

Frustration, connectivity, and the glass transition¹

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Abstract

The concepts of connectivity, localization, and frustration are explored in relation to glass formation in amorphous materials. First, the concept of eigenclusters to geometrically characterize correlations in amorphous materials is introduced, and discussed in detail for both the Ising ferromagnet and Ising spin glass models. Second, a new, glass-forming percolation model that contains frustration as the essential ingredient, and exhibits *two* percolation transitions, is discussed. This new model gives new insights into frustrated systems, and applications to the Ising spin glass model and other glass-forming systems are discussed. In particular, we propose the possibility that the occurrence of a percolation-type transition at temperatures above the glass transition temperature may be a general feature of glass-forming systems. The important role of computer simulations in probing the mechanism of glass formation is emphasized.

1. Introduction

The glass transition has been studied by physicists, chemists, engineers and materials scientists for over a century. Substantial efforts have been made by both experimentalists and theorists, but despite these numerous studies a universally accepted, comprehensive, and technologically useful theory of glass-forming materials remains elusive. Because of the many technological and scientific applications of a predictive theory of glasses, efforts to understand this complicated phenomenon continue. A variety of competing

theories based on such concepts as free volume, entropy, mode coupling, metastability, percolation, and localization have been introduced which each capture certain gross features of glasses. At a recent NIST workshop on *Glasses and the Glass Transition: Challenges in Materials Theory and Simulation*, many of these theories – and their testing by simulation – were discussed. A key point that was raised by the experimentalists at the workshop was the necessity for simple models and concepts that could (1) provide them with qualitative understanding of the nature of the glassy state, and (2) guide them in the preparation of glasses. In particular, the exploitation of computer models to examine length scales and time scales commensurate with those accessible to experiments, and thereby confirm or invalidate theories that predict phenomena on such scales, was stressed.

In this spirit, we examine in this paper the concepts of connectivity and frustration – and the inter-

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play between them – as tools in elucidating the nature of the glass transition. We argue that increased focus on the identification of clusters and the examination of frustration in glass-forming liquids through computer simulation offers a good prospect for advancement in our understanding of glasses. In particular, we propose that simulations at temperatures significantly above the computational glass temperature may yield important information concerning the effect of frustration in amorphous materials.

2. Clusters in unfrustrated systems

Attempts to describe the physics of amorphous systems in terms of groups of particles that collectively form individual units, or clusters, has a rich history in statistical mechanics. In particular, cluster descriptions have elucidated the nature of thermodynamic phase transitions in certain systems by providing a geometrical interpretation of correlations. For example, in the fruit-fly of statistical mechanical spin models – the Ising model – the paramagnetic–ferromagnetic transition may be described in terms of independent clusters of thermodynamically correlated spins [1,2]. In the Ising model in zero magnetic field, in which parallel (antiparallel) nearest-neighbor spins (represented by variables $s_i = \pm 1$) occupying the vertices of a d -dimensional lattice interact favorably (unfavorably) with energy $-J$ ($+J$), clusters may be constructed by randomly imposing fictitious bonds between nearest-neighbor parallel spins with probability $p_b = 1 - e^{-2J/k_B T}$. Coniglio and Klein [1] showed that these clusters of nearest-neighbor, bonded spins grow in size with decreasing temperature, and percolate at the paramagnetic–ferromagnetic transition. The critical exponents describing the divergence of the mean cluster linear dimension ξ_p and the mean cluster size S as the critical temperature is approached are identical to the critical exponents that describe the divergence of the thermodynamic correlation length ξ_T and the susceptibility χ , respectively. Thus, by defining the connectivity of spins in this particular way, the correlations between spins can be understood in terms of connectivity, and the *thermodynamic* transition can be understood in terms of a *percolation* transition [3]. In related work by Kastelyn and Fortuin [2], clusters were constructed by imposing bonds of infinite

strength between nearest-neighbor parallel spins with probability p_b , and zero interactions between all other pairs. Both approaches give the same cluster statistics.

The success of this geometric picture of a thermodynamic phase transition is further highlighted by the well-known Swendsen–Wang (SW) Monte Carlo cluster algorithm [4], a fast dynamical Monte Carlo algorithm that equilibrates the Ising model by flipping *clusters* of spins, rather than individual spins. In this algorithm, clusters are defined as above, and then flipped individually according to the Boltzmann probability calculated from the potential change in energy. Since by definition spins within a cluster are connected via bonds of infinite strength, and spins on different clusters are not connected, flipping an entire cluster of spins as a unit does not result in a change of energy, and thus the Boltzmann probability is simply 1/2. By updating independent groups of correlated spins in this way, the SW algorithm allows the system to take large steps in phase space directly to the equilibrium spin configuration, which drastically reduces the computational slowing down near the critical point. This algorithm has been successfully implemented and developed in other unfrustrated models, including, e.g., the XY model and the FM Potts model [5].

The reason for the success of this cluster picture of the Ising transition, and for the success of the SW algorithm in practically eliminating critical slowing down, is that with the particular choice of bond probability $p_b = 1 - e^{-2J/k_B T}$ found by Kastelyn and Fortuin (KF), and by Coniglio and Klein (CK), the pair connectedness function p_{ij} – which is the probability that two spins i and j belong to the same cluster – coincides with the pair correlation function $g_{ij} = \langle s_i s_j \rangle$ [6]. Thus, the correlations in the system are carried by particular clusters of spins which represent the relevant degrees of freedom. For example, whereas the structure factor $S(q)$ for a system of N spins would typically be written as (in zero field above T_c),

$$S(q) \propto \frac{1}{N} \left\langle \left| \sum_{i=1}^N e^{iq \cdot x_i} s_i \right|^2 \right\rangle, \quad (1)$$

where $\langle \dots \rangle$ indicates an ensemble average and x_i denotes the position of the i th spin on the lattice, we can in general partition the spins into arbitrarily-defined

clusters, and rewrite the sum as

$$S(q) \propto \frac{1}{N} \left\langle \left| \sum_{m=1}^{N_c} \sum_{i=1}^{N_m} e^{iq \cdot x_{mi}} s_{mi} \right|^2 \right\rangle, \quad (2)$$

where x_{mi} denotes the position of the i th spin within the m th cluster; the first sum ($\sum_{m=1}^{N_c}$) in Eq. (2) denotes a sum over clusters (N_c is the total number of clusters), and the second sum ($\sum_{i=1}^{N_m}$) denotes a sum over only the spins belonging to the m th cluster. If the clusters are defined correctly (i.e. according to the above prescription), the cross terms between clusters in Eq. (2) are identically zero, and the structure factor can be represented by a sum over individual, *independent* clusters:

$$S(q) \propto \frac{1}{N} \left\langle \sum_{m=1}^{N_c} \left| \sum_{i=1}^{N_m} e^{iq \cdot x_{mi}} s_{mi} \right|^2 \right\rangle. \quad (3)$$

Because these independent clusters form a basis set with which to describe the correlations, we refer to these clusters as *eigenclusters*. While there are many statistically equivalent sets of eigenclusters that can be identified for a given spin configuration, there is only one possible bond probability, and hence one rule for connectivity, that gives the eigenclusters for the system.

Because the Ising model is isomorphic to both the one-component and two-component lattice gas models of fluids, both the liquid–gas and liquid–liquid transitions that occur in these two models may be described in terms of eigenclusters by extending the KF–CK theory of connectivity used to describe the paramagnetic–ferromagnetic transition in the Ising model. Further extension of the theory to include hard-core interactions in off-lattice fluids should allow us to describe such transitions in a real fluid in terms of eigenclusters. This idea is currently being tested with molecular dynamics (MD) simulations of simple liquids [7]. However, incorporation of the repulsive, hard-core intermolecular interactions (which contribute to frustration and eventually a glass transition at high densities or low temperatures) into the bond probability is not at all trivial from a theoretical standpoint, and large-scale simulations will be required to test any predictions.

3. Clusters in frustrated systems

The question central to this paper is: Are clusters relevant to our understanding of the physics of the glass transition, and to relaxation of amorphous materials [8]? While the search for clusters in supercooled liquids and spin glasses is not new, the identification of *independent* clusters of particles or spins that carry the relevant correlations in frustrated systems [9] would provide a significant contribution to a geometric description of the glass transition. Attempts are currently being made to identify such clusters in the Ising spin glass model [10], in lattice models of polymers [11], and in supercooled simple liquids [11], via extension of the cluster theory developed by Coniglio et al. [12,13]

However, the question of whether the glass transition in fact has an underlying thermodynamic transition, and if so what kind, remains unanswered. A number of phenomena observed near the glass transition in simple liquids and polymers suggest that a thermodynamic singularity is indeed lurking nearby, most notably recent experiments [14] and simulations [15] which claim to observe evidence for a diverging length as T_g is approached. The possible existence of a diverging length associated with the structural glass transition is of fundamental importance, and simulations may have the best chance of answering it.

3.1. Clusters in the Ising spin glass model

The Ising spin glass model [16,17] is one example of a glass-forming spin system in which the glass transition (which in zero field is believed to be coincident with a second-order thermodynamic transition) can be described in terms of clusters [10]. In the spin glass, ferromagnetic (FM) and antiferromagnetic (AF) interactions are quenched randomly to the edges of a d -dimensional hypercubic lattice (instead of only FM (AF) interactions in the case of the FM (AF) Ising model.) As in the Ising model, the spins occupy the vertices of the lattice and can assume the values $s_i = \pm 1$. The competing interactions give rise to frustration when all the spins try to satisfy all the interactions simultaneously. While the spin glass – which is paramagnetic at high temperature – still exhibits a second-order thermodynamic transition at T_{sg} , the critical point shifts to a temperature lower

than the FM Ising T_c due to the frustration, and the values of the exponents (i.e. the universality class) change. As in the Ising model, the transition is known to be characterized by a diverging correlation length (which in the spin glass is associated with the *square* of the spin–spin correlation function $|g_{ij}|^2 = |\langle s_i s_j \rangle|^2$, averaged over all the interaction configurations) and is accompanied by a strong divergence in the nonlinear susceptibility, which above T_{sg} is given by $\chi^2 = \sum_{ij} |g_{ij}|^2$. However, the specific heat – which in the Ising model diverges at T_c – exhibits only a weak singularity at T_{sg} . Moreover, the breaking of ergodicity at T_{sg} is qualitatively different from that in the Ising model at T_c ; in particular, complex dynamical behavior characterized by stretched exponential relaxation of equilibrium autocorrelation functions is observed in the spin glass at temperatures well above the transition temperature [18].

How does one define eigenclusters in a spin glass? The usual definition of the KF–CK clusters described in the previous section leads to clusters which diverge in the spin glass at a temperature T_p that is *higher* than the spin glass transition temperature T_{sg} , and with exponents in the universality class of random percolation [13,19,20]. Moreover, because of the competing interactions, there are now two relevant connectedness functions to be considered when the pure Ising probability is used [13]:

$$p_{ij} = p_{ij}^{\parallel} + p_{ij}^{\vee}, \quad (4)$$

and

$$g_{ij} = p_{ij}^{\parallel} - p_{ij}^{\vee}, \quad (5)$$

where p_{ij}^{\parallel} (p_{ij}^{\vee}) is the probability that (1) spins i and j belong to the same KF–CK cluster and (2) spins i and j are parallel (antiparallel). The quantity g_{ij} coincides with the spin glass spin–spin correlation function. (In the absence of antiferromagnetic interactions, $p_{ij}^{\vee} = 0$, and thus $p_{ij} = g_{ij}$, so that both quantities coincide with the Ising spin–spin correlation function.) While $\sum_{ij} p_{ij}$ diverges at T_p , $\sum_{ij} |g_{ij}|^2$ diverges at T_{sg} . Thus, because of the frustration caused by the competing interactions – which essentially dilutes the thermodynamic correlations, pushing both T_p and T_{sg} to lower values than in the unfrustrated system – a revised definition of connectivity must be invoked to

identify those clusters which carry the relevant thermodynamic correlations.

The key requirement for constructing the eigenclusters is that the pair correlation function coincide with the pair connectedness function. Ideally, we would like to have an expression for the bond probability such that one dilution of the spin configuration with bonds would give the eigenclusters, in the same way as one dilution of the pure Ising spin configuration with $p_b = 1 - e^{-2J/k_B T}$ gives the Ising eigenclusters. Because of the disorder in the local environment, however, we suspect that the dilution of the spins cannot be performed uniformly in frustrated systems, and instead the bond probability may be spatially dependent; that is, p_b becomes $p_b(i, j)$ so as to be a function of the local disorder in the quenched interactions.

The reason for this generalization of the bond probability is that even above T_{sg} , some nearest-neighbor pairs of spins are more correlated than others at a given temperature – unlike in the unfrustrated Ising model, where $\langle s_i s_j \rangle$ for any nearest-neighbor ij pair is the same. This is exemplified by the temperature-dependent distribution of nearest-neighbor energies shown in Fig. 1 of Ref. [21] for the $\pm J$ Ising spin glass. This histogram of values of $\langle J_{ij} s_i s_j \rangle$, where $\langle \dots \rangle$ denotes a time average for the particular edge joining spins i and j for one given set of interactions, shows that at all $T > T_{sg}$ many different values of this quantity appear depending on the location of the spin pair on the lattice, and as T_{sg} is approached the distribution becomes extremely broad and asymmetric. The corresponding histogram for the pure ferromagnetic system would of course be a δ -function at any temperature, with the position of the δ -function moving from zero to one as T decreases from infinity to zero.

In the absence of an exact, general formula for $p_b(i, j)$ [22], one way to construct the eigenclusters in the spin glass in an approximate fashion [10] is to first construct the KF–CK clusters (which percolate at $T_p > T_{sg}$), and then dilute them in such a way that bonds between nearest-neighbor spins are retained with a probability reflecting the strength of the local correlation of that pair. Close to T_g , where the distribution of $\langle J_{ij} s_i s_j \rangle$ is strongly peaked, we may choose to retain only those nearest-neighbor spins whose correlation equals a value which falls under the peak of the distribution. This is appropriate if the spins which carry the *relevant* correlations are indeed those which

are connected by pairs most strongly correlated. Note that if a given pair of spins n and m is so strongly correlated that $\langle J_{nm}s_n s_m \rangle$ is close to unity, then n is effectively localized, or “quasi-frozen”, with respect to m . The resulting diluted clusters therefore consist of nearest-neighbor quasi-frozen spins connected by bonds with the same probability p_b used for the unfrustrated system.

Preliminary results from Monte Carlo simulation suggest that these clusters indeed percolate at T_{sg} with exponents in the spin glass universality class, and that the pair connectedness and pair correlation functions coincide close to T_g for large distances [10,23]. The cluster picture of the spin glass is therefore the following: as the temperature is lowered, clusters of nearest-neighbor spins connected by bonds with probability $p_b = 1 - e^{-2J/k_B T}$ grow and percolate at T_p . While this percolation transition does not correspond to a thermodynamic transition, it is found numerically [19] to coincide both with the onset of stretched exponential relaxation [18], and with the temperature at which the $\langle J_{ij}s_i s_j \rangle$ distribution first appears asymmetric [10]. As the temperature is lowered further, clusters of strongly-correlated, quasi-frozen nearest-neighbor spins connected by bonds grow within the former clusters, and percolate at T_{sg} [24].

Although the first (high T) percolation transition does not coincide with a thermodynamic transition, it is reasonable to believe that T_p “sets the stage” for the glass transition by marking the temperature below which inhomogeneity appears in the local environments, and that the inhomogeneity in the system – namely, the coexistence of mobile and localized clusters of spins – is responsible for the observed stretched exponential relaxation. Recent analytical work of Douglas and Hubbard [25] – which contains a number of ideas consistent with those discussed here — shows that an exponential distribution of cluster sizes may in general give rise to stretched exponential relaxation behavior. The connection between cluster size distribution and stretched exponential relaxation in supercooled liquids has also been discussed by Shlesinger and Bendler [26].

3.2. Frustrated percolation

How might this picture – and the concepts of connectivity that lead to it – be related to glass for-

mation in liquids? While the concept of frustration in glass-forming liquids and polymers is formally less clearly defined than in the spin glass, its effect is no less dramatic. Indeed, a large number of purported “crossover” phenomena occurring at temperatures significantly above T_g – the separation of time scales and onset of two-step relaxation of autocorrelation functions [8], the apparent “breakdown” of the Stokes–Einstein relation between translational diffusion and viscosity, and associated decoupling of translational and rotational diffusion [28–30,32], the decoupling of bulk and shear moduli [30], etc., as well as evidence for a weak transition above T_g in polymer melts [31,32] – all suggest a possible anticipation of the glass transition by a higher temperature “transition” marking a change from a liquid in which transport is homogeneous to a liquid in which transport is inhomogeneous [25,29,30,32]. It has been suggested that this inhomogeneity might arise at low temperature or high density due to geometric frustration of local molecular environments, which temporarily trap otherwise mobile molecules until a large-scale, cooperative rearrangement of many molecules takes place. This type of geometric frustration can be clearly seen in, for example, lattice models of polymer melts, where segments of polymers at low temperature become temporarily trapped and cannot move due to the local environment [27]. Moreover, recent models have shown that spatial inhomogeneity in an equilibrium fluid can lead to the aforementioned decouplings and breakdown of various transport properties [30].

To see why and how a higher temperature transition might arise in addition to the glass transition in structural glass-forming systems, we discuss a recently introduced lattice model [13,33] that contains geometric frustration as the essential ingredient, and exhibits a glass transition. Since percolation plays an important role in determining the critical behavior of this simple model, the model has been called “frustrated percolation” (FP). This model may also be viewed as a percolation model in a frustrated medium, and both site and bond versions of the model have been formulated. Both the static and dynamic properties of the FP model exhibit complex behavior with features in common with both structural glasses and spin glasses. This may suggest that the FP model may relate certain aspects of the glass transition in liquids to the spin glass transition.

The FP model has been described in detail elsewhere [33], so here we describe it only briefly and discuss its key properties. In the FP model, attractive (+) and repulsive (−) “interactions” are quenched randomly to each edge of a lattice. A loop (a closed path of edges) is said to be frustrated if the product over all the signs along the edges of the loop is negative. In the site version of the FP model, particles occupy the vertices of the lattice under the constraint that frustrated loops are not allowed to be fully occupied. While this geometric constraint will obviously be unimportant at low densities, packing difficulties will arise as more and more particles are placed on the lattice.

Because of the competing “interactions”, there are two relevant connectedness functions for this model:

$$p_{ij} = p_{ij}^+ + p_{ij}^-, \quad (6)$$

and

$$g_{ij} = p_{ij}^+ - p_{ij}^-, \quad (7)$$

where p_{ij}^+ (p_{ij}^-) is the probability that (1) sites i and j belong to the same cluster of nearest-neighbor particles, and (2) the product of all the signs along the path connecting i and j is +1 (−1). Renormalization group calculations on the bond version of the model [20] supported by numerical simulations [34] show that the lengths associated with these two quantities diverge at *different* temperatures, and consequently there are *two* critical points in the FP model – T_p , where the length ξ_p associated with the pair connectedness function p_{ij} diverges, and $T_g \ll T_p$, where the length ξ_g associated with the pair connectedness function g_{ij} diverges. The percolation transition at T_p is in the universality class of the ferromagnetic 1/2-state Potts model (as opposed to standard percolation which is in the same universality class as the ferromagnetic 1-state Potts model). The transition at T_g is in the spin glass universality class. Since p_{ij} (averaged over all possible interaction configurations) is the probability that i and j belong to the same cluster of particles, ξ_p corresponds to the linear dimension of these clusters. Consequently, T_p denotes a percolation transition of nearest-neighbor particles.

The physical meaning of the second diverging length is less straightforward. The second transition occurs at a temperature lower than the usual perco-

lation transition due to the interference of paths with different phases [35]. That is, different paths between particles i and j in a given configuration at time t will have the same phase (calculated by multiplying the signs along the path between the two particles), but the phase may change as the system evolves from one configuration to the next in time, or as different spin configurations are sampled. For a given pair of sites i and j , this interference effect vanishes if there is a “frozen” or strongly correlated path of particles between them, since the phase along this path will not change. Since a path can never be completely frozen at finite T , the major contribution to g_{ij} is thus due to those configurations in which particles on sites i and j are connected by *quasi-frozen*, or *localized*, particles. Therefore, $|g_{ij}|$ (averaged over all interaction configurations) roughly coincides with the probability that i and j belong to the same quasi-frozen cluster, and the length ξ_g associated with $|g_{ij}|^2$ roughly represents the linear dimension of these clusters. Since ξ_g diverges at T_g , the glass transition in the FP model coincides with the percolation of quasi-frozen, or localized, clusters of nearest-neighbor particles.

3.3. Frustrated percolation and the Ising spin glass model

The partition function for the bond version of the frustrated percolation model (generalized to include Potts variables) can be mapped exactly onto the partition function for the Ising spin glass model [36]. Consequently, T_p in the FP model maps precisely onto the percolation temperature T_p of the KF–CK clusters in the spin glass, while T_g in the FP model maps onto the percolation temperature T_{sg} of clusters of strongly-correlated, quasi-frozen spins in the spin glass. In the spin glass, the diverging correlation length ξ_T gives rise to a strong divergence in the nonlinear susceptibility (which is associated with the integral of the spin–spin pair correlation function), but only a weak singularity in the specific heat (which is associated with the integral of the energy–energy pair correlation function). In the FP model, the mean cluster size of the localized particles diverges with the same exponent as the nonlinear susceptibility of the spin glass, while the compressibility of the FP model exhibits a very weak singularity identical to that of the specific heat of the spin glass. That is, the density–density pair

correlation function of the FP model behaves as the energy–energy pair correlation function of the spin glass model:

$$g(r) = \frac{f(r/\xi)}{r^{d-2+\eta}}. \quad (8)$$

In both models, η is very large; consequently, as $\xi \rightarrow \infty$, $g(r) \rightarrow 0$ with a very large power, giving only a weak singularity in the compressibility. While the compressibility in non-spin systems is accessible via standard light scattering experiments, the mean cluster size of localized particles is not. Consequently, thermodynamic signatures of the glass transition in non-spin systems that behave like the FP model may be difficult to detect. Instead, perturbative, non-equilibrium experiments that “break” or deform the clusters (e.g., imposing shear) may be required.

3.4. Frustrated percolation, clusters, and glass-forming liquids

The frustrated percolation model suggests that systems containing disordered geometric frustration may exhibit *two* percolation transitions – one corresponding to a thermodynamic glass transition, and the other, at higher temperatures, corresponding to a dynamic transition and announcing the onset of heterogeneity in the local mobility. Depending on the nature of the disorder in the system, the higher temperature transition may or may not be thermodynamic. In fact, the spin glass free energy does not exhibit a singularity at T_p , and thus the transition is not thermodynamic in that system; nevertheless, the existence of the transition is a mathematically necessary prerequisite to the glass transition in this case, since $|g_{ij}| \leq |p_{ij}|$.

Certainly, the details of the glass transition will depend on whether the frustration is quenched in space, as in spin glasses, or annealed, as in simple liquids and polymers. If the frustration is not quenched, then both transitions (T_p and T_g) may be softened. In some systems, the frustration may even be annealed, but act “quenched” on short time scales (e.g., polymer melts). We point out that a great deal of experimental evidence suggests the possibility of a weak, thermodynamic transition at temperatures significantly above T_g in a number of polymer melts [31,32]. In these and other systems, complex dynamical behavior often accompanies the observed “thermodynamic” be-

havior, and many researchers who dispute the thermodynamic nature of the transition agree that the relaxation properties of the melt indeed appear to change at this high temperature “transition”. The frustrated percolation model suggests the possibility that this purported transition may indeed have some theoretical underpinnings, and may appear purely dynamic – or also thermodynamic – depending on the nature of the frustration, which may be dictated by such factors as polymer structure and the quenching process used in a particular experiment.

Nevertheless, even in systems where the first transition well above T_g may not be detectable with the same types of experiments that detect the glass transition, its influence may be detected through the onset of so-called *apparent* “non-ergodic”, or complex relaxation, behavior. Such behavior is already well known, and computer simulations which focus on the search for clusters – in particular, finite, quasi-immobile clusters of molecules *above* T_g – are within our reach today.

If there is a diverging length and underlying thermodynamic transition in glass-forming liquids – as in spin glasses and frustrated percolation – then it is tempting to apply the lessons learned from critical phenomena, and pursue the ideas that (1) clusters are relevant to the glass transition in polymers and liquids just as they are in spin glasses and frustrated percolation, and (2) different glass-forming systems (spin glasses, polymer melts, simple liquids, network-forming liquids, etc.) may belong to different universality classes. This would imply that a comprehensive theory of the glass transition is possible, with each universality class (determined not by the details of the interaction but by the symmetries of the system) being described by a different model, in analogy with the different universality classes of ordinary critical phenomena. The presence of a diverging length would also provide hope that the glass transition may be treated by a renormalization group theory as in the case of spin glasses where chaotic behavior in the recursion relations characterizes the glass phase.

If this is indeed the case, then theoretical and computational studies of lattice models would be extremely important in elucidating the essential features of glasses and glass-forming systems, just as are the Ising model and other lattice models in critical phenomena. In particular, extending the results of the FP model to structural glasses, we might expect a

diverging length corresponding to a spanning cluster of strongly-correlated, localized particles, to accompany the glass transition. In this framework, the glass transition looks very similar to the usual second-order phase transition of critical phenomena. However, the very large relaxation times associated with the relaxation of the localized clusters may mask the associated critical behavior, and thus the glass transition event would appear as only a kinetic event, perhaps described by a dynamic singularity as in mode-coupling theory [37]. If so, then the identification of the proper clusters might allow us to computationally study the statics of the transition without interference from the slow dynamics, in analogy with the Swendsen–Wang dynamics in the Ising model.

If localized clusters with a diverging length are indeed present in glass-forming liquids, how might they be detected? In spin glasses, the quasi-frozen clusters can be easily detected via the nonlinear susceptibility. In analogy with the susceptibility in a magnet, one might first think to look for density fluctuations to diverge as the glass transition is approached. However, the frustrated percolation model tells us that a glass transition may be accompanied by diverging connectivity and only a weak singularity in the compressibility. Indeed, the localized clusters in fluids may have a density closer to that of the mobile liquid that surrounds them, and therefore there should be no diverging density fluctuations, in agreement with experimental observation.

One of the interesting properties of the frustrated percolation model is that although the glass transition in that model is in the same static universality class as the spin glass, the dynamics compared to spin glasses is different due to the intrinsic difference in the diffusion-based dynamics of frustrated percolation as compared with the spin flip dynamics which is more appropriate in a spin system. Similarly, we may expect that different glass-forming systems are in the same (or just a few) *static* universality classes, but different *dynamic* ones due to the intrinsic difference in the actual molecular dynamics.

4. Summary

We have explored the concepts of connectivity, localization, and frustration in relation to glass forma-

tion in amorphous materials. The concept of eigenclusters to geometrically characterize correlations in amorphous materials was introduced, and discussed in detail for both the Ising ferromagnet and Ising spin glass models. We described a new, glass-forming percolation model that contains frustration as the essential ingredient, and exhibits *two* percolation transitions. This model gives new insights into frustrated systems, and we have discussed applications to the Ising spin glass model and other glass-forming systems. In particular, we have proposed the possibility that the occurrence of a percolation-type transition at temperatures above the glass transition temperature may be a general feature of glass-forming systems. This percolation transition should mark the onset of a complex relaxation behavior.

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