Gel Transition in Adhesive Hard-Sphere Colloidal Dispersions: The Role of Gravitational Effects

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The role of gravity in gelation of adhesive hard spheres is studied and a critical criterion developed for homogeneous gelation within the gas-liquid binodal. We hypothesize that gelation by Brownian diffusion competes with phase separation enhanced by gravitational settling. This competition is characterized by the gravitational Péclet number Pe_g, which is a function of particle size, volume fraction, and gravitational acceleration. Through a systematic variation of the parameters, we observe the critical Pe_g of ~0.01 can predict the stability of gels composed of adhesive hard spheres.

The adhesive hard-sphere reference system is the simplest reference system for colloidal and molecular fluids that exhibits enthalpically driven phase separations (gas-liquid [1] and liquid-crystal phase coexistence [2]). However, adding attraction to stable hard-sphere colloidal dispersions can also lead to a wide spectrum of arrested states spanning from attractive driven glasses [3] to gels [4], and to self-similar fractals [5]. Two model colloidal systems, depletion-driven colloid-polymer mixtures [6,7], and thermoreversibly gelling octadecyl silica adhesive hard spheres (AHS) [4,8] have been studied extensively in an effort to define the dynamic arrest boundaries. The effective attraction in colloid-polymer mixtures arise from an imbalance in the osmotic pressure exerted on the colloids by the polymer in solution when the particle center-to-center distance between adjacent colloids is smaller than the characteristic size of the polymer [7]. This complex interaction potential leads to a complicated multicomponent gas-liquid phase separation [9]. Using a density- and refractive-index-matched colloid-polymer system, gelation is shown to be preceded by local phase separation into a colloid-lean gas and a colloid-rich liquid [10]. The final percolated network, composed of connected, dense clusters, is unevenly distributed in the volume space [6,10]. The other model AHS system exhibits thermoreversible gelation and is well studied in literature. It is comprised of silica particles grafted with an octadecyl brush dispersed in organic solvent. Gelation in these dispersions is manifested upon lowering the temperature, which leads to either crystallization or a collapse of the brush depending on the molecular structure of a solvent [11]. Dynamic arrest leads to a homogeneous gel or attractive driven glass at higher volume fractions and temperatures that are well above the gas-liquid critical point. Despite the density- and refractive-index mismatch, this type of dispersion does not exhibit phase separation in the process of forming a gel.

In addition, the gel strength of the thermoreversible system at low volume fractions, φ, is located at or below the binodal curve, which is indicative of a possibility of a stable gel phase even in the theoretical two-phase region [12]. Hence, experimental results on these two model systems are contradictory with regards to the role of phase separation as a prerequisite for gelation.

Gravitational settling is known to be important in colloidal crystallization, as shown by microgravity experiments [13,14], and can lead to collapse of a gel for dilute suspensions of colloidal particles with attractive interactions [15]. Gravity may also affect gas-liquid phase separation in such systems. It has been previously proposed that there exists a φ limit below which phase separation can be observed, which is termed φ_{gel} [15]. This limit arises from a competition between perikinetic aggregation, leading to dynamic percolation and gelation, and gravitation sedimentation, which facilitates phase separation. The rates have a nontrivial dependence on the particle size and fractal dimension as the gravitational force acting on the particles in a cluster grows faster than the dependence of the hydrodynamic friction on the radius of gyration of a cluster [16]. This competition is captured by the gravitational Péclet number, Pe_g [15], which compares the relative rates of sedimentation to Brownian diffusion. Briefly, as increasing attraction between particles leads to aggregation, these particle clusters diffuse by Brownian motion and sediment by gravity due to the mismatch in the densities of particle and suspending medium. If the particle clusters diffuse sufficiently fast such that they can bind to neighboring clusters and form a percolated network, dynamic arrest and gelation results. On the other hand, if gravitational settling is faster, the particle clusters will sediment before forming a space-filling network. The resultant dispersion will have heterogeneities on length scales much larger than that of individual particles, and

will often show macroscopic phase separation into a clear fluid nearly devoid of particles in equilibrium with a colloid-rich sediment. As the rate of diffusion and sedimentation depend differently on the degree of particle aggregation and the aggregate microstructure, the behavior of a given dispersion depends on the initial concentration of particles as well as the size of the particles. Our goal here is to quantitatively study this phenomenon by preparing a homologous series of particles with the same interaction potential, but varying particle size, and measure their thermoreversible gelation over a broad range of φ. As the silica particles are not density matched to the suspending medium, this system enables identifying the critical gravitational Péclet number, Pe_g^{crit}, and φ_{gel} above which homogeneous gelation is possible without phase separation.

The thermoreversibly gelling systems are comprised of octadecyl-coated silica particles suspended in n-tetradecane [4,8,12] Three different silica particles (Ludox TM-50 from Sigma-Aldrich, NexSil 125 from Nyacol, and Seahostar KE-P30 from Nippon Shokubai) were coated with octadecyl chains following the procedure of van Helden *et al.* [8] and described in detail in [11]. The particles have a diameter of 28.0 ± 2.8, 108.4 ± 11.4, and 290.0 ± 6.2 nm, respectively, as determined by fitting the small-angle neutron scattering (SANS) intensities to a polydisperse core-shell model with Schultz distribution [17]. The sizes are referred to as 30, 100, and 300 nm, respectively. The polydispersity of $\sim 10\%$ suppresses crystallization and enables studying gelation and the underlying fluid-fluid phase separation. The shell layer thickness is determined to be 18.5 and 21.0 Å at 20 and 40 °C, respectively, via SANS and neutron reflectivity [11]. The volume fractions φ are calculated by converting the mass of the AHS particles into volume using the measured skeletal densities of the particles and are further confirmed with SANS [4]. Importantly, the strength of the interparticle attraction are determined to high precision by SANS measurements of the structure factor using a procedure previously published and validated against simulations [12].

Samples are fluid at 40 °C and gel or phase separate upon quenching the temperature. The temperature of gelation T_{gel} at each φ is determined via standard rheological methods following the seminal work by Winter and Chambon, which has demonstrated that the gel transition occurs when the congruence of storage and loss moduli is observed and both moduli are proportional to ω^n, with $n \sim 1/2$ over many decades, where ω is the oscillatory frequency [18]. The corresponding Baxter parameter τ_B is determined by SANS at the corresponding T_{gel}. This defines the locus of the gel line for the adhesive hard-sphere fluid [4,12].

Figure 1 shows that homogenous gelation occurs at progressively lower values of τ_B with decreasing φ and
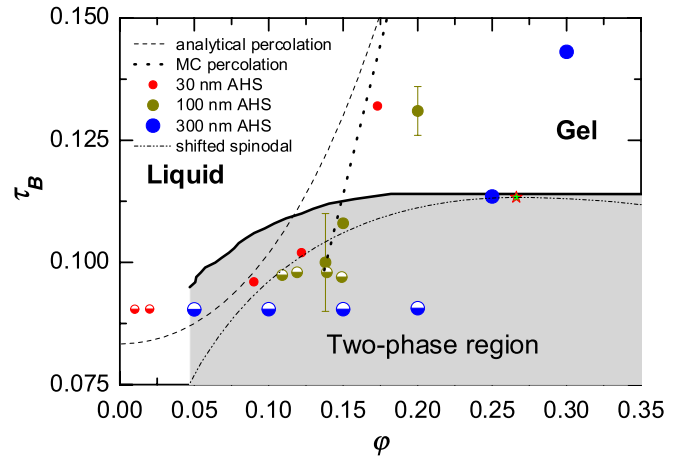

FIG. 1 (color online).   Filled symbols indicate τ_B of a homogeneous gel measured with SANS or ultra-small angle neutron scattering. Half-filled symbols refer to that of the colloid-rich phase of a phase-separated sample, where τ_B for the 100 nm particle dispersions (colloid-rich phase) were extracted from the SANS measurements, while τ_B of the 30 and 300 nm data points are determined via correlation (see Supplemental Material [24]). The dashed, dotted, and dash-dotted lines are the percolation line from the Percus-Yevick theory [25] and from Monte Carlo (MC) simulations [26] and the shifted spinodal boundary (see Supplemental Material [24]). The critical point is denoted by the green star at $\varphi = 0.266$, where φ is the volume fraction.

the gel line lies within the two-phase region at low φ. Lowering φ further does not induce a homogenous one-phase gel but leads to phase separation into an arrested, colloid-rich phase and a colloid-lean phase. This suggests that gels at such low φ are in a metastable state where the structure stability may be in competition with phase separation. Importantly, the lowest φ for which a homogenous gel forms, φ_{gel}, is observed to depend strongly on particle size. We find that φ_{gel} is 0.02, 0.14, and 0.20 for 30, 100, and 300 nm particles, respectively.

According to the corresponding state argument of Noro and Frenkel [19], the phase diagram for fluids with a range of attraction less than 14% of the hard-core diameter is universal. Since the relative ranges of attraction for these model systems are 1%, 0.3%, and 0.1%, respectively, this large difference in φ_{gel} cannot be a consequence of difference in the range of attraction. Rather, we refer to the work of Poon and Haw [15] and hypothesize that the reason for this strong particle size dependence lies with the effects of gravity competing with gelation. Gravitational effects have been well studied for sedimentation [20] and delayed settling of gels [21,22]. We extend the aforementioned argument to the gelation of AHS particles within the two-phase region [15]. When n particles of radius a aggregate and form a cluster, the cluster size scales with the mass fractal dimension d_f as $R/a \sim n^{1/d_f}$. Assuming a spherical geometry for the cluster leads to

$$v = \frac{2a^2 n^{1-(1/d_f)} |\Delta\rho| g}{9\eta}, \qquad (1)$$

where v is the sedimentation velocity, g is the gravitational acceleration, $\Delta\rho$ is the density difference between the particle and the suspension medium, and η is the suspension medium viscosity.

The corresponding rate for diffusion is given by the Stokes-Einstein-Southerland equation, where the cluster radius is used for the hydrodynamic particle size, is

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta a n^{1/d_f}}, \qquad (2)$$

where k_B is the Boltzmann constant, T is the temperature, and f is the drag coefficient.

A gel forms when φ_{eff} of the aggregates is ~ 1, such that $R \approx R_{\text{gel}}$, and then $R_{\text{gel}}/a \sim \varphi^{1/(d_f - S)}$, where S is the spatial dimension [23]. One can expect that a cluster will settle if Brownian motion is slower than sedimentation and vice versa. Therefore, comparing the time needed for a cluster to diffuse its characteristic size ($\tau_D = R^2/D$) to the corresponding time for sedimentation of a cluster over a distance comparable to its size ($\tau_S = R/v$) determines the relative importance between the two phenomena as

$$Pe_g = \frac{\tau_D}{\tau_S} = \frac{4\pi |\Delta\rho| g a^4}{3 k_B T} \varphi^{(d_f+1)/(d_f - S)}. \qquad (3)$$

Thus, gravitationally facilitated phase separation is anticipated when $Pe_g \gg 1$ and a homogenous gel phase when $Pe_g \ll 1$.

In our experiments, the parameters a, φ, and g in Eq. (3) are systematically varied to experimentally determine Pe_g^{crit}. The densities are measured by solution densitometry (Anton Paar DMA 4500 M) and the remaining parameter d_f is determined by fitting the fractal regime of the SANS spectra shown in Fig. 2 to a power law. d_f weakly decreases as a function of φ as verified in Ref. [4].

For each particle size, samples at sufficiently low φ are observed to phase separate, which is manifested by gravitational settling as the density of the particles (2.16, 2.08, and 2.05 g/cm³ in the order of increasing particle size) is higher than that of the fluid (0.760 g/cm³ [4]). Determining T_{gel} of dilute samples is not trivial as the samples sediment or fracture in the process of measurements. Therefore, we empirically estimate T_{gel} of such samples based on T_{gel} of homogeneous gels (see Supplemental Material [24]). The phase separation was visually observed to slow down after 1 week and practically cease after approximately 3 weeks of waiting time. Complete phase separation is frustrated by gelation when the strength of the gel's compressive yield stress is sufficient to arrest further gravitational settling of the dense phase. τ_B of the sedimented, gelled phase is determined by independent SANS measurements (see Fig. 1).
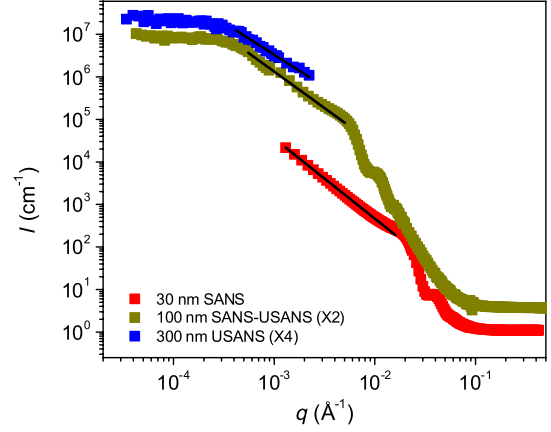

FIG. 2 (color online).   Scattering from colloidal gels with fits to determine the fractal dimension: $\varphi \sim 0.075$ (30 nm particles), $\varphi \sim 0.20$ (100 nm particles), and $\varphi \sim 0.25$ (300 nm particles). The power-law exponents correspond to the fractal dimensions (± 0.05) for each model system, which are $d_f = 1.9$, 1.7, and 1.5 for 30, 100, and 300 nm particle systems, respectively, 17. The data are vertically shifted for clarity.

Figures 3(a)–3(c) and Table I show results for systems under normal gravity at T_{gel} as discussed above. Note that all of these samples are located within the two-phase region of the AHS phase diagram (Fig. 1). Phase separation of some of the dispersions into cloudy, colloid-rich (bottom) and clear, colloid-lean phase (top) is evident within 10 hours to 3 days. In Figs. 3(a)–3(c) it is observed that for φ lower than φ_{gel}, increasing particle size at a fixed φ gives rise to a denser colloid-rich phase at the bottom and a larger volume of a colloid-lean phase at the top.

It is evident that whether gelation occurs prior to phase separation depends on the competition between diffusion and sedimentation, as captured by Pe_g. That is, as particles
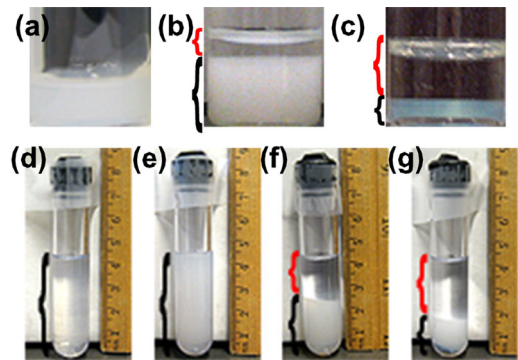

FIG. 3 (color online).   Induced phase separation in standard gravity with a systematic variation of a (a) $\varphi \sim 0.06$ (30 nm), (b) $\varphi \sim 0.075$ (100 nm), and (c) $\varphi \sim 0.05$ (300 nm). The red (upper) and black brackets indicate the colloid-lean and colloid-rich phases, respectively. (d) Nonphase separating dispersion of $\varphi \sim 0.075$ (30 nm) particles in normal gravity at 40 °C and after centrifuging in (e) $20g_0$, (f) $200g_0$, and (g) $2000g_0$ at 25 °C for 240 min.

TABLE I. Pe_g calculated for the experiments performed at normal gravity. Samples listed in black are homogeneous, stable gels [e.g., Fig. 3(a)], whereas samples listed in bold show evidence of sedimentation and phase separation-induced gelation [e.g., Figs. 3(b) and 3(c)]. The density-matched system is from Ref. [6]. It is demonstrated that the phase separation is observed when $Pe_g > 0.01$.

| | | Pe_g | | |
| | | Thermoreversible AHS | | Density matched |
	28 nm	108.4 nm	290 nm	1148 nm [6]
0.02	**0.012**	⋯	⋯	⋯
0.025	⋯	**0.29**	⋯	⋯
0.045	⋯	⋯	⋯	1.94
0.05	⋯	**0.067**	**0.89**	⋯
0.06	0.001	⋯	⋯	⋯
0.075	⋯	**0.028**	⋯	⋯
0.1	⋯	**0.015**	**0.28**	⋯
0.12	0.000	⋯	⋯	⋯
0.125	⋯	**0.010**	⋯	⋯
0.13	⋯	⋯	⋯	**0.08**
0.15	⋯	0.007	**0.14**	⋯
0.16	⋯	⋯	⋯	**0.043**
φ 0.17	0.000	⋯	⋯	⋯
0.2	⋯	0.004	0.088	⋯

aggregate and form a large structure, the structure becomes more susceptible to the gravitational pull, while the gel strength itself is controlled by the strength of attraction and the number of particles bonded in a unit volume. Therefore, a stronger attraction is needed for the larger particles to sustain their own weight and the ordering is consistent with this expectation, as shown in Fig. 3.

Pe_g is calculated for the cases shown in Fig. 3, as shown in Table I. Upon increasing the particle size at a fixed φ, Pe_g increases by a few orders of magnitude due to the fourth-power dependence on a [see Eq. (3)]. Based on the analysis shown in Table I, phase separation occurs when $Pe_g > \sim 0.01$. This defines a critical ratio Pe_g^{crit}, and hence φ_{gel}, below which phase separation precedes gelation.

Upon aggregation, the mass of a cluster m, and thus the gravitational pull, increases linearly with n while f increases linearly with R. Because m increases more quickly than f, v increases as particles aggregate. It is also true that D decreases as the cluster grows. Our work, to the best of our knowledge, quantitatively studies the interplay between Brownian diffusion and sedimentation of clusters upon dynamical arrest for the first time and establishes experimentally Pe_g^{crit} is ~ 0.01. That Pe_g^{crit} is less than order one is not surprising given that dynamic percolation leading to gelation requires more than just the initial, tenuous contacts between growing Brownian clusters to support the stress induced on the network by gravity. Thus, given the definition, it is reassuring that $Pe_g^{crit} < 1$, such

that Brownian diffusion must be significantly rapid to create a network capable of supporting the gravitational stress in order to form a stable, homogeneous gel.

The other parameter in Pe_g^{crit} that can be controlled is the gravitational acceleration. As a test of our identification of $Pe_g^{crit} \sim 0.01$ samples are gelled under centrifugation as shown in Figs. 3(d)–3(g). A dispersion of 30 nm particles at $\varphi \sim 0.075$ is subjected to 20, 200, and $2000g_0$ at T_{gel} for 240 min, where g_0 is the standard gravity. Here, 20, 200, and $2000g_0$ correspond to Pe_g of ~ 0.008, ~ 0.08, and ~ 0.8, respectively. The results show that samples phase separate in $200g_0$ and $2000g_0$ while no phase separation is observed in $20g_0$. This experiment independently confirms $Pe_g^{crit} \sim 0.01$ as the threshold between phase separation and gelation. The effect of gravitational acceleration is further corroborated with Monte Carlo simulations (see Supplemental Material [24]).

In summary, we studied the competition between homogeneous gelation and phase-separation-induced gelation in a model thermoreversible AHS system. Our results show that homogeneous gelation is possible within the two-phase region and below φ_c without phase separation as long as gravitational sedimentation does not overwhelm gelation by Brownian diffusion. Thus, this AHS system can gel without phase separation as long as gravitational sedimentation is not dominant. Further, by studying a homologous series of particles of varying size and by varying the gravitational acceleration, we demonstrate that a competition between gravitational sedimentation and diffusion as characterized by the gravitation Pe_g can be used to quantitatively predict the phenomenon, with $Pe_g^{crit} \sim 0.01$ the threshold.

Finally, we note that previous experiments using much larger, but nearly index-matched particles (~ 1000 nm), where the attraction is induced by an addition of a non-adsorbing polymer, always show heterogeneous phase separation for samples tested below the critical concentration [6,10]. We can estimate the conditions for these experiments and determine whether they exceed the Pe_g^{crit} identified in this work. The particles are density matched to eliminate settling. However, because these are relatively large particles, necessary for confocal imaging, an uncertainty in the density matching of only 1.5×10^{-4}, which is less than the reported uncertainty, leads to $Pe_g > 0.01$. We also note that this level of density mismatch could also be a result of thermal fluctuations of order $\pm 0.1\,°C$, which is comparable to experimental uncertainty in the temperature control in the confocal microscope. Such fluctuations would lead to fluctuations in the density mismatch and, consequently, body forces sufficient to compete with the Brownian diffusion of clusters and prevent homogeneous gelation. Hence, gelation induced by phase separation can be anticipated for these colloid-polymer mixtures, even without bulk sedimentation. It is important to recognize, however, that there are also additional differences between

these two different methods of inducing attractive interactions, as noted previously [4]. Homogeneous gels for our system are found near to the binodal and probably above the spinodal, which is given by the estimated line shown in Fig. 1 (as the exact spinodal line is not known for the AHS fluid). On the other hand, polymer depletion systems are thought to be quenched below the spinodal [6]. If so, this difference could also explain the heterogeneous gelation observed in the depletion flocculated systems. Further, the fact that the thermoreversible adhesive hard-sphere dispersions actually require contact for attraction may lead to long bond lifetimes that are not observed for the polymer-colloid mixtures [7]. Such long lifetimes may play an important role in stabilizing the homogeneous gel phase [7]. In conclusion, the experiments and their analysis presented here explain the important role of gravity in the gelation of dispersions of adhesive hard spheres. They also provide quantitative guidance for designing nanomaterials either by homogenous gelation or heterogeneous gels by phase separation.

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