

Characterization of free volume in atomic models of metallic glasses

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An analysis of interatomic space is presented for atomic models of amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ in the as-quenched state and in an annealed state. Interstitial voids are constructed as clusters of overlapping spheres that are placed in Delauney tetrahedra. It is found that the difference between as-quenched and annealed $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ predominantly lies in the quantity of the relatively large voids. More specifically, the number of voids surrounded by nine or less atoms ("intrinsic voids") increases, whereas the number of voids surrounded by ten or more atoms ("holes") strongly decreases. The interpretation is that during structural relaxation the holes break up into two or more intrinsic voids. Since in the annealed state the diffusivity is a factor 25 smaller than in the as-quenched state, the diffusion process is explained in terms of the occurrence of holes. The analysis of the volumes and shapes of the holes shows that (1) the volume distribution becomes narrower on structural relaxation, and (2) although holes with a volume of one atomic volume or more do occur, their shape is strongly nonspherical, and they certainly do not resemble crystalline vacancies. It is furthermore argued that, because of the importance of holes for the atomic mobility, the hole volume is to be regarded as the free volume appearing in the well-known free-volume model by Turnbull and Cohen.

I. INTRODUCTION

The structure of metallic glasses combines two properties that make these materials particularly interesting: a packing fraction as high as in most crystalline phases, and a liquidlike disorder in atomic coordinations. The question about the mechanism of atomic mobility (diffusion, viscous flow) in such structures has not yet been unambiguously answered. The atomic mobility is too strongly restricted by the high density and low temperature to be caused by liquidlike mechanisms like hydrodynamic flow. On the other hand, defects that often play a role for the atomic mobility in crystals, like vacancies or dislocations, cannot well be envisioned to be present. It is likely that a more or less spherical hole as large as a vacancy will not be stable in a disordered structure.¹ Still, the experimentally observed diffusivity in metallic glasses is not vanishing,² nor is their viscosity infinite.³ The atomic mobility also leads to changes in the disordered structure when the material is subjected to moderately high temperatures. At temperatures low enough to avoid crystallization, the properties of metallic glasses change significantly, notably the diffusivity and the viscosity. The relation between the kinetics of this structural relaxation and the atomic mobility has been treated in a number of studies.⁴ In general, the atomic mobility decreases when an as-quenched metallic glass is heat treated.^{2,3} For relatively stable glasses a metastable equilibrium state can be reached, in which the atomic mobility is no longer time dependent. Viscosity measurements during temperature-cycling experiments⁵ show that the equilibrium state is temperature dependent.

The concept of defects in metallic glasses appears in the application of the free-volume theory to this problem.^{6,7} A defect is defined as a site at which the free volume exceeds a critical value, which is on the order of

an atomic volume. According to the model, the atomic mobility, reflected by the viscosity and the diffusivity, is assumed to be proportional to the concentration of defects; for instance, when an as-quenched metallic glass is annealed, the decreasing diffusivity is caused by a decreasing defect concentration. Although this theory has been successful in the description of observations of structural relaxation,^{5,8} some questions remain: (1) What is the actual identity of a defect? (2) Why does a single defect appear to cause diffusive motion, whereas a pair of defects is needed for viscous flow?^{9,10} (3) Why does the diffusivity not reflect the temperature dependence of the equilibrium state?⁹ This paper deals primarily with the first two questions. Aiming to characterize free volume and defects in metallic glasses on a microscopic scale, we analyze two sets of atomic models of amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$, one for the as-quenched state and one for a relaxed state.

The changes in the disordered structure during structural relaxation can be studied by diffraction experiments. The most extensive study of this type has been performed by Schaal, Lamparter, and Steeb,¹¹ applying isotopic substitution in neutron diffraction to amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ in the as-quenched state and after annealing treatments. These data form a useful starting point for a study on the relation between structure and atomic mobility, since one of the annealing treatments that was applied (2 h at 570 K) reduces the atomic mobility by a factor of 25. This can be derived from diffusivity data for Au in amorphous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$,⁹ under the assumption that the composition difference and the type of diffusor have no strong influence. More generally, structural-relaxation studies on mobility related properties in a large array of different metallic glasses have shown great similarities. It can therefore be assumed that the present analysis is not pertinent to just $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$, but expresses

the general characteristics of metallic glasses.

Pusztai, Sietsma, and Thijsse¹² have derived atomic models of the atomic structure of $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ from Schaal's diffraction data by means of the reverse Monte Carlo technique.¹³ The resulting atomic structure and the changes therein induced by structural relaxation have been described in two previous papers.^{12,14} Although it was found that the atomic-volume distributions, especially for Pd atoms, respond to structural relaxation in a way that is consistent with the free-volume theory, no attention was paid to the identity and occurrence of defects. In the present paper we will study the characteristics of the interatomic space, primarily in search of a realistic picture of defects. With this goal in mind, interatomic voids are identified and analyzed in terms of the number of atoms surrounding them, their volume, and their shape. The relation with the atomic mobility in metallic glasses is discussed.

II. THE STRUCTURE OF INTERATOMIC SPACE

Eight of the 4096-atom models presented in Ref. 14 were used in the present study on amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$: four for the as-quenched state and four for the state after annealing for 2 h at 570 K. Each set of four models has been obtained by application of the reverse Monte Carlo (RMC) simulation technique to the experimental reduced radial distribution function $G(r)$, the structure factor $S(Q)$, the pair-correlation function $g(r)$, and the renormalized reduced radial distribution function $\Gamma(r) = G(r) / \langle |G(r)| \rangle$, where $\langle \dots \rangle$ denotes averaging over the r range.¹⁵ For both the as-quenched and the relaxed state a density of 75 atoms/nm³ has been used, resulting in an edge length of 3.794 nm for the cubic simulation box. The effect of structural relaxation on the atomic structure is exemplified in Fig. 1, giving the partial reduced radial distribution function $G_{\text{PdPd}}(r)$. For comparison, a random packing of 4096 hard Pd, Ni, and P spheres (RPHS), having the same density as the models for the metallic glass, is also included in this study. The RPHS model has been constructed using the same set of smallest allowed interatomic distances as the one used in

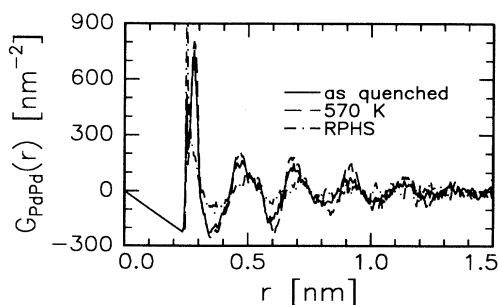


FIG. 1. Pd-Pd partial reduced radial distribution functions $G_{\text{PdPd}}(r)$ for the atomic models of amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$. Results for the as-quenched state and the 570 K state are obtained by the RMC simulation on $G(r)$. RPHS denotes a random packing model of hard spheres.

the RMC simulations.¹² Its $G_{\text{PdPd}}(r)$ is also shown in Fig. 1.

The definition of interatomic voids that is adopted in this paper has been recently proposed by Voloshin and Naberukin.¹⁶ In each atomic model a Voronoi tessellation is constructed. In order to account for the difference in atomic radii, the radical-plane method¹⁷ is applied, using atomic radii of 0.140 nm for Pd, 0.126 nm for Ni, and 0.090 nm for P.¹² The Voronoi tessellation is the starting point for the characterization of interatomic voids. To each vertex of the Voronoi network the largest possible sphere is assigned that can be fit in at that position without overlapping any of the neighboring atoms.^{16,18} These vertex spheres represent the open space inside all tetrahedral groups of four atoms (Delaunay tetrahedrons). The interconnection of the vertex spheres is an important characteristic of the interatomic space. In analogy with Ref. 16, vertex spheres are defined as being connected, and thereby forming a "void," if the separation of their centers is less than the sum of their radii. In other words: two vertices are part of the same void, if they touch or overlap, i.e.,

$$|\mathbf{r}_i - \mathbf{r}_j| \leq (1-f)(R_i + R_j), \quad (1)$$

with $\mathbf{r}_i, \mathbf{r}_j$ the position vectors of the vertices i and j , and R_i, R_j the radii of the spheres assigned to them. In this work, the overlap factor f is taken as zero, which means that spheres that merely touch belong to the same void. The choice $f=0$ is somewhat arbitrary, but is consistent with the idea that, if one would remove an atom, the resulting void should include both the volume of this atom and the voids adjacent to it. As a test, the procedure was applied to molecular-dynamics fcc crystals containing $N=1372$ atoms. It correctly yielded $2N$ tetrahedral voids and N octahedral voids. Temperature vibrations caused incidental splitting of some of the octahedral voids, which indicates that $f=0$ is not too small.

This definition of voids does not include all the space between the atoms. About 20% of the total volume is unaccounted for. More refined constructions are possible, such as centering spheres away from the vertices, or iteratively adding increasingly smaller spheres (e.g., Ref. 19). Nevertheless, the present method is believed to give a useful schematization of the interatomic space, and to provide a sufficiently realistic local measure of the available translational freedom of the atoms.

Each void can be characterized by two numbers: N_a , which is the number of atoms surrounding the void, and N_v , the number of vertices that make up the void. A simple example ($N_a=5, N_v=2$) is given in Fig. 2. In addition to these numbers we will also consider the volumes and shapes of the voids. Since the problem to determine analytically the total volume of an arbitrary number of spheres overlapping in an arbitrary way is quite complex, the void volumes are approximated by subdividing the simulation box into cubes of edge length 0.0076 nm (volume 0.44×10^{-6} nm³), and counting how many cubes each void contains. In this calculation, the uncertainty in the void volumes v is determined by the number of cubes that are only partly inside the void. The present cubes

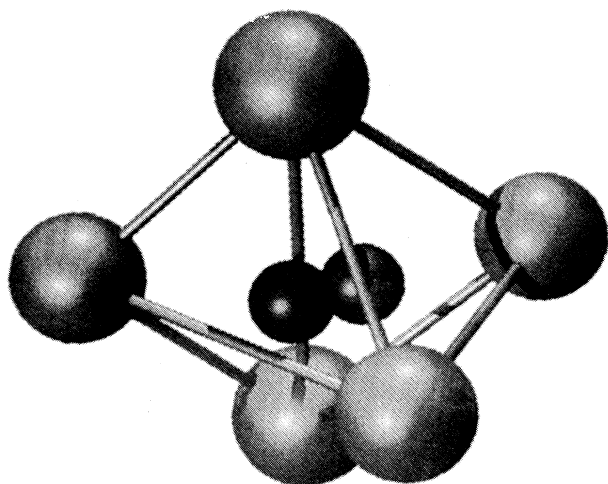


FIG. 2. Example of a void consisting of two vertex spheres ($N_v=2$, the small spheres), surrounded by five atoms ($N_a=5$, the larger spheres). The atoms are shown at 40% of their size.

lead to a relative uncertainty of about 0.009 for small voids, with $v \approx 0.3 \times 10^{-3} \text{ nm}^3$, and of about 0.002 for large voids, having $v \approx 20 \times 10^{-3} \text{ nm}^3$. These uncertainties are considerably smaller than the bin sizes used for the volume distributions, and hence can be ignored.

The shape of a void is characterized by a sphericity parameter ϕ , defined as the ratio of the volume of the void and the volume of its circumscribing sphere. For a perfectly spherical void ϕ has the value 1, for pancake or cigar shapes ϕ assumes smaller values. For instance, for three identical, touching spheres in a triangle $\phi=0.375$, for four spheres in a tetrahedron $\phi=0.5$. For a straight row of n touching spheres $\phi=n^{-2}$.

III. RESULTS

Numerical results of the analysis of the interatomic space are given in Table I. It is seen that all numbers follow a monotonous trend in the sequence RPHS-AQ-570 K. This clearly shows that the annealing treatment has enhanced the degree of ordering in the glass. In all cases the difference between RPHS and as-quenched (AQ) is larger than the difference between AQ and 570 K. The enhanced order in the atomic structure after structural relaxation is also visible in Fig. 1.

The structure of the 570 K state differs from the as-quenched structure in a lower number of vertices (Table I). Surprisingly, the number of voids increases slightly (10%) during structural relaxation, but their cumulative volume decreases from about 12.3% of the total simulation-box volume to 11.5%. Both the number and the volume of the large voids, called "holes" (these are

TABLE I. Results of the analysis of interatomic space in nine atomic models of amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$. RPHS, random packing of hard spheres; AQ, four RMC models for the as-quenched state; 570 K, four RMC models for the annealed state. The last column gives the function that was used in the RMC procedure to obtain the model. The parameter N_a denotes the number of atoms surrounding a void; holes are voids with $N_a \geq 10$.

	RPHS	AQ	570 K	RMC fit function
Number of atoms	4 096	4 096	4 096	
Number of vertices		25 079	24 746	$G(r)$
		25 098	24 744	$S(Q)$
		25 090	24 786	$\Gamma(r)$
		25 074	24 721	$g(r)$
		25 884	25 085	24 749
Number of voids		10 863	11 997	$G(r)$
		11 055	12 075	$S(Q)$
		10 728	11 723	$\Gamma(r)$
		10 921	12 157	$g(r)$
		7 153	10 892	11 988
Volume fraction of the voids			0.1227	$G(r)$
			0.1220	$S(Q)$
			0.1232	$\Gamma(r)$
			0.1222	$g(r)$
		0.1482	0.1225	0.1147
Number of holes		354	232	$G(r)$
		358	219	$S(Q)$
		344	253	$\Gamma(r)$
		351	221	$g(r)$
		623	351	231
Total hole volume (10^{-3} nm^3)		2 113	1 135	$G(r)$
		2 090	1 064	$S(Q)$
		2 024	1 226	$\Gamma(r)$
		2 074	1 063	$g(r)$
		4 793	2 075	1 122

voids with $N_a \geq 10$, a choice that will be explained below decrease considerably during structural relaxation.

The characterization of the voids by the number of atoms N_a and the number of vertices N_v leads to the distributions of Fig. 3. This figure gives the number of occurrences of voids, cumulated over the four models, as a function of N_a , subdivided for different values of N_v . For both the as-quenched state and the 570 K state a particular value of N_v is seen to be dominant for the voids with $N_a \leq 8$. In Fig. 4, showing the differences between the as-quenched and the 570 K state, this dominance is seen to become stronger upon structural relaxation. Also, for $N_a=9$ especially the ($N_v=9$) voids increase in number. An important feature in Fig. 4 is the zero crossing between $N_a=9$ and $N_a=10$. Voids with $N_a \leq 9$ increase in number upon structural relaxation, voids with $N_a \geq 10$ decrease in number. Figure 4 provides a strong clue to the type of change that voids undergo during structural relaxation: large voids break up into smaller ones, and small voids show a stronger preference for a distinct shape, i.e., a particular value for N_v . The net effect is that the total number of voids increases, but their volume (both the average volume per void and the total volume)

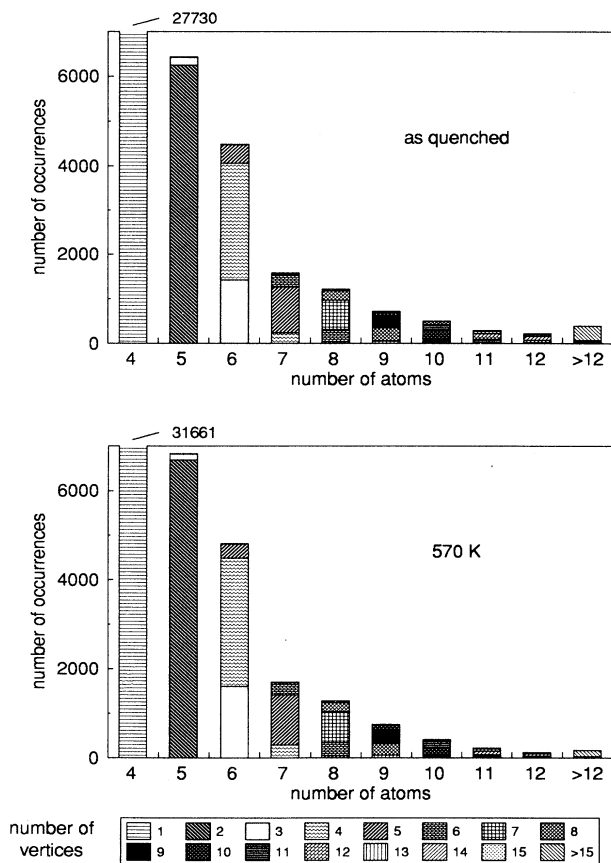


FIG. 3. Cumulative number of voids in four models of as quenched $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ (upper frame) and annealed $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ (lower frame) as a function of N_a , the number of atoms surrounding a void. Different shadings give the contribution of voids built up by different numbers of vertex spheres N_v .

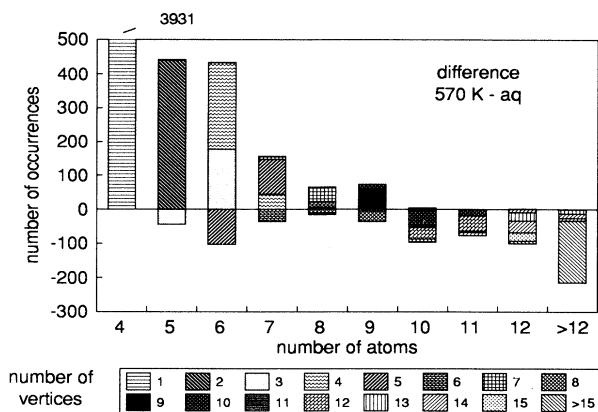


FIG. 4. Differences in numbers of voids between annealed and as-quenched $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$. A positive number means a greater number in the annealed state.

decreases. The persistent presence of the ($N_a \leq 9$) voids indicates that these voids should be seen as *intrinsic voids*, i.e., as voids that are intrinsically present in a dense packing of spheres. They are in this respect comparable to tetrahedral and octahedral voids in fcc crystals. This distinction between voids with $N_a \leq 9$ and voids with $N_a \geq 10$ is the reason that we use different terms for them. In view of the difference in character and in behavior between intrinsic voids and holes, we will treat them separately in the remainder of this paper.

Intrinsic voids. Arbitrarily chosen examples of the six preferential types of intrinsic voids are shown in Fig. 5. The top row gives the three most abundant intrinsic voids: the tetrahedral void ($N_a=4, N_v=1$), two tetrahedral voids merged into one ($N_a=5, N_v=2$), and the octahedral void ($N_a=6, N_v=4$). Figure 5 bears resemblance to Bernal's set of five canonical holes,²⁰ but it is not the same. A straightforward explanation of the differences is difficult, since Bernal only considered a monoatomic system and used the shape of the network of surrounding atoms as a classification criterion, rather than the number of surrounding atoms.

Figure 6 shows the volume distributions of the intrinsic voids for the as-quenched state and the 570 K state. It is found that they are not significantly different. This supports the interpretation that these small voids are "intrinsic" to the metallic glass structure, whatever its state of ordering. A somewhat different volume distribution is found for the RPHS model, notably in the range $v < 0.3 \times 10^{-3} \text{ nm}^3$. Since all the voids in this range are single or double tetrahedral voids, and 80% of these voids fall within this volume range, Fig. 6 shows that a distinct difference exists between the tetrahedral packing in a completely random structure and in structures having the short-range ordering of metallic glasses.

The total amount of undefined space increases from 19.2% in the as-quenched state to 19.9% in the 570 K state. Although no further specification can be made, the stable volume distributions of intrinsic voids indicate that no important changes in the character of the undefined

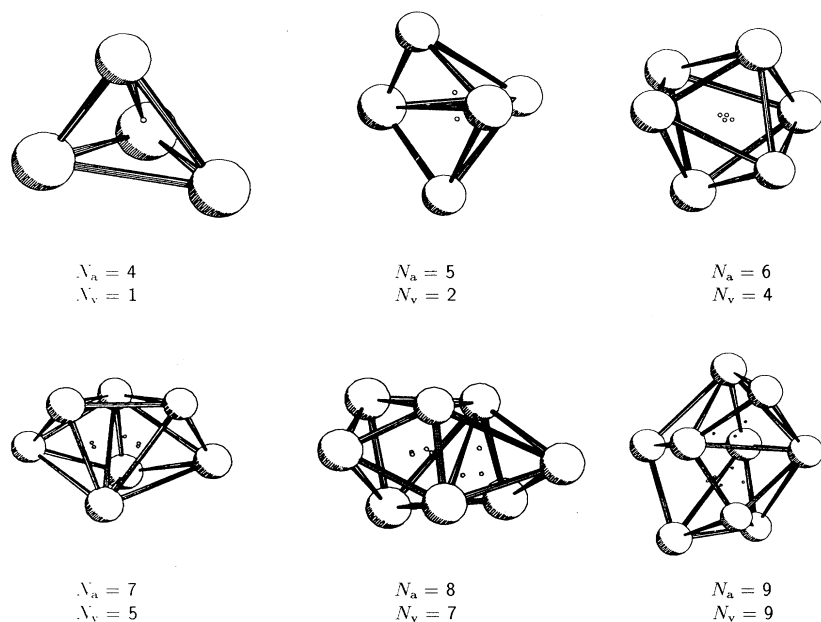


FIG. 5. The six types of preferred intrinsic voids. The large spheres represent atoms, the tiny spheres vertices.

space should be expected. The slight increase upon structural relaxation is trivially related to the increased number of voids.

Holes. A clear effect of structural relaxation is visible in the volume distributions of the holes in as-quenched and annealed $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ (Fig. 7). In addition to the decrease in the total number of holes (Table I), the volume distributions show a relatively strong decrease in the fraction of larger holes. The average volume of a hole changes from $5.9 \times 10^{-3} \text{ nm}^3$ for the as-quenched models to $4.9 \times 10^{-3} \text{ nm}^3$ for the 570 K models ($7.7 \times 10^{-3} \text{ nm}^3$ for RPHS). Since the atomic volume is about $15 \times 10^{-3} \text{ nm}^3$, the average hole is far too small to host a mobile atom like a vacancy does in crystalline structures. The total volume occupied by the holes amounts to 3.8% in the as-quenched state and 2.1% in the annealed state (8.8% for RPHS).

The sphericity distributions for the holes are given in Fig. 8 and the correlation between sphericity and volume in Fig. 9. The results show that ϕ assumes rather small values, indicating strongly nonspherical shapes for the holes. In particular, the sphericity of the holes that have a volume on the order of an atomic volume never exceeds

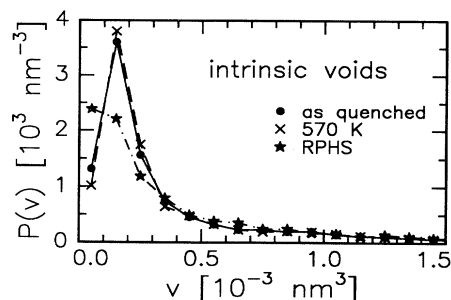


FIG. 6. Volume distributions for the intrinsic voids.

0.1. This indicates the complete absence of spherical, vacancylike defects in the amorphous structure. Since there is no significant effect of structural relaxation on the sphericity distribution, the probability of a void breaking up during structural relaxation does not seem to be related to its shape.

IV. DISCUSSION

The effect of structural relaxation on the volume distribution of the holes (Fig. 7) is the direct cause of the decrease in atomic mobility that has been experimentally observed (increasing viscosity,^{3,5} decreasing diffusivity^{4,9}). In this section the connection between atomic mobility and the occurrence of holes will be further discussed. One should bear in mind that the present study can only resolve differences in static structures. It can therefore at best merely give indications on the nature of the processes of atomic mobility. Besides, no information can be gained on the temperature dependence of the defect

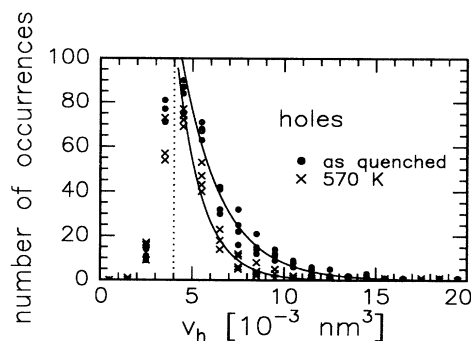


FIG. 7. Volume distributions for the holes. The symbols denote the individual models. The solid lines are the exponential fits to the tails of the distributions. The dotted line is drawn at $v_h = v_c$.

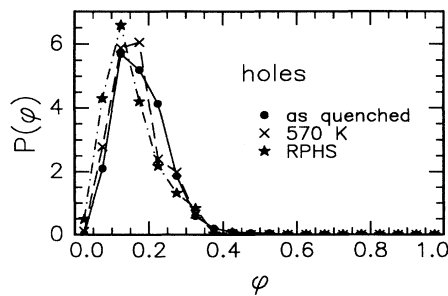


FIG. 8. Sphericity distributions for the holes.

structure, or the metastable equilibrium state, to which the diffusivity and the viscosity react differently.⁹ Molecular-dynamics studies focused on the behavior of the holes in metallic glasses will be undertaken to investigate these issues further. The present results do nevertheless contain revealing information, and give rise to the following interpretation.

(i) A number of experimental studies on *diffusion* in metallic glasses have shown that collective motions of atoms are more likely to take place than single-atom jumps. The isotope effect on the diffusivity indicates that at least ten atoms are involved in a diffusion event,²¹ and on the basis of experimental structural-relaxation data Van den Beukel²² estimates some 30 atoms to be involved in diffusion events. Expressed in terms of the results of the present work, it is plausible to assume that a collective motion of a group of atoms will only be possible if they are all adjacent to the same hole. In general, the mobility of a group of atoms will be determined by the void they share. Intrinsic voids do not play a role in the atomic mobility processes for two reasons. First, while during the heat treatment the atomic mobility decreases,

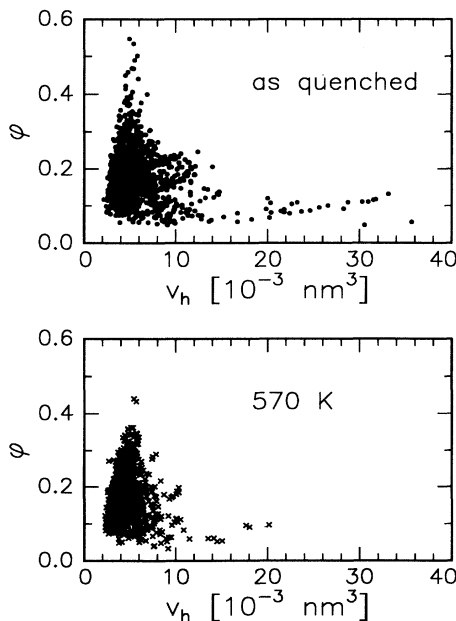


FIG. 9. Correlation between hole volume and sphericity. Each symbol represents a particular hole.

the abundance of intrinsic voids increases. Secondly, the number of atoms around intrinsic voids (on the order of 5 or 6) is considerably less than the 10–30 atoms mentioned above. Atomic mobility is therefore likely to take place at holes. A further experimental indication that holes are related to diffusion is found in studies on the pressure effect on the diffusivity. For the diffusivity of Au in amorphous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ (Ref. 23) an activation volume of $(11 \pm 4) \times 10^{-3} \text{ nm}^3$ is reported,²⁴ which is very well within the range of the hole-volume distribution in amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ (Fig. 7).

Diffusion events can be imagined to take place at a hole when strong thermal fluctuations cause a significant displacement of the atoms. If no other hole is present near the atoms in the next shell (i.e., the atoms surrounding the hole atoms), these atoms will not be able to follow the fluctuations, and push the hole atoms more or less back to their original positions. In this process the shape of the group of atoms changes only temporarily, but the atoms might swap places when they return to their positions.

(ii) Detailed studies on structural relaxation in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ by Van den Beukel and co-workers^{9,10} have led to the conclusion that *viscous flow* and diffusion are governed by different defects. In fact, they found that concentration c_d of defects for diffusion is related to the concentration c_f of defects for viscous flow by $c_d = c_f^{1/2}$. In case of a random distribution of defects over the structure, this relation implies that a diffusion defect is a single entity and that viscous flow can occur when two of these defects interact. This can be understood by extending the arguments given above: when, at the time of a strong thermal fluctuation around a diffusion defect, the atoms in the neighboring shell do have another hole at their disposition, the fluctuation in atomic positions can be accommodated, and the change in shape results in local shear. This leads to the conclusion that for a viscous-flow event two holes are needed.

(iii) During structural relaxation, the *reduction* of the defect concentration gives rise to a reduction of the atomic mobility. From the experimentally observed linear increase of the viscosity with time³ one can deduce that the reduction rate of the defect concentration ($-dc_d/dt$) is proportional to c_d^3 . This indicates that the mobility needed to break up holes is supplied only if three holes are interacting. Apparently, the shear that then takes place makes it possible for the atoms to change their local order in such a way that the holes break up in intrinsic voids. It is, however, not clear *why* at least three holes are necessary for this process.

Finally, the present interpretation is used to propose an alternative approach to the concept “free volume.” Contrary to the present work, the free-volume theory^{6,7} takes the atomic-volume distribution as a starting point.¹⁴ Atoms with a Voronoi-cell volume V larger than a certain value V_c are defined to have an amount of free volume equal to $V_f = V - V_c$. The critical value V_c represents the Voronoi volume of an atom in the densest state of the glass. According to Ref. 14, $V_c = 17.6 \times 10^{-3} \text{ nm}^3$ for Pd atoms in $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$. The assumption that this free volume is freely redistributed over the atoms in

the structure (i.e., without energy barriers) leads to an exponential distribution $P(V_f) = (1/\langle V_f \rangle) \exp(-V_f/\langle V_f \rangle)$, with $\langle V_f \rangle$ the average free volume per atom. One could, however, question the "free" character of free volume, since diffusion and viscous flow, as well as structural relaxation, are processes that involve an activation energy. Therefore, at least in those cases where the redistribution of free volume leads to diffusion, viscous flow, or annihilation of defects, it is no longer barrier free. Nevertheless, the exponentially decreasing tail of the volume distribution is important for the description of the atomic mobility. Defects are defined as those atoms that have $V_f > V^*$, with V^* a certain minimum volume for a defect. The defect concentration is thus given by $c_d = \exp(-1/x)$, with $x = \langle V_f \rangle / V^*$ the reduced average free volume. The description of experimental observations of structural relaxation by means of the free-volume theory makes no direct use of the definition of free volume in terms of the atomic-cell volume. It merely uses the quantity x to describe consistently the changes in widely different physical properties as resistivity ($\Delta\rho \propto \Delta x$), specific heat ($c_p \propto dx/dT$), and diffusivity [$D \propto c_d = \exp(-1/x)$]. This is successful primarily because free volume is defined as an *excess* volume, not because free volume is defined in terms of the atomic-cell volume.

In Ref. 14 the atomic-cell definition of free volume has been used for the present models of $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$, which yielded $\langle V_f \rangle = 0.58 \times 10^{-3} \text{ nm}^3$ for the Pd atoms in the as-quenched state, decreasing to $\langle V_f \rangle = 0.31 \times 10^{-3} \text{ nm}^3$ in the annealed state. Although the relative reduction of $\langle V_f \rangle$ is in agreement with the reduction from $x = 0.082$ to $x = 0.065$ ($c_d = 5 \times 10^{-6}$ to 2×10^{-7}) that was derived from diffusivity measurements,⁹ two problems remain. First, the atomic-cell concept of free volume strongly suggests that a single-atom mechanism is the principle carrier of atomic mobility. Secondly, in this interpretation defect concentrations turn out to be extremely low: if V^* is supposed to be equal to the activation volume for Au diffusion [$11 \times 10^{-3} \text{ nm}^3$ (Ref. 23)], the defect concentrations for Au diffusion result to be 5.8×10^{-9} per atom in the as-quenched state, and 3.9×10^{-16} in the annealed state. Not only are these values unphysically low, the reduction is also far larger than the experimentally ob-

served reduction in diffusivity by a factor of 25.

Here we propose an interpretation in which the concentration of holes is the determining factor for the atomic mobility, rather than the Voronoi-cell volume of single atoms. In order to establish a quantitative relation with atomic mobility we define free volume in terms of the hole volume. The distribution of the hole volumes v_h in the as-quenched and the 570 K state has been shown in Fig. 7. If the free volume is defined by $v_f = v_h - v_c$, with $v_c = 4 \times 10^{-3} \text{ nm}^3$, an exponential tail is found for the free-volume distributions. The critical volume v_c accounts for the fact that small voids having $N_a \geq 10$ may occur even in the densest state of the glass. On the one hand, the exponential decay is identical to the free-volume distribution in the original theory. Therefore, no modifications have to be made to the expressions for x and c_d (apart from substituting $\langle v_f \rangle$ for $\langle V_f \rangle$ and v_c for V_c), and this alternative free volume works equally well in the description of structural-relaxation effects on the different physical properties.^{5,8} On the other hand, the physical relevance of the present definition of free volume is much clearer. The hole volume is truly an excess volume, and its role in processes of collective atomic mobility can well be envisaged.

The high-volume tail of the hole-volume distributions can be represented by the average free volume per hole, being $2.2 \times 10^{-3} \text{ nm}^3$ for the as-quenched state, and $1.4 \times 10^{-3} \text{ nm}^3$ for the 570 K state. In the as-quenched state 75% of the holes is large enough to contribute to the free volume, in the 570 K state, 67%. Again using the activation volume as the smallest amount of free volume qualifying a defect, the holes with a volume $v_h > 15 \times 10^{-3} \text{ nm}^3$ can act as a vehicle for the diffusion of Au. In this way, the resulting defect concentrations are 4.3×10^{-4} per atom in the as-quenched state, and 1.5×10^{-5} in the annealed state. Not only are these values more reasonable than the ones obtained with the classical free-volume definition, but also the observed reduction of the diffusivity is very well reproduced.

Finally, Table II gives a number of features concerning the description of diffusion in metallic glasses by means of the free-volume theory. This table summarizes the main differences between the classical definition of free volume and the one presented in this paper.

TABLE II. Summary of differences between the classical free-volume theory (Ref. 6) and the present work. Numerical results are given for amorphous $\text{Pd}_{52}\text{Ni}_{32}\text{P}_{16}$ in the as-quenched state and after a heat treatment for 2 h at 570 K.

	Free-volume theory	This work
Volume entities	Atomic-cell volume V	Hole volume v_h
Centered at	Atoms	Open space
Critical volume	$V_c = 18 \times 10^{-3} \text{ nm}^3$	$v_c = 4 \times 10^{-3} \text{ nm}^3$
Annihilation mechanism	?	Holes break up into smaller voids
Diffusion process	Single-atom?	Ten or more atoms
Mean free volume, as quenched	$0.58 \times 10^{-3} \text{ nm}^3$	$2.2 \times 10^{-3} \text{ nm}^3$
Mean free volume, annealed	$0.31 \times 10^{-3} \text{ nm}^3$	$1.4 \times 10^{-3} \text{ nm}^3$
Defect concentration, as quenched	5.8×10^{-9}	4.3×10^{-4}
Defect concentration, annealed	3.9×10^{-16}	1.5×10^{-5}

V. CONCLUSIONS

The change in the degree of ordering of the atomic structure, induced by structural relaxation, is consistently reflected in the distributions of interatomic voids in the structure. As in crystalline atomic packings, intrinsic voids can be identified also in metallic-glass structures. These are voids that are surrounded by nine or less atoms. During structural relaxation, larger voids ("holes"), surrounded by ten or more atoms, break up into several intrinsic voids. This causes a decrease in the concentration of holes, and an increase in the concentration of intrinsic voids.

Holes play a determining role in atomic-transport processes. The concept of free volume can be naturally described in terms of the hole volumes, which has arguably

more physical reality than the original definition in terms of atomic-cell volumes. This also leads to a more consistent picture with respect to the experimental evidence on the diffusion process in metallic glasses.

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- ²⁴Some debate is still going on in the literature on the value of the activation volume. For instance, for amorphous CoFeNbB a zero activation volume has been found (Ref. 21).

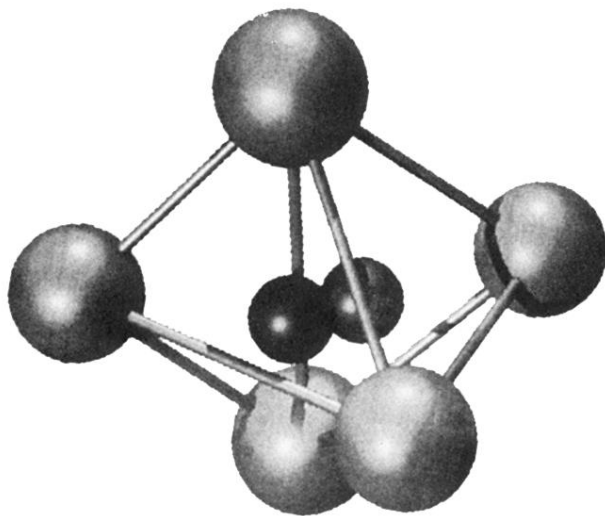


FIG. 2. Example of a void consisting of two vertex spheres ($N_v=2$, the small spheres), surrounded by five atoms ($N_a=5$, the larger spheres). The atoms are shown at 40% of their size.