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Water relationships in starch transitions

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A new understanding of water relationships in starch-based ingredients, products, and processes has been approached through 'food polymer science', an innovative research discipline that emphasizes the fundamental and generic similarities between synthetic and food polymers, and provides a new interpretive and experimental framework for the study of food systems that are kinetically constrained. This paper reviews the key elements of the food polymer science approach, including the concepts of 'water dynamics' and 'glass dynamics', and how the broad relevance of this approach to studies of state transitions and structure-function relationships that control starch gelatinization, retrogradation, and annealing has been confirmed in many recent reports.

INTRODUCTION

What is a glass? What is a glass transition? Why is the temperature at which a glass transition occurs (T_g) so important to the processing and storage stability of so many different types of foods, including cereal-based foods? Why is the effect of water as a plasticizer on T_g of such widespread relevance to starch-based ingredients, products, and processes? Why are considerations of non-equilibrium glassy solid and rubbery liquid states in foods (as described in terms of state diagrams), rather than equilibrium phases (described by phase diagrams), more germane to issues of food process control and product quality, safety, and storage stability? Why are the kinetics of heat/moisture processes for cereal polysaccharide-containing foods and of deteriorative changes in such food systems during storage more often appropriately interpreted in terms of the Williams–Landel–Ferry (WLF), rather than the Arrhenius, equation? What is the 'food polymer science' approach, with its integrated concepts of 'glass dynamics' and 'water dynamics', and why has this research approach proved so useful to the study of the glassy state phenomenon and glass transitions in foods, and therefore gained such widespread support from so many investigators? And why has there been, since the early 1980s, such interest in these questions, and such increasing research activity in both academia and industry, especially in the last few years, in this area of food science and technology?

The answers to these questions will be illustrated by this review paper that will emphasize: (a) theoretical principles from the field of synthetic polymer science that are applicable to studies of glasses and glass transitions, structure-functional property relationships, and water relationships in starch-based food materials and systems; and (b) a broad compilation of the literature, focusing primarily on the most recent experimental studies by a number of groups that have been especially active in this growing field of research. In this paper, we point out several key elements of the food polymer science approach, which, in a variety of recent studies, have been shown to be particularly relevant to starch-based products and processes. Results of these 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 starch-containing foods, with respect to (a) structure-functional property and water relationships, and (b) the influences of non-equilibrium glassy and rubbery states on time-dependent mechanical and rheological properties related to quality and storage stability.

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PHYSICOCHEMICAL PRINCIPLES FROM SYNTHETIC POLYMER SCIENCE — FOUNDATION OF THE 'FOOD POLYMER SCIENCE' APPROACH TO WATER RELATIONSHIPS IN STARCH TRANSITIONS

In the decade of the 1980s, the value of a polymer science approach to the study of glasses and glass transitions, and of their importance to structure-property relationships, in starch-based food materials, products, and processes was increasingly recognized by a growing number of food scientists. In this respect, food science followed the compelling lead of the synthetic polymers field. Researchers who have advocated the study of glasses and glass transitions in foods, and whose groups have been most active in this field, include: F. Franks; J.M.V. Blanshard; C. van den Berg; M. Karel and Y. Roos; P.J. Lillford; D.S. Reid; V.J. Morris, S.G. Ring, and A.C. Smith; R.C. Hoseney; D. Simatos, M. Le Meste, and V. Huang; T.J. Maurice and C.G. Biliaderis; T.W. Schenz; D.B. Lund; H.F. Zobel; M.C. Williams; and L. Slade and H. Levine. Pertinent references to their works are listed in Table 1 (Slade & Levine, 1993).

As reviewed in earlier publications (Slade/Levine references in Table 1), the research discipline of 'food polymer science' emphasizes the fundamental and generic similarities between synthetic polymers and food molecules, and provides 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 (references in Table 2 (Slade & Levine, 1993)), this innovative discipline has developed to unify structural aspects of foods, conceptualized as kinetically metastable, completely amorphous or partially crystalline, homologous polymer systems, with functional aspects dependent on mobility and viewed in terms of 'water dynamics' and 'glass dynamics' (Levine & Slade, 1988*a*, 1989*b*, 1992;

Table 1. References to studies of the glassy state phenomenon in foods by researchers and groups active in the field

Researcher	References
Franks	Franks *et al.* (1977, 1991), Franks (1982, 1983*a,b*, 1985, 1986*a,b*, 1989, 1990, 1991*a,b*), Franks & Grigera (1990), Franks & Hatley (1990), Finegold *et al.* (1989), Hatley *et al.* (1991), Franks & van den Berg (1991)
Blanshard	Blanshard (1986, 1987, 1988), Blanshard & Franks (1987), Blanshard *et al.* (1991), Marsh & Blanshard (1988), Kalichevsky *et al.* (1992*a,b,c,d*, 1993), Kalichevsky & Blanshard (1992, 1992*a,b*, 1993*a,b*), Tian & Blanshard (1992, 1993)
van den Berg	van den Berg (1981, 1986, 1991, 1993), van den Berg *et al.* (1993)
Karel and Roos	Karel & Flink (1983), Karel (1985, 1986, 1989, 1990, 1992), Karel & Langer (1988), Karel & Saguy (1991), Roos (1987, 1992*a,b*), Paakkonen & Roos (1990), Roos & Karel (1990, 1991*a,b,c,d,e,f,g*, 1992, 1993), Shimada *et al.* (1991), Buera *et al.* (1992), Karmas *et al.* (1992), Labrousse *et al.* (1992), Levi & Karel (1992, 1992*a*), Karel *et al.* (1993)
Lillford	Ablett *et al.* (1986, 1988, 1992*a,b*, 1993), Edwards *et al.* (1987), Lillford (1988), Attenburrow *et al.* (1989, 1990), Ablett & Lillford (1991), Davies *et al.* (1991), Izzard *et al.* (1991), Lillford *et al.* (1992), Attenburrow & Davies (1993)
Reid	Reid (1985, 1990), Lim & Reid (1991), Hsu & Reid (1992), Reid & Hsu (1992), Reid & McCarthy (1992), Reid *et al.* (1992, 1993), Taylor *et al.* (1992)
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, 1993), Ollett & Parker (1990), Smith (1990), Warburton *et al.* (1990), Whittam *et al.* (1990, 1991), Cairns *et al.* (1991*a,b*), Ollett *et al.* (1991), Ring & Whittam (1991), Botham *et al.* (1992), Noel & Ring (1992), Whittam (1992), Parker & Smith (1993)
Hoseney	Hoseney *et al.* (1986, 1992), Hoseney (1991), Hoseney & Rogers (1990), Yost & Hoseney (1986), Doescher *et al.* (1987), Zeleznak & Hoseney (1987*a,b*)
Simatos, Le Meste, and Huang	Simatos & Karel (1988), Simatos *et al.* (1989), Simatos & Blond (1991, 1993), Le Meste & Duckworth (1988), Le Meste & Simatos (1990), Le Meste & Huang (1991), Le Meste *et al.* (1990, 1991*a,b*, 1992), Blond (1989, 1992), Blond & Colas (1991), Blond & Simatos (1991), Matthiesen *et al.* (1991), Huang (1992), Huang *et al.* (1992), Aynie *et al.* (1993)
Maurice and Biliaderis	Maurice *et al.* (1985, 1991), Biliaderis *et al.* (1985, 1986*a,b,c*), Biliaderis & Galloway (1989), Biliaderis & Zawistowski (1990), Biliaderis & Seneviratne (1990*a,b*), Biliaderis (1990, 1991*a,b*), Caldwell *et al.* (1990), Biliaderis & Tonogai (1991), Goff *et al.* (1992), Michniewicz *et al.* (1992)
Schenz	Schenz *et al.* (1984, 1991, 1993)
Lund	Chungcharoen & Lund (1987), Lund (1989)
Zobel	Zobel (1988), Zobel *et al.* (1988)
Williams	Soesanto & Williams, (1981)
Slade and Levine	Slade (1984), Slade & Levine (1984, 1985, 1987*a,b*, 1988*a,b,c,d*, 1989, 1991*a,b*, 1992, 1992*a,b*, 1993), Slade *et al.* (1987, 1989), Levine & Slade (1986, 1988*a,b,c,d*, 1989*a,b,c,d*, 1990, 1991, 1992, 1992*a*, 1993), Levine *et al.* (1991, 1992), Cole *et al.* (1983, 1984)

(Courtesy of Slade & Levine, 1993)

Table 2. Selected references on structure–property relationships from synthetic polymer science literature

A. Textbooks:

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

B. Journal papers and book chapters:

Kauzmann (1948), Williams *et al.* (1955), Walton (1969), Brydson (1972), Sharples (1972), Hardy *et al.* (1973), Haward (1973), Roberts & White (1973), Flory (1974), Petrie (1975), Johari (1976), Baro *et al.* (1977), Buchanan & Walters (1977), Fuzek (1980), Johnson *et al.* (1980), Moy & Karasz (1980), Starkweather (1980), Bair (1981), Batzer & Kreibich (1981), Keinath & Boyer (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 & Russell (1986), Blum & Nagara (1986), Domszy *et al.* (1986), Hiltner & Baer (1986), Mandelkern (1986), Cheng & Wunderlich (1987), Aubin & Prud'homme (1988), Burchard (1988), Ellis (1988), Sichina (1988), Cheng (1989), Murthy *et al.* (1989), Ehlich & Sillescu (1990), Johari (1991), Pissis & Apekis (1991), Allen (1993)

(Courtesy of Slade & Levine, 1993)

Slade *et al.*, 1989; Slade & Levine, 1991*a,b*, 1993). These unified concepts have been used to explain and predict the functional properties of food materials during processing and product storage (Slade/Levine references in Table 1). Key elements of this interpretive approach to investigations of structure–function relationships in food systems, with demonstrated relevance to studies of water relationships in starch-containing foods and of state transitions that control starch gelatinization, retrogradation, and annealing, include recognition of the following (Slade & Levine, 1987*b*, 1988*a,b,c*, 1989, 1991*a,b*, 1992, 1993; Levine & Slade, 1988*a*, 1989*b*, 1992, 1993):

(a) the behaviour of foods and food materials as classical polymer systems, and that the behaviour is governed by dynamics rather than energetics;
(b) the importance of the characteristic temperature T_g, at which the glass–rubber transition occurs, as a physicochemical parameter that can determine processability, product properties, quality, stability, and safety of food systems;
(c) the central role of water as a ubiquitous plasticizer of natural and fabricated amorphous food ingredients and products;
(d) 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 $T > T_g$;
(e) the significance of non-equilibrium 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.

Glasses and glass transitions

A glass is operationally defined as an amorphous (i.e. non-crystalline) 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, called vitrification (Luyet, 1960), results in the 'freezing in' or immobilization of the disordered structure of the liquid state (Wunderlich, 1981; Allen, 1993), 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 (but not a change in phase (Allen, 1993)), from a glassy mechanical solid to a rubbery viscous liquid, capable of flow in real time (Ferry, 1980; Wunderlich, 1980). In terms of thermodynamics, the glass transition is operationally defined as a second-order transition (Sperling, 1986; Wunderlich, 1990; Allen, 1993), as opposed to a first-order transition, e.g. crystalline melting, which involves a change of phase as well as a change of state, and is denoted by: (a) a change in slope of the volume expansion (a first derivative of the free energy); (b) a discontinuity in the thermal expansion coefficient; and (c) 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 (Levine & Slade, 1988*a*) (adapted from Franks, 1982) shows that as the tem-

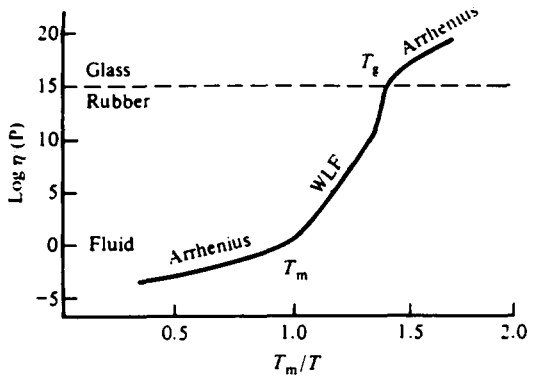

Fig. 1. Viscosity as a function of reduced temperature (T_m/T) for glassy and partially crystalline polymers. (Reproduced, with permission, from Levine and Slade (1988*a*).)

perature (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, non-linear form of kinetics referred to as WLF kinetics, derived from the WLF equation (Williams *et al.*, 1955), with an extraordinarily large temperature dependence (Angell, 1988; Franks & Grigera, 1990), becomes operative (Roberts & 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; Allen, 1993). At this glass transition temperature, the viscosity of a liquid is $\approx 10^{12}$ Pa s (10^{13} poise) (Koide *et al.*, 1990; Noel *et al.*, 1991), and the structural relaxation time as determined calorimetrically, e.g. by differential scanning calorimetry (DSC), for such a liquid is about 200 s (Angell, 1988). A 'mechanical' glass transition can be defined by combinations of temperature and deformation 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 & Walters, 1977; Angell, 1988; Green & Angell, 1989; Hosea *et al.*, 1990; Allen, 1993), 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), for which small-scale rotational motions of both solute and solvent (e.g. water) in solutions (Johari, 1991) do *not* become constrained as T falls below T_g (Allen, 1993), 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 & Slade, 1988*a*; 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 & Levine, 1988*b*).

Evolution of the 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 (1966) of glassy states in certain sugar-containing food products. They recognized: (a) 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 (b) 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 & Slade, 1986, 1988*a*; Slade & Levine, 1988*a*). White and Cakebread (1966) (see also Cakebread, 1969) were apparently the first food scientists to allude to the broader implications of non-equilibrium 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, (a) the work of White and Cakebread, (b) the even earlier (but somewhat better known by food technologists) work by Makower and Dye (1956) on the kinetics of crystallization of amorphous sucrose and glucose (from the water-plasticized, rubbery state at room $T > T_g$), (c) more recent work by other candy technologists such as Herrington and Branfield (1984) on the physicochemical properties of sugar glasses, and (d) 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, other workers (cited in Tables 1 and 3 (Slade & Levine, 1993)) have helped to advance, with increasing momentum, concepts and approaches based on recognition of the importance of non-equilibrium glassy and rubbery states in foods and on application of the underlying principles. The current state of accelerating activity and interest in this area is illustrated by the fact that 16 chapters in a recently published book on water relationships in foods (listed in Table 3B) include 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

Table 3. References to recent publications dealing with the practical significance of the glassy state and glass transition to food ingredients, products, and processes

A. General:

Flink (1983), Wittwer & Tomka (1984), Saleeb & Pickup (1985, 1989), Burke (1986), Chan *et al.* (1986), Atkins (1987), Gosline (1987), Russell (1987*a*), Gould & Christian (1988), Lineback & Rasper (1988), Quinquenet *et al.* (1988), BeMiller (1989), Cairault *et al.* (1989), Colonna *et al.* (1989), Fujio & Lim (1989), Russell & Oliver (1989), Shi & Seib (1989, 1992), Stepto & Dobler (1989), Hosea *et al.* (1990), Johnston-Banks (1990), Johnson *et al.* (1990), Kararli & Catalano (1990), Kararli *et al.* (1990), Lillie & Gosline (1990), Mita (1990), Oksanen & Zografi (1990), Pikal (1990*a,b*), Pikal & Shah (1990), Roozen & Hemminga (1990, 1991), Roper & Koch (1990), Rubin *et al.* (1990), Schiraldi (1990), Takushi *et al.* (1990), Van Scoik & Carstensen (1990), Yoshida *et al.* (1990), Belton (1991), Chang & Baust (1991*a,b,c*), Chinachoti *et al.* (1991*a*), Cocero & Kokini (1991), Davis (1991), Donhowe *et al.* (1991), Hartel & Shastry (1991), Hegenbart (1991), Karathanos *et al.* (1991), Karger & Ludemann (1991), Lai & Kokini (1991), Larsson (1991), Larsson & Eliasson (1991), Liu & Lelievre (1991*a,b*, 1992), Liu *et al.* (1991), Ma & Harwalkar (1991), MacDonald & Lanier (1991), Nakamura *et al.* (1991), O'Brien (1991), Parak & Nienhaus (1991), Patil (1991), Raemy & Lambelet (1991), Roozen *et al.* (1991), Roser (1991*a,b*), Scandola *et al.* (1991), Shukla (1991), Sochava *et al.* (1991), Spratt *et al.* (1991), Tanner *et al.* (1991), Cocero *et al.* (1992), Eliasson (1992), Gaines *et al.* (1992*a,b*), German *et al.* (1992), Goff (1992), Gudmundsson (1992), Gudmundsson & Eliasson (1992), Harrison *et al.* (1992), Kaletunc & Breslauer (1992), Karathanos & Saravacos (1992), Kim & Walker (1992), Lawton (1992*a,b,c*), Megret *et al.* (1992), Peleg (1992), Rajagopalan & Seib (1992), Shah & Ludescher (1992), Shogren (1992), Sochava & Belopolskaya (1992), Sochava & Smirnova (1992), Summers (1992), te Booy *et al.* (1992), Tolstoguzov & Nesmeyanov (1992), Watase *et al.* (1992), Zasypkin *et al.* (1992)

B. Chapters in *Water Relationships in Foods* (Plenum Press, New York, 1991):

Franks; Blanshard *et al.*; van den Berg; Karel & Saguy; Lim & Reid; Hoseney; Simatos & Blond; Le Meste *et al.*; Maurice *et al.*; Schenz *et al.*; Biliaderis; Slade & Levine; Given; Nishinari *et al.*; Tomka; Wasylyk & Baust

C. *Glass Transitions in Cereal-Based Foods* — AACC Symposium, 1992:

Botham *et al.*; Cocero *et al.*; Hoseney *et al.*; Huang *et al.*; Kalichevsky & Blanshard; Lillford *et al.*; Slade & Levine

D. Glass transitions in natural plant tissues:

Williams & Leopold (1989), Vertucci (1990), Bruni & Leopold (1991), Dereuddre *et al.* (1991), Koster (1991), Lin *et al.* (1991)

E. Chapters in *The Science and Technology of the Glassy State in Foods* (University of Nottingham Press, Nottingham, 1993):

Allen; Karel *et al.*; Slade & Levine; Reid *et al.*; Kalichevsky *et al.*; Hemminga *et al.*; Noel *et al.*; Ablett *et al.*; Roos & Karel; van den Berg *et al.*; Lillie & Gosline; Gidley *et al.*; Attenburrow & Davies; Levine & Slade; Donald *et al.*; Simatos & Blond; Peleg; MacInnes; Bolton *et al.*; Schenz *et al.*; Aynie *et al.*; Kalichevsky & Blanshard (1993*a,b*); Labuza; Livings & Donald; Nesvadba; Parker & Smith; Sala & Tomka (1993*a,b*); Willenbucher *et al.*; Tian & Blanshard; Sapru & Labuza

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

Chuy & Labuza; Cocero & Kokini; Hallberg & Chinachoti; Hsu & Reid; Huang; Leung *et al.*; Levi & Karel; Madeka & Kokini; Nelson *et al.*; Reid *et al.*; Roos; Taylor *et al.*

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

Blond; Nelson & Labuza; Reid & McCarthy; Slade & Levine

(After Slade & Levine, 1993)

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.A. Davis at the University of Minnesota's Food Science Department. Further indications of the recent prominence of this subject are as follows: (a) 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 the University of Nottingham, UK, in April, 1992 (references in Table 3E); (b) a symposium on 'Glass Transitions in Cereal-Based Foods' (references in Table 3C) was held at the American Association of Cereal Chemists' 77th Annual Meeting in Minneapolis, MN, in September 1992; and (c) many papers on the glassy state and glass transitions were presented at the Institute of Food Technologists' 1992 Annual Meeting in New Orleans, LA, in June 1992 (references in Table 3F) and at the ISOPOW-V Meeting on the Properties of Water in Foods in Valencia, Spain, in November 1992 (references in Table 3G).

In previous reports and reviews (Slade/Levine references in Table 1), we have described how recognition of the key elements of the food polymer science approach and their relevance to the behaviour of a broad range of different types of foods (e.g. intermediate-moisture, low-moisture, frozen, starch-based, gelatin-based, gluten-based, and other protein-based foods) and corresponding aqueous model systems increased markedly during the 1980s. We 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 (i.e. monomers, oligomers, and high polymers) of partially crystalline glassy polymer systems plasticized by water. Referring to the food polymer science approach, John Blanshard (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 food-stuffs, 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 praise for the food polymer science approach has come 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 ten 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's 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 an editorial on 'Characterizing food and its ingredients' in a recent issue of *Trends in Food Science and Technology*.

Significance of the glass transition in non-equilibrium food systems, including starch-containing foods, and methods for its analysis

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 & Darby, 1982). Eisenberg (1984) stated that 'the glass transition is perhaps the most important single parameter which one needs to know before one can decide on the application of the many non-crystalline [synthetic] polymers that are now available.' Especially in the last several years, a growing number of food scientists have increasingly recognized the practical significance of the glass transition as a physicochemical event that can govern food processing, product properties, quality, safety, and stability. Pertinent references are those in Tables 1, 3A, 3B, 3C, 3E, 3F, and 3G. Also noteworthy in this context are several recent reports in the biological literature (references in Table 3D) on glass transitions in plant cell walls, seeds, and other natural plant tissues.

This recognition of the importance of the glass transition in foods has gone hand-in-hand with an increasing awareness of the inherent non-equilibrium nature of most food products and processes (references in Tables 1 and 3), as exemplified by cereal-based, intermediate-moisture foods (IMF) such as various baked goods, in which amorphous polysaccharides (polymeric, oligomeric, and/or monomeric) and proteins are major functional components (Slade & Levine, 1988*a*). Selected 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 non-equilibrium nature include the following (Slade & Levine, 1987*b*, 1991*a,b*, 1993; Levine & Slade, 1988*a*, 1989*b*, 1992; Slade *et al.*, 1989): (a) microbiological activity; (b) water-vapor sorption/desorption hysteresis in concentrated food polymer systems; (c) graininess and iciness in ice cream, reduced survival of frozen enzymes and living cells, reduced activity and shelf-stability of freeze-dried proteins; (d) caking and other diffusion-limited, physical or chemical 'collapse' processes in amorphous powders; (e) recipe requirements for gelatin desserts; (f) cooking of cereals and grains; (g) expansion of bread or collapse of cake during baking, and effects of flour and sugar on cookie baking; (h) staling of baked products; and (i) effects of sugar-water glasses and rubbers on texture and storage stability of cookies. Selected references to recent studies are listed in Table 4 (Slade & Levine, 1993).

Thermal and thermomechanical analysis methods are particularly well suited for studying such non-equilibrium systems, and for defining structure–function relationships, e.g. of synthetic amorphous polymers, from measurements of their thermal and mechanical properties (Turi, 1981; Wunderlich, 1990). DSC and dynamic mechanical analysis (DMA) have become established methods for characterizing the kinetic (i.e. time- or frequency-dependent) transition from glassy solid to rubbery liquid state that occurs at T_g in completely amorphous or partially crystalline, synthetic

Table 4. Selected references to recent publications that have highlighted the non-equilibrium nature of food products and processes

Examples of non-equilibrium products and processes	References
Microbiological activity	Slade & Levine (1985, 1988*a,b*, 1991*a*), Gould & Christian (1988), Bolton *et al.* (1993), Sapru & Labuza (1993)
Sorption/desorption hysteresis	van den Berg (1981, 1986, 1991), Levine & Slade (1988*a*, 1989*b*), Lillford (1988), Cairault *et al.* (1989), Slade *et al.* (1989), Myers-Betts & Baianu (1990), Oksanen & Zografi (1990), Ablett & Lillford (1991), Franks (1991*a,b*), Slade & Levine (1991*a*)
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 & Slade (1986, 1988*c,d*, 1989*c,d*, 1990, 1992*a*), Blanshard & Franks (1987), Franks (1989, 1990), Franks & Hatley (1990), Le Meste & Simatos (1990), Pikal (1990*a,b*), Reid (1990), Belton (1991), Blond & Colas (1991), Chang & Baust (1991*a,b,c*), Franks & van den Berg (1991), Franks *et al.* (1991), Lim & Reid (1991), Roos & Karel (1991*f,g*), Goff (1992), Goff *et al.* (1992), Karel (1992)
Caking and other diffusion-limited, physical or chemical 'collapse' processes in amorphous powders	To & Flink (1978), Flink (1983), Karel & Flink (1983), Karel (1985, 1986, 1989, 1990), Levine & Slade (1986, 1988*b*, 1989*a*, 1992), Roos (1987), Karel & Langer (1988), Simatos & Karel (1988), Paakkonen & Roos (1990), Roos & Karel (1990, 1991*a,b,c,e*, 1992, 1993), Van Scoik & Carstensen (1990), Karel & Saguy (1991), Shimada *et al.* (1991), Karmas *et al.* (1992), Labrousse *et al.* (1992), Levi & Karel (1992), te Booy *et al.* (1992), Karel *et al.* (1993), Peleg (1993), Slade & Levine (1993)
Cooking of cereals and grains	Slade & Levine (1984, 1987*b*, 1988*b,c,d*, 1989), Reid & Charoenrein (1985), Burros *et al.* (1987), Paton (1987), Mestres *et al.* (1988), Levine & Slade (1989*b*), Knutson (1990), Lai & Kokini (1991), Larsson & Eliasson (1991), Liu & Lelievre (1991*a,b*, 1992), Liu *et al.* (1991), Rajagopalan & Seib (1992)
Expansion of bread or collapse of cake during baking, effects of flour and sugar on cookie baking	Blanshard (1986), Levine & Slade (1989*b*, 1993), Slade *et al.* (1989), Slade & Levine (1992)
Staling of baked products	Slade (1984), Miles *et al.* (1985*b*), Hoseney (1986), Slade & Levine (1987*b*, 1988*d*, 1989), Slade *et al.* (1987), Clark *et al.* (1989), Gidley & Bulpin (1989), Cairns *et al.* (1991*b*), Biliaderis (1991*b*), Cameron & Donald (1991), Patil (1991), Gudmundsson (1992), Michniewicz *et al.* (1992), Shogren (1992)
Recipe requirements for gelatin desserts	Slade & Levine (1987*a*), Levine & Slade (1988*a*)
Effects of sugar-water glasses and rubbers on texture and storage stability of cookies	Slade & Levine (1991*a,b*, 1992), Gaines *et al.* (1992*a,b*), Levine & Slade (1993)

(Courtesy of Slade & Levine, 1993)

and natural polymer systems (Fuzek, 1980; Wunderlich, 1990), including many food materials (Harwalkar & Ma, 1990). These methods and DMTA (dynamic mechanical thermal analysis (Davies *et al.*, 1991; Scandola *et al.*, 1991; Kalichevsky *et al.*, 1992*a,b,c,d*, 1993; Kalichevsky & Blanshard, 1992*a,b*; Shogren, 1992), a variation of DMA) have been the methods of choice in most recent investigations of glasses and glass transitions in food systems, including starch-containing products. In other studies (references in Table 5 (Slade & Levine, 1993)), complementary methods have also been employed 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. These methods include thermomechanical analysis (TMA), thermodielectrical analysis (TDEA), thermal stimulated current/relaxation map analysis (TSC/RMA) spectroscopy, electron spin resonance (ESR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, Brillouin scattering spectroscopy, phosphorescence spectroscopy, dielectric spectroscopy, Mossbauer spectroscopy, mechanical spectrometry, dynamic rheometry, viscometry, and Instron analysis. 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 and coworkers (Kalichevsky *et al.*, 1992*a,b,c,d*, 1993; Kalichevsky & Blanshard, 1992*a,b*) of the glass transition, at low moisture contents, of amylopectin (the branched polymer of starch), amylopectin-sugar mixtures, wheat gluten protein, gluten-sugar, gluten-lipid, gluten-emulsifier, and gluten-salt mixtures, casein, casein-sugar mixtures, and binary mixtures of amylopectin, gluten and casein, various combinations of DSC, DMTA, NMR, and Instron analysis 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 amylose (the linear polymer of starch), dextran, and

Table 5. References to studies employing methods other than DSC or DMA to investigate glass transitions and their effects in food ingredients and products

Method	References
Thermomechanical analysis (TMA)	Biliaderis *et al.* (1986*a,c*), Caldwell *et al.* (1990), Biliaderis (1990, 1991*a*), Le Meste & Huang (1991), Le Meste *et al.* (1991*a*), Maurice *et al.* (1991), Schenz *et al.* (1991), Goff (1992), Goff *et al.* (1992), Hoseney *et al.* (1992), Huang *et al.* (1992), Le Meste *et al.* (1992)
Thermodielectrical analysis (TDEA)	Quinquenet *et al.* (1988), Schiraldi (1990), Ollivon (1991), Scandola *et al.* (1991)
Thermal stimulated current/ relaxation map analysis (TSC/ RMA) spectroscopy	Matthiesen *et al.* (1991), Huang *et al.* (1992), Megret *et al.* (1992)
Electron spin resonance (ESR)	Le Meste & Duckworth (1988), Simatos & Karel (1988), Johnson *et al.* (1990), Le Meste & Simatos (1990), Le Meste *et al.* (1990, 1991*b*), Roozen & Hemminga (1990, 1991), Bruni & Leopold (1991), Roozen *et al.* (1991), Hemminga *et al.* (1993)
Nuclear magnetic resonance (NMR)	Simatos & Karel (1988), Rubin *et al.* (1990), Ablett & Lillford (1991), Belton (1991), Chinachoti *et al.* (1991*a*), Given (1991), Karger & Ludemann (1991), Tanner *et al.* (1991), Harrison *et al.* (1992), Kalichevsky *et al.* (1992*a,b,c,d*), Kalichevsky & Blanshard (1992), Lillford *et al.* (1992), Shogren (1992), Tian & Blanshard (1992), Ablett *et al.* (1993), Gidley *et al.* (1993), Willenbucher *et al.* (1993)
Brillouin scattering spectroscopy	Hosea *et al.* (1990)
Phosphorescence spectroscopy	Shah & Ludescher (1992)
Dielectric spectroscopy	Huang *et al.* (1992), Botham *et al.* (1992)
Mossbauer spectroscopy	Parak & Nienhaus (1991)
Mechanical spectrometry	Gosline (1987), Masi (1989), Lillie & Gosline (1990), Cocero & Kokini (1991), Roos & Karel (1991*f*), Sala & Tomka (1993*a*)
Dynamic rheometry	Mita (1990)
Viscometry	Ollett & Parker (1990), Noel *et al.* (1991)
Analysis by Instron (or other physical testing apparatus)	Attenburrow *et al.* (1990), Davies *et al.* (1991), Ollett *et al.* (1991), Cocero *et al.* (1992), Kalichevsky & Blanshard (1992*a*), Kalichevsky *et al.* (1992*a,b,c,d*), Lillford *et al.* (1992)

(After Slade & Levine, 1993)

pullulan; 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) (see also 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 & Levine, 1988*c*, 1991*a*; Orford *et al.*, 1989; Hosea *et al.*, 1990; Koide *et al.*, 1990; Noel *et al.*, 1990, 1991; Pissis & Apekis, 1991; Ring & Whittam, 1991; MacInnes, 1993)] of the measurement technique' (Kalichevsky *et al.*, 1992*a*) and that 'the various techniques are sensitive to different degrees of molecular mobility' (Kalichevsky *et al.*, 1992*a*).

The polymer science-based interpretive approach to thermal analysis studies of structure-function relationships in food systems (Slade/Levine references in Table 1), including starch-based ingredients and products, emphasizes insights gained by an appreciation of the fundamental similarities between synthetic amorphous polymers and glass-forming aqueous food materials with regard to their thermal, mechanical, and structural properties. Based on this approach, DSC 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 non-equilibrium physical states determine the time-dependent thermomechanical, rheological, and textural properties of food materials (Slade/Levine references in Table 1).

Plasticization by water

Plasticization, and its modulating effect on the temperature location of the glass transition, is another key technological aspect of synthetic polymer science (Sears & 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 & Darby, 1982). Characteristically, the T_g of an undiluted polymer is much higher than that of a typical low molecular

weight (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 (i.e. the volume of the mixture that is not occupied by molecules) increases (Ferry, 1980). A polymer science approach to the thermal and mechanical 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. 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.' It has become well documented, in large part through DSC studies, 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; Davies *et al.*, 1991; Ollett *et al.*, 1991; Kalichevsky *et al.*, 1992*a,c*; Kalichevsky & Blanshard, 1992*a*; Le Meste *et al.*, 1992), of completely amorphous or partially crystalline food ingredients, and that this T_g depression may be advantageous to product processing, functional properties, and storage stability (Levine & Slade, 1988*a*, 1989*b*, 1992; Slade *et al.*, 1989; Slade & Levine, 1991*a,b*). Recently, there has been expanding interest in the importance of the effect of water as a plasticizer of many different food materials and other biopolymers, including starch and its component polymers, amylose and amylopectin; starch hydrolysis products (SHPs); low MW sugars and polyhydric alcohols; non-starch polysaccharides; gluten and its component polymers, glutenin and gliadin; gelatin; collagen; elastin; zein and other proteins; lysozyme and other enzymes; poly(hydroxybutyrate); and the semicrystalline cellulose and amorphous hemicellulose and lignin components of wood. Pertinent references are compiled in Table 6 (Slade & Levine, 1993).

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 & Slade, 1988*a*)] 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 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 & Slade, 1988*a*), hemicelluloses (Kelley *et al.*, 1987), and elastin (Atkins, 1987).

A unified conceptual approach to research on glasses and glass transitions in aqueous 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 1). Lillford and his coworkers at Unilever have advocated a related 'materials science approach' to studies of: (a) the influence of water on the mechanical behavior of dough and batter before, during, and after baking (Ablett *et al.*, 1986); (b) the mechanical properties of solid food foams as affected by 'the plasticizing action of water' (Attenburrow *et al.*, 1989); (c) the influence of plasticization by water on the mobility and structural properties of non-equilibrium, kinetically metastable food polymer systems (Lillford, 1988; Ablett & Lillford, 1991); (d) the plasticizing effect of water on the mobility, rheological/mechanical properties, and glassy/rubbery behaviour of heat-set wheat gluten networks (Edwards *et al.*, 1987; Attenburrow *et al.*, 1990; Davies *et al.*, 1991); and (e) the mechanical properties and texture of cereal foods in and around the glassy state (Attenburrow & Davies, 1993). Similarity, in a review of structure-property relationships in starch and in another paper on starch gelatinization, Zobel and coworkers (Zobel, 1988; Zobel *et al.*, 1988) cited concepts used to characterize synthetic polymers and advocated this approach to provide increased understanding of the amorphous state and its role in determining physical properties of native and gelatinized starches. Others who have recently applied a synthetic polymers or materials approach to characterize the glass transition, melting, crystallization, annealing, or gelation/network formation behavior of food polymers such as starch or gluten include Blanshard, Hoseney, Morris, Ring, Smith, Biliaderis and Maurice, Le Meste and Huang, Lund, Russell, Seib, Eliasson, Lelievre, Tomka, Colonna, Fujio, Mita, Masi, Kokini, Shogren, Lawton, Reid, and Breslauer. References to their studies are listed in Table 7A (Slade & Levine, 1993). In recent years, many others have also supported the perspective based on the fundamental behavioural similarities between synthetic polymer-plasticizer and food molecule-water systems, first popularized by Slade and her coworkers (references in Table 1). Pertinent references are listed in Table 7B. Table 8 (Slade & Levine, 1993) lists specific references to publications dealing with the glassy state phenomenon in starch or gluten, and Table 9 (Slade & Levine, 1993) lists those applying a polymer science approach to various aspects of studies of starch gelatinization or retrogradation.

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 behaviour of water-soluble or water-miscible (collectively referred to as water-compatible) and water-sensitive amorphous materials or amorphous regions of partially crystalline materials (Levine & Slade, 1988*a*, 1989*b*, 1992; Slade *et al.*, 1989; Slade & Levine, 1991*a,b*). Plasticization, on a molecular level, leads to

Table 6. References to studies of effects of water as a plasticizer in food and biological materials

Material: References
Starch, amylose, amylopectin: Kainuma & French (1972), van den Berg (1981, 1986, 1991), Slade & Levine (1984, 1987*b*, 1988*c,d*, 1989), 1991*a,b*, 1992), Wittwer & Tomka (1984), Biliaderis *et al.* (1985, 1986*a,b,c*), Maurice *et al.* (1985), Ablett *et al.* (1986), Blanshard (1986, 1987, 1988), Yost & Hoseney (1986), Chungcharoen & Lund (1987), Ring *et al.* (1987), Russell (1987*a*), Slade *et al.* (1987), Tanner *et al.* (1987, 1991), Zeleznak & Hoseney (1987*a,b*), Levine & Slade (1988*a*, 1989*b*, 1992), Lillford (1988), Lineback & Rasper (1988), Marsh & Blanshard (1988), Zobel (1988), Zobel *et al.* (1988), Attenburrow *et al.* (1989), Biliaderis & Galloway (1989), Colonna *et al.* (1989), Hutchinson *et al.* (1989), Lund (1989), Orford *et al.* (1989), Russell & Oliver (1989), Shi & Seib (1989, 1992), Stepto & Dobler (1989), Biliaderis (1990, 1991*a,b*), Biliaderis & Seneviratne (1990*a,b*), Biliaderis & Zawistowski (1990), Ghiasi & Skarra (1990), I'Anson *et al.* (1990), Johnson, *et al.* (1990), Knutson (1990), Morris (1990), Noel *et al.* (1990), Roper & Koch (1990), Schiraldi (1990), Smith (1990), Warburton *et al.* (1990), Whittam *et al.* (1990, 1991), Cairns *et al.* (1991*b*), Chinachoti *et al.* (1991*a,b*), Garbow & Schaefer (1991), Given (1991), Karathanos *et al.* (1991), Lai & Kokini (1991), Larsson (1991), Larsson & Eliasson (1991), Liu & Lelievre (1991*b*, 1992), Ollett *et al.* (1991), Patil (1991), Roos & Karel (1991*d*), Scandola *et al.* (1991), Tomka (1991), Eliasson (1992), Gudmundsson (1992), Gudmundsson & Eliasson (1992), Huang *et al.* (1992), Kaletunc & Breslauer (1992), Kalichevsky & Blanshard (1992, 1992*b*, 1993*a*), Kalichevsky *et al.* (1992*a,b*, 1993), Karathanos & Saravacos (1992), Kim & Walker (1992), Le Meste *et al.* (1992), Lillford *et al.* (1992), Michniewicz *et al.* (1992), Noel & Ring (1992), Rajagopalan & Seib (1992), Shogren (1992), Tian & Blanshard (1992), Zasypkin *et al.* (1992), Gidley *et al.* (1993), Parker & Smith (1993), Sala & Tomka (1993*a,b*), Willenbucher *et al.* (1993)
Starch hydrolysis products: Cole *et al.* (1983, 1984), Flink (1983), Karel & Flink (1983), Saleeb & Pickup (1985, 1989), Levine & Slade (1986, 1988*a,b,c*, 1989*a,b,c*, 1990, 1991, 1992). Karel & Langer (1988), Orford *et al.* (1989), Levine *et al.* (1991), Lim & Reid (1991), Ring & Whittam (1991), Roos & Karel (1991*b,d*), Roozen & Hemminga (1991), Slade & Levine (1991*a,b*), Hemminga *et al.* (1993).
Low MW sugars: White & Cakebread (1966), Cakebread (1969), MacKenzie (1977), Soesanto & Williams (1981), Franks (1982, 1985, 1986*a*, 1989, 1990, 1991*a*), Herrington & Branfield (1984), Schenz *et al.* (1984, 1991), Karel (1985, 1986, 1989, 1992), Slade & Levine (1985, 1988*a,b*, 1991*a,b*, 1992), Chan *et al.* (1986), Blanshard & Franks (1987), Roos (1987, 1992*a*), Karel & Langer (1988). Levine & Slade (1988*a,b,c,d*, 1989*a,b,c,d* 1990, 1992, 1992*a*), Simatos & Karel (1988), Blond (1989), Finegold *et al.* (1989), Green & Angell (1989), Orford *et al.* (1989, 1990), Simatos *et al.* (1989), Williams & Carnahan (1989, 1990), Williams & Leopold (1989), Caldwell *et al.* (1990), Franks & Grigera (1990), Franks & Hatley (1990), Le Meste & Simatos (1990), Noel *et al.* (1990, 1991), Reid (1990), Roos & Karel (1990, 1991*a,c,d,e,f,g*, 1992, 1993), Roozen & Hemminga (1990, 1991), Rubin *et al.* (1990), Blond & Simatos (1991), Bruni & Leopold (1991), Franks & van den Berg (1991), Franks *et al.* (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Karel & Saguy (1991), Koster (1991), Le Meste & Huang (1991), Levine *et al.* (1991, 1992), Matthiesen *et al.* (1991), Maurice *et al.* (1991), Shimada *et al.* (1991), Simatos & Blond (1991), Ablett *et al.* (1992*a,b*), Karmas *et al.* (1992), Labrousse *et al.* (1992), Levi & Karel (1992), te Booy *et al.* (1992), Karel *et al.* (1993), van den Berg *et al.* (1993)
Polyhydric alcohols: Reid (1985), Levine & Slade (1988*a,b,c,d*, 1989*a,b,c*, 1990, 1992), Quinquenet *et al.* (1988), Slade & Levine (1988*b*, 1991*a*), Franks & Grigera (1990), Franks & van den Berg (1991), Koster (1991), Ablett *et al.* (1992*a*), Roos (1992*a*)
Non-starch polysaccharides: Kararli & Catalano (1990), Paakkonen & Roos (1990), Yoshida *et al.* (1990), Hegenbart (1991), Nishinari *et al.* (1991), Scandola *et al.* (1991), Slade & Levine (1991*a,b*), Gidley *et al.* (1993)
Gluten: Slade (1984), Ablett *et al.* (1986, 1988), Hoseney *et al.* (1986), Doescher *et al.* (1987), Edwards *et al.* (1987), Levine & Slade (1988*a*, 1989*b*, 1992), Lillford (1988), Attenburrow *et al.* (1989, 1990), Fujio & Lim (1989), Slade *et al.* (1989), Hoseney & Rogers (1990), Davies *et al.* (1991), Garbow & Schaefer (1991), Given (1991), Hoseney (1991), Slade & Levine (1991*a*, 1992), Cocero *et al.* (1992), Huang *et al.* (1992), Kalichevsky *et al.* (1992*c,d*, 1993), Kalichevsky & Blanshard (1992, 1992*b*), Lawton (1992*b*), Le Meste *et al.* (1992), Lillford *et al.* (1992), Michniewicz *et al.* (1992), Summers (1992), Tian & Blanshard (1992)
Glutenin: Cocero & Kokini (1991), Cocero *et al.* (1992), Kalichevsky *et al.* (1992*c*)
Gliadin: Cocero *et al.* (1992), Kalichevsky *et al.* (1992*c*), Madeka & Kokini (1992)
Gelatin: Jolley (1970), Yannas (1972), Borchard *et al.* (1980), Marshall & Petrie (1980), Slade & Levine (1984, 1987*a*, 1991*a*), Tomka (1986), Levine & Slade (1988*a*), Slade *et al.* (1989), Kalichevsky & Blanshard (1992)
Collagen: Yannas (1972), Batzer & Kreibich (1981), Levine & Slade (1988*a*), Slade *et al.* (1989), Slade & Levine (1991*a*)
Elastin: Kakivaya & Hoeve (1975), Hoeve & Hoeve (1978, 1980), Hoeve (1980), Atkins (1987), Gosline (1987), Levine & Slade (1988*a*), Slade *et al.* (1989), Lillie & Gosline (1990, 1993), Slade & Levine (1991*a*)
Zein: Cocero *et al.* (1992), Lawton (1992*a,c*), Madeka & Kokini (1992)
Other proteins: Le Meste & Duckworth (1988), Levine & Slade (1988*a*), Slade *et al.* (1989), Le Meste *et al.* (1990, 1991*b*), Pikal (1990*a*), Belton (1991), Slade & Levine (1991*a*), Sochava *et al.* (1991), Kalichevsky & Blanshard (1992, 1992*a,b*), Sochava & Smirnova (1992), Tolstoguzov & Nesmeyanov (1992), Zasypkin *et al.* (1992), Karel *et al.* (1993), Lillie & Gosline (1993)
Lysozyme: Bone & Pethig (1982, 1985), Poole & Finney (1983, 1984), Finney & Poole (1984), Morozov & Gevorkian (1985), Franks (1988), Levine & Slade (1988*a*), Lillford (1988), Slade *et al.* (1989), Myers-Betts & Baianu (1990), Slade & Levine (1991*a*), Sochava *et al.* (1991), Shah & Ludescher (1992)
Other enzymes: Poole & Finney (1984), Morozov & Gevorkian (1985), Levine & Slade (1988*a*), Slade *et al.* (1989), Slade & Levine (1991*a*), Sochava *et al.* (1991)
Cellulose, hemicellulose, lignin: Salmen & Back (1977), Kelley *et al.* (1987), Ostberg *et al.* (1990)
Poly(hydroxybutyrate): Harrison *et al.* (1992)

(After Slade & Levine, 1993)

Table 7. References to studies that have employed a synthetic polymers or materials approach to characterization of food molecule–water systems

A. Studies of starch or gluten (Researcher: References):

Blanshard: (1986, 1987, 1988), Edwards *et al.* (1987), Marsh & Blanshard (1988), Kalichevsky *et al.* (1992*a,b,c,d,* 1993), Kalichevsky & Blanshard (1992, 1993*a*), Tian & Blanshard (1992)
Hoseney: (1991), Hoseney *et al.* (1986, 1992), Yost & Hoseney (1986), Doescher *et al.* (1987), Zeleznak & Hoseney (1987*a,b*), Hoseney & Rogers (1990)
Morris: (1990), Ring *et al.* (1987), I'Anson *et al.* (1990), Cairns *et al.* (1991*b*)
Ring: Ring *et al.* (1987), Orford *et al.* (1989), Noel *et al.* (1990), Whittam *et al.* (1990, 1991), Ring & Whittam (1991), Botham *et al.* (1992), Noel & Ring (1992)
Smith: (1990), Hutchinson *et al.* (1989), Orford *et al.* (1989), Warburton *et al.* (1990), Ollett *et al.* (1991), Parker & Smith (1993)
Biliaderis and Maurice: Biliaderis *et al.* (1985, 1986*a,b,c*), Biliaderis & Galloway (1989), Biliaderis (1990, 1991*a,b*), Biliaderis & Seneviratne (1990*a,b*), Biliaderis & Zawistowski (1990), Biliaderis & Tonogai (1991)
Le Meste and Huang: Le Meste *et al.* (1991*a*, 1992), Huang *et al.* (1992), Aynie *et al.* (1993)
Lund: (1989), Chungcharoen & Lund (1987)
Russell: (1987*a*), Russell & Oliver (1989)
Seib: Shi & Seib (1989, 1992), Rajagopalan & Seib (1992)
Eliasson: (1992), Larsson (1991), Larsson & Eliasson (1991), Gudmundsson (1992), Gudmundsson & Eliasson (1992)
Lelievre: (1976), Liu & Lelievre (1991*a,b*, 1992), Liu *et al.* (1991)
Tomka: (1991), Wittwer & Tomka (1984), Sala & Tomka (1993*a,b*)
Colonna: Colonna *et al.* (1989)
Fujio: Fujio & Lim (1989)
Mita: (1990, 1992)
Masi: (1989)
Kokini: Cocero & Kokini (1991), Lai & Kokini (1991), Cocero *et al.* (1992)
Shogren: (1992)
Lawton: (1992*b*)
Reid: Taylor *et al.* (1992)
Breslauer: Kaletunc & Breslauer (1992)

B. Other studies:

Karel (1985, 1986, 1989, 1990, 1992), Campanella *et al.* (1987), Gosline (1987), Le Meste & Duckworth (1988), Simatos & Karel (1988), Cairault *et al.* (1989), Finegold *et al.* (1989), Franks (1989), Simatos *et al.* (1989), Franks & Grigera (1990), Johnson *et al.* (1990), Le Meste & Simatos (1990), Le Meste *et al.* (1990, 1991*b*), Lillie & Gosline (1990, 1993), Ollett & Parker (1990), Orford *et al.* (1990), Roos & Karel (1990, 1991*a,b,c,d,e,f,* 1992, 1993), Roozen & Hemminga (1990, 1991), Schiraldi (1990), Van Scoik & Carstensen (1990), Yoshida *et al.* (1990), Belton (1991), Blond & Simatos (1991), Bruni & Leopold (1991), Cameron & Donald (1991), Chang & Baust (1991*a,b,c*), Davis (1991), Franks *et al.* (1991), Given (1991), Izzard *et al.* (1991), Karathanos *et al.* (1991), Karel & Saguy (1991), Kohyama & Nishinari (1991), Le Meste & Huang (1991), Lim & Reid (1991), Lin *et al.* (1991), Matthiesen *et al.* (1991), Noel *et al.* (1991, 1993), O'Brien (1991), Parak & Nienhaus (1991), Raemy & Lambelet (1991), Scandola *et al.* (1991), Shukla (1991), Simatos & Blond (1991), Sochava *et al.* (1991), van den Berg (1991), Buera *et al.* (1992), Chuy & Labuza (1992), Goff (1992), Harrison *et al.* (1992), Huang (1992), Karmas *et al.* (1992), Lawton (1992*a*), Levi & Karel (1992), Nelson & Labuza (1992), Peleg (1992, 1993), Reid & Hsu (1992), Roos (1992*a*), Sochava & Belopolskaya (1992), Sochava & Smirnova (1992), te Booy *et al.* (1992), Zasypkin *et al.* (1992), Allen (1993), Gidley *et al.* (1993), Hemminga *et al.* (1993), Karel *et al.* (1993), Labuza (1993)

(Courtesy of Slade & Levine, 1993)

increased intermolecular space or free volume, decreased local viscosity, and concomitant increased mobility (Ferry, 1980; Lillie & 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 & Darby, 1982; Kalichevsky & Blanshard, 1992*a*). 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 & Darby, 1982). 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; Oksanen & Zografi, 1990; Harrison *et al.*, 1992; Kalichevsky & Blanshard, 1993*a*) and many readily soluble monomeric and oligomeric carbohydrates (Levine & Slade, 1986, 1988*a,b*, 1992; Slade & Levine, 1988*b*, 1991*a,b*; Orford *et al.*, 1989, 1990; Franks & Grigera, 1990; Noel *et al.*, 1990; Roos & Karel, 1990; 1991*d,e,f,g*; Blond & Simatos, 1991; Davies *et al.*, 1991; Franks *et al.*, 1991; Whittam *et al.*, 1991). This fact demonstrates two underlying precepts of the food polymer science approach: (a) synthetic amorphous polymers and glass-forming aqueous food materials are fundamentally similar in behaviour; and (b) food ingredients can be viewed generically as members of homologous families of completely amorphous or partially crystalline polymers, oligomers,

Table 8. References to publications dealing with the glassy state phenomenon in starch or gluten

A. References for methods used to determine T_g of starch, amylose, and/or amylopectin:

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

Measured by DSC: Slade (1984), Slade & Levine (1984, 1987*b*, 1988*c*), Wittwer & Tomka (1984), Maurice *et al.* (1985), Yost & Hoseney (1986), Zeleznak & Hoseney (1987*a*), Zobel *et al.* (1988), Orford *et al* (1989), Stepto & Dobler (1989), Biliaderis (1990, 1991*b*), Noel *et al.* (1990), Roper & Koch (1990), Warburton *et al.* (1990), Liu & Lelievre (1991*b*), Roos & Karel (1991*d,e*), Tomka (1991), Whittam *et al.* (1991), Kaletunc & Breslauer (1992), Noel & Ring (1992), Gidley *et al.* (1993), Kalichevsky & Blanshard (1993*a*)

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

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

Determined from DSC and NMR data: Given (1991)

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

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

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

Measured by DSC and mechanical spectroscopy: Sala & Tomka (1993*a*)

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

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

Other methods: van den Berg (1981, 1986)

B. References for methods used to measure T_g of gluten, glutenin, and/or gliadin:

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

TMA: Le Meste *et al.* (1991*a*, 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.* (1992*c*), Kalichevsky & Blanshard (1992)

DSC and mechanical spectrometry: Cocero & Kokini (1991)

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

DSC, DMTA, and NMR: Kalichevsky & Blanshard (1992)

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

C. References dealing with effects of T_g for starch and/or gluten on processing and product properties:

Slade (1984), Slade & Levine (1984, 1987*b*, 1991*a*, 1992), Maurice *et al.* (1985), Blanshard (1986), Levine & Slade (1988*a*, 1989*b*, 1992), Colonna *et al.* (1989), Shi & Seib (1989, 1992), Slade *et al.* (1989), Biliaderis (1990, 1991*a,b*), Hoseney & Rogers (1990), Noel *et al.* (1990), Schiraldi (1990), Warburton *et al.* (1990), Cairns *et al.* (1991*b*), Cocero & Kokini (1991), Davies *et al.* (1991), Given (1991), Hoseney (1991), Karathanos *et al.* (1991), Larsson (1991), Larsson & Eliasson (1991), Le Meste *et al.* (1991*a*, 1992), O'Brien (1991), Shukla (1991), Spratt *et al.* (1991), Tanner *et al.* (1991), Cocero *et al.* (1992), Gudmundsson (1992), Gudmundsson & Eliasson (1992), Huang *et al.* (1992), Kaletunc & Breslauer (1992), Kalichevsky *et al.* (1992*a,b,c*), Karathanos & Saravacos (1992), Lawton (1992*b*), Rajagopalan & Seib (1992), Shogren (1992), Tian & Blanshard (1992), Attenburrow & Davies (1993), Aynie *et al.* (1993), Donald *et al.* (1993), Labuza (1993), Parker & Smith (1993), Sala & Tomka (1993*a*)

(Courtesy of Slade & Levine, 1993)

and monomers, soluble in and/or plasticized by water (Levine & Slade, 1988*a*). The series from glucose through malto-oligosaccharides to the amylose and amylopectin components of starch exemplifies such a homologous polymer family.

Glass dynamics and water dynamics

On a theoretical basis of structure-property relationships for synthetic polymers, functional properties of food materials during processing and product storage can be successfully explained and often predicted (Slade/Levine references in Table 1). The food polymer science approach unifies structural aspects of foods, viewed as completely amorphous or partially crystalline polymer systems — the latter based on the classic 'fringed micelle' morphological model (Flory, 1953; Wunderlich, 1973; Billmeyer, 1984), shown in Fig. 2 (Slade & Levine, 1987*a*), which has been widely applied to starch (references in Table 9C — 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 the context of a 'dynamics map', shown in Fig. 3 (Slade & Levine, 1988*b*). This map was derived from a generic solute-solvent state diagram (Franks *et al.*, 1977; MacKenzie, 1977), in turn based originally on a more familiar equilibrium phase diagram of tem-

Table 9. References to publications describing a polymer science approach to studies of starch gelatinization and/or retrogradation

A. Retrogradation as a non-equilibrium polymer-crystallization process:

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

B. Gelatinization as a non-equilibrium polymer-melting process:

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

C. Application of the 'fringed micelle' structural model to starch:

Guilbot & Godon (1984), Slade (1984), Slade & Levine (1984, 1987*a,b*), Zobel (1988), Lund (1989), Chinachoti *et al.* (1991*b*), Kohyama & Nishinari (1991), Lai & Kokini (1991), Liu *et al.* (1991), German *et al.* (1992), Mita (1992)

D. Indirect plasticizing effect of water on T_m of partially crystalline starch:

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

E. Inappropriateness of the Flory–Huggins equilibrium thermodynamic treatment of gelatinization:

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

F. Antiplasticizing effect of sugars (i.e. sugar solutions relative to water alone) on gelatinization or retrogradation:

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

(Courtesy of Slade & Levine, 1993)

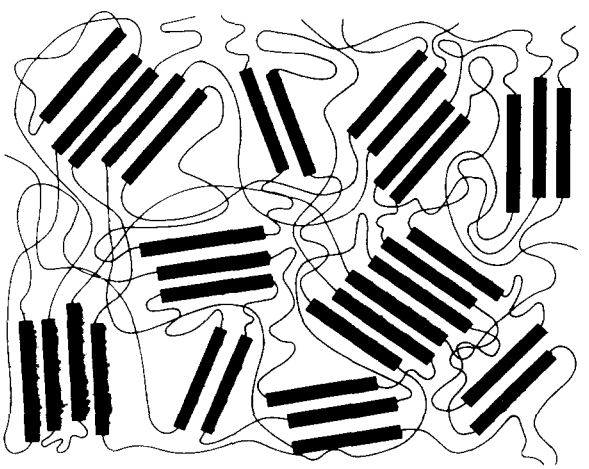

Fig. 2. 'Fringed micelle' model of the crystalline–amorphous structure of partially crystalline polymers. (Reproduced, with permission, from Slade and Levine (1987*a*).)

perature vs composition. The dynamics map, like the 'supplemented state diagram' (MacKenzie, 1977), is complicated by an attempt to represent aspects of both equilibrium and non-equilibrium thermodynamics in a single figure. The primary distinction at atmospheric pressure is that equilibrium regions are completely described, as shown, in two dimensions of temperature and composition, with no time dependence, while non-equilibrium regions emphatically require the third dimension of time, expressed as t/τ, where τ is a relaxation time. In this way, the time dependence of a dynamic process can be defined in terms of the relationship between the experimental time scale and the time frame of the relaxation process undergone by the system. The established principle of time–temperature superpositioning (Sichina, 1988) was extended to define 'mobility transformations' in terms of the critical variables of time, temperature, and moisture content,

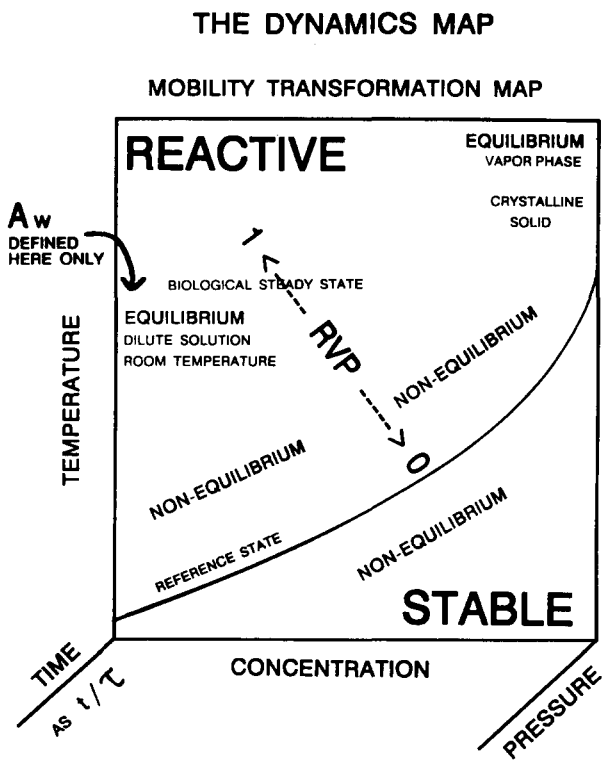

Fig. 3. A four-dimensional 'dynamics map', with axes of temperature, concentration, time, and pressure, which can be used to describe mobility transformations in non-equilibrium glassy and rubbery food systems. The reference state (the glass curve of T_g vs concentration) divides the map into metastable (glassy) and reactive (rubbery) regions. (Reproduced, with permission, from Slade and Levine (1988*b*).)

with pressure as another variable of potential technological importance (Slade & Levine, 1988*b*; Lillie & Gosline, 1990).

The dynamics map has been used (Slade & Levine, 1988*b*) to describe mobility transformations in water-compatible food polymer systems that exist in kinetically metastable glassy or rubbery states (Levine & Slade, 1988*a*, 1989*b*, 1992; Slade *et al.*, 1989; Slade & Levine, 1991*a,b*, 1992, 1993) always subject to conditionally beneficial or detrimental plasticization by water. For example, the non-Arrhenius kinetics of starch gelatinization and retrogradation have been explained in terms of mobility transformations, as illustrated by locating on the dynamics map the alternative pathways of complementary plasticization by heat and moisture (Slade & Levine, 1988*b,d*, 1989; Levine & Slade, 1989*b*). 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' to interpret and explain sorption isotherms and sorption hysteresis, have been treated alternatively in terms of water dynamics (Slade & Levine, 1988*a*, 1991*a,b*; Levine & Slade, 1988*a*). As the name implies, water dynamics focuses on: (a) the mobility (Chinachoti *et al.*, 1991*b*; Larsson, 1991; Tanner *et al.*, 1991; Goff, 1992) and eventual 'availability' (Ablett & Lillford, 1991; Franks, 1991*b*) of the plasticizing diluent, be it water alone or an aqueous solution; and (b) an interpretive approach to understanding how to control the mobility of the diluent in glass-forming food systems that would be inherently mobile, unstable, and reactive at $T > T_g$ and moisture content $W > W_g$. This concept, along with that of glass dynamics, has provided an innovative perspective on water relationships in foods (Duckworth, 1988; Ablett & Lillford, 1991; Franks, 1991*b*; Goff, 1992; Karel, 1992; references in Table 3B), including, e.g., moisture management and structural stabilization of IMF systems such as cereal-based products (Slade & Levine, 1988*a*, 1991*a*) and 'cryostabilization' of frozen, freezer-stored, and freeze-dried aqueous glass-forming food materials and products (Cole *et al.*, 1983, 1984; Levine & Slade, 1986, 1988*a,b,c,d*, 1989*a,b,c,d*, 1990). This perspective, the focal point of which is the critical importance of the glassy state phenomenon in foods, has received considerable recent support from many other workers (references in Table 10A (Slade & Levine, 1993)).

Glass dynamics deals with the time- and temperature-dependence of relationships among composition, structure, thermomechanical properties, and functional behavior (Levine & Slade, 1988*a*). As its name implies, glass dynamics focuses on: (a) the glass-forming solids in an aqueous food system; (b) T_g of the resulting aqueous glass that can be produced by cooling to $T < T_g$; and (c) 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, which may be deliberately chosen to be first above and then below T_g (Slade & Levine, 1991*a,b*). This concept emphasizes the operationally immobile (translationally), stable, and unreactive situation (actually one of kinetic metastability) that can obtain during product storage of a practical duration at temperatures below T_g and at moisture contents below W_g. It has been used to describe a unifying concept for interpreting 'collapse' phenomena (Levine & Slade, 1986, 1988*b*; Karel, 1992) which govern, e.g., the time-dependent caking of amorphous food powders during storage. Collapse phenomena in completely amorphous or partially crystalline food systems, investigated extensively by Karel and coworkers (references in Table 4), are translational diffusion-limited consequences of a material-specific structural and/or mechanical relaxation process (Levine & Slade, 1986). It was suggested (Slade & Levine, 1988*b*) and subsequently confirmed (Le Meste & Huang, 1991; Roos & Karel, 1991*a,b,e*, 1992; Roozen & Hemminga, 1991; Shimada *et al.*, 1991; Karmas *et al.*, 1992; Levi & Karel, 1992) that the microscopic and macroscopic manifestations of these consequences occur in real time at a temperature about 20°C or more above that of an underlying molecular state transformation. This trans-

Table 10. References to publications in which: A. Support is expressed for the perspective provided by the concepts of glass dynamics and water dynamics; B. The applicability of WLF kinetics to food systems at $T_g < T < T_m$ (in contrast to Arrhenius kinetics at $T < T_g$ or $T > T_m$) is discussed

A. Blanshard (1986, 1987, 1988), van den Berg (1986, 1991), Blanshard & Franks (1987), Chungcharoen & Lund (1987), Russell (1987*a*), Gould & Christian (1988), Karel & Langer (1988), Le Meste & Duckworth (1988), Lillford (1988), Lineback & Rasper (1988), Marsh & Blanshard (1988), Quinquenet *et al.* (1988), Simatos & Karel (1988), Zobel (1988), BeMiller (1989), Biliaderis & Galloway (1989), Cairault *et al.* (1989), Colonna *et al.* (1989), Franks (1989, 1990, 1991*a,b*), Finegold *et al.* (1989), Karel (1989, 1990, 1992), Lund (1989), Orford *et al.* (1989), Russell & Oliver (1989), Shi & Seib (1989, 1992), Simatos *et al.* (1989), Biliaderis (1990, 1991*a,b*), Biliaderis & Seneviratne (1990*a*), Biliaderis & Zawistowski (1990), Caldwell *et al.* (1990), Franks & Grigera (1990), Franks & Hatley (1990), Hosea *et al.* (1990), Hoseney & Rogers (1990), I'Anson *et al.* (1990), Johnson *et al.* (1990), Johnston-Banks (1990), Kararli & Catalano (1990), Kararli *et al.* (1990), Le Meste & Simatos (1990), Le Meste *et al.* (1990, 1991*a,b*, 1992), Morris (1990), Myers-Betts & Bainanu (1990), Noel *et al.* (1990, 1991), Oksanen & Zografi (1990), Ollett & Parker (1990), Paakkonen & Roos (1990), Pikal (1990*a,b*), Pikal & Shah (1990), Reid (1990), Roos & Karel (1990, 1991*a,b,c,d,e,f,g*, 1992, 1993), Roozen & Hemminga (1990, 1991), Rubin *et al.* (1990), Schiraldi (1990), Sobczynska *et al.* (1990), Warburton *et al.* (1990), Ablett & Lillford (1991), Belton (1991), Blond & Colas (1991), Blond & Simatos (1991), Cairns *et al.* (1991*b*), Chang & Baust (1991*a,c*), Chinachoti *et al.* (1991*a,b*), Cocero & Kokini (1991), Davis (1991), Franks & van den Berg (1991), Franks *et al.* (1991), Garbow & Schaefer (1991), Given (1991), Hatley *et al.* (1991), Hegenbart (1991), Izzard *et al.* (1991), Karathanos *et al.* (1991), Karel & Saguy (1991), Kohyama & Nishinari (1991), Lai & Kokini (1991), Larsson (1991), Larsson & Eliasson (1991), Le Meste & Huang (1991), Lim & Reid (1991), Liu & Lelievre (1991*a,b*, 1992), Liu *et al.* (1991), Ma & Harwalkar (1991), MacDonald & Lanier (1991), Matthiesen *et al.* (1991), Maurice *et al.* (1991), Nishinari *et al.* (1991), O'Brien (1991), Patil (1991), Ring & Whittam (1991), Roozen *et al.* (1991), Shimada *et al.* (1991), Shukla (1991), Simatos & Blond (1991), Tanner *et al.* (1991), Wasylyk & Baust (1991), Ablett *et al.* (1992*a,b*, 1993), Buera *et al.* (1992), Chuy & Labuza (1992), Cocero *et al.* (1992), Eliasson (1992), Gaines *et al.* (1992*a,b*), Goff (1992), Goff *et al.* (1992), Gudmundsson (1992), Gudmundsson & Eliasson (1992), Huang (1992), Kaletunc & Breslauer (1992), Kalichevsky *et al.* (1992*a,b,c,d*, 1993), Karathanos & Saravacos (1992), Karmas *et al.* (1992), Kim & Walker (1992), Kokini *et al.* (1992), Labrousse *et al.* (1992), Levi & Karel (1992), Michniewicz *et al.* (1992), Mita (1992), Nelson & Labuza (1992), Noel & Ring (1992), Peleg (1992, 1993), Rajagopalan & Seib (1992), Reid & Hsu (1992) Reid *et al.* (1992), Roos (1992*a*), Shogren (1992), Taylor *et al.* (1992), te Booy *et al.* (1992), Tian & Blanshard (1992), Watase *et al.* (1992), Zasypkin *et al.* (1992), Bolton *et al.* (1993), Gidley *et al.* (1993), Hemminga *et al.* (1993), Karel *et al.* (1993), Labuza (1993), Sapru & Labuza (1993)

B. Slade (1984), Slade & Levine (1985, 1987*a,b*, 1988*a,b,c*, 1989, 1991*a,b*, 1993), Levine & Slade (1986, 1988*a,b,c*, 1989*a,b,c,d*, 1990, 1992), Campanella *et al.* (1987), Gosline (1987), Kelley *et al.* (1987), Simatos & Karel (1988), Simatos *et al.* (1989), Slade *et al.* (1989), Biliaderis (1990, 1991*a,b*), Franks & Grigera (1990), Karel (1990, 1992), Le Meste & Simatos (1990), Lillie & Gosline (1990), Morris (1990), Reid (1990), Roos & Karel (1990, 1991*a,d,e,f,g*, 1992, 1993), Blond & Colas (1991), Franks & van den Berg (1991), Franks *et al.* (1991), Given (1991), Karathanos *et al.* (1991), Karel & Saguy (1991), Lim & Reid (1991), Patil (1991), Roozen & Hemminga (1991), Roozen *et al.* (1991), Shimada *et al.* (1991), Simatos & Blond (1991), Cocero & Kokini (1992), Cocero *et al.* (1992), Goff (1992), Huang (1992), Kalichevsky *et al.* (1992*b*, 1993), Karmas *et al.* (1992), Levi & Karel (1992), Nelson & Labuza (1992), Peleg (1992, 1993), Karel *et al.* (1993), Sapru & Labuza (1993)

(Courtesy of Slade & Levine, 1993)

formation from kinetically metastable amorphous solid to unstable amorphous liquid occurs at T_g (Levine & Slade, 1986). The effect of plasticization, leading to increased free volume and mobility in the dynamically constrained glass, by water on T_g is a key aspect of collapse and its mechanism (Levine & Slade, 1988*b*). This unifying concept for interpreting collapse phenomena has also been used to describe starch gelatinization and retrogradation (Slade & Levine, 1987*b*, 1991*a*; Levine & Slade, 1988*a*, 1989*b*).

A general physicochemical mechanism for collapse was described (Levine & Slade, 1986), based on occurrence of a material-specific structural transition at T_g, followed by viscous flow in the rubbery liquid state (Flink, 1983). The mechanism was derived from Williams-Landel-Ferry (WLF) free-volume theory for (synthetic) amorphous polymers (Williams *et al.*, 1985; Ferry, 1980). It was concluded (Levine & Slade, 1986, 1988*b*) and subsequently confirmed and widely accepted (Paakkonen & Roos, 1990; Pikal, 1990*a,b*; Roos & Karel, 1990, 1991*a,b,d,e,f*, 1992; Karel & Saguy, 1991; Shimada *et al.*, 1991; Karmas *et al.*, 1992; Levi & Karel, 1992; te Booy *et al.*, 1992; Peleg, 1993; Roos & Karel, 1993) that T_g is essentially identical to phenomenological transition temperatures observed for structural collapse (T_c) or recrystallization (T_r). The non-Arrhenius kinetics of collapse and/or recrystallization, or of any other diffusion-limited, physical or chemical relaxation process, in the high viscosity rubbery state are governed by mobility of the water-plasticized polymer matrix (Levine & Slade, 1986). It was hypothesized (Slade, 1984; Slade & Levine, 1984; Levine & Slade, 1986), and then confirmed and widely accepted (references in Table 10B), that these kinetics depend on the magnitude of $\Delta T = T - T_g$, as defined by a temperature-dependent exponential relationship derived from 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 & Slade, 1988*a*). 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 & Levine, 1984, 1987*b*, 1988*c*). Glass dynamics has also been used to describe the viscoelastic behavior of amorphous polymeric network-forming proteins such as gluten and elastin (Slade, 1984; Slade *et al.*, 1989).

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 mentioned earlier. As shown 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 non-equilibrium situation corresponding to the temperature–composition region of most far-reaching technological consequence to aqueous food systems (Slade & Levine, 1988*b*). The critical feature in the use of this map is identification of the glass transition as the reference state (Slade & Levine, 1988*a,b*; Franks & Grigera, 1990), a conclusion (Levine & Slade, 1988*a*; Ollett & Parker, 1990) based on WLF theory for glass-forming polymers. This line of demarcation, representing the so-called 'glass curve' of T_g vs composition (Levine & Slade, 1986; Simatos & Karel, 1988; Franks, 1989; Karel, 1992), provides a basis for description of the non-equilibrium thermo-mechanical, rheological, and textural (Kaletunc & Breslauer, 1992) behavior of water-compatible polymeric materials in glassy and rubbery states, in response to changes in moisture content, temperature, and time (Levine & Slade, 1988*a*). Mobility is the transcendent principle underlying definition of the glass transition as the appropriate reference state (Slade & Levine, 1988*a*), because mobility is key to all transformations in time (or frequency), temperature, and composition between different relaxation states for a technologically practical food (Slade & Levine, 1988*b*) or biological (Lillie & Gosline, 1990) system (Karel, 1992).

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, including starch-based ingredients and products (Levine & Slade, 1988*a*; Slade & Levine, 1988*b*). For example, the kinetics of all constrained relaxation processes, such as translational or rotational diffusion, and any chemical or physicochemical reaction dependent thereon, including starch gelatinization and retrogradation (Slade & Levine, 1987*b*, 1988*c*), which are governed by the mobility of a water-plasticized polymer matrix in glass-forming systems, vary (from Arrhenius-type to WLF-type) between distinct temperature/structure domains that are divided by this glass transition (Levine & Slade, 1986; references in Table 10B). 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 & Levine, 1988*b*). The WLF equation (Williams *et al.*, 1955; Ferry, 1980) defines the kinetics of molecular-level relaxation processes, 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 & Slade, 1986, 1988*b*, 1989*d*, 1992; Slade & Levine, 1988*b*; Franks & Grigera, 1980; Roos & Karel, 1990, 1991*a,d,e,f,g*, 1992; Franks *et al.*, 1991; Lim & Reid, 1991; Karel, 1992). 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 demarcate the upper boundary of the WLF region, where Arrhenius kinetics again apply (Levine & Slade, 1989*c*). 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 & Levine, 1988*b*). 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 & Slade, 1989*d*; Slade & Levine, 1991*a*). It should be noted 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, 1991*a,b*). In contrast, the actual measured relative vapor pressure (RVP) or relative humidity (RH) of a (non-equilibrium) 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 (or 100% RH) with increasing temperature above T_g and increasing moisture content above W_g (Slade & Levine, 1991*a,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, called T'_g (Franks *et al.*, 1977), on a state diagram for any particular solute. 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 & Slade, 1986; additional references in Table 11A (Slade & Levine, 1993)). A compilation of reported literature values of T'_g for many different low MW carbohydrates, as well as corresponding T_g values ('dry' T_g) for anhydrous solutes, was recently presented (Levine & Slade, 1992). As illustrated in the schematic state diagram shown in

Table 11. References to publications dealing with: A. T'_g; B. The importance of state diagrams and of the T'_g-C'_g point

A. Franks *et al.* (1977), Franks (1982, 1983*b*, 1985, 1986*a,b*, 1989, 1990, 1991*a*), Schenz *et al.* (1984, 1991, 1993), Slade (1984), Slade & Levine (1984, 1985, 1987*a,b*, 1988*a,b,c,d*, 1989, 1991*a,b*, 1992, 1993), Reid (1985, 1990), Levine & Slade (1986, 1988*a,b,c,d*, 1989*a,b,c,d*, 1990, 1991, 1992, 1992*a*, 1993), van den Berg (1986, 1993), Blanshard & Franks (1987), Lillford (1988), Marsh & Blanshard (1988), Karel (1989), Russell & Oliver (1989), Slade *et al.* (1989), Biliaderis (1990, 1991*b*), Caldwell *et al.* (1990), Franks & Grigera (1990), Le Meste & Simatos (1990), Noel *et al.* (1990), Paakkonen & Roos (1990), Pikal (1990*a,b*), Williams & Carnahan (1990), Blanshard *et al.* (1991), Blond & Colas (1991), Blond & Simatos (1991), Franks & van den Berg (1991), Franks *et al.* (1991), Given (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Karel & Saguy (1991), Le Meste & Huang (1991), Levine *et al.* (1991, 1992), Lim & Reid (1991), Ma & Harwalkar (1991), MacDonald & Lanier (1991), Matthiesen *et al.* (1991), Maurice *et al.* (1991), Roos & Karel (1991*c,d,e,f,g*, 1993), Roozen & Hemminga (1991), Roozen *et al.* (1991), Wasylyk & Baust (1991), Ablett *et al.* (1992*a,b*, 1993), Blond (1992), Cocero *et al.* (1992), Goff (1992), Goff *et al.* (1992), Huang (1992), Huang *et al.* (1992), Le Meste *et al.* (1992), Reid & Hsu (1992), Reid & McCarthy (1992), Reid *et al.* (1992, 1993), Roos (1992*a*), Hemminga *et al.* (1993), Karel *et al.* (1993), Simatos & Blond (1993), van den Berg *et al.* (1993)

B. Schenz *et al.* (1984, 1991, 1993), Slade (1984), Slade & Levine (1984, 1985, 1987*a,b*, 1988*a,b,c,d*, 1989, 1991*a,b*, 1992, 1993), Franks (1985, 1989, 1990), Burke (1986), Levine & Slade (1986, 1988*a,b,c,d*, 1989*a,b,c,d*, 1990, 1991, 1992, 1992*a*, 1993) van den Berg (1986), Blanshard & Franks (1987), Lillford (1988), Simatos & Karel (1988), Blond (1989), Green & Angell (1989), Karel (1989, 1992), Simatos *et al.* (1989), Williams & Leopold (1989), Biliaderis (1990), Caldwell *et al.* (1990), Franks & Grigera (1990), Le Meste & Simatos (1990), Noel *et al.* (1990), Williams & Carnahan (1990), Ablett & Lillford (1991), Blanshard *et al.* (1991), Blond & Colas (1991), Bruni & Leopold (1991), Chang & Baust (1991*b*), Franks & van den Berg (1991), Franks *et al.* (1991), Given (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Le Meste & Huang (1991), Lim & Reid (1991), Ma & Harwalkar (1991), MacDonald & Lanier (1991), Matthiesen *et al.* (1991), Roos & Karel (1991*d,e,f,g*, 1993), Simatos & Blond (1991), Ablett *et al.* (1992*a,b*, 1993), Cocero *et al.* (1992), Goff (1992), Huang *et al.* (1992), Reid & Hsu (1992), Roos (1992*a*), Karel *et al.* (1993)

(Courtesy of Slade & Levine, 1993)

Fig. 4 (Slade & Levine, 1991*a*), 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 non-equilibrium extension of the equilibrium liquidus curve for T_m of ice (Levine & Slade, 1986, 1988*a,b,c,d*, 1989*a,b,c,d*, 1990, 1991). This solute-specific location defines the composition of the glass that contains the maximum *practical* amount of plasticizing moisture — called W'_g, expressed as g UFW/g solute or weight % (wt%) water, or alternatively designated in terms of C'_g, expressed as wt% solute (Levine & Slade, 1986, 1988*a*) — and represents the transition from concentrated fluid to kinetically metastable, dynamically constrained solid that occurs on cooling to $T < T'_g$ (Slade & Levine, 1988*b*, 1991*a*). 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, 1983*a*, 1985, 1986*a,b*, 1989, 1990, 1991*a*; Levine & Slade, 1986, 1988*a*, 1989*b*; Slade *et al.*, 1989; Franks & Grigera, 1990; Oksanen & Zografi, 1990; Belton, 1991; Slade & Levine, 1991*a,b*; Tanner *et al.*, 1991; Goff, 1992).

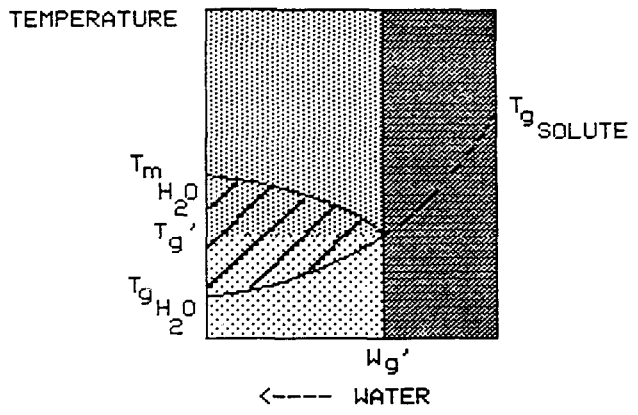

Fig. 4. Schematic state diagram of temperature vs wt% water for an aqueous solution of a hypothetical, glass-forming, small carbohydrate (representing a model frozen food system), illustrating how the critical locations of T'_g and W'_g divide the diagram into three distinguishable structure-property domains. (Reproduced, with permission, from Slade and Levine (1991*a*).)

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 & Williams, 1981; Slade & Levine, 1988*b*; Wunderlich, 1990). A theoretical calculation (Marsh & Blanshard, 1988) of T_g for a 50% wheat starch gel fell well below the measured value of -5 to -7°C for T'_g (Slade, 1984; Slade & Levine, 1984, 1987*b*), 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 & Levine, 1988*b*, 1991*a*), reconciled the difference between theoretical and measured values of T_g (Marsh & Blanshard, 1988). Moreover, the theoretical calculations supported the measured value of ≈ 27 wt% water (Slade, 1984; Slade & Levine, 1984, 1987*b*) for W'_g, the maximum practical water content of a homogeneous wheat starch-water glass. The calculated water content of a wheat starch

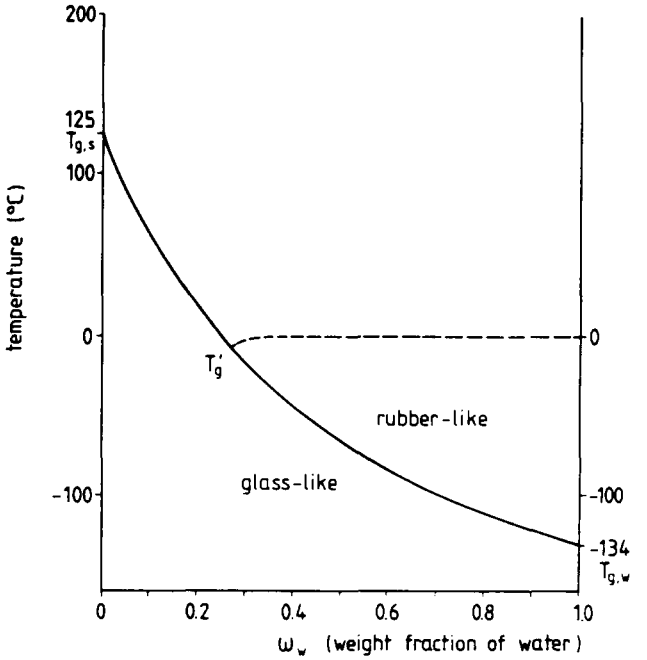

Fig. 5. State diagram, showing the approximate T_g temperatures as a function of mass fraction, for a gelatinized starch-water system. (Reproduced, with permission, from van den Berg (1986).)

glass with T_g of about −7°C is ≈28 wt% (Marsh & Blanshard, 1988), and 26 wt% for a measured T_g [i.e. T_g'] of −5°C (Roos & Karel, 1991*d*). These points are illustrated in the state diagram for a gelatinized starch-water system, shown in Fig. 5 (van de Berg, 1986).

In recent years, many workers have lent their strong support to advocacy of the importance of state diagrams (such as the ones in Figs 4 and 5), and of the solute-specific, invariant T_g'-C_g' as the focal point of such dynamics maps, to understanding structure-property relationships of food molecule-water systems (references in Table 11B). In fact, T_g' and C_g' values, especially of various low MW sugars widely used in starch-containing foods, have become a topic of so much current interest, as well as considerable controversy and debate, that many recent publications have been devoted to discussions of several different aspects of this subject, as outlined in Table 12 (Slade & Levine, 1993). It should also be noted, in passing, that T_g' corresponds to the subzero T_g mentioned by Atkins (1987) as being characteristic of many water-plasticized, rubbery biopolymers *in vivo*.

CONCLUSIONS AND FUTURE PROSPECTS

In this paper, we have outlined a food polymer science approach to the study of glasses and glass transitions in starch-containing foods. This approach has been used to define structure-functional property relationships and water relationships in starch-based food products and processes, and to assess and understand the effects of glass transitions, water plasticization, and WLF kinetics on product quality, safety, and stability. We have pointed out theoretical principles from the field of synthetic polymer science that are applicable to

Table 12. References to recent publications containing discussions of values of T_g' and C_g' and/or methods of determining those values for low MW carbohydrates

A. Methods of determining C_g' values:

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

B. T_g' value of −32°C for sucrose:

Schenz *et al.* (1984), Franks (1985, 1986*a,b*, 1989, 1990), Slade & Levine (1985, 1988*b*), Blanshard & Franks (1987), Levine & Slade (1988*b*, 1992), Caldwell *et al.* (1990), Blanshard *et al.* (1991), Franks *et al.* (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Lim & Reid (1991), Maurice *et al.* (1991), Roos & Karel (1991*f*), Roozen & Hemminga (1991), Schenz *et al.* (1991), Goff (1992), Goff *et al.* (1992), Reid & Hsu (1992), te Booy *et al.* (1992), Hemminga *et al.* (1993), MacInnes (1993), Reid (1993)

C. Different C_g' values for sucrose:

MacKenzie (1977), Franks (1983*b*, 1985, 1986*a,b*, 1989, 1990), Slade & Levine (1985, 1988*b*, 1991*a*), Blanshard & Franks (1987), Levine & Slade (1988*b*, 1992, 1993), Williams & Carnahan (1989, 1990), Franks & Grigera (1990), Blanshard *et al.* (1991), Dereuddre *et al.* (1991). Franks *et al.* (1991), Hatley *et al.* (1991), Izzard *et al.* (1991), Le Meste & Huang (1991), Roos & Karel (1991*c,e,f,g*, 1993), Ablett *et al.* (1992*a,b*, 1993), Goff (1992), Reid & Hsu (1992), Roos (1992*a*), Nesvadba (1993), Reid *et al.* (1993)

D. T_g' as the temperature at the midpoint, rather than the onset, of the transition:

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

(Courtesy of Slade & Levine, 1993)

studies of glasses and glass transitions in cereal-based foods, and have presented a broad overview of the literature, focusing primarily on the most recent experimental studies by a number of groups that have been especially active in this growing field of research. As a framework for this necessarily brief discussion, we have used the questions raised in the introduction, which we have attempted to address.

We hope we have succeeded, at least, in convincing the reader that the field of food science and technology has recently enjoyed a seemingly exponential growth of interest in the glassy state phenomenon in many foods, including starch-based products, and in 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 and structural characteristics), safety, and stability of foods. This state of affairs is evidenced by the fact that about 320 of the 464 references cited in this brief review deal with glasses and glass transitions in food materials and systems, and about 240 of these have been published since 1989. In the rest of the 1990s, 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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