

Phase Behavior in Highly Concentrated Assemblies of Microgels with Soft Repulsive Interaction Potentials

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Microgel particles with a soft repulsive interaction potential are investigated with particle tracking methods to study the phase behavior of soft-sphere systems. The use of poly(*N*-isopropylacrylamide) particles allows the effective volume fraction of a sample to be tuned via thermal modulation without altering the particle number density. This allows for investigation of the phase behavior of an assembly as a function of its initial packing density. In particular, we have elucidated the influence of soft colloid “overpacking” on the freezing effective volume fraction ($\phi_{\text{eff},f}$). These studies thereby illustrate the interplay between energetics/packing forces occurring at the colloidal and polymer chain length scales.

Introduction

Colloidal suspensions and assemblies have been studied extensively as model systems for fundamental interactions and ordering at the molecular level.^{1,2} Understanding colloidal phase behavior and crystallization properties is also essential for the development and implementation of photonic materials based on the periodic assembly of particles.^{3,4} Most studies have focused on model hard-sphere systems,^{1,5–7} but in recent years, suspensions of particles that are soft and deformable have been studied more extensively. For example, simulations carried out by Löwen and co-workers^{8–10} have explored the nature of star polymer dispersions by using arm density to modulate the softness of the particle interaction potential. They have found that soft interactions lead to much richer phase diagrams⁹ than are observed for the hard-sphere model. Polymer microgels, in particular poly(*N*-isopropylacrylamide) (pNIPAm), have been studied as a model system for soft interactions, with the rheological and structural properties,^{11,12} as well as phase behavior,^{13–15} being a topic of significant interest. Richtering and co-workers^{16,17} have recently reported rheological and small angle neutron scattering studies that illustrate the merit of using pNIPAm microgels as model systems for soft colloids. They have concluded that when structural properties, such as the radial decrease of polymer density, of the microgels are accurately accounted for, they can be considered a good model, especially for concentrated dispersions. Furthermore, thermoresponsive microgels provide an excellent “tunable” model system for probing soft-sphere interactions, because the particle volume and, hence, the overall volume fraction of the dispersion can easily be modulated with temperature while the particle number density is held constant.

Purely repulsive particle interactions can be modeled as a simple inverse power potential, $V \propto 1/r^n$, where r is the center-to-center distance between particles. Simulations carried out by

Hoover et al.¹⁸ and Agrawal and Kofke¹⁹ and more recently by Prestipino et al.²⁰ have shown that the phase behavior of a soft particle system changes as a function of the softness of the potential ($1/n$). For a hard-sphere model, for which $n_{\text{hs}} = \infty$, the volume fraction of freezing is $\phi_{\text{hs}} = 0.494$; this transition marks the volume fraction at which particles in a fluid dispersion begin to nucleate and form crystals. As n is made smaller, the potential becomes softer, shifting the density at which freezing occurs to higher volume fractions and decreasing the breadth of the fluid-crystal coexistence region. In the simulations described above, the freezing transition of soft particles did not diverge significantly from the hard-sphere model until $n \sim 20$.

Experimentally, this has been shown for polymer microgels modeled as softly repulsive via the inverse power potential. Poly(methylmethacrylate) (PMMA) microgels swollen in benzyl alcohol were observed to have a freezing transition of $\phi_f = 0.548$ with a coexistence region that spans a concentration range $\Delta\phi = 0.026$, as compared to the hard-sphere case of $\Delta\phi = 0.051$.²¹ Through experiment and comparison to the above-mentioned simulation data, the value of n was found to be ~ 20 . Microgels of pNIPAm with a cross-linking density of 1.4 mol % have also been examined in this manner, finding a freezing transition of $\phi_f = 0.59$, a coexistence region of $\Delta\phi = 0.02$, and ascribing to the particles a value of $n \sim 12$ – 13 .¹¹ These examples give a small glimpse into how the phase behavior of softly repulsive systems differs from the hard-sphere model. In this paper, we hope to better elucidate the phase diagram for assemblies of soft repulsive spheres. Specifically, we present experimental observations of the melting behavior of thermoresponsive pNIPAm microgel particles at volume fractions well above the maximum packing fraction of hard spheres to explore their behavior in a region of the phase diagram that is exclusive to soft particles and has to date been largely unexplored experimentally.

Experimental Section

Materials. The monomer *N*-isopropylacrylamide (NIPAm, Aldrich) was recrystallized from hexane (Fisher Scientific) prior to use. The cross-linker *N,N'*-methylenebis(acrylamide) (BIS)

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and the initiator ammonium persulfate (APS) were purchased from Aldrich and used as received. All water was purified to 18 M Ω with a Barnstead E-Pure system.

Synthesis. Cross-linked pNIPAm particles were synthesized in three batches via precipitation polymerization²² without the addition of a surfactant stabilizer. For all syntheses, the total monomer concentration was 140 mM in 100 mL of N₂-purged aqueous solution, and APS was warmed to 70 °C for 30 min prior to initiation of the reaction. All reactions were allowed to proceed for 4 h at 70 °C under a N₂ blanket. All particles were purified by repeated centrifugation/resuspension in distilled, deionized water. To synthesize 1 mol % cross-linked particles, the solution contained 138.6 mM (1.5687 g) NIPAm, 1.4 mM (0.0277 g) BIS, and 0.0346 g of APS. To synthesize 2 mol % cross-linked particles, the solution contained 137.2 mM (1.5529 g) NIPAm, 2.8 mM (0.0434 g) BIS, and 0.0235 g of APS. To synthesize 3 mol % cross-linked particles, the solution contained 135.8 mM (1.5367 g) NIPAm, 4.2 mM (0.0649 g) BIS, and 0.0369 g of APS.

Dynamic Light Scattering (DLS). Average hydrodynamic radii (R_h) and polydispersities of the particles were characterized by DLS (Protein Solutions, Inc). All data presented herein are an average of 25 measurements with 10 s acquisition times. Samples were equilibrated for 10 min at a given temperature before measurements were taken. The average R_h of the particles was calculated from the measured diffusion coefficients using the Stokes–Einstein equation by a regularization algorithm included in the manufacturer-supplied software (Dynamics v5.25.44, Protein Solutions, Inc).

Rheometry. Viscosity measurements were made on an MCR300 (Anton Paar) rheometer. All measurements were performed using a 50-mm/1° cone–plate geometry with Peltier temperature control. Dilute particle suspensions were equilibrated at each temperature for 10 min and measured with shear rates of 30–1000 s^{−1}; no shear-thinning is observed for these dilute suspensions so that the rheology can be described by a Newtonian viscosity.

Microscopy. Dispersions of varying concentrations were prepared and introduced into rectangular capillary tubes (Vitrocom), 0.1 mm × 2.0 mm × 50 mm, and sealed to form a closed system as described previously.¹³ On an Olympus IX71 microscope with a 100× oil immersion objective, bright field microscopy images (DIC mode) were recorded as a function of time with a Luca CCD camera (Andor) at the middle of the tube, ~50 μ m away from the wall to avoid perturbations from the glass interface. The sample temperature was controlled with a temperature stage (Physitemp) as well as an objective heater (Bioptechs) to within 0.1 °C. Images were recorded, starting at room temperature, at increasing 0.5 °C intervals. Samples were thermally equilibrated for 15 min between measurements. Images were recorded at 10 frames/s for 16.5 s.

We note that we have observed that following initial introduction of the sample into the capillary tubes, a nonequilibrium state is produced. This resulted in artificially high freezing transitions and low mean-squared displacements (MSD, vide infra) directly after preparation. Experiments in which a freshly prepared sample was monitored hourly for a 24 h period showed that the diffusion properties of the assemblies of 1 and 2 mol % cross-linked particles began to increase after ~10 h, and after ~16 h, the MSD remained consistent for the rest of the experiment. The MSD of assemblies of 3 mol % cross-linked particles was found to be stable after 48 h. Given this observation, samples of 1% and 2% particles were given at least 24 h to relax before starting any measurements, and samples

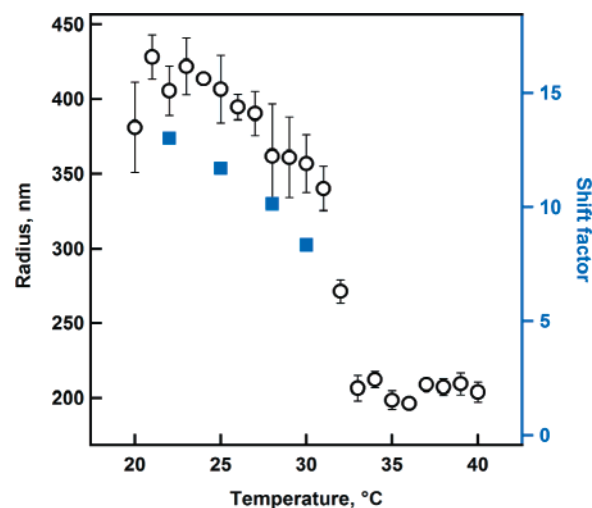


Figure 1. Temperature-dependent hydrodynamic radii of 2% particles measured via DLS (circles) and shift factors calculated from relative viscosities at different temperatures (squares).

from 3% particles were given at least 48 h to relax. We hypothesize that polymer chain entanglement, low levels of reversible aggregation due to incomplete redispersion of the polymer pellets, or both may be responsible. However, the exact nature of the initial nonequilibrium state and the process of relaxation have not been elucidated; these phenomena are currently being investigated in our laboratories.

Results and Discussion

A particular advantage of using pNIPAm lies in its lower critical solution temperature (LCST) behavior, with an LCST of ~31 °C in water.²³ In cross-linked particles, the LCST is closely correlated with a volume phase transition in which the polymer network collapses, expelling water and decreasing the size of the particle. The temperature dependence of R_h is shown for the 2 mol % cross-linked particles in Figure 1, where we observe a gradual decrease in size below the LCST, followed by a dramatic decrease in size as the temperature crosses the LCST. The same trend is observed for the 1 and 3 mol % cross-linked particles. The average R_h values for the particles as measured by DLS at 25 °C are listed in Table 1. The temperature range over which R_h decreases slowly (between 20 and 30 °C) is the range that has been utilized in this study to modulate assembly volume fraction in a controlled manner. It has been shown¹¹ through rheological studies that no significant change in the attractive portion of the particle interaction potential is evident for temperatures as high as 30 °C. Below this temperature, the particles can be considered purely repulsive.

Because microgels are highly solvent swollen polymer networks with a variable density, the particle volume fraction of a dispersion or assembly cannot be calculated directly from knowledge of the particle size or the mass of the particle components. A fairly straightforward way to establish an effective volume fraction ϕ_{eff} of the solvent-swollen particle is through the Einstein relation for hard spheres, which relates the relative viscosity, η_{rel} , of a dilute dispersion to the volume fraction of spheres. Inclusion of a second-order term derived by Batchelor is necessary to account for the effect of hydrodynamic interactions between particles.²⁴

$$\eta_{\text{rel}} = 1 + 2.5\phi_{\text{eff}} + 5.9\phi_{\text{eff}}^2 \quad (1)$$

In eq 1, $k \cdot c$ can be substituted for ϕ_{eff} , where c is the polymer

TABLE 1: Average Hydrodynamic Radii and Shift Factors for Particles Used in These Studies

particle [cross-linker]	R_h (25 °C) [nm]	k (22 °C) ^a	k (25 °C) ^a	k (28 °C) ^a	k (30 °C) ^a
1%	316 ± 8	22.01 ± 0.74	19.29 ± 0.62	15.83 ± 0.45	12.11 ± 0.35
2%	407 ± 22	12.45 ± 0.86	11.1 ± 0.54	9.39 ± 0.433	7.79 ± 0.38
3%	277 ± 5	12.02 ± 0.58	11.03 ± 0.38	9.67 ± 0.54	8.31 ± 0.74

^a Uncertainty in the shift factor k was calculated at a 90% confidence interval.

TABLE 2: Particle Density, Spacing, and Freezing Transitions of Assemblies

particle [cross-linker]	wt %	r^a [nm]	r/σ^b	$\phi_{\text{eff},f}^c$
1%	4.460	520.5	0.9182	58.29
	4.024	543.1	0.9581	54.95
	3.808	539.7	0.9521	56.69
	3.360	566.9	1.000	52.05
	3.142	594.0	1.0479	58.15
2%	7.977	872.8	0.9102	65.16
	7.206	899.5	0.9381	63.01
	6.797	927.8	0.9676	61.38
	6.385	953.9	0.9947	59.50
	5.995	958.9	1.000	59.31
	5.567	990.1	1.032	58.28
	5.180	1012	1.056	57.21
3%	7.508	623.3	0.9397	65.02
	7.104	636.7	0.9599	63.14
	6.692	656.7	0.9900	59.48
	6.241	663.3	1.000	55.47
	5.841	683.3	1.030	54.58
	5.346	690.0	1.040	53.61

^a Center-to-center distance of particles calculated from the radial pair distribution. ^b Noncompressed particle diameter derived from r at effective volume fractions of 0.74 at 22 °C. ^c Effective volume fraction of freezing.

concentration in wt/wt and k is a shift factor.²⁵ Once determined, k values can be used to calculate ϕ_{eff} for samples at concentrations outside the dilute regime. Experimental k values were obtained from a series of dilute suspensions ranging between 0.001 and 0.16 wt/wt of polymer. The suspensions were found to be Newtonian, and viscosities were plotted against the polymer concentration and then fit to eq 1. The k values obtained for the microgel particles used in this study at various temperatures are presented in Table 1. In Figure 1, the k values for the 2 mol % cross-linked particles can be seen overlaid on their hydrodynamic radius data. Note that the general trends of the two data sets correlate well, with the shift factor decreasing with temperature in the same fashion as the particle size. Thus, the effective particle volume fraction of any dispersion decreases as a function of increasing temperature.

Recorded image time series were analyzed with a modified form of particle-tracking routines originally developed by Crocker and Grier²⁶ to obtain particle trajectories and MSD values as a function of lag time, τ . Figure 2 shows the MSD versus τ and the corresponding trajectory images at three different temperatures for a typical assembly. Note that for all samples, at least 2000 particles are tracked in order to obtain statistically meaningful data. Occasionally, particle positions or trajectories cannot be rigorously defined due to particle displacement in the z -dimension. In these cases, the trajectory maps may show “empty” spaces in the map. These spaces should not be misconstrued as being due to the absence of a particle, but rather, as the absence of statistically robust data at that position. As described above, the MSD plots indicate the ensemble behavior of the dispersion and reflect the dynamic behavior of the assembly. Below the melting temperature, the assembly is frozen or caged, as indicated by the relatively flat MSD plot (circles and squares). As the particles deswell and the system becomes fluidlike, faster dynamics are observed in the MSD

plot as an increase in particle displacement with time (triangles). Interestingly, at 24.5 °C the MSD curve displays a prominent hump, which arises from a sample displaying equilibrium coexistence between a fluid and crystalline phase. Faster particles in the fluid fraction cannot be tracked for long lag times, as they tend to diffuse out of the focal plane. As a result, the MSD is weighted to the slower or caged particles at long lag times. If the trajectories are fractionated into fast and slow particle populations before calculating the MSD, the behavior of the individual phases is revealed. It should also be noted that the dynamics of individual particles could be observed by inspection of the trajectory images. These data show the 2D positions of the particles over the course of the experiment; confined or caged trajectories are observed for crystalline or glassy assemblies, and diffuse trajectories are observed for fluid samples.

Due to the soft thermoresponsive nature of the pNIPAm microgels described above, assemblies of particles can easily be packed and even ordered into crystals at particle concentrations equivalent to $\phi_{\text{eff}} > 0.74$ for fully swollen particles. In other words, the individual particles can be restricted to volumes smaller than their dilute solution equilibrium swelling volumes by simply increasing the polymer concentration to values for which $k \cdot c > 0.74$. Particle assemblies with such high number densities can be released from their kinetically trapped, high-energy glassy (or jammed) state via a thermal annealing process: heating, followed by slow cooling to form well-ordered crystals, as we have reported previously.^{13,27,28} This can be seen in Figure 3 where a sample containing 7.508 wt % of 3% particles was imaged in (a) an initially amorphous state, (b) at a temperature above the LCST of the polymer, and finally (c) after being cooled slowly for a period of hours to room temperature. In image c, the crystalline order of the sample is apparent from the multiple colors being diffracted from the sample (Bragg diffraction).

The transition shown pictorially in Figure 3 is typically characterized as a melting/freezing transition; however, the specific terminology associated with this transition is slightly more complex. The “freezing point” for colloidal dispersions is defined as the volume fraction where the onset of crystal formation is first observed, whereas the “melting point” is the volume fraction at which particles in a solid crystalline assembly first gain fluid mobility. In most cases, these transitions are separated by a small volume fraction range over which the assembly displays phase coexistence; for hard spheres, melting occurs at $\phi_m = 0.545$ and freezing at $\phi_f = 0.494$. Given these definitions, it is important to consider them in the context of our experimental procedures. In the experiments described below, changes in the colloidal phase behavior are observed as the volume fraction is *decreased* by applying incremental temperature *increases*. The critical information gleaned from these experiments is the volume fraction at which the assembly becomes *completely* fluid, i.e., the freezing point. Figure 4 illustrates this experimental procedure pictorially; the ϕ_{eff} , bright field images, particle trajectories, and MSD data of a sample are shown as the temperature is increased to the point of a total fluid transition. The red line indicates $\phi_{\text{eff},f}$. Experimentally, the

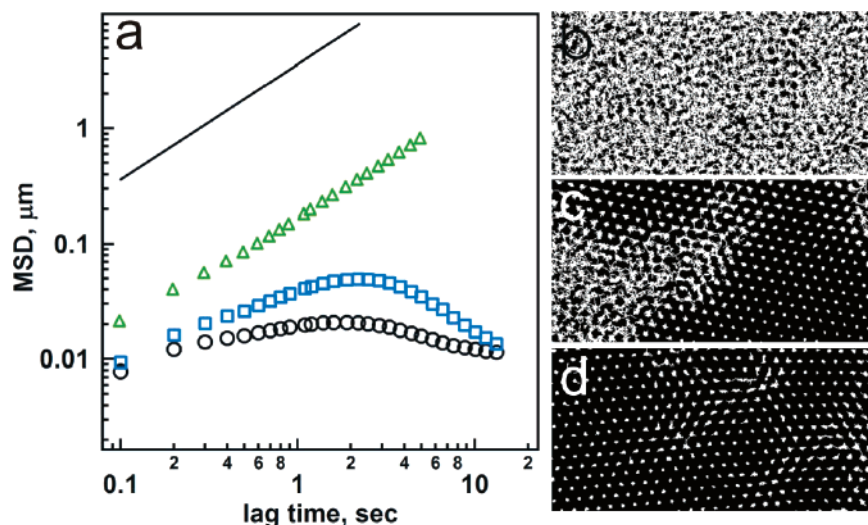


Figure 2. Colloid dynamics as a function of temperature. (a) MSD plots: MSD for an initially glassy assembly with a polymer weight percent of 5.18 at 24 °C [$\phi_{\text{eff}} = 59.5$ (circles)], 24.5 °C [$\phi_{\text{eff}} = 58.0$ (squares)], 25 °C [$\phi_{\text{eff}} = 56.5$ (triangles)]. The MSD for a freely diffusing particle calculated from the hydrodynamic radius of the particles at 25 °C is shown as the solid line. (b–d) Particle trajectories for assembly at (b) 25 °C; (c) 24.5 °C; and (d) 24 °C. The pronounced peak seen in the MSD curve for the assembly at 24.5 °C is due to the phase coexistence observable in c; this can also be seen to a lesser degree at 24 °C and in d.

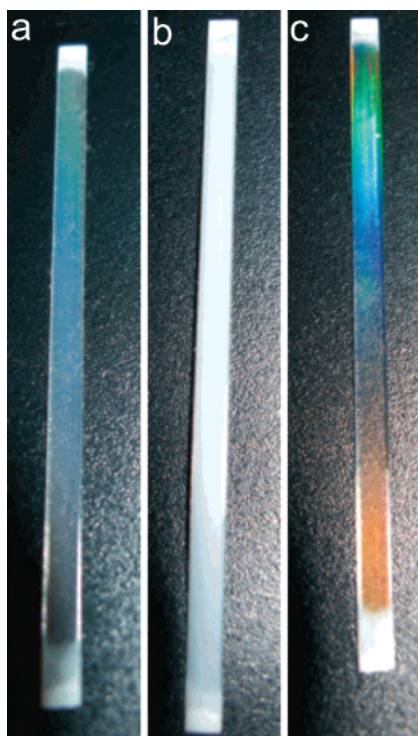


Figure 3. Assembly of 3% particles with a polymer wt % of 7.508 at room temperature (a) initially amorphous glassy state after introduction into the sample tube, (b) heated above the LCST of the polymer to a turbid fluid, and (c) showing Bragg diffraction due to crystalline order after slow cooling to room temperature over a period of hours.

freezing point was established from MSD data and was defined as being midway between the highest temperature at which crystals were observed and the lowest temperature at which all particles diffused freely. The effective volume fraction of freezing, $\phi_{\text{eff},f}$, was calculated from the experimentally determined freezing temperature and the corresponding k value. The error in $\phi_{\text{eff},f}$ was found to be approximately ± 4 –7% for all assemblies. This error was calculated by accounting for a temperature uncertainty of ± 0.25 °C along with all errors associated with the fitting of the k values.

Because of the difficulty in directly comparing the particle sizes in dilute solution with crystals of different packing densities, we employed a simple normalization method to determine packing densities in an internally consistent manner. The degree of “overpacking” or compression of each assembly was determined by a normalization of the crystal lattice constant, which was calculated from the radial pair distribution function. For all assemblies, the center-to-center distance r between particles was determined from the radial pair distribution nearest neighbor peak. For this normalization, we assume that the hard-sphere packing limit, $\phi_{\text{eff}} = 0.74$, is the highest volume fraction at which it is reasonable to assume little or no perturbations in microgel particle size and structure. The center-to-center distance, or r , of the assembly that has $\phi_{\text{eff}} = 0.74$ at 22 °C is defined here as σ . Our assumptions essentially define this as the diameter of a single unperturbed particle. The assembly “overpacking” or degree of particle compression is then defined as r/σ , where r is a function of particle concentration, and σ will be a constant for each particle type studied. For $r/\sigma < 1$ the particles in the assembly are compressed, and for $r/\sigma > 1$ the particles are crystalline but below maximum hard-sphere packing. In the case of hard spheres, the maximum packing is $r/\sigma = 1.0$, whereas at values of $r/\sigma \geq 1.11$, a crystal will lose order and begin melting. Table 2 contains r and r/σ values for all samples used in this study.

Given the above definitions of “overpacking” and the explanations of our experimental procedures, we can now consider the main results of this work. These data are summarized in Figure 5, which shows the $\phi_{\text{eff},f}$ as a function of compression (r/σ) for assemblies of 1%, 2%, and 3% cross-linked particles.²⁹ To reiterate, the $\phi_{\text{eff},f}$ axis is derived from the temperature-dependent particle tracking data; this value reflects the ease with which the sample melts upon heating induced particle shrinkage. It is, at first glance, odd to note that the assemblies composed of 2% and 3% particles tend to melt more easily as the degree of overpacking is increased. Furthermore, the slope of the line is larger for the 3% particles than for the 2% particles. The 1% particles do not show a clear trend in $\phi_{\text{eff},f}$ with packing density, however, regarding experimental uncertainty.

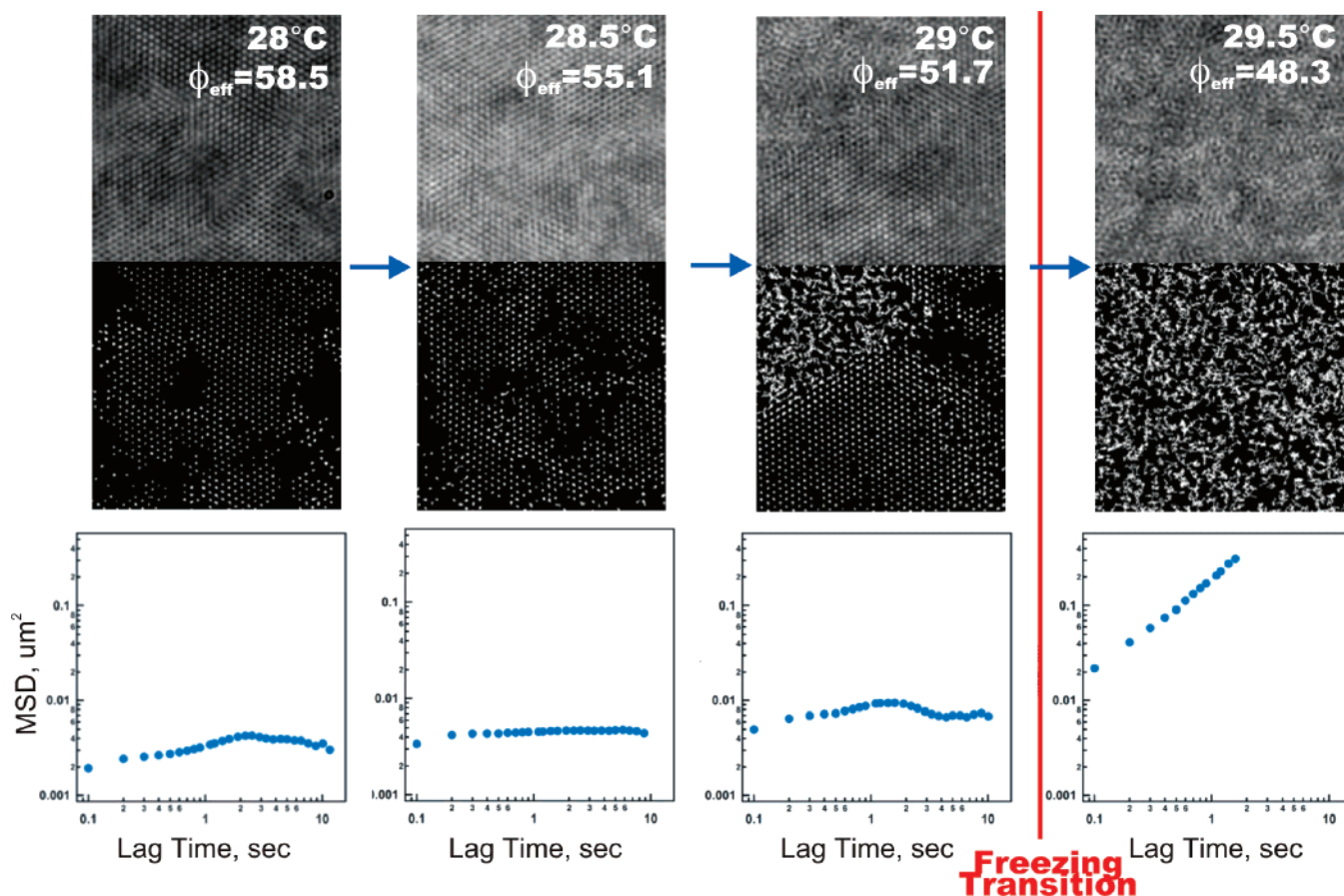


Figure 4. Illustration of the experimental process. The ϕ_{eff} , bright field image, particle trajectories, and MSD data are given for a sample at each temperature increment as the sample is heated to the point of melting. The red vertical line represents the point at which all order is lost to the fluid, that is, the freezing transition.

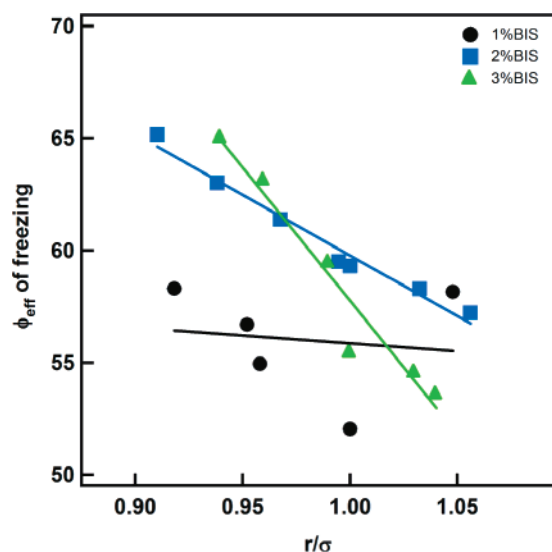


Figure 5. The freezing ϕ_{eff} as a function of compression for assemblies of 1% particles (triangles), 2% particles (circles), and 3% particles (squares). The lines are linear regressions to the data.

The increase in $\phi_{\text{eff},f}$ observed with decreasing r/σ can be rationalized by considering the growing osmotic pressure associated with overpacked assemblies composed of the 2% and 3% particles. In terms of the inverse power potential, as r approaches and then becomes smaller than σ , the interparticle potential increases exponentially as a function of n . For assemblies with greater degrees of overpacking, we therefore expect an overall increase in the repulsive (or internal) energy

as the polymer chains are asked to adopt a more condensed state. In other words, the particles are essentially sampling a higher energy portion of the interparticle potential as they are compressed more relative to their dilute-solution equilibrium swelling volume. This increased internal pressure in the particles will therefore cause the internal energy of the assembly to become higher as the particles are overpacked to a greater degree. This increase in the internal energy of the system will therefore require that less latent heat is necessary to induce a phase transition.³⁰

The different rates at which the freezing transition of 2% and 3% assemblies increase with overpacking, and the apparent lack of a consistent trend in the 1% assemblies can be attributed to the effect that cross-linking density should have on the particle compressibility. More highly cross-linked polymer networks are expected to be more rigid. In the case of microgel particles, this translates to an effective hardening of the particles, a larger value of n , and a steeper increase in energy closer to $r = \sigma$. Presumably, in the case of the 1% particles, the interaction potential is so soft that the concentration range utilized in this study was unable to probe small enough values of r to observe a marked increase in $\phi_{\text{eff},f}$ with packing density.

Conclusions

In conclusion, we have investigated phase transitions in highly concentrated assemblies of thermoresponsive microgels with soft repulsive interactions modeled as an inverse power potential. We have observed a rise in the freezing transition of assemblies as a function of particle concentration and have attributed this phenomenon to an increase in the internal energy of the system,

which is dependent on both particle softness and concentration. These results demonstrate that in the regime where soft colloids are “overpacked”, the phase transition behavior can be directly linked to the compressibility of the particles. Importantly, under these conditions, the increase in internal energy due to compression of the soft particles can result in a dramatic change in the effective volume fraction at which the colloidal crystal melts. Such phenomena may be of considerable importance as the use of soft building blocks in the assembly of nanostructured materials becomes more widespread.

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