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# Clusters and gels in systems of sticky particles

H Sedgwick<sup>1</sup>, S U Egelhaaf<sup>1,2</sup> and W C K Poon<sup>1</sup>

<sup>1</sup> School of Physics and Collaborative Optical Spectroscopy, Micromanipulation and Imaging Centre (COSMIC), The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

<sup>2</sup> School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JZ, UK

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## Abstract

We studied clustering and gelation in low-volume-fraction ( $\phi \lesssim 0.2$ ) hard-sphere colloids, some with charge, with added non-adsorbing polymers. The range of the effective ‘depletion’ attraction induced by the polymers between the particles is  $\gtrsim 2\%$  of the particles’ diameter. The effects of density mismatch between the particles and the solvent and unscreened charges on the particles were investigated. The onset of aggregation and gelation in a neutral, density-matched system is discussed in terms of mode-coupling theory (MCT) and a recent ‘renormalized’ version of MCT respectively. Gravity causes sedimentation of growing clusters and shifts the gelation boundary. In the charged and density-matched system, a ‘cluster phase’ in which finite-size aggregates ‘coexisted’ with monomers occurred before gelation. Its origins remain unclear.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Short-range interparticle attractions are ubiquitous in colloids. (Hereafter  $-\mathcal{E}$  is the contact strength of this attraction in units of the thermal energy  $k_B T$ , and  $\delta$  is its range in units of the particle diameter,  $2R$ .) If  $\mathcal{E}$  is large enough, the colloids can aggregate to form space-filling structures even at low particle volume fraction ( $\phi$ ). Such colloidal *gels* are non-ergodic (the particles are ‘stuck’), have finite low-frequency storage moduli, and occur widely in applications. Colloidal gelation in the limit of  $(\phi, \mathcal{E}^{-1}, \delta) \rightarrow 0$  has long been discussed in terms of diffusion-limited cluster aggregation (DLCA). Diffusing particles ‘bond’ permanently at contact; the growing, ramified, clusters do the same, eventually filling space. The practical aspects of colloidal gelation at finite  $(\phi, \mathcal{E}^{-1}, \delta)$  have been studied for many years. The underlying fundamental physics has recently become an area of intensive research.

This recent surge in interest is partly due to parallel developments in colloidal glasses. Experiments show that in dense ( $\phi \gtrsim 0.5$ ) suspensions with  $\delta \lesssim 0.1$ , two qualitatively distinct kinds of glasses exist: repulsion-dominated at low  $\mathcal{E}$ ; and attraction-dominated at high

$\mathcal{E}$  [1, 2]. Mode-coupling theory (MCT) predicts precisely such a scenario [3]. Interestingly, the predicted boundary separating ergodic fluid from attraction-dominated glass is continuous down to  $\phi \rightarrow 0$ . A question naturally arises—what is the significance of this MCT boundary at low  $\phi$ ? It has been proposed that increasing  $\mathcal{E}$  at low  $\phi$  (and fixed, small  $\delta$ ) across the MCT boundary should take the system from an ergodic fluid into a non-ergodic gel [4]. (If the particles are monodisperse, a region of crystallization at intermediate  $\mathcal{E}$  can also be expected.)

Surprisingly, there is little experimental support for a direct transition from ergodic fluid to non-ergodic gel (possibly via crystallization). Instead, the literature contains a confusing ‘zoo’ of observations. In particular, there have been reports of different kinds of amorphous sediments [5–7] or long-lived ‘clusters’ [8] at values of  $\mathcal{E}$  less than those needed for gelation. These diverse phenomena occur in different experimental systems, and no unified understanding exists to date.

In this work, we demonstrate that a variety of non-equilibrium phenomena in low- $\phi$  colloids with small- $\delta$  attractions can be generated *in a single, well-characterized model system* by tuning external conditions. Our results suggest that the plethora of literature observations may largely be due to the effects of gravity and charge. In particular, our data enable us to test directly a scaling prediction for charge-stabilized equilibrium clusters [9]. The gelation boundary at low  $\phi$  for a system with  $\delta \sim 0.02$  *without* gravity or charge effects is obtained for the first time, and compared to MCT and a recently proposed renormalized version of the theory applicable at low  $\phi$  [10].

## 2. The experimental system

Our basic experimental system consists of in-house synthesized spherical particles with poly(methylmethacrylate) (PMMA) cores fluorescently labelled with nitrobenzoxadiazole (NBD) and sterically stabilized by a thin ( $\sim 10$  nm) layer of chemically grafted poly-12-hydroxystearic acid suspended in *cis*-decalin. These behave as almost perfect hard spheres. PMMA (density  $\rho = 1.188$  g cm $^{-3}$ ) is considerably denser than *cis*-decalin ( $\rho = 0.897$  g cm $^{-3}$ ): the density mismatch is  $\Delta\rho \approx 0.3$  g cm $^{-3}$ . Addition of linear, non-adsorbing polystyrene (PS, Polymer Laboratory, molecular weight 212 400 g mol $^{-1}$ ) induces an effective attraction between the PMMA particles: exclusion of PS between the surfaces of two nearby particles results in a net osmotic force pushing them together. The depth and range of this ‘depletion’ attraction scale as the polymer concentration and the size of the polymer respectively. The latter can be estimated by twice the radius of gyration of a single coil, giving a dimensionless range of  $\delta \approx r_g/R$ .

The equilibrium phase behaviour, glass transitions, and gelation in the colloidal PMMA + non-adsorbing linear PS system *without* density matching has been studied extensively before [11]. We used a mixture of  $\approx 4:1$  cycloheptyl bromide (CHB):*cis*-decalin ( $\rho_{\text{CHB}} = 1.289$  g cm $^{-3}$ ) for density matching, with the precise ratio being adjusted empirically until no visible sedimentation was observed after centrifuging at 3000 rpm for 24 h.

It was found recently that CHB gave a positive charge,  $Q$ , to PMMA particles, with the value of  $Q$  being highly preparation dependent [12]. Our density-matched particles remained a fluid at  $\phi = 0.32$ , but crystallized at  $\phi = 0.36$ . The low freezing density,  $0.32 < \phi_F < 0.36$ , compared to that for hard spheres ( $\phi_F^{\text{HS}} = 0.494$ ) is consistent with  $Q \neq 0$ . Direct measurement of  $Q$  is hampered by the low solvent dielectric constant ( $\epsilon_r \approx 4$ ). An estimate can be made by assuming that each charge on a particle is balanced by a singly charged counter-ion in the solvent, and modelling the particles as effective hard spheres of radius  $R + \kappa^{-1}$  (where  $\kappa^{-1}$  is the Debye screening length) that crystallize at  $\phi_{\text{eff}} \approx 0.5$ . This gave  $Q \lesssim 10^3$ .

Following [12] we added tetrabutylammonium chloride (TBAC, from Fluka) to screen the charge. At a TBAC concentration of  $[\text{TBAC}] = 1$  mg cm $^{-3}$  ( $\approx 3.6$  mM),  $\kappa^{-1} = 1.1$  nm,

and we observed  $\phi_F \approx 0.5$ —i.e. the charges are sufficiently screened that the particles behave as uncharged hard spheres. The added TBAC left the sample density matched to within our experimental accuracy. We label these samples  $\bar{Q}\bar{G}$ . In pure *cis*-decalin we have samples of non-density-matched uncharged particles ( $\bar{Q}G$ ). On the other hand, density-matched samples of particles with bare (unscreened) charges ( $Q\bar{G}$ ) can be obtained by *not* adding any TBAC.

The swelling of single PS coils in 4:1 CHB:*cis*-decalin [13] and pure *cis*-decalin [14] have been documented, and are nearly identical near room temperature. For our polymer, literature data give  $r_g = 13.7$  nm in both cases. Particles used in the  $\bar{Q}\bar{G}$ ,  $\bar{Q}G$ , and  $Q\bar{G}$  experiments had radii  $R = 535, 527,$  and  $660$  nm respectively, giving  $\delta \approx 0.026, 0.026,$  and  $0.021$  in the three cases.

Each sample was prepared and homogenized in a cuvette. Then a small amount was pipetted for observation between a cover slip and a microscope slide in a confocal microscope (Nikon TE-300 with Biorad Radiance 2100 MP scanning head, excitation 488 nm, emission observed at 525 nm). The sample thickness was fixed by spacers at  $\approx 0.3$  mm.

### 3. Results

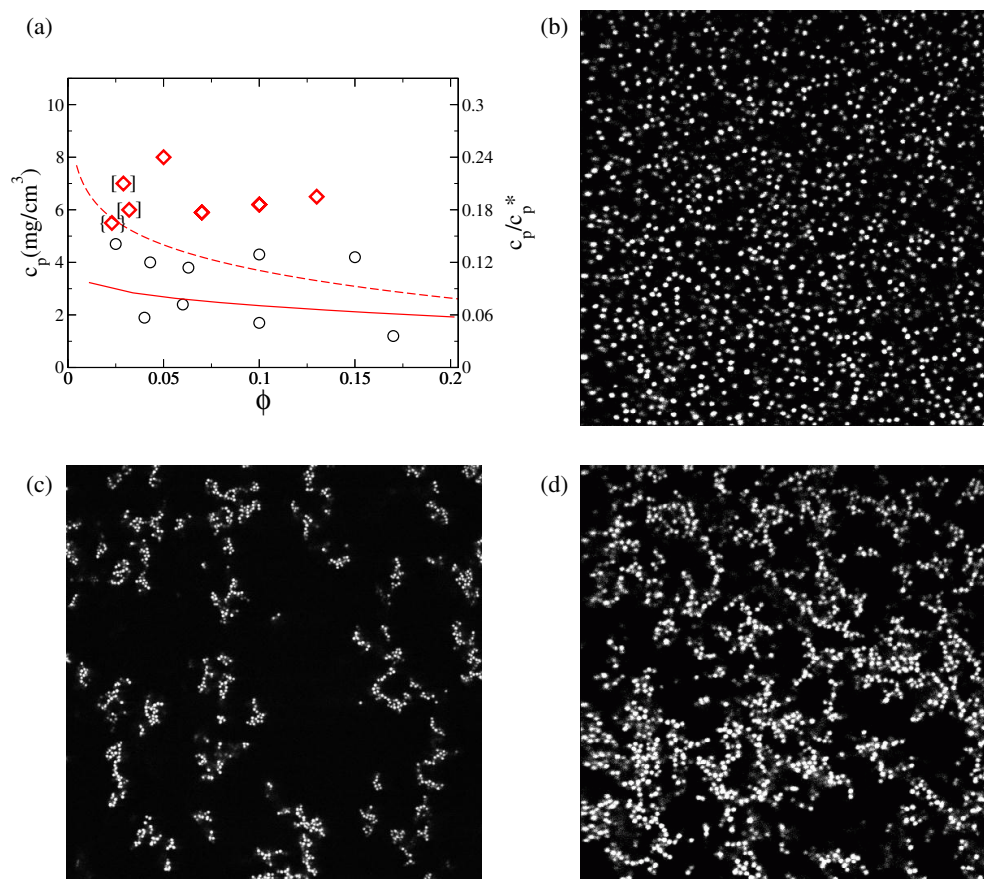
We observed the onset of aggregation in all three systems as  $c_p$  was increased. At high enough  $c_p$ , frozen system-spanning structures (gels) were formed, but the precise route to gelation was found to be strongly dependent on the degree of density matching and the presence of unscreened charges on the particles.

#### 3.1. The charge-screened, density-matched system ( $\bar{Q}\bar{G}$ )

Our observations for the charge-screened, density-matched system are summarized in figure 1(a). At low enough polymer concentrations,  $c_p \lesssim 5$  mg cm<sup>-3</sup>, individual particles exhibited Brownian motion; figure 1(b): these samples were ergodic fluids (o in figure 1(a)). At  $c_p \gtrsim 5$  mg cm<sup>-3</sup>, however, aggregation was observed which rapidly gave rise to rather large ( $\sim 50$  particle diameters) clusters ( $\diamond$ ; figure 1(a)). These clusters appeared ‘caged’ by each other, so the orientation and centre of mass of each cluster fluctuated without any net long-range motion. These fluctuations never disappeared during a two-hour observation period for the clustering sample with the lowest ( $\phi, c_p$ ) ( $\{\diamond\}$  in figure 1(a)). In other clustering samples, however, all discernible motion ceased after a period  $\tau$ , and the structure appeared frozen to the naked eye. The time interval  $\tau$  varied from 1 h to 5 min, rapidly decreasing as  $c_p$  and/or  $\phi$  increased. A handful of samples showed clusters with a lifetime of  $\tau \sim 1$  h before motion ceased ( $[\diamond]$  in figure 1(a)), but all other samples showed mobile large clusters over very significantly shorter timescales  $\tau \lesssim 20$  min. A confocal image of any of the frozen samples at any one observation depth apparently consisted of isolated clusters—figures 1(c), (d)—but images from different heights (hereafter, ‘z-scans’) revealed frozen clusters at every level, consistent with the whole sample consisting of a single, connected structure.

#### 3.2. The non-density-matched, neutral system ( $\bar{Q}G$ )

Our observations for the neutral non-density-matched particles,  $\bar{Q}G$ , are summarized in figure 2. The onset of aggregation occurred along a boundary almost identical to that found in the  $\bar{Q}\bar{G}$  system. Frozen structures were again found at high  $c_p$  ( $\diamond$ ; figure 2(a)). Over a range of intermediate polymer concentrations, however, a new type of behaviour was observed (\*; figure 2(a)). Here, images taken soon after loading showed clusters of particles, not dissimilar to the early stages of gelation in the  $\bar{Q}\bar{G}$  system. Taking z-scans, however,



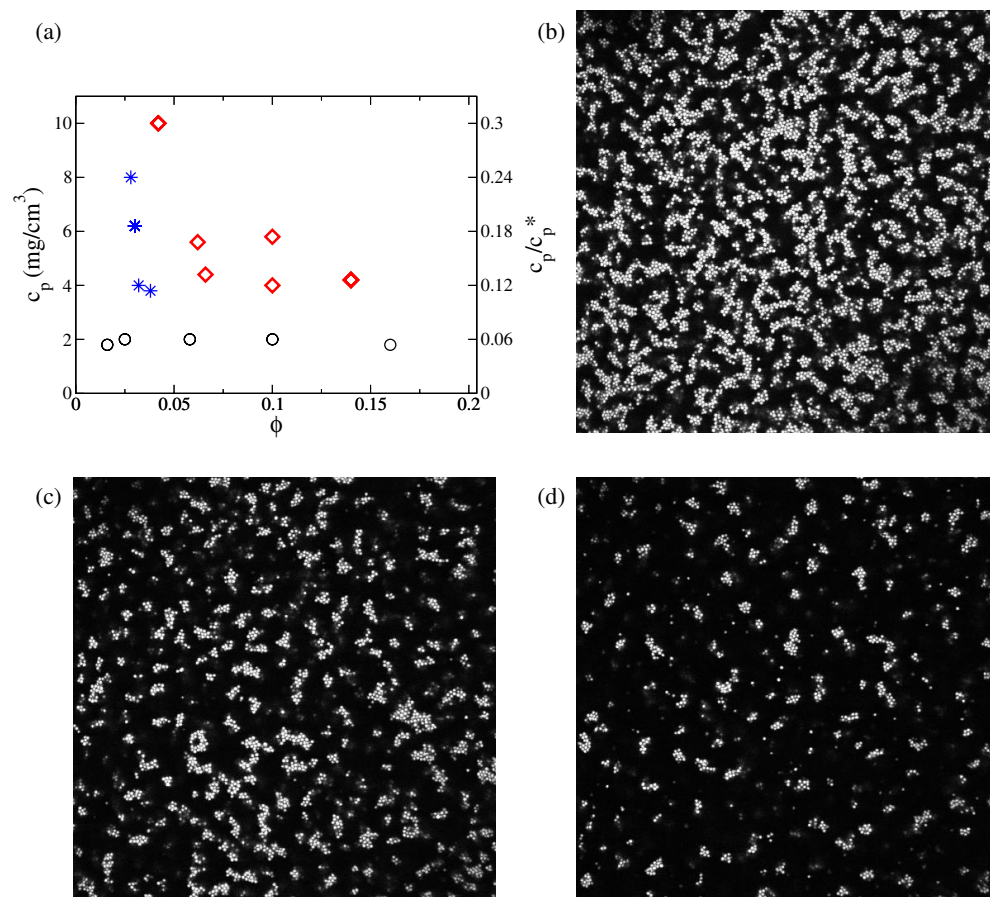
**Figure 1.** (a) Observations of the charge-screened, density-matched system ( $\bar{Q}\bar{G}$ ) of  $\delta \approx 0.026$ . Symbols represent the following: fluid—circle and aggregation—diamond. The MCT boundary is plotted for the parameters of our system (bold curve), and the corresponding CMCT gel line is also shown (dashed curve). Here and in other figures,  $c_p^*$  is the overlap concentration of the polymer. (b) A confocal micrograph of an ergodic fluid sample at  $\phi = 0.06$  and  $c_p = 2.4$  mg cm<sup>-3</sup>. (c) A confocal micrograph of the frozen structure in the sample with  $\phi = 0.029$  and  $c_p = 7$  mg cm<sup>-3</sup>. (d) A confocal micrograph of the frozen structure in the sample with  $\phi = 0.1$  and  $c_p = 6.2$  mg cm<sup>-3</sup>.

soon revealed that the clusters were undergoing rapid sedimentation. Soon a density gradient of clusters developed, ultimately giving rise to an amorphous sediment of clusters beneath a supernatant almost devoid of particles; figures 2(b)–(d).

### 3.3. The density-matched, charged system ( $Q\bar{G}$ )

Finally, we turn to density-matched particles with bare (unscreened) charges ( $Q\bar{G}$ ); figure 3(a). A transition from ergodic fluids in which individual particles exhibited Brownian motion ( $\circ$ ) to clustering ( $*$ ) was observed as  $c_p$  was increased. Thereafter, over an intermediate range of  $c_p$ , we found individual mobile clusters; figures 3(b), (c). At the highest  $c_p$ , we again found frozen structures (d).

At low  $\phi$ , it is immediately clear the clusters coexist with single particles; figure 3(b). At higher  $\phi$ —figure 3(c)—monomers are less immediately discernible, but are nevertheless



**Figure 2.** (a) Observations of the non-density-matched, neutral system ( $\bar{Q}G$ ) of  $\delta \approx 0.026$ . Symbols represent the following: fluid— $\circ$ , sedimenting clusters— $*$ , and frozen structures— $\diamond$ . (b)–(d) Confocal micrographs of the sedimenting clusters in a sample of  $\phi = 0.038$  and  $c_p = 3.8 \text{ mg cm}^{-3}$  at heights of (b) 12  $\mu\text{m}$ , (c) 24  $\mu\text{m}$  and (d) 36  $\mu\text{m}$  above the base of the sample, taken ten minutes after sample preparation.

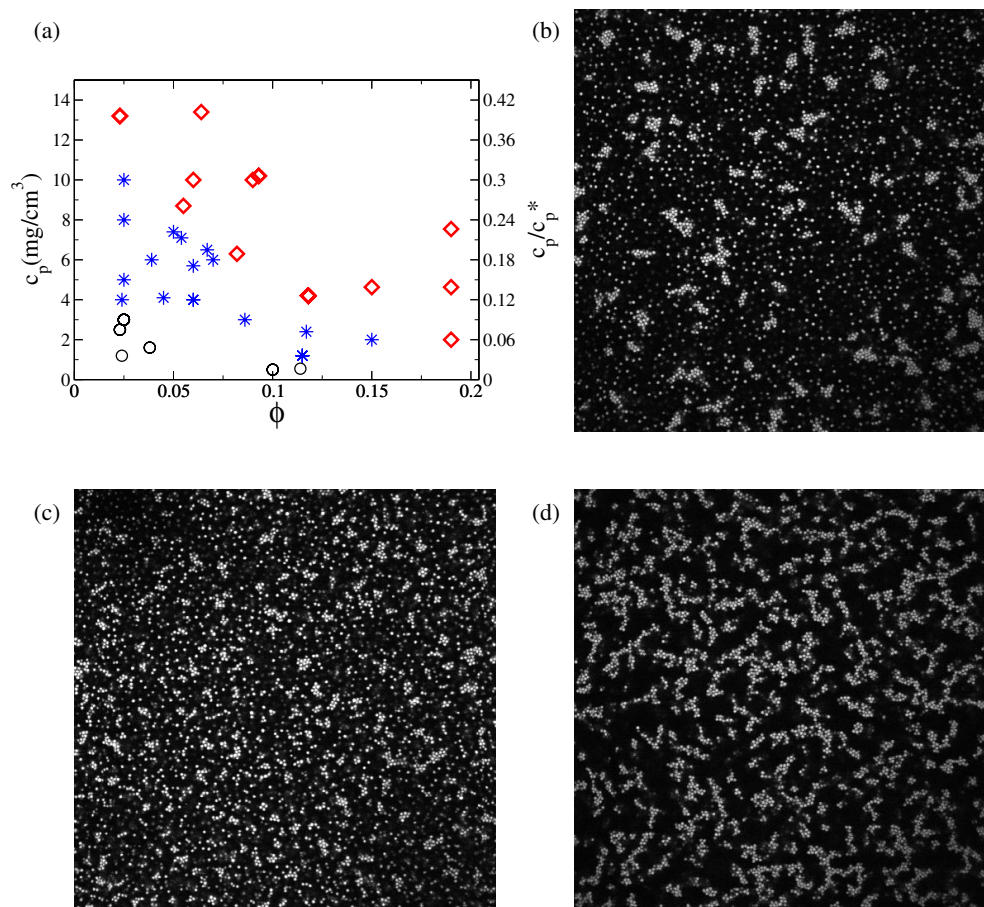
present. The clusters increased in size somewhat as  $c_p$  increased. These states of cluster–monomer coexistence seem to be long-lived: clusters were not found to grow by further aggregation. On the other hand, neither did we observe any particles joining or leaving the clusters.

#### 4. Discussion

Comparison of figures 1–3 immediately reveals our main finding: the route to gelation in three ostensibly very similar systems is highly dependent on the state of density matching and charge of the constituent particles. Below, we seek to interpret our findings in each case.

##### 4.1. The charge-screened, density-matched system ( $\bar{Q}\bar{G}$ )

The first significant result is the *sharp* onset of aggregation. One possible explanation is that we have crossed a gas–liquid binodal in the system. This is not likely for two reasons. First,



**Figure 3.** (a) Observations of the charged, density-matched system ( $Q\bar{G}$ ) of  $\delta \approx 0.021$ . Symbols represent the following: fluid—circle, mobile clusters—star, and frozen structures—diamond. (b) A confocal micrograph of the clusters in a sample with  $\phi = 0.086$  and  $c_p = 3 \text{ mg cm}^{-3}$ . (c) A confocal micrograph of the clusters in a sample with higher volume fraction,  $\phi = 0.15$ , and  $c_p = 1.9 \text{ mg cm}^{-3}$ . (d) A confocal micrograph of the frozen structure at  $\phi = 0.083$  and  $c_p = 6 \text{ mg cm}^{-3}$ .

our particles are monodisperse enough to crystallize; at  $\delta \approx 0.026$ , the gas–liquid binodal is metastable relative to the fluid–crystal binodal, so we would have expected to see crystallization first. Secondly, we do not see a coexisting population of dilute particles, which would have been expected in gas–liquid phase separation.

An alternative explanation of the onset of aggregation is given by mode-coupling theory (MCT), an approximation scheme that can predict when the local dynamics in a fluid first drops out of thermal equilibrium as a function of  $\phi$ ,  $\mathcal{E}$  (experimentally controlled by  $c_p$ ), and  $\delta$ . A closed form expression for the position of this ‘MCT boundary’ applicable at the low- $\phi$  limit in colloid–polymer mixtures has recently been obtained [15], and is plotted for the parameters of our system in figure 1(a). Its position is somewhat lower than the experimental clustering boundary—it is well known that MCT always overpredicts the tendency of systems to become non-ergodic; but the *shape* of the MCT boundary matches that of the experimental onset of aggregation rather well.

This calculated boundary is where MCT predicts that *single particles* should first drop out of thermal equilibrium. As aggregation proceeds, we need to apply MCT to the growing *clusters*, with renormalized parameters: the ramified internal structure of the clusters means that the cluster volume fraction continually increases; the growing size of the clusters means that the effective range of the attraction decreases; finally, the increasing number of sites at which a cluster can break (an entropic effect) can be modelled as a decreasing effective bond strength. A recent implementation of this scheme, known as ‘cluster MCT’ (CMCT), predicts that at some point, a glass of dense clusters—a colloidal gel—may result [10]. The CMCT gel line corresponding to the parameters of our system is also shown in figure 1(a).

The simplest interpretation of the CMCT scheme suggests that the region between the MCT and CMCT boundaries should give rise to rather large clusters that are internally non-ergodic but just fail to freeze into a glass of clusters, giving rise to a ‘cluster phase’ that is stable indefinitely. However, CMCT neglects thermal fluctuations and assumes perfect density matching. In a real system, where thermal rearrangements will occur, and density matching is never perfect, we expect the cluster phase to have a finite lifetime. Thus, for example, even a small amount of sedimentation would cause the clusters to jam.

In our experiments, it is tempting to identify the samples showing longer-lived clusters,  $\{\diamond\}$  and  $[\diamond]$  in figure 1(a), as belonging to the cluster phase, and ascribe the eventual cessation of fluctuations as due to imperfect density matching. Centrifugation over two days allowed us to estimate  $\Delta\rho \lesssim 10^{-1} \text{ g cm}^{-3}$ , so our largest clusters (tens of particle diameters) have a gravitational Peclet number (ratio of diffusive to sedimentation timescales) of  $\sim 1$ . Samples at higher  $(\phi, c_p)$  showed large clusters that remained mobile over very significantly shorter timescales,  $\tau \lesssim 20 \text{ min}$ . It is possible that the very rapid change in  $\tau$  from  $\gtrsim 1 \text{ h}$  down to  $\lesssim 20 \text{ min}$  can be associated with an underlying CMCT transition to a glass of clusters smoothed out by sedimentation. The position of this experimental boundary indeed compares rather well in shape with the CMCT prediction; figure 1(a).

#### 4.2. The non-density-matched, neutral system ( $\bar{Q}G$ )

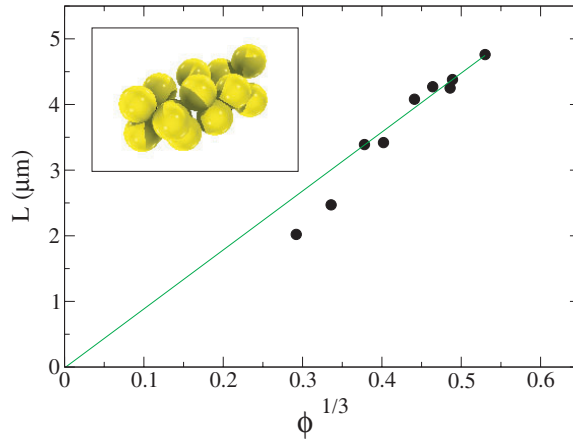
The onset of aggregation in the  $\bar{Q}G$  system occurs at approximately the same position as that in the corresponding density-matched system, and probably represents the MCT boundary. The gelation line is little affected by gravity at high enough  $\phi$ ; but now there is a sharp upturn at  $\phi \approx 0.05$ . In fact, we expect on qualitative grounds that there may exist a critical volume fraction,  $\phi^*$ , below which gelation would be impossible: clusters sediment faster than they can grow. The data in figure 2 suggest that in our system  $\phi^* \lesssim 0.02$ . Note that since the gravitational Peclet number of an object of size  $\mathcal{R}$  scales as  $\mathcal{R}^4$ , a small degree of density mismatching could have a very significant effect on large clusters and therefore the value of  $\phi^*$  [16].

Our observations are directly comparable to those made by Zukoski and co-workers for a system of silica particles where small polymers induced a depletion attraction of similar range ( $\delta \sim 0.02$ ) [7]. We believe that sedimentation was also important in the observations reported in [5, 6]; but in either case, the range of the effective interparticle attraction was considerably larger than the  $\delta \sim 0.02$  in the present work, so metastable gas–liquid phase separation almost certainly played an important part.

#### 4.3. The density-matched, charged system ( $Q\bar{G}$ )

Our observations at intermediate  $c_p$  are reminiscent of the ‘cluster phase’ identified by Segré *et al* [8]. (Since Segré *et al* used CHB for density matching, their particles were indeed charged.) The coexistence of clusters of well-defined average size with monomers





**Figure 4.** The cluster dimension  $L$  as a function of  $\phi^{1/3}$ . The line shows an unconstrained linear fit through all but the lowest two data points. The inset shows a typical cluster plotted using real particle coordinates from the sample with  $\phi = 0.086$  and  $c_p = 3 \text{ mg cm}^{-3}$ .

in aggregating charged particles has been predicted by Groenewold and Kegel [9, 17]. While the growth of a cluster lowers its energy because of the formation of more nearest-neighbour attractive ‘bonds’, it also increases its electrostatic self-energy. Eventually these two contributions balance, giving rise to finite clusters coexisting with monomers. Groenewold and Kegel further suggested that under the right conditions aggregation could bring about progressive counter-ion condensation, so the clusters would become unstable to unlimited growth, resulting ultimately in gelation. Qualitatively, our observations of a cluster phase followed by gelation as the attraction is deepened appear to fit this scenario.

Quantitatively, Groenewold and Kegel considered the balance between attraction and repulsion and the  $\phi$ -dependent degree of ionization of the particles and predicted the occurrence of clusters with characteristic dimension  $L$  [9]

$$L = K \left( \frac{E v b^3 e^{\ell_B/b}}{Q s \ell_B} \right)^{1/3} \phi^{1/3}. \quad (1)$$

Each particle of volume  $v$  and surface area  $s$  has  $Q$  ionizable sites each of which dissociates to give a counter-ion of size  $b$ . The solvent of dielectric constant  $\epsilon_r$  has Bjerrum length  $\ell_B = 56/\epsilon_r \text{ nm}$  at room temperature: this is the distance at which two electronic charges have potential energy equal to  $k_B T$ . Each particle in the interior of a cluster has energy  $-E$  due to interaction with its nearest neighbours. Groenewold and Kegel predicted disc-shaped clusters, for which the geometric factor  $K = 2.23$ .

To test whether the Groenewold–Kegel mechanism applies to our data, the size of a population of clusters (taken to be the largest dimension of each cluster) at  $c_p \approx 3 \text{ mg cm}^{-3}$  (corresponding to a contact attraction of  $\approx 5k_B T$  between neighbours) is plotted against  $\phi^{1/3}$  in figure 4. We find that except for the smallest clusters, an  $L \propto \phi^{1/3}$  scaling is satisfied. The cluster shape appears to be non-spherical; figure 4 inset. Using  $v$  and  $s$  calculated from the known particle radius,  $Q = 700$  (estimated from the freezing density at  $c_p = 0$ ; see section 2),  $E = 25k_B T$  (corresponding to 5 nearest neighbours) and  $\epsilon_r = 4.1$  (from  $\epsilon_r^{\text{decalin}} = 2.15$  and  $\epsilon_r^{\text{CHB}} = 5.3$ ), the fitted slope gave  $b = 0.49 \text{ nm}$ . This compares reasonably well with the radius of the likely counter-ion in our system ( $\text{Br}^-$ , from the photodissociation of the CHB, radius  $0.2 \text{ nm}$ ).

This apparent agreement with the predictions of Groenewold and Kegel is, however, surprising. According to these authors, there should be an *equilibrium* coexistence between finite clusters and monomers. In other words, we expect to see monomers joining and leaving clusters: no such processes could be observed in our system within two hours. Moreover, Groenewold and Kegel used approximations that only applied to large clusters (but which were nevertheless smaller than the Debye screening length), e.g. they neglected cluster entropy. Our clusters and Debye screening length are small—a few particle diameters. Another puzzling issue concerns the onset of aggregation in this system. There are three possibilities. First, in any system of attractive particles, we can expect transient clusters. Repulsion and the Groenewold–Kegel mechanism would serve to stabilize these clusters. Under this scenario, however, we expect to see a dynamic equilibrium between monomers and clusters, which we do not observe. Secondly, the onset of aggregation could be due to the crossing of an MCT boundary; but in this case, we would not expect the presence of unaggregated monomers. Finally, it may be surmised that what we are seeing is gas–liquid phase separation [18, 19]. This, however, is unlikely. We have already reasoned that the metastable gas–liquid binodal does not feature in our observations for the  $\bar{Q}\bar{G}$  and  $\bar{Q}G$  systems; we can expect repulsion to push this binodal to higher attraction strengths (or, equivalently, higher polymer concentrations).

Thus, while our observations in the  $\bar{Q}\bar{G}$  system are probably the most intriguing among those of the three systems studied, a consistent physical explanation for these observations remains to be worked out.

## 5. Summary and conclusions

We have studied aggregation and gelation in a model colloid with a very short-range ( $\delta \gtrsim 0.02$ ) polymer-induced depletion attraction between the particles. In the simplest case of density-matched and effectively neutral particles ( $\bar{Q}\bar{G}$ ), the onset of aggregation and gelation can perhaps be described by MCT [3] and CMCT [10] respectively. Gravity, by causing the sedimentation of growing clusters, gives rise to a sharp upturn of the gelation boundary, shifting it to higher polymer concentration (or, equivalently, attraction strength) in the uncharged and non-density-matched system ( $\bar{Q}G$ ). The observations for the charged and density-matched system ( $QG$ ) are the most intriguing. A cluster phase first formed, which ‘coexisted with monomers’; this was followed by gelation at the highest polymer concentrations. Some aspects of the cluster phase agreed with predictions by Groenewold and Kegel. But our failure to observe a dynamic equilibrium between clusters and monomers, and the smallness of our clusters, make us cautious in identifying what we observed with these predictions. The physical mechanism driving the onset of aggregation in this system remains unclear.

These remaining puzzles notwithstanding, we have shown that varying the degree of charging and density mismatch in a single, well-characterized model system can generate a rich ‘zoo’ of non-equilibrium behaviour.

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