)$, and the Laplace transform of the mean square displacement of the droplet, $\langle \Delta \tilde{r}^2(s) \rangle$,

$$G(s) = \frac{s}{6\pi a}\left[\frac{6k_BT}{s^2\langle \Delta \tilde{r}^2(s) \rangle}\right]$$

where s is the Laplace frequency. To implement this scheme, we first determined the mean square displacement from the DWS measurements of the temporal correlation function of the scattered intensity. We then calculated its Laplace transform numerically and obtained $\tilde{G}(s)$ using the above formula. Finally, $\tilde{G}(s)$ was fitted with a polynomial function which was then analytically continued using the substitution $s = i\omega$ to yield $G^*(\omega)$. The real and imaginary parts, $G'(\omega)$ and $G''(\omega)$, could then be identified. We note that since these are related by the Kramers–Kronig relations, we do not obtain two independent functions with this transformation. Transport mean free paths l^* used to invert measured intensity autocorrelation functions to mean-square displacements were obtained from measurements of the relative transmission with respect to a reference sample with known l^*. The values of l^* were larger than the typical void size in our gels by about 1 order of magnitude or more. We illustrate this in the case of $\phi = 0.35$ for which we measured $l^* = 72$ μm. In comparison, as can be seen in Figure 1, the typical void size is about 10 μm. Due to the diffusive transport of light on which it is based, the DWS technique inherently averages over many independent volumes in a sample. Nonetheless, we observed nonergodic behavior in our samples due to the extremely slow dynamics. This resulted in a random offset of the baseline of the intensity autocorrelation functions. Ergodic averaging was thus performed by averaging unnormalized correlation functions from 10 widely separated points in each sample (a measurement at each point lasting 30 min) in order to obtain a reliable measurement of the baseline and to determine the statistical error in our measurements. This small number of samples was sufficient to obtain a reliable average because each DWS measurement probes a very large volume of the sample due to the diffusive nature of the light transport. We experimentally verified that 10 samples were sufficient by comparing the results as each additional sample was obtained; no change in the data was observed after as few as seven samples were collected.

Results

Figure 2 shows the storage and loss moduli, $G'(\gamma)$ and $G''(\gamma)$, respectively, measured in an oscillatory experiment as a function of the strain amplitude γ at fixed frequency $\omega = 10$ rad/s. Both moduli are independent of strain only for very low values of gamma, $\gamma < 4 \times 10^{-4}$ for $c_p = 2$ mg/mL and $\gamma < 10^{-3}$ for $c_p = 4$ mg/mL, followed by a marked decrease at higher strains reflecting structural changes in the gel which relax only very slowly (over the course of several hours).

The frequency dependence of $G'(\omega)$ and $G''(\omega)$ measured mechanically for two gels with different polymer concentrations, but having the same volume fraction $\phi = 0.54$, is displayed in Figures 3a,b. These measurements were conducted with a small strain amplitude $\gamma \sim 10^{-3}$, within the range of values where $G'(\omega)$ and $G''(\omega)$ are strain-independent. At the lower polymer concentration, $c_p = 2$ mg/mL, the storage modulus $G'(\omega)$ is about 100 dyn/cm² at $\omega = 1$ rad/s and shows a very weak, monotonic increase with frequency, characteristic of a gel.[11] By contrast, the loss modulus, $G''(\omega)$, is smaller than $G'(\omega)$ and goes through a minimum at $\omega \sim 2$ rad/s, presumably becoming dominant at $\omega \sim 0.5$ rad/s, the lowest frequency measured. At the higher polymer concentration, $c_p = 4$ mg/mL, the magnitude of $G'(\omega)$ increases to a value of about 250 dyn/cm² at $\omega = 1$ rad/s; its frequency dependence becomes even weaker, while the minimum in $G''(\omega)$ is shifted to lower frequencies.

(a)

(b)

Figure 2. Strain-dependent storage modulus $G'(\gamma)$ (squares) and loss modulus $G''(\gamma)$ (triangles) measured at droplet volume fraction $\phi = 0.54$ and polymer concentrations $c_p = 2$ mg/mL (a) and $c_p = 4$ mg/mL (b). Experiments were performed by applying an oscillatory deformation, increasing the strain amplitude at fixed frequency $\omega = 10$ rad/s. The gel shows marked shear-thinning above strains of $\gamma = 10^{-3}$ for $c_p = 2$ mg/mL and $\gamma = 4 \times 10^3$ for $c_p = 4$ mg/mL, corresponding to reversible changes in the gel structure.

The intensity autocorrelation function $g_2(t)$ measured with DWS for a gel with $\phi = 0.54$ and $c_p = 4$ mg/mL is shown in Figure 4 (insert). At early times the decay of the correlation function reflects the local motion of individual emulsion drops and can be interpreted to determine $\langle \Delta r^2(t) \rangle$, which is also shown in Figure 4. Note that $\langle \Delta r^2(t) \rangle$ increases with time more slowly than in a free diffusion process, due to the restricted motion of droplets within clusters. At long times $\langle \Delta r^2(t) \rangle$ becomes time-independent and saturates at a value of about 60 Å, which is much smaller than both the range of the depletion potential ($2R_g = 94$ nm) and the droplet diameter. At even longer times not shown in the figure ($t > 10$ s), a final more noisy decay, probably due to large-scale rearrangements akin to the relaxation of foams,[13] was observed. However, this last decay cannot be interpreted in terms of a mean-square displacement, and thus, we do not expect a direct correspondence between this long-time decay in our DWS measurements and a relaxation in our measurements of the modulus. In addition, we do not observe any appreciable change of the modulus during the course of our measurements.

From the measured $\langle \Delta r^2(t) \rangle$, the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ were obtained as described in the previous section. Figure 5 shows $G'(\omega)$ and $G''(\omega)$ for droplet volume fractions between 0.10 and 0.52 measured with DWS. In
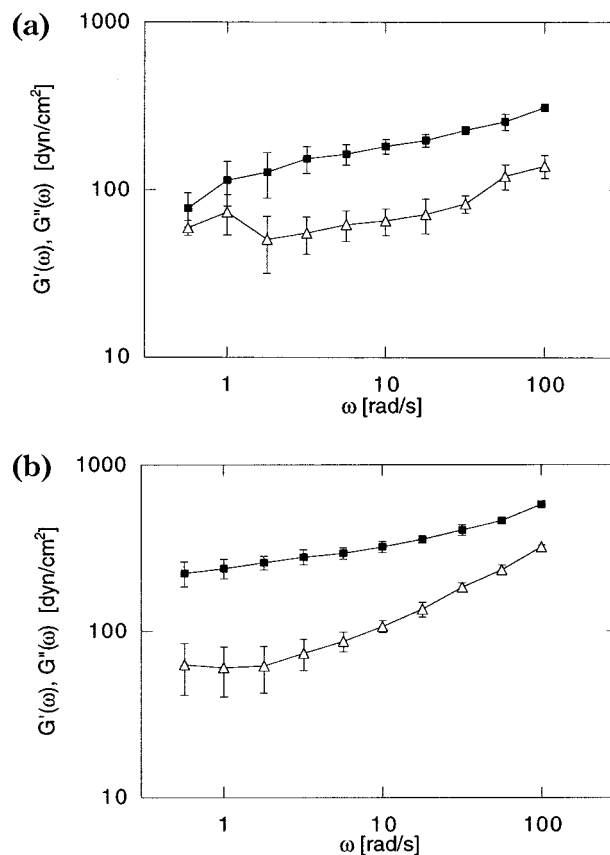
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(a)

(b)

Figure 3. Storage modulus $G'(\omega)$ (squares) and loss modulus $G''(\omega)$ (triangles) as a function of frequency ω at a droplet volume fraction $\phi = 0.54$ and polymer concentrations $c_p = 2$ mg/mL (a) and $c_p = 4$ mg/mL (b). Measurements were performed at a small strain amplitude of $\gamma = 10^{-3}$. The storage modulus dominates the loss modulus over a wide frequency range; at frequencies below 10 rad/s, $G'(\omega)$ and $G''(\omega)$ are only weakly dependent on frequency.
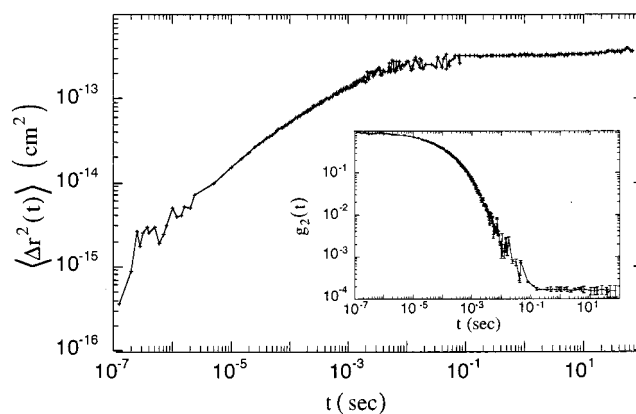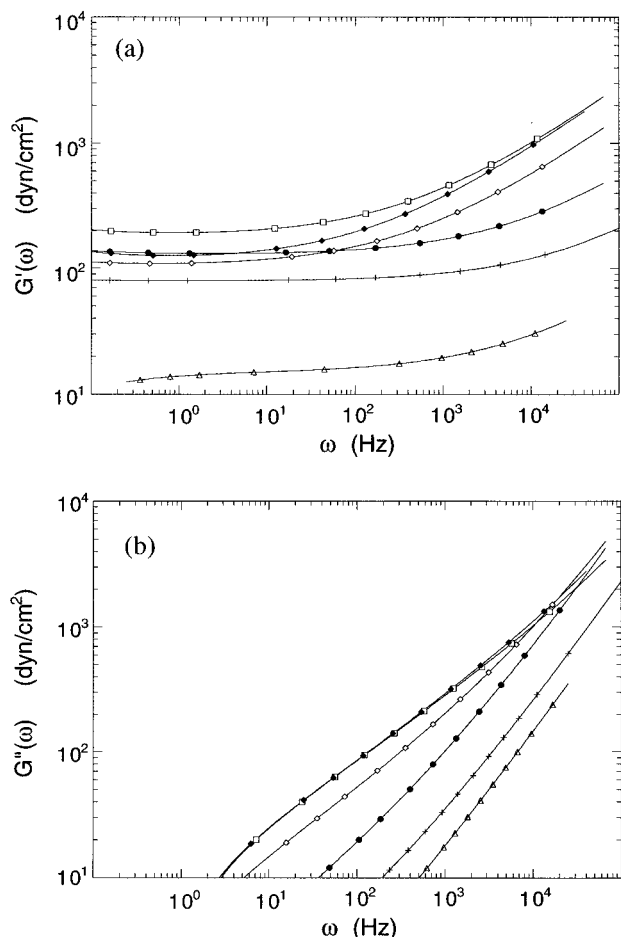

Figure 4. Mean-square displacement of droplets $\langle \Delta r^2(t) \rangle$ in an emulsion gel at droplet volume fraction $\phi = 0.54$ and polymer concentration $c_p = 4$ mg/mL measured with diffusing-wave spectroscopy. The droplet diameter is 1.8 μm. The normalized intensity autocorrelation function $g_2(t)$ (insert) decays to a plateau corresponding to the trapping of a single droplet due to elastic restoring forces. The transport mean free path measured by static transmission for this sample is $l^* = 56 \mu$m.

all these measurements the polymer concentration in the water phase was kept constant at $c_p = 4$ mg/mL. A comparison of the two moduli shows that as in the mechanical measurements, the storage modulus dominates over the loss modulus at low frequencies, in contrast to the behavior of emulsions without polymer at comparable volume fractions. At high frequencies, however,

Figure 5. Storage modulus $G'(\omega)$ (a) and loss modulus $G''(\omega)$ (b) measured with DWS at different droplet volume fractions ϕ: 0.52 (empty squares); 0.45 (solid diamonds); 0.35 (empty diamonds); 0.25 (solid circles); 0.15 (crosses); 0.10 (empty triangles). The polymer concentration is 4 mg/mL.

$G''(\omega)$ becomes comparable or larger than $G'(\omega)$, this feature being more pronounced for lower values of ϕ. $G'(\omega)$ exhibits a plateau at low frequencies followed by a monotonic increase with ω, which for sufficiently large ω increases as $\omega^{1/2}$, as for a concentrated hard sphere fluid.[13] Between $\phi = 0.10$ and $\phi = 0.15$, the plateau modulus G_p increases steeply from about 13 dyn/cm² at $\phi = 0.10$ to 80 dyn/cm² at $\phi = 0.15$; we attribute this strong ϕ-dependence to the proximity to the boundary between the gel phase and the two-phase (liquid plus gel) region. Interestingly, the measured plateau moduli scaled by the Laplace pressure $2\sigma/a$ are comparable to those obtained in dense emulsions for values of ϕ close to the random close packing $\phi_c = 0.64$,[14] even though ϕ in our gels is well below this value. This reflects the fact that the DWS measurements are more sensitive to the behavior of the concentrated regions, which scatter the light most strongly, than the regions of lower particle concentration, which neither scatter the light as effectively nor provide any contribution to the modulus.

The loss moduli shown in Figure 5b show a frequency dependence different from that measured with the rheometer: $G''(\omega)$ increases monotonically with ω for all volume fractions $0.10 < \phi < 0.54$, without the minimum observed in the mechanical experiments. This discrepancy

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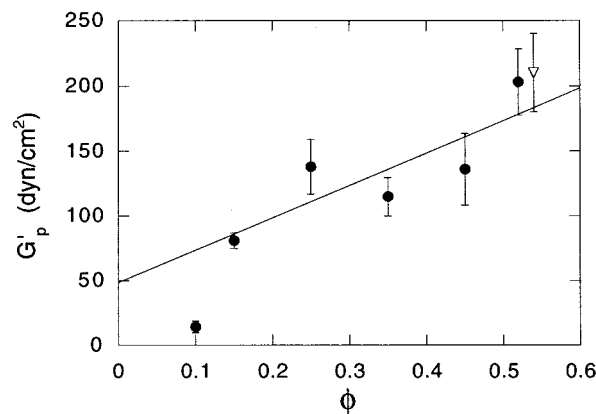

Figure 6. Volume-fraction dependence of the plateau modulus G_p of emulsion gels at $c_p = 4$ mg/mL as determined from the mean-square displacements measured by DWS (circles). The plateau measured with the rheometer (triangle) is consistent with the DWS data. Above the gelation transition at $\phi \sim 0.1$, $G_p(\phi)$ increases roughly linearly with volume fraction, indicating that the modulus of the gel is determined by the amount of the total volume occupied by droplet clusters that are able to store mechanical energy.

again reflects the difference between the behavior probed by the rheometer and that probed by DWS. The relaxation probed by the rheometer measurements may result from very large scale motion of the droplets, to which the DWS measurements are not sensitive.

Figure 6 shows the plateau modulus G_p measured as a function of volume fraction ϕ, at constant polymer concentration $c_p = 4$ mg/ml. We find that G_p increases roughly linearly with the droplet volume fraction, from $G_p \sim 80$ dyn/cm² at $\phi = 0.15$ to $G_p \sim 250$ dyn/cm² at $\phi = 0.52$, consistent with the mechanical measurements. This is somewhat surprising, considering that the osmotic pressure of the polymer (which is about 100 dyn/cm² at $c_p = 4$ mg/mL) and, hence, the depth of the attractive potential between two droplets are constant. The approximately linear dependence of G_p on ϕ which we observe contrasts with the rheological measurements of Patel and Russel,[3] who found an exponential dependence of G_p on ϕ in mixtures of hard colloids and polymers. Both measurements were conducted at similar values of the polymer volume fraction. However, the ratio of particle to polymer size was 6.9 in their case while it is nearly 20 in ours. This suggests that the dependence of the moduli on the size ratio may be an interesting issue for future investigations.

The DWS measurements reported here differ in a significant way from previous measurements that were interpreted in terms of the viscoelasticity of the medium. In previous studies, the media that were probed were homogeneous on length scales of the transport mean free path, l^*. As a result, the viscoelastic behavior measured with DWS correlated directly with the measurements using a rheometer. While l^* is also larger than the typical void size in our samples, light is scattered predominantly in those regions that have higher concentrations of particles. Since DWS measurements are sensitive to motions on small length scales, they may not provide a direct measure of the large scale viscoelasticity of the medium, as determined by a rheometer. Instead the DWS measurements more likely probe the behavior of the more concentrated regions. This may in part explain the discrepancy between the exponential dependence of G_p on ϕ measured with a rheometer by Patel and Russel[3] and the linear dependence we observed in our optical studies. Nevertheless, there is still a direct relationship between the properties probed by the DWS measurements and

those probed by the rheometer. The bulk elasticity of the gel must depend on both the basic modulus of the concentrated regions of particles, as well as on the connectivity of the network of these concentrated regions, which carry the stress. Thus, the modulus measured by the DWS measurements provides one key ingredient of the macroscopic modulus measured mechanically.

Within this qualitative picture, the observed scaling of G_p with volume fraction might be understood from a purely geometrical argument: the relatively weak attraction (< 5 kT) between the droplets results in a wide distribution of cluster sizes. The overall structure of the gel, on the other hand, is quite homogeneous as voids in the packing of the largest clusters can be filled with smaller clusters. Thus the shear stress will be distributed homogeneously over all the clusters of different sizes, i.e., the elastic modulus is given by the number of droplet−droplet contacts per unit volume. This number does not vary too much with increasing volume fraction, accounting for the relatively weak dependence. By contrast, for gels at low volume fractions and made with strong interparticle attraction, shear stresses are localized in a dilute backbone; this will result in a much stronger dependence of G_p on volume fraction, consistent with observations.[16]

In conclusion, we have presented measurements of elastic moduli of depletion-induced gels using rheology and light scattering techniques. Both methods yield comparable results for the low-frequency values of the storage modulus $G'(\omega)$; the differences in the frequency-dependence of $G''(\omega)$, however, reflect the different length scales probed by the two techniques. We find that using an isopycnic solvent is essential for preventing the gels from collapsing under their own weight, allowing us to measure very low elastic moduli in macroscopic samples. Perhaps the most important conclusion which emerges from our work is that the elasticity in these systems is controlled by structural features, i.e., the packing of clusters, and not by the osmotic pressure setting the attraction depth between the droplets.

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