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Inhomogeneity of the spatial distribution of vibrational modes in a computer model of amorphous argon

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The dynamic behavior of atoms in the more regular and more disordered regions in a molecular dynamics model of glassy argon is investigated. Partial velocity autocorrelation functions and their Fourier transforms are calculated for both types of regions. It is found that the more disordered regions are responsible for an excess density of low-frequency motions. The relation of this low-frequency excess to the so-called boson peak in the vibrational spectra of glasses is discussed.

Recently some experimental results have appeared in the physics of the amorphous state which could be interpreted as a manifestation of medium-range structure correlations[1] on the nanometer scale. Experiments on inelastic neutron scattering,[2–4] low-frequency Raman scattering (see, for example, Refs. 5 and 6), far-infrared absorption,[7,8] and data on the low-temperature specific heat[9,10] show that in the low-frequency (10–100 cm^{-1}) vibrational spectra of glasses there exists an excess density of vibrational states in comparison with the Debye one. This excess density of states forms the so-called boson peak which is a characterisic feature of the glassy state.[6] It is generally accepted that the excitations responsible for the boson peak are quasilocalized modes in which 10–100 atoms participate, i.e., their characteristic length is of the order of nanometers. This is verified by the soft potential model[11–13] and computer simulation analysis of the normal modes of a glass made up of soft spheres.[16] This is also in agreement with models in which the localization length is directly determined by the radius of the structural correlations or by the size of the glass structural inhomogeneity.[14,15]

Structural inhomogeneity on the medium-range scale seems to be of a general nature and is caused by the tendency of atoms to combine into configurations with the lowest local energy, on the one hand, and by the necessity to realize the energy minimum for the whole system, on the other hand. These two tendencies can come into conflict with one another, the result of which is a compromise structure. For example, it is known that packing in the form of a regular tetrahedron is the most efficient for four spherical atoms in three-dimensional (3D) space. However, it is impossible to fill up the whole space by such tetrahedra without gaps and overlaps. As a result, the most dense crystalline packings of spherical particles contain not only tetrahedra but also looser configurations—octahedra. On fast freezing of a glass-forming liquid no crystalline structure appears but both tendencies have to take place.

To study structural inhomogeneities of medium-range order it is convenient to use the geometrical approach of Voronoi-Delaunay.[17,18] In our recent paper[19] we investigated the form and mutual arrangements of the Delaunay simplexes in a molecular dynamics model of glassy argon and introduced the quantitative measure S for the description of the simplex shape. This parameter was defined as $S = \min(T, O)$, where T (tetrahedricity) and O (octahedricity) are the sums of the squared deviations of the edge lengths of a given simplex from those of the regular tetrahedra and quartoctahedra (a quarter of an octahedron) (see, e.g., Refs. 17, 18, and 20). The parameter S characterizes the "perfectness" of the Delaunay simplex shape. The lower the value of the parameter S the closer the shape of the Delaunay simplex to the shapes of these regular crystal types. It was shown that Delaunay simplexes which are close in shape to regular tetrahedra and quartoctahedra have a tendency to combine, forming regions of a perfect structure.[19] Between these perfect regions the packing of atoms is imperfect, i.e., the shape of the Delaunay simplexes there is far from the regular structures metioned above.

It is interesting to find out if there is a difference in the dynamic behavior of atoms in the given regions. In particular, where are the vibrations responsible for the boson peak localized? This question is reasonable because the localization length of the vibrations is of the order of the characteristic size of the structural inhomogeneity. In this paper we show that the low-frequency density of vibrational states is higher in the regions of imperfect structure. Other characteristics such as mean squared displacements of atoms and local density also demonstrate a correlation with the local order parameter S.

A molecular dynamics (MD) model of amorphous argon (500 atoms in a cube with periodic boundary conditions, interacting via a Lennard-Jones potential trun-

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cated at half the size of the cube) has been obtained from a model of a supercooled liquid ($T^* = 0.4$, $\rho^* = 0.818$) by relaxation in the NPT ensemble at constant temperature $T^* = 0.2$ and constant pressure $P = 0$. The relaxation process had 10 000 steps, each of 2×10^{-3} ps, and resulted in $\rho^* = 0.999$. The state obtained turned out to be a stable amorphous phase and just this state was used for our analysis. The MD evolution of this model during 20 000 steps did not lead to any statistically significant changes, so the structural inhomogeneities observed in the present model are not due to an incomplete relaxation process. This model has typical features of an amorphous phase: a negligibly small diffusion coefficient and a doublet splitting of the second peak of the pair correlation function. For more details, see Ref. 19.

Delaunay simplexes are very convenient for the description of structure patterns in noncrystalline systems.[20] However, in order to study physical properties we have to work with individual atoms, estimating their velocity or potential energy. The transition from simplexes to atoms is rather ambiguous because each simplex is determined by four atoms. On the other hand, each atom participates, on the average, in 24 simplexes[17] among which there can be both perfect and imperfect ones. In order to estimate the degree of perfectness for a given atom quantitatively, we propose to use the value of the parameter S averaged over all Delaunay simplexes which include this atom. Let us denote this new parameter as S_a:

$$S_a = \frac{1}{N}\sum_{k=1}^{N} S_k. \qquad (1)$$

Here N is the number of Delaunay simplexes which share the given atom and S_k is the measure of perfectness of the kth simplex. If all Delaunay simplexes containing the given atom were regular tetrahedra or quartoctahedra, the value of S_a would be equal to zero. Small values of S_a mean that all simplexes surrounding the atom resemble in their shapes regular polyhedra, or only a small number of simplexes have pronounced distortions. Thus smaller values of S_a testify to a higher perfectness of the surrounding structure.

For analysis of the spatial arrangement of atoms with various structural environments it is convenient to use the Delaunay network, which is a set of edges and vertices of all Delaunay simplexes of the given atomic system. The network vertices are the atom centers and the edges connect atoms participating in the same Delaunay simplex. To consider aggregates of atoms with the most perfect surroundings it is convenient to show (color) on the Delaunay network only those vertices (atoms) which have the S_a value less than some boundary value. Similarly, in order to study the regions with the most imperfect structure one can mark only those atoms for which S_a is greater than some boundary value.

To reduce the thermal noise, i.e., small displacements of atoms relative to their local equilibrium positions, we averaged the value of S_a for each atom over eight successive configurations separated by 0.4 ps along the time interval at which the autocorrelators were calculated. Such averaging of S_a decreases the influence of atoms located in the intermediate structure randomly fluctuating between perfect and imperfect states.

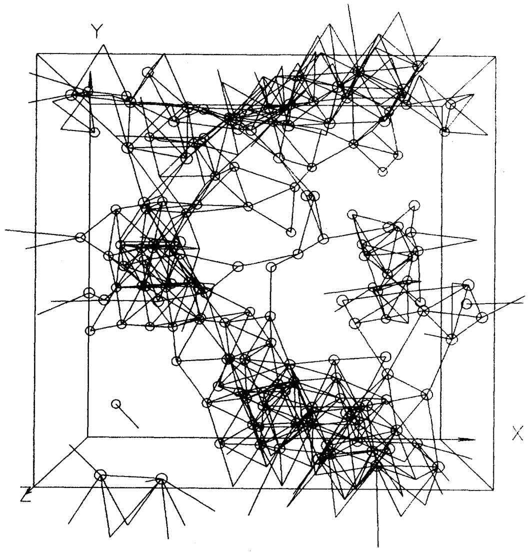

FIG. 1. Clusters of atoms with more regular (perfect) structural surroundings. 33% of all atoms with the smallest values of the characteristic S_a are shown. Circles represent the centers of atoms and bonds connect atoms belonging to the same Delaunay simplex.

In Fig. 1 vertices of the Delaunay network (and bonds connecting contiguous colored vertices) which have the value of $S_a < 0.61$ are colored. The number of such vertices corresponds to 33% of all atoms of the system. In such a manner we display aggregates of atoms with the most perfect structural surroundings. Similary, Fig. 2 shows the vertices of the network with $S_a > 0.75$. This boundary value has been chosen to provide the same percentage of atoms (33%) with the most imperfect structure. Figures 1 and 2 demonstrate a substantial inho-

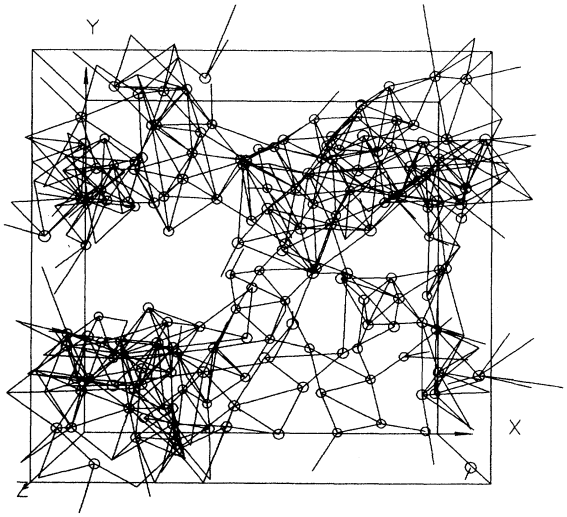

FIG. 2. Clusters of atoms with more disordered (imperfect) structural surroundings. 33% of all atoms with the greatest values of S_a are shown.

mogeneity in the spatial locations of the regions with definite types of structural order. There is a pronounced tendency for both types of atoms to group together. Localization regions are separated in the space but they are not compact "blobs,"[15] rather they are branched, mutually interwoven infinite clusters. The characteristic length for the regions of both types can be estimated as 3–5 interatomic distances, i.e., about 1–2 nm. This value determines the correlation length of structural inhomogeneities in the model.

As a characteristic of the dynamic behavior of the atoms let us consider the velocity autocorrelation function

$$K(\tau) = \langle \mathbf{v}(t)\mathbf{v}(t+\tau)\rangle_{t,n}, \qquad (2)$$

where the averaging is performed/calculated conventionally over all atoms of the system. However, this function can also be calculated for an individual atom or for any group of atoms. We calculated $K(\tau)$ for 20 000 time steps of 2×10^{-3} ps. In Fig. 3 we present an average function $K(\tau)$ for all atoms and partial autocorrelators for the perfect and imperfect atoms determined in Figs. 1 and 2. The behavior of $K(\tau)$ is typical for an amorphous phase of spherical atoms.[21] For atoms of a perfect structure one can see the deep first minimum and an excess over the average value at times 0.6–1.2 ps. In contrast, for atoms belonging to imperfect regions this function demonstrates a relatively shallow first minimum and then goes lower than the average function. Such behavior of the partial velocity autocorrelators implies relatively rigid surroundings for perfect atoms and softer ones for the imperfect.

The velocity autocorrelation function is connected by Fourier transformation with the spectrum of the vibrational density of states:

$$Z(\omega) = \frac{1}{\pi}\int_0^\infty \cos(\omega\tau)K(\tau)d\tau. \qquad (3)$$

A total spectrum for our model is shown in Fig. 4. It is a bump-shaped curve, typical for glasses, modulated by small oscillations. These oscillations are intrinsic features of the model. The analysis shows that they are not the cutoff effect: some fluctuations of $K(\tau)$ outside the upper integration limit in (3), which was 4 ps, provide rather small deviations from zero in $Z(0)$ but do not influence the overall spectrum shape. The most interesting peculiarity of the spectrum is a pronounced shoulder at low frequencies, 3 ps^{-1}. This shoulder is absent in the spectrum of crystalline argon whose MD model of 500 atoms with periodic boundary conditions has also been created and analyzed. The shoulder looks just like an excess density of vibrational states in the neutron spectra of glasses. One can see something like this feature in the spectra of model glasses in Fig. 4 of Ref. 21 and in Fig. 7 of Ref. 16.

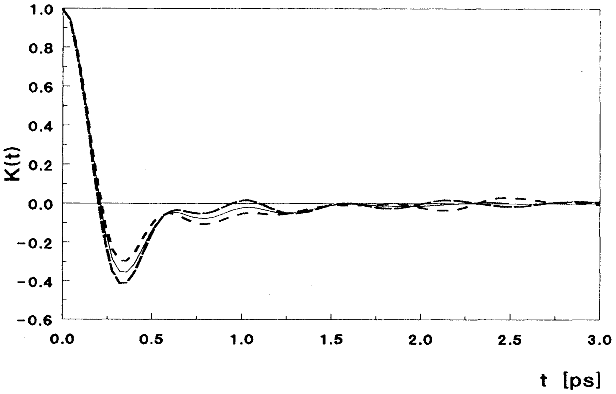

FIG. 3. Velocity autocorrelation functions. The solid line relates to the total system; the long-dashed line to atoms in regions of perfect structure; the short-dashed line to atoms in regions of imperfect structure.

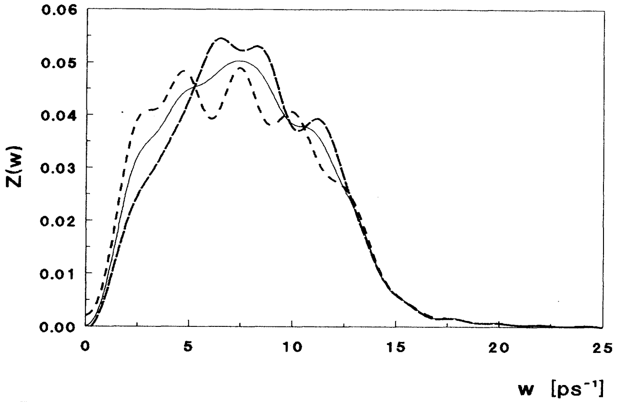

FIG. 4. Fourier transforms of the velocity autocorrelation functions. The solid line represents the total system, the long-dashed line atoms of the perfect structure, and the short-dashed line atoms of the imperfect structure.

The structural meaning of this shoulder can be revealed by the partial spectra of the vibrational density of states calculated as a Fourier transform of the partial velocity autocorrelation functions. We see that the low-frequency shoulder increases in the partial spectrum of the imperfect structure (Fig. 4). This means that the low-frequency modes are distributed preferably on the atoms with imperfect surroundings and are less characteristic of atoms with perfect surroundings. Note that atoms with an undetermined structure (the remaining 33% of atoms which are not attributed either to perfect or to imperfect regions) demonstrate a partial spectrum similar to the averaged one.

It is significant that the given low-frequency peak in the partial $Z(\omega)$ cannot be considered as an element of the spectrum oscillations which one observes in Fig. 4. When a subsystem of 33% of atoms was chosen at random, the partial spectra $Z(\omega)$ had similar oscillations as well. However, the mean of these oscillations for random subsystems strictly coincides with the average spectrum. On the other hand, for an imperfect structure (Fig. 4) the mean of oscillations in the partial spectrum goes above the average curve in the low-frequency range. We think the oscillations reflect some real peculiarities of the partial density of vibrational states of the clusters caused by their complicated geometry.

We have chosen one third of the total number of atoms to represent the regions of perfect structure (and an equal number for imperfect ones) in order to demonstrate more clearly their spatial arrangement (Figs. 1 and 2). Also carried out were calculations with other boundary values of S_a to select from 10% to 50% of atoms for both structural groups. In all cases the dynamical behavior is similar to that shown in Figs. 3 and 4. It is worth noting only that the "boson" peak seems more pronounced for an imperfect structure at lower percentages.

The development of the geometrical description of a disordered structure based on Voronoi and Delaunay tesselations makes it possible to investigate structural peculiarities quantitatively by computer simulations of an amorphous phase. The regions of perfect structure revealed by the analysis are noncrystalline although they are made up of elementary configurations inherent in crystals.[19] Their arrangement shows no translational symmetry and they are realized only on a nanometer scale. Aggregates of atoms with imperfect surroundings are made up of simplicial atomic configurations which are far from perfect. However, these regions of imperfect structure cannot be considered as defects of the structure in the usual sense. There is no pronounced physical boundary between these two types of regions and they have nearly the same local atomic density. Indeed, the average Voronoi polyhedron volume for atoms with imperfect surroundings exceeds the volume for atoms with perfect surroundings only by 4%. We found also that mean square atomic displacements in the imperfect regions are twice those in perfect regions.

In conclusion, the analysis of partial velocity autocorrelation functions calculated for atoms in the perfect and imperfect surroundings shows that there is inhomogeneity in the spatial distribution of low-frequency vibrations: they are localized preferably in the regions with more disordered structure. This result supports the soft potential model[11,13] in which the soft modes arise due to fluctuations of microscopical structural parameters of the glass. The regions of imperfect structure are places where soft modes may be realized. However, more analysis is needed to discuss the relation between the boson peak and the revealed tendency of atoms in more disordered configurations to contribute to lower-frequency motions.

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