Structure and dynamics of biphasic colloidal mixtures

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We investigate the structure and dynamics of biphasic colloidal mixtures composed of coexisting attractive and repulsive microspheres by confocal microscopy. Attractive gels formed in the presence of repulsive microspheres are more spatially homogeneous and, on average, are both more locally tenuous and have fewer large voids than their unary counterparts. The repulsive microspheres within these mixtures display heterogeneous dynamics, with some species exhibiting freely diffusive Brownian motion while others are trapped within the gel network during aggregation.

Colloidal gels, which consist of attractive colloidal particles that stick together to form a system-spanning interconnected network, are widely used in ceramics processing [1], inks [2], catalyst supports [3], and membranes [4]. To improve component performance, new strategies for designing concentrated gels with controlled structural and rheological properties are desired. The fundamental ties between local gel structure and bulk properties have received considerable attention, both theoretically and experimentally [5–7]. The overall connectivity of the gel network provides finite bending and stretching elasticity [8], contributing to the system's zero-shear elastic modulus. To date, most experimental studies have focused on colloidal gels composed of a single species with uniform interparticle interactions, in which the primary control parameters are the colloid volume fraction ϕ and the strength of the attractive interaction energy U [7,9,10]. Surprisingly, mixtures in which interparticle interactions are independently tuned have not been systematically studied, even though such systems may open new routes for tailoring gel properties even when both ϕ and U remain fixed.

In this Rapid Communication, we investigate the gel structure and suspension dynamics in biphasic colloidal mixtures using confocal laser scanning microscopy (CLSM). We selectively tune the interparticle interactions of attractive and repulsive microspheres, and create binary mixtures of these two species. In these mixtures, the attractive particles stick to one another yielding a gel network, while the repulsive particles are stable, sticking neither to the attractive particles nor to one another. This system differs from most colloidal dispersions in which attractive interactions are uniformly controlled via the addition of depletants [7,9,10], salt [11], or acid or base to solution [2]. By imaging and quantifying the two particle populations independently, we elucidate the role of the excluded volume of repulsive particles in mediating the local and the long-range structure of the gel phase as well as the effect of the arrested gel network on the dynamics of the repulsive particles.

We use three separate particle batches of silica microspheres, all with similar diameters. Their average diameters, assessed from scanning electron microscopy photomicrographs, are $\langle \sigma_1 \rangle = 0.68 \pm 0.04$ μm, $\langle \sigma_2 \rangle = 0.72 \pm 0.02$ μm, and $\langle \sigma_3 \rangle = 0.62 \pm 0.03$ μm. The first batch (diameter σ_1) is labeled with rhodamine dye, and rendered "attractive" by partially coating their surface with hydrophobic n-octyldimethylchlorosilane following a standard silane-coupling procedure [12]. These particles rapidly flocculate when suspended in an index-matched polar mixture of H_2O-dimethylsulfoxide. The second batch (diameter σ_2) is labeled with fluorescein dye; these uncoated particles are "repulsive" due to their negatively charged surface [12]. The third batch (diameter σ_3) is synthesized without dye; however, their surfaces are rendered hydrophobic and thus they are "plain attractive" particles similar to the first batch. To prepare biphasic colloidal mixtures, the appropriate amounts of each species are mixed with the solvent in custom-made vials for CLSM, and sonicated for 30 s at a 1 s on/off cycle. We confirm that this sonication step is sufficient to break up the hydrophobic particle clusters, by imaging the attractive particles in a representative biphasic mixture at ϕ_{att}=0.05, ϕ_{rep}=0.42, immediately after sonication (data not shown). Here, ϕ_{att} and ϕ_{rep} denote the volume fractions of the attractive and repulsive particles, respectively. For the range of ϕ_{att} studied, the attractive particles rapidly aggregate within a few seconds after sonication to yield a colloidal gel. All samples contain a total volume fraction ϕ_{total} of 0.47 and are imaged 5–15 min after sonication, unless otherwise noted.

CLSM is carried out on two separate instruments. A Leica SP2 confocal microscope with a $60\times$ objective (N.A.=1.4) is used to characterize the three–dimensional (3D) structure of these mixtures. Rhodamine and fluorescein dye molecules are separately detected by the confocal microscope (using two photomultiplier tubes for simultaneous imaging of the two dyes). Volumetric image stacks are acquired at heights $z > 10$ μm to quantify the gel structure away from container boundaries. By comparing the known values of ϕ_{att} to those obtained from the imaged volumes, we confirm that sedimentation effects are minimized over the range of ϕ_{att} investigated [13]. A Vt-Eye confocal fast scanner attached to an inverted Olympus microscope with a $100\times$ objective (N.A. =1.32) is used for imaging the suspension dynamics. 2D

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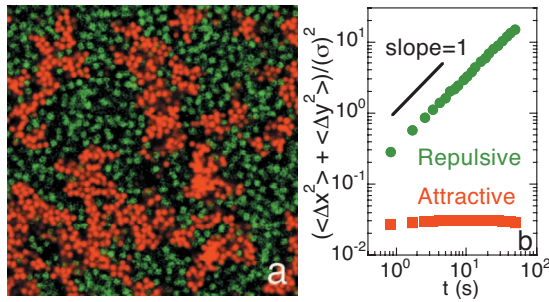
FIG. 1. (Color) (a) Confocal two-dimensional (2D) image of the biphasic colloidal mixture containing attractive and repulsive particles ($\phi_{att}=\phi_{rep}=0.05$). (b) MSD of the respective populations.

images are acquired at a rate of 1 image/s, at a depth z ~ 15 μm into the specimen.

Figure 1(a) shows a CLSM image of a sample with ϕ_{att} $=\phi_{rep}=0.05$. Attractive and repulsive microspheres are shown as red and green, respectively. The attractive microspheres form a gel, confirming that their hydrophobic interactions are sufficiently strong to induce gelation even at this low ϕ_{att}. These gelled particles coexist with individually dispersed, repulsive microspheres [green in Fig. 1(a); see supporting information for a time series of CLSM images]. Analysis of the mean squared displacements (MSD) in Fig. 1(b) shows that the attractive particles are completely arrested, while the repulsive particles remain nearly freely diffusive. Together, our observations demonstrate the biphasic nature of these model colloidal mixtures.

We first explore whether the presence of repulsive microspheres influences the structure of the gel phase formed within these biphasic mixtures. A simple way to characterize the gel structure is to quantify the Voronoi polyhedra volumes V_{VP} of the attractive particles. This is a measure of the local free space around each microsphere; small values of V_{VP} are associated with dense regions of the gel, while large values of V_{VP} indicate that the gel has internal voids. Figure 2 compares the distribution of V_{VP} for gels formed in the biphasic mixtures to their unary counterparts at ϕ_{att} $=0.33, 0.23$, and 0.14. Here, a unary counterpart is defined as a suspension with the same ϕ_{att} that contains no repulsive microspheres ($\phi_{rep}=0$). For the biphasic samples, the repulsive particle volume fraction is chosen so that $\phi_{rep}+\phi_{att}$
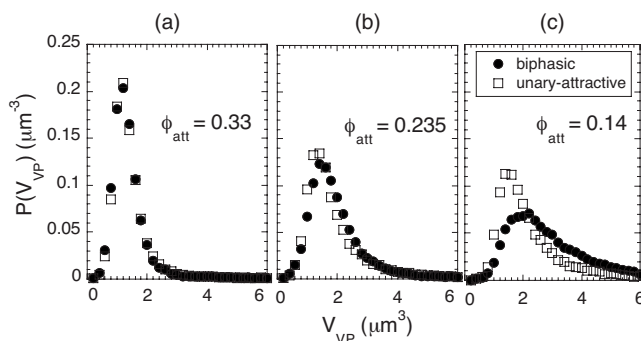

FIG. 2. Probability distribution of Voronoi polyhedra volumes of the gel phase, assembled from attractive particles within biphasic ($\phi_{total}=0.47$) and unary ($\phi_{rep}=0$) systems.
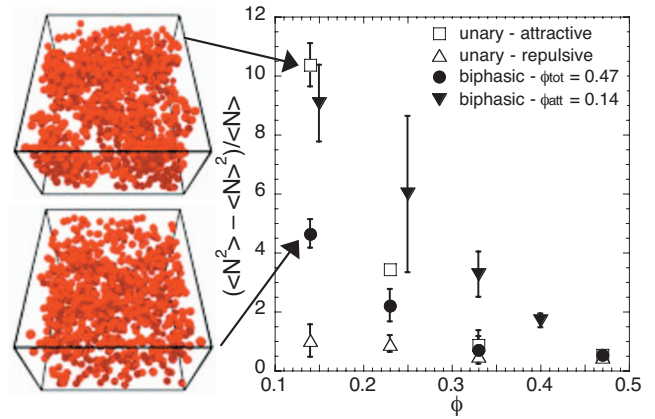

FIG. 3. (Color) Local number density fluctuations. The open squares correspond to a unary sample composed of purely attractive particles. The solid symbols represent the number density fluctuations of the gel phase assembled from biphasic mixtures; the solid triangles correspond to a fixed $\phi_{total}=0.47$ where the horizontal axis represents ϕ_{att}, and the solid circles correspond to a fixed ϕ_{att} $=0.14$ where the horizontal axis represents ϕ_{rep}. Number density fluctuations of unary repulsive suspensions at the corresponding ϕ are also plotted for comparison (open triangles). Each point reports the average of three independent experiments, with standard deviations shown as error bars. The inset shows 3D reconstructions of the gel structures.

$=0.47$. All distributions show an initial peak at small V_{VP} followed by a long tail, indicating the gel structures are primarily comprised of dense clusters and a few long-range voids, consistent with that previously reported for thermoreversible colloidal gels at $\phi>0.1$ [14]. At $\phi_{att}=0.33$, the Voronoi volume probability distributions $P(V_{VP})$ for the binary and unary samples are nearly identical. In this case, the addition of a small population of repulsive microspheres ($\phi_{rep}=0.14$) to the dense gel ($\phi_{att}=0.33$) does not significantly affect the gel's long-range structure. By contrast, for lower values of ϕ_{att} [Figs. 2(b) and 2(c)], the gel structure for the biphasic mixture deviates from its unary counterpart, with a lower peak height at small V_{VP} and a less steep descent at moderate V_{VP} compared to the unary samples. In these biphasic mixtures, the gel structure is more homogeneous, i.e., more attractive particles are associated with moderate void space (moderate V_{VP}). We have confirmed this trend by studying a series of samples with $\phi_{att}=0.14$, but with differing quantities of added repulsive particles with ϕ_{rep} between 0.15 and 0.40, and noting that again the voids in the gel become more homogeneous and moderate in size [13]. Note the voids contain only solvent in the unary samples, whereas they typically contain repulsive microspheres in the biphasic mixtures, as shown in Fig. 1(a).

To further investigate the effect of repulsive microspheres on the long-range gel structure, we compute the ratio of mean squared number density fluctuations in the gel to its average density, $(\langle N^2 \rangle - \langle N \rangle^2)/\langle N \rangle$, where N denotes the number of particles counted in a bin of $5 \times 5 \times 5$ μm^3, and the angle brackets $\langle \ \rangle$ denote an averaged quantity over the entire image volume. The results for the biphasic mixtures and their unary counterparts are plotted as a function of ϕ_{att} in Fig. 3 (solid circles and open squares, respectively). The large mag-
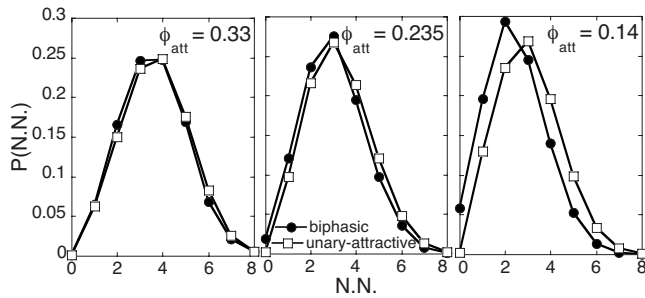
FIG. 4. Probability distribution of the number of interparticle bonds per particle, for gels assembled from biphasic ($\phi_{total}=0.47$) and unary ($\phi_{rep}=0$) systems.

nitude of density fluctuations at low ϕ for the unary gels is a manifestation of long-range structural heterogeneity [14]. For the biphasic mixtures (solid circles), the magnitudes of gel density fluctuations are still large, but smaller than the unary gel counterparts at all values of ϕ_{att} investigated. For comparison, we plot the same measure of density fluctuations for unary suspensions of repulsive particles at the corresponding ϕ (open triangles). As expected, the density fluctuations in the repulsive dispersions are of significantly lower magnitude, since these particles adopt a homogeneous spatial configuration. Finally, Fig. 3 also demonstrates the influence of adding repulsive particles to a system with fixed $\phi_{att}=0.14$ (solid triangles). It is clear that the gel structure becomes more homogeneous as ϕ_{rep} increases.

We also present 3D reconstructions of the gel structure at $\phi_{att}=0.14$ from representative $15 \times 15 \times 10$ μm^3 volumes in the unary and binary samples (Fig. 3). As can be seen, the unary gel structure consists primarily of dense clusters and long-range voids. By contrast, the biphasic system adopts a more uniform distribution of particles. We compared $(\langle N^2 \rangle - \langle N \rangle^2)/\langle N \rangle$ for three different bin sizes and found that a bin size of $5 \times 5 \times 5$ μm^3 reveals the largest difference between the biphasic and unary gels. However, we note that this is sensitive to the imaged region within the gels, and is thus only suggestive of the length scales at which the gel types differ most.

We quantify the local structure of the gels by their bond number distributions. Two attractive microspheres are assumed to form a bond when the distance between their centers of mass is less than the distance corresponding to the first minimum in the radial distribution function, $g(r)$. In Fig. 4, the distribution of interparticle bonds in the gel phase is compared for the binary and unary samples. At $\phi_{att}=0.33$, the bond number distribution is unaffected by the biphasic nature of the system, similar to the behavior observed with the distribution of Voronoi polyhedra volumes. As the ratio ϕ_{att}/ϕ_{rep} is decreased, the local gel structure for the biphasic mixture deviates from its unary counterpart, favoring fewer bonds per attractive particle. The increasing number of microspheres with 2 or fewer bonds indicates the gel becomes more locally tenuous, with more linear chains. Furthermore, the nontrivial number of particles with 0 bonds indicates the presence of freely diffusing attractive particles that have not yet found any other attractive particles with which to bond. Thus, even on the scale of individual particles, the presence

of the repulsive species strongly influences the local gel structure. This trend is again confirmed in a series of samples with fixed $\phi_{att}=0.14$ and varying ϕ_{rep}; as ϕ_{rep} increases, the nearest neighbor distribution increasingly reflects locally tenuous connections and a higher population of freely diffusing attractive particles (see [13]).

To verify that our system is kinetically trapped, we examined its structural evolution between 5 and 50 min after preparing the sample. Over this time period, only minimal structural changes were found in the distributions of V_{VP} and nearest neighbors (NN), far smaller than the variations seen between samples in Figs. 2 and 4. The most significant change was a slow decrease in the number of attractive particles with zero NNs (from ~8% to ~5%), as some isolated particles move and find other attractive particles to stick to. However, this does not affect our main observation that the biphasic gels are more spatially homogeneous.

Collectively, the results shown in Figs. 2–4 reveal important implications of the presence of repulsive microspheres in biphasic mixtures for both the long-range and local structure of the gel phase. The repulsive particles have significantly slower dynamics than the solvent molecules, especially at the large total volume fractions examined here. When randomly distributed among a population of attractive particles, these species can frustrate the particle association process thereby yielding aggregated systems that are kinetically trapped in a more structurally uniform state (Figs. 2 and 3) and which are composed of attractive particles that, on average, share less contacts with other attractive species (Fig. 4).

The differences in the distribution of elastic bonds observed in Fig. 4 suggest a larger density of attractive microspheres with less than three bonds (NN < 3) in biphasic mixtures. These singly connected points along the gel backbone can serve as soft pivots [15], significantly altering the system's nonlinear rheology [16]. The addition of repulsive particles changes both the number density and the distribution of elastic bonds within the structure in a nontrivial manner. By simply adjusting the fraction of particles that are able to form interparticle elastic bonds, the system's rheology may be tuned even when ϕ_{total} and the strength of interparticle interactions remain fixed. This is because the bonds between attractive particles make larger contributions to the system's zero-shear elastic modulus than contacts involving repulsive particles. Although the precise consequences of the biphasic nature of these mixtures on their viscoelasticity warrant future investigation, our findings suggest a new route for engineering disordered colloidal structures with tunable properties.

While the presence of repulsive microspheres affects the gel structure, the gel network in turn modifies the dynamics of the repulsive particles. Figure 5(a) shows the distribution of repulsive particle displacements, $P(\Delta x)$, in a biphasic mixture at $\phi_{att}/\phi_{rep}=0.14/0.33$, computed from time-lapsed 2D CLSM images which use the "plain attractive" particles (invisible to the confocal) so that the dynamics of the repulsive particles are easier to follow. For this mixture, $P(\Delta x)$ appears to comprise two distinct functional forms: a Gaussian distribution, consistent with freely diffusing Brownian particles, and a separate peak near $\Delta x=0$, indicating a second
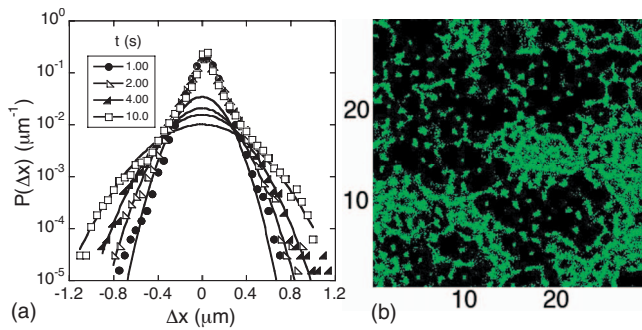
FIG. 5. (Color) (a) Probability distribution of repulsive particle displacements in a biphasic mixture at $\phi_{att}=0.14$, $\phi_{rep}=0.33$. (b) Repulsive particle trajectories over 125 s.

population of localized particles. In Fig. 5(b) we plot the repulsive particle trajectories for 500 images collected over 125 s. The black areas represent gel-rich regions, since attractive particles are invisible in this experiment. In these regions, the area covered by the trajectory of a repulsive particle is, on average, smaller than that in the gel-free (green) regions. Therefore, repulsive particles that reside in gel-rich regions appear to be more localized. This immobilization, which is responsible for the dynamical heterogeneity observed in Fig. 5(a), likely arises due to trapping of repulsive particles inside gel clusters during the aggregation process, and is directly responsible for the more uniform biphasic gel structures quantified in Figs. 2–4. The population densities of fast and slow particles can, in principle, be quantified by further analysis of $P(\Delta x)$.

In summary, we have developed a model system for tailoring colloidal gelation and particle dynamics, in which freely suspended repulsive particles coexist with a gel comprised of attractive particles. This design paradigm has important implications for direct-write assembly [2,11], microfiltration membranes [4], and catalyst supports [3]. The use of biphasic mixtures may also open avenues for studying the origins of dynamical arrest [9,17,18] and heterogeneity [19,20] in colloidal suspensions as well as particle diffusion and deposition in model porous media [21].

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