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Construction of amorphous structures

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Conditions for modeling amorphous structures from first principles are minimization of the free energy and a certain degree of continuity with the liquid state. We achieve the minimization of the total energy due to pair potentials or pseudopotentials by a variational method and the use of a seed structure as boundary condition. The seed structure, which has to be selected from several possible structures according to the shape of the pseudopotential is more or less propagated by these so-constructed structures. A rather flat pseudopotential is required for a bcc solution, while a sharper one results in an amorphous structure which extends the icosahedron structure. Planar cuts, the pair-distribution function, packing efficiency, energy, and coordination number are derived for this fairly stable complex structure. Numerous excited states of low energy are shown to occur because of inhomogeneities and defects such as vacancies.

INTRODUCTION

For the last thirty years the number and variety of the observed amorphous or glassy systems have increased so much that now one can speak of a fourth state of matter as already introduced by Gibbs and DiMarzio.[1] Because of the improvement of the cooling techniques, amorphous systems are observed even in the cases of simple metal atoms interacting via simple pseudopotentials.[2] The definition of an amorphous structure which can generate numerous low-energy excited states,[1,3] and thus introduces nearly continuously the liquid state, implies several conditions. Even when one neglects the dynamic conditions the amorphous structure is submitted to two conditions. First, because it is a metastable structure, i.e., physically stable, at 0 K it must minimize the free energy $F=E-TS$ and, therefore, the total energy E. Second, it must have a large number of low-lying excited states in order to have a large entropy and to give rise to a minimum of free energy at a finite temperature. The previous studies of amorphous structures have emphasized one of these two features. Dense random packing (DRP) emphasizes the energy minimization by means of geometrical remarks with hard spheres and later with soft spheres.[4–6] On the other hand, Monte Carlo techniques used in molecular dynamics enabled several authors to obtain liquid structures and then to freeze them.[7] In their case one may not be sure of the complete relaxation, and the structure is quite complex, while in the case of DRP the choice of the initial structure is rather arbitrary and the number of the low-lying excited states is not very well known. In this paper we use a systematic method to obtain metastable states at 0 K and determine a solution which satisfies a stable cluster nucleation. Some excited states of this solution are studied and the evidence for a great number of low-energy excited states is given. The large number of these states is due to the abundance of large holes in the structure in spite of its density and this is quite in accordance with the free-volume theory.[3]

Section I deals with the principles of the calculation while results are given in Sec. II. In Sec. III we study some excited states and make some concluding remarks.

I. PRINCIPLES OF CALCULATION

A. Total-energy minimization

In terms of the local density $n(\vec{x})$ and of the pair potential or pseudopotential $V(\vec{x})$ the total energy E reads

$$E=\frac{1}{2}\sum_{i,j} V(\vec{x}_j-\vec{x}_i)n(\vec{x}_i)n(\vec{x}_j)\ , \qquad (1)$$

where the $\vec{x}_i$ belong to a simple-cubic lattice of lattice parameter arbitrarily small.

One can use a continuum representation of the atomic density $n(\vec{x})$ and then make infinitesimal variations of n. Or, one can express the Hamiltonian in a local form on $n(\vec{x})$ and its derivatives while keeping the discrete character of x. Then one can admit infinitesimal Dirac-function-like variations of the density for this generalized Landau-Ginzburg Hamiltonian. In both cases the result of the variational method is the equation[8]

$$n(\vec{k})V(\vec{k})=0 \tag{2}$$

in the reciprocal space. This equation neglects the boundary conditions which give other contributions. Its general solution reads[9]

$$n(\vec{x})=\sum_j C_j \exp(i\vec{k}_j\cdot\vec{x}) , \tag{3}$$

where the constants C_j are defined for the nodes $\vec{k}_j$ of the Fourier transform $V(\vec{k})$ of the pair potential $V(\vec{x})$.

One can notice the continuity of the solution obtained for the density. As it is classical when going from discrete to continuous problems,[10] one will take the location $\vec{x}_{\max}$ of the maxima of $n(\vec{x})$ to make the discrete density $N(\vec{x})$ of the network:

$$N(\vec{x})=\sum_{\{x_{\max}\}} \delta(\vec{x}-\vec{x}_{\max}) . \tag{4}$$

Because of the variational method used here, $N(\vec{x})$ which is not very different from $n(\vec{x})$ will still give rise to an extremum value of E the total energy.

B. Boundary condition on a cluster

The boundary condition is expected to determine which among the C_j and k_j's of Eq. (3) are the compatible ones. In the case of a radial potential such as the LJ one used here, there is a complete angular indeterminacy for the $\vec{k}_j$, and the restriction to a few parameters will be quite convenient for the sake of simplicity. We choose to express the boundary conditions on a small stable cluster because in the picture of the nearly continuous glassy transition,[3] a series of stable or metastable configurations is expected to occur from the first nucleation step to the amorphous "ground state": the amorphous phylum. Equation (3) defines at the same time a series of configurations of different sizes, so this choice of boundary condition ensures a clear link between the first step of nucleation and the last ones of the amorphous structure.

Now the choice of a small stable cluster is easily reduced to a choice among a few ones because of the size and stability conditions. Namely, the simplest clusters are the nine-atom cluster "BCC," which is the unit cell of the bcc lattice, and four 13-atom clusters, which correspond to the fcc unit cell (FCC), one hexagonal cell (H), and two pentagonal structures: one with a planar symmetry (P) and the other one with a central symmetry (I). Among the 13-atom cluster Frank[11] demonstrated that if some relaxation is allowed, i.e., if the pair potential is not too sharp, the icosahedral structure I is the stable one because it is the more isotropic one and a central contraction can be used to improve the coordination of all the peripheral atoms at the same time. The central coordination number N_c is 12 while N_c for the peripheral atoms is 5. If the pair potential is sharper, fcc and hexagonal clusters are more stable. Now in the bcc structure, the coordination number is 14 if the pair potential is rather flat and allows a 13% central contraction. After the eight or six first neighbors located at a distance $a\sqrt{3}/2$ of one typical atom, there are six or eight next-nearest atoms located at a distance a, which is the bcc lattice parameter, so a smoother potential gives rise preferably to a bcc structure with a lattice spacing larger by a few percent than the optimal interatomic distance deduced from the potential minimum. In other words, there are three types of solidification of the materials which have a purely radial pseudopotential: If the potential well is soft, they crystallize with the bcc structure; if it is sharper, they produce stable pentagonal clusters; if it is very sharp, they crystallize in the fcc or hexagonal structures. Such a remark is well in accordance with the observations.[12] As has been already noticed by Alexander and MacTague,[13] the high-temperature crystal structures of all the metallic elements on the left-hand side of the Periodic Table (groups I*A*, II*A*, III*B*—VI*B*), with the exception of Mg together with almost all the lanthanides and actinides, are known to be bcc near the melting line at low pressure. Most, however, transform to other structures at low temperature. Altogether there are at least 40 elements with bcc as their high-temperature phase.

There are also indications that monocrystalline solids, presumably representing the situation when crystal nucleation was inhibited, tend to have icosahedral local structure.[14] There is a close agreement with the previous prediction because metallic elements with a few external electrons are expected to have a radial smooth pseudopotential and that the pseudopotential is softened at high temperature because of the thermal dilation.

Here we want to study the typical amorphous structure so we choose the icosahedron I for defining the boundary condition. We use a Lennard-Jones (L-J) potential,

$$V(\vec{x})=\left[\frac{x}{a}\right]^{-12}-2\left[\frac{x}{a}\right]^{-6}, \qquad (5)$$

with a for atomic unit length a.u., which allows some relaxation to occur. In order to define the pertinent $\vec{k}_j$ we made a Fourier transform of the density of I and classified its maximum values. To each node of the transform of L-J potential corresponds a sphere in the three-dimensional reciprocal space. On the first and on the second sphere ($k_1 \approx 2\pi/a$ and $k_2 \approx 4\pi/a$), one finds twice twelve peaks of the Fourier transform of I, which are, of course, dual of the twelve summits of I. Because of convenience it appears more useful to introduce in Eq. (3) the peaks of the second sphere ($k=13.85$) than the first one. But the practical result of the construction does not depend on this choice. When selecting only twelve $\vec{k}_j$ we select one special order of interference. Because of the symmetry of the icosahedron I all C_j have the same modulus and a good choice is to take them all equal to 1, so the density given by Eq. (3) reduces to a sum of twelve exponential terms, i.e., because of the central symmetry to a sum of six cosine terms. Each of these cosine terms has a maximum value 1 reached for a series of regularly spaced parallel planes. The maximum values of this equation will define a simple-cubic lattice in a six-dimensional space.

C. Operating rules

As already said, we take the maximum value of $n(\vec{x})$ in order to define a discrete network, i.e., it defines a projection from a six-dimensional simple-cubic lattice into a three-dimensional amorphous structure. This involves the loss of some of the maxima. The convenient rule used in our numerical calculations if two locations of maxima of n are closer than $d=0.9a$ is to take into account only the one with the highest value of n. The list of sites starts at the origin and then on spherical shells of increasing radii. So we built a 1681-atom cluster computed on the IRIS 80 of CII Honeywell Bull at Université Paris VII. This 1681-atom cluster A defines a part of an amorphous structure. A contains 663 peripheral atoms and so it is convenient to define a central cluster C of 1018 atoms which is the internal part of A.

Thus too closed a contact is avoided, but holes may appear because of the selection. Such holes were sought in a systematic way. There are 12 holes $0.96a$ in diameter at a distance $1.96a$ from the origin and 20 at a distance $3.26a$ from the origin. One can define a completed cluster CC of 1050 atoms and a completed amorphous cluster CA of 1713 atoms.

The practical interest of these structures lies in their stability which can be checked from relaxation processes such as used hereafter. In these relaxation studies, at each step the forces $\vec{F}_i=-\partial E/\partial \vec{r}_i$ are calculated on each site, then all sites are moved by the respective displacements $\vec{\delta}_i=\lambda\vec{F}_i$ and the energy E is computed for this configuration. After a smooth decrease of the energy E during the first steps of relaxation, E becomes constant, i.e., we reached a rather correct metastable state with relative fluctuations of about 10^{-5}.

One can notice that this relaxation process does not break the symmetry of the initial state, and thus the convergence is quite rapid. We define two kinds of relaxation according to different boundary conditions, i.e., different external hydrostatic pressures. In the cluster relaxation all atoms relax; we speak of a relaxed configuration X' obtained from an initial one X. In the amorphous relaxation, the peripheral atoms remain blocked and the others relax; we speak of a relaxed configuration X''. The interest of these small perturbations of the initial configuration and of their shifts after a relaxation process is an accurate determination of the actual amorphous ground state. As a matter of fact, during the relaxation process we admit a strong screening effect realistic in metallic alloys by cutting off the L-J interaction after a distance 1.3.

II. RESULTS

A. Planar cuts

Different planar cuts regularly spaced and perpendicular to a given direction, here pentagonal axis Oz of the 13-atom cluster, are given. Each atom or element has been taken as a sphere of diameter D ($=0.96$ a.u.) because in the 13-atom cluster I there is a central contraction and the shortest distance between atoms is $0.96a$.[11] These small spheres do not overlap. The choice of the plane direction brings out the extension of the pentagonal structure. These planes have the equations $z=h$, with the respective

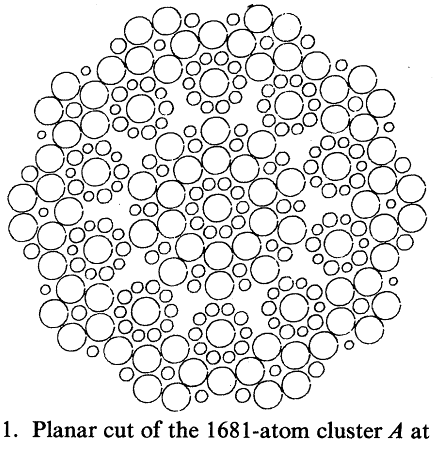

FIG. 1. Planar cut of the 1681-atom cluster A at $h=0$.

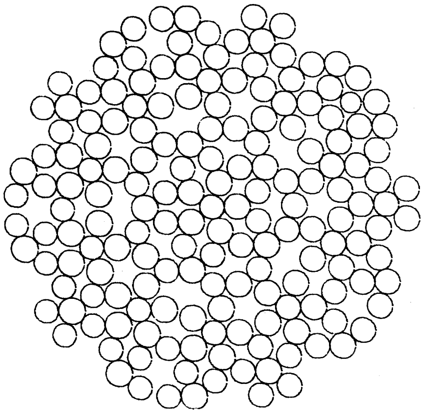

FIG. 2. Planar cut of the 1681-atom cluster A at $h=0.25D$.

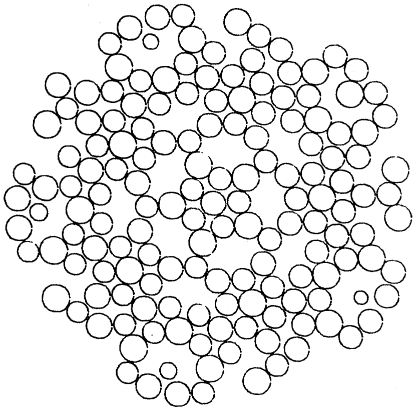

FIG. 4. Planar cut of A at $h=0.75D=0.72$ a.u.

values: Fig. 1, $h=0$; Fig. 2, $h=D/4$; Fig. 3, $h=D/2$; Fig. 4, $h=3D/4$. These figures show the cluster A. One has to point out that similar clusters of about 500 atoms have been calculated with a center far from the origin, i.e., (10,10,10) or (20,20,20). One sees the propagation of the fivefold symmetry without that of a translational periodicity. When one tries to define some packing units[6] for the network, one may distinguish icosahedra I and 43-atom clusters M which are shown in Fig. 5. In the surroundings of this cluster M there are many other M's which are imbricated together and thus incomplete, as can be shown in the central cut reported in Fig. 1.

The relaxation process tends towards a better balance of forces, i.e., a reduction of the inhomogeneities. This is shown in the planar cuts of CA′, the completed amorphous cluster after amorphous relaxation given in Figs. 6–9. These cuts are along the $z=h$ plane at different levels h as in Figs. 1–4. One can notice that the general features of the initial configuration A, such as the fivefold symmetry, remain conserved. It is a proof of the stability of this configuration and of the fivefold symmetry as recently observed in simulated liquids.[15] We did not reproduce all the data on these different perturbations of the initial configuration A, but we want to point out two main features of the relaxation process. As a consequence of the relaxation process

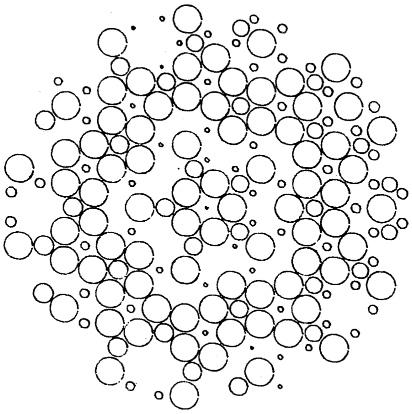

FIG. 3. Planar cut of the 1681-atom cluster A at $h=0.5D$.

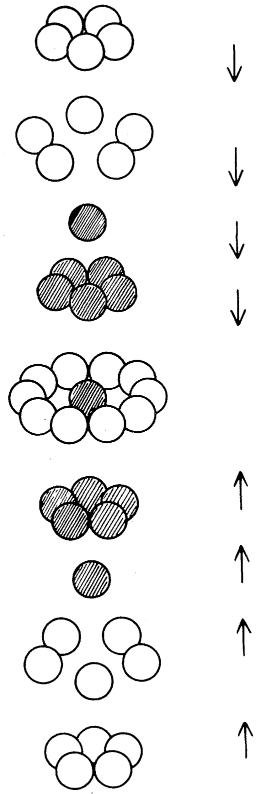

FIG. 5. Stacking sequence of the 43-atom cluster according Oz axis. Hatched atoms belong to the internal 13-atom icosahedron.

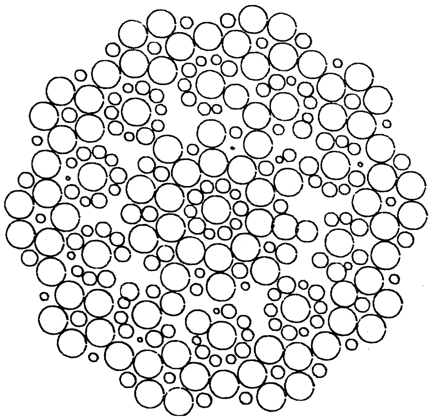

FIG. 6. Planar cut of the relaxed completed amorphous cluster CA′ of 1713 atoms with $h=0$.

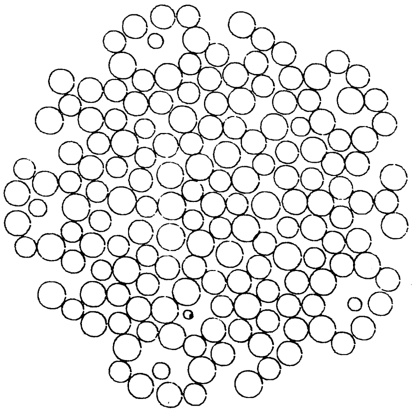

FIG. 8. Planar cut of CA′ with $h=0.75D=0.72$ a.u.

there is a general dilation of the configuration, especially for the cluster relaxation when large holes have been filled, i.e., CA′. And the configurations A and A'' are the closer ones, i.e., A is nearly insensitive to an amorphous relaxation. In other words, A is stable.

One can notice different kinds of inhomogeneities. First of all, at the global level of blocks of about 50 atoms there are packing units rather well defined, which are joined by interfaces more badly defined. This is due to the impossibility of building a regular set with fivefold symmetry as is well known.[16] Moreover, such a superstructure of inhomogeneities has been observed in the results of Egami and coworkers on relaxed frozen liquid structures.[7] On the local point of view there is an inhomogeneity of the coordination number N_c. By setting the minimal coordination distance at 1.3 we obtain for CA and CA″ the following results: 80% of the 1000 inner atoms have eleven nearest neighbors while about 10% have twelve or ten nearest neighbors. A few inner atoms have nine nearest neighbors. The high level of binding in this structure and the absence of bcc clusters may be noticed.

B. PDF and RDF

The pair-distribution function (PDF) and radial-distribution function (RDF) of the computed models are displayed as histograms with a 0.01-a.u. pitch. The results with the cluster C of 1018 atoms without relaxation, extracted from the cluster A of 1681 atoms, are plotted on Fig. 10 for the PDF and Fig. 11 for the RDF. The first peak on these figures lies at a distance 0.96 a.u. This justifies the extensive

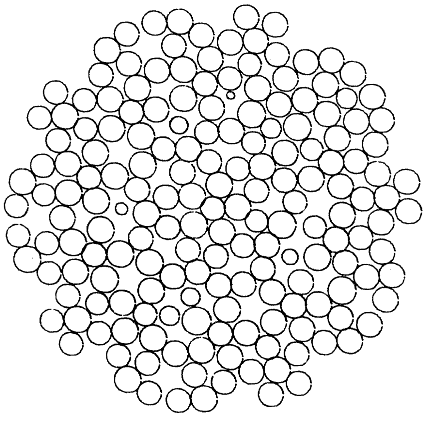

FIG. 7. Planar cut of CA′ with $h=0.25D=0.24$ a.u.

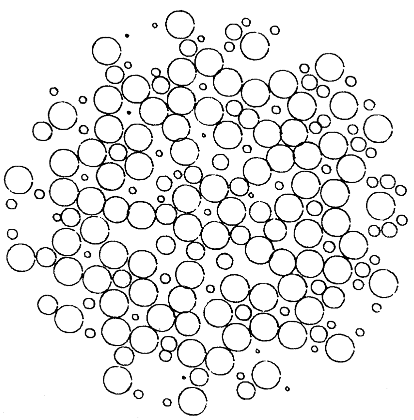

FIG. 9. Planar cut of CA′ with $h=0.5D=0.48$ a.u.

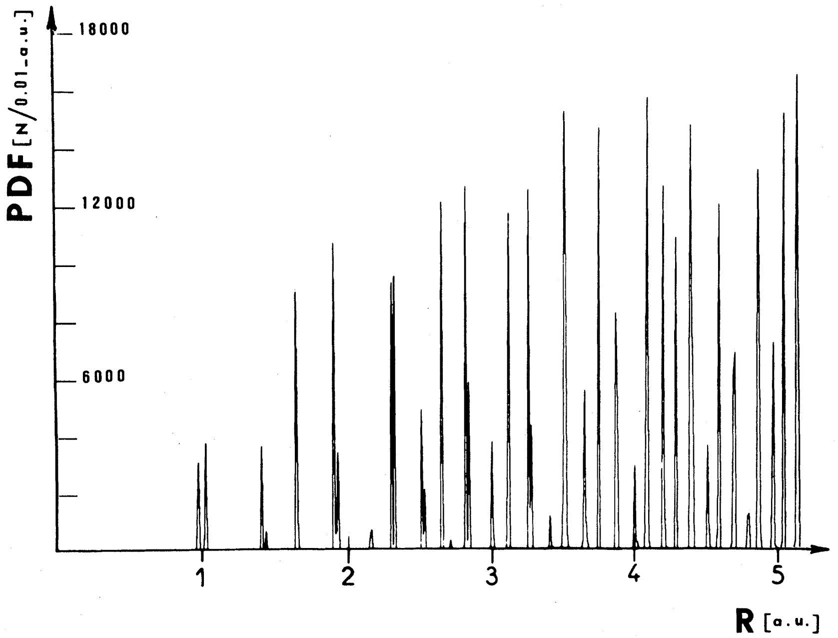

FIG. 10. Pair-distribution function (PDF) as a function of distance in atomic units for the 1018-atom cluster *C*.

use of this value for the contracted diameter, especially when comparing with the hard-sphere problem and in the planar cuts. The other peaks of the PDF occur at 1.4 a.u. with two distinct peaks at 1.40, 1.43, 1.64, and 1.90 a.u., which is distinct from 1.93, 2.16, 2.30, and 2.32 a.u. These peaks are rather sharp but their positions are typical of amorphous structures.[6]

On the PDF curve given in Fig. 10, the two peaks near 1 a.u. at 0.96 and 1.02 are characteristic of the icosahedral structure with a central contraction and an external dilation. The distances 1.64 and 1.90 or 1.92 a.u. are the other characteristics of the icosahedron. The peak which appears at 1.40 a.u. is characteristic of the internal structure of the 43-atom cluster shown in Fig. 5. The same distance separates the atoms of the internal icosahedron from those of the external crown of 30 atoms. Thus the intensity of this peak at 1.4 is rather weak compared with the intensity of such a peak for a fcc structure where this distance stands between next-nearest neighbors. Thus this amorphous structure is very different from the fcc one. Other peaks of the 43-atom cluster shown in Fig. 5 are located at 2.30,

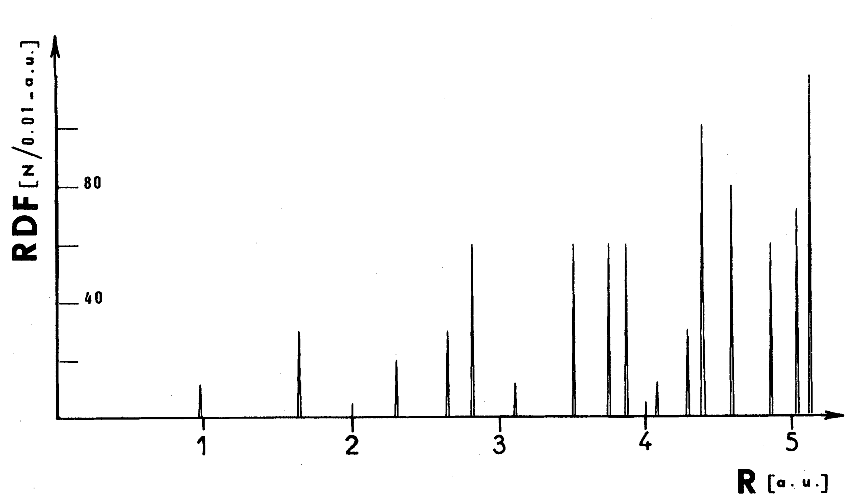

FIG. 11. Radial-distribution function (RDF) as a function of distance in atomic units, for the 1018-atom cluster *C*.

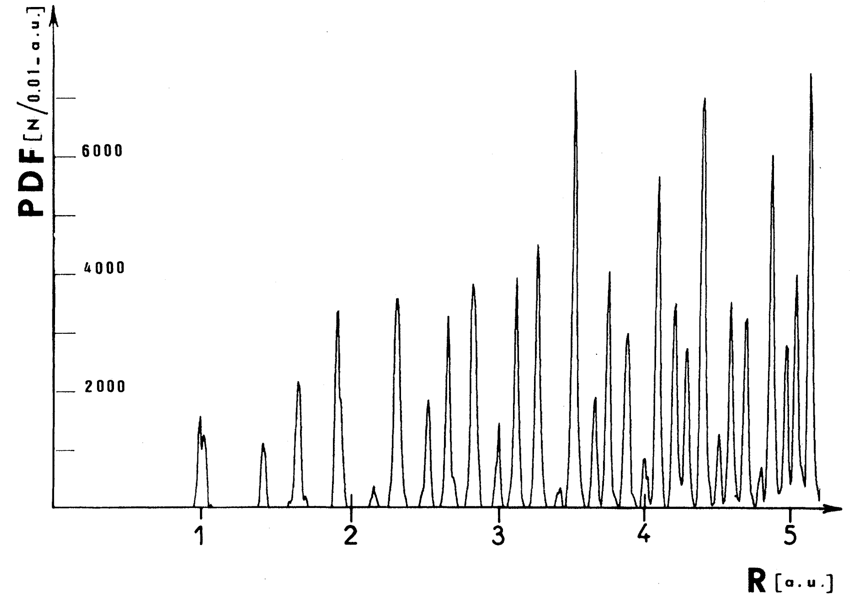

FIG. 12. PDF of the central part of the relaxed amorphous cluster A'' in atomic units.

2.32, 2.51, 2.65, 2.84, 3.11, and 3.27 a.u. All these peaks appear in Fig. 10. This confirms that these 43-atom clusters are amorphous. The PDF and RDF of the amorphous cluster A' are shown in Figs. 12 and 13. One can see a weak broadening of the lines because of randomization and a general shift of the peaks towards higher distances because of the expected dilation. As a matter of fact, the experimental results, such as those quotes by Cargill[6] for instance, show a stronger broadening. And the usual theoretical results show stronger broadening than in the experimental situation. However, here we are speaking of a cluster of N atoms, so there can be only N^2 distances between pairs of atoms, while in numerous theoretical results the size of the cluster was increased by a large number of reflections on

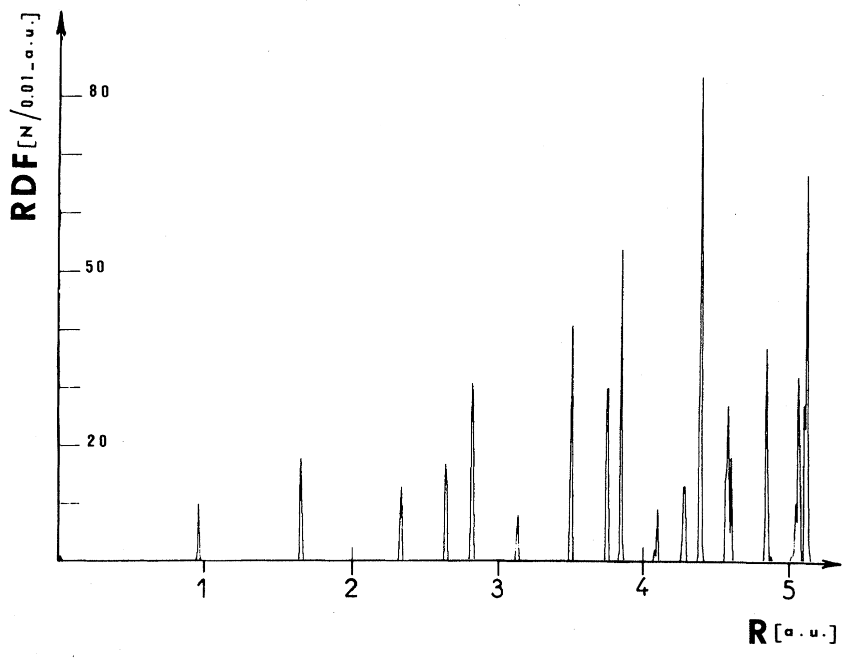

FIG. 13. RDF of the central part of the relaxed amorphous cluster A'' in atomic units.

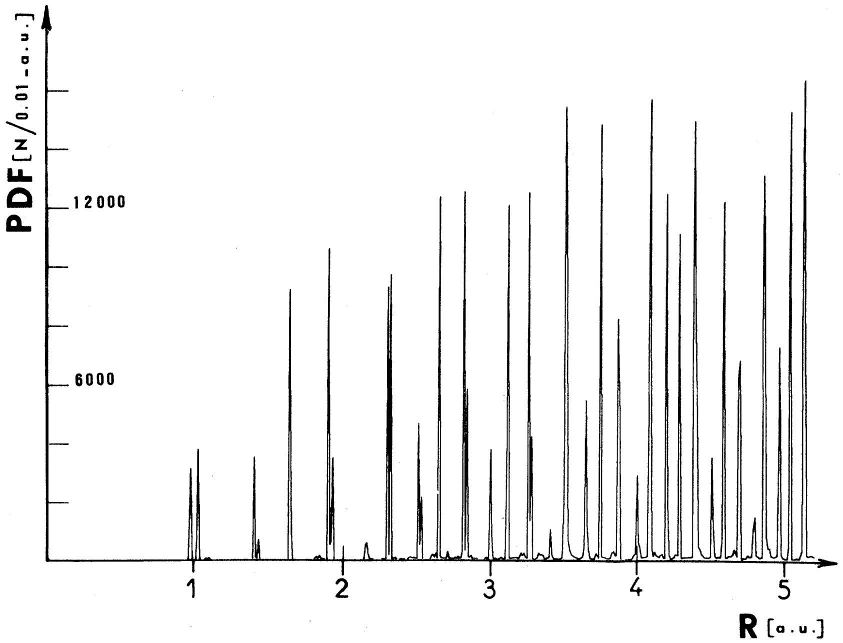

FIG. 14. PDF of the completed cluster CC of 1018 atoms, in atomic units.

the walls of boundaries. This process increases tremendously N and introduces a modulation in the reciprocal space which tends to modulate the calculated PDF. Thus there is no contradiction between these results and the other ones deduced either from other models of clusters or from experimental observations. Moreover, the observation of diffraction patterns from electron microscopy on small samples of Au (Ref. 17) or Ni (Ref. 18) prepared at low temperatures indicates a well-organized system with narrow diffraction peaks. These observations are interpreted on the basis of a 55-atom cluster with a fivefold symmetry. It seemed to us they can be interpreted on the basis of our larger clusters. In any

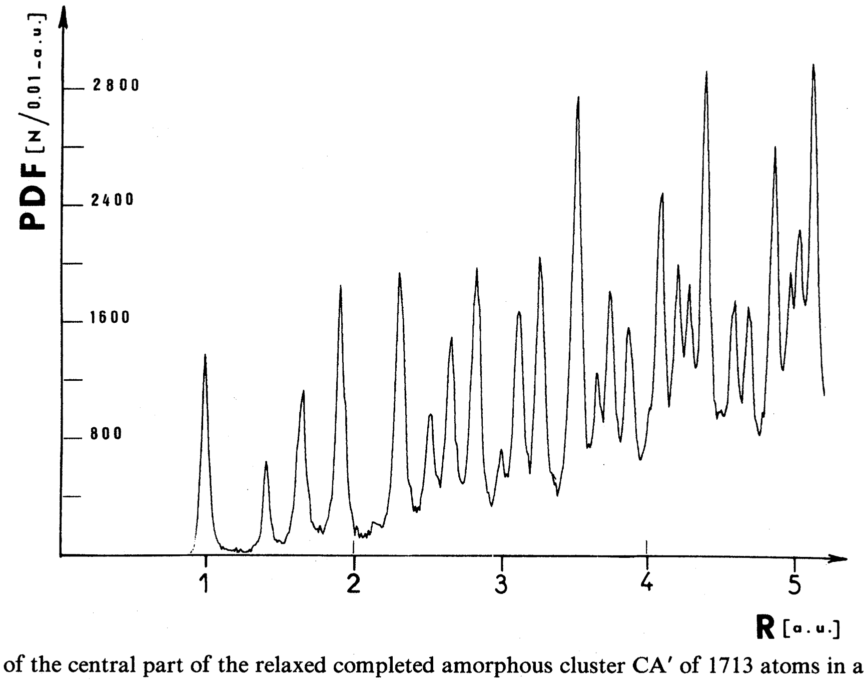

FIG. 15. PDF of the central part of the relaxed completed amorphous cluster CA′ of 1713 atoms in atomic units.

event, it is a proof for the existence of such long-range networks.

When filling the holes with extra atoms, new interatomic distances appear as shown in Fig. 14 where the PDF of the completed cluster CC is shown. This gives rise to a number of extra small peaks in this figure. After a cluster relaxation one obtains CA′, the PDF of which is plotted down in Fig. 15. Here both the dilation and the stability of the main features are obvious.

C. Density

Density is a main feature of structural models. Although this model does not deal with hard spheres, it is interesting to calculate the packing efficiency of the hard-sphere model with which it can be associated. Because of the previous remarks on the peaks on the PDF, we choose hard spheres with a diameter of 0.96 a.u. while considerations based upon the potential minimum give a diameter of 1 a.u., which will give a density value higher by about 12%. The packing efficiency is calculated according to the method used by Mason[19] and by Adams and Matheson[20] for spheres $S(R)$ centered at the origin as a function of their radius R. First the atoms lying completely in $S(R)$ are counted. Then for all the atoms cut by $S(R)$, the volume of the atom inside $S(R)$ is computed. The volume common to two spheres of radii r and r_0 with a distance d between the centers is

$$V=(\pi/3)[2r^3+2r_0^3+d^3-3d(a^2-r_0^2)]\ , \qquad (6)$$

where

$$a=(r^2+d^2-r_0^2)/2d$$

and

$$r>r_0\ .$$

The density calculated for the initial cluster A of 1681 atoms is plotted in Fig. 16. After some classical Friedel-type oscillations of decreasing amplitude, there is a maximum of density of 0.614 for a radius of 4.93 a.u., then a slight decrease to 0.59 for 6 a.u. When one takes into account the amorphous relaxation, there is a slight change of the density curve but only for radii smaller than 2 a.u. In the case of a cluster relaxation, i.e., with free boundaries, there is a small decrease of the density as shown in Fig. 16. This decrease corresponds to the dilation already shown. These results are close to those obtained for hard spheres by Scott and Kilgour,[21] Matheson,[22] and Ichikawa.[23] They are about 5% lower than the admitted limit for a hard-sphere packing: 0.64. We are dealing with a soft-sphere model, so it is quite reasonable to admit a diameter unity for r_0 instead of the used 0.96 a.u. and to introduce the interstitial atoms. Then, as shown in Fig. 17, the density reaches a value of 0.722 for a radius of 4.90 a.u. and decreases to a value of 0.68 for a radius 6 a.u. This packing efficiency is quite close to that obtained by Egami *et al.*,[17] 0.73 using soft spheres and smaller interstices. In other words, this model, easily tractable because of its analyticity, consistent with the assumption of local order, is practically as efficient for the density as the best random models now available.

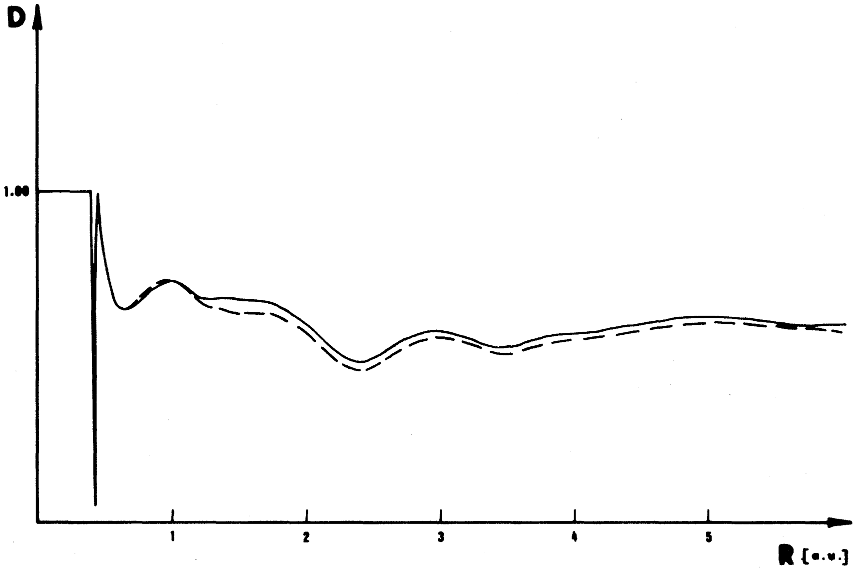

FIG. 16. Atomic density $D(R)$ as a function of the distance R from the origin for spheres $S(R)$ centered on the origin, with hard-sphere diameter 0.96 a.u. The solid line is the plot of the density of the 1681-atom cluster A while by the dashed line one considers the fully relaxed 1013-atom cluster C'.

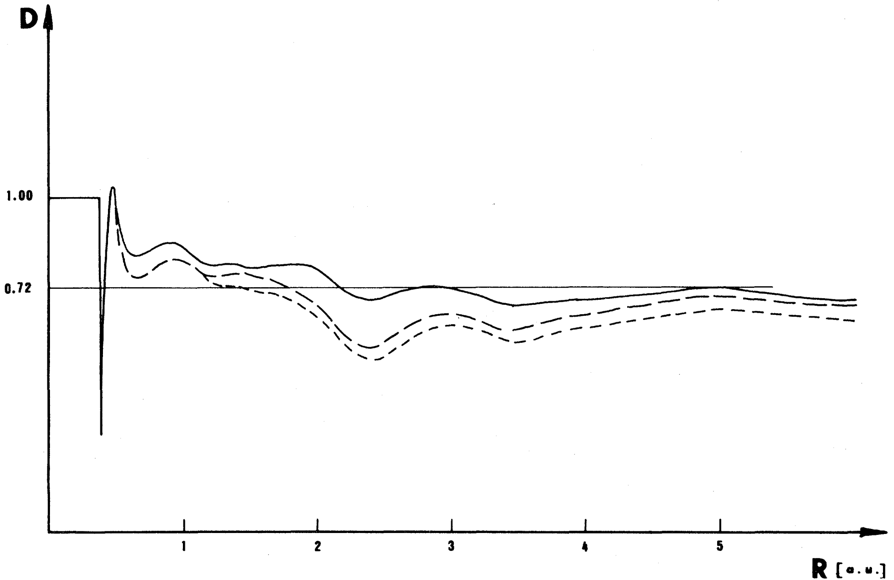

FIG. 17. Atomic density $D(R)$ for spheres $S(R)$ centered at the origin, with hard-sphere diameter 1 a.u. The solid line shows the density of the relaxed completed amorphous cluster CA′ while clusters A and C' are shown by the long- and short-dashed line, respectively. One notes the uniformity of the solid curve, which is due to the filling of holes near $R=2$ and 3 a.u. The crystalline value of D is 0.74.

D. Interaction energy

This model has been defined theoretically by a minimization of the total energy in order to obtain stable and metastable configurations. As has been shown in the previous sections dealing with the relaxation process, one obtains from the theoretical considerations quite metastable configurations which are relaxed after a few cycles with small changes only. Of course, it is of interest to consider the actual value of the total energy of interaction. It has been shown that in the last steps of relaxation the total energy fluctuates with an amplitude of tenths of an energy unit, where the energy unit (e.u.) is the binding energy of two atoms interacting via the Lennard-Jones potential when placed at the potential minimum, i.e., distant from 1 a.u. Thus the fluctuation operates on only 0.1 bond for the total cluster, i.e., 10^{-4} bond for each atom.

In order to avoid the boundary effect when measuring the total energy, we consider a central cluster, the centers of which are located in a sphere centered at the origin and of radius 6 a.u. Thus such centers have their full number of neighbors. Here we screened the Lennard-Jones potential totally at a distance of 1.5 a.u. The alternative of the total energy when changing this cutoff values from 1.5 to 1.3 a.u. is of about 10% in relative values. For the 1018 central centers taken into A'', the total energy is $-11\,296$ e.u. which gives a mean energy per atom of -11.2 e.u. For the 1050 central centers taken into the completed CA′, the total energy is 11 165 e.u., with a mean energy per atom of -10.65 e.u. The occupancy of interstitial sites by the same atoms does not modify strongly the mean energy. Of course, one can expect that with smaller atoms this occupancy will be more favorable, even for smaller interstices. Different potentials have been used by workers working on these sphere packings, so the comparisons are not so easy. Thus the value of 11 e.u. is a mean bonding energy per atom, which means there is an average number of eleven neighbors per atom. It confirms the value 11 for the coordination number N_c. As for the other features, the result is consistent with a dense nonuniform packing, and this complex structure looks like a random one.

CONCLUDING REMARKS

From the interaction given by a pair potential, and by means of a variational method, with reference to an initial 13-atom cluster we built a metastable structure. This structure follows the symmetry of the seed structure which has been chosen to be the icosahedron in conformity with the deductions of stability for the small cluster.[11] As a matter of fact, this structure propagates the seed structure with the necessary transition regions. Moreover, the imbrication of amorphous units which are icosahedra and systems of 43 atoms is well proved and occurs in a rather complex manner which seems to have been unattainable from simple considerations.

In order to study the stability of this amorphous structure we have considered several other structures which can be derived from the same one or by adjunction of some vacancies or by a relaxation process due to external forces. In other words, we have studied several accessible excited states, and it has been proved that their energies lie in a narrow range, exactly within a relative fluctuation of 5% of the binding energy of the cluster. Thus one deals with low-lying excited states as expected for an amorphous structure.[1,3] Practically amorphous structures of isotropic atoms are obtained from a rapid cooling of the liquid state; the amorphous structure keeps a memory of this high-temperature state because of the nonequilibrium process. From a freezing temperature T_f, one can define a Boltzmann factor $\exp(-U/NkT_f)$ for an excited state of N atoms of excitation energy U. Thus the occurrence of such excited structures in a large sample is quite probable. This explains the extra modulation of the experimental PDF and RDF. Finally, before a study of the excited states of this amorphous structure can be complete, one must notice the evidence for other low-energy excited electronic states. As a matter of fact, this amorphous structure is fairly nonuniform; hence crystalline fields cannot be expected to be uniform, and locally excited electronic states occur. This is an explanation for the well-known local fluctuations of anisotropy in magnetic amorphous materials.[24] Quite obviously the occurrence of many low-energy excited states is due to the inhomogeneities which include vacancies, i.e., to a free-volume effect as in the free-volume theory of the glassy state.[3] Finally the amorphous structure described here and its excited state define a "phylum" to the liquid state when the effective pseudopotential is radial and displays a well neither too sharp nor too flat.

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