

15

Glass Transition and State Diagram of Foods

Mohammad Shafiur Rahman

CONTENTS

15.1	Introduction.....	336
15.1.1	Background	336
15.1.2	Glass Transition and Glassy State.....	337
15.2	State Diagram and Its Components	337
15.2.1	State Diagram	337
15.2.2	Components of State Diagram	338
15.2.3	Equilibrium and Nonequilibrium State	340
15.2.3.1	Thermodynamic Equilibrium	340
15.2.3.2	Metastable Equilibrium.....	340
15.2.3.3	Nonequilibrium	340
15.2.4	Cooling and Metastability	340
15.2.4.1	Typical Cooling Curves	340
15.2.4.2	Cooling Rate and Thermodynamic Equilibrium.....	341
15.2.5	State of Water in Foods	343
15.2.6	Differential Scanning Calorimetry	344
15.2.7	Dynamic Mechanical Thermal Analysis	346
15.2.8	Freezing Point	346
15.3	Theoretical Progresses in Glassy State.....	347
15.3.1	Free Volume Theory	347
15.3.2	Relaxation in the Glassy State	348
15.4	Applications of Glassy State Concept in Food Systems	349
15.4.1	Diffusion Process.....	349
15.4.2	Texture and Structure	350
15.4.3	Crystallization	350
15.4.4	Stickiness.....	350
15.4.5	Grain Damage by Drying	350
15.4.6	Pore Formation in Foods.....	351
15.4.7	Microbial Stability.....	352
15.4.8	Desiccation-Tolerant Organisms	352
15.4.9	Oxidation	353
15.4.10	Nonenzymatic Browning.....	353
15.4.11	Enzymatic Reaction.....	354
15.4.12	Denaturation of Protein	354
15.4.13	Hydrolysis	354
15.4.14	Enzyme Inactivation and Other Chemical Reactions	355
15.4.15	Sensory Properties.....	355
	References	356

15.1 Introduction

15.1.1 Background

In the literature, new concepts and hypotheses are being developed and proposed in the areas of food properties to bring food science from empiricism to a strong scientific foundation [130]. The stability of foods is of utmost interest to both food scientists and engineers, and a better understanding of the factors controlling stability or reaction rates is clearly needed [96,132]. In the middle of the twentieth century, scientists began to discover the existence of a relationship between the water contained in a food and its relative tendency to spoil [164]. In the 1980s, Labuza and his group generated significant data on food stability as a function of water activity. They also began to realize that the active water could be much more important to the stability of a food than the total amount of water present. Thus, it is possible to develop generalized rules or limits for the stability of foods using water activity. For example, there is a critical water activity below which no microorganisms can grow. For most foods, this critical range is in the 0.6–0.7 values of water activity. Pathogenic bacteria cannot grow below a water activity of 0.85–0.86, whereas yeasts and molds are more tolerant to a reduced water activity of 0.80, but usually no growth occurs below a water activity of about 0.62. A food product is most stable at its monolayer moisture content, which varies with the chemical composition and structure. This was the main reason why food scientists started to emphasize on water activity rather than total water content. Since then, the scientific community has explored the great significance of water activity in determining the physical characteristics, processes, shelf life, and sensory properties of foods. It is now used to predict the end point of drying, process design and control, ingredient selection, product stability, and packaging selection.

Recently, the limitations of water activity were elucidated and alternatives proposed. Water activity is defined at equilibrium, whereas foods with low and intermediate water content may not be in a state of equilibrium and it is time-temperature-moisture dependent. The critical limits of water activity may also be shifted to higher or lower levels by other factors such as pH, salt, antimicrobial agents, heat treatment, and temperature to some extent [136]. The third limitation is the effect of specific solutes [39]. It has been demonstrated that minimum water activity for the growth of microbial organisms is dependent on the solutes employed to adjust the water activity of a medium [164]. Also, it was observed later that some solutes were more inhibiting than others. Thus, the water activity of a medium is not the only determining factor regulating microbial response. The nature of the solute used also plays an important role, thus the concept of generalization with water activity is questioned. Moreover, water activity does not provide any indication of the state of the water present and how it is bound to the substrate [65]. In addition, many physical characteristics such as crystallization, caking, stickiness, gelatinization, collapse, molecular mobility, and diffusivity could not be explained based on the basis of water activity concept [136]. Therefore, the glass transition concept was put forward.

Glassy materials have been known for centuries, but it is only in the last 70 years or so that scientific understanding of these systems has evolved [55]. Early attempts to describe the vitrification phenomenon concluded that glass is a liquid that has lost its ability to flow, thus instead of taking the shape of its container, glass itself can serve as a container for liquids. Food materials are in an amorphous or non-crystalline state below the glass transition temperature, and are rigid and brittle. Glasses are not crystalline with a regular structure, but retain the disorder of the liquid state. Physically it is solid, but thermodynamically it is a liquid. Molecular mobility increases 100-fold above glass transition. In kinetic terms, Angell [9] described a glass as any liquid or supercooled liquid whose viscosity is between 10^{12} and 10^{13} Pa s, thus effectively behaving like a solid that is able to support its own weight against flow due to gravity. To put this viscosity into context, a supercooled liquid with a viscosity of 10^{14} Pa s would flow 10^{-14} m/s in the glassy state compared with the flow rate of a typical liquid in the order of 10 m/s. In other words, a glass is a liquid that flows about 30 μm in a century [30]. This is evidenced by the fact that ancient stained glass windows are thicker at their base due to flow under gravity [81].

The earliest papers on the glass transition concept in food and biological systems can be found in the literature of the 1960s [103,139,188]. White and Cakebread [188] first highlighted the importance of the glassy state of foods in determining its stability. They were perhaps the first food scientists to discuss the importance of the glassy and rubbery states in relation to the quality control of a number of

high-solids systems. In the 1980s, significant applications of the glass transition concept in food processing emerged when Levine and Slade [97] and Slade and Levine [177] identified its major merits. In the 1990s, Roos, Karel, and other groups generated significant data on glass transition and components of state diagram for a number of food components. It has been mentioned in the literature that foods can be considered very stable at the glassy state, since below glass temperature the compounds involved in the deterioration reactions take many months or even years to diffuse over molecular distances and approach each other to react [178]. A hypothesis put forth recently states that this transition greatly influences food stability, as the water in the concentrated phase becomes kinetically immobilized and therefore does not support or participate in reactions. Formation of a glassy state results in a significant arrest of translational molecular motion, and chemical reactions become very slow [127]. The rules of glass transition concept are: (i) the food is most stable at and below its glass transition, and (ii) higher the $T-T_g$ (i.e., above glass transition), higher the deterioration or reaction rates. Similarly, mechanical and transport properties could also be related with glass transition. It is very interesting to see that this concept has been so widely tested in foods. In many instances, glass transition concept does not work alone; thus, it is now recommended to use both the water activity and glass transition concepts in assessing processability, deterioration, food stability, and shelf-life predictions [145,148].

15.1.2 Glass Transition and Glassy State

Phase transitions in foods can be divided into two groups: first-order and second-order. At first-order transition temperature, the physical state of a material changes isothermally from one state to another (e.g., solid to liquid, liquid to gas) by release or absorption of latent heat (e.g., melting, crystallization, condensation, evaporation). Second-order transition occurs (e.g., amorphous state to glassy state) without release or absorption of latent heat [126]. Glass transition is a nature of second-order time-temperature-dependent transition, which is characterized by a discontinuity or change in slope in physical, mechanical, electrical, thermal, and other properties of a material when plotted as a function of temperature [126]. A process is considered to be of second-order thermodynamic transition if the material undergoes a change in state but not in phase. It is more meaningful to define glass transition as the nature second-order change in the properties since each measurement technique is based on monitoring change in a specific property, and since change or break in properties is achieved within a certain temperature range rather than a specific temperature. A perfect second-order transition occurs at a specific temperature.

Glasses are formed when a liquid or a rubbery system is cooled so rapidly that there is no time for the molecules to rearrange themselves and pack into crystalline domains [68]. With continued cooling, the system exhibits a significant change in thermal, mechanical, and other physical properties at the glass transition region. Experimentally, this is supported by calorimetric studies on supercooled glycerol, which produces a steep change in heat capacity as a function of temperature at 190 K [8]. During heating, devitrification of polydisperse food materials does not occur at a fixed point with the change of specific heat. Instead, networks soften over quite a large range of temperatures [81]. Researchers may prefer to refer the molecular processes as glass transition rather than as second-order transitions to avoid implying a thermodynamic state at which equilibrium conditions are achieved. This is due to the fact that increasing rates of cooling shift the glass transition at higher temperatures and produce a less dense glass, arguing that equilibrium glass conditions lie below the experimentally accessible values [43].

15.2 State Diagram and Its Components

15.2.1 State Diagram

State diagram is the map of different states of a food as a function of water or solids content and temperature [129]. The main advantages of drawing a map are to help in understanding the complex changes when the food's water content and temperature are changed. It also assists in identifying the food's stability during storage as well as selecting a suitable temperature and moisture content for processing. [Figure 15.1](#) shows a state diagram indicating different states as a function of temperature and solids mass fraction.

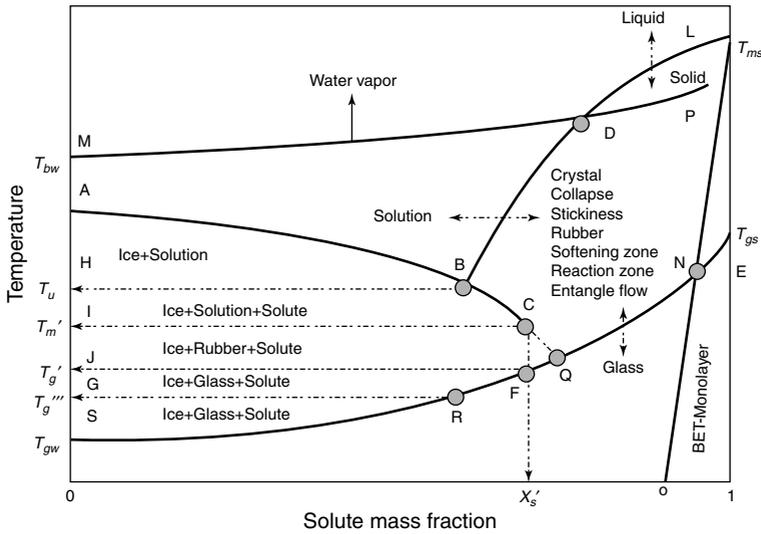


FIGURE 15.1 State diagram showing different regions and state of foods (T_{bw} : boiling point, T_u : eutectic point, T_m' : end point of freezing, T_g' : glass transition at end point of freezing, T_{gw} : glass transition of water, T_{ms} : melting point of dry solids, T_{gs} : glass transition of dry solids. (From Rahman, M. S. 2006. *Trends Food Sci. Technol.* 17: 129–141.)

15.2.2 Components of State Diagram

Earlier, a state diagram was constructed with only freezing curve and glass transition line. Now, attempts are being made to add other structural changes with the glass line, freezing curve, and solubility line in the state diagram. Numbers of microregions and new terminologies are also being included in constructing the state diagram. The state diagram presented in Figure 15.1 was updated from Rahman (130). In Figure 15.1, the freezing line (ABC) and solubility line (BD) are shown in relation to the glass transition line (EFS). The point F (X_s' and T_g') lower than T_m' (point C) is a characteristic transition (maximal-freeze-concentration condition) in the state diagram, defined as the intersection of the vertical line from T_m' to the glass line EFS [131]. The water content at point F or C is considered as the unfreezable water ($1-X_s'$). Unfreezable water mass fraction is the amount of water remaining unfrozen even at very low temperature. It includes both uncrystallized free water and bound water attached to the solids matrix. The point Q is defined as T_g'' and X_s'' as the intersection of the freezing curve to the glass line by maintaining the similar curvature of freezing curve. Matveev [106] proposed a method to estimate the T_g'' and X_s'' intersection point in the state diagram of frozen solution using glass transition temperature of the solute. Point R is defined as T_g''' as the glass transition of the solids matrix in the frozen sample, which is determined by differential scanning calorimetry (DSC). This is due to the formation of some solid matrix-associated unfreezable water and transformation of all free water into ice, although the sample contains different levels of total water before the start of DSC scanning [136]. In the region AHB, the phases present are ice and solution. Below point B, first crystallization of solute occurs, thus HBCI region transforms to three states: ice, solution, and solute crystal. No free water (i.e., able to form ice) exists on the right side of point C (T_m' , end point of freezing with maximal-freeze-concentration condition) and then the very concentrated solution is transformed to rubber state. The maximal-freeze-concentration condition could be achieved using optimum conditions by slow cooling and annealing of the samples. The region ICFJ contains ice, rubber, and solute crystal. Point F is the T_g' , below which point a portion of the rubber state is transformed to glass state, thus region JFS contains glass, ice, and solute crystal. The rate of cooling can shift the points B, C, and F. More detailed effects of cooling on the shift of line ABC are discussed by Rahman [129].

The region BQEL is important in food processing and preservation; many characteristics such as crystallization, stickiness, and collapse are observed in this region [146,150]. In case of cereal proteins using G' and G'' , Kokini et al. [87] determined the entangled polymer flow region when both G' and G''

decreased with the increase of temperature. A reaction zone was defined from thermo-mechanical analysis by plotting G' and G'' as a function of temperature when both G' and G'' increased from a minimum value and start separation each other and then decreased again starting the softening region. All these transitions are observed in the region BQEL. The line BDL is the melting line that is important when products reach high temperatures during processing, such as frying, baking, roasting, and extrusion cooking. In the case of multicomponent mixtures such as food, a clear melting is difficult to observe at high temperature due the reactions between components. In this case, Rahman [129] defines it as decomposition temperature. Line MDP is the boiling line for water evaporation from the liquid (line MD) and solid phases (line DP). This line does not intersect the y-axis on the right.

Recently, many papers presented data on water activity as well as glass transition as a function of water content. However, the link between water activity and glass transition—in order to determine stability—was not identified. Karel et al. [77] attempted to relate water activity and glass transition by plotting equilibrium water content and glass transition as a function of water activity. By drawing a vertical line on the graph, stability criterion can be determined from the isotherm curve and glass transition line. However, at any given temperature (say 25°C), the stability moisture content from glass transition line is much higher than the stability moisture from the isotherm. So the question is how to use them both. Even at present, it is a real challenge to link them. In his first attempt, Rahman [131] plotted BET-monolayer value as LO line—shown in Figure 15.1. It intersects at point N with the glass line ES, which shows that at least in one location (point N) glass and water activity concepts provide the same stability criterion. This approach forms more microregions, which could give different stability in the state diagram. More studies regarding stability need to be undertaken on the left (above and below glass) and right sides (above and below) of the line LO. A successful combination of water activity and glass transition could provide more in-depth knowledge on stability criteria. In addition, how could other factors such as pH and preservatives be linked with these concepts. Are we too far away to develop a unified theoretical basis? The region of drying and freezing process can be easily visualized in the diagram, and product stability could be assessed based on moisture content and temperature. The sources of state diagram of different foods and foods components are compiled in Table 15.1. Most of the transitions defined in the state diagram are commonly measured by the DSC method using appropriate protocol. The thermo-mechanical analysis (TMA) and oscillation methods are less commonly used; however, these methods are more sensitive. More details of measurement methods are presented by Rahman [126,132].

It is evident from the review by Rahman [131] that the degree of variation of food stability below glass transition are not following the rule indicating only the glass transition temperature for developing the stability rule could not be enough. The types or characteristics of glassy state in different types of foods with variations of composition and water content should be used to characterize the stability criterion. In addition, the effect of temperature below T_m' , T_g'' , T_g' , and T_g''' should also be explored. Samples having freezable water are more complex and the four temperatures are defined as: $T_m' > T_g'' > T_g' > T_g'''$ [136]. There are only few references available that include all the four characteristic temperatures

TABLE 15.1

State Diagram Developed for Different Foods and Food Components

Material	Components	References
Apple, grape, onion, strawberry, sucrose, fructose, bacterial suspension, tomato, garlic	Freezing curve, glass line, X_s'' , and T_g''	[4,5,15,24,57,69,88, 137,157,158,165,166]
Honey	Freezing curve, glass line, X_s'' , T_g'' , and T_g'''	[74]
Sucrose	X_s'' , T_g''	[2]
Sucrose, lactose, maltose, glucose, maltodextrins, starch, arabinosylyan	Freezing curve, glass line, X_s' , T_m' , and T_g'	[56,149,150–152]

with their moisture content. It is important to know how these temperatures affect the stability of foods. It would be interesting to explore what other differences in stability exist in products within these different ranges [131].

15.2.3 Equilibrium and Nonequilibrium State

Complex foods exist in states of either unstable nonequilibrium or metastable equilibrium, but never in true thermodynamic equilibrium [51]. Fennema [53] defined the terminology as follows.

15.2.3.1 Thermodynamic Equilibrium

Any food consisting of only one phase requires minimization of free energy to attain thermodynamic equilibrium. For foods containing two or more phases, thermodynamic equilibrium requires that the chemical potential be equal, in every part of the system, for each substance present. Chemical potential determines whether a substance will undergo a chemical reaction or diffuse from one part of a system to another. An equilibrium state can be attained through many possible paths, i.e., the same properties must be obtainable at a given temperature regardless of whether the temperature is approached by cooling or warming.

15.2.3.2 Metastable Equilibrium

Metastable equilibrium refers to a state of pseudoequilibrium, or apparent equilibrium, which is stable over practical time periods but is not the most stable state possible. A metastable state can exist (i.e., conversion to a more stable equilibrium state will not occur) when the activation energy for conversion to a more stable equilibrium state is so high that the rate of conversion is of no practical importance.

15.2.3.3 Nonequilibrium

Nonequilibrium refers to a state that is inherently unstable, i.e., change to a more stable state is likely to occur at a rate of practical importance. The exact rate at which destabilization occurs depends on the particular system and the conditions to which it is exposed.

15.2.4 Cooling and Metastability

15.2.4.1 Typical Cooling Curves

Typical cooling curves during freezing are shown in Figure 15.2 [126]. The abrupt rise in temperature due to liberation of the heat of fusion after initial supercooling represents the onset of ice crystallization. Cooling below the initial freezing point of the sample without formation of ice is defined as supercooling [53]. Pure water can be supercooled by several degrees before the nucleation phenomenon begins. Once the critical mass of nuclei is reached, the system nucleates at point a in Figure 15.2 and releases its latent heat faster than the rate at which it is being removed from the system [126]. The temperature then increases instantly to the initial or equilibrium freezing temperature at point b.

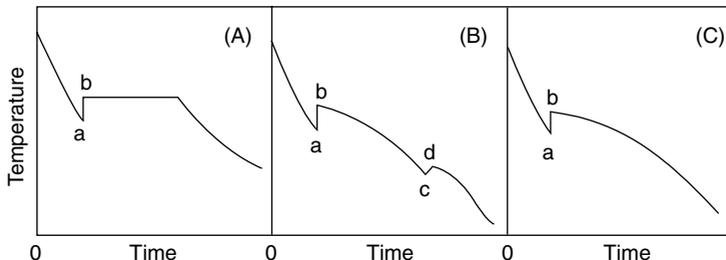


FIGURE 15.2 Typical cooling curves; A: water, B: solution, C: food; a: ice crystallization, b: equilibrium freezing point, c: initiation of solute crystal, d: eutectic point. (From Rahman, M. S. 1995. *Food Properties Handbook*. CRC Press, Boca Raton, FL.)

In aqueous solutions, point a is not as low as in the case of pure water since the added solute will promote heterogeneous nucleation, thereby accelerating the nucleation process. Solute greatly decreases the amount of supercooling for two reasons: faster nucleation and lowered freezing point. In very concentrated solutions, it is sometimes difficult to even induce supercooling [58].

After crystallization is completed, the temperature drops as the sensible heat is released in case of water (Figure 15.2A). In solutions, supersaturation continues due to the freezing of water, and solute crystals may form by releasing latent heat of solute crystallization, causing a slight jump in temperature from c to d (Figure 15.2B). These points are known as eutectic points. However, in reality it is very difficult to trace the points c or d using the cooling curve.

In solutions with multiple solutes or foods, it is difficult to determine the eutectic points. Many different eutectic points might be expected, but each plateau would be quite short if small quantities of solutes were involved (Figure 15.2C). If a material is heated from a frozen or glass state, then the onset of ice melting is called melting point of ice. The freezing point or melting point is considered as an equilibrium process, i.e., neither cooling or heating nor its rate affects the phase transition point of ice crystallization.

15.2.4.2 Cooling Rate and Thermodynamic Equilibrium

Fennema's [53] schematic depiction of a binary system is used to simplify the presentation. The basic format of the figures is shown in Figure 15.3, a plot of sample temperature versus equilibrium state. The columns represent different rates of cooling: equilibrium cooling, moderate cooling, and rapid cooling. The left column (equilibrium cooling) represents cooling at an exceedingly slow rate, the middle column (moderate cooling) represents cooling at a moderate rate consistent with commercial practice, and the right column (very rapid cooling) represents cooling at a rate that is exceedingly rapid. Cooling will follow a downward path in the columns.

15.2.4.2.1 Equilibrium Cooling

Cooling in the first column in Figure 15.3 is in accordance with thermodynamic equilibrium, which is not possible under practical circumstances, nor is it desirable. Thermodynamic freezing is, however, worthy of consideration for conceptual reasons. The path begins at point S, which represents an aqueous solution containing one solute at thermodynamic equilibrium (Figure 15.4). Cooling must occur at an exceedingly slow rate to preserve equilibrium conditions [192], which will eventually bring the solution to its initial

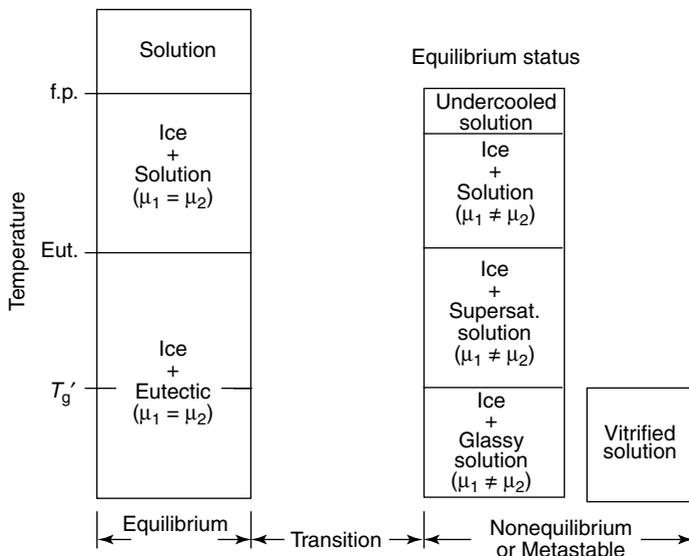


FIGURE 15.3 Equilibrium status based on rate of cooling. (From Fennema, O. 1995. In: *Food Preservation by Moisture Control: Fundamentals and Applications*. Technomic Publishing, Lancaster, PA. pp. 243.)

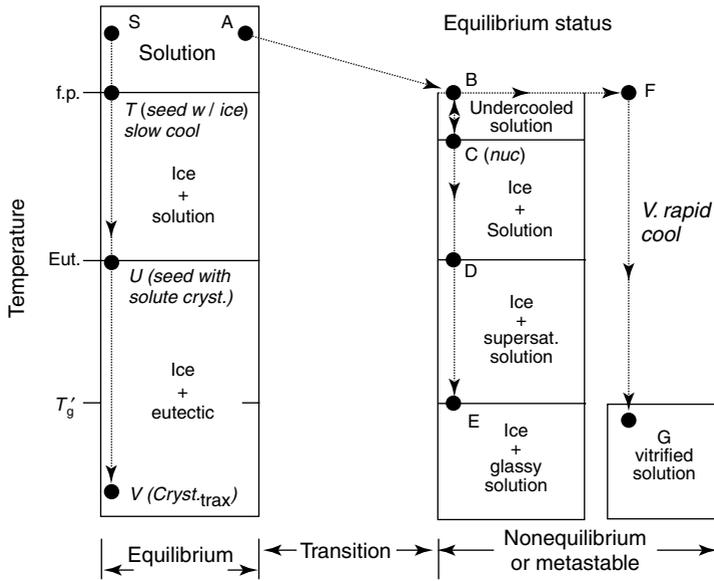


FIGURE 15.4 Equilibrium status and path of cooling. (From Fennema, O. 1995. In: *Food Preservation by Moisture Control: Fundamentals and Applications*. Technomic Publishing, Lancaster, PA. pp. 243.)

freezing point T . At this point, an ice crystal must be added to avoid undercooling and subsequent nucleation of ice, both of which are nonequilibrium events. With the ice crystal in place, further cooling will result in the formation of additional pure ice crystals and a decline in the freezing point of the unfrozen phase. Eventually, the temperature decreases to the saturation or eutectic point U . At this point, a small crystal of solute must be added to avoid supersaturation and subsequent nucleation of solute, both of which are nonequilibrium events. Fennema [53] noted that solute crystallization is mandatory to sustain thermodynamic equilibrium, and it is common even in the presence of seed crystals of solute that the solute will not crystallize at a subeutectic temperature. However, here it is assumed here to form solute crystallization. Further cooling results in crystallization of ice and solute in constant proportion, leaving the unfrozen phase unchanged in composition and freezing point. This dual crystallization process continues at constant temperature until crystallization of water and solute is as complete as possible. Further cooling will simply lower the sample temperature with no further change in physical state.

15.2.4.2.2 Moderate Cooling

The metastable or nonequilibrium pathways are quite different from equilibrium cooling. Both paths start in the solution at point A , and cooling brings the sample to its initial freezing point B . At this point, further cooling at a moderate rate, consistent with commercial practices, results in undercooling to point C . This nonequilibrium supercooling eventually results in nucleation, release of latent heat of crystallization, and, if cooling is relatively slow, a reversal in temperature almost to the initial freezing point B . As ice forms with further cooling, the freezing point of the solution phase declines. With further cooling, more of the original water converts to ice and the solute eventually attains its saturation concentration D (eutectic point). Further cooling typically does not result in nucleation of solute crystals, rather the solution becomes increasingly supersaturated with solute, and this condition is normally metastable. Continued cooling to point E will cause the supersaturated unfrozen phase to convert to a metastable, amorphous solid (a glass) with a very high viscosity (about 10^{12} Pa s). This temperature is the glass transition temperature (T_g), which is usually determined by the composition of the sample and the rate of cooling. If cooling has been slow by commercial standards, the unfrozen solution can be maximally freeze concentrated, and T_g , under this circumstance, will assume quasiinvariant value known as T_g' , which is dependent only on the solute composition of the sample. In practice, maximum freeze concentration is usually not obtained, and the observed T_g differs from T_g' . Numerical data for different food components have been compiled by Rahman [126].

15.2.4.2.3 Very Fast Cooling

A third possible cooling pathway (Figure 15.4) involves very rapid removal of heat from very small samples. This path has no commercial significance for foods. Thus, the ABFG path results in vitrification of the entire sample. The glass temperature is not an equilibrium process, and the cooling rate also affects the glass temperature. With very slow cooling during freezing there is a possibility of heterogeneous nucleation of ice and less possibility of ice formation. In the extreme case (fast cooling), the material may transform from liquid to glass at the melting point without further ice formation.

15.2.5 State of Water in Foods

Different states of water, such as bound, free, capillary, mobile, nonsolvent water, and unfreezable, are defined in the literature [126]. The state of water can be measured with different techniques or methods. The water sorption isotherm is based on three types of water: monolayer, multilayer, and mobile or free water [143]. The BET-monolayer is estimated from water sorption isotherm and commonly presented in the literature. It could be mentioned that only BET-monolayer has strong theoretical basis and should be used in stability determination. The BET-monolayer for a large number of foods and their components has been compiled by Rahman and Labuza [136]. It is not recommended to use GAB-monolayer value due to the number of defects in estimating its real value, although it is popular for its validity up to water activity of 0.9 [126].

Unfreezable water content can be estimated by comparing DSC enotherms of samples having freezable water. Paakkonen and Plit [115] measured the unfreezable water of cabbage using this method. Unfreezable water, can be estimated from the plot of melting enthalpy as a function of water content. This procedure was used for model crackers [62], strawberry [147], date flesh [129], sucrose [2], and garlic [136]. Usually, unfreezable water is independent of total water, present in the system. In case of chitin, unfreezable water increased with the increase of total water, and the amount of freezable water is relatively very low compared to the unfreezable water [116]. In case of water–gellan systems, unfreezable water increased with the size of junction zone [66]. Using NMR technique, Li et al. [99] studied the mobility of freezable and unfreezable water in waxy cornstarch determined by DSC. Water was found to be isotropically mobile for samples over a range of water contents (6.3%–47%) at room temperature. Mobility increased with increasing water content and temperature. A large fraction of unfreezable water was relatively mobile, comparable to a liquid state down to -32°C . The decreasing fraction of mobile water with decreasing temperature suggested that only some of the so-called unfreezable water could be progressively immobilized as temperature decreased. Much of the water remained high in mobility, regardless of the relatively rigid starch molecules in the glassy solid state. This means that water in the glassy state of starch can greatly influence reactions at both ambient and freezing temperatures. At least in this example, the glassy state of the solid materials is not an appropriate term to imply or to predict the molecular dynamics of water and its influence on food stability. Bell et al. [17] determined water mobility in a polyvinyl pyrrolidone (PVP) system, as determined via NMR, and found that water mobility was not affected by glass transition. PVP systems at constant water activities and water contents, but different physical states (glassy and rubbery), had the same water mobility. An evaluation of four chemical reactions showed no relation between water mobility and kinetic data. The effect of water on chemical reactions is multidimensional and cannot be reduced to a single physicochemical parameter.

From the state diagram shown in Figure 15.1, unfreezable water can be estimated from points C and F. Comparisons of determining unfreezable water using different methods were presented for dates [129] and garlic [136]. It is always found that BET-monolayer values are much lower than that of unfreezable water [50]. Other techniques used to determine the state of water are dielectric spectroscopy, Fourier transformation infrared spectroscopy (FTIR), x-ray scattering, nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI), electrical resistance, and self-diffusion [1,65,72,92]. Three states of water (polymer, capillary, and free) were identified in whey by NMR [118]. The NMR and dielectric measurements of starch paste showed one type of water, while agar gels contain two types of water, in samples containing less than 55% moisture [117]. Lang and Steinberg [94] studied the types of water in cornstarch, sugar, sodium chloride, and a mixture of starch and sugar using NMR. It was found that sucrose is a structure former, while sodium chloride is a structure breaker. Three types of water mobility were observed in sucrose solution by NMR techniques [140]. Solute–solvent and solute–solute interactions via hydrogen bonding are suggested as

the mechanisms to explain the observed decrease in water mobility. Lai et al. [93] studied the water mobility in starch-based food products when fat is replaced by fat mimetic components. The active water in starch–sucrose system was strongly dependent on sucrose content [38]. Molecular mobility of starch and water in starch–water mixtures was studied with the NMR technique and related with water sorption isotherm [42]. The effect of bound water on glycinin was studied by FTIR spectra [1]. In addition to the techniques mentioned above, many techniques are being used to determine the mobility, and state of water and solutes available for chemical reactions, but their interpretation is far from straightforward [65].

15.2.6 Differential Scanning Calorimetry

The glass transition temperature is difficult to determine in real food systems due to their complexity and heterogeneity [34]. The most common and popular method used to determine glass transition is the DSC that detects the change in heat capacity occurring over the transition temperature range. For almost half a century, most of the work in these systems has been carried out by DSC, which measures as a function of temperature the difference in energy inputs into a substance and its reference, with both materials subjected to a control temperature program. In the 1990s, modulated DSC (MDSC) was commercialized to increase the sensitivity and resolution of thermal analysis, and provide the heat capacity and heat flow in a single experiment [81,185]. It is common to use mainly heating DSC curve to study the characteristic transitions, and usually a heating rate of 5°C/min is used. However, heating rate affects the values of glass transition. Experimental conditions such as cooling rate, sample size, and annealing conditions used should always be reported with glass transition values. Calorimetric or spectroscopic techniques have some limitations in terms of sample size and shape, and water content control. In some cases, for example, in case of starch it is less sensitive.

The typical DSC curves shown in Figures 15.5 through 15.7 are based on the level of moisture content and types of the samples. Figure 15.5 shows DSC graphs for low moisture content (i.e., high solids) when there is no freezable water in the sample. In the case of samples with unfreezable water, the DSC curve is shown in Figure 15.5, indicating no ice formation during cooling or ice melting during heating. Many foods or food components showed an exothermic (Figure 15.5B) or endothermic (Figure 15.5C) peak. Kaspis [81] pointed out that (at a low moisture content <30%) regardless of the polysaccharide types, an endothermic peak appeared consistently within the 45°C–80°C temperature band during the first heating scan on a calorimeter. The position of the peak remained constant and independent of the temperature shifts of the glass transition (when it appeared), but the associated enthalpy increased with moisture content [12]. This was interpreted on the basis of stabilizing enthalpic associations between water molecules and ordered macromolecular sequences. The endothermic overshoot may be deliberately used to help in detecting the glass transition, with materials for which the heat capacity jump is particularly small and smeared out over a broad temperature range. There is no consensus for the definition of the glass transition point on a DSC curve among the various points that may be chosen as onset (T_{gi}), mid (T_{gp}), and end (T_{ge}). Earlier data presented in the literature dealt mainly with the mid or peak point; however, the recent trend is to present onset, mid, and end points. Champion et al. [34] pointed out that a glass transition should be characterized by at least two parameters indicating its onset or mid and the width of the transition.

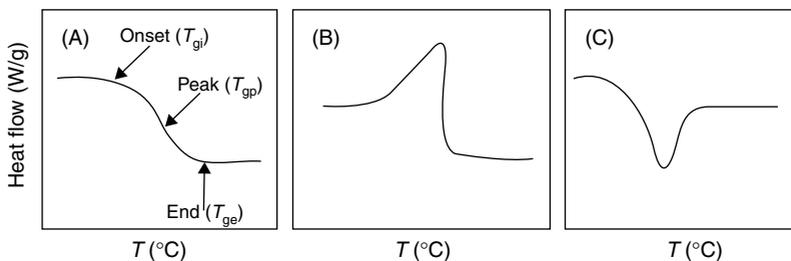


FIGURE 15.5 Typical DSC thermograms for glass transition of samples containing unfreezable water. (From Rahman, M. S. 2006. *Trends Food Sci. Technol.* 17: 129–141.)

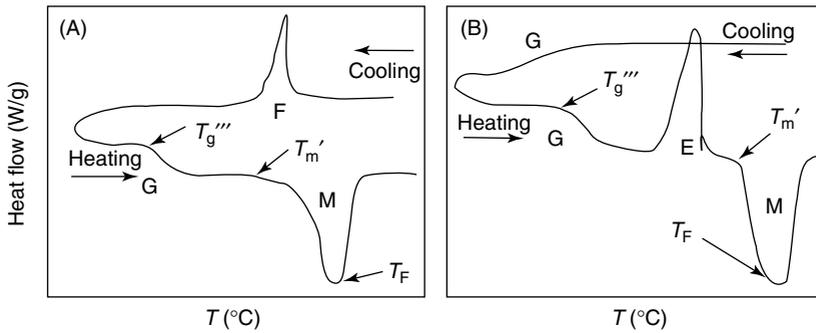


FIGURE 15.6 Typical DSC thermograms showing glass transition, freezing and melting endotherms for sample containing freezable water. (From Rahman, M. S. 2006. *Trends Food Sci. Technol.* 17: 129–141.)

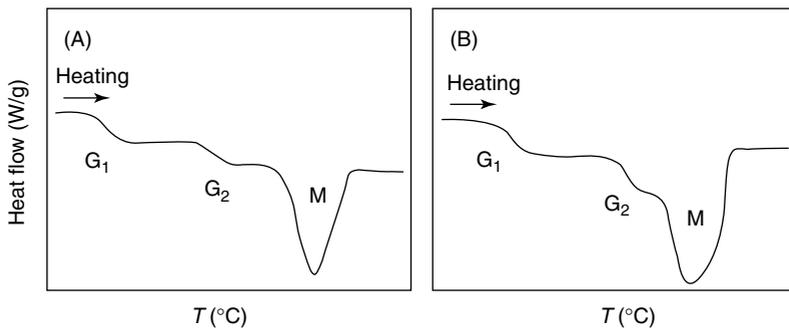


FIGURE 15.7 Typical DSC thermograms showing two glass transitions and melting endotherm for a sample containing freezable water. (From Rahman, M. S. 2006. *Trends Food Sci. Technol.* 17: 129–141.)

Figure 15.6 shows DSC cooling and heating curves for samples containing freezable water. If the moisture content is high and the cooling rate is relatively slow, freezing of the water is observed during cooling—as shown by F in Figure 15.6A. If the sample contains relatively low freezable water and the cooling rate is relatively fast, the freezing exotherm does not appear—as shown in Figure 15.6B. The location of T_g''' and T_m' is shown in Figure 15.6. In many samples, the exothermic peaks E (Figure 15.6B) are observed after glass transition and melting endotherm in the heating DSC curve. To determine T_m' , optimum annealing needs to be performed to maximize the ice formation at a temperature between T_g''' and apparent T_m' (without annealing). It is common to perform annealing at $T_m' - 1$. Owing to kinetic constraints, solutions with high initial solutes (60%–80%) may require several days or even weeks of annealing at $T_g' < T < T_m'$ until the maximally freeze-concentrated state is achieved [77]. The observed exothermic enthalpy relaxation peak during rewarming, between the glass transition and the melting endotherm, may disappear after annealing or rescanning [15,130]. This process, generally called devitrification, corresponds to ice crystallization. Freezable water that had remained unfrozen due to hindered crystallization during fast cooling, crystallizes during warming [104].

In many cases, two glass transitions are observed—as shown in Figure 15.7—even with annealing [57,130]. In extreme cases, a second glass transition may be observed with the melting endotherm (Figure 15.7B). Different hypotheses are proposed for two or more glass transitions. The two transitions occurred, one due to the backbone of a large polymer or less mobile component, and the other due to the less mobile or side chains [129]. Another reason could be due to the incompatibility of different solutes in the mixture [110]. Yet another proposed concept for solutions with a single solute is: it is the result of the formation of a solute-crystal-rich, unequilibrated phase trapped around or within the rapidly nucleated ice crystals, and solute inclusion within the ice crystals itself [64]. Li and Chen [100] used these two glass transitions to identify the degree of compatibility of rice starch–hydrocolloid mixtures. In the case of compatible samples, such as rice starch–high methoxyl pectin mixture, a new single glass transition

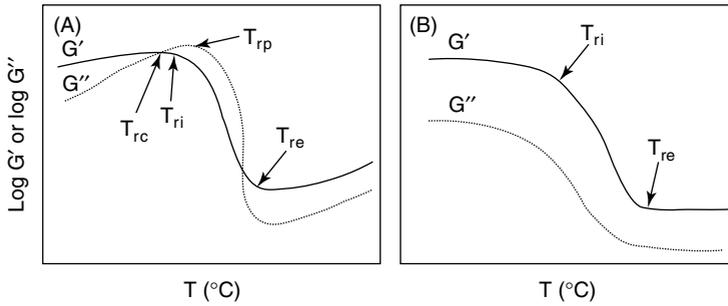


FIGURE 15.8 The typical plots of $\log G'$ or $\log G''$ showing the glass transition. (From Rahman, M. S. et al. 2002. *J. Food Eng.* 53: 301–313.)

was exhibited, which is between the transitions of two individual components. In contrast, incompatible rice starch–low methoxyl pectin and rice starch–locust bean gum showed two transitions corresponding to the two individual components. In the case of concentrated samples with freezable water, no ice crystallization was observed during cooling, indicating that vitrification was accomplished.

15.2.7 Dynamic Mechanical Thermal Analysis

Other useful and sometimes more sensitive methods include thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), dynamic mechanical thermal analysis (DMTA), and dynamic oscillation method. In DMTA, structural properties are examined with G' and G'' as a function of temperature at a constant frequency or time of measurement. Figure 15.8 shows the typical curves. Again, it is necessary to specify how the transition temperature (T_r) is defined from the experimental curves. The temperature is commonly taken from the maximum of the loss factor ($\tan \delta$), which is more easily determined. The maximum of the loss modulus (E'' or G'') is much better for transition determined from the point of view of its physical meaning [34]. Moreover, no $\tan \delta$ peak is expected with small molecular weight systems. In Figure 15.8A, it was proposed that the rheological glass transition was the point between the glass transition and the glassy state [83]. The transition from T_g (DSC glass) and T_r (mechanical or rheological glass) should not be considered as fully equivalent. Shalaev and Kanev [167] mentioned that mechanical glass transition occurs above DSC glass due to the sample's ability to keep its form. In DSC and DMTA, the sample is subjected to stresses of different physical nature (change of temperature in DSC, shearing or compression in DMTA). The experimental time may also be different (depending on cooling–heating rates and annealing in DSC, on measurement frequency in DMTA). Blond [23] and Kasapis et al. [82] compared the results for glass transition from DSC and mechanical methods. A different coupling of the imposed perturbations with the structural units (with particular relaxation times) may be responsible for discrepancies in the data obtained with different techniques. In Figure 15.8B, a cross over between G' and G'' is not observed. In general, it can be recommended to present T_{ri} , T_{re} , T_{rc} , and T_{rp} in comparison with glass transition by DSC.

15.2.8 Freezing Point

Cooling curve is one of the most simple and popular methods to measure the freezing point of foods. The complete discussion is not presented here since details of the cooling curve method are given by Rahman [126] and Rahman et al. [134]. The cooling curve method was used to measure the freezing point of milk [36,37], coffee extract [14], dates [84], tuna flesh [135], and garlic [136].

Typical melting endotherms for melting of ice are shown in Figure 15.9. The ice melting or freezing point is commonly characterized from the endothermic peak during melting [63,130]. This method provides very accurate determination for a sharp peak. In case of a wider peak (Figure 15.9C), it is difficult to determine from the peak. A wider peak appears due to the wide variation in the state of water in foods; in this case, the maximum slope of the endotherm (point b in Figure 15.9C) or the extra-plotted peak is used as onset temperature of the ice melting [57,63]. When the sample contains mainly free water, it shows a sharp endothermic peak at melting similar to pure water (Figure 15.9C). Multiphase natures of the DSC curves are

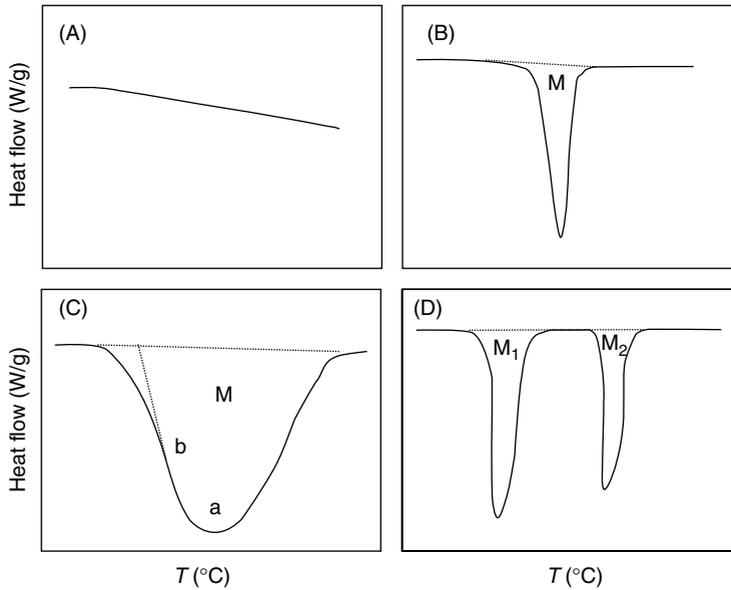


FIGURE 15.9 Typical thermogram for sample containing unfreezable water and different types of melting endotherms of ice. (From Rahman, M. S. 2006. *Trends Food Sci. Technol.* 17: 129–141.)

found for the metastable states of water in gum from *Acacia senegal* [124] and gellan [66] (Figure 15.9D). The sample containing nonfreezing water shows no first-order transition (Figure 15.9A).

15.3 Theoretical Progresses in Glassy State

Kasapis [81] provided scientific progress of the science of the glassy phenomenon, which cuts across several domains of science. The present knowledge about glass transition is essentially phenomenological, very little is known about theoretical aspects [34]. Champion et al. [34] reviewed different proposed theories for understanding the glass transition, including free volume theory, entropy-controlled cooperative motions, mode coupling theory, frustration-limited domains, and hierarchical correlated molecular motions. Basic and deeper understanding could determine their real applications in food technology.

15.3.1 Free Volume Theory

Among all the theories, the free volume theory and relaxation phenomenon are beginning to contribute in explaining some changes in foods below glass temperature. Although there is as yet no fully satisfactory theory of the glass transition in polymers, the free volume approach has been widely employed in a quantitative fashion to interpret glassy phenomenon in terms of molecular processes [48]. The useful and simple concept argues that the total volume per mole of a material is the sum of the free volume and occupied volume. The latter includes not only the van der Waals radii but also the volume associated with vibrational motion of atoms. The free volume is therefore that extra volume required for larger scale vibrational motions than those found between consecutive atoms of the same chain [13]. On the free volume concept, glass transition is defined as that temperature at which free volume collapses sensibly to zero and the mobility is restricted keeping only movement allowed by the occupied volume [109]. Quantitatively, Williams–Landel–Ferry (WLF) equation is proposed as [189]:

$$\log\left(\frac{\mu}{\mu_g}\right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (15.1)$$

where T and T_g are the experimental and reference temperature, and C_1 and C_2 the WLF constants (phenomenological coefficients), which are related to the free volume. Other properties, such as shift factor (a_T), G' , G'' , and rate constant could also be used instead of μ . The universal values of C_1 and C_2 are -17.4

and 51.6, respectively, as given by Williams et al. [189]. Soesanto and Williams [180] found these coefficients valid for the WLF correlation of the viscosity of sugars. Ferry [54] identified that these values fluctuate slightly as a function of material types. The VTF equation is also used and expressed as

$$\mu_g = A \exp\left(\frac{BT_o}{T - T_o}\right) \quad (15.2)$$

where T_o is the reference temperature and A and B are the parameters. Angell et al. [11] and Angell [10] classified material as strong/fragile through the glass transition based on the variations of B and C_2 . The fragility parameter m was introduced to differentiate fragile systems ($100 < m < 200$), which are highly sensitive to temperature changes above glass transition, from strong ones ($16 < m < 100$), which are less disturbed by passage through the glass transition. The application of various methods to estimate m for food materials is available in the literature [174,175]. Champion et al. [34] discussed different values of m for food components and their practical significance of the strong/fragile classification with respect to foods. They mentioned that a small variation in the value of m for two products may result in a large difference in stability, as the sensitivities to temperature around glass transition are different. It could also benefit from a better knowledge of the strong/fragile behavior of the material processed, such as extrusion, puffing, or flaking. The theory of free volume has been quite successful in following the temperature dependence of viscoelastic functions in the glass transition region and relating parameters to molecular characteristics. Complex nonlinearity and nonexponentiality could not be explained much with free volume approach. The popularity of WLF/free volume approach is due to its simplicity, and it considers that all relaxation processes have the same temperature dependence. In addition, it does not consider the intermolecular interactions, which are more fundamental, and the ultimate determining factor of molecular dynamics in densely packed polymers [112].

15.3.2 Relaxation in the Glassy State

The glass transition temperature is a kinetic and relaxation process associated with the primary relaxation of the material [34]. The relaxation time (characteristic time of mobility) is the time that is necessary for the recovery of equilibrium conditions after perturbation of one property of the material. As a relaxation phenomenon, glass transition temperature can be studied with techniques such as mechanical or impedance spectroscopies, termed as α -relaxation (main relaxation). When the temperature is well above glass transition, the molecules or the structural units (such as the repetitive element of a polymer) can move independently from each other because there is enough free volume between the entities. The molecular organization in the material is strongly dependent on temperature above glass transition, but it is relatively stable below glass: molecules stay in an isoconfigurational state, the cooperativity effect being restricted [34]. Within the glassy state, the change in dynamic properties obeys the Arrhenius law. Relaxation processes can be observed in the glassy state with mechanical or impedance spectroscopies. This is also evident with the endothermic features on DSC curves. In addition to the main relaxation α , several secondary relaxations β are observed. Its origin is still being investigated and it corresponds to: more localized molecular motions (for example, in the case of sugar molecules it is linked to the presence and motions of $-OH$ groups), molecular structure of carbohydrate, and rotation of the whole molecule in heterogeneity of the matrix [25,35,61,70,73,156]. Below glass, a microstructural change may take place, which corresponds to the system approaching the metastable equilibrium, with some extra loss in enthalpy and volume. This *physical aging* can be regarded as a continuation of the α relaxation. The more compact molecular organization and the strengthening of interactions result in changes in mechanical and also in transport properties. Its relevance is being increasingly recognized with cereal products [25,34]. Physical aging is responsible for the appearance of various features on DSC curves: endothermic overshoot that expresses rapid enthalpy recovery after aging below glass transition, but also an exothermic event when rapid cooling is followed by a much slower rewarming [175]. Two other characteristics need to be explained in the glass transition domain – nonlinearity, which means that the characteristic changes with time, as it depends on the structure of the glass and nonexponential behavior, which means that the process of α -relaxation cannot be described by a single relaxation function, due to microstructural heterogeneities.

Nonexponentiality is most commonly interpreted as a distribution of relaxation times and mathematically represented by a so-called stretch exponential function [34]:

$$\Phi = \exp[-(\theta/\tau)^k] \quad (15.3)$$

where Φ is the mechanical property and exponent k close to 1 for strong liquids (nearly exponential relaxation). For fragile liquids, it changes from near 1 at high temperature to a value close to 0.3–0.5 near glass transition [34]. In this situation, Ngai et al. [112] used stretched exponential function of Kohlrausch, Williams, and Watts (KWW). In case of stress relaxation modulus

$$\Phi = (\Phi_g - \Phi_e)[\exp(\theta/\tau)^{1-n}] + \Phi_e \quad (15.4)$$

where Φ_g is the glassy mechanical property, Φ_e the equilibrium mechanical property of the local segmental motion, θ the time after the application of a fixed strain, τ a measured relaxation time, and n the coupling constant, which ranges from 0 to 1.0. It was found that strongly coupled (interacting) systems have high values of n and an apparently broad distribution of relaxation times, which is the cornerstone of the coupling theory [144]. The parameter n need not be constant during a relaxation, hence the theory is not thermorheologically simple. Kasapis [81] anticipated that much attention would be focused in the area of coupling theory in the future. Other types of theoretical models are discussed by Champion et al. [34].

15.4 Applications of Glassy State Concept in Food Systems

A low glass transition means that at room/mouth temperature, the food is soft and relatively elastic, and at higher temperatures it may even flow. In contrast, a food with a high glass transition temperature is hard and brittle at ambient temperature. Glass transition and state diagram concepts are widely applied in foods to explore its validity. The following section provides a review on this aspect.

15.4.1 Diffusion Process

The glass transition affects diffusion-controlled chemical reactions through the decrease of diffusion coefficient [79,179]. The decrease in diffusivity is due to the changes in viscosity and mobility. The diffusion time of a water molecule over 1 Å distance should be more than 10^6 years at room temperature in a glassy matrix based on the Stoke–Einstein relation [34]. The timescale for the loss of stability in food at low water content is not so large. Ablett et al. [3] measured translational diffusion coefficients of water using the pulsed-field gradient NMR technique in 81% pullulan. They showed that diffusivity of water is around 4×10^{-11} m²/s at glass transition. There was no significant drop below the glass transition, instead there was a change in slope above or below the glass transition when diffusivity was plotted as a function of temperature. The diffusion coefficient of water in low-moisture food polymers decreased with the decrease in moisture content, without any break in the glass transition when diffusivity was plotted versus water content. The diffusivity depends mainly on moisture content and exhibits a low sensitivity to the nature of the surrounding polymer [27]. In the case of water diffusivity in maltose–water mixtures above and below glass transition, Parker and Ring [119] plotted diffusivity and viscosity as a function of T_g/T and found that the slopes for diffusivity and viscosity with temperature were not parallel, but instead were extremely divergent when $T_g/T > 0.8$. This decoupling evidence (between viscosity of the diffusion medium and diffusion of small molecule) indicated that the decrease in diffusivity near or below glass is not solely due to the decrease in viscosity. Another important factor affecting diffusivity, in addition to glassy state, is the porosity, porous structure, and structural collapse of foods. The release of entrapped volatiles and flavors is also important to food stability. Arrhenius plot of diffusivity of helium, methanol, and ethyl bromide and glass transition temperature of sucrose: raffinose matrix showed changes in the slope at glass transition [77].

When the molecular size of the diffusing molecule is very small, compared to the molecules of the matrix, the Stokes–Einstein relation is inadequate to predict the reactant diffusion. In this case, solute diffusion and macroscopic viscosity did not significantly reduce the diffusion of small molecules [46,95,105]. The decoupling effect from Stokes–Einstein relation based on viscosity was also observed for diffusion of fluorescein in sucrose solutions [33]. The decoupling started at $T_g/T > 0.86$, and the discrepancy increases as temperature reaches glass transition. The motion of small probes in such viscous materials may be facilitated by the presence of nanodefects or by local motions in the material (secondary relaxations).

15.4.2 Texture and Structure

If the moisture content of crispy products such as chips, crackers, cornflakes, and extruded products increases due to water sorption or if the temperature is increased during storage, the crispy structure is lost [34]. Roudaut et al. [155] showed that the loss of the crispy texture of dried white bread corresponds to a critical water content of 9%–10% for which samples are in the glassy state. A sharp decreasing trend was observed when compressive failure stress of the frozen sample is plotted as a function of temperature. This change was defined as brittle–ductile transition. It is not generally true that brittle–ductile appears at glass transition, although in certain cases the brittle–ductile transition coincided with the glass transition temperature [120]. Nicholls et al. [113] clearly demonstrated that the brittle–ductile transition occurred within gelatinized starch, while it was still in the glassy state as defined by the DSC. Watanabe et al. [187] found that there was a remarkable difference between the brittle–ductile and glass transitions temperature in case of fish meat. They pointed out that to ascertain the reasons as to why these are different, lengthy and detailed experimentation is necessary because the brittle–ductile transition depends on a number of extrinsic factors, including strain rate, temperature, stress state, specimen geometry, and the presence of notches and flaws.

15.4.3 Crystallization

Temperatures above glass allow molecular mobility and rearrangement of molecules to the crystalline state [97]. Crystallization releases adsorbed water, which in closed containers further plasticizes the remaining amorphous portion of the material [85,154]. Crystallization causes the most drastic changes to the physical properties of food polymers. It may considerably affect food stability and it may impair the rehydration properties of food powders [85,154,169]. It also affects textural properties, e.g., crystallization of starch in bakery products during staling [179]. Lactose crystallization in milk powders leads to increased free fat and flavor deterioration, and it may also promote nonenzymatic browning [85,160]. The crystalline materials are not able to entrap other compounds, which become completely released due to crystallization, thus volatiles are lost and lipids become exposed to oxygen. Increasing $T-T_g$ raises the rate of crystallization, with increasing crystallinity. Sandiness in ice cream resulted from lactose crystallization [150]. The crystallization time for amorphous lactose can be predicted using WLF equation [154]. The extent of crystallization and melting behavior of gelatinized cornstarch was affected by $(T-T_g)$ [71]. Crystallization under low $T-T_g$ conditions appears to produce smaller and less perfect crystallites than those produced under high $T-T_g$ conditions, owing to lower molecular mobility. The crystallization of isomalt in plasticized form was reduced by adding hydrogenated starch hydrolysates (HSH). The low-molecular HSH appeared to be more effective in reducing crystallization than high-molecular HSH, which indicates that high glass transition is not necessarily the best inhibitor of isomalt crystallization [108]. In honey stored at 20°C, coarse crystals were formed with melting temperatures between 45°C and 65°C, whereas honey stored at –20°C granulated as a finely grained, fondant-like honey, melting between 25°C and 45°C. In honeys stored at 10°C and 4°C, big and small crystals were produced having intermediate characteristics when compared with honeys stored at 20°C and –20°C [102].

15.4.4 Stickiness

Initiation of viscous flow, caking, and stickiness depends on the glass transition temperature. In the case of spray-dried lactose, caking and collapse increased with increase in $T-T_g$ [101]. The sticky point of an amorphous sucrose and fructose was found to be 10°C higher than glass transition [153].

15.4.5 Grain Damage by Drying

It was found that for a Bengal variety of rice grain, at a moisture content of 15% (wet basis) the values for thermal expansion coefficients β_{glass} and β_{rubber} were $8.60 \times 10^{-5}/^\circ\text{C}$ and $4.99 \times 10^{-5}/^\circ\text{C}$, respectively [121]. Similarly, for Cypress at 14% moisture content, the values for β_{glass} and β_{rubber} were $8.80 \times 10^{-5}/^\circ\text{C}$ and $4.26 \times 10^{-5}/^\circ\text{C}$, respectively. It can be seen that there is a considerable difference between the values

of β_{glass} and β_{rubber} in the two zones of the state diagram. A hypothesis based on glass transitions inside rice kernels was proposed to explain rice fissure formation during the drying process [44,122,170]. Similarly, when drying occurred in the glassy region, head rice yield was not reduced noticeably after drying. When drying occurred in the rubbery region and no tempering was performed immediately following drying, head rice yield reduction would be marginal if the drying durations were shorter than the maximum moisture content gradient time [190,191].

15.4.6 Pore Formation in Foods

The glass transition theory is one of the concepts that has been proposed to explain the process of shrinkage, collapse, fissuring, and cracking during drying [45,75,76,89,129]. The *hypothesis* indicates that a significant shrinkage can be noticed during processing only if the drying temperature is higher than the glass transition of the material at that particular moisture content [6]. The methods of freeze-drying and hot-air drying can be compared based on this theory. In freeze-drying, if the drying temperature is below or close to T_g' (maximally freeze-concentrated glass transition temperature, which is independent of solids content) or T_g (glass transition as a function of solids content), the material is in the glassy state. Hence shrinkage is negligible. As a result, the final product is very porous. With hot-air drying, however, if the drying temperature is above T_g' or T_g , the material is in the rubbery state and substantial shrinkage occurs causing a lower level of pores. Karel et al. [77] performed freeze-drying under high vacuum (0.53 Pa) and reduced vacuum conditions (90.64 and 209.28 Pa) to obtain varying initial sample temperatures that were below (-55°C), near (-45°C), and above (-28°C) for the three vacuum pressure. Collapse was determined by measuring apparent shrinkage before and after freeze-drying of apple, potato, and celery. Samples dried at -55°C showed no shrinkage (more pores), while shrinkage increased with an increase in drying temperature, justifying the glass transition concept. Recent experimental results dictate that the concept of glass transition is not valid for freeze-drying of all types of biological materials, thereby indicating the need to incorporate other concepts [159], and thus a unified approach ought to be used. In the case of freeze drying, pore formation in food materials showed two distinct trends when shelf temperatures were maintained at a constant level between -45°C and 15°C [159]. The materials in group I (i.e., abalone, potato, and brown date) showed a decreasing trend, whereas those in group II (i.e., apple and yellow date) showed an increasing trend in pore formation. This may be due to the structural effects of the materials. However, none of the papers measured the actual temperature history of the sample passing during freeze drying. The temperature and moisture history of the sample during freeze drying could shed more fundamental knowledge and thus help explain the real process of pore formation or collapse.

In many cases of convection air-drying, observations related to collapse or pore formation are just the *opposite of the glass transition* concept [47,137,138,186]. The mechanism proposed for this was the concept of case hardening, and internal pressure development [6,137,138]. They indicated that at a low drying rate (low temperature), the moisture gradient within the product is small and internal stresses are low and hence the material shrinks down fully onto a solid core, and shrinkage is uniform. At a high drying rate (higher temperature), the surface moisture decreased very rapidly so that the surface became stiff (i.e., case hardening phenomenon), limiting subsequent shrinkage, thus increasing pore formation [133]. In this instance of case hardening, the permeability and integrity of the crust play a role in maintaining the internal pressure inside the geometric boundary. Internal pressure always tries to puff the product by creating a force to the crust. Glass transition concept cannot explain the effect of crust and internal pressure. In the case of tuna meat, vacuum-drying produced higher porosity compared to air drying when both samples were dried at 70°C [132]. The porosity of dehydrated products increased as vacuum pressure decreased, which means shrinkage can be prevented by controlling pressure [90]. Microwaving creates a massive vaporization situation causing puffing [123]. This indicates that in addition to the temperature effect, environment pressure also affects pore formation, and this effect cannot be explained by the glass transition concept. Similarly, in the case of extrusion, after the processing temperature exceeds 100°C , porosity also increases correspondingly, which is contrary to the glass transition concept [7]. This is due to the rapid vaporization of water vapor at the exit of the die. After analyzing experimental results from literature, Rahman [128] identified that the glass transition theory does not hold true for all products or processes. Other concepts, such as surface tension, pore pressure, structure, environment pressure, and mechanisms of

moisture transport, also play important roles in explaining the formation of pores. Rahman [128] hypothesized that as capillary force is the main force responsible for collapse, counterbalancing this force causes formation of pores and lower shrinkage. The counterbalancing forces are a result of the generation of internal pressure due to vaporization of water or other solvents, variations in moisture transport mechanism, and pressure outside the material. The other factor could be strength of the solid matrix (i.e., ice formation; case hardening; surface cracks formation; permeability of water through crust; change in tertiary and quaternary structure of polymers; presence or absence of crystalline, amorphous, and viscoelastic nature of solids; matrix reinforcement; and residence time). However, some of these factors are related to glass transition.

15.4.7 Microbial Stability

The microbial stability of food has long been estimated by its water activity. The rule is: (i) lower the water activity, more microbiologically stable the food, and (ii) foods are most stable at its BET-monolayer moisture content. The water activity at the monolayer water content is also called the *critical water activity*. One defect in this concept is that microbial stability is affected by the nature and type of the solute at a given water activity. Another weakness is that water activity is defined at equilibrium, whereas foods at low and intermediate moisture are not in a state of equilibrium. In the dynamic state, water may be migrating from one component of food to another. This nonequilibrium state is difficult to predict by the equilibrium state defined by water activity.

What are the alternatives? Slade and Levine [176] and Franks [59] maintained that water activity could serve as a useful, but not the sole indicator of microbial safety. Slade and Levine's [176] hypothesis was that water dynamics or glass-rubber transition may be applied instead of water activity to predict the microbial stability of concentrated and intermediate-moisture foods. Sapru and Labuza [161] studied the inactivation of bacterial spores and their glass transition temperature. Spores at glass transition have high heat resistance, and above glass they are easy to inactivate. At a given temperature, the inactivation rate decreases with the increase of glass transition temperatures of spores. Chirife and Buera [40] maintained that glass-rubber transition would not be useful in predicting with confidence the microbial stability of foods. They analyzed data from the literature and concluded that water activity and glass transition are two different entities. The mobility factors (i.e., glass transition) in addition to water activity are not useful for a better definition of microbial stability of foods. Water activity is a solvent property and glass is a property related to the structure of food. Thus, both properties are needed for understanding food-water relationships at different conditions [40,182,184].

Macroscopic heterogeneities in a food material can induce the presence of areas with a higher mobility [34]. Chirife et al. [41] investigated microbial stability in glassy white bread and maltodextrins. They showed that mold growth may be possible below glass transition if nonglassy microregions exist. Champion et al. [34] stressed the need for further studies to investigate the effects of nonhomogeneous water distribution and phase separation on reaction rates. Hills et al. [67] first studied using NMR relaxation and electrical conductivity to actually distinguish the effect of local rather than global water activity on microbial stress in porous media. They found that microbial stress does not correlate with the global water activity measured for the whole assembly, but rather with the local water activity of the water actually surrounding the cells.

15.4.8 Desiccation-Tolerant Organisms

Desiccation-tolerant organisms (anhydrobiotes), such as seed and pollen, are capable of surviving the removal of their cellular water. The life span of seeds can be remarkably long, ranging from decades to centuries [86,125,181] and even millennia [168]. In the late 1980s, Burke [31] forwarded the hypothesis that the cytoplasm of seeds could enter into a glassy state. He suggested that in dry anhydrous organisms, glasses could be formed from cell solutes like sugars that were known to provide protection from denaturation of large molecules and formation of molecular aggregates, and high viscosity may stop all chemical reactions that require molecular diffusion. Thus, the glass concept turned out to be an interesting hypothesis to account for survival in the dry state. The physiological importance of the glassy state in desiccation tolerance and storage longevity was also assessed. More recently, in addition to the measurement of glass transition temperature, efforts focused on the assessment of additional physical properties such as molecular density and local viscosity of the intracellular glassy matrix [30]. When the concept of glasses

was introduced in seed science, sugars were thought to play an important part in the composition and properties of the glassy matrix. Many studies were conducted to explore the biological and physicochemical properties of the intracellular glassy matrix. Several techniques have been developed to provide further insights into the molecular properties of glasses, such as electron paramagnetic resonance (EPR) and Fourier transform infrared (FTIR) spectroscopy. Recently, Buitink and Leprince [30] reviewed the molecular properties of glasses. It is considered that the protective effect is improved by hydrogen bonding, water replacement of the sugars with proteins, increasing T_g and T_c (collapse), and filling the small voids. A *perfect biological glass* would exhibit a high T_g and T_c , low molecular mobility, and high density, existing of a mixture of molecules that have high hydrogen bonding capacity to undergo direct interactions with their neighboring molecules as well as to prevent phase separation and crystallization [30].

15.4.9 Oxidation

The oxidation phenomenon, such as fat or ascorbic acid oxidation, occurs in low-moisture food systems. The oxidation of unsaturated lipids entrapped in sugar-based matrices is affected by physical changes such as collapse or crystallization occurring above glass transition [91,169]. The encapsulated oil is released as a consequence of the crystallization of amorphous lactose. The released oil undergoes rapid oxidation, while encapsulated oil remains unoxidized.

15.4.10 Nonenzymatic Browning

Karmas et al. [80], Karel et al. [78], and Buera and Karel [29] indicated that phase transitions with physical aspects of the matrix are factors affecting the rates of nonenzymatic browning reactions. Nonenzymatic browning below glass transition was very slow. The systems used were vegetables, dairy products, and model food systems with amino acids and sugars in a PVP matrix. Karmas et al. [80] showed that the rate of the reaction is low at temperatures below glass and increases with increase in $T-T_g$. They also pointed that the reaction is also controlled by several other factors such as structural changes and water content independent of its plasticizing effect. In this case, both moisture and glass transition affected the reaction rate [29]. This is due to the changes in diffusion coefficient below glass transition when nonenzymatic reactions take place in the diffusion-limited region. Roos and Himberg [148] also showed that it is not stopped by the glass transition temperature of the maltodextrin, lysine, and xylose matrix, and is possible in the glassy state. The WLF equation was found valid in predicting the reaction rate constant as a function of moisture and temperature above glass [29].

There is no general rule as to whether water activity or glassy state of the system, as dictated by glass transition temperature, impacts the rates of chemical reactions in reduced moisture solid food systems. Bell [16] studied the kinetics of nonenzymatic browning pigment formation in a model PVP (different molecular weight) matrix. The browning rates of matrices having different glass temperature, but constant water activity, were significantly different except when all were in the glassy state. As the system changed from a glassy state to a rubbery state, the rate of browning increased sevenfold. The rate of browning also increased as water activity increased from 0.33 to 0.54, but then appeared to plateau with further increases in water activity. In addition, the concentration of reactants in the aqueous microenvironment had a significant impact on the rate of brown pigment formation.

Bell et al. [21] studied the glycine loss and Maillard browning as a function of glass transition temperature. At a water activity of 0.54, pH 7, and stored at 25°C, the rate constants were very low when $T-T_g$ is close to zero and increased with the increase in $T-T_g$. O'Brien [114] studied the rate of nonenzymic browning in freeze-dried model systems containing lysine with glucose, sucrose, or trehalose at pH 2.5 and a water activity of 0.33. The temperatures were at 40°C, 60°C, and 90°C. All systems were in rubbery state at 90°C, whereas at 40°C and 60°C trehalose was in mixed amorphous glass-crystalline system while glucose and sucrose were in rubbery state. The rate of nonenzymatic browning in the trehalose system was much lower than that in sucrose or glucose, depending on temperature. The rate constant was in the order: glucose > sucrose > trehalose. The presence of crystalline material in the trehalose system at 40°C and 60°C may have influenced the overall rate of hydrolysis, stabilizing the system. At 90°C, all systems were in rubbery state, and there were substantial differences between the stability of sucrose and trehalose. Thus, glass transition is not only the controlling factor for rate of browning, but mainly the

rate-limiting sucrose hydrolysis step since glucose had a very high rate than sucrose. The effect of glass transition was much less than previously reported. Karel et al. [77] developed correlation for the browning rate constant as a function of $1/T$, moisture content, and $T-T_g$.

Bell and Hageman [18] studied the kinetics of aspartame degradation in the PVP model system at constant temperature (25°C) and pH (7.0) as a function of water activity and glass transition independently. Degradation reaction rates at constant water activity, but different glass transition temperature, were not significantly different and rates at a similar distance from T_g , but different water activities, were significantly different. Thus, the rate of aspartame degradation was significantly influenced by the water activity, while the effect of the glass transition temperature on the reaction was negligible.

15.4.11 Enzymatic Reaction

Several enzymatic reactions can occur at low water contents [49,171] or in the frozen state [52,53,60,172,173] such as those catalyzed by alkaline phosphatase, lipoxygenase, lipase, or invertase. The effect of temperature on the reaction rate depends on the relative value of the diffusion of the reactants and the activity of the enzyme in such a concentrated media. Champion et al. [34] pointed that there is risk of proposing a unified theoretical model to predict the reactions in such concentrated materials. Torreggiani et al. [183] found no clear relationship between the anthocyanin loss and $T-T_g'$ of strawberry juices. Other important factors such as the pH of the unfrozen phase could influence anthocyanin pigment stability. It could be hypothesized that sorbitol showing stability could alter the nucleophilic power of the water or could play a specific protective role, due to its chemical nature, in the enzymatic breakdown of the anthocyanin pigments.

15.4.12 Denaturation of Protein

The properties and functionality of the protein depend on whether it exists in the native or denatured state; maintaining protein structure and functionality is important in food science. The kinetics of aspartame degradation was evaluated in poly(vinyl) pyrrolidone model system [18,20]. Reaction rates at constant water activity but different glass transition values were not significantly different. Moreover, rates at the same values of $T-T_g$ were significantly different with changing water activity. The temperature of denaturation decreased with increasing moisture content to some plateau, where further increases in moisture no longer influenced the denaturation temperature [19]. Bell and Hageman [19] studied the denaturation temperature of globular proteins (β -lactoglobulin, ovalbumin, and ribonuclease) in dry state as a function of glass transition temperatures of polyhydroxy compounds (water, glycerol, sorbitol, sucrose, and trehalose). The component was in the 25%–33% w/w range. They found that the thermal stability of protein correlated with glass transition temperatures of polyhydroxy component, and lower the T_g of the component, greater was the degree of protein destabilization. They hypothesized that in dry state, the additives were acting as plasticizers, enhancing the mobility and thus the unfolding of the globular proteins.

15.4.13 Hydrolysis

The effect of glass transition on different chemical reactions is not as clear as in the cases with physical changes. This is due to the multiple roles of water in foods, such as plasticizer, reactant or product of chemical reactions, and pH [28]. One of the chemical reactions that was proposed to occur only in the rubbery phase (i.e., above glass transition) is sucrose inversion in acid-containing amorphous powders [98]. Buera et al. [28] investigated the effect of glass transition on the rate of acid-catalyzed sucrose hydrolysis in an amorphous polymeric matrix of PVP. No direct relationship was found between sucrose hydrolysis in a PVP matrix and T_g or $T-T_g$. Glass transition is not a key factor determining the rate of sucrose hydrolysis. The major effect on the rate of hydrolysis was related to changes in pH, which is moisture dependent. Knowledge of the actual pH of a system and the possible changes that may occur during concentration or drying is necessary for better understanding of chemical changes in low- and intermediate-moisture foods. Sucrose hydrolysis in an acid-containing (low pH 3.1) amorphous starch powder (native or pregelatinized) occurred to a significant extent in the glassy state [162]. The mobility effects do not control the extent of reaction. Hydrolysis (31%–85% remaining sucrose) was observed at

different water content and temperature below glass. Little reaction occurred at moisture contents below the so-called BET-monolayer. Temperature was a critical factor controlling sucrose inversion.

15.4.14 Enzyme Inactivation and Other Chemical Reactions

The stability of enzymes in low-water systems was analyzed based on the glass concept. The stability of lactase during heating at 70°C was studied in different amorphous glassy matrices: trehalose, maltodextrin, or poly(vinyl) pyrrolidone [107]. The protective effect of the maltodextrin and poly(vinyl) pyrrolidone matrices on the enzyme was attributed to their glass transition temperature, but the trehalose matrix is much more efficient for enzyme stability independent of its glass transition value. Schebor et al. [163] studied the stabilization of the enzyme invertase (β -fructofuranosidase) by its incorporation in aqueous model systems of trehalose, maltodextrin, and poly(vinyl) pyrrolidone followed by freeze-drying and desiccation to zero moisture content. When the systems were heated to 90°C for thermal inactivation of invertase, the enzyme was protected by maltodextrin and PVP, but not significantly protected by trehalose, although all systems were in the glassy state. Cardona et al. [32] observed significant inactivation of invertase when maltodextrin and PVP were kept well below their glass transition, but the enzyme was fairly stable in rubbery trehalose systems. At moisture contents that allowed trehalose crystallization, rapid thermal inactivation of invertase was observed. The invertase inactivation in heated systems of reduced moisture could not be predicted on the basis of glass transition, and this was particularly true for trehalose for which it was evident that the glassy state was not the main stabilizing factor.

The relevance of glass transition as a reference temperature for predicting the rate of chemical or enzymatic reactions was studied, but no clear relationship has been established [34]. Bell and White [22] studied thiamin loss as a function of water activity and glass transition temperature. The maximum rate constant appeared to be around $T - T_g = -23^\circ\text{C}$. Below glass transition (i.e., lower $T - T_g$), the rate constant decreased and correlated reasonably well with the decreasing values of $T - T_g$. In the rubbery region (i.e., water activity more than 0.4), the rate constants no longer correlated with $T - T_g$, but correlated instead with water activity. The reason could be attributed to the collapse of the matrix.

15.4.15 Sensory Properties

The effect of molecular weight on the glass temperature of starch hydrolysis products (SHP) is shown in Figure 15.10. The plateau region in Figure 15.10 indicates the useful range of gelation, encapsulation,

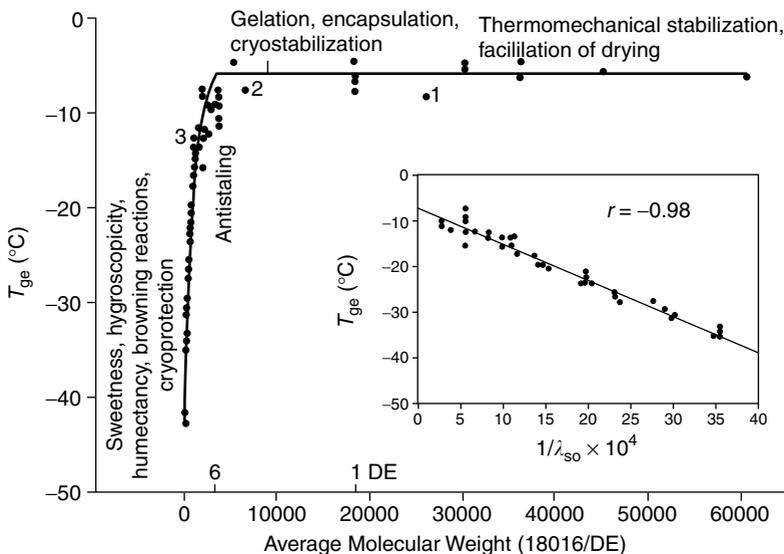


FIGURE 15.10 Effect of molecular weight on glass transition of starch hydrolysis product (SHP). (From Levine, H., Slade, L. 1986. *Carbohydr. Polym.* 6: 213–244.)

cryostabilization, thermochemical stabilization, and facilitation of drying process. The lower end corresponds to the area of sweetness, browning reactions, and cryoprotection. The intermediate region at the upper end of the steeply rising portion represents the area of antistaling ingredients. The map can be used to choose individual SHPs or mixtures of SHPs and other carbohydrates to achieve the desired complex functional behavior for specific product applications [97]. For example, the synthesis of SHPs capable of gelation from solution should be designed to yield materials of dextrose equivalent (DE) ≤ 6 and $T_g' \geq 8^\circ\text{C}$. Similarly, potato starch maltodextrins of 5–6 DE (25% w/w) produced thermoreversible, fat-mimetic gels, and tapioca SHPs of DE ≤ 5 also form fat-mimetic gels from solution to develop fat-replaceable ingredients [26,141,142]. Levine and Slade [97] developed a linear relation between DE and glass transition temperature of maximally freeze-concentrated solution of commercial SHPs. Thus, the correlation can be used to approximately calculate DE for dextrin and maltodextrin of unknown SHPs, which can do away with the more tedious and time-consuming classical experimental methods for DE determination [111].

Glass transition alone could not be considered as a generic rule for food stability criteria since in a number of instances, such as pore formation, diffusion, microbial stability, and nonenzymatic browning, other factors or mechanisms play an important role. However, glass transition is definitely one of the factors affecting stability, and presents a future challenge to combine the glass concept with other mechanisms or factors such as water activity, pH, and preservatives [131].

References

1. Abbott, T. P., Nabetani, H., Sessa, D. J., Wolf, W. J., Liebman, M. N., Dukor, R. K. 1996. Effects of bound water on FTIR spectra of glycinin. *J. Agric. Food Chem.* 44: 2220–2224.
2. Ablett, S., Darke, A. H., Izzard, M. J., Lillford, P. J. 1992. Modelling of heat capacity–temperature data for sucrose–water systems. *J. Chem. Soc. Faraday Trans.* 88(6): 795–802.
3. Ablett, S., Darke, A. H., Izzard, M. J., Lillford, P. J. 1993. Studies of the glass transition in malto-oligomers. In: *The Glassy States in Foods*. Blanshard, J. M. V., Lillford, P. J. Eds. Nottingham Press, Nottingham. pp. 189–206.
4. Ablett, S., Izzard, M. J., Lillford, P. J. 1992. Differential scanning calorimetric study of frozen sucrose and glycerol solutions. *J. Chem. Soc. Faraday Trans.* 88(6): 789–794.
5. Ablett, S., Izzard, M. J., Lillford, P. J., Arvanitoyannis, I., Blanshard, J. M. V. 1993. Calorimetric study of the glass transition occurring in fructose solutions. *Carbohydr. Res.* 246: 13–22.
6. Achanta, S., Okos, M. R. 1996. Predicting the quality of dehydrated foods and biopolymers – research needs and opportunities. *Drying Technol.* 14(6): 1329–1368.
7. Ali, Y., Hanna, M. A., Chinnaswamy, R. 1996. Expansion characteristics of extruded corn grits. *Food Sci. Technol.* 29: 702–707.
8. Allen, G. 1993. A history of the glassy state. In: *The Glassy State in Foods*. Blanshard, J. M. V., Lillford, P. J. Eds. Nottingham University Press, Nottingham. pp. 1–12.
9. Angell, C. A. 1988. Perspective on the glass transition. *J. Phys. Chem. Solids.* 49: 863–871.
10. Angell, C. A. 1991. Relaxation in liquids, polymers and plastic crystals–strong/fragile patterns and problems. *J. Non-Cryst. Solids.* 13–31 and 131–133.
11. Angell, C. A., Bressel, R. D., Green, J. L., Kanno, H., Oguni, M., Sare, E. J. 1994. Liquid fragility and the glass transition in water and aqueous solutions. *J. Food Eng.* 22: 115–142.
12. Appelqvist, I. A. M., Cooke, D., Gidley, M. J., Lane, S. J. 1993. Thermal properties of polysaccharides at low moisture: 1 an endothermic melting process and water carbohydrate interactions. *Carbohydr. Polym.* 20: 291–299.
13. Arridge, R. G. C. 1975. The glass transition. In: *Mechanics of Polymers*. Clarendon Press, Oxford. p. 24–50.
14. Barnett, S. 1973. Freezing of coffee extract to produce a dark colored freeze-dried product. *AIChE Symposium Series.* 69(132): 26–32.
15. Baroni, A. F., Sereno, A. M., Hubinger, M. D. 2003. Thermal transitions of osmotically dehydrated tomato by modulated temperature differential scanning calorimetry. *Thermochim. Acta.* 395: 237–249.
16. Bell, L. N. 1996. Kinetics of nonenzymatic browning in amorphous solid systems: distinguishing the effects of water activity and the glass transition. *Food Res. Int.* 28: 591.

17. Bell, L. N., Bell, H. M., Glass, T. E. 2002. Water mobility in glassy and rubbery solids as determined by oxygen-17 nuclear magnetic resonance: impact on chemical stability. *Food Sci. Technol.* 35: 108–112.
18. Bell, L. N., Hageman, M. J. 1994. Differentiating between the effects of water activity and glass transition dependent mobility on a solid-state chemical reaction: aspartame degradation. *J. Agric. Food Chem.* 42: 2398–2401.
19. Bell, L. N., Hageman, M. J. 1996. Glass transition explanation for the effect of polyhydroxy compounds on protein denaturation in dehydrated solids. *J. Food Sci.* 61: 372–374 and 378.
20. Bell, L. N., Labuza, T. P. 1991. Aspartame degradation kinetics as affected by pH in intermediate and low moisture food systems. *J. Food Sci.* 56: 17–20.
21. Bell, L. N., Touma, E., White, K. L., Chen, Y. 1998. Glycine loss and Maillard browning as related to the glass transition in a model food system. *J. Food Sci.* 63(4): 625–628.
22. Bell, L. N., White, K. L. 2000. Thiamin stability in solids as affected by the glass transition. *J. Food Sci.* 65(3): 498–501.
23. Blond, G. 1994. Mechanical properties of frozen model solutions. *J. Food Eng.* 22: 253–269.
24. Blond, G., Simatos, D., Catte, M., Dussap, C. G., Gros, J. B. 1997. Modeling of the water-sucrose state diagram below 0°C. *Carbohydr. Res.* 298: 139–145.
25. Borde, B., Bizot, H., Vigier, G., Emery, J., Buleon, A. 1999. Sub T_g relaxations and physical ageing in hydrated glassy polysaccharides. In: *Biopolymer Science: Food and Non Food Applications*. Colonna, P., Guilbert, S. Eds. INRA Editions, Paris. pp. 167–172.
26. Braudo, E. E., Belavtseva, E. M., Titova, F. F., Plashchina, I. G., Krylov, V. L., Tolstoguzov, V. B., Schierbaum, F. R., Richter, M. 1979. Struktur und Eigenschaften von maltodextrin-hydrogelen. *Starch.* 31:188 .
27. Bruin, S., Luyben, K. 1980. In: *Advances in Drying*. Mujumdar, A. Ed. Hemisphere, Washington, DC.
28. Buera, M. D. P., Chirife, J., Karel, M. 1995. A study of acid-catalyzed sucrose hydrolysis in an amorphous polymeric matrix at reduced moisture contents. *Food Res. Int.* 28: 359–365.
29. Buera, M. P., Karel, M. 1993. Application of the WLF equation to describe the combined effects of moisture and temperature on nonenzymatic browning rates in food systems. *J. Food Process. Preserv.* 17: 31–45.
30. Buitink, J., Leprince, O. 2004. Glass formation in plant anhydrobiotes: survival in the dry state. *Cryobiology.* 48: 215–228.
31. Burke, M. J. 1986. The glassy state and survival of anhydrous biological systems. In: *Membranes, Metabolism and Dry Organisms*. Leopold, A. C. Ed. Cornell University Press, Ithaca, New York. pp. 358–363.
32. Cardona, S., Schebor, C., Buera, M. P., Karel, M., Chirife, J. 1997. Thermal stability of invertase in reduced-moisture amorphous matrices in relation to glassy state and trehalose crystallization. *J. Food Sci.* 62: 105–112.
33. Champion, D., Hervet, H., Blond, G., Le Meste, M., Simatos, D. 1997. Translation diffusion in sucrose solutions in the vicinity of their glass transition. *J. Phys. Chem.* B10: 10674–10679.
34. Champion, D., Le Meste, M., Simatos, D. 2000. Towards an improved understanding of glass transition and relaxations in foods: molecular mobility in the glass transition range. *Trends Food Sci. Technol.* 11: 41–55.
35. Chan, R. K., Pathmanthan, K., Johari, G. P. 1986. Dielectric relaxations in the liquid and glassy states of glucose and its water mixtures. *J. Phys. Chem.* 90: 6358–6362.
36. Chen, P., Chen, X. D., Free, K. W. 1996. Measurement and data interpretation of the freezing point depression of milks. *J. Food Eng.* 30: 239–253.
37. Chen, X. D., Chen, P. 1996. Freezing of aqueous solution in a simple apparatus designed for measuring freezing point. *Food Res. Int.* 29(8): 723–729.
38. Chinachoti, P., Stengle, T. R. 1990. Water mobility in starch/sucrose systems: an oxygen-17 NMR. *J. Food Sci.* 55(6): 1732–1734.
39. Chirife, J. 1994. Specific solute effects with special reference to *Staphylococcus aureus*. *J. Food Eng.* 22: 409–419.
40. Chirife, J., Buera, M. D. P. 1994. Water activity, glass transition and microbial stability in concentrated/semimoist food systems. *J. of Food Sci.* 59(5): 921–927.
41. Chirife, J., Buera, M. P., Gonzalez, H. L. 1999. The mobility and mold growth in glassy/rubbery substances. In: *Water Management in the Design and Distribution of Quality Foods*. ISOPOW 7. Roos, Y. H., Leslie, R. B., Lillford, P. J. Eds. Technomic, Lancaster. pp. 285–298.

42. Choi, S., Kerr, W. L. 2003. ^1H NMR studies of molecular mobility in wheat starch. *Food Res. Int.* 36: 341–348.
43. Christensen, R. M. A. 1977. A thermodynamical criterion for the glass-transition temperature. *Trans. Soc. Rheol.* 21: 163–181.
44. Cnossen, A. G., Siebenmorgen, T. J., Yang, W., Bautista, R. C. 2000. An application of glass transition temperature to explain rice kernel fissure occurrence during the drying process. *Drying Technol.* 19(8): 1661–1682.
45. Cnossen, A. G., Siebenmorgen, T. J. 2000. The glass transition temperature concept in rice drying and tempering: effect on milling quality. *Trans. ASAE.* 43(6): 1661–1667.
46. Contreras-Lopez, E., Champion, D., Hervet, H., Blond, G., Le Meste, M. 1999. Effet de differents polysaccharides sur la mobilite rotationnelle et translationelle de petites molecules dans des solutions concentrees de saccharose. In: *Les Produits Alimentaires et l'Eau*. Agoral-99, Paris. pp. 253–258.
47. Del Valle, J. M., Cuadros, T. R. M., Aguilera, J. M. 1998. Glass transitions and shrinkage during drying and storage of osmosed apple pieces. *Food Res. Int.* 31(3): 191–204.
48. Dlubek, G., Fretwell, H. M., Alam, M. A. 2000. Positron/positronium annihilation as a probe for the chemical environment of free volume holes in polymers. *Macromolecules.* 33: 187–192.
49. Drapon, R. 1972. Reactions enzymatiques en Milieu Peu Hydrate. *Annal. Technol. Agric.* 21: 487–499.
50. Duckworth, R. B., Smith, G. M. 1963. The environment for chemical change in dried and frozen foods. *Proc. Nutr. Soc.* 22: 182–189.
51. Fennema, O. 1975. Activity of enzymes in partially frozen aqueous systems. In: *Food Sci. Technol. A Series of Monograph*. Duckworth, R. B. Ed. Academic Press, London. pp. 397–412.
52. Fennema, O. 1978. Enzyme kinetics at low temperature and reduced water activity. In: *Dry Biological Systems*. Crowe, J. H., Clegg, J. S. Eds. Academic Press, London. pp. 297–342.
53. Fennema, O. 1995. Metastable and nonequilibrium states in frozen food and their stabilization In: *Food Preservation by Moisture Control: Fundamentals and Applications*. Barbosa-Canovas, G. V., Welti-Chanes J. Eds. Technomic Publishing, Lancaster, PA. pp. 243.
54. Ferry, J. D. 1980. *Viscoelastic Properties of Polymers*. Wiley, New York.
55. Ferry, J. D. 1991. Some reflections on the early development of polymer dynamics: viscoelasticity, dielectric dispersion, and self-diffusion. *Macromolecules.* 24: 5237–5245.
56. Fessas, D., Schiraldi, A. 2001. State diagram of arabinoxylan-water binaries. *Termochim. Acta.* 370: 83–89.
57. Fonseca, F., Obert, J. P., Beal, C., Marin, M. 2001. State diagrams and sorption isotherms of bacterial suspensions and fermented medium. *Termochim. Acta.* 366: 167–182.
58. Franks, F. 1985. Complex aqueous systems at subzero temperatures. In: *Properties of Water in Foods*. Simatos, D., Multon, J.L. Eds. Martinus Nijhoff Publishers, Dordrecht.
59. Franks, F. 1991. Water activity: a credible measure of food safety and quality? *Trends Food Sci. Technol.* 2(3): 68–72.
60. Franks, F., Hatley, R. H. M. 1992. Stable enzymes by water removal. In: *Stability and Stabilization of Enzymes*. Van Den Tweel, W. J. J., Harde, R. A., Buitelaar, R. M. Eds. Elsevier Science, Amsterdam. pp. 45–54.
61. Gidley, M. J., Cooke, D., Ward-Smith, S. 1993. Low moisture polysaccharide systems: thermal and spectroscopic aspects. In: *Glassy State of Foods*. Blanshard, J. M. V., Lillford, P. J. Eds. Nottingham University Press, Nottingham. pp. 303–316.
62. Given, P. S. 1991. Molecular behavior of water in a flour-water baked model system. In: *Water Relationships in Food*. Levine, H., Slade, L. Eds. Plenum Press, New York. pp. 465–483.
63. Goff, H., Caldwell, K. B., Stanley, D. W., Maurice, T. P. 1993. The influence of polysaccharides on the glass transition in frozen sucrose solutions and ice cream. *J. Dairy Sci.* 76: 1268–1277.
64. Goff, H. D., Montoya, K., Sahagian, M. E. 2002. The effect of microstructure on the complex glass transition occurring in frozen sucrose model systems and foods. In: *Amorphous Food and Pharmaceutical Systems*. Levine, H. Ed. The Royal Society of Chemistry, Cambridge. pp. 145–157.
65. Hardman, T. M. 1986. Interaction of water with food component. In: *Interaction of Food Components*. Birch, G. G., Lindley, M. G. Eds. Elsevier Applied Science Publishers, London. pp. 19–30.
66. Hatakeyama, T., Quinn, F. X., Hatakeyama, H. 1996. Changes in freezing bound water in water-gellan systems with structure formation. *Carbohydr. Polym.* 30: 155–160.
67. Hills, B. P., Manning, C. E., Ridge, Y., Brocklehurst, T. 1996. NMR water relaxation, water activity and bacterial survival in porous media. *J. Sci. Food Agric.* 71: 185–194.
68. Hutchinson, J. M. 1995. Physical aging of polymers. *Prog. Polym. Sci.* 20: 703–760.

69. Izzard, M. J., Ablett, S., Lillford, P. J. 1991. Calorimetric study of the glass transition occurring in sucrose solutions. In: *Food Polymers, Gels, Colloids*. Dickinson, E. Ed. The Royal Society of Chemistry, London. pp. 289–300.
70. Johari, G. P. 1976. Glass transition and secondary relaxations in molecular liquids and crystals. *Ann. NY Acad. Sci.* 2: 177–140.
71. Jouppila, K., Roos, Y. H. 1997. The physical state of amorphous cornstarch and its impact on crystallization. *Carbohydr. Polym.* 32: 95–104.
72. Kaatze, U. 1990. On the existence of bound water in biological systems as probed by dielectric spectroscopy. *Phy. Med. Biol.* 35(12): 1663–1681.
73. Kalichevsky, M. T., Blanshard, J. M. V. 1992. A study of effect of water on the glass transition of 1:1 mixtures of amylopectin, casein and gluten using DSC and DMTA. *Carbohydr. Polym.* 19: 271–278.
74. Kantor, Z., Pitsi, G., Thoen, J. 1999. Glass transition DSC temperature of honey as a function of water content as determined by differential scanning calorimetry. *J. Agric. Food Chem.* 47: 2327–2330.
75. Karathanos, V., Angelea, S., Karel, M. 1993. Collapse of structure during drying of celery. *Drying Technol.* 11: 1005.
76. Karathanos, V. T., Kanellopoulos, N. K., Belessiotis, V. G. 1996. Development of porous structure during air drying of agricultural plant products. *J. Food Eng.* 29: 167–183.
77. Karel, M., Angelea, S., Buera, P., Karmas, R., Levi, G., Roos, Y. 1994. Stability-related transitions of amorphous foods. *Thermochim. Acta.* 246: 249–269.
78. Karel, M., Buera, M. P., Roos, Y. 1993. Effects of glass transitions on processing and storage. In: *The Science and Technology of the Glassy State in Foods*. Blanshard, J. M. V., Lillford, P. J. Eds. Nottingham University Press, Nottingham.
79. Karel, M., Saguy, I. 1991. Effects of water on diffusion in food systems. In: *Water Relationships in Foods*. Levine, H., Slade, L. Eds. Plenum Press, New York. p. 157.
80. Karmas, R., Buera, M. P., Karel, M. 1992. Effect of glass transition on rates of nonenzymatic browning in food systems. *J. Agric. Food Chem.* 40: 873.
81. Kasapis, S. 2005. Glass transition phenomena in dehydrated model systems and foods: a review. *Drying Technol.* 23(4): 731–758.
82. Kasapis, S., Al-Marhoobi, I. M., Mitchell, J. R. 2003. Testing the validity of comparisons between the rheological and the calorimetric glass transition temperatures. *Carbohydr. Res.* 338: 787–794.
83. Kasapis, S., Al-Marhobi, I. M. A., Sworn, G. 2001. α and β mechanical dispersions in high sugar/acyl gellan mixtures. *Int. J. Biol. Macromol.* 29: 151–160.
84. Kasapis, S., Rahman, M. S., Guizani, N., Al-Aamri, M. K. S. 2000. State diagram of temperature vs. date solids obtained from the mature fruit. *J. Agric. Food Chem.* 48: 3779–3784.
85. Kim, M. N., Saltmarch, M., Labuza, T. P. 1981. Nonenzymatic browning of hygroscopic whey powders in open versus sealed pouches. *J. Food Process Preserv.* 5: 49–57.
86. Kivilaan, A., Bandurski, R. S. 1981. The one-hundred-year period for Dr. Beal's seed viability experiment. *Am. J. Bot.* 68: 1290–1292.
87. Kokini, J. L., Cocero, A. M., Madeka, H., De Graaf, E. 1994. The development of state diagrams for cereal proteins. *Trends Food Sci. Technol.* 5: 281–288.
88. Kramkowski, R., Kaminski, E., Serowik, M. 2001. Characterisation of garlic freeze drying with the use of differential scanning calorimetry. *Electron. J. Polish Agric. Univ.* 4(2): 1–6.
89. Krokida, M. K., Karathanos, V. T., Maroulis, Z. B. 1998. Effect of freeze-drying conditions on shrinkage and porosity of dehydrated agricultural products. *J. Food Eng.* 35: 369–380.
90. Krokida, M., Maroulis, Z. 2000. Quality changes during drying of food materials. In: *Drying Technology in Agricultural and Food Sciences*. Mujumdar, A. S. Ed. Science Publishers, Enfield. pp. 61–106.
91. Labrousse, S., Roos, Y., Karel, M. 1992. Collapse and crystallization in amorphous matrices with encapsulated compounds. *Sci. Aliments.* 12: 757.
92. Labuza, T. P., Hayman, C. R. 1998. Moisture migration and control in multi-domain foods. *Trends Food Sci. Technol.* 9: 47–55.
93. Lai, H. M., Schmidt, S. J., Chiou, R. G., Slowinski, L. A., Day, G. A. 1993. Mobility of water in a starch-based fat replacer by ^{17}O NMR spectroscopy. *J. Food Sci.* 58(5): 1103–1106.
94. Lang, K. W., Steinberg, M. P. 1983. Characterization of polymer and solute bound water by pulsed NMR. *J. Food Sci.* 48: 517–538.
95. Le Meste, M., Champion, D., Roudaut, G., Contreras-Lopez, E., Bond, G., Simatos, D. 1999. Mobility and reactivity in low moisture and frozen foods. In: *Water Management in Design and Distribution of*

- Quality Foods*. ISOPOW Roos, Y. H., Leslie, R. B., Lillford, P. J. Eds. Technomic Publisher, Lancaster. pp. 267–284.
96. Le Meste, M., Roudaut, G., Rolee, A. 1997. The physical state and quality of cereal-based foods. In: *Food Engineering 2000*. Fito, P., Ortega-Rodriguez, E., Barbosa-Canovas, G. V. Eds. Chapman & Hall, New York. pp. 97–113.
 97. Levine, H., Slade, L. 1986. A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPs). *Carbohydr. Polym.* 6: 213–244.
 98. Levine, H., Slade, L. 1989. Interpreting the behavior of low moisture foods. In: *Water and Food Quality*. Hardman, T. M. Ed. Elsevier Applied Science, New York. pp. 71–134.
 99. Li, S., Dickinson, L. C., Chinachoti, P. 1998. Mobility of “unfreezable” and “freezable” water in waxy cornstarch by ^2H and ^1H NMR. *J. Agric Food Chem.* 46: 62–71.
 100. Li, T. Y., Chen, J. T. 2001. Evaluation of rice starch-hydrocolloid compatibility at low-moisture content by glass transitions. *J. Food Sci.* 66(5): 698–704.
 101. Lloyd, R. J., Chen, X. D., Hargreaves, J. B. 1996. Glass transition and caking of spray-dried lactose. *Int. J. Food Sci. Technol.* 31: 305–311.
 102. Lupano, C. E. 1997. DSC study of honey granulation stored at various temperatures. *Food Res. Int.* 30(9): 683–688.
 103. Luyet, B., Rasmussen, D. 1968. Study by differential thermal analysis of the temperatures of instability of rapidly cooled solutions of glycerol, ethylene glycol, sucrose and glucose. *Biodynamica.* 10: 167–191.
 104. MacFarlane, D. R. 1986. Devitrification in glass forming aqueous solutions. *Cryobiology.* 23(3): 230–244.
 105. Martin, D. R., Ablett, S., Sutton, M., Sahagian, M. E. 1999. Diffusion of aqueous sugar solutions as affected by locust bean gum studied by NMR. *J. Food Sci.* 64: 46–49.
 106. Matveev, Y. I. 2004. Modification of the method for calculation of the C_g' and T_g' intersection point in the state diagrams of frozen solutions. *Food Hydrocolloids.* 18: 363–366.
 107. Mazzobre, M. F., Buera, M. P., Chirife, J. 1997. Protective role of trehalose on thermal stability of lactose in relation to its glass and crystal forming properties and effect of delaying crystallization. *Food Sci. Technol.* 30: 324–329.
 108. McFetridge, J., Rades, T., Lim, M. 2004. Influence of hydrogenated starch hydrolysates on the glass transition and crystallization of sugar alcohols. *Food Res. Int.* 37: 409–415.
 109. Moonan, W. K., Tschoegl, N. W. 1985. The effect of pressure on the mechanical properties of polymers. IV. Measurements in Torsion. *J. Polym. Sci.: Polymer Physics Edition.* 23: 623–651.
 110. Morales-Diaz, A., Kokini, J. L. 1998. Understanding phase transitions and chemical complexing reactions in 7S and 11S soy protein fractions. In: *Phase/State Transitions in Foods*. Rao, M. A., Hartel, R. W. Eds. Marcel Dekker, New York. pp. 273–311.
 111. Murray, D. G., Luft, L. R. 1973. Low-DE cornstarch hydrolysates. *Food Technol.* 27: 32.
 112. Ngai, K. L., Magill, J. H., Plazek, D. J. 2000. Flow, diffusion and crystallization of supercooled liquids: revisited. *J. Chem. Phys.* 112: 1887–1892.
 113. Nicholls, R. J., Appleqvist, I. A. M., Davies, A. P., Ingman, S. J., Lillford, P. J. 1995. Glass transitions and the fracture behavior of gluten and starches within the glassy state. *J. Cereal Sci.* 21: 25–36.
 114. O'Brien, J. 1996. Stability of trehalose, sucrose and glucose to nonenzymic browning in model systems. *J. Food Sci.* 61: 679–682.
 115. Paakkonen, K., Plit, L. 1991. Equilibrium water content and the state of water in dehydrated white cabbage. *J. Food Sci.* 56(6): 1597–1599.
 116. Paakkonen, K., Plit, L. 1991. The state of water and chitin in the northern milk cup mushroom (*Lactarius trivialis*). *Food Sci. Technol.* 24(3): 204–207.
 117. Padua, G. W. 1993. Proton NMR and dielectric measurements on sucrose filled agar gels and starch pastes. *J. Food Sci.* 58(3): 603–626.
 118. Padua, G. W., Richardson, S. J., Steinberg, M. P. 1991. Water associated with whey protein investigated by pulsed NMR. *J. Food Sci.* 56(6): 1557–1561.
 119. Parker, R., Ring, S. G. 1995. Diffusion in maltose-water mixtures at temperatures close to the glass transition. *Carbohydr. Res.* 273: 147–155.
 120. Parker, R., Smith, A. C. 1993. The mechanical properties of starchy food materials at large strains and their ductile-brittle transitions. In: *The Glassy States in Foods*. Blanshard, J. M. V., Lillford, P. J. Eds. Nottingham University Press, Leicestershire. pp. 519–522.

121. Perdon, A. A. 1999. Amorphous state transition in rice during the drying process. Ph.D. dissertation, University of Arkansas, Fayetteville, AR.
122. Perdon, A. A., Siebenmorgen, T. J., Mauromoustakos, A. 2000. Glassy state transition and rice drying: development of a brown rice state diagram. *Cereal Chem.* 77(6): 708–713.
123. Pere, C., Rodier, E., Schwartzentruber, J. 1998. Effects of the structure of a porous material on drying kinetics in a microwave vacuum laboratory scale dryer. *IDS '98. 11th International Drying Symposium.* pp. 1922–1929.
124. Phillips, G. O., Takigami, S., Takigami, M. 1996. Hydration characteristics of the gum exudate from *Acacia senegal*. *Food Hydrocolloids.* 10(1): 11–19.
125. Priestley, D. A., Cullinan, V. I., Wolf, J. 1985. Differences in seed longevity at the species level. *Plant Cell Environ.* 8(8): 557–562.
126. Rahman, M. S. 1995. *Food Properties Handbook*. CRC Press, Boca Raton, FL.
127. Rahman, M. S., 1999, Glass transition and other structural changes in foods, In: *Handbook of Food Preservation*, Rahman, M. S., Ed. Marcel Dekker, New York. pp. 75–93.
128. Rahman, M. S. 2001. Toward prediction of porosity in foods during drying: a brief review. *Drying Technol.* 19(1): 1–13.
129. Rahman, M. S. 2004. State diagram of date flesh using differential scanning calorimetry (DSC). *Int. J. Food Prop.* 7(3): 407–428.
130. Rahman, M. S. 2005. Dried-food properties: challenges ahead. *Drying Technol.* 23(4): 695–715.
131. Rahman, M. S. 2006. State diagram of foods: its potential use in food processing and product stability. *Trends Food Sci. Technol.* 17: 129–141.
132. Rahman, M. S., Al-Amri, O. S., Al-Bulushi, I. M. 2002. Pores and physico-chemical characteristics of dried tuna produced by different methods of drying. *J. Food Eng.* 53: 301–313.
133. Rahman, M. S., Al-Zakwani, I., Guizani, N. 2005. Pore formation in apple during air drying as a function of temperature and pore size distribution. *J. Sci. Food Agric.* 85(6): 979–989.
134. Rahman, M. S., Guizani, N., Al-Khaseibi, M., Al-Hinai, S., Al-Maskri, S. S., Al-Hamhami, K. 2002. Analysis of cooling curve to determine the end point of freezing. *Food Hydrocolloids.* 16(6): 653–659.
135. Rahman, M. S., Kasapis, S., Guizani, N., Al-Amri, O. 2003. State diagram of tuna meat: freezing curve and glass transition. *J. Food Eng.* 57(4): 321–326.
136. Rahman, M. S., Labuza, T. P. 1999. Water activity and food preservation. In: *Handbook of Food Preservation*. Rahman, M. S. Ed. Marcel Dekker, New York. pp. 339–382.
137. Rahman, M. S., Sablani, S. S., Al-Habsi, N., Al-Maskri, S., Al-Belushi, R. 2005. State diagram of freeze-dried garlic powder by differential scanning calorimetry and cooling curve methods. *J. Food Sci.* 70(2): E135–E141.
138. Ratti, C. 1994. Shrinkage during drying of foodstuffs. *J. Food Eng.* 23: 91–105.
139. Rey, L. R. 1958. Etude Physiologique et Physico-chimique de l'Action des Basses Temperatures sur Tissus Animaux Vivants. Ph.D. thesis, 122 p.
140. Richardson, S. J., Baianu, I. C., Steinberg, M. P. 1987. Mobility of water in sucrose solutions determined by deuterium and oxygen-17 nuclear magnetic resonance measurements. *J. Food Sci.* 52(3): 806–812.
141. Richter, M., Schierbaum, F., Augustat, S., Knoch, K. D. 1976. U.S. Patent 3,396,245, 8 June.
142. Richter, M., Schierbaum, F., Augustat, S., Knoch, K. D. 1976. U.S. Patent 3,986,890, 19 October.
143. Rockland, L. B. 1969. Water activity and storage stability. *Food Technol.* 23: 11–21.
144. Ronald, C. M., Santangelo, P. G., Ngai, K. L. 1999. The application of the energy landscape model to polymers. *J. Chem. Phys.* 111: 5593–5598.
145. Roos, Y. 1995. Characterization of food polymers using state diagrams. *J. Food Eng.* 24: 339–360.
146. Roos, Y. 1995. Water activity and glass transition temperature: how do they complement and how do they differ? In: *Food Preservation by Moisture Control. Fundamentals and Applications*. Barbosa-Canovas, G.V., Welti-Chanes, J. Eds. Technomic Publishing Company, PA, pp. 133–154.
147. Roos, Y. H. 1987. Effect of moisture on the thermal behavior of strawberries studied using differential scanning calorimetry. *J. Food Sci.* 52(1): 146–149.
148. Roos, Y. H., Himberg, M. J. 1994. Nonenzymatic browning behavior, as related to glass transition of food model at chilling temperature. *J. Agric. Food Chem.* 42: 893–898.
149. Roos, Y., Karel, M. 1991. Water and molecular weight effects on glass transitions in amorphous carbohydrates and carbohydrate solutions. *J. Food Sci.* 56(6): 1676–1681.

150. Roos, Y., Karel, M. 1991. Applying state diagrams in food processing and product development. *Food Technol.* 45(12): 66–71, 107.
151. Roos, Y., Karel, M. 1991. Nonequilibrium ice formation in carbohydrate solutions. *Cryo-Letter.* 12: 367–376.
152. Roos, Y., Karel, M. 1991. Amorphous state and delayed ice formation in sucrose solutions. *Int. J. Food Sci. Technol.* 26: 553–566.
153. Roos, Y., Karel, M. 1991. Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *J. Food Sci.* 56: 38–43.
154. Roos, Y., Karel, M. 1992. Crystallization of amorphous lactose. *J. Food Sci.* 57: 775–777.
155. Roudaut, G., Dacremont, C., Le Meste, M. 1998. Influence of water on the crispness of cereal based foods—acoustic, mechanical, and sensory studies. *J. Texture Stud.* 29: 199–213.
156. Roudaut, G., Maglione, M., Le Meste, M. 1999. Sub- T_g relaxations in cereal-based systems. *Cereal Chem.* 76: 78–81.
157. Sa, M. M., Figueiredo, A. M., Sereno, A. M. 1999. Glass transitions and state diagrams of fresh and processed apple. *Thermochim. Acta.* 329: 31–38.
158. Sa, M. M., Sereno, A. M. 1994. Glass transitions and state diagrams for typical natural fruits and vegetables. *Thermochim Acta.* 246: 285–297.
159. Sablani, S. S., Rahman, M. S. 2002. Pore formation in selected foods as a function of shelf temperature during freeze drying. *Drying Technol.* 20(7): 1379–1391.
160. Saltmarch, M., Vagnini-Ferrari, M., Labuza, T. P. 1981. Theoretical basis and application of kinetics to browning in spray-dried whey food systems. *Prog. Food Nutr. Sci.* 5: 331–344.
161. Sapru, V., Labuza, T. P. 1993. Glass state in bacterial spores predicted by polymer glass-transition theory. *J. Food Sci.* 58: 445–448.
162. Schebor, C., Buera, M. D. P., Chirife, J., Karel, M. 1995. Sucrose hydrolysis in glassy starch matrix. *Food Sci. Technol.* 28: 245–248.
163. Schebor, C., Buera, M. P., Chirife, J. 1996. Glassy state in relation to the thermal inactivation of enzyme invertase in amorphous dried matrices of trehalose, maltodextrin and PVP. *J. Food Eng.* 30(3–4): 269–282.
164. Scott, W. J. 1953. Water relations of *Staphylococcus aureus* at 30°C. *Aust. J. Biol. Sci.* 6: 549.
165. Sereno, A. M., Sa, M. M., Figueiredo, A. M. 1995. Low temperature phase transitions in natural and osmotic dehydrated fruits. In: *Osmotic Dehydration of Fruits and Vegetables*. Lenart, A., Lewicki, P. P. Eds. Warsaw Agricultural University Press, Warsaw. pp. 50–68.
166. Sereno, A. M., Sa, M. M., Figueiredo, A. M. 1998. Glass transitions and state diagrams for freeze-dried and osmotically dehydrated apple. *Proceedings of the 11th International Drying Symposium (IDS '98)*, Halkidiki, Greece, August 19–22.
167. Shalaev, E. Y., Kanev, A. N. 1994. Study of the solid–liquid state diagram of the water–glycine–sucrose system. *Cryobiology.* 31: 374–382.
168. Shen-Miller, J., Mudgett, M. B., Schopf, J. W., Clarke, S., Berger, R. 1995. Exceptional seed longevity and robust growth: ancient sacred lotus from China. *Am. J. Bot.* 82: 1367–1380.
169. Shimada, Y., Roos, Y., Karel, M. 1991. Oxidation of methyl linoleate encapsulated in amorphous lactose-based food models. *J. Agric. Food Chem.* 39: 637–641.
170. Siebenmorgan, T. J., Yang, W., Howell, T. A., Meullenet, J. F., Wang, Y. J., Cnossen, A. G. 2000. Fissure formation in rice kernels during the drying process: a glass transition perspective. *Proc. of the 2000 Rice Technical Working Group Conference*, Biloxi, MS.
171. Silver, M., Karel, M. 1981. The behavior of invertase in model systems at low moisture content. *Food Chem.* 5: 283–311.
172. Simatos, D., Blond, G. 1991. DSC studies and stability of frozen foods. In: *Water Relationships in Foods*. Levine, H., Slade, L. Eds. Plenum Press, New York. pp. 139–156.
173. Simatos, D., Blond, G. 1993. Some aspects of the glass transition in frozen food systems. In: *The Glassy State in Food*. Blanshard, J. M. V., Lillford, P. J. Eds. Nottingham University Press, Nottingham. pp. 395–415.
174. Simatos, D., Blond, G., Perez, J. 1996. Basic physical aspects of glass transition. In: *Food Preservation by Moisture Control Fundamentals and Applications*. Barbosa-Canovas, G. V., Welti-Chanes, J. Eds. Technomic Publishing, Lancaster. pp. 3–31.
175. Simatos, D., Blond, G., Roudaut, G., Champion, D., Perez, J., Faivre, A. L. 1996. Influence of heating and cooling rates on the glass transition temperature and the fragility parameter of sorbitol and fructose as measured by DSC. *J. Thermal Anal.* 47: 1419–1436.

176. Slade, L., Levine, H. 1987. Structural stability of intermediate moisture foods—a new understanding. In: *Food Structure—Its Creation and Evaluation*. Mitchell, J. R., Blanshard, J. M. V. Eds. Butterworths, London. pp. 115.
177. Slade, L., Levine, H. 1988. Nonequilibrium behavior of small carbohydrate-water systems. *Pure Appl. Chem.* 60: 1841–1864.
178. Slade, L., Levine, L. 1991. A food polymer science approach to structure property relationships in aqueous food systems: nonequilibrium behavior of carbohydrate-water systems. In: *Water Relationships in Food*. Levine, H., Slade, L., Eds. Plenum Press, New York.
179. Slade, L., Levine, L. 1991. Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. *Crit. Rev. Food Sci. Technol.* 30: 115.
180. Soesanto, T., Williams, M. C. 1981. Volumetric interpretation of viscosity for concentrated and dilute sugar solutions. *J. Phys. Chem.* 85: 3338.
181. Steiner, A. M., Ruckebauer, P. 1995. Germination of 110-year-old cereal and weed seeds, the Vienna sample of 1877. Verification of effective ultra-dry storage at ambient temperature. *Seed Sci. Res.* 5: 195–199.
182. Taylor, J. R. 1995. Glass-state molecular mobility. *Food Ind. South Africa.* 48: 29–31.
183. Torreggiani, D., Forni, E., Guercilena, I., Maestrelli, A., Bertolo, G., Archer, G. P., Kennedy, C. J., Bone, S., Blond, G., Contreras-Lopez, E., Champion, D. 1999. Modification of glass transition temperature through carbohydrates additions: effect upon colour and anthocyanin pigment stability in frozen strawberry juices. *Food Res. Int.* 32: 441–446.
184. Van den Berg, C. 1991. Food–water relations: progress and integration, comments and thoughts. In: *Water Relations in Foods*. Levine, H., Slade, L. Eds. Plenum Press, New York. pp. 21.
185. Verdonck, E., Schaap, K., Thomas, L. C. 1999. A discussion of the principles and applications of modulated temperature DSC (MTDSC). *Int. J. Pharmaceutics.* 192: 3–20.
186. Wang, N., Brennan, J. G. 1995. Changes in structure, density and porosity of potato during dehydration. *J. Food Eng.* 24: 61–76.
187. Watanabe, H., Tang, C. Q., Suzuki, T., Mihori, T. 1996. Fracture stress of fish meat and the glass transition. *J. Food Eng.* 29: 317–327.
188. White, G. W., Cakebread, S. H. 1966. The glassy state in certain sugar-containing food products. *J. Food Technol.* 1: 73–82.
189. Williams, M. L., Landel, R. F., Ferry, J. D. 1955. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *J. Amer. Chem. Soc.* 77: 3701–3707.
190. Yang, W., Jia, C. C., Howell, T. A. 2003. Relationship of moisture content gradients and glass transition temperatures to head rice yield during cross-flow drying. *Biosys. Eng.* 86(2): 199–206.
191. Yang, W., Jia, C. C., Siebenmorgen, T. J., Pan, Z., Cnossen, A. G. 2003. Relationship of kernel moisture content gradients and glass transition temperatures to head rice yield. *Biosys. Eng.* 85(4): 467–476.
192. Zhao, J., Notis, M. R. 1993. Phase transition kinetics and the assessment of equilibrium and metastable states. *J. Phase Equil.* 14: 303.