A Geometrical Model of the Structure of Liquid Silicon Incorporating the Local- and Medium-Range Orders

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A new structure model of liquid silicon is tested by incorporating the local bond orientational order and the medium-range radial distribution. The shoulder observed on the high Q side of the principal peak in the structure factor of liquid silicon appears to be mainly caused by the atomic radial distribution in the range from 0.4 to 0.6 nm. On the other hand, a molecular dynamics simulation on liquid silicon shows that the angular distribution of neighboring atoms has tetrahedral-like features, similar to those in the β-tin type crystal structure with $c/a = 0.7$. With these facts in mind, a new geometrical model of liquid silicon is proposed which simultaneously satisfies the experimental density, radial distribution, calculated bond orientational order, and typical liquid nature of random orientation in the long range.

Key words: Liquid silicon; Pair distribution function; Structure factor; Bond orientational order; Structure model.

1. Introduction

Several X-ray and neutron diffraction studies of liquid silicon, germanium, and other III to V group elements [1–6] have shown that some of the structure factors $S(Q)$ of these liquids have shoulders at the high Q side of the first peak, and relatively small coordination numbers of about 6 to 9 [6]. These features are considered to indicate the coexistence of different types of bonding, for example covalent and metallic [7, 8]. Orton [9] proposed the coexistence in liquid silicon and germanium of two kinds of atoms having different radii. Later he proposed a quasi-crystalline model [10] assuming tetrahedral and random configurations in the first and outer coordination shells, respectively. Davidović et al. [3] proposed that in liquid germanium the interatomic distances between the atoms around a vacancy are shortened. Badirkhan et al. [11] assumed in liquid germanium hypothetical "bond particles". Most of these works, however, include somewhat ambiguous concepts and hence are not widely accepted.

There exist also theoretical approaches for the structure of liquid silicon and other III to V group elements. Regnaut et al. [12] calculated the structure of liquid gallium and tin by using nonlocal Shaw pseudopotential with the optimized random phase approximation and suggest that their characteristic structural feature is due to the long-range part of the potential. Beck and Oberle [13] calculated the structure of liquid gallium and did show that the position of the shoulder in the structure factor is correlated with the period of the Friedel oscillation. Hafner and his coworkers [14] extended this idea to other liquid III to V elements including silicon and germanium by assuming characteristic distances of the short-ranged hard-core diameter and the long-ranged Friedel wavelength.

On the other hand, the characteristic features of these liquids are also reproduced by short-ranged manybody interaction alone. Stillinger and Weber (hereafter referred to as SW) proposed empirical interatomic potentials for silicon and germanium with cutoff distances smaller than 0.4 nm [15]. The agreement between the experimental structure factor and the simulated one using the SW potential is fairly good, and hence many similar approaches have been tested [16]. Use of the SW potential did show that three-body interaction must be included for reproducing the tetrahedral arrangement even in the liquid. A tetrahedral-like angular distribution in liquid silicon was also suggested by the Car-Parrinello method [17] and other ab initio techniques [18–20] in which the inherent interaction is short-ranged due to a small system size. Hence there are two successful approaches for

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reproducing the structure of liquid silicon and germanium based on long-ranged pair interactions and short-ranged many-body interactions, respectively.

Although these studies deal with three-dimensional atomic positions and claim "good" agreement with the experimental results, few efforts have been made to characterize the relation between near-neighbor and long-range structures, and the three-dimensional atomic arrangement in these liquids is not fully understood yet. Recently, Petkov et al. [5] proposed an empirical model for liquid germanium in which the atomic arrangement is represented by a topologically disordered β-tin structure. In their case, the structure factor can be adjusted to the experimental one by slightly shifting the atomic positions to preferable ones. This is considered to be a necessary condition at best, but its meaning is unclear because the modification includes many arbitrary rearrangements of atomic positions.

The main purpose of the present study is to construct a simple three-dimensional model for liquid silicon based on new aspects extracted from experimental and molecular dynamics (MD) results. The goal of this study is to provide a clear picture of the atomic arrangement in liquid silicon, based on published X-ray and neutron diffraction experiments.

2. Experimental Properties and the Molecular Dynamics Calculation

As for the atomic number density,

$$\varrho_N = N/V, \tag{1}$$

where N is the number of atoms in volume V, Glazov et al. [21] reported for liquid silicon 54.0 nm^{-3} (corresponding to 2.52 $\mathrm{g/cm^3}$). They used a floating tungsten bob. Recently Sasaki et al. [22] reported a higher value, 55.1 nm^{-3} (2.57 $\mathrm{g/cm^3}$) on using an improved apparatus and a floating SiC bob. In this study the latter value is used because SiC is less reactive than tungsten [22].

With the pair distribution function,

$$g(r) = \frac{\mathrm{d}N(r - \mathrm{d}r/2, r + \mathrm{d}r/2)}{4\pi r^2\, \mathrm{d}r\, \varrho_N}, \tag{2}$$

the structure factor $S(Q)$ is defined as,

$$S(Q = 1 + \int 4\pi r^2 \varrho_N \{g(r) - 1\} \frac{\sin(Q r)}{Q r}\, \mathrm{d}r, \tag{3}$$

where Q is the wavenumber [6]. The pair distribution function and the structure factor can be obtained experimentally and by computer simulation [23]. There exist several experimental $g(r)$ and $S(Q)$ data for liquid silicon [1, 2, 24]. The X-ray result [1] was mainly used in this work.

The bond orientational order (hereafter referred to as BOO) is the two-dimensional information on the atomic configuration around a central atom. The fundamental idea of BOO is to consider the directional distribution of "bonds" in 4π solid angles around the central atom and to expand it by spherical harmonics [25]. The expansion coefficients Q_{lm} of the bond orientation $\hat{r}_{ij}$ are given by

$$Q_{lm} = \sum_j w_{ij}\, Y_{lm}(\hat{r}_{ij}), \tag{4}$$

where i denotes the central and j its neighboring atoms, and Y_{lm} is the spherical harmonic. The weighting factor w_{ij} is introduced to take the "strength" of each bond into account. In order to apply the BOO to a disordered system, the rotational invariant should be considered as,

$$Q_l \equiv \left\langle \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} | Q_{lm} |^2 \right]^{1/2} \right\rangle_i, \tag{5}$$

hence the two-dimensional, angular distribution of bonds is decomposed into a series with expansion coefficients, $Q_1, Q_2, \ldots, Q_\infty$.

Although the definition of the "bond" is not unique, especially in disordered systems such as liquids and glasses, the present work is to use the most unambiguous definition that "bonds" are formed toward the direct, indirect, or quasi-direct neighbors composing the Voronoi polyhedron [26] from a particular central atom. The weighting factor w_{ij} for each bond is scaled by the solid angle looking out of the faces of the polyhedron from the central atom. This definition is simple and also applicable to crystal structures where the Voronoi polyhedron becomes to be the Wigner-Seitz cell.

Although the BOO is a useful concept for discussing the three-dimensional structure, its experimental determination is quite difficult. For this reason we used the molecular dynamics (MD) method with the SW potential, which is considered the best one among several empirical potentials for analyzing the liquid properties of silicon [27, 28]. The MD simulation was carried out with 4096 atoms in the periodic box under the condition of constant-NVT [29] at 1430 °C with a time step of 0.5 fs. Details of the simulation are almost identical to our previous studies [23, 30].

3. Results and Discussion

3.1. Origin of the Shoulder in the Structure Factor

First we consider the most attracting feature of the liquid structure of silicon: the shoulder on the high Q side of the first peak in the structure factor. Many discussions have concentrated on this point [1–3, 5, 7–14]. As easily understood through (3), the oscillation in the interference with the period Q^* is caused by the pair correlation at $r = 2\pi/Q^*$. In this sense, the main oscillatory feature with the period of $Q^* \sim 25$ nm^{-1} shown in Fig. 1 denotes a strong correlation at $r \sim 0.25$ nm, which coincides with the first peak position in $g(r)$. On the other hand, since the characteristic shoulder is located at a 1.25 times larger wave number than the principal peak [6], the short range nature of the order of $r \sim 0.20$ nm has to be considered. For example, Orton [9] assumed in liquid germanium smaller atoms with diameters of 0.207 nm beside the normal atoms of 0.270 nm.

Another possible origin of the shoulder in the structure factor of liquid silicon and germanium is the fact that the inherent periodicity in the liquid is not 1.25 times the main oscillation but only one third of it, hence the correlation length generating the shoulder is about 0.60 nm. In fact, there are large broad peaks at about 0.57 nm in the pair distribution functions of liquid silicon and germanium [1]. To confirm the feasibility of this idea, we divided the pair distribution function into two parts, "short" and "long", as shown in Fig. 1, and calculated their contributions to the structure factor, using (3). The threshold of the division into short and long parts was set at $r = 0.41$ nm, where $g(r)$ becomes almost unity. The contribution based on the "short" part of $g(r)$ represents the global feature of the total structure factor. On the other hand, the contribution of the "long" part of $g(r)$ appears in the lower Q range and modifies the shape of the principal peak to have a shoulder on the high-Q side as shown in Figure 1. Then the shoulder may qualitatively be explained by the features of $g(r)$ at longer distances: the dip at ~ 0.45 nm, the peak at ~ 0.57 nm, etc., which are completely different from those of simple metallic liquids [1, 6].

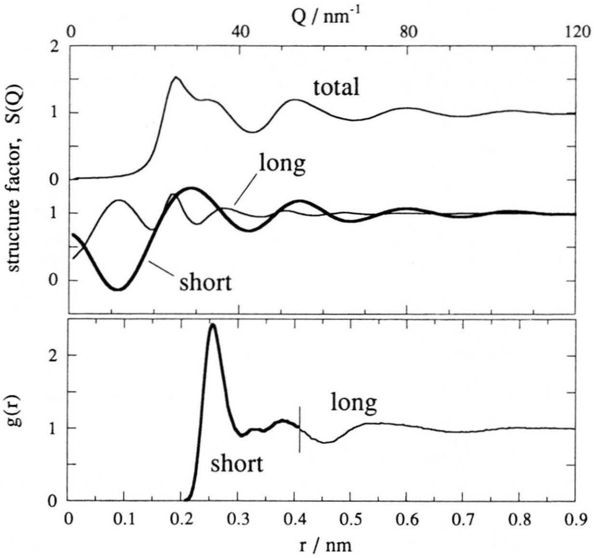

Fig. 1. Contributions to the structure factor from the short ($r \leq 0.41$ nm) and long ($r > 0.41$ nm) parts of the simulated $g(r)$ of liquid silicon.

Taken these points, it is strongly suggested that any structure model for liquid silicon or germanium should incorporate the medium range ordering in the range from 0.4 to 0.6 nm. This contrasts to some of the empirical models [3, 9, 10] based on the short range order only.

3.2. Similarity in the Medium-Range Radial Distribution between the Liquid Structure and High Pressure Crystal Forms of Silicon

Next we investigate the three-dimensional picture of atomic arrangement in the range from 0.4 to 0.6 nm. Petkov et al. suggested that the β-tin type crystal structure has a similar medium-range order to that in liquid germanium (see Fig. 5 in [5]). We extended this idea to other crystal forms related to silicon to investigate their similarities with the liquid structure. We used nine existing or hypothetical polymorphs of silicon under high pressure [31–33] as listed in Table 1.

For comparison with respect to the one-dimensional structures, we could not use the original definition of $g(r)$ given in (2) for crystals since $\mathrm{d}N/\mathrm{d}r$ becomes a summation of delta functions. This difficulty can be reduced by substituting an artificial distribution function for the delta functions. This operation is derived for mathematical convenience, but its physical

Table 1. High pressure forms of silicon crystals and their structural properties. The coordination number counts the neighbors in the first coordination shell. The scaled density is the value for which cell sizes are scaled by the nearest neighbor distance to be 0.245 nm.

Index	Structure	Designation	Coord. number	Scaled density g/cm^3
dia	diamond	Si-I	4	2.06
BC8	body centered cubic	Si-III	1+3	2.13
T12	tetragonal	(Ge-III)	4 (complex)	2.25
β-tin	centered tetragonal	Si-II	4+2	3.23
sc	simple cubic	hypothetical	6	3.17
sh	simple hexagonal	Si-V	2+6	3.23
bcc	b.c.c.	hypothetical	8	4.12
hcp	h.c.p.	Si-VII	12	4.49
fcc	f.c.c.	Si-VIII	12	4.49

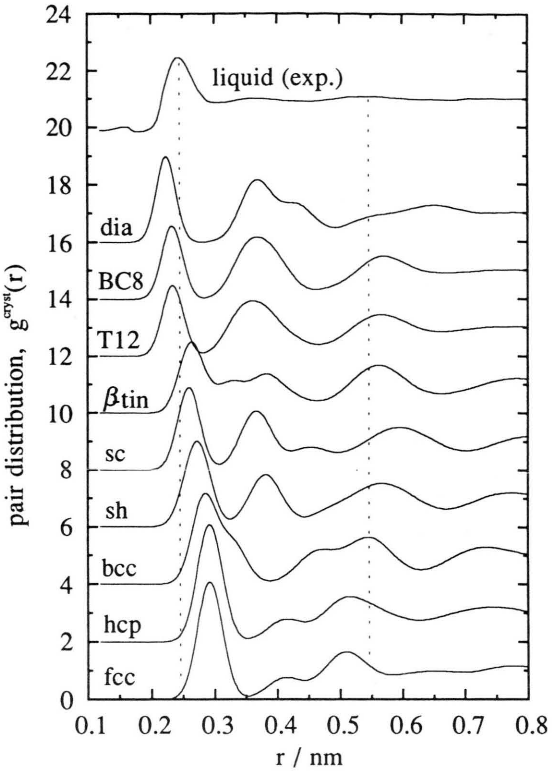

Fig. 2. A comparison of the calculated $g(r)$ of nine crystal structures with the experimental one of liquid silicon [1]. The cell dimension was adjusted to have the same density as that of liquid silicon.

meaning can be attributed to thermal vibration or structural disorder in the long range region. For the simulation with crystals we used $g(r)$ as modified in the following way:

$$g^{\mathrm{cryst}}(r) = \sum_{j}^{\infty} \frac{N_j f(r; r_j)}{4\pi r^2 \varrho_N}, \tag{6}$$

where r_j and N_j are the interatomic distance and the coordination number of j-th neighbor, and the distribution function f was assumed to be a Gaussian at r_j. The standard deviation σ of the Gaussian distribution was assumed to be $0.067\,r_j$ which was adjusted by the experimental data of liquid $g(r)$. In order to maintain the accuracy of $g^{\mathrm{cryst}}(r)$ at long distances, more than 700 neighboring atoms were counted in the summation.

The choice of the atomic density ϱ_N is arbitrary. If the cell dimension of the crystal is scaled by using the first-neighbor distance, then the resultant macroscopic density becomes much different from the experimental value 2.57 g/cm^3. In Table 1 such scaled densities of crystals are listed, of which the nearest neighbor distances were adjusted to be equal to the first peak position, 0.245 nm, of the experimental $g(r)$ data [34]. They suggest a difference of the order of -20 to $+30\%$ from the experimental liquid density value. In other words, the atomic distances should be different from the experimental ones if the cell dimension of the crystal is adjusted to the experimental atomic density. The $g^{\mathrm{cryst}}(r)$ of each crystal calculated in this manner is shown in Fig. 2 together with the experimental $g(r)$ of liquid silicon [1] for comparison. The first peak position of each $g^{\mathrm{cryst}}(r)$ differs significantly from that of the liquid. For example, the BC8 and T12 crystals, which have already been used as model structures of amorphous silicon or germanium [33], show their first peak at ~0.23 nm, i.e. at an about 5% shorter distance than the experimental value. On the other hand, the structures of β-tin, sc and sh crystals indicate first neighbor distances of ~0.27 nm which are by about 10% longer than that in the liquid.

However, with respect to the medium range order between 0.4 and 0.6 nm, the BC8, T12, β-tin, sc and sh crystals show an oscillating behavior which is rather similar to that in the liquid; therefore these crystal forms are considered as candidates for modeling the liquid. A characteristic structural feature of liquid silicon is given by an anomalous flat $g(r)$ in the range between 0.3 and 0.4 nm. Such a plateau can only be reproduced by the β-tin structure. For this reason, further consideration is made with the β-tin structure although its atomic density is much higher than that of the liquid.

3.3. Structural Similarity between the Bond Orientational Order (BOO) of Liquid and Crystal

Beside the one-dimensional information, a two-dimensional property such as the BOO is also important for discussing why the medium-range order in liquid silicon arises. Wang and Stroud [35] discussed the BOO in liquid silicon only for the lower order of Q_1 to Q_3. However, as shown by Steinhardt et al. [25], the BOO in higher orders is necessary for the comparison of any structure of liquid and crystals. Therefore the values of Q_1 to Q_{12} in liquid silicon were estimated in this work by using molecular dynamics simulation.

It may be asked why we did not employ ab initio molecular dynamics such as the Car-Parrinello method for estimating the BOO. The medium-range order between 0.4 and 0.6 nm is the main interest in this work, but at present, the ab initio methods can deal with typically only 64 atoms [17–20]. For this small number of atoms, the half size of the basic cell is about 0.52 nm, which means that the simulated structure in the medium-range is deformed by the periodic boundary conditions. This kind of structural deformation in a small system has already been pointed out by Grabow [36]. Steinhardt et al. [25] suggested that the bond orientational order in simulated structures becomes modified by the periodic boundary conditions even in a larger system of 512 atoms. For these reasons we decided to choose the classical molecular dynamics method with 4096 atoms, of which half the cell size in the liquid state is 2.13 nm, which may be large enough for discussing the BOO in the liquid structure.

Figure 3 is a graphical representation of the estimated values of Q_l for each l in liquid silicon together with those of the nine crystal forms. The Q_l values for $l \leq 4$ in the liquid strongly deviate from the asymptotic value 0.33. This fact implies that the angular distribution of the neighboring atoms in liquid silicon is not random. Among the higher order values $l \geq 5$, Q_7 and Q_8 seem to be slightly higher than the asymptotic value. The similarity of BOO between liquid and crystal can be evaluated by calculating the correlation factor. When assuming the series of Q_l in $l_{\min} \leq l \leq l_{\max}$ to be the vector in $(l_{\max} - l_{\min} + 1)$-dimensions, then the correlation can be defined as the vector product, $\hat{Q}^{\text{liquid}} \cdot \hat{Q}^{\text{cryst}}$. In Table 2 the resultant correlation factors are listed together with the values of Q_1 to Q_6 in each crystal and the liquid. The highest correlation factors are found in the cases of T12, β-tin, and BC8 crystals.

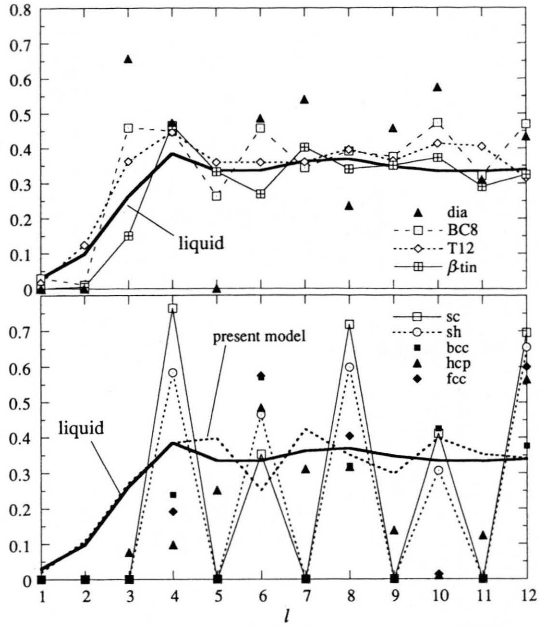

Fig. 3. The bond orientational order, Q_l, in the nine crystals and the simulated liquid structure. The thick dotted line in the lower half denotes the values in the model configuration given in Figure 7.

Table 2. Bond orientational order Q_l in nine crystal forms and the simulated structure of liquid silicon. The last column shows the correlation factor of each crystal structure with the liquid structure by considering the series of Q_1 to Q_6 as a vector.

	Q_1	Q_2	Q_3	Q_4	Q_5	Q_6	Corr. factor
dia	0	0	0.65697	0.47144	0	0.48588	0.815
BC8	0.02963	0.01093	0.45968	0.44942	0.26304	0.45765	0.960
T12	0.01642	0.12440	0.36243	0.44603	0.35956	0.35917	0.995
β-tin	0	0.00473	0.15051	0.46591	0.33246	0.26922	0.963
sc	0	0	0	0.76376	0	0.35355	0.729
sh	0	0	0	0.58301	0	0.46507	0.759
bcc	0	0	0	0.23849	0	0.57007	0.682
hcp	0	0	0.07607	0.09722	0.25159	0.48476	0.808
fcc	0	0	0	0.19094	0	0.57452	0.654
liquid	0.0289	0.0974	0.2617	0.3842	0.3345	0.3352	1

The physical meaning of these results may be easily understood by plotting the values of Q_3 and Q_4, as shown in Figure 4. The values of Q_3 and Q_4 represent the atomic configurations based on tetrahedral and octahedral arrangements, respectively. It is found in Fig. 4 that there is a smooth trend from diamond to BC8, T12 and β-tin, which corresponds to the order of the non-metallic to metallic phase transition under

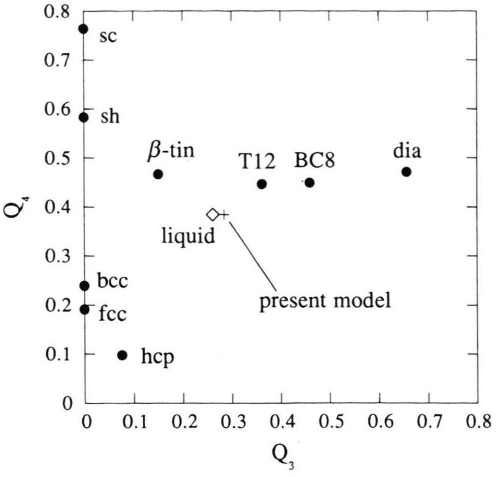

Fig. 4. Two-dimensional plot of Q_3 and Q_4 for the nine crystals and the simulated structure of liquid silicon. The cross denotes the Q_3 and Q_4 values for the model configuration given in Figure 7.

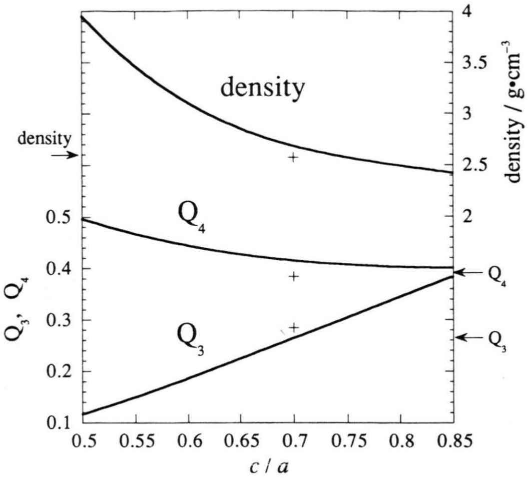

Fig. 5. Variation of the scaled density by the first-neighbor distance, Q_3 and Q_4 in the β-tin like structures as functions of c/a. The arrows denote the experimental density and simulated BOO. The three crosses denote the values in the model configuration given in Figure 7.

compression [31, 33, 37]. The BOO of liquid silicon locates between the T12 and β-tin structures, and thus a partial breaking of sp^3 bonding induced by melting is suggested. It may be concluded that the tetrahedral arrangement related to sp^3 bonding exists in liquid silicon but this atomic arrangement is not exactly identical to those found in the β-tin or T12 structures.

3.4. A New Structure Model of Liquid Silicon

We have now obtained new information for describing the structure of liquid silicon. In this section, a new model is proposed. The new model should conform with a three-dimensional structure which,

(a) reproduces the experimental density,
(b) reproduces the experimental data of $g(r)$ and $S(Q)$,
(c) shows a reasonable agreement with the simulated BOO, and
(d) satisfies the liquid nature of random orientation at long distances.

As a starting structure, we took the β-tin type which is closest to, but different from the actual liquid with respects to the density, the BOO, and the directional anisotropy originating from the c-axis.

The discrepancies in density and BOO can be reduced simultaneously by increasing the c/a ratio from the original value of 0.55 [31]. Figure 5 shows the variation of the scaled density and the values of Q_3 and Q_4 in the β-tin like structure as functions of c/a. As shown in this figure, a c/a ratio of 0.7 provides good coincidence with the density as well as the BOO characterized by Q_3 and Q_4. This implies that the β-tin structure with a ratio $c/a = 0.7$ satisfies the conditions (a) and (c). It should be pointed out, however, that the simulated $g(r)$ of this structure model shows a clear dip and peak at 0.29 and 0.35 nm, respectively, and the flat plateau is not seen any more. Hence some further modifications are needed for satisfying the condition (b).

It may be helpful to stress that the conditions (b) and (d) can be satisfied simultaneously by introducing different local orientations in the model structure. Generally speaking, coexistence of different orientations with special axes may lead to significant boundary mismatches. In case of the β-tin type, however, this can be released by introducing a slight modification of the atomic position if two regions contact with their (011) faces of body-centered tetragonal geometry, as shown in Figure 6. In this figure, the orientations of the local c-axis in two regions differ by about 120°. At the same time, the radial distribution near the boundary is modified from distinct peaks of first and third neighbor distances, 0.245 and 0.335 nm, to that of an averaged distance at about 0.29 nm. Hence the dip and peak at near neighbor distances

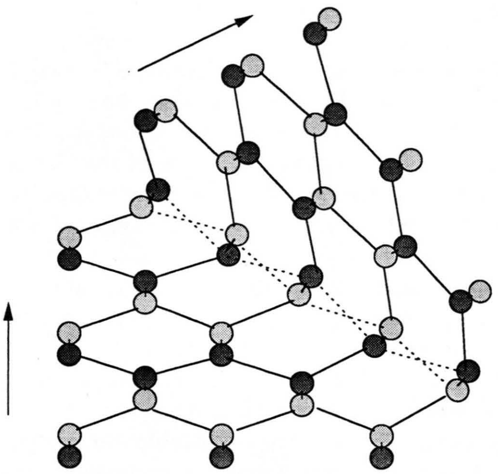

Fig. 6. Schematic diagram of the phase boundaries between β-tin like regions. The two types of atoms (black and gray) denote the they lie in different (100) layers. The arrow denotes the local orientation of [001] in each region.

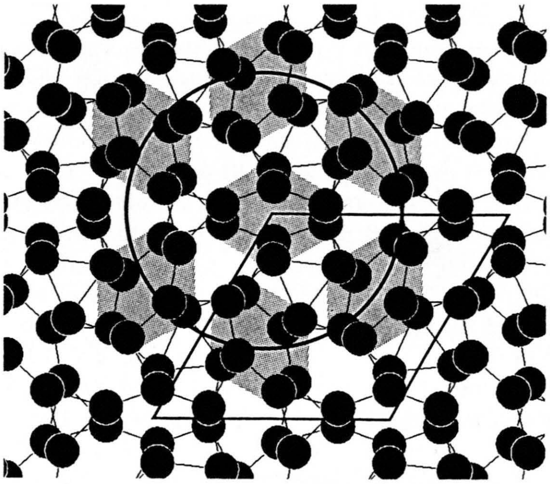

Fig. 7. Two dimensional view of the atomic arrangement of the present model for liquid silicon. The rhombic cell denotes the translational primitive cell in this configuration, and the gray areas show the local crystal-like regions. The circle with $r = 0.6$ nm was added as a guide for eyes.

found in $g^{\mathrm{cryst}}(r)$ with $c/a = 0.7$ are modified to a plateau-like distribution. By using this idea, a model structure of liquid silicon is constructed as illustrated in Figure 7. The present idea is to fill up the three-dimensional space by small β-tin like regions with different c-axis orientation. They are represented by the gray regions where the c-axis orientations differ by 60° to 120°, and then six different orientations are included. It may be noted that the distance between the centers of these gray regions is about 0.6 nm, which is comparable to the characteristic length scale in the medium range order.

After adjusting the values of the cell dimension of the local β-tin like region and the total atomic density

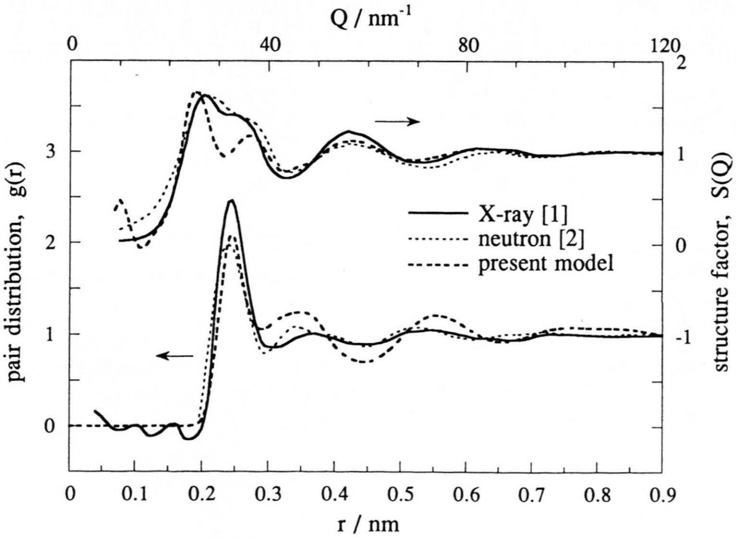

Fig. 8. A comparison of calculated $g(r)$ and $S(Q)$ of the present model with the experimental data obtained by X-ray [1] and neutron [2] diffraction.

based on the experimental data, the present model still has one additional free parameter, namely the gliding distance of two regions on the boundary. After selecting an appropriate value for this parameter, 0.05 nm, the pair distribution function in this configuration was calculated by (5), and the results are shown in Fig. 8 together with the structure factor calculated by (3). The present geometrical model is found to reproduce the essential structure features of liquid silicon, for example the first peak position with the flat plateau from 0.3 to 0.4 nm and the medium-range order between 0.4 and 0.6 nm in $g(r)$. The usefulness of the present model structure is also confirmed by finding agreement in the BOO results as shown in Figs. 3 and 4.

The significant difference between the experimental data and the present model is seen in the shape of the shoulder at the principal peak in $S(Q)$, which is mainly arising from the discrepancy in the amplitude of the medium-range order in $g(r)$. In other words, our model still keeps the regularity in the original crystalline structure too much. The authors maintain the view that further improvement is possible when considering the degree of freedom in the atomic configuration so as to allow more appropriate atomic positions for reproducing the liquid structure. This can be done by using, for example, the reverse Monte Carlo method but is beyond the purpose of the present work.

4. Concluding Remarks

The motivation of the present study is to understand the structure of liquid silicon based on a known atomic configuration with only minor modification. Our intention is, of course, not to insist that liquid silicon consists of collective microscopic crystals, but to show that the essential feature of liquid silicon, exemplified by the shoulder in the experimental structure factor, can be reproduced by considering the medium-range ordering. In the present approach, local atomic configurations of β-tin type with $c/a = 0.7$ are assumed, and their orientations are rearranged so as to have a nearly random distribution in the long distance. It includes only a few adjustable parameters, namely the experimental density, experimental first neighbor distance, and the gliding distance at the boundary. Although some further improvements of the model are requested, it would be interesting to extend the present result to the subject of physical properties of liquid silicon or germanium.

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[1] Y. Waseda and K. Suzuki, Z. Physik **B20,** 339 (1975).
[2] J. P. Gabathuler and S. Steeb, Z. Naturforsch. **34a,** 1314 (1979).
[3] M. Davidović, M. Stojić, and Dj. Jović, J. Phys. C: Solid State Phys. **16,** 2053 (1983).
[4] P. S. Salmon, J. Phys. F: Met Phys. **18,** 2345 (1988).
[5] V. Petkov, S. Takeda, Y. Waseda, and K. Sugiyama, J. Non-Cryst. Solids **168,** 97 (1994).
[6] Y. Waseda, The Structure of Non-crystalline Materials. McGraw-Hill, New York 1980.
[7] N. W. Ashcroft, Nuovo Cim. **12,** 597 (1990).
[8] M. Popescu, J. Physique **42,** C4-1043 (1981).
[9] B. R. Orton, Z. Naturforsch. **30a,** 1500 (1975). – B. R. Orton, J. Phys. Coll. **41,** C8-280 (1980).
[10] B. R. Orton, Inst. Phys. Conf. Ser. No. 101, 77 (1990).
[11] Z. Badirkhan, A. Ferrante, M. Rovere, and M. P. Tosi, Nuovo Cim. **12,** 619 (1990).
[12] Regnaut, C. J. P. Badiali, and M. Dupont, Phys. Lett. **74A,** 245 (1979).
[13] H. Beck and R. Oberle, J. Phys. Coll. **41,** C8-289 (1980).
[14] G. Kahl an J. Hafner, Solid State Commun. **49,** 1125 (1984). – W. Jank and J. Hafner, Phys. Rev. B **41,** 1497 (1990).
[15] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31,** 5262 (1985).
[16] See for example: M. D. Kluge, J. R. Ray, and A. Rahman, Phys. Rev. B **36,** 4234 (1987). – U. Landman, W. D. Luedtke, M. W. Ribarsky, R. N. Barnett, and C. L. Cleveland, Phys. Rev. B **37,** 4637 (1988). – Z. Q. Wang and D. Stroud, Phys. Rev. B **38,** 1384 (1988).
[17] I. Štich, R. Car, and M. Parrinello, Phys. Rev. Lett. **63,** 2240 (1989). – I. Štich, R. Car, M. Parrinello, and S. Baroni, Phys. Rev. B **39,** 4997 (1989). – I. Štich, R. Car, and M. Parrinello, Phys. Rev. B **44,** 4262 (1991).
[18] G. Kresse and J. Hafner, J. Non-Cryst. Solids **156–158,** 956 (1993).
[19] J. R. Chelikowsky and N. Binggeli, Solid State Commun. **88,** 381 (993).
[20] A. P. Horsfield and P. Clancy, Modelling Simul. Mater. Sci. Eng. **2,** 277 (1994).
[21] V. M. Glazov, S. N. Chizhevskaya, and N. N. Glagoleva, Liquid Semiconductors, Plenum, New York 1969.
[22] H. Sasaki, E. Tokizaki, K. Terashima, and S. Kimura, J. Cryst. Growth **139,** 225 (1994).
[23] H. Ogawa, K. Sugiyama, Y. Waseda, and Y. Shiraishi, J. Non-Cryst. Solids **143,** 201 (1992).
[24] Yu. G. Poltavtsev, Sov. Phys. Cryst. **16,** 387 (1971).
[25] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28,** 784 (1983).

[26] W. Brostow, J. P. Dussault, and B. L. Fox, J. Comp. Phys. **29,** 81 (1978).
[27] H. Balamane, H. T. Halicioglu, and W. A. Tiller, Phys. Rev. B **46,** 2250 (1992).
[28] S. J. Cook and P. Clancy, Pys. Rev. B **47,** 7686 (1993).
[29] S. Nose, J. Chem. Phys. **81,** 511 (1984).
[30] H. Ogawa, Y. Shiraishi, K. Kawamura, and T. Yokokawa, J. Non-Cryst. Solids **119,** 151 (1990). – H. Ogawa and Y. Waseda, J. Cryst. Growth **128,** 945 (1993).
[31] in: Properties of Silicon, EMIS Data Reviews Series No. 4, INSPEC, London 1988, p. 8 and references therein.
[32] J. S. Kasper and S. M. Richards, Acta Cryst. **17,** 752 (1964).
[33] Biswas, R. R. M. Martin, R. J. Needs, and O. H. Nielsen, Phys. Rev. B **30,** 3210 (1984).
[34] Waseda and Suzuki [1] derived 0.25 nm for the first neighbor distance by the Gaussian fitting of the radial distribution in $4\pi r^2 \varrho(r)$ form. This value is transferred to the first-peak position at about 0.245 nm in the $g(r)$ form adopted in this study.
[35] Z. Q. Wang and D. Stroud, J. Chem. Phys. **94,** 3896 (1991).
[36] N. H. Grabow, in: Materials Theory and Modelling Symposium, Master. Res. Soc., Pittsburgh 1993, p. 171.
[37] M. T. Yin and M. L. Cohen, Phys. Rev. B **26,** 5668 (1982); Phys. Rev. Lett. **45,** 1004 (1980).

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