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GLASS TRANSITIONS AND WATER–FOOD STRUCTURE INTERACTIONS

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I. INTRODUCTION

In the decade of the 1980s, the value of a polymer science approach to the study of the glassy state phenomenon and glass transitions, and of their importance to water–food structure interactions, in food materials, products, and processes was increasingly recognized by a growing number of food scientists and technologists (Table I). Why did this happen, and

TABLE I

REFERENCES TO STUDIES OF GLASSY STATE PHENOMENON AND GLASS TRANSITIONS IN FOODS AND FOOD MATERIALS BY RESEARCHERS AND GROUPS MOST ACTIVE IN FIELD IN 1980s[a]

Researchers	References
Franks	Franks *et al.* (1977, 1991), Franks (1982, 1983a,b, 1985, 1986a,b, 1989, 1990, 1991a,b,c, 1992a,b, 1993a,b), Finegold *et al.* (1989), Hatley *et al.* (1989), Franks and Grigera (1990), Franks and Hatley (1990, 1992, 1993), Franks and van den Berg (1991), Hatley (1991), Hatley and Franks (1991), Hatley *et al.* (1991), Hatley and Mant (1993), Ramanujam *et al.* (1993), Suzuki and Franks (1993)
Blanshard	Blanshard (1986, 1987, 1988), Blanshard and Franks (1987), Marsh and Blanshard (1988), Blanshard *et al.* (1991), Arvanitoyannis *et al.* (1992, 1993), Blanshard and Mitchell (1992), Kalichevsky and Blanshard (1992a–e), Kalichevsky *et al.* (1992a–d, 1993a,b), Tian and Blanshard (1992a,b,c), Arvanitoyannis and Blanshard (1993a,b)
van den Berg	van den Berg (1981, 1986, 1991, 1992), van den Berg *et al.* (1992, 1993)
Karel and Roos	Karel and Flink (1983), Karel (1985, 1986, 1989, 1990, 1991a,b,c, 1992, 1993), Roos (1987, 1992a–d), Karel and Langer (1988), Paakkonen and Roos (1990), Roos and Karel (1990, 1991a–h, 1992, 1993), Karel and Saguy (1991), Shimada *et al.* (1991), Aguilera *et al.* (1992), Anglea *et al.* (1992a,b), Buera and Karel (1992), Buera *et al.* (1992), Jouppila and Roos (1992), Karathanos *et al.* (1992), Karmas *et al.* (1992, 1993), Labrousse *et al.* (1992), Levi and Karel (1992a, 1993a,b), Karel *et al.* (1993a,b)
Lillford	Ablett *et al.* (1986, 1988, 1992a,b,c, 1993), Edwards *et al.* (1987), Lillford (1988), Attenburrow *et al.* (1989, 1990, 1992), Ablett and Lillford (1991), Davies *et al.* (1991), Izzard *et al.* (1991), Lillford *et al.* (1992), Attenburrow and Davies (1993)
Morris, Ring, and Smith	Ring *et al.* (1987), I'Anson *et al.* (1988, 1990), Hutchinson *et al.* (1989), Orford *et al.* (1989, 1990), Morris (1990), Noel *et al.* (1990, 1991, 1992, 1993), Ollett and Parker (1990), Smith (1990, 1992a,b,c), Warburton *et al.* (1990, 1992), Whittam *et al.* (1990, 1991), Cairns *et al.* (1991a,b), Ollett *et al.* (1991, 1993a,b), Ring and Whittam (1991), Botham *et al.* (1992), Noel and Ring (1992), Parker and Smith (1992), Whittam (1992), Donald *et al.* (1993), Kirby *et al.* (1993)

(*continues*)

TABLE I (*Continued*)

Researchers	References
Reid	Reid (1985, 1990, 1992a,b), Lim and Reid (1991, 1992), Hsu and Reid (1992), Reid and Hsu (1992), Reid *et al.* (1992, 1993a,b), Taylor *et al.* (1992), Kerr *et al.* (1993)
Hoseney	Hoseney *et al.* (1986, 1992), Yost and Hoseney (1986), Doescher *et al.* (1987), Zeleznak and Hoseney (1987a,b), Faubion and Hoseney (1989), Hoseney and Rogers (1990, 1993), Hoseney (1991, 1992), Dong (1992)
Simatos, Le Meste, and Huang	Simatos and Karel (1988), Le Meste and Duckworth (1988), Blond (1989, 1992, 1993), Simatos *et al.* (1989), Le Meste and Simatos (1990), Le Meste *et al.* (1990, 1991a,b, 1992), Blond and Colas (1991), Blond and Simatos (1991), Le Meste and Huang (1991), Matthiesen *et al.* (1991), Simatos and Blond (1991, 1993), Aynie *et al.* (1992a,b), Huang (1992, 1993a,b), Huang *et al.* (1992, 1993), Simatos (1994)
Maurice and Biliaderis	Maurice *et al.* (1985, 1991), Biliaderis *et al.* (1985, 1986a,b,c), Biliaderis and Galloway (1989), Biliaderis (1990, 1991a,b, 1992a,b), Biliaderis and Seneviratne (1990a,b), Biliaderis and Zawistowski (1990), Caldwell *et al.* (1990), Biliaderis and Tonogai (1991), Michniewicz *et al.* (1992), Goff *et al.* (1993)
Schenz	Schenz *et al.* (1984, 1991, 1992)
Tomka	Wittwer and Tomka (1984), Tomka (1986, 1991), Sala and Tomka (1992a,b), Willenbucher *et al.* (1992)
Slade and Levine	Slade (1984), Slade and Levine (1984, 1985, 1987a,b, 1988a–d, 1989, 1990, 1991a,b, 1992a–c, 1993a–c), Slade *et al.* (1987, 1989, 1993), Levine and Slade (1986, 1988a–d, 1989a–d, 1990, 1991, 1992a,b, 1993), Levine *et al.* (1991, 1992), Cole *et al.* (1983, 1984)

[a] Modified from Levine and Slade (1992b).

why do many current workers in the field consider this polymer science approach to be a significant advance in food research?

In this chapter, we attempt to answer these questions by reviewing the so-called "food polymer science" approach and various recent examples of how it has been used to define structure–function relationships in food products and processes, and to assess and understand the effects of glass transitions and water plasticization on food quality, safety, and stability. We review some theoretical principles from the field of synthetic polymer science that have been shown to be applicable to studies of the glassy state phenomenon in foods, and illustrate those applications by means of a broad overview focusing primarily on the most recent experimental studies by a number of groups that have been especially active in this rapidly growing field of research. In so doing, we attempt to convince readers, especially those previously unfamiliar with the food polymer science approach, of the importance of such an approach to food R&D. It is our hope that this review is sufficiently comprehensive and self-contained to enlighten those readers not previously acquainted with its subject matter. At the same time, we intend that it should build on our several earlier reviews (Levine and Slade, 1988a, 1989b, 1992b; Slade *et al.,* 1989; Slade and Levine, 1991a,b, 1993b,c), by emphasizing critical coverage of the most up-to-date studies, applications, and remaining (and/or resulting) questions concerning glass transitions and water–food structure interactions, in order to satisfy those readers already familiar with this subject. All readers are referred to those previous reviews for discussions of various earlier studies and applications exhaustively detailed there but not here.

II. FOUNDATION OF THE "FOOD POLYMER SCIENCE" APPROACH

The research approach known as "food polymer science" (Slade/Levine references in Table I) emphasizes the fundamental and generic similarities between synthetic polymers and food molecules, and has provided a new interpretive (rather than theoretical) and experimental framework for the study of food systems that are kinetically constrained. Based on established structure–property relationships from the field of synthetic polymer science (Table II), this innovative approach was developed to unify structural aspects of foods, viewed as kinetically metastable, completely amorphous or partially crystalline, homologous polymer systems, with functional aspects, dependent on mobility and conceptualized in terms of "water dynamics" and "glass dynamics." These unified concepts have been widely applied to explain and predict functional properties of food materials during processing and product storage (Slade/Levine references in Table I). Key elements of this interpretive approach to investigations of structure–function relationships in food systems, with demonstrated relevance to moisture management and water relationships (Slade and Levine, 1991a), include recognition of the following:

1. The behavior of foods and food materials as classical polymer systems, and that the behavior is governed by dynamics rather than energetics

TABLE II

SELECTED REFERENCES ON STRUCTURE–PROPERTY RELATIONSHIPS FROM SYNTHETIC POLYMER SCIENCE LITERATURE[a]

(A) Textbooks

Flory (1953), Wunderlich (1973, 1976, 1980, 1990), Cowie (1973), Nielsen (1977), Ferry (1980), Rowland (1980), Turi (1981), Sears and Darby (1982), Billmeyer (1984), Sperling (1986), Elliott (1990), Gray (1991), Matsuoka (1992)

(B) Journal Articles and Book Chapters

Kauzmann (1948), Gordon and Taylor (1952), Williams *et al.* (1955), Walton (1969), Brydson (1972), Sharples (1972), Hardy *et al.* (1973), Haward (1973), Roberts and White (1973), Flory (1974), Petrie (1975), Johari (1976, 1991), Baro *et al.* (1977), Buchanan and Walters (1977), Couchman and Karasz (1978), Fuzek (1980), Johnson *et al.* (1980), Moy and Karasz (1980), Starkweather (1980), Bair (1981, 1985), Batzer and Kreibich (1981), Keinath and Boyer (1981), Maurer (1981), Prime (1981), Shalaby (1981), Wunderlich (1981), Fried *et al.* (1982), Gaeta *et al.* (1982), Angell (1983, 1988), Eisenberg (1984), Ellis *et al.* (1984), Graessley (1984), Jin *et al.* (1984), Boyer *et al.* (1985), Matsuoka *et al.* (1985), Robertson (1985), Alfonso and Russell (1986), Blum and Nagara (1986), Domszy *et al.* (1986), Hiltner and Baer (1986), Mandelkern (1986), Cheng and Wunderlich (1987), Huang *et al.* (1987), Aubin and Prud'homme (1988), Burchard (1988), Ellis (1988), Sichina (1988), Cheng (1989), Murthy (1989), Murthy *et al.* (1989, 1993), Ehlich and Sillescu (1990), Angell *et al.* (1991, 1992), Cassel and Twombly (1991), Pissis and Apekis (1991), Roland and Ngai (1991, 1992), Chin *et al.* (1992), Lomellini (1992), Xenopoulos *et al.* (1992), Allen (1993), Compan *et al.* (1993), Ngai and Roland (1993)

[a] Modified from Levine and Slade (1992b).

2. The importance of the characteristic temperature, T_g, at which the glass–rubber transition occurs, as a physicochemical parameter that can determine processibility, product properties, quality, stability, and safety of food systems
3. The central role of water as a ubiquitous plasticizer of natural and fabricated amorphous food ingredients and products
4. The effect of water as a plasticizer on T_g, and the resulting non-Arrhenius, diffusion-limited behavior of amorphous polymeric, oligomeric, and monomeric food materials in the rubbery liquid state at $T > T_g$
5. The significance of nonequilibrium glassy solid and rubbery liquid states (as opposed to equilibrium thermodynamic phases) in most "real world" food products and processes, and their effects on time-dependent structural and mechanical properties related to quality and storage stability.

A. GLASSES AND GLASS TRANSITIONS

A glass is operationally defined as an amorphous (i.e., noncrystalline) solid (Haward, 1973). In fact, a glass is actually an undercooled liquid of such high viscosity [$\eta > 10^{10}$–10^{14} Pa s (Ferry, 1980; Wunderlich, 1981; Sperling, 1986)] that it exists in a metastable, mechanical solid state, in which it is capable of supporting its own weight against flow due to the force of gravity (Haward, 1973). A glass forms when a typical liquid, with a disordered molecular structure, is cooled to a temperature generally about 100°C (for many pure liquids) below its equilibrium crystalline melting temperature (T_m) or freezing point, at a cooling rate sufficiently high to avoid crystallization of the liquid (Ferry, 1980). This solidification process, known as vitrification (Luyet, 1960), results in the "freezing in" or immobilization of the disordered structure of the liquid state (Wunderlich, 1981), such that the resulting glassy solid is spatially homogeneous, but without any long-range lattice order, and is incapable of exhibiting any long-range, cooperative relaxation behavior (e.g., translational mobility) on a practical time scale (Ferry, 1980; Wunderlich, 1990).

A glass transition in amorphous systems is a temperature-, time- (or frequency-), and composition-dependent, material-specific change in physical state, from a glassy mechanical solid to a rubbery viscous liquid (capable of flow in real time) (Ferry, 1980; Wunderlich, 1990). In terms of thermodynamics, the glass transition is operationally defined as a second-order transition (Sperling, 1986; Wunderlich, 1990) (as opposed to a first-order transition, e.g., crystalline melting) and denoted by (1) a change in slope of the volume expansion (a first derivative of the free energy); (2) a discontinuity in the thermal expansion coefficient; and (3) a discontinuity in the heat capacity (a second derivative of the free energy) (Kauzmann, 1948; Wunderlich, 1990). The glass transition is also operationally defined, based on mechanical properties, in terms of a mechanical relaxation process such as viscosity (Ferry, 1980). Figure 1 shows that as the temperature (T) is lowered from that of the low-viscosity liquid state above T_m, where familiar Arrhenius kinetics apply, through a temperature range from T_m to T_g, a completely different, nonlinear form of kinetics, with an extraordinarily large temperature dependence (Angell, 1988; Franks and Grigera, 1990; Angell *et al.,* 1991, 1992), becomes operative (Roberts and White, 1973). Then, at a temperature where cooperative mobility becomes limiting, a state transition occurs, typically manifested as a three orders-of-magnitude change in viscosity, modulus, or mechanical relaxation rate (Eisenberg, 1984; Sperling, 1986; Noel *et al.,* 1990, 1991). At this glass transition temperature, the viscosity of a liquid is $\approx 10^{12}$ Pa s (10^{13} p) (Koide *et al.,* 1990; Noel *et al.,* 1991), the structural relaxation time [as determined calorimetrically, e.g., by differential scanning calorimetry (DSC)] for such a liquid is $\approx$200 seconds (Angell, 1988; Angell *et al.,* 1991, 1992), and, equivalently, the relaxation frequency is $\approx 10^{-3}$ Hz (Murthy *et al.,* 1993). A "mechanical" glass transition can be defined by combinations of temperature and deformation

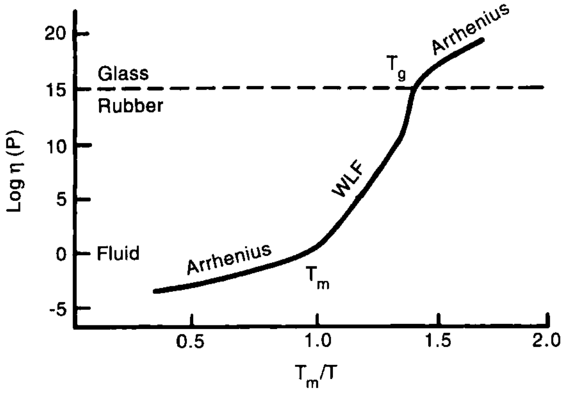

FIG. 1. Viscosity as a function of reduced temperature (T_m/T) for glassy and partially crystalline polymers. Reprinted from Levine and Slade (1988a) with permission of Cambridge University Press. Copyright 1988 Cambridge University Press. Adapted from Franks (1982).

frequency for which, as temperature decreases, sufficiently large numbers of mobile units (e.g., small molecules or backbone-chain segments of a macromolecule) become cooperatively immobilized (in terms of large-scale rotational and translational motions) during a time comparable to the experimental period (Buchanan and Walters, 1977; Angell, 1988; Green and Angell, 1989; Hosea *et al.,* 1990), such that the material becomes a mechanical solid capable of supporting its own weight against flow. Perhaps the most important distinction between dimensionally extended (alpha) relaxations, which give rise to the glass transition as translational motions become constrained at T_g, and small-scale (beta and gamma) relaxations (Scandola *et al.,* 1991; Botham *et al.,* 1992; Noel *et al.,* 1992), for which small-scale rotational motions do *not* become constrained as T falls below T_g, is the cooperative nature of alpha relaxations (Johari, 1976; Ferry, 1980; Wunderlich, 1981). Arrhenius kinetics become operative once again in the glassy solid at $T < T_g$ (Noel *et al.,* 1991), but the rates of all diffusion-limited processes are much lower in this high-viscosity solid state than in the liquid state at $T > T_g$ (Levine and Slade, 1988a; Karmas *et al.,* 1992). In fact, the difference in average relaxation times between the two Arrhenius regimes (at $T < T_g$ and $T > T_m$) is typically more than 14 orders of magnitude (Slade and Levine, 1988b).

B. EVOLUTION OF THE "FOOD POLYMER SCIENCE" APPROACH

The genesis of a polymer science approach to the study of glasses and glass transitions in foods dates back at least to 1966 and a seminal review by White and Cakebread on the glassy state and T_g in certain sugar-containing food products. They recognized (1) the importance of the glassy state, and of the glass transition temperature and its location relative to the temperature of storage (either ambient or subzero), in a variety of aqueous food systems, including but not limited to boiled sugar candies, and (2) the critical role of water as a plasticizer of food glasses and the quantitative T_g-depressing effect of increasing content of plasticizing moisture, whereby T_g of a particular glass-forming solute–water mixture depends on the corresponding content of plasticizing water (W_g) in that glass at its T_g (Levine and Slade, 1986, 1988a; Slade and Levine, 1988a). White and Cakebread (1966; Cakebread, 1969) were apparently the first food scientists to allude to the broader implications of nonequilibrium glassy and rubbery states to the quality, safety, and storage stability of a wide range of glass-forming aqueous food systems. Evidently, outside a small community of candy technologists, (1) the work of White and Cakebread, (2) the even earlier (but somewhat better known by food technologists) work of Makower and Dye (1956) on the kinetics of crystallization of amorphous sucrose and glucose (from the water-plasticized, rubbery state at room $T > T_g$), (3) the more recent work by other candy technologists such as Herrington and Branfield (1984) on the physicochemical properties of sugar glasses, and (4) the broader relevance of this body of work to the field of food science and technology went largely unnoticed until the early 1980s.

Since that time, many other workers (Tables I and IIIA) have helped to advance, with increasing momentum since 1984, concepts and approaches based on recognition of the importance of, and application of the principles underlying, nonequilibrium glassy solid and rubbery liquid states in foods. The current situation of accelerating activity and interest in this area is illustrated by the fact that 16 different chapters in a recent book on water relationships in foods (Table IIIB) included discussions of glasses and glass transitions in food systems. Another strong indication of the emergence of this subject is the fact that a new graduate course, "Advanced Topics in Food Science: Glass Transitions, T_g, A_w, and the Physical Properties of Foods," was offered for the first time in the summer of 1990 by Professors T. Labuza and E. Davis at the University of Minnesota's Food Science Department. Still another indication of the recent prominence of this subject is the fact that (1) an entire 4-day-long international conference on "The Science and Technology of the Glassy State in Foods" was held as one of the well-known "Easter Schools" at Nottingham University (UK) in April 1992) (Table IIIE), to mark the completion of phase I of the groundbreaking ACTIF (Amorphous and Crystalline Transitions in Foods) research program at Nottingham; (2) a symposium on "Glass Transitions in Cereal-Based Foods" (Table IIIC) and another on "Developments in

TABLE III

REFERENCES TO RECENT PUBLICATIONS DEALING WITH THE PRACTICAL SIGNIFICANCE OF THE GLASSY STATE PHENOMENON AND GLASS TRANSITION TO THE PROCESSING, QUALITY, SAFETY, AND STABILITY OF FOOD AND BIOLOGICAL INGREDIENTS AND PRODUCTS[a]

(A) General

Soesanto and Williams (1981), Flink (1983), Saleeb and Pickup (1985, 1989), Chan *et al.* (1986), Hardman (1986), Atkins (1987), Gosline (1987), Russell (1987a), Gould and Christian (1988), Lineback and Rasper (1988), Quinquenet *et al.* (1988), Skarra *et al.* (1988), Takahashi *et al.* (1988), Zobel (1988, 1992a,b), Zobel *et al.* (1988), BeMiller (1989, 1993), Cairault *et al.* (1989), Colonna *et al.* (1989), Doublier (1989), Eliasson (1989, 1992), Fujio and Lim (1989), Russell and Oliver (1989), Shi and Seib (1989, 1992), Stepto and Dobler (1989), Ahlneck and Zografi (1990), Hosea *et al.* (1990), Johnston-Banks (1990), Johnson *et al.* (1990), Kararli and Catalano (1990), Kararli *et al.* (1990), Lillie and Gosline (1990), Mita (1990), Oksanen and Zografi (1990, 1993), Pikal (1990a,b, 1993), Pikal and Shah (1990), Pikal *et al.* (1990, 1991a,b), Roozen and Hemminga (1990, 1991), Roper and Koch (1990), Rubin *et al.* (1990), Schiraldi (1990), Stauffer (1990, 1992), Takushi *et al.* (1990), Van Scoik and Carstensen (1990), Williams *et al.* (1990), Yoshida *et al.* (1990, 1992), Belton (1991), Chang and Baust (1991a,b,c), Chinachoti *et al.* (1991a), Cocero and Kokini (1991), Davis (1991, 1992a,b), Donhowe *et al.* (1991), Fujio *et al.* (1991), Gaines (1991, 1993), Graf and Saguy (1991), Hartel and Shastry (1991), Hegenbart (1991, 1993), Karathanos *et al.* (1991), Karger and Ludemann (1991), Lai and Kokini (1991), Larsson (1991), Larsson and Eliasson (1991), Liu and Lelievre (1991a,b, 1992a,b), Liu *et al.* (1991), Ma and Harwalkar (1991), MacDonald and Lanier (1991), Nakamura *et al.* (1991), O'Brien (1991), Parak and Nienhaus (1991), Patil (1991), Raemy and Lambelet (1991), Roozen *et al.* (1991), Roser (1991a,b), Scandola *et al.* (1991), Shukla (1991), Sochava *et al.* (1991), Spratt *et al.* (1991), Tanner *et al.* (1991), Tolstoguzov (1991, 1992), Young and Scholl (1991), Bagley (1992), Berail *et al.* (1992), Best (1992), Bizot *et al.* (1992), Boskovic *et al.* (1992), Bruin (1992), Caldwell *et al.* (1992), Chang and Randall (1992), Chinachoti (1992a, 1993), Cocero *et al.* (1992a), Colaco *et al.* (1992), Colonna and Buleon (1992), de Graaf *et al.* (1992), Eerlingen and Delcour (1992), Finley *et al.* (1992), Gaines *et al.* (1992a–c, 1993a,b), German *et al.* (1992), Goff (1992), Gontard *et al.* (1992a,c), Gudmundsson (1992), Gudmundsson and Eliasson (1992), Hanover (1992), Harrison *et al.* (1992), Hartel (1992, 1993), Jovanovich *et al.* (1992), Jurgens *et al.* (1992), Kaletunc and Breslauer (1992), Karathanos and Saravacos (1992), Katsuta *et al.* (1992), Kawai *et al.* (1992), Kim and Setser (1992), Kim and Walker (1992), Kokini (1992), Kokini *et al.* (1992a,b), Kresin and Rau (1992), Labuza and Baisier (1992), Lawton (1992a,b), Lim *et al.* (1992), Magoshi *et al.* (1992), Megret *et al.* (1992), Milczarek *et al.* (1992), Nelson and Labuza (1992b), Newman (1992), Peleg (1992), Pissis *et al.* (1992), Rajagopalan and Seib (1992), Rao *et al.* (1992), Roy *et al.* (1992), Sahagian and Goff (1992, 1993), Sapru and Labuza (1992b), Saunders *et al.* (1992), Schroeter and Hobelsberger (1992), Shah and Ludescher (1992), Shogren (1992), Shogren *et al.* (1992), Sochava and Belopolskaya (1992), Sochava and Smirnova (1992), Stute (1992), Summers (1992), te Booy *et al.* (1992), Tolstoguzov and Nesmeyanov (1992), Watase *et al.* (1992), Zasypkin *et al.* (1992), Zhang and Jackson (1992), Anonymous (1993a,b), Appelqvist *et al.* (1993), Carpenter *et al.* (1993), Crowe and Crowe (1993), Crowe *et al.* (1993), Eerlingen *et al.* (1993), Eliasson and Larsson (1993), Ford and

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TABLE III (*Continued*)

Dawson (1993), George (1993), Hancock and Zografi (1993), Haynes and Locke (1993), Haynes *et al.* (1993), Lawton and Wu (1993), Mancini (1993), Mestres *et al.* (1993), Nelson (1993), O'Donnell (1993), Ohshima *et al.* (1993), Peppas (1993), Rohde *et al.* (1993), Roser and Colaco (1993), Seow and Teo (1993), Seow and Thevamalar (1993), Shalaev and Kanev (1993), Yano (1993), Zanoni *et al.* (1993)

(B) Chapters in "Water Relationships in Foods" (Plenum Press, New York 1991)

Franks (1991a), Blanshard *et al.* (1991), van den Berg (1991), Karel and Saguy (1991), Lim and Reid (1991), Hoseney (1991), Simatos and Blond (1991), Le Meste *et al.* (1991b), Maurice *et al.* (1991), Schenz *et al.* (1991), Biliaderis (1991a), Slade and Levine (1991b), Given (1991), Nishinari *et al.* (1991), Tomka (1991), Wasylyk and Baust (1991)

(C) "Glass Transitions in Cereal-Based Foods" Symposium and Other Papers at AACC Annual Meeting (1992)

Amemiya and Menjivar (1992), Botham *et al.* (1992), Cocero *et al.* (1992b), Hoseney *et al.* (1992), Huang *et al.* (1992), Kalichevsky and Blanshard (1992c), Lelievre (1992b), Lillford *et al.* (1992), Slade and Levine (1992a), Smith (1992b)

(D) Glass Transitions in Natural Plant Tissues

Burke (1986), Hirsh (1987), Koster and Leopold (1988), Williams and Leopold (1989), Vertucci (1990), Bruni and Leopold (1991, 1992), Dereuddre *et al.* (1991), Koster (1991), Lin *et al.* (1991), Williams (1991), Leopold *et al.* (1992), De Bry (1993), Koster *et al.* (1993), Williams *et al.* (1993)

(E) Chapters in "The Glassy State in Foods" (Nottingham University Press, Loughborough, 1993)

Allen (1993), Karel *et al.* (1993a), Slade and Levine (1993c), Reid *et al.* (1993a), Kalichevsky *et al.* (1993a), Hemminga *et al.* (1993), Noel *et al.* (1993), Ablett *et al.* (1993), Roos and Karel (1993), van den Berg *et al.* (1993), Lillie and Gosline (1993), Gidley *et al.* (1993), Attenburrow and Davies (1993), Levine and Slade (1993), Donald *et al.* (1993), Simatos and Blond (1993), Peleg (1993), MacInnes (1993), Bolton *et al.* (1993)

Poster Papers at Easter School Conference (1992)

Schenz *et al.* (1992), Aynie *et al.* (1992a), Kalichevsky and Blanshard (1992d,e), Labuza (1992), Livings *et al.* (1992), Nesvadba (1992a), Parker and Smith (1992), Sala and Tomka (1992a,b), Willenbucher *et al.* (1992), Tian and Blanshard (1992c), Sapru and Labuza (1992a)

(F) Papers at IFT '92 Annual Meeting (1992)

Attwool *et al.* (1992), Chinachoti (1992a), Chuy and Labuza (1992), Cocero and Kokini (1992), Hallberg and Chinachoti (1992), Hsu and Reid (1992), Huang (1992), Jeffery (1992), Leung *et al.* (1992), Levi and Karel (1992a), Madeka and Kokini (1992b), Nelson *et al.* (1992), Reid *et al.* (1992), Roos (1992b), Taylor *et al.* (1992)

(G) Papers at ISOPOW-V Conference (1992)

Blond (1992), Nelson and Labuza (1992a), Reid (1992a), Slade and Levine (1992b), Blanshard and Mitchell (1992), Angell *et al.* (1992), Kokini *et al.* (1992d), MacInnes (1992), Nesvadba (1992b), Jouppila and Roos (1992), Chinachoti (1992b), Gontard *et al.* (1992b), Aynie *et al.* (1992b)

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TABLE III (*Continued*)

(H) Papers at CoFE '92 Meeting (1992)

Labuza and Nelson (1992), Anglea *et al.* (1992b), Roos (1992c), Madeka and Kokini (1992a), Lim and Reid (1992)

(I) Chapters in "Developments in Carbohydrate Chemistry" (AACC, St. Paul, 1992)

Zobel (1992a), Lelievre (1992a), Biliaderis (1992a), Sullivan *et al.* (1992), Thompson (1992)

(J) Papers at ICEF 6 Congress (1993)

Karel (1993), Cocero *et al.* (1993), Roos and Jouppila (1993), Huang (1993a), Nesvadba (1993)

(K) Papers at IFT '93 Annual Meeting (1993)

Barrett *et al.* (1993), Cherian and Chinachoti (1993), Cocero and Kokini (1993), Huang (1993b), Karmas *et al.* (1993), Kim and Taub (1993), Levi and Karel (1993a), Madeka and Kokini (1993), McCurdy *et al.* (1993), Nelson and Labuza (1993), Shah and Ludescher (1993), Wang and Chinachoti (1993)

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[a] Modified from Levine and Slade (1992b).

Carbohydrate Chemistry" (Table IIII) were held at the AACC 77th Annual Meeting in Minneapolis in September 1992; and (3) many papers on the glassy state and glass transitions were also presented in 1992 and 1993 at the following: IFT '92 Annual Meeting in New Orleans (Table IIIF); CoFE–AIChE 1992 Summer National Meeting in Minneapolis (Table IIIH); ISOPOW-V Meeting on the Properties of Water in Foods in Valencia (Spain) in November 1992 (Table IIIG); ICEF-6 Congress in Chiba (Japan) in May 1993 (Table IIIJ); and IFT '93 Annual Meeting in Chicago (Table IIIK).

Recognition of several key elements (mentioned earlier) of the food polymer science approach and their relevance to the behavior of a broad range of different types of foods [e.g., intermediate-moisture (IMF), low-moisture, frozen, starch-based, gelatin-, gluten-, and other protein-based foods] and corresponding model systems increased markedly during the 1980s (Slade and Levine, 1991a). Various studies have illustrated the perspective afforded by using this conceptual framework and demonstrated the technological utility of this new approach to understand and explain complex behavior, design processes, and predict product quality, safety, and storage stability, based on fundamental structure–property relationships of food systems viewed as homologous families of partially crystalline glassy polymer systems plasticized by water (Slade/Levine references in Table I). Referring to the food polymer science approach, John Blanshard, in the proposal for the ACTIF research program (personal communication, 1987), stated that "it is not often that a new concept casts fresh light across a whole area of research, but there is little doubt that the recognition of the importance of the transition from the glassy to the crystalline or rubbery state in foodstuffs, though well known in synthetic polymers, has opened up new and potentially very significant ways of thinking about food properties and stability." In a lecture on historical developments in industrial polysaccharides, James BeMiller (1989) echoed Blanshard's words by remarking that a key point regarding the future of polysaccharide research and technology is "the potential, already partly realized, in applying ideas developed for synthetic polymers to polysaccharides; for example, the importance of the glassy state in many polysaccharide applications." More support for the food polymer science approach came in two recent columns in *Cereal Foods World,* one on food technology, entitled "A New Development in Carbohydrate Research," in which Triveni Shukla (1991) said "a recent breakthrough in fundamental research on starches [translated from basic concepts of synthetic polymers] concerns glass transition behavior and the glass transition temperature, T_g," and the other on methodology, entitled "The "Nobel" Science of Foods," in which Eugenia Davis (1991) said "we are seeing an explosion of polymer science application to food polymers in the last 10 years. For example, the study of glass transitions (T_g) in formulated and fabricated foods as they go from the glassy to the rubbery state is found in virtually every food science-related journal. Calorimetric, rheological, and spectroscopic methods are used. As a result, it has become imperative that we incorporate such basic scientific information into our courses and research programs." As if to support Davis' and Shukla's observations, John O'Brien (1991) commented on "the rapid advances in starch chemistry and technology . . . the manipulation of glass transition temperatures, and controlled crystallization/gelatinization" in a recent editorial in *Trends in Food Science and Technology* on "Characterizing Food and Its Ingredients." The food polymer science approach and the importance of glass transitions in foods have even become subjects of increasing discussion in several recent food trade magazine articles (Hegenbart, 1991, 1993; Best, 1992; Anonymous, 1993a; Mancini, 1993; O'Donnell, 1993).

C. T_g AND METHODS OF ITS MEASUREMENT IN FOODS

The technological importance of the glass transition in amorphous polymers and of the characteristic temperature at which it occurs (T_g) is well known in synthetic polymer science (Ferry, 1980; Rowland, 1980; Sears and Darby, 1982; Eisenberg, 1984). Especially in the last several years, a growing number of food scientists from both academia and industry have increasingly recognized the practical significance of the glass transition as a physicochemical event [i.e. a change of state but not a change of phase

(Allen, 1993)] that can govern food processing, product properties, quality, safety, and stability (Tables I and III). This recognition of the importance of the glass transition in foods [as well as in related biological materials (Table IIID), such as plant cell walls, seeds (with emphasis on the glassy state, produced by sucrose and various other sugars at low moisture, as the mechanism of control of the dormant state), and other natural plant tissues, and pharmaceutical materials] has gone hand-in-hand with an increasing awareness of the inherent nonequilibrium nature of most food products and processes (Table IV). Many examples of food systems whose behavior is governed by dynamics far from equilibrium and of practical problems of food science and technology posed by their nonequilibrium nature have been described (e.g., Slade/Levine references in Table I).

The polymer science-based interpretive approach to studies of structure–function relationships in food systems emphasizes insights gained by an appreciation of the fundamental similarities between synthetic amorphous polymers and glass-forming aqueous food materials with respect to their thermal, mechanical, and structural properties (Slade and Levine, 1991a). Such properties, for synthetic polymers as well as food materials, are most commonly measured by thermal analysis methods such as DSC and dynamic mechanical [thermal] analysis (DMA [DMTA]) (Turi, 1981; Wunderlich, 1990; Harwalkar and Ma, 1990). DSC and DMA have become established methods for characterizing glass transitions in completely amorphous or partially crystalline polymer systems (Fuzek, 1980), and have been the ones of choice in most recent investigations of glasses and glass transitions in food systems. However, in many other recent experimental studies, other methods (listed in Table V), complementary to DSC and DMA, have also been used to measure glass transitions in food ingredients and products and/or aspects of molecular mobility and diffusivity related to the effects of glass transitions in aqueous food glasses and rubbers. Probably the most powerful instrumental approach to the study of glass transitions in foods would involve combined use of several of these different but complementary experimental techniques (Noel *et al.*, 1990). For example, in recent studies by Kalichevsky *et al.* (1992a–c) of the glass transition of amylopectin (the branched polymer of starch), amylopectin–sugar mixtures, wheat gluten protein, and gluten–sugar mixtures at low moisture contents, DSC, DMTA, NMR, and Instron analyses were utilized. Similarly, Shogren (1992) combined DSC, DMTA, and NMR measurements to study the effect of moisture content on physical aging of extruded corn starch glasses; Scandola *et al.* (1991) combined DSC, DMTA, and TDEA measurements to investigate the glass transition of dry dextran, pullulan, and amylose; Sahagian and Goff (1992) used DSC, TMA, and NMR to determine the influence of xanthan gum on the thermomechanical behavior of a frozen sucrose solu-

TABLE IV

SELECTED REFERENCES TO RECENT PUBLICATIONS THAT HAVE HIGHLIGHTED THE NONEQUILIBRIUM NATURE OF FOOD (OR PHARMACEUTICAL) PRODUCTS AND PROCESSES[a]

Examples of nonequilibrium products and processes	References
Microbiological activity	Slade and Levine (1985, 1988a,b, 1991a), Gould and Christian (1988), Sapru and Labuza (1992a,b), Bolton *et al.* (1992)
Sorption/desorption hysteresis	van den Berg (1981, 1986, 1991), Hardman (1986), Levine and Slade (1988a, 1989b), Lillford (1988), Cairault *et al.* (1989), Slade *et al.* (1989), Myers-Betts and Baianu (1990), Oksanen and Zografi (1990), Paakkonen and Roos (1990), Ablett and Lillford (1991), Franks (1991a,b), Pikal *et al.* (1991a), Slade and Levine (1991a), Reid (1992b), Yano (1993)
Graininess and iciness in ice cream, reduced survival of frozen enzymes and living cells, reduced activity and shelf stability of freeze-dried proteins	Cole *et al.* (1983, 1984), Levine and Slade (1986, 1988c,d, 1989c,d, 1990, 1992a), Blanshard and Franks (1987), Hirsh (1987), Franks (1989, 1990, 1991c, 1992b, 1993a,b), Franks and Hatley (1990, 1992, 1993), Le Meste and Simatos (1990), Noel *et al.* (1990), Pikal (1990a,b, 1993), Pikal and Shah (1990), Pikal *et al.* (1990, 1991a,b), Reid (1990, 1992a), Belton (1991), Blond and Colas (1991), Chang and Baust (1991a,b,c), Franks and van den Berg (1991), Franks *et al.* (1991), Hatley (1991), Hatley and Franks (1991), Lim and Reid (1991, 1992), Roos and Karel (1991f,g), Berail *et al.* (1992), Best (1992), Blond (1992, 1993), Caldwell *et al.* (1992), Chang and Randall (1992), Goff (1992), Karel (1992), Nesvadba (1992a), Reid *et al.* (1992), Sahagian and Goff (1992, 1993), van den Berg (1992), van den Berg *et al.* (1992, 1993), Carpenter *et al.* (1993), Crowe and Crowe (1993), Crowe *et al.* (1993), Ford and Dawson (1993), Goff *et al.* (1993), Huang *et al.* (1993), Kerr *et al.* (1993), Ohshima *et al.* (1993), Williams *et al.* (1993)
Caking and other diffusion-limited, physical or chemical "collapse" processes in amorphous powders	Tsourouflis *et al.* (1976), To and Flink (1978), Downton *et al.* (1982), Flink (1983), Karel and Flink (1983), Karel (1985, 1986, 1989, 1990, 1991c), Levine and Slade (1986, 1988b, 1989a, 1992b), Roos (1987, 1992b–d), Karel and Langer (1988), Simatos and Karel (1988), Wallack and King (1988), Ahlneck and Zografi (1990), Paakkonen and Roos (1990), Roos and Karel (1990, 1991a,b,c,e, 1992, 1993), Van Scoik and Carstensen (1990), Karel and Saguy (1991), Levine *et al.* (1991, 1992), Shimada *et al.* (1991), Aguilera *et al.* (1992), Anglea *et al.* (1992b),

(continues)

TABLE IV (*Continued*)

Examples of nonequilibrium products and processes	References
	Best (1992), Bruin (1992), Buera and Karel (1992), Chuy and Labuza (1992), Karathanos *et al.* (1992), Karmas *et al.* (1992, 1993), Labrousse *et al.* (1992), Levi and Karel (1992a, 1993a,b), Nelson and Labuza (1992a,b), te Booy *et al.* (1992), van den Berg (1992), Hartel (1993), Hegenbart (1993), Huang (1993a), Karel *et al.* (1993a,b), Nelson (1993), Peleg (1993), Slade and Levine (1993c)
Cooking of cereals and grains (including, e.g., by extrusion)	Slade and Levine (1984, 1987b, 1988b,c,d, 1989), Reid and Charoenrein (1985), Burros *et al.* (1987), Paton (1987), Mestres *et al.* (1988), Levine and Slade (1989b), Knutson (1990), Lai and Kokini (1991), Larsson and Eliasson (1991), Liu and Lelievre (1991a,b, 1992a), Liu *et al.* (1991), Colonna and Buleon (1992), Rajagopalan and Seib (1992), Tolstoguzov (1992), Warburton *et al.* (1990, 1992), Zobel (1992a), BeMiller (1993), Donald *et al.* (1993), Seow and Teo (1993), Seow and Thevamalar (1993)
Expansion of bread or collapse of cake during baking, effects of flour and sugar on cookie baking	Blanshard (1986), Slade *et al.* (1989, 1993), Levine and Slade (1989b, 1993), Slade and Levine (1990, 1993b,d), Hoseney and Rogers (1993)
Staling of baked products	Slade (1984), Miles *et al.* (1985b), Hoseney (1986), Slade and Levine (1987b, 1988d, 1989), Slade *et al.* (1987), Skarra *et al.* (1988), Clark *et al.* (1989), Gidley and Bulpin (1989), Biliaderis (1991b, 1992a,b), Cairns *et al.* (1991b), Cameron and Donald (1991), Patil (1991), Chinachoti (1992b), Gudmundsson (1992), Hallberg and Chinachoti (1992), Michniewicz *et al.* (1992), Rao *et al.* (1992), Shogren (1992), Zhang and Jackson (1992), Hoseney and Rogers (1993)
Effects of sugar–water glasses and rubbers on texture and storage stability of cookies	Slade and Levine (1990, 1991a,b, 1993b,d), Amemiya and Menjivar (1992), Gaines *et al.* (1992a–c, 1993a,b), Gaines (1991, 1993), Levine and Slade (1993), Slade *et al.* (1993)
Recipe requirements for gelatin desserts	Slade and Levine (1987a), Levine and Slade (1988a)

[a] Modified from Levine and Slade (1992b).

tion; Cocero and Kokini (1991) used combined mechanical spectrometry and DSC measurements in a study of the glass transition, at low moisture contents, of the glutenin component of gluten; Rubin *et al.* (1990) investigated vitrification of honey, using DSC and NMR; Johnson *et al.* (1990) examined the interactions of starch and sugar–water, using ESR and DSC; Ollivon (1991; Quinquenet *et al.*, 1988) employed DSC and TDEA measurements to analyze solute–water interactions in aqueous glasses and rubbers of various sugars and polyhydric alcohols; Huang *et al.* (1992) used TMA, TSC, and dielectric spectroscopy measurements to study the glass transition, at low moisture contents, of starch, gluten, and white bread; Ollett and Parker (1990) showed that both viscosity and DSC measurements yielded comparable T_g values for undercooled melts of fructose or glucose; and Noel *et al.* (1991) showed the same for low-moisture maltose–water mixtures. Results of such studies have graphically demonstrated "the fact that the glass transition is not observed at a unique temperature, but is related to the frequency [or time scale (Gosline, 1987; Slade and Levine, 1988c, 1991a; Orford *et al.*, 1989; Hosea *et al.*, 1990; Koide *et al.*, 1990; Noel *et al.*, 1990, 1991; Pissis and Apekis, 1991; Ring and Whittam, 1991; Nelson, 1993)] of the measurement technique" (Kalichevsky *et al.*, 1992a) and that "the various techniques are sensitive to different degrees of molecular mobility" (Kalichevsky *et al.*, 1992a).

Based on a polymer science approach, various DSC, DMA, and other results have been used to demonstrate that product quality and stability often depend on maintaining foods in kinetically metastable, dynamically constrained, time-dependent glassy and/or rubbery states, and that these nonequilibrium physical states determine the time-dependent thermomechanical, rheological, and textural properties of foods (Slade/Levine references in Table I).

D. EFFECT OF PLASTICIZATION ON T_g

Plasticization, and its modulating effect on the temperature location of the glass transition, is another key technological aspect of synthetic polymer science (Sears and Darby, 1982). A polymer science approach to the analysis of both model and real food systems involves recognition of the critical role of water as an effective plasticizer of amorphous polymeric, oligomeric, and monomeric food materials (Karel, 1985; Levine and Slade, 1988a, 1989b; Slade *et al.*, 1989). It has become well documented that plasticization by water depresses the T_g [and the melt viscosity (Smith, 1990) and elastic or Young's modulus (Ablett *et al.*, 1986; Hutchinson *et al.*, 1989; Smith, 1990, 1992a,c; Davies *et al.*, 1991; Ollett *et al.*, 1991; Kalichevsky *et al.*, 1992a,c; Le Meste *et al.*, 1992; Schroeter and Hobelsberger, 1992)] of completely

TABLE V

REFERENCES TO STUDIES EMPLOYING METHODS OTHER THAN DSC OR DMA TO INVESTIGATE GLASS TRANSITIONS AND THEIR EFFECTS IN FOOD INGREDIENTS AND PRODUCTS[a]

Method	References
Thermomechanical analysis (TMA)	Biliaderis *et al.* (1986a,c), Caldwell *et al.* (1990), Biliaderis (1990, 1991a), Le Meste and Huang (1991), Le Meste *et al.* (1991a, 1992), Maurice *et al.* (1991), Schenz *et al.* (1991), Chang and Randall (1992), Davis (1992b), Dong (1992), Goff (1992), Hoseney *et al.* (1992), Huang *et al.* (1992), Sahagian and Goff (1992, 1993), Goff *et al.* (1993), Huang (1993a,b), Reid *et al.* (1993b)
Thermodielectrical analysis (TDEA)	Chan *et al.* (1986), Quinquenet *et al.* (1988), Schiraldi (1990), Ollivon (1991), Scandola *et al.* (1991), Botham *et al.* (1992), Hsu and Reid (1992), Noel *et al.* (1992), Reid *et al.* (1993b)
Thermal stimulated current/relaxation map analysis (TSC/RMA) spectroscopy	Matthiesen *et al.* (1991), Bruni and Leopold (1992), Huang *et al.* (1992), Leopold *et al.* (1992), Megret *et al.* (1992), Pissis *et al.* (1992)
Electron spin resonance (ESR)	Le Meste and Duckworth (1988), Simatos and Karel (1988), Johnson *et al.* (1990), Le Meste and Simatos (1990), Le Meste *et al.* (1990, 1991b), Roozen and Hemminga (1990, 1991), Bruni and Leopold (1991, 1992), Roozen *et al.* (1991), Leopold *et al.* (1992), Hemminga *et al.* (1993)
Nuclear magnetic resonance (NMR)	Ablett *et al.* (1986, 1993), Simatos and Karel (1988), Rubin *et al.* (1990), Ablett and Lillford (1991), Belton (1991), Chinachoti *et al.* (1991a), Given (1991), Karger and Ludemann (1991), Pikal *et al.* (1991a), Tanner *et al.* (1991), Chinachoti (1992a), Harrison *et al.* (1992), Kalichevsky *et al.* (1992a–d, 1993a), Kalichevsky and Blanshard (1992c), Kawai *et al.* (1992), Lillford *et al.* (1992), Newman (1992), Sahagian and Goff (1992), Shogren (1992), Tian and Blanshard (1992b), Willenbucher *et al.* (1992), Cherian and Chinachoti (1993), Gidley *et al.* (1993), Oksanen and Zografi (1993)
Fourier-transform infrared (FTIR)	Young and Scholl (1991), Tian and Blanshard (1992a)
Brillouin scattering spectroscopy	Hosea *et al.* (1990)
Phosphorescence spectroscopy	Shah and Ludescher (1992, 1993)
Fluorescence microscopy	Nelson (1993)
Dielectric spectroscopy	Huang *et al.* (1992), Haynes and Locke (1993), Haynes *et al.* (1993)

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TABLE V (*Continued*)

Method	References
Mossbauer spectroscopy	Parak and Nienhaus (1991)
Mechanical spectrometry	Gosline (1987), Masi (1989), Lillie and Gosline (1990, 1993), Cocero and Kokini (1991, 1993), Roos and Karel (1991f), Anglea *et al.* (1992a), Davis (1992a), de Graaf *et al.* (1992), Kokini (1992), Sala and Tomka (1992a), Barrett *et al.* (1993), Karel *et al.* (1993b), MacInnes (1993), Simatos and Blond (1993)
Dynamic rheometry	Mita (1990), Madeka and Kokini (1992a, 1993), Yano (1993)
Viscometry	Ollett and Parker (1990), Noel *et al.* (1991), Cocero and Kokini (1992), Cocero *et al.* (1992b)
Analysis by Instron (or other physical testing apparatus)	Attenburrow *et al.* (1990, 1992), Davies *et al.* (1991), Ollett *et al.* (1991), Amemiya and Menjivar (1992), Cocero *et al.* (1992a,b), Kalichevsky and Blanshard (1992b), Kalichevsky *et al.* (1992a–d, 1993b), Lillford *et al.* (1992), Smith (1992a), Attenburrow and Davies (1993), Hegenbart (1993), Kirby *et al.* (1993), Rohde *et al.* (1993)
Gas permeability or vapor sorption	van den Berg (1981, 1986, 1991), Slade and Levine (1985, 1991a), Levine and Slade (1988a), Slade *et al.* (1989), Oksanen and Zografi (1990, 1993), Arvanitoyannis *et al.* (1993), Hancock and Zografi (1993)

[a] Modified from Levine and Slade (1992b).

amorphous or partially crystalline food ingredients and products, and that this T_g depression may be advantageous or disadvantageous to ingredient and product processing, functional properties, and storage stability (Slade and Levine, 1991a; Levine and Slade, 1992b). Recently, there has been expanding interest in the importance of the effect of water as a plasticizer of many different food materials and biopolymers (Table VI).

A unified conceptual approach to research on the glassy state phenomenon and glass transitions in food polymer systems, based on principles translated from synthetic polymer science, has enhanced our qualitative understanding of structure–function relationships in a wide variety of food ingredients and products (Slade/Levine references in Table I). Many workers have recently applied a synthetic polymers or "materials science" (see references of Lillford and co-workers at Unilever in Table VIIA) approach to characterize the glass transition, melting, crystallization, annealing, or

TABLE VI

REFERENCES TO STUDIES OF EFFECTS OF WATER AS A PLASTICIZER OF FOOD AND BIOLOGICAL MATERIALS[a]

Starch, amylose, amylopectin: Kainuma and French (1972), van den Berg (1981, 1986, 1991, 1992), Slade (1984), Slade and Levine (1984, 1987b, 1988c,d, 1989, 1991a,b, 1992c, 1993a,b), Wittwer and Tomka (1984), Biliaderis *et al.* (1985, 1986a,b,c), Maurice *et al.* (1985), Ablett *et al.* (1986), Blanshard (1986, 1987, 1988), Yost and Hoseney (1986), Chungcharoen and Lund (1987), Ring *et al.* (1987), Russell (1987a), Slade *et al.* (1987), Tanner *et al.* (1987, 1991), Zeleznak and Hoseney (1987a,b), Levine and Slade (1988a, 1989b, 1992b), Lillford (1988), Lineback and Rasper (1988), Marsh and Blanshard (1988), Skarra *et al.* (1988), Zobel (1988, 1992a), Zobel *et al.* (1988), Attenburrow *et al.* (1989, 1992), Biliaderis and Galloway (1989), Colonna *et al.* (1989), Hutchinson *et al.* (1989), Lund (1989), Orford *et al.* (1989), Russell and Oliver (1989), Shi and Seib (1989, 1992), Stepto and Dobler (1989), Biliaderis (1990, 1991a,b, 1992b), Biliaderis and Seneviratne (1990a,b), Biliaderis and Zawistowski (1990), Ghiasi and Skarra (1990), I'Anson *et al.* (1990), Johnson *et al.* (1990), Knutson (1990), Morris (1990), Noel *et al.* (1990), Roper and Koch (1990), Schiraldi (1990), Smith (1990, 1992a,c), Warburton *et al.* (1990, 1992), Whittam *et al.* (1990, 1991), Cairns *et al.* (1991b), Chinachoti *et al.* (1991a,b), Garbow and Schaefer (1991), Given (1991), Karathanos *et al.* (1991), Lai and Kokini (1991), Larsson (1991), Larsson and Eliasson (1991), Liu and Lelievre (1991b, 1992a,b), Ollett *et al.* (1991, 1993a,b), Patil (1991), Roos and Karel (1991d), Scandola *et al.* (1991), Tomka (1991), Bizot *et al.* (1992), Colonna and Buleon (1992), Dong (1992), Eerlingen and Delcour (1992), Eliasson (1992), Gudmundsson (1992), Gudmundsson and Eliasson (1992), Hallberg and Chinachoti (1992), Huang *et al.* (1992), Jovanovich *et al.* (1992), Kaletunc and Breslauer (1992), Kalichevsky and Blanshard (1992a–d), Kalichevsky *et al.* (1992a,b, 1993a), Karathanos and Saravacos (1992), Kim and Walker (1992), Kokini *et al.* (1992c), Le Meste *et al.* (1992), Lelievre (1992a), Lillford *et al.* (1992), Lim *et al.* (1992). Michniewicz *et al.* (1992), Noel and Ring (1992), Parker and Smith (1992), Rajagopalan and Seib (1992), Roos (1992d), Sala and Tomka (1992a,b), Schroeter and Hobelsberger (1992), Shogren (1992), Shogren *et al.* (1992), Thompson (1992), Tian and Blanshard (1992b), Tolstoguzov (1992), Willenbucher *et al.* (1992), Zasypkin *et al.* (1992), Zhang and Jackson (1992), Arvanitoyannis *et al.* (1993), Attenburrow and Davies (1993), BeMiller (1993), Donald *et al.* (1993), Eliasson and Larsson (1993), Gidley *et al.* (1993), Huang (1993b), Kirby *et al.* (1993), Seow and Teo (1993), Seow and Thevamalar (1993)

Starch hydrolysis products: Cole *et al.* (1983, 1984), Flink (1983), Karel and Flink (1983), Saleeb and Pickup (1985, 1989), Levine and Slade (1986, 1988a,b,c, 1989a,b,c, 1990, 1991, 1992b), Karel and Langer (1988), Orford *et al.* (1989), Levine *et al.* (1991, 1992), Lim and Reid (1991, 1992), Ring and Whittam (1991), Roos and Karel (1991b,d), Roozen and Hemminga (1991), Slade and Levine (1991a,b), Roos (1992b), Ablett *et al.* (1993), Hemminga *et al.* (1993), Nelson (1993), Ollett *et al.* (1993a)

Low-MW sugars: White and Cakebread (1966), Cakebread (1969), MacKenzie (1977), Soesanto and Williams (1981), Franks (1982, 1985, 1986a, 1989, 1990, 1991a, 1992b, 1993a,b), Herrington and Branfield (1984), Schenz *et al.* (1984, 1991), Karel (1985, 1986, 1989, 1992), Slade and Levine (1985, 1988a,b, 1991a,b, 1992c, 1993b), Chan *et al.* (1986), Blanshard and Franks (1987), Roos (1987, 1992a,b,d), Karel and Langer (1988), Levine and Slade (1988a–d, 1989a–d, 1990, 1992a,b), Simatos and Karel (1988), Blond (1989, 1993), Finegold *et al.* (1989), Green and Angell (1989), Orford *et al.* (1989, 1990),

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TABLE VI (*Continued*)

Simatos *et al.* (1989), Williams and Carnahan (1989, 1990), Williams and Leopold (1989), Ahlneck and Zografi (1990), Caldwell *et al.* (1990), Franks and Grigera (1990), Franks and Hatley (1990, 1992, 1993), Le Meste and Simatos (1990), Noel *et al.* (1990, 1991), Reid (1990), Roos and Karel (1990, 1991a,c–h, 1992, 1993), Roozen and Henminga (1990, 1991), Rubin *et al.* (1990), Blond and Simatos (1991), Bruni and Leopold (1991, 1992), Franks and van den Berg (1991), Franks *et al.* (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Karel and Saguy (1991), Koster (1991), Le Meste and Huang (1991), Levine *et al.* (1991, 1992), Matthiesen *et al.* (1991), Maurice *et al.* (1991), Shimada *et al.* (1991), Simatos and Blond (1991), Ablett *et al.* (1992a,b,c, 1993), Berail *et al.* (1992), Chinachoti (1992a), Huang (1993a,b), Jouppila and Roos (1992), Karmas *et al.* (1992), Labrousse *et al.* (1992), Levi and Karel (1993b), Nesvadba (1992b), te Booy *et al.* (1992), van den Berg (1992), Arvanitoyannis and Blanshard (1993b), Karel *et al.* (1993a), Nelson (1993), van den Berg *et al.* (1993), Williams *et al.* (1993)

Polyhydric alcohols: Reid (1985), Levine and Slade (1988a–d, 1989a,b,c, 1990, 1992b), Quinquenet *et al.* (1988), Slade and Levine (1988b, 1991a), Franks and Grigera (1990), Franks and van den Berg (1991), Koster (1991), Ablett *et al.* (1992a), Jouppila and Roos (1992), Roos (1992a)

Nonstarch polysaccharides: Kararli and Catalano (1990), Paakkonen and Roos (1990), Yoshida *et al.* (1990, 1992), Hegenbart (1991), Nishinari *et al.* (1991), Scandola *et al.* (1991), Slade and Levine (1991a,b), Ablett *et al.* (1993), Appelqvist *et al.* (1993), Gidley *et al.* (1993), Yano (1993)

Gluten: Slade (1984), Ablett *et al.* (1986, 1988), Hoseney *et al.* (1986), Doescher *et al.* (1987), Edwards *et al.* (1987), Levine and Slade (1988a, 1989b, 1992b), Lillford (1988), Attenburrow *et al.* (1989, 1990, 1992), Fujio and Lim (1989), Slade *et al.* (1989), Hoseney and Rogers (1990), Stauffer (1990), Davies *et al.* (1991), Garbow and Schaefer (1991), Given (1991), Hoseney (1991, 1992), Slade and Levine (1991a, 1992c, 1993b), Aynie *et al.* (1992a,b), Cocero *et al.* (1992a,b), de Graaf *et al.* (1992), Dong (1992), Gontard *et al.* (1992a,b,c), Hallberg and Chinachoti (1992), Huang *et al.* (1992), Kalichevsky *et al.* (1992c,d, 1993a), Kalichevsky and Blanshard (1992a,c), Kokini (1992), Kokini *et al.* (1992d), Le Meste *et al.* (1992), Lillford *et al.* (1992), Michniewicz *et al.* (1992), Saunders *et al.* (1992), Summers (1992), Tian and Blanshard (1992b), Attenburrow and Davies (1993), Huang (1993b), Lawton and Wu (1993)

Glutenin: Cocero and Kokini (1991), Cocero *et al.* (1992a,b), de Graaf *et al.* (1992), Kalichevsky *et al.* (1992c), Kokini *et al.* (1992d)

Gliadin: Cocero *et al.* (1992a,b), de Graaf *et al.* (1992), Kalichevsky *et al.* (1992c), Kokini *et al.* (1992d), Madeka and Kokini (1992a,b)

Gelatin: Jolley (1970), Yannas (1972), Borchard *et al.* (1980), Marshall and Petrie (1980), Slade and Levine (1984, 1987a, 1991a), Tomka (1986), Levine and Slade (1988a), Slade *et al.* (1989), Kalichevsky and Blanshard (1992c)

Collagen: Yannas (1972), Batzer and Kreibich (1981), Levine and Slade (1988a), Slade *et al.* (1989), Slade and Levine (1991a)

Elastin: Kakivaya and Hoeve (1975), Hoeve and Hoeve (1978, 1980), Hoeve (1980), Atkins (1987), Gosline (1987), Levine and Slade (1988a), Slade *et al.* (1989), Lillie and Gosline (1990, 1993), Slade and Levine (1991a)

Zein: Cocero *et al.* (1992a,b), Kokini *et al.* (1992d), Lawton (1992a,b), Madeka and Kokini (1992a,b), Magoshi *et al.* (1992)

(*continues*)

TABLE VI (*Continued*)

Other proteins or polypeptides: Le Meste and Duckworth (1988), Le Meste *et al.* (1990, 1991b), Levine and Slade (1988a), Slade *et al.* (1989), Pikal (1990a, 1993), Pikal and Shah (1990), Pikal *et al.* (1990), Belton (1991), Franks (1991c), Fujio *et al.* (1991), Slade and Levine (1991a), Sochava *et al.* (1991), Tolstoguzov (1991, 1992), Aguilera *et al.* (1992), Angell *et al.* (1992), Kalichevsky and Blanshard (1992a,c), Milczarek *et al.* (1992), Pissis *et al.* (1992), Roy *et al.* (1992), Sochava and Smirnova (1992), Tolstoguzov and Nesmeyanov (1992), Zasypkin *et al.* (1992), Kalichevsky *et al.* (1993b), Karel *et al.* (1993a), Lillie and Gosline (1993)

Lysozyme: Bone and Pethig (1982, 1985), Poole and Finney (1983, 1984), Finney and Poole (1984), Morozov and Gevorkian (1985), Franks (1988), Levine and Slade (1988a), Lillford (1988), Slade *et al.* (1989), Myers-Betts and Baianu (1990), Slade and Levine (1991a), Sochava *et al.* (1991), Pissis *et al.* (1992), Shah and Ludescher (1992), Sochava and Smirnova (1992)

Other enzymes: Poole and Finney (1984), Morozov and Gevorkian (1985), Levine and Slade (1988a), Slade *et al.* (1989), Slade and Levine (1991a), Sochava *et al.* (1991)

Cellulose, hemicellulose, lignin: Salmen and Back (1977), Kelley *et al.* (1987), Ostberg *et al.* (1990), Pissis *et al.* (1992), Newman (1992)

Poly(hydroxybutyrate): Harrison *et al.* (1992)

[a] Modified from Levine and Slade (1992b).

gelation/network formation behavior of major food polymers such as starch and gluten (Table VIIA). Table VIII lists specific references to publications dealing with the glassy state phenomenon in starch or gluten, and Table IX lists those applying a polymer science approach to various aspects of studies of starch gelatinization or retrogradation. In recent years, many other workers have also supported the perspective based on the fundamental behavioral similarities between synthetic polymer–plasticizer and food molecule–water systems (Table VIIB), first popularized by Slade and Levine.

A central theme of the food polymer science approach focuses on the effect of water as a plasticizer on the glass transition and resulting diffusion-limited behavior of water-compatible or water-sensitive amorphous materials or amorphous regions of partially crystalline materials (Levine and Slade, 1988a, 1989b, 1992b; Slade *et al.*, 1989; Slade and Levine, 1991a,b). Water-compatible food polymers such as starch, gluten, and gelatin, for which water is an efficient plasticizer but not necessarily a good solvent, exhibit essentially the same physicochemical responses to plasticization by water as do many water-compatible synthetic polymers (Ellis, 1988; Ahlneck and Zografi, 1990; Oksanen and Zografi, 1990, 1993; Buera *et al.*, 1992; Harrison *et al.*, 1992; Kalichevsky and Blanshard, 1992d; Hancock and Zografi, 1993) and many readily soluble monomeric and oligomeric carbohydrates (Table XE). This fact illustrates two underlying precepts of

TABLE VII

REFERENCES TO STUDIES THAT HAVE EMPLOYED A SYNTHETIC POLYMERS OR MATERIALS SCIENCE APPROACH TO CHARACTERIZATION OF FOOD MOLECULE–WATER SYSTEMS[a]

(A) Studies of Starch or Gluten (*Researcher:* References)

Slade and Levine: Slade (1984), Slade and Levine (1984, 1985, 1987b, 1988a–d, 1989, 1990, 1991a,b, 1992a–c, 1993a–c), Slade *et al.* (1987, 1989, 1993), Levine and Slade (1986, 1988a,b,c, 1989a,b,c, 1990, 1991, 1992b, 1993), Levine *et al.* (1991, 1992)

Lelievre: Lelievre (1976, 1992a,b), Liu and Lelievre (1991a,b, 1992a,b), Liu *et al.* (1991)

Tomka: (1991), Wittwer and Tomka (1984), Sala and Tomka (1992a,b), Willenbucher *et al.* (1992)

Biliaderis and Maurice: Biliaderis *et al.* (1985, 1986a,b,c), Maurice *et al.* (1985), Biliaderis and Galloway (1989), Biliaderis and Zawistowski (1990), Biliaderis and Seneviratne (1990a,b), Biliaderis (1990, 1991a,b, 1992a,b), Biliaderis and Tonogai (1991)

Blanshard: Blanshard (1986, 1987, 1988), Edwards *et al.* (1987), Marsh and Blanshard (1988), Blanshard and Mitchell (1992), Kalichevsky *et al.* (1992a–d, 1993a), Kalichevsky and Blanshard (1992b,c,d), Tian and Blanshard (1992b), Arvanitoyannis *et al.* (1993)

Lillford: (1988), Ablett *et al.* (1986, 1988, 1993), Edwards *et al.* (1987), Attenburrow *et al.* (1989, 1990, 1992), Ablett and Lillford (1991), Davies *et al.* (1991), Lillford *et al.* (1992), Attenburrow and Davies (1993)

Hoseney: Hoseney (1991, 1992), Hoseney *et al.* (1986, 1992), Yost and Hoseney (1986), Doescher *et al.* (1987), Zeleznak and Hoseney (1987a,b), Hoseney and Rogers (1990, 1993), Faubion and Hoseney (1989), Dong (1992)

Russell: (1987a), Russell and Oliver (1989)

Lund: (1989), Chungcharoen and Lund (1987)

Morris: (1990), Ring *et al.* (1987), I'Anson *et al.* (1990), Cairns *et al.* (1991b)

Ring: Ring *et al.* (1987), Orford *et al.* (1989), Noel *et al.* (1990), Whittam *et al.* (1990, 1991), Ring and Whittam (1991), Botham *et al.* (1992), Noel and Ring (1992)

Zobel: Zobel (1988, 1992a,b), Zobel *et al.* (1988)

Lineback: Lineback and Rasper (1988), Saunders *et al.* (1992)

Ghiasi: Skarra *et al.* (1988), Ghiasi and Skarra (1990)

Seib: Shi and Seib (1989, 1992), Rajagopalan and Seib (1992)

Smith: Smith (1990, 1992a,b,c), Hutchinson *et al.* (1989), Orford *et al.* (1989), Warburton *et al.* (1990, 1992), Ollett *et al.* (1991, 1993a,b), Parker and Smith (1992), Donald *et al.* (1993), Kirby *et al.* (1993)

Eliasson: Eliasson (1989, 1992), Larsson and Eliasson (1991), Larsson (1991), Gudmundsson and Eliasson (1992), Gudmundsson (1992), Eliasson and Larsson (1993)

Colonna: Colonna *et al.* (1989), Colonna and Buleon (1992)

Doublier: Doublier (1989)

Fujio: Fujio and Lim (1989)

Masi: Masi (1989)

Mita: Mita (1990, 1992)

Le Meste and Huang: Le Meste *et al.* (1991a, 1992), Aynie *et al.* (1992a,b), Huang *et al.* (1992)

Kokini: Kokini (1992), Cocero and Kokini (1991, 1993), Lai and Kokini (1991), Cocero *et al.* (1992a,b), de Graaf *et al.* (1992), Kokini *et al.* (1992a,d), Madeka and Kokini (1992a, 1993)

Stauffer: Stauffer (1990)

Shogren: Shogren (1992), Shogren *et al.* (1992)

(*continues*)

TABLE VII (*Continued*)

Lawton: Lawton (1992c), Lawton and Wu (1993)
Reid: Taylor *et al.* (1992)
Breslauer: Kaletunc and Breslauer (1992)
Stute: Stute (1992)
Setser: Kim and Setser (1992)
Schroeter: Schroeter and Hobelsberger (1992)
Guilbert: Gontard *et al.* (1992a,b,c)
Thompson: Thompson (1992)
Rollings: Sullivan *et al.* (1992)
Delcour: Eerlingen and Delcour (1992), Eerlingen *et al.* (1993)
Anon: Jovanovich *et al.* (1992)
Jackson: Zhang and Jackson (1992)
Haynes: Haynes *et al.* (1993)
Seow: Seow and Teo (1993), Seow and Thevamalar (1993)
Schiraldi: Zanoni *et al.* (1993)

(B) Other Studies

Karel (1985, 1986, 1989, 1990, 1991a,b,c, 1992), Campanella *et al.* (1987), Gosline (1987), Le Meste and Duckworth (1988), Simatos and Karel (1988), Cairault *et al.* (1989), Finegold *et al.* (1989), Franks (1989, 1991c, 1992a, 1993a,b), Simatos *et al.* (1989), Franks and Grigera (1990), Johnson *et al.* (1990), Katsuta and Kinsella (1990), Le Meste and Simatos (1990), Le Meste *et al.* (1990, 1991b), Lillie and Gosline (1990, 1993), Noel *et al.* (1990, 1991, 1992, 1993), Ollett and Parker (1990), Orford *et al.* (1990), Roos and Karel (1990, 1991a–f,h, 1992, 1993), Roozen and Hemminga (1990, 1991), Schiraldi (1990), Van Scoik and Carstensen (1990), Yoshida *et al.* (1990, 1992), Belton (1991), Blond and Simatos (1991), Bruni and Leopold (1991), Cameron and Donald (1991), Chang and Baust (1991a,b,c), Davis (1991), Franks *et al.* (1991), Fujio *et al.* (1991), Given (1991), Izzard *et al.* (1991), Karathanos *et al.* (1991, 1992), Karel and Saguy (1991), Kohyama and Nishinari (1991), Le Meste and Huang (1991), Lim and Reid (1991, 1992), Lin *et al.* (1991), Matthiesen *et al.* (1991), O'Brien (1991), Parak and Nienhaus (1991), Raemy and Lambelet (1991), Roozen *et al.* (1991), Scandola *et al.* (1991), Shukla (1991), Simatos and Blond (1991, 1993), Sochava *et al.* (1991), Tolstoguzov (1991), van den Berg (1991, 1992), Young and Scholl (1991), Aguilera *et al.* (1992), Amemiya and Menjivar (1992), Angell *et al.* (1992), Anglea *et al.* (1992a), Bagley (1992), Berail *et al.* (1992), Best (1992), Bruin (1992), Buera and Karel (1992), Buera *et al.* (1992), Chinachoti (1992a), Chuy and Labuza (1992), Franks and Hatley (1992, 1993), Goff (1992), Harrison *et al.* (1992), Huang (1992, 1993a,b), Jouppila and Roos (1992), Karmas *et al.* (1992), Lawton (1992a), Levi and Karel (1992b, 1993b), Milczarek *et al.* (1992), Nelson and Labuza (1992a–c, 1993), Nelson *et al.* (1992), Newman (1992), Peleg (1992, 1993), Pissis *et al.* (1992), Reid (1992b), Reid and Hsu (1992), Roos (1992a–d), Roy *et al.* (1992), Sahagian and Goff (1992, 1993), Sapru and Labuza (1992a,b), Sochava and Belopolskaya (1992), Sochava and Smirnova (1992), te Booy *et al.* (1992), Tian and Blanshard (1992a), Zasypkin *et al.* (1992), Allen (1993), Anonymous (1993a), Appelqvist *et al.* (1993), Arvanitoyannis and Blanshard (1993a,b), Blond (1993), De Bry (1993), Gidley *et al.* (1993), Hancock and Zografi (1993), Hartel (1993), Haynes and Locke (1993), Haynes *et al.* (1993), Hegenbart (1993), Hemminga *et al.* (1993), Huang *et al.* (1993), Kalichevsky *et al.* (1993b), Karel *et al.* (1993a,b), Kerr *et al.* (1993), MacInnes (1993), Madeka and Kokini (1993), Nelson (1993), O'Donnell (1993), Oksanen and Zografi (1993), Pikal (1993), Ramanujam *et al.* (1993), Suzuki and Franks (1993), Williams *et al.* (1993), Yano (1993), Simatos (1994)

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[a] Modified from Levine and Slade (1992b).

TABLE VIII

REFERENCES TO PUBLICATIONS DEALING WITH THE GLASSY STATE PHENOMENON IN STARCH OR GLUTEN[a]

(A) References for Methods Used to Determine T_g of Starch, Amylose, and/or Amylopectin

Calculated from theory: Blanshard (1986, 1988), Marsh and Blanshard (1988)

DSC: Slade (1984), Slade and Levine (1984, 1987b, 1988c), Wittwer and Tomka (1984), Maurice *et al.* (1985), Yost and Hoseney (1986), Zeleznak and Hoseney (1987a), Zobel *et al.* (1988), Orford *et al.* (1989), Stepto and Dobler (1989), Biliaderis (1990, 1991b), Noel *et al.* (1990), Roper and Koch (1990), Warburton *et al.* (1990, 1992), Liu and Lelievre (1991b, 1992b), Roos and Karel (1991d,e), Tomka (1991), Whittam *et al.* (1991), Bizot *et al.* (1992), Eerlingen and Delcour (1992), Kaletunc and Breslauer (1992), Kalichevsky and Blanshard (1992d), Lelievre (1992a), Noel and Ring (1992), Zobel (1992a), Donald *et al.* (1993), Eliasson and Larsson (1993), Gidley *et al.* (1993), Seow and Teo (1993), van den Berg *et al.* (1993)

TMA: Le Meste *et al.* (1991a, 1992), Dong (1992), Hoseney *et al.* (1992)

DSC and TMA: Biliaderis *et al.* (1986a), Biliaderis (1991a)

DSC and NMR: Given (1992), Shogren *et al.* (1992)

DMTA and NMR: Lillford *et al.* (1992)

DSC, DMTA, and NMR: Kalichevsky *et al.* (1992a,b), Kalichevsky and Blanshard (1992c), Shogren (1992)

DSC, DMTA, and TDEA: Scandola *et al.* (1991)

DSC and mechanical spectroscopy: Sala and Tomka (1992a)

TMA, TSC, and dielectric spectroscopy: Huang *et al.* (1992)

Mechanically (as T at which characteristic orders-of-magnitude decrease in modulus is observed): Noel *et al.* (1990), Smith (1990, 1992a), Ollett *et al.* (1991), Kalichevsky *et al.* (1992a,b), Kalichevsky and Blanshard (1992b,c)

Instron (acoustics): Attenburrow *et al.* (1992)

Other methods: van den Berg (1981, 1986), Schroeter and Hobelsberger (1992)

(B) References for Methods Used to Determine T_g of Gluten, Glutenin, and/or Gliadin

DSC: Slade (1984), Hoseney *et al.* (1986), Doescher *et al.* (1987), Levine and Slade (1988a), Fujio and Lim (1989), Slade *et al.* (1989), Hoseney and Rogers (1990), Noel *et al.* (1990), Hoseney (1991), Cocero *et al.* (1992a,b), Cherian and Chinachoti (1993), Lawton and Wu (1993)

TMA: Le Meste *et al.* (1991a, 1992), Dong (1992), Hoseney *et al.* (1992)

DMA: Mita (1990), Summers (1992)

Mechanically (as T at which characteristic orders-of-magnitude decrease in modulus is observed): Attenburrow *et al.* (1990), Davies *et al.* (1991), Kalichevsky *et al.* (1992c), Kalichevsky and Blanshard (1992c)

DSC and mechanical spectrometry: Cocero and Kokini (1991, 1993), de Graaf *et al.* (1992), Madeka and Kokini (1993)

DMTA and NMR: Lillford *et al.* (1992)

DSC and DMTA: Gontard *et al.* (1992a,b)

DMTA and Instron (acoustics): Attenburrow *et al.* (1992)

Instron (acoustics): Attenburrow and Davies (1993)

DSC, DMTA, and NMR: Kalichevsky *et al.* (1992c), Kalichevsky and Blanshard (1992c)

TMA, TSC, and dielectric spectroscopy: Huang *et al.* (1992)

(*continues*)

TABLE VIII (*Continued*)

(C) References Dealing with Effects of T_g for Starch and/or Gluten on Processing and Product Properties

Slade (1984), Slade and Levine (1984, 1987b, 1990, 1991a, 1992c, 1993a,b), Maurice *et al.* (1985), Blanshard (1986), Hoseney *et al.* (1986), Yost and Hoseney (1986), Doescher *et al.* (1987), Zeleznak and Hoseney (1987a), Levine and Slade (1988a, 1989b, 1992b), Zobel (1988, 1992a,b), Colonna *et al.* (1989), Faubion and Hoseney (1989), Shi and Seib (1989, 1992), Slade *et al.* (1989, 1993), Biliaderis (1990, 1991a,b, 1992b), Hoseney and Rogers (1990, 1993), Noel *et al.* (1990), Schiraldi (1990), Stauffer (1990), Warburton *et al.* (1990, 1992), Cairns *et al.* (1991b), Cocero and Kokini (1991), Davies *et al.* (1991), Given (1991), Hoseney (1991, 1992), Karathanos *et al.* (1991), Larsson (1991), Larsson and Eliasson (1991), Le Meste *et al.* (1991a, 1992), O'Brien (1991), Ollett *et al.* (1991, 1993a,b), Shukla (1991), Spratt *et al.* (1991), Tanner *et al.* (1991), Amemiya and Menjivar (1992), Attenburrow *et al.* (1992), Aynie *et al.* (1992a,b), Best (1992), Bizot *et al.* (1992), Blanshard and Mitchell (1992), Cocero *et al.* (1992b), Colonna and Buleon (1992), Dong (1992), Gontard *et al.* (1992a,c), Gudmundsson (1992), Gudmundsson and Eliasson (1992), Hallberg and Chinachoti (1992), Huang *et al.* (1992), Jovanovich *et al.* (1992), Kaletunc and Breslauer (1992), Kalichevsky *et al.* (1992a,b,c), Karathanos and Saravacos (1992), Kokini *et al.* (1992c,d), Lawton (1992b), Livings *et al.* (1992), Parker and Smith (1992), Rajagopalan and Seib (1992), Rao *et al.* (1992), Roos (1992d), Sala and Tomka (1992a), Saunders *et al.* (1992), Shogren (1992), Shogren *et al.* (1992), Smith (1992b,c), Stute (1992), Sullivan *et al.* (1992), Tian and Blanshard (1992b), Tolstoguzov (1992), van den Berg (1992), Zasypkin *et al.* (1992), Zhang and Jackson (1992), Anonymous (1993b), Attenburrow and Davies (1993), BeMiller (1993), Cherian and Chinachoti (1993), Donald *et al.* (1993), Eerlingen *et al.* (1993), Eliasson and Larsson (1993), Kirby *et al.* (1993), Lawton and Wu (1993), Mestres *et al.* (1993), Rohde *et al.* (1993), Seow and Teo (1993), Seow and Thevamalar (1993), Zanoni *et al.* (1993)

[a] Modified from Levine and Slade (1992b).

the food polymer science approach: (1) synthetic amorphous polymers and glass-forming aqueous food materials are fundamentally similar in behavior; and (2) food ingredients can be viewed generically as members of homologous families of completely amorphous or partially crystalline polymers, oligomers, and monomers, soluble in and/or plasticized by water (Levine and Slade, 1988a).

E. "WATER DYNAMICS" AND "GLASS DYNAMICS"

On a theoretical basis of structure–property relationships for synthetic polymers (Table II), functional properties of food materials during processing and product storage can be successfully explained and often predicted (Slade/Levine references in Table I). The food polymer science approach unifies structural aspects of foods, viewed as completely amorphous or partially crystalline polymer systems [the latter based on the classical

TABLE IX

REFERENCES TO PUBLICATIONS DESCRIBING A POLYMER SCIENCE APPROACH TO STUDIES OF STARCH GELATINIZATION AND/OR RETROGRADATION[a]

(A)Retrogradation as a Nonequilibrium Polymer Crystallization Process

Slade (1984), Slade and Levine (1984, 1987b, 1989d, 1989), Miles *et al.* (1985a,b), Ring (1985a,b), Ablett *et al.* (1986), Blanshard (1986), Ring and Orford (1986), Ring *et al.* (1987), Russell (1987b), I'Anson *et al.* (1988), Mestres *et al.* (1988, 1993), Skarra *et al.* (1988), Zobel (1988), Clark *et al.* (1989), Colonna *et al.* (1989), Gidley (1989), Gidley and Bulpin (1989), Levine and Slade (1989b), Lund (1989), Russell and Oliver (1989), Biliaderis (1990, 1991a,b, 1992b), Morris (1990), Schiraldi (1990), Biliaderis and Tonogai (1991), Cairns *et al.* (1991a,b), Cameron and Donald (1991), Chang and Liu (1991), O'Brien (1991), Patil (1991), Shukla (1991), Tanner *et al.* (1991), Colonna and Buleon (1992), German *et al.* (1992), Gudmundsson (1992), Jurgens *et al.* (1992), Michniewicz *et al.* (1992), Mita (1992), Rao *et al.* (1992), Roos (1992d), Shi and Seib (1992), Shogren (1992), Shogren *et al.* (1992), Zhang and Jackson (1992), Eerlingen *et al.* (1993)

(B) Gelatinization as a Nonequilibrium Polymer Melting Process

Slade (1984), Slade and Levine (1984, 1987b, 1988b,c,d, 1989), Kuge and Kitamura (1985), Maurice *et al.* (1985), Reid and Charoenrein (1985), Biliaderis *et al.* (1986a), Blanshard (1986, 1987, 1988), Yost and Hoseney (1986), Burros *et al.* (1987), Chungcharoen and Lund (1987), Paton (1987), Russell (1987a), Zobel (1988, 1992a), Zobel *et al.* (1988), Levine and Slade (1989b), Lund (1989), Russell and Oliver (1989), Shi and Seib (1989, 1992), Biliaderis (1990, 1991a,b, 1992b), Knutson (1990), Morris (1990), Schiraldi (1990), Whittam *et al.* (1990), Chinachoti *et al.* (1991a), Gidley and Cooke (1991), Kohyama and Nishinari (1991), Larsson and Eliasson (1991), Liu and Lelievre (1991a,b, 1992b), Liu *et al.* (1991), O'Brien (1991), Patil (1991), Shukla (1991), Colonna and Buleon (1992), Eerlingen and Delcour (1992), Gudmundsson (1992), Gudmundsson and Eliasson (1992), Kalichevsky *et al.* (1992a), Karathanos and Saravacos (1992), Lelievre (1992a), Noel and Ring (1992), Rajagopalan and Seib (1992), Roos (1992d), BeMiller (1993), Eliasson and Larsson (1993), Seow and Teo (1993), Seow and Thevamalar (1993), Zanoni *et al.* (1993)

(C) Application of the "Fringed Micelle" Structural Model to Starch

Guilbot and Godon (1984), Slade (1984), Slade and Levine (1984, 1987a,b), Zobel (1988, 1992a), Lund (1989), Chinachoti *et al.* (1991b), Kohyama and Nishinari (1991), Lai and Kokini (1991), Liu *et al.* (1991), Colonna and Buleon (1992), Eerlingen and Delcour (1992), German *et al.* (1992), Kokini *et al.* (1992a), Lelievre (1992a), Mita (1992), Stute (1992), Seow and Thevamalar (1993)

(D) Indirect Plasticizing Effect of Water on T_m of Partially Crystalline Starch

Lelievre (1976, 1992a), Slade (1984), Slade and Levine (1984, 1987b), Maurice *et al.* (1985), Biliaderis *et al.* (1985, 1986a,b,c), Zobel (1988), Zobel *et al.* (1988), Biliaderis and Galloway (1989), Biliaderis (1990, 1991a,b, 1992b), Biliaderis and Seneviratne (1990a,b), Biliaderis and Zawistowski (1990), Whittam *et al.* (1990, 1991), Liu and Lelievre (1991b, 1992a), Gudmundsson (1992), Gudmundsson and Eliasson (1992), Kim and Walker (1992), BeMiller (1993), Seow and Thevamalar (1993)

(*continues*)

TABLE IX (*Continued*)

(E) Inappropriateness of the Flory–Huggins Equilibrium Thermodynamic Treatment of Gelatinization

Slade (1984), Slade and Levine (1984, 1987b, 1988c,d, 1989), Biliaderis *et al.* (1986a), Burros *et al.* (1987), Paton (1987), Russell (1987a), Mestres *et al.* (1988), Levine and Slade (1989b, 1992b), Lund (1989), Biliaderis (1990, 1991a,b, 1992b), Knutson (1990), Whittam *et al.* (1990, 1991), Liu and Lelievre (1991b), Ring and Whittam (1991), Colonna and Buleon (1992), Gudmundsson (1992), Lelievre (1992a), Roos (1992d), Eliasson and Larsson (1993)

(F) Antiplasticizing Effect of Sugars (i.e., Sugar Solutions Relative to Water Alone) on Gelatinization or Retrogradation

Slade (1984), Slade and Levine (1984, 1987b, 1988b,d, 1989, 1993b), Blanshard (1987, 1988), Chungcharoen and Lund (1987), Levine and Slade (1989b, 1992b), Lund (1989), Biliaderis (1990, 1992a), Biliaderis and Seneviratne (1990a,b), Hoseney and Rogers (1990, 1993), I'Anson *et al.* (1990), Johnson *et al.* (1990), Morris (1990), Sobczynska *et al.* (1990), Cairns *et al.* (1991b), Chinachoti *et al.* (1991a,b), Kohyama and Nishinari (1991), Nishinari *et al.* (1991), Shukla (1991), Chinachoti (1992a), Eerlingen and Delcour (1992), Eliasson (1992), Gudmundsson (1992), Kim and Setser (1992), Kim and Walker (1992), Lim *et al.* (1992), Rajagopalan and Seib (1992), Roos (1992d), Eliasson and Larsson (1993)

[a] Modified from Levine and Slade (1992b).

"fringed micelle" morphological model (Flory, 1953; Wunderlich, 1973; Billmeyer, 1984) shown in Fig. 2 (Slade and Levine, 1987a)], with functional aspects, dependent on mobility and described in terms of the integrated concepts of "water dynamics" and "glass dynamics." Through this unification, the appropriate kinetic description of the non-equilibrium thermomechanical behavior of food systems has been illustrated in terms of state diagrams of temperature vs. composition, viewed in the context of a "dynamics map," shown in Fig. 3 (Slade and Levine, 1988b). The dynamics map has been used (Slade and Levine, 1988b) to describe the behavior of water-compatible food polymer systems that exist in kinetically metastable glassy or rubbery states always subject to conditionally beneficial or detrimental plasticization by water. The map domains of moisture content and temperature, traditionally described with only limited success using concepts such as "water activity" (A_w) and "bound water," have been treated alternatively in terms of water dynamics (Slade and Levine, 1991a). As the name implies, water dynamics focuses on (1) the mobility (Chinachoti *et al.*, 1991b; Larsson, 1991; Tanner *et al.*, 1991; Goff, 1992) and eventual "availability" (Franks, 1991b; Ablett and Lillford, 1991; Chinachoti, 1992a) of the plasticizing diluent, be it water alone or an aqueous solution; and (2) an interpretive approach to understanding how to control the mobility

TABLE X

REFERENCES[a]

A. Publications in Which Support Is Expressed for the Perspective Provided by the Concepts of Glass Dynamics and Water Dynamics

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TABLE X (*Continued*)

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C. Publications in Which Evidence Suggesting That the Glass Curves of Many Polysaccharides and Proteins Show Common Characteristics Is Reported

Slade (1984), Slade and Levine (1985, 1987b, 1991a, 1993b), Hoseney *et al.* (1986), van den Berg (1986), Atkins (1987), Kelley *et al.* (1987), Zeleznak and Hoseney (1987a), Blanshard (1988), Le Meste and Duckworth (1988), Levine and Slade (1988a, 1989b,

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TABLE X (*Continued*)

1992b), Takahashi *et al.* (1988), Orford *et al.* (1989), Le Meste and Simatos (1990), Lillie and Gosline (1990, 1993), Noel *et al.* (1990), Yoshida *et al.* (1990, 1992), Cocero and Kokini (1991), Liu and Lelievre (1991b, 1992b), Ollett *et al.* (1991), Roos and Karel (1991b,d), Scandola *et al.* (1991), Sochava *et al.* (1991), Tanner *et al.* (1991), Angell *et al.* (1992), Attenburrow *et al.* (1992), Chang and Randall (1992), Cocero *et al.* (1992a,b), de Graaf *et al.* (1992), Dong (1992), Gontard *et al.* (1992c), Gudmundsson (1992), Gudmundsson and Eliasson (1992), Hallberg and Chinachoti (1992), Huang *et al.* (1992), Kaletunc and Breslauer (1992), Kalichevsky and Blanshard (1992a,b), Kalichevsky *et al.* (1992a,c, 1993a,b), Kokini *et al.* (1992d), Kresin and Rau (1992), Lawton (1992a,b), Lelievre (1992a), Le Meste *et al.* (1992), Madeka and Kokini (1992a,b), Magoshi *et al.* (1992), Milczarek *et al.* (1992), Newman (1992), Noel and Ring (1992), Roos (1992b), Sala and Tomka (1992a), Shogren (1992), Sochava and Smirnova (1992), Ablett *et al.* (1993), Appelqvist *et al.* (1993), Attenburrow and Davies (1993), Blond (1993), Cherian and Chinachoti (1993), Crowe *et al.* (1993), Gidley *et al.* (1993), Kirby *et al.* (1993), Lawton and Wu (1993), Slade *et al.* (1993), Yano (1993)

D. Publications in Which the General Correlation between Carbohydrate MW and Dry T_g Is Described

Franks (1985, 1989, 1990, 1993b), Slade and Levine (1985, 1988b, 1991a,b, 1993b), Levine and Slade (1986, 1988a,b,c, 1989a, 1992a,b), Finegold *et al.* (1989), Green and Angell (1989), Orford *et al.* (1989, 1990), Noel *et al.* (1990), Williams *et al.* (1990), Franks and van den Berg (1991), Franks *et al.* (1991), Levine *et al.* (1991, 1992), Lim and Reid (1991), Ring and Whittam (1991), Roos and Karel (1991b,d,e), Franks and Hatley (1992), Jouppila and Roos (1992), Roos (1992a,c), te Booy *et al.* (1992), van den Berg (1992), Karel *et al.* (1993b), Nelson (1993), O'Donnell (1993), Slade *et al.* (1993), van den Berg *et al.* (1993)

E. Publications in Which the Similarities between Water Plasticization of Low-Molecular-Weight Carbohydrates and of Synthetic Polymers Are Pointed Out

Slade and Levine (1985, 1988b, 1991a,b), Levine and Slade (1986, 1988a,b, 1992b), Orford *et al.* (1989, 1990), Franks and Grigera (1990), Noel *et al.* (1990), Blond and Simatos (1991), Davies *et al.* (1991), Franks *et al.* (1991), Roos and Karel (1990, 1991d–g), Whittam *et al.* (1991), Nesvadba (1992b), Slade *et al.* (1993)

F. Publications in Which T_g of Food Polymer–Polymer or Food Polymer–Plasticizer (Water) Blends Is Calculated Using One of Several Equations [(1) Gordon–Taylor, (2) Couchman–Karasz, or (3) Other]

(1) Roos and Karel (1991b,d–h, 1993), Aguilera *et al.* (1992), Buera *et al.* (1992), Cocero *et al.* (1992a,b), de Graaf *et al.* (1992), Jouppila and Roos (1992), Roos (1992a–d), Cocero and Kokini (1993), Huang (1993a), Kalichevsky *et al.* (1993b), Karel *et al.* (1993b), Nelson (1993)

(2) Finegold *et al.* (1989), Orford *et al.* (1989, 1990), Ring and Whittam (1991), Roozen *et al.* (1991), Kalichevsky and Blanshard (1992a,b), Kalichevsky *et al.* (1992a–d), Noel and Ring (1992), Yoshida *et al.* (1992), Arvanitoyannis and Blanshard (1993a), Blond (1993), Donald *et al.* (1993), Franks (1993b), Suzuki and Franks (1993)

(3) Pikal and Shah (1990), Kalichevsky and Blanshard (1992d), Roy *et al.* (1992), Huang (1993b), Oksanen and Zografi (1993)

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[a] Modified from Levine and Slade (1992b).

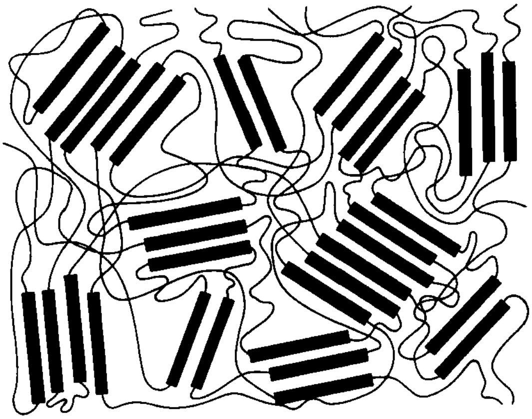

FIG. 2. "Fringed micelle" model of the crystalline–amorphous structure of partially crystalline polymers. From Slade and Levine (1987a) with permission of Van Nostrand Reinhold/AVI.

of the diluent in glass-forming food systems that would be inherently mobile, unstable, and reactive at temperatures and moisture contents corresponding to the rubbery liquid state at $T > T_g$ (Slade and Levine, 1991a). This concept, along with that of glass dynamics, has provided an innovative perspective on water relationships in foods (Duckworth, 1988; Simatos and Karel, 1988; Franks, 1991b; Ablett and Lillford, 1991; Goff, 1992; Karel, 1992; Nelson and Labuza, 1992a; Reid, 1992b; Roos, 1992b; Hegenbart, 1993; Nelson, 1993) (Table IIIB), including, e.g., moisture management and structural stabilization of IMF systems (Slade and Levine, 1985, 1988a, 1991a) and "cryostabilization" of frozen, freezer-stored, and freeze-dried aqueous glass-forming food materials and products (Cole *et al.*, 1983, 1984; Levine and Slade, 1986, 1988a–d, 1989a–d, 1990). This perspective, the focal point of which is the critical importance of the glassy state phenomenon in foods, has received a great deal of recent support from many workers in the field (Table XA).

Glass dynamics deals with the time and temperature dependence of relationships among composition, structure, thermomechanical properties, and functional behavior (Levine and Slade, 1988a). As its name implies, glass dynamics focuses on (1) the glass-forming solids in an aqueous food system; (2) T_g of the resulting aqueous glass that can be produced by cooling to $T < T_g$; and (3) the effect of the glass transition and its T_g on processing and process control, via relationships between T_g and the temperatures of individual processing steps (Slade and Levine, 1991a,b). This concept emphasizes the operationally immobile (translationally), stable, and unreac-

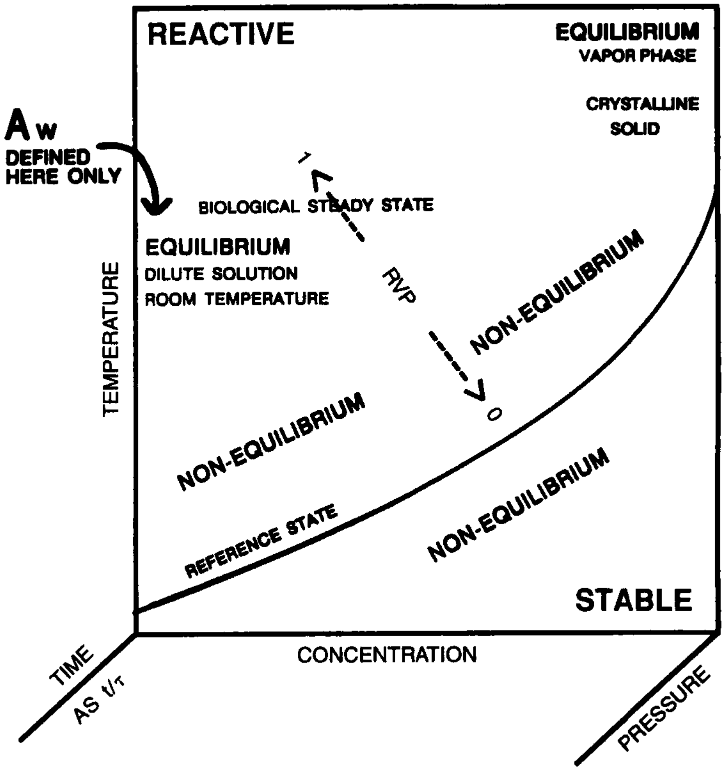

FIG. 3. Four-dimensional "dynamics map," with axes of temperature, concentration, time (expressed as t/τ, where τ is a relaxation time), and pressure, which can be used to describe mobility transformations in nonequilibrium glassy and rubbery systems. From Slade and Levine (1988b) with permission.

tive situation (actually one of kinetic metastability) that can obtain during product storage (of a practical duration) at temperatures and moisture contents corresponding to the glassy solid state at $T < T_g$. It has been used to describe a unifying concept for interpreting "collapse" phenomena (Levine and Slade, 1986, 1988b; Franks, 1989, 1990; Pikal, 1990a,b; Reid, 1990; Roos and Karel, 1991b, 1993; Shimada *et al.*, 1991; Anglea *et al.*, 1992b; Chang and Randall, 1992; Chuy and Labuza, 1992; Karel, 1992; Levi and Karel, 1992a, 1993a,b; Roos, 1992b,c; te Booy *et al.*, 1992; Peleg, 1993; Sahagian and Goff, 1993; van den Berg *et al.*, 1993), which govern a host of time-dependent, translational diffusion-limited, deterioration processes (physical, chemical, or enzymatic) (Karel *et al.* references in Table IV) that can occur in amorphous food or pharmaceutical materials and products during storage in the rubbery liquid state at $T > T_g$ (Levine and Slade, 1986, 1988b; Roos, Karel, and coworkers references in Table IV). This unifying concept for interpreting collapse phenomena has also been used to describe starch gelatinization, retrogradation, and annealing in baked goods and other starch-based food systems (Slade, 1984; Slade and Levine, 1984, 1987b; Levine and Slade, 1988a, 1989b; Zobel, 1988, 1992a,b; Larsson and Eliasson, 1991; Shi and Seib, 1992; Seow and Teo, 1993; Seow and Thevamalar, 1993) (Table IX).

A physicochemical mechanism for collapse, derived from Williams–Landel–Ferry (WLF) free-volume theory for (synthetic) amorphous polymers (Williams *et al.*, 1955; Ferry, 1980), has been described (Levine and Slade, 1986). The non-Arrhenius kinetics of collapse in the rubbery liquid state are governed by the mobility of the water-plasticized food polymer matrix. These so-called WLF kinetics (Table XB) depend on the magnitude of $\Delta T = T - T_g$ (Slade, 1984; Slade and Levine, 1985; Levine and Slade, 1986), as defined by WLF theory. Glass dynamics has proved a useful concept for elucidating the physicochemical mechanisms and kinetics of structural/mechanical changes involved in various melting, annealing, and (re)crystallization processes (Levine and Slade, 1988a). Such phenomena are observed in many partially crystalline food polymers and processing/storage situations, including, e.g., the gelatinization, retrogradation, and annealing of starches (Slade, 1984; Slade and Levine, 1984, 1987b, 1988c; Whittam *et al.*, 1990; Lelievre, 1992a,b; Stute, 1992; Taylor *et al.*, 1992; Zanoni *et al.*, 1993). Glass dynamics has also been used to describe the viscoelastic behavior of amorphous network-forming proteins such as wheat gluten (Slade, 1984; Slade *et al.*, 1989).

F. STATE DIAGRAMS

The fundamental importance of state diagrams (e.g., Fig. 4), and of the glass transition as the critical reference state on such diagrams (which determines technological performance), to understanding and controlling the nonequilibrium behavior of water-containing food systems during processing and product storage, as influenced by the variables of moisture content, temperature, and time, has become widely recognized (Table XIB). The interdependent concepts of water dynamics and glass dynamics, embodied in the state diagram as a dynamics map, have provided insights into the relevance of the glassy reference state to functional aspects of a variety of food systems (Levine and Slade, 1988a; Slade and Levine, 1988b). Process control, product quality, safety, and shelf-life are all dictated by WLF kinetics (Table XB), which are applicable above T_g in the viscoelastic, rubbery liquid state of accelerating mobility and translational diffusion

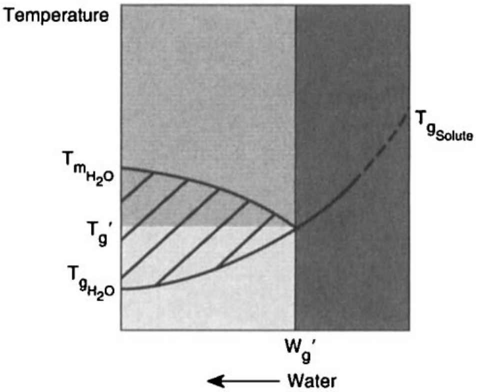

FIG. 4. Schematic state diagram of temperature versus weight percent (w%) water for an aqueous solution of a hypothetical, glass-forming, small carbohydrate, illustrating how the critical locations of T_g' and W_g' divide the diagram into three distinguishable structure–property domains. Reprinted with permission from Slade, L., and Levine, H. 1991a. Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. *CRC Crit. Rev. Food Sci. Nutr.* **30**, 115–360. Copyright CRC Press, Inc. Boca Raton, FL.

(Slade and Levine, 1991a, 1993c). In recent years, many workers (Table XIB) have lent their strong support to advocacy of the importance of state diagrams (e.g., Fig. 4), and of the solute-specific, invariant point, $T_g' - C_g'$ (defined below), as the focal point (see Fig. 4) of such dynamics maps, to understanding structure–property relationships of food molecule–water systems. Most recently, a three-dimensional state diagram for a ternary system [two solutes (sucrose and glycine) plus water] has been reported by two groups (Suzuki and Franks, 1993; Shalaev and Kanev, 1993). As pointed out in both reports, this complex state diagram contains a metastable, three-dimensional glass transition *surface* (as opposed to the typical two-dimensional glass transition curve for a binary solute–water system), which Suzuki and Franks have proposed as a novel concept important to, e.g., the formulation of multicomponent mixtures to be freeze-dried.

T_g' represents the solute-specific subzero T_g of the maximally freeze-concentrated, amorphous solute/unfrozen water (UFW) matrix surrounding the ice crystals in a frozen solution (Franks *et al.*, 1977; Schenz *et al.*, 1984; Levine and Slade, 1986) (Table XIA); C_g' is the solute concentration of the T_g' glass, while W_g' is its concentration of UFW. As discussed further later, T_g' and C_g' values, especially of various low-molecular-weight (MW) sugars widely used in foods, have become a topic of so much current interest, as well as considerable controversy and debate (Slade and Levine, 1991a; Levine and Slade, 1992b), that many recent publications have been devoted

TABLE XI

REFERENCES[a]

A. Publications Dealing with T_g'

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B. Publications Dealing with the Importance of State Diagrams and of the T_g'–C_g' Point

Schenz *et al.* (1984, 1991, 1992), Slade (1984), Slade and Levine (1984, 1985, 1987a,b, 1988a–d, 1989, 1990, 1991a,b, 1992c, 1993b,c), Franks (1985, 1986a, 1989, 1990, 1991c, 1992b, 1993a,b), Burke (1986), Levine and Slade (1986, 1988a–d, 1989a–d, 1990, 1991, 1992a,b, 1993), van den Berg (1986, 1992), Blanshard and Franks (1987), Lillford (1988), Simatos and Karel (1988), Blond (1989, 1993), Green and Angell (1989), Karel (1989, 1992), Simatos *et al.* (1989), Slade *et al.* (1989, 1993), Williams and Leopold (1989), Ahlneck and Zografi (1990), Biliaderis (1990, 1991b), Caldwell *et al.* (1990), Franks and Grigera (1990), Le Meste and Simatos (1990), Noel *et al.* (1990), Williams and Carnahan (1990), Ablett and Lillford (1991), Blanshard *et al.* (1991), Blond and Colas (1991), Bruni and Leopold (1991), Chang and Baust (1991b), Franks and van den Berg (1991), Franks *et al.* (1991), Given (1991), Hatley (1991), Hatley and Franks (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Le Meste and Huang (1991), Lim and Reid (1991), Ma and Harwalkar (1991), MacDonald and Lanier (1991), Matthiesen *et al.* (1991), Roos and Karel (1991d,e–h, 1993), Simatos and Blond (1991, 1993), Ablet *et al.* (1992a,b,c, 1993), Berail *et al.* (1992), Best (1992), Chang and Randall (1992), Chinachoti (1992a), Cocero *et al.* (1992a,b, 1993), Colonna and Buleon (1992), de Graaf *et al.* (1992), Eerlingen and Delcour (1992), Goff (1992), Huang *et al.* (1992), Jouppila and Roos (1992), Kawai *et al.* (1992), Kokini (1992), Kokini *et al.* (1992b,d), Kresin and Rau (1992), Labuza and Nelson (1992), Leopold *et al.*

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TABLE XI (*Continued*)

(1992), Madeka and Kokini (1992a,b, 1993), Nelson and Labuza (1992b, 1993), Reid (1992b), Reid and Hsu (1992), Roos (1992a–d), van den Berg *et al.* (1992, 1993), Cocero and Kokini (1993), Franks and Hatley (1993), Hartel (1993), Hegenbart (1993), Karel *et al.* (1993a,b), MacInnes (1993), Nelson (1993), Ohshima *et al.* (1993), Reid *et al.* (1993a,b), Shalaev and Kanev (1993), Suzuki and Franks (1993)

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[a] Modified from Levine and Slade (1992b).

to discussions of different aspects of this subject (Table XII). Table XIII presents a survey of recent literature values of T_g' and C_g' for various low-MW carbohydrates.

III. KEY ELEMENTS AND APPLICATIONS OF THE "FOOD POLYMER SCIENCE" APPROACH

A. EFFECT OF MOLECULAR WEIGHT ON T_g

For pure synthetic polymers, in the absence of diluent, T_g varies with MW in a characteristic and theoretically predicted fashion, which has a significant impact on resulting mechanical and rheological properties (Ferry, 1980; Levine and Slade, 1989b). As illustrated in Fig. 5, for a homologous series of amorphous linear polymers, T_g increases with increasing number-average MW ($\overline{M}_n$) [due to decreasing free volume (Ferry, 1980)], up to a plateau limit for the region of entanglement coupling in rubberlike viscoelastic random networks [typically at $\overline{M}_n = 1.25 \times 10^3$ to 10^5 (Graessley, 1984)], then levels off with further increases in $\overline{M}_n$ (Ferry, 1980; Billmeyer, 1984). Below the entanglement $\overline{M}_n$ limit, there is a theoretical linear relationship between increasing T_g and decreasing inverse $\overline{M}_n$ (Sperling, 1986). The difference in three-dimensional morphology and resultant mechanical and rheological properties between a collection of nonentangling, low-MW polymer chains and a network of entangling, high-MW, randomly coiled polymer chains can be viewed as analogous to the difference between masses of elbow macaroni and spaghetti (Levine and Slade, 1989b). For synthetic polymers, $\overline{M}_n$ at the boundary of the entanglement plateau often corresponds to about 600 backbone-chain atoms (Sperling, 1986). Since there are typically about 20 to 50 backbone-chain atoms in each polymer segmental unit involved in the cooperative, long-range, translational motions that can occur only at or above T_g (Brydson, 1972), entangling high polymers are those with at least about 12 to 30 such segmental units per chain (Levine and Slade, 1989b).

TABLE XII

REFERENCES TO RECENT PUBLICATIONS CONTAINING DISCUSSIONS OF VALUES OF T_g' AND C_g' AND/OR METHODS OF DETERMINING THOSE VALUES FOR LOW-MOLECULAR-WEIGHT CARBOHYDRATES[a]

(A) Methods of Determining C_g' Values

Levine and Slade (1986, 1988b, 1992a,b), Slade and Levine (1988b, 1991a), Blond (1989), Hatley *et al.* (1989, 1991), Noel *et al.* (1990), Orford *et al.* (1990), Schiraldi (1990), Vertucci (1990), Blond and Colas (1991), Blond and Simatos (1991), Hatley (1991), Hatley and Franks (1991), Izzard *et al.* (1991), Ma and Harwalkar (1991), Raemy and Lambelet (1991), Roos and Karel (1991c,d,f,g,h), Schenz *et al.* (1991, 1992), Simatos and Blond (1991, 1993), Ablett *et al.* (1992a,b,c, 1993), Franks (1992b, 1993b), Jouppila and Roos (1992), Kawai *et al.* (1992), Kresin and Rau (1992), Reid and Hsu (1992), Roos (1992a,c,d), Hatley and Mant (1993), MacInnes (1993), Reid *et al.* (1993a,b)

(B) T_g' Value of −32°C for Sucrose

Schenz *et al.* (1984, 1991), Franks (1985, 1986,a,b, 1989, 1990, 1991c, 1992b, 1993a,b), Slade and Levine (1985, 1988b), Blanshard and Franks (1987), Levine and Slade (1988b, 1992b), Caldwell *et al.* (1990), Blanshard *et al.* (1991), Izzard *et al.* (1991), Franks *et al.* (1991), Hatley (1991), Hatley and Franks (1991), Hatley *et al.* (1991), Lim and Reid (1991, 1992), Maurice *et al.* (1991), Roos and Karel (1991f), Roozen and Hemminga (1991), Chang and Randall (1992), Chinachoti (1992a), Goff (1992), Leung *et al.* (1992), Reid and Hsu (1992), Roos (1992d), Sahagian and Goff (1992), te Booy *et al.* (1992), van den Berg (1992), Goff *et al.* (1993), Hartel (1993), Hatley and Mant (1993), Hemminga *et al.* (1993), Kerr *et al.* (1993), McCurdy *et al.* (1993), Reid *et al.* (1993a), Suzuki and Franks (1993), van den Berg *et al.* (1993)

(C) Different C_g' Values for Sucrose

MacKenzie (1977), Franks (1983b, 1985, 1986a,b, 1989, 1990, 1991c, 1992b, 1993a,b), Slade and Levine (1985, 1988b, 1991a), Blanshard and Franks (1987), Levine and Slade (1988b, 1992b, 1993), Williams and Carnahan (1989, 1990), Franks and Grigera (1990), Williams *et al.* (1990), Blanshard *et al.* (1991), Dereuddre *et al.* (1991), Franks *et al.* (1991), Hatley (1991), Hatley and Franks (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Le Meste and Huang (1991), Roos and Karel (1991c–h, 1993), Ablett *et al.* (1992a,b, 1993), Chinachoti (1992a, 1993), Goff (1992), Hanover (1992), Jouppila and Roos (1992), Kawai *et al.* (1992), Nesvadba (1992a), Reid and Hsu (1992), Roos (1992a,c,d), van den Berg (1992), Blond (1993), Franks and Hatley (1993), Hartel (1993), Reid *et al.* (1993a), Suzuki and Franks (1993), van den Berg *et al.* (1993)

(D) T_g' as the Temperature at the Midpoint, Rather Than the Onset, of the Transition

Franks *et al.* (1977, 1991), Franks (1982, 1985, 1986a, 1989, 1990, 1992b), Schenz *et al.* (1984, 1991, 1992), Reid (1985, 1990), Levine and Slade (1986, 1988a–d, 1992b), Blanshard and Franks (1987), Hatley *et al.* (1989, 1991), Caldwell *et al.* (1990), Franks and Grigera (1990), Franks and Hatley (1990), Le Meste and Simatos (1990), Williams and Carnahan (1990), Blanshard *et al.* (1991), Blond and Simatos (1991), Hatley (1991), Hatley and Franks (1991), Izzard *et al.* (1991), Lim and Reid (1991, 1992), Maurice *et al.* (1991), Wasylyk and Baust (1991), Ablett *et al.* (1992a,b,c), Berail *et al.* (1992), Chang and Randall (1992), Reid and Hsu (1992), Blond (1993), Goff *et al.* (1993), Hatley and Mant (1993), Reid *et al.* (1993b), Suzuki and Franks (1993), van den Berg *et al.* (1993)

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[a] Modified from Levine and Slade (1992b).

TABLE XIII

T_g' AND C_g' VALUES FOR LOW-MW CARBOHYDRATES: SURVEY OF RECENT LITERATURE DATA[a]

Compound	MW	T_g' (°C) [refs. a–d]	Other T_g' values [refs.]	C_g' (w%) [refs. b–e]	Other C_g' values [refs.]
Ethylene glycol	62.1	−85		34.5	
Propylene glycol	76.1	−67.5		43.9	
1,3-Butanediol	90.1	−63.5		41.5	
Glycerol	92.1	−65	−65 [f,h,i,j,k,aa,ddd], −95 [q], −100 [eee]	54.1	54 [j,k,ddd], 54.1 [f,h,i], 80 [q]
Erythrose	120.1	−50		41.8	
Threose	120.1	−45.5			
Erythritol	122.1	−53.5			
Thyminose (deoxyribose)	134.1	−52		43.1	
Ribulose	150.1	−50			
Xylose	150.1	−48	−48 [j,k,l,aa,ddd,eee], −47 [h,i], −60 [z]	69.0	69 [h,i,j,k,l,ddd], 78.9 [z]
Arabinose	150.1	−47.5	−48 [h,i], −48.5 [l], −61 [z]	44.8	44.8 [h,i,l], 79.3 [z]
Lyxose	150.1	−47.5	−47.5 [aa]		
Ribose	150.1	−47	−47 [h,i,j,k,aa,ddd,eee], −49 [y], −62 [z]	67.1	67 [j,k,ddd], 67.1 [h,i], 81.4 [z]
Arabitol	152.1	−47	−48 [1]	52.9	52.9 [l]
Ribitol	152.1	−47		54.9	
Xylitol	152.1	−46.5	−46.5 [j,k,aa,ddd], −47 [eee], −67 [z]	57.1	57.1 [j,k,ddd], 80.2 [z]
Methyl riboside	164.2	−53		51.0	
Methyl xyloside	164.2	−49		49.8	
Quinovose (deoxyglucose)	164.2	−43.5		47.4	
Fucose (deoxygalactose)	164.2	−43	−57 [z]	47.4	78.4 [z]
Rhamnose (deoxymannose)	164.2	−43	−55 [z]	52.6	82.8 [z]
Talose	180.2	−44	−44 [aa]		
Idose	180.2	−44			
Psicose	180.2	−44			
Altrose	180.2	−43.5	−43.5 [aa]		
Gulose	180.2	−42.5			
Glucose	180.2	−43	−43 [f,h,i,j,k,l,r,s,aa,zz,ddd,eee], −43.5 [ccc], −36.5 [m], −52 [ss], −53 [z], −57 [tt,uu], −42.4 [vv], −50 [ww]	70.9	70.9 [f,j,k,l], 67.1 [xx], 71.4 [h,i], 74.7 [vv], 79.2 [ss,tt], 80.0 [z,ww], 82 [xx], 83 [zz,ddd,eee]

Fructose	180.2	−42	−42 [f,h,i,j,k,l,s,t,aa,zz,ccc,ddd,eee], −48 [v], −53 [z,ss], −58 [tt,uu]	51.0	51 [f,j,k,l], 51.3 [h,i], 79 [v], 82.5 [z], 78.6 [ss,tt], 85 [zz,ddd,eee]
Fructose : glucose (1 : 1 blend)		−42.5	−42.5 [j,k,ddd]	52.0	52 [j,k,ddd]
Galactose	180.2	−41.5	−41.5 [f,aa], −42 [h,i], −40.5 [j,k,ddd], −41[eee], −43 [p], −50 [ww], −51 [z]	56.5	55 [j,k,ddd], 56.5 [f], 57.1 [h,i], 71 [p,xx], 79 [ww], 80.5 [z], 84 [xx,eee]
Allose	180.2	−41.5		64.1	
Sorbose	180.2	−41	−52 [z]	69.0	81.0 [z]
Mannose	180.2	−41	−41 [j,k,aa,ddd,eee], −53 [z]	74.1	74.1 [j,k,ddd], 67.6 [xx], 80.1 [z], 83.3 [xx], 84 [eee]
Tagatose	180.2	−40.5		42.9	
Inositol	180.2	−35.5	−36 [h,i]	76.9	76.3 [h,i]
Mannitol	182.2	−40	−35 [o]		
Galactitol	182.2	−39			
Sorbitol	182.2	−43.5	−43.5 [f,j,k,aa,zz,ddd], −43 [h,i], −44 [l,ccc,eee], −57 [z]	81.3	81.3 [f,h,i,j,k,l,ddd], 70.4 [xx], 81.7 [z], 84.7 [xx], 88 [zz,eee]
Glucoheptose	210.2	−37.5			
Mannoheptulose	210.2	−36.5			
Glucoheptulose	210.2	−36.5		56.5	
Perseitol (mannoheptitol)	212.2	−32.5			
Isomaltulose (palatinose)	342.3	−35.5			
Nigerose	342.3	−35.5			
Cellobiulose	342.3	−32.5			
Isomaltose	342.3	−32.5	−32 [l]	58.8	58.8 [l]
Sucrose	342.3	−32	−32 [f,h,i,j,k,l,n,o,r,t,x,aa,cc,dd,ee,ff,aaa, ddd,eee,hhh], −33 [gg,hh,zz,ggg], −33.5 [ccc], −34 [g,yy], −35 [ii,bbb], −37 [ww], −40 [q,ss], −41 [z,mm,nn,rr], −41.5 [q], −46 [aa,kk,nn,jj,tt,uu]	64.1	64.1 [f,h,i,j,k,l], 66 [qq], 73 [kk], 75.0 [bb], 77 [bbb], 78 [hh], 79.5 [kk,ll,nn,pp,ss,tt], 80 [aa,ii,jj,mm], 81 [ww], 81.2 [q], 81.7 [z], 83.0 [ff,zz,eee], 83.3 [hhh], 84 [eee]
Gentiobiose	342.3	−31.5		79.4	
Laminaribiose	342.3	−31.5			
Turanose	342.3	−31	−31 [aa]	61.0	
Mannobiose	342.3	−30.5	−30.5 [aa]	52.4	

(*continues*)

TABLE XIII (*Continued*)

Compound	MW	T_g' (°C) [refs. a–d]	Other T_g' values [refs.]	C_g' (w%) [refs. b–e]	Other C_g' values [refs.]
Melibiose	342.3	−30.5	−37 [z]		81.7 [z]
Lactulose	342.3	−30		58.1	
Maltose	342.3	−29.5	−29.5 [f,j,k,aa,zz,ddd], −29.7 [vv], −30 [h,i,l,eee], −31.6 [ccc], −41 [pp,tt], −37 [z], −36 [ss]	80.0	80 [f,h,i,j,k,l,pp,ddd], 81.6 [z], 74.5 [bb], 76.7 [vv], 81.5 [ss,tt,zz,eee]
Maltulose	342.3	−29.5			
Trehalose	342.3	−29.5	−27 [o], −29.5 [j,k,aa,ddd], −30 [h,i,l,eee], −35 [z], −32 [fff]	83.3	83.3 [j,k,l,ddd], 81.6 [z], 82.6 [h,i], 80 [eee], 70.5 [bb]
Cellobiose	342.3	−29			
Lactose	342.3	−28	−28 [h,i,o,aa,zz], −35 [ss], −36 [z], −40 [tt], −41 [uu], −45 [oo]	59.2	58.8 [h,i], 80 [oo], 81.3 [z], 82.5 [ss]
Maltitol	344.3	−34.5	−42 [z]	62.9	82.9 [z]
Isomaltotriose	504.5	−30.5		66.7	
Panose	504.5	−28		62.9	
Raffinose	504.5	−26.5	−26 [h,i]	58.8	58.5 [h,i]
Maltotriose	504.5	−23.5	−23.5 [f,j,k,aa,zz,ddd], −23 [h,i,w], −23.1 [vv], −24 [l,eee,ggg], −29 [u]	69.0	69 [f,h,i,j,k,l,ddd], 81 [u], 78.5 [bb], 81.6 [vv], 75 [zz]
Nystose	666.6	−26.5			
Stachyose	666.6	−23.5		47.2	
Maltotetraose	666.6	−19.5	−19.3 [vv]	64.5	75.5 [bb], 82.1 [vv]
Maltopentaose	828.9	−16.5	−15.8 [vv], −18 [w]	68.0	74.0 [bb], 76.5 [vv]
Maltohexaose	990.9	−14.5	−14.5 [zz], −14.7 [vv]	66.7	72.5 [bb], 75 [zz], 76.4 [vv]
Maltoheptaose	1153.0	−13.5	−13.2 [vv], −14 [w], −18 [u]	78.7	77.4 [vv], 78 [u], 79.0 [bb]

References

[a]	Levine and Slade (1986)	[aa]	Roos (1992d)
[b]	Levine and Slade (1988b)	[bb]	Kawai *et al.* (1992)
[c]	Levine and Slade (1988c)	[cc]	Blanshard and Franks (1987)
[d]	Levine and Slade (1988d)	[dd]	Caldwell *et al.* (1990)
[e]	Slade and Levine (1988b)	[ee]	Schenz *et al.* (1984)
[f]	Goff (1992)	[ff]	Hatley *et al.* (1991)
[g]	Goff *et al.* (1993)	[gg]	Lim and Reid (1991)
[h]	Franks (1985)	[hh]	Reid and Hsu (1992)
[i]	Franks (1986a)	[ii]	Izzard *et al.* (1991)
[j]	Franks (1990)	[jj]	Le Meste and Huang (1991)
[k]	Franks and Grigera (1990)	[kk]	Roos and Karel (1991c)
[l]	Franks (1989)	[ll]	Reid *et al.* (1993b)
[m]	Franks (1982)	[mm]	Williams and Carnahan (1990)
[n]	Franks (1986b)	[nn]	Roos and Karel (1991g)
[o]	Chang and Randall (1992)	[oo]	Roos and Karel (1991e)
[p]	Blond (1989)	[pp]	Roos and Karel (1991d)
[q]	Ablett *et al.* (1992a)	[qq]	Nesvadba (1992a)
[r]	Maurice *et al.* (1991)	[rr]	MacInnes (1993)
[s]	Rubin *et al.* (1990)	[ss]	Roos and Karel (1991f)
[t]	Schenz *et al.* (1991)	[tt]	Roos and Karel (1991h)
[u]	Ablett *et al.* (1993)	[uu]	Roos and Karel (1993)
[v]	Ablett *et al.* (1992c)	[vv]	Schenz *et al.* (1992)
[w]	Roozen *et al.* (1991)	[ww]	Simatos and Blond (1993)
[x]	Roozen and Hemminga (1990)	[xx]	Simatos and Blond (1991)
[y]	Wasylyk and Baust (1991)	[yy]	te Booy *et al.* (1992)
[z]	Roos (1992a)	[zz]	van den Berg (1992)
[aaa]	Suzuki and Franks (1993)	[bbb]	Shalaev and Kanev (1993)
[ccc]	Kerr *et al.* (1993)	[ddd]	Franks (1991c)
[eee]	Franks (1993a)	[fff]	Crowe *et al.* (1993)
[ggg]	Berail *et al.* (1992)	[hhh]	Hatley and Mant (1993)

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[a] Modified from Levine and Slade (1992b).

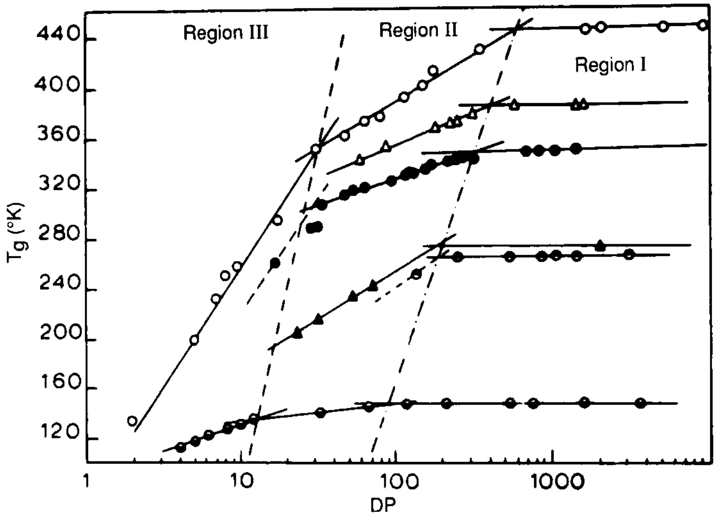

FIG. 5. Plot of T_g as a function of log DP (degree of polymerization, a measure of molecular weight), for poly (α-methylstyrene) (open circles); poly(methylmethacrylate) (open triangles); poly(vinyl chloride) (solid circles); isotactic polypropylene (solid triangles); atactic polypropylene (circles, top half solid); and poly(dimethylsiloxane) (circles, bottom half solid). From Sperling, L. H. 1986. "Introduction to Physical Polymer Science." Copyright © 1986 Wiley (Interscience), New York. Reprinted by permission of John Wiley & Sons, Inc.

Within a homologous family of food polymers [e.g., from the glucose monomer through maltose, maltotriose, and higher maltooligosaccharides (e.g., maltodextrins) to the amylose and amylopectin high polymers of starch], both T_g (Slade and Levine, 1988b; Levine and Slade, 1989a; Orford *et al.*, 1989, 1990; Ring and Whittam, 1991; Roos and Karel, 1991b; Jouppila and Roos, 1992; Karel *et al.*, 1993b) and T_g' (Levine and Slade, 1986, 1988a–d; Lim and Reid, 1991; Roos and Karel, 1991e; Jouppila and Roos, 1992; Karel *et al.*, 1993b) increase in the same characteristic fashion with increasing solute MW, as demonstrated in Figs. 6 (Levine and Slade, 1986), 7 (Levine and Slade, 1988a), and 8 (Levine and Slade, 1989a). This finding has been shown to be in full accord with the established variation of T_g with MW for homologous families of pure synthetic amorphous polymers (Ferry, 1980; Billmeyer, 1984; Sperling, 1986), described above. The insights resulting from this finding have proved pivotal to the characterization of structure–function relationships in many different types of completely amorphous and partially crystalline food polymer systems (Slade and Levine, 1991a).

The general correlation between increasing saccharide MW and increasing T_g (Levine and Slade, 1988a,b, 1989a; Roos, 1992a) was also confirmed

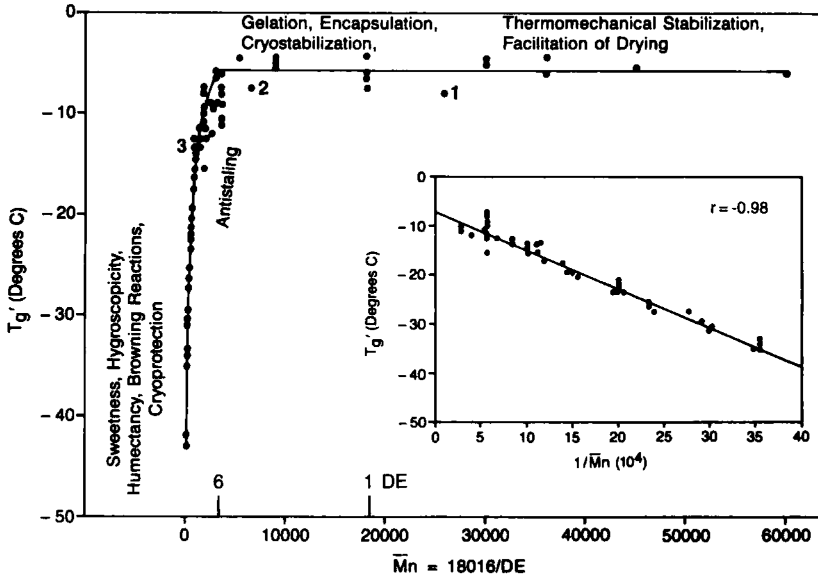

FIG. 6. Variation of the glass transition temperature, T_g', for maximally frozen 20 w% solutions against $\overline{M}_n$ [expressed as a function of dextrose equivalent (DE)] for a homologous family of commercial starch hydrolysis products (SHPs). DE values are indicated by numbers marked above the x axis. Areas of specific functional attributes, corresponding to the three regions of the diagram, are labeled. Inset: Plot of T_g' versus $1/\overline{M}_n$ (× 10,000) for SHPs with $\overline{M}_n$ values below the entanglement limit, illustrating the theoretically predicted linear dependence. From Levine and Slade (1986) with permission.

in recent studies of the T_g behavior of amorphous mixtures of low-MW carbohydrates reported by Finegold *et al.* (1989) and Orford *et al.* (1990). Results of their studies demonstrated that measured T_g values of various dry binary mixtures of mono- and di- or oligosaccharides can be roughly approximated from a mole fraction-weighted average of the individual dry T_g values of each saccharide in a given amorphous blend. However, while the general correlation between carbohydrate MW and dry T_g has now become well established and widely accepted (Table XD), it should be carefully noted, as illustrated by the T_g data in Table XIV, that T_g can vary substantially, even within a series of compounds of the same MW and only the most subtle differences in chemical structure. The reasons for this are not known.

1. T_g of Polymer–Polymer and Polymer–Plasticizer Blends

As alluded to above and reviewed elsewhere (Levine and Slade, 1988a), the correlation between polymer MW and T_g can be extended to cover

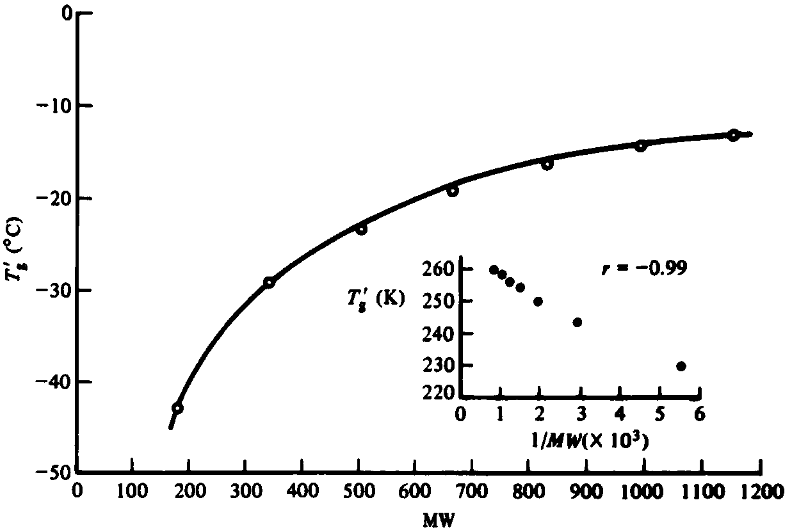

FIG. 7. Variation of the glass transition temperature, T_g', for maximally frozen 20 w% solutions against MW for a homologous series of maltooligosaccharides from glucose through maltoheptaose. Inset: Plot of T_g' versus 1/MW (× 1000) of solute, illustrating the theoretically predicted linear dependence. Reprinted from Levine and Slade (1988a) with permission of Cambridge University Press. Copyright 1988, Cambridge University Press.

homogeneous amorphous blends of two or more miscible neat polymers, a polymer plus a plasticizer, or two or more polymers plus a plasticizer. To a first approximation, T_g of a homogeneous, multicomponent blend can be estimated from the weight-average composition of a mixture of components with individual T_g values of T_{g1}, T_{g2}, T_{g3}, etc. (Sperling, 1986). This simple approach has been shown to work well for various glass-forming food systems (Levine and Slade, 1988c, 1989a; Berail *et al.*, 1992), in addition to those studied by Finegold *et al.* (1989) and Orford *et al.* (1990). For example, the DSC-measured T_g' value of −37.5 ± 1.0°C for various samples of orange juice is well approximated by a calculated value of −37.25°C for a 2:1:1 blend of sucrose (T_g' = −32°C), fructose (T_g' = −42°C), and glucose (T_g' = −43°C), which constitutes the predominant water-soluble solids of typical orange juice (Levine and Slade, 1989c). Similarly, the homogeneous glass formed by a molten 1:1 mixture of pure crystalline glucose (dry T_g = 31°C) and fructose (lower dry T_g = 11°C) has a DSC-measured T_g value of 20°C (Slade and Levine, 1988b; Finegold *et al.*, 1989), which is within 1°C of the calculated value.

Beyond such a simple empirical approach to estimating T_g of a polymer–polymer or polymer(s)–plasticizer blend (which, in any event, was used,

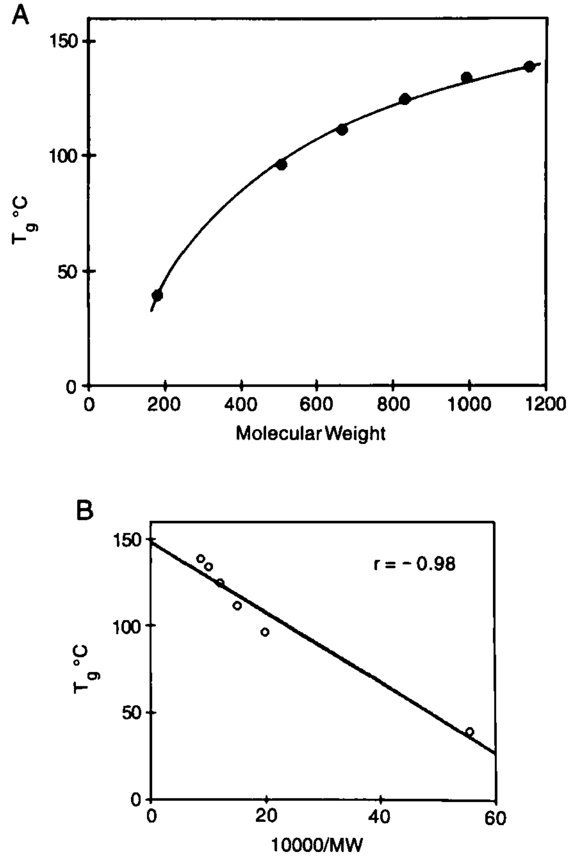

FIG. 8. Variation of the glass transition temperature, T_g (measured for dry powders), against (A) MW and (B) 10,000/MW, for a homologous series of maltooligosaccharides from glucose through maltoheptaose. From Levine and Slade (1989a) with permission.

in the cases described above, to corroborate measured data, rather than to replace experimental measurements), efforts to predict T_g of such blends, based on theoretical approaches using equations derived empirically or from classical thermodynamics, represent largely an academic exercise. Franks (1993b) has recently stated that "the prediction of glass transition temperatures of mixtures from the properties of the pure components and the mixture composition is uncertain, because the very nature of the glass transition itself is not yet fully understood." If one needs to know, with confidence, an accurate value for T_g of a blend, in order, e.g., to design a process [e.g., freeze-drying without "melt-back" (Levine and Slade, 1986,

TABLE XIV

T_g VALUES FOR LOW-MW CARBOHYDRATES: SURVEY OF RECENT LITERATURE DATA[a]

Compound	MW	T_g (°C) [Refs. a–c]	Other T_g values [Refs.]
Xylose	150.1	9.5	9 [d,e,f,ll], 9.5 [z], 13 [g,h], 14 [i]
Arabinose	150.1		3 [i], 4 [g]
Lyxose	150.1	8	8 [z]
Ribose	150.1	−10	−10 [d,e,z,ll], −11 [g], −13 [i]
Xylitol	152.1	−18.5	−18.5 [z], −19 [g], −23 [i], −39 [d,e,ll]
Fucose (deoxygalactose)	164.2		31 [i]
Rhamnose (deoxymannose)	164.2		0 [i], 27 [g]
Talose	180.2	11.5	11.5 [z]
Tagatose	180.2		40.5 [ll]
Altrose	180.2	10.5	10.5 [z]
Glucose	180.2	31	21 [f], 29 [j,k,hh], 30 [l], 31 [e,m,z,bb], 33 [n], 36 [i,aa,mm], 37 [l], 38 [g,h], 38.5 [dd], 39 [d,e,o,y,ll]
Fructose	180.2	11, 100	5 [bb], 7 [g,z,gg], 10 [i,ff], 11 [aa], 13 [d,e,o,p], 16 [dd,ll], 17 [f], 100 [e]
Fructose : glucose (1 : 1 blend)		20	13 [g], 20 [d,e,ll], 21 [o]
Galactose	180.2	≈30, 110	32 [g,h], 38 [i], 110 [e,z,ll]
Sorbose	180.2		27 [i]
Mannose	180.2	30	30 [d,e,z,ll], 31 [i], 36 [g]
Sorbitol	182.2	−2	−2 [q,z,dd], −3 [d,e,f], −4 [i], 0 [o,ll]
Isomaltose	342.3		78 [g]
Sucrose	342.3	52	52 [e,f,r], 57 [d,e,o,s,t,u], 55 [nn,oo], 56 [v,ii], 56.6 [jj], 61 [mm], 62 [z,bb], 66 [n], 67 [i,j,aa,cc,kk], 69.5 [dd], 70 [g,y,e,ll]
Turanose	342.3	52	52 [z]
Mannobiose	342.3	90	90 [z]
Melibiose	342.3		91 [i], 95 [g]
Maltose	342.3	43	43 [d,e,f], 70 [n], 87 [w,z,bb], 91 [i], 92 [h,i,aa], 94 [v], 95 [g,y,dd], 100 [ll]
Trehalose	342.3	79	79 [n,z], 77 [e,ll], 107 [i]
Cellobiose	342.3	77	77 [d,e,ll]
Lactose	342.3		100 [dd], 101 [i,s,u,x,bb,ii], 103 [z], 106 [aa]
Maltitol	344.3		44 [i]
Maltotriose	504.5	76	76 [d,e,f,z,ll], 130 [y,dd], 131 [v], 134 [g], 135 [i]

(continues)

TABLE XIV (*Continued*)

Compound	MW	T_g (°C) [Refs. a–c]	Other T_g values [Refs.]
Nystose	666.6	77	
Maltotetraose	666.6	111.5	147 [l]
Maltopentaose	828.9	125	165 [l]
Maltohexaose	990.9	134	173 [v], 175 [g,l,y,dd]
Maltoheptaose	1153.0	138.5	

References

[a] Slade and Levine (1988b)
[b] Slade and Levine (1991a)
[c] Levine and Slade (1989a)
[d] Franks (1990)
[e] Franks and Grigera (1990)
[f] Franks (1989)
[g] Orford *et al.* (1990)
[h] Noel *et al.* (1990)
[i] Roos (1992a)
[j] Soesanto and Williams (1981)
[k] Chan *et al.* (1986)
[l] Orford *et al.* (1989)
[m] Ollett and Parker (1990)
[aa] Roos and Karel (1991f)
[cc] te Booy *et al.* (1992)
[ee] Suzuki and Franks (1993)
[gg] Kalichevsky and Blanshard (1992b)
[ii] Arvanitoyannis and Blanshard (1993a)
[kk] Blond (1993)
[mm] Murthy *et al.* (1993)
[oo] Hatley and Mant (1993)
[n] Green and Angell (1989)
[o] Finegold *et al.* (1989)
[p] Wasylyk and Baust (1991)
[q] Quinquenet *et al.* (1988)
[r] Blanshard and Franks (1987)
[s] Roos and Karel (1991a)
[t] Roos and Karel (1991c)
[u] Roos and Karel (1990)
[v] Franks *et al.* (1991)
[w] Roos and Karel (1991b)
[x] Shimada *et al.* (1991)
[y] van den Berg *et al.* (1993)
[z] Roos (1992d)
[bb] Roos and Karel (1991h)
[dd] van den Berg (1992)
[ff] Ablett *et al.* (1992c)
[hh] Tian and Blanshard (1992a)
[jj] Levi and Karel (1992a)
[ll] Franks (1993a)
[nn] Franks and Hatley (1992)

[a] Modified from Levine and Slade (1992b).

1988b,c, 1989c; Franks, 1989, 1990, 1991c, 1992b; Pikal, 1990a,b, 1993)] or specify a temperature for product storage (Levine and Slade, 1986, 1988b,c, 1989a,c), one must measure it, rather than rely on an uncertain, predicted value. Nevertheless, a great deal of recent research effort, especially in the food area (Table XF), has gone into studies aimed at predicting T_g of binary or ternary systems, using equations commonly employed in the synthetic polymers field for different types of binary mixtures, including polymer–polymer and polymer–plasticizer systems (Levine and Slade, 1988a). The oldest and simplest of these equations is that of Gordon and Taylor (1952),

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

where T_{g1}, T_{g2}, and T_g are the T_g values (in °K) of components 1 and 2 and of the blend, respectively, w_1 and w_2 are the weight fractions of components 1 and 2 in the blend, and k is an empirical constant. (Note that if $k = 1$, this equation reduces to the straightforward weight-averaging approach described above for orange juice.) This Gordon–Taylor equation was subsequently refined by Couchman and Karasz (1978), who defined k as $\Delta C_{p2}/\Delta C_{p1}$, where ΔC_{p1} and ΔC_{p2} are the changes in heat capacity at the T_g of components 1 and 2, to yield the Couchman–Karasz equation. In either of these equations, extra terms can be added for mixtures with three or more components. As reviewed elsewhere (Levine and Slade, 1988a), both of these equations have been used, successfully only in certain instances, to predict T_g of blends of synthetic amorphous polymers and of synthetic polymers and plasticizers (i.e., water or organic diluents). As summarized in Table XF, both of these equations, as well as others, have also been used in recent years by various workers to predict (1) extents of depression of polymer T_g by plasticizing water and/or (2) T_g of homogeneous blends of glass-forming food materials, including binary and ternary mixtures of various small sugars (i.e., saccharide monomers and oligomers), or sugar alcohols, and/or food polymers (e.g., starch, amylose, amylopectin, maltodextrins, dextran, xanthan gum, hyaluronic acid, gluten, glutenin, gliadin, casein, sodium caseinate, and fish protein), in the presence or absence of water. As in the case of synthetic polymers, these studies of food polymer systems have generally met with only mixed success, i.e., the agreement between results for measured vs. predicted T_g has sometimes been good and sometimes not (Huang, 1993b).

B. PLASTICIZATION BY WATER

As mentioned earlier, plasticization, and its modulating effect on the temperature location of the glass transition, is a key technological aspect of synthetic polymer science (Sears and Darby, 1982). In that field, the classical definition of a plasticizer is "a material incorporated in a polymer to increase the polymer's workability, flexibility, or extensibility" (Sears and Darby, 1982). Characteristically, the T_g of an undiluted polymer is much higher than that of a typical low-MW, glass-forming diluent. As the diluent concentration of a solution increases, T_g decreases monotonically, because the average MW of the homogeneous polymer–plasticizer mixture decreases, and its free volume, (the volume of the mixture that is not occupied by molecules) increases (Ferry, 1980). Plasticization, on a molecular level, leads to increased intermolecular space or free volume, decreased local viscosity, and concomitant increased mobility (Ferry, 1980; Lillie and Gosline, 1990; Harrison *et al.*, 1992). Plasticization implies intimate mixing and molecular compatibility, such that a plasticizer is homogeneously blended in a polymer, or a polymer in a plasticizer (Sears and Darby, 1982; Kalichevsky *et al.*, 1993b). Note that a true solvent, capable of cooperative dissolution of ordered crystals and having high thermodynamic compatibility and miscibility at all proportions, is always also a plasticizer, but a plasticizer is not always a solvent (Sears and Darby, 1982).

It is well known that water, acting as a plasticizer, affects the T_g of completely amorphous polymers and both the T_g and T_m of partially crystalline polymers (Rowland, 1980; Levine and Slade, 1988a, 1989b, 1992b; Slade *et al.*, 1989; Slade and Levine, 1991a,b). Water is a "mobility enhancer"; its low MW leads to a large increase in mobility, due to increased free volume and decreased local viscosity (Ferry, 1980), as moisture content is increased from that of a dry solute to a solution (Slade and Levine, 1988a,b). The direct plasticizing effect of increasing moisture content at constant temperature is equivalent to the effect of increasing temperature at constant moisture and leads to increased segmental mobility of chains in amorphous regions of glassy and partially crystalline polymers, allowing, in turn, a primary structural relaxation transition at decreased T_g (Rowland, 1980; Sears and Darby, 1982). Lillie and Gosline (1990) explained plasticization this way: "The plasticizing action of water or heat on an amorphous polymer can be explained in terms of free volume, a loosely defined parameter quantifying the space available for movement of the polymer chain segments. Increasing free volume through the introduction of a low MW solvent, such as water, or through thermal expansion reduces the barriers to rotational and translational motion. This reduction increases molecular mobility and shifts the viscoelastic properties away from the glass point as predicted by the WLF equation."

Sears and Darby (1982) stated unequivocally that "water is the most ubiquitous plasticizer in our world." Karel (1985) noted that "water is the most important . . . plasticizer for hydrophilic food components." Atkins (1987) succinctly stated the important observation that "water acts as a plasticizer, dropping the T_g of most biological materials from about 200°C [for anhydrous polymers, e.g., starch, gluten, gelatin (Levine and Slade, 1988a)] to about −10°C or so [under physiological conditions of water content], without which they would be glassy" [in their native, *in vivo* state]. The latter T_g of about −10°C [corresponding to T_g' (Levine and Slade, 1988a)] is characteristic of high-MW biopolymers at or above moisture contents, near 30%, corresponding to physiological conditions. This fact has been reported for many polysaccharides and proteins, including starch, gluten, and gelatin (Levine and Slade, 1988a), hemicelluloses (Kelley *et al.,* 1987), and elastin (Atkins, 1987). Recently, there has been increasing evidence (Table XC) to suggest that most, if not all, high-MW biopolymers appear to share a common glass curve (or, at least, very similar ones) (Slade and Levine, 1991a, 1993b; Levine and Slade, 1992b). With the weight of this evidence has come recognition (Slade and Levine, 1992a,b, 1993a–c) that the following rule of thumb appears to be widely applicable to many glass-forming polysaccharides and proteins (including starch, amylopectin, amylose, maltooligosaccharides and maltodextrins, hydroxyethyl starch, cellulose, hemicellulose, carboxymethyl celluose, dextran, pullulan, xanthan, hyaluronic acid, gluten, glutenin, gliadin, zein, collagen, gelatin, elastin, keratin, albumins, globulins, casein, poly-L-asparagine, lysozyme, and ribonuclease), and fully describes the "practical" portion of the glass curve [i.e., from dry T_g to T_g' (Slade and Levine, 1991a)], which is relevant to many food applications of such high-MW biopolymers: (1) dry $T_g \approx 200 \pm 50°C$, (2) T_g decreases by $\approx 10 \pm 5°C/w\%$ water at low moisture contents ($\leq \approx 10$ w% water), (3) $T_g \approx$ room temperature at $W_g \approx 20 \pm 5$ w% water, and (4) $T_g' \approx -10 \pm 5°C$ and $W_g' \approx 25–30$ w% water.

State diagrams illustrating the extent of the T_g-depressing effect of water, as well as the above rule of thumb, have been reported for a wide variety of natural, as well as synthetic, water-compatible, glassy and partially crystalline polymers (Rowland, 1980; Levine and Slade, 1988a, 1989b, 1992b; Slade *et al.,* 1989; Slade and Levine, 1991a,b; Nelson, 1993). In such diagrams, exemplified by the schematic one in Fig. 4, the smooth "glass curve" of T_g versus w% composition demonstrates the dramatic effect of water on T_g, especially at low moisture contents, where T_g typically decreases by $\approx 10 \pm 5°C/w\%$ water (Levine and Slade, 1988a), from the neighborhood of 200°C for an anhydrous polymer (Atkins, 1987). An example of such a state diagram (Fig. 9) depicts the amylopectin of freshly gelatinized starch as a typical water-compatible, completely amorphous polymer that exhibits a T_g curve from >125°C for pure anhydrous starch to about −135°C, the T_g of pure amorphous solid water (Mayer, 1991), passing through T_g' at about −5°C (and $W_g' \approx 27$ w% water) (Slade, 1984; Slade and Levine, 1984). Figure 9 shows T_g of starch decreasing by $\approx 6°C/w\%$ water for the first 10 w% moisture, in good agreement with another glass curve for starch, calculated from free volume theory (Blanshard, 1988; Marsh and Blanshard, 1988). Another recently published glass curve for completely amorphous amylopectin (waxy maize starch) samples with moisture contents in the 10–25 w% range, measured by DSC (Kalichevsky *et al.,* 1992a), showed T_g continuing to decrease by $\approx 7°C/w\%$ water in this range, in agreement with another DSC-measured glass curve, this one for native wheat starch, reported by Zeleznak and Hoseney (1987a). Like the glass curve

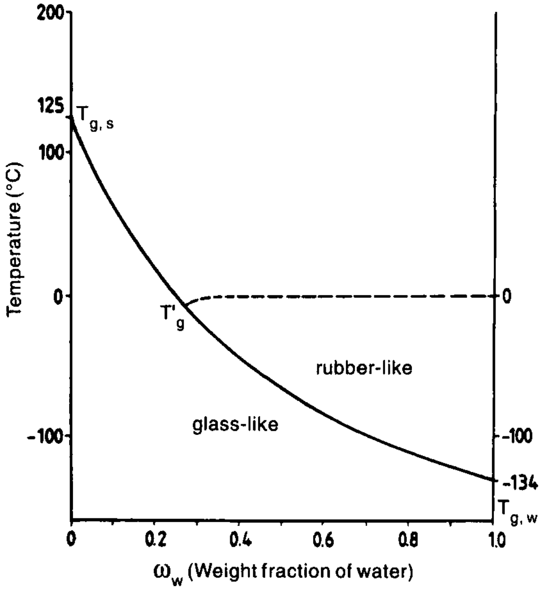

FIG. 9. State diagram, showing the approximate T_g values as a function of mass fraction, for a gelatinized starch–water system. From van den Berg (1986) with permission.

in Fig. 9, the experimental curve reported by Kalichevsky *et al.* could be smoothly extrapolated to the T_g'–W_g' point for starch (Levine and Slade, 1992b).

Similarly, the glass curve for water-compatible, amorphous wheat gluten in Fig. 10 (Hoseney *et al.,* 1986) shows a decrease in T_g from >160°C at <1 w% water to ≈15°C at ≈16 w% water, a depression of ≈10°C/w% water in this moisture range (Fujio and Lim, 1989; Kalichevsky *et al.,* 1992c). The plasticizing effect of water on gluten continues at higher moisture contents, until T_g falls to $T_g' \approx -7.5$°C and W_g reaches $W_g' \approx 26$ w% water (Slade *et al.,* 1989). As in the glass curve for starch in Fig. 9, a smooth curve of T_g versus w% composition results for gluten, when one connects the DSC-measured data points for (1) T_g of gluten samples at <2 w% moisture (Fujio and Lim, 1989); (2) T_g of commercial vital wheat gluten powder at 6 w% "as is" moisture [from Slade's (1984) original report of a glass transition in gluten]; (3) T_g'–W_g' (Slade *et al.,* 1989); and (4) T_g of water. Another experimentally measured glass curve, this one for the glutenin component of gluten, likewise shows a monotonic decrease in T_g from ≈110–130°C at 4 w% water to ≈20°C at 14 w% water, a depression of ≈9–11 C/w% water in this moisture range (Cocero and Kokini, 1991, 1993). These results for glutenin were recently confirmed by Kalichevsky *et al.* (1992c), who also

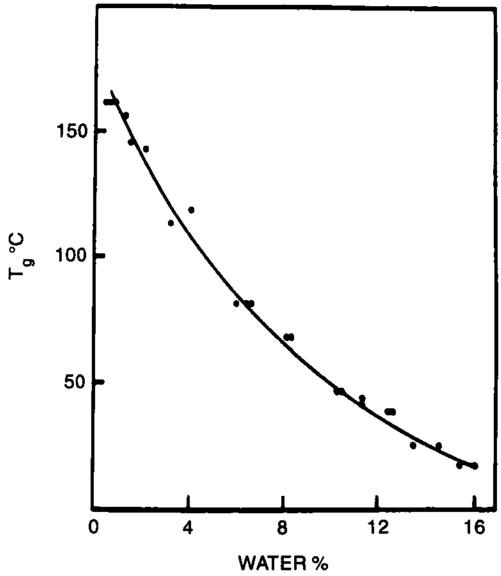

FIG. 10. Change in T_g as a function of moisture for a hand-washed and lyophilized wheat gluten. From Hoseney *et al.* (1986) with permission.

measured T_g for the gliadin component of gluten [as did Cocero *et al.* (1992a), de Graaf *et al.* (1992), and Madeka and Kokini (1992a,b, 1993)] and reported that "the T_gs of both glutenin and gliadin are very similar to the T_g of whole gluten."

Since the first reports of a glass transition in starch (van den Berg, 1981, 1986; Slade, 1984; Slade and Levine, 1984, 1987b, 1988c; Maurice *et al.*, 1985) and in gluten (Slade, 1984; Levine and Slade, 1988a; Slade *et al.*, 1989), and recognition by these workers of the importance of the glass transition temperature, and its dependence on water content, to the structure–function relationships of starch and gluten in baked products and other wheat flour-based foods, the aqueous glass curves of these two major food polymers, and the effect of plasticization by water on their T_gs, have been actively investigated by many other workers (references in Tables VIIIA and VIIIB). Since starch and gluten are the major storage polymers of wheat endosperm, and they are synthesized, stored in the mature seed, and hydrolyzed by enzymes of germination in the same temperature and moisture environment, it appears biochemically and physiologically logical that their aqueous glass curves should be similar, if not identical (Levine and Slade, 1992b). That is, since conditions of synthesis, storage, and use are identical for the two storage polymers, equivalent performance should reflect equivalent glass curves. In fact, the results and conclusions of many of the studies cited in Table VIII seem to support this suggestion. Parts A and B of that table list references to studies of the T_gs of starch, gluten, and/or their component polymers and to methods used to determine them. Taken together, these T_g results appear to fall in the same region of temperature and moisture content, i.e., a T_g around "room temperature" (≈15–25°C) at a moisture content around 15 to 20 w% (Levine and Slade, 1992b). The technological implications of such a T_g and moisture content to the processing and product properties of starch- and/or gluten-based food products (e.g., doughs and baked goods) are obviously profound, as discussed in the references listed in Table VIIIC. Particularly noteworthy in this regard are recent results from Le Meste *et al.* (1992) on the glass transition of white pan bread, measured (in terms of onset temperature for softening) by TMA. In this first study of the thermomechanical glass transition in an actual, complex food product, they reported a glass curve of T_g versus moisture content for bread, which begins at ≈165°C at 0 w% water, decreases by ≈10°C/w% water from 0 to 10 w% moisture and by ≈5°C/w% water from 10 to 20 w% moisture, thereby passing through $T_g \approx 20°\text{C}$ at ≈16.5 w% water, and then levels off at $T_g \approx -12°\text{C}$ (i.e., T_g') for moisture contents above ≈25 to 27 w% (i.e., W_g'). Such a glass curve is just what one might expect for a water-plasticized, amorphous, mixed matrix of developed gluten and gelatinized starch, which comprises the continuous, three-dimensional, structural network of fresh-baked bread crumb (Levine and Slade, 1989b; Aynie *et al.*, 1992a,b; Dong, 1992; Le Meste *et al.*, 1992; Hallberg and Chinachoti, 1992; Huang *et al.*, 1992; Kim and Taub, 1993).

In a related vein, also noteworthy are the recent interest and research activity concerning the glass transition and the effect of water plasticization on T_g and resulting rheological properties of corn zein protein and zein-containing doughs (Lawton, 1992a,b; Cocero *et al.*, 1992a,b; Kokini *et al.*, 1992d; Madeka and Kokini, 1992a,b, 1993; Magoshi *et al.*, 1992). Particular attention is due to the meticulous DSC studies by Sochava and co-workers on the glass transition and the effect of water plasticization on T_g in lysozyme and various other globular proteins (Sochava *et al.*, 1991; Sochava and Belopolskaya, 1992; Sochava and Smirnova, 1992).

Returning to the subject of water plasticization of starch, we note the importance of the fact that plasticization of the amorphous regions (e.g., backbone segments and branch points of amylopectin molecules) of native granular starches by sorbed water is neither instantaneous nor simultaneous with the initial swelling caused by water uptake (Slade and Levine, 1991a). It was demonstrated by Aguerre *et al.* (1989) that "the uptake of water takes place between the concentric layers" of the granule, leading to "interlamellar expansion of the starch granule structure." This sorbed water must subsequently diffuse from interlamellar spaces to the amorphous regions of the granule before plasticization of polymer molecules or chain segments in those amorphous regions can begin (Yost and Hoseney, 1986; Slade and Levine, 1991a). The salient point is that while water is unquestionably an effective plasticizer of starch and all other water-compatible food polymers, the mere presence of water does not attest that plasticization has already occurred (Slade and Levine, 1991a). Thus, when one reads the following quote from Hoseney (1986),

> When starch is placed in water, the granule is freely penetrated by water, or for that matter, by most small molecules. The starch can hold about 30% of its dry weight as moisture. The granule swells slightly; its increase is generally considered to be about 5%. The volume change and water absorption are reversible, and heating the system to just below its gelatinization temperature will not bring about any other changes,

one must be careful not to equate rapid penetration (e.g., through preexisting channels and voids) with rapid plasticization by water, as some have done (Liu and Lelievre, 1991b; Lelievre, 1992a). In fact, plasticization at T below the initial T_g of a material is very slow, but it occurs much more rapidly at T above the initial T_g (Slade and Levine, 1991a). This was graphically demonstrated by some remarkable swelling studies of poly(vinyl chloride) (PVC) described by Sears and Darby (1982). It was found that several "common PVC plasticizers . . . would not swell an unplasticized PVC sheet at room temperature in two years' time . . . . Yet, all of the plasticizers swelled the rigid PVC sheet at 76°C, the approximate T_g of the resin. When the same PVC was hot-compounded with a plasticizer, cooled, and then immersed in various other plasticizers, it would imbibe more plasticizer."

A new diagnostic experiment (a "thought" experiment, i.e., designed but not yet conducted), outlined in Table XV (Slade and Levine, 1993b), was conceived to reinforce the critical distinction between "presence of water" and "plasticization by water."

1. Plasticization and Antiplasticization by Sugars

An interesting phenomenon to discuss in this section on plasticization concerns what we have always thought of as the "schizophrenic" behavior of sucrose (or other typical low-MW sugars such as glucose or fructose) in a starch–sucrose–water system (Slade and Levine, 1987b, 1993b; Levine and Slade, 1988c, 1989c). By schizophrenic, we mean showing either of two very different (essentially opposite) personalities, depending on which of two different situations exists; where the two different behaviors can each be

TABLE XV

DIAGNOSTIC EXPERIMENT TO DISTINGUISH "PRESENCE OF WATER" FROM "PLASTICIZATION BY WATER"[a]

A. Native commercial wheat starch at room temperature and "as is" moisture content:
  1. Observe *low* relative vapor pressure (RVP) at 25°C; this implies that room temperature, T, is below initial T_g and $\approx$ 6 w% moisture, W, is below W_g'.
  2. So, water is present *and* acts as a plasticizer, but it is insufficient to depress initial T_g to below 25°C.

B. Add water at room temperature to achieve W such that $W_g' > W > 20$ w%:
  1. Observe *high* RVP at 25°C; this implies that T is below initial T_g and $W_g' > W > 20$ w%.
  2. So, *more* water is present, but it does *not* act as an instantaneous plasticizer, because T is below initial T_g, even though total (but nonplasticizing) water is sufficient to depress T_g to below T after *long* relaxation time.

C. Add water at a different temperature, T, such that initial $T_g < T <$ initial T_m (i.e., gelatinization peak temperature, from DSC), to achieve W such that $W_g' > W > 20$ w% (*same* W as in part B, above), then cool to room temperature to complete treatment:
  1. Both T and W are the same as in part B when RVP is measured at room temperature, but the path was different, because water was added below (part B) versus above (part C) initial T_g.
  2. So, observe *low* RVP, such that part A RVP < part C RVP < part B RVP.

D. Add water at T such that initial $T_g < T <$ initial T_m (i.e., gelatinization peak temperature, from DSC), to achieve higher W such that $W > W_g'$, then cool to room temperature:
  1. Amylopectin is still partially crystalline, but it is completely plasticized.
  2. So, observe *high* RVP, such that part A RVP < part C RVP < part D RVP < part B RVP.

E. Add water at higher T such that $T \approx$ amylose $T_g >$ initial T_m (amylopectin), to achieve W such that $W > W_g'$ (same W as in part D), then cool to 25°C:
  1. Amylopectin is completely amorphous and plasticized, and its short branches depress $\overline{M}_w$ of amylopectin, but amorphous, high-MW amylose is also plasticized and contributes to overall T_g (also to network T_g?).
  2. So, observe *high* RVP, perhaps part A RVP < part C RVP < part E RVP < part D RVP < part B RVP.

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[a] Modified from Slade and Levine (1993b).

described and explained in terms of established concepts, but the underlying reason for the manifestation of two different personalities is not completely understood. As indicated in Table IXF, the "antiplasticizing" effect of sucrose and other sugars (i.e., of a sugar–water solution relative to water alone) on the gelatinization of native starches [normal or waxy (all amylopectin)] (Slade and Levine, 1987b) is well established and widely accepted. In the presence of native starch and excess water (i.e., $W > W_g'$), sugar behaves as a plasticizing cosolvent with water, such that the sugar–water co-plasticizer, of higher average MW [and lower free volume, so higher T_g

(Ferry, 1980)] than water alone, plasticizes [depresses the temperature of the glass transition of the amorphous regions, which immediately precedes the gelatinization of native, partially crystalline (Slade and Levine, 1988c)] starch less than does water alone, so that the gelatinization temperature (as well as the T_g that precedes it) in the presence of sugar (whether initially added to the mixture as a crystalline solid or predissolved in water) is elevated (hence, "anti") relative to the gelatinization temperature of starch in water alone. Moreover, with increasing concentration of sugar in the three-component mixture (thus, a sugar–water co-plasticizer with increasing average MW, decreasing free volume, and increasing T_g, relative to water alone), the magnitude of the antiplasticizing effect increases, and so do T_g and the gelatinization temperature (Slade and Levine, 1987b).

If we then take the very same sample and immediately freeze it, we see that T_g' of the homogeneous, completely amorphous, three-component matrix (gelatinized starch or amylopectin + sugar + unfrozen water) surrounding the crystals of pure ice is lower than the corresponding T_g' of gelatinized starch in water alone, falling somewhere between the T_g' values of the sugar–water alone (e.g., −32°C for sucrose, −43°C for glucose) and gelatinized starch–water alone (≈ -5°C), as determined by the weight ratio of starch:sugar in the sample (Levine and Slade, 1988c, 1989c). Thus, in the freeze-concentrated matrix, sugar has changed its behavior by assuming the role of a low-MW co-solute with starch, which lowers the average MW and increases the free volume of the starch–sugar mixture, thus depressing T_g' relative to the T_g' of gelatinized starch–water in the absence of sugar. In other words, in this situation, sugar is acting as a plasticizer of starch, which is the behavior one would ordinarily expect of a low-MW oligomer in a homogeneous blend with a high-MW polymer with which it is thermodynamically compatible (Ferry, 1980; Wunderlich, 1980; Sears and Darby, 1982). Analogous behavior, i.e., various sugars (e.g., sucrose, glucose, fructose) and polyols (e.g., glycerol) acting as plasticizers and depressing T_g of amorphous starch or amylopectin in three-component aqueous mixtures at low moisture contents ($W < W_g'$), has been described in several reports (Ollett *et al.*, 1991; Roozen *et al.*, 1991; Kalichevsky *et al.*, 1992b; Kalichevsky and Blanshard, 1992b,c; Shogren *et al.*, 1992; Arvanitoyannis *et al.*, 1993; Attenburrow and Davies, 1993; Barrett *et al.*, 1993; Kirby *et al.*, 1993; Sala and Tomka, 1992a).

Let us summarize the apparent symptoms of sugar's schizophrenia. In the first situation (gelatinization), sugar acts as a co-solvent with water, whereas starch acts as the sole solute, and its T_g is elevated in the presence of sugar. In contrast, in the second situation (frozen or low-moisture systems), sugar acts as a co-solute with starch, whereas water acts as the sole solvent, and starch's T_g is depressed in the presence of sugar. Such schizophrenic behavior of sugars is evidently not limited only to starch-containing systems, but may be generalizable to other polysaccharide- (Levine and Slade, 1989c) and protein-containing systems (Slade *et al.*, 1989) as well. For example, the effect of sucrose and other sugars to elevate the denaturation temperature of various enzymes (e.g., lysozyme) and globular proteins (e.g., egg white, soy) in aqueous solution is well known (Franks, 1988; Harwalkar and Ma, 1990; Ma and Harwalkar, 1991), although the mechanism of this action of sugars to raise the heat-set-gelation temperature of proteins had not previously been ascribed to "antiplasticization" (Slade and Levine, 1993b), even though such native proteins are known to have amorphous regions that undergo glass transitions (Slade *et al.*, 1989; Sochava *et al.*, 1991; Sochava and Smirnova, 1992). In contrast to this stabilizing effect of sugars, the behavior of various sugars (e.g., sucrose, glucose, fructose) acting as plasticizers and depressing T_g of amorphous gluten or caseinate in three-component aqueous mixtures at low moisture contents ($W < W_g'$) has been described in several reports (Kalichevsky *et al.*, 1992c, 1993b; Kalichevsky and Blanshard, 1992c). The analogous effect of sucrose to depress T_g' of a frozen gluten–sugar–water mixture (with $W > W_g'$), relative to the corresponding T_g' of gluten–water in the absence of added sugar, had been reported earlier (Slade *et al.*, 1989).

C. THE DYNAMICS MAP

The key to our perspective on concentrated, water-plasticized food polymer systems relates to recognition of the fundamental importance of the dynamics map shown earlier in Fig. 3. The major area of the map (i.e., the area surrounding the reference state in two dimensions and projecting into the third, time, dimension) represents a nonequilibrium situation corresponding to the temperature–composition region of most far-reaching technological consequence to aqueous food systems (Slade and Levine, 1988b). The critical feature in the use of this map is identification of the glass transition as the reference state (Slade and Levine, 1988a,b; Franks and Grigera, 1990), a conclusion (Levine and Slade, 1988a; Ollett and Parker, 1990) based on WLF theory for glass-forming polymers. This line of demarcation (representing the glass curve of T_g versus composition) (Levine and Slade, 1986; Simatos and Karel, 1988; Franks, 1989, 1990; Karel, 1992; Karel *et al.*, 1993b) provides a basis for description of the nonequilibrium thermomechanical behavior of water-compatible polymeric materials in glassy and rubbery states (Levine and Slade, 1988a), in response to changes in the key variables of moisture content, temperature, and time (Tsourouflis *et al.*, 1976). Mobility is the transcendent principle underlying definition of the glass transition as the appropriate reference state (Slade and Levine, 1988a), because mobility is key to all transformations in time (or frequency), temperature, and composition between different relaxation states for a technologically practical food (Slade and Levine, 1988b) or biological (Lillie and Gosline, 1990) system (Karel, 1992; Karel *et al.*, 1993b).

As mentioned earlier, the interdependent concepts of water dynamics and glass dynamics embodied in the dynamics map have provided insights into the relevance of the glassy reference state to functional aspects of a variety of food systems (Levine and Slade, 1988a; Slade and Levine, 1988b). For example, the kinetics of all constrained relaxation processes, such as translational or large-scale rotational diffusion (and any chemical or enzymatic reaction dependent thereon), which are governed by the mobility of a water-plasticized polymer matrix in glass-forming systems, vary (from Arrhenius- to WLF-type) between distinct temperature/structure domains, which are divided by this glass transition (Table XB). Thus, while Arrhenius kinetics are applicable below T_g in the glassy solid state of very low mobility and very slow diffusion (the domain of glass dynamics, labeled STABLE in Fig. 3), WLF kinetics (Ferry, 1980) are applicable above T_g in the viscoelastic, rubbery liquid state of accelerating mobility and diffusion (the domain of water dynamics, labeled REACTIVE in Fig. 3) (Slade and Levine, 1988b). The WLF equation (Williams *et al.*, 1955; Ferry, 1980) defines the kinetics of molecular-level relaxation processes (such as the collapse phenomena referred to earlier), which will occur in practical time frames only in the rubbery state above T_g, in terms of an exponential, but non-Arrhenius, function of ΔT above this boundary condition (Levine and Slade, 1986, 1988b, 1989d, 1992b; Slade and Levine, 1988b, 1991a, 1993c; Franks and Grigera, 1990; Roos and Karel, 1990, 1991a,d–h, 1992, 1993; Franks *et al.*, 1991; Lim and Reid, 1991, 1992; Shimada *et al.*, 1991; Buera and Karel, 1992; Karathanos *et al.*, 1992; Karel, 1992; Karmas *et al.*, 1992, 1993; Labrousse *et al.*, 1992; Levi and Karel, 1992a, 1993a,b; Nelson and Labuza, 1992a, 1993; Reid *et al.*, 1992, 1993b; Karel *et al.*, 1993a,b; Kerr *et al.*, 1993; Nelson, 1993). The highest mobility and most rapid diffusion occur in the region above a second set of reference lines, the equilibrium liquidus and solidus curves, which demark the upper boundary of the WLF region, where Arrhenius kinetics again apply (Levine and Slade, 1989c). Within the WLF region, kinetics accelerate according to the WLF equation, from the extremely steep temperature dependence of WLF kinetics just above T_g to the moderate temperature dependence of Arrhenius kinetics on approaching T_m (Slade and Levine, 1988b, 1993c). The WLF equation describes the profound range of kinetics between T_g and T_m, with correspondingly profound implications for process control, product quality, safety, and shelf life (Levine and Slade, 1989d; Slade and Levine, 1991a). It should be noticed in Fig. 3 that A_w is correctly defined only in the region of the map corresponding to a dilute solution at equilibrium at room temperature (Franks, 1991a,b). In contrast, the actual measured relative vapor pressure (RVP) of an (nonequilibrium) IMF system would approach zero in the limit of the glassy reference state at temperatures below T_g and moisture contents below W_g, but would increase toward 1.0 with increasing temperature above T_g and increasing moisture content above W_g (Slade and Levine, 1991a,b).

One particular location among the continuum of T_g values along the reference glass curve in Fig. 3 results from the behavior of water as a *crystallizing* plasticizer and corresponds to an operationally invariant point [defined earlier as T_g' (Table XIA)] on a state diagram for any particular solute. A compilation of recently reported literature values of T_g' for many different low-MW carbohydrates, along with corresponding C_g' values, is shown in Table XIII. As illustrated in the schematic state diagram shown earlier in Fig. 4, T_g' corresponds to, and is determined by, the point of intersection of the kinetically determined glass curve for homogeneous solute–water mixtures and the nonequilibrium extension of the equilibrium liquidus curve for T_m of ice (Levine and Slade, 1986, 1988a–d, 1989a–d, 1990). This solute-specific location defines the composition of the glass that contains the maximum *practical* amount of plasticizing moisture [W_g', expressed as g UFW/g solute or w% water, or alternatively defined in terms of C_g', expressed as w% solute (Levine and Slade, 1986, 1988a)] and represents the transition from concentrated fluid to kinetically metastable, dynamically constrained solid that occurs on cooling to $T < T_g'$ (Slade and Levine, 1988b, 1991a). In this homogeneous, freeze-concentrated, solute–water glass, the water represented by W_g' is not "bound" energetically, but rather rendered unfreezable in a practical time frame due to the immobility imposed by the extremely high local viscosity of $\approx 10^{12}$ Pa s at T_g' (Franks, 1982, 1983a, 1985, 1986a,b, 1989, 1990, 1991a; Levine and Slade, 1986, 1988a, 1989b; Slade *et al.,* 1989; Franks and Grigera, 1990; Oksanen and Zografi, 1990, 1993; Belton, 1990, 1991; Slade and Levine, 1991a,b; Tanner *et al.,* 1991; Goff, 1992).

Marsh and Blanshard (1988) documented the technological importance of freeze-concentration in such situations and the practical implication of water being a readily crystallizable plasticizer, characterized by a high value of T_m/T_g ratio ≈ 2 (Soesanto and Williams, 1981; Slade and Levine, 1988b; Wunderlich, 1990). A theoretical calculation (Marsh and Blanshard, 1988) of T_g of a 50% wheat starch gel fell well below the measured value of −5° to −7°C for T_g' (Slade, 1984; Slade and Levine, 1984, 1987b; Liu and Lelievre, 1991b, 1992b), because the calculation, based on free volume theory, did not account for ice formation and resulting freeze-concentration that occur below about −3°C. Recognition of the practical limitation of water as a plasticizer of water-compatible solutes, due to phase separation of ice (Slade and Levine, 1988b, 1991a; Hancock and Zografi, 1993; Lillie and Gosline, 1993), reconciled the difference between theoretical and measured values of T_g (Marsh and Blanshard, 1988). Moreover, the theoretical calculations supported the measured value of ≈27 w% water (Slade, 1984; Slade and Levine, 1984, 1987b) for W_g', the maximum practical water content of a homogeneous wheat starch–water glass. The calculated water content of a wheat starch glass with T_g of about −7°C is ≈28 w% (Marsh and Blanshard, 1988), and 26 w% for a measured T_g [i.e., T_g'] of −5°C (Roos and Karel, 1991d).

In the context of the present discussion of the practical importance of T_g', as well as the earlier discussion of collapse phenomena, a report by Chang and Randall (1992) is particularly noteworthy. They used a combination of DSC and TMA to determine optimum freeze-drying conditions for various multicomponent aqueous solutions of proteins with sugars and/or salts. Their DSC results showed measured values of T_g' [taken as the midpoint, rather than the onset, of the transition (Table XIID), as obtained from derivative heat-flow curves (Levine and Slade, 1986)] for various maximally freeze-concentrated matrices, as well as corresponding lower-temperature values of T_g (arising from only partial freeze-concentration), which were in excellent agreement with previously published results (Levine and Slade, 1988c, 1989c; Slade *et al.,* 1989). More importantly, their TMA results for the same samples (measured in terms of probe penetration, as a consequence of mechanical softening of the ice-containing matrix, at $T > T_g'$), which agreed with their DSC data, verified that structural collapse ("melt-back") of the amorphous matrix during the ice sublimation stage of their freeze-drying experiments was only observed at freeze-drying temperatures above T_g', but not at $T_g < T < T_g'$. They concluded that T_g' represents "the true collapse temperature," while the lower-temperature T_g "is not related to collapse" (Chang and Randall, 1992). Their conclusion was in full agreement with a concept for interpreting collapse phenomena in frozen food systems, which had been advocated in earlier reports dealing with the theory and practice of "cryostabilization technology" (Levine and Slade, 1986, 1988b,c, 1989c; Slade and Levine, 1991a), but aspects of which have subsequently been questioned by other workers (Simatos and Karel, 1988; Blond, 1989, 1993; Simatos *et al.,* 1989; Blond and Simatos, 1991; Izzard *et al.,* 1991; Karel, 1991c, 1992; Karel and Saguy, 1991; Le Meste and Huang, 1991; Roos and Karel, 1991c–h, 1993; Simatos and Blond, 1991, 1993; Ablett *et al.,* 1992a,b,c, 1993; Roos, 1992a,c,d; Kerr *et al.,* 1993; MacInnes, 1993; Reid *et al.,* 1993a,b). According to this concept of cryostabilization against collapse, T_g' (rather than the lower-temperature T_g) is the only glass transition temperature relevant to the stability of ice-containing foods, against any translational diffusion-limited deterioration process (e.g., structural collapse), during freeze-drying or freezer storage (Levine and Slade, 1989c; Slade and Levine, 1991a). The previous questioning of certain aspects of this concept (discussed further in the next section) has concerned (1) the true identity of the transition (i.e., glass transition or ice melting?) labeled T_g' in typical DSC profiles of frozen sugar solutions [e.g., Fig. 1 in Levine and Slade (1986)], and (2) which of the two DSC-measured transitions, T_g' or the lower T_g, is the predominant one governing stability against collapse processes in frozen foods. The results and conclusions of Chang and Randall (1992) seem to lend strong support to the original interpretation of the cryostabilization concept.

1. T_g' and C_g': Current Issues

As mentioned earlier and discussed in previous reviews (Slade and Levine, 1991a; Levine and Slade, 1992b), T_g' and C_g' values, especially of various low-MW sugars widely used in foods, are a topic of much current interest, controversy, and debate (Table XII). The wide variations in recently published T_g' and C_g' values for many low-MW carbohydrates were illustrated earlier in Table XIII. The present discussion focuses on the current status of several key issues.

a. T_g' Values. The following issues around published T_g' values, which relate mainly to different interpretations of the DSC-measured transitions, were summarized in introductory notes (prepared by Unilever Colworth House and Wageningen University) for an informal discussion conference on "glass transitions in foods," held at Wageningen University in The Netherlands in May 1990, and attended by about two dozen invited specialists in this area.

1. "The major transition (the "T_g' glass transition" [measured as the midpoint temperature (Table XIID)]) is the glass transition of the maximally freeze-concentrated solution, and this is assumed to be the only transition of real significance. The other minor transitions [including a lower-temperature T_g arising from only partial freeze-concentration during initial freezing (Levine and Slade, 1986, 1988c, 1989c)] tend to be ignored" (Schenz *et al.*, 1984, 1991, 1992; Slade and Levine, 1984, 1985, 1988a,b, 1991a; Franks, 1985, 1986a,b, 1989, 1990, 1991c, 1992b, 1993a,b; Reid, 1985, 1990; Levine and Slade, 1986, 1988a–d, 1989a–d, 1990, 1991, 1992b; Hatley *et al.*, 1989, 1991; Pikal, 1990a,b, 1993; Roozen and Hemminga, 1990, 1991; Blanshard *et al.*, 1991; Franks *et al.*, 1991; Hatley, 1991; Hatley and Franks, 1991; Lim and Reid, 1991, 1992; Maurice *et al.*, 1991; Roozen *et al.*, 1991;

Attwool *et al.*, 1992; Chang and Randall, 1992; Goff, 1992; Hsu and Reid, 1992; Reid and Hsu, 1992; Reid *et al.*, 1992, 1993b; Sahagian and Goff, 1992, 1993; Taylor *et al.*, 1992; van den Berg, 1992; Goff *et al.*, 1993; Hatley and Mant, 1993; Hemminga *et al.*, 1993; Kerr *et al.*, 1993; McCurdy *et al.*, 1993; van den Berg *et al.*, 1993).

2. "There are two glass transitions, which correspond to either two different conformations or two concentrations of the sugar present, i.e. due to inhomogeneity within the sample" (Simatos and Karel, 1988; Blond, 1989, 1993; Simatos *et al.*, 1989; Blond and Simatos, 1991).

3. "There is only a single glass transition, and the complex nature of the DSC transition is due to an additional stress relaxation process which occurs at the glass transition" (Blond, 1989; Blond and Simatos, 1991; Simatos and Blond, 1991, 1993; Hatley and Mant, 1993).

4. "There is only a single glass transition, and the second major transition in the thermograph, the so-called 'T_g' transition', is not a glass transition at all, but is due to the onset of ice melting, which starts to occur soon after the sample goes through the glass transition, and represents the temperature at which the sample changes from kinetic to thermodynamic control" (Le Meste and Simatos, 1990; Noel *et al.*, 1990; Izzard *et al.*, 1991; Le Meste and Huang, 1991; Roos and Karel, 1991c–h, 1993; Ablett *et al.*, 1992a–c, 1993; Jouppila and Roos, 1992; Karel, 1992; Roos, 1992a,c; Karel *et al.*, 1993a,b; MacInnes, 1993).

The above issues were still current in 1993, as demonstrated by the dates of the above-cited references, and by summary notes prepared by M. Karel following (a) the April '92 Easter School on The Glassy State in Foods and (b) the November 1992 ISOPOW-V Meeting (mentioned earlier with regard to Tables IIIE and IIIG, respectively). After (a), Karel remarked: "With respect to T_g' and C_g', a consensus is forming, largely due to studies on carefully annealed systems using both mechanical spectrometry and calorimetry. It is evident that the transition phenomenon initiated at T_g' merges with ice melting." It should be noted that the latter point has never been at issue; the original description of T_g', according to (1) above and consistent with the schematic state diagram in Fig. 4 (the validity of which is unquestioned), made it clear that the DSC-measured T_g' value coincides, in the time frame of the DSC experiment, with the temperature at which ice formation ceases during cooling and ice melting begins during subsequent warming (Levine and Slade, 1986, 1988b,c, 1989c). After (b), Karel noted that "frozen food stability could be described with reference to a "critical temperature" (T_{cr}), but the data do not allow a confirmation of the correspondence of T_{cr} to T_g or T_g'." Despite this statement, the fact remains that many workers currently support the view that $T_{cr} \equiv T_g'$ [based on (1)]; e.g., $T_g' = -32°C$ for sucrose (Table XIIB).

Although not necessarily part of the consensus referred to above by Karel, the following points about interpretations (1) to (4) are worthy of mention. The proponents of (3), who had earlier been proponents of (2), have consistently reported that annealing experiments, performed with galactose solutions to confirm the hypothesis, were not completely successful (Blond, 1989; Blond and Simatos, 1991; Simatos and Blond, 1991, 1993). One of the major arguments against (1), by some proponents of (4), has been the claim that the "T_g' glass transition" cannot be a glass transition at all, but rather must be an ice-melting onset transition, because ΔC_p at T_g' (e.g., for sucrose) is *too large* (Izzard *et al.,* 1991; Ablett *et al.,* 1992a,c, 1993), when compared, e.g., to results from theoretical modeling simulations of C_p–T data for sucrose–water systems (Ablett *et al.,* 1992b). However, results of other concurrent analyses of ΔC_p data [for galactose–water (Blond and Simatos, 1991), maltooligosaccharide–water (Schenz *et al.,* 1992), and sucrose–water and stachyose–water (Hatley and Mant, 1993) systems] have shown this argument to be questionable. Moreover, according to the criteria for "fragile" glass-forming liquids described by Angell *et al.* (1992) (discussed further later), one would expect that ΔC_p at T_g' would increase with increasing "fragility" of aqueous solutions of a series of sugars. Franks (1993b) has concluded that "the origin of the relationship between the heat capacity change accompanying the glass transition and the degree of polymerization of the substrate is obscure." Most recently, Ablett *et al.* (1993) have conceded that their "explanation for the origin of the single transition [$\equiv T_g'$, based on (1)] for biopolymers [as opposed to the two transitions they claim to observe for low-MW sugars] does mean that it would be valid to use this transition to characterize the T_g' temperature in the case of biopolymers, even though the observed transition probably arises from a different phenomenon." Similarly, Roos and Karel (1991d,e) have conceded that the two transitions they advocate [as proponents of (4)], T_g' and T_m' (as onset temperatures), merge to a single transition for high-MW carbohydrates such as starch and low-DE maltodextrins, with a midpoint temperature identical to the corresponding T_g' values [based on (1)] previously reported for starch and the same low-DE maltodextrins (Slade and Levine, 1984, 1987b, 1988c; Levine and Slade, 1986, 1988b).

As mentioned earlier, a large body of evidence has been built [e.g., references in (1) above, including the freeze-drying study by Chang and Randall (1992), described earlier, and the studies by Lim and Reid (1991, 1992) and Kerr *et al.* (1993; Reid *et al.,* 1992) of reaction kinetics in relation to T_g' in frozen model systems, described later], on a foundation of the "cryostabilization technology" concept, which supports the practical importance of T_g' [based on (1)] as the temperature [$\equiv$ Karel's T_{cr} (Hsu and Reid, 1992; van den Berg, 1992; van den Berg *et al.,* 1993)] critical to frozen food stability and successful freeze-drying, because below T_g', translational diffusion-limited processes will not occur, on a practical time scale, in ice-containing frozen food systems. The current situation is perhaps best summed up by the pragmatic view espoused by Reid in the following remarks: "Whilst, as scientists, we are deeply committed to determining the true nature of the events which lead to the "humps" and "bumps" in the calorimeter traces, for practical purposes it may not be so important. If product stability can be correlated with any particular bump, then this is of practical value, and should not be overlooked" (Reid *et al.,* 1993a), and "While the discussion of the true nature of these transitions is very important, it does not invalidate the observation that in many ways reaction kinetics are affected by the temperature of the event labelled T_g' by Levine and Slade" (Reid *et al.,* 1993b).

b. C_g' Values. The introductory notes from the above-mentioned Wageningen conference had this to say about the issue of C_g' values:

> There is concern about how the concentration of the freeze-concentrated glass can be measured. The most widely publicized method [e.g., Levine and Slade, 1986, 1988b] is to determine the total amount of heat required to melt the ice in a known weight of sample [i.e., a single 20 w% solution]. The amount of ice present is then calculated from the known latent heat of ice. However, there is now evidence [references for "other C_g' values" in Table XIII] to show that this method consistently underestimates the amount of ice present, and consequently underestimates the freeze-concentrated concentration (C_g'). Therefore there is some concern about the validity of published C_g' data on numerous food compounds [i.e., Levine and Slade, 1988b,c].

Two years later, this statement was followed up by Karel's earlier-quoted remark, at the close of the Easter School at Nottingham, about a consensus forming with regard to C_g' values. He was referring to a widely held belief that C_g' values for many low-MW sugars and polyols all appear to fall in a narrow range around 80 ± 5 w% solute (references in Table XIII). This point of view has been supported by painstaking analyses [as exemplified by that of Hatley *et al.* (1991)] of actural state diagrams, such as the most popular one for sucrose–water, and of the C_g' concentration [by definition, the solute concentration of a solution with *no* "freezable" water (Levine and Slade, 1986)] corresponding to the point at which measured T_g' coincides with the glass curve constructed from measured values of T_g as a function of solute concentration for highly concentrated [in many instances, supersaturated, and therefore unstable with respect to solute crystallization during instrumental cooling (e.g., MacInnes, 1993)], completely vitrified solutions with values of C_g surrounding C_g' (Blond, 1989, 1993; Simatos *et al.,* 1989; Williams and Carnahan, 1990; Blanshard *et al.,* 1991; Franks, 1991c, 1992b, 1993a,b; Franks and van den Berg, 1991; Franks *et al.,* 1991; Hatley *et al.,* 1991; Izzard *et al.,* 1991; Le Meste and Huang, 1991; Roos and Karel, 1991d–h, 1993; Simatos and Blond, 1991, 1993; Ablett *et al.,* 1992a–c, 1993; Leung *et al.,* 1992; Roos, 1992a,c; van den Berg, 1992; Hatley and Mant, 1993; van den Berg *et al.,* 1993).

Today, it seems safe to say that different values of C_g' *can* result, depending on the method used to determine it for a given low-MW carbohydrate (Tables XIIA, XIIC, and XIII). For example, for sucrose, the "state diagram" method has produced a "rigorous" C_g' value of ≈80 (±4) w% (Tabe XIII), whereas analysis of uncorrected DSC data for a single freeze-concentrated 20 w% solution (*not* annealed) produced a much lower "apparent" C_g' value of ≈64 w% (Levine and Slade, 1988b), which has subsequently been confirmed by several other workers (Hatley *et al.,* 1991; Izzard *et al.,* 1991; Ablett *et al.,* 1992a,b; Nesvadba, 1992a; Reid and Hsu, 1992; Reid *et al.,* 1993a). As shown by the data compiled in Table XIII, similarly large differences between reported C_g' values determined by these two methods result for many other sugars. It should also be noted, as has been widely reported for sucrose (as well as various other sugars and polyols), that it is generally (1) very difficult to force ice to form, in supersaturated solutions of ≈65 to 70 w% concentration, without extensive annealing, temperature cycling, or in the absence of stress cracking (which serves to heterogeneously nucleate ice formation) of an otherwise totally vitrified glass (Williams and Carnahan, 1989, 1990; Hosea *et al.,* 1990; Williams *et al.,* 1990, 1993), and (2) essentially impossible, in a realistic experimental time frame, to force ice to form in solutions of $> \approx 70$ w% concentration, even with extensive annealing (MacKenzie, 1977; Franks, 1982; Levine and Slade, 1988a; Blond, 1989, 1993; Simatos *et al.,* 1989; Williams and Carnahan, 1989, 1990; Hosea *et al.,* 1990; Roozen and Hemminga, 1990, 1991; Williams *et al.,* 1990; Blond and Simatos, 1991; Chang and Baust, 1991b; Dereuddre *et al.,* 1991; Hatley *et al.,* 1991; Izzard *et al.,* 1991; Le Meste and Huang, 1991; Roos and Karel, 1991c,f–h, 1993; Schenz *et al.,* 1991; Simatos and Blond, 1991, 1993; Ablett *et al.,* 1992a–c, 1993; Nesvadba, 1992a; Roos, 1992a,c,d; Hatley and Mant, 1993; Karel *et al.,* 1993b; MacInnes, 1993). Such findings have inadvertently lent support to the *practical* relevance of the lower "apparent" C_g' values (obtained using freeze-concentrated 20 w% sugar solutions as models for real frozen food systems), rather than the higher "rigorous" C_g' values, to technological issues concerning the ice content of actual frozen foods (Cole *et al.,* 1983, 1984; Slade and Levine, 1991a; Levine and Slade, 1992b).

Despite these facts, or perhaps because of them, the opinion expressed by Karel, about a consensus over C_g' values, glosses over some real problems yet to be confronted and resolved. One of these is the remaining mystery about why, for most of the low-MW carbohydrates listed in Table XIII, the difference between values of "rigorous" C_g' (determined from measurements on highly concentrated solutions, produced, in essence, by hydrating the dry solute) and "apparent" C_g' (determined from DSC measurements made of the ice-melting endotherm after freeze-concentrating a fairly dilute solution) is quite large (with "rigorous" $\gg$ "apparent" C_g' in all such cases) (Hatley and Mant, 1993), while for several others (i.e., glucose, mannose, maltose, trehalose, sorbitol), the difference is much smaller or nonexistent. Trehalose is especially unusual in this regard, in that, depending on the experimental method used to determine C_g', trehalose's C_g' value can be the highest (Levine and Slade, 1988b) or lowest (Kawai *et al.,* 1992) among those for a series of common sugars. Possibly, the answer to this mystery might lie in the relative kinetics of ice formation in undercooled, concentrated versus dilute aqueous solutions of small sugars (Slade and Levine, 1991a; Levine and Slade, 1992b; Roos, 1992a,d), which, evidently, are usually (Franks, 1982), but not always, quite different. But why not always? Of course, it should be kept in mind that both T_g' and C_g' are kinetic parameters measured under nonequilibrium conditions, for solutions whose behavior is under kinetic rather than thermodynamic control (Levine and Slade, 1986, 1988a,b,c; Franks, 1985, 1993a; Noel *et al.,* 1990). As if to balance Karel's opinion about consensus, Franks (1993b) has offered the following note of caution: "however, the endotherm profile also contains contributions from the heat of dilution and the heat capacity of fusion, which make the exact determination of unfrozen water an uncertain affair."

Another part of the mystery is illustrated by the C_g' data for the homologous series of maltooligosaccharides listed in Table XIII, which show that, as a general trend, "apparent" C_g' increases and "rigorous" C_g' decreases with increasing solute MW, until the two values essentially merge for maltoheptaose (Levine and Slade, 1988b; Schenz *et al.,* 1992; Ablett *et al.,* 1993). As alluded to earlier, once MW increases to the range of all the high-MW polysaccharide and protein biopolymers (e.g., starch and gluten) characterized to date, the C_g' range moves to $\approx$70 to 75 w% solute (Slade and Levine, 1993a–c), and the difference between "rigorous" and "apparent" C_g' values essentially disappears (Slade and Levine, 1984, 1987b, 1991a; Marsh and Blanshard, 1988; Roos and Karel, 1991d; Ablett *et al.,* 1993). Part of the explanation for this lies in the fact that the DSC data corrections (e.g., temperature dependence of latent heat of fusion of ice) alluded to above, necessary to convert "apparent" into "rigorous" C_g', are known to decrease in significance with increasing solute MW (Hatley *et al.,* 1991; Reid and Hsu, 1992). However, this fact does not explain why one obtains the same C_g' value, whether one starts with a dilute or a highly concentrated biopolymer solution; i.e., why the relative kinetics of ice formation in dilute versus concentrated solutions are evidently the same, without exception, for high-MW, but not for low-MW, solutes. Why do the kinetics of ice formation appear to differ the way they do in aqueous solutions of mono-, oligo-, and polysaccharides of equivalent weight concentration? The expected differences in bulk viscosity among undercooled, rubbery solutions of different MW solutes (Franks, 1982) would seem not to completely account for the C_g' results obtained. Moreover, why do values of "rigorous" C_g' appear to *decrease* with increasing solute MW (e.g., from ≈80 w% for mono- and disaccharides to ≈70 to 75 w% for polysaccharides) (Roos and Karel, 1991d; Ablett *et al.,* 1993), when one might intuitively expect the opposite relationship, as is, in fact, evidenced by "apparent" C_g' values (Slade and Levine, 1991a)? Before there can be a true consensus about C_g' values, there is obviously much work still to be done on the question of kinetics of ice formation [as well as on the possibly related question of stress relaxation in the freeze-concentrated glass at T_g' (Hatley and Mant, 1993)] in aqueous food carbohydrate solutions, as functions of solute MW and concentration, not to mention molecular conformation (for solutes of equal MW).

2. *Diffusion of Water and Solute in Aqueous Food Glasses at $T < T_g$*

Let us quote once again from the introductory notes for the 1990 Wageningen conference, this time on the subject of mobility of water in glassy materials:

> It has been proposed that the residual UFW in a frozen solution is kinetically controlled, and not an equilibrium property. During freezing, the solution viscosity rapidly increases until [the solution] finally becomes an amorphous solid, i.e., a glass. One definition of a glass is that the Stokes viscosity of the sample is in excess of 10^{14} Pa s, and it is assumed that this is also the local viscosity of the water molecules present. Translated into molecular motion terms, this is equivalent to a diffusion rate for the water molecules of a few microns per [decade] [Franks *et al.,* 1991]. It has been proposed that the reason why UFW is detected in frozen solutions is not because it becomes "bound," but because the mobility of the water in the glass is so slow. This means that on a practical time scale, the water molecules will stop diffusing to the ice interface, with the result that ice crystallization stops [Franks, 1982, 1985]. The problem with this model is that there is an increasing amount of evidence [from NMR, ESR, and sorption studies] to suggest that the mobility of the UFW is much higher than has been proposed.

It should be noted, of course, that the skepticism expressed above begs the question: If the unfrozen, plasticizing water in a glass at $T < T_g'$ is so mobile, why can't it continue to crystallize to ice? The fact that it does not, in real time, continue to freeze is not at issue (Slade and Levine, 1991a), and past rationalizations based on the concept of "bound" water are no longer widely accepted (Simatos and Karel, 1988; Ahlneck and Zografi, 1990; Belton, 1990, 1991; Ablett and Lillford, 1991; Franks, 1991a; Slade and Levine, 1991a; Chinachoti, 1992a; Gidley *et al.*, 1993; Hegenbart, 1993). The Wageningen notes went on to say: "All these observations [of much higher water mobility in glasses] may be a result of inhomogeneity within the samples, which could arise due to either the structure being porous, or due to there being different domains with different water mobilities. However, if this is the case, then the effect of sample inhomogeneity needs to be built into the model." This issue of potential sample heterogeneity is certainly valid, even more so for real, complex food products than for simpler model systems, and it needs to be more widely recognized and stressed (Slade and Levine, 1991a; Nelson, 1993), even though, as discussed below, it may account for some but not all such observations of higher-than-expected mobility of water or solute in glasses.

The above question about the "unfreezability" of the plasticizing water in glasses leads to another obvious question. Since UFW is evidently not mobile enough to continue to crystallize in real time at $T < T_g'$, why is it that this UFW *can* be removed, albeit slowly, by diffusion from a glass, e.g., during the desorption (or secondary drying) stage of freeze-drying? As pointed out by Franks (1993b): "The migration of water within, and its removal from, amorphous matrices containing hydrogen-bonding groups is of particular scientific interest and technological importance." There has been much recent study of the diffusion of water in glassy matrices, with regard to the freeze-drying of proteins, other biologicals, and pharmaceuticals (Franks, 1990, 1992b; Pikal and Shah, 1990; Pikal *et al.*, 1990; Pikal, 1993). The specific question of the mobility and desorbability of UFW from glasses during freeze-drying has been explicitly addressed and investigated in detail by Pikal and co-workers, who measured rates of water removal from glassy systems. Their quantitative data led to the conclusion that "while water mobility is greatly restricted in a glassy system (relative to a system above T_g), sufficient [translational] mobility does exist to allow moderate secondary-drying rates even well below T_g" (Pikal and Shah, 1990; Pikal *et al.*, 1990). However, Franks (1990) noted that "clearly, the geometry (texture) of the freeze-concentrate is an important factor, as is also its structural uniformity and the distribution of the residual water" [after the vacuum sublimation or primary drying stage].

The subject of diffusion in aqueous food polymer glasses and rubbers has also been extensively discussed in many previous reports by Karel and co-workers, with regard, e.g., to aspects of food dehydration technology, encapsulation and controlled release, and quality of dehydrated foods (Karel and Flink, 1983; Karel, 1985, 1986, 1989, 1990, 1991c, 1992; Karel and Langer, 1988; Simatos and Karel, 1988; Le Meste and Simatos, 1990;

Karel and Saguy, 1991; Shimada *et al.*, 1991; Karmas *et al.*, 1992, 1993; Labrousse *et al.*, 1992; Levi and Karel, 1992a, 1993a,b; Karel *et al.*, 1993a,b). Encapsulation of labile food components, such as volatile flavors and aromas, in glassy matrices produced, e.g., by freeze-drying, spray-drying, or extrusion is a well-established and well-founded technology. Its fundamental technological basis, indeed its very reason for being, is the greatly enhanced stability that results from successful entrapment of labile, otherwise highly mobile, small molecules in low-moisture food glasses at $T < T_g$ (Karel and Flink, 1983; Karel, 1985, 1986, 1990; Saleeb and Pickup, 1985, 1989; Karel and Langer, 1988; Levine *et al.*, 1991, 1992; Shimada *et al.*, 1991; Boskovic *et al.*, 1992; Bruin, 1992; Karmas *et al.*, 1992, 1993; Labrousse *et al.*, 1992; Levi and Karel, 1992a, 1993a,b; Nelson *et al.*, 1992; Karel *et al.*, 1993a,b; Nelson, 1993; Nelson and Labuza, 1993; Peppas, 1993). In other words, minimized diffusion of small, labile components within and out of aqueous glassy matrices is the established functional basis of glass-encapsulation technology. The same technological basis underlies the use of freeze-drying (or other drying methods) for the stabilization of high-value biological and pharmaceutical materials, including enzymes, proteins, and drugs, in low-moisture glassy matrices (Franks, 1989, 1990, 1991a,c, 1992b, 1993a,b; Levine and Slade, 1989c, 1992a; Franks and Hatley, 1990, 1992, 1993; Pikal, 1990a,b, 1993; Pikal and Shah, 1990; Pikal *et al.*, 1990, 1991a,b; Franks and van den Berg, 1991; Franks *et al.*, 1991; Hatley, 1991; Hatley and Franks, 1991; Roser, 1991b; Roy *et al.*, 1992; te Booy *et al.*, 1992; van den Berg *et al.*, 1992, 1993; Ramanujam *et al.*, 1993; Roser and Colaco, 1993). But these facts just lead to another obvious question that one should ask. Since water can be removed from a glass during the desorption stage of freeze-drying, why is it that other volatile molecules, encapsulated in the same glass, are effectively retained, at least partially? Is this due, at least in part, to the fact that water has a lower MW, smaller molecular size, lower T_g, and, therefore, higher mobility than most molecules that one would attempt to glass-encapsulate? The answer to the last question, although not known with certainty (Bruin, 1992), is probably yes. In the context of such questions with, at best, uncertain answers, the following remark by Schlotter (1990) is especially interesting: "It should be noted that above the T_g, and in the melt, diffusion is well behaved compared to that in glassy materials."

Two years after the Wageningen conference, Karel, in his summary notes for the Easter School, said the following about mobility, of water and solute, in glasses:

> It has been shown by many of the participants, using many different techniques, that T_g represents an important transition point for "mobility" in foods. However, stability

> of foods is far from assured below T_g. Processes [e.g., chemical reactions that are *not* translational diffusion-limited, including free-radical reactions such as lipid oxidation (Karel, 1986; Nelson and Labuza, 1992b)] continue below this temperature, some at very respectable rates . . . . Water remains highly mobile below T_g. Vapor pressure measurements, NMR spectroscopy, as well as computer modeling indicate water binding to specific sites is very transient (picosecond scale [Brady and Ha, 1991]). There is no discontinuity in properties of water, itself, in polymer glasses [i.e., with regard to properties such as, or related to, translational or rotational diffusion rates of water, there appears to be no change in their temperature dependence at T_g (Franks, 1993b; Pikal, 1993; Simatos and Blond, 1993), as measured, e.g., by NMR (Pikal *et al.*, 1991a; Kalichevsky *et al.*, 1992b; Ablett *et al.*, 1993; Cherian and Chinachoti, 1993) and/or sorption studies (Oksanen and Zografi, 1993; Pikal, 1993); this behavior of water is in sharp contrast to that of the same properties of the polymer segmental units in amorphous food polymer–water blends (Tanner *et al.*, 1991; Ablett *et al.*, 1993; Franks, 1993b; Pikal, 1993; Reid *et al.*, 1993b; Simatos and Blond, 1993) or of other molecules [probes (Shah and Ludescher, 1993) or reporters] much larger than water, such as dyes (Wesson *et al.*, 1982; Huang *et al.*, 1987; Ehlich and Sillescu, 1990; Nelson, 1993) or ESR spin probes (Le Meste and Duckworth, 1988; Le Meste *et al.*, 1991b; Roozen and Hemminga, 1990, 1991; Bruni and Leopold, 1991, 1992; Roozen *et al.*, 1991; Hemminga *et al.*, 1993), as discussed further below] . . . . Ordering of polymer segments, or of polymer segment–water structures, below T_g is implied by the existence of low temperature endotherms [purportedly due to melting of microcrystalline regions that form during aging] in [many glassy] polysaccharides [Bizot *et al.*, 1992; Kalichevsky *et al.*, 1992a; Livings *et al.*, 1992; Shogren, 1992; Appelqvist *et al.*, 1993; Donald *et al.*, 1993; Gidley *et al.*, 1993].

It should be noted that the latter phenomenon, which has generated much current interest (in his summary of advances reported at ISOPOW-V, Karel referred to it alternately as the "so-called Gidley endotherm" and an "apparition" deserving further study), could be due simply to the kind of sample heterogeneity mentioned earlier. In such a case, even for a polysaccharide–water model system, multiple amorphous domains of different size, with different compositions (e.g., moisture contents) and T_g values, could coexist, and at least one of these T_gs (but not the major one observed by DSC) could be below the storage ("aging") temperature, thus allowing recrystallization to occur in *that* (rubbery) domain, as one would expect (Slade and Levine, 1991a). Alternatively, the endothermic event in question might be due to slow "enthalpic relaxation" of a glassy component, which is a phenomenon quite widely and generally observed after sub-T_g annealing ("physical aging") of plastics and other synthetic amorphous polymers (Petrie, 1975; Wunderlich, 1981; Roos, 1992d; Williams *et al.*, 1993). Enthalpic relaxation, which occurs as a consequence of sufficient *short-range* mobility at $T < T_g$, has recently also been reported for low-moisture glasses of food polymers such as starch (Bizot *et al.*, 1992; Shogren, 1992; Seow and Teo, 1993) and gluten (Lawton and Wu, 1993), as well as for low-MW carbohydrates such as sucrose (Hatley and Franks, 1991), maltose (Noel *et al.*, 1991), glycerol and sorbitol (Chang and Baust, 1991a,c;

Franks, 1993b). Indeed, Appelqvist *et al.* (1993) have mentioned the possibility of enthalpic relaxation as an explanation for their observations, and even pointed out that certain aspects of their results, e.g., dependence on thermal history and time/temperature dependence of the recovery, were consistent with established criteria for enthalpic relaxation (Wunderlich, 1981). If this alternative interpretation were correct, then one would expect the endothermic transition to change in appearance and temperature location under different DSC cooling and heating protocols, and to disappear after a first heating scan that would erase the sample's thermal history (Wunderlich, 1981). Such an experimental approach, which to date has not been applied to aqueous food polymer glasses that have exhibited the low-temperature endotherm in question, would be the surest way to distinguish between a relaxation process under kinetic control and a first-order melting transition under energetic control and thus unaffected by the kinetics of its measurement (Wunderlich, 1990).

Certain other facts, relating to diffusional mobility below versus above T_g, are well established. For example, in the synthetic polymers literature, it has been clearly shown that plots of diffusivity or permeability as a function of temperature, for the diffusion of gases [or of dye molecules (Ehlich and Sillescu, 1990)] in amorphous polymers, exhibit a sharp change in slope at T_g [see, e.g., Fig. 5.105 in Sears and Darby (1982)], demonstrating that the translational mobility of small probe molecules in amorphous matrices, which is very low (but not zero) at $T < T_g$, increases dramatically as free volume likewise increases at $T > T_g$. This behavior is so diagnostic that the breakpoint in such plots can actually be used to determine a T_g value that agrees precisely with the T_g measured by DSC (Compan *et al.*, 1993). Exactly the same type of behavior has recently been reported for (1) the diffusivity and permeability of gases in completely amorphous, water-plasticized films of potato or rice starch (with or without added sugars), for which T_g as a function of moisture and sugar content was measured by DSC and DMTA [see Figs. 2–13 in Arvanitoyannis *et al.* (1993)]; (2) the temperature-dependent rate of water vapor transmission as a function of RVP for water-plasticized films of wheat gluten [see Fig. 8 in Gontard *et al.* (1992c)], for which T_g as a function of moisture content was measured by DSC and DMTA (Gontard *et al.*, 1992b); and (3) the diffusion coefficient of water during gelatinization of raw rice (Lin, 1993), although, in this case [and others involving the kinetics of starch gelatinization, reviewed by Lai and Kokini (1991)], it was not recognized that such behavior is a direct consequence of a glass transition at 63.5°C during heating of partially crystalline glassy starch in excess moisture (i.e., $W > W_g'$) (Maurice *et al.*, 1985; Slade and Levine, 1987b, 1988c). Similarly, the same kind of extreme increase in diffusional mobility with increasing free volume and decreasing local viscosity at $T > T_g$ has been demonstrated by (1) ESR data for local rotational diffusion of spin probes in frozen aqueous solutions of sugars and maltooligosaccharides, when compared to the DSC-measured T_g' values of Levine and Slade (1988b–d) for the same solutes (Roozen and Hemminga, 1990, 1991; Roozen *et al.*, 1991; Hemminga *et al.*, 1993); (2) ESR data for rotational diffusion coefficient of a spin probe in water-plasticized samples of soybean seeds [or of caseinate proteins (Le Meste and Duckworth, 1988; Le Meste *et al.*, 1991b)], when compared to T_g data for the same samples measured by TSC (Bruni and Leopold, 1991, 1992); (3) Brillouin scattering data, when compared to DSC-measured T_g data, for aqueous sucrose solutions (Hosea *et al.*, 1990); (4) rate data for a diffusion-limited chemical reaction (nonenzymatic browning) in model aqueous amorphous food matrices above and below T_g, which show a clear change in slope at T_g (signifying a sharply increasing reaction rate at $T > T_g$), in so-called Arrhenius plots of log browning rate versus $1/T$ (Karmas *et al.*, 1992; Karel *et al.*, 1993b); and (5) water vapor absorption isotherm data for various glassy food polymers, which show a sharp increase in the extent of water sorption at $T > T_g$, once the sorbing polymer transforms from glassy solid to rubbery liquid as a consequence of dynamic plasticization by the sorbed water (van den Berg, 1981, 1986, 1991; Slade and Levine, 1985, 1991a; Levine and Slade, 1988a; Cairault *et al.*, 1989; Slade *et al.*, 1989; Oksanen and Zografi, 1990, 1993; Franks, 1991b; Gontard *et al.*, 1992c; Reid, 1992b; Roos, 1992b; Hancock and Zografi, 1993; van den Berg *et al.*, 1993; Yano, 1993).

Most recently, Franks (1993b) has summed up the current state of our understanding about mobility and diffusion in aqueous food glasses this way: "In the glass, the water [i.e., UFW] molecule motions are severely retarded [i.e., retarded enough so that this water cannot crystallize to ice], but hardly to the extent of complete inhibition . . . the available evidence suggests that the water molecules constituting the 'residual moisture' in a solid solution are able to diffuse rapidly, compared to the motions of the molecules (or polymer segments) making up the glassy phase. The mobility of water within glassy matrices may contribute to the observed chemical reactions that can occur at measurable rates, even below the measured (DSC) T_g." Others have recently reached quite similar conclusions (Johari, 1991; Ablett *et al.*, 1993; Reid *et al.*, 1993b; Simatos and Blond, 1993).

Relevant new learning, in a recent paper from the synthetic polymers literature by Chin *et al.* (1992), could be important in advancing our understanding of the diffusional mobility of water in aqueous food polymer glasses. Chin *et al.* used NMR to investigate the rotational diffusional motion of polymer chain segments, as a function of temperature, in a two-component, compatible amorphous blend of two polymers with individual

T_gs different by 110°C. They pointed out that such a large difference in T_gs could also apply to typical polymer–diluent blends. As usual, their compatible blend exhibited only a single T_g by DSC, which was intermediate in value between the T_gs of the two pure polymers. Chin *et al.* stated that this "large T_g gap indicates a significant difference in the intrinsic mobility of the individual components of the blend." By analogy, we would expect the same to be true of a compatible amorphous blend of water ($T_g \approx -135°C$) and a typical food polymer (dry $T_g \approx 200°C$) or food monomer (e.g., a monosaccharide of dry $T_g \approx 30°C$). Chin *et al.* asked the following questions: "To what degree, if any, is this difference preserved in the dynamics of the two chains near the DSC T_g of the blend? Is there extensive cooperativity between the motions of the two types of chains in the blend or does each component retain certain aspects of the intrinsic mobility indicated by their respective T_gs as pure polymers?" They found evidence of segmental motions in the blend, beginning at temperatures significantly below the blend's T_g, under experimental conditions in which a one-component polymer glass would only begin to show such local motions at temperatures above its T_g. They also found that these rotational diffusional motions in the blend showed a much broader distribution of relaxation times than would be shown by a single-component polymer glass under the same conditions (Chin *et al.*, 1992).

Let us suggest an explanation, built on fairly self-evident analogies to the findings of Chin *et al.* (1992) [as well as earlier results of (1) Ehlich and Sillescu (1990) on tracer diffusion below and above T_g, and (2) Roland and Ngai (1991) on dynamical heterogeneity in miscible polymer blends], for why the diffusion rate of water is always greater than the diffusion rate of the solute(s) in an aqueous glass, as a means to explain why water can be slowly removed from an aqueous glass by freeze-drying at a sample temperature below the instantaneous T_g of the blend, but above that of water itself.

The T_g of a binary blend of a compatible diluent (often a fluid solvent or plasticizer at the experimental temperature) with a monomeric material (often a solid solute at the experimental temperature) is determined by the $\overline{M}_w$ of the blend (Ferry, 1980); T_g corresponds to the limiting free volume associated with the $\overline{M}_w$ of the blend (Slade and Levine, 1991a). In other words, only the average free volume, not its distribution, governs the glass transition (Roland and Ngai, 1991). Thus, the T_g of the blend is higher than that of the diluent (since the material with the lower T_g is designated as the diluent) and lower than that of the solute. The operational interpretation of this rule (which depends on the introduction of a reporter molecule as a third species, at a concentration that is insufficient to alter the T_g of the original blend) is that only a diagnostically selected reporter molecule, which has a hydrodynamic volume corresponding to that of a species with the same $\overline{M}_w$ as the $\overline{M}_w$ of the blend, would experience, at the T_g of the blend, a change in slope of the temperature dependence of its relaxation times, such that diffusion below T_g would be constrained to a rate several orders-of-magnitude smaller than the diffusion rate measured at a temperature about 20°C above T_g [rather than several times smaller, as expected for Arrhenius kinetics (Levine and Slade, 1989d)]. [Such behavior can be inferred from the experimental data reported by Furuta *et al.* (1984) for the diffusion coefficient of water in aqueous maltodextrin glasses and rubbers.] That is, at the T_g of the blend, the conditions of free volume and local viscosity required for cooperative motions over 100-Å dimensions are just met for the exogenous reporter molecule, but they are still more than adequate for diluent molecules. A corollary to this rule is that, if the experimental temperature were set equal to the T_g of the blend, then the diffusion rate of the diluent, if the diluent were unwarily considered as an endogenous reporter molecule, would be not only higher than the respective rates for the exogenous reporter molecule or for a solute molecule, but would also be more extremely temperature dependent [according to WLF kinetics, themselves temperature dependent! (Slade and Levine, 1988b)] than those rates. In contrast, if the monomeric solute could be monitored as an endogenous reporter molecule, its diffusion rate not only would be lower than that of the exogenous reporter molecule, but would also be much less temperature dependent (according to Arrhenius kinetics). As a result, a small temperature increment of a few degrees near the instantaneous T_g of the blend could have an order-of-magnitude effect to increase the diffusion rate of diluent molecules, with an almost negligible effect on the diffusion rate of solute molecules. Alternatively, if the experimental temperature were set equal to the T_g of the pure diluent, constrained diffusion, characteristic of the solid state, would be observed for all three molecular species. In the case of a nonentangling oligomer, the rules would be the same, but the temperature window between the T_g of the diluent and that of the solute would be wider [as seen from NMR results (Ablett *et al.*, 1993)], such that the disparity would be greater between the diffusion rate of the diluent and that of the solute at an intermediate temperature equal to the T_g of the blend. In the case of a high-MW, entangling polymer, the T_g of the blend should be calculated from the $\overline{M}_w$ of the diluent with the segmental unit of the polymer, using the T_g of the pure diluent and the molecular or segmental T_g of the polymer, rather than its higher network T_g (Levine and Slade, 1989b). We also note another potential consequence of such situations [inferred from the findings of Roland and Ngai (1991)]: for an aqueous food polymer glass, a very broad glass transition can result from the very different dynamics of the water and solute components of the miscible blend.

D. WLF THEORY AND WLF KINETICS

With the first sentence of their classic paper, Williams, Landel, and Ferry (1955) introduced their new equation by saying "in an amorphous polymer above its glass transition temperature, a single empirical function can describe the temperature dependence of all mechanical and electrical relaxation processes." Over 30 years later, Sperling (1986) remarked that "for a generation of [synthetic] polymer scientists and rheologists, the WLF equation has provided a mainstay both in utility and theory." It has become increasingly recognized (Table XB) that (1) the amorphous polymers referred to by Williams *et al.* include many food polymer, oligomer, and/or monomer systems; (2) in the last several years, Sperling's remark has begun to apply to food scientists and technologists; and (3) even after decades of investigations and applications by synthetic polymer scientists, there are still new and useful insights to be gleaned from the WLF equation, which are relevant to the behavior of amorphous food molecules and systems (Slade and Levine, 1993c).

1. The WLF Equation

At temperatures above T_g, plasticization (by either water or heat) affects the viscoelastic, thermomechanical, electrical, guest/host diffusion, and gas permeability properties of completely amorphous and partially crystalline polymer systems (Levine and Slade, 1988a; Lillie and Gosline, 1990). In the rubbery range, above T_g for completely amorphous polymers or between T_g and T_m for partially crystalline polymers [in either case, typically from T_g to about T_g + 100°C for well-behaved synthetic polymers (Slade and Levine, 1988b)], the dependence of viscoelastic and other properties on temperature (i.e., the effect of increasing temperature on relative relaxation times) is successfully predicted (Cowie, 1973; Gray, 1991) by the WLF equation, an empirical equation whose form was originally derived from the free volume interpretation of the glass transition (Williams *et al.,* 1955; Ferry, 1980). The WLF equation can be written as (Williams *et al.,* 1955; Soesanto and Williams, 1981)

$$\log\left(\frac{\eta}{\rho T} \Big/ \frac{\eta_{g},}{\rho_g T_g}\right) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}, \qquad (2)$$

where η is viscosity or other diffusion-limited relaxation process, ρ is density, and C_1 and C_2 are coefficients that describe the temperature dependence of the relaxation process at temperatures above the reference temperature. For an undiluted polymer, when T_g is used as the reference temperature, C_1 is proportional to the inverse of the free volume of the system at T_g, while C_2 is the ratio of the free volume at T_g over the expansion coefficient of the free volume. The expansion coefficient of the free volume is the constant that describes the linear dependence, on ΔT above T_g, of the increase in free volume due to thermal expansion above T_g (i.e., the difference between the volumes of the rubbery liquid and glassy solid states). C_1 and C_2 are material-specific constants (i.e., not temperature-dependent) for an undiluted polymer, but, importantly, their numerical values vary with composition in the presence of a diluent (Ferry, 1980), such as water (Slade and Levine, 1988b, 1991a, 1993c; Lillie and Gosline, 1990; Nelson, 1993). C_1 and C_2 take on values of "universal constants" [17.44 and 51.6, respectively, as extracted from experimental data on many synthetic amorphous polymers (Williams *et al.*, 1955)] for well-behaved, diluent-free polymers (Slade and Levine, 1988b).

The WLF equation describes the kinetic nature of the glass transition and has been shown to be applicable to any glass-forming polymer, oligomer, or monomer (Ferry, 1980). The equation, with the same values of the "universal constants" (in most cases), has also been reported, especially recently (Table XB), to apply to experimental data (for viscosity, or other mechanical relaxation processes, as a function of temperature) for an ever-increasing variety of food materials and systems, including (1) molten glucose (Williams *et al.*, 1955); (2) concentrated solutions of mixed sugars (Soesanto and Williams, 1981); (3) ice cream and frozen desserts (Slade and Levine, 1985, Levine and Slade, 1989c); (4) amorphous glucose–water mixtures (Chan *et al.*, 1986); (5) hydrated elastin rubbers (Gosline, 1987); (6) American process cheese (Campanella *et al.*, 1987; Peleg, 1992); (7) concentrated, thermoset, aqueous gels of whey protein (Katsuta and Kinsella, 1990); (8) undercooled melts of fructose or glucose (Ollett and Parker, 1990); (9) amorphous lactose and sucrose powders at low moisture contents (Roos and Karel, 1990, 1991a,e, 1992; Shimada *et al.*, 1991; Levi and Karel, 1992a, 1993a,b; Nelson and Labuza, 1992a; Peleg, 1992); (10) freeze-concentrated solutions of fructose or glucose (Roos and Karel, 1991f); (11) supersaturated sucrose solutions (Roos and Karel, 1991g); (12) frozen solutions or low-moisture powders of maltodextrins (Lim and Reid, 1991, 1992; Reid, 1992a; Nelson and Labuza, 1992a, 1993); (13) frozen fruits and juices (Huang, 1992; Huang *et al.*, 1993); (14) dehydrated vegetables (Karmas *et al.*, 1992; Nelson and Labuza, 1992a; Karel *et al.*, 1993a); (15) gelatinized starch (Taylor *et al.*, 1992); and (16) bacterial spores (Sapru and Labuza, 1992a,b). Notably, Lillie and Gosline (1990) extended Gosline's (1987) work on rubbery elastin by showing that, over a range of water contents, the WLF coefficients, determined from elastic modulus data, had (nonuniversal) average values of $C_1 = 9.7$ and $C_2 = 28.8$. Similarly, Cocero and Kokini (1992) reported that the temperature dependence of shear viscosity data for water-plasticized glutenin above its T_g fits the WLF equation with $C_1 = 10.8$ and $C_2 = 40.2$. In a related vein, the issue of nonuniversal values of the WLF coefficients, as determined from experimental data, for various synthetic polymers and food systems has been discussed in several papers (Slade and Levine, 1988b, 1993c; Angell *et al.*, 1991, 1992; Buera and Karel, 1992; Huang, 1992; Nelson and Labuza, 1992a, 1993; Peleg, 1992; Huang *et al.*, 1993; Karel *et al.*, 1993a; Reid *et al.*, 1993b) and in notable depth, in the context of a detailed comparison of the applicability of WLF and Arrhenius kinetics to food systems, in the thesis by Nelson (1993). It is also notable that the WLF equation, with values of the coefficients dictated by experimental data, has been shown to correctly describe the kinetics of chemical degradation, of amorphous freeze-dried drug–excipient mixtures at low moisture contents, at storage temperatures 5°–30°C above T_g (Roy *et al.*, 1992).

The WLF equation defines mobility in terms of the non-Arrhenius temperature dependence of the rate of any diffusion-limited relaxation process occurring at a temperature T, compared to the rate of the relaxation at the reference temperature T_g, expressed in terms of how log η depends on ΔT, where $\Delta T = T - T_g$. The equation is valid in the temperature range of the rubbery or undercooled liquid state, where it is typically used to describe time-/temperature-dependent behavior of polymers (Roberts and White, 1973). The equation is based on the assumptions that polymer free volume increases linearly with increasing temperature above T_g, and that segmental or mobile-unit viscosity, in turn, decreases rapidly with increasing free volume (as illustrated implicitly in Fig. 1) (Ferry, 1980). Thus, the greater the ΔT, the faster a system is able to move (due to increased free volume and decreased mobile-unit viscosity); so the greater is the mobility, and the shorter is the relaxation time (Slade and Levine, 1988b; Lillie and Gosline, 1990).

In essence, the WLF equation and resulting master curve of log (η/η_g) versus $T - T_g$ (Williams *et al.*, 1955; Soesanto and Williams, 1981) represent a mobility transformation, described in terms of a time–temperature superposition (Slade and Levine, 1988b). Such WLF plots typically show a five orders-of-magnitude change in η [or in rates of other relaxation processes, such as diffusion (Ehlich and Sillescu, 1990; Karathanos *et al.*, 1991; Karel and Saguy, 1991; Roozen and Hemminga, 1991; Levi and Karel, 1992a, 1993b) or crystallization (Roos and Karel, 1990, 1991a,e, 1992; Shimada *et al.*, 1991; Levi and Karel, 1993b)] over a 20°C interval immediately above T_g (Franks, 1985; Lillie and Gosline, 1990), which is characteristic of WLF behavior in the rubbery fluid range (Slade and Levine, 1988b; Levine and Slade, 1989c; Noel *et al.*, 1990; Franks *et al.*, 1991; Roos and Karel, 1991g). For example, as demonstrated by Soesanto and Williams (1981), the effects of temperature and concentration on mobility of fluids above T_g can be combined to create a single master curve, which represents the WLF equation. The viscosity data shown in Fig. 11 were obtained for highly concentrated (> 90 w%) aqueous mixtures of sucrose and fructose. These results showed a five orders-of-magnitude change in η of concentrated sugar solutions, over a 20°C interval near T_g, a finding in excellent accord with the behavior predicted by the quantitative form of the WLF equation, with its "universal constants" of $C_1 = 17.44$ and $C_2 = 51.6$. These results constituted the first experimental demonstration that concentrated sugar solutions obey the WLF equation quantitatively as well as do synthetic high polymers. As

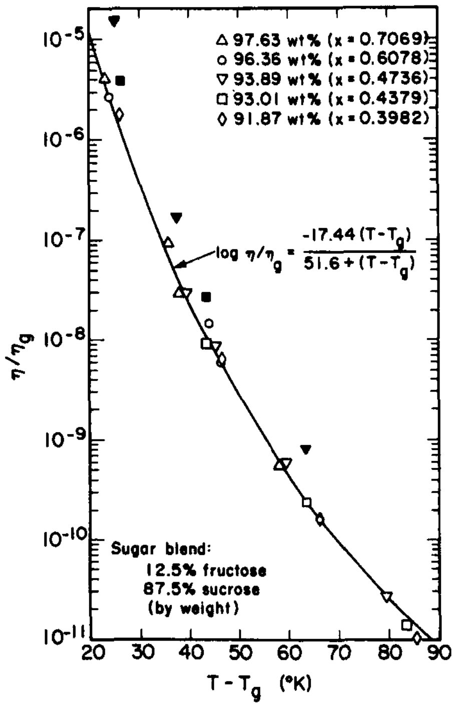

FIG. 11. Temperature dependence of viscosity for aqueous solutions of a 12.5:87.5 (w/w) fructose:sucrose blend, illustrating the fit of the data to the curve of the WLF equation. Reprinted with permission from Soesanto, T., and Williams, M. C. 1981. Volumetric interpretation of viscosity for concentrated and dilute sugar solutions. *J. Phys. Chem.* **85**, 3338–3341. Copyright 1981 American Chemical Society.

mentioned earlier, it had been shown decades before that viscosity data for a completely amorphous, diluent-free glucose melt fit the WLF equation with the same coefficients, and thus that glucose also behaves like a typical well-behaved synthetic polymer (Williams *et al.,* 1955; Matsuoka *et al.,* 1985). In a related vein, it has been confirmed experimentally that undercooled melts of diluent-free fructose or glucose exhibit a five orders-of-magnitude change in η over a 20°C interval above T_g (Noel *et al.,* 1990; Ollett and Parker, 1990), as predicted by the WLF equation. Similarly, as illustrated in Fig. 12, Roos and Karel (1990, 1991a,e, 1992; Shimada *et al.,* 1991) showed that the rates of crystallization of sucrose or lactose in completely amorphous powders at low moisture contents change by five orders of magnitude over a 20°C interval above T_g, in accord with the WLF, but not the Arrhenius, equation. Likewise, Levi and Karel (1992a, 1993a,b) showed that (1) the rate of diffusion of propanol in low-moisture sucrose rubbers increases by five orders of magnitude, and (2) the relaxation times for propanol release, crystallization, and collapse in anhydrous sugar matrices decrease by five orders of magnitude, from T_g to T_g + 20°C, and that their experimental data fit a curve of the WLF equation with its "universal" values for C_1 and C_2. It is also interesting to note that Le Meste and Huang (1991), in a TMA study of frozen sucrose solutions, found that for a 20 w% sucrose sample, softening and concomitant flow during heating were observed to be gradual in the temperature range −32°C (i.e., T_g') to −10°C, but above −10°C (i.e., 22°C above T_g), sample volume decreased much more rapidly as a consequence of compression, as expected, based on WLF kinetics (Slade and Levine, 1988b).

Description of the time-/temperature-dependent behavior of food systems by the WLF equation requires selection of the appropriate reference T_g for any particular glass-forming material [of any given MW and extent of plasticization (Williams *et al.,* 1955; Soesanto and Williams, 1981; Chan *et al.,* 1986)], be it T_g for a low-moisture system (with $W < W_g'$) or T_g' for a frozen system (with $W > W_g'$) (Levine and Slade, 1986, 1988b, 1989a; Roos and Karel, 1990, 1991a,d–g, 1992; Biliaderis, 1991b; Franks *et al.,* 1991; Shimada *et al.,* 1991; Slade and Levine, 1991a; Karmas *et al.,* 1992, 1993; Levi and Karel, 1992a, 1993a,b). For a typical, diluent-free polymer, T_g of the undercooled liquid is defined in terms of an iso-free volume state of limiting free volume (Ferry, 1980), and also, very approximately, as an iso-viscosity state somewhere in the range 10^9 to 10^{14} Pa s (Soesanto and Williams, 1981; Franks, 1982, 1989, 1990; Angell, 1988; Levine and Slade, 1988a; Simatos and Karel, 1988; Hofer *et al.,* 1989; Koide *et al.,* 1990; Ollett and Parker, 1990; Angell *et al.,* 1991, 1992; Slade and Levine, 1991a; Kalichevsky *et al.,* 1992b; Karel, 1992). This iso-viscosity state refers to local, not macroscopic, viscosity (Ferry, 1980), a fact that constitutes a

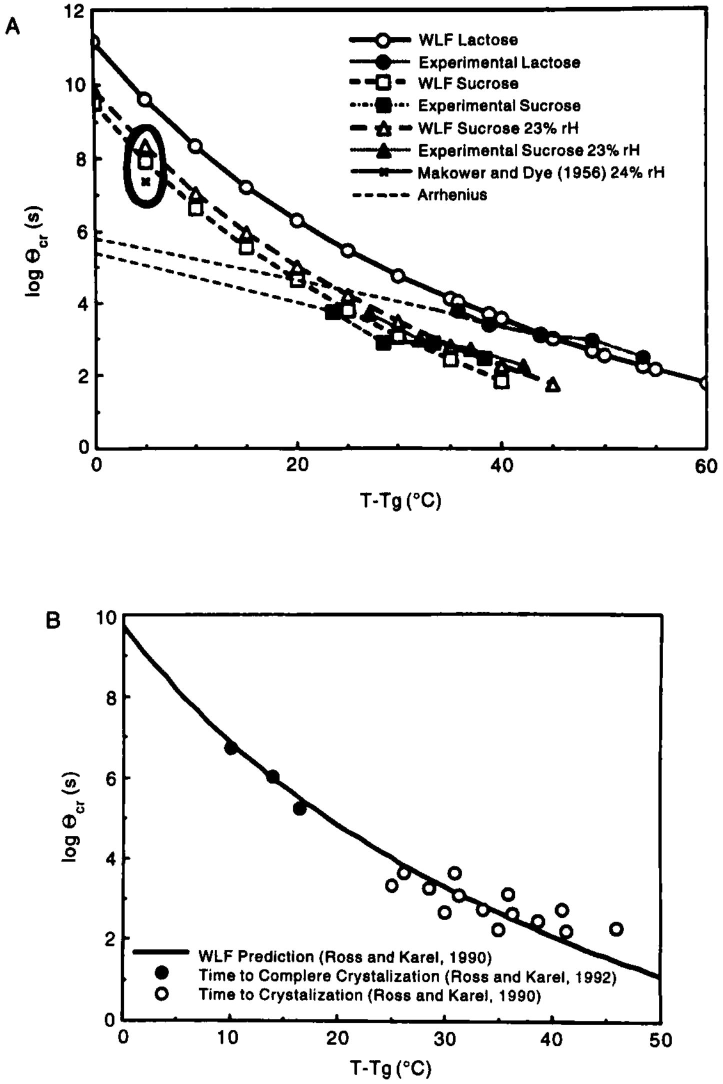

FIG. 12. WLF- versus Arrhenius-type temperature dependence of the crystallization time [expressed as log Θ_{cr} (s)], as a function of $\Delta T = T - T_g$, for (A) completely amorphous sucrose and lactose [adapted from Roos and Karel (1991a) with permission] and (B) completely amorphous lactose [adapted from Roos and Karel (1992) with permission] at low moisture contents.

critical conceptual distinction (Slade and Levine, 1988b), as explained later with regard to Fig. 14D.

a. Viscoelastic Behavior of Aqueous Food Polymer Systems. In the context of the utility of the WLF equation, the underlying basis of the principle of time–temperature superpositioning is the equivalence between time (or frequency) and temperature as they affect molecular relaxation processes that influence the viscoelastic behavior (i.e., the dual characteristics of viscous liquids and elastic solids) of polymeric materials and glass-forming small molecules (Ferry, 1980; Sichina, 1988; Lillie and Gosline, 1990; Mita, 1990). This principle is illustrated in Fig. 13 (Levine and Slade, 1989b), which shows a master curve of modulus as a function of temperature or frequency for a typical partially crystalline synthetic high polymer (Graessley, 1984). Figure 13 has been widely used to describe the viscoelastic behavior of such materials, as exemplified by molten starch during extrusion (Lai and Kokini, 1991) or by a kinetically metastable gelatin gel in an undercooled liquid state, in the context of WLF theory (Borchard *et al.,* 1980; Slade and Levine, 1987a). At $T > T_g$, gelatin gels manifest a characteristic rubberlike elasticity (Tomka *et al.,* 1975), due to the existence of a network of entangled, randomly coiled chains (Yannas, 1972). With increasing temperature, a gelatin gel traverses the five regions of viscoelastic

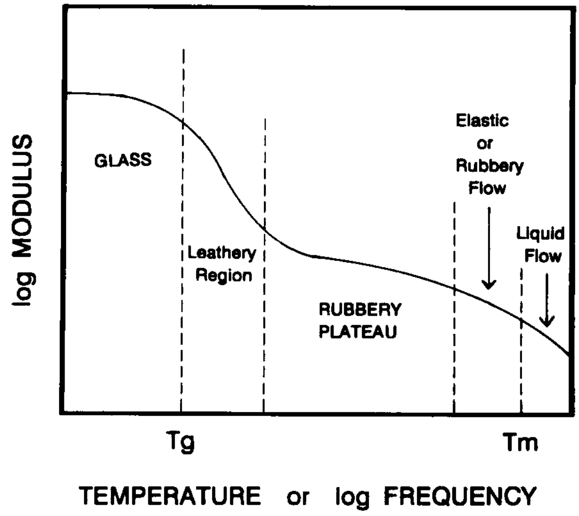

FIG. 13. Master curve of modulus as a function of temperature or frequency, illustrating the five regions of viscoelastic behavior characteristic of synthetic partially crystalline polymers. From Levine and Slade (1989b) with permission of Van Nostrand Reinhold/AVI.

behavior characteristic of synthetic partially crystalline polymers (Yannas, 1972), as illustrated in Fig. 13: (1) at $T < T_g$, vitrified glass; (2) at $T = T_g$, glass transition to leathery region, typically manifested as a three orders-of-magnitude decrease in modulus (Sperling, 1986); (3,4) at $T_g < T < T_m$, rubbery plateau to rubbery flow; and (5) at $T > T_m$, viscous liquid flow (Le Meste and Simatos, 1990; Le Meste *et al.*, 1992). It is interesting to note that at $T_g < T < T_m$, a gelatin gel is freely permeable to diffusion of dispersed dyes and molecules as large as hemoglobin (Slade *et al.*, 1989); only at $T < T_g$ is such dye diffusion greatly inhibited (Wesson *et al.*, 1982). In light of this fact, it is not at all surprising that the self-diffusion coefficient of water in a gelatin gel at $T > T_g$ has been shown to be close to that of water in bulk liquid water (Mel'nichenko *et al.*, 1993). Thus, the local viscosity inside the pores of a gelatin gel network, as measured by the diffusion of water [which shows Arrhenius kinetics (Mel'nichenko *et al.*, 1993) at an experimental temperature >150°C above water's molecular T_g], is essentially the same as that of bulk water.

The typical decrease in modulus (usually by ≈2–4 orders of magnitude) at the glass transition, illustrated in Fig. 13, has also been shown in similar plots of mechanical modulus data (as functions of either temperature or moisture content) recently reported for (1) completely amorphous, water-plasticized matrices of amylopectin and amylopectin–sugar mixtures (Kalichevsky *et al.*, 1992a,b), gluten and mixtures of gluten with sugars, lipids, emulsifiers, or salts (Kalichevsky *et al.*, 1992c,d), other proteins such as ovalbumin, gelatin, casein, and sodium caseinate (Kalichevsky *et al.*, 1993a,b), mixtures of casein or caseinate with sugars (Kalichevsky *et al.*, 1993b), and 1:1 mixtures of amylopectin, casein, and gluten, as well as other multicomponent biopolymer mixtures (Kalichevsky and Blanshard, 1992a,c); (2) extruded starch and starch–glucose mixtures (Noel *et al.*, 1990; Ollett *et al.*, 1991; Smith, 1990, 1992a); (3) dry amorphous dextran and pullulan (Scandola *et al.*, 1991); (4) water-plasticized films of amorphous carboxymethyl cellulose (Yano, 1993); (5) elastic networks of thermoset (via covalent crosslinking) gluten (Attenburrow *et al.*, 1990, 1992; Davies *et al.*, 1991); and (6) hydrated elastin rubbers (Gosline, 1987; Lillie and Gosline, 1990, 1993).

Le Meste *et al.* (1991a) used TMA to study flour-based food products and found that their viscoelastic properties, as functions of temperature and moisture content, correspond to those characteristic of the glassy state, the glass transition region, or the rubbery plateau. More recently, they published the first thermomechanical study of the glass transition in a complex food product, fresh white pan bread, and reported (Le Meste *et al.*, 1992) that the rigidity modulus drops by three orders of magnitude at T_g [i.e., $T_g' = -12°C$, as measured by TMA, for bread with moisture content > $W_g' = 25$–30 w%, in comparison to $T_g' = -5°C$, as measured by DSC (Levine and Slade, 1989b; Slade and Levine, 1991a)]. Those results on the glass transition in white bread were confirmed in follow-up work using DMA (Aynie *et al.*, 1992a,b), which also illustrated the plasticizing effect of water on Young's modulus. Colleagues of ours at Nabisco (Amemiya and Menjivar, 1992) recently reported the first measurements of the glass transition in commercial cookies and crackers. Their plots [see Fig. 5 in Slade and Levine (1993b)] of Young's modulus as a function of moisture content (fat-free dry solids basis), as measured by an Instron three-point-bend test done at room temperature, showed a room-temperature glass transition occurring at a moisture content coinciding with the point at which the modulus shows a sharp drop from its high value at the glassy plateau (Sperling, 1986), as illustrated in Fig. 13. Their results showed that the moisture content at the glass transition decreased from ≈10 w% for a lean cracker to < ≈5 w% for a high-sugar, wire-cut cookie (Slade and Levine, 1993b). Attenburrow and Davies (1993) reported similar results for Young's modulus (measured at room temperature) versus moisture content for another baked product, ice cream wafers, which showed a glass transition at ≈10 w% moisture. Also noteworthy is a report by Sauvageot and Blond (1991) of the effect of water plasticization on crispness of breakfast cereals, which included plots of sensory crispness versus moisture content [as well as RVP, which they called A_w] for two commercial grain-based products (Kellogg's Corn Flakes and Rice Krispies). These plots bear a striking resemblance to the portion of the curve in the glass–leathery–rubbery plateau region of Fig. 13, as well as to previously published plots of modulus versus moisture content for amorphous starch or starch–sugar mixtures (Noel *et al.*, 1990; Ollett *et al.*, 1991; Smith, 1990, 1992a; Kalichevsky *et al.*, 1992a,b). They appear to indicate an abrupt transition, occurring over a narrow range of moisture contents around 10%, from a glassy product of high crispness to a leathery/rubbery one of low crispness. Nevertheless, Sauvageot and Blond surprisingly did not point out the possible connection between the behavior they observed and an underlying glass transition in the water-plasticized products. In contrast, Kaletunc and Breslauer (1992) have reported a direct correlation between increasing sensory crispness and increasing T_g (measured by DSC) for low-moisture corn–flour extrudates, while Labuza and Nelson (1992), Lillford *et al.* (1992), Parker and Smith (1992), and Tolstoguzov (1992) have all described how the glass transition governs the texture (i.e., hard, brittle, crispy, and/or crunchy below T_g; soft, leathery, rubbery, and/or soggy above T_g) of various low-moisture, cereal-based materials and products, including extruded products. In a related vein, in an older report by Andrieu and Stamatopoulos (1986) on durum wheat pasta drying, a plot of Young's modulus (measured at

20°C) versus moisture content shows obvious evidence of a glass transition occurring at ≈16 w% moisture, which those authors discussed in terms of a change in the pasta's mechanical behavior from plastic to elastic type. It is also interesting to note the results reported by Ollett *et al.* (1993a,b) on the powder-compaction behavior measured at room temperature for hydrated native potato starch. These results appear to indicate a clearly observable change from glasslike to rubberlike response, at a moisture content (20 w%) coinciding with that at which Young's modulus, measured at room temperature, exhibits the characteristic drop indicative of the glass transition of completely amorphous starch– or amylopectin–water mixtures (Ollett *et al.*, 1991; Kalichevsky *et al.*, 1992a).

From modulus results for starch-, gluten-, and other protein- and polysaccharide-based systems (Attenburrow *et al.*, 1990; Lillie and Gosline, 1990, 1993; Noel *et al.*, 1990; Smith, 1990, 1992a; Davies *et al.*, 1991; Ollett *et al.*, 1991; Scandola *et al.*, 1991; Gontard *et al.*, 1992b; Kalichevsky and Blanshard, 1992a,b; Kalichevsky *et al.*, 1992a–d, 1993a,b; Attenburrow and Davies, 1993; Yano, 1993), it can be seen that the decrement in modulus from below T_g to above T_g for an aqueous glass of a compatible water–solute blend is not identical to the decrement in modulus for a neat glass of the same solute. No explanation for this observation has previously been given; we offer a possible one here.

When the distribution of water is spatially homogenous in the amorphous regions of a compatible aqueous blend, and the water content is less than W_g', then all of the water functions as plasticizing water, so that the T_g of the blend is intermediate between the lower T_g of pure water and the higher (molecular or segmental) T_g of the solute (Slade and Levine, 1991a). (A binary blend is considered here, to avoid complications due to the order of addition of components to the blend.) Addition of water as a plasticizer has a predictable effect on the *kinetics* of the primary mechanical relaxations of the blend, compared to those of the neat solute. That is, the characteristic decrement in modulus, as the temperature passes from below to above T_g during an experimental temperature sweep, would be observed to occur at lower and lower temperatures for aqueous blends with increasing water content than for the neat solute (Cocero and Kokini, 1991; Scandola *et al.*, 1991; Aynie *et al.*, 1992a; de Graaf *et al.*, 1992; Gontard *et al.*, 1992b; Kalichevsky and Blanshard, 1992a; Kalichevsky *et al.*, 1992c, 1993a; Lillie and Gosline, 1993). In this context, the term "plasticization" refers unambiguously to "depression of the T_g of a compatible blend, relative to the T_g of the undiluted solute," i.e., a kinetic process (Sears and Darby, 1982). Alternatively, at a constant experimental temperature, an inflection point in the decreasing modulus of the sample would be observed as the sample moisture content is increased (Andrieu and Stamatopoulos, 1986; Gosline, 1987; Attenburrow *et al.*, 1990; Lillie and Gosline, 1990, 1993; Smith, 1990, 1992a,c; Davies *et al.*, 1991; Ollett *et al.*, 1991; Amemiya and Menjivar, 1992; Kalichevsky and Blanshard, 1992b; Kalichevsky *et al.*, 1992a–d, 1993b; Attenburrow and Davies, 1993; Yano, 1993). In this case, the term "plasticization" could refer ambiguously either to the kinetic effect of altering the temperature difference between the experimental temperature and the depressed T_g of the blend relative to the undiluted solute (Slade and Levine, 1991a) or to a mechanical softening effect. The ambiguity arises from the fact that the mechanical softening may be solely an indirect reflection of the kinetic effect, or it may represent an additional direct mechanical effect independent of the kinetic effect of the plasticizer to depress the T_g of the solute–water blend below the T_g of the undiluted solute, and thereby change the relationship between the experimental temperature and the instantaneous T_g of the sample. Indeed, the kinetic effect of a plasticizer to depress T_g (the α or primary relaxation of the backbone of a polymer or molecular relaxation of a monomer) may be accompanied by either a plasticizing or antiplasticizing effect on T_β (the β or secondary, sub-T_g, relaxations) (Levine and Slade, 1988a), as is suggested by the tan δ curves reported for carboxymethyl cellulose (Yano, 1993), dextran, amylose, and pullulan (Scandola *et al.*, 1991). As a result, even in the glassy state, water may serve to decrease *or* increase the modulus of the glassy aqueous blend, relative to the modulus of the undiluted glass.

A thought experiment, to help clarify the distinction between the kinetic effect of depression of T_g by water as a plasticizer and the mechanical effect on the absolute modulus observed at a particular temperature for a particular composition of an aqueous blend, is as follows. Part I of the experiment would demonstrate the ambiguous dual aspects of plasticization by water. At a constant experimental temperature, typically room temperature for convenience, the modulus of an undiluted solute in the glassy state would be compared to the moduli of a series of aqueous blends, prepared so that the distribution of water would be spatially homogeneous throughout the sample (thought experiments allow such a luxurious criterion). Alternative conventions would define a value of W_g corresponding to T_g = room temperature as the water content at the onset or at the inflection of the decreasing modulus profile.

Part II of the experiment would demonstrate unambiguously the independent mechanical aspect of plasticization by water. The absolute modulus of each sample in the series would be measured at an experimental temperature below the respective T_g of each sample and at a series of equivalent temperature increments above the respective T_g of each sample. The maximum water content in any sample should be less than W_g', so that the modulus of ice would not be convoluted with that of a glassy matrix at any experimental temperature in a practical time frame. The absolute values of the glassy modulus below the respective T_g and of the rubbery modulus at each equivalent temperature increment above T_g of each sample in the series, with water content in the range 0% to $W_g < W_g'$, would reflect the *mechanical* aspect of water as a plasticizer or antiplasticizer of the solute. At each equivalent temperature, relative to the respective values of T_g, the moduli of the aqueous blends might be the same, or larger, or smaller than that of the undiluted parent sample, independent of the kinetic effect of water as a plasticizer that actually determines those respective values of T_g. Although the typical decrement in modulus between the glass below T_g and the deformable rubber above T_g of the undiluted solute would be ≈3 orders of magnitude (Sperling, 1986), the corresponding decrement for the aqueous blends could be the same, or larger, or smaller than three orders of magnitude. For starch or gluten blends with water, the decrement is often smaller than 3 log units (Andrieu and Stamatopoulos, 1986, Noel *et al.*, 1990; Smith, 1990, 1992a,c; Cocero and Kokini, 1991; Davies *et al.*, 1991; Ollett *et al.*, 1991; Attenburrow *et al.*, 1992; Aynie *et al.*, 1992a; Gontard *et al.*, 1992b; Kalichevsky and Blanshard, 1992a,b; Kalichevsky *et al.*, 1992a–d, 1993a; Attenburrow and Davies, 1993). This might be due to the role of network crosslinking (Ollett *et al.*, 1991; Kalichevsky *et al.*, 1993a) and resultant network T_g (Levine and Slade, 1989b) in these cases, e.g., for thermoset gluten, the amorphous glutenin network formed by covalent crosslinking via intermolecular disulfide bonding (Schofield *et al.*, 1984; Slade *et al.*, 1989; Kalichevsky *et al.*, 1993a), and for gelatinized/retrograded starch, the partially crystalline amylopectin network formed by a combination of interchain entanglements in the amorphous regions and hydrogen-bonded junction zones comprising the microcrystalline regions (Slade, 1984; Miles *et al.*, 1985b; Slade and Levine, 1987b; Smith, 1990, 1992a; Ollett *et al.*, 1991).

Part III of the experiment would demonstrate the unambiguous kinetic aspect of plasticization by water. The interpolated temperature location at the onset or at the inflection of the decrement in modulus, determined from the quantized temperature sweep of part II of the experiment (or from a judicious continuous temperature sweep experiment, recognizing that use of a constant heating rate results in a variable, increasing value of t/τ as the temperature increases above the respective T_g of the blend), for each sample of the series, would define the kinetic effect of water as a plasticizer to depress the T_g of the undiluted solute to the respective T_g values of the aqueous blends.

2. *Comparison of WLF and Arrhenius Behavior*

The WLF equation is not intended for use much below T_g (i.e., in the glassy solid state) or in the very low viscosity liquid state [$\eta < 10$ Pa s

(Soesanto and Williams, 1981)], typically 100°C or more above T_g, where Arrhenius kinetics apply (Roberts and White, 1973; Johari, 1976; Nielsen, 1977; Ferry, 1980; Robertson, 1985; Levine and Slade, 1988a; Ehlich and Sillescu, 1990; Chang and Baust, 1991c; Franks *et al.,* 1991; Gray, 1991; Karathanos *et al.,* 1991; Noel *et al.,* 1991; Scandola *et al.,* 1991). For partially crystalline polymers, the breadth of the temperature range of the rubbery domain of WLF behavior corresponds to the temperature interval between T_g and T_m (Wunderlich, 1976; Ferry, 1980), as illustrated in Fig. 1. Cheng (1989) noted that the size of this temperature interval between T_g and T_m may be as much as several hundred degrees for synthetic high polymers. We reported an analysis of the variation of the size of this temperature interval with the T_m/T_g ratio of representational synthetic polymers and glass-forming, low-MW carbohydrates (Slade and Levine, 1988b). The study compared the WLF behavior of kinetically metastable carbohydrate–water systems to the corresponding knowledge base for synthetic polymers. According to the conventional description, a typical well-behaved synthetic high polymer (e.g., a representational elastomer) would manifest its T_g around 200 K in the completely amorphous state, and its T_m around 300 K in the completely crystalline state (Wunderlich, 1980), so that the ratio of T_m for the pure crystalline material to T_g for the completely amorphous material is ≈ 1.5 (or $T_g/T_m \approx 0.67$) (Brydson, 1972; Wunderlich, 1990). Such a polymer would also have a local viscosity of $\approx 10^{12}$ Pa s and a free volume fraction of $\approx 2.5\%$ at T_g (Ferry, 1980). For this typical well-behaved polymer, WLF kinetics are considered to be operative in a temperature range about from T_g to T_g +100°C (Williams *et al.,* 1955). It can be seen that this operational definition is related to the typical T_m/T_g ratio of 1.5, since in such a case, the difference in temperature between T_g and T_m would be $\approx$100°C. Figure 14A (Slade and Levine, 1988b) illustrates this conventional description of the relaxation behavior of a typical well-behaved polymer [e.g., the classic model, Hevea rubber (Brydson, 1972; Ferry, 1980; Sperling, 1986), or polyvinyl acetate (Johnson *et al.,* 1980; Matsuoka *et al.,* 1985)], which would obey the standard form of the WLF equation with coefficients $C_1 = 17.44$, and $C_2 = 51.6$. In this plot of log a_T versus ΔT [where a_T = WLF shift factor, expressed as relative relaxation times (Ferry, 1980)], relaxation time progresses from WLF behavior very near T_g to Arrhenius behavior at $\approx$100°C above T_g. Within this temperature range, where technological process control would be expected, relaxation times for WLF behavior near T_g would change by a factor of 10 for every 3°C change in temperature. In contrast, for Arrhenius behavior with familiar $Q_{10} = 2$ kinetics above T_m, a factor-of-10 change in relaxation time would require a 33°C change in temperature (Slade and Levine, 1988b).

A second class of amorphous polymers was described as typical but not well behaved (Slade and Levine, 1988b), in the sense that they are readily

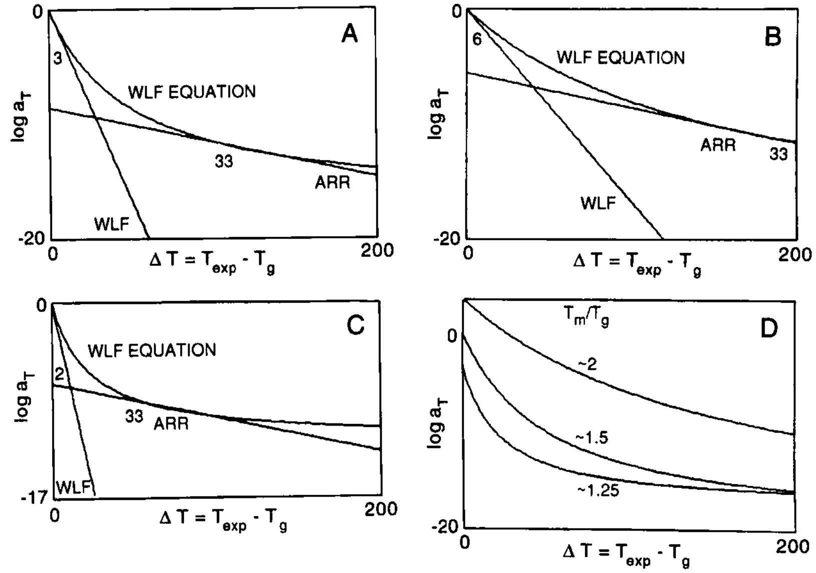

FIG. 14. WLF plots of the time–temperature scaling parameter (WLF shift factor, expressed as relative relaxation times), a_T, as a function of the temperature differential above the reference state, T_g, with the limiting regions of low and high ΔT defined by the WLF and Arrhenius kinetic equations, respectively. The curves of the WLF equation (with coefficients C_1 and C_2 as noted) illustrate the temperature dependence of the relaxation time behavior for hypothetical polymers with T_m/T_g ratios of (A) 1.5 (C_1 = 17.44, C_2 = 51.6); (B) 2.0 (C_1 = 26.4, C_2 = 154.8); (C) 1.25 (C_1 = 10.8, C_2 = 23.3); (D) 2.0, 1.5, and 1.25. From Slade and Levine (1988b) with permission.

crystallizable (Brydson, 1972; Haward, 1973; Ferry, 1980; Wunderlich, 1980) and thus have a decreased glass-forming tendency (Murthy *et al.,* 1993). Highly symmetrical polymers such as poly(vinylidene chloride) and poly(vinyl cyclohexane), which manifest crystalline melting enthalpies of ≈170 J/g, fit this class (Wunderlich, 1980). For such polymers, the T_m/T_g ratio is frequently ≫ 1.5, so the temperature range between T_g and T_m is ≫ 100°C. Different WLF coefficients would be required to describe their relaxation profile, as illustrated by the plot in Fig. 14B drawn for a hypothetical case where $C_1 = 26.4$ and $C_2 = 154.8$. For a representational case of T_g ≈200 K (with $\eta_g > 10^{12}$ Pa s and/or free volume fraction < 2.5%) and $T_m/T_g \approx 2$ ($T_g/T_m \approx 0.5$), T_m would be ≈400 K. Thus, there would be a region of ≈200°C in which relaxation times would change from WLF behavior near T_g (in this schematic case, by a factor of 10 for every 6°C) to Arrhenius behavior near T_m (by a factor of 10 for every 33°C) (Slade and Levine, 1988b). A notable example of a material with $T_m/T_g \approx 2$ is water (Soesanto and Williams, 1981; Wunderlich, 1990). It is also interesting to note a recent report by Lomellini (1992) that both polystyrene and polycarbonate exhibit WLF behavior, with regard to their melt viscoelastic data, over a surprisingly large temperature range from T_g to about T_g + 185°C. Like synthetic polymers in this class, low-MW carbohydrates with high T_m/T_g ratios are reported to have high values of crystalline melting enthalpy and to crystallize readily (Roos, 1992a).

A third class of polymers, often characterized by highly unsymmetrical structures, was described as atypical and poorly behaved (Slade and Levine, 1988b), in that T_g is near T_m (Brydson, 1972; Wunderlich, 1980). Murthy *et al.* (1993) have reported a correlation between decreasing T_m/T_g and increasing glass-forming tendency. For such polymers, with $T_m/T_g \ll 1.5$ (e.g., ≈ 1.25, or $T_g/T_m \approx 0.8$), a quantitatively different form of the WLF equation would be required to describe their relaxation profile. For a representational polymer in this class, as illustrated in Fig. 14C, using a hypothetical case where $C_1 = 10.8$ and $C_2 = 23.3$, $T_g \approx 200$ K (with $\eta_g \ll 10^{12}$ Pa s and/or free volume fraction $\gg 2.5\%$) and $T_m \approx 250$ K. Thus, the temperature range in which WLF kinetics would be operative is much smaller than usual. Relaxation times would change from WLF behavior near T_g (in this case, by a factor of 10 for every 2°C) to Arrhenius behavior above T_m (by a factor of 10 for every 33°C) over a region of only ≈50°C (Slade and Levine, 1988b). The synthetic polymer cited as the classic example of this behavior, which was attributed to anomalously large free volume and high mobility at T_g, is bisphenol polycarbonate, with $T_m/T_g \approx 1.18$ (Brydson, 1972; Ehlich and Sillescu, 1990). Another important example of this case, with $T_m/T_g \approx 1.25$, is poly(dimethyl siloxane), which was singled out (Ferry, 1980) for its anomalously high mobility, manifested as anomalously low local effective viscosity (Slade and Levine, 1988b). This category of behavior was also reported (Levine and Slade, 1988a, 1989a) to be exemplified by food materials such as gelatin and native starch (due to nonuniform distribution of moisture in amorphous and crystalline regions of these high polymers at low moisture), as well as the sugars fructose and galactose (due to an anomalously large requirement for rotational free volume of these anhydrous monosaccharides and concomitantly large availability of translational free volume at a given extent of rotational mobility) (Slade and Levine, 1988b).

The three types of behavior exemplified in Figs. 14A–C, in which the T_m/T_g ratio is either the typical value of 1.5, or much greater, or much less, were compared, in order to examine how the respective relaxation profiles change in the temperature interval between T_m and T_g for representational, diluent-free polymers with a common value of T_g (Slade and Levine, 1988b). As illustrated in Fig. 14D, this analysis revealed the critical significance of the T_m/T_g ratio for any given glass-forming polymer. For sufficiently similar values of T_g, either different values of the ratio, T_m/T_g, or the difference, $T_m - T_g$, for different polymers (e.g., food carbohydrates) can be used as an inherent normalizing parameter to compare relative mobilities at T_g and at $T \gg T_g$. The greater the value of T_m/T_g or $T_m - T_g$, the greater is the inherent rigidity of the material at its T_g, and the more constrained is its mobility at any given ΔT above its T_g. The case of polymers with similar values of T_g is illustrated by a comparison of the local translational mobility of Hevea rubber and polyisobutylene (Ferry, 1980) at an experimental temperature 100 K above their respective values of T_g ($T_g = 200$ K for Hevea rubber, 202 K for polyisobutylene). The local viscosity in Hevea rubber was more than two orders of magnitude lower than that in polyisobutylene (Ferry, 1980), and either the smaller ratio of T_m/T_g (1.49 for Hevea rubber, 1.57 for polyisobutylene) or the smaller difference of $T_m - T_g$ (98 K for Hevea rubber, 115 K for polyisobutylene) served to predict the greater mobility in Hevea rubber (Slade and Levine, 1988b). However, for dissimilar values of T_g, the ratio T_m/T_g, is still a predictive normalizing parameter for relative mobilities, but the difference, $T_m - T_g$, may no longer be predictive. This case of polymers with dissimilar values of T_g is illustrated (Ferry, 1980) by a comparison of the local translational mobility of polystyrene and polyisobutylene at an experimental temperature 100 K above their respective values of T_g ($T_g = 373$ K for polystyrene). The local viscosity in polystyrene was even lower than that in Hevea rubber, which could be successfully predicted by the even smaller value of T_m/T_g (1.37 for polystyrene), but not by the value, even greater than that of polyisobutylene, of $T_m - T_g$ (138 K for polystyrene) (Slade and Levine, 1988b). In Fig. 14D, the behavior of log a_T versus ΔT is compared for different values of T_m/T_g (i.e., ≈2, 1.5, and 1.25), to determine how mobility varies in the kinetically constrained regions of this mobility transformation map. At $T \gg T_g$, the overall free volume for different polymers may be similar (Ferry, 1980), yet individual free volume requirements for equivalent mobility may differ significantly, as reflected in the T_m/T_g ratio. Anisotropy in either rotational mobility [which depends primarily on free volume (Ferry, 1980)] or translational mobility [which depends primarily on local viscosity, as well as free volume (Ferry, 1980)] may be the key determinant of a particular polymer's relaxation behavior.

In the context of discussing the comparison between WLF and Arrhenius behavior, it is interesting to note the connection between the analysis illustrated in Fig. 14 and Angell's framework for classifying the behavior of glass-forming liquids (including synthetic amorphous polymers and organic and inorganic liquids) as either "strong" or "fragile" (Angell, 1988; Murthy, 1989; Angell *et al.*, 1991, 1992). The potential for useful insights resulting from application of Angell's classification scheme for glass-forming liquids to the behavior of glass-forming food materials (e.g., sugars and polyols), with regard to stability against translational diffusion-limited relaxation processes such as crystallization, was first mentioned by Noel *et al.* (1990, 1991) and subsequently discussed in depth by Angell, himself (Angell *et al.*, 1992). According to Angell's terminology, "strong" liquids (exemplified by the network glass former, SiO_2) are those with (1) a three-dimensional structural network of bonds; (2) resistance of the short-range order of the glassy structure to thermal disruption on heating to $T > T_g$; (3) Arrhenius or almost-Arrhenius relaxation behavior (e.g., linear dependence of log η on $1/T$) at $T > T_g$ (as well as $T < T_g$); (4) approximately constant $\eta_g \approx 10^{12}$ Pa s at T_g [i.e., the glass transition is an iso-viscous phenomenon only for "strong" liquids (Angell *et al.*, 1991)]; and (5) generally, a small or even undetectable increase in C_p at T_g. In contrast, "fragile" liquids [exemplified by molecular (e.g., terphenyl) and ionic (e.g., aqueous solutions of LiCl) glass formers] are those with (1) no three-dimensional structural network of bonds; (2) loss of the short-range order of the glassy structure, accompanying the thermal transition at T_g; (3) an increasingly exaggerated departure from Arrhenius relaxation behavior at $T > T_g$; (4) variable η_g at T_g (η_g decreases from $\approx 10^{12}$ Pa s for "strong" liquids to as low as $\approx 10^{9}$ Pa s for the most "fragile" liquids) [i.e., the glass transition is *not* an iso-viscous phenomenon for "fragile" liquids (Angell *et al.*, 1991)]; and (5) generally, a large increase in C_p (as much as a doubling of the glassy-state C_p in some cases) at T_g. Angell has illustrated the contrasting relaxation behavior of "strong" and "fragile" glass-forming liquids by means of so-called "T_g-scaled Arrhenius plots" of log η or log(segmental relaxation time, τ) versus T_g/T, referred to as "fragility plots" or "'strong-to-fragile' patterns" (Angell, 1988; Angell *et al.*, 1991, 1992). Others have used similar "T_g-scaled Arrhenius plots" of log η versus $\log(T - T_g)$ (Murthy, 1989) or log τ versus T_g/T (Ngai and Roland, 1993) or log a_T versus T_g/T (Roland and Ngai, 1992) as alternative representations of Angell's "fragility plots." Roland and Ngai (1992) prefer to call theirs "cooperativity plots," since the synthetic amorphous polymers they have discussed do not undergo any modification of structure at the glass transition.

There is a revealing analogy between Angell's "fragility plot" and the WLF plot in Fig. 14D, both of which are normalized to T_g as the reference state. The upper curve in Fig. 14D (taken from Fig. 14B) corresponds to that of a "strong" liquid, while the lower curve in Fig. 14D (taken from Fig. 14C) corresponds to that of a "fragile" liquid. Moreover, just as the curves in Fig. 14D intersect the left-hand ordinate (at $T = T_g$) at different values of log a_T, so too do Angell's "fragility curves" not all pass through the same point (in terms of log η or log τ) at $T_g/T = 1$ (Angell *et al.*, 1991, 1992), thus demonstrating that the glass transition is rigorously neither an iso-viscous (Murthy, 1989) nor an iso-relaxation time phenomenon for all glass-forming liquids. Let's explore the basis of the analogy, in an effort to glean further insights. Angell has described the "strong"-to-"fragile" pattern of increasing deviations from Arrhenius-type behavior (with its mild dependence of η on temperature), using the Vogel–Tammann–Fulcher (VTF) form of the dependence of η on temperature,

$$\eta = \eta_0 \exp (DT_0/[T - T_0]), \tag{3}$$

with D as the only variable (Angell *et al.,* 1992). "Strong" liquids are those with large values of D, while "fragile" liquids, with small values of D, are those that show a much greater dependence of η on temperature at $T > T_g$. Angell noted that (1) the VTF and WLF equations have identical mathematical forms and so are interconvertible; (2) for the entire spectrum of glass-forming liquids, including synthetic polymers, existence of a range of D values in the VTF equation implies a range of values for the WLF constant, C_2, rather than one universal value; (3) the values of D in the VTF equation and C_1 in the WLF equation are numerically proportional; and (4) the WLF constant, C_2, is numerically identical to $T_g - T_0$, where T_g is the WLF reference temperature and T_0 is a constant from the VTF equation (Angell *et al.,* 1991, 1992). Therefore, "strong" liquids, with large values of D, are those with large values of C_1 (i.e., larger than the "universal" value of 17.44, e.g., the polymer represented in Fig. 14B, with $C_1 = 26.4$), while "fragile" liquids, with small values of D, are those with small values of C_1 (i.e., smaller than the "universal" value of 17.44, e.g., the polymer represented in Fig. 14C, with $C_1 = 10.8$). For glass-forming liquids that are also crystallizable, such as the representational polymers described with regard to Fig. 14, it follows that Angell's classification of "strong" corresponds to those liquids with values of T_m/T_g ratios $\gg 1.5$ (see, e.g., the top curve in Fig. 14D), his description of "fragile" corresponds to those liquids with $T_m/T_g \ll 1.5$ (see, e.g., the bottom curve in Fig. 14D), while liquids with intermediate "strong–fragile" behavior should be those with $T_m/T_g \approx 1.5$ (see, e.g., the middle curve in Fig. 14D).

The synthetic polymers mentioned by Angell as being known to be most "strong" [polyisobutylene (PIB)] and most "fragile" [bisphenol polycarbonate (BPPC), poly(dimethyl siloxane) (PDMS)] in their relaxation behavior (Angell *et al.,* 1991, 1992) are the same ones that were noted for their extraordinarily high or low T_m/T_g values (PIB, 1.57; BPPC, 1.18; PDMS, 1.25), in the context of Fig. 14. Hevea rubber and polyvinyl acetate are synthetic polymers with $T_m/T_g \approx 1.50$ (Ferry, 1980), which would be expected to show intermediate "strong–fragile" behavior. With regard to glass-forming food materials (e.g., low-MW carbohydrates), glycerol has an extraordinarily high value of $T_m/T_g = 1.62$ (Slade and Levine, 1991a), and Angell noted that it has a large *D*, commensurate with "strong" behavior of this hydrogen-bonded liquid (Angell *et al.*, 1992). Angell also remarked that the behavior of glassy water near its T_g (−137°C) appears to be that of a very "strong" liquid (Angell *et al.*, 1992). This is particularly noteworthy, since water has the highest known T_m/T_g value of 2.0 (Wunderlich, 1990), as mentioned earlier with regard to Fig. 14B. In contrast to such "strong" hydrogen-bonded liquids as glycerol and water, with T_m/T_g values $\gg 1.5$, other hydrogen-bonded liquids, including sorbitol and sugars such as glucose, fructose, maltose, and sucrose, all of which have T_m/T_g values ≤ 1.43 (Slade and Levine, 1991a) and values of η_g at T_g significantly less than 10^{12} Pa s (Angell *et al.*, 1992), have been classified as somewhat "fragile" (Noel *et al.*, 1990; Angell *et al.*, 1992). As mentioned earlier and noted elsewhere in various contexts by many workers (Williams *et al.*, 1955; Soesanto and Williams, 1981; Slade and Levine, 1988b; Noel *et al.*, 1990; Ollett and Parker, 1990; Roos and Karel, 1991g), one manifestation of the relaxation behavior (WLF-type) of liquids as "fragile" as glucose, fructose, and sucrose (in the form of either anhydrous melts or highly concentrated aqueous solutions) is a drop in viscosity of five orders of magnitude over the 20°C interval immediately above T_g. Consequently, as T_g is approached from above in this temperature region, the rate of translational diffusion, and thus of diffusion-limited processes such as crystallization that cause time-dependent changes in the quality of foods, will be greatly reduced (Slade and Levine, 1988b; Noel *et al.*, 1990). Noel *et al.* (1990) have stated that "for 'fragile' liquids, small differences in storage temperature in the vicinity of T_g will have dramatic effects on stability and will determine whether a material is stable for ten days or for hundreds of days. . . . The classification of 'strong' and 'fragile' behavior on the basis of the dependence of liquid viscosity on temperature can give useful insights into stability with respect to crystallization." Further insight results from the recognition that, for glass-forming liquids that can crystallize, "fragility" evidently increases with decreasing value of T_m/T_g, whereas "strength" appears to increase with increasing value of T_m/T_g.

The relaxation phenomena manifested at T_g represent thermomechanical or electrical properties controlled by the local small-molecule or segmental, rather than macroscopic, environment of a polymer, because the molecular glass transition is a cooperative transition (Roberts and White, 1973; Wunderlich, 1981; Angell, 1988; Cheng, 1989) resulting from concerted constraints on both translational and rotational mobility. On cooling a viscous fluid of relatively symmetrical mobile units with relatively isotropic mobility, translational motions would be expected to be "locked in" at a higher temperature before rotational motions, because of the slower structural relaxations associated with larger-scale translational diffusion (Slade and Levine, 1988b). In this case, cooperative constraints of local viscosity and free volume on translational diffusion determine the temperature at which the glass transition is manifested, as a dramatic increase in relaxation times compared to the experimental time frame. However, in the case of motional anisotropy, molecular asymmetry has a much greater effect on rotational than translational diffusion, so rotational motions could be "locked in" before translational motions as the temperature is lowered (Slade and Levine, 1988b).

As revealed by Fig. 14D, a very small T_m/T_g ratio (i.e., close to 1.0) is accounted for by an anomalously large free volume requirement for rotational diffusion (Brydson, 1972). When the free volume requirement is so large, a glass transition (i.e., vitrification of the viscous liquid) on cooling can actually occur even when the local viscosity of the system is relatively low (Slade and Levine, 1988b). Thus, instead of the typical "firmness" for a glass ($\approx 10^{12}$ Pa s), such a glass (e.g., of bisphenol polycarbonate, or anhydrous fructose or galactose, or any other "fragile" liquid) may manifest a $\eta_g \ll 10^{12}$ Pa s (Soesanto and Williams, 1981; Angell, 1988; Levine and Slade, 1988a; Slade and Levine 1988a; Angell *et al.*, 1992). In such a glass, the time constant for translational diffusion may be anomalously small, indicative of high translational mobility. In contrast, in the glass of a typical well-behaved polymer, the time constant for translational diffusion would be greater than that for rotational diffusion, so an increase in local viscosity would be concomitant with a decrease in free volume (Slade and Levine, 1988b). The above analysis pointed out the critical significance of anomalously low values of T_m/T_g (for the dry solute) close to 1.0 on the mobility, resultant relaxation behavior, and consequent technological process control for nonequilibrium food polymer systems (in the *presence* of water) in their supraglassy fluid state well above T_g (Slade and Levine, 1988b), in terms of the WLF kinetics of various translational diffusion-limited, mechanical/structural relaxation processes, such as gelatinization, annealing, and recrystallization of starch (Slade and Levine, 1988c; Biliaderis, 1991b).

Interestingly, Ollett and Parker (1990) have reported a measured value of $\eta = 4.5$ Pa s [reported as $10^{4.5}$ Pa s by Noel *et al.* (1990)] for a fructose melt at 100°C. This temperature was selected for discussion, because it represents the higher of the two values of T_g measured by DSC for undiluted, amorphous fructose as 11° and 100°C (Slade and Levine, 1988b) and as 13° and 100°C (Finegold *et al.*, 1989), not 30° and 100°C as stated by Ollett and Parker (1990) and Noel *et al.* (1990), who took the low value of viscosity at 100°C to mean that the DSC transition at 100°C could not be a glass transition. The dismissal of the higher-temperature DSC transition as a glass transition appeared to be supported by the fact that similar values of 10° and 13°C for T_g of fructose were obtained by analysis of the temperature dependence of their η data according to the VTF and WLF equations, respectively. However, Ollett and Parker measured shear viscosity (i.e., related to translational mobility), and we hypothesized that the constraint at 100°C relates to rotational restraint to reorientation, in a way in which fructose and galactose have been suggested to be anomalous (Slade and Levine, 1988b). It would be expected, when cooperative relaxations are overwhelmingly predominated by translational constraints, so that a measurement of shear viscosity or translational diffusion can be used to characterize the plasticizing effect of temperature, time, or diluent on mobility (Slade and Levine, 1991a), that the WLF equation, which describes the influence of both translational and rotational constraints on relaxations, would be equivalent to the VTF equation that describes the temperature dependence of viscosity (Ferry, 1980; Angell *et al.,* 1992). In fact, as mentioned earlier, the VTF parameters, D and T_0, can then be redefined directly in terms of the WLF coefficients, C_1 and C_2. In contrast, when relaxations are predominated by rotational constraints or depend on both rotational (primarily limited by free volume) and translational (primarily limited by local viscosity) mobility, then analysis of measurements of shear viscosity by the VTF equation, as a means to estimate the value of T_g, would not be expected to match values of T_g obtained from analysis of measurements of C_p (by DSC) or dielectric loss according to the WLF equation (Ferry, 1980). The change in C_p at the glass transition reflects the change in the expansion coefficient of free volume from that of the glass to that of the undercooled liquid (Wunderlich, 1981, 1990), such that an anomalous requirement of free volume for cooperative, asymmetrical rotations could result in the observation by DSC of an anomalously elevated value of T_g, at a temperature where the measured value of local viscosity [e.g., shear viscosity of sufficiently small molecules, to avoid the complication that would be caused by the presence of entanglement networks (Ferry, 1980)] would be anomalously depressed. Similarly, observation of dielectric relaxations, which reflect the combined extent of cooperative rotational constraints and the effects of local viscosity on reorientation of dipoles (Sears and Darby, 1982), would not necessarily provide the same estimation of T_g as a measurement of shear viscosity alone.

Angell has recently suggested an alternative explanation (Angell *et al.,* 1992) for the high-temperature glasslike transition exhibited by a melt of β-D-fructose, which he too has observed at 100°C by DSC (personal communication, 1993). This explanation is based on his principle of "superstructuring" effects, which involve dynamic phenomena, e.g., slow (much longer than the relaxation time associated with shear viscosity) structural relaxations, that can occur in glass-forming liquids at $T \gg T_g$ and then become "locked in" before vitrification of the liquid at T_g, as exemplified by the lambda transition in liquid sulfur (Angell *et al.*, 1987). As a consequence of such "superstructuring" effects, "the properties of a subsequently formed glass can be influenced by heat treatments that are administered at temperatures far above the glass transformation range . . . the structures trapped by quenching through the 'slow' superstructuring region are stable against relaxation to the original lower-T_g structures, even when [the glass is] heated well above T_g where thermal history effects are usually removed" (Angell *et al.*, 1987). In other words, such a "superstructuring" effect on the properties of the glass would not be susceptible to the normal effects of annealing near T_g (Angell *et al.*, 1992). The critical consequence of "superstructuring" is that diffusion-limited reactions in low-moisture glass-forming food materials could be arrested at temperatures well above the glass transition. Such diffusional arrest would be "an important deciding factor in the shelf life of both dried and [frozen] foods" (Angell *et al.*, 1992). Angell believes that the high-temperature glasslike transition exhibited by anhydrous melts of fructose (at 100°C) and galactose (at 110°C) (Slade and Levine, 1988b) represents such a "superstructuring" effect, i.e., a slow $\alpha \rightarrow \beta$ conformational relaxation (personal communication, 1993). Obviously, this intriguing phenomenon in fructose and galactose, which is *not* observed in other monosaccharides such as glucose and mannose (Slade and Levine, 1988b), is worthy of further study that might help us better understand the dramatic, and technologically important, differences between fructose and glucose as moisture-management agents with respect to microbiological activities (e.g., mold-spore germination) in foods (Slade and Levine, 1985, 1988a,b, 1991a).

The temperature location of T_g is determined by free volume, which is proportional to $\overline{M}_n$ of a material blend (Ferry, 1980). Variations in $\overline{M}_n$, of a material of a single chemical type with an intrinsic distribution of MWs or of a materials blend with a compatible diluent, result in variations in the number of free chain ends and small mobile units, which in turn give rise to variations in free volume. The local viscosity of a series of materials or materials blends, evaluated while maintaining constant values of $\overline{M}_n$ and temperature, is proportional to weight-average MW ($\overline{M}_w$) (Ferry, 1980). Local viscosity is inversely related to translational diffusion and sufficiently asymmetric rotational diffusion, and equivalent to bulk viscosity for nonentangling materials, but dramatically lower than bulk viscosity when entanglement occurs (Ferry, 1980; Slade and Levine, 1988b). The onset of glassy behavior has been related to constraints in free volume for high-MW materials and to constraints in local viscosity for low-MW materials or highly plasticized blends with low-MW diluents (Ferry, 1980).

The location of a particular value of T_g on the state diagram in Fig. 4 for a diluent-plasticized material requires identification of the explanations for both the temperature location and weight-composition location of T_g. For a given composition, the temperature location of T_g for both the diluent-free material and the diluent-plasticized blend depends on free volume and $\overline{M}_n$ (Ferry, 1980). For a given temperature, explanation of the composition location of T_g relates to local viscosity and $\overline{M}_w$, as previously demonstrated (Slade and Levine, 1988b) by the relationships between T_g', inverse $\overline{M}_n$ (Fig. 6), and inverse $\overline{M}_w$ for a diverse series of low-MW sugars and polyhydric alcohols and, more clearly, for a homologous series of nonentangling glucose oligomers (Fig. 7). This explanation leads to the expectations, for comparison of materials, that anomalies in the temperature location of T_g arise from anomalies in the free volume requirement for mobility, while anomalies in the composition location of T_g arise from anomalies in the local viscosity requirement for mobility. In turn, these expectations provide intuition for comparison of the effects of materials on particular relaxation processes that become limited primarily by constraints in either rotational or translational mobility (Slade and Levine, 1988b). Examples of relaxation processes that manifest primary rotational constraints include (1) absorption of microwave energy, and (2) creation of critical nuclei during the prerequisite nucleation step of crystallization in the absence of seeding. Examples of relaxation processes that become translationally limited include (1) mositure migration/sorption, which is measured as apparent RVP but often called A_w, and (2) growth of crystals during the subsequent propagation step of crystallization (Slade and Levine, 1991a).

Experimental conditions that are located above the reference glass curve result in free volumes greater than those in the glassy state. Typically, free volumes that are sufficient for α relaxations (cooperative translational motions and cooperative, anisotropic rotational motions) are much more than sufficient for β relaxations (noncooperative, isotropic rotational motions). This typical behavior is reflected in (1) WLF kinetics of α relaxations above T_g versus Arrhenius kinetics of β relaxations below or above T_g, and (2) a dramatic extension of time scales for α relaxations below T_g, resulting from a discontinuity in the temperature dependence of time scales at T_g versus continuation of local isotropic rotational motions below T_g, without a discontinuity in time scale (Ferry, 1980). Moreover, free volumes that are sufficient for α relaxations are typically coincident with local viscosities that are sufficient for α relaxations, and therefore, also sufficient for β relaxations. Accordingly, both the temperature and composition locations of T_g would typically coincide for mobile units of the same molecular volume. However, if free volumes that are sufficient for α relaxations are coincident with local viscosities that are *not* sufficient for α relaxations, then it is possible that even β relaxations would become constrained and probable that small extents of anisotropy could become more important. Thus, it is this departure from the normal coincident behavior that gives interesting clues for comparison of materials that show anomalies in either the temperature location or composition location of points on a reference glass curve, and of T_g'-W_g' in particular (Slade and Levine, 1991a).

3. *Interesting Analogy between the Michaelis–Menten and WLF Equations*

As mentioned earlier, the coefficients of the WLF equation, C_1 and C_2, have previously been compared to constants that appear in other empirical, descriptive equations that relate viscosity to temperature, such as the VTF equation (e.g., Gray, 1991; Angell *et al.*, 1992). The WLF constants have also previously been related to free volume in the glassy state and the expansion coefficient of free volume above T_g (Ferry, 1980). However, despite the practical importance of the WLF equation (Sperling, 1986), some simple, intuitive implications of the WLF coefficients were previously overlooked in the 38 years since the classic WLF paper appeared. Recognition that the WLF equation has the form of a rectangular hyperbola has revealed such useful, intuitive implications about the WLF coefficients (Slade and Levine, 1993c), in much the same way that recognition of the Michaelis–Menten (MM) equation as a section from a rectangluar hyperbola has made it one of the most useful tools available to the biochemist to study enzyme reaction kinetics and other ligand-binding phenomena (Dixon and Webb, 1964). Perhaps the practical utility of the WLF equation will become even more conceptually appealing to food scientists and other biochemists by consideration of the analogy between the MM and WLF equations, as illustrated by the side-by-side comparison in Fig. 15 (Slade and Levine, 1993c).

A preliminary consideration of the elegance of the generic rectangular hyperbola shown in Fig. 15 will serve to introduce the descriptive analogy. Hyperbolas are distinguished from parabolas by the fact that hyperbolas have asymptotes, and rectangular hyperbolas are further distinguished by the fact that the angle between the asymptotes is 90° (Schwartz, 1960; Strang, 1991). The special case of the rectangular hyperbola of practical interest, familiarly exemplified by Boyle's gas law ($P * V =$ constant), is represented by the equation $X * Y =$ constant, whose asymptotes coincide with the Cartesian coordinate axes (Schwartz, 1960). When experimental data are observed to have the empirical form of a section from a rectangular hyperbola with the Cartesian coordinate axes as asymptotes, but the origin ($x = 0$, $y = 0$) of the experimental data is not

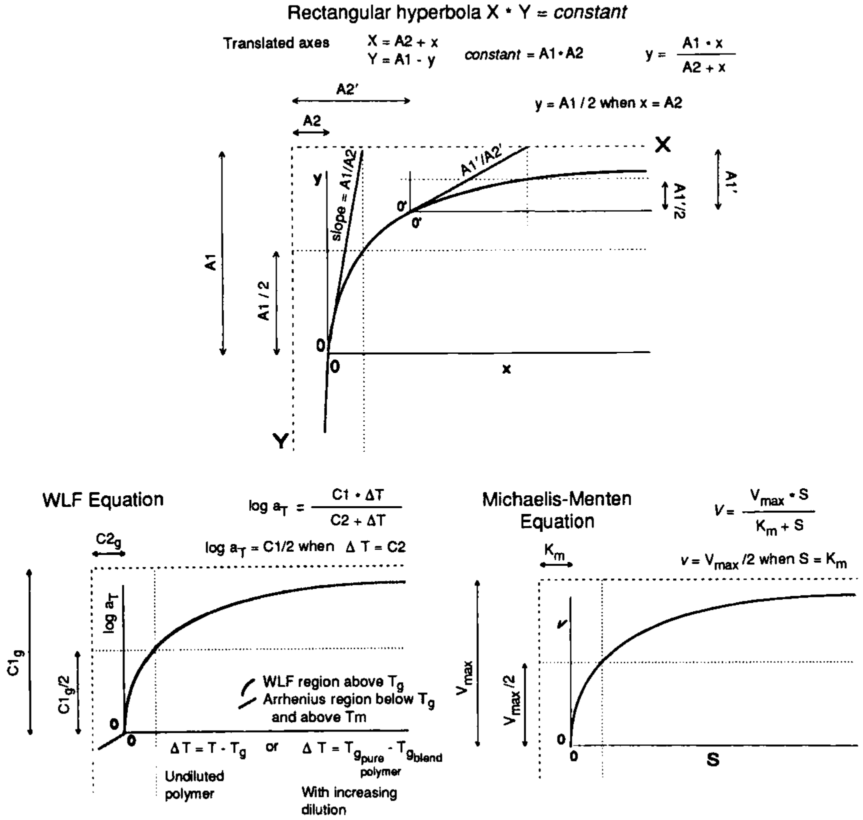

FIG. 15. Comparative diagrams illustrating the analogy between Michaelis–Menten and WLF kinetics. From Slade and Levine (1993c) with permission. See text for explanation of symbols.

coincident with the origin ($X = 0$, $Y = 0$) of the coordinate axes, the coordinates of the experimental values can be translated, so that they relate to the origin of the coordinate axes (Schwartz, 1960). If A_1 is the distance along the Y axis between the origin of the experimental data and the origin of the coordinate axes that represent the asymptotes of the experimental data, and A_2 is the distance along the X axis between the origin of the experimental data and the origin of the asymptotic coordinate axes, then the equation describing the rectangular hyperbolic form of the translated experimental data may be written,

$$X * Y = \text{constant} \qquad (\text{where } X = A_2 + x,\ Y = A_1 - y, \text{ and constant} = A_1 * A_2), \qquad (4)$$

and rearranged as

$$y = (A_1 * x)/(A_2 + x). \tag{5}$$

For the experimentalist, the great practical utility of these variations of the equation for the rectangular hyperbola derives from the fact that a simple visual inspection of a graphical display of experimental data that conform to them yields both an initial estimate for the values of the coefficients A_1 and A_2 and immediate intuition about their physical interpretation. The visual inspection is facilitated by the generic attributes of the rectangular hyperbola, as illustrated in Fig. 15: (1) the experimental data x,y represent a section from the rectangular hyperbola defined by $X * Y = A_1 * A_2$, with the coordinate axes X, Y as asymptotes; (2) the origin of the experimental axes is translated from the origin of the coordinate axes, such that $X = A_2 + x$ and $Y = A_1 - y$; (3) in the limit as x approaches ∞, the slope approaches 0, as y approaches A_1, the horizontal asymptote; (4) in the limit as y approaches $-\infty$, the slope approaches 1, as x approaches $-A_2$, the vertical asymptote, which is outside of the experimental region of immediate interest, i.e. at values of $x < 0$; (5) for any value of $\infty > x > 0$, in the limit as x approaches 0, the slope approaches its maximum value, which is equivalent to the ratio A_1/A_2; (6) the intermediate value of $\infty > x > 0$, at which y attains a value of $A_1/2$ (half of the asymptotic value of y), is equivalent to A_2; and (7) the inherent property of scaling allows the selection of any alternative experimental origin ($x' = 0' > 0$, $y' = 0' > 0$), so that $X = A_2' + x'$, $Y = A_1' - y'$, $A_2' > A_2$, $A_1' < A_1$, and $A_1 * A_2 = A_1' * A_2'$.

It is this translated form of the equation for a rectangular hyperbola, whose asymptotes coincide with the Cartesian coordinate axes, that is most familiar to food scientists and other chemists, because measurements that relate the concentration of bound ligand to the free ligand concentration for any type of ligand-binding process that involves a simple dissociation of ligand from independent and equivalent sites, such as Langmuir adsorption (Dixon and Webb, 1964), would be described by this equation. In particular, in the absence of allostery, in nearly all cases where the initial rate of an enzymatic reaction is plotted against the free substrate concentration, the data are observed to fall on a section from a rectangular hyperbola (Dixon and Webb, 1964) described by an equation of this form, the well-known MM equation,

$$v = (V_{\max} * S)/(K_m + S), \tag{6}$$

as shown in Fig. 15, where y is the initial reaction velocity, v; x is the substrate concentration, S; A_1 is the asymptotic rate, $V_{\max}$, attained as the ultimate initial reaction velocity at infinite substrate concentration, when all binding sites are occupied by substrate (i.e., at saturation); and A_2 is the Michaelis constant, K_m, defined as the substrate concentration that results in a half-maximal reaction rate. As seen in Fig. 15, in analogy with the generic attributes of the rectangular hyperbola, V_{max} can be estimated from the horizontal asymptote, and K_m can be estimated from the value of the substrate concentration that results in an intial velocity of $V_{max}/2$ or from the initial slope (V_{max}/K_m) of the experimental curve. The classic theory of enzyme kinetics proposed by Michaelis and Menten in 1913 is based on the suggestion that a dissociation constant $K_s = K_m$ of an enzyme–substrate complex accounts for the rectangular hyperbolic form of the kinetic data (Dixon and Webb, 1964). Even though the proof for any particular theoretical interpretation *cannot* be inferred from the fact that experimental data exhibit the empirical form of a rectangular hyperbola, the MM equation (and its linearized or logarithmic variations) has maintained its preeminence with physical biochemists (Wyman and Gill, 1990), and every introductory course in food science extends its popularity.

Analogously, the WLF equation (2) also exhibits the form of a section from a rectangular hyperbola, as shown in Fig. 15, where y is the log of the relaxation shift factor expressed as relative relaxation rates, log a_T; x is the differential of the experimental temperature above T_g as the reference temperature, ΔT; A_1 is the asymptotic value of log a_T, C_1, corresponding in number to the ultimate orders-of-magnitude change in relaxation rates from the limit of WLF temperature dependence of kinetics (just above the sub-T_g Arrhenius region), through the region where Arrhenius behavior is again achieved (typically above T_m), and finally to the limiting region of elevated temperatures, such that kinetics are no longer temperature dependent; and A_2 is C_2, the value of ΔT at which log a_T attains a value of $C_1/2$, half of the ultimate orders-of-magnitude change in relaxation rates above T_g, and also the difference in temperature of the reference temperature, T_g, above the asymptotic temperature (equivalent to T_0, the VTF parameter). Ferry (1980) stated the "rule of thumb that T_0 is usually ≈50°C below the glass transition temperature," but a visual inspection of Fig. 15 shows that $C_2 \approx 50$ only pertains to certain well-behaved systems, typically with $T_m/T_g \approx 1.5$. One particularly useful aspect of Fig. 15 can be appreciated by the analogy of the scaling property, shown for the generic rectangular hyperbola, to the description by Ferry (1980) of the consequence of increasing dilution on the values of C_1 and C_2. Just as the value of A_1 decreases to A_1' and the value of A_2 increases to A_2', when the experimental origin is translated from (0,0) to (0′,0′), a depression of the T_g of the undiluted polymer with increasing dilution results in an effective translation along the ΔT axis, so that with increasing dilution, "C_2 increases while C_1 decreases" (Ferry, 1980). As mentioned earlier, the numerical value of C_1 is "universally" (Sperling, 1986) 17.44, meaning that there would be a

17+ orders-of-magnitude change in relaxation rates between the sub-T_g and super-T_m Arrhenius regions for a model "universal" polymer. The "universal" value of C_2 is 51.6, which would correspond to an 8+ orders-of-magnitude increase in relaxation rates in the temperature interval between T_g and 50°C above T_g. Near T_g, the limiting slope corresponds to C_1/C_2, so that an order-of-magnitude increase in relaxation rates is achieved in the 3°C interval above T_g for the "universal" polymer. For a typical well-behaved polymer with $T_m/T_g \approx 1.5$, the slope of the rectangular hyperbola achieves a value near 0.03 (such that Arrhenius $Q_{10} \approx 2$ kinetics are observed) at a $\Delta T \approx 100°\text{C}$ above T_g, coincident with the value of $T_m = 300\text{ K}$ for the classic model polymer with $T_g = 200\text{ K}$. Thus, this intuition about the physical basis of the WLF constants, revealed by the analogy between MM and WLF kinetics illustrated in Fig. 15, has recently been related to previous empirical observations about implications of the value of the T_m/T_g ratio on mobility (Slade and Levine, 1988b), described earlier in the context of Fig. 14. In essence, the T_m/T_g ratio serves as a normalizing factor for intrinsic rigidity, i.e. as a normalizing factor for inherent constraints on relaxation within the WLF rubbery range (Slade and Levine, 1993c).

4. *Contrast between WLF and Arrhenius Kinetics*

WLF kinetics differ from Arrhenius kinetics in several important respects (Slade and Levine, 1988b; Levine and Slade, 1989c, 1990), and we have emphasized the contrast, because we believe that the qualitative differences are as influential as the quantitative differences in their impact on both experimental approach and technological significance (Levine and Slade, 1989d, 1992b; Slade and Levine, 1991a). A comparison between WLF and Arrhenius kinetics begins with recognition that the temperature dependence of microscopic relaxation parameters (including self-diffusion coefficient, viscosity, rotational and translational relaxation rates or times, and macroscopic processes that rely on them, such as crystallization) changes monotonically from a steep dependence of log relaxation rate on temperature just above T_g to a shallow dependence above T_m, i.e., over a material-specific temperature range from T_g to far above T_g (Franks, 1982; Angell, 1988; Slade and Levine, 1988b; Ehlich and Sillescu, 1990; Pikal and Shah, 1990; Franks *et al.,* 1991; Karathanos *et al.,* 1991; Karel and Saguy, 1991; Karmas *et al.,* 1992; Levi and Karel, 1992a). This realization reveals two underlying diagnostic characteristics that distinguish WLF from Arrhenius kinetics (Levine and Slade, 1989d).

First, the coefficient of the temperature dependence (so-called "activation energy") is defined as a constant in the expression for Arrhenius kinetics, and a plot of log relaxation rate versus $1/T$ is a straight line (Le

Meste and Simatos, 1990; Chang and Baust, 1991c; Noel *et al.,* 1991; Scandola *et al.,* 1991). But the coefficient itself is temperature dependent in the WLF expression; a plot of log relaxation rate versus $1/T$ is characteristically curvilinear in the material-specific, rubbery temperature range above T_g (up to T_m) (Campanella *et al.,* 1987; Karel, 1989; Ehlich and Sillescu, 1990; Koide *et al.,* 1990; Pikal and Shah, 1990; Karel and Saguy, 1991; Nelson and Labuza, 1992a; Nelson, 1993), approaching linearity only below T_g or above T_m (Levine and Slade, 1989c). Examples of food materials/systems exhibiting such curvilinear plots were recently reported by (1) Ollett and Parker (1990), log η versus $1/T$ for undercooled melts of fructose and glucose; (2) Noel *et al.* (1991), log η versus $1/T$ for low-moisture maltose–water mixtures; (3) Lillie and Gosline (1990), log a_T versus T for hydrated elastin; (4) Karmas *et al.* (1992; Buera and Karel, 1992; Karel *et al.,* 1993b), log rate of nonenzymatic browning versus $1/T$ for amorphous model systems; (5) Levi and Karel (1992a), log diffusion factor versus $1/T$ for diffusion of volatiles in amorphous sucrose–water matrices; and (6) Nelson (1993), log rate of ascorbic acid oxidation versus $1/T$ for amorphous maltodextrin–water matrices. The absolute value of the derivative of log relaxation parameter versus $1/T$ increases as T approaches T_g from above, and decreases abruptly to an approximately constant value as T falls below T_g, or decreases gently to an approximately constant value as T is elevated above T_m and far above T_g, where the constant value corresponds to the Arrhenius coefficient (activation energy) that characterizes a given system and relaxation process (Levine and Slade, 1989d). The shape of the derivative profile and the temperature range over which the derivative varies are material-specific properties: typically, a range of >100°C for materials with $T_m/T_g > 1.5$, or a range of <100°C for materials with $T_m/T_g < 1.5$ (Slade and Levine, 1988b). Clearly, it is the fact that the derivative varies in a material-specific and temperature-dependent fashion, rather than the particular magnitude of the derivative (Simatos *et al.,* 1989; Le Meste and Simatos, 1990; Simatos and Blond, 1991, 1993), that constitutes the salient feature of WLF kinetics (Levine and Slade, 1989d). It is also important to note, as has been stressed by various workers (Huang, 1992; Huang *et al.,* 1993; Peleg, 1992; Nelson and Labuza, 1992a; Nelson, 1993), that an apparent absence of curvature, at $T > T_g$, in a plot of log reaction rate versus $1/T$ should not be assumed to indicate that the kinetics in question cannot be described by the WLF equation, and so Arrhenius kinetics must apply. Rather, such a linear plot should be taken to indicate that the temperature range over which the experimental reaction rate data were examined was probably too narrow to reveal the curvature expected of WLF-type behavior, illustrated in Fig. 16.

It was previously noted (Slade and Levine, 1991a) that such curvilinear plots of log rate versus $1/T$ (still referred to as so-called "Arrhenius plots"

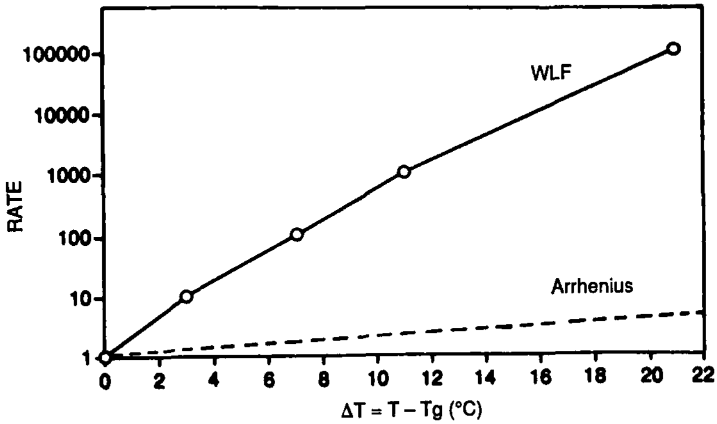

FIG. 16. Variation of the rate of a diffusion-limited relaxation process against $\Delta T = T - T_g$, as defined by the WLF equation with its "universal" numerical constants of $C_1 = 17.44$ and $C_2 = 51.6$ (solid line), or by the Arrhenius equation ($Q_{10} = 2$ form) (dashed line). Adapted from Levine and Slade (1989c) by permission of Gordon and Breach Science Publishers, Inc. and Franks *et al.* (1991) with permission.

by their authors) have also been reported (e.g., LeBlanc *et al.*, 1988) from studies of storage stability (e.g., against different enzymatic activities) of various frozen food systems stored at different freezer temperatures (Duden and Scholz, 1982; LeBlanc *et al.*, 1988; Lee *et al.*, 1988; Baardseth and Naesset, 1989), all above the relevant T_g' reference state of the foods in question (Levine and Slade, 1989d). Results of the cited studies demonstrated that enzymatic reaction rates and corresponding rates of quality loss manifest a WLF-type, rather than Arrhenius-type, temperature dependence on ΔT of the freezer temperature above T_g' (Levine and Slade, 1989d; Slade and Levine, 1991a). In a related vein, Lim and Reid (1991, 1992) and Kerr *et al.* (1993; Reid *et al.*, 1992) have reported an excellent correlation, predicted from WLF theory and "cryostabilization technology" concepts (Levine and Slade, 1988c; Reid, 1990), between increasing rates of diffusion-limited deterioration reactions (e.g., model reaction systems involving enzyme hydrolysis, protein aggregation, or nonenzymatic oxidation of ascorbic acid) and increasing ΔT above T_g'. This correlation was demonstrated by results of their experimental studies of reaction kinetics in frozen aqueous model systems [formulated using a series of sugars and commercial maltodextrins with a range of previously measured T_g' values (Levine and Slade, 1986, 1988b)] stored at a range of different subzero freezer temperatures. Their results also confirmed the expectation (Levine and Slade, 1988c; Reid, 1990) [based on earlier experimental results for a frozen enzyme–substrate model system (Levine and Slade, 1986) and more recent results for an amorphous enzyme–substrate model system at low moisture (Leopold *et al.,* 1992)] of an essentially zero rate of reaction for each storage situation in which the freezer temperature was below T_g' of the particular sugar–maltodextrin-based model system (Lim and Reid, 1991, 1992; Reid *et al.,* 1992; Kerr *et al.,* 1993). Most recently, Nelson (1993; Nelson and Labuza, 1993) has analyzed reaction kinetics data from the literature for a wide variety of rubbery food systems, and has reported results that can be seen to confirm the applicability of WLF-type kinetics and the inappropriateness of Arrhenius kinetics.

The second diagnostic characteristic that distinguishes WLF from Arrhenius kinetics is that there is no explicit reference temperature in the expression for Arrhenius kinetics (Levine and Slade, 1989d), because, in fact, the implicit reference temperature is taken generically to be 0 K (Slade and Levine, 1991a; Nelson and Labuza, 1992a; Franks, 1993a), regardless of the distinctive thermomechanical properties of a system, and even though Arrhenius kinetics are applicable only below T_g and above T_m (Ferry, 1980; Franks, 1982; Levine and Slade, 1988a). In contrast, the WLF equation benefits from an explicit material-specific reference temperature, which is T_g of a component or compatible blend (Ferry, 1980). Therefore, it is critical to note that when the rate or time scale of a relaxation process can be shown to depend on a material-specific reference T_g (e.g., Anonymous, 1993b), Arrhenius kinetics are not applicable to describe mobility transformations (time–temperature–moisture superposition) for that process in the rubbery range from T_g to T_m, regardless of whether the average slope of a log k versus $1/T$ curve can be empirically fitted by a $Q_{10} = n$ rule and regardless of the particular magnitude of n (Levine and Slade, 1989d; Peleg, 1992). Even today, some food engineers seem to be especially prone to overlook or disregard this fundamental distinction between Arrhenius and WLF kinetics; while they acknowledge the benefits to be gained by treating kinetics data using a material-relevant reference temperature, they still insist on incorrectly characterizing their results in terms of Arrhenius kinetics (Nunes *et al.,* 1993; Lin, 1993). Similarly, in various recent studies of the kinetics of starch gelatinization (reviewed by Lai and Kokini, 1991) and protein denaturation (reviewed by Ma and Harwalkar, 1991), so-called "Arrhenius plots" have been presented, each of which exhibits a sharp break at the material-specific reference temperature, i.e., the gelatinization temperature [actually, at $T > T_g$ (Slade and Levine, 1987b)] for starch or the denaturation temperature [actually, at $T > T_g$ (Slade *et al.,* 1989; Sochava *et al.,* 1991; Sochava and Smirnova, 1992; Tolstoguzov, 1991, 1992)] for protein.

In the temperature–composition domain sufficiently above T_g, where equilibrium and steady-state thermodynamics apply, the coefficient of the temperature dependence of log relaxation rate on $1/T$ is defined by Arrhenius kinetics to be a constant and is observed to approximate a relatively small constant value over a typical experimental range of about 20°C (Levine and Slade, 1989d). In the increasingly nonequilibrium domain of temperature–composition approaching T_g from above, the coefficient of the temperature dependence of log relaxation rate on $1/T$ is not a constant and increases ever more rapidly over a range of 20°C (Slade and Levine, 1988b). Typically, Arrhenius rates for aqueous systems above T_m might increase fourfold over a temperature range of 20°C (Levine and Slade, 1989d), while WLF rates near T_g would increase by four or five orders of magnitude (Franks, 1985; Slade and Levine, 1988b; Levine and Slade, 1989c). As an example illustrating the significance of the difference between WLF and Arrhenius kinetics, Chan *et al.* (1986) noted that the dielectric relaxation behavior of amorphous glucose plasticized by water is "remarkably similar" to that of synthetic amorphous polymers in glassy and rubbery states. They showed that the rates of this mechanical relaxation process, which depends on rotational rather than translational mobility, follow the WLF equation for water-plasticized glucose mixtures in their rubbery state above T_g, but follow the Arrhenius equation for glucose–water glasses below T_g (Chan *et al.*, 1986). Also noteworthy is Angell's (1983) pertinent observation that the temperature dependence of the transport and relaxation properties of undercooled liquid water is strikingly non-Arrhenius in the temperature range from T_m to the homogeneous nucleation temperature at −40°C. This non-Arrhenius temperature dependence also typifies the case for many other viscous liquid systems that undergo restructuring processes that require the "cooperative involvement of other molecular motions" (Angell, 1983, 1988). Included in these other viscous liquid systems that exhibit non-Arrhenius behavior are concentrated aqueous solutions (analogous to frozen foods) at subzero temperatures (Pikal and Shah, 1990), according to a suggestion by Hofer *et al.* (1989).

The impact of WLF behavior on the kinetics of diffusion-limited relaxation processes in water-plasticized, rubbery food polymer systems has been conceptually illustrated by the schematic curves shown in Fig. 16 (Levine and Slade, 1989c; Franks *et al.*, 1991). Relative relaxation rates, calculated from the WLF equation with its "universal" numerical constants, demonstrate the nonlinear logarithmic relationship: For $\Delta T = 0°, 3°, 7°, 11°$, and 21°C, corresponding relative rates would be 1, 10, 10^2, 10^3, and 10^5, respectively. These rates illustrate the five orders-of-magnitude change, over a 20°C interval above T_g, typically shown by WLF plots, as mentioned earlier with regard to Fig. 11. They are dramatically different from the rates defined by the $Q_{10} = 2$ rule of Arrhenius kinetics for dilute solutions, as shown for comparison in Fig. 16. As pointed out earlier with regard to

Fig. 14A, for Arrhenius behavior above T_m, a factor-of-10 change in relaxation rate would require a 33°C change in temperature, in contrast to a 3°C change for WLF behavior near T_g of a partially crystalline polymer of $T_m/T_g = 1.5$ (Slade and Levine, 1988b). An illustration of the effect of such WLF kinetics, relating to the striking contrast between the relative time frames involved in slow caking and spontaneous agglomeration in amorphous food powders (Levine and Slade, 1989a), is represented by the schematic state diagram in Fig. 17. Caking and agglomeration are identical, translational diffusion-limited collapse processes that can occur in low-moisture, amorphous powders sensitive to plasticization by water and/or heat (Levine and Slade, 1986, 1988b; Peleg, 1993). As implied in Fig. 17, caking and agglomeration are distinguishable only by a WLF-type time–temperature transformation (Slade and Levine, 1988b). It has been shown (Downton *et al.*, 1982; Tardos *et al.*, 1984; Wallack and King, 1988) that spontaneous agglomeration of solid powder particles occurs, at a so-called "sticky point" temperature (T_{sp}), when η of the liquid phase at the surface of a particle drops to $\approx 10^7$ Pa s. This η is $\approx 10^5$ lower than η_g. From the WLF equation (which treats viscosity as a diffusion-limited relaxation process), as defined above in Fig. 16, this five orders-of-magnitude difference between η_g and η_{sp} corresponds to a ΔT of $\approx$21°C between the T_g that governs caking and the T_{sp} that governs spontaneous agglomeration of a given powder at a given moisture content. Thus, as indicated on the state diagram in Fig. 17, WLF theory would predict that the T_g and T_{sp}

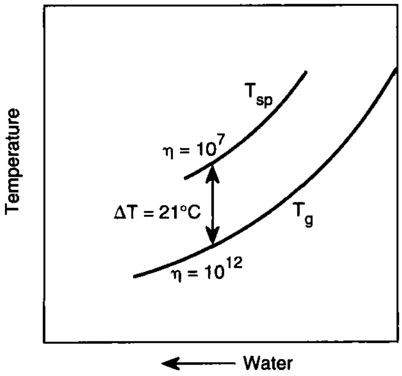

FIG. 17. Schematic state diagram of temperature versus water content for an amorphous food powder, illustrating the WLF-governed temperature differential (at a given moisture content) between the iso-viscosity lines representing the T_g curve, just above which slow caking can occur, and the "sticky point" temperature (T_{sp}) curve, above which spontaneous agglomeration can be effected.

curves should represent parallel iso-viscosity lines. The T_{sp} curve for fast agglomeration (in seconds at $T > T_{sp}$) during processing would lie above the T_g curve for slow caking (after months at T just above T_g) during storage, and the ΔT of 21°C would reflect the very different time scales for these two collapse processes (Levine and Slade, 1986, 1988b, 1989a; Slade and Levine, 1988b). Recently reported experimental results for amorphous powders of mixed sugars and of maltodextrins (Roos and Karel, 1991a,b) have confirmed the quantitative relationship between T_g and T_{sp} predicted by Fig. 17. Peleg (1993), too, has recently reassessed and endorsed this relationship.

Another example of WLF-governed relaxation behavior involves the kinetics of (re)crystallization (Levine and Slade, 1988a, 1989b; Slade *et al.*, 1989). Crystallization kinetics, with regard to such common sugars as glucose, sucrose, and lactose, has been a subject with a long history of study by food scientists and technologists (Makower and Dye, 1956; White and Cakebread, 1966; Cakebread, 1969), which has seen much renewed interest in recent years (Slade and Levine, 1988b, 1991a; Levine and Slade, 1989a, 1992b; Roos and Karel, 1990, 1991a,e, 1992, 1993; Van Scoik and Carstensen, 1990; Blanshard *et al.*, 1991; Noel *et al.*, 1991; Shimada *et al.*, 1991; Karel, 1992; Levi and Karel, 1992a, 1993b; Roos, 1992a,c; Arvanitoyannis and Blanshard, 1993a,b; Hartel, 1993; Karel *et al.*, 1993a,b). Crystallization is a diffusion-limited process (Baro *et al.*, 1977) that, on a time scale of technological significance, can only occur within the WLF rubbery domain bounded by the temperature limits of T_g and T_m (Wunderlich, 1976). As illustrated in Fig. 18 (Levine and Slade, 1989b), the propagation step in the crystallization mechanism approaches a zero rate at $T < T_g$ for an amorphous but crystallizable solute [either polymeric (Wunderlich, 1976) or monomeric (Levine and Slade, 1988a)], initially quenched from the melt or liquid solution state to a kinetically metastable solid state. Due to immobility in the glass, migratory diffusion of either large main-chain segments or small molecules, required for growth of crystals from metastable nuclei, would be inhibited over realistic times (Levine and Slade, 1988a; Chang and Baust, 1991c; Noel *et al.*, 1991). However, propagation rate increases exponentially with increasing ΔT above T_g (up to T_m) (Marsh and Blanshard, 1988; Morris, 1990; Biliaderis, 1991b, 1992b; Arvanitoyannis and Blanshard, 1993a), due to the mobility allowed in the rubbery liquid state. Thus, a recrystallization transition from unstable (i.e., undercooled) amorphous liquid to (partially) crystalline solid may occur at $T > T_g$ (White and Cakebread, 1966; Karel, 1986; Phillips *et al.*, 1986; Levine and Slade, 1988b, 1989a; Noel *et al.*, 1991; Ring and Whittam, 1991; Tian and Blanshard, 1992a; Arvanitoyannis *et al.*, 1993; Eerlingen *et al.*, 1993), with a rate defined by the WLF

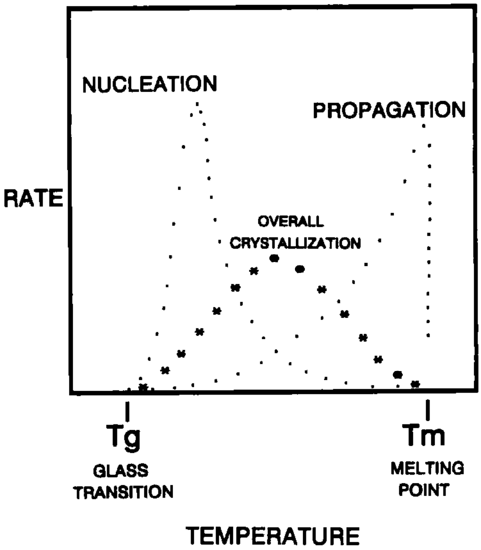

FIG. 18. Crystallization kinetics of partially crystalline polymers, expressed in terms of crystallization rate as a function of temperature. From Levine and Slade (1989b) with permission of Van Nostrand Reinhold/AVI.

equation (Levine and Slade, 1986). Brydson (1972) illustrated the extreme temperature dependence of, and the remarkably contrasting time frames that resulted for, the crystallization kinetics for a water-plasticized, well-behaved (i.e., $T_m/T_g \approx 1.5$), synthetic amorphous polymer, nylon-66. When that polymer's water-plasticized T_g was ≈ room temperature, slow crystallization occurred during room-temperature storage for a period of up to 2 years; however, when the polymer was annealed at a higher temperature, $T_a \approx (T_g + T_m)/2$ [i.e., the temperature corresponding to the peak maximum of the overall crystallization rate curve in Fig. 18, also corresponding to the maximum rate of annealing at $T_a \approx 0.83T_m$ (Brydson, 1972; Slade and Levine, 1988d)], a comparable extent of crystallization was achieved in only ≈30 minutes.

The facts that time-dependent recrystallization can only occur at temperatures above T_g, with a rate increasing with increasing ΔT above T_g, and manifests kinetics defined by the quantitative WLF (rather than Arrhenius) equation (Levine and Slade, 1988b) have been confirmed in recent experimental studies of the recrystallization of amorphous, freeze-dried sugars (sucrose and lactose) by Karel, Roos, and co-workers (Roos and Karel, 1990, 1991a,e, 1992, 1993; Shimada *et al.*, 1991; Karel, 1992; Levi and Karel, 1992a, 1993a,b; Roos, 1992a,c; Karel *et al.*, 1993a,b). As shown earlier in

Fig. 12A, which combined data for sucrose and lactose from Roos and Karel with a critical datum point (the x highlighted in the oval) from the classic study of sucrose crystallization by Makower and Dye (1956), and in Fig. 12B, experimental curves of the temperature dependence (in terms of ΔT above T_g) of crystallization times for completely amorphous sucrose and lactose at low moisture contents (in the water-plasticized, rubbery liquid state at various ΔT values above T_g) fit the theoretical curve of the WLF equation (with $C_1 = 17.44$ and $C_2 = 51.6$), but not that of the Arrhenius equation. Other specific examples of such a recrystallization process [i.e., a collapse phenomenon (Levine and Slade, 1988b)] include ice (Roos and Karel, 1991e–g) and solute [e.g., lactose in dairy products (Blanshard and Franks, 1987)] recrystallization in frozen aqueous food systems at $T > T_r \equiv T_g'$ (Levine and Slade, 1986).

A critical message to be distilled from this section is that the structure–property relationships of water-compatible food polymer systems are dictated by a moisture–temperature–time superposition (Starkweather, 1980; Flink, 1983; Levine and Slade, 1986; Lillie and Gosline, 1990). Referring to the schematic state diagram in Fig. 4 as a conceptual mobility map (representing an extension of the dynamics map in Fig. 3), one sees that the T_g curve represents a boundary between nonequilibrium glassy solid and rubbery liquid physical states in which various diffusion-limited processes [e.g., collapse phenomena involving mechanical and structural relaxations (Levine and Slade, 1988b)] either can (at $T > T_g$ and $W > W_g'$, the high-moisture portion of the water dynamics domain corresponding to the upper left part of Fig. 4, or $T > T_g$ and $W < W_g'$, the low-moisture portion of the water dynamics domain corresponding to the upper right part of Fig. 4) or cannot occur (at $T < T_g$, in the domain of glass dynamics corresponding to the bottom part of Fig. 4) over realistic times (Levine and Slade, 1986, 1988a; Franks, 1989, 1990; Karel, 1992; Karel *et al.,* 1993b). The WLF equation defines the kinetics of molecular-level relaxation processes [e.g., the diffusion-limited chemical and enzymatic reactions studied by Lim and Reid (1991) and Kerr *et al.* (1993), mentioned earlier], which will occur in practical time frames only in the rubbery state above T_g, in terms of an exponential, but non-Arrhenius, function of ΔT above this boundary condition (Levine and Slade, 1986).

E. THERMOSETTING OF AMORPHOUS POLYMERS

The classical thermosetting process for synthetic amorphous polymers, e.g., in the production of rigid epoxy resins and flexible natural or synthetic rubbers, is typically described by a time–temperature transformation (TTT) reaction diagram (Prime, 1981). As illustrated in Fig. 19 (Sperling, 1986), this TT diagram has been "used to provide an intellectual framework for understanding and comparing the cure and glass transition properties of thermosetting systems" (Sperling, 1986). As reviewed by Prime (1981), thermosetting polymers become infusible (i.e., unmeltable) and insoluble due to chemical crosslinking reactions during curing, which produce a three-dimensional network with essentially infinite MW. Curing of amorphous polymers at a curing temperature (T_{cure}), somewhat above the initial molecular T_g of the polymer reactant (T_{g_0}), allows very slow conversion with concomitant elevation of molecular T_g, until molecular T_g approaches T_{cure}, and the system vitrifies. The molecular T_g depends only on the extent of conversion and not on T_{cure} (Bair, 1985). At a sufficiently higher T_{cure}, gelation occurs before vitrification, at a characteristic extent of conversion. At this system-specific degree of cure, the partially cured polymer thermosets by undergoing a sudden and thermally irreversible transformation from a viscous liquid ($T_{\text{cure}} \gg T_{g_0}$ of the polymer reactant) to a nonflowable,

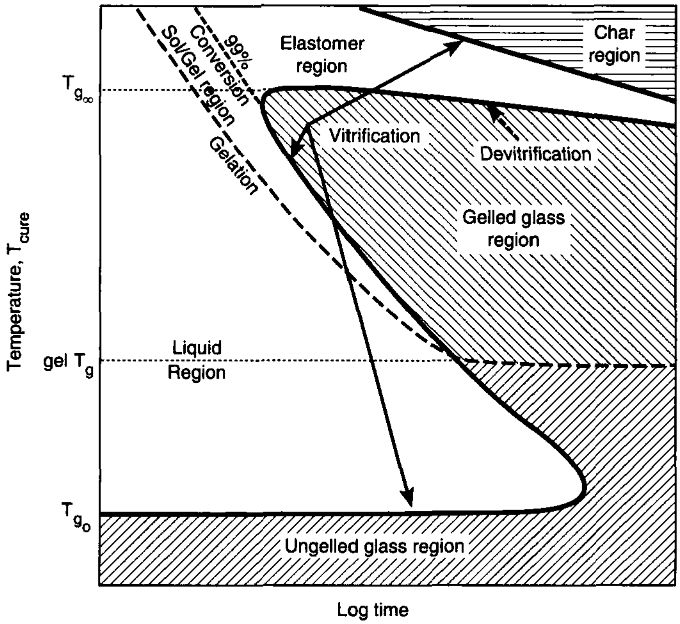

FIG. 19. Thermosetting process for amorphous polymers, as illustrated by a time–temperature transformation reaction diagram. See text for explanation of symbols. From Sperling, L. H. 1986. "Introduction to Physical Polymer Science." Copyright © 1986 Wiley (Interscience), New York. Reprinted by permission of John Wiley & Sons, Inc.

elastic network ($T_{cure} >$ the gel point, initial gel-T_g), which rapidly approaches infinite macroscopic viscosity as gel-T_g approaches T_{cure}, and the system vitrifies. Gelation, per se, does not retard the rate of the curing reaction (which is chemically, rather than diffusion, controlled as long as T_{cure} is well above the effective instantaneous network T_g), and is detectable by the inability of large gas bubbles to rise in a thermosetting mass (Prime, 1981). In Fig. 19, the S-shaped curing curve between T_{g0} and $T_{g\infty}$ (the network T_g of the fully cured system) results, because the reaction rate increases with increasing temperature (Sperling, 1986). Thus, the gel point, initial gel-T_g, is the critical minimum value of gel-T_g that represents the temperature at which gelation and vitrification (of the elastic gel to a glass) occur simultaneously. As described above, at temperatures between gel-T_g and $T_{g\infty}$, the thermosetting mass first reacts chemically to form a crosslinked rubbery network, then vitrifies as the continuously increasing network T_g becomes coincident with T_{cure}, essentially quenching the curing reaction (now diffusion-controlled) before completion, but giving the illusion that the product is completely cured (Sperling, 1986). Once the network T_g exceeds T_{cure}, the diffusion of reactants becomes so restricted that the reaction rate decreases by more than three orders of magnitude (Bair, 1985). The resulting incompletely cured network would have a T_g denoted as ult-T_g, where gel-$T_g <$ ult-$T_g < T_{g\infty}$ (Prime, 1981). However, since vitrification is thermally reversible, curing can be extended by a postcure heat treatment of the rubbery thermoset at $T >$ ult-T_g, or rapidly completed by a postcure heat treatment at $T > T_{g\infty}$.

Importantly, the TTT diagram in Fig. 19 refers to the curing and vitrification kinetics of a neat polymer system, in the absence of plasticizer or solvent. Sorption of, or dilution by, plasticizer has a profound effect on the time frame of the TTT diagram, due to depression of all operative T_g values and concomitant acceleration of the curing reactions at a given T_{cure}. The role of water as a plasticizer is perhaps even more critical for the storage stability of both the original reaction mixture and the final cured product. Moisture sorption or loss has been shown to be a major factor in the aging behavior of synthetic thermosets (Prime, 1981). Plasticization of the thermoset network depresses network T_g and modulus, whereas loss of plasticizer leads to toughness or brittleness.

The TTT diagram in Fig. 19 illustrates the four material states encountered during curing: liquid, rubber (elastomer), ungelled glass, and gelled glass. The time axis signifies measured times to gelation and to vitrification, as a function of cure temperature (Prime, 1981; Sperling, 1986), and underlines the importance of the kinetics of curing reactions in thermosettable polymers. For example, in a DSC experiment, if a polymer sample (of $T_g = T_{g0}$) is heated to $T >$ gel-T_g in an initial scan, but then immediately cooled to $T < T_{g0}$ and rescanned, the extent of curing achieved during the first scan may be undetectably small (Slade *et al.*, 1989). Consequently, T_{g0} in the rescan may appear unchanged, and the sample may behave as a thermoplastic polymer. In contrast, if the same sample is heated to $T \gg$ gel-T_g, or to $T >$ gel-T_g and then held for a longer time before cooling and rescanning, the curing reaction can proceed. In this case, the rescan would not show T_{g0}, but rather a new network $T_g > T_{g0}$, and the sample would appear to be thermoset (Slade *et al.*, 1989). An actual example of this contrasting behavior has been reported for curing of an epoxy–amine system in a DSC (Prime, 1981). On holding at T_{cure} a few degrees above gel-T_g, about an hour was required to achieve the characteristic extent of cure to thermoset. When T_{cure} was more than 80°C above gel-T_g, the same extent of cure was achieved in about 3 minutes, so that thermosetting could occur within the time frame of a dynamic DSC experiment. Indeed, in the latter case, because T_{cure} was more than 20°C above $T_{g\infty}$, complete curing was achieved within 10 minutes.

The apparent parallels between the established behavioral characteristics of thermosetting synthetic amorphous polymers, described above, and the empirically known structure–funtion relationships of wheat gluten protein in various baking applications (and postbaking heat treatments, e.g., microwave "refreshening") have been described (Slade *et al.*, 1989) and are reviewed below.

1. *Wheat Gluten as a Viscoelastic Polymer System*

Unique among cereal grain storage proteins, native ("vital") wheat gluten is a major functional food ingredient, especially as a flour component in baked goods (Bloksma, 1978; Kasarda *et al.*, 1978; Pomeranz, 1978; Magnuson, 1985). The structure–property relationships of gluten have been described in terms of a highly amorphous, multipolymer system, water-plasticizable but not water-soluble, and capable of forming continuous, multidimensional, viscoelastic films and networks (Schofield *et al.*, 1984; Slade, 1984; Hoseney *et al.*, 1986; Levine and Slade, 1988a; Doescher *et al.*, 1987; Edwards *et al.*, 1987). Gluten also appears to function as either a thermoplastic or thermosetting amorphous polymer in response to the heat–moisture treatment constituted by baking (Slade *et al.*, 1989, 1993; Slade and Levine, 1992c; Levine and Slade, 1993). The thermosetting behavior, when it occurs at practical heating rates and sample concentrations, is considered to be a typical consequence of irreversible protein denaturation and "heat-set gelation" above a critical temperature (Schofield *et al.*, 1984; Magnuson, 1985; Davies, 1986; Schofield, 1986; Ablett *et al.*, 1988; Blanshard, 1988; Masi, 1989). The resulting dramatic changes in mechanical and rheological properties (i.e., large increases in viscosity and elastic modulus at temperatures between about 50° and 100°C) of bread dough during baking are responsible in part (along with starch gelatinization) for the transformation from a predominantly viscous dough to a predominantly elastic baked crumb (Schofield *et al.*, 1984; Schofield, 1986; Bloksma, 1986; Blanshard, 1988; Bloksma and Bushuk, 1988; Dreese *et al.*, 1988b; Masi, 1989). The mechanism of such thermo-irreversible "heat-set" gelation involves formation of permanent networks, due to rheologically effective, intermolecular crosslinks composed of covalent disulfide bonds, resulting in a polymerization of the gluten proteins (Bloksma, 1978, 1986; Pomeranz, 1978; Cantor and Schimmel, 1980; Schofield *et al.*, 1984; Ablett *et al.*, 1988; Dreese *et al.*, 1988a; Shewry *et al.*, 1988; Attenburrow *et al.*, 1990; Hoseney and Rogers, 1990; Davies *et al.*, 1991; Hoseney, 1991). Such completely amorphous, thermoset gel networks (which may also contain entangled polypeptide chains) represent a separate category from two other common types of food polymer gels, i.e., partially crystalline, thermoreversible gels (e.g., starch–water and gelatin–water) and completely amorphous, topologically reversible "entanglement" gels (e.g., sodium caseinate–water, not heat-treated) that can be dispersed by dilution (Slade and Levine, 1987a,b; Burchard, 1988; Slade *et al.*, 1989; Levine and Slade 1988a, 1989b).

Wheat gluten's unique combination of cohesive, viscoelastic, film-forming, thermoplastic or thermosetting, and water-absorbing properties (Schofield *et al.*, 1984; Magnuson, 1985) is derived from the structure of the native proteins (Payne, 1987). Gluten is a complex of interacting proteins that have been categorized traditionally into two major groups, gliadins and glutenins, based on their solubility and insolubility, respectively, in 70 to 90% aqueous ethanol. An alternative classification has been proposed, which reflects the chemical and genetic relationships of the component polypeptides of gluten (Tatham *et al.*, 1985; Payne, 1987). The groups are (1) sulfur-poor prolamins (ω-gliadins), (2) sulfur-rich prolamins (α-, β-, and γ-gliadins; low-MW glutenin subunits), and (3) high-MW prolamins (high-MW glutenin subunits). The broad correspondence between the two classification schemes relates to identification of proteins present as monomers (single polypeptide chains) associated by hydrogen bonding and hydrophobic interactions as gliadins, and proteins present as polymers (multisubunit aggregates) linked by interchain disulfide bonds as glutenins (Payne *et al.*, 1985; Schofield, 1986; Payne 1987). In this context, gliadins are lower-MW proteins ($< 10^5$) that can adopt globular conformations with intramolecular disulfide bonds, α-helical segments, and/or β-turns, and act as the viscous, extensible, plasticizing component of gluten (Schofield, 1986; Payne, 1987; Blanshard, 1988; Slade *et al.*, 1989). Glutenins are higher-MW ($> 10^5$) with broader MW distribution, highly elastic, multisubunit proteins [which contain a significant amount of secondary structure in the form of β-turns (Tao *et al.*, 1989)] crosslinked by intersubunit disulfide bonds (Schofield, 1986). Glutenins act as the elastic component (Lasztity, 1986; du Cros, 1987; Edwards *et al.*, 1987; Payne, 1987; Blanshard, 1988) of the viscoelastic network that forms in a flour–water dough via crosslinking by thiol–disulfide interchange reactions catalyzed by rheologically active thiols (Kasarda *et al.*, 1978; Pomeranz, 1978; Bloksma, 1978; Schofield, 1986; Ewart, 1988). In this functionality, glutenins are similar to elastin, in that these are the only two protein systems known to exhibit high segmental mobility at high MW and to form hydrated, three-dimensional, open-structured, rubberlike elastic networks via disulfide bonding (Schofield, 1986; Edwards *et al.*, 1987; Ablett *et al.*, 1988; Shewry *et al.*, 1988; Slade *et al.*, 1989).

It is important to stress the distinction between local intermolecular disulfide crosslinking of gliadins (Schofield *et al.*, 1984) and long-range intermolecular disulfide network formation of high-MW glutenins (Weegels *et al.*, 1988; Shewry *et al.*, 1988). "Gluten" defies the usual biological rule of thumb for genetic design of stable proteins (Cantor and Schimmel, 1980): single polypeptide chains should contain *either* free thiols (cysteine) *or* disulfides (cystine), but not both in a single gene product. Coexistence of both –SH and –S–S– results in dynamic catalysis of disulfide exchange and consequent lack of definition of highly probable, predominant subunit conformations in the gluten population (Cantor and Schimmel, 1980). Disulfide exchange, crosslinking, and thermosetting reactions during heat–moisture treatments, such as baking, result in (1) progressive depletion of the least stable crosslinks and catalytically effective thiols and (2) eventual establishment of permanent local crosslinks in gliadins, a permanent long-range (cooperative) network by high-MW glutenins, and residual catalytically ineffective thiols. Extensibility and viscous flow of film-forming gliadins in doughs with moisture contents $> W_g'$ are diminished by disulfide crosslinking during baking (Schofield *et al.*, 1984), resulting in decreased extensibility and increased hardness, but not increased elasticity. Elasticity and rigidity of network-forming high-MW glutenins in such doughs are enhanced by disulfide thermosetting during heat treatment (Weegels *et al.*, 1988; Shewry *et al.*, 1988), which results in an increased number of permanent disulfide junction zones, such that loss of extensibility *is* accompanied by increased elasticity. Thus, increased firmness results from an increase in loss modulus due to gliadin crosslinking (Schofield *et al.*, 1984) and an increase in elastic modulus due to high-MW glutenin (Weegels *et al.*, 1988; Shewry *et al.*, 1988) network thermosetting. Clearly, simple determination of neither residual thiol content nor the amount of insolubilized protein (Rogers *et al.*, 1990; Huang *et al.*, 1991) is sufficient for interpretation of the mechanism of firming or development of rubbery texture during heat–moisture treatment of gluten doughs, such as microwave baking or reheating of bread (Slade and Levine, 1992c). The causative insolubilized proteins should be identified by demonstration of gel electrophoresis bands, high-pressure liquid chromatography (HPLC) peaks (Lookhart *et al.,* 1987; Pomeranz *et al.,* 1987; Menkovska *et al.,* 1987; Ng and Bushuk, 1987), or antigens to monoclonal antibodies (Skerritt *et al.,* 1988; Hill *et al.,* 1988), which are present in doughs but missing in baked products. Missing gliadin subunits could account for increased firmness and decreased extensibility without increased rubberiness, while missing glutenin subunits could account for a dramatic increase in rubberiness with only moderate increase in firmness (Levine and Slade, 1989b). These structure–property relationships of gluten are critical to the processing, product quality, and storage stability of various types of flour-based doughs and finished baked goods (Schofield *et al.,* 1984; Davies, 1986; Schofield, 1986; Blanshard, 1988; Slade *et al.,* 1989; Levine and Slade, 1989b; Hoseney and Rogers, 1990; Hoseney, 1991, 1992; Slade and Levine, 1992c).

2. *Thermosetting Behavior of Amorphous Gluten*

Slade (1984) reported DSC results of T_g measurements from a study of commercial vital wheat gluten, approached as an amorphous, water- and lipid-compatible polymer. Isolated wheat gluten at low moisture (i.e., 6 w% "as is" water content) manifested a T_g of 66°C (Slade, 1984; Levine and Slade, 1988a). Once heated through this glass transition, gluten has sufficient mobility, due to thermal and water plasticization, to form a thermoset network, via disulfide crosslinking. This thermally irreversible thermosetting reaction was suggested (Levine and Slade, 1988a) to be analogous to chemical "curing" of epoxy resin and "vulcanization" of rubber. As described earlier, such classical thermosetting reactions of synthetic amorphous polymers are also only possible at $T > T_g$ (Prime, 1981; Sperling, 1986). In contrast to its response to plasticization by water alone, gluten remained thermoplastic (i.e., its glass transition was reversible) in 1:1 comelts with nonaqueous plasticizers such as triacetin and B12K, the latter a blend of lipids commonly used as a bread-shortening system. However, higher T_g values of 73° and 79°C demonstrated the more dramatic plasticizing effect on gluten of only 6 w% water, compared to 50 w% triacetin or B12K, respectively (Slade, 1984; Levine and Slade, 1988a). This finding, that water is far superior to lipids in its ability to plasticize gluten, was recently corroborated by results of Kalichevsky *et al.* (1992c,d).

In the context of effects on bread-baking performance, Slade (1984) deduced that the interaction of aqueous gluten with lipids represents another example of relative "antiplasticization" of a polymer by a higher-

MW plasticizer [analogous to the effect of different sugar–water co-solvents on the gelatinization of starch (Slade and Levine, 1987b)], relative to plasticization by water alone. Slade's (1984) conclusion, that the thermomechanical and rheological properties of wheat gluten can be explained based on recognition of gluten as a water- and lipid-plasticizable, highly amorphous polymer system, was verified, in part, by T_g measurements from a subsequent DSC study by Hoseney *et al.* (1986). As shown earlier in Fig. 10, their glass curve of T_g versus w% water is a smooth curve from >160°C for the glassy polymer at ≤1 w% moisture to 15°C for the rubbery polymer at 16 w% moisture. As discussed earlier, these results exemplified the typical extent of plasticizations by water (i.e., depression of T_g by ≈10°C/w% water), previously illustrated for a variety of other water-compatible, amorphous food polymers (Levine and Slade, 1988a, 1989b; Slade *et al.,* 1989). However, Hoseney *et al.* (1986) did not observe the thermosetting behavior of aqueous gluten, reported by Slade (1984); we suggested that this could have been due to differences in the DSC measurement techniques employed (Slade *et al.,* 1989). More recently in Hoseney's laboratory, Dong (1992) conducted a TMA study of gluten at low moisture contents and reported that gluten's T_g was observed to increase to higher temperatures with increasing time of heat treatment at T slightly above T_{g0}, as a consequence of thermosetting via intermolecular disulfide crosslinking. Dong explained the contrast between her results and the earlier ones of Hoseney *et al.* (1986) by pointing out that TMA showed greater sensitivity than did DSC to changes caused by heat treatment of gluten, because TMA is known to be more sensitive to rheological changes occurring at and below the gel point of a thermosetting polymer (Prime, 1981). Slade's (1984) original conclusion, regarding the basis of its structure–property relationships in the amorphous polymeric nature of wheat gluten, was also verified by another DSC study (Fujio and Lim, 1989) of the effect of moisture content on T_g and the resulting properties of gluten. Fujio and Lim's results showed that heat treatment of native gluten at low moisture produced an amorphous polymeric material that, once softened to a rubbery liquid (of increased compressibility under pressure and resulting higher density) due to plasticization by heat and moisture, underwent a diagnostic color change (as a consequence of the pressure-induced increase in density) above a critical temperature (which decreased with increasing moisture) corresponding to T_g. Additionally, a recent DSC study by Lawton and Wu (1993) on the thermal behavior of annealed wheat gluten produced new experimental results that confirmed the findings of earlier workers, with regard to gluten's behavior as an amorphous, water-plasticizable polymer, which is analogous to the behavior of many synthetic amorphous polymers.

It has been suggested (Slade *et al.,* 1989) that the enhanced ability of amorphous gluten in hard wheat flour–water doughs heated to $T > T_g$ to thermoset (i.e., undergo an irreversible structural transformation from viscous liquid polymer system with transient crosslinks to elastic, permanently crosslinked gel with a higher network T_g) represents a critical aspect of the baking/volume-determining mechanism for white pan bread, and is partly responsible (along with starch gelatinization) for the mechanical and rheological differences between dough and baked bread. Recent results that lend direct support to this suggestion have come from a study by Van Vliet *et al.* (1992) of the mechanism of gas retention in bread doughs from hard wheat flours. Their results showed that in biaxially extended doughs, hydrated gluten is oriented and birefringent [as also reported previously by Slade *et al.* (1989)], and that gluten in this condition can thermoset during baking, thus contributing to the setting of the bread crumb and its transformation from foam to sponge. In a related vein, the dramatic increases in viscosity and elastic modulus of starch-free gluten–water doughs heated to temperatures between ≈50° and 100°C, leading to gelation via network formation by protein–protein aggregation at $T > 80°C$ (Schofield *et al.,* 1984; Davies, 1986; Ablett *et al.,* 1988; Blanshard, 1988; Dreese *et al.,* 1988a; Shewry *et al.,* 1988; Weegels *et al.,* 1988; Masi, 1989), are strongly suggestive of a molecular mechanism involving a classical thermosetting process via covalent crosslinking in an amorphous polymer system (Levine and Slade, 1989b). It is well known that the effect of shortening (mixed lipids) on flour–water bread doughs produces breads of increased baked loaf volume, by allowing greater oven spring during baking (Moore and Hoseney, 1986). This effect has been interpreted (Slade *et al.,* 1989) as arising from lipid plasticization of gluten to extend its period of thermoplasticity early in the baking process, prior to thermosetting of the water-plasticized gluten network at the end of baking, in addition to the better known role of lipid to retard starch pasting. It has also been suggested (Slade *et al.,* 1989) that the characteristically rubbery/leathery texture produced by microwave reheating of bread and other baked products results in large part from a postcure heat treatment of the thermoset gluten polymer, which effects a further increase in crosslinking density with a concomitant further elevation of network T_g. In a related vein, we have described a new hypothesis [reviewed elsewhere (Slade *et al.,* 1989)] for the role of gluten in the "spreading"/baking mechanism of sugar-snap cookies. This hypothesis differentiates, based on flour functional properties, between certain glutens that thermoset during baking (as in bread) of inferior cookies made from poor-cookie-quality hard wheat flours and other glutens that remain thermoplastic until structural collapse occurs during baking of superior cookies made from excellent-quality soft wheat flours (Stauffer, 1990, 1992).

In the context of the earlier description of the gelation mechanism and viscoelastic properties of thermosetting amorphous polymers, the parallels seem obvious (Slade *et al.*, 1989) among the established behavioral characteristics of thermosetting synthetic amorphous polymers, the equally well-documented behavior of thermosetting partially crystalline and paracrystalline keratin biopolymer systems (Whewell, 1977; Milczarek *et al.*, 1992), and the empirically known structure–function relationships of hard wheat glutens in the baking of excellent breads and inferior sugar-snap cookies (Bloksma, 1978; Kasarda *et al.*, 1978; Pomeranz, 1978). Moreover, the general response of fully baked products to subsequent microwave heating is consistent with a postcure reaction stage in a continuous, thermoset gluten network. Such a partially thermoset network, incompletely cured during baking, with incident T_g = ult-T_g (as a result of removal from the oven, rather than intervening vitrification), could have its curing process extended or even completed during microwaving, where superheated steam could provide internal temperatures greater than those during oven baking. Consequently, the network T_g would increase to a higher ult-T_g or even to $T_{g\infty}$. The resulting texture of a product after cooling to room temperature would be characterized by increased rubberiness/leatheriness, due to increased macroscopic viscosity, owing to the change in ΔT between network T_g and room temperature (Slade *et al.*, 1989). The maximum elevation of T_g effected by curing, from molecular T_{g0} to network $T_{g\infty}$, varies significantly depending on the system, e.g., from <30°C for an unidentified DuPont elastomer (Maurer, 1981) to >170°C for a bisphenol-A epoxy (Prime, 1981). Considering the approximate value of T_{g0} for developed gluten in unbaked bread dough [i.e., gluten T_g' of about −7.5°C (Slade *et al.*, 1989)] and the comparative textural attributes at room temperature of the dough, the fresh oven-baked loaf, and the product microwaved after baking, we have speculated (Slade *et al.*, 1989) on the values of ult-T_g after baking or after microwaving. For $\Delta T \approx 33°C$ (room $T - T_{g0}$), dough firmness is characteristically low. Fresh-baked and cooled bread is clearly elastic (diagnostic of a critical extent of network formation), but also quite deformable, so that ΔT must exceed 0. Thus, baked ult-T_g is between −7.5° and 25°C. The leathery texture of microwave-reheated bread is diagnostic of $\Delta T \ll 20°C$. In the worst case, microwaved ult-T_g may reach 25°C or above! As observed for the aging of commercial synthetic polymer thermosets, moisture will play a critical role in aging of the baked product. Thus, ult-T_g and product modulus could be elevated even further by moisture redistribution or drying (as an additional consequence of microwave heating) or depressed by humidification (Slade *et al.*, 1989).

Such apparent analogies imply a relatively high potential for displacement of the distribution of free thiol groups and intramolecular disulfide bonds toward intermolecular disulfide crosslinking and network thermosetting during baking in glutens from hard wheat flours, without underestimating the contribution of leached-amylose networks [especially from chlorinated flours, as emphasized by Blanshard (1986)] or pentosan networks (Slade *et al.*, 1989; Slade and Levine, 1992c). Blanshard (1986) described the progressive firming of cakes during cooling after baking in terms of T_g of amylose and the plasticizing effect of moisture and short amylopectin branches. Because the cake crumb structure depends on leached-amylose networks [so that replacement of wheat starch by waxy corn starch results in cake collapse (Blanshard, 1986)], the operative T_g is network T_g. In glutens from excellent cookie-quality soft wheat flours used in optimized cookie formulations, the converse argument, suggested by cookie-baking results reviewed elsewhere (Slade *et al.*, 1989, 1993; Slade and Levine, 1992c; Levine and Slade, 1993), implies a lower potential for such a displacement of the distribution toward disulfide crosslinking during baking. These speculative conclusions were offered (Slade *et al.*, 1989) to stress the importance of network T_g, rather than molecular or segmental T_g, to the rheological behavior of baked products (Levine and Slade, 1989b; Slade and Levine, 1992c), in the hope that they would stimulate future research.

Subsequent research in several laboratories (Attenburrow *et al.*, 1990, 1992; Rogers *et al.*, 1990; Davies *et al.*, 1991; Huang *et al.*, 1991; Dong, 1992; Tian and Blanshard, 1992b) has focused on the suggestion that thermosetting of water-plasticized gluten, through high-temperature treatment by microwave or conventional heating, results from disulfide-crosslinked network formation and concomitant elevation of gluten's T_g, which could account for the textural toughening of reheated bread (Slade *et al.*, 1989). The previously mentioned findings of Dong (1992) appear to lend strong support to this concept. In contrast, workers at Unilever (Davies *et al.*, 1991; Attenburrow *et al.*, 1992) reported "anomalous behavior" that could call the concept into question. They made DMTA measurements of storage modulus for hydrated glutens (21% moisture) and found, unexpectedly, a lower T_g for gluten heat-set at 150°C than for gluten heat-set at 90°C. This finding appeared to contradict results of their earlier study (Attenburrow *et al.*, 1990), which were interpreted as showing that increasing temperature treatments (up to ≈130°C) of rubbery gluten dough result in an increased amount of intermolecular crosslinking. A possible explanation for the "anomalous behavior" they observed [which they speculated could be due to a reduction in polymer chain length (Attenburrow *et al.*, 1992)] is that it resulted from a thermosetting reaction ("curing") carried out in air, leading not only to crosslinking but also to oxidative degradation at 150°C (but not at 90°C) and, thus, to a net reduction in T_g; if the reaction had been carried out in a nitrogen atmosphere, the gluten heat-set at 150°C would have shown a higher T_g than that for gluten heat-set at 90°C. This possibility is suggested by a recent finding for synthetic polyimide thermosets; i.e., postcuring a thermoset polyimide in air can oxidatively degrade the polymer, but postcuring it in nitrogen will raise its T_g (Studt, 1992). Further support for this explanation could come from the fact that the measured T_g for gluten heat-set at 150°C was around −10°C (Davies *et al.*, 1991; Attenburrow *et al.*, 1992), a value more suggestive of a molecular T_g (i.e., close to $T_g' \approx -7.5°C$) for somewhat degraded gluten than of a network T_g (expected to be well above 0°C) for extensively crosslinked gluten (Slade *et al.*, 1989). In a related study by Tian and Blanshard (1992b), who used NMR to investigate the toughening of bread by microwave reheating, their data could be interpreted as showing that microwave heating results in a thermoset gluten network with a rheologically unique distribution of disulfide crosslinks, rather than an increase in the number of crosslinks (Schofield *et al.*, 1983). Such an interpretation would contrast with the questionable conclusion reached by Rogers *et al.* (1990) that disulfide crosslinking of gluten cannot explain the toughening of bread heated or baked in a microwave. Obviously, still more research is warranted, to clarify the relationship among gluten thermosetting, disulfide crosslinking, network T_g, and the practical problem of textural toughening of microwaved or conventionally reheated baked goods.

3. *Thermoplastic and Thermoset Behavior of Aqueous Gluten Systems*

As mentioned earlier, gluten–water blends are capable of exhibiting thermoplastic or thermoset behavior. With respect to gluten model systems, it has been shown that heat damage in gluten–water blends depends on both temperature and moisture content, and that thiol–disulfide exchange reactions are a critical feature of the changes in both mechanical and thermodynamic properties. These effects of heat–moisture treatment were measured by changes in interfacial behavior, distribution, and reactivity of thiol and disulfide groups; rheology; solubility; and gel electrophoresis to identify the missing bands in the solubilized protein (Schofield *et al.*, 1983; Weegels *et al.*, 1988, 1991; Weegels, 1991; Weegels and Hamer, 1991; Eliasson and Silverio, 1991). At 65% moisture, progressive disulfide exchange leading to enhanced thermostability of crosslinking of high-MW (HMW) glutenins begins below 70°C, and unfolding and disulfide crosslinking of relatively heat-labile, sulfur-rich (α) gliadins occur above 70°C, while relatively heat-stable, sulfur-poor (ω) gliadins are not polymerized even at 100°C (Schofield *et al.*, 1983). At 25% moisture and 80°C, HMW glutenins become crosslinked by disulfides, leading to a more rigid glutenin matrix, but lower-MW glutenins are less affected, and gliadins are essentially unchanged (Weegels *et al.*, 1988; Ablett *et al.*, 1988). At moisture contents below 21%, even the HMW glutenins are progressively less affected (Weegels *et al.*, 1988).

Similar experiments have not been conducted in gluten model systems containing sucrose, which would be much more appropriate for understanding gluten functionality in rich cracker and cookie products (Slade and Levine, 1992c). Actual baking experiments, followed by protein solubilization and gel electrophoresis, give clues to the expected behavior for ternary gluten–sucrose–water model systems. During baking of lean white pan bread (high moisture, low sugar), both HMW glutenins and gliadins (sulfur-rich α-, β-, and γ gliadins most affected, sulfur-poor ω-gliadins least affected) become crosslinked and insoluble in the absence of β-mercaptoethanol (Lookhart *et al.*, 1987; Menkovska *et al.*, 1987, 1988). During baking of sugar-snap cookies with high-quality soft wheat flours, HMW glutenins are unaffected, and gliadins are essentially unaffected (Pomeranz *et al.*, 1987, 1989). The absence of extensive polymerization of glutenins and S-rich gliadins in cookie systems, compared to the presence of disulfide crosslinking of glutenins and S-rich gliadins in bread crumb (even greater in bread crust), was said to be "unexpected and unexplainable" (Pomeranz *et al.*, 1987), since the internal temperature of the cookie exceeded that of the bread crumb during baking. However, the high sucrose concentration in the AACC sugar-snap cookie dough retarded thermosetting of glutenins and S-rich gliadins, just as it retards the gelatinization of starch, compared to the extent of starch gelatinization in bread crumb (Slade and Levine, 1992c).

It is important to stress that the thermosetting of gluten proteins by disulfide crosslinks occurs with essentially no change in the measurable content of total free –SH groups; rather, there is a progressive shift in the location of free –SH groups from a sodium dodecyl sulfate (SDS)-extractable to an SDS-inextractable form (Schofield *et al.*, 1983). Thus, it is the progressive disulfide exchange, from the relatively thermolabile distribution characteristic of native gluten proteins in aqueous doughs toward an ultimate thermostable distribution characteristic of gluten networks with maximum rigidity and network T_g, that accounts for the mechanical changes from a thermoplastic gluten system in dough to a thermoset gluten in baked products (Schofield *et al.*, 1984; Levine and Slade, 1989b). As mentioned earlier, this mechanism of thermosetting is entirely analogous to the thermosetting of synthetic polymers (Slade *et al.*, 1989); with increasing reaction temperature, the instantaneous value of macroscopic T_g increases from an initial minimum value for the thermoplastic polymer chain (T_g), through an intermediate higher value for the partially thermoset network (gel-T_g or ult-T_g), to an ultimate maximum T_g (T_{g_∞}) of the maximally thermoset network (Sperling, 1986). For a homopolymer system, progressive thermosetting and increase in network T_g occur with a progressive increase in crosslink density and network rigidity (Prime, 1981). But, the very key to gluten functionality is that gluten is *not* a homopolymer system! The intra- and intermolecular locations and distribution of thermolabile disulfide bonds among the different native gliadin and glutenin proteins of gluten differ from the progressively more thermostable population of disulfide bonds that results from disulfide exchange among gluten proteins that have undergone conformational (secondary and tertiary) and associative (quaternary) changes during heat–moisture treatments (Schofield *et al.*, 1984). These differences in the spatial and energetic *distribution* of covalent disulfide linkages, from the thermoplastic distribution associated with the dominance of molecular T_g in the dough to the thermoset distribution associated with the dominance of network T_g in the baked product, and the decreased tendency for ongoing disulfide exchange to depart from the thermoset distribution (Weegels, 1991), compared to the relatively facile disulfide exchange in the thermoplastic distribution, account for the characteristic difference in mechanical properties of a dough at room temperature from a baked product that has been cooled to room temperature (Schofield, 1986; Levine and Slade, 1989b).

With respect to the mechanical behavior and sensory texture of heat–moisture-treated gluten-based systems, it may be instructive to distinguish possible pathways that lead to different "ultimate thermosets." A critical feature of nonequilibrium systems, such as thermosets, whose behavior depends on plasticization by time, temperature, and diluents of molecular and network glass transitions, is that the previous history of the system may be even more important than its final steady state (Slade and Levine, 1991a). We could compare the ultimate thermosets that would result from a two-step heating process with that from a single-step process. The ultimate distribution of disulfide linkages that would result from a two-step process of slow heating through the 55°–75°C temperature region where glutenins crosslink (Schofield *et al.*, 1983) to a resilient network noted for its elastic recovery, followed by generation of a tough, leathery, elastic network resulting from postcuring of the glutenin network and participation of gliadins (Schofield *et al.*, 1983), on continued heating past 130°C (Attenburrow *et al.*, 1990; Cocero *et al.*, 1992b), would not be the same as the distribution that would result, on instantaneously rapid heating to, and spontaneous crosslinking of gliadins above, 130°C, in a hard, brittle, short network via a one-step process. The generation of fewer crosslinks with greater rheological effectiveness, in terms of elastic recovery and chewy sensory texture, by the two-step process might well be associated with greater protein extractability, compared to the generation of greater insolubilization of protein and short, brittle sensory texture by the one-step process. The two-step process might be identified with conventional bread baking, followed by microwave reheating, or with atmospheric steam cooking, followed by microwave superheated-steam treatment, whereas the one-step process could represent initial microwave baking. The protein extractability, rheological behavior, and sensory attributes of the final steady states resulting from such alternative pathways would not be expected to be, and have in fact been shown not to be (Rogers *et al.,* 1990; Huang *et al.,* 1991), the same. In contrast, the direct contribution of apolar interactions to the mechanical behavior of heat–moisture-treated gluten systems is not expected to be a dominant feature. Although an increasing extent of hydrophobic interactions among gluten proteins with increase in temperature during heat–moisture treatments is expected to be indirectly important to gluten functionality, through their modulation of disulfide exchange reactions during baking (Weegels *et al.,* 1991), the relative importance of hydrophobic interactions is diminished on cooling (Privalov and Gill, 1988), when the baked product is returned to room temperature.

IV. RESEARCH NEEDS: OUTSTANDING PROBLEMS, ISSUES, AND UNANSWERED QUESTIONS

In the context of this concluding section on research needs and unsolved problems, it is apropos to quote the following remark by Franks (1992a), contained in a recent editorial on "the importance of being glassy:"

> It is clear that amorphous solids and glass transitions impinge directly on several aspects of low temperature science. What is not clear to some of the practitioners who rush to apply these concepts is that the actual physical nature of the glass transition and its proper description are still subject to some very basic mysteries which continue to baffle physicists and chemists alike. We thus possess several applicable technologies and phenomenologies but lack a proper scientific understanding. Perusal of the relevant literature reveals much point scoring, overt and covert, rather than genuine attempts to solve the major outstanding problems.

In Section II, C, we discussed the wide variety of experimental methods that have been used recently to determine T_g in aqueous food polymer systems (Table V). As a practical matter, there is a need for further research with regard to the issue of the agreement, or lack of agreement, among T_g values measured for the same sample by different methods, or even by the same method (e.g., DSC) using different experimental conditions. Since the glass transition is a kinetically controlled change in state, but not an equilibrium thermodynamic change of phase (Ferry, 1980), it is not at all surprising that the measured value of T_g (be it dry T_g, T_g at $0 < W_g < W_g'$, or T_g') depends on the temperature–time (or –frequency) conditions of its measurement (Wunderlich, 1981, 1990). For example, for T_g measured by DSC, an order-of-magnitude decrease in heating rate (e.g., from 10° to 1°C/min) would generally result in a decrease in T_g of ≈3°C (Wunderlich, 1981; Noel *et al.*, 1991) [as predictable from the WLF equation (Slade and Levine, 1991a)]. Similarly, for T_g measured by DMA, a decade drop in measurement frequency would result in a decrease in T_g of about 3°–6°C (MacInnes, 1993). Consequently, a review of earlier reported T_g values for pure amorphous glucose (Slade and Levine, 1991a), measured [mainly by DSC or differential thermal analysis (DTA)] over the past 60+ years, showed a spread of 10°C, while the more recent T_g values for glucose listed in Table XIV show an even bigger spread of nearly 20°C. In contrast, as shown by Schenz *et al.* (1984; Levine and Slade, 1990), when the same sample is measured by different thermal analysis methods, using essentially the same time–temperature conditions of measurement, it is possible to obtain the same T_g value, at least for a simple model system. For a 20 w% sucrose–water solution, measured by DSC (transition midpoint temperature), DMA (loss modulus peak temperature), and TMA (midpoint temperature of dimension change), Schenz *et al.* observed the same T_g' value of −32°C, in agreement with other measurements subsequently made by many other workers (Table XIIB). As shown by the detailed studies by Kalichevsky *et al.* (1992a–c), when the samples to be measured are model systems much more complex than a sucrose solution (e.g., aqueous amylopectin or gluten, with or without added sugars), and the techniques employed to determine T_g are as diverse in their measurement aspects as are DSC, DMTA, NMR, and Instron, less than perfect agreement among measured T_g values is only to be expected. Of special note, the results of Kalichevsky *et al.* (1992a–c) demonstrated that T_g, as determined by NMR [which can measure T_g for a sample in terms of the onset of mobility (above a so-called "rigid lattice limit") on a size scale of ≤10 Å], was generally observed at a significantly lower temperature (for a given sample composition and moisture content) than was the T_g determined by DSC or DMTA, which are considered to be able to detect the onset of longer-range, cooperative mobility in a glassy domain of >100-Å dimension (Wunderlich, 1981, 1990; Slade and Levine, 1991a). Also noteworthy are the recent results of a careful thermal analysis study by Cassel and Twombly (1991), who compared the T_g values measured by DSC, DMA, and TMA for a well-characterized sample of epoxy resin. They reported that "the best agreement in T_g values between the various measurement methods was obtained between: DSC heat flow midpoint; TMA onset of expansion, flexure or stress relief; and the onset of the storage modulus for DMA data taken at 0.1 Hz. These were all within one degree . . . . The best correlation with the DSC and

TMA data to be obtained from a 1-Hz DMA run was that of the onset of the loss modulus peak." As reviewed elsewhere (Levine and Slade, 1990; Schenz *et al.,* 1991), thermomechanical methods such as DMA or TMA are generally considered to have greater inherent sensitivity, for the detection of lower-intensity transitions such as glass transitions (in comparison to crystalline melting transitions), than do thermal methods such as DSC or DTA (Kalichevsky *et al.,* 1993a). Thus, for T_g measurements on real, multicomponent, complex food products, in which moisture and water-compatible solids can be heterogeneously distributed, which can result in the existence of multiple amorphous domains (large and small) with different T_g values (Slade and Levine, 1991a), it is generally recommended that DMA or TMA be used, in addition to or in place of DSC (e.g., Dong, 1992; Le Meste *et al.,* 1992; Hoseney *et al.,* 1992), when one has a choice among these techniques. In a related vein, it has been noted that, from a food technology/product development point of view, it would be desirable to have alternative experimental methods that would be easier to use, faster to perform, and less expensive than DSC, DMA, or TMA, for the accurate measurement of T_g of real foods (Hegenbart, 1993). Such methods do not currently exist.

There is a widely agreed need for further research with regard to several questions, of more academic interest, about T_g values. One unanswered question concerns the fundamental relationship (presumably, cause-and-effect) between the molecular structure of a given glass former and its T_g (i.e., dry T_g, T_g', or low-moisture T_g). This question was alluded to in Section III, A, with reference to the dry T_g values compiled in Table XIV, which showed that T_g can vary substantially, even within a series of carbohydrates of the same MW and only the most subtle differences in molecular structure.

Another question, discussed in detail in Section III,C,1,a, relates specifically to the significant differences among reported T_g' values (as illustrated in Table XIII) and the various diverse interpretations of experimental DSC heat-flow curves, which have given rise to such differences. Although much of the recent debate and controversy over T_g' values has centered around the T_g' for sucrose, which has been by far the most studied sugar, the T_g' value for glycerol, as reported by only a few groups (Levine and Slade, 1988b; Franks, 1985, 1993a; Ablett *et al.,* 1992a; Roos, 1992d), has nevertheless also become a bone of contention. We have long considered glycerol a unique (at least, in our experience) and perplexing case, in that its T_g' value, as we have measured it [−65°C (Levine and Slade, 1988b)], cannot be made to fit on a smooth glass curve drawn between the T_g for water (−135°C) and that for neat glycerol [−78° (Ablett *et al.,* 1992a) or −93°C (Hatley and Franks, 1991; Roos, 1992d; Franks, 1993a)], because, as right-fully pointed out by Ablett *et al.* (1992a), our T_g' value is ***higher*** than glycerol's dry T_g. In contrast, the T_g' values of −95° or −100°C are lower than the corresponding dry T_g values reported by Ablett *et al.* (1992a) and Franks (1993a), respectively, and so can be made to fit a smooth glass curve for the glycerol–water system, as would ordinarily be required (Slade and Levine, 1991a). In the absence of any evidence to support the possibility of glycerol–water hydrate formation as an explanation for our anomalously high T_g' value, glycerol stands alone as the only low-MW carbohydrate, among hundreds we have analyzed, for which our measured T_g' value cannot be made to fit a smooth glass curve anchored by the measured dry T_g value for the solute (Slade and Levine, 1988b). It would certainly be desirable to understand the reason for, and possible functional significance of, this anomalous behavior of glycerol.

As discussed in detail in Section III,C,1,b, another part of the recent T_g'–C_g' controversy has involved the issue of the disparity between reported C_g' values (Table XIII) for many low-MW carbohydrates. There is an obvious polarization between the "rigorous" C_g' values, all of which fall around 80 w% solute, and the "apparent" C_g' values, which appear to vary with T_g' and solute MW [i.e., show a general trend of increasing C_g' with increasing T_g' and MW (Levine and Slade, 1986, 1988b,c)] in a way that one might intuitively expect and view as consistent with practical, albeit empirical, experience. That experience begs the following questions: 1) Doesn't every food technologist "know" that, to fabricate a frozen product (e.g., ice cream) with minimum ice content and maximum textural softness, or an IMF with minimum "A_w" (RVP) [if one accepts the premise that C_g' and RVP both depend in a related fashion on plasticizer mobility (Slade and Levine, 1991a)], one would formulate with low-MW sugars (e.g., glucose) rather than polymeric carbohydrates (e.g., maltodextrin)? (2) Doesn't everyone accept the rule of thumb that ice content in a frozen product, or RVP of an IMF, would generally increase (and so would C_g') with increasing MW for a homologous series of solutes (Slade and Levine, 1991a)? Such deliberately prejudicial questions are simply intended to emphasize the need for a deeper understanding [rather than the point scoring referred to by Franks (1992a)] of the reasons underlying the polarization between "rigorous" and "apparent" values of C_g'.

Also in need of a deeper understanding is the relationship between "A_w" and T_g, where these properties of a food system represent the traditional ("water activity" concept) versus the modern approach ("food polymer science," sometimes referred to as "glass transition theory") to assessment of food quality, safety, and stability (Slade and Levine, 1991a). As alluded to in Section II,E, the relationship between these properties has been dealt with in considerable depth by various groups in recent years (Slade and

Levine, 1985, 1988a, 1991a; Simatos and Karel, 1988; Karel, 1989; Roos and Karel, 1990, 1991a,b, 1993; Franks, 1991a,b; Chuy and Labuza, 1992; Nelson and Labuza, 1992a,b, 1993; Nelson *et al.*, 1992; Reid, 1992b; Roos, 1992b; Sapru and Labuza, 1992a,b; Karel *et al.*, 1993a,b; Nelson, 1993). Worthy of special note in this regard is Roos' novel and original treatment of experimental data for water adsorption isotherm at 25°C, water content at $T_g = 25°C$, and corresponding "A_w", all plotted together on a single graph to highlight "the critical water content and "A_w" values . . . that depress T_g to ambient temperature" for various food materials (Roos, 1992b). Despite such useful and informative approaches, there is still a need for greater understanding that would be more directly applicable to practical food technology/product development problems (Hegenbart, 1993).

Another much-debated issue, in need of resolution through further research, concerns the breadth of applicability of WLF-type kinetics (in place of Arrhenius kinetics) to predict rates of deterioration processes in food products at $T > T_g$ (Levine and Slade, 1986, 1988b,c, 1989d; Simatos *et al.*, 1989; Slade and Levine, 1991a; Buera and Karel, 1992; Nelson and Labuza, 1992a; Peleg, 1992; Nelson, 1993). As discussed in Section III,D,1, with reference to Table XB, the recent controversy about the appropriateness of the WLF equation to describe kinetics in rubbery food systems has focused primarily on two aspects: (1) the specific values (i.e., "universal" versus nonuniversal) of the WLF coefficients, C_1 and C_2; and (2) the correct T_g to define as the WLF reference state. With regard to the question about the WLF coefficients, experimental results from Reid's group (Lim and Reid, 1991, 1992; Reid *et al.*, 1992, 1993b; Kerr *et al.*, 1993) and Labuza's group (Nelson and Labuza, 1992a; Sapru and Labuza, 1992a,b; Nelson, 1993), when viewed together with those from Karel and co-workers (references in Table XB), have clearly indicated that whatever the most suitable values of C_1 and C_2 may be, the temperature dependence of reaction rates on $T - T_g$, as defined by the WLF equation, evidently applies to a wide range of diffusion-limited processes in food systems. Nevertheless, a better understanding of the reasons behind case-by-case differences in C_1 and C_2 values would certainly be desirable.

The question about the correct T_g reference state for use in the WLF equation, when this equation is applied to reaction kinetics data for translational diffusion-limited deterioration processes in partially melted, rubbery frozen food systems at $T_g' < T < T_m$, has become one of the most controversial and passion-filled issues of the day. We have argued that the appropriate reference state for an ice-containing, rubbery product should be T_g', rather than a lower T_g corresponding to a less freeze-concentrated solute–UFW mixture (Levine and Slade, 1988c, 1989c,d; Slade and Levine, 1991a). Our reasoning [based on the conceptual framework of WLF theory (Ferry, 1980)] is that the correct glassy reference state for an ice-containing system should represent the composition (C_g') that a maximally freeze-concentrated sample would have come from on warming (from $T \leq T_g'$ to $T_g' < T < T_m$), and that it would, in practice, go back to on recooling (from $T_g' < T < T_m$ to $T \leq T_g'$) at a realistic rate, as the ice-containing, partially melted (at $T_g' < T < T_m$) sample would slowly track along the liquidus curve between the temperature limits of T_g' and maximum T_m (e.g., see Fig. 4) during fluctuations in freezer-storage temperature. On the other side of this heated argument, Karel (in his summary notes from both the Easter School and ISOPOW-V conferences) and others (Kerr *et al.,* 1993; Reid *et al.,* 1993b; Simatos and Blond, 1993) have claimed that the proper reference state should be a lower T_g than T_g', which would represent the more dilute solute–UFW glass (of $C = C_g < C_g'$) that could result if the partially melted, rubbery sample at $T_m > T > T_g'$ were quench-cooled [at an unrealistically high rate (Levine and Slade, 1989c)] to a temperature below the glass curve (i.e., $T < T_g$ at C_g), but they have not presented any experimental evidence that would unequivocally support this claim. [Results reported by Kerr *et al.* (1993) and Reid *et al.* (1993b) were inconclusive on this issue, showing essentially the same excellent correlations of reaction rates with $T - T_g'$ and with $T - T_g$ ($r^2 = 0.98$ and 0.99, respectively).] On the contrary, as discussed in Section III,C, Chang and Randall (1992) showed convincingly that T_g', not the lower T_g, is the relevant T_g that governs collapse during freeze-drying. Moreover, Reid *et al.* (1993b) have conceded that "the empirical observation remains that $T - T_g'$ is linearly correlated to reaction rates, whatever the event signified by T_g'." Obviously, this controversial question needs to be addressed dispassionately and resolved by further research.

Some other unresolved issues that have been highlighted in this review include the following:

1. The usefulness of theoretical equations for predicting T_g of mixtures (Section III,A,1)
2. The functional significance of the similarities versus differences in the aqueous glass curves for high-MW food polymers (Section III,B)
3. The underlying reason for the "schizophrenic" behavior of small sugars as plasticizers or antiplasticizers of food polymers (Section III,B,1)
4. The extent of the diffusional mobility of water (and other low-MW, volatile or labile components) and matrix solutes in aqueous food glasses at $T < T_g$, and of the instability that could result from diffusion-controlled deterioration reactions, were they to occur at appreciable rates in the glassy solid (Section III,C,2)

5. The reason for the difference in the decrement in modulus at T_g for aqueous versus anhydrous food polymer glasses (Section III,D,1,a)
6. The relationship and underlying significance of "strong/fragile" behavior and T_m/T_g ratio of glass-forming liquids (Section III,D,2)
7. The origin and functional significance of the higher-temperature, glass-like transition in pure amorphous fructose and galactose (Section III,D,2)
8. The role of wheat gluten in the mechanism of toughening of high-moisture baked goods during postbake heat treatments—classical thermosetting behavior of amorphous polymers? (Section III,E).

In view of the many unanswered questions and unresolved issues highlighted in this section, it is not surprising that the subject of this review has represented a powerful force capable of drawing scientists from several different disciplines (e.g., food, pharmaceutical, biotechnology) together in recent years to confer and debate. Two previous conferences devoted to the subject of glasses and glass transitions in foods, one in 1990 at Wageningen University and the other the 1992 Easter School at Nottingham University, have already been discussed. Another such meeting, an extraordinary 2-day discussion symposium on the "Chemistry and Application Technology of Amorphous Carbohydrates," conceived by Professor Felix Franks, took place in the Spring of 1995. Professor Franks described as follows the situation that prompted him to propose this symposium:

> The physical properties of amorphous carbohydrates in the anhydrous state or at a low moisture content play an important role in the processing and product quality of cereal-based and various other foods and the stabilization of pharmaceutical and biotechnological products (e.g., as excipients in freeze-drying). There is an increasing awareness that, in all such applications, thermomechanical properties partly determine the choice of suitable formulations. Despite their increasing importance in food and pharmaceutical process technology, the chemistry of such amorphous sugars, perhaps containing a small amount of moisture, is substantially unexplored. Formulations and recipes are usually arrived at on a hit-or-miss basis with little basic understanding of the reasons for success or failure.

About 30 invited experts were brought together

> to discuss and define the relevant problems, rank them in order of importance, and suggest effective experimental, theoretical, and computational methods for their study. The following properties and attributes are among those that require an improved understanding:
>
> Relationships between molecular structure and glass transition [discussed above and in Section III,A];
>
> Chemical reactivity of solid sugars [discussed in Section III,C,2];
>
> Chemical and biochemical reactions and kinetics in supersaturated carbohydrate mixtures [discussed above and in Section III,D];

Physical processes (e.g., crystallization) of, and within, amorphous carbohydrates; effects of residual moisture [discussed in Section III,D,4];

Solid solutions involving carbohydrates [Franks, 1993b];

Dynamics of small molecules (e.g., water) within amorphous carbohydrates [discussed in Section III,C,2];

Suitable model systems and analytical methods [discussed above and in Section II,C];

Role of carbohydrates as bioprotectants against desiccation [Green and Angell, 1989; Franks *et al.*, 1991; Roser, 1991,a,b; Colaco *et al.*, 1992; Levine and Slade, 1992a; Carpenter *et al.*, 1993; Crowe and Crowe, 1993; Crowe *et al.*, 1993; Franks, 1993a,b; Roser and Colaco, 1993; Table IIID].

A summary report of the proceedings and recommendations of the symposium will be prepared and issued by the conveners (Professor Franks and H. Levine).

Also worthy of note here was the commencement in late 1993 of phase II of the ACTIF research program at Nottingham University. Following up on the work of ACTIF I, ACTIF II proposed "to investigate the significance of the 'rubbery state' in foods in relation to processing, quality and storage life" (John Blanshard *et al.*, personal communication, 1993).

V. CONCLUSIONS AND FUTURE PROSPECTS

The field of food science and technology has recently enjoyed a seemingly exponential growth of interest in concepts and studies centered around the glassy state phenomenon and glass transition in foods, the applications of state diagrams, WLF kinetics, and the plasticizing effect of water on T_g. This spurt of interest stems from a growing realization of the importance of glassy and rubbery states to the quality (including textural, structural, and rheological attributes), safety, and stability of foods. This state of affairs is evidenced by the fact that more than 500 of the references cited in this review deal with the glassy state phenomenon and glass transitions in food materials and systems, and more than 400 of those have been published since 1990. Results of such studies have demonstrated the major opportunity offered by the food polymer science approach to expand not only our quantitative knowledge but also, of broader practical value in the context of industrial applications, our qualitative understanding of food products and processes, with respect to (1) structure–functional property and water relationships and (2) the influences of nonequilibrium glassy and rubbery states on time-dependent mechanical and rheological properties related to quality and storage stability. In the rest of this decade, we expect to witness even greater growth and interest in this exciting area, because it offers so many challenging questions still to be answered, while promising so many opportunities for technological advancement.

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