Local stresses and pressures always exist in glasses. In this letter we consider their effects on the structure and structural correlations in simple glasses. We find that extreme values of local pressures are related to well defined local structures. The correlations related to these extreme stresses extend to full system size and decay as a power law with the distance. This result is especially striking, since at large scales, the total density fluctuation exhibits exponentially damped decay similar to the decay in simple liquids. Thus at medium and large distances, the atoms with extreme values of local pressures exhibit higher degree of correlation than the rest of the system. These results were found for glasses with very different short range structure, indicating their general nature.

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The nature of correlations in amorphous solids and super cooled liquids poses a fascinating question that has received a lot of attention (see e.g. [1,2]). While in crystals there is a clear cut definition of structural correlations that uses the period of the crystalline lattice, how to define structural correlation in glasses and liquids is an open question that may have various answers.

A related question is which physical quantity should be used in looking for correlations. There are various possibilities. The simplest one is to analyze the average number of atoms at a distance \( r \) from a central atom, using the radial distribution function (RDF). For simple liquids with a known atomic pair potential, the RDF can be calculated from integral equations supplemented by a closure relation and requirements for thermodynamic consistency [3]. The same methods cannot be applied for the glassy phase, because glasses are non ergodic systems. The RDFs describe average radial correlations and thus fail to touch the finer details of the structure for glasses and liquids. They tend to average out variances in the local structure.

A second option is to find some strongly varying local property of the system, like the local stress, distribution of energy wells, Voronoi volume or another local structural parameter, and use it in the calculation of conditional correlation functions. An obvious question in such case is whether these parameters are manifestations of random statistical noise, or do they exhibit a more basic nature of the glass.

Local stresses and pressures always exist in glasses. They result from variations in the local environments, which persist even in a zero-temperature glass, where all the local forces on the atoms vanish. The average stress and pressure might be zero, but the local stresses have a wide distribution [4]. The glass can be described as a discrete atomic network in which the stresses balance each other throughout the network. To understand such a network one should study the correlations between the stressed configurations. The role of the most compressed/stretched sites is an important issue. We show that they are manifestation of the basic structure of glasses. Thus they are relevant for classification of the local structural units and the degree of randomness in a glass.

The characterization of stressed networks is naturally complicated since they involve tensorial description and statistical noise. However, even without knowledge of the full details of the network, one can use the local stresses to obtain an elastic and structural description of a glass [4]. An appropriate scalar, such as the trace of the site stress tensor [4], or the local pressure [5], can be used as a parameter for the study of correlations in the glass. In this letter we present our study of the effects of extreme values of local pressures on structural correlations in simple glasses.

For mono-atomic systems where atoms interact through a pair potential \( U(\mathbf{r}_{ij}) \), where \( \mathbf{r}_{ij} \) is the distance between atoms \( i \) and \( j \), we define the term [4]

\[
J_i = \sum_j \frac{dU(\mathbf{r}_{ij})}{dr} \tag{1}
\]

as "local effective pressures" (LEP). \( J \)'s so defined are related to an effective pressure \( p_i^{eff} \) on a sphere of radius \( r \) around atom \( i \) by \( p_i^{eff} = J_i/(4\pi r^2) \). Since the local pressures depend on the choice of the cell [7], using \( J \)'s as the conditional parameter enables us to investigate directly the effect of simple elastic features on structural correlations. Unlike the forces \( \mathbf{f}_i = \sum_j \nabla U(\mathbf{r}_{ij}) \) that vanish at zero temperature, LEP as well as local pressures do not vanish in amorphous solids, even when the total (bulk) pressure is zero. The probability distribution of \( J \) is generally quite wide, although most of the atoms feel relatively small pressures (see examples in [4]).

The conditional radial pair distribution function \( n_{ij}(r) \) is defined as the average number of neighbors at distance
density as in [9]. The initial LJ liquids were prepared and equilibrated at $T = 1$. LJ glass was prepared by steepest decent quench to zero temperature glass. The initial IC liquids were prepared and equilibrated at $T = 1.6$. Glasses at various temperatures were prepared by coupling to a heat bath and then equilibrating the systems till the systematic decrease in energy stops. To subtract the effects of thermal noise, all the glasses were quenched to zero temperature by steepest descent procedure. We used 4 independent systems of IC glass and 3 independent systems of LJ glass. Results reported below are similar for all systems. All the quantities are expressed in the LJ reduced units and the distances are given in atomic distances.

First, we briefly discuss the density correlation function $\rho(r) = n(r)/4\pi r^2$. It is well known that in simple liquids, long range decay of $\rho(r)$ is (e.g. [1])

$$\rho(r) - \rho_0 \sim \exp^{-\alpha_0 r} \cos(\alpha_1 r + \phi)$$

where $\rho_0$ is the bulk value, $\alpha_0$ is decay length and $\alpha_1$ is the wavelength of the decay. For simple liquids, $\alpha_0$ depends on the temperature.

We calculated numerically the variations of $\rho(r)$ for both potentials in the liquid phase and in zero temperature glass. In liquid phase, after the first coordination shell, $\rho(r)$ decays in accord to eq. 2. Fig. 1 shows the variations in $\log(\rho(r) - \rho_0)$ for both potentials in the zero temperature glass. After a few coordination shells, the glassy correlations exhibit decays of the type of eq. 3 with $\alpha_1 \approx 1.12 \cdot 2\pi, \alpha_0 \approx 0.56$ for IC glass and $\alpha_1 \approx 1.14 \cdot 2\pi, \alpha_0 \approx 0.62$ for LJ glass at $T = 0$. A comparison with the liquids at $T = 1$ shows that the differences in the wavelength $\alpha_1$ are very minor, and the variations in the decay length $\alpha_0$ are about 20%. Thus it is apparent that density fluctuations at longer scales in glasses are similar to those in liquids. This result is in accord with the view that ‘inherent’ glasses and liquids have a very similar structure but the temperature disguises it. The main qualitative effect of the temperature on $\rho(r)$ is to smooth structural details in the 2-4 coordination shells. For similar results on different systems see in [3].

![FIG. 1. log($\rho(r) - \rho_0$) vs r for an LJ (a) and IC (b) glasses at 0k. We fit the decay exponents by the straight lines.](image)

As stated before, the probability distribution of $J$ is quite wide. Its width and shape are similar for the LJ and the IC glasses. To evaluate the effects of the stresses we calculated $n_J(r)$ for the extreme parts of the $J$ distributions (4 percent of the particles). As shown in Fig. 2, the first 3 peaks of the conditional distributions are considerably narrower than the peaks of $n_J(r)$. The peaks are shifted relative to each other by about 0.1 atomic distance. This shift in the position is a result of the different compression of the environments. The shift toward smaller $r$ for small $J$’s indicates compressed local environments whereas the shift toward larger $r$’s for large $J$’s indicates stretched local environments. The radii of those environments are consistent with effective potential estimates [3]. The shifts in $r$ in the first coordination shell are analog to variations in volume in a Voronoi scheme.

The apparent differences between LJ and IC glasses (Fig. 2a and 2b) are a manifestation of the different finer structural details. For the LJ glass, the $n_{J_2}(r)$ look similar but shifted regardless of the values of $J$, indicating the absence of a well defined local structure. However, in the IC glass case, the width of the first peak is much narrower for small $J$s than for the larger ones (a factor of about 2). The structural origin of this becomes even more apparent when the ratios between the positions of the 1st and 2nd peaks in $n_J(r)$ are calculated. In the LJ glass the ratio is $\approx 1.7$ for both high/small values of $J$. In the IC glass, the ratio is $\approx 1.7$ for small $J$s and $\approx 1.63$ for large $J$’s. The
ratio of 1.7 does not suggest any specific local structure, although it is very pronounced in IC glass, where atoms barely appear in the interval between the peaks. The 1.63 ratio corresponds to the distances between atoms on the faces of an Icosahedron! Thus the non-compressed environments are consistent with atoms that sit on the faces of empty icosahedra. Those icosahedra are the voids with radius of one atomic distance observed in [11]. On the other hand, the compressed environments have an almost full icosahedral nature, i.e. there are exactly 12 neighbors to an atom, and almost all atoms in the first neighbor shell have five nearby neighbors. The neighbors in the second peak of the compressed environments, are very sharply defined (the ratio between the stressed and compressed 2nd peaks is about 3.) They are held by the more diffuse, stretched empty icosahedral packing.

The stretched and compressed environments are spread throughout the system. Since the average number of neighbors in the glass is about 12, the two sets and their first neighbors span the whole glass. Thus the two types of extremely stressed environments define all of the glass. Note that in both glasses, the average nearest neighbor distances change as a function of the distance from these sets of atoms. Those changes happen up to second/third peak position in order to balance compressed environments with stretched ones and vice versa. This is a result of radial gradients of the stress around these atoms. The tensorial nature of the glasses is manifested in the adjustment of the local distances.

The next obvious question is whether these special environments are correlated at a longer range. To answer this question, we use the functions $dn_J(r)$, defined in eq. 2 for extreme values of $J$, to identify variations from the ‘average structure’. In Figure 3 we present $dn_J(r)$ for the compressed sites of the LJ and the IC glasses. This difference indicates the existence of excess correlations between the subset $J$ and the total lattice. Similar results have been obtained for the stretched subsets except for a phase shift in the position of the peaks. We checked that for randomly chosen sets of atoms one observes no correlations at all in $dn_J$, as is indeed expected. The intensity of the difference in short distances is larger by a factor of two in the IC glass. The correlation lengths can be seen from the integrals of $dn_J$. In the IC glass they are constant up to half of the system size (14 atomic units). On the the LJ case the correlations decay from a scale of 2-3 until they are randomized at a distance of 10.
glass. This is the probable cause for the cutoffs in the correlations in the LJ glass. The limited range of excess correlations in the LJ glass is also consistent with the lack of glass transition in the LJ glass.

The additional structure and additional correlations can also be observed in the Fourier transform which also reduce the statistical noise. We performed Fourier transforms on the sets using \( d_{nJ}(q) = \sum_j \exp(iqr_j)dn_{rJ}(r_j) \). In Figure 4 we present \( |dn_{nJ}(q)|^2 \) for lowest values of \( J \) for LJ and IC glasses. Very similar figures were obtained for \( |n_{rJ}(q)|^2 \) for highest values of \( J \). A sharp pronounced peak at \( q = q_{\text{peak}} \) exists for both glasses indicating that the period of the oscillations is about one atomic distance. In the IC glass, \( |n_{rJ}(q)|^2 \) exhibits additional structure at \( q > q_{\text{peak}} \) which is absent in the LJ glass. The intensity of the peaks in the IC glass is much stronger. Inverse transforms confirmed the previous ranges of the correlations.

![FIG. 4. \( dn_{J}(q)^2 \) for the LJ (a) and for the IC (b) glasses.](image)

The normalized conditional densities \( dn_{J}(r)/(4\pi r^2) \) decay with the radius as \( r^{-2} \). The interpretation of these results is that though the total correlations in the system are randomized there are long range correlations within the stressed networks. A possible explanation for such correlations is the existence of correlated chains.

In this letter we demonstrated how additional structural features, which are not apparent in \( n(r) \) due to its wide peaks, emerge when one considers \( n_J(r) \). For two simple glasses with very different short range structure, we have shown that whereas the averaged structural correlations have exponentially dumped decay analog to dense liquids, stronger and extended structural correlations are revealed throughout the system when one considers finer measures using LEP.

We have demonstrated the existence of two critical subsets of atoms in the structure. These subsets are not random structures but a result of interrelations between local structure (and packing) and local elastic features (see also ref. [4]). We have shown that those sets induce long range structural correlations which decay much slowly than the total radial distribution function. These finding suggest a fascinating picture of simple glasses.

There are natural extensions of this study. First, using LEP one can proceed to study more complicated glasses, where the need to identify structural correlations is even more acute. One might expect that for stronger type of local organization there might be stronger and longer range correlations. It is thus interesting to study different kind of potentials to see what are the universality classes of the decay of the conditional correlations.

It is natural to assume that atomic diffusion near the glass transition will be dominated by movements in the stretched environments. This is obviously related to the existence of free volume due to the icosahedral voids [2]. The existence of correlations between these states suggest that atomic diffusion, in temperatures slightly above the glass transition, will occur as a correlated set of jumps in the stresses network. Below the glass transition such correlated movements are inhibited. Since one expect LEPs to vary smoothly at the glass transition, this parameter is especially convenient for study and comparison of structural correlations in glasses in a wide range of temperatures as well as supper cooled liquids near glass transition.

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