Fluid structure in colloid-polymer mixtures: the competition between electrostatics and depletion

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Abstract.
We studied the structure of a colloid-polymer mixture, in the one-phase region, as a function of polymer concentration. Using confocal microscopy, and Fourier transformation of the image data, we accessed the system in real and reciprocal space simultaneously, at the single particle level. We found no change in the colloidal fluid structure as a function of polymer concentration. The fluid phase persisted to higher concentrations of polymer than expected, before an abrupt gelation transition. Furthermore, we found a dramatic change in the local structure around each particle at the onset of gelation. We attribute these phenomena to a screened electrostatic repulsion between the colloids, which, although weak, suppressed the depletion attraction due to the polymer. The repulsive and attractive interactions have a similar range, which results in behaviour distinct both from pure depletion and the recently observed cluster phase formed in the presence of long-ranged electrostatic repulsions. Instead, these results are qualitatively similar to the competition between van der Waals and electrostatic interactions in the Derjaguin-Landau-Verwey-Overbeek theory. We compare our experiments with Monte Carlo simulation and find agreement with a combination of the Asakura-Oosawa-Vrij and Yukawa potentials.

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1. Introduction

Colloid-polymer mixtures have attracted a great deal of attention, as they provide convenient ways to study phenomena as diverse as fluid-fluid demixing and dynamical arrest (Poon 2002, Tuinier *et al* 2003). Attractions between the colloids are driven by the depletion mechanism of the polymers (Asakura and Oosawa 1954, 1958, Vrij 1976), while electrostatic interactions lead to repulsions between the colloids, polymers or both (Verwey and Overbeek 1949). The depletion attractions between the colloids are easy to manipulate: the depth of the potential well is controlled by the polymer concentration, allowing precise control of the thermodynamic stability of the system. The interaction range is set by the polymer-colloid size ratio q. For $q \geq 0.25$, fluid-fluid

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phase separation is observed, while smaller ratios give colloidal gels and fluid-crystal coexistence (Ilett *et al* 1995, Poon *et al* 1997, de Hoog *et al* 2001).

The colloids are often treated as hard spheres (Gast *et al* 1983, Lekkerkerker *et al* 1992), but in the case of aqueous systems, it was necessary to incorporate electrostatic repulsions between the colloids to obtain quantitative agreement between experiment and theory (Sperry 1984, Gast *et al* 1986). The use of non-aqueous solvents suppresses the charge, so the colloids behave more like hard spheres and the agreement with Asakura-Oosawa-Vrij (AOV) theory is better (Gast *et al* 1983, Ilett *et al* 1995). The trend of electrostatic interactions to inhibit phase separation is well-captured in recent work (Denton and Schmidt 2005, Fortini *et al* 2005).

A charged depletant can enhance the depletion interaction (Mondain-Monval *et al* 1995, Petekidis *et al* 2002, Helden *et al* 2004). In density and refractive index matched systems, with weak but very long-ranged electrostatic repulsions (Yethiraj and van Blaaderen 2003), a cluster phase has been found prior to gelation (Segre *et al* 2000, Sedgwick *et al* 2004, Campbell *et al* 2005).

Even in the one-phase region, when there is insufficient polymer to cause phase separation, there can be a change in the structure of the colloidal fluid due to depletion. While some scattering studies have been carried out (Ye *et al* 1996, Shah *et al* 2003), at present real-space studies are limited to simulation work (Dijkstra *et al* 1999). Real space analysis, yielding the radial distribution function, $g(r)$, is expected to be particularly interesting: in the dilute limit $g(r)$ is related to the pair interaction $u(r)$ simply by a Boltzmann factor:

$$g(r)_{\eta \to 0} \approx \exp(-\beta u(r)) \qquad (1)$$

where η is the colloid volume fraction and β is $1/k_B T$ with k_B Boltzmann's constant and T absolute temperature (Louis 2001, Hansen and Macdonald 1976).

We studied a colloidal model system, similar to that employed by Sedgwick *et al* (2004). This we observed at the single particle level with 3d confocal microscopy. By determining the colloid radial distribution function, and Fourier transforming images we can study the system in real and Fourier space simultaneously. We limit our attention to the one phase region, as gels have already received considerable attention (e.g. Dinsmore and Weitz 2002, Campbell *et al* 2005).

2. Experiment and Simulation Methods

We used a density and refractive index matched colloidal model system. The polymethyl methacrylate (PMMA) colloids were sterically stabilised and labelled with rhodamine isothiocyanate (Bosma *et al* 2002). The diameter was σ=1.95 μm and the polydispersity was 4.7 % as determined with static light scattering. The PMMA was dispersed in a mixture of cyclohexyl bromide (CHB) and cis decalin. 260 μM of tetrabutyl ammonium bromide salt was dissolved in the solvent mixture to screen the electrostatic interactions between the colloids, so that the phase behaviour was reminiscent of hard spheres (Yethiraj & van Blaaderen 2003). However the Debye screening length, of order 100 nm, is not negligibly small and the interactions can be distinguished from hard spheres (Royall *et al* 2005). We added polystyrene (PS) as the non-adsorbing polymer, of two molecular weights (M_w=8.5$\times$10^6, M_w/M_n=1.05) and (M_w=3.0$\times$10^7, M_w/M_n=1.3). For the 8.5×10^6 molecular weight PS we found the radius of gyration R_G to be around 88 ± 9 nm at 22° C with dynamic light scattering, while for the 3.0×10^7 molecular weight polymer, we estimate the radius of

gyration to be 160 nm (Vincent 1990). These values of R_G are consistent with a theta solvent, in accordance with previous measurements in this solvent mixture (Campbell *et al* 2005). The colloid volume fraction was fixed at $\eta=0.05$, and we only varied the polymer volume fraction $\phi_P = (4/3)\pi R_G^3 \rho_P$ where ρ_P is the polymer number density. In each case, we sampled several state points in the one phase region, and established the polymer concentration required for gelation. The colloidal fluid samples showed no significant change over several hours.

The confocal microscope system used was a Olympus BX51W1 microscope with a 60x Planapo oil-immersion lens, fitted with a Yokogawa CSU21 scan-head whose disk rotated at 5000 rpm. We imaged the system with an Andor D-721-10 CCD camera. Scanning in the z direction was performed with a Pi PV8285 piezo scanner. Typically we took images at 60 frames per second (500×500 pixels). In the z direction each 2d image was separated by around 200 nm.

We tracked the colloid coordinates and determined the radial distribution function $g(r)$ as described previously (Royall *et al* 2003). It is possible to learn more about the colloid interactions by comparing the experimental radial distribution function with the results of (eg) Monte Carlo (MC) simulations, where we input a specific colloid-colloid potential. While it is in principle possible to explicitly determine such parameters as the colloid charge in this way (Royall *et al* 2003), here we restrict ourselves to comparing the structure with that predicted by simulation. In particular we consider the fluid-gelation boundary. As before (Royall *et al* 2003, 2005), we described the screened Coulomb interactions between the colloids with a Yukawa potential with a hard core,

$$\beta u_{YUK}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ \beta\epsilon \dfrac{\exp(-\kappa(r-\sigma))}{r/\sigma} & \text{for } r \geq \sigma \end{cases} \tag{2}$$

where r is the centre to centre separation of the two colloids. The contact potential is given by

$$\beta\epsilon = \frac{Z^2}{(1+\kappa\sigma/2)^2}\frac{l_B}{\sigma} \tag{3}$$

where Z is the colloid charge, κ is the inverse Debye screening length and l_B is the Bjerrum length. Due to the steric stabilisation and refractive index matching, the van der Waals interactions are reduced to a fraction of $k_B T$ and therefore neglected.

We describe the depletion attractions following Asakura and Oosawa (1954, 1958)

$$\beta u_{AO}(r) = \begin{cases} \infty & \text{for } r < \sigma \\ \dfrac{\pi(2R_G)^3 z_P}{6}\dfrac{(1+q)^3}{q^3} & \\ \times\{1 - \dfrac{3r}{2(1+q)\sigma} + \dfrac{r^3}{2(1+q)^3\sigma^3}\} & \text{for } r \geq \sigma < \sigma_C + (2R_G) \\ 0 & \text{for } r \geq \sigma + (2R_G) \end{cases} \tag{4}$$

where the polymer fugacity z_P is equal to the number density ρ_P for ideal polymers. To determine simulated radial distribution functions, we carried out MC simulation in the canonical ensemble with periodic boundary conditions (Frenkel and Smit 2002).

We can also obtain Fourier space information by making a radial average of the Fourier transform of a 2d micrograph (Tanaka *et al* 1986). Although confocal
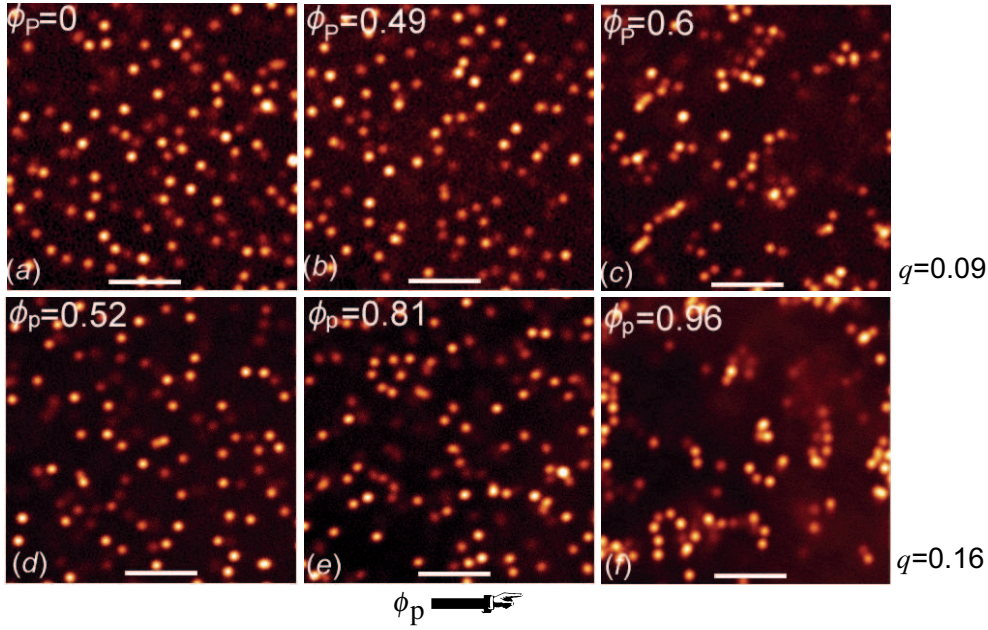
Figure 1. COLOR ONLINE. Confocal microscopy images as a function of polymer concentration. $q=0.09$, (a)-(c) $q=0.16$, (d)-(f) (a,b) and (d,e) are colloidal fluids with no apparent change in structure, despite the difference in polymer concentration ϕ_P. Increasing the polymer concentration results in a gel (c), (f) with connectivity in 3D. The bars denote 10μm.

microscopy is a 3d technique, slightly inhomogenous light levels and the anisotropy in resolution hamper Fourier transformation of 3d images. We return to the interpretation of Fourier transforms of 2d images below.

3. Results and Discussion

We divide this section as follows. First a selection of confocal microscopy images is presented, followed by the real space analysis, yielding $g(r)$. The Fourier space results are shown next and finally the interactions underlying the phase behaviour are discussed.

The images shown in figure 1 are confocal micrographs around 50 μm into the sample. Figures 1 (a-c) concerns the $q = 0.09$ system, (d-f) the $q = 0.16$ system. Both undergo gelation, at $\phi_{GEL} = 0.545 \pm 0.055$ and $\phi_{GEL} = 0.88 \pm 0.084$ for $q = 0.09$ and $q = 0.16$ respectively. Here ϕ_{GEL} denotes the polymer volume fraction required for gelation. Although the 2d 'slices' in figures $1(c)$ and $1(f)$ do not show connectivity, 3d particle tracking reveals a percolating structure. What is surprising about these images is that the colloidal fluid in the one-phase region shows very little change in structure, in either case. This contrasts with scattering studies, where the static structure factor changed with polymer concentration (Ye *et al* 1996, Shah *et al* 2003). For mixtures of hard sphere and ideal polymers, phase separation is predicted at $\phi_P \approx 0.25$ for $q = 0.09$ and $\phi_P \approx 0.3$ for $q = 0.16$ (Lekkerkerker *et al* 1992). While larger size ratios ($q > 0.4$) deviate from theory assuming ideal polymer behaviour (Aarts
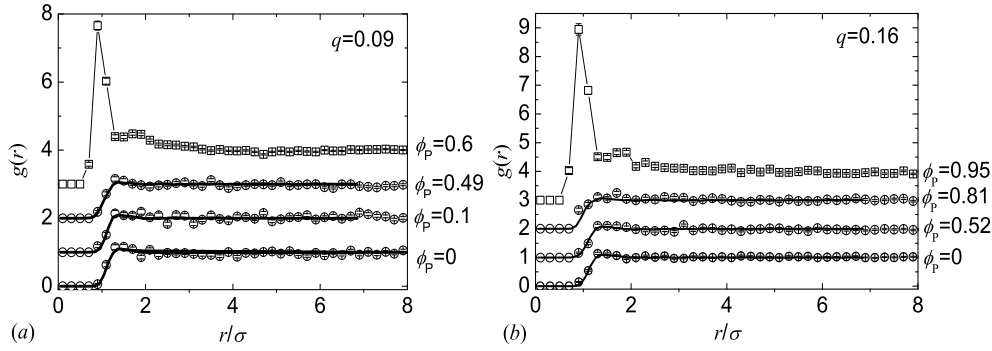
Figure 2. Pair correlation functions at various polymer concentrations, for $q = 0.09$ (a) and $q = 0.16$ (b). Unfilled circles are experimental data for the one phase region, squares are gels and black lines follow from MC simulation. Lines are offset for clarity.

et al 2002), the magnitude of our discrepancies, even considering the significant error in the polymer volume fraction, seems worthy of some further explanation. We believe that the electrostatic interactions between the colloids are responsible for both the suppression of phase separation, and the fact that the fluid structure shows no discernable change upon addition of polymer.

Pair correlation function data are shown in figure 2. The one phase data are overlaid with the results of simulations. Like the images, there is no apparent change in the fluid structure, until gelation, where a strong peak at $r = \sigma$ is seen. Here the $g(r)$ in the case of the gel takes rather longer to decay to unity ($r \sim 5\sigma$), showing that density fluctuations persist over longer length-scales, as noted by Campbell *et al* (2005). That hardly anything happens in the fluid, is in marked contrast to work on a similar system without added salt, where a cluster phase is found in the one-phase region and very little change at the particle level is seen upon gelation (Sedgwick *et al* 2004, Campbell *et al* 2005). Upon adding salt, Sedgwick *et al* (2004) found no clusters, in agreement with the observations here.

We fitted the experimental radial distribution functions with the Yukawa potential (eq. (2)), for $\phi_P = 0$. For these parameters, only a qualitative fit can be made as a considerable change in $\beta\epsilon$ gave a small variation in $g(r)$. We set $\kappa\sigma = 20$ ($\kappa^{-1} = 100$ nm) in accordance with previous structural (Royall *et al* 2005) and conductivity (Royall *et al* 2003) measurements. However, by combining equations (2) and (4), it was possible to model the addition of polymer. Furthermore, we identified the point at which the simulation began aggregating, as determined by a continuous decrease in the potential energy, as (approximately) the gelation point ϕ_{GEL}. It goes beyond the scope of this work to rigorously model a dynamically arrested gel, but our approach did provide a convenient way to estimate the contact potential $\beta\epsilon$, which was found by adjusting it such that ϕ_{GEL} in the simulation matched that of the experimental system. In this way, we arrived at $\beta\epsilon = 8$ and 9 for $q=0.09$ and 0.16 respectively, corresponding to $Z = 422$ and 448 respectively.

While $g(r)$ is sensitive to local structure, longer-ranged correlations may more easily be detected by Fourier analysis. We therefore calculated 'structure factors' from 2d confocal microscopy images, as shown in figures 3(a) and (b) for $q = 0.09$ and $q = 0.16$ respectively. The single-particle level structure is clearly visible at $k\sigma \approx 2\pi$,
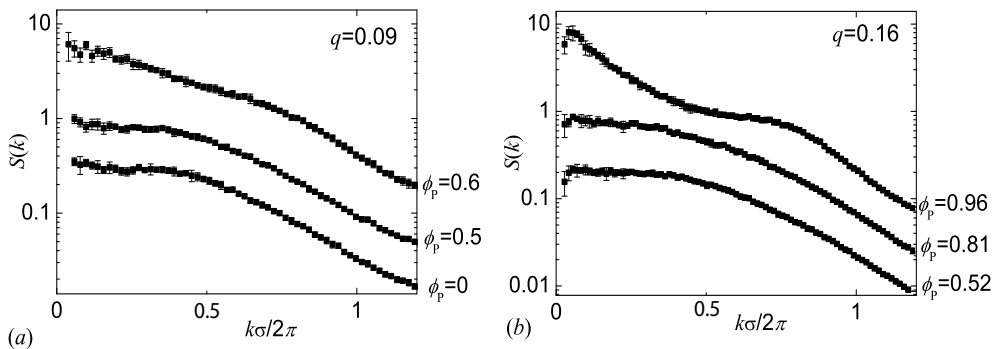
Figure 3. The 'structure factor' resulting from Fourier transforms of 2d confocal microscopy images at various polymer concentrations, for $q = 0.09$ (*a*) and $q = 0.16$ (*b*). Lines are offset for clarity.

where k is the wavevector. Like the $g(r)$ data, there is very little change in the colloidal fluid prior to gelation. From Ornstein-Zernike theory, for length-scales considerably larger than the particle diameter, the structure factor is proportional to

$$S(k) \propto \frac{1}{1 + \xi^2 k^2} \tag{5}$$

where ξ is the correlation length. While the above relation is valid for a 3d system, it turns out to be possible to fit data obtained from a 2d image with this equation. A full and rigorous investigation of the validity of fitting the 2d image data with a 3d function such as equation (5) lies beyond this work, but here we proceeded as follows: As mentioned above, the experimental data is unsuitable for 3d Fourier transformation so we made digital images from simulation data, which we analysed in 2d and 3d. We took parameters to match the gelation boundary for $q = 0.09$. Two such 'structure factors' are shown in figure 4(*a*), inset, corresponding to the experimental data in figure 3(*a*). We fitted the simulation data with equation (5) for $k\sigma < \pi$. In the 3d case, we obtained values of $\xi = 1.0 \pm 0.3\sigma$ and $\xi = 1.6 \pm 0.5\sigma$ for $\phi_P = 0.5$ and 0.6 respectively, while for 2d we found $\xi = 1.2 \pm 0.4\sigma$ for $\phi_P = 0.5$ and $\xi = 1.6 \pm 0.5\sigma$ for $\phi_P = 0.6$. Although these data are preliminary, they do suggest that simply fitting equation (5) is at least a reasonable approach.

Figure 4(*a*) shows the correlation length obtained by fitting the 'structure factor' with equation (5). The data are plotted as the fraction of ϕ_{GEL} since this allows a direct comparison between the two experiments. The correlation length shows a marked increase upon gelation, while in the one-phase region, there is little change. As in figures 1-3, we see relatively little difference between the experiments: the correlation length increases sharply upon gelation. There is a hint of a more gradual increase in $\xi(\phi_P)$ for $q = 0.16$ approaching the gelation point, but more data are needed to be certain. The topmost 'structure factor' in figure 3(*b*) has a slight peak at low k, suggesting that the density fluctuations have sufficient magnitude to regard the system as phase separated. However both the 'peak' value and fitting equation (5) give similar correlation lengths. In the gel, the correlation length is longer in the $q = 0.16$ system but it is expected to evolve as a function of time (Bibette *et al* 1992) so similar values are not anticipated.

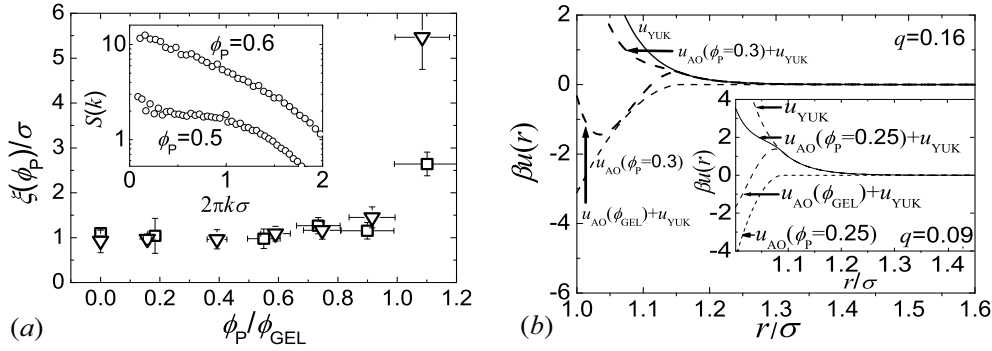The potentials used to model the system, equations (2) and (4), are plotted in

Figure 4. (*a*) The correlation length as determined from Ornstein-Zernike fits as a function of scaled polymer volume fraction $q = 0.09$, squares, $q = 0.16$, triangles. Inset shows 3d 'structure factors' from simulation data. (*b*) pair potentials used in the Monte Carlo simulation to model the fluid structure, for $q = 0.16$. Inset shows the $q = 0.09$ system.

figure 4(*b*) for $q=0.16$ and as an inset for $q=0.09$. In both cases, we plot the individual contributions from the electrostatic screening (u_{YUK}) and depletion (u_{AO}). In the case of u_{AO}, we set the polymer volume fraction around that required for phase separation in the *absence* of electrostatic repulsions, i.e. $\phi_P = 0.24$ and 0.3 for $q = 0.09$ and 0.16 respectively. We sum these 'pure' depletion potentials with u_{YUK} in each case and show the combined $u_{YUK} + u_{AO}(\phi_{GEL})$ interactions.

The reason for the suppressed phase separation now becomes clearer. First we consider the case when we would expect phase separation in the absence of electrostatics, $\phi_P = 0.25$ and 0.3 for $q = 0.09$ and 0.16 respectively. In this case the Yukawa potential is only perturbed by the addition of the depletion interaction. The electrostatic repulsions dominate. However, upon increasing the polymer concentration to ϕ_{GEL}, an attractive well develops in each case.

4. Summary

To conclude, we studied the structure of a model colloid-polymer mixture, in the one-phase region. We accessed both real and Fourier space, which gave similar results. Contrary to expectations, we found that the fluid structure did not change significantly as a function of polymer concentration, but that a marked change occurred at the particle level upon gelation. Furthermore, we found that phase separation appeared to be suppressed. We attribute these effects to an electrostatic repulsion between the colloids which has a similar range to the depletion attraction. With Monte Carlo simulation, assuming Yukawa and Asakura-Oosawa-Vrij behaviour, we found agreement with our experimental results. By considering the Asakura-Oosawa and Yukawa contributions to the pair potential, we found that the depletion attraction is suppressed by electrostatic repulsions, but at elevated polymer concentrations where we find aggregation in experiments, an attractive well is formed. Our system provides an analogue with aqueous colloidal dispersions in which the electrostatics may be tuned to compete with van der Waals interactions: here the attractions are tuned to compete with the electrostatics.

Acknowledgments

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