The Chemical Physics of Food
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The idea of this book started out with my long-held conviction that the complexity of food materials, and the difficulty of describing them in a quantitative manner, has sometimes led food scientists to think that the rigour required of them was less than that required by the traditional physical sciences. However, a number of food scientists are trying to approach the treatment of materials with precisely this level of rigour. This is not an easy task. A working definition of food, which I have found useful, is that it is slightly decayed organic matter that somebody wants to eat. As such the material is intractable, highly variable and is not characterized by parameters that are easily measured. These challenges require a higher, not lower, level of rigour in thinking and experimental design in order to produce useful models of material properties.

The topics I have chosen for this book are areas where the authors exemplify the chemical physics approach. By this I mean a combination of the applications of chemical and physical methods, often of the most advanced kind, together with a clear quantitative consideration of the data. It is my hope that the approach taken here will come to be the norm in food science.

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Chapter 1
Emulsions

John N. Coupland

1.1 Introduction

Oil and water are almost completely mutually insoluble yet commonly coexist in foods in the form of emulsions. The oil forms a separate dispersed phase in the aqueous material (or vice versa, although the topic of water-in-oil emulsions will not be considered here). There is a thermodynamic pressure for a complete phase separation but this is kinetically retarded largely by amphiphilic material adsorbed at the interface. Example food emulsions include beverage cloud emulsions, flavour emulsions, fluid milk, ice cream mix, mayonnaise, salad dressing and soups. Other foods including cake batter, hot-dog mix and frozen ice cream are not precisely emulsions but their behaviour can be understood in similar terms. Additionally, the language of dispersions as revealed in the study of emulsions can inform our understanding of foods as diverse as dough foams and fluid chocolate.

Despite the great diversity of foods containing emulsions, each with its own unique qualities, food emulsions have some common features that make them worth examining as a group. Firstly, the droplets present are of the order of a micrometre in diameter and so scatter light very efficiently, consequently most food emulsions appear opaque and white. Secondly, the presence of a dispersed phase increases the viscosity of the aqueous continuous phase, and interdroplet interactions can lead to dramatic non-Newtonian rheological properties and even gelation. Finally the presence of nonpolar domains within an aqueous continuum enables the partitioning of solutes and a change in their reactivity. All of these properties can be related quantitatively to the structure of the emulsions and will change as the emulsion structures changes.

To understand the functional properties of an emulsion, it is therefore necessary to start with a proper description of its structure and the mechanisms of its destabilization and then consider how these structures affect bulk properties. The study of food emulsions is a mature field and the subject of many books (see, e.g., refs 1–6). A comprehensive review of the depth of knowledge is beyond the scope of this work; instead I have tried to guide the reader through the core topics in a logical way and provide guidance to good sources for a more thorough treatment.
1.2 Emulsion structure

Emulsion structure can be described by a limited number of parameters. Changes in these parameters will reflect changes in the stability of the product and may affect its functional properties as discussed below.

1.2.1 Size

The drive to minimize interfacial area makes emulsion droplets spherical under all but the most extreme conditions and thus they can be characterized by a single length dimension. Real emulsions contain a broad range of droplet sizes (i.e. polydisperse) typically ranging from about a tenth to some tens of micrometres. The range of particle sizes present can be represented as a particle size distribution in which the percentage of the dispersed phase volume (or area, length or number of particles) within a given size range is expressed as a histogram. Very often the histogram is replaced with a scatter plot when the number of size bands is large. The distinction between volume, area, length and number distributions is important and each offers distinct insights into the properties of the emulsion. For example, Fig. 1.1 shows the properties of a typical food emulsion. When expressed on a volume basis the distribution appears bimodal, but as relatively few large droplets contain much of the oil, when the same distribution is expressed on an area or particularly a number basis the distribution appears unimodal. Very often it is preferable to express a distribution in terms of a mean, and some of the many useful means are listed in Table 1.1.

![Fig. 1.1 Particle size distribution of a typical food emulsion. The same emulsion is represented as a volume-, area- and number-based distribution. Note: the x-axis is a logarithmic scale and is a representation of a histogram as a scatter plot; the y-axis shows the proportion of the droplets of a characteristic size.](image-url)
1.2.2 Concentration

The concentration of droplets is typically expressed as a mass fraction of the dispersed phase, though in certain cases a volume fraction is more relevant and these can be readily inverted knowing the density of both phases. In foods the concentration of dispersed-phase oil can vary between a fraction of a percent (e.g. beverage flavour emulsions) and about 75% in mayonnaise. As the volume fraction increases, the particles increasingly interact with one another until they are close packed.\(^7\) The maximum theoretical close packing of identical spheres is 0.7405, but in reality this type of highly organized structure does not occur and random close packing occurs at much lower volume fractions (~0.64). Polydisperse emulsions can pack to a higher volume fraction as the smaller droplets can fit within the gaps left between the large.

Droplet volume fractions beyond close packing are only attainable by deforming the spherical droplets and forming a highly concentrated emulsion, also known as a liquid foam. While in dilute systems the properties of the emulsions are governed by the interactions between the continuous and dispersed phases, as concentration is increased droplet–droplet interactions become increasingly important until in highly concentrated emulsions the droplet–droplet interactions dominate.\(^7\) A striking example of this is mayonnaise, which is a viscoelastic solid formed from a concentrated dispersion of one Newtonian liquid in another. The elastic properties of the concentrated emulsion are due to the reversible deformation of the droplets in response to deformation.

### Table 1.1 Different means that can be used to describe emulsion distributions (adapted from Hunter\(^3\)).

<table>
<thead>
<tr>
<th>Mean</th>
<th>Definition</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>(d_{\text{mean}} = \frac{\sum n_i d_i}{\sum n_i})</td>
<td>Typical ruler measurement</td>
</tr>
<tr>
<td>Area</td>
<td>(d_s = \sqrt[3]{\frac{\sum n_i d_i}{\sum n_i}})</td>
<td>Important when the area of the emulsion is important, for example when droplets act as a catalyst. Often results for image analysis measurement</td>
</tr>
<tr>
<td>Volume</td>
<td>(d_v = \sqrt[3]{\frac{\sum n_i d_i^3}{\sum n_i}})</td>
<td>Volume (or weight) of particles. Measured by electrozone sensing</td>
</tr>
<tr>
<td>Surface-volume</td>
<td>(d_{\text{Sauter}} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2})</td>
<td>The Sauter mean is useful for surface-active material. The surface area per unit volume is given by (6\phi / d_{\text{Sauter}}) ((\phi = \text{volume fraction}))</td>
</tr>
<tr>
<td>Equivalent volume</td>
<td>(d_{\text{equivalent}} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3})</td>
<td>Typical output of some light-scattering instruments. Divide by length average to get a polydispersity index</td>
</tr>
</tbody>
</table>

1.2.2 Concentration

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1.2.3 Surface properties

The short-range molecular interactions responsible for holding liquids together as separate phases also lead to interfacial tension. In an oil-in-water emulsion, water molecules are strongly attracted to other water molecules via a network of hydrogen bonds and so there is a net force acting on surface molecules pulling them back into the bulk. At a macroscopic scale this can be seen (and measured) as a force acting normal to a line of unit length drawn in the surface (i.e. the interfacial tension, $\gamma$). Alternatively surface tension can be seen as the proportionality constant linking interfacial area to the energy cost of generating it.$^{6,8}$

Although at a molecular scale surfaces are inevitably somewhat diffuse, it is convenient to imagine them as an infinitesimally thin plane (Fig. 1.2b). The Gibbs definition of this plane is the surface drawn so that the deficit concentration on one side is equal to the excess concentration on the other (Fig. 1.2c).

The surface properties of emulsion droplets are further complicated by the fact that they are highly curved. Curved surfaces lead to more interfacial molecular contact than the corresponding planar interface and so are higher energy structures. At a molecular level this can be interpreted as the molecules at the interface being more exposed to the other phase whereas macroscopically this is seen as an increased pressure on the concave side of a curved surface – the Laplace pressure, $P_L$, i.e:

$$P_L = \frac{2\gamma}{r} \tag{1.1}$$

where $r$ is the radius of curvature. High internal pressure makes small fluid droplets spherical and hard to deform and also leads to the phenomenon of capillary rise. The high pressure inside very fine droplets importantly increases the solubility of their contents (the logarithm of relative solubility increases with inverse radius – the Kelvin equation). If oil has some

---

Fig. 1.2  Illustrations of the oil–water interface. (a) Optical micrograph of an oil droplet in water; at a bulk scale the interface is seen as a clean line (the thick line seen in most microscopy is an optical artefact). At a molecular scale (b) there is some diffusion in one phase into the other although the bulk solubility is negligible. This mixing can be drawn (c) as a decaying concentration of oil with distance moving into the aqueous phase and vice versa. The Gibbs surface is drawn so the deficit concentration on one side is equal to the excess on the other.
solubility in the continuous phase, the difference in surface curvature will favour the diffusion of oil from a small droplet to a larger (i.e. Ostwald ripening). The smaller droplets will eventually disappear and there will be a net increase in average droplet size without any direct contact between the droplets. In most food emulsions the solubility of triglycerides in water is so low that the rate of this process is negligible; however, certain flavour oils are moderately polar and may diffuse faster. Furthermore, surfactants may incorporate oil molecules in their core and hence increase their effective aqueous phase solubility and the rate of Ostwald ripening.9

1.2.3.1 Modified surfaces

Unmodified surfaces are only present for a very short period of time following emulsion formation because amphiphilic material (see below) absorbs rapidly to reduce the interfacial free energy. The kinetics of accumulation of material is first limited by diffusion times from the bulk and second by any energy barriers of adsorption. Important consequences are the limited efficiencies of homogenization processes (i.e. droplets recoalesce before an amphiphilic layer can form so limiting the minimum droplet size that can be achieved) and the preferential accumulation of one surfactant over another (e.g. small molecule surfactants diffuse faster than proteins).10

For an individual amphiphilic molecule, the energetics of adsorption are governed by a balance between loss of translational entropy and the largely enthalpic interactions that will bind it to the surface. In food emulsions the hydrophobic forces acting on the nonpolar parts of the molecule are largely responsible for the adsorption process but these can be modified by attractive and repulsive interactions between adsorbed molecules. For example, sodium dodecyl sulfate is a negatively charged surfactant. Its surface adsorption is driven by a need to remove the dodecyl hydrocarbon chain from the aqueous environment but opposed by the loss of molecular entropy and by the electrostatic repulsion between a molecule approaching the surface and the negatively charged molecules already there. The relationship between amount of surfactant present and amount adsorbed to the interface is given by the sorption isotherm. Although the values will vary greatly between systems, some common salient features can be seen in Fig. 1.3. First, the amount adsorbed increases at a decreasing rate with bulk concentration over a limited range to a plateau above which the concentration remains constant. The plateau value represents a surface saturated with surfactant, typically at monolayer thickness. The monolayer value in most food emulsions is in the order of a few milligrams per square metre. Adsorbed amphiphilic material reduces the interfacial free energy by shielding the oil from the water. The amount the interfacial tension is reduced by adsorbed surfactant is given as the surface pressure (\(\pi\)) where \(\pi = \gamma - \gamma_0\) (\(\gamma\) is the interfacial tension of the modified surface and \(\gamma_0\) the interfacial tension of the bare surface) (Fig. 1.3). The relationship between the amount of bulk and adsorbed amphiphilic material and the surface pressure is given by the Gibbs adsorption isotherm:

\[
d\pi = -d\gamma = RT\Gamma \text{dln}a
\]

where \(\Gamma\) is the surface excess concentration of the amphiphilic material (i.e. amount adsorbed per unit interfacial area), \(a\) is its bulk activity (or concentration in some dilute systems), and
T and R are the absolute temperature and gas constant, respectively. Different materials have different surface tension lowering properties but one of the important distinctions in foods is that protein surfactants tend to lower the surface tension less than small molecules. A consequence of this is that small molecule surfactants can competitively displace polymers from the interface.11 Recently similar exchanges between bound and unbound proteins have been observed.12,13

1.2.3.2 Types of interfacial material

Many food ingredients are surface active and can have a role in stabilizing food emulsions. Polymeric surfactants (MW > ~1000) are usually a linear chain whose monomers have varying water solubility. This group comprises chiefly proteins,14 but some polysaccharides are also usefully surface active and have similar properties.15 In proteins, the hydrophobic amino acids will tend to partition into the lipid phase while leaving the hydrophilic amino acids in the aqueous phase. Protein adsorption is largely irreversible because, although the energy cost of moving one hydrophobic amino acid from the oil phase is relatively low, the overall cost of simultaneously moving many residues is prohibitive. (However, as noted above, proteins can be displaced from a surface.)

The different affinities for the amino acid residues for the water and oil phases lead a disordered protein to form a series of loops, trains and tails at the interface (Fig. 1.4a). The thickness of a disordered protein film is often large (~10 nm) and in some cases the structure formed is in good accordance with the distribution of hydrophobic amino acids in

Fig. 1.3 Typical sorption isotherm. The amount of adsorbed material increases at a decreasing rate with bulk concentration until a plateau is reached corresponding to surface saturation. The surface tension decreases with surface coverage.
the primary structure (e.g. α and β-casein). In globular proteins, the strong secondary and tertiary structure opposes protein unfolding at the surface and the protein tends to adsorb more or less intact. The protein will then subsequently progressively unfold to improve its conformation. Although the gross changes in protein morphology are relatively small, enzymes particularly can be surface denatured. Films of globular proteins are thinner than disordered proteins (~2–3 nm) but often much more dense (Fig. 1.4b).

There are striking parallels between the three-dimensional reactivity of polymers in solution and polymers adsorbed at an interface.17 For example, thermally treated solutions of β-lactoglobulin will gel through the formation of disulfide bonds (or through cross-links formed by transglutaminase) whereas the same protein adsorbed at a surface will form a cross-linked film stabilized by similar disulfide bonds (or transglutaminase-catalysed bonds). Another example is the observation that gum arabic and β-casein are thermodynamically incompatible in bulk and will also phase-separate when both are adsorbed at an interface.20

The second important class of amphiphilic materials in foods are small-molecule surfactants (Fig. 1.4c). Whereas the hydrophobic portions of most surfactants are most often hydrocarbon-based, the hydrophilic group can be charged (anionic, cationic, zwitterionic) or merely polar. Their lower molecular weight means small-molecule surfactants diffuse more rapidly than proteins both in bulk and laterally at the surface of the droplet. Surfactant adsorption is also reversible because only one hydrophobic group need be detached from the surface to enable complete molecular desorption. Although each surfactant molecule is mobile, the average amounts at the surface and in bulk will remain constant. Many sur-

---

Fig. 1.4 Diagrammatic representation of the conformation of (a) disordered polymer, (b) globular protein, (c) small-molecule surfactants and (d) fine particles at an interface. This diagram is not to scale; in reality the thickness of the surface layer would be three orders of magnitude smaller than the droplet (perhaps less for surface particles) and the curvature of the surface would not be detectable on the scale of the surfactant molecules.
factants will self-assemble in polar and nonpolar media to form a rich variety of dynamic yet thermodynamically stable structures.\textsuperscript{5}

The final class of amphiphilic materials comprises some fine particles. Fine solid particles \((r << r_{\text{droplet}})\) (e.g. some flours, spices and crystals) are observed to adsorb to the interface and stabilize the emulsion (Fig. 1.4d). Although the theoretical basis of this functionality is less well developed, it is thought that the intermediate wetting properties of the solid forces it to adhere at a certain angle to the interface (i.e. Pickering stabilization).\textsuperscript{21}

Figure 1.4 is a representation of the four types of amphiphilic material adsorbed to a single droplet. To facilitate the diagram the surface is shown highly curved relative to the scale of the surface layer. This representation shows that in a water-continuous dispersion the preponderance of the amphiphilic material is water soluble. The molecular asymmetry forces some surface curvature to the droplet and favours the formation of oil droplets rather than an oil continuous phase.

### 1.2.4 Interdroplet potentials

The discussion of emulsion structure so far has treated the droplets as hard spheres, but in fact a number of intermolecular forces act between the droplet, the interface, the continuous phase and other droplets.\textsuperscript{22} These are best understood in terms of attractive and repulsive forces acting around the droplets. The effects can be expressed as a force–distance function (Fig. 1.5a) showing the net forces acting on a droplet at a given distance from a second droplet or as an interdroplet pair potential (Fig. 1.5b), that is, the free energy change to bring one droplet to a given distance from a second droplet. Of course these are two representations of the same phenomena as energy is the integral of work over distance. As illustrated in Fig. 1.5, the net force field may be:

(I) Repulsive at all ranges and the dispersion will be stable.

(II) Attractive at all ranges and there will be rapid coalescence.

(III) Repulsive at large separations but attractive at small ones. At infinite range the forces tend to zero and so the particles will tend to remain separated. If the height of the energy barrier is large enough (>several kT, where k is the Boltzmann constant and T absolute temperature; the product kT is a measure of the thermal energy of the system) the emulsion will be stable but as it decreases particles will ‘jump’ the barrier and begin to coalesce.

(IV) Attractive at large separations but repulsive at short separations. Droplets will tend to accumulate in the energy minima; probably corresponding to flocculation rather than coalescence. Again the droplets may approach closer if the repulsive barrier is small enough.

The theoretical basis of these forces is reasonably well understood and can be measured experimentally with a colloidal force balance.\textsuperscript{23} Some of the more important contributors to the stability of food emulsions are described below:

#### Electrostatic forces

Like-charge repulsion is largely a function of charge on adsorbed surfactant/protein. The amount of charge on a surface can be altered by pH or by specific ion binding. A charged
surface disturbs the ionic distribution in the continuous phase and sets up a double layer of an accumulation of oppositely charged counterions near the surface and similarly charged co-ions opposite. When the double layers of similar droplets overlap they repel one another. A simple formulation of the electrostatic potential between similar spheres ($w_{\text{electrostatic}}$) at separation $h$ is given by McClements:\footnote{McClements, 2003}

$$w_{\text{electrostatic}} = 2\pi\varepsilon_0 \varepsilon_r \psi_0^2 \ln(1 + e^{-\kappa h})$$  \hfill (1.3)

where $\varepsilon_0$ and $\varepsilon_r$ are the dielectric constants of a vacuum and the relative dielectric constant on the continuous phase, respectively, and $\psi_0$ is the surface potential (formally as measured at the plane of slip, a small distance away from the charged droplet surface incorporating some entrained ions and solvent). The parameter $\kappa$ is the reciprocal Debye length, a measure of the thickness of the double layer, which is inversely related to the ionic strength of the medium. According to this formulation the magnitude of the potential therefore decays with separation distance, the rate of decay increases with ionic strength and the magnitude

---

**Fig. 1.5** Schematic representations of the (a) Gibbs free energy change required to bring a droplet from infinity to a given separation with another droplet, and (b) the forces acting on the approaching droplets as a function of distance during the approach. The four functions (I–IV) shown in each case represent forms of the interaction potential discussed in the text.
of the potential depends on both the surface potential and the dielectric constant of the continuous phase.

**van der Waals forces**

Even neutral molecules will attract one another via the van der Waals or dispersion forces. Although a nonpolar molecule by definition has zero average electrical dipole, the instantaneous distribution of electrons usually leads to some polarity. The electrical field generated polarizes adjacent groups and sets up a weak attraction between the transient dipole and the resultant induced dipole. van der Waals forces are the dominant interaction in nonpolar fluids but, importantly for emulsion stability, the net action of many intermolecular forces leads to an interdroplet attractive force. A simple formulation for the van der Waals potential between two similar droplets of radius $r$ at separation $h$ is:

$$w_{\text{van der Waals}} = -\frac{A r}{12h}$$

The proportionality constant $A$ is the Hamaker function ($\sim 0.75 \times 10^{-20}$ J in food emulsions). The precise value of the Hamaker function depends on the frequency-dependent dielectric properties of the component phases. According to this formulation the force is relatively long range (decays as the reciprocal of distance and often effective out to $\sim 10$ nm).

**Steric interactions**

Adsorbed material acts as a barrier to coalescence at very short range (i.e. when the surface layers begin to overlap). The two main contributions to this mechanism are compression (volume exclusion) and mixing (osmotic) effects. Compression is always strongly repulsive but mixing can be attractive at slightly longer ranges depending on the solvent–polymer interactions.

**Hydrophobic forces**

Water molecules strongly interact with one another to form a dynamic hydrogen-bonded structure. Water molecules adjacent to a hydrophobic (nonpolar) surface arrange their interactions to minimize the water–surface contacts and in doing so become more ordered and lose entropy. Bringing two hydrophobic surfaces together reduces the volume of low-entropy water and is the basis for the hydrophobic attraction between nonpolar surfaces in water. Partially covered surfaces or surfaces covered with certain (denatured) polymers will experience an attractive hydrophobic force. Hydrophobicity is only recently becoming understood as a force, but it is believed to decay exponentially with distance and to be relatively long range.

### 1.3 Emulsion dynamics

As seen above, the large interfacial free energy of emulsions means that they are thermodynamically unstable structures and will tend to phase-separate. There are various mechanisms
that are important in emulsion destabilization, and although in reality they often occur simultaneously and catalyse one another, here we will start by examining them in isolation.

1.3.1 Creaming

The density of water is approximately 1000 kg m\(^{-3}\) while food oils are about 970 kg m\(^{-3}\). The 30 kg m\(^{-3}\) difference provides buoyancy for oil droplets in water and they will eventually float to the surface and form a separate cream layer. (In some cases, e.g. solid fat droplets, the particles may be denser than the continuous phase and will sediment. The rates of both processes can be described in a similar manner.) A creamed layer has a higher fat content, and extensive creaming can lead to visible and textural differences in the product. A cream layer can initially be redispersed by mixing but, if left, the closely packed droplets may begin to flocculate and coalesce, in which case reversing the destabilization is less easy.

The stability of an emulsion to creaming can be calculated from the creaming velocity of a single particle.\(^{24}\) The movement of a buoyant droplet is opposed by a frictional force from the continuous phase and counterbalancing these forces yields a simple Stokes expression for the terminal velocity (\(v_{\text{Stokes}}\)) for a creaming droplet:

\[
v_{\text{Stokes}} = -\frac{2gr^2\Delta\rho}{9\eta}
\]

where \(r\) is particle radius (in fact \(r_{54}\), \(\Delta\rho\) is the density of the dispersed phase minus the difference of the continuous phase, \(\eta\) is the continuous phase viscosity and \(g\) the acceleration due to gravity. Stokes’ law is only true for isolated, noninteracting spheres, and several approaches have been used to modify it to account for finite droplet concentrations. Even in dilute systems, the movement of particles upwards is retarded by the countermovement of continuous phase downwards. This can be accounted for by modifying Stokes velocity in a volume fraction-dependent manner (e.g. \(v = v_{\text{Stokes}} (1 - 6.5\phi)\); however, this approach will only work in dilute systems (roughly <2\%) beyond which a semiempirical function must be applied (cf. Krieger–Dougherty equation below):

\[
v = v_{\text{Stokes}} \left( 1 - \frac{\phi}{\phi_c} \right)^{1+b}
\]

where \(\phi_c\) is introduced as a critical concentration (often approximately close packing) where creaming is drastically retarded, and \(k\) is a constant. Even this formulation deals poorly with polydisperse emulsions where there is a range of creaming rates. Large particles that cream rapidly can be particularly destabilizing if they flocculate with smaller particles as they move upwards.

Moderate flocculation increases creaming rate because the larger effective radius of the floc is weighted more heavily in Equation 1.5 than the loss of density difference due to the presence of entrained continuous phase. More extensive flocculation has the effect of lowering \(\phi_c\).
### 1.3.2 Flocculation

Flocculation is the permanent or semipermanent association of droplets without mixing of their contents. Flocculation requires first that two particles collide, and second that they react in some way to bond together. Collision rates \( (F_b, \text{ collisions per unit volume per second}) \) under Brownian motion can be calculated from Smoluchowski kinetics:\(^{25}\)

\[
F_b = k_b n^2 = \frac{3kT\phi^2}{2\eta \pi r^6}
\]  

(1.7)

where \( k_b \) is a second-order rate constant for the process and \( n \) is the number density of the particles. In fact, only about one collision in a million leads to reaction, and the Smoluchowski expressions given above proportionally overestimate the flocculation rate. In principle the proportion of collisions leading to interaction can be calculated from the interdroplet pair potential but in practice flocculation is usually considered more qualitatively. For example, electrostatic repulsive forces are reduced when the net charge is zero or their effects are shielded by high ionic strengths. Consequently, a whey protein-stabilized emulsion may flocculate when \( \text{pH} > \text{pI} \) or in the presence of salts.\(^{26}\) Other forces are affected in other cases; for example, the surface proteins in similar emulsions were denatured by a heating step.\(^{27}\) The denatured protein is more hydrophobic and its presence at the interface leads to increased hydrophobic attraction between droplets and flocculation. In all cases the balance of forces acting is important rather than the absolute magnitude of an individual contributor (Fig. 1.6a).

In other cases it is more profitable to consider the mechanism of flocculation as the simultaneous binding of two (or more) droplets to a third structural element (i.e. bridging flocculation, Fig. 1.6b). For example, emulsions prepared with a low protein:oil ratio may have the same protein chain adsorbed onto different droplets and therefore be flocculated. Similarly an oppositely charged added aqueous polymer may adsorb to multiple droplets and bind them together (Fig. 1.6b).\(^ {15}\)

The formation of a floc represents another level of emulsion structure not examined in Section 1.2. Floc structure has a strong effect on the properties of emulsions, particularly rheology (see Section 1.4.1). Figure 1.7 shows two simulated flocs formed from the same number of particles. Figure 1.7a is a more open structure than Fig. 1.7b and the effective volume entrained within the floc (i.e. the radius of gyration around the centre of mass) is greater. In many cases it is possible to ascribe a fractal dimension to the flocculated structure. All objects show some relation between their length and mass. For Euclidean solids, planes and lines it is a cubic, quadratic or linear relationship, respectively (e.g. an emulsion droplet is a three-dimensional Euclidean object – its mass is proportional to the cube of its radius). For fractal objects (e.g. Fig. 1.7) the relationship between length and volume (or mass) is noninteger. For a flat fractal the closer the fractal dimension to two, the more efficiently the object fills the space and the denser the aggregate (e.g. Fig. 1.7b is denser than 1.7a). Similarly, for a realistic three-dimensional aggregate, the closer the fractal dimensionality to three, the more dense the object and the lower its effective volume. Fast aggregation has been shown to give a more open structure than slower aggregation. Flocs can also rearrange after formation to maximize attractive interparticle interactions.