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An experimental study of a model colloid-polymer mixture

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Abstract. — We report an experimental study of the phase behaviour of a model hard sphere colloid + non-adsorbing polymer mixture – sterically stabilised PMMA (radius = 217 nm) and polystyrene ($r_{\rm H} = 12.8$ nm) in cis-decalin. It was found that the main effect of adding polymer was to expand the fluid-crystal coexistence region of the colloidal suspension, which spans $0.494 < \phi < 0.545$ ($\phi =$ colloid volume fraction) at zero polymer concentration. The separated dilute and dense colloidal phases showed marked polymer partitioning, giving rise to strong osmotic compression of the colloidal crystal phase. These findings are shown to compare favourably with a recent statistical mechanical model [Lekkerkerker *et al. Europhys. Lett.* 20 (1992) 559)]; possible sources of discrepancies are discussed. In addition the presence of a small amount of polymer in colloidal glasses ($\phi > 0.58$) was shown to induce crystallization. At high enough polymer concentrations crystallization was inhibited at all ϕ and a « gel » state was obtained. Finally, the effect of temperature on the phase behaviour is reported. Increasing temperature lowers the amount of polymer needed to cause fluid-crystal phase separation as well as transition into the « gel » state.

1. Introduction.

It is known from experiment (see, for example, [1-6]) that the addition of enough nonadsorbing polymer to a suspension of colloidal particles causes phase separation to occur. Understanding this phenomenon is of practical importance, as well as of fundamental interest, since many industrial products are, in essence, colloid + non-adsorbing polymer mixtures. Nevertheless, despite a considerable amount of research, uncertainties remain in both experiment and theory. Here we report a study, which includes several new features, of the phase behaviour of a model colloid-polymer mixture in which the two components are individually well characterized.

The earliest theoretical discussion of this subject is that of Asakura and Oosawa [7]. When the surfaces of two colloidal particles are separated by a distance less than the size of a polymer coil, polymer is excluded from a *depletion region* between the particles. The polymer therefore exerts a net osmotic force which pushes the two particles towards one another. The effect of polymer can thus be described by adding a polymer-induced attractive potential to the bare interparticle interaction (V_c) . The range of this « depletion potential » (V_{dep}) is determined by the polymer size (e.g. as given by its radius of gyration, r_g), while its depth is proportional to the polymer concentration. Various theoretical attempts have been made to determine the form of V_{dep} . In the simplest approximation [8, 9], all internal degrees of freedom of the polymer are ignored, and the polymer coils are treated as interpenetrable. More realistic modelling of the polymer gives qualitatively similar results [10-12]. The total interaction between two colloidal particles is then given by $V_{tot} = V_c + V_{dep}$. The phase behaviour of particles interacting via V_c is assumed to be known. The effect of V_{dep} is treated by thermodynamic perturbation theory.

The paradigmatic case of hard-sphere colloids of radius a, $V_c(r) = \infty$ for r < 2a. $V_c(r) = 0$ for r > 2a, has been studied in some detail [4, 13]. In the unperturbed system (no added polymer), a colloidal fluid phase is stable at volume fraction $\phi < 0.494$ [14, 15]. When $\phi > 0.545$, the stable phase is a colloidal crystal. Coexistence of fluid and crystalline phases occurs for $0.494 < \phi < 0.545$ [14, 15]. Effective potential calculations of the type described above predict that the effect of added polymer depends on the polymer size ratio,

 $\frac{r_g}{a}$ When this ratio is less than about 0.3, added polymer is predicted to expand the fluidcrystal coexistence region. When $\frac{r_g}{a} > 0.3$, however, a fluid-fluid type phase separation is also

possible. The case when V_c takes the Yukawa form, appropriate for charged colloids, has also been investigated [16].

Until recently most theoretical treatments of polymer-induced phase separation in colloidal suspensions have used this effective potential approach. Predictions resulting from this approach have also dominated the interpretation of experimental data. In recent years, however, a number of authors [16-19] have questioned the validity of treating the effect of added polymer *via* an effective two-body depletion potential, since this method is not able to deal with the likely occurrence of the *partitioning* of polymer between the various separated phases. Indeed, one attempt [17] at treating the colloidal and polymeric translational degrees of freedom on an equal footing using thermodynamic perturbation theory for mixtures strongly suggests that such partitioning will occur.

Experimentally also the situation is less than satisfactory. Much work has been performed on systems, particularly charged mixtures (charged colloid + polyelectrolyte), in which the behaviour of each component individually is far from fully characterized. Little detailed study of the structure and composition of the separated phases has been reported. Since data interpretation has been influenced predominantly by theories based on an effective potential, only one experiment to date has provided evidence for polymer partitioning [5].

In a recent theoretical paper Lekkerker *et al.* have addressed the issue of polymer partitioning [20]. The colloidal particles are taken to be hard spheres of radius a; the polymers are assumed to interact with the particles as hard spheres of radius δ , but to be interpenetrable « points » so far as their interaction with each other is concerned. A treatment of this model, using a physically transparent statistical mechanical approximation, predicts marked partitioning of the polymer between separated phases. Theoretical phase diagrams in the experimentally accessible density-density representation (polymer concentration *versus* colloid volume fraction), which show this partitioning, were presented for the first time (Fig. 1).

In this paper, we report the experimental phase diagram of a model colloid-polymer mixture – colloidal poly-methylmethacrylate (PMMA) + polystyrene (PS) in *cis*-decahydronaphthalene (*cis*-decalin) at room temperature. The PMMA particles [21] themselves have been studied extensively in recent years [15, 22-24] and appear to behave like hard spheres. PS is a well known and well characterized model polymer. Its theta point in *cis*-decalin is a little below



Fig. 1. — The predicted phase diagram for a colloid-polymer mixture in which the polymer to colloid size ratio (δ/a) is 0.08 according to the theory of [20]. The phase diagram is plotted in terms of an effective polymer fraction, $\eta = (4/3) \pi \delta^3 (N_p/V)$, and the colloid volume fraction $\phi = (4/3) \pi a^3 (N_c/V)$. Tie lines are shown in the two-phase crystal-fluid (C-F) coexistence region. Note that the oblique tie lines imply considerable partitioning of the polymer among the coexisting phases.

room temperature, so that it is reasonable to assume coil interpenetrability as a first approximation under our experimental conditions. The mixture studied here therefore makes direct contact with the theoretical work of Lekkerkerker *et al.*; the data presented below provide significant confirmation of the predicted phase behaviour. At one concentration of colloid we have investigated the effect of temperature on the phase boundaries. The existence and some properties of a « gel » state obtained at high polymer concentrations are also reported (compare [2, 6]).

2. Materials and samples.

The particles used in this study consisted of PMMA cores, stabilised sterically by thin, 10-15 nm, chemically-grafted layers of poly-12-hydroxystearic acid [21]. They were suspended in *cis*-decahydronaphthalene (*cis*-decalin). Suspensions of this type (without added polymer) have been studied extensively with emphasis on particle dynamics [22], phase behaviour [15], crystallization [23], and glass formation [24]. These studies have established that the interparticle interaction is steep and repulsive and is well approximated by that of hard spheres. Samples were made by dilution or concentration of a stock solution. As described previously [15], the effective hard sphere volume fractions (ϕ) of the samples were calculated using literature values of the densities, $\rho_{PMMA} = 1.18 \text{ gcm}^{-3}$ and $\rho_{decalm} = 0.894 \text{ gcm}^{-3}$, and scaled so that freezing occurs at the hard sphere value $\phi = 0.494$. The particle radius was determined to be $a = 217 \pm 5$ nm from a measurement by powder light crystallography of the lattice parameter of a colloidal crystal at the melting volume fraction, $\phi = 0.545$ [23]. The polydispersity in the particle radius was determined by electron microscopy and dynamic light scattering [25] to be $\approx 5 \%$.

The polystyrene (PS) was obtained from Pressure Chemical Company. The quoted molecular weight was $M_w = 390,000$ with $\frac{M_w}{M_n} < 1.10$. The theta temperature of PS in *cis*-

decalin is $T_{\theta} = 12.5$ °C [26]. The hydrodynamic radius of the polymer was calculated from its diffusion constant, measured by dynamic light scattering in dilute solution; we obtained $r_{\rm H} = 12.8 \pm 0.6$ nm.

Samples were prepared by mixing PMMA suspensions with a PS stock solution. Each sample was then homogenised in a vortex mixer and tumbled. The volume fractions of PMMA colloid were in the range $0.015 < \phi < 0.63$, while the concentrations c_p of PS spanned $0 < c_p < 0.008 \text{ gcm}^{-3}$. The first set of experiments described here were performed at room temperature, 19 ± 2 °C.

The effect of temperature was studied with a set of samples, each with a colloid volume fraction of $\phi = 0.2 \pm 0.0015$, but with varying polymer concentrations ranging from $c_p = 0.00385$ to $c_p = 0.00540$ gcm⁻³ These samples were observed in the temperature range 8 °C to 28 °C, using a bath of liquid whose temperature was controlled to better than ± 0.5 °C.

3. Results.

Samples were inspected visually at regular intervals. The difference in refractive indices of the particles and the decalin, ≈ 1.49 -1.481, is large enough that the samples appeared quite cloudy; however they were sufficiently translucent that processes, such as crystallization, occurring in their bulk could be seen.

3.1 ROOM TEMPERATURE. — The different types of phase behaviour observed at room temperature are mapped out in the ϕ - c_p plane in figure 2a.

Samples with low colloid volume fractions ($\phi < 0.49$) and low polymer concentrations remained in single phases and appeared homogeneous (circles in Fig. 2a). (After days to weeks some gravitational settling of the particles was observed; however this settling was much slower than that of the crystalline or gel states discussed below.) The spatial arrangement of the colloidal particles in these samples is apparently « fluid-like », and individually particles can explore the whole sample volume by diffusion. This single phase behaviour is an extension of the colloidal fluid phase at $0 < \phi < 0.494$ in the polymer free system.

In samples with higher polymer concentrations (squares in Fig. 2a), colloidal crystallites, iridescent « specks » under white light illumination, began to be observed a few hours after mixing. Nucleation appeared to be homogeneous throughout the sample volumes. Within a day

Fig. 2. — a) The experimental phase diagram for a mixture of PMMA colloid and polystyrene. The \blacktriangleright vertical axis is polymer concentration (c_p) in gcm⁻³; the horizontal axis is colloid volume fraction (ϕ) . Circles = single phase colloidal fluid; squares = fluid-crystal coexistence; triangles = « gel »; asterisks = fully crystalline; diamonds = glass. The compositions of the two phases into which sample A separates are marked by filled squares. The various lines are added as guides to the eye as to the approximate locations of various phase boundaries. b) Comparison between experiment and theory. The expanded crystal-fluid coexistence region due to added polymer as determined by experiment (lower continuous lines, taken from (a)) and as predicted by the theory of Lekkerkerker *et al.* [20] using $\delta/a = 0.08$ (dotted lines). The upper continuous line represents the experimentally observed onset of the gel state.



a)



Polymer Concentration ($C_p \times 10^3$ g cm⁻³)

or so the crystallites settled under gravity, leaving supernatant colloidal fluid separated from the polycrystalline phases by well defined boundaries. In appearance, samples in this region resembled those at $0.494 < \phi < 0.545$ in the polymer free system [15].

At still higher polymer concentrations (triangles in Fig. 2a) crystallization was inhibited. Immediately after mixing, samples in this region were visually identical to samples in the single-phase region found at lower polymer concentrations. Preliminary studies by dynamic light scattering showed these samples to be effectively « non-ergodic » [27] on the timescale (> 10³ s) of the measurement. The amplitudes of the measured normalized intensity correlation functions were smaller than those for fluid-like samples, indicating the presence of very slowly decaying density fluctuations and the effective suppression of long-distance diffusion [27]. This, together with the absence of iridescence, suggest an amorphous but almost rigid arrangement of colloid particles interspersed with polymer molecules. We will label this as the « gel » state. The closest analogue to this in the polymer free system is the colloidal glass observed above $\phi \approx 0.58$ in the polymer free system [15, 24].

After a few hours, the gel state was observed to settle, leaving a clear supernatant devoid of colloidal particles. When this settling was complete after a few days, the volume of sediment was consistent with a random close packed arrangement ($\phi \approx 0.64$) of *all* the colloidal particles originally present. This sediment was observed to crystallize at the interface with the supernatant after some months.

Polymer-free samples at high colloid volume fractions ($\phi \ge 0.53$) showed fluid-crystal coexistence, fully crystalline (asterisks in Fig. 2a) and glassy (diamonds in Fig. 2a) behaviour with increasing ϕ , as observed previously [15]. On the addition of increasing amounts of polymer, samples which were initially fully crystalline ($0.545 < \phi < 0.58$) underwent partmelting to give a coexisting colloidal fluid. A small amount of polymer in a glassy sample was found to induce full crystallization. At even higher concentrations of polymer the sample then moved into crystal-fluid coexistence. At the highest added polymer concentrations, two samples at high colloid concentration failed to give any crystals, suggesting gel formation.

The actual compositions of the two phases in one particular sample (sample A in Fig. 2a, initial composition $\phi = 0.151$, $c_p = 0.0048 \text{ gcm}^{-3}$) showing fluid-crystal coexistence were determined. The ratio of the volumes of fluid and crystalline phases was 4.8 : 1. The volume fraction of colloid in the crystalline phase was determined by light crystallography. The crystal structure was assumed to be that of a hard-sphere colloidal crystal without polymer, a stacking of hexagonally arranged layers of particles [23]. The spacing of the hexagonal layers was determined from their Bragg reflection and ϕ_{crystal} calculated from this spacing and the previously measured particle radius, 217 nm. This procedure gave $\phi_{\text{crystal}} = 0.655 \pm 0.01$. The measured volume ratio of fluid to crystalline phases and the lever rule then requires $\phi_{\text{fluid}} = 0.063$.

The two phases were then carefully separated. Colloidal particles in the supernatant phase were spun down using a centrifuge, and the polymer concentration was determined by comparing scattered light intensities with those of PS solutions in decalin of known concentrations, giving $c_p(\text{fluid}) = 0.0058 \pm 0.0008 \text{ gcm}^{-3}$. The crystal phase was redispersed in an equal volume of decalin and the polymer concentration in the resultant suspension estimated using the same procedure, giving $c_p(\text{crystal}) = 0.0019 \pm 0.0003 \text{ gcm}^{-3}$ (See the appendix for more details of these calculations. The rather large error bars on c_p reflect the uncertainties in estimating the amount of polymer in the sediment after centrifuging.)

3.2 TEMPERATURE DEPENDENCE. — The temperature dependent phase behaviour of a series of twelve samples (all at $\phi = 0.2 \pm 0.0015$) was also investigated. The polymer concentrations in these samples ranged from $c_p = 0.00385 \text{ gcm}^{-3}$ to $c_p = 0.00540 \text{ gcm}^{-3}$ At room tempera-

ture, these samples span (see Fig. 2) all three types of possible phase behaviour : single phase fluid, fluid-crystal coexistence and gel. The samples were remixed by tumbling before being allowed to equilibrate at each new temperature in the temperature bath. Visual inspection then determined the phase behaviour.

The phase diagram for the $T-c_p$ plane at $\phi = 0.2$ is shown in figure 3. The same three types of phases as at room temperature were found at all temperatures studied. The major effect of temperature was to change the range of c_p over which fluid-crystal coexistence was observed.



Fig. 3. — The effect of temperature. All samples have colloid volume fraction $\phi = 0.2$; the vertical axis gives polymer concentration (c_p) in gcm⁻³ Circles = single phase colloidal fluid; squares = fluid-crystal coexistence; triangles = « gel ».

4. Discussion.

The ratio of polymer ($r_{\rm H} = 12.8 \text{ nm}$) and colloidal particle (a = 217 nm) sizes in our experiments is about 0.06. For this situation all previous theoretical studies predict that the effect of the added polymer is to expand the fluid-crystal coexistence region, which spans $0.494 < \phi < 0.545$ at $c_{\rm p} = 0$. Our room temperature results, shown in figure 2a, clearly confirm this prediction. The lines in figure 2a are drawn to guide the eye. The lower lines separate the region of fluid-crystal coexistence from the fluid region at $\phi < 0.494$ and from the crystal/glass region at $\phi > 0.545$; the upper line indicates the onset of the gel state; the dotted line separates the fully crystalline region from the glassy region.

The solid squares in figure 2a indicate the measured compositions of the two phases into which sample A separated (see Sect. 3.1 and the appendix). These should lie on the lower phase boundary lines, and on a straight tie line which includes the overall composition of sample A. It is evident that this is the case, when allowance is made for experimental errors in the measurement of the polymer concentrations. These results directly indicate significant partitioning of polymer between the separated phases.

The increased polymer concentration in the fluid phase results in osmotic compression of the coexisting crystal. The volume fraction of the crystal in sample A, $\phi_{crystal} = 0.655$, is much larger than that, $\phi \approx 0.58$, at which a glass transition of the pure (polymer free) colloid has been found [15, 24]. We note that osmotic compression of colloidal crystals has also been observed in mixtures of colloidal PMMA particles of two different sizes [28].

Quantitative comparison of the measured phase boundaries with the predictions of [20] is not straightforward. As mentioned in section 1, Lekkerkerker et al. [20] assumed that the polymer coils were interpenetrable to one another, but that the centre of each coil was excluded from a sphere of radius $a + \delta$ centred on any colloidal particle. The polymer concentration was quoted as an effective polymer volume fraction $\eta = \frac{4}{3} \pi \delta^3 \frac{N_p}{V}$, where N_p is the number of polymer coils in the sample volume V. Conversion to the experimental variable c_p is via the relation $\frac{4}{3}\pi\delta^3 c_p = \eta M$, where M is the mass of one polymer coil. While M is known, it is not immediately obvious what value should be used for δ . The theoretical phase boundaries shown in figure 2b were obtained by regarding δ simply as a « fitting parameter » used to connect theory and experiment. The value of δ required to fit the experimental fluid-crystal phase boundary at colloid volume fraction $\phi \approx 0.3$ (near the middle of the range of ϕ spanned by our data) is $\delta = 18$ nm. We see that the predicted phase boundaries are then in qualitative agreement with the experimental results at other colloid volume fractions, but that there are clear quantitative differences. In particular, the theoretically predicted left-hand phase boundary is steeper than that found experimentally, and the polymer concentrations in the dense colloidal phase (the high ϕ phase boundary) are significantly underestimated by the theory.

The fitted value of δ can be compared with various theoretical candidates. The hydrodynamic radius of the polymer used in our experiments, measured by dynamic light scattering at room temperature and low polymer concentration ($c_p = 0.002 \text{ gcm}^{-3}$), was $r_H = 12.8 \pm 0.6 \text{ nm}$. For a Gaussian coil, the relationship between the radius of gyration r_g and the hydrodynamic radius r_H is $r_g = 1.51 r_H$ [29], giving $r_g = 19.3 \pm 0.9 \text{ nm}$. Possibly the most realistic quantity with which δ should be compared is the thickness of the depletion layer, ξ , near a hard wall in a polymer solution. A self consistent field calculation [30] of this quantity gives $\xi = (2/\pi^{1/2}) r_g$ for unswollen (Gaussian) coils at infinite dilution. Using $r_g = 19.3 \text{ nm}$, we get $\xi = 21.8 \pm 1 \text{ nm}$. It is reassuring that the fitted value of $\delta = 18 \text{ nm}$ is close to this value.

Our measurement of r_g , via r_H , can be compared with the data of Berry [26]. He reported that for PS in decalin, $r_g(T_\theta) = 0.0270 \sqrt{M_w}$, giving $r_g(T_\theta) = 17.0$ nm for $M_w = 390,000$. He also gave $r_g(T)/r_g(T_\theta)$ as a function of the Fixman two-body interaction parameter z, a measure of the monomer-monomer excluded volume interaction in units of kT. Berry's measurements yielded the experimental relation

$$z = 0.00975 \sqrt{M_{\rm w} [1 - T_{\theta}/T]},$$

so that z = 0.13 for our experimental conditions ($T \approx 292$ K, $T_{\theta} = 286$ K). At this value of z, Berry's results predict that, for $r_g(T_{\theta} = 12.5 \text{ °C}) = 17.0 \text{ nm}$, $r_g(T = 19 \text{ °C}) = 19 \text{ nm}$ which compares well with the value deduced from the measured hydrodynamic radius,

 $r_g(T = 19 \text{ °C}) = 19.3 \pm 0.9 \text{ nm}$ (above). Berry's data also indicate that PS coils in *cis*-decalin are only slightly swollen at room temperature.

As noted above, even if δ is regarded simply as a parameter to be fitted, there is still clear disagreement between experiment and theory. We discuss possible origins of this disagreement, starting with the dependence of the properties of the polymer on concentration. The theory of Lekkerkerker *et al.* [20] assumes that the polymer is ideal in the sense that the polymer size is independent of concentration and that its osmotic pressure is given by the ideal form, $\Pi = N_p kT/\alpha V$ (where α is the free volume fraction, see below). In reality, the thickness ξ of the depletion layer (and therefore δ) will be concentration dependent [31], and the osmotic pressure will be non-ideal. (At high enough concentrations c_p , this will be true even at the theta temperature.) Thus the depletion potential, which scales as $\Pi \delta^2 a$ (see [18] and [20]), will in general have a concentration dependence more complicated than that assumed in the theory.

The fraction η' of the volume of *solvent* occupied by polymer is given in terms of the overall effective volume fraction of polymer η defined above by $\eta' = \eta/(1 - \phi)$, where as before ϕ is the colloid volume fraction. In terms of this variable, crossover from the dilute to the semidilute regime (i.e. polymer coil overlap) will occur at $\eta' \approx 1$. Reference to figure 1 shows that at $\delta/a \leq 0.1$, we can expect the maximum value of η' to be around 0.3, which can be described as « pre-crossover ». We therefore expect that correcting the ideal gas osmotic pressure used for the polymer in [20] by including the effect of a second virial coefficient would be a good starting point for accounting for the c_p dependence of Π . The full theory of the effect of concentration on ξ in this concentration regime is, however, apparently not yet available (see [31] for a discussion of concentration effect in the fully semi-dilute regime).

A second potential source of disagreement between experiment and theory is revealed when it is recognised that the diameter of the PS polymer coils, ≈ 40 nm, and the thicknesses of the polymer coatings on the PMMA particles, $\approx 10-15$ nm, are comparable in magnitude. The coatings of poly-12-hydroxystearic acid on the particles are thought to be quite tightly packed [32] but, almost certainly, the « surfaces » of the composite particles are neither smooth nor hard on the scale of a few nm. Limited penetration of the particles by the polymer is therefore possible.

Finally the theory of [20] is essentially a *mean field* theory. The free energy of a mixture of N_c colloidal particles and N_p polymer molecules in total volume V is written in the form

$$F = F_{\rm c}(N_{\rm c}, V) + F_{\rm p}(N_{\rm p}, \alpha V) \tag{1}$$

where the first term corresponds to pure colloid in a volume V, and the second term to pure polymer in a volume αV , where the « free volume fraction » α is the fraction of the total sample volume which is accessible to the polymer molecules. In general α is, of course, a function of the coordinates of all N_c colloidal particles, $\alpha = \alpha (\{r_c\})$. The total free energy only separates into the above form if one makes the mean field approximation

$$\alpha(\{r_{c}\}) \to \langle \alpha \rangle = \alpha(\phi)$$
⁽²⁾

where $\langle \cdots \rangle$ denotes averaging over colloidal configurations. This procedure means that the interaction between polymer and colloid is contained solely in the dependence of α on the colloid volume fraction $\phi = \frac{N_c}{V} \frac{4}{3} \pi a^3$. This formulation ignores the effect of *fluctuations* in the colloidal coordinates, which would give rise to a term proportional to $kT \langle \delta \phi^2 \rangle$ in the fractional free volume. Such fluctuations could be included in the theory for phase behaviour by a self-consistent calculation using a Ginzburg-Landau type approach.

It should also be pointed out that the free energy approximation (1) puts colloids and polymers on an unequal footing. The polymer part, F_p , depends on the colloidal volume

fraction via $\alpha(\phi)$, while there is no polymer concentration dependence in the colloid part, $F_{\rm c}$. In reality, however, we expect that the presence of added polymer will perturb the configuration of the colloids and therefore their free energy [17]. In turn, this means that the averaging indicated in (2) should be performed over the *perturbed* configuration of colloidal particles, giving rise to a c_p dependence of α . The actual expression used for α (see the Appendix) does not allow for this possibility.

Work to extend the theory of [20] to include some of these complications, and therefore to determine their effect on the predicted phase diagram, is in progress.

We note that this appears to be first experimental study of the effects of adding polymer to colloidal crystals and glasses i.e. of the high- ϕ branch of the phase boundary in figure 2a. A particularly interesting observation is the ability of added polymer to induce crystallization in the colloidal glass. The reasons for this are unclear at present, although it can be speculated that the presence of polymer may cause increased fluctuations of the free volume (see above), giving rise to local configurations that offer low free energy barriers to crystallization.

The effect of temperature on the phase behaviour is striking. At the colloid concentration studied in this work ($\phi = 0.2$), the fluid-crystal coexistence region is apparently at its narrowest round about room temperature (Fig. 3). Both heating and cooling lead to a significant expansion of this region. The progressive decrease in the amount of polymer needed to cause the single phase fluid to separate into two phases as the temperature is increased can be understood qualitatively as a combination of two effects : individual coils expand (thus increasing δ), and the contribution of the second virial term to the osmotic pressure (Π) increases. Since the depletion potential (in units of kT) scales as $c_p \Pi \delta^2 a$ [18, 20] we expect that, in agreement with the observations, the amount of polymer needed to cause phase separation should decrease with increasing temperature. Presumably this effect is also relevant when it comes to considering the effect of temperature on the formation of the gel state. A more detailed study of temperature effects, both experimentally and theoretically, is in progress.

The gel state observed in our experiments has not been predicted by theory ; little is known about this state at present. It has been speculated that, under the influence of a strong enough depletion attraction, the particles adopt a tenuous, metastable, fractal-like arrangement interspersed with polymer molecules [2]. The slow settling of this state, leaving a colloid-free supernatant, suggests that the both the polymer molecules and colloidal particles are still somewhat mobile. However our preliminary dynamic light scattering measurements, performed on a sample soon after mixing, indicate that these motions must be very slow. We intend to investigate in more detail both the structure and dynamics of this intriguing state.

Two previous studies have reported observations similar to ours, regions of fluid-crystal coexistence at moderate polymer concentrations and « gel states » with more added polymer. Sperry [2] investigated aqueous mixtures of hydroxyethyl cellulose polymer and charged particles of acrylic copolymer. Particle arrangements were inferred from low magnification optical microscopy. Smits *et al.* [6] studied mixtures of uncharged silica spheres, sterically-stabilised by alkane (octadecyl) chains, and polystyrene or poly(dimethyl siloxane) polymer in cyclohexane. In the first experiment the interactions between the various species were quite complicated; in the second, the fact that silica particles on their own often fail to crystallize [6] at $\phi > 0.494$ diminishes somewhat their value as « model » hard-sphere colloids. Both experiments predate [20], so that comparison with that theory was not possible.

In conclusion we have shown that mixtures of hard-sphere PMMA colloids and polystyrene constitute a promising model system which we intend to study comprehensively in the future. We have shown that the phase diagrams are in reasonable agreement with recent theoretical predictions, particularly with regard to partitioning of the polymer between separated phases.

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Appendix.

Calculation of the polymer concentrations in the separated phases.

Consider a single phase colloid-polymer mixture of total volume V. This sample is spun in a centrifuge to sediment the colloidal particles. After spinning down, the sediment is observed to occupy a fraction f of the total volume. The polymer concentration in the supernatant (now devoid of particles) can be measured by light scattering. Let this concentration be c'_p (in grammes per cm³). The question is — what is the polymer concentration c_p in the original single-phase sample ? To answer this question, we need to know the amount of polymer in the sediment. At the low centrifuging speeds used in our work (≤ 3000 rpm) we do not expect significant sedimenting of the polymer. We therefore can reasonably assume that the concentration of polymer in the « free volume » of the sediment is c'_p .

The free volume is that portion of the volume of the sediment which is available for the insertion of a polymer coil. Assume the polymer coil is excluded from coming closer than a distance δ to the surface of a colloid particle, and that the colloidal particles (volume fraction ϕ) are randomly distributed hard spheres (radius *a*). Then the *free volume fraction*, α , can be estimated by an expression derivable from the scaled particle theory of mixtures [33]

$$\alpha = (1 - \phi) \exp[-A\gamma - B\gamma^2 - C\gamma^3]$$

where $\gamma = \phi/(1 - \phi)$, $A = 3 \xi + 3 \xi^2 + \xi^3$, $B = 9 \xi^2/2 + 3 \xi^3$ and $C = 3 \xi^3$ (where $\xi = \frac{\delta}{a}$).

The sediment will be a random close packing of particles, so that $\phi \approx 0.64$. In our experiments a = 217 nm and $\delta \approx 18$ nm (see Sect. 4 of main text), giving $\alpha = 0.20$.

The amount of polymer in the sediment is then $c'_p \alpha f V$. The total amount of polymer $c_p V$ in the original sample is therefore $c'_p \alpha f V + c'_p (1 - f) V$, giving finally

$$c_{\rm p} = c_{\rm p}'(\alpha f + 1 - f) = c_{\rm p}'[1 - f(1 - \alpha)].$$

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