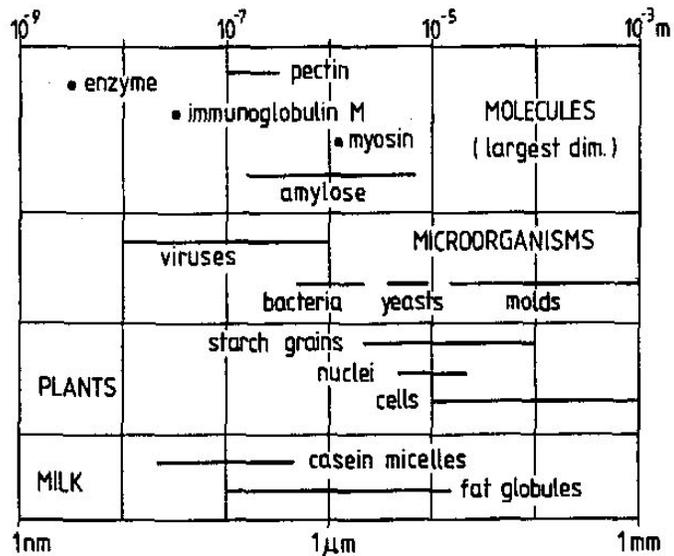


3. Dispersed Systems

Introduction. Many food ingredients are completely immiscible and so will form separate phases within the food. However the sizes of these phases can be very small, so to the naked eye the food will appear homogeneous. The techniques and principles of *colloid science* are suited to dealing with the properties of fine particles and their applications to foods will be explored in this section. A colloidal particle is many times larger than an individual molecule but many times smaller than anything that can be seen with the naked eye. Some examples of colloidal particles in foods are listed in the adjacent table (Table is reproduced from Fennema text). A colloidal particle has at least one length dimension in the range (approximately) of tens of nanometers and tens of micrometers. Although colloidal particles are small, each contains a huge number of molecules. To get an idea of the number of molecules needed to form a colloidal particle: a 10 nm droplet of water would contain about 10^5 molecules, a 10 μm about 10^{14} molecules. To stretch the analogy, if a water molecule was a person, a 10 nm droplet would be have as many people as a city the size of Bethlehem (PA), while a 10 μm droplet 10,000 times the population of the planet.



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Particles must be dispersed in a second phase. (Note that the particles are the dispersed phase and the phase they are dispersed in is the continuous phase). Depending what the phases are (solid, liquid, gas) it is possible to generate different types of colloidal system. Their names and some examples are given in the following table:

Continuous phase

		Solid	Liquid	Gas
Dispersed phase	Solid	<i>Solid Glass (e.g., frozen food)</i>	<i>Sol (e.g., molten chocolate)</i>	<i>Smoke</i>
	Liquid		<i>Emulsion (e.g., cream)</i>	<i>Aerosol (e.g., spray)</i>
	Gas	<i>Solid foam (e.g., whipped candy)</i>	<i>Foam (e.g., beer)</i>	

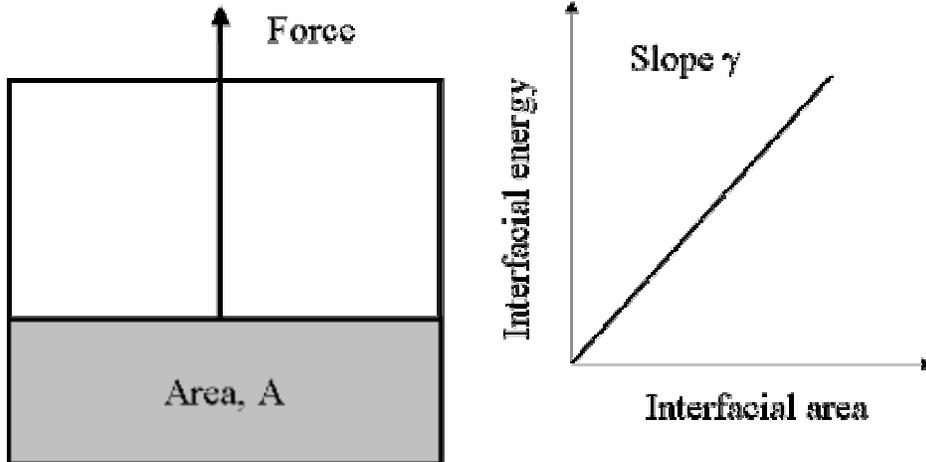
Surface Chemistry. The behavior of large objects is governed by gravity. The behavior of very small objects is governed by thermal motion. Colloidal objects will diffuse randomly in response to thermal energy (Brownian motion) but may also settle out slowly. In addition, for colloidal objects surface properties are important.

Interfacial energy depends on the chemical dissimilarity between the continuous and dispersed phases. At a molecular level, like molecules are more attracted to like. Therefore a molecule at the surface will have a net attraction back into the bulk. Any attempt to increase the surface area will force more molecules to the surface and increase the net pull opposing the expansion. The magnitude of the pull depends on the extent of the molecular dissimilarity (i.e., how much more the surface molecules would rather interact with similar molecules).

A classic experiment to measure this type of surface force is to measure the force it takes to stretch out a soap bubble. Pulling back the plunger forces more molecules to the air-solution interface and is opposed by a force related to the molecular dissimilarity between soap solution molecules and air. The slope of the surface energy with interfacial area graph is γ – the interfacial tension.

$$dG = \gamma dA$$

where dG is the change in surface excess free energy caused by a change in interfacial area (dA). As in all things there is a drive to minimize Gibbs free energy. For surface energy this can either be done by reducing the surface area (i.e., increasing the size of the droplets by allowing them to merge) or reducing the interfacial tension (i.e., by adsorbing a surfactant to the interface).



Complicating the issue of surface tension is the impact of surface curvature. Surface tension pulls surface molecules towards the center of a droplet, slightly increasing the pressure inside. If a droplet is small (i.e., the surface is highly curved) there are more molecules pulling in per unit volume so the pressure is even higher. The increase in pressure (over atmospheric pressure) is the Laplace pressure (P_L) a function of interfacial tension (γ) and the radius of curvature:

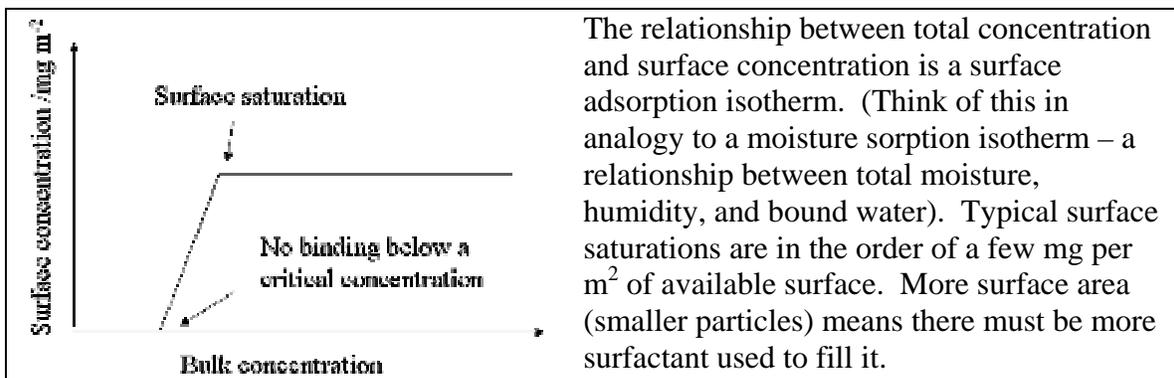
$$P_L = \frac{2\gamma}{r}$$

Laplace pressure has two important consequences for food colloids:

1. Small fluid (gas or liquid droplets in foams or emulsions) colloids behave as hard spheres. Any attempt to deform them means the curvature changes and the pressure in some parts of the droplet is higher than in others. To equalize the pressure the droplet (or bubble) reverts to its spherical shape. Smaller droplets are obviously more rigid than larger ones because the surface-volume ratio is greater.
2. Small droplets/bubbles are more soluble than large ones because solubility increases with pressure. The solubility differential will drive the diffusion of dispersed phase material from small to large particles through a process known as Ostwald ripening. When the solubility of the dispersed phase in the continuous is intrinsically very low Ostwald ripening is unlikely to be significant (e.g., oil is very insoluble in water so food emulsion have little tendency to Ostwald ripen). On the other hand more soluble dispersed phase is more prone to Ostwald ripening (e.g., carbon dioxide in a foam, ice crystals in ice cream).

Surfaces provide an ideal environment for amphiphilic molecules. An amphiphile has part of its structure water-soluble and part water insoluble. Examples include polymers (e.g., proteins) and small molecules (i.e., surfactants, e.g., soaps, Tween, lecithin). By aligning at an interface they can solubilize their water-soluble parts in the aqueous phase and their hydrophobic parts in the less polar phase (e.g., oil or air).

Surface adsorption represents an entropy cost and well as an entropy/enthalpy benefit for the surface-active material. Free surface-active material is able to diffuse freely about the system and is thus has higher entropy than if it were bound. On the other hand bound surface-active material does not have to pay the entropy cost of having hydrophobic portions of their structure in contact with water. The trade-off between cost and benefit means that there needs to be some finite concentration of surface-active material added before there is surface adsorption. The amount of adsorbed surface-active material will increase as more as added until the surface becomes saturated and there is no more available space (i.e., monolayer adsorption).



Each surface-active molecule that adsorbs at the surface blocks some unfavorable contact between the immiscible phases and goes some way to stabilize the system. If the surface tension in the absence of surfactant is γ_0 and in the presence of surface active material is γ then the surface pressure (the extent of surface tension lowering) is $\pi (= \gamma_0 - \gamma)$. The greater the surface pressure, the lower the interfacial free energy and the more stable the system. The more surface-active material adsorbed, the lower the surface pressure (i.e., lower the surface tension). Because the surface load reaches a plateau at high [surfactant] the surface tension reaches its minimum at a similar concentration (and surface pressure its maximum).

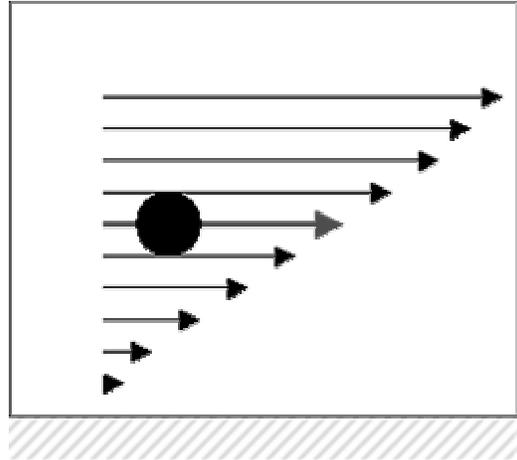
[Small molecule surfactants have a lower surface affinity than a polymeric (protein) surfactant so it is necessary to add more to get any surface adsorption. However the surfactant can lower the interfacial tension more than the protein. (Imagine the surfactant molecule “packing” more efficiently at the surface and better block the phases from each other.) An important consequence for foods is that if a mixture of surfactant and protein are used to create a dispersed system, the surfactant will predominate at the interface. Secondly, if surfactant is added to a protein-stabilized dispersed system, it may displace the protein. The competitive adsorption of surfactant in place of protein is important in understanding the role of added small-molecule emulsifiers in ice cream.]

Properties of Dispersed Systems. The key parameters governing the properties of all dispersed systems are the type (i.e., which phase is continuous?), particle concentration, and particle size.

- The type of emulsion can usually be readily determined – the system “feels” and behaves most like the continuous phase (e.g., mayonnaise disperses relatively easily in water but not in oil because it is an oil-in-water emulsion).
- There is always a distribution of sizes in any real dispersed system. The presence of even a few large particles can lead to much more rapid destabilization. Particle size can be reduced (within limits) by increasing the energy used in preparing the dispersion or by adding more surfactant during the dispersion process.
- The concentration of the particles (usually given as a volume-fraction ϕ) can increase from zero to close-packing. Close-packing is a geometric constraint on the number of spheres that can be physically fitted into an available space (e.g., there is a limited number of basketballs that can fit into a room and there will still be some unfilled space). Close packing for monodisperse spheres is about 69% and much higher for polydisperse particles.

Dispersed systems are always more viscous than the pure continuous phase and the viscosity is greater the more dispersed particles present. Viscosity is the intermolecular friction that must be overcome to make a liquid flow. At its simplest, fluid flow is seen as a velocity gradient with one layer (streamline) of fluid flowing relative to another. The boundary layer of fluid adjacent to a stationary surface can only flow at an infinitesimally small speed. The layer beyond that an infinitesimal amount faster and so on. The more friction between the layer, the more energy needed to achieve a given velocity gradient and the higher the viscosity.

When particles are included in the fluid stream they disrupt the streamlines as they force liquid to flow around them. This increases the amount of energy needed to achieve a given velocity gradient and increases the viscosity. Another, more systematic, way of looking at this is to imagine the particles as blocking some streamlines. To achieve the same overall velocity gradient, the velocity gradient over the liquid parts of the system (the unblocked streamlines) must be higher. To achieve the same overall velocity gradient as the particle-free system it costs more energy because a higher velocity gradient in the remaining liquid parts of the system.



However you conceptualize the mechanism of viscosity-building by particles the magnitude of the effect can be described by the Einstein equation:

$$\eta = \eta_0 (1 + 2.5\phi)$$

where η is the viscosity of the dispersion, η_0 is the viscosity of the continuous phase (i.e., no particles) and ϕ is the volume fraction of particles present. The Einstein equation only works quantitatively up to a few percent particles, at higher concentrations the viscosity will increase even more quickly than predicted.

Creaming (Sedimentation). The effect of particles on a flowing liquid are the basis of the increased viscosity of dispersed systems. However particles will also diffuse and move in a stationary liquid. Very small particles will be most affected by temperature and diffuse randomly by Brownian motion. Large particles diffuse less and are affected more by gravity so tend to either float or sink depending on their density. Oil is less dense than water so will tend to float to the surface of an emulsion (i.e., creaming). The speed of the droplet as it floats upwards is retarded by the friction it experiences with the continuous phase.

The tendency of a particle to float is the buoyancy – a product of the amount of material trying to float (i.e., particle volume) and the density difference between phases ($\Delta\rho$) and the acceleration due to gravity (g):

$$F_b = \frac{\pi d^3 g}{6} \Delta\rho$$

The frictional force opposing a spherical particle as it moves upwards is proportional to its surface area, its speed and the viscosity of the continuous phase (η_c).

$$F_f = 3\pi\eta_c r v$$

A droplet will float upwards at ever increasing speeds in response to the buoyancy force until the velocity is sufficient to allow the frictional force to exactly match it. When $F_b = F_f$ the particle will continue to move upwards at its terminal velocity (v_s):

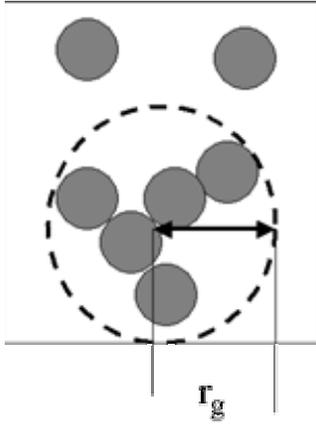
$$v_s = \frac{d^2 \Delta \rho g}{18 \eta_c}$$

The Stokes-Einstein equation provides an estimate of the speed of a creaming particle. The lower v_s , the more stable the emulsion will be to creaming. Stokes-Einstein is rarely quantitatively applicable but it gives some ideas to reduce creaming rate (increase continuous phase viscosity, reduce particle size, increase oil density).

Foams. Foams can be formed either by whipping a gas into a liquid or by bubble nucleation (e.g., from yeast cells or from a supersaturated CO_2 solution). Foams are similar in many ways to emulsions but have some distinctive feature worth consideration:

- Gasses are more soluble in water than oils so the rate of Ostwald ripening is much more rapid.
- Bubbles tend to be much larger than droplets because lower energy levels are used to form them and because very small bubbles tend to disappear quickly by Ostwald ripening.
- Creaming is typically much faster in foams as the density difference and the bubble size is much larger.
- Large foam bubbles are more capable of deformation than small oil droplets so it is possible to reach very high volume fractions ($\phi > 99\%$)
- Dilute foams (e.g., soda) break down by rapid creaming. Concentrated foams (e.g., meringue) break down by (i) drainage and (ii) film rupture.

Particle Aggregation. The mechanisms of emulsion stability considered so far (i.e., creaming – very important especially for large droplets, and Ostwald ripening – rarely important unless the oil has significant water-solubility) require no droplet-droplet contact. Droplet-droplet collisions and interactions are essential for droplet aggregation. There are two types of aggregations: fluid droplets can coalesce when they collide and merge to form one larger droplet. Fluid droplets can also collide, form a semi-permanent link, but maintain their individual identity and do not merge (i.e., flocculation). (Solid droplets can only flocculate). Flocculation usually precedes coalescence and in practice most food emulsions spoil before significant coalescence has occurred.



Flocculated networks of particles are open structures that include a proportion of continuous phase in their structure. The effective volume fraction of a flocculated system is therefore larger than a corresponding non-flocculated system. In fact, most sudden changes in viscosity for a dispersed system depend on the formation or fracture of flocs. A second major consequence of flocculation is because the effective particle size (the hydrodynamic radius) is larger the creaming rate is much faster. Very extensive flocculation allows the formation of an extended particle network spanning the sample. The heavily flocculated fluid will now behave as a gel and will not cream at all because all the particles are interconnected.

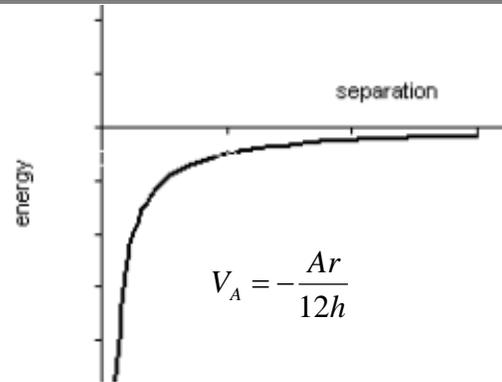
The rate of droplet aggregation processes depends on the number of droplet collisions and their effectiveness (i.e., how many of the collisions lead to particles “sticking” and forming a floc). Collision kinetics is a second order process (i.e., rate depends on the square of the number of particles present). The second order rate constant can be calculated from the diffusion coefficient of the particles present as:

$$k_{fast} = \frac{4kT}{3\eta}$$

where T is absolute temperature, k is the Boltzmann constant and η is the continuous phase viscosity. The rate predicted by this equation (i.e., Smoulokowski kinetics) is very high. In practice not every collision leads to droplet aggregation and we must reduce this rate by a collision efficiency w (usually >1): $k = k_{fast}/w$. The collision efficiency is related to an energy barrier preventing the droplets colliding. If the size of the energy barrier (or w) is large, k will tend to zero and the particles will not aggregate.

We can imagine the energy barrier as a “force field” that surrounds the droplets. There are some non-covalent attractive forces and some repulsive forces that surround each droplet. Their sum gives the magnitude of the effective force field and the energy barrier that may prevent droplets reacting.

Van der Waals forces are weak transient-dipole attractions between all matter. Particles will attract each other by these forces. However, they have a limited range and their effectiveness decreases as $1/\text{separation}$. The force is conventionally expressed as a pair potential – the free energy cost (or gain) to bring one a particle from infinite separation to a distance h from a second similar particle. The Van der Waals function is negative because it is attractive (so $\Delta G < 0$ to bring particles closer). While weak, Van der Waals force can attract particles over several nanometers.



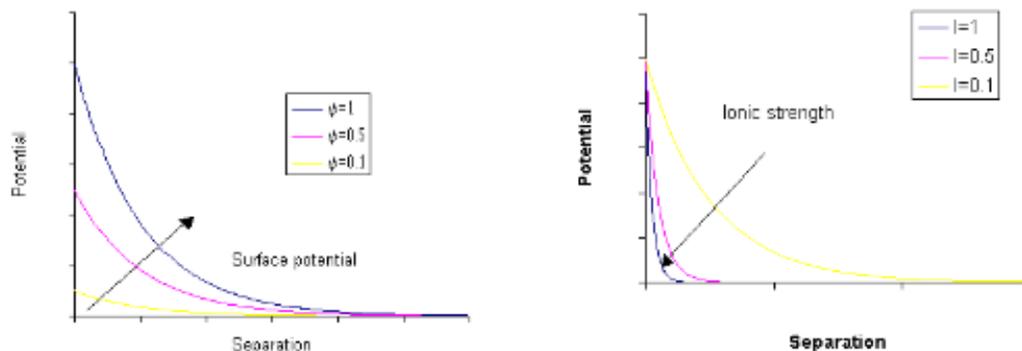
where r is the particle radius and h the particle separation and A is the Hamaker constant.

Electrostatic interactions are repulsive between similarly charged particles. Most particles are charged because the proteins adsorbed to their surface

The effective magnitude of the repulsive force depends on the surface charge (i.e., potential). It decays in magnitude exponentially moving away from the charge and the rate of decay is greater in higher ionic strength systems. The formulation commonly used is:

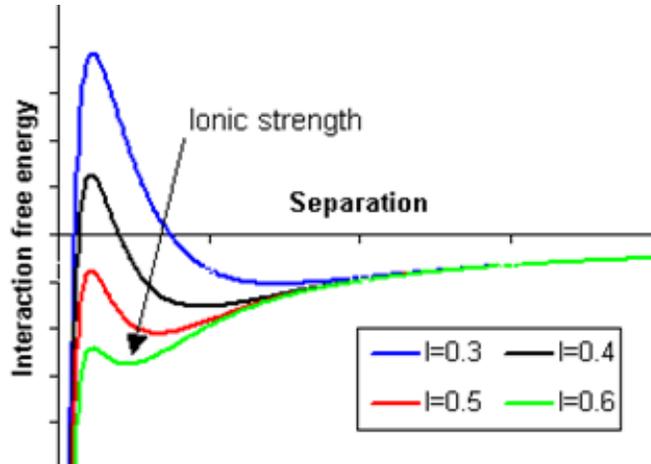
$$V_E = kr\psi^2 \ln(1 + e^{-kh})$$

where ψ is the surface potential, r is the droplets radius, h is the particle separation, k is a constant and κ is the reciprocal Debye length – a constant whose magnitude increases with ionic strength (concentration of ionic charge in the aqueous phase).



Note the potential is positive – it costs energy to bring one particles closer to a similarly-charged particle.

According to the DVLO theory, the net potential between droplets is given by the sum of the Van der Waals attractive forces and electrostatic forces. The sum of forces is attractive at some separations and repulsive at others. It provides the interdroplet pair potential. A pair potential represents an energy surface a particle must move across to approach and collide with a second. If the



potential is repulsive at all separations, collisions will be difficult. If the potential is attractive (negative) at all separations the particles will deviate from their trajectories towards one another and collide. If there is an energy barrier (a positive slope) in the potential it will provide the energy barrier needed to calculate the collision efficiency (w). For example, the Figure shows the effect of increasing ionic strength (and decreasing the range of electrostatic repulsion) on the DVLO potential. At long ranges the potential is attractive and droplets will approach. However, at shorter ranges the electrostatic repulsion will dominate and create a repulsive barrier, that if large enough ($>2-3$ kT) will prevent further droplet approach (some ionic strengths give a small secondary minima that may hold particles at a finite separation in loose flocs). Beyond the repulsive energy barrier the Van der Waals attraction again dominates and droplets that can overcome the barrier will rapidly coalesce in the energy well.

Question 1: DVLO Theory. DVLO theory can predict the interaction potential between droplets in an emulsion. The main adjustable parameters in the equation are the surface potential (related to the charge density on the surface of the droplet – increase by either adsorbing more protein or increasing the charge on the each protein, pH-pI) and the ionic strength ($=\sum cz^2$, where c is the concentration of ions of charge z . Increase by adding salts). In this exercise, use the Excel spreadsheet on the class website to calculate DVLO potentials between droplets with different surface potential and ionic strength. For surface potentials in the range 0.1-1, calculate the maximum ionic strength that can maintain an energy barrier opposing aggregation. Present your answer as graph of maximum ionic strength (y) against surface potential (x) and one or two sentences explaining what this stability map tells us about the types of emulsion composition we can expect to be stable.

The DVLO approach is in reality an oversimplification. There are many more forces that may be important and a truly successful theory would incorporate all of these. Among the most important are steric repulsion forces. A thick layer of surfactant surrounding a particle can prevent the approach of a second particle and inhibit aggregation. Steric repulsion is very powerful but very short range. They can typically hold droplets at a close separation in flocs without allowing them to merge and coalesce. The two mechanisms of steric repulsion are:

- (i) Osmotic. As the droplets approach one another the aqueous portion of the surfactants overlap. Locally the concentration of surfactant molecules increases and the concentration of water decreases. This sets up an osmotic pressure gradient between the overlap area and the outside solution. Water will diffuse in according to the Osmotic pressure and force the particles apart.
- (ii) Mechanical. The physical space taken up by the aqueous portions of the surfactant molecules cannot be taken up by other molecules. When a second droplet approaches the physical presence of one layer prevents the other getting too close.

Any tendency for the surface proteins on one droplet to bond with the surface proteins on another droplet will quickly favor aggregation.