PHASE TRANSITIONS

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Contents

Summary

Phase transitions are transformations occurring between the three basic physical states: 1) solid, 2) liquid, and 3) gas. State transitions are transformations occurring between the physical states of amorphous materials (e.g., solid and liquid states of supercooled materials) or could refer to time-dependent changes in the physical state of materials, as in time-dependent flow causing structural changes and collapse of structure. Glass transition has received much attention as one of the most important transitions affecting the physicochemical properties of low-moisture and frozen foods, including food stability. Phase behavior of water is extremely important in freezing foods, dehydration, evaporation, and high pressure food processing. Water in food systems acts as a solvent, but also as a plasticizer of low-water food solids and of freeze-concentrated solids in the unfrozen phase. Water plasticization is observed from the decreasing transition temperatures of non-lipid food solids with increasing water content. Melting of sugar occurs in some food processes or evaporation in which sugar water syrup is produced (e.g., in manufacture of confectionery). Crystallization of sugars occurs at temperatures below melting, but sufficiently rapid cooling of a sugar melt results in an amorphous state, in which solidification takes place below the glass transition temperature. Stickiness and caking of food powders, as well as collapse of porous, dehydrated food structures, have been shown to be controlled by glass transition. Recrystallization and increase of ice crystal size is a typical quality defect of frozen foods. At temperatures below glass transition (i.e., in glassy foods), the rates of diffusion-controlled reactions have been found to be relatively low or insignificant. A rapid increase in reaction rates within or above the glass transition temperature range may be observed because of enhanced diffusion.

1. Introduction

Natural substances, including foods, are complicated systems composed of a large number of organic and inorganic compounds. These materials may exist in several physical forms and states. They may also be rather homogeneous systems or highly heterogeneous materials with several different phases in their physical structure. Therefore, knowledge of biomaterials and food properties, including phase and state transitions, is extremely important in food design and engineering.

The phase transitions of water in food systems are relatively well-known, and applied in such operations as freezing, evaporation, and dehydration to remove water and provide extended microbiological stability. Water may also affect the behavior and the physical state of other components, particularly, water miscible and water soluble food components. Non-polar compounds, mainly lipids, exist in a separate phase from the aqueous phase and exhibit their own phase transitions. Transitions in the lipid phase include crystallization and melting of fats, which are extremely important in giving desired quality characteristics to dairy foods, spreads, and emulsions, to mention a few examples (see *Crystallization, Food Emulsions*).

Most low-water and frozen foods are solids, but only a few food materials exist in a thermodynamic equilibrium, crystalline solid state. Crystalline equilibrium structures of water miscible and water soluble food components are highly exceptional. These are typical of only crystalline sugars, salts, and other chemically pure substances. Crystalline materials are stable and not susceptible to chemical changes or microbial

spoilage. In contrast, most food products contain compounds of varying molecular weight and structure, and are likely to exist in the non-crystalline, amorphous state. Simple examples of solid amorphous food material include cereal foods like breakfast cereals, confectionery, dehydrated foods, food powders, snacks, and frozen food solids. Many of these foods, however, are shelf stable when manufactured, distributed, and stored properly.

The non-lipid phase of low-water and frozen food solids is predominantly composed of water miscible carbohydrates and proteins. The phase behavior and interactions with water of these compounds define their physical state and possible phase and state transitions occurring in processing and storage. In low-water foods, water is absorbed by carbohydrates and proteins. In these materials, water is a softener or a plasticizer of food solids, thereby contributing significantly to food structure. In frozen foods, most of the water exists in a separate, solid ice phase. However, it is extremely important to note that during freezing, water miscible compounds become freeze-concentrated and some of the water remains unfrozen within the freeze-concentrated solids. The extent of freeze-concentration at a given temperature is dependent on food composition and solutes in the unfrozen phase. At sufficient temperature, the solids-unfrozen water phase may become maximally freeze-concentrated, and then vitrify as a glass below a given composition-dependent temperature. Both low-water and frozen foods are considered stable when stored below their glass transition temperature, i.e., in the glassy solid state.

Glass transition, i.e., the change in state between the amorphous, supercooled liquid and the solid glassy state, is the state transition governing the structure's physico-chemical and structural properties, acceptability, and shelf life (of numerous low-water and frozen foods). Many low-water solid foods, such as breakfast cereals and snack foods, have solid, porous, crispy structures. These materials are crispy in the glassy state, but crispness may be lost due to water sorption and plasticization during storage at high relative humidity. Another structure-related property is the flowability of food powders. Glassy food powders, e.g., lactose-containing dairy powders, are free flowing in the glassy state. Water sorption and thermal plasticization of powders may result in reduced surface viscosity of powder particles, which is observed in stickiness and caking. Supercooled, plasticized, viscous liquid materials may flow, allowing surface adhesion of particles, shrinkage, and loss of structure. Loss of structure in dehydrated foods is often accompanied by other deteriorative changes, such as change in color, loss of flavor, and oxidation of encapsulated lipids. Transformation of material into a supercooled liquid state over the glass transition may in some cases allow crystallization of component compounds, for example, lactose in milk powders and several pharmaceutical preparations, and retrogradation of starch, which is often considered the main cause of the staling of bread. Crystallization of component compounds and recrystallization of ice in frozen foods, particularly, frozen deserts (including ice cream), may be controlled by the glass transition of the freeze-concentrated solids phase.

Important issues related to the glass transition of solid food and pharmaceutical matrices are diffusion, translational mobility of molecules, and rates of deteriorative changes, including enzymatic activity and rates of chemical reactions. It is often assumed that

rates of diffusion-controlled changes become insignificant below glass transition, as materials solidify and molecules freeze in the glassy state. However, according to several studies on water mobility in glassy food structures, water remains relatively mobile in glassy food systems. It has also been observed that many deteriorative changes and growth of some microorganisms may occur, although with significantly reduced rates in glassy food structures.

Obviously, the physical state and physicochemical properties of food materials affect their behavior in processing, storage, distribution, and consumption. The physical state and structure of biological materials is also important to material stability and long-term maintenance of biological activity. This has been recognized in several areas of biological sciences, including studies on the stability of seeds, cryopreservation of microorganisms (starter cultures) and living organs, and dormancy of organisms in extreme conditions. This article, however, is based on studies of phase transitions in foods, including state transitions and their effects on food properties in processing and storage, as well as the kinetics of desired and detrimental changes in quality.

2. Phase and State Transitions

Phase transitions are transformations occurring between the three basic physical states: 1) solid, 2) liquid, and 3) gas. State transitions cannot be defined in thermodynamic terms as precisely as phase transitions, but rather as transitions occurring between the physical states of amorphous materials (e.g., the solid and liquid states of supercooled materials), or as time-dependent changes in the physical state of materials (e.g., time-dependent flow causing structural changes and collapse). However, state transitions are typical of non-equilibrium materials, and are characterized by relaxations towards the stable, equilibrium state. The effect of water on the phase and state behavior of food solids is well recognized and important in determining processability, stability, and quality.

2.1. The Equilibrium State

Thermodynamics helps characterize the differences in physical properties between various equilibrium states and the driving forces towards equilibrium. A change in temperature or pressure may introduce the driving force of a system leading to another equilibrium state, for example, transformation between the solid and liquid states. The equilibrium state is defined by pressure, p, temperature, T, and volume, V. Possible combinations of coexisting phases of the same compound are solid and liquid, solid and gas, and liquid and gas. All three phases may coexist only at the triple point, which has exact temperature and pressure conditions. Equilibrium between the various phases only exists when the molecules are not being driven towards another phase (i.e., at transition temperatures, at constant pressure). The driving force behind a phase transition is the chemical potential, μ, and the conditions allowing equilibrium can be defined by chemical potential, pressure, and temperature.

2.2. Types of Transitions

A change in chemical potential or Gibbs energy at a phase transition temperature shifts

the equilibrium state to one with lower chemical potential and Gibbs energy, as described in Figure 1. The first derivatives of chemical potential and Gibbs energy functions show discontinuity at the first-order transition temperature, and step changes in enthalpy, entropy, and volume that occur during first-order phase transitions. These include transitions between the solid, liquid, and gas states of pure compounds, i.e., melting and crystallization, and vaporization and condensation, which have defined latent heat in the phase transition.
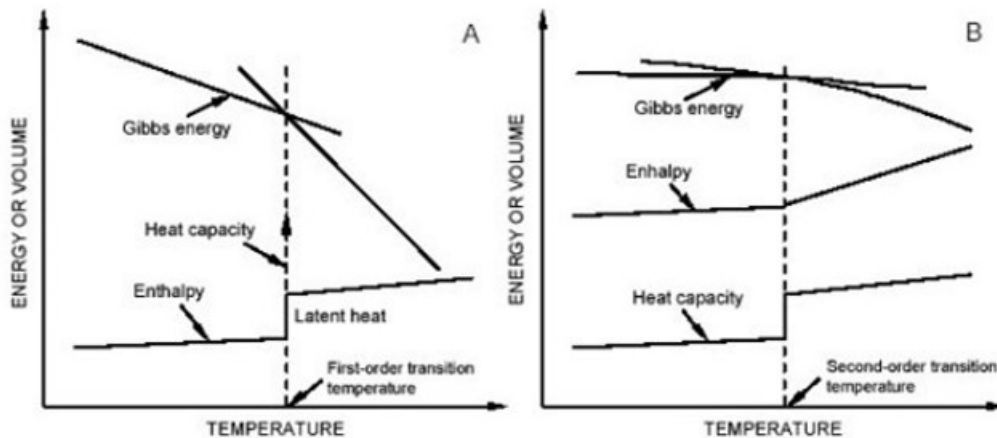

Figure 1. A. Changes in Gibbs energy and enthalpy at a first-order phase transition. B.

Changes in Gibbs energy, enthalpy, and heat capacity at a second-order phase transition. In second-order phase transitions, the second derivatives of chemical potential and Gibbs energy show a discontinuous change at the transition temperature (Figure 1). Therefore, a second-order transition has no latent heat, but there is a discontinuity in heat capacity, Cp, and thermal expansion coefficient, α. These properties are different in both phases and show a step change at the transition temperature.

Glass transition, the transition between the solid and supercooled liquid states of amorphous materials, has the thermodynamic properties of second-order transitions. Although glass transitions involve a change in heat capacity, they occur over a temperature range in which no exact transition temperature can be measured. However, glass transition temperatures are often taken as the onset or midpoint temperature in the glass transition temperature range, determined using differential scanning calorimetry (DSC). Glass transitions in food systems are observed in amorphous or partially amorphous structures formed in various processes that allow a sufficiently short time for removal of water, or cooling of concentrated solids. The equilibrium melting temperature of crystals of several glass formers, mostly sugars, is located at about 100°C above the glass transition.

2.3. Measurement of Transitions

Several instrumental methods are available for determination of phase and state transitions in food systems. Obviously, transition temperatures can be measured by direct visual observation of the change in state of the material using microscopy or

methods that allow determination of thermal property changes in solid and liquid samples at various temperatures. Common methods include dilatometry to observe volume changes and thermal analysis to measure thermal properties as a function of temperature.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are most frequently used in the determination of transition temperatures and heat of transitions, respectively. Spectroscopic techniques and x-ray diffraction measurements are also used to observe the physical state and changes in crystallinity at various conditions.

Most of these methods are common in the determination of solid-liquid transitions in food fats and lipids, frozen foods, and in the determination of glass transitions and the physical state of amorphous, low-water food systems.

Glass transition has received much attention as one of the most important transitions affecting the physicochemical properties of low-water and frozen foods, and their stability and shelf life. Glass transition involves no latent heat, but is detected by observing changes in various dielectric (dielectric constant) (see *Electrical Properties*), mechanical (modulus, viscosity) (see *Mechanical Properties*, *Food Rheology and Texture*), and thermodynamic (enthalpy, free volume, heat capacity, thermal expansion coefficient) properties (see *Thermal Properties*).

These changes allow observation of the transition with various methods that can detect these changes as a function of frequency, f, temperature, or time, t. The most common method used to observe glass transitions is DSC, which detects the change in heat capacity occurring over the transition temperature range. Other useful and often more sensitive and complementary methods include DMA or mechanical spectroscopy, which measures changes in material response to oscillating mechanical stress as a function of temperature, and DEA, which measures material response to changing voltage and gives information on dielectric properties as a function of temperature.

Both methods may also be used isothermally to detect material response to the changing frequency of applied stress. Important techniques from studies on molecular mobility and diffusion, and their dependence on the physical state and phase and state transitions, include nuclear magnetic resonance (NMR) spectroscopic methods and electron spin resonance spectroscopy (ESR), which can detect changes in mobility at molecular levels. Both DEA and DMA measurements have suggested that amorphous food systems show low temperature relaxation below the glass transition.

These relaxations indicate molecular vibrations and rotations occurring in the solid, glassy state. Calorimetric glass transition is accompanied by the onset of translational motions of molecules, which in DEA and DMA measurements are observed from primary relaxations. Spectroscopic measurements also suggest increasing molecular motions taking place over the calorimetric glass transition temperature range. However, small plasticizer molecules, such as water, have high mobility below the glass transition of food materials.
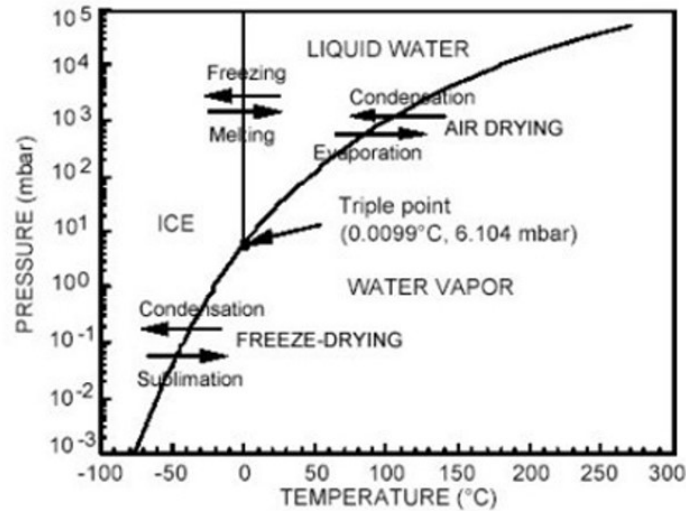
2.4. Transitions and Water

Figure 2. Phase diagram of water. The solid curves indicate pressure and temperature values at the phase transitions, where two phases may coexist. All three phases coexist at the triple point.

The phase transitions of water govern thermal behavior and the properties of most food materials. For example, ice formation occurs in biological materials, including foods, when temperature is below freezing or when pressure is reduced to below the triple point pressure of water (Figure 2). Food materials, however, do not have exact freezing temperatures, since the extent of ice formation below the initial freezing temperature is dependent on temperature and food composition. Usually, supercooling precedes ice formation, which in some foods occurs at low temperatures, well below common freezer temperatures. At high temperatures, the boiling temperature and water vapor pressure may set limits on food processing conditions. Evaporation of water and consequent evaporative cooling are other important phenomena in food processing. In high-pressure food processing, the common transition temperatures of water are significantly altered and may be applied to achieve, for example, instant freezing or melting of water in foods.

2.4.1. Phase Behavior of Water

Phase behavior of water is extremely important in food freezing, dehydration, evaporation, and high pressure food processing, and is described in the phase diagram showing equilibrium lines between the various phases (Figure 2). However, the presence of solutes in the water phase of foods causes solute-dependent depression of the freezing temperature and elevation of the boiling temperature, which should be taken into account during food processing. Freezing of water results in separation of ice from solutes and food solids as almost pure ice crystals. Removal of ice crystals from partially frozen foods is the basis of freeze-concentration as a food concentration technique. Freeze-drying is another food processing operation that is based on the removal of ice crystals from frozen foods by sublimation.

2.4.2. Amorphous Water

Amorphous, non-crystalline solid water can be produced by extremely rapid cooling of water to below its glass transition to avoid crystallization, through vapor deposition and pressure amorphization. Most studies agree that the glass transition of amorphous water occurs between –130 and –140°C, of which –135°C is often the glass transition temperature. Amorphous water tends to crystallize rapidly, almost instantly above the glass transition. In food systems, the glass transition of water represents the lowest glass transition of water soluble and water miscible solids, as their glass transition temperature (in mixtures with water) decreases with increasing water content.

2.4.3. Water in Foods

Properties of water in both solutions and foods differ from those of pure water. Water in foods is the most important solvent, and the depressing effect of solutes on the freezing temperature of water in foods has been well established. Both melting temperature depression and boiling temperature elevation of water in foods results from the vapor pressure depressing effect of the solutes.

Below the freezing temperature, vapor pressure of ice is lower than that of water, and the equilibrium state becomes the solid state. Ice formation in a solution with decreased vapor pressure requires that the vapor pressure of ice be lower than that of unfrozen water. Consequently, ice formation in foods occurs below the freezing temperature of pure water. During freezing, separation of water from foods as ice results in a freeze-concentration of solutes, and the vapor pressure of unfrozen water decreases further. The increasing solute concentration and decreasing vapor pressure cause further depression of the equilibrium freezing temperature of water. Therefore, the extent of ice formation in foods is temperature dependent and often continues at relatively low temperatures. Foods with high amounts of low molecular weight sugars show considerable freezing temperature depression and contain higher amounts of unfrozen water at lower temperatures than foods composed of polymeric compounds. The freezing temperature depression and unfrozen water content are mainly dependent on particular solutes in the water and are apparently independent of the lipid fraction. However, first-order phase transitions of lipids may occur over the same temperature ranges as those of ice and water, which also affect the physical characteristics of foods containing lipids. Various inorganic salts form eutectic solutions with water. One of the most common eutectic salts is sodium chloride, which crystallizes with water from a binary solution at the eutectic temperature, –21.1°C. At this temperature, the solution becomes supersaturated and both water and solute are transformed into the crystalline state. The eutectic behavior of organic compounds (e.g., sugars) is more complicated, as their supersaturated solutions often solidify into a glassy state before eutectic crystallization occurs. In sugar mixtures, crystallization is retarded since the component compounds affect the eutectic behavior and crystallization properties. One of the lowest eutectic temperatures is that of $CaCl_2$ at –55°C. Eutectic temperatures for glucose, lactose, and sucrose are at –5, –0.7, and –9.5°C, respectively. Eutectic crystallization in foods, however, is probably rare due to the complex nature of the materials.

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Biographical Sketch

Yrjö H. Roos is Professor of Food Technology at University College, Cork, Ireland. He has actively contributed to the area of phase and state transitions in foods, and his monograph on "Phase Transitions in Foods" (1995, Academic Press) is a widely used reference book on glass transitions in food systems. His research interests are in the area of physical chemistry of foods and particularly in thermal and time-dependent properties of food systems affecting food properties and rates of food quality changes in processing and storage. His research contributes to understanding phase changes and reaction kinetics in concentrated and frozen foods, explaining time-dependent changes in crystallinity and water sorption, changes in rates of non-enzymatic browning reactions, and enzyme activity and recrystallization of ice.