# Chapter **7** PARTICULATE GELS

# 7.1 INTRODUCTION

Ceramic coatings, films, and parts, such as fibers and catalyst supports, are often manufactured using the "sol-gel" process, in which a liquid suspension, or "sol," of colloidal particles, such as  $ZrO_2$ ,  $SiO_2$ , or  $Al_2O_3$ , is "gelled," or flocculated, into a quasi-solid mass by addition of a chemical agent (Brinker and Scherer 1990). Solvent is then removed from the gel by drying or extraction, any organics are burned out, and the gel is sintered at high temperature to form a useful glass or ceramic coating or part. Sometimes the particles are themselves grown in solution from monomeric species such as aqueous tetraethoxysilane (TEOS) by polymerization reactions; these particles then flocculate into a gel under appropriate pH and salinity conditions (Brinker and Scherer 1990).

For an initially stable sol composed of colloidal particles, the gelling agent, which is usually a pH modifier, an electrolyte, or a polymer, produces gelation by reducing repulsive particle–particle interactions, so that attractive van der Waals forces can draw particles into near contact. If the particle concentration is high enough (around a few volume percent or higher), a sample-spanning network of such contacts forms, producing a solid-like gel phase.

Given the universality of attractive van der Waals forces, the gelation phenomenon is perhaps less in need of explanation than is the existence of a stable dispersed particulate sol phase under appropriate conditions. Clumping of micron- and submicron-sized particles is in fact the norm; preparation of stable sols, on the other hand, requires special techniques, of which there are several. One is simply to match the index of refraction of the particles to that of the suspending medium, so that the Hamaker constant, which determines the magnitude of the van der Waals interactions, is small. Such a dispersed phase cannot be conveniently gelled, however, except perhaps by changing the temperature enough to increase the van der Waals interactions among the particles.

A more useful way to produce a sol phase is to use particles whose surfaces in solution are charged, resulting in *electrostatic stabilization* of the sol. Many oxide particles, such as SiO<sub>2</sub> or TiO<sub>2</sub>, contain hydroxyl (–OH) groups at their surfaces that can hydrolyze in aqueous media to form negatively charged  $-O^-$  groups; these can stabilize the suspension (Israelachvili 1991; Adamson and Gast 1997). Addition of an acid or an acid former tends to neutralize these groups, producing gelation. Alternatively, salt can be added, which at high enough concentration, often around 0.1 M, collapses the diffuse electrostatic double layer so that particles can approach closely enough to be drawn into near contact by van der Waals forces. Yet another way to stabilize colloidal dispersions is to *graft* or *adsorb* surfactant, hydrocarbon, or polymer chains to the surfaces of particles, producing a steric barrier to flocculation (Russel et al. 1989). If the chains are long enough and interact favorably with the solvent, the particles are kept at arm's length from each other and cannot flocculate. When desired, flocculation can then be induced by changing the temperature so that the solvent is repelled from the adsorbed chains, and the chains then "stick" to each other, thereby binding together the particles to which they are attached.

As discussed below, a dispersion that has been somehow stabilized can also be made to flocculate by adding to the suspension a *nonadsorbing* polymer, which induces *depletion flocculation* (Asakura and Oosawa 1954, 1958; Vrij 1976; Fleer and Scheutjens 1982; Liin-on et al. 1975; Vincent et al. 1988; Liang et al. 1994).

Long polymer molecules that strongly adsorb to the particle surfaces can also induce flocculation by *bridging* the gap between neighboring particles (Russel et al. 1989; Otsubo 1993). The rheological properties of mixtures of particles and adsorbing polymers in a solvent bear a resemblance to those of polymeric physical gels (see Section 5.4), wherein the particles play the role of cross-linkers, binding different polymer molecules together. When the concentration ratio of particles to polymers is not too extreme, these suspensions form bridging-flocculated gels. An example is silica particles and polyethylene oxide polymer in water, which gels and exhibits shear-thickening transitions (Cabane et al. 1997), analogous to the behavior of polymeric physical gels.

# 7.2 PARTICLE INTERACTIONS IN SUSPENSIONS

## 7.2.1 Interparticle Potentials

In principle, it should be possible to predict the critical conditions for flocculation and the rheological properties of the flocculated gel from the effective interparticle potential W(D), where D is the distance or gap separating the surfaces of neighboring particles. Typically, W(D) is estimated by adding together contributions from hard-core steric interactions, van der Waals interactions, electrostatic interactions, and possibly other interactions such as those from absorbed, grafted, or dissolved chains, or from thin (so-called Stern) layers of adsorbed ions, along with their hydration shells (Israelachvili 1991; Russel et al. 1989; Adamson and Gast 1997).

For spherical particles, some of these interactions can be described by simple formulas. The hard-core steric potential is simply

$$W_{\text{steric}} = \begin{cases} \infty & D < 0 \\ 0, & D \ge 0 \end{cases}$$
(7-1)

The van der Waals potential is [Russel et al. 1989; see Eq. (2-36)]

$$W_{\rm vdw} = -\frac{A_H}{12} \left\{ \frac{4a^2}{4aD + D^2} + \left(\frac{2a}{2a+D}\right)^2 + 2\ln\left[1 - \left(\frac{2a}{2a+D}\right)^2\right] \right\}$$
(7-2)

where  $A_H$  is the Hamaker constant and *a* is the particle radius. For small separations *D*, this reduces to simply

$$W_{\rm vdw} \approx -\frac{aA_H}{12D}$$
 for  $D \ll a$  (7-3)

The electrostatic potential, in the limit that the the gap between particles is small and the surface potential  $\psi_s$  is constant, is [Eq. (2-59)]

$$W_e = 2\pi\varepsilon_0\varepsilon a\psi_s^2 \ln[1 + \exp(-\kappa D)]$$
(7-4a)

while in the limit of constant surface charge [Eq. (2-60)] we obtain

$$W_e = 2\pi\varepsilon_0\varepsilon a\psi_s^2 \ln\left[\frac{1}{1 - \exp(-\kappa D)}\right]$$
(7-4b)

Here  $\varepsilon_0 = 8.8 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$  is the permittivity of space,  $\varepsilon$  is the dielectric constant of the medium,  $\psi_s$  is the electrostatic potential at the particle surfaces, and  $\kappa^{-1}$  is the Debye screening length,  $\kappa \equiv (\sum_i n_{\infty i} e^2 z_i^2 / \varepsilon \varepsilon_0 k_B T)^{1/2}$ . For simple 1:1 electrolytes such as NaCl at room temperature,  $\kappa^{-1}$  is given by (Israelachvili 1991)

$$\kappa^{-1} = \frac{0.304}{\sqrt{[\text{NaCl}]}} \quad \text{nanometers} \tag{7-5}$$

where [NaCl] is the molarity of the salt. For particle separations greater than a Debye length  $\kappa^{-1}$ , there is little difference between  $W_e$  for the constant-potential boundary condition and that for the constant-surface-charge boundary condition.

The surface potential  $\psi_s$  is often equated with the *zeta potential*  $\zeta$ , which is obtained by measuring the rate of migration of particles under an electric field. The zeta potential is the potential at the particle's *shear surface*, which can be displaced from the true particle surface when there is a Stern layer of tightly bound ions. The pH at which the zeta potential is zero is known as the *isoelectric point*; in general it can be different from the *point of zero charge*, which is the pH required to neutralize the surface of the particle.

The potentials (7-1), (7-2), and (7-4a), when combined, form the basis of the celebrated DLVO (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) theory of colloid stability. This theory is useful in predicting the conditions of surface potential, ionic strength, and so on, under which flocculation will occur. But the theory has important limitations, in part because it only considers van der Waals, electrostatic, and hard-core interactions.

The theory can be extended to include additional interactions. For example, if nonadsorbing polymer is present in solution, exclusion of this polymer from regions where the particles are closer together than the radius of gyration of the polymer molecules produces a potential  $W_{depl}$  that is roughly the osmotic pressure  $\Pi$  times the volume of layers from which polymer is depleted. Thus (Patel and Russel 1987; Russel et al. 1989)

$$W_{\text{depl}} = \begin{cases} -\frac{4\pi}{3} (a + \Delta_d)^3 \left[ 1 - \frac{3(2a+D)}{4(a+\Delta_d)} + \frac{(2a+D)^3}{16(a+\Delta_d)^3} \right] \Pi, & 0 \le D < 3\Delta_d \\ 0, & D > 3\Delta_d \end{cases}$$
(7-6)

where  $\Delta_d$  is the depletion-layer thickness. In dilute solutions,  $\Delta_d$  is roughly the polymer radius of gyration  $R_g$ . In more concentrated semidilute solutions, where polymer molecules overlap,  $\Delta_d$  is smaller than this.

The osmotic pressure  $\Pi$  is given by

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$$\Pi \approx \nu^{(R)} k_B T \left( 1 + \frac{A_2 M_n^2 \nu^{(R)}}{N_A} \right)$$
(7-7)

where  $\nu^{(R)}$  is the number of polymer molecules per unit volume of "free solution"—that is, solution not occupied by colloidal particles or their depletion regions (Ilett et al. 1995).  $\nu^{(R)}$  is also the number of coils per unit volume of a particle-free polymer solution in osmotic equilibrium with the sample.  $\nu^{(R)}$  is related to  $\nu$ , the number of polymer molecules per unit total volume of colloidal solution by  $\nu = f \nu^{(R)}$ , where f is the fraction of solution that is "free." It can be obtained from (Lekkerkerker et al. 1992; Ilett et al. 1995):

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

with  $\gamma \equiv \phi/(1-\phi)$ ,  $A \equiv 3\xi + 3\xi^2 + \xi^3$ ,  $B \equiv 4.5\xi^2 + \xi^3$ , and  $C \equiv 3\xi^3$ , with  $\xi \equiv \Delta_d/a$ .  $M_n$  in Eq. (7-7) is the number-averaged polymer molecular weight, and  $A_2$  is the second virial coefficient; for a theta solvent,  $A_2 = 0$ , while in a good solvent,  $A_2 > 0$ . The better the solvent, the stronger the depletion flocculation.

When the particles are in contact,  $W_{depl}$  is at its minimum value, which is

$$(W_{\text{depl}})_{min} = -\frac{4\pi\Delta_d^3}{3}\left(1 + \frac{3a}{2\Delta_d}\right)\Pi$$
(7-8)

Recently, direct experimental measurements of the depletion force using the surface forces apparatus were reported by Kuhl et al. (1996); the magnitude of the force was found to be in agreement with theoretical expectations.

Figure 7-1 gives examples of some of the above interaction potentials. The total interaction potential is usually assumed to be just the sum the individual contributions:

$$W = W_{\text{steric}} + W_{\text{vdw}} + W_e + W_{\text{depl}} + W_{\text{hyd}}$$
(7-9)

where  $W_{hyd}$  is the "hydration layer" potential to be discussed shortly. Although the individual potentials are typically monotonic functions of particle separation D, the sum of all contributions has one or more local minima. Since the magnitude of the van der Waals interaction grows more steeply with decreasing separation than any other interactions except very short range steric interactions, there is a deep (in theory, infinitely deep) attractive "well" at separations near zero. This well is called the *primary minimum*. There may also be a much shallower *secondary minimum* at larger separations (see Fig. 7-1).

In principle, spherical particles that come close enough together should always fall into an infinitely deep van der Waals primary minimum. In practice, as particle separations shrink to a couple of nanometers or less, there are strong steric forces that can prevent closer approach. In aqueous systems, steric forces are generated by adsorbed ions and hydration layers—that is, water that is hydrogen-bonded with ions adsorbed onto the particle surface. The effective potential,  $W_{hyd}$ , produced by these ions and hydration layers is sensitive to the type of absorbed ions that are present on the surface.  $W_{hyd}$  has been represented as an exponentially decaying function of the particle–particle separation (Israelachvili 1991):

$$W_{\rm hyd} = W_0 \, \exp(-D/2\Delta_{\rm hyd}) \tag{7-10}$$



Figure 7.1 Schematic diagram of interaction potential versus separation distance D for van der Waals and electrostatic "double-layer" interactions. The lower inset shows the collapse of the repulsive barrier as the electrolyte concentration is increased or the surface potential is decreased. At a separation distance of zero, there is an infinitely steep hard-core repulsive (or positive) interaction. (From Israelachvili 1991, reprinted with permission from Academic Press.)

where  $W_0$  is typically around 3–30 mJm<sup>-2</sup> and the range of the interaction is small, so that  $\Delta_{hyd} \approx 1$  nm. Because of its short range, the "hydration" interaction is sometimes incorporated into the total potential W simply by slightly enlarging the effective hard-core radius of the particles used to compute  $W_{steric}$  from Eq. (7-1), while using just the "bare" radius a in the formula for the van der Waals interaction. In this way, the infinite van der Waals well is cut off, and it is replaced by a well of finite depth.

Once flocculation has occurred, the properties of the flocculated dispersion depend strongly on the details of the interaction at separations near the primary minimum, including the depth of this primary minimum. This depth is often estimated simply by evaluating the potential W at the separation  $D_0$  given by twice the thickness  $\Delta_{hyd}$  of the assumed hydration or Stern layer. Since  $\Delta_{hyd}$  is very small, on the order of a nanometer or so, the electrostatic interaction is sensitive to the choice of a constant potential or a constant surfacecharge boundary condition (see Fig. 2-14). The electrostatic potential  $W_e$  obtained using the constant potential boundary condition, Eq. (7-4a), is bounded at small separation distances, while  $W_e$  from the constant charge boundary condition, Eq. (7-4b), is singular as  $D \rightarrow 0$ , although it is less singular than the van der Waals potential. Experimental data from the surface-forces apparatus (Israelachvili 1991) indicate that the electrostatic contribution lies between the two limits, but is closer to that for a constant surface charge. Rheological measurements also seem to support the constant-surface-charge condition (Friend and Hunter 1971). Thus, considering only van der Waals interactions and electrostatic interactions with a constant surface charge, one obtains for the depth of the primary minimum

$$W_{\min} \approx -\frac{aA_H}{12D_0} + C\zeta^2 a \tag{7-11a}$$

where

$$C \equiv 2\pi \varepsilon_0 \varepsilon \ln\left[\frac{1}{1 - \exp(-\kappa D_0)}\right]$$
(7-11b)

and we have replaced the surface potential  $\psi_s$  with the more easily measurable zeta potential  $\zeta$ .

If  $D_0$  is small, the van der Waals interaction usually dominates the electrostatic one, and the primary attractive minimum is then very deep, so that  $-W_{\min}/k_BT \gg 1$ . Particles that fall into this minimum will therefore "stick" to other particles, and at thermodynamic equilibrium all particles will be clumped together into a single mass. Note, however, that the depth of the well can be reduced by increasing the magnitude of the zeta potential  $\zeta$ .

#### 7.2.2 Electrostatic Stabilization

The stabilization produced by electrostatic forces is often a *kinetic* effect. As one increases the surface potential  $\psi_s$ , or the Debye length  $\kappa^{-1}$ , the local maximum in W becomes increasingly positive (see inset in Fig. 7-1). When  $W_{\text{max}}$  exceeds many  $k_BT$ , particles that are initially separated from each other rarely acquire enough kinetic energy to surmount the high repulsive potential barrier  $W_{\text{max}}$  and fall into the deep van der Waals primary minimum. [When  $D_0$  and  $\zeta$  are unusually large, the van der Waals minimum disappears altogether (Frens and Overbeek 1972; Israelachvili 1991).] The probability that a particleparticle collision will be energetic enough to overcome the barrier is proportional to  $\exp[-W_{\text{max}}/k_BT]$ . Since the time scale for a particle to diffuse a distance a equal to its own radius is  $\sim a^2/D_0$ , where  $D_0$  is here the diffusivity of the particle, the time  $t_D$  required for particles to diffuse into their attractive minima scales as (Russel et al. 1989)

$$t_D \approx \frac{a^2}{D_0} \exp\left(\frac{W_{\text{max}}}{k_B T}\right) = \frac{6\pi \eta_s a^3}{k_B T} \exp\left(\frac{W_{\text{max}}}{k_B T}\right)$$
(7-12)

where we have used the Stokes-Einstein value for the diffusivity,  $D_0 = k_B T / 6\pi \eta_s a$ , and  $\eta_s$  is the viscosity of the solvent medium. Because of the exponential dependence of  $t_D$  on

 $W_{\text{max}}$ , even small 100-nm-diameter particles in a low-viscosity solvent take months or even years to aggregate if the potential barrier  $W_{\text{max}}/k_BT$  exceeds 25 or so.

Thus, although thermodynamic stability is not attained, surface charges can generate *kinetic stability* of essentially indefinite duration, provided that the sol is stored in conditions that keep  $W_{\text{max}}/k_BT$  high, and provided that the sol is not subjected to strong flows that might impart to the particles enough kinetic energy to induce flocculation (Russel et al. 1989).

#### 7.2.3 Flocculation and Gelation

If desired, flocculation of the stabilized sol can be deliberately induced. This can be done, for example, by adding electrolyte to the suspension or by changing the surface charge by altering the pH. A condition for rapid flocculation can be derived (Russel et al. 1989) by finding the electrolyte concentration at which the potential barrier is eliminated, so that  $W_{\text{max}} = 0$ . Using Eq. (7-3) for the van der Waals interactions, using Eq. (2-57) for the electrostatic interactions, and applying the condition W' = 0 at W = 0 gives for a symmetric electrolyte the critical bulk electrolyte concentration (number of cations per unit volume)  $n_{\text{crit}}$ :

$$n_{\rm crit} = \frac{49.6}{z^6 \ell_b^3} \left[ \frac{k_B T}{A_H} \right]^2 \tanh^4 \left( \frac{e z \psi_s}{4k_B T} \right)$$
(7-13)

where

$$\ell_b \equiv \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \tag{7-14}$$

is the *Bjerrum length*. At room temperature,  $\ell_b \approx 58/\varepsilon$  nm.

Note from Eq. (7-13) that when  $e_{z}\psi_{s}/4k_{B}T > 1$ , there is a strong dependence of the critical electrolyte concentration on charge valency, namely  $n_{crit} \propto z^{-6}$ . Thus, multivalent ions are predicted to be very effective at inducing flocculation; this is called the Schulze-Hardy rule (Russel 1989; Israelachvili 1991).

For a symmetric electrolyte and a weak surface potential, using Eq. (2-51) for the relationship between the surface potential  $\psi_s$  and the surface charge density  $\sigma$  (Coulombs per unit area) and using Eq. (2-48) for  $\kappa$  (with  $n_1 = n_2 = n_{\text{crit}}$ ), we obtain

$$n_{\rm crit} = \frac{0.36\ell_b^{-1} z^{-2} \sigma^{4/3}}{(\varepsilon \varepsilon_0 A_H)^{2/3}}$$
(7-15)

This result implies that for the typical values  $A_H \approx 10^{-20}$  J and  $\varepsilon \approx 50$ , a suspension of particles with a surface charge of 0.1 charges/nm<sup>2</sup> will be rapidly flocculated by a 0.1 M solution of univalent electrolyte (see Worked Example 7.4 at the end of this chapter).

As flocculation continues, particle pairs, or doublets, become triplets, and so on, so that flocs containing many particles appear. This growth process has been studied by light scattering in dilute or modestly concentrated suspensions, with particle volume fractions  $\phi$  less than 0.10. These studies (Dimon et al 1986; Schaefer et al. 1984; Aubert and Cannell 1986) show that the radius  $a_k$  of a floc containing k particles scales as a power law with k; that is,

$$\frac{a_k}{a} \approx k^{1/D_f}, \qquad k \approx \left(\frac{a_k}{a}\right)^{D_f}$$
 (7-16)

If the flocs had consisted of densely packed particles, then the exponent  $D_f$  would equal 3, the dimensionality of space. Instead, experiments with aggregated neutral gold particles show  $D_f \approx 1.7-1.8$ ; and for slightly charged silica particles,  $D_f \approx 2.0-2.2$ . A power-law scaling with  $D_f < 3$  implies that the flocs are open, ramified structures, or *fractals* (see Fig. 7-2). In general, a fractal is a self-similar object which looks the same at different magnifications. The smaller the dimension  $D_f$ , the more open and porous the fractal floc. Theoretical models show that  $D_f = 1.75$  is consistent with a "fast flocculation" process called "diffusion-limited aggregation" (Jullien et al. 1984; Russel 1989), in which flocs grow predominantly by fusing with other flocs as soon as they come into contact with them.



**Figure 7.2** Transmission electron micrographs of flocculated gold sols with particle radii  $a = 7.2 \pm 0.8$  nm. (From Weitz and Huang 1984, with permission.)

If flocs can interpenetrate to some extent after contacting, the floc becomes denser and  $D_f$  increases to  $D_f \approx 2.0-2.2$ , which corresponds to "slow flocculation," or "reaction-limited aggregation."

As a floc grows, its porosity increases. The volume fraction of solid in a floc containing k particles decreases with increasing k as

$$\phi_k \sim \left(\frac{a_k}{a}\right)^{D_f - 3} \approx k^{(D_f - 3)/D_f} \tag{7-17}$$

Hence, as the flocs grow larger, the volume fraction of solution they encompass increases. Once the volume fraction permeated by the flocs fills the entire solution, the flocs connect together to form a percolating (sample-spanning) network (Feng and Sen 1984). This is *gelation*, and it occurs when the floc size k reaches a value  $k^*$  such that  $\phi_{k^*}$ , the volume fraction of particles in the floc, equals  $\phi$ , the volume fraction of particles in solution. This condition gives

$$k^* \sim \phi^{-D_f/(3-D_f)} \tag{7-18}$$

From this equation, we find that there will be isolated flocs containing 100 or more particles only when  $\phi$  is small,  $\phi < 0.1$ . Since the particles are usually denser than the suspending medium, isolated large flocs, formed when  $\phi$  is small, can sediment under gravity. For larger  $\phi$ , however, gelation usually occurs, and sedimentation is then avoided, unless the gel structure is so fragile that it collapses under its own weight.

### 7.2.4 Thermoreversible Gelation

Chemically induced gelation, produced for example by addition of an electrolyte as described above, often produces a hard gel that cannot easily be restored to a fluid state. To study the gelation process in more detail and to probe the rheology of gels as a function of the strength of interparticle bonds, it is desirable to study *thermoreversible* gelation, in which the gel transition can be traversed in either direction as many times as desired with a single sample, merely by lowering and raising the temperature.

Since particles within a few angstroms of contact bind together strongly by van der Waals forces, weak gels only form if the particle surfaces are somehow prevented from coming into near contact. One successful method for accomplishing this is to adsorb or graft polymeric or oligomeric chains onto the particle surfaces (Russel et al. 1989). The required thickness of the adsorbed layer can be estimated from the van der Waals interaction potential  $W_{vdw} \approx -aA_H/12D$ . This potential will readily be overcome by Brownian motion if  $-W_{vdw} < k_BT$ . Thus, the spacing D between particles must be kept larger than  $D_{crit} \approx aA_H/12k_BT$ . This can be accomplished by adsorbing or grafting a layer of thickness  $\Delta_{graft} = \frac{1}{2}D_{crit} = aA_H/24k_BT$  onto each particle's surface. Since a typical value of  $A_H/k_BT$  is 2.5, we predict that we shall need a layer whose thickness is about a/10, about 10% of the particle's radius. For lower values of  $A_H/k_BT$ , layers even thinner than this will suffice.

If these particles are suspended in a solvent that is marginal for the grafted chains, then at high temperature, above the "theta" point for the chains in the solvent (see Section 2.3.1.2), the chains repel each other, and the particles remain dispersed. If, however, the temperature

T is reduced below the theta temperature  $\theta$ , attractive particle-particle interactions occur, eventually producing flocculation at low enough T. Thus, in such a dispersion, the strength of the particle-particle interactions can be controlled by adjusting the temperature, and a dispersion that has been flocculated at a low temperature can be redispersed merely by increasing T.

One system with these desirable features is a suspension of small ( $a \approx 50$  nm) silica particles onto which octadecyl chains have been densely grafted (Stöber et al. 1968; van Helden et al. 1981; Woutersen and de Kruif 1991). The octadecyl chains have a theta point near room temperature in various solvents, including benzene, dodecane, and hexadecane.

The properties of the above system at modest particle concentrations are relatively simple to model, because the grafted octadecyl layer is thin compared to the particle radius and because the particle-particle interactions are weak enough that the properties of the dispersion are not sensitive to the detailed shape of the particle-particle interaction potential. These considerations have motivated the use of a simple "square-well potential" as a model of the particle-particle interactions (Woutersen and de Kruif 1991) (see Fig. 7-3). This potential consists of an infinite repulsion at particle-particle contact (where D = 0), bounded by an attractive well of width  $\Delta$  and depth  $\varepsilon$ . There are no interactions at particleparticle gaps greater than  $\Delta$ . Near the theta point, the well depth  $\varepsilon$  depends on temperature as follows (Flory and Krigbaum 1950):

$$\varepsilon = \alpha \left(\frac{\theta}{T} - 1\right) k_B T \quad \text{for } T < \theta$$
 (7-19)

where  $\alpha$  is a constant.

The strength of the particle-particle interactions produced by this potential depend on both the depth  $\varepsilon$  and width  $\Delta$  of the potential. However, for narrow wells,  $\Delta/a \ll$ 1, the particle-particle interactions are controlled only by the combination parameter (Baxter 1968)



**Figure 7.3** The square well potential where r = 2a + D is the separation of the particles' centers of mass. (From Woutersen and de Kruif, reprinted with permission from J. Chem. Phys. 94:5739, Copyright © 1991, American Institute of Physics.)

$$\tau_B = \frac{2a + \Delta}{12\Delta} \exp\left(\frac{-\varepsilon}{k_B T}\right) \tag{7-20}$$

In the limit  $\Delta/a \rightarrow 0$  at fixed  $\tau_B$ , the structure and rheology of the suspension depend only on  $\tau_B$  and not on  $\Delta$  and  $\varepsilon$  separately. This limit is Baxter's "adhesive hard-sphere," or "sticky hard-sphere," model (Baxter 1968). The parameter  $\tau_B$  of the model is a monotonically increasing function of temperature, and thus it can be thought of as a rescaled temperature. The predictions of the adhesive hard-sphere model are in reasonable agreement with lightscattering data for the weakly flocculated silica particles with grafted octadecyl chains at low and modest volume fractions of particles. However, at high particle volume fractions, neutron scattering shows substantial deviations between the measured structure factor and the theoretical one (Woutersen et al. 1993).

## 7.2.5 Gelation and Phase Separation

For the adhesive hard-sphere model, the theoretical phase diagram in the  $\tau_B - \phi$  plane has been partially calculated (Watts et al. 1971; Barboy 1974; Grant and Russel 1993). According to this model, there is a critical point  $\tau_{B,c} = 0.0976$  below which the suspension is predicted to *phase separate* into a phase dilute in particles and one concentrated in them (see Fig. 7-4). The particle concentration at the critical point of this phase transition is  $\phi_c = 0.1213$ . This phase transition is analogous to the gas-liquid transition of ordinary



**Figure 7.4** Phase diagram for adhesive hard spheres as a function of Baxter temperature  $\tau_B$ . The solid line is the spinodal line for liquid–liquid phase separation (the dense liquid phase is probably metastable), the dot–dashed line is the "freezing" line for appearance of an ordered packing of spheres, and the dashed line is the percolation transition. (Adapted from Grant and Russel 1993, reprinted with permission from the American Physical Society.)

small-molecule fluids. The phase dilute in colloidal particles is analogous to the "gas," and the concentrated phase corresponds to "liquid" phase of small molecules. (The phase separation of a concentrated from a dilute colloidal fluid phase is known as *coacervation*, if it is induced by addition of nonadsorbing polymer.)

At high particle concentrations, the adhesive hard-sphere model also predicts a transition from the dense disordered "liquid" phase to a macrocrystalline solid-like packing of spheres, analogous to a freezing transition of ordinary small molecules (see Fig. 7-4). (The freezing line in Fig. 7-4 terminates at a relatively high value of  $\tau_B$  because of computational difficulties in extending it to lower  $\tau_B$ .) The phase behavior of adhesive hard spheres is in some respects similar to that of ordinary small molecules because both systems are driven by a balance of van der Waals attraction, hard-core repulsion, and thermal agitation.

There are, however, important differences between the phase behavior of "sticky" spheres and that of small molecules, which arise from differences in the relative ranges of the attractive potentials. These differences have been explored in a wonderful set of calculations and experiments by Gast et al. (1983) and Pusey and coworkers (Ilett et al. 1995) for suspensions of spheres that are made to attract each other by the polymer-depletion mechanism. In such systems, the range of the attractive potential relative to the sphere size can be varied by controlling the ratio  $\xi \equiv \Delta_d/a$  of the polymer depletion-layer thickness to the sphere radius. For  $\xi \to 0$  the potential is short-ranged, like that of sticky hard spheres, while for  $\xi \approx 1$  the potential is long-ranged, like that of ordinary molecular liquids. Figure 7-5 shows the phase diagrams computed for the depletion potential, Eq. (7-6), with  $\xi = 0.08, 0.33$ , and 0.57. These predicted diagrams were confirmed by experiments on PMMA



**Figure 7.5** Theoretical phase diagrams for mixtures of polymers and colloids for size ratios  $\Delta_d/a = (\mathbf{a}) \ 0.08$ ,  $(\mathbf{b}) \ 0.33$ , and  $(\mathbf{c}) \ 0.57$  of depletion layer thickness (or polymer radius of gyration) to colloidal sphere radius. The ordinate  $\nu^{(R)}$  is the number of polymer molecules per unit volume of "free solution." In (**a**), the range of the attractive depletion interaction is short, and when the potential becomes strong at high  $\nu^{(R)}$ , the coexistence region of colloidal crystal and disordered fluid becomes broad. For a long-ranged potential in (**c**), a fluid-fluid coexistence region emerges with a dilute colloidal fluid, or "gas" coexisting with a concentrated colloidal fluid, or "liquid." CP denotes the fluid-fluid critical point, and TP is the triple point, which is a line on these diagrams. (From Ilett et al. 1995, reprinted with permission from the American Physical Society.)

spheres stabilized with a thin layer of grafted chains, in decaline, with added long-chain polystyrene. The ordinate in Fig. 7-5 is the polymer concentration in a hypothetical polymer phase in osmotic equilibrium with the colloidal phase, as discussed in Section 7.2.1; it is closely related to the chemical potential of the polymer. For the long-ranged potential in Fig. 7-5c, the phase diagram is analogous to that of ordinary molecular substance such as water, where  $\nu^{(R)}$  is analogous to an inverse temperature, since it controls the strength of the attractive interaction. Thus, if the ordinate of Fig. 7-5c is inverted, the phase diagram is similar to that of a molecular liquid, with its gas, liquid, and crystalline phases.

As the range of the potential is narrowed (Fig. 7-5a), the gas-liquid coexistence region disappears, and at modest  $v^{(R)}$  the coexisting macrocrystalline solid phase appears at much lower volume fractions of spheres. Comparing Fig. 7-5a with Fig. 7-4 (and inverting the ordinate of Fig. 7-5a, since increasing  $v^{(R)}$  corresponds to decreasing  $\tau_B$ ), we conclude that in the limit of a very short range interaction, that of adhesive spheres, the ordering line shown in Fig. 7-4, if calculations could be performed to extend it to lower values of  $\tau_B$ , would curve toward much lower volume fractions, and the fluid-fluid coexistence region in Fig. 7-4 is almost certainly a metastable one. The *equilibrium* phase diagram of sticky hard spheres is thus probably similar to Fig. 7-5a, with the ordinate inverted. Although the fluid-fluid coexistence region in Fig. 7-4 is probably not *thermodynamically* stable, it may play an important role in the *kinetics* of phase separation and gelation of these systems.

The phase diagram of the adhesive hard-sphere model suggests analogies between the *gelation* and *phase separation*. For example, when a dilute suspension is flocculated, large isolated flocs form, which settle under gravity to form a dense "phase" that is separated macroscopically from the remaining dilute suspension. An analogous process occurs in molecular fluids, such as dilute polymer solutions from which solid polymer is precipitated by addition of a nonsolvent. In the latter, the precipitated polymer particles are usually crystalline, while obvious crystalline order is usually absent from particulate flocs. Nevertheless, dense-phase crystalline order can also be produced in particulate flocs, if the particles are nearly monodisperse and if the repulsive barrier is reduced gradually, giving the attracting particles time to develop crystalline structure before they lose the ability to rearrange (Brinker and Scherer 1990). Even rather rigid gels formed by primary van der Waals attractions in dense suspensions manage to contract slowly in volume over a period of hours and days, by exuding solvent; this process is called *syneresis* (Brinker and Scherer 1990).

These examples suggest that at least in some cases of gelation there is a thermodynamic driving force for separation of a dense particulate phase from a more dilute one. But exactly what is the relationship between gelation and phase separation? Figures 7-4 and 7-5 suggest that for low and modest particle volume fractions not far from the critical concentration, an increase in the interparticle forces (by lowering  $\tau_B$  or raising  $\nu^{(R)}$ ) ought to produce macroscopic phase separation. This prediction is supported by experiments of Rouw et al. (1989), who temperature-quenched initially stable dispersions of 24-nm octadecyl-grafted silica particles ( $\phi = 0.13$ ) in benzene, and then monitored structural changes by light scattering. Several aspects of the observed structural changes were analogous to the process of *spinodal decomposition* in simple liquids, to be described in Section 9.2.1. In particular, soon after the quench, there was an early growth regime characterized by a rapidly growing scattering peak at a constant scattering angle. Later, the peak shifted to smaller angles, corresponding to coarsening of a well-developed pattern of inhomogeneities in particle concentration.

While these aspects of gelation are similar to those of classical spinodal decomposition, the power-law exponents governing the late-stage coarsening in the particulate system differ greatly from the classical values for spinodal decomposition. This is perhaps not surprising, since late-stage coarsening in spinodal decomposition of liquid–liquid mixtures involves interfacial-tension-driven compaction of continuum fluid labyrinths, while aggregated or flocced particles, on the other hand, lack continuum interfaces and may be too rigid to form compact structures. Thus, the fluid-like spinodal pattern of inhomogeneities that appears at short times after quenching a modestly concentrated particle dispersion evidently develops into a rigid fractal-like structure at later times.

When rigid fractal-like structures link up to span the medium, a gel is formed. Hence, the process of gelation has been compared to *percolation* (see Section 5.2.1). From the sticky hard-sphere model, the percolation line on the  $\tau_B - \phi$  phase diagram can be calculated (see Fig. 7-4). At the percolation transition, the theory gives for the Baxter parameter

$$\tau_{B,\text{perc}} = \frac{19\phi^2 - 2\phi + 1}{12(1-\phi)^2}$$

Below the percolation line, there is predicted to be a sample-spanning cluster of contacting spheres. Woutersen et al. (1994) found that the gel point for 47-nm octadecyl-grafted silica spheres in benzene is in reasonable agreement with the predicted percolation transition. However, Grant and Russel (1993) found that the gelation line is below the percolation line for a similar suspension in hexadecane. According to Fig. 7-4, when a dispersion with particle concentrations well above the critical point  $\phi_c \approx 0.12$  is cooled, the percolation transition is encountered well before the liquid–gas phase boundary. Hence, if gelation does correspond to the percolation line, Fig. 7-4 implies that gelation can occur without phase separation or syneresis, if  $\tau_B$  is not too small—that is, if the gel is not too strongly flocculated. We should note, however, that since the possibility that gelation of adhesive spheres corresponds not to percolation, but to an arrested fluid–solid transition. The relationship between gelation and phase separation is no mere academic issue; phase separations produce inhomogeneities in density and structure that are deleterious to a gel body's strength, rigidity, and resistance to cracking (Brinker and Scherer 1990).

# 7.3 RHEOLOGY OF PARTICULATE GELS

Rheological measurements on concentrated, strongly flocculated gels are hampered by the following difficulties (Buscall et al. 1986, 1993; Rueb and Zukoski 1997):

- 1. Poor reproducibility
- 2. Sensitivity to gel preparation
- 3. Sensitivity to shear history
- 4. Extremely limited range of linear viscoelastic response
- 5. Slip

The first three or four of these experimental difficulties arise because of the nonequilibrium structure of strongly flocculated gels. Particles bound strongly together in their primary van der Waals potential minima are unable to rearrange within laboratory time scales; hence the structures cannot relax to achieve thermodynamic equilibrium. Therefore, the gel structure depends on preparation history, including any deformation experienced by the gel prior to the rheological measurement.

These problems can be avoided in weakly flocculated gels, which attain thermodynamic equilibrium on experimental time scales. Since an understanding of weakly flocculated gels can form the basis for study of strongly flocculated gels, we shall consider the former first.

#### 7.3.1 The Rheology of Weakly Flocculated Gels

Figure 7-6 shows the viscosity of thermoreversible dispersions (discussed in Section 7.2.4) of  $a \approx 50$ -nm silica particles onto which octadecyl chains have been densely grafted in benzene at particle volume fractions  $\phi = 0.088-0.133$ , as a function of temperature T (Woutersen and de Kruif 1991). For  $T \ge \theta = 316$  K, the viscosity relative to that of the solvent,  $\eta_r \equiv \eta/\eta_s$ , is independent of temperature, and its dependence on volume fraction  $\phi$  is exactly as expected for hard spherical particles without attractive interactions. As T is lowered below  $\theta$ , however, the viscosity rises rapidly, because of the onset of attractive interactions.

The effect of these attractive interactions is even more dramatic at higher particle concentrations. Figure 7-7 shows the relative viscosity at  $\phi = 0.47$ , as well as the longest relaxation time for  $\phi = 0.40$  and 0.47, at low shear rates. Note that there is a large increase in  $\eta_r$  as the temperature is lowered. Figure 7-8 shows the shear-rate dependence of  $\eta_r$  for  $\phi = 0.367$  at several temperatures. The bland, Newtonian behavior at high T gives way to strong shear thinning when  $T \leq \theta - 13$  K = 303 K. The complex viscosity  $\eta^*$  scales roughly as  $\omega^{-1/2}$  at high frequency  $\omega$  (Woutersen et al. 1994).

The expression for the zero-shear viscosity for the adhesive hard-sphere model at modest particle volume fraction is (Woutersen and de Kruif 1991)

$$\eta_{r,0} = 1 + 2.5\phi + \left(6.2 + \frac{2.1}{\tau_B}\right)\phi^2 \tag{7-21}$$



**Figure 7.6** Relative viscosity as a function of temperature *T* for dispersions in benzene of octadecyl-grafted silica spheres with radii a = 47 nm at volume fractions  $\phi$  of 0.133 ([]), 0.106 (()), and 0.088 ( $\Delta$ ). The lines are the predictions of Eq. (7-21), with square well parameters of  $\Delta = 0.3$  nm,  $\alpha = 117$  and  $\theta = 316$  K. (From Woutersen and de Kruif, reprinted with permission from J. Chem. Phys. 94:5739, Copyright © 1991, American Institute of Physics.)



**Figure 7.7** (a) Relative viscosity as a function of temperature *T* for a dispersion described in Fig. 7-6 at a volume fraction  $\phi$  of 0.47, extrapolated to low shear rates ( $\bigcirc$ ,  $\triangle$ ), and at low shear frequencies ( $\square$ ), from steady shearing and oscillatory shearing, respectively. (b) Longest relaxation time  $\tau_1$  as a function of temperature for  $\phi = 0.40$  ( $\square$ ) and 0.47( $\bigcirc$ ). (From Woutersen et al., reprinted with permission from J. Chem. Phys. 101:542, Copyright © 1994, American Institute of Physics.)



**Figure 7.8** Shear-rate dependence of the relative viscosity for a dispersion similar to that described in Fig. 7-6 at a volume fraction  $\phi$  of 0.367 and at temperatures (from bottom to top) of 317.28 K, 308.13 K, 306.20 K, 304.17 K, 303.16 K, and 302.16 K. (From Woutersen and de Kruif, reprinted with permission from J. Chem. Phys. 94:5739, Copyright © 1991, American Institute of Physics.)

The lines in Fig. 7-6 show that this expression fits the temperature-dependence of the viscosity for  $\phi \leq 0.15$ . Combining this with Eq. (7-20), we find that the attractive interactions between particles contribute a term proportional to  $\phi^2 \exp(\varepsilon/k_B T)$  to the relative viscosity. Thus, the viscosity increases exponentially with the depth of the potential well.

A similar, and even more dramatic, viscosity enhancement was observed by Buscall et al. (1993) for dispersions of 157-nm acrylate particles in "white spirit" (a mixture of high-boiling hydrocarbons). These particles were stabilized by an adsorbed polymer layer, and then they were depletion-flocculated by addition of a nonadsorbing polyisobutylene polymer. Figure 7-9 shows curves of the relative viscosity versus shear stress for several concentrations of polymer at a particle volume fraction of  $\phi = 0.40$ . Note that a polymer concentration of 0.1% by weight is too low to produce flocculation, and the viscosity is only modestly elevated from that of the solvent. For weight percentages of 0.4–1.0%, however, there is a 3–6 decade increase in the zero-shear viscosity!

Figure 7-10 shows the zero-shear viscosity  $\eta_{r,0}$  plotted semilogarithmically against polymer concentration. The lines through the data are fits to an exponential dependence of  $\eta_{r,0}$  on the depth of the potential well  $-W_{\min}$ , that is,

$$\eta_{r,0} \propto \exp\left(\frac{-\alpha W_{\min}}{k_B T}\right)$$
(7-22)

(Keep in mind that  $W_{\min}$  is negative.) The potential well depth was calculated using Eq. (7-8) for depletion flocculation. At the highest polymer concentrations, the dimensionless well depth reaches  $-W_{\min}/k_BT \approx 18$ . (At polymer concentrations high enough that polymer coils begin to overlap, which is the beginning of the semidilute regime, the depletion layer thickness begins to decrease with increasing polymer concentration, which



Figure 7.9 Shear-stress dependence of the relative viscosity for dispersions in "white spirit" of acrylic copolymer particles of radius a = 157 nm at a volume fraction of  $\phi = 0.40$ for differing concentrations of nonadsorbing polyisobutylene polymer of molecular weight 411,000. The particles had been stabilized by addition of a comb-graft copolymer of PMMA backbone (which adsorbed to the particles) with non-adsorbing poly(12hydroxystearic acid) teeth. The concentrations (in weight per unit volume) of polyisobutylene are 1.0%  $(\mathbf{V}), \ 0.85\%(\mathbf{I}), \ 0.6\%(\mathbf{I}), \ 0.5\%(\mathbf{V}),$ 0.4%(), and 0.1%(). (From Buscall et al. 1993, with permission from the Journal of Rheology.)



**Figure 7.10** The effect of polyisobutylene (PIB) concentration on the zero-shear viscosity of the suspensions described in Fig. 7-9. The lines were calculated assuming  $\eta_{r,0}(0) = K \exp(-\alpha W_{\min}/k_BT)$ , with values of the second virial coefficient  $A_2$  of  $6 \times 10^{-5}$ ,  $8 \times 10^{-5}$ , and  $10^{-4}$ . (From Buscall et al. 1993, with permission from the Journal of Rheology.)

is apparently responsible for the turnover of  $\eta_{r,0}$  at the highest polymer concentration in Fig. 7-10.)

The increased zero-shear viscosity of more strongly flocculated gels is a consequence of an increase in the *relaxation time*  $\tau$  required for particles to rearrange their positions (see Fig. 7-7). The relaxation time  $\tau$  is estimated to be

$$\tau \approx \frac{a^2}{D_0} \exp\left(\frac{-\alpha W_{\min}}{k_B T}\right) = \frac{6\pi \eta_s a^3}{k_B T} \exp\left(\frac{-\alpha W_{\min}}{k_B T}\right)$$
(7-23)

where  $D_0$  is the particle free diffusivity. Hence, as noted earlier, the larger  $-W_{\min}/k_BT$  is and the more strongly a gel is flocculated, the longer it takes to reach thermodynamic equilibrium. In a strongly flocculated alkoxide silica gel formed by polymerization of tetrethyl orthosilicate (TEOS), a slow creep test showed the relaxation time to be a day or longer (Scherer et al 1988) and showed the low-shear-rate viscosity to be as high as  $10^{12}$  Pa!

Note in Fig. 7-9 that as the gel becomes more strongly flocculated, not only does the low-shear-rate plateau viscosity becomes larger, but the drop in viscosity in the shear thinning region becomes steeper (Fedotova et al. 1967). The onset of shear thinning occurs at a critical shear stress of about 3 Pa. An even more sudden decrease in viscosity at a stress of about 10 Pa is shown in Fig. 7-11 for 2.5% flocculated silica particles in methyl laurate. When the plateau viscosity becomes very high, it is only accessed at very low shear rates,  $\dot{\gamma} \sim 10^{-5}$ - $10^{-3}$  sec<sup>-1</sup>. Since experiments at shear rates less than  $10^{-3}$  sec<sup>-1</sup> require hours or days to carry out, plateaus that exist only at shear rates less than  $\sim 10^{-3}$  sec<sup>-1</sup> will usually not be observed in rheological experiments, unless great patience is exercised. Instead, at the lowest experimental shear rates, a steep decrease in viscosity with increasing shear stress will be seen. Figure 7-12 is an example of such viscosity curves (Patel and Russel 1987), obtained for depletion-flocculated dispersions of surfactant-stabilized polystyrene particles ( $\phi = 0.20, 0.30$ ; a = 115 nm). Behavior of this sort—a sudden decrease in viscosity above



Figure 7.11 Viscosity versus shear stress for flocculated 2.5% silica particles in methyl laurate. The open triangles are from a stress-controlled instrument, while the other symbols are from a shear-rate-controlled one. (Reprinted from Coll. Surf., 69:15, Van der Aerschot and Mewis (1992), with kind permission from Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

Figure 7.12 Shear-stress dependence of the relative viscosity for dispersions in water of charged polystyrene particles of radius a = 115nm with nonadsorbing Dextran T-500 polymer (synthesized from glucose) added as a depletion flocculant. The polymer molecular weight is 298,000, and its radius of gyration  $R_{e}$  is 15.8 nm. Volume fractions and polymer concentrations are:  $\phi = 0.3$ ,  $C_p =$ 2.5 wt% ( $\blacksquare$ ),  $\phi = 0.2, C_p = 2.5$  wt% (**•**), and  $\phi = 0.2$ ,  $C_p = 0.5$  wt%  $(\bigcirc)$ . (From Patel and Russel 1987, with permission from the Journal of Rheology.)

a critical shear stress—is often referred to as *yield*, and the critical stress is called the *yield* stress  $\sigma_y$ .

There has been debate in the literature regarding the propriety of referring to a critical stress as a yield stress when there is a possibility of a Newtonian flow region at suitably low shear stress (Barnes and Walters 1985). However, from a practical point of view, the sudden onset of a measurable rate of shear above a critical shear stress, and no measurable rate of shear below it, is a useful experimental criterion for defining the yield phenomenon. Still, the possible presence of Newtonian creep at very low rates of strain should not be forgotten, since this such behavior can affect the drying and sagging behavior of gel bodies.

## 7.3.2 The Rheology of Strongly Flocculated Gels

Let us now consider strongly flocculated dispersions at particle concentrations high enough to produce rigid gel networks. The term "strong flucculation" is ambiguous, but for practical purposes we take it to refer to gels in which the attractive potential minimum is large,  $-U_{\min}/k_BT \ge 20$ . In such cases, once particle-particle contacts are formed, they are released by thermal agitation so infrequently that particle rearrangements are strongly suppressed. Thus, the time for equilibration of the structure, given by a relaxation time  $\tau$ , is too long to occur within the experimental time frame, which is usually no more than several hours. The "Newtonian" zero-shear viscosity is only attained at shear rates  $\dot{\gamma} \lesssim \tau^{-1}$ , and these rates are too low to be accessed. Thus, strongly flocculated gels are characterized by a yield stress, rather than a zero-shear viscosity. Other rheological quantities that are important for strongly flocculated gels include compactive strength, linear (and nonlinear) elastic moduli at high and low frequencies, and the shear-rate-dependent viscosity. The dependencies of these on particle size, particle concentration, and particleparticle interactions are of obvious importance for the processing of colloidal gels. One would like to develop theoretical understanding of such dependencies, or even quantitative models, if possible.

Rheological measurements are difficult on strongly gelled colloids, and data often do no reproduce well. Multiple runs often must be averaged together to reduce data scatter. Strongly flocculated suspensions are by definition not at equilibrium, and so their properties are sensitive to preparation technique and deformation history. In addition, in large-deformation or continuous shearing, slipping of the gel against the surfaces of the rheometer tools is always a danger, although using roughened tools (Buscall et al. 1993) or vane-type rheometer fixtures (Dzuy and Boger 1985; Leong et al. 1993) seems to be an effective countermeasure.

Despite these difficulties, several experimental studies have established trends that seem to be generic for the rheological properties of these materials. In particular, Buscall et al. (1986, 1987, 1988) have reported extensively on suspensions of well-characterized silica and polystyrene spheres coagulated by addition of electrolyte. Figure 7-13 shows measured values of the compactive strength  $P_y$  and yield stress  $\sigma_y$  as functions of particle volume fraction  $\phi$  for a = 245-nm polystyrene particles coagulated at 0.1 M BaCl<sub>2</sub>. Analogous results were obtained with a = 13-nm silica particles. The compactive strength  $P_y$  is a compressive yield stress above which compression of the gel occurs in a centrifuge. A similar volume-fraction dependence was found for the high-frequency modulus  $G_{\infty}$ , obtained by measuring the velocity of propagation of a shear wave; the characteristic frequency of this wave is high (around  $\sim 10^3 \sec^{-1}$ ), and its amplitude is small (around  $3 \times 10^{-4}$ ). Just above  $\phi_g \approx 0.05$ , the minimum particle concentration for gelation, one expects the gel modulus to depend on  $\phi$  as  $G_{\infty} \propto (\phi - \phi_g)^n$  (de Gennes 1976; Feng and Sen 1984; Stauffer 1985). However, over most of the range of  $\phi$ , both  $G_{\infty}$  and  $P_y$  increase with  $\phi$  roughly as (Buscall et al. 1987; Rueb and Zukoski 1997)

$$P_y \propto G_\infty \propto \phi^\mu$$
 (7-24)

The power-law exponent  $\mu$  is around 4.0–5.0. A similar result is obtained for the yield stress in shear  $\sigma_y$ , except the exponent is smaller,  $\sigma_y \propto \phi^{3.0}$ , and  $\sigma_y$  is a couple of decades smaller in magnitude than  $P_y$ . Chen and Russel (1991) found a similar power law for flocculated octadecyl-coated silica particles. Such power laws have been derived from theories that model the gel as a network of interconnected fractal clusters (Buscall et al. 1988; Shih et al. 1990; Potanin et al. 1995).

The influence of particle size on the yield stresses  $P_y$  and  $\sigma_y$  have also been measured; Buscall et al. (1988) found the power-law dependencies



**Figure 7.13** Compressional,  $P_y$ , and shear,  $\sigma_y$ , yield stresses versus particle volume fraction  $\phi$  for dispersions in water of charged polystyrene particles of radius a = 245 nm coagulated by addition of BaCl<sub>2</sub>. (From Buscall et al. 1987). (reprinted from J Non-Newt Fluid Mech 24:183, Buscall et al. (1987), with kind permission from Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

$$P_y \sim a^{-2.3}, \qquad \sigma_y \sim a^{-2}$$
 (7-25)

Data for  $\sigma_y$  versus *a*, corroborating the above scaling, are reported in Fig. 7-14.

The low-frequency modulus  $G_0$  for flocculated polystyrene particles, measured by creep tests at small stresses and strains as low as  $10^{-4}$ , was found to be nearly identical to the high-frequency modulus  $G_{\infty}$  (Buscall et al. 1987). Thus, these strongly flocculated systems are highly elastic at small strains, with little relaxation over a wide range of frequencies. Figure 7-15 confirms this interpretation, showing for a strongly flocculated dispersion of silica particles that there is little frequency dependence of the elastic storage modulus G' over a wide range of frequencies, and that the loss modulus G'' is much smaller than G'.

The modulus of strongly flocculated gels tends to be highly strain-dependent, with linear behavior confined to very low strain amplitudes (Buscall et al. 1988). Figure 7-16 shows the low-frequency modulus in creep versus normalized strain amplitude for strongly flocculated polystyrene particles with volume fractions  $\phi$  between 0.1 and 0.25. In



**Figure 7.14** Shear yield stress  $\sigma_y$  versus particle volume fraction  $\phi$  for charged polystyrene particles aggregated in water by addition of BaCl<sub>2</sub>.  $\sigma_y$  is normalized by the square of the particle radius to account for the scaling  $\sigma_y \propto a^{-2}$ . Data for particles of radii 245 nm, 480 nm, and 1700 nm are included, with  $a_{ref} = 245$  nm. The line has a slope of 3.0. (From Buscall et al. 1988, reproduced by permission of The Royal Society of Chemistry.)



**Figure 7.15** Storage and loss moduli G' and G'' as functions of frequency in small-amplitude oscillatory straining at a strain amplitude of 0.5% for a silica particulate dispersion ( $\phi \approx 0.25$ ,  $a \approx 25$  nm) gelled by reduction of pH.



**Figure 7.16** Low-frequency shear modulus  $G(\gamma)$  divided by the smallamplitude modulus G(0), versus normalized strain  $\gamma/\gamma_{ref}$  for charged polystyrene particles of radii a = 245 nm and 1300 nm and volume fractions between 0.1 and 0.25 aggregated in water by addition of BaCl<sub>2</sub>.  $\gamma_{ref}$  ranges from 0.015 to 0.073. (From Buscall et al. 1988, reproduced by permission of The Royal Society of Chemistry.)

Fig. 7-16,  $\gamma$  is normalized by a reference strain  $\gamma_r$  to bring the data for different values of  $\phi$  into superposition;  $\gamma_r$  varies from 0.073 at  $\phi = 0.1$  to 0.015 at  $\phi = 0.25$ . Thus, according to Fig. 7-16, for the most concentrated gels, the modulus is strain-independent only when  $\gamma \leq \gamma_c = 0.0005$ , or 0.05%! Above this tiny strain, the modulus shows strain softening. The strain  $\gamma_y$  required for yield is, however, much higher than this, around 3% or so. Another surprise is that if a strain of 1% or so is imposed on the sample, and then the stress is suddenly removed, a large percentage, around 80%, of the imposed strain is recovered, even though the imposed strain is high enough for the modulus to be highly nonlinear.

Weakly flocculated gels are less strain sensitive than the strongly flocculated gels discussed above. Figure 7-17 shows the elastic modulus G versus strain  $\gamma$  for two gels made from weakly flocculated octadecyl-coated silica spheres (Chen and Russel 1991). For the more weakly flocculated of the two, obtained by lowering the temperature to 29°C, nonlinearity occurs above a critical strain  $\gamma_c$  of around 10%, while for a somewhat more



**Figure 7.17** Shear elastic modulus G' divided by the small-strain modulus G'(0) versus strain  $\gamma$  for dispersions in hexadecane of octadecylgrafted silica spheres with radius a = 56 nm and concentration  $\phi = 0.182$ . The temperatures are 29°C ( $\bigcirc$ ), and 20°C ( $\square$ ). (From Chen and Russel 1991, reprinted with permission from Academic Press.)

strongly flocculated gel at 20°C,  $\gamma_c$  is only 1%. As we saw, for the strongly flocculated gels of Buscall and coworkers,  $\gamma_c$  is around 0.05%. Thus, as the flocculation becomes stronger, the strain sensitivity increases. In addition, *strongly flocculated gels are likely to be more brittle than weakly flocculated ones*, in that although they are harder than weakly flocculated gels, they cannot be deformed as much without fracturing (Velamakanni et al. 1990). This finding is of considerable importance for the processing of gel bodies.

Thus, the mechanical properties of a gel depend not only on particle radius a and concentration  $\phi$ , but also on the flocculation strength. For gels in aqueous media, the mechanical properties therefore depend on the charge on the particle surfaces, as well as on the type of ions that might be bound to them. Figure 7-18a from Leong et al. (1993) shows the yield stress for suspensions of zirconia particles (a = 150 nm) with particle volume fractions ranging from 0.12 to 0.24, flocculated by addition of a strong acid (nitric acid, HNO<sub>3</sub>) or a strong base (potassium nitrate, KOH). These pH adjusters change the surface charge of the particles, presumably through surface binding of  $H^+$  or  $OH^-$ . The surface charge of the particles was probed by measurements of electroacoustic mobility of the particles in diluted suspensions (see Fig. 7-18b). The electroacoustic-mobility data were converted to an approximate surface potential, or zeta potential  $\zeta$  (see below). (Although the extrapolation of these electroacoustic data for diluted suspensions to a  $\zeta$  potential for concentrated suspensions is not entirely proper, the electroacoustic technique is a simple and useful means of obtaining a qualitative estimate of the surface potential, at least near the isoelectric point.) Note in Fig. 7-18 that the maximum yield stress occurs at the pH  $(\sim 7)$  for which the dynamic mobility, and hence the surface charge, is zero.

Figure 7-19 makes this point even more dramatically, showing that the yield stress  $\sigma_y$  decreases linearly with the square of the zeta potential, for both positive and negative  $\zeta$ . *Thus*  $\sigma_y$  *is maximum at*  $\zeta = 0$ ; that is, at pH = 7 for the zirconia particles. A similar finding was reported much earlier by Hunter and Nicol (1968) and by Friend and Hunter (1971). This linear dependence of  $\sigma_y$  on  $\zeta^2$  can be predicted directly from the linear dependence on  $\zeta^2$  of the primary minimum  $(-W_{min})$  of the interparticle potential [see Eq. (7-11a)].

The pH at which  $\zeta$  is zero can be adjusted by adding surface-binding anions, such as phosphate, citrate, or sulfate, to the suspension (Leong et al. 1993). Figure 7-20 shows



**Figure 7.18** (a) Shear yield stress  $\sigma_y$  versus pH for dispersions in water of "blocky"-shaped ZrO<sub>2</sub> particles with radius a = 150 nm and volume fractions  $\phi = 0.124$ , 0.145, 0.184, 0.213, and 0.242. These correspond to the mass percentages 45.4%, 50.0%, 57.0%, 61.4%, and 65.3%. The pH was adjusted using HNO<sub>3</sub> and KOH. (b) The dynamic mobility of particles in diluted suspensions as a function of pH. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)



**Figure 7.19** Shear yield stress versus square of the zeta potential  $\zeta^2$  for the dispersions described in Fig. 7-18 at particle volume fractions  $\phi = 0.184$  and 0.213, or mass percentages of 57.0% and 61.4%. The zeta potential was obtained at low  $\phi$  from the dynamic mobility. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)



**Figure 7.20** (a) Shear yield stress  $\sigma_y$  versus pH for dispersions described in Fig. 7-18 at a volume fraction  $\phi = 0.184$ , with varying amounts of added phosphate shown as a percentage on a dry weight basis. (b) The dynamic mobility of diluted ( $\phi = 0.025$ ) suspensions as a function of pH with varying amounts of added phosphate. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)

the yield stress versus pH and the dynamic mobility versus pH for a series of zirconia suspensions containing varying amounts of phosphate ion. As they are added to the suspension, phosphate anions bind to the particle surfaces, rendering it more negatively charged; to neutralize this charge, the pH must be lowered to supply H<sup>+</sup> ions. Thus, the pH at which  $\zeta = 0$  is less when phosphate is present in solution than when it is absent (see Fig. 7-20b). Note in Fig. 7-20a that the pH at which  $\sigma_y$  is maximum corresponds well with the pH at which  $\zeta = 0$  for various concentrations of phosphate (see Fig. 7-21). A similar result holds for other anions, although different ions differ in their ability to bind to the surface and shift the isoelectric point (i.e.p.) (see Fig. 7-22).

Thus, the yield stress  $\sigma_y$  is maximized at the isoelectric point. Note, however, in Fig. 7-20 that when the i.e.p. is shifted by the binding of ions to the particle surfaces, the maximum yield stress is reduced. As noted in Section 7.2.1, the binding of ions to the particle surfaces is likely to increase the thickness of the hydration layers on the particles that keep the particle surfaces from coming closer than a few nanometers from each other. Leong et al. (1993) have found a correlation between the size of the adsorbed anion and the magnitude of the decrease in the yield stress. However, the size of the hydrated ion, rather than the size of the ion itself, should, in principle, control the closest approach of the particles (Israelachvili 1991).



**Figure 7.21** pH at which the yield stress  $\sigma_y$  is maximum ( $\bullet$ ) and pH at the isoelectric point ( $\bigcirc$ ) measured electroacoustically, versus concentration of phosphate, for suspensions described in Fig. 7-20. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)

**Figure 7.22** pH at which the yield stress  $\sigma_y$  is maximum versus concentration of lactate ( $\bigcirc$ ), malate ( $\bigcirc$ ), and citrate ( $\triangle$ ) for suspensions described in Fig. 7-18, with  $\phi = 0.184$ . (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)

Analogous results have been reported by Velamakanni et al. (1990) for the shearthinning viscosity of alumina-particle suspensions ( $a \approx 100$  nm,  $\phi = 0.20$ ). Gels produced by raising the electrolyte (NH<sub>4</sub> Cl) concentration at a pH away from the i.e.p. have lower viscosities than those produced at the i.e.p. Velamakanni et al. refer to the former as "coagulated" gels and the latter as "flocculated" gels; they argue that "coagulated" gels are more easily sedimented or filter-pressed to high density than are "flocculated" gels. High-density gels are desirable because they are more easily dried and sintered.

#### 7.3.3 Theory

#### 7.3.3.1 Yield Stress and Elastic Modulus

We have seen that the rheological properties of weakly flocculated gels can be predicted at least qualitatively using reasonable particle–particle interaction potentials derived from van der Waals and polymer depletion forces. Can a similar approach succeed in predicting the mechanical properties of strongly flocculated gels?

Developing accurate theories for strongly flocculated gels is challenging, since the structures of such gels are not at thermodynamic equilibrium. At best, one might assume that such gels are in a state of *static equilibrium* in which the forces acting on each particle are in balance. Since the interaction potential between particles in a strongly flocculated gel has a minimum  $W_{\min} = W(D_0)$  that is deep compared to  $k_B T$ , gaps between neighboring particle surfaces in such gels will presumably almost always be close to  $D_0$ , unless the gel is subjected to a mechanical strain. Therefore, the shape of the potential W(D) near  $D_0$  is important in determining the gel's mechanical properties.

Sensitivity to the shape of W(D) differentiates weakly from strongly interacting particles. For the former, the precise shape of the potential is not important; we saw in Section 7.2.4 that even a simple square-well potential is an adequate approximation. But insensitivity to the shape of the potential can only be expected when the particles are only weakly bound by that potential, so that rapid, thermally driven changes in particle–particle separation average out the details of the shape of the potential. For strongly flocculated gels, the particle–particle separations remain trapped near the minimum in the potential well, and the shape of the well near this minimum matters much more.

Nevertheless, if one assumes a static, rather than a thermodynamic, equilibrium, one can attempt to estimate the dependence of the yield stress  $\sigma_y$  and the modulus G on the shape and depth of the interparticle potential. Imagine that a gel is subjected to a shear strain  $\gamma$  that *homogeneously* displaces particles from their positions of static equilibrium. Pairs of particles are pulled apart by this strain, and separations between particle centers of mass should increase roughly by an amount  $\gamma r_0$ , where  $r_0 \equiv 2a + D_0$  is the separation between centers of mass in the absence of strain. Hence, the imposition of a strain  $\gamma$  increases the gap between particle surfaces from  $D_0$  to

$$D \approx D_0 + \gamma (2a + D_0) \tag{7-26}$$

(Some particles will be tend to be pushed together by a homogeneous strain, but these can't move much closer together, because they encounter hard steric repulsions.) If  $\gamma$  is small, this increased separation of particles is small *relative to the initial separation of centers of mass*. But the increase is much larger *relative to the initial gap*  $D_0$ . Thus, the ratio of the gap between particles *after* the strain to that *before* the strain is  $(\gamma r_0 + D_0)/D_0 = [\gamma(2a + D_0) + D_0]/D_0 \approx 2\gamma a/D_0$ . Since the ratio  $2a/D_0$  is usually large  $(\geq 100)$ , even a strain of only 1% multiplies the gap between neighboring particles by a factor of two or more! From this, we can see why strongly flocculated gels, with particle–particle gaps as low as 1 nm, are so strain-sensitive (Buscall et al. 1987).

A force F = -W'(D) with  $D = \gamma (2a + D_0) + D_0$  is produced by this increased separation between the particles, where W' is the derivative of W with respect to D. This force would restore the original interparticle spacing if the shearing stress were removed.

The macroscopic stress  $\sigma$  is this force times the number of interparticle bonds that cross a unit area of the sample; this latter factor should scale as  $\phi^2/a^2$  (Russel et al. 1989). As long as the local applied force increases with increased strain,  $\sigma$  increases with increasing strain, and the gel maintains its mechanical stability. But once the strain reaches the point that the slope W' of the potential is a maximum (see Fig. 7-23), any further strain produces a decreasing force, and the interparticle structure breaks apart. This corresponds to the point of *yield*. Thus, the yield strain  $\gamma_y$  is given by the condition that the second derivative W'' of W(D) is zero; that is, W''(D<sub>y</sub>) = 0, where  $D_y = 2\gamma_y a + (\gamma_y + 1)D_0$  is the value of D for which W'' = 0. Very roughly, we might expect that W' is a maximum (W'' = 0) when separation  $D = D_y$  is on the order of twice  $D_0$ , the value of D at static equilibrium. This would imply that the yield strain  $\gamma_y$  is roughly  $D_0/2a$ ; hence, for particles 100 nm in radius,  $\gamma_y \approx 0.005$  (0.5%), or less, not too far from experimental observations.

The yield stress (i.e., the stress at the yield point) is proportional to  $F_{\text{max}} = W'_{\text{max}} = W'(D_y)$  times the number of interparticle bonds that cross a unit area of the sample,  $\phi^2/a^2$ ; thus

$$\sigma_{\rm y} \sim \frac{\phi^2}{a^2} W'(D_{\rm y}) \tag{7-27}$$

We can estimate W' at the yield point to be roughly  $-W_{\min}/D_0$ . Hence, from Eqs. (7-11a) and (7-11b) we obtain

$$\sigma_{y} \sim \frac{\phi^2}{a} \left( \frac{A_H}{12D_0^2} - \frac{C}{D_0} \zeta^2 \right) \tag{7-28}$$

where  $C \equiv 2\pi \varepsilon_0 \varepsilon \ln[(1 - \exp(-\kappa D_0))^{-1}]$ . For a specific example, let us take 0.01 M 1:1 electrolyte so that  $\kappa \approx 0.3 \text{ nm}^{-1}$ . For zirconia particles in water,  $A_H \approx 6 \times 10^{-20} \text{ J}$  (Leong et al. 1993). Taking  $D_0 \approx 2 \text{ nm}$ , and  $a \approx 100 \text{ nm}$ , we obtain from Eq. (7-28)

$$\sigma_{y}[Pa] \sim \phi^{2}(1.2 \times 10^{4} - 14\zeta^{2}[(mV)^{2}])$$
(7-29)



Figure 7.23 Schematic of pair potential W(D), showing location of maximum slope, which should control the yield stress and yield strain, and the curvature of the potential at its minimum, which in theory controls the low-strain modulus. (Adapted from Russel et al. 1989, with permission.) For a particle volume fraction of  $\phi = 0.2$ , this predicts a yield stress of 500 Pa at the i.e.p., and it also predicts that this yield stress is reduced to zero when  $\zeta$  is increased to about 30 mV. These results are within about a factor of two of the experimentally measured yield stresses (see Fig. 7-19 for example). However, the scaling of  $\sigma_y$  with particle size and concentration ( $\sigma_y \propto \phi^3 a^{-2}$ ) is stronger than predicted by Eq. (7-28), and so agreement is not as good at other volume fractions.

The linear modulus G can be estimated by an analogous argument (Russel et al. 1989). G is defined as the stress divided the strain  $\gamma$ , where  $\gamma$  is small enough that G is independent of  $\gamma$ . As we argued above, the stress  $\sigma$  is given roughly by  $(\phi^2/a^2)W'(D)$ , with D given by Eq. (7-26). If the quantity  $\sigma/\gamma$  is to be independent of strain, then  $\gamma$  must be small enough that W' can be linearized in D; that is,  $W'(D) \approx W''(D_0)(D - D_0) \approx W''(D_0)2a\gamma$ . Hence  $G \sim (\phi^2/a^2)W'/\gamma$  is

$$G \sim \frac{2\phi^2}{a} W''(D_0)$$
 (7-30)

Thus, the linear modulus is controlled by the *curvature* of the particle-particle potential W at its minimum. Of course, this local curvature is extremely sensitive to the details of the particle-particle interactions at close separations (Goodwin et al.1986), and thus the modulus will also depend strongly on these details. Nevertheless, if we estimate  $W''(D_0) \approx -W_{\min}(D_0)/D_0^2$ , then Eq. (7-30), combined with Eqs. (7-11a) and (7-11b), gives

$$G \sim \frac{2\phi^2}{D_0^2} \left( \frac{A_H}{12D_0} - C\zeta^2 \right)$$
(7-31)

Or, for the example considered above, we have

$$G \,[\text{kPa}] \sim \phi^2 (1.2 \times 10^3 - 1.4 \zeta^2 \,[(mV)^2])$$

For  $\phi = 0.2$  and  $\zeta = 0$ , this gives  $G \sim 50$  kPa. The above arguments imply that  $G/\sigma_y \approx 2a/D_0$ ; that is, the modulus is a couple of orders of magnitude larger than the yield stress. This is consistent with the data of Buscall et al. (1987). Note in Eq. (7-31) that the modulus is predicted to be *independent* of the particle size a, a prediction consistent with the data of Chen and Russel (1991) and Goodwin et al. (1986); see also Russel et al. (1989). However, again, the dependence on  $\phi$  in Eq. (7-30) is considerably weaker than that found experimentally (Buscall et al. 1988).

The steeper dependences of  $\sigma_y$  and G on  $\phi$  found in the experiments can be understood if one notes that Eqs. (7-28) and (7-30) assume that every interaction between neighboring particles contributes to the modulus or yield stress. However, as  $\phi$  decreases, because of the fractal character of the gel structure, an ever smaller fraction of these contacts is likely to support the stress applied to the gel, while the remaining are "dead-end," or "ineffective," contacts. The growing fraction of "ineffective" contacts as  $\phi$  decreases implies that G and  $\sigma_y$  should depend more strongly on  $\phi$  than  $\phi^2$ , and that Eqs. (7-28) and (7-30) will be most accurate at large  $\phi$ . And, indeed, the concentration dependences of the yield stress data of Buscall and coworkers do show a tendency to bend over toward a lower power law at large  $\phi$  (see Fig. 7-13).

#### 7.3.3.2 Shear Viscosity at High Shear Rates

At high shear rates, when the gel network is broken down, the dominant viscoelastic contribution comes from flocs that break apart and reform rapidly. For such dispersions, at modest particle volume fractions, a typical relationship between steady-state shear stress  $\sigma$  and shear rate  $\dot{\gamma}$  is shown in Fig. 7-24 (Friend and Hunter 1971). Note that at the highest shear rates, the  $\dot{\gamma}$ - $\sigma$  relationship appears to be linear, but the extrapolation of this linear relationship to zero shear rate intersects the stress axis at a positive value,  $\sigma_B$ , rather than zero. This intercept is called the "Bingham" yield stress, derived from the Bingham equation for shear stress (Friend and Hunter 1971):

$$\sigma = \eta_{\rm pl} \dot{\gamma} + \sigma_B \tag{7-32}$$

where  $\eta_{pl}$ , the "plastic viscosity," is the slope of the linear relationship between  $\sigma$  and  $\dot{\gamma}$ . As Fig. 7-24 shows, the Bingham yield stress  $\sigma_B$  differs from the "true" yield stress  $\sigma_y$ ;  $\sigma_y$  is measured at small shearing strains by finding the minimum stress required to induce flow.

Theories for the steady-shear viscosity are complex. They involve assumptions about the dependences on shear rate of floc size, shape, and floc-floc interactions. The simplest case one might consider is the limit of very high shear rates and not-too-high particle concentrations. In this limit,  $\sigma_B$  is assumed to arise from the work that must be done to break apart *particle pairs* (Friend and Hunter 1971). These particle pairs re-form again because of shear-induced collisions. At steady state, the rate at which particle pairs are produced by the collisions must equal the rate at which shearing pulls these pairs apart. This rate, per unit volume of suspension, can be estimated from simple kinetic theory as  $3\phi^2\dot{\gamma}/\pi^2a^3$ . Each time a particle pair is pulled apart, the energy expended is  $-W_{\min}$ , given by Eq. (7-11), which assumes that the particles must be separated from their primary attractive minima. Thus, the rate at which energy is dissipated by this process is  $(-W_{\min})3\phi^2\dot{\gamma}/\pi^2a^3$ . This dissipation rate is then set to  $\sigma_B\dot{\gamma}$ , so that (Friend and Hunter 1971)



Figure 7.24 Shear stress versus shear rate for dispersions in water of polymethylmethacrylate particles with radius a = 220 nm and volume fraction  $\phi = 0.070$  at ionic strength 0.02 g ions/liter of NaCl and zeta potentials of +14.6 (1), +21.6 (2), +29.3 (3), +35.9 (4), +55 (5), and supernatant (6). (From Friend and Hunter 1971, reprinted with permission from Academic Press.)

$$\sigma_B = \frac{3\phi^2}{\pi^2 a^3} \left( -W_{\min} \right) = \frac{3\phi^2}{\pi^2 a^3} \left[ \frac{aA_H}{24D_0} - C\zeta^2 a \right]$$
(7-33)

The second equality is obtained by using Eq. (7-11a) for  $W_{\min}$ . Equation (7-33) predicts that  $\sigma_B$  should scale with particle volume fraction as  $\sigma_B \propto \phi^2$ , and with zeta potential as  $\sigma_B \approx \sigma_{B,0} - k\zeta^2$ , where  $\sigma_{B,0}$  is the Bingham yield stress at zero zeta potential, and k is a constant. These scalings have been observed in several experiments (Firth 1976).

Despite these successes, this "particle-pair" model is untenable at the shear rates typical of most experiments, because, as pointed out by Firth and Hunter (1976a), the maximum hydrodynamic force available to pull two spheres apart is orders of magnitude too small to pull the spheres out of their deep potential well. This maximum hydrodynamic force is given by

$$F_H = 6.12\pi \eta_s a^2 \dot{\gamma} \sim 10^{-13} \,\mathrm{N} \tag{7-34}$$

for  $\dot{\gamma} = 10^3 \text{ sec}^{-1}$ , while the van der Waals force  $F_{\text{vdw}}$  holding the spheres together is obtained by differentiating Eq. (7-3) with respect to the separation D. At the i.e.p., we have

$$F_{\rm vdw} \approx \frac{aA_H}{12D^2} \sim 10^{-10} \,\mathrm{N}$$
 (7-35)

The above estimates of these forces are based on the following typical parameter values:  $D = 1 \text{ nm}, a = 100 \text{ nm}, \eta_s = 10^{-3} \text{ Pa} \cdot \text{s}, A_H = 10^{-20} \text{ J}, \text{ and } \dot{\gamma} = 10^3 \text{ sec}^{-1}$ . Of course, if D is taken to be much larger, say 20 nm or so, then the van der Waals force would be weak enough that the particles could be pulled apart by the hydrodynamic force. But if somehow D were as large as this, then Eq. (7-33) would predict a value for the Bingham yield stress that is orders of magnitude smaller than the measured values. Also, if the sheared suspension consists mainly of sphere singlets and doublets, the plastic viscosity  $\eta_{\text{pl}}$  would not be much larger than that for a suspension of noninteracting hard spheres; but in fact,  $\eta_{\text{pl}}$  is much larger than this. Furthermore, both direct visualization and scattering measurements show that even under flow, the flocs are bigger than doublets (Reich and Vold 1957; Firth 1976; Rueb and Zukoski 1997). Using a Coulter counter, Hunter and Frayne (1980) report that the floc radius R scales with shear rate roughly as  $R \sim \dot{\gamma}^{-0.4}$ .

Thus, it seems that only at much higher shear rates,  $\dot{\gamma} \sim 10^5 \text{ sec}^{-1}$  or so, will the stresses be dominated by doublets and single particles. Starting with Firth and Hunter (1976a), several models of the sheared dispersions have been developed that attempt to account for stresses generated by shear-induced distortion and breakage of larger flocs. A general framework seems to be provided by the "elastic floc model" of Firth and Hunter (1976a, 1976b; see also Hunter 1992). According to this model, most of the stress is generated by tension in particle–particle bonds within large flocs. Large values of the plastic viscosity are accounted for by assuming that individual flocs can be treated as "hard spheres" whose volume exceeds that occupied by individual particles in the floc, because of the flocs' open structure. A more recent theory by Potanin et al. (1995) differentiates between "soft" and "rigid" bonds between particles, with only the latter contributing to the stress. This model has been used to interpret the rate at which the elastic modulus of a gel rebuilds after being broken down in a strong shearing flow (Rueb and Zukoski 1997). Such predictions are potentially important in designing suspensions as thixotropic agents

for commercial applications, such as encapsulants of microelectronic devices. However, to date, the detailed experimental probes of floc structure necessary to validate models of this kind, and to provide measurements of the parameters that go into them, are still lacking.

• Problems and Worked Examples 7.1 through 7.4 test your practical working knowledge of colloidal gels.

# 7.4 SUMMARY

Many experimental data are now available on the rheology of particulate gels, including the effects of particle concentration, size, and strength of interaction. For weakly flocculated gels, reasonable theories exist that allow for at least qualitative, and even quantitative, prediction of the zero-shear viscosity. These theories predict that the relaxation time  $\tau$  and the zero-shear viscosity  $\eta_0$  increase with the depth  $-W_{\min}$  of the attractive potential well as  $\tau \sim \eta_0 \sim \exp(-W_{\min}/k_BT)$ . For strongly flocculated gels with  $-W_{\min}/k_BT \gtrsim 20$ ,  $\tau$  becomes too long for equilibration of the gel structure to occur within reasonable experimental times. Also, for strongly flocculated gels, the zero-shear viscosity is so large, and is accessed at such low shear rates, that these gels are characterized by a yield stress, rather than a zero-shear viscosity.

Rheological data on strongly flocculated gels are hard to reproduce and are sensitive to sample preparation, pre-shearing, and experimental protocol. Nevertheless, clear trends are evident in the experimental dependences of yield stress  $\sigma_y$  and modulus G of strongly flocculated gels on particle volume fraction  $\phi$ , radius a, and zeta potential  $\zeta$ . The magnitudes of  $\sigma_y$  and G can be estimated theoretically based on an estimate of the gap  $D_0$  between particles;  $D_0$  appears to be sensitive to the presence and type of ions adsorbed onto the particle surfaces. The predicted dependence of  $\sigma_y$  on  $\zeta$  is in good agreement with experiment, while experiments show a steeper dependence on  $\phi$  than is predicted by the simplest theory. In general, as the net interparticle attractions are made stronger (for example, by reducing electrostatic repulsions), the particles become more tightly bonded to each other, and the elastic modulus and yield stress increase. Also, strongly flocculated gels yield or weaken at smaller strains, and hence are more brittle than more weakly flocculated ones. Since optimization of gel properties usually requires that the modulus be as high as possible, while the brittleness be minimized, understanding and control of the rheology of gels is of considerable importance in the processing of colloidal gel bodies.

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# PROBLEMS AND WORKED EXAMPLES

**Problem 7.1** Name two ways of inducing flocculation in a suspension of electrostatically stabilized spheres.

**Problem 7.2** Consider a suspension of charged spheres. Suppose the suspension is a soft solid (i.e., with a yield stress) when no electrolyte has been added. After adding 0.01 M NaCl, the suspension becomes a runny liquid. After adding an additional 0.1 M NaCl, it is a solid again! Can you give an explanation?

**Problem 7.3(a) (Worked Example)** Consider a flocculated suspension, 20% by volume, of silica particles of 100-nm radius in 0.1 M KNO<sub>3</sub>, where  $A_H = 10^{-20}$  J,  $\varepsilon = 50$ , and the particles are held 2 nm apart by adsorbed ions. Estimate the yield stress at the i.e.p.

#### ANSWER:

From Eq. (7-28), we obtain

$$\sigma_{\rm y} \sim \frac{\phi^2}{a} \left( \frac{A_H}{12D_0^2} - \frac{C\zeta^2}{D_0} \right) \tag{A7-1}$$

At the isoelectric point  $\zeta = 0$ . Hence in mks units, Eq. (A7-1) gives

$$\sigma_y \sim \frac{(0.2)^2}{10^{-7} \mathrm{m}} \left( \frac{10^{-20} \mathrm{ J}}{12(2 \times 10^{-9})^2 \mathrm{m}^2} \right) = 83 \mathrm{ J/m^3} \mathrm{ or } \mathrm{Pa}$$

**Problem 7.3(b) (Worked Example)** At what  $\zeta$  potential (in mV) do you expect the colloidal gel to lose its yield stress?

## ANSWER:

From Eq. (A7-1), the yield stress will disappear when

$$\zeta^2 = \frac{A_H}{12CD_0} \tag{A7-2}$$

Now, from Eq. (7-11b), we obtain

$$C = 2\pi \varepsilon \varepsilon_0 \ln \left[ \frac{1}{1 - \exp(-\kappa D_0)} \right]$$
(A7-3)

In 0.1 M KNO<sub>3</sub>, Eq. (7-5) gives the following for the Debye length of any 1:1 electrolyte:

$$\kappa^{-1} = \frac{0.3}{\sqrt{0.1}} \approx 1 \text{ nm}$$

Therefore  $\kappa D_0 = 2$ . Hence,  $\ln[(1 - \exp(-\kappa D_0))^{-1}] = \ln[(1 - \exp(-2))^{-1}] = 0.15$ . Also,

$$2\pi\varepsilon\varepsilon_0 = 6.28 \times 4.4 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} = 27.6 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

Therefore, C in Eq. (A7-3) is  $4 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ . Then, from Eq. (A7-2), we obtain

$$\zeta^{2} = \frac{10^{-20} \text{ J}}{12 \times 4 \times 10^{-10} \times 2 \times 10^{-9} \text{ C}^{2} \text{ J}^{-1}} = 10^{-3} \text{ J}^{2}/\text{C}^{2}$$

which implies that

$$\zeta = 0.03 \text{ J/C} = 30 \text{ mV}$$
 (A7-4)

**Problem 7.3(c) (Worked Example)** The electrostatic contribution in Eq. (A7-1) is valid in the limit of a weak electrostatic force, so that the Debye–Hückel theory applies. Show that this limit is applicable under the conditions described in part (a).

#### ANSWER:

According to Section 2.2, just before Eq. (2-49), the Debye-Hückel theory applies when  $ez\psi_s/4k_BT < 1$ . Since  $\zeta = \psi_s$  and the charge valence z is unity 1, we have the following from Eq. (A7-4):

$$\frac{ez\psi_s}{4k_BT} = \frac{1.6 \times 10^{-19} \times 0.03 \text{ J}}{4 \times 4 \times 10^{-21} \text{ J}} = 0.3 < 1$$

Thus, the electrostatic forces are weak enough for Eq. (A7-1) to be valid.

**Problem 7.4 (Worked Example)** Consider a suspension of silica particles in water for which the Hamaker constant is  $10^{-20}$  J and the dielectric constant is  $\varepsilon = 50$ . If the surface charge is 0.1 charges/nm<sup>2</sup>, calculate how high the molarity of NaCl must be to induce flocculation. Remember, each surface charge is that of an electron,  $e = 1.6 \times 10^{-19}$  C, the permittivity of space is  $\varepsilon_0 = 8.8 \times 10^{-12}$  C<sup>2</sup> J<sup>-1</sup> m<sup>-1</sup>, and the Bjerrum length is  $\ell_b = 58/\varepsilon$  nm. Assume a weak surface potential.

#### ANSWER:

According to Eq. (7-15), flocculation is induced when the number of cations per unit volume reaches the value

$$n_{\rm crit} = \frac{0.36\ell_b^{-1} z^{-2} \sigma^{4/3}}{(\varepsilon \varepsilon_0 A_H)^{2/3}}$$
(A7-5)

where  $\ell_b = 58/50 = 1.16$  nm  $= 1.6 \times 10^{-9}$  m. For NaCl, the valence z is unity. Converting the charge density into coulombs per square meter, we obtain

$$\sigma = 0.1 \times 10^{18} \text{ charges}/\text{m}^2 = 0.1 \times 10^{18} \times 1.6 \times 10^{-19} \text{C}/\text{m}^2 = 1.6 \times 10^{-2} \text{C}/\text{m}^2$$

Hence,

$$\sigma^{4/3} = 4 \times 10^{-3} \,\mathrm{C}^{4/3} \mathrm{m}^{-8/3} \tag{A7-6}$$

Now

$$\varepsilon \varepsilon_0 A_H = 50 \times 8.8 \times 10^{-12} \times 10^{-20} \text{ C}^2 \text{m}^{-1} = 4.4 \times 10^{-30} \text{ C}^2 \text{m}^{-1}$$

Then

$$(\varepsilon \varepsilon_0 A_H)^{2/3} = 2.7 \times 10^{-20} \text{ C}^{4/3} \text{ m}^{-2/3}$$
 (A7-7)

From Eqs. (A7-6) and (A7-7), we find

$$\frac{\sigma^{4/3}}{(\varepsilon\varepsilon_0 A_H)^{2/3}} = 1.5 \times 10^{17} \,\mathrm{m}^{-2}$$

Inserting this into Eq. (A7-5) gives

$$n_{\rm crit} = \frac{0.36}{1.16 \times 10^{-9} {
m m}} \, 1.5 \times 10^{17} {
m m}^{-2} \approx 0.5 \times 10^{20} {
m cm}^{-3} = 0.5 \times 10^{23} \, {
m liter}^{-1}$$

This can be converted to molarity by dividing by Avogadro's number,  $6 \times 10^{23}$ , giving 0.08 M for the critical salt concentration to induce flocculation.

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