

## The laboratory glass transition

Prabhat K. Gupta

*Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio 43210*

John C. Mauro

*Science and Technology Division, Corning Incorporated, SP-TD-01-1, Corning, New York 14831*

(Received 2 March 2007; accepted 17 April 2007; published online 11 June 2007)

The phenomenology of the laboratory glass transition is examined in the enthalpy landscape framework. It is shown that a generic description of the glassy state based on partitioning of the phase space caused by the finiteness of the time of observation explains all universal features of glass transition. Using this description of glass, which is referred to as the extrinsically constrained liquid, expressions are derived for properties of glass and for property changes at the laboratory glass transition. A model enthalpy landscape is used to illustrate the basic concepts of this description. Additional new consequences of this description, such as the role of complexity in glass transition and the zero residual entropy of a glass, are discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2738471]

### I. INTRODUCTION

Interest in the physics of supercooled liquids, glass transition, and the glassy state has seen explosive growth during the last decade. New conceptual tools have been introduced (such as the energy landscape<sup>1</sup>), new theoretical directions have been pioneered (for example, the random first order transition<sup>2</sup> and the random energy models<sup>3</sup>), new insights have been gained from simulations (particularly in simple systems such as the binary Lennard-Jones systems<sup>4</sup>), and new results have been established experimentally (for example, the spatially heterogeneous dynamics<sup>5</sup>). Excellent reviews<sup>6,7</sup> are available that summarize much of this work. Notwithstanding these significant advances, a generic, comprehensive, and theoretically sound framework for rationalizing the relaxation behavior of supercooled liquids and structural glasses is still lacking.<sup>8</sup> While there are many facets to this complex topic, the transition of a liquid as a result of a finite observation time to a solid glass—called the laboratory glass transition (LGT)—is of special importance as it provides the basis for many important technological applications. These applications include (to list just a few) tempering, annealing, optical homogeneity, and viscous forming of structural glasses.<sup>9</sup> The LGT is the primary focus of this paper. The so-called ideal glass transition that is hypothesized to occur in supercooled liquids at a low temperature (known as the Kauzmann temperature) is not a concern of this paper.

A key concept in the physics of LGT is that of the observation (or experimental or extrinsic) time ( $t_{\text{obs}}$ ). At some temperature ( $T$ ) and pressure ( $P$ ), a liquid behaves like a solid (i.e., exhibits a finite shear modulus) when  $t_{\text{obs}}$  is much less than the intrinsic average structural relaxation time  $\tau(T, P)$  of the liquid. This solidlike state is called glass.<sup>10</sup> As  $t_{\text{obs}}$  approaches  $\tau$ , a glass begins to relax spontaneously towards its liquid state. When  $t_{\text{obs}} \gg \tau$ , the system exhibits liquid state properties. Denoting an observable by  $Q$ , it follows that

$$Q(t_{\text{obs}} \ll \tau, T, P) \equiv Q_G(T, P, t_{\text{obs}}) \quad \text{and}$$

$$Q(t_{\text{obs}} \gg \tau, T, P) \equiv Q_L(T, P). \quad (1)$$

It should be noted that while glass properties  $Q_G$  depend on  $t_{\text{obs}}$ , the liquid state properties  $Q_L$  do not. The difference  $\Delta Q$  defined as

$$\Delta Q(T, P, t_{\text{obs}}) \equiv Q_L(T, P) - Q_G(T, P, t_{\text{obs}}) \quad (2)$$

is called a configurational property and represents the change in  $Q$  upon relaxation of a glass to the liquid state. Relaxation in liquids and glasses, at some fixed pressure, can be investigated either by varying  $t_{\text{obs}}$  at fixed  $T$  (using, for example, either aging experiments or ultra-hypersonic techniques<sup>11</sup>) or by varying  $T$  at fixed a fixed value of  $t_{\text{obs}}$  (such as by cooling a liquid at constant rate that is inversely proportional to  $t_{\text{obs}}$ ). The two methods study the same phenomenon. For the present work, we focus on LGT during the cooling of a liquid.

At high temperatures,  $\tau$  is small compared to  $t_{\text{obs}}$ . As a result, the system behaves like a liquid. At low temperatures (where  $t_{\text{obs}} \ll \tau$ ), the system behaves like a glass. The laboratory glass transition is characterized by a temperature  $T_g$ , where  $\tau$  is equal to  $t_{\text{obs}}$

$$\tau(T_g(P)) = t_{\text{obs}}. \quad (3)$$

$T_g$  is called the (laboratory) glass transition temperature. Equation (3) can, in principle, be solved for  $T_g(t_{\text{obs}})$  from the knowledge of  $\tau(T, P)$ :

$$T_g(t_{\text{obs}}, P) = T_g(t_{\text{obs}}, \tau(T_g, P)). \quad (4)$$

Thus, measurements at high temperatures ( $T > T_g$ ) provide properties of the liquid state,

$$Q(T > T_g(t_{\text{obs}}, P)) = Q_L(T, P), \quad (5a)$$

and low temperature measurements provide glassy state properties,

$$Q(T < T_g(t_{\text{obs}}, P)) = Q_G(T, P, t_{\text{obs}}). \quad (5b)$$

A large amount of relaxational data<sup>12,13</sup> around  $T_g$  has been collected for the past several decades in a diverse variety of systems (ionic, covalent, metallic, and hydrogen bonded) in both liquid and glassy states (particularly at  $P=1$  atm). Collectively, these studies show a strong universality in the observed features of LGT. These universal (or generic) features are the following.<sup>14,15</sup>

- (1) LGT is not a sharp transition. Properties change smoothly across  $T_g$ .
- (2)  $T_g(t_{\text{obs}})$  increases with decrease in  $t_{\text{obs}}$ .<sup>16</sup> This behavior is in contrast to that of a first order thermodynamic transition (such as crystallization) that is kinetically suppressed to lower temperatures as cooling rate is increased (or  $t_{\text{obs}}$  is decreased). This anomalous  $t_{\text{obs}}$  dependence of LGT is an indication that LGT is not a thermodynamic transition but a consequence of arrested relaxation dynamics.
- (3) There is no change in the enthalpy of the system (i.e., no latent heat in LGT),  $\Delta H=0$ .<sup>17</sup> Also, there is no change in the volume,  $\Delta V=0$ .<sup>18</sup>
- (4) There are rounded discontinuities in (second order) properties such as isobaric heat capacity ( $C$ ), isothermal compressibility ( $K$ ), and thermal expansion coefficient ( $\alpha$ ). These changes are similar to that for an Ehrenfest second order transition ( $\Delta C > 0$  and  $\Delta K > 0$ ). However, LGT is not a second order transition because the so-called Prigogine-Defay ratio  $[\Delta C \Delta K / T_g V (\Delta \alpha)^2]$  is observed to be greater than unity.<sup>19</sup> This ratio is unity for an Ehrenfest second order transition.
- (5) A glass relaxes spontaneously to the liquid state. This process—referred to as structural relaxation (SR)—typically exhibits two stages: a fast process (called secondary or  $\beta$  relaxation) and a slow process (called primary or  $\alpha$  relaxation). Both stages exhibit near-stretched exponential dynamics.<sup>20</sup>
- (6) A glass is homogeneous at the mesoscopic level due to frozen-in spatial variations in structure. These structural variations result in density and entropy variations that can be measured by either Rayleigh light scattering<sup>21,22</sup> or small angle X-ray scattering<sup>23</sup> techniques. It has been suggested<sup>24</sup> that these frozen-in variations are the source of spatially heterogeneous dynamics in glasses.

The universality of these experimental features suggests that the underlying physics of LGT is insensitive to the details of the interatomic potentials. It should, therefore, be feasible—and certainly desirable—to develop a generic statistical mechanical framework for LGT. Such a framework will provide a common basis for rationalizing data in different systems and “macroscopic boundary conditions” for developing microscopic models of LGT. This paper discusses such a generic framework for the glassy state (and for LGT) which we refer to as the “extrinsically constrained liquid” (ECL) description.

The notion of constraining (confining or arresting or freezing) some aspect of the liquid state during LGT is not new. The conventional phenomenological thermodynamic

formalism postulates the existence of a set of internal (or order) parameters.<sup>15,16,25</sup> The internal parameters assume their equilibrium values in the liquid state and are frozen in the glassy state. This approach predicts correctly the signs of changes in the second order properties at  $T_g$ , a Prigogine-Defay ratio greater than unity, and first order properties that do not change at the glass transition. By adding a phenomenological rate equation for the internal parameters, this approach is also capable for analyzing the relaxation kinetics. The well-known Tool-Narayanaswamy model is a testimonial to this.<sup>25</sup> However, the internal parameter approach does not answer questions such as how many internal parameters are needed and does not provide any clue about the physical meanings of internal parameters. Most importantly, it does not provide any insight into the  $T$  dependence of the relaxation time.

Jäckle<sup>26,27</sup> was the first to propose a generic statistical mechanics of LGT. He examined two different statistical mechanical formulations of the glassy state. The one called the quenched liquid (QL) view is widely accepted at present.<sup>28,29</sup> In the QL view, a glass is considered as an ensemble of configurations with a probability density in the phase space which is frozen at the value equal to that in the liquid state at  $T_g$ . The QL view has the following implications about LGT.

- (a) The glass and the liquid are one and the same macrostate at  $T_g$ .
- (b) There is no entropy change at LGT. As a consequence, the glass has higher configurational entropy than the liquid at temperatures below  $T_g$  and a positive residual entropy at  $T=0$ .

The first consequence is inconsistent with observed feature #4. The second cannot be tested experimentally and, as we show later, remains controversial. The statistical mechanical framework for broken-ergodic systems was developed by Palmer.<sup>30</sup> Broken ergodicity corresponds to confinement of the system configuration point in one of the many sub-regions (components) of the phase space because of a finite observation time. His treatment showed that all glasses (structural and spin) can be treated as broken-ergodic systems. Palmer’s formalism, however, requires a choice for the probabilities of the “component ensemble.” Palmer examined in detail the “unbiased component ensemble” which ignores all history dependence. Palmer’s formalism, with Jäckle’s history dependent component probability distribution,<sup>26</sup> forms the basis of our analysis.

Jäckle also proposed a second formulation, termed the disordered solid (DS) view. According to Jäckle,<sup>26</sup> in the DS view “the glass free energy is determined by the vibrational degrees of freedom alone, and is similar to the free energy of the corresponding crystal.” The DS view is associated with an entropy loss  $[\Delta S(T_g) > 0]$  in LGT. This raises questions since there is no latent heat in LGT.

The energy landscape approach is known to provide relatively transparent and generic view of various thermodynamic changes and kinetic processes taking place in a liquid near  $T_g$ .<sup>1,31</sup> The energy landscape framework has renewed interest in Palmer’s broken-ergodicity formalism. It has been discovered that dynamics in a landscape involves regions of

phase space—called metabasins—where a system resides for extended periods of time. These metabasins resemble the “components” proposed by Palmer. The main objective of our paper is to examine a synthesis of the following four well-established concepts assuming that the landscape is known: (1)  $t_{\text{obs}}$  as a key extrinsic time scale of LGT, (2) existence of  $t_{\text{obs}}$ -dependent metabasins in the landscape, (3) application of broken-ergodicity concepts to systems confined to metabasins, and (4) a history dependent (QL) probability distribution for metabasins.

A somewhat similar approach has been reported by Wales and Doye.<sup>32</sup> However, their focus is on detailed analysis of a particularly simple landscape model to examine fragility values as a function of system parameters. Unlike their work, our goal is to develop a generic framework for examining LGT and to point out certain related issues which previously have not received much attention. We do not analyze a landscape model to learn about LGT. We use an analytically soluble model to demonstrate the consistency of concepts involved in ECL.

The outline of this paper is as follows. Section II presents the ECL description. Section III illustrates the ECL description using a model landscape. Section IV compares the ECL description with existing models of LGT. New consequences of ECL are reported in Sec. V. The last section concludes this work.

## II. GLASS AS A EXTRINSICALLY CONSTRAINED LIQUID

Since the enthalpy landscape plays a key role in our discussion, we review the relevant features of such a landscape in Sec. II A. We then introduce the relevant concepts of activated dynamics in Sec. II B discuss the phase space partitioning in Sec. II C, and present the ECL description of glass in Sec. II D. Expressions for the property changes at LGT are derived thereafter.

### A. Enthalpy landscape

As described by Debenedetti and Stillinger,<sup>31</sup> an enthalpy landscape (HL) is an enthalpy hypersurface as a function of the system’s microstate described by  $3N-6$  positional coordinates of atoms and a coordinate for the system volume. Here,  $N$  is the total number of particles in the system. Because crystallization plays no role in LGT,<sup>33</sup> we consider only the HL of a supercooled liquid (SCL). This is obtained from the HL of an equilibrium liquid after removing all microstates containing crystals of size greater than (or equal to) the critical crystal nucleus size. Geometric features of an HL of interest to LGT are as follows.

#### 1. Inherent structure (IS)

The rugged HL consists of a large number of enthalpy minima. Each minimum represents a mechanically stable state and is known either as a “configurational state” or as an “inherent structure” (IS).<sup>34</sup> The total number ( $\Omega$ ) of ISs is extremely large, on the order of  $(N!) \exp(\text{constant } N)$ . The enthalpy distribution of IS states,  $H_i^{(\text{IS})}$  ( $i=1, \dots, \Omega$ ), determines the thermodynamic properties of the system.

#### 2. Basins (B)

Associated with each IS is a set of mechanically unstable microstates that drain into the IS upon energy minimization. This set is called the basin of the IS. The basin states represent the “vibrational” states at  $T > 0$ . The system is at the IS only at  $T=0$  K. The shape of a basin, especially its principal curvatures at the IS, determines the vibrational frequencies in the basin. For convenience, we assume that all basins have the same shape. As a consequence, the vibrational states of all basins are identical. Further, for simplicity, we assume that basins are isotropic, harmonic, and are characterized by a single vibrational frequency ( $\nu$ ).

#### 3. Activation free energy (F)

Transitions between two ISs may occur along several possible paths (possibly transiting through multiple intermediate ISs). Each of these paths goes through a maximum in the enthalpy at some configuration called the saddle point configuration. The difference between the saddle point enthalpy and the enthalpy of the originating IS is called the barrier enthalpy  $\underline{H}$ . In the hyperdimensional space, there may exist a number, say,  $n_{ij}(H_{ij})$ , of different paths having the same barrier enthalpy. The most probable path (called the activation path) is the one having the lowest activation free energy  $\underline{F}_{ij}$ , from IS( $i$ ) to IS( $j$ ):

$$\underline{F}_{ij} = \underline{H}_{ij} - k_B T \ln(n_{ij}). \quad (6)$$

A point to emphasize is that barrier enthalpies (and hence free energies) of activation paths in the two opposite directions are, in general, not equal:  $\underline{H}_{ij} \neq \underline{H}_{ji}$ . In principle, all activation pathways of a given HL can be identified and the range of barrier free energies  $\underline{F}_{ij}$  (from a minimum  $\underline{F}_K$  to a maximum  $\underline{F}_C$ ) can be determined. The distribution of barrier free energies  $\{\underline{F}_K \leq \underline{F}_{ij} \leq \underline{F}_C\}$  determines the activated dynamics in the HL.

### B. Activated dynamics in an enthalpy landscape

Two qualitatively different dynamical processes can be distinguished in an HL:

- Intrabasin (or vibrational) relaxation (VR) is a very fast nonthermally activated process that occurs within each basin. Physically, VR corresponds to temperature equilibration between the basin and the thermal reservoir. The configuration (IS) of the system does not change during VR. In the following, we assume that VR is fast enough so that, at any instant, the temperatures of all basins are equal and the same as that of the heat reservoir.
- Interbasin transitions (or basin hopping) are slow, thermally activated processes in which the system configuration hops among different basins. These interbasin transitions are the source of structural relaxation and of LGT.

According to the transition state theory,<sup>35</sup> the transition rate  $\gamma_{ij}$  from IS ( $i$ ) to IS( $j$ ) at a temperature  $T$  is expressed as follows:

$$\gamma_{ij} = \nu \exp[-F_{ij}/k_B T]. \quad (7)$$

Here,  $k_B$  is Boltzmann's constant.

The probability  $W_{ij}$  of transition from IS( $i$ ) to IS( $j$ ) in time  $t$  is

$$W_{ij}(T, t) = 1 - [1 - \exp(-F_{ij}/k_B T)]^{\nu t}. \quad (8)$$

The activation pathways from  $i$  to  $j$  are considered impassable (or closed) when

$$W_{ij} \leq \varepsilon, \quad (9)$$

where  $\varepsilon$  is a small positive number. Using Eqs. (8) and (9), a maximum passable free energy barrier  $F^*$  can be defined as follows:

$$F^*(T, t_{\text{obs}}, \varepsilon) \equiv k_B T \ln \frac{1}{[1 - (1 - \varepsilon)^{(1/\nu t_{\text{obs}})]}}. \quad (10)$$

Only pathways with  $F_{ij} < F^*$  are passable (i.e., open) in the observation time. When the maximum barrier energy  $F_C$  is less than  $F^*$ , all barriers are passable and the system is able to sample an adequate number of basins within the time of observation so that the average of a property over  $t_{\text{obs}}$  is effectively equal to the infinite time average (and the phase average for ergodic systems). This state is called ergodic and describes the liquid state.

When  $F_K < F^* < F_C$ , some pathways become impassable. However, the system may still remain ergodic as alternative paths may still be available in the hyperdimensional landscape for the system to sample a representative number of ISs. As  $F^*$  decreases further [as a consequence of cooling, see Eq. (10)], more and more pathways become impassable. At low temperatures, the HL partitions into a set of nonoverlapping components among which no transitions occur during the observation time. A system with a partitioned HL is called broken ergodic within the observation time.

In principle, it is possible to determine whether an HL is partitioned at a given temperature and for a given  $t_{\text{obs}}$ . The HL can be mapped into a graph whose vertices are the ISs. Each pair of vertices, between which transition paths are allowed during  $t_{\text{obs}}$  in both directions, is connected by two directed edges. One edge, from vertex  $i$  to vertex  $j$ , is assigned the value  $F_{ij}$  and the other the value  $F_{ji}$ , representing the (reverse) transition from  $j$  to  $i$ . Pairs of vertices having allowed transitions only in one direction is connected by a single directed edge. Vertices that do not have any allowed transitions in either direction between them do not share an edge. Such a "transition graph" of the HL is connected at high temperatures (i.e., there exists at least one path between any two vertices). At a sufficiently low temperature, the graph breaks up into pieces among which there are no connecting edges. We refer to such a broken-ergodic system, having a partitioned HL because of a finite time of observation, as an "extrinsically constrained" system. Stein and Newman<sup>36</sup> have used the term "structural confinement" for such systems. However, we prefer the term extrinsic constraining as it describes more appropriately the fact that the confinement is strictly a consequence of the finite time of observation. It is also useful to point out that extrinsic constraining is different from "trapping" where a system remains

trapped even when  $t_{\text{obs}}$  becomes large (a phenomenon sometimes referred to as "weakly broken ergodicity"<sup>37</sup>).

### C. The LGT partition and metabasins

The ECL description considers a glass as a broken-ergodic state, the LGT as the process of breaking ergodicity, and the finite  $t_{\text{obs}}$  as the cause of ergodicity breaking. The time of observation is an externally imposed constraint on the observed behavior of the system and plays an important role in defining a laboratory glass. It is clear that the impassability of pathways begins, upon cooling, at a temperature  $T_C$  [corresponding to the highest barrier  $F_C$  and defined in a manner similar to Eq. (10)]. As the temperature decreases, more of the remaining barriers become impassable in the order of decreasing barrier free energies.  $T_g(t_{\text{obs}})$  is the onset temperature below which a given HL becomes partitioned. We refer to this partition of the HL at  $T_g(t_{\text{obs}})$  as the LGT partition. The LGT partition is not an intrinsic property of the landscape as it depends on  $T$  and  $t_{\text{obs}}$ .

Following Stillinger,<sup>38</sup> we refer to the components of the LGT partition as metabasins (MBs), each of which may contain many single basins. There is ample evidence from simulations for the existence of the well-defined MBs.<sup>39,40</sup> The process of partitioning continues as the temperature decreases below  $T_g$  and comes to a stop at some low temperature,  $T_K(t_{\text{obs}})$ , where the smallest barrier free energy ( $F_K$ ) becomes equal to  $F^*$ . The value of  $T_K(t_{\text{obs}})$  is greater than that of the well-known Kauzmann temperature  $T_K$ , which is defined only in the limit of large  $t_{\text{obs}}$ .<sup>3,6,7,31</sup>

The question of interest is that, given an HL and  $t_{\text{obs}}$ , how one can determine the LGT partition (and the value of  $T_g$ ). In principle, the LGT partition can be identified as follows. For given values of  $T$  and  $t_{\text{obs}}$ ,  $F^*$  can be calculated [using Eq. (10)] and all IS pairs can be classified as having transitions or not. Then, using the transition graph, one can determine if the HL is connected. At high  $T$ , the HL is fully connected (i.e., there is no partitioning and the number of components is simply 1). At low  $T$ , the HL is partitioned. Thus, if one studies the number of components of the HL as a function of  $T$  (keeping  $t_{\text{obs}}$  fixed),  $T_g$  can be determined.

In MD simulations, one can determine whether an HL is partitioned at a given temperature by starting the system configuration point in a randomly selected IS, propagating the system for a time equal to  $t_{\text{obs}}$ , and keeping track of all the different basins that the system visits in this process. By repeating such experiment several times from the same starting basin (but with different randomly selected initial velocity directions), one can identify the MB containing that particular starting IS. Then, by repeating the process from different ISs, one can determine the remaining MBs. Finally, this procedure can be repeated at different temperatures. One can determine  $T_g$  as the temperature where the partitioning begins upon cooling.

### D. The extrinsically constrained liquid description of the glassy state

The ECL description consists of two postulates about the metabasins (MBs):

- (i) For  $T < T_g(t_{\text{obs}})$ , the HL partitions into a set of MBs among which there are no transitions. The system is confined in a MB with a probability equal to the fraction of the relaxation time spent in that particular MB by the liquid at  $T_g(t_{\text{obs}})$ .
- (ii) At  $T_g(t_{\text{obs}})$ , each MB is ergodic.

While the first postulate provides a method of calculating the probability of confinement in a particular MB, the second postulate permits the calculation of the thermodynamic properties of MBs. The two together are needed to calculate the properties of a glass. The underlying assumption behind the ECL postulates is

$$\tau_{\text{MB}}(T_g) < t_{\text{obs}} < \tau_{\text{HL}}(T_g). \quad (11)$$

In the following, we assume that the LGT has been identified and has a total of  $M$  metabasins. Using the first ECL postulate, the probability  $P_K^{(\text{MB})}$  for the system configuration point to be confined in the  $K$ th MB ( $K=1, \dots, M$ ) is given by

$$P_K^{(\text{MB})}(T_g(t_{\text{obs}})) = \sum_{i \in K(t_{\text{obs}})} P_{i,L}^{(B)}(T_g(t_{\text{obs}})). \quad (12)$$

Here,  $p_{i,L}^{(B)}(T_g)$  is the probability that, in the liquid state at  $T_g$ , the system configuration point is in the  $i$ th basin. The MB probabilities  $P_K$  remain unchanged unless the glass is allowed to relax.

A property  $Q_K$  of the  $K$ th MB at some temperature  $T$  ( $\leq T_g$ ) is the restricted ensemble average of all basins within that MB:

$$Q_K^{(\text{MB})}(T, T_g(t_{\text{obs}})) = \sum_{i \in K} \frac{p_i^{(B)}(T)}{P_K^{(\text{MB})}(T_g(t_{\text{obs}}))} Q_i^{(B)}(T). \quad (13)$$

The property  $Q_G(T, T_g(t_{\text{obs}}))$  of a glass can now be expressed as the weighted average of  $Q_K^{(\text{MB})}$  over all MBs:

$$Q_G(T, T_g(t_{\text{obs}})) = \sum_K P_K^{(\text{MB})}(T_g(t_{\text{obs}})) Q_K^{(\text{MB})}(T, T_g(t_{\text{obs}})). \quad (14)$$

### E. Some terminology: Vibrational, relaxational, and configurational properties

A property  $Q$  of a system is given by the weighted average of its values,  $Q_i^{(B)}$ , in all basins:

$$Q(T) = \sum_{i=1}^{\Omega} p_i(T) \{Q_i^{(B)}(T)\}. \quad (15)$$

The change in  $Q$ ,  $\delta Q$ , as a result of a temperature change is given by

$$\delta Q = \sum_{i=1}^{\Omega} \delta p_i \{Q_i^{(B)}(T)\} + \sum_{i=1}^{\Omega} p_i \left\{ \frac{dQ_i^{(B)}}{dT} \right\} \delta T. \quad (16)$$

The last term in Eq. (16) is the basin contribution  $\delta Q_B$ . This term accounts for the changes in the vibrational states of basins with temperature. The first term on the right hand side is due to changes in  $p_i$  due to inter-MB transitions. We refer to this term as the relaxational contribution  $\delta Q_R$ .<sup>10</sup> When

relaxation is sufficiently fast so that the system maintains equilibrium at all times, the relaxational part is called configurational property  $\Delta Q$  of the liquid:

$$\Delta Q = \sum_{i=1}^{\Omega} \frac{dp_{i,L}}{dT} Q_i^{(B)}(T). \quad (17)$$

### F. Property changes in observables at LGT

From Eq. (15), an observable property  $Q_L(T)$  of the liquid is given by

$$Q_L(T) = \sum_i P_{i,L}^{(B)}(T) Q_i^{(B)}(T). \quad (18)$$

From Eqs. (14) and (18), it follows that

$$\begin{aligned} Q_G(T_g, T_g(t_{\text{obs}})) &= \sum_K P_K^{(\text{MB})}(T_g) \sum_{i \in K} [p_i^{(B)}(T_g) / P_K^{(\text{MB})}(T_g)] Q_i^{(B)}(T_g) \\ &= Q_L(T_g). \end{aligned} \quad (19)$$

In other words, there is no change in any observable first order property at  $T_g$ . In particular, there is *no change in enthalpy*, implying no latent heat in LGT.

The relaxational contributions to properties show significant changes at LGT. For example, Palmer<sup>30</sup> and Jäckle<sup>26,27</sup> have shown that there is always a drop in the heat capacity in going from the liquid to the glassy state. The configurational entropy of a liquid is

$$\delta S_{R,L}(T_g) = -k_B \sum_i P_{i,L}^{(B)}(T_g) \ln \{p_{i,L}^{(B)}(T_g)\}. \quad (20)$$

Using Eq. (18), the relaxational entropy of a glass,  $\delta S_{R,G}(T_g)$ , is given by

$$\delta S_{R,G}(T_g) = \sum_{K=1}^M P_K^{(\text{MB})}(T_g) \delta S_{R,K}^{(\text{MB})}(T_g). \quad (21)$$

Here,  $\delta S_{R,K}^{(\text{MB})}(T_g)$  is the relaxational entropy of the  $K$ th MB. The entropy loss at LGT is the difference  $\delta S_{R,L}(T_g) - \delta S_{R,G}(T_g)$  and is given by [using Eqs. (20) and (21)]

$$\Delta S(T_g(t_{\text{obs}})) = -k_B \sum_K P_K^{(\text{MB})}(T_g(t_{\text{obs}})) \ln P_{K,L}^{(\text{MB})}(T_g(t_{\text{obs}})). \quad (22)$$

There is a growing trend to refer to  $\Delta S$  as the “complexity.”<sup>41</sup>  $\Delta S$  is also equal to the “relative entropy” of the glass.<sup>42</sup> If all MBs had equal probability, the complexity will take its maximum value  $k_B \ln(M)$ , much like Boltzmann’s expression for the entropy ( $k_B \ln \Omega$ ). Using Eqs. (19) and (22), the free energy change  $\Delta F$  at LGT is given by

$$\Delta F(T_g(t_{\text{obs}})) = -T_g \Delta S(T_g(t_{\text{obs}})). \quad (23)$$

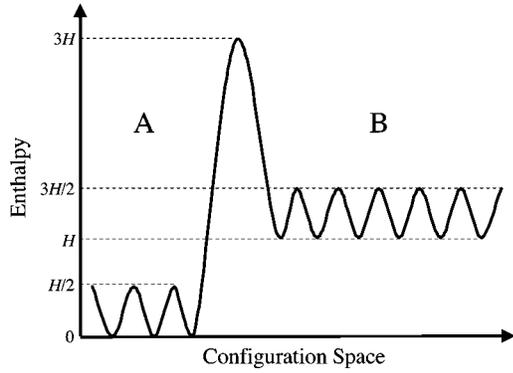


FIG. 1. Model HL containing two metabasins. Metabasin A has three and B has six ISs. All ISs have the same vibrational frequency ( $\approx 0.5$  GHz).

### III. ECL IN A MODEL LANDSCAPE

#### A. A model HL

We illustrate the concepts of the ECL description of the glassy state by simulating dynamics *during cooling at constant rate* for a simple model landscape. The model HL is designed to be extremely simple so that the equilibrium and the constrained equilibrium properties can be solved analytically. The model HL (see Fig. 1) has two well-defined MBs: the ground state MB (labeled A) and the excited state MB (labeled B). All ISs within each MB are degenerate. The IS energy in B is greater than the IS energy of A (which is taken as the ground level) by an amount equal to  $H$ . There are a total of  $n_A$  ISs in A and  $n_B$  in B. There are two sets of barriers in this model HL. All intra-MB barriers (referred to as  $\beta$  barriers) have equal enthalpy ( $=H/2$ ). The inter-MB barrier (i.e., the  $\alpha$  barrier) has a height of  $3H$  (from the A side).

#### B. Entropies of the liquid and the glassy states

Since, in this model HL, all ISs within a MB have equal probability, the liquid configurational entropy is expressed as

$$\delta S_{R,L}(T) = k_B \left[ P_{A,L}(T) \ln \left( \frac{n_A}{P_{A,L}(T)} \right) + P_{B,L}(T) \ln \left( \frac{n_B}{P_{B,L}(T)} \right) \right]. \quad (24)$$

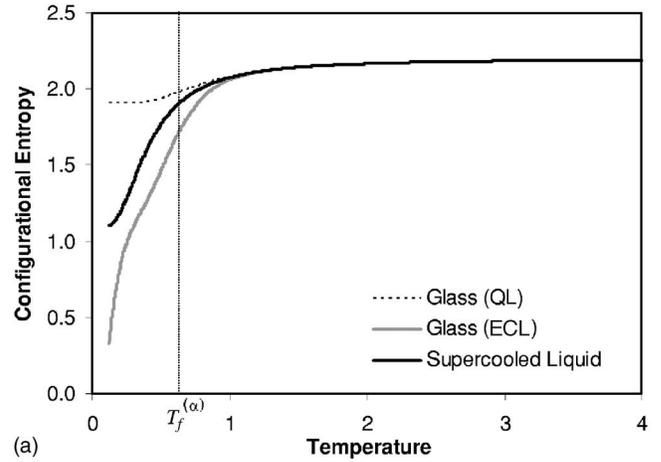
Depending on the value of  $t_{\text{obs}}$ , two types of glasses may form in this HL. For a sufficiently small  $t_{\text{obs}}$  (or high cooling rate), the system is trapped within a single basin and the entropy of the resulting glass is zero. We refer to it as the “zero entropy glass.” When the cooling rate is slow, the system is first trapped in one of the MBs forming an  $\alpha$  glass (i.e., a normal glass). The relaxational entropy of such a glass (when ISs within each MB are degenerate) is, using Eq. (20),

$$\delta S_{R,G}(T_g) = k_B [P_{A,L}^{(\text{MB})}(T_g) \ln n_A + P_{B,L}^{(\text{MB})}(T_g) \ln n_B]. \quad (25)$$

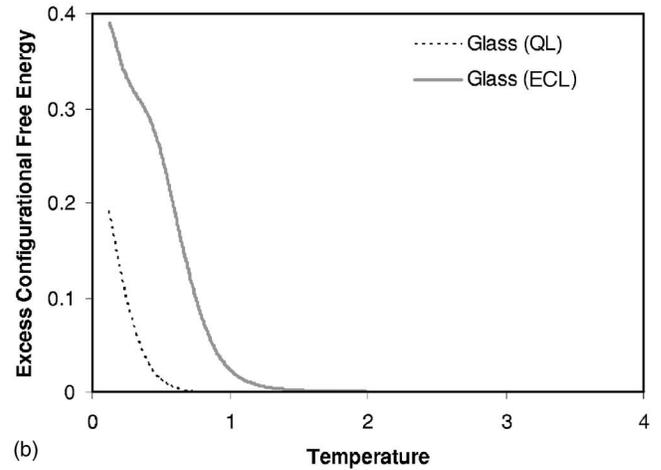
Using Eq. (22), the entropy loss (i.e., the complexity) in LGT is given by

$$\Delta S(T_g) = -k_B (P_A \ln P_A + P_B \ln P_B). \quad (26)$$

For the model HL,  $\Delta S$  can be calculated analytically and its



(a)



(b)

FIG. 2. (a): Relaxational entropy (in units of  $k_B$ ) for a liquid cooled at a constant nondimensional rate of  $10^3$  (in the model HL of Fig. 1) from a nondimensional temperature of 4. The dark curve in the middle (labeled SCL) gives the equilibrium entropy of the supercooled liquid. The lower curve corresponds to the ECL description. The upper curve (QL) corresponds to the commonly accepted view of glass (see Sec. IV). Temperature is in the units of  $H/k_B$  ( $3H$  is the maximum barrier height in Fig. 1). The value of  $T_f^{(\alpha)}$  gives the temperature where the entropy of the supercooled liquid equals that which is “frozen” in the glass under the traditional (QL) view of the glass transition. (b) Variation of the excess relaxational free energy (over that of the liquid free energy) during cooling at a constant rate [same experiment as in (a)].

variation with  $T_g$  goes through a maximum  $k_B \ln(2)$  before saturating to the high temperature limit of  $0.637k_B$ .

#### C. Evolution of properties during linear cooling

The evolution of IS probabilities was studied for the model system by solving a system of master equations.<sup>43</sup> Results for a constant cooling rate are shown in Fig. 2(a). It shows that the loss of entropy occurs continuously over a range of temperatures. Inter-MB transitions, going over the largest barrier, are the first to freeze and the intra-MB transitions going over the lowest barriers are the last to freeze. The vertical line in Fig. 2(a) shows the glass transition temperature calculated according to the Moynihan method,<sup>25</sup> which assumes that there is no loss of entropy at  $T_g$  [depicted by the dotted curve labeled QL in Fig. 2(a)].

Figure 2(b) shows the change in the relaxational free energy corresponding to Fig. 2(a),

$$\delta F_R(T) = \delta H_R(T) - T\delta S_R(T). \quad (27)$$

This figure shows that the relaxational free energy of a glass is always greater than that of the liquid. This is expected since liquid state is the minimum free energy state.<sup>19</sup>

#### D. Isothermal structural relaxation of a glass

During SR of a glass, the constraint of  $t_{\text{obs}}$  is relaxed and the laboratory time becomes equal to  $t_{\text{obs}}$ . As a consequence of removing the  $t_{\text{obs}}$  constraint, the inter-MB transitions become active. SR begins rapidly over  $\beta$  barriers within MBs. During this  $\beta$  relaxation, the probability of being confined in a MB and the complexity value do not change with time. Nonetheless, the entropy of the system increases as the probability distribution within each MB “spreads out.”

In the  $\alpha$  relaxation, entropy changes with time primarily because of inter-MB transitions. The complexity increases from a value of zero in the glassy state to its equilibrium value at  $T$ . Since intra-MB relaxation is always present even during inter-MB relaxation, there is a contribution from the intra-MB term as well during the  $\alpha$  relaxation. Figure 3(a) shows entropy change during isothermal relaxation of an  $\alpha$  and of a zero entropy glass.

Notice that, during relaxation in this model HL, the system exchanges enthalpy with the reservoir. Figure 3(a) shows that entropies of both glasses exhibit a maximum during relaxation. Even though the entropy shows a maximum, the free energy decreases in both cases as shown in Fig. 3(b). This is expected since relaxation is a spontaneous irreversible isothermal process and, by the second law, the free energy must decrease monotonically.

#### IV. COMPARISON OF ECL DESCRIPTION WITH OTHER MODELS OF GLASSY STATE

As mentioned earlier, Jäckle<sup>26</sup> argued in favor of the QL view of glass. Figure 2(a) shows the configurational entropy variation according to the QL view for the liquid cooled at a constant rate in the model HL. Note that the entropy of the QL glass remains above that of the liquid at low temperatures leading to a finite residual entropy. Since in this view the liquid and the glass are considered identical macrostates at  $T_g$ , a glass should not exhibit any relaxation at  $T_g$ .

The ECL description is more general than Jäckle’s second formulation—the disordered solid (DS) view.<sup>26</sup> A glass is confined in a single MB containing many basins. This permits a glass to have some configurational degrees of freedom and allows a possibility for secondary (intra-MB) relaxations at lower temperatures.

#### V. DISCUSSION OF THE ECL DESCRIPTION OF THE GLASSY STATE

##### A. ECL and the observed features LGT

It is useful to recap how the observed features of LGT (listed in Sec. I) are satisfied by the ECL description of glass.

(i) *LGT is not a sharp transition.* As mentioned earlier, the pathways start to become impassable at a temperature  $T_C$  that is higher than  $T_g$ . Gradually, more and more pathways

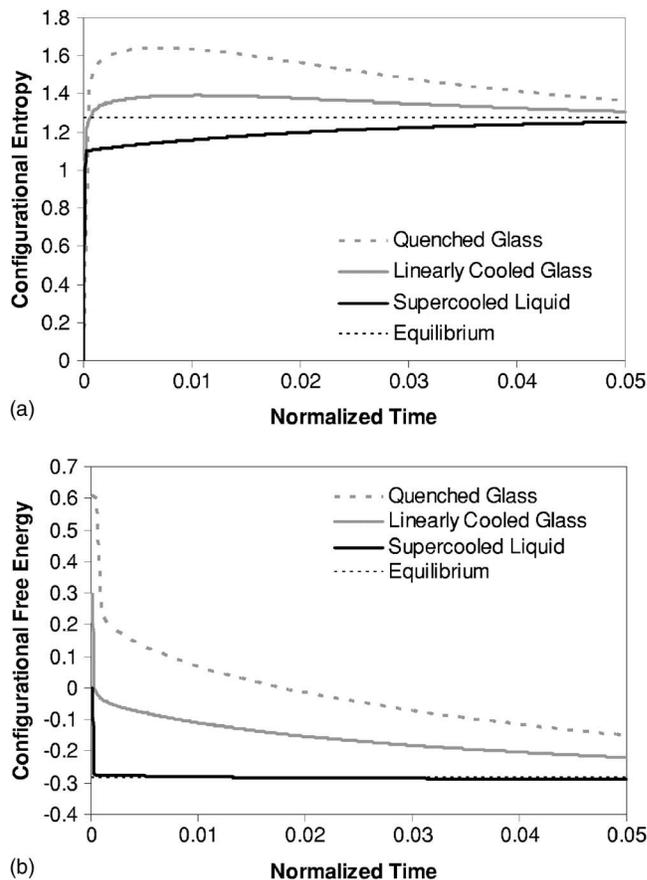


FIG. 3. (a): Entropy evolution during isothermal structural relaxation at a temperature of  $\frac{1}{4}$ . The dashed curve represents a zero entropy glass (quenched and confined to a single IS by quenching from  $T=4$  to  $T=\frac{1}{4}$ ), the thin continuous curve represents an  $\alpha$  glass formed by cooling at a constant rate from  $T=4$  to  $T=\frac{1}{8}$  and then immediately up quenching to  $T=\frac{1}{4}$ , and dark continuous curve the thermal equilibration of an up-quenched liquid from  $T=\frac{1}{8}$  to  $T=\frac{1}{4}$ . Also shown is the equilibrium value of the configurational entropy of the liquid at  $T=\frac{1}{4}$ . (b) Change in relaxational free energy during isothermal relaxation for cases corresponding to those shown in (a). Note that the free energy decreases in all cases. The units are the same as in Fig. 2.

become impassable upon cooling. Thus, LGT is intrinsically a continuous transition.

(ii)  $T_g$  decreases as  $t_{\text{obs}}$  increases. This follows directly from Eq. (10) since increase in  $t_{\text{obs}}$  leads to an increase in the value of  $F^*$  and requiring a lower  $T_g$  to make pathways impassable. The  $t_{\text{obs}}$  dependence of  $T_g$  is the key to understanding the history dependence of the properties of glass.

(iii) *No latent heat in LGT.* This follows directly from Eq. (19) because of the fact that volume and energy being basin properties are not changed in LGT.

(iv) *Changes in higher order properties.* Since LGT is a transition from an ergodic to a broken-ergodic state, the second order properties (like the heat capacity, compressibility, and expansion coefficient) show finite changes. This is a signature property of broken ergodicity as has been shown by Palmer.<sup>30</sup> The discontinuities appear rounded for finite cooling rates.

(v) *Glass relaxes spontaneously to the liquid state.* During a relaxation experiment (where a glass is held at a fixed temperature), the laboratory time ( $t$ ) becomes equal to the

$t_{\text{obs}}$ . As  $t$  increases, so does  $t_{\text{obs}}$ . Because of the removal of the  $t_{\text{obs}}$  constraint, the glass relaxes spontaneously.

(vi) *Glass and liquid are not equivalent macrostates at  $T_g$ .* In the ECL description, all pathways are passable in the liquid state and the HL remains connected. This is not the case in the glassy state (with partitioned HL) even though both are at the same temperature (i.e.,  $T_g$ ). Since they are different, a glass being the nonequilibrium state relaxes to the equilibrium liquid state (even at its own  $T_g$ ).

## B. The crossover effect

The crossover effect refers to observing a nonmonotonic change in a property during isothermal isobaric relaxation of a glass. In the ECL view, the crossover effect has a natural explanation. During relaxation, the entropy of the system changes because of the changes in vibrational contribution (intrabasin relaxation) and because of the complexity term (due to inter-MB transitions). The complexity term always increases [see Eq. (22)] since its starting value in the glassy state is zero. However, the sign of the vibrational contribution depends on whether the system is up quenched or down quenched to the relaxation temperature (prior to the start of the relaxation). The vibrational contribution to entropy decreases after down quenching because of a drop in temperature (but increases after up quenching). Thus, after down quenching, the two contributions vary in opposite directions (increase of complexity and decrease of vibrational entropy). Thus, only after down quenching, the entropy may show a maximum (indicating a crossover effect) during relaxation. Whether the crossover effect is actually observed depends on the magnitude and the kinetics of the two contributions. This is in agreement with the results of a recent MD simulation study of *o*-terphenyl<sup>44</sup> according to which “we find that only for sufficiently deep quenching temperatures and long aging times, it is possible to reproduce in simulations the crossover effects.”

## C. ECL and the second law

According to Eq. (18), there is no change in enthalpy at LGT. However, there is a loss of relaxational entropy in going from liquid to glass as the inter-MB transitions freeze out. A loss of entropy in LGT has also been suggested by Wales and Doye,<sup>32</sup> by Thirumalai *et al.*,<sup>45</sup> by Speedy,<sup>46</sup> by Balmakov,<sup>47</sup> and by Kivelson and Reiss.<sup>48</sup> A loss of entropy accompanied by no change in enthalpy appears to violate the second law of the thermodynamics. How to resolve this contentious issue?

First, we reiterate that even though we are considering a nonisolated system, the system is effectively isolated at  $T_g$  since there is no change in energy or in the volume at LGT. Thus, the conflict is not because the system is not isolated.

Second, this apparent violation of the second law is also not because of some concern with the definition of entropy for the glassy state. The glassy state is a broken-ergodic state and each MB, being ergodic, follows the same definition of entropy as that for an equilibrium state as long as all the appropriate constraints are properly accounted for.<sup>49</sup>

Third, there is no disagreement about the absence of latent heat in LGT. This is an experimentally established fact and is accepted by all previous treatments. Thus, the absence of latent heat in LGT is not an issue.

It seems to us that as long as the glassy state is restricted to a subset of the phase space, there has to be loss of configurational entropy. Theories that conclude no entropy loss at  $T_g$  use a thermodynamic definition of entropy (namely, as the temperature derivative of the free energy). Thus, the issue comes down to the definition of configurational entropy: Is it given by the number of thermodynamically allowed microstates or the number of kinetically accessible microstates visited by the system during the time of observation? There is apparently no clear answer to this question in the literature.<sup>42,43,49</sup> If we assume the latter (as we do in this paper), then the loss of entropy at LGT is real.

However, we suggest that a loss of entropy without latent heat at LGT does not violate the second law. This is because the constraint of  $t_{\text{obs}}$ , responsible for LGT, is an external constraint imposed on the system by the observer. The application of this constraint “drives” the LGT. The LGT is, therefore, not a spontaneous process. The second law applies only to spontaneous processes and, therefore, does not apply to LGT.

It is useful to point out that the process which is the inverse of LGT, namely, the structural relaxation of a glass (to the liquid state) at  $T_g$ , as a consequence of removal of the constraint of  $t_{\text{obs}}$ , is a spontaneous process. During this relaxation process, the entropy increases as is required by the second law. This increase of entropy during relaxation at  $T_g$  is consistent with the entropy loss during LGT.

## VI. SUMMARY

In summary, we conclude that there is convincing support for the “extrinsically constrained liquid” description of glass. According to the ECL view, LGT is essentially an “entropy reducing,” nonspontaneous ergodicity-breaking process without any latent heat. The description provides a natural explanation of crossover experiments, of existence of secondary relaxations, of the existence of excess heat capacity in the glassy state, and of the effects of thermal history (i.e., cooling rates) on the properties of glass.

## ACKNOWLEDGMENTS

Discussions with Arun Varshneya, Roger Loucks, and Jitendra Balakrishnan were extremely helpful and are gratefully appreciated.

<sup>1</sup>D. J. Wales, *Energy Landscapes* (Cambridge University Press, Cambridge, 2003).

<sup>2</sup>V. Lubchenko and P. G. Wolynes, *Annu. Rev. Phys. Chem.* **58**, 235 (2007).

<sup>3</sup>M. Sasai, *J. Chem. Phys.* **118**, 10651 (2003).

<sup>4</sup>H. C. Anderson, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 6686 (2005).

<sup>5</sup>M. D. Ediger, *Annu. Rev. Phys. Chem.* **51**, 99 (2000).

<sup>6</sup>J. Jäckle, *Rep. Prog. Phys.* **49**, 171 (1986).

<sup>7</sup>M. D. Ediger, C. A. Angell, and S. R. Nagel, *J. Phys. Chem.* **100**, 13200 (1996).

<sup>8</sup>C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, *J. Appl. Phys.* **88**, 3113 (2000).

<sup>9</sup>A. K. Varshneya, *Fundamentals of Inorganic Glasses*, 2nd ed. (Society of

- Glass Technology, Sheffield, 2007).
- <sup>10</sup>T. A. Litovitz and C. A. Davis, *Phys. Acoust.* **IIA**, 281 (1965).
- <sup>11</sup>H. Z. Cummins, H. Zhang, J. Oh, J. A. Seo, H. K. Kim, Y. H. Hwang, Y. S. Yang, Y. S. Yu, and Y. Im, *J. Non-Cryst. Solids* **352**, 4464 (2006).
- <sup>12</sup>J. D. Stevenson and P. G. Wolyne, *J. Phys. Chem. B* **109**, 15093 (2005).
- <sup>13</sup>B. O. Mysen and P. Richet, *Silicate Glasses and Melts* (Elsevier, New York, 2005).
- <sup>14</sup>M. Goldstein, in *Relaxation in Complex Systems*, edited by K. Ngai and G. B. Wright (US Dept of Commerce, Springfield, VA, 1985), p. 13.
- <sup>15</sup>P. K. Gupta, *Rev. Solid State Sci.* **3**, 221 (1989).
- <sup>16</sup>C. T. Moynihan, A. J. Easteal, M. A. deBolt, and J. Tucker, *J. Am. Ceram. Soc.* **59**, 12 (1976).
- <sup>17</sup>X. Xia and P. G. Wolyne, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 2990 (2000).
- <sup>18</sup>P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1996).
- <sup>19</sup>P. K. Gupta and C. T. Moynihan, *J. Chem. Phys.* **65**, 4136 (1976).
- <sup>20</sup>J. C. Dyre, *Rev. Mod. Phys.* **78**, 953 (2006).
- <sup>21</sup>A. J. Ikushima, T. Fujiwara, and K. Saito, *J. Appl. Phys.* **88**, 1201 (2000).
- <sup>22</sup>D. M. Krol, K. B. Lyons, S. A. Brawer, and C. R. Kurkjian, *Phys. Rev. B* **33**, 4196 (1986).
- <sup>23</sup>R. LePrac, B. Champagnon, L. David, A. Faivre, C. Levelut, Ph. Guenot, J. L. Hazemann, C. Rochas, and J. P. Simmon, *Philos. Mag. B* **82**, 431 (2002).
- <sup>24</sup>C. T. Moynihan and J. Schroeder, *J. Non-Cryst. Solids* **160**, 52 (1993).
- <sup>25</sup>G. W. Scherer, *Relaxation in Glass and Composites* (Wiley, New York, 1986), 171.
- <sup>26</sup>J. Jäckle, *Philos. Mag. B* **44**, 533 (1981).
- <sup>27</sup>J. Jäckle, *Physica B* **127**, 79 (1984).
- <sup>28</sup>S. Langer, J. P. Sethna, and E. C. Grannan, *Phys. Rev. B* **41**, 2261 (1990).
- <sup>29</sup>P. Richet, D. de Ligny, and E. F. Westrum, *J. Non-Cryst. Solids* **315**, 20 (2003).
- <sup>30</sup>R. G. Palmer, *Adv. Phys.* **31**, 669 (1982).
- <sup>31</sup>P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).
- <sup>32</sup>D. J. Wales and J. P. K. Doye, *J. Chem. Phys.* **63**, 214204 (2001).
- <sup>33</sup>F. H. Stillinger, *J. Chem. Phys.* **88**, 7818 (1988).
- <sup>34</sup>F. H. Stillinger and T. A. Weber, *Science* **225**, 983 (1984).
- <sup>35</sup>R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, Oxford, 2001).
- <sup>36</sup>D. L. Stein and C. M. Newman, *Phys. Rev. E* **51**, 5228 (1995).
- <sup>37</sup>C. Monthus and J.-P. Bouchaud, *J. Phys. A* **29**, 3847 (1996).
- <sup>38</sup>F. H. Stillinger, *Science* **267**, 1935 (1995).
- <sup>39</sup>A. Heuer, B. Doliwa, and A. Saksengwijit, *Phys. Rev. E* **72**, 021503 (2005).
- <sup>40</sup>G. Fabricius and D. A. Stariolo, *Physica A* **331**, 90 (2004).
- <sup>41</sup>K. Binder and W. Kob, *Glassy Materials and Disordered Solids* (World Scientific, Singapore, 2005).
- <sup>42</sup>S. Goldstein and J. L. Lebowitz, *Physica D* **193**, 53 (2004).
- <sup>43</sup>J. C. Mauro and A. K. Varshneya, *J. Am. Ceram. Soc.* **89**, 1091 (2006).
- <sup>44</sup>S. Mossa and F. Sciortino, *Phys. Rev. Lett.* **92**, 045504 (2004).
- <sup>45</sup>D. Thirumalai, R. D. Mountain, and T. R. Kirkpatrick, *Phys. Rev. A* **39**, 3563 (1989).
- <sup>46</sup>R. J. Speedy, *Biophys. Chem.* **105**, 411 (2003).
- <sup>47</sup>M. D. Balmakov, *Glass Phys. Chem.* **22**, 344 (1996).
- <sup>48</sup>D. Kivelson and H. Reiss, *J. Phys. Chem. B* **103**, 8337 (1999).
- <sup>49</sup>J. L. Lebowitz, *Phys. Today* **46**(9), 32 (1993).