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***Ab initio* molecular dynamics studies on volume stability of Voronoi polyhedra under pressures in a metal glass**

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We study volume stability of Voronoi polyhedra under hydrostatic pressures in a sodium glass. We optimize the atom positions under the pressures by an *ab initio* molecular dynamics method with an orbital-free density functional. The number of atoms in the supercell is 128. The change of the volumes is insensitive to pressure for the Voronoi polyhedra with smaller volumes. We introduce a method to evaluate the average charge density around individual atom. The average electron charge density around individual atom increases with decreasing Voronoi volume. The volume change of Voronoi polyhedron with signature (0,0,12,0) is the most stable to the applied pressures. The density around the atoms with the signature (0,0,12,0) is the greatest among the signatures. © 1996 American Institute of Physics. [S0021-9606(96)04017-6]

I. INTRODUCTION

The bulk modulus of the metallic glasses is one of the fundamental quantities. The moduli of the metallic glasses have been studied by use of empirical molecular dynamics (EMD) methods.¹ The experimental studies² have demonstrated that the bulk moduli of glasses are smaller by several percentages than those of the crystals. Almost earlier studies, however, have discussed the average bulk moduli in the glasses. Since the atom positions in glasses are random, the system has a variety of local environments of atoms. It is interesting to clarify the response of the local volumes to hydrostatic pressures in the system. Many methods exist to analyze the geometrical random structures. Among them Voronoi analysis is used to study the local structure in the glasses.³ In the analysis a signature (n_3, n_4, n_5, n_6) is used to identify the local environment of atoms, where n_i is the number of i -edged faces on the polyhedron. The number of atoms with signature (0,0,12,0) is several percentages and increases with decreasing cooling rate.⁴ It has been found, by using the EMD method, that the atom with the signature has the lowest potential energy.

In the present paper we study the volume stability of Voronoi polyhedra to the pressures in the sodium glasses. The volume stability depends on the local environment of the atom. We define the volume stability as an inverse of the proportion of the Voronoi volume to the average volume per atom under the pressure. The stability can be a measure of the stiffness of Voronoi polyhedra. In the case of simple metal crystals, the bulk moduli are explained by free-electron approximation⁵ with an average charge density. The difference of the local environments in the glasses gives rise the charge density fluctuation. A theoretical interest arises in the relation between the charge density around the atom and the local volume stability in the glasses. We clarify this point by introducing a method to evaluate the average charge density around individual atom. In order to optimize the atom positions in the glass states, first we produce a model glass by the EMD method. Then the electron charge density and the atom

positions are optimized by use of an *ab initio* molecular dynamics (AIMD) method with an orbital-free density functional.^{6,7}

The density functional theory⁸ (DFT) has made great progress with the development of theories, computational techniques, and computer hardwares. Especially the DFT with local density approximation has succeeded in describing the ground-state properties. The AIMD technique by Car and Parrinello⁹ (CP) is one of the powerful tools to explore the dynamical and statistical properties of the condensed systems. In the last decade many efforts focus on reducing CPU time of the CP method. For instance, they are modifications of the pseudopotentials,¹⁰ accelerated algorithms of optimization in an electron system such as a conjugate gradient method,¹¹ and order- N method.¹² The last method allows us to treat large systems such as disordered systems, layered structures, large clusters, and so on. Recently Madden group^{6,7} has proposed an AIMD method with an orbital-free density functional, which is one of the order- N method. The kinetic energy functional in the Kohn–Sham scheme is represented by single-electron wave function. This method, however, uses a Perrot functional¹³ as a kinetic energy functional that is represented by the electron charge density. The Perrot functional is a modified version of Thomas–Fermi–von Weizsäcker functional by using the linear response theory. The functional gives a good agreement with experimentals.^{6,7}

II. THEORETICAL METHOD

A. *Ab initio* molecular dynamics method

We use the AIMD method with an orbital-free density functional presented by Pearson, Smargiassi, and Madden.⁶ In the description of the DFT,⁸ the total energy E_{tot} of the system is given by

$$E_{\text{tot}}[\rho, \{\mathbf{q}\}] = E_{\text{kin}}[\rho] + E_C[\rho] + E_{\text{xc}}[\rho] + E_{\text{ext}}[\rho, \{\mathbf{q}\}] + E_{\text{II}}[\{\mathbf{q}\}], \quad (1)$$

where $\rho(\mathbf{r})$ is the electron charge density, \mathbf{q} is the atom positions, E_{kin} is the kinetic energy functional of a noninteracting electron gas, E_C is the electron–electron Coulomb energy functional, E_{xc} is the exchange–correlation energy functional, E_{ext} is the electron–ion interaction energy functional that is represented by using pseudopotential, and E_{II} is the ion–ion interacting Coulomb energy. We use Perrot kinetic energy functional $E_P[\rho]$ for E_{kin} given by

$$E_P[\rho] = E_{\text{vW}}[\rho] - E_{\text{lin}}[\rho] + E_{\text{HK}}[\rho] \quad (2)$$

with

$$E_{\text{vW}}[\rho] = E_{\text{TF}}[\rho] + \frac{1}{8} \int_{\Omega} \frac{\nabla \rho(\mathbf{r}) \nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} d\mathbf{r}, \quad (3)$$

$$E_{\text{lin}}[\rho] = E_{\text{TF}}[\bar{\rho}] + \frac{\Omega}{2} \sum_{\mathbf{G}} \rho_{\mathbf{G}}^* \rho_{\mathbf{G}} \left(-\frac{1}{\chi_{\text{vW}}(\mathbf{G})} \right) \quad (4)$$

and

$$E_{\text{HK}}[\rho] = E_{\text{TF}}[\bar{\rho}] + \frac{\Omega}{2} \sum_{\mathbf{G}} \rho_{\mathbf{G}}^* \rho_{\mathbf{G}} \left(-\frac{1}{\chi_0(\mathbf{G})} \right), \quad (5)$$

where the $\bar{\rho}$ is the average charge density, the first term $E_{\text{vW}}[\rho]$ is the von Weizsäcker functional which is constructed by the Thomas–Fermi energy functional $E_{\text{TF}}[\rho]$ and the correction term including the charge density gradient, the second term $E_{\text{lin}}[\rho]$, which is linearized form of $E_{\text{vW}}[\rho]$, is represented by using the response function $\chi_{\text{vW}}(\mathbf{G})$,¹⁴ and the last term $E_{\text{HK}}[\rho]$, which is Hohenberg–Kohn linear response functional, is represented by using the Lindhard function $\chi_0(\mathbf{G})$.¹⁵ The charge density $\rho(\mathbf{r})$ is expanded as Fourier series

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}). \quad (6)$$

The density $\rho(\mathbf{r})$ and the atom positions \mathbf{q} are optimized by using a CP type coupled equations given by

$$\mu_G \ddot{\rho}_G = -\frac{\delta E_{\text{tot}}}{\delta \rho_G} \quad (7)$$

and

$$M_q \ddot{\mathbf{q}} = -\nabla_{\mathbf{q}} E_{\text{tot}}. \quad (8)$$

In order to solve the above equations we use the steepest decent (SD) procedure, i.e.,

$$\rho_{\mathbf{G}}(t + \Delta t) = \rho_{\mathbf{G}}(t) - \frac{\Delta t^2}{\mu_{\mathbf{G}}} \frac{\delta E_{\text{tot}}}{\delta \rho_{\mathbf{G}}} \quad (9)$$

and

$$\mathbf{q}(t + \Delta t) = \mathbf{q}(t) - \frac{\Delta t^2}{M_q} \nabla_{\mathbf{q}} E_{\text{tot}}. \quad (10)$$

We set the “fake mass” $\mu_{\mathbf{G}}$ as $-\mu_0/F(\mathbf{G})$, where μ_0 is a constant and $F(\mathbf{G})$ is the response function of the free-electron gas at the same average density of the system within

the random phase approximation.^{6,16} We set parameters as the mass $\mu_0 = 10^6$ a.u., time mesh $\Delta t = 500$ a.u., ion mass $M_q = 20\,953.8920$ a.u., energy cutoff $E_{\text{cut}} = 15.0$ Ry, and the number of FFT meshes is $32\,768 (= (2^5)^3)$. We use the Topp–Hopfield local pseudopotential¹⁷ and the Ceperley–Alder exchange–correlation energy functional.¹⁸ Initial charge density is obtained from superposition of the charge density of isolated atoms. The initial atom positions of the glasses are obtained by the EMD method which we will give later. We scale the atom positions depending on the volumes of the systems and optimize the charge density for 30 steps for the fixed atom positions. Then the positions and the charge density are optimized simultaneously for 2200 steps using the SD method. We choose the extent of scaling so as for the Voronoi signature of each atom to be unchanged.

B. Initial atom positions

We obtain the initial atom positions by use of the EMD method with the pair potential for sodium.¹⁹ We choose the unit of length $\sigma = 3.24 \times 10^{-10}$ m, ion mass $M_q = 3.82 \times 10^{-26}$ kg, and energy $\epsilon = 599 k_B$ where k_B is the Boltzmann constant. The unit of time is $\tau = 6.96 \times 10^{-13}$ s and the time mesh of integration is 0.00718τ (5.00×10^{-15} s). The equation of motion is integrated by a modified Verlet algorithm. We construct the system of 128 atoms with bcc structure of which the density is $0.920 \times 10^3 \text{ kg m}^{-3}$. The system is heated to a temperature of 381 K and held at the temperature for 6000 steps (30 ps). The temperature is controlled by a modified momentum scaling method.²⁰ Then the system is cooled by 40 K and held at the temperature for 100 steps. This procedure is repeated down to 21 K. The cooling rate corresponds to $8.00 \times 10^{13} \text{ K s}^{-1}$.

C. Average charge density around individual atom

In order to characterize the charge distribution around an individual atom, we introduce an average charge density around atom q given by

$$\bar{\rho}_q = \frac{Z_{Sq}}{\Omega_{Sq}}, \quad (11)$$

where Z_{Sq} is the electron charge in the sphere S_q shown in Fig. 1 and Ω_{Sq} is the volume of a sphere S_q . We define the radius R_q of the sphere S_q as twice as large as the radius r_q of the atomic sphere. The number of electron charge within the distance of the nearest-neighbor atoms can be a measure of the atomic bonding. In order to obtain the charge Z_{Sq} , we expand the charge density $\rho(\mathbf{r}_q)$ using spherical harmonics as

$$\rho(\mathbf{r}_q) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) = \sum_{lm} \rho_{lm}(r_q) Y_{lm}(\hat{r}_q) \quad (12)$$

with

$$\rho_{lm}(r_q) = 4\pi i^l \sum_{\mathbf{G}} \rho_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{q}) j_l(Gr_q) Y_{lm}^*(\hat{G}), \quad (13)$$

where $\mathbf{r}_q = \mathbf{r} - \mathbf{q}$. Thus the electron charge Z_{Sq} in the sphere S_q is given by

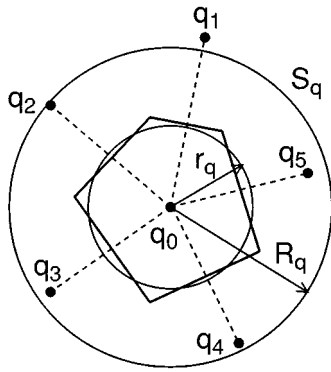


FIG. 1. The schematic representation of sphere S_q of which radius R_q is twice of the atomic sphere with radius r_q . The volume of the atomic sphere is the same as that of the Voronoi polyhedron. The polyhedron centered atom q_0 is constructed by planes that are perpendicular bisector planes of the lines drawn from atom q_0 to the surrounded atoms q_1, \dots, q_5 .

$$\begin{aligned}
 Z_{S_q} &= \int_{S_q} \rho(\mathbf{r}_q) d\mathbf{r}_q \\
 &= 4\pi \sum_{G \neq 0} \frac{\rho_G}{G} \exp(i\mathbf{G} \cdot \mathbf{q}) \\
 &\quad \times \left(-\frac{R_{S_q}}{G} \cos(GR_{S_q}) - \frac{1}{G^2} \sin(GR_{S_q}) \right) \\
 &\quad + \delta(G=0) \Omega_{S_q} \rho_{G=0}.
 \end{aligned} \quad (14)$$

III. RESULTS AND DISCUSSION

The initial atom positions have been obtained by use of the EMD method. The positions and the atom charge density are optimized for five volumes by AIMD until the values of the total energy have converged down to 10^{-6} Ry. The pair distribution function of the system had a split of the second peak, in which the inside peak was higher than the outside peak. It has been well recognized that the splitting is a characteristic feature of the metal glasses.³ In the crystallized states the outside peak is higher than the inside peak.³

We have obtained the total energy curve as a function of the volume Ω_{cell} of the supercell. The equilibrium volume has been found to be $\Omega_{\text{eq}} = 35\,047.757$ a.u. by a least square fitting procedure. We have calculated the pressure curve of the system as a function of volume Ω_{cell} of the supercell using the equation²¹ as

$$\begin{aligned}
 P(\Omega_{\text{cell}}) &= \frac{2}{3\Omega_{\text{cell}}} E_{\text{kin}} + \frac{1}{3\Omega_{\text{cell}}} E_H + \frac{1}{3\Omega_{\text{cell}}} E_{\text{II}} \\
 &\quad + \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} \{ \mu_{\text{xc}}[\rho(\mathbf{r})] - \epsilon_{\text{xc}}[\rho(\mathbf{r})] \} \rho(\mathbf{r}) d\mathbf{r} \\
 &\quad + \frac{1}{\Omega_{\text{cell}}} E_{\text{ps}} + \frac{1}{3} \sum_{\mathbf{G}} S(\mathbf{G}) G \rho^*(\mathbf{G}) \frac{\partial V_{\text{ps}}(\mathbf{G})}{\partial G}.
 \end{aligned} \quad (15)$$

Using the pressure curve we have calculated the bulk modulus at the volume of Ω_{eq} . In Table I we show the bulk moduli of the present glass and the bcc crystal. The bulk modulus of

TABLE I. The bulk moduli B of glass and crystals at the equilibrium edge length a_{eq} of the supercell including 128 atoms.

Structure	Method	a_{eq} (a.u.)	B (GPa)
Relaxed glass	AIMD	32.694	6.386
bcc crystal	AIMD	32.556	6.717
bcc crystal	EXPT.	31.92 ^a	6.8

^aIn Ref. 22.

the glass is smaller than the calculated bulk modulus of the crystal by 4.8%. This feature coincides with the earlier studies for other metallic glasses.^{1,2} The difference can be explained by the theory of free-electron bulk modulus⁵ for simple metal crystals with the average charge density $\bar{\rho}$. In the free-electron approximation the bulk moduli B of the simple metals are given by $B \approx r_s^{-5}$, where r_s is density parameter that is given by $\frac{4}{3}\pi r_s^3 = 1/\bar{\rho}$. Thus $B \approx \bar{\rho}^{5/3}$. It has been found that the experimental bulk moduli of simple metal crystals satisfy this relation.⁵

We have analyzed the local structures in the glass with the Voronoi polyhedron analysis. We have applied pressures so as not to change the population of the signatures. Figure 2 shows the fractions of the signatures of Voronoi polyhedra appeared abundantly. The number of (0,0,12,0) Voronoi polyhedron has been five, which shows the present glass corresponds to a relaxed state of the sodium glass.⁴

Figure 3 shows the variation of the Voronoi volumes $\bar{\Omega}_q(n_3, n_4, n_5, n_6)$ of the glass as a function of the volume $\Omega_a = \Omega_{\text{cell}}/N_a$, where Ω_{cell} is the volume of the supercell and N_a is the number of atoms in the cell. We have averaged the Voronoi volumes over the same signature. The Voronoi volumes decrease linearly with decreasing the volume Ω_a . We define the volume stability $\bar{K}_q^{-1}(n_3, n_4, n_5, n_6)$ as

$$\bar{K}_q(n_3, n_4, n_5, n_6) \equiv \frac{d\bar{\Omega}_q(n_3, n_4, n_5, n_6)}{d\Omega_a}. \quad (16)$$

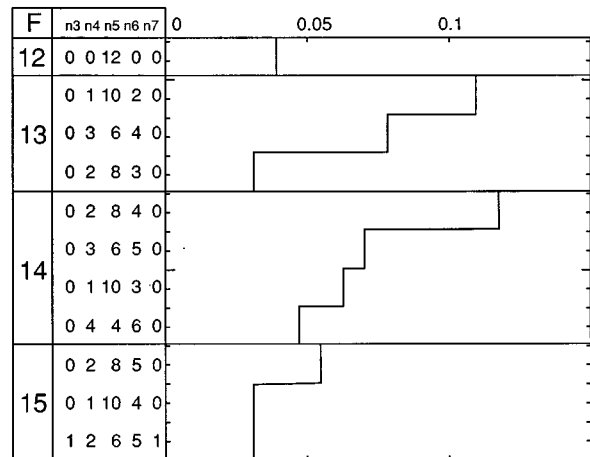


FIG. 2. Histogram of fraction of the Voronoi signatures, where n_i of (n_3, n_4, n_5, n_6) is the number of i -edged faces on the polyhedron, F is the total number $\sum n_i$ of faces on the polyhedron.

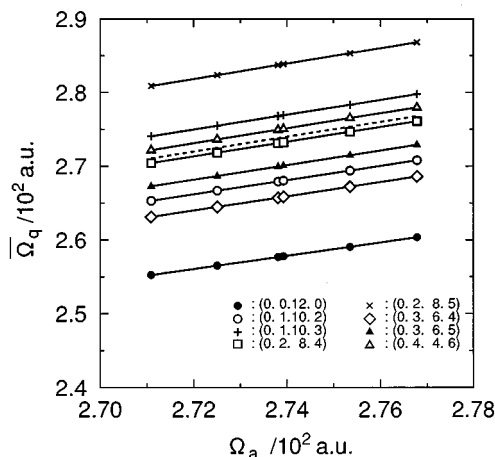


FIG. 3. Variation of the volumes $\bar{\Omega}_q(n_3, n_4, n_5, n_6)$ of Voronoi polyhedra as a function of the volume Ω_a per atom in crystal state. The dashed line corresponds to the variation for crystal.

The volume stability can be a measure of the stiffness of the polyhedra. We have obtained it by use of the least square fitting of the relations shown in Fig. 3. Figure 4 shows the stability as a function of $\bar{\Omega}_q(n_3, n_4, n_5, n_6)$ at the volume Ω_{eq} for each signature. The dotted line in Fig. 4 corresponds to the volume stability of the sodium crystal. The stability $\bar{K}_q^{-1}(n_3, n_4, n_5, n_6)$ increases with the decreasing volume of the Voronoi polyhedra. This indicates that the volume changes with small Voronoi polyhedra are insensitive to the pressure, i.e., the small Voronoi polyhedron seems to have large local bulk modulus. The largest $\bar{K}_q^{-1}(n_3, n_4, n_5, n_6)$ of the (0,0,12,0) polyhedron is about 1.15 times that of (0,2,8,5) polyhedron. The Voronoi polyhedron with signature (0,0,12,0) seems to have the greatest local bulk modulus.

In order to explain this behavior, we obtain the average charge density $\bar{\rho}_q$ around each atom using the Eq. (11). The differences of the local environments yield the charge density fluctuation. Thus the average densities are different for each signature. Figure 5 shows the average densities as a

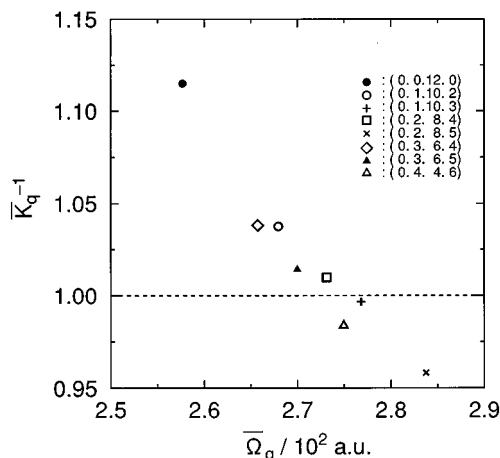


FIG. 4. Change of the volume stability $\bar{K}_q^{-1}(n_3, n_4, n_5, n_6)$ as a function of volume $\bar{\Omega}_q(n_3, n_4, n_5, n_6)$ of Voronoi polyhedron.

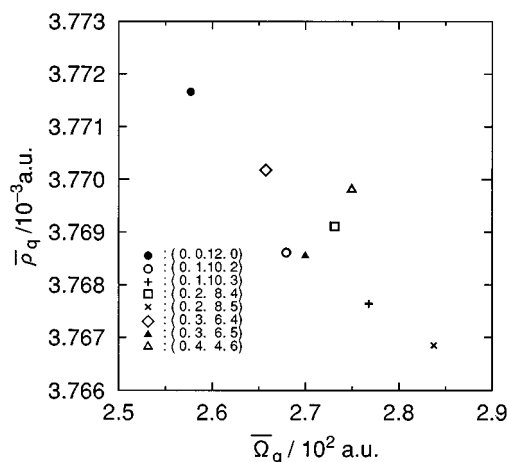


FIG. 5. Average charge densities $\bar{\rho}_q$ as a function of Volume $\bar{\Omega}_q(n_3, n_4, n_5, n_6)$ of Voronoi polyhedron.

function of volume of the polyhedra. The densities increase with decreasing the volume of Voronoi polyhedra. The density $\bar{\rho}_q$ is the highest for the signature (0,0,12,0) which has icosahedral cluster. Using the theory of the free-electron bulk modulus⁵ for the simple metal crystals, we found that the Voronoi polyhedron with the high average charge density has large local bulk modulus. This is the origin of the high stability of the small Voronoi polyhedron. Thus the icosahedral cluster has the greatest local bulk modulus in the sodium glass.

IV. CONCLUDING REMARKS

We have studied the volume stability of Voronoi polyhedra under hydrostatic pressures in a sodium glass by use of the *ab initio* molecular dynamics method with an orbital-free density functional. The change of the volumes is insensitive to pressure for the Voronoi polyhedra with small volumes. We have introduced a method to evaluate the average charge density around an individual atom. The average charge density around an atom increases with decreasing the volume of Voronoi polyhedron. We have applied the theory of the free-electron bulk modulus to the volume stability in the sodium glass and found that the volume of Voronoi polyhedron with signature (0,0,12,0) is the most stable in the sodium glass.

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