CHAPTER

# Physical properties of food materials

# 1

## 1.1 INTRODUCTION

Dr. Alina Szczesniak defined the physical properties of foods as "those properties that lend themselves to description and quantification by physical rather than chemical means" (Szczesniak, 1983). This seemingly obvious distinction between physical and chemical properties reveals an interesting historical fact. Indeed, until the 1960s, the chemistry and biochemistry of foods were by far the most active areas of food research. The systematic study of the physical properties of foods (often considered a distinct scientific discipline called "food physics" or "physical chemistry of foods") is of relatively recent origin.

The physical properties of foods are of utmost interest to the food engineer, for many reasons:

- Many of the characteristics that define the quality (e.g., texture, structure, and appearance) and stability (e.g., water activity) of a food product are linked to its physical properties.
- One of the most active areas of "cutting edge" food research deals with the development of foods with novel physical structures. The incorporation of man-made nanoscale elements is one example of application in this area which requires in-depth understanding of physical structure.
- Quantitative knowledge of many of the physical properties, such as thermal conductivity, density, viscosity, specific heat, enthalpy, and many others, is essential for the rational design and operation of food processes and for the prediction of the response of foods to processing, distribution, and storage conditions. These are sometimes referred to as "engineering properties," although most physical properties are significant from the product quality and process engineering points of view.

In recent years, the growing interest in the physical properties of foods is conspicuously manifested. A number of books dealing specifically with the subject have been published (e.g., Mohsenin, 1980; Peleg and Bagley, 1983; Jowitt, 1983; Lewis, 1990; Balint, 2001; Scanlon, 2001; Walstra, 2003; Sahin and Sumnu, 2006; Figura and Teixeira, 2007; Belton, 2007; Lillford and Aguilera, 2008; Rahman, 2009; Arana, 2012). The number of scientific meetings on related subjects held every year is considerable. Specific courses on the subject are being included in most food science, engineering, and technology curricula.

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Some of the “engineering” properties will be treated in connection with the unit operations where such properties are particularly relevant (e.g., viscosity and rheology in fluid flow, particle size in size reduction, thermal properties in heat transfer, diffusivity in mass transfer, etc.). Properties of more general significance and wider application are discussed in this chapter.

## 1.2 MASS, VOLUME, AND DENSITY

Some of the most important characteristics of foods are physical attributes such as size, shape, volume, weight, density, and appearance (color, turbidity, and gloss). Most of these properties are immediately perceivable and easily measurable.

*Density* is the mass per unit volume. Its symbol is the Greek letter $\rho$ and its units in the SI system are kg $m^{-3}$. If $m$ (kg) is the mass and $V$ ($m^3$) is the volume, then:

$$\rho = \frac{m}{V} \tag{1.1}$$

*Specific gravity* (also known as *relative density*) is the ratio of the density of a substance to the density of another substance taken as reference. Nearly always the reference material is water. Unlike density, specific gravity is dimensionless.

Density is an important engineering property as it appears in almost every equation describing a process where mass and gravity are involved. At the same time, it is a factor that must be taken into account in technological considerations. For example, the density of a finished product must be known and controlled, as food packages are most often filled volumetrically but sold by weight.

Density of foods is usually determined by straightforward but often inaccurate methods including the Archimedes technique of liquid displacement. In some cases, density can be evaluated from chemical composition. Iezzi et al. (2013) found that the true density of cheese can be predicted quite accurately, using linear equations based on composition, provided that the air content is taken into account. Nondestructive methods based on X-ray imaging, including computed X-ray tomography and X-ray linear attenuation (Kelkar et al., 2015; Guelpa et al., 2016), have been found to compare with traditional methods within 10%. Methods for the prediction of density, based on three-dimensional (3D) scanning of the food volume, have been proposed (Kelkar et al., 2011; Uyar and Erdoğdu, 2009).

In *porous foods*, one distinguishes between the *apparent density* (density of the food including the pores) and the *true density* (density of the solid matrix without the pores). *Bulk density* is used to characterize powders. It depends on the relative position of the powder particles inside the interparticle void space. Two values of powder bulk density are measured. *Loose bulk density* is the bulk density of noncompressed powder. Tap bulk density is the bulk density of powder compressed by tapping. The ratio of tap density to loose density is known as the *Hausner Ratio*. It is an important characteristic, extensively used to predict compressibility and flowability of powders

(Barbosa-Cánovas et al., 2005). Román-Ospino et al. (2016) describe a method based on near-infrared spectroscopy for real-time monitoring of powder bulk density.

Density data for various materials are given in Table A.3 (Appendix).

## 1.3 MECHANICAL PROPERTIES

### 1.3.1 DEFINITIONS

By mechanical properties, we mean those properties that determine the behavior of food materials when subjected to external forces. As such, mechanical properties are relevant both to processing (e.g., conveying, size reduction) and to consumption (texture, mouth feel).

The forces acting on the material are usually expressed as *stress*, that is, intensity of the force per unit area (N $\text{m}^{-2}$ or Pa). The dimensions and units of stress are like those of pressure. Very often, but not always, the response of materials to stress is deformation, expressed as *strain*. Strain is usually expressed as a dimensionless ratio, such as the elongation as a percentage of the original length. The relationship between stress and strain is the subject matter of the science known as *rheology* (Steffe, 1996).

We define three ideal types of deformation (Szczesniak, 1983):

- *Elastic deformation*: This kind of deformation appears instantly with the application of stress and disappears instantly with the removal of stress. For many materials, the strain is proportional to the stress, at least for moderate values of the deformation. The condition of linearity, called Hooke's Law (Robert Hooke, 1635–1703, English scientist), is formulated in Eq. (1.2):

$$E=\frac{\text{Stress}}{\text{Strain}}=\frac{F/A_0}{\Delta L/L_0} \tag{1.2}$$

where:

$E$ = Young's modulus (after Thomas Young, 1773–1829, English scientist) (Pa).
$F$ = force applied ($N$).
$A_0$ = original cross-sectional area ($\text{m}^2$).
$\Delta L$ = elongation (m).
$L_0$ = original length (m).

- *Plastic deformation*: This kind of deformation does not occur as long as the stress is below a limit value known as *yield stress*. Deformation is permanent, that is, the body does not return to its original size and shape when the stress is removed.
- *Viscous deformation*: This kind of deformation (flow) occurs instantly with the application of stress and it is permanent. The *rate* of strain is proportional to the stress (see Chapter 3).

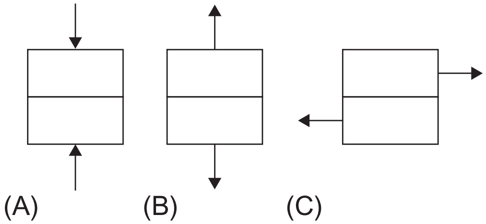

**FIG. 1.1**

Types of stress. (A) Compression, (B) tension, and (C) shear.

The types of stress are classified according to the direction of the force in relation to the material. *Normal stresses* are those that act in a direction perpendicular to the material's surface. Normal stresses are *compressive* if they act toward the material and *tensile* if they act away from it. *Shear stresses* act in a direction parallel (tangential) to the material's surface (Fig. 1.1).

The increase in the deformation of a body under constant stress is called *creep*. The decay of stress with time, under constant strain, is called *relaxation*.

Many of the important quality attributes, collectively known as "texture," actually reflect the mechanical properties of foods. The objective study of food texture is therefore based on the quantitative determination of basic mechanical properties with the help of appropriate instruments (Steffe, 1996).

### 1.3.2 RHEOLOGICAL MODELS

The stress-strain relationship in food materials is usually complex. It is therefore useful to describe the real rheological behavior of foods with the help of simplified mechanical analogs or mathematical expressions (Pomeranz and Meloan, 2000; Myhan et al., 2012). The mechanical analogs are constructed by connecting ideal elements (elastic, viscous, friction, rupture, etc.) in series, in parallel, or in combinations of both. The ideal solid (elastic) behavior is graphically represented as a spring, while the ideal fluid (viscous) behavior is introduced as a dashpot. Models consisting of a combination of springs and dashpots represent *viscoelastic* behavior. Some of these models are shown in Fig. 1.2. The mechanical models are useful in the development of mathematical models (equations) for the description and prediction of the complex rheological behavior of foods. The Maxwell model and the Kelvin model are used to simulate stress relaxation and creep, respectively (Figura and Teixeira, 2007). More complex rheological behavior is simulated, adding to the mechanical model, slides (representing friction), and shear pins (representing limit flow).

The technique known as "dynamic mechanical analysis" (abbreviated as DMA) is extensively used to study viscoelastic behavior. In DMA, a sinusoidal oscillating stress $\sigma$ is applied to the sample and the response (strain $\varepsilon$) of the material is recorded (Menard, 2008). In the case of an ideal elastic material, the recorded strain $\varepsilon$ is in

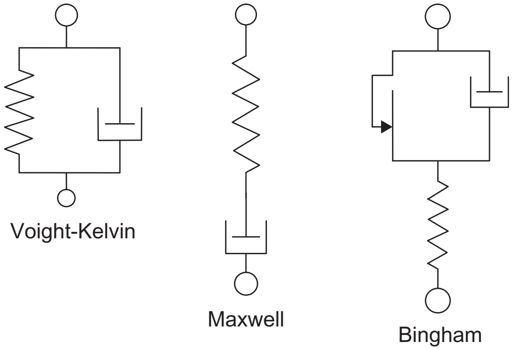

**FIG. 1.2**

Three rheological models.

phase with the applied stress $\sigma$. In a purely viscous material, the strain lags after the stress by 90 degrees. In the case of a viscoelastic material, the lag angle $\delta$ will be between 0 and 90 degrees (Eqs. 1.3a, 1.3b).

$$\varepsilon = \varepsilon_0 \sin(\omega t) \tag{1.3a}$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \tag{1.3b}$$

where $\omega$ is the oscillation frequency and $t$ is time.

Two tensile moduli are defined as follows (Eqs. 1.4a, 1.4b):

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos\delta \tag{1.4a}$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin\delta \tag{1.4b}$$

$E'$ is the "storage modulus," representing the elasticity and $E''$ is the "loss modulus" representing viscosity (portion of the energy converted to heat). The ratio of $E''$ to $E'$ is the tangent of the lag angle $\delta$. In a similar manner, two moduli, $G'$ and $G''$, are defined for shear. $G'$ and $G''$ are frequently used in the study of dough rheology by DMA.

DMA measurements can be taken at constant or varying temperature. Techniques for DMA at varying temperature are known as TMA (thermomechanical analysis). One application of TMA is in the determination of the glass transition temperature (see Section 2.8).

## 1.4 THERMAL PROPERTIES

Almost every process in the food industry involves thermal effects such as the heating, cooling, or phase transition. The thermal properties of foods are therefore of considerable relevance in food process engineering. The following properties are of particular importance: thermal conductivity, thermal diffusivity, specific heat, latent heat of phase transition, and emissivity. A steadily increasing volume of information on experimental values of these properties is available in various texts (e.g., Mohsenin, 1980; Choi and Okos, 1986; Rahman, 2009) and electronic databases. In addition, theoretical or empirical methods have been developed for the prediction of these properties in the light of the chemical composition and physical structure of food materials.

*Specific heat*, $c_p$ (kJ $\text{kg}^{-1}$ $\text{K}^{-1}$), is among the most fundamental of thermal properties. It is defined as the quantity of heat (kJ) needed to increase the temperature of one unit mass (kg) of the material by one degree (K) at constant pressure. The specification of "at constant pressure" is relevant to gases where the heat input needed to cause a given increase in temperature depends on the process. It is practically irrelevant in the case of liquids and solids. A short survey of the methods for the prediction of specific heat is included below. Most of the other thermal properties of foods are defined and discussed in detail in Chapter 3, dealing with transport phenomena.

The definition of specific heat can be formulated as follows:

$$c_p = \frac{1}{m}\left(\frac{dQ}{dT}\right)_P \tag{1.5}$$

The specific heat of a material can be determined experimentally by static (adiabatic) calorimetry or differential scanning calorimetry or calculated from measurements involving other thermal properties. It can be also predicted quite accurately with the help of a number of empirical equations.

The simplest model for solutions and liquid mixtures assumes that the specific heat of the mixture is equal to the sum of the pondered contribution of each component. The components are grouped in classes: water, salts, carbohydrates, proteins, and lipids. The specific heat, *relative to water*, is taken as: salts = 0.2; carbohydrate = 0.34; proteins = 0.37; lipids = 0.4; water = 1. The specific heat of water is 4.18 kJ $\text{kg}^{-1}$ $\text{K}^{-1}$. The specific heat of a solution or liquid mixture is therefore:

$$c_p = 4.18\left(0.2X_{\text{salt}} + 0.34X_{\text{carbohyd}} + 0.37X_{\text{prot}} + 0.4X_{\text{lip}} + X_{\text{water}}\right) \tag{1.6}$$

where $X$ represents the mass fraction of each of the component groups (Rahman, 2009).

For mixtures that approximate solutions of sugar in water (e.g., fruit juices), Eq. (1.6) becomes:

$$c_p = 4.18\left[0.34X_{\text{sugar}} + 1\left(1 - X_{\text{sugar}}\right)\right] = 4.18\left(1 - 0.66X_{\text{sugar}}\right) \tag{1.7}$$

Another frequently used model assigns to the total dry matter of the mixture a single relative specific value of 0.837 kJ $\text{kg}^{-1}$. The resulting approximate empirical expressions for temperatures above and below freezing are given in Eq. (1.8):

$$\begin{aligned} c_p &= 0.837 + 3.348X_{\text{water}} \quad \text{for temperatures above freezing} \\ c_p &= 0.837 + 1.256X_{\text{water}} \quad \text{for temperatures below freezing} \end{aligned} \tag{1.8}$$

### EXAMPLE 1.1

Meat loaf contains 21% protein, 12% fat, 10% carbohydrates, 1.5% minerals (salt), and 0.555% water. Estimate the specific heat of the loaf.

#### Solution

We substitute the data in Eq. (1.6):

$$C_P = 4.18(0.2 \times 0.015 + 0.34 \times 0.1 + 0.37 \times 0.21 + 0.4 \times 0.12 + 0.555) = 3.00\,\mathrm{kJ/kgK}$$

### EXAMPLE 1.2

Estimate the specific heat of 65 Bx. orange juice concentrate.

#### Solution

We consider the concentrate as a solution of sugar in water and we read 65 Bx. as 65% sugar w/w. We apply Eq. (1.7):

$$C_P = 4.18(1 - 0.66 \times 0.65) = 2.39\,\mathrm{kJ/kgK}$$

### EXAMPLE 1.3

Raw salmon contains 63.4% water. Estimate, approximately, the specific heat of salmon at temperatures above freezing and below freezing.

#### Solution

Since an approximate solution is acceptable, we shall apply Eq. (1.8):

$$c_p = 0.837 + 3.348 \times 0.634 = 2.96\,\mathrm{kJ/kgK} \quad \text{for temperatures above freezing}$$
$$c_p = 0.837 + 1.256 \times 0.634 = 1.63\,\mathrm{kJ/kgK} \quad \text{for temperatures below freezing}$$

## 1.5 ELECTRICAL PROPERTIES

The electrical properties of foods are particularly relevant to microwave and ohmic heating of foods and to the effect of electrostatic forces on the behavior of powders. The most important properties are electrical conductivity and the dielectric properties. These are discussed in Chapter 3, in relation to ohmic heating and microwave heating, respectively.

## 1.6 STRUCTURE

Very few foods are truly homogeneous systems. Most foods consist of mixtures of distinct physical phases in close contact with each other. The heterogeneous nature of foods may be visible to the naked eye or perceived only when examined under a microscope or electron microscope. In foods, the different phases are seldom in complete equilibrium with each other and many of the desirable properties of "fresh" foods, such as the crispiness of fresh bread crust, are due to the lack of equilibrium between the phases. The structure, microstructure, and lately nanostructure of foods are extremely active areas of research (e.g., Skytte et al., 2015; Aguilera, 2011; Kokini, 2011; Markman and Livney, 2011; Frisullo et al., 2010; Anon, 2008; Chen et al., 2006; IFT, 2006; Graveland-Bikker and de Kruif, 2006; Garti et al., 2005; Morris, 2004).

Following are some of the different structural elements in foods.

1. Cellular structures: Vegetables, fruits, and muscle foods consist in large part of cellular tissue. The characteristics of the cells and more particularly of the cell walls determine the rheological and transport properties of cellular foods. One of the characteristics particular to cellular foods is *turgidity* or *turgor pressure*. Turgor is the intracellular pressure resulting from osmotic differences between the cell content and the extracellular fluid (Taiz and Zeiger, 2006). This is the factor responsible for the crisp texture of fruits and vegetables and for the "fleshy" appearance of fresh meat and fish. Cellular food structures may also be created artificially. Wheat bread consists of gas-filled cells with distinct cell walls. The numerous puffed snacks and breakfast cereals produced by extrusion owe their particular crispiness to their cellular structure with brittle cell walls (see "Foams" below.)
2. Fibrous structures: In this context, we refer to physical fibers, that is, to solid structural elements with one dimension much larger than the other two, and not to "dietary fiber," which is a notion related to dietary function. The most obvious of the fibrous foods is meat. Indeed, protein fibers are responsible for the chewiness of muscle foods. The creation of a man-made fibrous structure is the main challenge of the meat analog developer.
3. Gels: Gels are macroscopically homogeneous colloidal systems, where dispersed particles (generally polymeric constituents such as polysaccharides or proteins) have combined with the solvent (generally water) to create a tridimensional semirigid solid structure. Gels are usually produced by first dissolving the polymer in the solvent than changing the conditions (cooling, concentration, and cross-linking) so that the solubility is decreased (Banerjee and Bhattacharya, 2012). Gelation is particularly important in the production of set yogurt, dairy desserts, custard, tofu, jams, and confectionery. The structural stability of food gels subjected to shear and certain kinds of processing (e.g., freezing-thawing stability) is an important consideration in product formulation and process design.
4. Emulsions: Emulsions (Dickinson, 1987; McClements, 2005) are intimate mixtures of two mutually immiscible liquids, where one of the liquids is dispersed as fine globules in the other (Fig. 1.3). In the case of foods, the two liquid media are, in most cases, fats, and water.

   Two possibilities exist for emulsions consisting of oil and water:

   a. The dispersed phase is oil (oil-in-water, o/w emulsions). This is the case of milk, cream, sauces, and salad dressings.

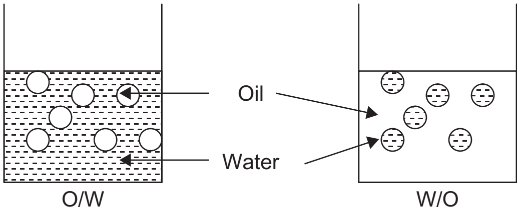

**FIG. 1.3**

Schematic structure of oil-in-water and water-in-oil emulsions.

**b.** The dispersed phase is water (water-in-oil, w/o emulsions). Butter and margarine are w/o emulsions.

Emulsions are not thermodynamically stable systems (Macclements, 2007). They do not form spontaneously. Emulsification requires energy input (mixing, homogenization) in order to shear one of the phases into small globules and disperse them in the continuous phase (see Section 7.6). Emulsions tend to break apart as the result of coalescence (fusion of the dispersed droplets into larger ones) and creaming (separation of the original emulsion into a more concentrated emulsion or cream, and some free continuous phase). Emulsions are stabilized with the help of surface-active agents known as emulsifiers.

**5.** Foams: Foams are cellular structures consisting of gas (air) filled cells and liquid cell walls (Bikerman, 1973). Owing to surface forces, foams behave like solids. Ice cream is essentially frozen foam, since almost half of its volume is air. Highly porous solid foods, such as many cereal products, may be considered as solid foams (Guessasma et al., 2011). Foams with specific characteristics (bubble size distribution, density, stiffness, and stability) are important in milk containing beverages and beer. On the other hand, the spontaneous excessive foaming of some liquid products (e.g., skim milk) during transportation and processing may create serious engineering problems. Undesired foaming is controlled by proper design of the equipment, mechanical foam breakers, or through the use of food grade chemical antifoaming (prevention) and defoaming (foam abatement) agents such as oils and certain silicone-based compounds.

**6.** Powders: Solid particles, 10–1000 μm in size, are defined as powders (Barbosa-Cánovas et al., 2005). Smaller particles are conventionally called “dust” and larger particles are “granules.” Some food products and many of the raw materials of the food industry are powders. Powders are produced by size reduction, precipitation, crystallization, or spray drying. One of the main issues related to powders in food engineering is the flow and transportation of particulate materials, discussed in Chapter 3.

**7.** Nanostructure: Natural structural/functional elements measuring a few nanometers occur abundantly in all foods (Magnuson et al., 2011). Nanoemulsions, casein micelles, and very thin films measuring a few nanometers in thickness are but a few examples of nanomaterials naturally present in foods.

Although the study of the occurrence, structure, and function of natural nanomaterials is of considerable importance, "food nanotechnology" deals primarily with the creation of man-made nanoelements that can perform, because of their size and structure, specific useful functions in foods (Weiss et al., 2006). Many of these elements can be prepared from food biopolymer systems, taking advantage of the capability of these systems to form nanoparticles of specific shape through mechanisms of *self-assembly*. Following are a few of the potential applications of engineered nanoelements in the food industry:

- Nanosizing of antimicrobial agents to enhance their effectiveness (Weiss et al., 2009). One of the most promising applications is the incorporation of nanosized silver (Chen and Schluesener, 2008).
- Nanoemulsification to improve dispersibility/solubility and bio-availability (Magnuson et al., 2011).
- Controlled and efficient delivery of nutrients and nutraceuticals through nanoencapsulation (Chen et al., 2006; McClements, 2010).
- Improved protection of sensitive nutrients through nanoencapsulation and coating (Weiss et al., 2006).
- Use of nanostructures as biosensors for detecting pathogens and providing information related to food traceability (Charych et al., 1996).
- Incorporation of specific nanoelements (nanofibers, nanotubes, and nanoclays) in polymers, in order to improve mechanical, barrier, and delivery characteristics as coating or packaging materials (Kumar et al., 2011; Arora and Padua, 2010; Sanchez-Garcia et al., 2010; Imran et al., 2010; Brody, 2006).

It should be pointed out that the technical/economic feasibility of these and similar applications of nanotechnology to foods at industrial scale remains to be demonstrated. Furthermore, extensive further research is needed regarding the safety of the inclusion of engineered nanoelements in foods.

## 1.7 WATER ACTIVITY

### 1.7.1 THE IMPORTANCE OF WATER IN FOODS

Water is the most abundant constituent in most foods. Indicative values of water content in a number of food products are shown in Table 1.1. Classification of foods into three groups, according to their water content (high, intermediate, and low moisture foods), has been suggested (Franks, 1991). Fruits, vegetables, juices, raw meat, fish, and milk belong to the high moisture category. Bread, hard cheeses, and sausages are examples of intermediate moisture foods while the low moisture group includes dehydrated vegetables, grains, milk powder, and dry soup mixtures.

The functional importance of water in foods goes far beyond its mere quantitative presence in their composition. On the one hand, water is essential for the

**Table 1.1** Typical water content of some foods

| Food | Water (%) |
|---|---|
| Cucumbers | 95–96 |
| Tomatoes | 93–95 |
| Cabbage | 90–92 |
| Orange juice | 86–88 |
| Apples | 85–87 |
| Cow milk | 86–87 |
| Eggs, whole | 74 |
| Chicken, broiled | 68–72 |
| Hard cheese | 30–50 |
| White bread | 34 |
| Jams, preserves | 30–35 |
| Honey | 15–23 |
| Wheat | 10–13 |
| Nuts | 4–7 |
| Dehydrated onion | 4–5 |
| Milk powder | 3–4 |

good texture and appearance of fruits and vegetables. In such products, loss of water usually results in lower quality. On the other hand, water, being an essential requirement for the occurrence and support of chemical reactions and microbial growth, is often responsible for the microbial, enzymatic, and chemical deterioration of food.

It is now well established that the effect of water on the stability of foods cannot be related solely to the quantitative water content. As an example, honey containing 23% water is perfectly shelf-stable while dehydrated potato would undergo rapid spoilage at a moisture content half as high. To explain the influence of water, a parameter that reflects both the quantity and the "effectiveness" of water is needed. This parameter is *water activity*.

## 1.7.2 WATER ACTIVITY, DEFINITION, AND DETERMINATION

Water activity, $a_w$, is defined as the ratio of the water vapor pressure of the food to the vapor pressure of pure water at the same temperature.

$$a_w = \frac{p}{p_0} \tag{1.9}$$

where:

$p$ = partial pressure of water vapor of the food at temperature $T$.
$p_0$ = equilibrium vapor pressure of pure water at temperature $T$.

The same type of ratio also defines the relative humidity of air, RH (usually expressed as a percentage):

$$\mathrm{RH} = \frac{p'}{p_0} \times 100 \tag{1.10}$$

where:

$p'$ = partial pressure of water vapor in air.

If the food is in equilibrium with air, then $p = p'$. It follows that the water activity of the food is equal to the relative humidity of the atmosphere in equilibrium with the food. For this reason, water activity is sometimes expressed as the *equilibrium relative humidity*, ERH.

$$a_w = \frac{\mathrm{ERH}}{100} \tag{1.11}$$

Many of the methods and instruments for the determination of water activity are based on Eq. (1.11). A sample of the food is equilibrated with a small headspace of air in a close chamber and then the relative humidity of the headspace is measured by an appropriate hygrometric method such as the "chilled mirror" technique (Fig. 1.4).

Typical water activity values of some food products are given in Table 1.2.

**FIG. 1.4**

Measurement of water activity.

**Table 1.2** Typical water activities of selected foods

| $a_w$ range | Product examples |
|---|---|
| 0.95 and above | Fresh fruits and vegetables, milk, meat, and fish |
| 0.90–0.95 | Semihard cheeses, salted fish, and bread |
| 0.85–0.90 | Hard cheese, sausage, and butter |
| 0.80–0.85 | Concentrated fruit juices, jelly, and moist pet food |
| 0.70–0.80 | Jams and preserves, prunes, dry cheeses, and legumes |
| 0.50–0.70 | Raisins, honey, and grains |
| 0.40–0.50 | Almonds |
| 0.20–0.40 | Nonfat milk powder |
| Less than 0.2 | Crackers, roasted ground coffee, and sugar |

### 1.7.3 WATER ACTIVITY: PREDICTION

The principal mechanisms responsible for the depression of vapor pressure of water in foods are solvent-solute interaction, binding of water molecules to the polar sites of polymer constituents (e.g., polysaccharides and proteins), adsorption of water on the surface of the solid matrix, and capillary forces (Le Maguer, 1987). In high moisture foods, such as fruit juices, the depression may be attributed entirely to water-solute interaction. If such foods are assumed to behave as "ideal solutions," then their water vapor pressure obeys Raoult's Law (see Section 13.2). In this case:

$$p = x_w p_0 \Rightarrow x_w = \frac{p}{p_w} = a_w \tag{1.12}$$

where $x_w$ is the water content (in molar fraction) of the food. It follows that the water activity of an ideal aqueous solution is equal to the molar concentration of water $x_w$. The water activity of high moisture foods (with $a_w$ of 0.9 or higher) can be calculated quite accurately by this method.

### EXAMPLE 1.4

Estimate the water activity of honey. Consider honey of as an 80% w/w aqueous solution of sugars (90% hexoses, 10% disaccharides).

**Solution**

The composition of 100 g of honey is:

| | | |
|---|---|---|
| Water | 20 g | 20/18 = 1.11 gmol |
| Hexoses | 72 g | 72/180 = 0.40 gmol |
| Disaccharides | 8 g | 8/342 = 0.02 gmol |

Assuming Raoult's Law, the water activity of honey is equal to the molar fraction of water:

$$a_w = x_w = \frac{1.11}{1.11 + 0.40 + 0.02} = 0.725$$

As the water content is reduced, water binding by the solid matrix and capillary forces become increasingly significant factors and overshadow water-solute interaction. Furthermore, the assumption of ideal solution behavior can no longer be applied because of the elevated concentration of the liquid phase. The relationship between water content and water activity, $a_w = f(X)$, becomes more complex. This is discussed in the next section.

Water activity is temperature dependent. Considering the definition of water activity, as given in Eq. (1.8), one would be tempted to conclude in the opposite. Temperature affects both $p$ and $p_0$ in the same manner (the law of Clausius-Clapeyron); therefore, their ratio should not be affected by the temperature. This is true for the liquid phase and, indeed, the water activity of high moisture foods is affected by temperature very slightly, if at all. The situation is different at lower levels of water content. Temperature affects not only the water molecules but also the solid matrix interacting with water. Therefore, temperature affects water activity at intermediate and low moisture levels where the adsorption and capillary effects are strong. The direction and intensity of temperature effects are not predictable.

## 1.7.4 WATER VAPOR SORPTION ISOTHERMS

The function representing the relationship between water content (e.g., as grams of water per gram of dry matter) and water activity at constant temperature is called the "water vapor sorption isotherm" or simply the "moisture sorption isotherm" of a food. The general form of a hypothetical sorption isotherm is shown in Fig. 1.5.

Sorption isotherms of a large number of foods have been compiled by Iglesias and Chirife (1982).

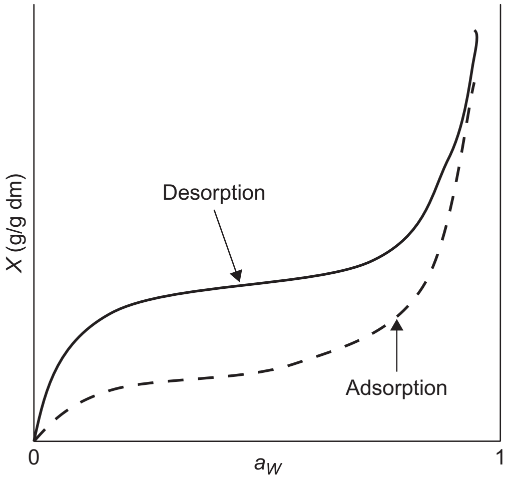

**FIG. 1.5**

General form of a sorption isotherm.

Sorption isotherms are determined experimentally. Basically, samples of the food are equilibrated at constant temperature with atmospheres at different known relative humidities. After equilibration, the samples are analyzed for water (moisture) content. Each pair of ERH-moisture content data gives one point on the isotherm. The experimental methods for the determination of sorption isotherms fall into two groups, namely, static and dynamic procedures. In static methods, weighed samples of food are placed in jars, over saturated aqueous solutions of different salts, and left to equilibrate at constant temperature. At constant temperature, the concentration of saturated solutions is constant and so is their water vapor pressure. The relative humidity of the atmosphere in equilibrium with saturated solutions of some salts is given in Table 1.3.

In dynamic methods (Yu et al., 2008), the sample is equilibrated with a gas stream, the relative humidity of which is continuously changed. The quantity of moisture adsorbed or desorbed is determined by recording the change in the weight of the sample.

The two curves shown in Fig. 1.5 indicate the phenomenon of "hysteresis" often encountered. One of the curves consists of experimental data points where the food sample came to equilibrium by losing moisture (desorption). The other curve represents points obtained by the opposite path, i.e., by gain of moisture (adsorption). The physical explanation of the sorption hysteresis has been the subject of many studies. Generally, hysteresis is attributed to the condensation of some of the water in the capillaries (Labuza, 1968; Kapsalis, 1987; deMann, 1990). The observation that, depending on the path of sorption, food can have two different values of water activity at the same moisture content casts doubt on the thermodynamic validity of the concept of sorption equilibrium (Franks, 1991).

Numerous attempts have been made to develop mathematical models for the prediction of sorption isotherms (Chirife and Iglesias, 1978; Lievonen and Roos, 2002). Some of the models developed are based on physical theories of adsorption (see Chapter 12). Others are semiempirical expressions developed by curve-fitting techniques. A model based on the distinction of "surface absorption water" and "solution water" has been suggested (Yanniotis and Blahovec, 2009). A distributive algorithm,

**Table 1.3** Saturated salt solutions commonly used in the determination of sorption isotherms

| Salt | $a_w$ at 25°C |
|---|---|
| Lithium chloride | 0.11 |
| Potassium acetate | 0.22 |
| Magnesium chloride | 0.33 |
| Potassium carbonate | 0.44 |
| Sodium chloride | 0.75 |
| Potassium sulfate | 0.97 |

based on the sorption characteristics of the main constituents (glucose, fructose, sucrose, salt, protein, and fiber), has been reported to predict successfully the water sorption isotherms of vegetables and fruits (Moreira et al., 2009).

One of the best-known models is the Brunauer-Emmett-Teller (BET) equation. The basic assumptions on which the BET model is based are discussed in Section 12.2 (Adsorption). Applied to water vapor sorption, the BET equation is written as follows:

$$\frac{X}{X_m} = \frac{Ca_w}{(1-a_w)[1+a_w(C-1)]} \tag{1.13}$$

where:

$X$ = water content, grams water per gram of dry matter.
$X_m$ = a parameter of the equation, interpreted as the value of $X$ for the saturation of one monomolecular layer of water on the adsorbing surface (the BET monolayer).
$C$ = a constant, related to the heat of adsorption.

To find $X_m$ and $C$ from experimental sorption data, the BET equation is written as follows:

$$\frac{a_w}{(1-a_w)X} = \Phi = \frac{1}{X_m C} + \frac{C-1}{X_m C} a_w \tag{1.14}$$

If the group $\Phi$ is plotted against $a_w$, a straight line is obtained (Fig. 1.6). $X_m$ and $C$ are calculated from the intercept and the slope.

The BET model has been found to fit well sorption isotherms, up to water activity values of about 0.45.

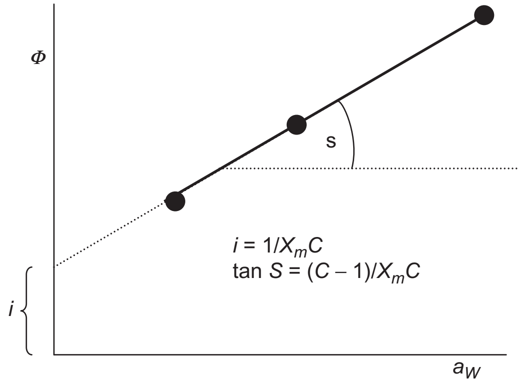

**FIG. 1.6**

Linearization of the BET equation with three experimental points.

## EXAMPLE 1.5

Following are three points from the sorption isotherm of potato at 20 degrees:

| $a_w$ | $X$ (g water per g dry matter) |
|---|---|
| 0.12 | 0.05 |
| 0.47 | 0.11 |
| 0.69 | 0.18 |

*Estimate the monolayer value of potato, based on the data.*

### Solution

We calculate the group $\Phi$ in Eq. (1.14) as a function of $a_w$. We find:

| $a_w$ | $\Phi$ |
|---|---|
| 0.12 | 2.73 |
| 0.47 | 8.06 |
| 0.69 | 12.36 |

The equation of the linear plot of $\Phi$ versus $a_w$ is found to be: $\Phi = 16.74\ a_w + 0.57$

$$\frac{C-1}{X_m C} = 16.74 \quad \frac{1}{X_m C} = 0.57$$

Solving for $C$ and $X_m$, we find $\mathbf{C = 30.36}$ and $\mathbf{X_m = 0.058}$.

Another equation which is often used to predict sorption isotherms is the GAB (Guggenheim-Anderson-de Boer) model shown below:

$$\frac{X}{X_m} = \frac{CKa_w}{(1-Ka_w)[1-Ka_w+CKa_w]} \tag{1.15}$$

where $C$ and $K$ are constants, both related to the temperature and heat of adsorption. The range of applicability of the GAB equation is wider than that of the BET model.

### 1.7.5 WATER ACTIVITY: EFFECT ON FOOD QUALITY AND STABILITY

Bacterial growth does not occur at water activity levels below 0.9. With the exception of osmophilic species, the water activity limit for the growth of molds and yeasts is between 0.8 and 0.9. Most enzymatic reactions require water activity levels of 0.85 or higher. The relationship between water activity and chemical reactions (Maillard browning, lipid oxidation) exhibit more complex behavior with maxima and minima (Fig. 1.7).

## 1.8 PHASE TRANSITION PHENOMENA IN FOODS

### 1.8.1 THE GLASSY STATE IN FOODS

With few exceptions, foods should be regarded as metastable systems capable of undergoing change. Stability is a consequence of the rate of change. In turn, the rate of change depends on molecular mobility. In recent years, molecular mobility has

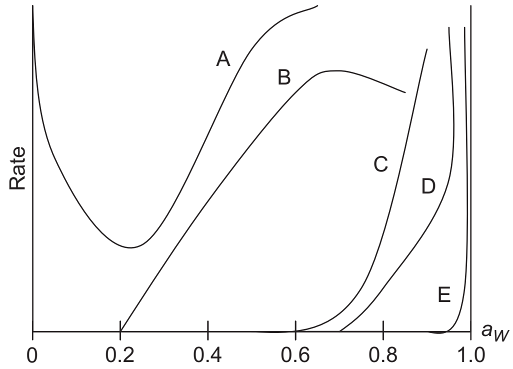

**FIG. 1.7**

Relative rate of deterioration mechanisms as affected by water activity. (A) Lipid oxidation, (B) maillard browning, (C) enzymatic activity, (D) mold growth, and (E) Bacteria growth.

become a subject of strong interest among food scientists. The subject is particularly important in solid and semisolid foods with low to intermediate water content. In the majority of foods belonging to this category, the interaction between polymeric constituents, water, and solutes is the key issue in connection with molecular mobility, diffusion, and reaction rates. Accordingly, concepts and principles developed by polymer scientists are now being applied to foods (Slade and Levine, 1991, 1995; Le Meste et al., 2002).

Consider a liquid food product, such as honey, consisting of a concentrated aqueous solution of sugars. The physical properties and stability of such a solution depend on two variables: concentration and temperature. If the concentration is increased by slowly removing some of the water and the temperature is lowered gradually, solid crystals of sugar will be formed. If the process of concentration and cooling is carried out under different conditions, crystallization will not take place, but the viscosity of the solution will increase until a rigid, transparent, glass-like material will be obtained. The familiar transparent hard candy is an example of glassy (vitreous) food. The glassy state is not limited to sugar-water systems. Intermediate- and low-moisture foods often contain glassy regions consisting of polymer materials (e.g., gelatinized starch) and water. The phenomenon of passage from the highly viscous, rubbery semiliquid to the rigid glass is called "glass transition" and the temperature at which that occurs is the "glass transition temperature, $T_g$."

Physically, glass is an *amorphous solid*. It is also sometime described as a supercooled liquid of extremely high viscosity. Conventionally, the viscosity assigned to glass is on the order of $10^{11}$–$10^{13}$ Pa s, although it is practically impossible to verify this convention experimentally. The molecules of glass do not have an orderly arrangement as in a solid crystal, but they are sufficiently close and sufficiently immobile to possess the characteristic rigidity of solids. Owing to the negligible molecular mobility, the rate of chemical and biological reactions in glassy material is extremely low. Therefore, the glassy state in foods represents a condition of maximum stability (Sablani et al., 2007; Akköse and Aktaş, 2008; Roos, 2010; Syamaladevi et al., 2011). The rigidity of the glassy regions affects the texture of the food. The staling of bread is due to the transition of the starch-water system from a rubbery to glassy state. The crunchiness of many snack products is due to their glassy structure.

## 1.8.2 GLASS TRANSITION TEMPERATURE

The different physical states of an aqueous solvent-solute system capable of forming an amorphous solid and the processes of passage from one state to another have been described by Roos and Karel (1991a) in a frequently cited diagram (Fig. 1.8).

Boiling of a liquid or melting of a crystal are "thermodynamic" phase transitions, also known as "first-order transitions" (Roos, 1995). They occur at a fixed, definite set of conditions (temperature, pressure), independent of the rate. The phases in transition are mutually in equilibrium. In contrast, glass transition is of kinetic nature. It does not involve large step changes in properties and does not require a considerable latent heat of transition. The glass transition temperature of a given rubbery material is not a fixed point. It varies somewhat with the rate and direction of the change (e.g., rate of heating or cooling); therefore, the procedure for its determination has to be specified exactly.

Glass transition temperatures of pure dry sugars are given in Table 1.4.

Glass transition temperature is strongly dependent on concentration. Dilute solutions have lower $T_g$. This led Roos and Karel (1991b) to conclude that water acts on the amorphous food as a *plasticizer* in a polymer system. The effect of concentration on $T_g$ is shown in Fig. 1.9 for a solution of sucrose.

It has been suggested that the glass transition temperature of a binary blend can be predicted, using the Gordon-Taylor equation, borrowed from polymer science and shown in Eq. (1.14):

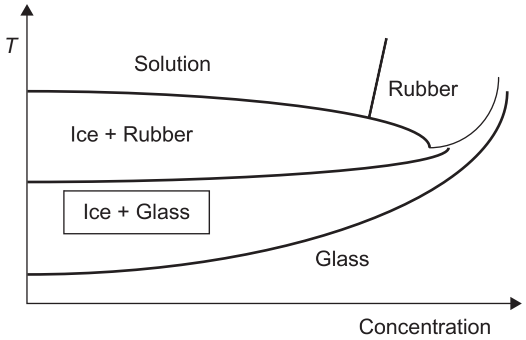

**FIG. 1.8**

State diagram of a carbohydrate solution.

*From Roos, Y., Karel, M., 1991a. Applying state diagrams to food processing and development. Food Technol. 45(12), 66, 68–71, 107.*

**Table 1.4** Glass transition temperatures of sugars

| Substance | $T_g$ (°C) |
|---|---|
| Sorbitol | −2 |
| Xylose | 9.5 |
| Glucose | 31 |
| Fructose | 100 |
| Maltose | 43 |
| Sucrose | 52 |

*From Belitz, H.D., Grosch, W., Schieberle, P., 2004. Food Chemistry, third ed. Springer-Verlag, Berlin.*

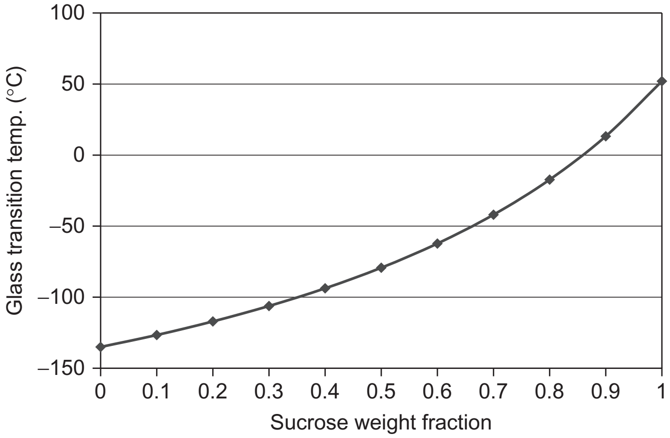

**FIG. 1.9**

Effect of temperature on $T_g$ of sucrose solutions.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{1.16}$$

where:

$T_g$ = glass transition temperature of the mixture.
$T_{g1}$, $T_{g2}$ = absolute glass transition temperatures (K) of components 1 and 2, respectively. The subscript 2 refers to the component with the higher $T_g$.
$w_1$, $w_2$ = weight fractions of components 1 and 2, respectively.
$k$ = a constant.

A simpler approximate expression is the Fox equation (Schneider, 1997):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1.17}$$

According to Johari et al. (1987) the $T_g$ of water is 138 K or −135°C. Glass transition temperatures of some carbohydrates are shown in Table 1.4.

---

## EXAMPLE 1.6

Estimate the glass transition temperature of honey. Consider honey of as an 80% w/w aqueous solution of dextrose.

### Solution

We use the Fox equation. We index water as 1 and dextrose as 2. We take the $T_g$ of water as 138 K and the $T_g$ of dextrose as 304 K (31°C).

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} = \frac{0.2}{138} + \frac{0.8}{304} = 0.00408$$

$$T_g = 245\,\text{K} = -28^\circ\text{C}$$

---

The viscosity of solutions increases sharply as $T_g$ is approached. Near $T_g$, the effect of temperature on viscosity does not comply with the Arrhenius Law (Chapter 4, Section 4.2.3) but follows the Williams-Landel-Ferry (WLF) relationship (Roos and Karel, 1991c), as shown in Eq. (1.15):

$$\log \frac{\mu}{\mu_g} = \frac{-17.44\left(T - T_g\right)}{51.6 + \left(T - T_g\right)} \tag{1.18}$$

where $\mu$ and $\mu_g$ stand for the viscosity at the temperatures $T$ and $T_g$, respectively.

Just like water activity, glass transition temperature has become a key concept in food technology, with applications in quality assessment and product development. Since the glassy state is considered as a state where molecular mobility is at a minimum, it has been suggested to study food properties and stability not as a function of the temperature $T$ but as a function of the difference $T - T_g$ (Simatos et al., 1995).

Several methods exist for the determination of $T_g$ (Otles and Otles, 2005). The results may vary somewhat, depending on the method used. The most commonly applied method is differential scanning calorimetry (DSC). DSC measures and records the heat capacity (i.e., the amount of heat necessary to increase the temperature by 1°C) of a sample and of a reference as a function of temperature. A sharp increase or decrease in heat capacity indicates an endothermic or exothermic phase transition at the temperature where this occurs. In the case of first-order transitions, such as melting, the amplitude of the change is considerable. In contrast, glass transition is detected as a subtle inflexion in the heat capacity curve (Fig. 1.10).

Since the change occurs over a temperature range and not sharply at one temperature, the decision where to read $T_g$ is subject to interpretation. The two most common conventions are the midpoint of the step and the point representing the onset of the transition (Simatos et al., 1995).

Other techniques, such as a rheological method applicable to spray-dried dairy powders, have been proposed (Hogan et al., 2010). The technique consists of constant rate heating of powder under compression and measurement of changes in

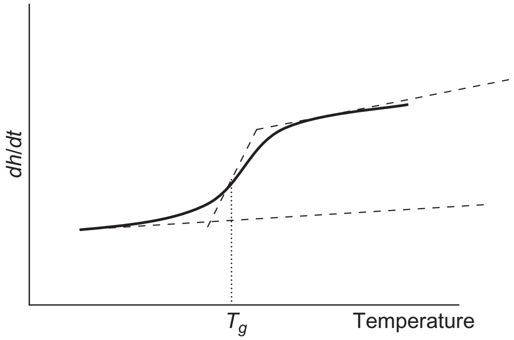

**FIG. 1.10**

Glass transition temperature from DSC plot.

either gap distance or normal force. A considerable increase in the rate of change of these values seems to occur at $T_g$. Another frequently utilized method makes use of TMA (thermomechanical analysis, as discussed in Section 1.3). The method assumes that the tangent of the lag angle ($tg\ \delta$) passes through a maximum at $T_g$.

## 1.9 OPTICAL PROPERTIES

By optical properties, we refer to the reaction of the food to electromagnetic radiation, particularly to visible light. Practically, the important optical properties are **transparency**, **turbidity**, and **color**. As a quality attribute, high transparency is expected in drinking water, wine, most beers, some juices, jellies, oils, etc. Turbidity is a consequence of light scattering by dispersed particles or droplets in emulsions and suspensions. A dispersed system will be turbid if the dispersed phase is opaque or has a refractive index different from that of the continuous phase *and* if the dispersed particles are larger than the wavelength of the light.

Light is *refracted* when it passes from one transparent medium to another. Refraction is a consequence of the difference in velocity of the light in the two media. The amplitude of refraction is a function of the *index of refraction* of the two media, as shown in Fig. 1.11, and Eq. (1.19), known as Snell's Law.

$$\frac{\sin\alpha}{\sin\beta} = \frac{n_2}{n_1} \tag{1.19}$$

where:

$\alpha$, $\beta$: incidence and refraction angles, respectively.
$n_1$, $n_2$: refractive indexes of the two media against air (or vacuum).

If the light penetrates from air into a liquid, $n_1 = 1$ and Eq. (1.19) becomes:

$$\frac{\sin\alpha}{\sin\beta} = n \tag{1.20}$$

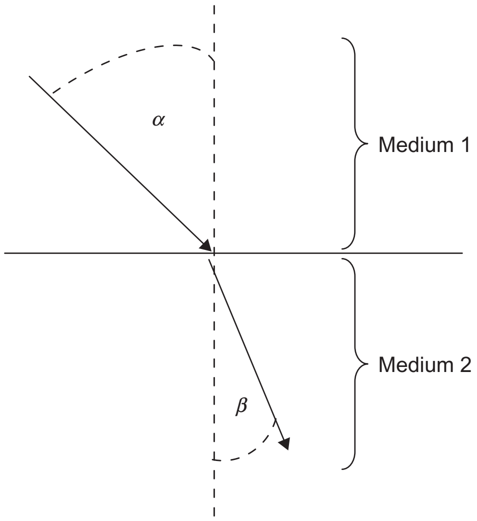

**FIG. 1.11**

Refraction of light.

where $n$ is the refractive index of the liquid.

The *refractive index* of solutions depends on their concentration. Indeed, refractometry is extensively used for the rapid determination of concentration, particularly in solutions of sugar and sugar-like solutes.

Another important area related to the optical properties of foods is the reaction of foods to electromagnetic radiation in the wavelength range of 800–2500 μm, known as the "near-infrared (NIR) range" (Ozaki et al., 2007). The principal components of foods (water, proteins, fats, and carbohydrates) have characteristic absorption spectra when exposed to NIR radiation. In recent years, *NIR spectroscopy* (*NIRS*) (Christy et al., 2004) has become a most valuable tool for the rapid approximate analysis of foods. More recently, the potential use of NIRS for process control, food safety assurance, and food traceability through monitoring of material properties has been demonstrated (Bock and Connelly, 2008; Fu and Ying, 2016).

Color as a physical property will be discussed in Chapter 5.

## 1.10 SURFACE PROPERTIES

The molecules at the surface of a liquid or solid body are in a state different from that of the molecules inside the body. While the molecules in the bulk are subjected to balanced attraction by the molecules all around, the molecules at the free surface of the body are attracted on one side only. While the molecules in the bulk are arranged at random, the molecules at the surface assume a more or less orderly arrangement approaching that of a solid film under tension. Energy has to be supplied in order to increase the free surface of a liquid or the interface surface between two immiscible liquids. The energy increment $\Delta E$ needed to increase the free surface by one unit is named the *surface tension* of the liquid. It is designated by the symbol $\gamma$ (sometimes $\sigma$) and its units in the SI system are J m$^{-2}$ or N m$^{-1}$.

$$\gamma = \frac{\Delta E}{\Delta A} \tag{1.21}$$

Surface tension is relevant in many areas of food technology such as: capillary phenomena, emulsions and suspensions, homogenization, foams, bubble formation, spraying, coating, wetting, washing, cleaning of solid surfaces, adsorption, etc.

The surface tension of water at room temperature is approximately $73 \times 10^{-3}$ N m$^{-1}$. Surface tension decreases with increasing temperature. For pure substances, it becomes 0 at the critical temperature. Surface tension data for a number of additional liquids are tabulated in Table A.18 (Appendix).

## 1.11 ACOUSTIC PROPERTIES

Solid foods emit audible sounds when fractured (Lewicki et al., 2009). The sound generated in the mouth cavity when solid foods are fractured during mastication is an important quality factor, particularly in crunchy/crispy foods. Loss of the ability to emit sound when fractured (e.g., as a result of moisture adsorption) is detected by the consumer as a loss of quality. Analysis of the emitted sound has become an important tool in the study of crunchiness/crispiness as well as a useful technique in quality assessment (Duizer, 2001; Castro-Parada et al., 2007). Salvador et al. (2009) and Taniwaki and Kohyama (2012) investigated the effect of crispness on the acoustic behavior of potato chips.

Feeling the acoustic response (echo) of solid foods to contact or knocking is a well-established popular method for the evaluation of texture quality in some foods, such as melons and hard cheeses. It has been shown that the analysis of the acoustic response can be used for the evaluation of fruit texture (Zdunek et al., 2011). Mao et al. (2016) worked on the optimization of the technique for the nondestructive evaluation of watermelon firmness.

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