Chapter 6

Surface Properties of Foods

SUMMARY

In this chapter, the principles and measurement methods of surface tension and interfacial tension are discussed. Information about colloidal systems in foods is also given.

Surface tension is defined as work required to extend a surface under isothermal conditions. If the surface forces take place at the interfaces, it is called interfacial tension. The methods for measuring surface tension are capillary rise, drop weight, bubble pressure, tensiometer, and dynamic methods. Substances that reduce the surface tension of a liquid are known as surface-active materials. Emulsifiers and hydrocolloids used in food systems are typical examples of surface-active materials. With certain modifications, the same methods used for surface tension can also be used for measuring interfacial tension.

Colloidal dispersion is the two-phase system in which the particles in the dispersed phase are between 1 and 1000 nm in diameter. Colloidal systems in foods can be categorized into four groups—sol, gel, emulsion, and foam—based on the states of matter in the continuous and dispersed phases. Proteins can act as both emulsifiers and stabilizers in food systems. The major difference between an emulsifier and a stabilizer is that the emulsifier is used to obtain short-term stabilization but stabilizers supply long-term emulsion stability.

6.1 SURFACE TENSION

You might have noticed water in spherical droplets on the surface of a leaf or emerging from tap. This can be explained by surface tension.

A molecule in the bulk of the liquid is attracted in all directions that cancel each other (Fig. 6.1). However, on the surface, the molecules are attracted across the surface and inward since the attraction of the underlying molecules is greater than the attraction of the vapor molecules on the other side of the surface. Therefore, the surface of the liquid is in a state of tension. This causes water to pull itself into a spherical shape which has the least surface area. Molecules at the surface of the liquid are attracted inward because of the van der Waals intermolecular attractions. This creates a force in the surface that tends to minimize the surface area and this force is known as surface tension. Surface tension can be defined as the tendency of a surface of a liquid to behave like a stretched elastic membrane. If the surface is stretched, the free energy of the system is increased.

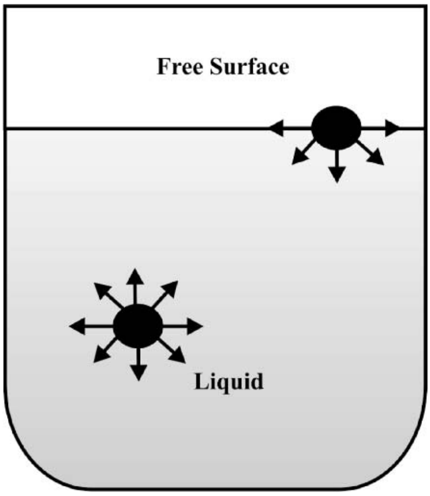

Figure 6.1 Interactions of water molecules inside and near the surface of liquid.

As can be seen in Fig. 6.2, the small droplet adapts its shape to an almost perfect sphere since it has the least surface area per unit volume. The shape becomes flatter as the size increases because of gravity since gravity is a function of unit volume whereas surface tension is a function of surface area. Therefore, gravity is more important for particles having larger sizes.

You can observe the effects of surface tension by conducting a simple experiment at home. When you shake black pepper into a glass of water, you will observe that the pepper will float because of surface tension. When a drop of soap or detergent is added to the water, the pepper will sink. Soap or detergents have the ability to reduce the surface tension of liquids.

The surface tension (σ) is expressed as free energy per unit surface area or work required to extend a surface under isothermal conditions. It is also defined as the force per unit length on the surface that opposes the expansion of the surface. This definition can be seen in Fig. 6.3, in which a bar is pulled with force F to expand a liquid film that is stretched like a bubble film on a wire frame.

$$\sigma = \frac{\text{Work done}}{\text{Increase in area}} = \frac{FL}{2Ld} = \frac{F}{2d} \tag{6.1}$$

where d is the distance between wires A and B, L is the distance that the bar is advanced to the left, and the factor 2 is introduced since there are two liquid surfaces (one at the front and one at the back).

The surface tension has dimensions of force per unit length. In the SI system, the unit for surface tension is N/m. The surface tension values of some liquid foods are given in Table 6.1.

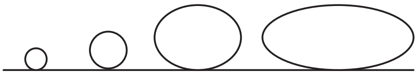

Figure 6.2 Effects of surface tension on droplets having different sizes.

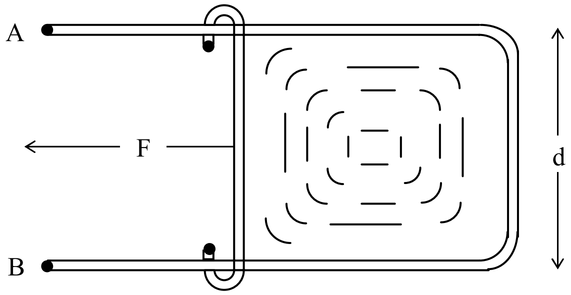

Figure 6.3 Schematic diagram for determination of the surface tension of a liquid.

Water has a very high surface tension value (Table 6.1). Liquids that have high surface tension values also have high latent heat values. The surface tensions of most liquids decrease as the temperature increases. The surface tension value becomes very low in the region of critical temperature as the intermolecular cohesive forces approach zero. The surface tensions of liquid metals are large in comparison with those of organic liquids. For example, the surface tension of mercury at 20°C is 435.5 mN/m (Weast, 1982). As can be seen in Table 6.1, alcohol in wine reduces the surface tension.

When dealing with surface properties, several equations give us some insight into the physical phenomena occurring during the processes related to surface rather than volume. They are the Laplace, Kelvin, Young, and Gibbs adsorption equations.

Table 6.1 Surface Tensions of Some Liquids at 20°C

Liquid	*Surface Tension (mN/m)*
Water[a]	72.75
Milk[b]	42.3–52.1
Skim milk (0.04% milk)[c]	52.7
Cream (34% milk)[c]	45.5
Cotton seed oil[d]	35.4
Coconut oil[d]	33.4
Olive oil[e]	33.0
Sunflower oil[f]	33.5
Wine (Chardonnay) (10.8% ethanol)[g]	46.9
Diluted wine (Chardonnay) (2.7% ethanol)[g]	60.9

[a] From data of Weast (1982).
[b] From data of Jenness, Shipe, and Sherbon (1974).
[c] From data of Witnah (1959).
[d] From data of Flingoh and Chong Chiew(1992).
[e] From data of Powrie and Tung (1976).
[f] From data of Ould-Eleya and Hardy (1993).
[g] From data of Peron et al. (2000).

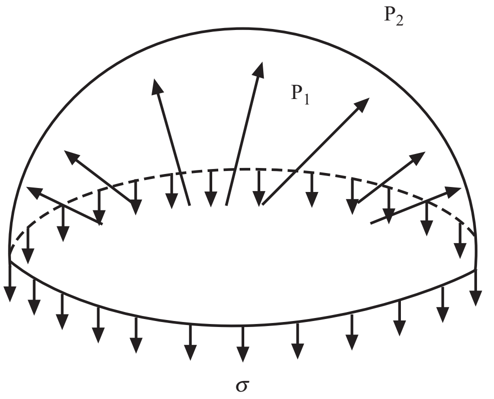

Figure 6.4 Half shape of a liquid droplet in vapor.

6.2 LAPLACE EQUATION

Consider a liquid droplet in spherical shape in vapor (Fig. 6.4). The internal pressure of the liquid is at pressure P_1 while the environment is at P_2. The surface tension of the liquid tends to cause the bubble to contract while the internal pressure P_1 tries to blow apart. Therefore, two different forces need to be considered.

Force due to a pressure difference between the pressure inside the droplet and the vapor outside is:

$$F = (P_1 - P_2)\pi r^2 \tag{6.2}$$

Force due to surface tension is:

$$F = 2\pi r\sigma \tag{6.3}$$

At equilibrium, these two forces are balanced. Then:

$$\Delta P = P_1 - P_2 = \frac{2\sigma}{r} \tag{6.4}$$

Equation (6.4) is known as the Laplace equation. This equation can be used to determine the relationship between the surface tension and the rise or depression of a liquid in a capillary as shown in Fig. 6.5. When a capillary tube is immersed in a liquid vertically, the liquid rises or depresses in the tube. The rise or depression of the liquid depends on the contact angle that liquid makes with the wall. The contact angle is the angle between the tangent to the surface of a liquid at the point of contact with a surface and the surface itself. If the contact angle is less than 90°, liquid will rise whereas it will depress for a contact angle greater than 90°.

If the capillary is of very small diameter, the meniscus will be in the shape of a sphere and the radius of curvature of liquid surface in the capillary can be expressed as:

$$r = \frac{r_t}{\cos\theta} \tag{6.5}$$

where r_t is the capillary tube radius and θ is the contact angle.

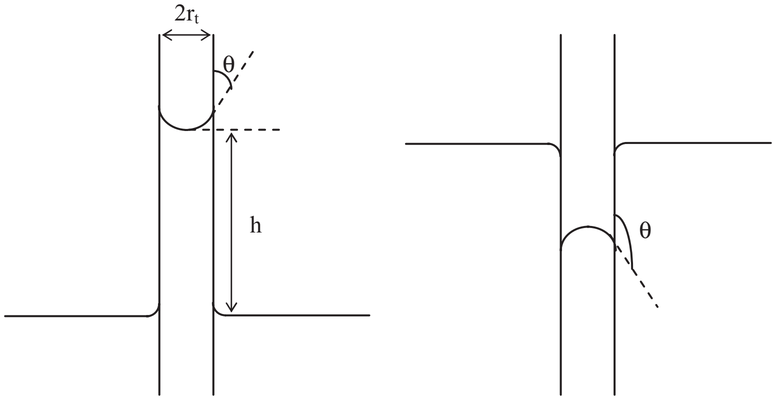

Figure 6.5 Rise or depression of a liquid in a capillary.

The difference between pressure in the liquid at the curved surface and pressure at the flat surface is:

$$\Delta P = \frac{2\sigma \cos\theta}{r_t} \tag{6.6}$$

Atmospheric pressure pushes the liquid up until pressure difference between liquid at the curved surface and liquid at the plane surface is balanced by the hydrostatic pressure:

$$\frac{2\sigma \cos\theta}{r_t} = hg(\rho_l - \rho_v) \tag{6.7}$$

where ρ_l is the density of the liquid, ρ_v is the density of vapor, and h is the height of the column.

Since the density of vapor is very small compared to that of the liquid, the equation can be approximated as:

$$\sigma = \frac{h\ g\ \rho_l\, r_t}{2\cos\theta} \tag{6.8}$$

Example 6.1. Calculate the height of rise of water in a clean capillary tube of radius 0.001 cm if the density of water is 997 kg/m^3, surface tension is 73 dynes/cm, and the contact angle of water to the glass is 10°.

Solution:

$$\sigma = \left(73\frac{\text{dyne}}{\text{cm}}\right)\left(\frac{10^{-5} N}{1\ \text{dyne}}\right)\left(\frac{100\ \text{cm}}{1\ \text{m}}\right) = 7.3 \times 10^{-2}\ \text{N/m}$$

From Eq. (6.8):

$$\sigma = \frac{h\ g\ \rho_l\, r_t}{2\cos\theta} \tag{6.8}$$

$$\Rightarrow h = \frac{2\cos(10^\circ)\left(7.3 \times 10^{-2}\,\frac{\text{N}}{\text{m}}\right)}{\left(9.81\,\frac{\text{m}}{\text{s}^2}\right)\left(997\,\frac{\text{kg}}{\text{m}^3}\right)\left(10^{-5}\,\text{m}\right)} = 1.47\,\text{m}$$

6.3 KELVIN EQUATION

In addition to capillarity, another important consequence of pressure associated with surface curvature is the effect it has on thermodynamic activity. For liquids, the activity is measured by the vapor pressure. In another words, curvature of a surface affects the vapor pressure. This is expressed by the relationship of differential change in the area of the interface and the differential change in Gibbs free energy of the system. Starting from the first law of thermodynamics:

$$dU = dQ + dW \tag{6.9}$$

For a system in equilibrium:

$$dQ = TdS \tag{6.10}$$

and

$$dW = -PdV + \sigma dA \tag{6.11}$$

Combining the first and second laws of thermodynamics for an open-component system:

$$dU = TdS - PdV + \sigma dA + \mu dn \tag{6.12}$$

In the last term in Eq. (6.12), μ is the chemical potential and *dn* is the change in the number of moles in the system. This term gives the change in Gibbs free energy when *dn* moles of a substance are added to the droplet without changing the area of the surface, which is the case for a planar surface.

The Gibbs free energy of the system can be expressed by:

$$G = H - TS \tag{6.13}$$

Substituting $H = U + PV$:

$$G = U + PV - TS \tag{6.14}$$

Differentiating Eq. (6.14):

$$dG = dU + PdV + VdP - TdS - SdT \tag{6.15}$$

Inserting Eq. (6.12) for *dU*:

$$dG = \sigma dA + \mu dn - SdT + VdP \tag{6.16}$$

For a sphere, volume change is $dV = 4\pi r^2 dr$ and area change is $dA = 8\pi r dr$. Thus:

$$dA = \frac{2dV}{r} = \frac{2\overline{V}dn}{r} \tag{6.17}$$

where $\overline{V}$ is the molar volume of the liquid. Combining Eq. (6.17) with (6.16), Eq. (6.18) is obtained:

$$dG = \left(\frac{2\overline{V}\sigma}{r} + \mu_{\text{planar}}\right) dn - SdT + VdP \tag{6.18}$$

The chemical potential of the liquid in the droplet is given by:

$$\mu_{\text{droplet}} = \frac{2\overline{V}\sigma}{r} + \mu_{\text{planar}} \tag{6.19}$$

If the vapor behaves like a perfect gas:

$$\mu_{\text{droplet}} = \mu_{\text{planar}} + RT \ln \frac{P}{P^0} \tag{6.20}$$

where P^0 is the vapor pressure of the planar surface. Combining Eq. (6.20) with Eq. (6.19), the Kelvin equation is obtained:

$$\ln\left(\frac{P}{P^0}\right) = \frac{2\overline{V}\sigma}{rRT} \tag{6.21}$$

This equation gives the vapor pressure (P) of a droplet having a radius r. The assumption to obtain the Kelvin equation is that the surface tension is independent of the curvature of the surface. If the sign of one part of the equation changes, it results in vapor pressure of the concave surface of a liquid in the capillary or a small bubble.

Example 6.2. The vapor pressure of water is 3167.7 Pa at 25°C. Calculate the vapor pressure of water at 25°C in droplets of radius 10^{-8} m if the surface tension for water is 71.97 dyne/cm at 25°C. Density and molecular weight of water are 997 kg/m^{3}and 18 kg/kg-mole, respectively. The gas constant, R, is 8314.34 J/kg-mole K**.**

Solution:

$$\sigma = \left(71.97\,\frac{\text{dyne}}{\text{cm}}\right)\left(\frac{10^{-5}\,\text{N}}{1\,\text{dyne}}\right)\left(\frac{100\,\text{cm}}{1\,\text{m}}\right) = 7.2 \times 10^{-2}\,\text{N/m}$$

Molar volume is calculated by dividing molecular weight by density of sample:

$$\overline{\text{V}} = \frac{18\,\text{kg/kgmole}}{997\,\text{kg/m}^3} = 0.018\,\text{m}^3\text{/kgmole}$$

Using the Kelvin equation (6.21):

$$\ln\left(\frac{P}{P^0}\right) = \frac{2\overline{V}\sigma}{rRT} \tag{6.21}$$

$$\ln\left(\frac{P}{3167.7}\right) = \frac{2(0.018)(7.2 \times 10^{-2})}{(10^{-8})(8314.34)(298)}$$

P is calculated as 3517 Pa.

6.4 SURFACE ACTIVITY

Substances that reduce the surface tension of a liquid at very low concentrations are called surface active. Emulsifiers and hydrocolloids are good examples for surface-active materials. These materials have both polar or hydrophilic and nonpolar or lipophilic groups. They orient themselves at the interface between the two phases. These substances concentrate at the surface and give large decreases in surface tension. This can be expressed quantitatively by the Gibbs adsorption isotherm.

$$\Gamma = -\frac{1}{mRT}\frac{d\sigma}{d\ln a} \cong -\frac{1}{RT}\frac{d\sigma}{d\ln c} \tag{6.22}$$

where Γ is adsorption (excess concentration) of solute at the surface (kg-mole/m^2), σ is surface tension (N/m), R is the gas constant (8314.34 J/kg-mole · K), a is activity of solute in the bulk solution, c is concentration of solute in the bulk solution (kg-mole/m^3), and m is a constant with a value of 1 for dissociating substances.

The sign of excess concentration (Γ) is opposite to the sign of the change of surface tension with concentration or activity of solute in solution.

Example 6.3. The surface tension of aqueous solution of butanol was measured at 20°C and the results were given in Table E.6.3.1. Use the Gibbs isotherm to find the surface excess at $c = 0.1$ mol/L.

Solution:

Using Gibbs adsorption isotherm (Eq. 6.22), σ is plotted with respect to ln c (Fig. E.6.3.1).

$$\Gamma \cong -\frac{1}{RT}\frac{d\sigma}{d\ln c} \tag{6.22}$$

The slope of Fig. E.6.3.1 at $c = 0.1$ mol/L will give the surface excess at that point.
The polynomial equation of the curve is:

$$\sigma = -6.145(\ln c)^2 - 45.143(\ln c) - 15.253$$

$$\frac{d\sigma}{d(\ln c)} = -12.29(\ln c) - 45.143$$

at $c = 0.1$ or at $\ln c = -2.302$:

$$\frac{d\sigma}{d(\ln c)} \text{ is found as } -16.85 \text{ mN/m.}$$

Table E.6.3.1. The Surface Tension Values of Aqueous Butanol Solutions at Different Concentrations

c (mol/L)	*σ (mN/m)*
0.0264	68.17
0.0536	62.78
0.1050	56.36
0.2110	40.12
0.4330	18.05

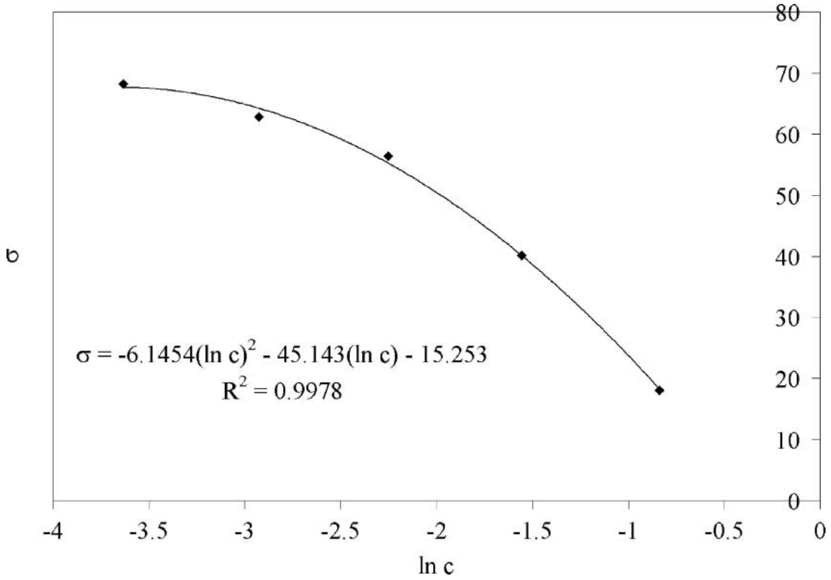

Figure E.6.3.1 Surface tension versus ln *c* graph.

Inserting the value of $\frac{d\sigma}{d(\ln c)}$ into Eq. (6.22), the excess concentration of solute at surface is determined as:

$$\Gamma = -\frac{1}{\left(8314.34\,\frac{J}{\text{kgmole}\cdot K}\right)(293K)}\left(\frac{1J}{1N\cdot m}\right)\left(-16.85\times 10^{-3}\,\frac{N}{m}\right) = 6.92\times 10^{-9}\,\frac{\text{kgmol}}{m^2}$$

6.5 INTERFACIAL TENSION

Surface tension appears in situations involving either free surfaces (liquid–gas or liquid–solid boundaries) or interfaces (liquid–liquid boundaries). If it takes place in interfaces, it is called interfacial tension.

Interfacial tension arises at the boundary of two immiscible liquid due to the imbalance of intermolecular forces. Emulsifiers and detergents function by lowering the interfacial tension. Generally, the higher the interfacial tension, the lower is the solubility of the solvents in each other. Interfacial tension values between water and some organic solvents and oils are given in Table 6.2.

6.6 YOUNG AND DUPRE’ EQUATIONS

In a liquid droplet on a solid surface, the interfacial tensions involving solid–liquid, solid–vapor, and liquid–vapor should be considered (Fig. 6.6). All the interfacial tensions are acting to minimize interfacial energy. The forces acting are balanced at equilibrium and Young’s equation is

Table 6.2 Interfacial Tension Values Between Water and Some Materials

Material	*Temperature (°C)*	*Interfacial Tension (mN/m)*
n-Hexane[a]	20	51.1
Peanut oil[b]	25	18.1
Olive oil[b]	25	17.6
Coconut oil[b]	25	12.8
Mercury[c]	20	375.0

[a] From data of Kaye and Laby (1973).
[b] From data of Powrie and Tung (1976).
[c] From data of Shaw (1970).

obtained:

$$\sigma_{sv} = \sigma_{lv} \cos\theta + \sigma_{sl} \tag{6.23}$$

where θ is the contact angle; σ is surface tension (N/m); and the subscripts s, l, and v denote solid, liquid, and vapor, respectively.

If θ is greater than 90°, the liquid does not wet the solid and tends to move about on the surface and does not enter capillary pores. A liquid completely wets the solid only when θ is zero (Adamson, 1990).

Young's equation relates solid and liquid surface tensions (work necessary to create one solid or liquid surface unity), solid–liquid interfacial tension (work necessary to create one interface unity between solid and liquid), and the contact angle.

An energy balance known as the Dupre' equation defines work of adhesion between solid and liquid. The Dupre' equation relates adhesive and adherent surface tensions and the work of adhesion (W_a) (McGuire, 2005):

$$W_a = \sigma_{sv} + \sigma_{lv} - \sigma_{sl} \tag{6.24}$$

The theory of thermodynamic adsorption was based on Young and Dupree energy equations (Michalski, Desobry, & Hardy, 1997). The thermodynamic adsorption theory was broadly developed by various researchers (Dann, 1970; Fowkes, 1964, 1972, 1983; Girifalco & Good, 1957; Li & Neumann, 1992: Van Oss, Good, & Busscher, 1990). These researchers showed that adhesion was

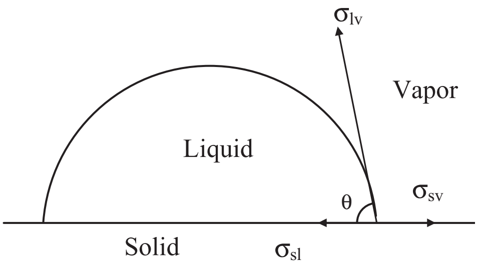

Figure 6.6 Forces involved in Young's equation.

due to electrodynamic intermolecular forces acting at the liquid–liquid, liquid–solid, and solid–solid interfaces. Interfacial attraction was then expressed in terms of reversible work of adhesion related to the surface tensions of materials. The details of mechanisms of adhesion can be found in the review of Michalski et al. (1997).

6.7 COLLOIDAL SYSTEMS IN FOODS

All colloidal systems have two phases: a continuous phase and a discontinuous or dispersed phase. Colloidal dispersion is a two-phase system in which the particles in the dispersed phase are between 1 and 1000 nm in diameter. For this reason, most manufactured foods can be considered as food colloids and many contain hydrocolloids that are added to control stability and rheological properties. Food hydrocolloids are high molecular weight hydrophilic biopolymers used in food products to control their texture, flavor, and shelf-life.

Colloidal systems in foods can be categorized into four groups based on the states of matter constituting the two phases, which are sols, gels, emulsions, and foams.

6.7.1 Sols

A sol can be defined as a colloidal dispersion in which a solid is the dispersed phase and liquid is the continuous phase. Gravy, stirred custard, and other thick sauces can be given as examples of sols. The proper ratio of the ingredients is necessary to achieve the desired viscosity of the sols at a certain temperature. If they are unacceptably thick, they can either be heated or more water can be added to reduce their viscosity.

Pectin is hydrophilic and attracts a layer of water that is bound tightly to the molecules by hydrogen bonds, like other carbohydrates and many proteins. Thus, water forms an insulating shield for the pectin or other hydrophilic colloid, providing a layer that inhibits bonding between the molecules of the colloidal substances (Fig. 6.7). Sols can be transformed into gels as a result of reduction in temperature. The solids in the discontinuous phase move with increasing difficulty through the continuous liquid phase and eventually start to associate with each other. In a pectin gel, the pectin molecules are the continuous phase and the liquid is the dispersed phase while in the pectin sol, the pectin molecules are the dispersed phase and the liquid is the continuous phase. Sols may be formed as a preliminary step in making a gel. Jams and jellies made with pectin are common examples that form a sol prior to the desired gel structure.

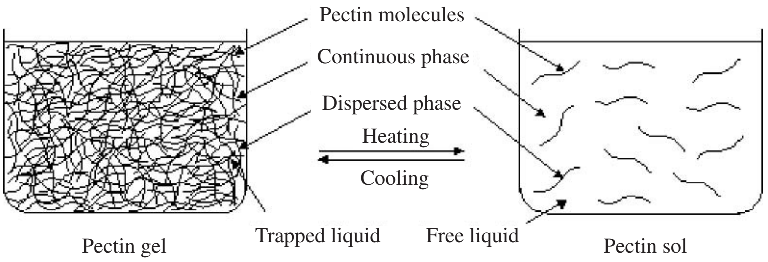

Figure 6.7 Pectin gel and sol.

6.7.2 Gels

A gel is the reverse of a sol in which a solid matrix is the continuous phase and a liquid is the discontinuous phase. The solid in the gel is sufficiently concentrated to provide the structure needed to prevent flow of the colloidal system.

Some of the free liquid may be released if the gel structure is cut. This phenomenon is known as syneresis. The type of solid and its concentration in the gel are important in determining the amount of syneresis. Syneresis may be undesired in some products such as jelly but may be useful in cheese production.

6.7.3 Emulsions

An emulsion is a colloidal system in which a liquid is dispersed as droplets in another liquid with which it is immiscible. Emulsions can be classified as oil-in-water (o/w) and water-in-oil emulsions (w/o). In oil-in-water emulsions, oil is dispersed in water as droplets. The typical example for o/w emulsions is mayonnaise. In water-in-oil emulsions, such as butter, droplets of water are dispersed in oil.

Viscosities of the emulsions are very high as compared to the viscosities of either of the liquids. For example, the viscosity of mayonnaise is higher than that of the vinegar and oil used in preparing mayonnaise. The stability of emulsions can be determined by the viscosity of the continuous phase, the presence and concentration of emulsifier, the size of the droplets, and the ratio of dispersed phase to the continuous phase.

When an emulsion is subjected to some stress such as freezing or centrifugation, it may break. That is, the two liquids separate into discrete phases.

In emulsion systems it is necessary to determine the difference between an emulsifier and a stabilizer (Dickinson, 1992). The emulsifiers aid emulsion formation and short-term stabilization by interfacial action. An emulsifier is a small molecule surfactant that is amphiphilic, having both polar or nonpolar parts, and thus has attraction toward both phases of the emulsion. The emulsifying agent collects around the surface of the dispersed spheres; as a result the droplets cannot touch each other directly and coalescence. Monoglycerides, polysorbates, sucrose esters, and lecithin are examples for emulsifiers. Egg yolk is the best common food naturally containing emulsifying agents. The primary emulsifying agent found in egg yolk is lecithin. Small molecules are not so effective for supplying long-term stability.

The amount of emulsifying agent present has a significant effect on the stability of the emulsion. Enough agent must be present to form a complete monomolecular layer around each droplet but there is no benefit of using more emulsifying agent than the required amount.

Stabilizers, on the other hand, are generally proteins or polysaccharides supplying long-term emulsion stability, possibly by an adsorption mechanism but not necessarily so. The main stabilizing action of food polysaccharides is by modifying viscosity or gelation in aqueous phase. Proteins act as both emulsifier and stabilizer since they have high tendency to adsorb at oil–water interfaces to form stabilizing layers around oil droplets (Dickinson, 2003).

An emulsifier should be surface active, meaning that it has an ability to reduce the surface tension at the oil–water interface. The lower the interfacial tension, the greater the extent to which droplets can be broken up during intense shear or turbulent flow (Walstra & Smulders, 1998).

An amphiphilic characteristic is required for a polymer to be surface-active. If it is a hydrocolloid, it must contain numerous hydrophobic groups. These groups will enable adsorbing molecules to adhere to and spread out at the interface which will protect the newly formed droplets. An ideal emulsifier is composed of species with relatively low molecular weight, with good solubility in aqueous continuous phase. For a biopolymer to be effective in stabilizing dispersed particles or emulsion droplets, it should have a strong adsorption characteristic, complete surface coverage, formation of a thick steric, and charged stabilizing layer (Dickinson, 2003). Strong adsorption implies that the amphiphilic polymer has a substantial degree of hydrophobic character to keep it permanently at the interface. Complete surface coverage means that the polymer is sufficient to fully saturate the surface. Formation of a thick steric stabilizing layer implies that the polymer is hydrophilic and has a high molecular weight (10^4–10^6 Da) within an aqueous medium with good solvent properties. Formation of a charged stabilizing layer implies the presence of charged groups on the polymer that contribute to the net repulsive electrostatic interaction between particle surfaces, especially at low ionic strength.

Proteins are surface-active compounds and comparable with low molecular weight surfactants (emulsifiers). They result in lowering of the interfacial tension of fluid interfaces. Proteins emulsify an oil phase in water and stabilize the emulsion. The increased resistance of oil droplets to coalescence is associated with protein adsorption at the interfacial surface and the formation of interfacial layer having high viscosity. In comparison to the low molecular weight surfactants, proteins have the ability to form an adsorption layer with high strength and increase the viscosity of the medium which results in high stability of emulsion (Garti & Leser, 2001). Low molecular weight surfactants (LMW) commonly used in foods are mono- and diglycerides, polysorbates, sorbitan monostearate, polyoxyethylene sorbitan monostearate, and sucrose esters. They lower the interfacial tension to a greater extent than high molecular weight surfactants such as proteins and gums (Table 6.3). LMW surfactants have higher adsorption energies per unit area than proteins and gums but proteins and gums can adsorb at the interface with several segments. Although LMW surfactants are more effective than the others in reducing interfacial tensions, emulsions formed by them are less stable. This is due to the fact that steric repulsion between the protein-covered oil droplets is very effective against aggregation. In addition, since proteins have higher molecular weight, their adsorption and desorption are slower than the adsorption and desorption of LMW surfactants (Bos & van Vliet, 2001).

Surfactants can be classified as nonionic or ionic according to the charge of the head group. They are also categorized based on their ability to dissolve in oil or water. A measure of this is expressed by hydrophilic/lipophilic balance (HLB). HLB number can be calculated by using the

Table 6.3 General Characteristics of Interfacial Properties of LMW Surfactants and Proteins[a]

Interfacial Properties	*LMW Surfactants*	*Proteins*
Number of molecules	10^{-5} mol/m^2	10^{-7} mol/m^2
Adsorbed amount	1.0–2.0 mg/m^2	2.0–3.0 mg/m^2
Adsorption	Reversible	Practically irreversible
Molecular size and shape	Cylindrical (1 × 1 × 2 nm)	Often globular (4–5 nm)
Conformational changes upon adsorption	No	Yes
Equilibrium interfacial tension at air-water interface	40–22 mN/m	57–47 mN/m
Value of surface tension gradient	High	Low

[a] From Bos, M. A., & van Vliet, T. Interfacial rheological properties of adsorbed protein layers and surfactants: A review. *Advances in Colloid and Interface Science, 91*, 437–471. Copyright © (2001) with permission from Elsevier.

Table 6.4 Ranges of HLB Values for Different Applications.[a]

HLB Value	*Application*
3–6	Emulsifiers of w/o emulsions
7–9	Wetting agents
8–18	Emulsifiers of o/w emulsions
13–15	Detergents
15–18	Solubilizers

[a] From Bos, M. A., & van Vliet, T. Interfacial rheological properties of adsorbed protein layers and surfactants: A review. *Advances in Colloid and Interface Science, 91*, 437–471. Copyright © (2001) with permission from Elsevier.

relationship:

$$\mathrm{HLB} = 7 + \sum \text{hydrophilic group numbers} - \sum \text{lipophilic group numbers} \tag{6.25}$$

HLB value is the rate of the weight percentage of hydrophilic groups to the weight percentage of hydrophobic groups in the emulsifier molecule. Emulsifiers with HLB values below 9 are lipophilic, those with HLB values between 8 and 11 are intermediate, and those with HLB values between 11 and 20 are hydrophilic (Lewis, 1996). Table 6.4 shows the application of surfactants and their HLB values. Diacetyl tartaric acid ester of monoglycerides (DATEM), which is a common emulsifier used in baked products has a HLB value of 9.2 (Krog & Lauridsen, 1976). Sorbitan monostearate, with a HLB value of 5.7, can be used in cake mixes and cacao products.

Generally a combination of emulsifiers is necessary to achieve a stable emulsion. HLB value of a mixed emulsifier system $(\mathrm{HLB})_\mathrm{m}$ containing emulsifier A and B can be calculated by using HLB values ($\mathrm{HLB_A}$ and $\mathrm{HLB_B}$) and mass fraction (X_A^w and X_B^w) of individual emulsifiers:

$$(HLB)_m = X_A^w(HLB_A) + X_B^w(HLB_B) \tag{6.26}$$

Some food hydrocolloids are sufficiently surface active and act as emulsifying agents in oil-in-water emulsions. Their emulsifying properties come from the proteinaceous material covalently bound or physically associated with carbohydrate polymer. The emulsions produced are coarser than those with low molecular weight water soluble surfactants or milk proteins at the same emulsifier/oil ratio. After hydrocolloids are strongly adsorbed at the oil–water interface, hydrocolloids can be more effective than proteins or others. Polysaccharides affect emulsion stabilization by increasing the viscosity of the dispersing phase and surface adsorption. Surface tension values of several gums are given in Table 6.5.

Locust bean gum and guar gum were shown to decrease the surface tension of water at low concentrations (up to 0.5%) and surface tension of gum solutions was time dependent. Surface tensions decreased and adsorption rates increased significantly by increasing gum concentration (Garti & Leser, 2001).

Guar gum and locust bean gum are used for their thickening, water holding, and stabilizing properties. Although there are no hydrophobic groups in these gums, they function by modifying the rheological properties of aqueous phase.

Xanthan gum is used as a thickening agent in foods. Xanthan gum is used as a stabilizer for oil-in-water emulsions. It was proposed by some researchers that its stabilizing ability comes from the viscosity effect (Coia & Stauffer, 1987; Ikegami, Williams, & Phillips, 1992). The adsorption

Table 6.5 Surface Tension Values of Selected Gums[a]

Gum	*Gum Weight (%)*	*σ (mN/m)*
Tragacanth	0.6	42
Xanthan	0.6	43
Guar	0.7	55
Locust bean gum	0.7	50

[a] From Garti, N., & Leser, M.E. Emulsification Properties of Hydrocolloids. *Polymers for Advanced Technologies, 12*, 123–135. Copyright © (2001) with permission from John Wiley & Sons.

characteristic of xanthan gum was also studied. In general, the adsorption of gum onto liquid droplets needs different requirements than proteins. The steric stabilization of proteins on oil–water droplets cannot be observed in hydrocolloids since they lack the flexibility to reorient at the surface and hydrophobic moieties.

A possible adsorption mechanism of hydrophilic compounds onto the oil–water interphase is not well known. On the other hand, proteins containing hydrocolloids are good steric stabilizers because they contain a significant proportion of flexible hydrophobic groups to act as anchoring points and many hydrophilic groups to form the stabilizing chains. However, most polysaccharide polymers are sufficiently hydrophilic to be regarded as nonadsorbing.

6.7.4 Foams

Foams can be defined as a colloidal dispersion in which gas is the dispersed phase and liquid is the continuous phase. The dispersion medium is usually a liquid that is sometimes modified into a solid by heating or strengthened by a solid. Ice cream, whipped cream, or cake batter are some examples of foams. There is usually a third phase such as oil or fat in foam used in food systems. Foams are important because of their contribution to volume and texture of food products.

The inclusion of air reduces the density of the product. The term overrun is used in relation to foams to describe the amount of air incorporated. It is defined as the percentage increase in volume attributed to air and expressed as:

$$\text{Overrun} = \frac{V_f - V_l}{V_l}100 \tag{6.27}$$

where V_f is the volume of the foam and V_l is the volume of the original liquid.

Liquids should have low surface tension to form foams. As a result of low surface tension, the liquid can be stretched or spread easily and does not coalescence. If the surface tension is high, formation of the foam will be difficult because of its resistance to spreading and strong tendency to expose the least surface area. If the liquid has high surface tension, the foam collapses quickly as a result of the tendency to coalescence.

Liquids should have low vapor pressure to prevent evaporation. This will help retain the gaseous phase within the liquid and minimize its tendency to break out into the surrounding medium.

Stability can be provided to foams if some solid matter can be incorporated into the films to increase the rigidity of the walls surrounding the gas. In protein foams, the denaturation of the protein provides stability to cell walls.

Table 6.6 The Relevance of the Surface and Bulk Properties to Bread Baking

Stage in Bread Baking Process	*Surface Tension*	*Strain-Hardening*	*Resistance to Extension*	*Extensibility*
Mixing	+	−	−	−
First proof	++	++	++	−
Final proof	−	++	+	+
Baking	?	++	+	++

++, very relevant; +, relevant; − , not relevant. From Kokelaar et al. (1994).

The interfacial properties of foam-based products are controlled by competition between surface-active agents that adsorb at the oil–water and air–water interfaces in these systems. Static (equilibrium) interfacial tension, dynamic interfacial properties, interfacial rheology, diffusion, and adsorption and desorption properties of the surfactants and proteins are important for the stability of foam-based foods (Xu, Nikolov, Wasan, Gonsalves, & Borwankar, 2003).

If a bubble in foam is considered, there are two forces acting on the bubble—dynamic forces and surface tension forces. The dynamic forces can be regarded as shear stress. The ratio of these forces, which is the Weber number, is used to determine the maximum stable bubble size possible (Walstra, 1983):

$$\mathrm{We} = \tau \frac{D_{\max}}{\sigma} \tag{6.28}$$

where τ is shear stress, σ is surface tension, and D is the diameter of the bubble.

During bread making in the mixing stage, air bubbles are entrapped in the gluten network. If We is greater than $\mathrm{We}_{\mathrm{critical}}$ the bubble breaks. The critical Weber number depends on the type of flow and the ratio of viscosity of gas in the bubble (gas) to that of continuous phase (dough). Lipids and added surfactants will lower the minimum air bubble radius formed during mixing which may lead to more and smaller bubbles in the dough resulting in a finer crumb structure. After mixing, the growth of large bubbles at the expense of smaller ones will occur, which is called disproportion. This can be retarded by the addition of surfactants. If the dough has enough strain-hardening properties, the gas bubbles that are large enough to expand at the existing carbon dioxide partial pressure will have a narrow bubble size distribution. This will lead to a regular crumb structure in the product (Kokelaar, Van Vliet, & Prins, 1994). The relevance of the surface and bulk properties to bread baking were studied and are summarized in Table 6.6.

6.8 MEASUREMENT OF CONTACT ANGLE AND SURFACE TENSION

6.8.1 Contact Angle Measurement Methods

Contact angle can be measured with a contact angle goniometer. This instrument consists of a light source, an illuminating stage on which the liquid drop–solid material three-phase system (liquid, vapor, solid) rests, and a telescope. By viewing the drop through the telescope, the contact angle is measured.

An inexpensive instrument of a video-based contact angle meters is also available to measure contact angle (McGuire, 2005). A detailed discussion about measurement of contact angle can be found in Michalski et al. (1997).

6.8.2 Surface Tension Measurement Methods

The methods for measuring surface tension are capillary rise, drop weight, bubble pressure, tensiometer, and dynamic methods. The same methods with certain modifications can be used for measuring interfacial tension.

The capillary rise method is a simple method. However, it is limited to the measurement of surface tension of pure liquids (Aveyard & Haydon, 1973). In the capillary rise method, a capillary tube is immersed in liquid vertically which then rises to a height h inside the tube. When equilibrium is reached, the upward forces of surface tension balance the downward forces due to the height of the column of liquid. Then:

$$\sigma = \frac{\rho_l\, g\, h\, r_t}{2\cos\theta} \tag{6.8}$$

In the case of mercury, there may be a complete nonwetting of surface where angle of contact is 180° which leads $\cos\theta$ to be (–1). This causes capillary depression.

In the drop weight method, either the weight or the volume of the drop formed at the end of a capillary tube is measured. The droplet will grow to a size at which its weight overcomes the surface tension force. At this moment, the droplet will detach from the tube and its weight can be measured by collecting it in a small pan and weighing it. By equating the forces acting on the droplet, surface tension force, and gravitational force as the droplet breaks, surface tension can be determined as:

$$\sigma = \frac{mg}{2\pi\, r_t} \tag{6.29}$$

where m is the mass of the droplet and r_t is the external radius of the capillary tube.

This equation is an approximation since in practice the entire drop never falls completely from the tip. Therefore, a correction factor (F) is incorporated into Eq. (6.29) (James, 1967).

$$\sigma = \frac{Fmg}{r_t} \tag{6.30}$$

Problems of absolute determinations can also be overcome by using a fluid of known surface tension. If m_1 and m_2 are the drop masses of two fluids of surface tension σ_1 and σ_2, then the ratio can be written as:

$$\frac{\sigma_1}{\sigma_2} = \frac{m_1}{m_2} \tag{6.31}$$

There are some studies in literature in which the drop weight method was used to determine surface tension of whole and skim milk (Bertsch, 1983) and milk protein solutions (Arnebrant & Naylander, 1985).

For measuring surface tension of viscous and heterogeneous fluids such as batter, the bubble pressure method is used. In this method, a capillary tube is immersed into the sample (Fig. 6.8). Distilled water is then dropped into a vertical sigmoidal tube connected to a capillary to increase its internal pressure. A small bubble is formed at the end of capillary and floated to the surface of the product. When the radius of curvature is minimum, surface tension of the sample is calculated from the internal pressure

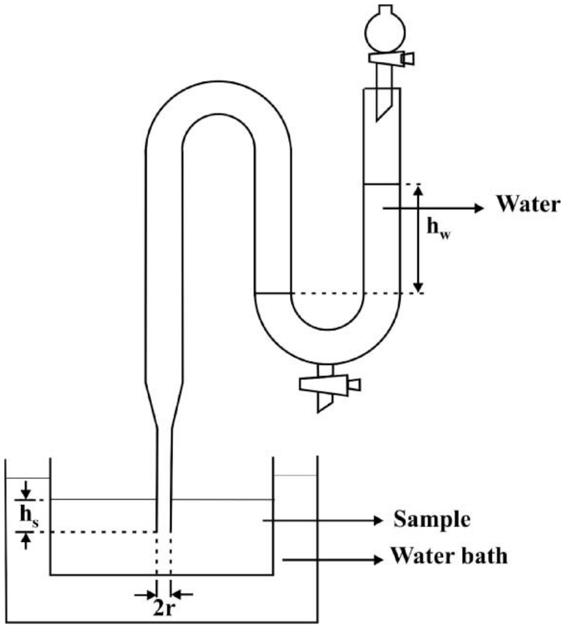

Figure 6.8 Bubble method. [From Sasaki,K., Shimaya, Y., Hatae, K., & Shimada, A. Surface tension of baked food batter measured by the maximum bubble pressure method. *Agricultural & Biological Chemistry, 55*, 1273–1279. Copyright © (1991) with permission from Japan Society for Bioscience, Biotechnology and Agrochemistry.]

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of bubble by using the Laplace equation:

$$\rho_w g h_w - \rho_s g h_s = \frac{2\sigma}{r} \tag{6.32}$$

where h_w is the height difference between water surfaces in the sigmoidal tube, h_s is the length from the sample surface to the capillary, ρ_w is the water density, and ρ_s is the sample density.

Surface tensions of solutions containing surface-active compounds can be determined by the Du Nouy ring tensiometry method. In the literature, various studies are described in which this method was used to measure surface tension of oils (Flingoh & Chong Chiew, 1992), milks (Duthie & Jenson, 1959; Watson, 1956, 1958), aqueous solutions of hydroxymethylcellulose (HPMC) (Riedl, Szklenarik, Zelko, Marton, & Racz, 2000), and chitosan coating solution (Choi, Park, Ahn, Lee, & Lee, 2002).

In the Du Nouy method, a platinum ring is suspended above the liquid sample. It is dipped into the sample and pulled out. The force necessary to pull the ring through the surface is measured. The equation for the ring method is:

$$\sigma = \frac{mg}{2c} \tag{6.33}$$

where m is the mass and c is the circumference of the ring.

Equation (6.33) gives apparent surface tension and it is necessary to use a correction factor. The magnitude of the correction factor depends on the dimension of the ring and density of the liquid. The correction factors are supplied with the manufacturer of the instrument. This method gives static surface tension for fast-adsorbing substances. Otherwise, it gives dynamic surface tension.

The oscillating jet method is a dynamic method that is used to determine the surface tension of skim milk (Kubiak & Dejmek, 1993). This method is based on the mechanical instability in a jet of liquid sample emerging from an elliptical orifice. The circular shape of the drops tends to be restored by sample surface tension. However, as a result of the liquid inertia, oscillations around a circular cross-sectional shape occur. A parallel light beam applied perpendicular to the jet axis will then deviate on the drops. Then, sample surface tension can be calculated from oscillation wavelength (λ) (distance between the observed stripes), flow rate (Q), sample density (ρ_s), and mean radius of the jet (r) which is the average of maximum and minimum radii $r_{\max}$ and $r_{\min}$:

$$\sigma = \frac{4}{6}\frac{\rho_s Q^2\left[1+\frac{37}{24}\left(\frac{r_{\max}-r_{\min}}{r_{\max}+r_{\min}}\right)^2\right]}{r\lambda^2\left[1+\frac{5}{3}\pi^2\frac{r^2}{\lambda^2}\right]} \tag{6.34}$$

Example 6.4. The capillary tube method was used to measure the surface tension of liquid helium-4 which has a density of 145 kg/m^3. A tube of radius 1.1 mm was immersed to a depth of 3.56 cm and the pressure was read as 51.3 Pa. If the contact angle is 0°, calculate the surface tension of liquid helium-4.

Solution:

Using Eq. (6.6):

$$\sigma = \frac{\Delta\,\mathrm{Pr}_t}{2\cos\theta}$$

For 0° contact angle $\cos\theta = 1$

$$\Delta P = P - \rho g h$$

Then:

$$\sigma = \frac{(P-\rho g h)\,r_t}{2}$$

$$\sigma = \frac{\left[51.3\,\mathrm{Pa} - (145\,\mathrm{kg/m^3})(9.81\,\mathrm{m/s^2})(3.56\times10^{-2}\,\mathrm{m})\right](1.1\times10^{-3}\,\mathrm{m})}{2}$$

$$\sigma = 3.63\times10^{-4}\,\mathrm{N/m}$$

Example 6.5. Pressure (gauge) of 2.91 MPa was necessary to blow water out of a glass filter with uniform pore width. What will be the mass of the drops leaving the filter at 20°C if the surface tension at that temperature is 0.07275 N/m? The density of water at 20°C is 997 kg/m^{3}and the contact angle is 0°.

Solution:

Using Eq. (6.6):

$$\Delta P = \frac{2\sigma\cos\theta}{r_t} \tag{6.6}$$

$$\cos\theta = 1$$

Then:

$$\Rightarrow r_t = \frac{2\left(0.07275\,\frac{\text{N}}{\text{m}}\right)(1)}{2.91 \times 10^6\,\text{Pa}} = 5 \times 10^{-8}\,\text{m}$$

The volume of the spherical drop can be calculated as:

$$\begin{aligned} V &= \frac{4}{3}\pi r^3 \\ &= \frac{4}{3}\pi\left(5 \times 10^{-8}\right)^3 \\ &= 5.23 \times 10^{-22}\,\text{m}^3 \end{aligned}$$

Multiplying the determined volume by the density of the drop, the mass of the drop is found as:

$$\begin{aligned} m &= \rho V \\ &= \left(997\,\frac{\text{kg}}{\text{m}^3}\right)\left(5.24 \times 10^{-22}\,\text{m}^3\right) \\ &= 5.22 \times 10^{-19}\,\text{kg} \end{aligned}$$

PROBLEMS

6.1. A water droplet has a radius of 2×10^{-8} m. The surface tension of water at 30°C is 0.07 N/m. If the vapor pressure of a flat surface of water is 3160 Pa at 30°C, calculate the vapor pressure of water at that temperature.

6.2. Using a capillary rise method, the surface tension of olive oil was measured as 33×10^{-3} N/m. The height of rise in capillary glass tube that has a radius of 0.05 mm is 0.1 m. If the oil density is 800 kg/m^3, calculate the contact angle.

6.3. To find the degree of supersaturation required to nucleate water droplets spontaneously, water vapor is rapidly cooled to 20°C. It is found that the vapor pressure of water must be five times its equilibrium vapor pressure. If the surface tension of water is 73×10^{-3} N/m, calculate the radius of the water droplet formed at this degree of supersaturation.

6.4. Calculate the surface tension of milk if the height of rise of milk in a capillary of radius 0.001 cm is 30 cm and the contact angle is 70° ($\rho_{\text{milk}} = 1030$ kg/m^3).

6.5. An open glass tube that has a radius of 1 mm is inserted vertically into a dish of mercury at 20°C. Is there a rise or depression in the capillary? Calculate the amount of rise or depression. **Data:** Density of mercury: 13,600 kg/m^3, surface tension of mercury: 4.66×10^{-1} N/m, $\theta = 130°$

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