Chapter 6

Conclusion

'The many men, so beautiful
And they all dead did lie:
And a thousand, thousand slimy things
Lived on; and so did I'

- **Rime of the Ancient Mariner**, Samuel Taylor Coleridge (1797).

6.1 Thesis summary

A detailed study of non-equilibrium aggregation in a model colloid-polymer mixture has been presented. Although aggregation has been observed frequently in colloid-polymer mixtures both the static and dynamic structure of these aggregates, and accordingly the aggregation kinetics, have remained uninvestigated. In this study it was shown that the non-equilibrium region in the phase diagram can be split into three distinctly different kinetic regimes. At low colloid and polymer concentrations one finds behaviour reminiscent of classical nucleation and growth, characterised by a stationary ring of scattered light which forms at small angles only after a finite time. At higher colloid and polymer concentrations one observes behaviour analogous to classical spinodal decomposition as one finds a continuously brightening and collapsing small angle ring.

The static structure of these states is found to be consistent with atomic systems which undergo spinodal decomposition. The dynamics suggest that the particles are relatively free to diffuse throughout the aggregation process, consistent with the observation of a continuously evolving speckle pattern. At still higher colloid or polymer concentrations one finds that the depletion potential becomes sufficiently large to cause the system to gel. In this case one finds a ring which initially collapses but becomes arrested at a finite wavevector. The early stage growth is found to follow a DLCA-type mechanism. Accordingly one finds retarded particle dynamics and the persistence of frozen-in density fluctuations. After a finite time the ring suddenly collapses roughly coincident with visible gravitational settling, attributed to a slow particle rearrangement. In the absence of gravity this slow Brownian-driven rearrangement leads to the formation of dense discrete droplets.

As yet the origin of non-equilibrium aggregation has received little attention. It was suggested that the non-equilibrium behaviour observed here is induced by the presence of an incipient metastable gas-liquid phase boundary, calculated using a recent mean-field theory. The distinctly different kinetic regimes observed in the non-equilibrium region can be explained once analogies have been drawn between the colloid-polymer system and recent Ising-like simulation.

6.2 Comparison with the study of Allain et al.

Here I draw analogies between this work and a very recent study of aggregation phenomena, which in particular studies the effect of gravity on aggregation kinetics. Aggregation almost always occurs under the influence of gravity, but the effect of gravity has received little attention. A study which does examine the effects of both aggregation and sedimentation is that of Allain et al. [93], [145], who investigate the formation of calcium carbonate aggregates formed under a van der Waals attraction. As bond

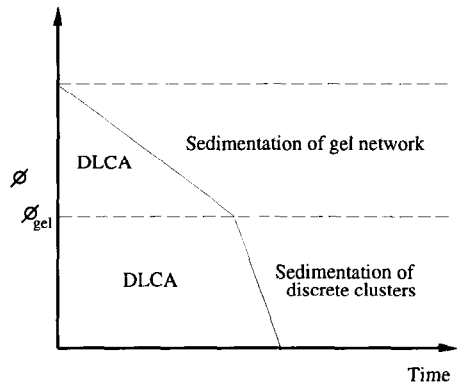

Figure 6.1. The different effects of gravity on the late stages of colloidal aggregation.

breaking and bond rotation are always suppressed, due to the very strong interparticle bonds, they always observe behaviour analogous to DLCA i.e. equivalent to the transient-gelation regime observed here. In contrast to our study their system is poorly characterised with a large polydispersity, hindering detailed comparison with the work presented here. They identify two different kinetic regimes to the aggregation process when the system is subject to the influence of gravity:

- The early stage kinetics are dominated by diffusion i.e. a DLCA-type mechanism.
- The late stage kinetics are primarily governed by gravitational effects.

The late stage growth, i.e. once the clusters have grown sufficiently large to be affected by gravity, is found to be strongly dependent upon the initial colloid volume fraction. If ϕ is sufficiently small, $\phi < \phi_{gel}$, they observe the formation of discrete clusters which rapidly sediment *before* the formation of a system-spanning gel. If ϕ is sufficiently large, $\phi > \phi_{gel}$, a percolating structure forms and after an initial latency time the whole network sediments. This behaviour is summarised in figure 6.1.

Analogous behaviour has been observed here. At low volume fractions of colloid and large polymer concentrations, e.g. sample 4 at $\phi \sim 0.02$, one observes early stage DLCA kinetics. Despite a partially retarded speckle pattern the small angle ring never becomes

completely arrested. It was conjectured that the effect of gravity was sufficiently large to prevent gelation so that only discrete clusters were formed which sedimented before the system could percolate. Consistent with this hypothesis there appears to be little latency time before visible sedimentation.

As the volume fraction was increased, yet still with a sufficiently large polymer concentration, e.g. sample 9 at $\phi \sim 0.1$, the early stage kinetics again follow a DLCA-type mechanism, to yield a system-spanning gel. The gel slowly breaks up due to the effect of Brownian motion, which tends to break interparticle bonds and compactify the local short-range structure. Discrete clusters are formed under this slow rearrangement, which rapidly sediment under gravity. Consistent with this hypothesis the gel was observed to break up into independent amorphous clusters once the effect of gravity had been removed. If the collapse was purely gravity driven then the collapse of the structure would be initiated at the bottom of the sample and a small angle ring would persist at the top, contrary to what is observed. Consistent with our study they find that the gel latency time increases and sediment velocity decreases with increasing colloid volume fraction (see figures 4.4 and 4.5).

Allain et al. estimate the critical volume fraction required to form a system-spanning gel, ϕ_{gel}, which can be written,

$$\phi_{gel} \sim \left(\frac{4\pi \, \Delta\rho \, g a^4}{3 k_B T} \right)^{(3-d_f)/(1+d_f)} \tag{6.1}$$

This equation arises from equating the Brownian and gravitational time scales for a ramified cluster to diffuse a distance comparable to its own diameter. If one assumes that a fractal dimension of 1.7 is necessary for a fully frozen gel structure, one finds $\phi_{gel} \sim 0.10$ in the system studied in this thesis, consistent with the lack of a completely frozen ring or latency time at $\phi \sim 0.02$, no matter the polymer concentration. In the

same model system, but with a larger particle radius ($a \sim 300nm$), very recent observations suggest that the structure fails to gel at any colloid or polymer concentration until $\phi \gtrsim 0.2$, consistent with equation (6.1) which suggests $\phi_{gel} \sim 0.18$ [146].

The study of Allain et al. was only restricted to a deep interparticle attraction and therefore they failed to observe the rich variety of aggregation kinetics observed here i.e. neither nucleation-like or spinodal-like behaviour which were observed at low interparticle attractions. Without light scattering data they also did not determine the exact nature of the structures formed; neither did they link their observed phenomena to the underlying equilibrium phase behaviour. In our study it was argued that non-equilibrium aggregation is induced by the presence of an incipient metastable gas-liquid boundary. Once analogies have been made to Ising-like simulation all the different kinetic regimes can be explained.

6.3 Possible future work

In contrast to the work of Allain et al. the colloid-polymer system represents a binary mixture and throughout this work the role of the polymer molecules has been largely ignored. In all theoretical treatments the system has been regarded as a single one-component colloidal fluid, subject to a deep, short-ranged interparticle attraction which becomes sufficiently large to induce non-equilibrium aggregation. In future studies the role of the polymer should be examined in more detail. Ideally one would have a colloidal suspension which could be exactly index-matched, so that only the polymer molecules scattered light. Alternatively one could fluorescently tag the polymer molecules, which could be studied using fluorescence techniques such as confocal microscopy or fluorescence recovery after photobleaching.

Rather than simply studying aggregation kinetics the fundamental relation between atomic and colloidal phase kinetics requires more investigation, and the model colloid-polymer system provides an ideal opportunity to do so. One can now readily examine

very early stage phase separation kinetics, due to the very slow diffusion rates in colloid-polymer systems, and their dependence upon gravity, effects which cannot be studied in atomic systems. One can also examine the very short scale structure throughout the phase separation process. There are a number of different regions of the phase diagram which could be studied, through the use of small angle scattering techniques in particular. These include the gas-liquid phase, gas-crystal phase and three phase regions of the phase diagram, found in a colloid-polymer mixture with a sufficiently large size ratio. If the predicted solid-solid phase transition is observed, in a colloid-polymer mixture with a sufficiently small size ratio, then one would expect to find an enhanced small angle scattering which could be used to study kinetics. Also the kinetics of the crystal-fluid phase separation, observed for all size ratios less than 0.33, could be studied in more detail.

Finally in a recent computer simulation it was shown that C_{60} may not have a stable liquid phase, as the inter-molecular potential is too short-ranged. Hagen et al. [62] mapped out a metastable gas-liquid boundary which showed a marked similarity to the non-equilibrium region observed in colloid-polymer mixtures. Whether there is a stable liquid phase remains a contentious issue. Would one observe similar kinetic regimes within a metastable gas-liquid phase of C_{60}, similar to those seen in colloid-polymer mixtures? Would one even observe a C_{60} gel state? As yet these questions remain open.

Appendix A

Scattered electric field from a sphere

Equation (3.4) can be written,

$$b(Q) = 4\pi \int_0^a dr\ r^2(n - n_0)\frac{sin(Qr)}{Qr} \tag{A.1}$$

assuming a spherical particle of radius a. Ignoring the phase factor in the resulting electric field (which will make no contribution to the form factor),

$$E(Q) = \frac{4\pi a^2}{(Qa)^2}(n - n_0)\int_0^a Qrsin(Qr)\ dr \tag{A.2}$$

$$= \frac{4\pi a^3}{(Qa)^3}(n - n_0)(sin(Qa) - (Qa)cos(Qa)) \tag{A.3}$$

$$= V_{sphere}\frac{3}{(Qa)^3}(n - n_0)(sin(Qa) - (Qa)cos(Qa)) \tag{A.4}$$

where $V_{sphere} = \frac{4}{3}\pi a^3$ is the volume of the sphere.

Appendix B

Scattered electric field from a shell

Consider a shell of inner radius a, outer radius $a + \Delta$ and refractive index n_s. Using the result derived in Appendix A, equation (A.3) can be written,

$$E(Q) = \frac{4\pi a^3}{(Qa)^3}(n_s - n_0)\ |sin(Qr) - (Qr)cos(Qr)|_a^{a+\Delta} \tag{B.1}$$

$$\begin{aligned} &= \frac{4\pi a^3}{(Qa)^3}(n_s - n_0)(sin(Qa)cos(Q\Delta) + cos(Qa)sin(Q\Delta) \\ &\quad - [Qa + Q\Delta][cos(Qa)cos(Q\Delta) - sin(Qa)sin(Q\Delta)] \\ &\quad -sin(Qa) + (Qa)cos(Qa)) \end{aligned} \tag{B.2}$$

Assuming a thin shell $\Delta << a$ this can be written,

$$E(Q) \sim \frac{4\pi a^3}{(Qa)^3}(n_s - n_0)\left((Q^2 a\Delta)sin(Qa) - (Q\Delta)^2 sin(Qa)\right) \tag{B.3}$$

$$\sim 4\pi a^2 \Delta(n_s - n_0)\frac{sin(Qa)}{Qa} \tag{B.4}$$

$$= V_{shell}(n_s - n_0)\frac{sin(Qa)}{Qa} \tag{B.5}$$

where $V_{shell} = 4\pi a^2\Delta$ is the volume of the shell.

Appendix C

The relation between $S(Q)$ and $g(r)$

Equation (3.10) can be written,

$$S(Q) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle e^{(i\mathbf{Q}.(\mathbf{r}_i-\mathbf{r}_j))}\rangle \tag{C.1}$$

$$= 1+\frac{1}{N}\langle\sum_{i\neq j}^{N}\sum_{j\neq i}^{N} e^{(i\mathbf{Q}.(\mathbf{r}_i-\mathbf{r}_j))}\rangle \tag{C.2}$$

separating the $i=j$ and $i\neq j$ terms. Introducing the Dirac delta function $\delta(\mathbf{r})$,

$$S(Q) = 1+\frac{1}{N}\langle\sum_{i\neq j}^{N}\sum_{j\neq i}^{N}\int\int e^{(i\mathbf{Q}.(\mathbf{r}-\mathbf{r}'))}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)\rangle\, d\mathbf{r}d\mathbf{r}' \tag{C.3}$$

$$= 1+\frac{1}{N}\int\int e^{(i\mathbf{Q}.(\mathbf{r}-\mathbf{r}'))}.\langle\sum_{i\neq j}^{N}\sum_{j\neq i}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)\rangle\, d\mathbf{r}d\mathbf{r}' \tag{C.4}$$

$$= 1+\frac{1}{N}\int\int e^{(i\mathbf{Q}.(\mathbf{r}-\mathbf{r}'))}\rho^{(2)}(\mathbf{r},\mathbf{r}')\, d\mathbf{r}d\mathbf{r}' \tag{C.5}$$

The function $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ is known as the two-particle distribution function and is related to the pair correlation $g(r)$,

$$g(r) \equiv \frac{\rho^{(2)}(\mathbf{r})}{\rho^2} \tag{C.6}$$

where ρ is the homogeneous density. Therefore,

$$S(Q) = 1 + \rho \int e^{i\mathbf{Q}.\mathbf{r}} g(r)\, d\mathbf{r} \tag{C.7}$$

by integrating out the dummy variable $\mathbf{r}'$.

In a very dilute gas $g(r) = 1$ due to a lack of pair correlations (i.e. $\rho^{(2)}(\mathbf{r}) = \rho^2$) and the structure factor is simply a delta function which can be regarded as a contribution to the forward scattering. It is common practice to ignore this contribution and rewrite equation (C.7) as,

$$S(Q) = 1 + \rho \int e^{i\mathbf{Q}.\mathbf{r}} (g(r) - 1)\, d\mathbf{r} \tag{C.8}$$

Appendix D

Second Virial coefficients

The second virial coefficient is defined as,

$$B_2 \equiv -\frac{1}{2}\int f(\mathbf{r}) d^3r \tag{D.1}$$

$$= -\frac{1}{2}\int \left(exp\left[-\frac{\epsilon}{k_B T}\right] - 1 \right) d^3r \tag{D.2}$$

Therefore for a hard sphere fluid,

$$B_{2,HS} = -\frac{1}{2}\int_{r=0}^{a} \left(exp\left[-\frac{\epsilon = \infty}{k_B T}\right] - 1 \right) d^3r$$

$$-\frac{1}{2}\int_{r=a}^{\infty} \left(exp\left[-\frac{\epsilon = 0}{k_B T}\right] - 1 \right) d^3r \tag{D.3}$$

$$= \frac{1}{2}\int_{r=0}^{a} d^3r \tag{D.4}$$

$$= \frac{2\pi a^2}{3} \tag{D.5}$$

In the case of the AHS model,

$$
\begin{aligned}
B_{2,AHS} &= -\frac{1}{2}\int_{r=0}^{a}\left(exp\left[-\frac{\epsilon=\infty}{k_BT}\right]-1\right)d^3r \\
&\quad -\frac{1}{2}\int_{r=a}^{a+\delta}\left(\frac{(a+\delta)}{12\tau_B\delta}-1\right)d^3r \\
&\quad -\frac{1}{2}\int_{r=(a+\delta)}^{\infty}\left(exp\left[-\frac{\epsilon=0}{k_BT}\right]-1\right)d^3r \qquad \text{(D.6)} \\
&= \frac{1}{2}\int_{r=0}^{a}d^3r-\frac{1}{2}\int_{r=a}^{a+\delta}\frac{(a+\delta)}{12\tau_B\delta}d^3r+\frac{1}{2}\int_{r=a}^{a+\delta}d^3r \qquad \text{(D.7)} \\
&= \frac{2\pi a^2}{3}\left(1-\frac{1}{4\tau_B}\right) \qquad \text{(D.8)}
\end{aligned}
$$

in the limit $\delta \to 0$.

For the SW fluid,

$$
\begin{aligned}
B_{2,SW} &= -\frac{1}{2}\int_{r=0}^{a}\left(exp\left[-\frac{\epsilon=\infty}{k_BT}\right]-1\right)d^3r \\
&\quad -\frac{1}{2}\int_{r=a}^{a+\delta}\left(exp\left[-\frac{\epsilon}{k_BT}\right]-1\right)d^3r \\
&\quad -\frac{1}{2}\int_{r=(a+\delta)}^{\infty}\left(exp\left[-\frac{\epsilon=0}{k_BT}\right]-1\right)d^3r \qquad \text{(D.9)} \\
&= \frac{1}{2}\int_{r=0}^{a}d^3r-\frac{1}{2}exp\left[-\frac{\epsilon}{k_BT}\right]\int_{r=a}^{a+\delta}d^3r+\frac{1}{2}\int_{r=a}^{a+\delta}d^3r \qquad \text{(D.10)} \\
&= \frac{2\pi a^2}{3}-\left(exp\left[-\frac{\epsilon}{k_BT}\right]-1\right).\frac{2\pi}{3}\left((a+\delta)^2-a^2\right) \qquad \text{(D.11)} \\
&= \frac{2\pi a^2}{3}\left[1-\left(exp\left[-\frac{\epsilon}{k_BT}\right]-1\right)\left(2\left(\frac{\delta}{a}\right)+\left(\frac{\delta}{a}\right)^2\right)\right] \qquad \text{(D.12)}
\end{aligned}
$$

Appendix E

Structure factor of a doublet

$$S(Q) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} e^{i\mathbf{Q}.(\mathbf{r_i}-\mathbf{r_j})} \tag{E.1}$$

$$= \frac{1}{N}\sum_{i=1}^{N} e^{i\mathbf{Q}.\mathbf{r_i}}\sum_{i=1}^{N} e^{-i\mathbf{Q}.\mathbf{r_i}} \tag{E.2}$$

$$= \frac{1}{N}|\sum_{i=1}^{N} e^{i\mathbf{Q}.\mathbf{r_i}}|^2 \tag{E.3}$$

as the two sums $\sum_i, \sum_j$ are independent. In the case shown in figure E.1, for two particles of radius a, centred at a and $-a$, this can be written,

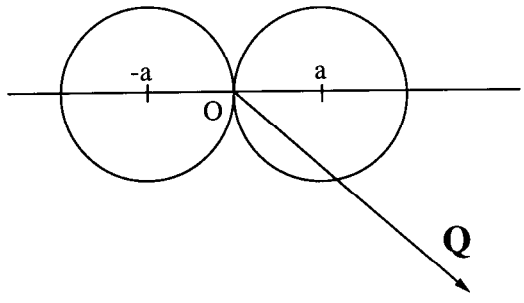

Figure E.1. Scattering geometry.

$$\frac{1}{N}|\sum_{i=1}^{N} e^{i\mathbf{Q}.\mathbf{r}_i}|^2 = 2\,cos^2\left((Qa)cos(\theta)\right) \tag{E.4}$$

Averaging around $\mathbf{Q}$,

$$\frac{1}{N}\langle|\sum_{i=1}^{N} e^{i\mathbf{Q}.\mathbf{r}_i}|^2\rangle = \frac{1}{4\pi}\int\int 2\,sin(\theta)\;cos^2((Qa)cos(\theta))\;d\theta d\phi \tag{E.5}$$

$$= \left[\frac{sin(2Qa)}{2Qa}\right] + 1 \tag{E.6}$$

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Publications:

Work from this thesis which has either been published or submitted for publication:

'An experimental study of a model colloid-polymer mixture'
J. Phys. II France **3** 1075 (1993).

'Aggregation Dynamics in a Model Colloid-Polymer Mixture'
Analytical Proceedings **30** 493 (1993).

'Dynamics of Colloid-Polymer mixtures'
Physica A **201** 322 (1993).

'Gelation in Colloid-polymer mixtures'
To appear in Faraday Discussion 101: 'Gels'.

The DIC microscopy presented in chapter 4 has been included in:

'Developments in Wide Field Microscopy:
3D Spatial Investigations using Differential Interference Contrast
(DIC) Microscopy'
Scott Singleton *Unilever internal report* June (1994).