Modelling Viscosity Temperature Dependence of Supercooled Sucrose Solutions−The Random-Walk Approach

Mafalda Quintas,*,† Teresa R. S. Brandão,† Cristina L. M. Silva,† and Rosiane L. Cunha‡

Laboratório de Optimização de Processos Alimentares, Escola Superior de Biotecnologia, Universidade Católica Portuguesa, R. Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal, and Laboratório de Engenharia de Processos, Departamento de Engenharia de Alimentos, Faculdade de Engenharia de Alimentos, UNICAMP, Cidade Universitária "Zeferino Vaz," Caixa Postal 6121, CEP 13081-970 Campinas, SP, Brasil

Sucrose and its supersaturated or supercooled solutions are of the utmost importance in areas as different as food and pharmaceutical industries or cryopreservation of biological systems. In the supercooled "state", such amorphous solutions are fragile systems, presenting extremely high viscosity with decreased mobility of molecules, impairing experimental determinations at low temperatures (below critical temperature, T_c). This work proposes the random walk (RW) approach to study relaxation behavior in the supercooled melt, using only viscosity data at temperatures above T_c. For comparison purposes, the Vogel−Fulcher−Tamman (VFT) model was fitted to th data. The random walk approach is based on the distribution of molecular energies, thus having a theoretical support not found in the VFT model. The RW estimated parameters can be correlated with system characteristics, showing their dependence on water content or sucrose concentration. RW and VFT model description was evaluated from the mathematical and physical points of view, but the random walk model led to more consistent regression results and parameter estimates with improved precision.

Introduction

All materials exist in a physical state resulting from their composition and temperature, and their mechanical properties are dependent on molecular mobility. Amorphous system viscosity reflects molecular mobility, which in turn is mainly proportional to the relaxation time. When a liquid is cooled below the melting temperature and crystallization is avoided, a rubbery region or supercooled melt "state" is observed. With further cooling of the system, the "glassy state" is achieved at a determined temperature, named glass transition temperature (T_g). The glass transition temperature is dependent on both the composition and solid content of a material.[1] It has been described as the temperature at which molecules take at least 100 s to move from one position to another.[2] T_g is also considered as the temperature limit for physical stability of a material, which justifies the great importance that areas like food science dedicate to this subject.[3] Not without controversy,[4] the "glassy state" is generally accepted to be an isoviscous state, with a viscosity (η_g) of approximately 10^{12} Pa.s.[5]

Relaxation behavior in supercooled liquids has interested scientists for a long time. Experimentally, two types of temperature dependence behavior have been observed: (i) the Arrhenius behavior, where viscosity varies exponentially with the reciprocal of temperature, and (ii) the VFT behavior, where viscosity temperature dependence presents a nonlinear behavior in the Arrhenius plot.[6] These different behaviors have been classified as strong (Arrhenius following) and fragile (VFT following) supercooled liquids.[5] The fragility (m) concept has been proposed to measure the deviation from strong behavior

in the "supercooled state" and to characterize the steepness of the viscosity temperature dependence.[6]

Several theories have been proposed to explain the differences in strong and fragile behavior, e.g., the theory of the liquid state[7] for the former and the theories of free volume[8,9] and the entropy-controlled cooperative motions[10] for the latter. However, these theories do not consider the experimentally observed dynamical singularity in the response of a fragile supercooled system at a critical (or divergence) temperature, T_c ($T_c > T_g$), described by the mode coupling theory.[11] Determination of T_c is difficult. However, some typical values of T_g/T_c around 0.83 can be found in literature.[12] Also, for semirigid polymers this ratio was found to be around 0.9,[13,14] and studies on glycerol indicated a 0.77 ratio.[4] For sucrose solutions, T_g/T_c was found to be approximately 0.86, in a wide concentration range.[15]

More recently, Arkhipov and Bässler[12,16] used the random walk (RW) approach to develop a model that is able to describe the temperature dependence of viscosity in both strong and fragile liquids. A random-walk is a statistical tool that can be used to predict the final state of a system when a physical phenomenon, usually associated with movement, occurs in a complex way. Arkhipov and Bässler[12,16] considered that a unit structure (i.e., a molecule or a subunit embedded in the molecular environment) in the configurational space cannot change its position without a transition in the configurational space. This transition can be considered as a jump of a unit structure in a highly complex energy landscape. After each jump, the structural unit finds a new environment and the configurational space phase memory is lost. This "no memory" process can be modeled as a random walk on a disordered network of hopping sites in configurational space, characterized by a broad distribution of energies. The energy of a structural unit depends on a large number of random configurational co-ordinates and a normalized function can be realistically assumed for the

---

* Corresponding author.

† Universidade Católica Portuguesa. Tel: +351 22 558 00 58, Fax: +351 22 509 03 51.

‡ Cidade Universitária "Zeferino Vaz" UNICAMP. Tel: +55 19 3788 4047, Fax: +55 19 3788 4027.

Supercooled Sucrose Solutions

J. Phys. Chem. B, Vol. 111, No. 12, 2007 **3193**

distribution of possible metastable states. The jump frequency of structural units, which is proportional to system viscosity, can be determined using a master equation for the normalized energy distribution function of the structural units.[12,16] In the case of supercooled fragile systems, due to the strong effect of temperature on the energy of molecules, two regimes are considered: (i) the lower-temperature regime (at $T < T_c$), where the activation energy of a jump upward in energy is larger than the difference between site energies; and (ii) the higher-temperature regime (at $T > T_c$), where the energy landscape is fluctuating at a frequency large enough to allow an unit jump to an adjacent site, and the activation energy of a jump upward in energy is the difference between site energies.

Sucrose and its supercooled solutions are of the utmost importance in areas as different as food and pharmaceutical industries or cryopreservation of biological systems. Sucrose solutions behave as Newtonian fluids in a wide concentration range[17−19] and are fragile glass formers.[20] In the supercooled state, such amorphous solutions present extremely high viscosity with decreased mobility of molecules. The torque of most commercial rheometers is not able to support such high viscosities, and in order to measure viscosity near T_g (i.e., in the low-temperature regime), it is necessary to replace the transducer[21] or recur to comparison techniques that introduce a larger experimental error.[4]

The research presented in this paper aims at testing the usefulness of the random walk model to describe sucrose viscosity behavior in the "supercooled state" and determine solution fragility when only data from the high-temperature regime is available. The VFT description of such data is also studied for comparison purposes. The comparison between the two models was done in two ways: (i) by assessing the quality of mathematical description of experimental data and (ii) by discussing the parameters physical meaning.

Theoretical Considerations

Modeling Relaxation Behavior in Supercooled Liquids. As mentioned above, in supercooled liquids, viscosity temperature dependence may follow an Arrhenius type equation,[22] which is an empirical model developed from the theory of the liquid state,[7] or present deviation from such behavior. The Vogel−Fulcher−Tammann (VFT) model (eq 1) is often used to model fragile behavior:[5]

$$\eta = \eta_{0_{VFT}} \exp\left(\frac{B}{T - T_{0_{VFT}}}\right) \quad (1)$$

where $\eta_{0_{VFT}}$, B and $T_{0_{VFT}}$ are model parameters and correspond, respectively, to (i) the viscosity at infinite temperature, (ii) a temperature that can be correlated with the function curvature and thus with the system fragility, and finally, (iii) a temperature ($<T_g$), which experimental evidence suggests coincides with the Kauzmann temperature[23] (i.e., the temperature where the extrapolated liquid entropy meets the crystal entropy[24]).

Mathematically, the Arrhenius equation may be considered a particular case of the VFT model (eq 1), with $T_{0_{VFT}} = 0$ and B proportional to the activation energy. However, when VFT model is applied to viscosity data outside the "supercooled state," the physical interpretation of the parameters is impaired.

Arkhipov and Bässler[12,16] developed a theory able to explain relaxation behavior in strong and fragile supercooled liquids, which accounts for the observed changes at T_c in fragile systems. Such approach allowed the development of mathematical models that describe viscosity temperature dependence above and below T_c.

Applying a random walk to fragile glass forming liquids, the lower temperature regime ($T < T_c$) yields[12,16]

$$\eta = \eta_{0_{RW}}\left[\frac{\pi}{2(\alpha - 1)}\right]^{1/2} \alpha^{(2\alpha-3)/2(\alpha-1)}\left[\Gamma\left(\frac{1}{\alpha}\right)\right]^{-1}\left(\frac{T_{0_{RW}}}{T}\right)^{(2-\alpha)/2(\alpha-1)}$$
$$\exp[(\alpha - 1)(T_{0_{RW}}/\alpha T)^{\alpha/(\alpha-1)}] \quad (2)$$

where Γ is the gamma function and α a shape parameter of energy distribution, $\eta_{0_{RW}}$ accounts for the contribution of structural unit jumps toward viscosity, and $T_{0_{RW}}$ is a temperature that reflects the spread of the self-energies of the structural units.

For the higher temperature regime ($T > T_c$), the relation is given by[12,16]

$$\eta = \eta_{0_{RW}} 2^{(2\alpha-1)/2(\alpha-1)} 1/\alpha \Gamma\left(\frac{1}{\alpha}\right)\left(\frac{T_{0_{RW}}}{T}\right)$$
$$\exp[(\alpha - 1)(1 - 2^{-1/\alpha-1})(T_{0_{RW}}/\alpha T)^{\alpha/(\alpha-1)}] \quad (3)$$

Assessing Fragility of a Glass Forming Liquid. Several methods have been proposed to "measure" fragility (m) of a system, i.e., to characterize the steepness of viscosity temperature dependence.[6] The most popular form is to measure the slope of the VFT equation near T_g:[4,6,25−27]

$$m_{VFT} = \frac{d \log \eta}{d(T_g/T)}\Big|_{T=T_g} = B\frac{T_g}{(T_g - T_{0_{VFT}})^2} \quad (4)$$

The RW model also allows for a description of the function steepness through the α parameter. In fact, strong glass forming fluid behavior (Arrhenius-like) show $\alpha \rightarrow 2$ and fragile glass forming liquids behavior (VFT-like) present $\alpha \rightarrow 1$.[16] Furthermore, a correlation of fragility m and α has been successfully established:[28]

$$m_{RW} = \frac{1}{\ln 10}\left[\left(\frac{2 - \alpha}{2(\alpha - 1)}\right) + \alpha(T_{0_{RW}}/\alpha T_g)^{\alpha/(\alpha-1)}\right] \quad (5)$$

Data Analysis and Modeling Procedures

As explained before, experimental measurements of sucrose solutions viscosity in the "supercooled state" are difficult, especially in the temperature range from T_c to T_g. In this paper, studies were carried out using authors published viscosity data of sucrose solutions[18] with different concentrations (79.9%, 82.9%, and 85.2% (w/w)) and at temperatures corresponding to the "supercooled state" (i.e., above the saturation point, or at temperatures below the melting temperature). Data were only available in the high-temperature regime, since T_g/T was <0.86 for every case[15] (T_g was determined as a function of solution composition, by the Gordon-Taylor's relationship, using $T_{g,water}$ = −135 °C and $T_{g,pure\ sucrose}$ = 62 °C[29]).

Although the studied concentration range appears to be quite narrow, the large differences in measured viscosity allowed studying temperature behavior in the "supercooled state."

The VFT model and the random walk model (high-temperature regime), eqs 1 and 3, respectively, were fitted to viscosity data of the different sucrose solutions. Due to added difficulties in optimizing an equation containing the gamma function, the pre-exponential terms of eq 3 were substituted by a constant c, as follows:

$$c = \eta_{0_{RW}} 2^{(2\alpha-1)/2(\alpha-1)} 1/\alpha \Gamma\left(\frac{1}{\alpha}\right) \quad (6)$$

TABLE 1: Results of Fitting the VFT Model Using: (a) Only Experimental Data and (b) Experimental Data and η_g Calculated from Literature[a]

data	concentration (w/w)	VFT model regression results					predictions from VFT regression results	
		Estimated parameters (95% SHW)						
		$\eta_{0_{VFT}}$	$T_{0_{VFT}}$	B	R^2	MSE	m_{VFT}	η_g
experimental (a)	79.9	9.08×10^{-6} (918%)	186 (918%)	1576 (3%)	>0.9999	1.67	275	1.47×10^{14}
	82.9	1.78×10^{-6} (1250%)	182 (1479%)	2026 (4%)	0.9997	4.18	191	1.03×10^{12}
	85.2	5.87×10^{-6} (1617%)	199 (1630%)	1798 (5%)	0.9988	7.61	258	7.43×10^{13}
experimental + literature η_g (b)	79.9	2.37×10^{-4} (101%)	190 (95%)	1210 (0.6%)	>0.9999	4.35×10^{-2}	262	6.15×10^{12}
	82.9	3.53×10^{-4} (33%)	198 (30%)	1230 (0.2%)	>0.9999	1.31×10^{-2}	263	6.13×10^{12}
	85.2	8.94×10^{-5} (66%)	201 (64%)	1496 (0.3%)	>0.9999	3.15×10^{-2}	241	6.13×10^{12}

[a] Estimated parameters (corresponding 95% SHW) and evaluation of the regression on the basis of R^2 and MSE. Fragility calculated from eq 4 and viscosity at T_g predicted by the model.

Nonlinear regression analysis was performed using the simplex algorithm for function minimization,[30] programmed in Fortran 77 language (Fortran 5.1, Microsoft Corporation, 1990). With the exception of the mentioned cases (see later in the text), the objective function for minimization was the sum of the squared residues (least-squares estimation).

The 95% standard error of the parameters was calculated using the variance-covariance matrix. Parameters precision was determined through the 95% standard halved width (i.e., the 95% standard error divided by parameter estimate). The use of the variance-covariance matrix for the calculation of the standard error in nonlinear regression procedures must be carefully interpreted, since it leads to underestimated confidence intervals for the parameters.[31] However, this approximation can be used for comparison of different models parameters' precision.

The quality of the regressions was evaluated on the basis of the determination coefficient, R^2, the mean square error, MSE (i.e., the sum of the squared residuals divided by the regression degrees of freedom) and residuals visual inspection.

Results and Discussion

Fitting the VFT Model to Supercooled Sucrose Solution Viscosity Data. As already mentioned, measuring viscosity near the glass transition (especially at $T < T_c$ is difficult. In the past, studies of viscosity near T_g were performed typically by fitting the VFT model to high-temperature ($T > T_c$) viscosity data and then extrapolating model behavior near T_g.[26]

The fitted parameters obtained using this approach (fragility determination and prediction of viscosity near or at T_g) lack physical significance, since these are extrapolated results. Furthermore, this approach raises substantial mathematical issues, as following described.

A typical example of VFT model (eq 1) fitting to sucrose viscosity data can be observed in Figure 1 (dashed line) and Table 1 includes the regression results for the three studied concentration levels. It can be concluded that (i) parameter estimates have high associated errors (evaluated through the 95% SHW), which impairs conclusions on the effect of sucrose concentration on VFT parameters, and (ii) η_g prediction is poor, due to extrapolation to a distant point of the function. From the above, the determination of fragility (m)—through the slope of the VFT equation near T_g—becomes a mere academic exercise, which may in some cases and with proper caution be used to compare results from different molecules or solutions. In the present case, m_{VFT} results clearly lack statistical significance ($T_{0_{VFT}}$, used in their determination, presents 95% standard errors 10 times higher than the parameter itself). Furthermore, fragility is expected to increase with sucrose content,[20] which could not be observed.
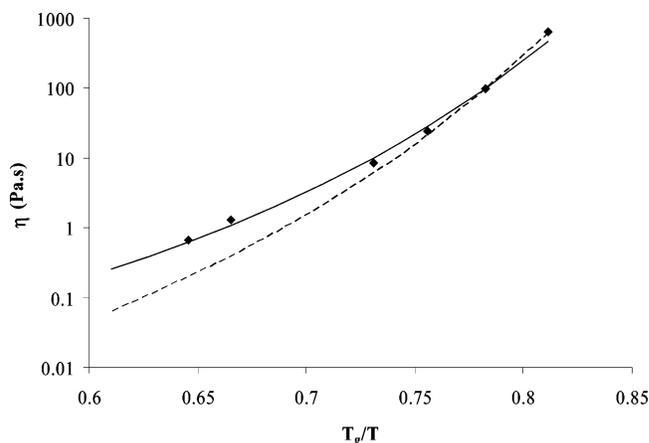

Figure 1. Typical VFT model fitting to experimental data (dashed line) and to experimental data including viscosity at T_g calculated from literature (solid black line). Points indicate experimental values and example is for a 79.9% (w/w) sucrose solution.

Fitting the VFT Model using a Theoretical Viscosity at T_g. To study the effect of extrapolating the VFT model in calculating η_g, the model was fitted using experimental data and a theoretical "pseudo-experimental point" at the glass transition temperature: the viscosity at T_g calculated from literature.[32-34] Results are also presented in Figure 1 and Table 1. As it can be observed, there is an indication of an increase in regression quality through the observed increase in R^2. However, the MSE cannot be compared. Due to large differences in viscosity values' magnitudes, drawbacks occurred in residuals sum of squares minimization. In this case, a mathematical artifice was used: the objective function used for the regression was the sum of the squared residuals divided by the experimental value (normalized residuals sum of squares). Such artifice also impairs comparison between estimates' precision: the 95% standard errors are not comparable (nevertheless, the observed decrease in the 95% SHW may be a reflection of improved estimate precision). Furthermore, the determination of fragility (m_{VFT}) still lacks statistical significance: $T_{0_{VFT}}$ estimate still presents large 95% SHW. This is even worsen by the facts that (i) the 95% standard errors calculated through the variance-covariance matrix are, as previously discussed, underestimated and (ii) the use of normalized residuals sum of squares in the regression procedure aggravates the underestimation of the 95% standard errors.

From the parameter physical meaning point of view, this approach also presents problems. Since it does not take into account the behavioral change at T_c, which may influence the shape of the function, predictions of viscosity near T_g, and even of fragility, may be compromised.[4] Furthermore, in this ap-

Supercooled Sucrose Solutions

J. Phys. Chem. B, Vol. 111, No. 12, 2007 **3195**
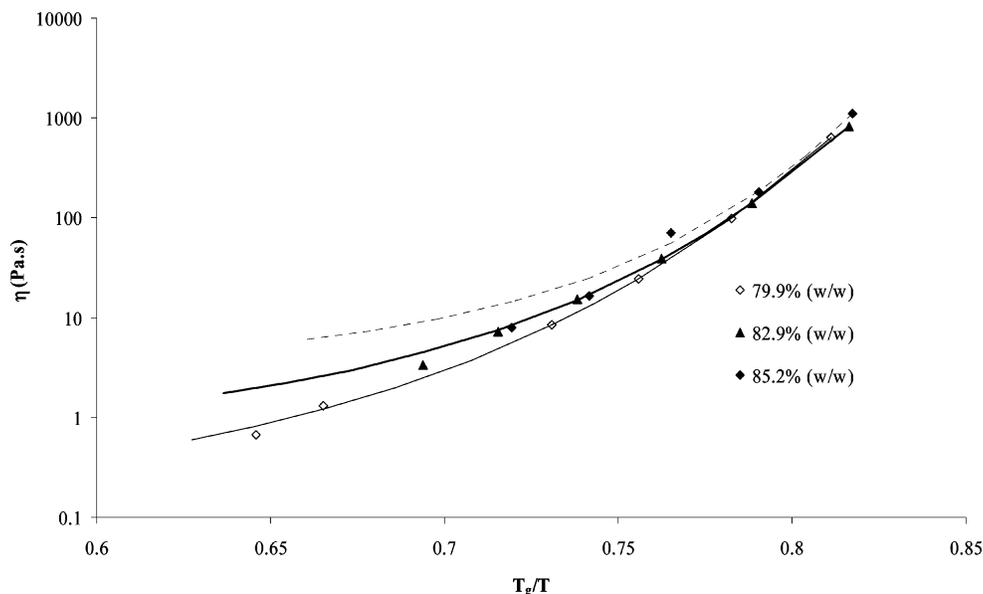

Figure 2. Random walk (RW) model fitting to experimental data of viscosity for the three sucrose concentration levels: 79.9% (w/w), solid gray line; 82.9% (w/w), solid black line; and 85.2% (w/w), dashed line—high-temperature regime (eq 3).

TABLE 2: Results from Fitting the Random Walk (RW) Model to Experimental Data, at Different Sucrose Concentrations[a]

concentration (w/w)	RW model regression results					predictions from RW regression results	
	estimated parameters (95% SHW)			R^2	MSE	$\eta_{0_{RW}}$	m_{RW}
	c	$T_{0_{RW}}$	α				
79.9	0.116 (15%)	542 (1%)	1.16 (0.3%)	>0.9999	0.03	6.88×10^{-3}	119
82.9	0.597 (24%)	502 (2%)	1.13 (0.5%)	>0.9999	1.22	2.13×10^{-2}	151
85.2	3.061 (8%)	455 (0.7%)	1.09 (0.2%)	0.9996	173.11	4.03×10^{-2}	285

[a] Estimated parameters (corresponding 95% SHW) and evaluation of the regression on the basis of R^2 and MSE. Fragility calculated from eq 5 and $\eta_{0_{RW}}$ determined from eq 6.

proach, η_g is seldom experimentally determined, but rather calculated either from (i) literature data obtained by extrapolations[32−34] or, (ii) assuming a constant and theoretical value of 10^{12} Pa.s, diminishing any physical interpretation of the results. These facts, associated with the lack of parameter significance, impair any consistent conclusions on relaxation behavior in the supercooled melt using only high-temperature relaxation data.

Fitting the RW Model to Supercooled Sucrose Solutions Viscosity Data. The RW model is based on the assumption of molecule energy distribution and thus is supported by a theoretical background not found in the VFT model. In this section, the RW prediction of relaxation behavior (both from the mathematical and physical points of view) will be analyzed.

The results of fitting the RW model (eq 3, with the pre-exponential factors substituted by c (eq 6)) can be observed in Figure 2 and Table 2. Comparing the results with VFT model fitting (Table 1a), a remarkable increase on the estimates' precision was observed. The R^2 values increased in all cases, together with a significant decrease of MSE for 79.9% and 82.9% (w/w) sucrose solutions, indicating an enhanced regression procedure. However, a strong increase in MSE was observed in the case of 85.2% (w/w) sucrose solution. This may be due to the fact that (i) the available experimental data was near the literature value for T_c (i.e., such solution may be near a change in the relaxation behavior regime and better predictions could have been obtained if the low-temperature regime model (eq 2) was used) and/or (ii) few experimental points are available for the regression (Figure 2).

The results are relevant for the physical interpretation of the observed phenomena: $\eta_{0_{RW}}$, which was calculated from esti-

mated c (Table 2), is proportional to the structural units jump contribution to viscosity, increasing with sucrose content (i.e., with number of sucrose molecules in the solution).

The spread of the self-energies of the structural units due to configurational disorder, which is described by $T_{0_{RW}}$, decreases with increasing sucrose content. This fact may be due to the existence of less water molecules in the solution, decreasing molecular interaction and leading to an energetically "more homogeneous" configurational space.

The calculated fragility index (α) was significantly different for the studied sucrose solutions and approaches 1 with increasing sucrose content, as expected.[16,20] Furthermore, the calculated m_{RW} (from eq 5; Table 2) is in agreement with literature values.[26]

These results are even more significant when the small concentration range of this study is considered, and are a good indication of the potential of the random-walk (RW) approach to the study of molecular relaxation behavior in the supercooled "state," using only high-temperature regime data.

Conclusions

The random walk model is able to provide the viscosity temperature dependence in the supercooled state, with a theoretical support not found in the widely used VFT model.

Furthermore, the RW approach allows for fragility determination avoiding experimental measurements in $T < T_c$ region with improved precision of estimated parameters. These results are an indication of the RW model usefulness in describing relaxation behavior in supercooled systems. This approach may be applied to other systems, in order to access its validity for a wider range of materials.

Glossary

m	fragility
m_{VFT}	fragility by VFT model
m_{RW}	fragility by RW model
MSE	mean square error
R^2	determination coefficient
T	temperature (°C or K)
T_c	critical temperature (°C or K)
T_g	glass transition temperature (°C or K)
T_{0RW}, c	RW model parameters (°C or K and Pa.s, respectively)
T_{0VFT}, B	VFT model parameters (°C or K)

Greek Symbols

α	shape parameter of energy distribution
Γ	gamma function
η	viscosity (Pa.s)
η_g	viscosity at glass transition (Pa.s)
η_{0RW}	RW model parameter (Pa.s)
η_{0VFT}	VFT model parameter (Pa.s)

References and Notes

(1) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley & Sons, Inc: New York, 1980.

(2) Bueche, F. *J. Chem. Phys.* **1959**, *30*, 748−752.

(3) Slade, L.; Levine, H. *Crit. Rev. Food Sci. Nutr.* **1991**, *30*, 115−360.

(4) Schroter, K.; Donth, E. *J. Chem. Phys.* **2000**, *113*, 9101−9108.

(5) Angell, C. A. *J. Phys. Chem. Solids* **1988**, *49*, 863−871.

(6) Angell, C. A. *Chem. Rev.* **2002**, *102*, 2627−2649.

(7) Eyring, H.; Hirschefelder, J. *J. Phys. Chem.* **1937**, *41*, 249−257.

(8) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471−1475.

(9) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164−1169.

(10) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139−146.

(11) Gotze, W.; Sjorgen, L. *Rep. Prog. Phys.* **1992**, *55*, 241−376.

(12) Arkhipov, V. I.; Bassler, H. *J. Phys. Chem.* **1994**, *98*, 662−669.

(13) Saiter, A.; Bureau, E.; Zapolsky, H.; Saiter, J. M. *J. Non-Cryst. Solids* **2004**, *345−46*, 556−561.

(14) Saiter, A.; Bureau, E.; Cabot, C.; Saiter, J. M. *J. Non-Cryst. Solids* **2006**, *352*, 5067−5071.

(15) Champion, D.; Hervet, H.; Blond, G.; Le Meste, M.; Simatos, D. *J. Phys. Chem. B* **1997**, *101*, 10674−10679.

(16) Arkhipov, V. I.; Bassler, H. *J. Non-Cryst. Solids* **1994**, *172*, 396−400.

(17) Mathlouthi, M.; Génotelle, J. Rheological properties of sucrose solutions and suspensions. In *Sucrose. Properties and Applications*; Mathlouthi, M., Reiser, P., Eds.; Blackie Academic & Professional: London, 1995; pp 126−154.

(18) Quintas, M.; Brandao, T. R. S.; Silva, C. L. M.; Cunha, R. L. *J. Food Eng.* **2006**, *77*, 844−852.

(19) Saggin, R.; Coupland, J. N. *J. Food Eng.* **2004**, *65*, 49−53.

(20) Angell, C. A.; Bressel, R. D.; Green, J. L.; Kanno, H.; Oguni, M.; Sare, E. J. *J. Food Eng.* **1994**, *22*, 115−142.

(21) Shi, X. F.; Mandanici, A.; McKenna, G. B. *J. Chem. Phys.* **2005**, *123*.

(22) Barnes, H. A.; Hutton, J. F.; Walters, K. *An Introduction to Rheology*, 1st ed.; Elsevier Science Publishers B.V.: Amsterdam, 1989.

(23) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131*, 13−31.

(24) Kauzmann, W. *Chem. Rev.* **1948**, *43*, 219−256.

(25) Saiter, A.; Saiter, J. M.; Grenet, J. *Eur. Polym. J.* **2006**, *42*, 213−219.

(26) Branca, C.; Magazu, S.; Maisano, G.; Migliardo, F.; Migliardo, P.; Romeo, G. *J. Phys. Chem. B* **2001**, *105*, 10140−10145.

(27) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222−1224.

(28) Saiter, A.; Bureau, E.; Zapolsky, H.; Marais, S.; Saiter, J. M. *J. Non-Cryst. Solids* **2002**, *307*, 738−743.

(29) Roos, Y. H. *Phase Transitions in Foods*; Academic Press: San Diego, California, 1995.

(30) Nelder, J. A.; Mead, R. *Computer J.* **1965**, *7*, 308−313.

(31) Bates, D.; Watts, D. *Non-linear Regression Analysis and its Applications*; John Wiley & Sons: New York, 1988.

(32) Braga da Cruz, I.; MacInnes, W. M.; Oliveira, J. C.; Malcata, F. X. Supplemented state diagram for sucrose from dynamic mechanical thermal analysis. In *Amorphous Food and Pharmaceutical Systems*; Levine, H., Ed.; The Royal Society of Chemistry: Cambridge, 2002; pp 59−70.

(33) Parker, R.; Ring, S. G. *Cryo-Lett.* **1995**, *16*, 197−208.

(34) Soesanto, T.; Williams, M. C. *J. Phys. Chem.* **1981**, *85*, 3338−3341.