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We study colloidal gels formed upon centrifugation of dilute suspensions of spherical colloids (radius 446 nm) that interact through a long-range electrostatic repulsion (Debye length ≈ 850 nm) and a short-range depletion attraction (~ 12.5 nm), by means of confocal scanning laser microscopy (CSLM). In these systems, at low colloid densities, colloidal clusters are stable. Upon increasing the density by centrifugation, at different stages of cluster formation, we show that colloidal gels are formed that significantly differ in structure. While significant single-particle displacements do not occur on the hour time scale, the different gels slowly evolve within several weeks to a similar structure that is at least stable for over a year. Furthermore, while reference systems without long-range repulsion collapse into dense glassy states, the repulsive colloidal gels are able to support external stress in the form of a centrifugal field of at least 9g.

Introduction

Colloidal dispersions can exhibit a wide variety of interparticle interactions as a function of particle (surface) composition, solvent, and additives. These interactions vary from pure excluded volume (hard spheres)¹ to quite complex ones. Effective attraction between colloids can for example be induced by addition of nonadsorbing polymers, referred to as depletion interaction.^{2,3} Colloids can also have a charged surface, resulting in mutual screened-Coulomb repulsion, or can possess even more complex pair potentials, such as a long-range repulsion combined with a short-range attraction. Systems with the latter kind of potential exhibit a rich phase behavior. Theory^{4,5} has predicted the existence of stable colloidal clusters as well as percolating network gels for this case. Experiments⁶⁻⁹ and simulations^{10–12} have confirmed the existence of these states. A highly ordered gel consisting of Bernal spiral branches was also observed⁷ and its structure was confirmed by computer simulations.^{11,13} It has further been suggested that colloidal clusters in these systems might be useful models for atomic nuclei, at least in a classical sense.⁵ Indeed, nucleons are held together by the strong, short-range nuclear force, similar to a short-range depletion interaction, while the finite size of atoms is stabilized by the long-ranged Coulomb forces between protons in the nucleus. These forces are also present in suspensions of charged colloids, particularly if the Debye screening length is long. Periodic phases, such as lamellae and columnar, have been observed in computer simulations of dense nuclear matter (see ref 14) but also in concentrated suspensions of colloids with long-ranged repulsion and short-ranged attraction¹⁵ being a clear indication of the similarity between nuclear matter and these types of colloidal suspensions.

Here we investigate the structure, stability, and formation pathways of colloidal gels in systems with long-range repulsion and short-range attraction potentials. The repulsion originates from charges on the colloid surfaces (induced by the solvent mixture), while the attractions stem from depletion interactions (by addition of nonadsorbing polymer). We did not only observe the predicted colloidal clusters and gels for these systems but we also encountered gels with highly different structures. These structures are nearly arrested, but nonetheless show dynamics over the course of weeks, leading to a similar gel structure that is at least stable for over a year.

Experimental Methods

Materials. Spherical poly(methylmethacrylate) (PMMA) colloids, fluorescently labeled with 4-methylaminoethylmethacrylate-7-nitro-2-oxa-1,3-diazoal (NBD-MAEM), were synthesized through a procedure described in detail elsewhere.¹⁶ The colloids were sterically stabilized with poly(12-hydroxystearic acid) or PHS. Their (dry) mass density ρ was found to be 1.17 g cm⁻³, their refractive index $n_D^{20} = 1.50$, and their average radius a = 446 nm with a polydispersity of 2.9% (determined by scanning electron microscopy; SEM).¹⁶ *cis*-Decalin "for synthesis" (Dec; with $\rho = 0.897$ g cm⁻³ and $n_D = 1.4810$) and NaHCO₃ p.a. pure were obtained from Merck. Cycloheptyl bromide 97% (CHB; with $\rho = 1.289$ g cm⁻³ and $n_D = 1.5050$) was obtained from Aldrich and polystyrene powder ($M_w = 200\ 000\ \text{g}\ mol^{-1}$) from Pressure Chemical Co.

Charged Colloid–Polymer Dispersions. The investigated colloidal systems consisted of PMMA colloids and polystyrene dissolved in mixtures of *cis*-decalin and CHB. The *cis*-decalin/ CHB mixture is known to induce surface charges on PMMA colloids.⁹ Prior to use, CHB was washed with an equal volume of 37% HCl, deionized water, 5% (w/w) NaHCO₃ aqueous solution and twice more with deionized water. Drying was done

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 TABLE 1: Characteristics and Treatment of the Studied

 Colloidal Systems^a

				stable phase	
sample	$\phi_{ m p}$	solvent	$\phi_{\rm c}({\rm final})$	1g	9g
1	0.17	Dec/CHB	0.15	cluster fluid	
2	0.28	Dec/CHB	0.15	cluster fluid	
3	0.35	Dec/CHB	0.15	gel	
4	0.38	Dec/CHB	0.15	gel	
5	0.25	Dec/CHB	0.24		gel
6	0.24	Dec/CHB	0.24		gel
7	0.24	Dec/Tet/CCl ₄	0.64		glass

^{*a*} The initial colloid volume fraction was $\phi_c = 0.05$. Subsequent sedimentation under normal gravity (1g), or through centrifugation at 9g, resulted in a local volume fraction ϕ_c (final) near the bottom of the sample cells, where the analysis took place. The polystyrene polymer volume fraction ϕ_p , solvent composition, the observed stable phase and the formation route (two right columns) are indicated. The abbreviations Dec, CHB, and Tet refer to the solvents *cis*-decalin, cycloheptyl bromide, and tetralin. See the text for the definitions of cluster fluid and gel used here.

by adding 50 g L^{-1} CaCl₂ powder and stirring overnight. The powder was filtered out in a dust-free hood (Millipore Mitex Membrane filter type 10 μ m LS). The colloids were dispersed in *cis*-decalin and mixed with polystyrene in *cis*-decalin. CHB and cis-decalin were added subsequently such that the overall mass ratio of cis-decalin:CHB was ~3:10. At this composition the colloids were refractive index and almost density matched, allowing for CLSM studies and minimizing the influence of gravity on the studied systems. All samples (with a typical volume of 0.6 mL) were thoroughly shaken after preparation. Table 1 summarizes the sample details. The samples were initially prepared with a colloid volume fraction (ϕ_c) of 0.05 and polymer volume fraction (ϕ_p) as indicated in Table 1. Sedimentation under normal gravity (1g), or by means of centrifugation at 9g, increased the local volume fraction near the bottom of the sample cells. This is where the samples were analyzed. These volume fractions were quantified by image analysis and are indicated in Table 1 as $\phi_{\rm c}$ (final). These values were extracted from 2D images by comparing the numbers of particles per slice to homogenized samples where the true (3D) volume fraction was known. For samples 1–4 the final $\phi_{\rm c} \approx$ 0.15 while for samples 5 and 6 the volume fraction stabilized at $\phi_{\rm c} \approx 0.24$. Clearly, denser colloidal gels are formed by centrifugation at 9g than under normal gravity. Sample 7 consisted of 38.7%:39.3%:22.0% (v/v) of respectively cisdecalin, tetralin (Tet), and carbon tetrachloride (CCl₄) and was used as a control sample. This mixture induces a negligible charge on PMMA colloids¹⁷ and such dispersions thus do not exhibit electrostatic repulsions. The last column in Table 1 indicates in what stable state the colloids assembled (at least over a year) and the formation route (normal gravity or centrifugation at 9g). We refer to a suspension of clusters consisting of $\sim 2-20$ colloids that are at least stable over a year as the "stable cluster fluid phase". We define a colloidal gel as a sample with ϕ_c significantly below 0.5 in which the averaged particle mean square displacements do not significantly deviate from zero over a time window of at least an hour.

Interaction Potential Characterization. The short-range attractive and long-range repulsive interactions between the colloids were quantified as follows. The mean radius of gyration $\langle r_g \rangle$ of polystyrene with a molar mass of 200 000 g mol⁻¹ was estimated at 12.5 nm in *cis*-decalin.¹⁸ This results in a typical length scale ξ over which the depletion force acts relative to the colloid size of $\xi = r_g/a \approx 0.028$. Neglecting excluded

volume effects of the polymers, the depth of the attraction well between colloids as a function of polymer concentration is given by $-\beta U = \frac{1}{2}\phi_p(3/\xi + 2)$,¹⁹ with $\beta = 1/k_bT$. It is easy to verify that in the range $0.17 \le \phi_p \le 0.38$, the well depth in units of thermal energy lies within $9 \le -\beta U \le 21$.

The colloid charge was quantified by electrophoresis, using a Coulter Delsa 440SX and the procedure as described by Royall et al.²⁰ The suspension consisted of $\phi_c = 0.05$ in a mixture of CHB and 23.1% *cis*-decalin by weight (no polymer added). The run parameters were 100 V, 2.0 s on/0.5 s off, and a total run time of 300 s. We measured an electrophoretic mobility of $(0.023 \pm 0.003) \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and related it to the zeta potential with a standard electrokinetic model.²¹ Using the empirical relationship of Loeb et al.,²² we calculated the colloid charge Z to be $Z = 40 \pm 10 e$, where e is the elementary charge. We estimate the Debye screening length, $\kappa^{-1} \approx 850$ nm, by comparing with measurements on similar mixtures of cyclohexyl bromide and *cis*-decalin.²³ The addition of polystyrene polymer likely causes a further increase of the screening length, as it is nonionic and has a low (bulk) dielectric constant ($\varepsilon \sim 2-2.8$).

Confocal Laser Scanning Microscopy and Image Analysis. For imaging and quantitative analysis, samples were studied with a Nikon TE 2000U inverted microscope, equipped with a Nikon C1 confocal scanning head in combination with an Ar ion laser $\lambda = 488$ nm, Spectra Physics) and an oil-immersion lens (100× CFI Plan Apochromat, NA 1.4, Nikon). The typical imaged area was 50 × 50 μ m² with a frame resolution of 512 × 512 pixels and a rate of about 1 frame/s. Statistics were typically averaged over 100 images measured at heights separated by 0.3 μ m. Standard image analysis algorithms were used to track particle positions²⁴ and to extract nearest neighbor, string length, and cluster size distributions.²⁵

Results and Discussion

We observed that at polymer volume fractions $\phi_p < 0.028$ stable colloidal cluster fluids formed (Table 1). These stable cluster fluids have been seen before for similar systems ($\xi =$ 0.021) at these polymer and colloid volume fractions.⁹ Interestingly, we observed that the morphology of the clusters in these fluids changed over the course of days. Figure 1(A1) shows the presence of single colloids, doublets, and a few colloidal strings (linear aggregates of colloids) in sample 5 a few hours after preparation. Figure 1(B1) shows sample 6, identical in composition to sample 5, but now 3 days after preparation. Contrary to sample 5, mainly small compact clusters were present and hardly any colloidal strings were seen. The more compact clusters (from now on simply referred to as clusters; Figure 1(B1)) were found to be more favorable colloidal aggregate morphologies than the linear colloidal strings: stable cluster fluids consisted largely of clusters and only few strings. In order to study colloidal gel structures and dynamics, both samples 5 and 6 were now centrifuged at 9g (for 18 and 32 h respectively) to a colloid concentration of $\phi_c \approx 0.20$. This resulted in the formation of very different colloidal gel structures as shown in Figure 1(A2,B2). The gel in sample 5 (A2) clearly consisted of thinner colloidal branches than the gel in sample 6 (B2). The morphology of the colloidal clusters prior to centrifugation, mainly doublets and strings (sample 5) or clusters (sample 6), determined the thickness of the colloidal gel branches and thus the structure of the gel. We note that the branches in sample 6 resemble Bernal spiral branches as reported previously in highly similar system,⁷ but we did not determine the exact branch structure. The evolution of the colloidal gels in samples 5 and 6 was subsequently followed over time. Figure



Figure 1. 2D confocal microscopy images (50 × 50 μ m²) of samples 5 and 6 and control sample 7; see Table 1. (A1) Sample 5 a few hours after its preparation and before centrifugation. (A2) Sample 5 after centrifugation at 9*g* to $\phi_c \approx 0.20$. (A3) Sample 5, 3 weeks after centrifugation. (B1) Sample 6, with the same composition as sample 5, 3 days after its preparation, but before centrifugation. (B2) Sample 6 after centrifugation at 9*g* to $\phi_c \approx 0.20$ and (B3) 3 weeks later. Sample 7, before and after centrifugation are shown in (C1) and (C2), respectively. (C3) The same sample 3 weeks later. Note that the scale bar in (A1) applies to all of the images.

1(A3) shows the gel in sample 5 which evolved during 3 weeks after the density quench. On average, a thickening of the gel branches was observed, as compared to the gel that formed just after centrifugation. Figure 1(B3) shows the resulting gel in sample 6. In sharp contrast to sample 5, the gel branches became thinner over 3 weeks time. It is remarkable that the initially different gels in samples 5 and 6 evolved to a similar gel structure, which was stable over the course of a year. This observation implies that colloidal gels in the systems studied here are not structurally arrested, but slowly evolve toward a particular (meta)stable structure. In general, the kind of structural rearrangements as shown here has not been observed earlier (for example in uncharged colloid—polymer mixtures),²⁶ even though exchange of particles with a dilute monomer gas has been observed.²⁷

To check whether similar colloidal gels formed in uncharged colloid—polymer systems, control sample 7 was studied. Figure 1(C1) shows large colloidal aggregates, spanning the whole sample volume in freshly prepared sample 7, that are very different from the small aggregates in samples 5 and 6. Sample 7 after 18 h of centrifugation at 9g is shown in (C2). A dense, glassy colloidal phase formed, which did not change over 3 weeks time (C3). This result emphasizes the importance of charges on the colloid surfaces, in the formation of both cluster fluids and colloidal gels. In the systems studied here, gels only supported external stress in the form of a centrifugal field of

 \sim 9g if charges were present. In the absence of charge, glassy states formed as shown in Figure 1(C2,C3).

Further characterization of the colloidal cluster fluids and the colloidal gels was done by image analysis. Based on counting nearest neighbors, we identify the fractions of colloids in monomers, doublets, strings, and clusters. Strings are defined as aggregates containing more than two colloids, without particles that have more than two nearest neighbors and with single nearest-neighbor particles at their ends. Clusters are other aggregates. Figure 2A shows schematic representations of how a colloidal monomer, doublet, string or cluster was defined in the image analysis. Despite our data analysis in 2D, it clearly discriminates between colloidal cluster fluids and colloidal gels, and even quantifies differences in gel structures.

In Figure 2B the evolution of the aggregate composition of sample 2, a typical example of a stable cluster fluid (Table 1), is shown over 3 weeks' time. One day after preparation, 85% of the colloids appeared as monomers in 2D analysis. Over time, more colloidal doublets, strings, and clusters were present, but even after 3 weeks the sample was still a cluster fluid and no colloidal gel formed. We note that strings mainly formed initially, after which they collapsed to form clusters. Figure 2C shows the aggregate composition evolution of sample 3, a typical example of a colloidal gel formed under normal gravity (see Table 1). First, the number of single colloids decreased and the numbers of doublets, strings, and clusters increased. Subse-



Figure 2. (A) Definitions of a monomer, doublet, string (NN = nearest neighbor), and cluster as used in the 2D image analysis. (B) and (C) show the evolution in the aggregate compositions of samples 2 and 3 (Table 1). The difference between a stable cluster fluid (sample 2 in B) and a colloidal gel (sample 3 in C) is clearly reflected in the highly different aggregate compositions. In (C) the transition from a cluster fluid to a gel is indicated by the dotted line. In (D) and (E), the time evolution in aggregate composition of samples 5 and 6 is shown. The difference in their respective gel structures is reflected in the aggregate compositions. (D) shows that the gel branches in sample 5 got thicker over time, while (E) shows that the gel branches in sample 6 narrowed slightly over time. The legend in (B) also applies to (C–E), where it is emphasized that this is how the colloidal aggregates appeared in 2D (see text for more extensive explanation). Note that fractions are in percentages of all detected colloids.

quently, the number of doublets decreased to form a colloidal gel with branches that appear as strings or clusters in 2D analysis (the transition from a cluster fluid to a gel is indicated by the dotted line in Figure 2C). The analyses for gels obtained by centrifugation at 9g are shown in Figure 2, D and E, for sample 5 and 6, respectively. The aggregate composition in sample 5 prior to centrifugation (as in Figure 1(A1)) was analyzed and set as t = 0. After centrifugation, a gel formed whose branches were mainly detected as colloidal strings in 2D analysis (see Figure 1(A2)). Over time, more gel branches were detected as clusters, i.e. the gel branches thickened on average. For sample 6 the aggregate composition prior to centrifugation (as in Figure 1(B1)) was also analyzed and set as t = 0. Right after centrifugation, a colloidal gel formed with branches that were almost solely identified as clusters (see Figure 1(B2)). Upon aging, more branches were detected as strings; i.e., the gel branches thinned over time. The composition of the colloidal gels for samples 5 and 6 evolved over several weeks, but then both formed a gel with a similar structure that was stable over the course of 1 year at least.

More extensive analyses were performed on a stable cluster fluid (sample 2) and on aged (at least 3 weeks old) colloidal gels (samples 3–6). The results are shown in Figure 3. In the first analysis the percentages of colloids with a given number of nearest-neighbors (NN) were determined from 2D images. Figure 3A shows these nearest-neighbor distributions. This emphasizes that gels formed under normal gravity (samples 3 and 4) are in a different state than gels formed through centrifugation (samples 5 and 6). That is, in samples 5 and 6, the overall number of nearest neighbors is higher than in samples 3 and 4. This is in agreement with the higher local volume fraction ϕ_c (final) (Table 1) and the observed thicker branches



Figure 3. (A) Nearest-neighbor (NN) distributions of the stable phases of samples 2-6. (B) The fraction of colloids in gel branches that appeared as strings for samples 5 and 6, immediately and several weeks after centrifugation at 9*g*. All fractions are in percentages of all colloids as they appear in two-dimensional CLSM images.

in the gels of samples 5 and 6 (not shown). The nearest-neighbor distributions for samples 5 and 6 were almost identical, as was expected from the similar confocal images (Figure 1, A3 and B3) and aggregate composition (Figure 2, D and E).

A final illustration of the evolution of the two gels in samples 5 and 6 to a similar final state is shown in Figure 3B. It shows the size distribution of gel branches that are detected as strings in 2D analysis. Initially, in sample 5, the fraction of colloids detected in strings is high, while this is low for sample 6. In their stable gel states however, both gels have similar percentages of colloids in strings of all sizes. Note that the shallow yet persistent maxima at two colloids per branch might be an artifact of our two-dimensional analysis, which does not affect our main conclusion that dissimilar gels evolve to quantifiably similar structures.

The intriguing question that remains is whether at still longer times the gel state evolves to a periodic structure (lamellar or columnar) as predicted to be the ground-state in these systems.¹⁵ Because of the enormous time scales involved, we believe the only way to test this possibility is to try other formation routes in order to avoid the systems getting trapped in a gel state.

Conclusions

In summary, we have shown that similar colloidal gels can form through different pathways. The initial structure of the gels sensitively depends on the history of the samples before a density quench, in the form of centrifugation, takes place. The monomers, strings, or clusters form the building blocks for the gel branches that initially appear. One gel consisted mainly of thick, possibly Bernal spiral-like branches, whereas the other consisted of thin, string-like branches. These are not dynamically arrested states as they evolved over time into gels with similar characteristics (aggregate composition, nearest-neighbor distribution, and string size distributions). The formed colloidal gel was at least stable for over a year at room temperature and we showed that the presence of charge allowed the gels to support external stress in the form of a centrifugal field of at least 9g. In the absence of charge, gels formed under normal gravity conditions collapse into a high-density glassy state upon centrifugation.

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