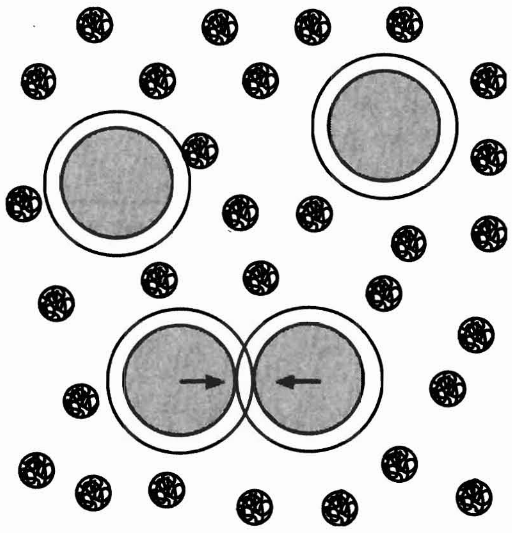

Fig. 4.5 The depletion interaction. Polymer coils are excluded from a depletion zone near the surface of the colloidal particles; when the depletion zones of two particles overlap there is a net attractive force between the particles arising from unbalanced osmotic pressures.

- The chains can be attached to the surface either by chemical bonds or by physical interactions. In either case, the strength of the bond anchoring the polymer to the surface needs to be rather greater than $k_B T$, otherwise there will be a tendency for the chain to become detached from the surface.

4.3.5 Depletion interactions

The final interaction we consider is, like the electrostatic interactions and polymer stabilisation, ultimately due to osmotic pressure, but in this case the interaction is **attractive** rather than repulsive. **Depletion interactions** arise whenever the solution contains, in addition to the suspended particles, other particles intermediate in size between the suspended particles and the size of the solvent molecules. The most common case occurs when the suspension contains a dissolved polymer which does not adsorb onto the surface of the particles.

The situation is illustrated in Fig. 4.5. The polymer molecules, depicted here as spheres, are excluded from a region of thickness L away from the surface of the particles—the depletion zone. As the particles approach, the depletion zones overlap, with the result that there is a volume of solution between the particles in which the concentration of polymer molecules is less than it is in the bulk solution. This means that the difference in osmotic pressure between the bulk solution and the depletion zone leads to a force pushing the particles together.

For a dilute solution of polymers, or indeed any other particles, which do not interact, the osmotic pressure P_{osm} is given simply by the ideal gas expression

$$P_{\text{osm}} = \frac{N}{V} k_B T, \tag{4.40}$$

where there are N polymer molecules in volume V of solution. The net interaction potential between the particles F_{dep} is simply

$$F_{\text{dep}} = -P_{\text{osm}} V_{\text{dep}}, \tag{4.41}$$

where V_{dep} is the total volume between the particles from which the polymers are excluded. For two spheres of radius a, at a centre-to-centre separation r, simple geometry gives

$$V_{\mathrm{dep}} = \frac{4\pi}{3}(a + L^3)\left(1 - \frac{3r}{4(a + L)} + \frac{r^3}{16(a + L)^3}\right). \tag{4.42}$$

The depletion interaction is never very large, but it is always attractive, and the depth of the well can become comparable to $k_{\mathrm{B}}T$; thus increasing the strength of the depletion interaction by addition of free polymer can lead to phase separation or aggregation in colloidal systems.

4.4 Stability and phase behaviour of colloids

We have seen how a variety of interactions between colloidal particles may lead to the particles either repelling or attracting each other; these interactions lead to interesting phase behaviour. In some ways this phase behaviour can be considered to be analogous to the phase behaviour of matter, with the colloidal particles taking the role of atoms or molecules. One can envisage a phase transition from a solid-like phase to a liquid-like phase, driven by attraction between the particles. More usually, however, the attractive energy is much greater than $k_{\mathrm{B}}T$. Rather than having an equilibrium between a dense liquid-like phase and a gas-like phase, whenever two particles meet, they stick irreversibly. This leads to the formation of open flocs which eventually fall out of suspension (flocculate).

We can summarise some of the ways in which the interaction between colloidal particles can be changed from repulsive to attractive:

- we can **add salt** to an electrostatically stabilised colloid, reducing the Debye screening length and decreasing the magnitude of the electrostatic repulsion relative to the van der Waals attraction;
- we can **add poor solvent** to a polymerically stabilised colloid; the resulting attractive polymer/polymer interactions will lead to a net attraction between the colloid particles;
- we can **physically or chemically remove** grafted polymer chains from the surface of the colloidal particles;
- we can **add non-adsorbing polymer** to cause an increase in the size of the depletion interaction.

4.4.1 Crystallisation of hard-sphere colloids

When the forces between colloidal particles are repulsive at all separations one has a stable suspension. If the particles are spherical with a rather narrow size distribution, then as one increases the concentration of particles (e.g. if the dispersing liquid is allowed to evaporate) one finds a remarkable transition from a disordered arrangement of particles, analogous to a liquid, to a crystalline packing of the particles. These **colloidal crystals** have true long-range order; often the diameter of the colloidal particles falls between 100 nm and 1 μm, and in this case the crystal will diffract light, resulting in striking opalescent

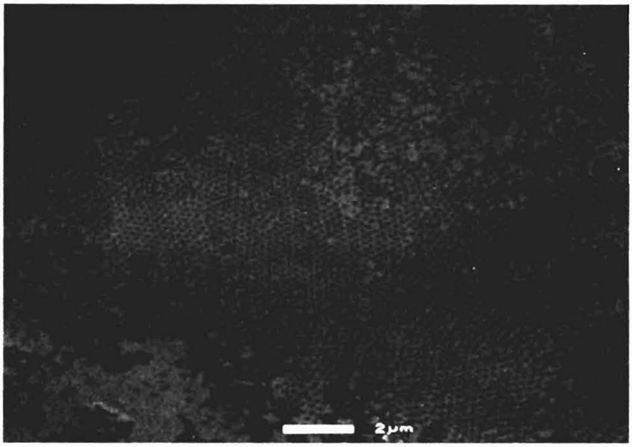

Fig. 4.6 A water-borne latex suspension imaged by environmental scanning electron microscopy, showing the formation of ordered regions. Reprinted with permission from He and Donald (1996). Copyright 1996 American Chemical Society.

interference effects. In fact, the gemstone opal is a natural colloidal crystal composed of submicrometre-sized silicon dioxide particles. The systems typically studied in the laboratory are composed of submicrometre polymer particles produced by a so-called emulsion polymerisation process, which yields rather a narrow particle size distribution. The particles are stabilised against coagulation by coating them with a layer of short polymer chains grafted to the surface. In fact, these systems are very similar to the latices produced on a vast industrial scale to form the basis of emulsion paints and water-based varnishes. An environmental scanning electron micrograph of one such material is shown in Fig. 4.6, showing clearly the tendency of the particles to form close-packed ordered regions.

A good starting point for understanding the phenomenon of colloidal crystallisation is to be found in a very simple model developed by theorists to understand liquids—the **hard-sphere** model. As its name suggests, in this model we consider an assembly of perfect spheres which interact via a potential which is zero except where two spheres overlap, in which case it is infinite. This model is in fact rather a good approximation to a sterically stabilised colloid in which the thickness of the stabilising polymer layer is much less than the radius of the particles.

We know that the maximum density one can achieve in packing hard spheres is obtained when they are arranged in a regular close-packed structure, in which case the volume fraction of spheres is 0.7404. If the spheres are packed randomly as closely as possible, then the maximum volume fraction obtainable (**random close packing**) can be shown to be around 0.63. So one can see that at very high volume fractions simple packing constraints force the spheres to take up a close-packed crystalline structure.

However, this provides only a very partial explanation of colloidal crystallisation. What is surprising is that crystals appear at a much lower volume fraction of spheres than that for either regular close packing or random close packing. In fact, at a volume fraction of 0.494 there is an abrupt transition to a crystal with a volume fraction of 0.545. This is a true phase transition; if one prepares a suspension with an intermediate volume fraction it will separate into two coexisting phases.

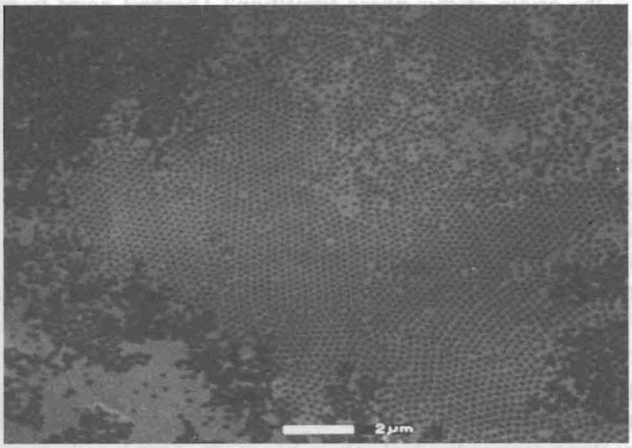

Fig. 4.6 A water-borne latex suspension imaged by environmental scanning electron microscopy, showing the formation of ordered regions. Reprinted with permission from He and Donald (1996). Copyright 1996 American Chemical Society.

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What is the origin of this phase transition? The first point to note is that temperature does not directly enter into the problem. Because the only possible energies for any configurations of the sphere are either zero (if no spheres overlap) or infinity (if two spheres do overlap) the Boltzmann weights for any configuration can only be either unity or zero, with no dependence on temperature. So the volume fractions of the coexisting liquid and solid phases are completely independent of temperature. The transition between solid and liquid must be driven entirely by **entropy**.

This seems paradoxical. How can it be that for some volume fractions, a regular crystal with long-range order can have a higher entropy—that is, be more disordered—than a random, liquid-like, arrangement? The reason is related to the difference between random and regular close-packing densities. In the crystal state, we lose entropy compared to the amorphous state by virtue of the long-range order, but because crystalline packing is more efficient than random packing each individual sphere has more space locally to explore, and thus has a higher entropy in the crystalline state compared to the amorphous state.

Another way of thinking about this involves the idea of **excluded volume**. The fact that two spheres cannot overlap leads to an effective repulsive force between spheres of entropic origin. We can understand this by remembering how excluded volume is dealt with in the van der Waals theory of non-ideal gases. Recall that for a perfect gas one can write the entropy per atom S_{ideal} of N atoms in a ideal V as

$$S_{\text{ideal}} = k_{\text{B}} \ln \left(a \frac{V}{N} \right) \tag{4.43}$$

where a is a constant. Now, if the gas atoms have a finite volume b this reduces the volume accessible to any given atom from V to $V - Nb$, and we must modify our expression for the entropy accordingly:

$$S = k_{\text{B}} \ln \left(a \frac{(V - Nb)}{N} \right). \tag{4.44}$$

We can rewrite this in terms of S_{ideal} as

$$S = S_{\text{ideal}} + k_{\text{B}} \ln \left(1 - \frac{bN}{V} \right), \tag{4.45}$$

and if the volume fraction of atoms is low we can expand the logarithm to yield,

$$S = S_{\text{ideal}} - k_{\text{B}} \left(\frac{N}{V} \right) b, \tag{4.46}$$

with a corresponding free energy given by

$$F = F_{\text{ideal}} + k_{\text{B}} T \left(\frac{N}{V} \right) b. \tag{4.47}$$

Thus there is an effective repulsion between the atoms, and in the case of a hard-sphere colloid it is an effective interaction of this kind that causes the particles to arrange themselves on a crystal lattice.

Of course, at the volume fractions at which hard spheres crystallise the approximations used in this simple expression have long since broken down,

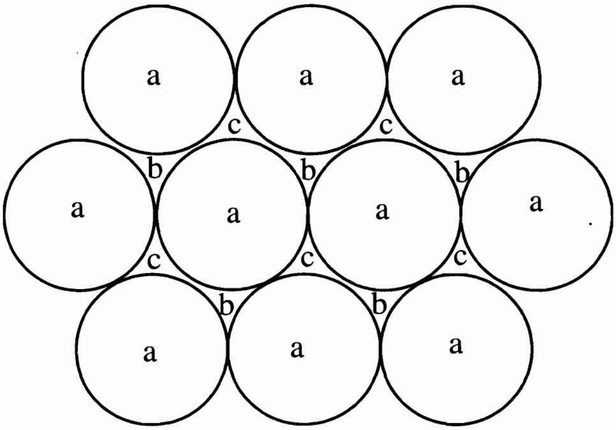

Fig. 4.7 A single close-packed layer, illustrating that there are two sites on which a second close-packed layer can be placed: b and c.

and the theory needs to be considerably refined to take into account the possibility that more than two particles may be interacting simultaneously, and to lift the mathematical approximations appropriate to a low particle volume fraction. Nonetheless developments of this approach form the basis of modern statistical mechanical theories of the hard-sphere fluid.

Before we leave the subject of crystallisation in hard-sphere systems, there is one subtle point that needs to be addressed. There are two different crystal structures which are close packed, namely face-centred cubic (FCC) and hexagonal close packed (HCP), and both have an identical maximum packing fraction. The difference between the two types of packing is best understood in terms of Fig. 4.7. Once one close-packed layer is laid down, there are two different ways in which subsequent layers can be placed. In the HCP structure, the sequence of layers alternates as ababab..., while in an FCC structure the sequence is abcabc....

Experimentally it is found that colloidal crystals as normally prepared have a random sequence of close-packed planes, corresponding to an HCP structure with a very large number of stacking faults. This is of some practical significance, as potentially colloidal crystals could have important applications in photonics, as materials with a so-called **photonic bandgap**. In such a material diffraction effects can lead to a situation in which light of a certain wavelength is unable to propagate in any direction. The existence of such bandgaps does, however, depend on the crystal structure being largely defect free. Quite recently, it has been found that there is a tiny difference in entropy between the FCC and HCP structure, and that it is the FCC structure that is always at equilibrium (Woodcock 1997, Mau and Huse 1999). Thus with careful preparation techniques it should be possible to prepare defect-free colloidal crystals with interesting optical properties.

4.4.2 Colloids with longer ranged repulsion

We have seen that we can produce a repulsive interaction between colloidal particles with a relatively long range either by having an electrostatic repulsion between the particles in a solution with a relatively low salt content, and thus a large Debye length, or by having long polymers grafted to the interface. Often

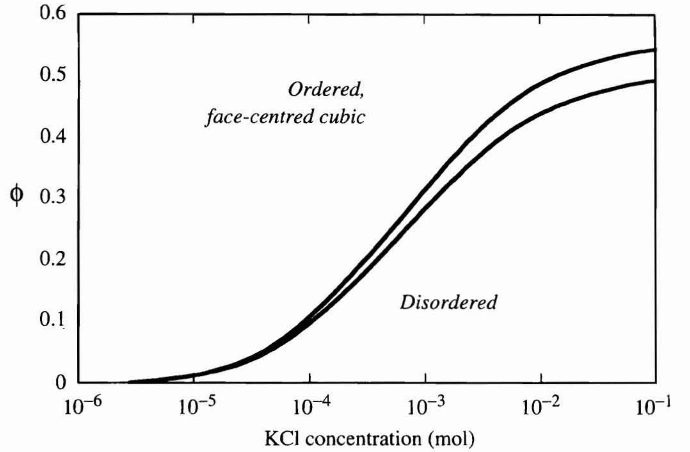

Fig. 4.8 Phase diagram for charged spheres in a polyelectrolyte solution as a function of the volume fraction of spheres ϕ and the concentration of salt, as calculated for spheres of radius 0.1 μm with surface charge $5000e$. After Russel *et al.* (1989).

the range of the repulsion is large compared to molecular sizes, but still small compared to the radius of the particle, and in this case the repulsive force can be treated as a perturbation of the hard-sphere interaction. Thus we anticipate a transition from a liquid state to a solid state, but this transition will occur at lower volume fractions than for a pure hard-sphere interaction. The effective hard-sphere radius of the colloid particles is greater than their physical radius because of the additional long-ranged repulsion.

This is illustrated in Fig. 4.8, which shows the predictions of a perturbation theory for the phase behaviour of the order–disorder transition for charged spheres in a solution of an electrolyte. At high concentrations of salt, the Debye screening length is very small and the order–disorder transition occurs at concentrations very close to those expected for ideal hard spheres. As the salt concentration is reduced, the Debye length—and thus the range of the repulsive interaction—increases and the volume fraction at which the order–disorder transition takes place is correspondingly reduced.

4.4.3 Colloids with weakly attractive interactions

If the interaction between colloidal particles is attractive, then we expect the system to undergo a transition to a **disordered, condensed phase**; this is analogous to a gas–liquid transition in a molecular system. The best way to realise this situation in practice is to add non-adsorbing polymer to a colloidal system that is stabilised by electrostatic interactions or by a grafted polymer layer; this creates a relatively weak attractive part of the potential whose magnitude depends on the volume fraction of added polymer. An example of the kind of phase diagram obtained by plotting the volume fraction of particles on one axis and the amount of added polymer—and thus the size of the attractive interaction—is sketched in Fig. 4.9. This diagram has been compared to experiment and found to be in agreement. One should compare this diagram to a phase diagram for a simple fluid plotted in the density/temperature plane, as sketched in Fig. 2.3. In fact the statistical mechanical theories which can be used to predict phase diagrams for simple fluids are easily adapted to predict the phase diagrams for colloidal dispersions.

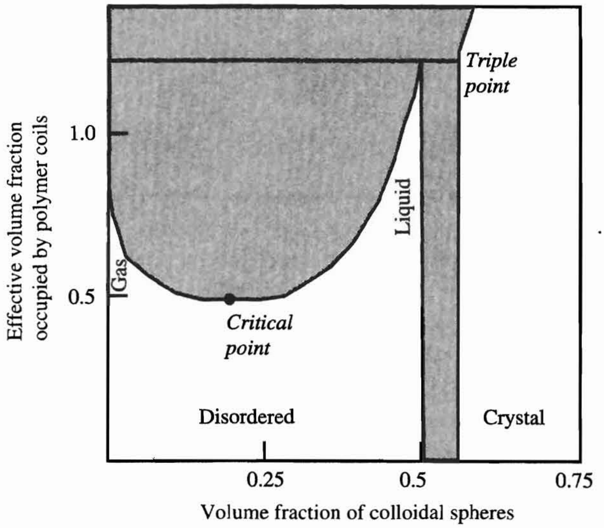

Fig. 4.9 Calculated phase diagram for a colloid of hard spheres with non-adsorbing polymer added to the solution. The ratio of the sizes of the colloidal spheres to the radii of the polymer molecules is 0.57. After Illett *et al.* (1995).

The qualitative features of this phase diagram are relatively straightforward to understand. When the attractive interactions are weak, we get a liquid–solid transition driven by the effective repulsion between the particles. This repulsion includes both the repulsion of entropic origin that underlies the excluded volume effect and any physical repulsion due to electrostatic or polymer-mediated interactions. The liquid–solid interaction is always first order; because there is a change in symmetry between the two phases the transition cannot take place gradually and thus there can be no critical point. When the attractive part of the potential becomes more important, we can have a gas–liquid phase separation which is analogous to the liquid–liquid unmixing transition discussed in Chapter 2. This transition can take place continuously, and thus there is a critical point. However, when the coexisting volume fraction for the liquid phase is large enough, this phase can lower its free energy even further by going over to an ordered state. Thus, according to the amount of added polymer, one can have a phase transition as a function of particle concentration from a gas to a liquid state, from a gas to a solid state, and indeed at one special condition there is a **triple point**, where gas, liquid, and solid coexist.

4.4.4 Colloids with strongly attractive interactions

The phase diagrams discussed in the section above are **equilibrium** phase diagrams; if one drives a system from the gas to the solid state by increasing the particle volume fraction, say, and if one subsequently adds more solvent then the transition should be completely reversible, and one should recover a low-density disordered state. If the depth of the attractive well in the potential curve is only a few times $k_B T$, equilibrium is easily reached. However, as the attraction becomes larger, it is more and more difficult to reach equilibrium: if two particles come into contact and stick then they take longer and longer to unstick and try another configuration, even if the first arrangement of particles does not correspond to the equilibrium state. This has a profound effect on the structure of the aggregates, as illustrated in Fig. 4.10.

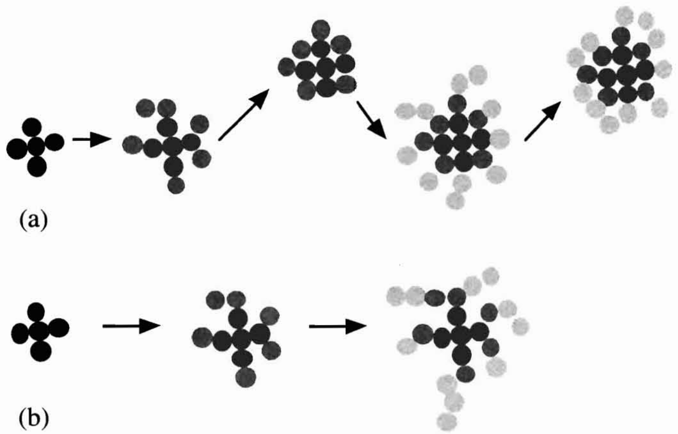

Fig. 4.10 Aggregation with and without rearrangement. In (a) the attraction is weak enough to allow the particles to rearrange following aggregation—this produces relatively compact aggregates. In (b) the attractive energy is so strong that once particles make contact, they remain stuck in this position. Particles arriving later tend to stick on the outside of the cluster, as access to its interior is blocked, resulting in much more open aggregates with a fractal structure.

If particles, once they have joined the aggregate, are able to rearrange, the resulting aggregate is likely to be rather compact. However, if once stuck the energy of attraction is too large for the particle to move again, the aggregate will be much more open in structure, because particles arriving at the aggregate later will tend to find access to the interior of the aggregate blocked by the earlier arrivals. In fact, the resulting structure is **fractal** in character. For a three-dimensional compact object the relationship between the size of the aggregate R and its mass M can be written $R \sim M^{1/3}$; for a fractal the corresponding relation is $R \sim M^{1/d_\mathrm{f}}$, where d_f is a fractal dimension which is less than three but greater than one.[2]

In an idealised model of aggregation, known as **diffusion-limited aggregation**, particles are considered to diffuse randomly until they touch a member of the cluster, after which they stick without further movement. Computer simulations reveal that for this model $d_\mathrm{f} \approx 1.71$, corresponding to very open, ramified structures. A more realistic model of aggregation would allow clusters themselves to aggregate; such **diffusion-limited cluster–cluster aggregation** models yield a slightly larger value of $d_\mathrm{f} \approx 1.78$.

Experiments reveal that if aggregation takes place in circumstances in which aggregation is very fast, with very deep potential wells of attraction, open aggregates are found with fractal dimensions of around 1.75, while in experiments carried out in slower conditions, when some rearrangement is presumably permitted, fractal dimensions are somewhat larger.

4.5 Flow in concentrated dispersions

Adding particles to a liquid might be expected to produce a dispersion with a viscosity greater than that of the pure liquid; this is indeed what happens, but in addition to an increased viscosity concentrated dispersions can show pronounced non-Newtonian effects in their flow, in particular **shear thinning**.

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[2] Of course, this relationship is valid for values of R between an upper limit, set by the overall size of the aggregate, and a lower limit defined by the size of the constituent particles. This is the difference between a mathematical fractal, for which such a relationship holds for all values of R, and a physical fractal, for which the relationship holds only for a limited range of lengths.