Numerical Test of Stillinger's Argument Concerning the Kauzmann Paradox[†]

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Received: July 8, 2004; In Final Form: October 11, 2004

Many aspects of glass forming liquids, including the existence and nature of a thermodynamic glass transition, continue to be the subject of considerable scientific investigation. In particular, much recent work has been based on the inherent structure approach developed by Stillinger and co-workers. Within the inherent structure framework, Stillinger formulated an argument with the conclusion that a finite temperature ideal glass transition of the type associated with the Kauzmann paradox cannot occur for substances with limited molecular weight and with conventional intermolecular interactions. The argument, which relies on considerations concerning local defects that may occur in amorphous inherent structures, is tested numerically by generating inherent structures for a model liquid. The results concerning defects in inherent structures conform to Stillinger's description. The implications of these results are briefly discussed.

1. Introduction

Most liquids transform into a crystalline solid when cooled to low temperatures, undergoing a thermodynamic phase transition at the freezing temperature. Under suitable experimental conditions, however, a liquid can be *supercooled*, i.e., retained in the liquid state at temperatures lower than the freezing temperature. Such supercooled liquids transform into an amorphous solid, or a glass, at the glass transition temperature, T_g. This transformation has some characteristics of a thermodynamic phase transition, and has been described as such in various theoretical analyses.[1−5] The historical impetus for these theories stems from the observation by Kauzmann[6] that the excess entropy of the liquid (over that of the crystal phase in the supercooled regime) appears to vanish at a finite temperature. Starting with the work of Gibbs and DiMarzio,[1] there have thus been various formulations of *entropy theories* of the ideal glass transition, wherein the vanishing of the excess entropy (or the configurational entropy which it is a surrogate for) is the essential hallmark of the thermodynamic transition. In addition, there have been other theories of a thermodynamic transition, such as free volume theory,[7,8] as well as kinetic theories that place no special emphasis on a static transition, such as mode coupling theory,[9] and studies of models of kinetic facilitation etc.[10−13] In the laboratory, the liquid close to the glass transition becomes extremely viscous, and hence the transformation observed in the laboratory is strongly affected by the rate at which the liquid is cooled and occurs over a finite transformation range, rather than a sharply defined temperature. Such observations have lead to the suggestion that no genuine thermodynamic transition (the "ideal glass transition") underlies glass formation in the laboratory, which is argued instead to be a *kinetic* phenomenon arising from the enormous increase in the liquid's viscosity at low temperatures. Even within the context of theories that emphasize thermodynamic considerations, the existence of the ideal glass transition has been challenged.[14,15] Stillinger[15] presented one such argument against the existence of an ideal glass transition based on analyzing the distribution of local energy minima (inherent structures) sampled by the liquid. In the present paper, some issues relevant to Stillinger's argument are tested numerically by generating inherent structures for a range of energies and system sizes.

The rest of the paper is organized as follows. In section 2, a brief review is given of the inherent structure formalism. In section 3, Stillinger's argument regarding the Kauzmann paradox and a finite ideal glass transition are described. Section 4 describes the numerical study performed. Section 5 describes the results. Section VI contains a discussion of the implications of the results obtained, and a summary.

2. Inherent Structure Approach

The inherent structure approach[16−27] is premised on the observation that the disordered structure of the liquid implies the existence of a large number of local minima of the potential energy, as a function of the $3N$ coordinates of the atoms (in the case of an atomic liquid) in the liquid, and that the existence of these minima must become significant for the thermodynamics and dynamics of the liquid at low temperatures. Accordingly, one considers the decomposition of the $3N$ dimensional configuration space of the liquid into basins of individual local potential energy minima, termed inherent structures (IS). A basin of a given minimum is defined as the set of points in the configuration space (or configurations) that map to that minimum under a local energy minimization. The canonical partition function of the liquid can then be expressed as a sum over IS basins, the summand being partial partition functions defined for individual basins. In turn, the sum over basins is written in terms of (a) a distribution of minima in energy, and (b) the free energies of basins, as follows:

$$Q(N,\rho,T) = \Lambda^{-3N}\frac{1}{N!}\int d\boldsymbol{r}^{\mathbf{N}}\exp[-\beta\Phi]$$

$$= \sum_{\alpha}\exp[-\beta\Phi_{\alpha}]\Lambda^{-3N}\int_{V_{\alpha}}d\mathbf{r}^{N}\exp(-\beta(\Phi-\Phi_{\alpha}))$$

$$= \int d\Phi\ \Omega(\Phi)\exp[-\beta(\Phi + F_{\text{vib}}(\Phi,T))]$$

$$= \int d\Phi\ \exp[-\beta(\Phi + F_{\text{vib}}(\Phi,T) - TS_{\text{c}}(\Phi))] \quad (1)$$

where Φ is the total potential energy of the system, α indexes individual IS, Φ_α is the potential energy at the minimum, $\Omega(\Phi)$ is the number density of IS with energy Φ. The configurational entropy density is defined, within this approach, as $S_c \equiv k_B \ln \Omega$. The *basin free energy* $F_{vib}(\Phi_\alpha,T)$ is obtained by a restricted partition function sum over a given IS basin, V_α. Λ is the de Broglie wavelength, N is the number of atoms, T is the temperature, and ρ is the density of the liquid. The configurational entropy of the liquid arises from the multiplicity of local potential energy minima sampled by the liquid at temperature T (and density ρ, suppressed here for simplicity) and is related to the configurational entropy density above by

$$S_c(T) = \int d\Phi \, S_c(\Phi) \, P(\Phi,T) \qquad (2)$$

where

$$P(\Phi,T) = \Omega(\Phi) \exp[-\beta(\Phi + F_{vib}(\Phi,T))]/Q(N,\rho,T)$$

$$= \exp[-\beta(\Phi + F_{vib}(\Phi,T) - TS_c(\Phi))]/Q(N,\rho,T) \quad (3)$$

is the probability density that IS of energy Φ are sampled at temperature T.

3. Stillinger's Argument

Based on the description above, it is possible in principle for the system to reach the lowest possible energy minima (indicated by Φ_K below) at a finite temperature, depending on the properties of the distribution $\Omega(\Phi)$. The ideal glass temperature is defined as the temperature where the degeneracy of the most probable energy minima becomes nonextensive, or equivalently, where the configurational entropy vanishes. (a) Accepting the definition of the configurational entropy as being given by the degeneracy of local energy minima and (b) assuming that derivative of the basin free energy on the inherent structure energy is not singular, it is clear that for Φ_K to become most probable at a finite temperature T_K, the derivative of $S_c(\Phi)$ with respect to Φ must be finite at Φ_K, with the inverse of the slope determining the value of T_K. Ideal glass transitions have indeed been estimated using this approach for many model systems, although in each case, through assumptions about how the inherent structure behaves at low temperatures/high densities.[17,21,23−25]

Given an inherent structure, Stillinger argues[15] that it is always possible to create new inherent structures through structural excitations that are local in nature and have finite energy cost, such as point defects and interstitials. At low concentration of such defects, it is legitimate to assume that they do not interact. In such a case, the log of the density of such new minima varies with energy as $-\Delta\Phi \log(\Delta\Phi)$, where $\Delta\Phi$ is the cost of creating a single defect. This has the implication that the overall density of states of inherent structures would possess a configurational entropy density whose slope at Φ_K is infinite, thereby disallowing the possibility of a strict ideal glass transition at a finite temperature, because Φ_K would only be reached at zero temperature. There are, however, a few possible exceptions that are listed by Stillinger that would invalidate the above argument: (i) Systems where the molecular weight of the components diverges, such as polymeric glass formers, (ii) the possibility of localized defects is restricted to a subextensive set of positions in the system, and (iii) the excitation enthalpy diverges as the concentration of excitations goes to zero.

In this paper, the above considerations are tested by analyzing the inherent structures for a model atomic glass former. Specifically, the third of the possible alternatives listed by Stillinger is considered. A large set of inherent structures are analyzed and classified by their energies. Clearly, the behavior of inherent structures possessing high energies is not relevant to the question being addressed, and the properties of only the lowest energy inherent structures matter. Because the ability to produce inherent structures of very low energies is limited computationally, it is important to consider the trend in the studied behavior as a function of the inherent structure energies. For the inherent structures considered, point defects are created by the removal of an arbitrarily chosen particle, and the system potential energy is reminimized to obtain a new inherent structure. The difference in the energy of the old and new inherent structures yields the energy cost of creating the point defect. The mean squared displacement of the particles in the system is also calculated as a measure of the "perturbation" required to create the new inherent structure. It is clear that for the energy cost to increase arbitrarily as the inherent structure energy decreases, the process of creating a point defect must perturb the inherent structure over a length scale that must also grow with the lowering of the inherent structure energy. In other words, as the inherent structure energy is decreased, the particle positions must become more strongly correlated, and the configurations must respond to a perturbation more like a house of cards, the lower the inherent structure energy. To quantify this, the energy cost and particle displacement is calculated as a function of the distance from the point defect created. The above procedures are then repeated, this time by moving the selected atom to a new "low density" location in the system, thereby creating a point defect-interstitial pair. The procedure adopted thus tests whether the generation of new inherent structures necessarily involves collective rearrangement of particles, or whether it can happen by the displacement of a small number of particles.

4. Computational Procedure

The model liquid studied is the Kob−Andersen binary Lennard-Jones liquid.[28] Systems consisting of $N = 256$ (204 type A and 52 type B) particles and $N = 10000$ particles (8000 type A and 2000 type B) have been simulated through molecular dynamics. The particles interact via the Lennard-Jones (LJ) potential, with parameters $\epsilon_{AB}/\epsilon_{AA} = 1.5$, $\epsilon_{BB}/\epsilon_{AA} = 0.5$, $\sigma_{AB}/\sigma_{AA} = 0.8$, and $\sigma_{BB}/\sigma_{AA} = 0.88$, and $m_B/m_A = 1$. The LJ potential is modified with a quadratic cutoff and shifting at $r_c^{\alpha\beta} = 2.5\sigma_{\alpha\beta}$. The reduced density is 1.2. For $N = 256$ the temperature range spans $T = 0.39$ to $T = 0.57$, at which T the liquid is equilibrated. In addition, low energy inherent structure configurations are also generated by a search procedure that does not produce any equilibrium distribution (Sastry, unpublished). Further details are as in ref 19. The $N = 10000$ system is studied between $T = 0.377$ and $T = 0.7$. The liquid is not in equilibrium below $T = 0.552$.

For each case considered, inherent structures are generated by energy minimization. The energy minimization, if seen as a quenching procedure, amounts to an infinitely fast quench to zero temperature. As such, the only temperature of relevance is the temperature at which the liquid is equilibrated. Alternately, the monotonic relationship between the inherent structure energy and the equilibrium temperature may be used in assigning a temperature to the inherent structures considered. For $N = 10000$, 20 inherent structures are considered in each bin of width 0.01, whereas for $N = 256$, between 100 and 200 inherent structures are considered in each run (which span more than one energy bin of width 0.01). In all cases, 10 point defects are generated at random positions using the following procedure:
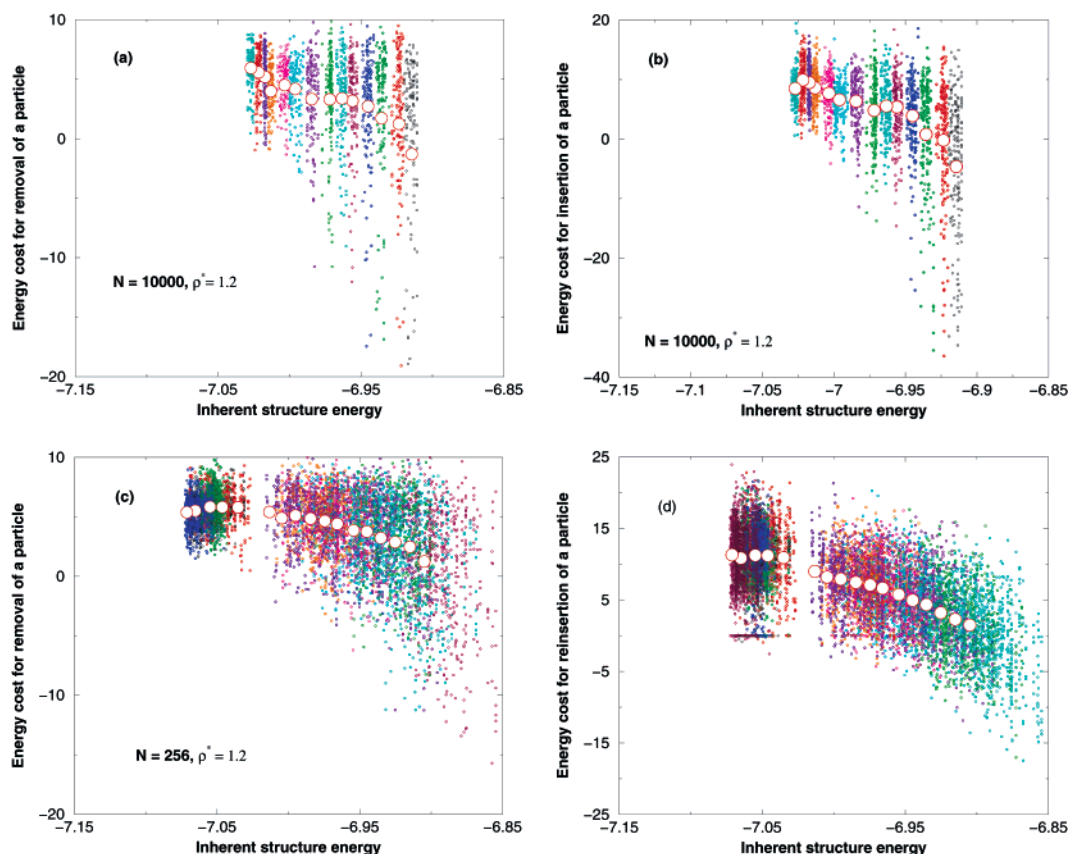
Figure 1. Energy cost of (a) removal of a particle for $N = 10000$, (b) insertion of a particle in a low-density region for $N = 10000$, (c) removal of a particle for $N = 256$, and (d) insertion of a particle in a low-density region for $N = 256$. The inherent structure energies per particle of the initial configuration are plotted on the x-axis, and the total energy cost is shown on the y-axis. The range of the x-axis is the range from Φ_K to the location of the maximum of the density of states, as estimated in ref 24. The inherent structure energies at $T \sim 1.0$, 0.47, and 0.3 respectively are -0.687, -6.983, and (estimated[25]) -7.15. The different symbols correspond to different energy bins ($N = 10000$) or different runs ($N = 256$), and the open circles superimposed are the bin-wise averages. The same representation is used in Figure 2.

A tessellation is performed using the radical plane construction[29,30] (which is the generalization of the Voronoi construction appropriate for the polydisperse configurations considered here), followed by an identification of ten Voronoi vertices[31] that have the largest distance away from surrounding particles. For each chosen vertex, a search is made to find the particle that is farthest away, subject to the minimum image convention. The selected atom is removed, and the resulting configuration minimized. The energy change or "cost" of creating the point defect is calculated as the difference of the energy of the original inherent structure and the final inherent structure. The corresponding quantity to monitor for constant pressure systems would be the enthalpy cost, which is expected to behave in a similar fashion. The mean squared distance between the two inherent structures (not counting the removed particle) as well as the energy and displacement averages as a function of the distance from the location of the particle removed are calculated. Starting again with the original inherent structure, the selected atom is inserted (interstitial defect) at the location of the chosen Voronoi vertex, and the resulting configuration is reminimized. The energy cost, mean squared displacement, and the corresponding distance dependent quantities (as a function of the distance from the location of insertion) are calculated as before.

5. Results

Figure 1a shows the energy cost of removing a particle for the $N = 10000$ system, showing each individual data point as well as the bin-wise averages. It is seen that the energy cost rises as inherent structure energy decreases. However, from the

available data, it is hard to ascertain what might be the behavior as one approaches the lowest energy inherent structures. Figure 1b displays the energy cost of removing a particle and reinserting it in a loose-packed region of the configuration. The trend in the energy costs is similar. It should be noted that the magnitude of the energy cost in each case is in the range of the energy per particle in the original inherent structure.

Figure 1c shows the energy cost of removing a particle for the $N = 256$ system, which shows data consistent with the $N = 10000$ particle system in the energy range spanned in both cases. However, the lowest energies accessed for $N = 256$ are considerably lower than the $N = 10000$ particle system, and for the lower end of the sampled energy range, the energy cost is seen to flatten with respect to energy and approach a constant value. The same trend is observed for the reinsertion of particles shown in Figure 1d. In Figure 1d, the data points clustered around zero energy cost arise from the curious but inconsequential (for our purposes) situation where the procedure of relocating a particle and reminimizing the energy results in a cyclic shift of coordinates of a small subset of particles (particle 1 takes the position of particle 2, ..., particle n takes the position of particle 1).

The conclusion to be drawn from the data in Figure 1 is that the energy cost of creating a point or interstitial defect (a) is roughly the energy per particle in the parent inherent structure and (b) does not grow as the inherent structure energy decreases but instead appears to approach a constant value. To understand these results better, the displacements of particle positions resulting from the procedure for creating defects is examined
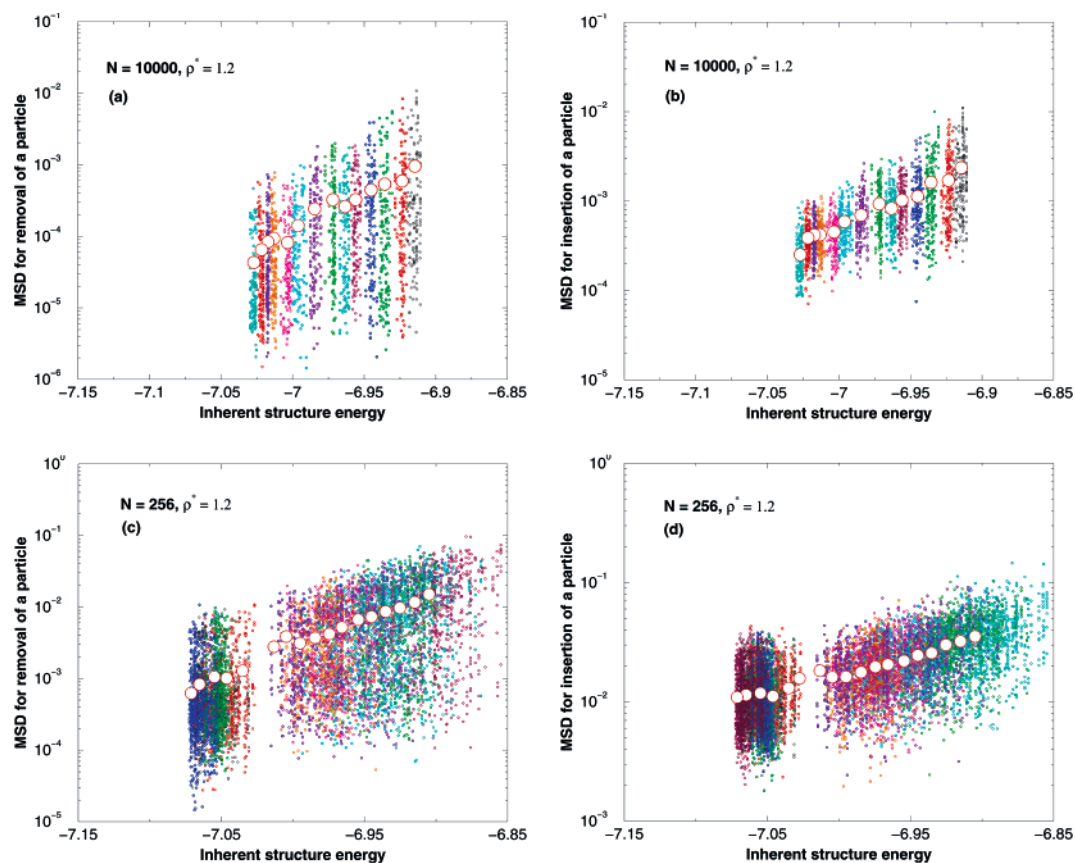
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Figure 2. Mean squared displacement resulting from the (a) removal of a particle for $N = 10000$, (b) insertion of a particle in a low-density region for $N = 10000$, (c) removal of a particle for $N = 256$, and (d) insertion of a particle in a low-density region for $N = 256$. Symbols as in Figure 1.
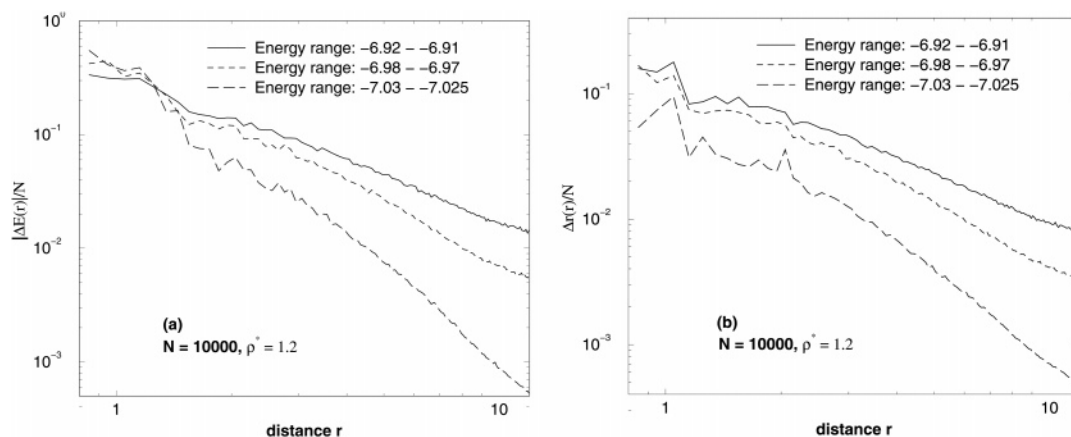

Figure 3. Average magnitude of the (a) energy cost and (b) displacement of particles, as function of distance from a particle removed, for $N = 10000$.

next. Figure 2a shows the squared displacement per particle when a particle is removed from the system (not counting the particle that is removed) for the $N = 10000$ case. Figure 2 b shows the corresponding data when the removed particle is reinserted in a new location in the system. Parts c and d of Figure 2 show the corresponding data for $N = 256$. In each case, the position of the particle that is removed or displaced is not included. It is seen that the displacement caused to the positions of particles as a result of the creation of defects decreases strongly as the inherent structure energy decreases. Indeed, instead of changing toward a *house of cards*, the inherent structures approach a *brick wall* as their energy decreases.

The same trend is confirmed when one considers the energy cost and displacement as a function of distance from the defect

site. Figure 3a shows the average of the magnitude of the energy cost from a point defect as a function of distance from the defect, for $N = 10000$. It is seen that as the energies of the inherent structures decreases, this quantity becomes shorter ranged. The same trend is demonstrated by the average of the displacement suffered by particles, as a function of distance, shown in Figure 3b. The same behavior is also observed in the case of reinsertion of the removed particle (data not shown).

6. Discussion and Summary

The results presented here confirm that the properties of localized defects and excitations as presented by Stillinger[15] are indeed valid for the model liquid studied here. However, the conclusion of the absence of a finite Kauzmann temperature

needs further evaluation. One may consider the magnitude of the effect to be expected for the rounding off of the transition due to the possibility of finite energy cost excitations, which have been argued to come into effect extremely close to the ideal glass transition in structural glass formers.[32] One may also consider whether the definition of the configurational entropy in terms of the degeneracy of inherent structures should indeed be accepted as more than a good approximation (see, e.g., ref 33). For instance, the transition between wells in a "two level system"[34] in a glass constitutes a transition between distinct inherent structures, but not, from a physical point of view, a transition between distinct glasses. Therefore, a natural question to ask concerns the possibility of grouping inherent structures together in a manner that would conform more closely to the physical notion of a glass, and how such a grouping would affect discussion of an ideal glass transition. Indeed, there has been some discussion of such *metabasins*.[35−37] Results of such an analysis as an extension of the work described in this paper will be presented in a forthcoming manuscript.

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