Stress-induced structural transformation and shear banding during simulated nanoindentation of a metallic glass

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Received 13 December 2006; received in revised form 23 March 2007; accepted 24 March 2007

Available online 25 May 2007

Abstract

Simulated nanoindentation tests on a three-dimensional model of a binary metallic glass-forming alloy reveal how the stress field and material structure interact to control deformation beneath the indenter. Initially, the stress field follows the Hertzian solution with fluctuations due to heterogeneities. Homogeneous or localized plastic deformation arises, depending on the processing history of the material. In the case of localized deformation, the first shear band initiates sub-surface, relaxing the local shear stress. The subsequent shear band morphology is observed to be rate-dependent. Deformation induced changes in material structure are characterized in terms of short-range ordering and free volume, with the former providing significantly greater signal-to-noise.

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Keywords: Molecular dynamics; Nanoindentation; Metallic glasses; Shear bands; Incipient plasticity

1. Introduction

Metallic glass (MG) is of great technological interest because of its excellent mechanical properties and its potential for wider use in structural applications and emerging nanoelectromechanical systems [1–4]. Like many nanocrystalline materials [5], however, when MG materials are mechanically loaded in unconfined testing geometries the plastic deformation localizes into shear bands while the rest of the material deforms elastically, resulting in little overall ductility. Strain localization in MG appears to arise from structural rather than thermal softening [6,7]. The temperature rise for final fracture of MG samples can be well above the melting point [7], but estimates of the temperature rise inside a shear band before failure have ranged from less than a few degrees Kelvin to thousands of degrees [6,8]. Recent reports indicate that the temperature rise is delayed with respect to the plastic deformation [9] and the width of the heated zone is much larger than the shear band width [7]. Furthermore, suppression of localized deformation by high strain rate has been demonstrated both experimentally [10] and numerically [11]. These results all provide evidence that the instability does not arise from thermal softening.

The most often considered atomistic structural softening mechanism, local free volume creation [12–15], has been measured experimentally [16], but the difficulty of measuring free volume in situ with sufficient temporal and spatial resolution has prevented its role in localized deformation from being directly confirmed experimentally. In simulations this is not an issue, but in recent studies the signal-to-noise ratio of such a signature in the density was observed to be low [9]. Although density or free volume are promising candidates, there are other more subtle changes in structure that can be quantified and related to liquid structure and glass formability [17,43,44]. For example, we have shown in previous simulations of a particular two-dimensional glass-forming system that there is depletion of short-range order (SRO) within the shear band which results in a structural softening mechanism [18]. Similar observations have been made in several three-dimensional systems as well [19]. Recently, work-hardening...
accompanied by exceptional ductility has been observed in a CuZrAl alloy, which is attributed to the existence of nanoscale structural inhomogeneities [20]. However, the precise nature of these inhomogeneities and the means by which they control the mechanical response remain to be determined. A coherent understanding of the underlying physics of deformation capable of explaining both worksoftening and work-hardening in MG and its composites is needed.

Nanoindentation has become the preferred testing method to measure the mechanical properties of bulk materials as well as nanometer scale structures [21–24] because it provides the means to apply load to a confined sample region. However, the resulting plastic deformation occurs primarily sub-surface. As a result, only the consequences of the deformation in forming external surface steps and in influencing the load–displacement curves are immediately accessible. Moreover, it has been observed that both the contact area and stress distribution within the contact deviate from continuum theory due to atomic-scale roughness making the load displacement curves difficult to analyze [25]. It is not yet clear whether contact theory holds for the stress distribution inside the bulk of the loaded sample on the nanometer scale.

Here, we present simulations of a three-dimensional binary Lennard–Jones model glass mechanically tested in a nanoindentation geometry. The incipient plasticity is characterized by the deformation morphology and stress field pattern underneath the surface. Furthermore, we quantify the structural difference between the material inside the shear bands and that outside for the sample that exhibits the most localized deformation. It is found that the degree of ductility of metallic glass is controlled by structural transformations on the atomic scale induced by deformation. These transformations are quantified in terms of free volume and SRO.

2. Simulation setup

We have performed a molecular dynamics simulation on a three-dimensional binary alloy interacting with a Wahnstrom potential [26]. The alloy consists of two species, which will be referred to as S and L for small and large, interacting via a Lennard–Jones potential of the form

$$\phi_{ij} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]$$

where $\epsilon$ represents the bonding energy and $\sigma$ provides a length scale, the distance at which the interaction energy is zero. The SS and LL bond energies are equal to that of the SL bond energy so that $\epsilon_{SS} = \epsilon_{SL} = \epsilon_{LL}$. The SS and LL length scales are related to the SL length scale by

$$\sigma_{SS} = \frac{5}{6} \sigma_{LL}, \quad \sigma_{SL} = \frac{11}{12} \sigma_{LL}$$

The reference length scale is chosen to be $\sigma_{LL}$ and the reference energy scale to be $\epsilon_{LL}$. The two types of atoms have different masses such that $m_L = 2m_0, m_S = m_0$. The reference time scale is $t_0 = \sigma_{LL} \sqrt{m_0/\epsilon_{LL}}$. $T_{MCT}$, the mode coupling temperature, was measured to be $0.57\epsilon_{LL}/k$ [27], where $k$ is the Boltzmann factor. The closest binary metallic glass, in terms of composition and atom radius ratio, is perhaps Ni$_{50}$Nb$_{50}$, with Nb being the larger species. Both quantities match the current model glass exactly. However, a less important quantity, the mass ratio for Ni$_{50}$Nb$_{50}$ is 1.6 instead of 2.0. Therefore the reduced units for this Wahnstrom system can be matched to physical units: $t_0 \approx 0.5$ ps, $\sigma_{LL} \approx 2.7$ Å, $m_0 \approx 46$ amu and $T_{MCT} \approx 1000$ K [28,29].

The glassy samples were created by starting from supercooled liquids equilibrated at 2100 K. Subsequent to equilibration, the temperature of the liquid was reduced to 6% of $T_{MCT}$ or 60 K. We employed a three-step cooling scheme to carefully control the rate of the quench at temperatures near the glass transition (Table 1). The temperature and pressure of the system were continuously reduced during each cooling step. There were three samples produced by this procedure which are referred to as samples I–III, with cooling rates increased 50-fold progressively in step II (Table 1). All three samples were then tiled eight across by three down to create a single slab of 600,000 atoms (50% Nb atoms and 50% Ni atoms) in a box of size $\sim 100 \times 35 \times 2.5$ nm$^3$ for the three samples. Periodic boundary conditions were imposed along the $X$- and $Z$-directions. This thin-slab geometry was selected to maximize the in-plane spatial dimension and to mimic the plane strain condition.

During nanoindentation tests, a frictionless cylindrical indenter was lowered into the glassy thin films as illustrated in Fig. 1. The indenter was modeled by a purely repulsive potential with the form:

$$\phi_h = \epsilon_{LL} \left[ \frac{R_h - R_i}{0.6 \sigma_{LL}} \right]^{-12}$$

where $R_h$ and $R_i$ are the indenter and film radii, respectively.

A coherent understanding of the underlying physics of deformation capable of explaining both work-softenening and work-hardening in MG and its composites is needed.

Table 1

<table>
<thead>
<tr>
<th>Cooling schedule for three samples</th>
<th>$T_{\text{start}}$ (K)</th>
<th>$T_{\text{end}}$ (K)</th>
<th>$P_{\text{start}}$ (GPa)</th>
<th>$P_{\text{end}}$ (GPa)</th>
<th>$t_{\text{cool}}$ (ps), sample I</th>
<th>$t_{\text{cool}}$ (ps), sample II</th>
<th>$t_{\text{cool}}$ (ps), sample III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step I</td>
<td>2100</td>
<td>1290</td>
<td>16.23</td>
<td>9.73</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Step II*</td>
<td>1290</td>
<td>790</td>
<td>9.73</td>
<td>5.77</td>
<td>25,000</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Step III</td>
<td>790</td>
<td>60</td>
<td>5.77</td>
<td>0.00</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

* This temperature range crosses the glass transition point where most of the TCS SRO will be formed. Therefore the structure of the final glassy sample depends most sensitively on the quenching rate of step II.
where \( r_{ii} \) is the distance between atom \( i \) and the center of the cylindrical indenter projected to the \( X-Y \) plane. \( R_i \), the radius of the indenter, was chosen to be 40 nm. The indenter acted as a material of infinite stiffness with no surface friction. The lower edge of the slab was held fixed as if the amorphous film were deposited upon a substrate of infinite stiffness. The indenter was lowered into the substrate under displacement control at a velocity of 0.54 m s\(^{-1}\) to a maximum displacement of 5.0 nm. Although these indentation rates are high compared to typical experimental rates, they are still well below the rates at which shock waves or other high-impact phenomena become important. This can be quantified by noting that the sound speed of the glassy sample is \( C_2 = 2400 \text{ms}^{-1} \) for sample I. Therefore, the indenter speed was more than three orders of magnitude smaller than the sound speed. A sound wave needs roughly 50 ps to travel along the longest spatial dimension of the specimen, the time it takes to depress our indenter by \( 0.3 \text{Å} \). During indentation, the system was maintained at a constant temperature of 6\% \( T_{MCT} \), or 60 K, using a Nose–Hoover thermostat [30,31].

3. Simulation results

3.1. Hertzian contact

The vertical force on the indenter rises elastically from zero according to Hertz theory before the inception of plastic deformation. The load follows [32]:

\[
P = \frac{\pi a^2 E^*}{4R} L_z
\]

where \( P \) is load, \( R \) is the reduced elastic constant and \( a \) is half of the projected contacted length. Atoms are considered in contact with the indenter if they are within 0.22 nm of the surface of the indenter. \( L_z \) is the length of the simulation box in the \( Z \)-direction. \( E^* \) is the reduced Young’s modulus in plain strain conditions:

\[
\frac{1}{E^*} = \frac{1}{E_s} + \frac{1}{E_i} \left( 1 - \nu_s^2 \right) + \frac{1}{E_i} \left( 1 - \nu_i^2 \right)
\]

where \( E_s \) and \( E_i \) are the elastic modulus of the sample and the indenter and \( \nu \) is the Poisson’s ratio. For sample I, \( E_s \) is measured to be 70 GPa, and \( \nu_s = 0.364 \). \( E_i \) is infinite for the rigid indenter. Fig. 2 shows the simulated load–displacement curves as well as the Hertzian solution for sample I. Although the overall load on the indenter follows Eq. (4), it is also important to determine whether the spatial distribution of the stress underneath the indenter obeys continuum elasticity. This is done by calculating the stress tensor for each volume element with dimensions \( 1.0 \times 1.0 \times 2.5 \text{nm}^3 \), over the entire system. The stress profile for \( \sigma_{xx}, \sigma_{yy} \) and maximum shear directly beneath the indenter for sample I just before the incipient plasticity is shown in Fig. 3. The result agrees well with the Hertzian solution.

![Fig. 1. Illustration of the nanoindentation testing geometry. Periodic boundary conditions (PBC) apply on the \( X-Y \) and \( Y-Z \) planes.](image1)

![Fig. 2. The load displacement curves from nanoindentation simulations performed on samples I (red), II (green) and III (blue). The dotted line shows the elastic prediction for indentation in a material for sample I. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)](image2)

![Fig. 3. Local in-plane stresses along the center line of the sample directly underneath the indenter just before the incipient of plasticity for sample I. The indenter is held at a nominal indentation depth of 1.22 nm for 100 ps in order to reduce temporal local stress fluctuations. \( Y \) is the depth away from the contact surface in the \( Y \)-direction; \( a \), the half projected contact length, is measured to be 7.2 nm and \( p_0 \), the maximum pressure, is measured to be 6.6 GPa. The solid lines are Hertzian solutions for stress in the \( X \)-direction, the \( Y \)-direction and maximum shear stress.](image3)
3.2. Incipient plasticity

As later demonstrated, sample I exhibits the most localized deformation underneath the indenter among the three samples. Therefore, we focus on the onset of plasticity in sample I. The first shear band nucleates at a displacement between ~1.24 nm and 1.30 nm. The plastic deformation causes a discontinuity on the load–displacement curve, as shown in Fig. 4a. The local atomic rearrangements can be characterized by the deviatoric shear strain using the numerical method introduced in Ref. [33]. Fig. 4b shows the plastic deformation of the system evolving from a nominal displacement of 1.22–1.27 nm, the midpoint of the nucleation process. Fig. 4c shows the plastic deformation from a nominal displacement of 1.22–1.32 nm, the end of the first nucleation of a band. The initial shear band nucleus runs from the upper-left to the lower-right following the $\alpha$-lines in the slip-line field. This initial shear band nucleus is apparently off-center and away from the locus of maximum shear. There is also very little shear band growth along this direction. Instead, the shear band propagates along the $\beta$-lines as shown in Fig. 4c. The center point of the shear band lies ~5.4 nm below the surface and is ~45° away from the vertical direction. At a nominal displacement of 1.22 nm where elasticity still holds, Hertzian theory predicts that the maximum shear will be located

![Fig. 4](image-url)

Fig. 4. (a) The load displacement curve for sample I during the formation of the first shear band; (b and c) local shear strain distribution during the nucleation of the first shear band of sample I. The local shear strain is calculated by comparing the configurations at a nominal indentation depth of 1.22 nm to those at a depth of 1.27 nm (b) and 1.22 nm to 1.32 nm (c). Black denotes 10% strain while white denotes 0% strain. The scale bar is 2.7 nm; (d) local shear stress distribution before the nucleation of the first shear band of sample I. The indenter is held at a nominal indentation depth of 1.22 nm for 100 ps in order to reduce temporal local stress fluctuations; (e) local shear stress distribution after the nucleation of the first shear band of sample I. The indenter is held at a nominal indentation depth of 1.32 nm for 100 ps in order to reduce temporal local stress fluctuations. The size and orientation of cross denotes the magnitude and direction of the maximum shear for each volume element with dimensions of 0.54 $\times$ 0.54 $\times$ 2.5 nm$^3$. The cross on the right denotes the maximum shear stress (1.99 GPa) predicted by elasticity.
at 0.78 a or 5.37 nm beneath the indenter, with a 45° orientation away from the vertical direction, both in excellent agreement with simulation results.

We also calculate the stress field before and after the first shear band nucleated to see whether there is any signature in the stress field that would predict the resulting shear band morphology. The stress field at a nominal indentation displacement of 1.22 nm is shown in Fig. 4d. The stress field fluctuates spatially due to structural heterogeneities, but there was no recognizable high shear stress region that correlated to the shear band later observed. The orientation of the shear band, however, does follow the local maximum shear direction. As shown in Fig. 4e, the stress field in the area where the shear band emerges diminished significantly, resulting in a considerably more inhomogeneous stress field. The resulting stress field is crucial for determining the morphology of further shear band development.

3.3. The effect of quenching rates

As shown in Fig. 2, sample I, produced at the slowest quench rate, exhibits the highest hardness, while sample III, produced at the fastest quench rate, exhibits the lowest. After yield, serrated flow is evident in the load displacement data for sample I while the load displacement curves are progressively smoother for the other two samples. The discontinuities in the load–displacement curves correspond directly to shear band activity [18, 34].

Fig. 5Ia, Ila and IIIa show images of the regions of high local strain in all three samples at the maximum indentation depth. The deformation morphology follows the prediction of the slip-line theory [35]. A few shear bands carry the majority of the plastic flow in sample I. Two of these grow to the surface causing surface steps and pile-ups. Sample III exhibits the majority of deformation in a region immediately beneath the indenter and the plastic flow is more evenly distributed with smaller spacing between plastic events. Sample II exhibits an intermediate behavior; the deformation is much less localized than that of the sample I, yet one shear band still propagates to the surface. The reason for this relationship between quench rate and plastic flow will be discussed further in the context of the structural analysis to follow.

3.4. The effect of strain rates

To study the strain rate effects, we have indented all three samples using two additional indenter rates, 2.7 and 13.5 m s\(^{-1}\), which are five and twenty-five times the original rate, respectively. For each sample, the load–displacement curves with different indenter rates are rather similar, with an overlapping elastic regime and only showing higher load...
for higher indenter rate at the maximum indentation depth. However, the deformation morphology is quite sensitive to the indenter rate. As shown in Fig. 6, two types of shear band arise: (1) wing-like shear bands propagating to the surface, such as the left wing of sample I for the lowest indentation rate and (2) wedge-like shear bands penetrating into the film, such as the one from upper-right to lower-left of sample I at the lowest indentation rate. For sample I, two wing-like shear bands emerge on both the left and the right for the lowest indentation rate. At the intermediate indentation rate, the right wing-like shear band disappears. At the highest indentation rate, there are no wing-like shear bands in sample I. The same holds for sample II. Indentation rate does not seem to affect the homogeneous deformation morphology of sample III.

The formation of wing-like shear bands usually leads to larger discontinuities in the load–displacement curves [36]. Therefore, it is conceivable that higher strain rate suppresses wing-like shear bands, leading to fewer discontinuities in the load–displacement curves as seen in experiments [21].

4. Structural analysis

In order to reveal the structural difference between the shear band region and the undeformed region, we used an analysis based on the idea of efficient local packing for hard spheres by quantifying the triangulated coordination shell (TCS) SRO [19] as well as the free volume. TCS SRO is defined as the fraction of atoms in configurations that maximize the tetrahedral packing as determined by a hard-sphere approximation. A criterion derived from Euler’s theorem can be written for the coordination polyhedron [37]:

$$\sum_q (6 - q)v_q = 12$$

(6)

Here, the surface coordination number, $q$, is defined for each atom in the coordination shell as the number of neighboring atoms also residing in the coordination shell; $v_q$ is the number of atoms in the coordination shell with a surface coordination number $q$. The near-neighbor cutoffs are approximately 0.39, 0.36 and 0.33 nm for the AA, AB and BB bonds, respectively, as determined by the average of the first and second peak positions in the radial distribution function. We refer to atoms with a coordination shell satisfying Eq. (6) as SRO atoms. By constraining the surface coordination number to be only 5 or 6, Frank and Kasper [37] found four of such triangulated coordination shells with coordination numbers of 12 (icosahedron), 14, 15 and 16. Such restriction of the surface coordination number is appropriate only for nearly identical atoms. Here, we do not limit the range of $q$ so that such a criterion can be applied to general binary systems. However, for the Wahnstrom system, $q$ ranges from 3 to 7.

Free volume is defined by Cohen and Turnbull [38] as follows:

$$v_f = \bar{v} - v_0$$

(7)

where $\bar{v}$ is the average volume per molecule and $v_0$ is the van der Waals volume of the molecule. We have found that our ability to resolve variations in free volume depends critically on how we define the van der Waals volume. In fact, the most straightforward definition, i.e., that the
The hard-sphere radius of the small atoms is simply $\sigma_S/2$ and the large atoms are $\sigma_L/2$, results in any free volume contrast becoming entirely lost in the noise. To obtain an appreciable signal we find that we need to define the van der Waals volume of each atom to be a spherical volume associated with the largest radius the atom could adopt without overlapping other atoms similarly approximated as spheres. Formally, we express the radius of this sphere as

$$r_i = \min_{j \in N} \left( \frac{\sigma_i}{\sigma_i + \sigma_j} d_{ij} \right)$$

where atom $j$ is one of the $N$ near neighbors of atom $i$, and $d_{ij}$ is the distance between atom $i$ and atom $j$. If the neighboring atom, $j$, is of the same species as atom $i$, then the maximum effective van der Waals radius of $i$ is half of the distance between these two atoms. If $j$ is a different species, then the upper bound on the van der Waals radius of $i$ due to atom $j$ is calculated by multiplying the interatomic separation between $i$ and $j$ by the ratio of the hard-sphere radius of $i$ to the sum of the hard-sphere radii of $i$ and $j$. For the potential used here, $\sigma_i$ takes on the value $\sigma_{LL}$ for $L$ atoms (Nb) and $\sigma_{SS}$ for $S$ atoms (Ni). The smallest value of all the candidate radii for a given atom becomes its van der Waals radius. During coarse-graining, the system is divided into a number of cells. The boundaries of each cell may cut through the spherical shells of many atoms. In that case, the van der Waals volume of each atom is partitioned among the cells accordingly. The average free volume in each cell is then defined as:

$$\bar{v}_i = v - \sum_j P_j \cdot \frac{4}{3} \pi \cdot r_i^3$$

where $v$ is the volume of each cell, $r_i$ is the hard-sphere radius for each atom and $P_j$ is the partitioning factor of each atom with respect to this specific cell. It is important to note that in this free volume characterization method we follow Cohen and Turnbull by considering all the space between the atoms. This method is different than that proposed by Sietsema and Thijsse [39], which is closer to the TCS SRO method since in that method spherical voids are constructed to exist at tetrahedral centers.

The coarse-grained distributions of the TCS SRO are shown in Fig. 5b. Iib and IIb and those of the free volume are shown in Fig. 5c, Iic and IIIc, for all three samples at the maximum indentation depth. For sample I, the TCS SRO maps clearly resemble the plastic deformation behavior, while the free volume maps only exhibit marginal features with significantly higher noise.

To evaluate the correlation of the structural signature to the deformation behavior quantitatively, we calculated the signal-to-noise ratio for both structural analysis methods. If a particular coarse-grained volume element contains a majority of atoms with a local strain larger than 10%, then the element is designated as heavily deformed. We estimated the noise to be the standard deviation of the TCS SRO or free volume in regions that are not heavily deformed, and the signal to be the absolute difference of the average SRO or free volume between the heavily deformed and not heavily deformed regions. The signal-to-noise ratio of the TCS SRO map is $\sim 50%$ higher than that of the free volume. It is not surprising that the free volume maps correlate to some degree with the TCS SRO measurements, since the latter is based on efficient packing, but the degree to which the TCS SRO maps clearly delineates the region of deformation is notable. Unlike sample I, sample III appears to be structurally homogenous and there is no structural signature resembling the deformation morphology in Fig. 5Iia. The structural feature in sample II is marginal.

The structural evolution of the material during deformation is depicted in Fig. 7. Although similar transformation is evident in both sets of histograms, the changes in the distribution of the TCS SRO is clearer. For this reason the following discussions only refer to the TCS SRO. Fig. 7 shows that due to the interplay between mechanical disordering and thermal reordering upon deformation, the structure converges toward a common flow state. Depending on the initial state, each sample fares differently: sample I undergoes significant disordering; sample II undergoes moderate disordering; and sample III undergoes reordering facilitated by plastic deformation. Since the yield stress of the sample is a positive function of the degree of TCS SRO [19], sample I can be structurally softened due to its highly ordered initial state. Consequently, sample I exhibits the most dramatic strain localization. Sample III hardens due to the deformation induced enhancement of its SRO. Therefore, plastic deformation in sample III is nearly homogenously distributed.
5. Conclusions

We present a systematic study of a model three-dimensional binary glass-forming system subjected to simulated nanoindentation. The elastic and later plastic response of the specimen is determined by the combined effects of the external mechanical force as well as the structure of the glassy material itself. The external mechanical force varies with the indenter shape, indentation rate and depths. The structure of the specimen varies sensitively with its thermal history. In the elastic regime, continuum elasticity theory holds down to a spatial scale of ~5–10 atomic spacing, below which the stress field fluctuates due to structural heterogeneities. There is no recognizable region with high shear stress that leads to the nucleation of the first shear band, which agrees with the picture that incipient plasticity comes from the instability due to structural transformations instead of stress concentration. The first shear band emerges off-center in a location that does not coincide with the location of maximum shear predicted by elasticity. However, the subsequent shear band that eventually propagates occurs at the location of maximum shear stress predicted by elasticity theories. The formation of the shear band relaxes the local shear stress field significantly, leading to a non-uniform stress field.

Quenching rate determines the structure of the glassy material, which in turn controls the qualitative nature of the plastic deformation in the material. Gradually quenched samples exhibited a higher initial degree of SRO and a consequently increased degree of strain localization. The conversion of material from ordered to disordered plays a crucial role in the softening process that emerges in glasses subjected to deformation [40–42]. Encouragingly, such structural signatures could, in principle, be obtained experimentally [17,43,44].

Acknowledgements

The authors acknowledge the support of the NSF under grant DMR-0135009 and in part under Grant No. PHY99-07949. The authors thank Drs. Naida Lacevic, Sharon Glotzer, Michael Atzmon and John Kieffer for stimulating discussions. We are also grateful for the support of the Center for Advanced Computing (CAC) at the University of Michigan.

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