Structural Transitions and Glass Formation

J. Kieffer

Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

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Independent results from experiment and computer simulations, pertaining to the change in physical properties of glass-forming liquids throughout the transition range, have been examined in the context of a two-state model. The complex mechanical moduli for a number of glass-forming oxides have been determined as a function of the temperature, using Brillouin light scattering. The temperature dependence of these moduli, which is characterized by the lack of thermo-rheological simplicity, can be adequately and consistently described by a two-state model. The relaxational modulus can be attributed solely to a peculiar viscoelastic structural state, which gradually comes into existence at high temperatures, as a result of structural transitions from the glassy to the viscoelastic state. The temperature dependence of inherent structure energies, as obtained by computer simulations of a Lennard-Jones fluid, by Sastry et al., can be described with the same two-state model. The ubiquitous behavior in these independent findings provides support for the concept that thermodynamically driven structural transitions underlie the glass transition.

1. Introduction

Glass formation is commonly perceived as the result of cooling of a liquid below its melting point, provided the rate is sufficiently fast to avoid the growth of a crystalline phase. In this picture, the removal of thermal energy would allow for the structure to settle into the nearest attainable potential energy minimum, to form a glass, and furthermore, this glass would act like a solid because the characteristic relaxation times have grown far beyond the frame of observation.[1] Of course a number of ubiquitous features associated with the glass transition, such as the discontinuity in the temperature dependence of thermodynamic state functions at T_g, cannot be explained with such a simple picture. Hence, the exact nature of the structural rearrangements associated with the relaxations in supercooled liquids, i.e., a detailed geometric description of relaxed and unrelaxed configurations, and the mechanisms that lead from one to the other, remain a matter of great interest.

Structural characterization of glasses and corresponding melts using techniques that are most sensitive to nearest-neighbor configurations, such as X-ray and neutron diffraction, infrared and Raman spectroscopies, or nuclear magnetic resonance, reveal subtle differences that can be attributed to the increased degree of disorder in the liquid. However, for strong glass formers, a significant change in the elementary structural building blocks is not observed.[2,3] This suggests that, if there is any structural reorganization associated with the glass transition, it might manifest itself more clearly in the intermediate- to extended-range order of the substance.

In this context, we found it to be particularly insightful to examine the gigahertz-frequency mechanical response of glass-forming liquids, because it probes the structural integrity on the scale of about 100 nm. To this end, we employed the Brillouin light scattering technique and measured the complex mechanical modulus of various glass-forming systems as a function of temperature, in particular across the glass transition regime. A complete account of our data is given in several publications.[4,5] Here we want to concentrate on one particular aspect of our analysis and put it in the context of some recent

computer simulations. The aim of this comparison is to raise the reader's awareness for the ubiquitous shape that reappears in the temperature dependence of various properties of glass-forming systems. As will be argued below, this reoccurrence supports the concept that thermodynamically driven structural transitions are associated with the glass transition. This paper is organized as follows: First we will illustrate the model that we developed in order to interpret the thermo-mechanical behavior of several glass-forming liquids in a consistent way. In this model, $\phi(T)$ describes the temperature dependence of the static modulus. The functional form for $\phi(T)$ is derived from the assumption that the static modulus is controlled by the presence of a rigid structural state and that with increasing temperature a gradual transition between this rigid and a viscoelastic state takes place. In the original conception of this model, $\phi(T)$ was embedded in a more complex formalism, and effort is made here to identify measurable quantities, which provide more direct access to the fraction of substance in either structural state. Such quantities are found in the relaxational modulus for pure boron oxide, based on Brillouin and ultrasonic measurements, and in the inherent structure energies recently reported by Sastry et al.[6]

2. Complex Mechanical Modulus in the Glass Transition Range

We have used Brillouin light scattering to determine the complex mechanical moduli in glass-forming liquids, as a function of the temperature. For details about the experiments and the analysis of the spectrum of scattered light, we refer to earlier publications[4,5] and the pertinent literature.[7−9] In short, this spectrum contains Brillouin peaks, which result from inelastic interactions between the light and thermal phonons that always exist in condensed matter at finite temperatures. The underlying process is analogous to the Doppler effect for sound. Hence, the frequency shift, ω_S, between the elastically and inelastically scattered light can be related to the velocity of thermal phonons at a given wavevector. Furthermore, since this

wavevector is being selected by the scattering geometry according to $q = 2n/\lambda \sin \theta/2$, where θ is the angle between the incident and scattered light, n is the refractive index of the scattering medium, and λ the wavelength of the light, we can evaluate its elastic storage modulus,

$$M'(\omega) = \frac{\rho_0 \omega_S^2}{q^2} \tag{1}$$

with knowledge of the average density ρ_0 of the substance. The full widths at half-maximum of the peaks is $2q^2\Gamma$. In glass-forming melts the line widths of the Brillouin peaks are predominantly affected by viscous processes,[4] and in a good approximation one can relate Γ to the viscosity of the scattering medium,

$$\Gamma_s \approx \nu(\omega) = \frac{\eta_0}{\rho_0} + \frac{c_\infty^2 - c_0^2}{1 + (\omega_S \tau_B)^2} \tau_B \tag{2}$$

In this expression, η_0 is the steady-state viscosity, c_∞ and c_0 are the velocities of sound at infinite and zero frequency, respectively, and τ_B is a characteristic relaxation time of the structure. From this we obtain the loss modulus according to

$$M''(\omega) = \rho_0 \omega_S \nu(\omega) \tag{3}$$

In this manner, the Brillouin scattering experiment furnishes both components of the complex mechanical modulus, $M^*(\omega) = M'(\omega) + iM''(\omega)$, within a single measurement. Given a laser source within the visible range of light, these measurements typically provide access to phonons in the gigahertz frequency regime. In a solid, elastic deformations at such frequencies can be considered adiabatic, and the corresponding sound velocity is c_∞. In a simple liquid far above the melting temperature, on the other hand, structural constituents completely rearrange within a nanosecond to accommodate any momentary mechanical perturbations and, except for the resistance to isotropic deformations, exhibit no elasticity. The corresponding sound velocity is c_0.

This circumstance makes the gigahertz frequency range particularly interesting for investigating the temperature range between the glass transition and the melting point. In fact, we should expect to see the storage modulus vary between its infinite- and zero-frequency limits, when going from T_g to the highest temperature attainable in our experiments. At first sight, our results give that impression. As representative examples, in Figures 1 and 2, the longitudinal storage and loss moduli for a sodium borate and a potassium tellurite system are shown as a function of temperature. Below T_g, the storage modulus varies only slightly, due to the effect of thermal expansion. Above T_g, the storage modulus decreases precipitously and approaches a high-temperature plateau. The magnitude of this plateau corresponds to the bulk modulus.

Based on the appearance of these data, it is tempting to describe the temperature dependence of the complex modulus with a Debye expression, which is based on Maxwell's model for viscoelastic media.[10] Assuming that the relaxation processes are thermally activated, one can change the value of the characteristic relaxation time by means of varying the temperature, since $\tau_B = \tau_0 e^{E_A/k_B T}$, where τ_0 is the fundamental time constant and E_A is the activation energy of the process. Hence the expression for the complex mechanical modulus becomes
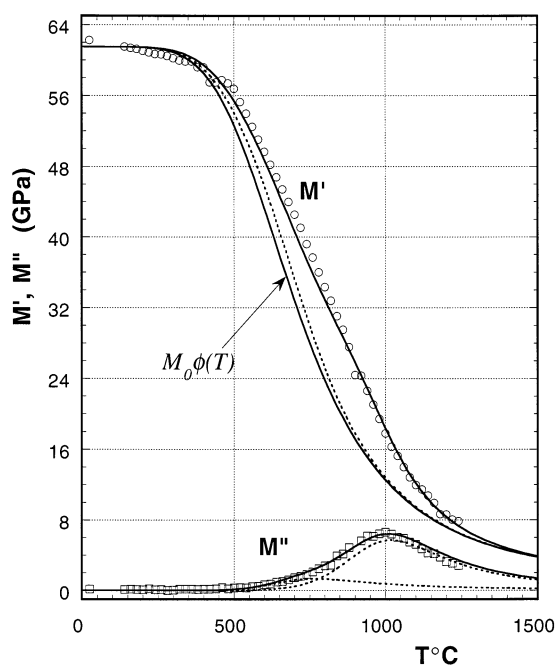

Figure 1. Storage and loss modulus of a binary alkali borate containing 32 mol % Na_2O, as a function of the temperature. Best fits of the data using eq 7 are superimposed. The lowest solid curve associated with the storage modulus represents the static modulus. Two relaxation mechanisms were identified for this system. Individual contributions are shown as dotted lines, and the sum of all contributions as solid lines passing through the data points. The distance between the solid line fitting the storage modulus and that corresponding to the static modulus amounts to the relaxational modulus, which is active at a given temperature.

a function of frequency as well as temperature,

$$M^*(\omega, T) + M_0 + M_2 \frac{\omega^2 \tau_0^2 e^{2E_A/k_B T}}{1 + \omega^2 \tau_0^2 e^{2E_A/k_B T}} + iM_2 \frac{\omega \tau_0 e^{E_A/k_B T}}{1 + \omega^2 \tau_0^2 e^{2E_A/k_B T}} \tag{4}$$

The factor M_2, which precedes the frequency- and temperature-dependent terms, is called the relaxational modulus.

3. Viscous Relaxation vs Structural Transitions

3.1. Rigid-Domain Model. As we have shown in previous papers, however, eq 4 does not fit the data shown in Figures 1 and 2 (or that of any of the other systems we have studied). In particular, the complex conjugate components of the mechanical modulus do not conform to a Kramers–Kronig transformation with respect to the variable $e^{E_A/k_B T}$, as would be expected for a linear susceptibility. Or, in other words, over the transition range, one cannot assume time–temperature superposition for these glass-forming systems. We therefore made the working assumption that the structures of the high-temperature melt and of the glass are inherently different. Because the mechanical response of the substance on the 10–100 nm scale is so sensitive to the structural changes that take place in the transition range, it is likely that these changes affect primarily the pattern and extent of chemical bonds between structural constituents. As such, the actual atomic displacements upon reorganization may be minute. However, the path for force transmission is changed in a systematic way. In other words, while the statistical representation of atomic positions may be hardly changed, as
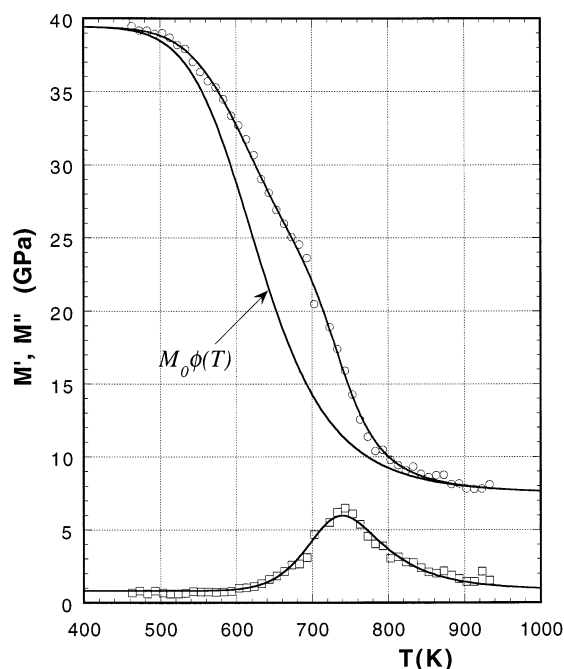
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supercooled liquid, and therefore capable of viscoelastic relaxation. When the slope of G changes to that of the solid phase (glass or crystal), the structure relinquishes certain degrees of freedom, and we consider it rigid, or purely elastic. Obviously, the transition between these structural states can occur at various degrees of supercooling, and throughout a macroscopic specimen, a distribution of structural states can coexist. Such coexistence is furthermore facilitated by the innate disorder of amorphous structures, which allows the system to overcome the need for creating distinct interfaces between the viscoelastic and rigid structural domains.

The formalism derived below is for the simplest case of two distinct structural states. The concept of two-level or two-state systems has been used as a modeling approach for numerous phenomena, including the anomalous behavior in the low-temperature heat capacity,[11,12] the thermal expansion,[13] the temperature dependence of the elastic properties in silica glass,[14,15] and the glass transition.[16–20] A more detailed discussion of the two-state concept, in the context of the existing literature, is presented below. The formalism presented here exhibits a qualitative behavior similar to that of other authors. In fact, it is based on simple Boltzmann statistics, which describes the partition of a system between two thermodynamic states as

$$\frac{n_V}{n_R} = e^{-(G_V - G_R)/k_B T} = e^{-\Delta G/k_B T} \tag{5}$$

where n_V and n_R refer to the number of moles in the viscoelastic and rigid state respectively, and $\Delta G = G_V - G_R$ is the free energy difference between the states. One can then express the fraction of substance in either the rigid or viscoelastic state by $\phi(T)$ and $1 - \phi(T)$ respectively, with

$$\phi(T) = \frac{n_R}{n_R + n_V} = [1 + e^{-[\Delta H(T_c - T)/k_B T_c T]}]^{-1} \tag{6}$$

ΔH is the enthalpy difference and T_c is the temperature at which the supercooled liquid and the glass have the same free energy. To eliminate the entropy, we assumed that G varies linearly near T_c. The modulus of such a system is then a composite of the moduli of either phase, in a first approximation, a linear combination of the two,

$$M^*(\omega, T) = M_0 \phi(T) +$$

$$(1 - \phi(T)) \sum_j M_{2,j} \frac{\omega^2 \tau_{0,f}^2 e^{2E_{A,j}/k_B T} + i\omega \tau_{0,j} e^{E_{A,j}/k_B T}}{1 + \omega^2 \tau_{0,j}^2 e^{2E_{A,j}/k_B T}} \tag{7}$$

By virtue of the factor $\phi(T)$ the static modulus in eq 7 is now temperature dependent, and the relaxational moduli are now affected by two opposing temperature influences. The relaxational term has been formulated as a sum, to account for the possibility of several relaxation mechanisms (denoted by "j") to be active simultaneously.

Using this model we were able to describe both components of the complex mechanical modulus consistently, for all systems we investigated. When the data for the storage and loss moduli for a given system were fitted independently, using eq 7, the magnitudes for M_2, τ_0, and E_A are the same within the boundaries of the experimental error. The fact that this procedure worked well for all systems we investigated provides strong support for the concept that the structural states of the liquid and the glass are inherently different from each other. In

Figure 2. Storage and loss modulus of a binary alkali tellurite containing 20 mol % K$_2$O, as a function of the temperature. Best fits of the data using eq 7 are superimposed. The lowest solid curve associated with the storage modulus represents the static modulus. Only one relaxation mechanisms was identified for this system. The distance between the solid line fitting the storage modulus and that corresponding to the static modulus amounts to the relaxational modulus, which is active at a given temperature.
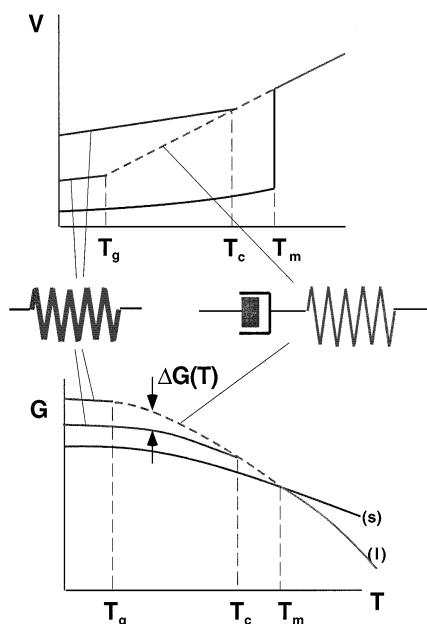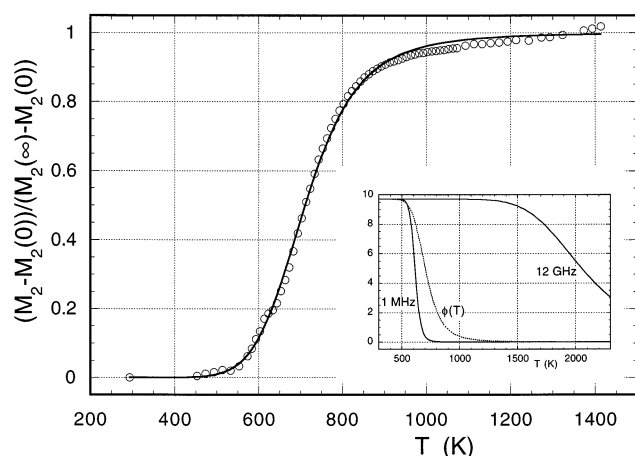

Figure 3. Schematic illustrating the stability regimes of the elastic and viscoelastic structural states, by means of the temperature dependence of the specific volume and free energy of the system.

revealed by diffraction experiments, bonding patterns characteristic of the glass and the liquid must differ significantly.

Changing the bonding pattern in a structure is also likely to involve a change in internal energy and entropy. We can therefore assume a free energy difference between the structure most characteristic of the glass and that of the liquid. A schematic of a free energy diagram for the presumed situation is shown in Figure 3. As long as the free energy, G, follows the slope of that of the liquid, we consider the structure a

Figure 4. Relaxational modulus for pure B_2O_3, as determined by comparing the sound velocities measured at 1 MHz and 12 GHz. The ability to relax is attributed only to the viscoelastic (i.e., liquid) structural state. The apparent temperature dependence reflects that of the fraction of material in the viscoelastic state. Inset: Relaxation window for the ultrasonic and Brillouin probes. The drops in the solid lines mark the temperatures at which liquid B_2O_3 starts to relax within each oscillatory period of a given probe. The dotted line represents $\phi(T)$; its decay indicates the ability of the structure to transform.

previous publications we have described possible scenarios for the mechanisms of structural transitions. These mechanisms were derived by combining information from various experimental studies of these systems, and from computer simulations, and they inferred concrete details with regard to the structural differences between liquid and glass.

Nevertheless, since the function $\phi(T)$, which describes the relative amounts of the glassy and liquid structural states, enters into eq 7 as only one of two temperature-dependent terms, support for this concept is indirect. In the following, we present fits of $\phi(T)$ (or its complement) to more direct measures of the change of the structural state. One of these measures is derived from the measurement of sound velocities at different frequencies, the other one from computer simulations.

3.2. Relaxational Modulus. Tauke et al. measured sound velocities of pure boron oxide as a function of temperature, using ultrasonic techniques.[21] At the lowest frequency they report, 1 MHz, their data for the longitudinal sound velocity drops almost precipitously to its high-temperature plateau, right at the glass transition. On the basis of the loss modulus data from our Brillouin measurements, we know that the characteristic relaxation time associated with the viscous relaxation in liquid boron oxide, for this temperature regime range is between 100 and 0.2 ns. This is shorter than the reciprocal of the ultrasound probing frequency. Hence, on the time scale of the ultrasound measurement, the liquid relaxes nearly completely to the constraints imposed by the pressure fluctuations of the sound waves. It is therefore legitimate to approximate the 1 MHz data with the isothermal sound velocity of the system. On the other hand, Brillouin measurements probe the system at a more than 4 orders of magnitude higher frequency, which is close to the adiabatic sound velocity of the substance. Hence, the difference between the Brillouin and ultrasonic data directly provides a measure for the relaxational modulus, M_2. The validity of this assertion is illustrated in the inset of Figure 4 (see figure caption for discussion).

The aforementioned difference between the elastic characteristics of B_2O_3 supercooled melts, measured at two different frequencies, is expressed as a mechanical modulus (because this eliminates the effect of thermal expansion) and is plotted in

Figure 4. Since M_2 is associated only with the high-temperature structure, it is a good measure for the amount of material existing in this structural state. (Note that, by definition, the relaxational component of the modulus must act in parallel to any existing static components.) The line represents the best fit of the data, using the expression for $(1 - \phi(T))$. The values for ΔH and T_c for this fit are in excellent agreement with those obtained from the simultaneous fit of the complex modulus data of boron oxide using eq 7, namely 65 kJ/mol and 710 K. Note that above 800 °C the mechanical properties of boron oxide melts are controlled by a new mechanism, which cause all elastic constants to increase monotonically, up to at least 1600 °C.[15] The data shown in Figure 4 have been corrected for this effect, by assuming an overall linear contribution, for which the slope was determined at the highest temperatures. At T_g, the longitudinal storage modulus exhibits a cusp, which is more or less pronounced depending on the cooling rate with which the glass has been produced. The irregularities near T_g in the data shown in Figure 4 can therefore be understood as resulting from the difference in thermal histories of the glasses used in the ultrasonic and Brillouin measurements. Furthermore, only above about 650 K has the mechanical response curve at 1 MHz (see inset in Figure 4) dropped to low enough values for the determination of M_2 to be sufficiently accurate. Nevertheless, the temperature dependence of the relaxational modulus is quite well described by the functional form of $(1 - \phi(T))$, given by eq 6, especially the characteristic asymmetry in the changeover. On the basis of the above arguments, the changeover in the relaxational modulus can be attributed to the generation of the high-temperature structural state, and we would like to submit this comparison as further support for the existence of distinct structural states between the glass and melt of a substance.

3.3. Inherent Structures of Simulated Simple Glass-Forming Liquids. Stillinger et al. introduced the concept of inherent structures of liquids as the configurations corresponding to the nearest minimum in the potential energy landscape, associated with a given high-temperature system.[22] The inherent structure of a liquid can be considered as its ground state, from which it is being displaced at finite temperatures due to thermal motion. Because they are devoid of thermal disorder, inherent structures are likely to reveal a "cleaner" representation of atomic configurations in amorphous systems. It is therefore perhaps more fruitful to examine these inherent structures for characteristic patterns in a given amorphous configuration, if such patterns should exist.

In a recent study, Sastry et al. have examined the inherent structures of a binary Lennard-Jones fluid as a function of temperature, by computer simulation.[6] In their study, configurations were equilibrated at various temperatures, and then "quenched" to the closest potential energy minimum using the conjugate gradient method. The potential energies corresponding to the quenched states, for one system size, are reproduced in Figure 5. Accordingly, these authors found that at high temperatures quench energies are relatively independent of the temperature, but when approaching the mode-coupling critical temperature (which for this system is 0.435 in reduced units), the energies exhibit a precipitous decline toward a low-temperature plateau.

The changeover between the two limiting levels of quench energies exhibits the same characteristic asymmetry as the elastic modulus data examined in the previous section. Not surprisingly, the expression for $(1 - \phi(T))$ provides an excellent fit to these data. Note that the way such a fit should be done properly is not immediately obvious. In Figure 5, data for three different
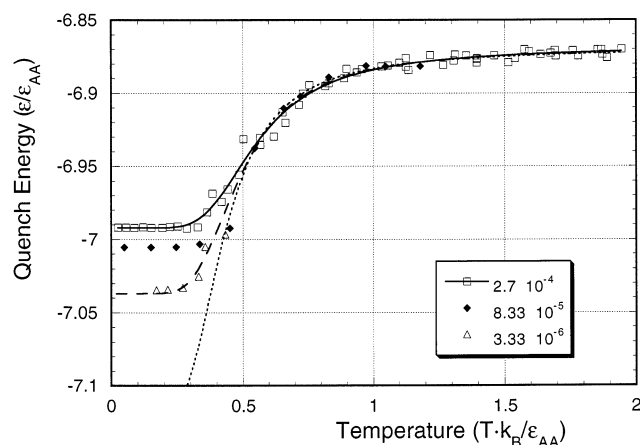
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Figure 5. Inherent structure energies of a binary Lennard-Jones mixture, as a function of the temperature. The reader is referred to ref 6 for a complete description of the system and simulation details. Data for different cooling rates (in units of $(\epsilon_{AA} m_A \sigma_{AA}^2)^{1/2} k_B^{-1}$) are shown, indicating that the magnitude of the low-temperature plateau is uncertain. Best fits of these data sets by $(1 - \phi(T))$ are shown as solid or dashed lines. The dotted line fits the high-temperature data that overlap for all cooling rates and a fictitious low-temperature plateau at -7.15. The dotted line serves to illustrate that, regardless of the quench energy values at low temperatures, all fits overlap at high temperatures.

cooling rates (referring to the equilibration schedules for the configurations at finite temperatures) are shown. The lower the cooling rate, the deeper the quench energies for the most supercooled configurations. Considering that even the slowest cooling rate in these simulations is still extremely fast in comparison to experimentally achievable rates, it is likely that the inherent structures below $T \sim 0.4$ K do not correspond to equilibrated configurations. This implies that neither the magnitude of the quench energies below this temperature, nor the exact form of their temperature dependence are known with certainty. Fitting a functional form to these data might be risky. However, as demonstrated in Figure 5, the fit of $(1 - \phi(T))$ to the data is surprisingly good, regardless of what the actual level of the low-temperature quench energies might be. Several data sets were fit. In all cases the curves overlap at high temperatures. The shape described by $(1 - \phi(T))$ seems to evolve rather independently on either side of the inflection point.

Consequently, a two-state model appears to provide an adequate description for the temperature dependence of the inherent structure energies. This observation is evidently far from proving that structural transitions are underlying to glass formation, but at least it reintroduces the concept of structurally and energetically distinct states as a plausible paradigm into the current thinking about the glass transition. While at the time of this writing inherent structure configurations were not available to us for examination, we have been assured by the authors of ref 6 that no obvious differences in the structural patterns could be discerned between the high- and low-temperature inherent structures.[23] For the Lennard-Jones system studied in ref 6, generally a split in the second peak of the pair correlation function upon cooling is reported, and on the basis of the changes in the void size distributions it has recently been concluded that the low-temperature configurations tend to assume FCC-like short-range order.[24] However, a satisfactory description of the differences between melt and glass structures requires more advanced analyses than the conventional spatial correlation functions. If, indeed, the inherent structures provide a more unencumbered glimpse onto the underlying geometries in amorphous structures, the success with which a two-state model describes the temperature dependence of the quench

energies should provide incentive for developing the necessary diagnostic tools to identify such structural characteristics.

4. Conclusions

In the foregoing sections we have presented experimental observations and results from computer simulations pertaining to the changes in materials characteristics upon going through the glass transition range. What these data have in common is that they all conform to a two-state model. When analyzing the temperature dependence of the complex mechanical modulus, as determined by Brillouin light scattering, for a number of glass-forming systems, we found it indispensable to assume that structures undergo a gradual transition between structural states, with vastly different mechanical properties. Using a two-state model, not only could we fit the data, but we were able to provide a description that is consistent across all systems we investigated. For highly networked glass formers, such as boron oxide, we estimated the magnitude of the relaxational modulus, by comparing elastic constants measured at vastly different frequencies. Because the relaxational modulus is a direct measure of the fraction of material existing in viscoelastic domains, we could directly validate our assumption of a two-state scenario.

Naturally, these isolated observations by themselves would not make a compelling case for pursuing this concept in the context of the glass transition, if it were not for the many past occurrences where researchers have been able to rationalize their observations on the basis of two-state scenarios. To name a few, as early as 1966, Macedo et al. have proposed a two-state model in order to describe the density dependence in boron oxide glass and melts.[16] Angell et al. put forth their bond lattice model for the glass transition in 1972.[18] In this model, the relative amounts of broken and intact bonds is described by a partition function similar to that of eq 5. More recently, Fischer et al., used a two-fluid model for interpreting the anomalous quasi-elastic light scattering results in a one-component fluid.[20] While the aforementioned researchers have based their analysis on the same statistical approach as we did, more complex formalisms have been developed, still pertaining to the general idea of two distinct structural states. The free volume model by Cohen and Grest, which also distinguishes between rigid and fluid domains, is an example.[25]

While it is worth noting how well a two-state model describes the thermo-mechanical behavior of glass-forming oxide melts, the true incentive for raising the awareness in the community for the usefulness of this concept results from two current developments in the field of glasses. One is the growing amount of evidence for the concept of polyamorphism, i.e., the existence of more than one noncrystalline structure for the same substance.[26,27] Polyamorphism directly implies two thermodynamically distinct states. As of now, polyamorphism has been inferred from observations that physical properties of a given material can be vastly different, depending on the conditions of preparation, while in an amorphous state in either case. The other development is the insight recently gained from computer simulations, following the development of new analysis procedures more sensitive to the pertinent features in structure and dynamics of glass-forming systems. Strong support for a spatially heterogeneous character in such systems can be derived from the variations in the local dynamic behavior in glass-forming liquids.[28]

One such analysis, i.e., the inherent structure studies by Sastry et al., has prompted the writing of this paper. The quality with which the inherent structure energies can be fitted with a two-

state model is remarkable, and it strongly encourages consideration of the following concepts: (i) inherent structures represent more faithfully the essence of the amorphous state, and (ii) thermodynamically driven structural transitions underlie the glass transition phenomenon.

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