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Simple view of waterlike anomalies of atomic liquids with directional bonding

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We propose that the shape of the equilibrium T-P phase diagram of a liquid is strongly correlated with the thermodynamic anomalies and the ease of vitrification. The T-P phase diagram of water is characterized by its V shape. By using this specific shape of the phase diagram as a fingerprint, we classify five elements Si, Ge, Sb, Bi, and Ga into water-type atomic liquids. Similarly, some group III-V (e.g., InSb, GaAS, and GaP) and II-VI compounds (e.g., HgTe, CdTe, and CdSe) are also classified into water-type liquids. We demonstrate that the phase behaviors and the thermodynamic and kinetic behaviors of these liquids can be described by the two-order-parameter model that deals with not only density ordering but also bond ordering. In these liquids, the former represents the metallic-bond nature favoring the isotropic symmetry and tries to increase the density upon ordering, while the latter represents the covalent-bond nature favoring the tetrahedral symmetry and tries to decrease it upon ordering. Thus, they are intrinsically competing. This model well explains the shape of the phase diagram, the temperature dependence of the structure factor, and the thermodynamic anomalies of density and heat capacity of liquid Si in a coherent manner. It also predicts that these water-type liquids will be very poor glass formers at ambient pressure, but their glass-forming ability should increase with increasing pressure. This increase in the glass-forming ability is not only due to the thermodynamic reasons, but also due to the kinetic ones.

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I. INTRODUCTION

The atomic liquid, which has no obvious internal degrees of freedom, apparently looks like the simplest ideal liquid. But it is not necessarily the case. This is due to anisotropic electronic interactions reflecting the symmetry of the electronic wave function. Thus, some atomic liquids can hardly be regarded as simple Lennard-Jones fluids. For example, some group-IV elements (Si,Ge) and semimetals (Sb,Bi,Ga) are famous for a number of unusual behaviors.[1–5] Despite the fact that Si and Ge are extremely important elements for semiconductor applications, their liquid-state properties and phase behaviors still remain to be clarified. Here we summarize unusual behaviors of Ge (Refs. 1–6) as a typical example to illustrate some common universal features of these atomic liquids. In a crystalline state (Ge-I), Ge is a diamond-structure semiconductor with a direct band gap of about 0.9 eV and an indirect gap of about 0.7 eV. Each Ge atom is surrounded by four covalently bonded first-nearest neighbors in a tetrahedral symmetry. With increasing pressure, the open tetrahedral bond network is broken and, thus, the number of neighbors and the density increase. Around 10 GPa a phase transition to the metallic *b*-Sn structure (Ge-II) occurs, and at even higher pressures a hexagonal phase and a close-packed phase are produced. At ambient pressure, the melting point of *c*-Ge (Ge-I) is $T_m=1210$ K but it decreases with increasing pressure. Upon melting, Ge undergoes a semiconductor-metal transition, accompanying the density increase by about 4.7% and the increase in the coordination number from 4 in the crystal to 6.8 in the liquid. The electrical conductivity increases upon melting by more than an order of magnitude and the band gap disappears. It is much suggested that these unusual features originating from the directional covalent bonding survive even in a liquid state. These behaviors are also observed for Si.

Interestingly, the behaviors of these atomic liquids look quite similar to those of water except for electronic properties: Water is known to increase its density and the coordination number upon the melting of hexagonal ice at 0 °C and to have the density maximum at 4 °C and polymorphism.[7,8] The physical origin of these anomalous behaviors of liquid water has recently been studied intensively,[9,10] focusing on its tetrahedral network-forming tendency. On noting the similar directional nature of covalent and hydrogen bonding, the similarity between water and the above-mentioned atomic liquids was suggested by Angell and co-workers[6,9,11] and Poole *et al.*[12] This view was also supported by recent computer simulations, as reviewed in Refs. 8, 11, and 12 Thus, these liquids are now sometimes called tetrahedral liquids.[9]

These unusual behaviors of atomic liquids are related to fundamental questions about the structure of a liquid: Is it completely disordered or partially ordered? If the latter is the case, does it contain an atomic configuration reminiscent of the equilibrium crystalline structure or other metastable competing local structures, such as icosahedral ordering?[13] And what physical factors determine the answers to these questions?

In addition to the thermodynamic anomalies, we point out an interesting common feature of these liquids, which may be a clue to answer the above questions. Molten Si, Ge, and Ga can be supercooled to a considerable degree, but they can never be quenched into the glassy state *in bulk* even with the fastest cooling rates available. On the other hand, solid Si, Ge, and Ga can be directly deposited in amorphous forms by evaporation or sputtering techniques. These features are again common to water: Amorphous forms of water can never be formed in bulk by a simple temperature quench and can be made only by hyperquenching or vapor deposition. The only reason why the glassy amorphous state of these

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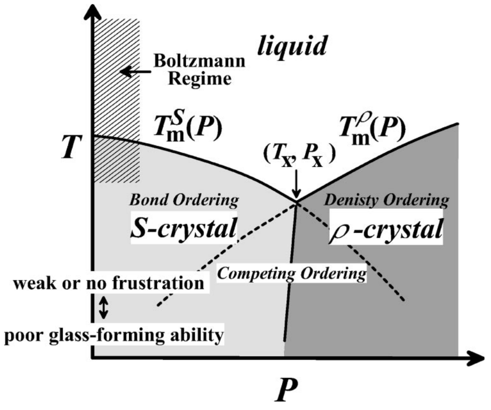

FIG. 1. A schematic figure of the phase diagram of water-type liquids including Si, Ge, Bi, Sb, Ga, and water itself. T_m^i is the melting point of an i crystal. The melting curve of a water-type liquid is thus characterized by its V shape; namely, it has the crossover pressure (P_x) at a positive pressure (Ref. 1). Our model tells us that this unusual phase diagram is directly related to the thermodynamic and kinetic anomalies of these liquids and also to the poor glass forming ability at ambient pressure. Here we also consider a possible liquid-liquid phase transition, or bond ordering in a liquid state (Refs. 8–12 and 19). According to our two-order-parameter model (Ref. 19), a gas-liquid critical point is identified as a critical point of liquid-state density (ρ) ordering, while a second-critical point is that of liquid-state bond (S) ordering. Our model suggests that water-type atomic liquids such as Si and Ge may have hidden liquid-liquid transitions below the melting point with a high possibility, as in the case of liquid water. However, it should not be the cause of the water-type anomalies (Refs. 18 and 19), which are discussed in this paper. Amorphous-amorphous transitions in Si and Ge, if they exist, should be a new type of semiconductor-metal transitions.

extremely poor glass formers are successfully produced with much effort is that these atomic liquids and water are so important, respectively, in semiconductor applications or in nature. It is known that the glass-forming ability of these liquids (at least, water and Ge) drastically increases with an increase in pressure. This poor glass-forming ability of these atomic liquids and water at ambient pressure and the drastic increase of their glass-forming ability at a high pressure[14,15] is an interesting problem for any theory of liquid or of liquid-glass transition and, at the same time, it may be a key to understand the above-mentioned unusual features of atomic liquids.

In this paper, we demonstrate that our two-order-parameter model of liquid can reasonably explain the above-described unusual behaviors of atomic liquids. On noting that the P-T phase diagrams[1] of five atomic liquids (Si, Ge, Sb, Bi, and Ga) are essentially the same as that of water, which is characterized by its V-shape (see Fig. 1), we classify them into "water-type atomic liquids."[16] We argue that the shape of the phase diagram is strongly correlated with not only the thermodynamic anomalies but also the ease of vitrification. We propose to use the shape of the P-T phase diagram as a fingerprint for specifying liquids having water-type behaviors.

The structure of the paper is as follows. In Sec. II, we briefly describe our two-order-parameter model of liquids. In Sec. III, we propose a physical scenario that the short-range bond ordering is responsible for the thermodynamic anomalies of water-type atomic liquids, and check its validity by using liquid Si as an example. In Sec. IV, we explain how the shape of the equilibrium phase diagram is related to the ease of vitrification and discuss the roles of short-range bond ordering in liquid-glass transition. In Sec. V, we summarize our paper.

II. TWO-ORDER-PARAMETER MODEL OF LIQUIDS

First we explain our model of atomic liquids. Our model is based on the idea[17–19] that (i) there exist unique locally favored structures in any liquids and (ii) such structures are created in a sea of normal-liquid structures and their number density increases upon cooling since they (in a ground state) are energetically more favorable by ΔE than normal-liquid structures (in an excited state). We identify a locally favored structure as a minimum structural unit [symmetry (or volume) element].[20] For atomic liquids such as Si and Ge, it should be tetrahedron, which has a larger specific volume by Δv (>0) than the corresponding normal-liquid structure does. Note that there are many different configurations as well as various bonding states for normal-liquid structures, while there is a unique configuration for locally favored structures. Thus, the degeneracy of the state of normal-liquid structures (g_ρ) should be much larger than that of locally favored structures (g_S). The relevance of this two-order-parameter model of liquids was supported by the successful description of water's anomalies.[18,21]

To express the short-range bond ordering in liquids, we introduce the so-called bond-orientational order parameter Q_{lm} (Refs. 22 and 23): $Q_{lm}(\mathbf{R})=Y_{lm}(\theta(\boldsymbol{R}),\Psi(\boldsymbol{R}))$, where $Y_{lm}(\theta(\boldsymbol{R}),\Psi(\boldsymbol{R}))$ are the spherical harmonics, and $\theta(\boldsymbol{R})$ and $\Psi(\boldsymbol{R})$ are the polar angles of the bond measured with respect to some reference coordinate system, and $\boldsymbol{R}$ is the midpoint of a bond. Then we take the normalized average of Q_{lm} over a small volume located at $\boldsymbol{r}$, which we express by $\overline{Q}_{lm}(\boldsymbol{r})$. Then, its rotationally invariant combination can be defined as

$$Q_l(\boldsymbol{r})=\left[\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|\overline{Q}_{lm}(\boldsymbol{r})|^2\right]^{1/2}. \tag{1}$$

We can use this $Q_l(\boldsymbol{r})$ to define the local bond order parameter: $S(\boldsymbol{r})\equiv Q_l(\boldsymbol{r})$. For example, $l=3$ for a tetrahedron,[23] while $l=6$ for an icosahedron.[22]

On the basis of a two-state model,[18,19] the equilibrium average of the fraction of locally favored structures S, $\overline{S}$, can be straightforwardly obtained, if we assume $\overline{S}\ll 1$, as

$$\overline{S}=\frac{g_S}{g_\rho}\exp[\beta(\Delta E-P\Delta v)], \tag{2}$$

where $\beta=1/k_BT$. We call a temperature region, where $\overline{S}$ is small enough and is given by the above Boltzmann factor, a "Boltzmann regime." It should be noted that this condition of $\overline{S}\ll 1$ is satisfied even for $\beta\Delta E>1$ since $g_S\ll g_\rho$. We also note that although the average fraction is described by the above thermodynamic relation, locally favored structures are created and annihilated in a rather short time scale and thus the system should not be regarded as a simple mixture of the two components. From kinetic consideration, we can say that the lifetime of locally favored structures is longer than that of normal-liquid ones.

We argue that the Boltzmann regime almost entirely covers the experimentally accessible liquid state of bulk atomic liquids (see Fig. 1), which was confirmed for the case of liquid water.[18] At a low temperature, the cooperativity in excitation of locally favored structures may play an important role and in some cases it would lead to a liquid-liquid phase transition[9–12] (see the caption of Fig. 1). Such behavior can also be described in a natural manner by our model,[19] which takes the cooperativity of short-range bond ordering into account.

III. SHORT-RANGE ORDERING AND THE RESULTING THERMODYNAMIC ANOMALIES

Here we demonstrate that the thermodynamic anomalies of water-type liquids can simply be explained by the short-range tetrahedral ordering. We choose liquid Si as an example, since accurate experimental data for the structure factor, density, and heat capacity are available for it.

A. Structural change upon cooling in liquid Si: Evidence of short-range bond ordering

The existence of the short-range order with tetrahedral symmetry is evidenced by the shoulder in the high wave number (q) side of the first peak of the structure factor $F(q)$, or the second peak of the radial distribution function $g(r)$, for liquid Si, Ge, and Ga. For Si, for example, the first peak of $g(r)$ is located around $r_1 = 2.4$ Å, while the second one is around $r_2 = 3.5$ Å.[3–5,24] The ratio of 3.5/2.4=1.46 is compatible with that of the two characteristic interatomic distances of the tetrahedral unit, $2\sqrt{6}/3 = 1.63$. We analyze the temperature dependence of the ratio of the height of the second peak to that of the first one of $g(r), g(r_2)/g(r_1)$ of liquid Si, which is a direct measure of the population of tetrahedral units. We assume the following functional form:

$$g(r_2)/g(r_1) = a + b\,\exp(\Delta E/k_B T). \tag{3}$$

Here a, b, and ΔE are positive constants, which are used as the adjustable parameters in the fitting. As shown in Fig. 2, the temperature dependence of $g(r_2)/g(r_1)$ is found to be well described by $\overline{S}$ with $\Delta E = 8107$ K. This result supports the validity of our argument from the structural viewpoint.

B. Thermodynamic anomalies of Si

Along the same line, we next consider the thermodynamic anomalies of density[25] and heat capacity[25] of Si, which are similar to those of water.[7,8] According to our two-state model, the specific volume v_{sp} is given by

$$v_{sp} = v_{sp}^B + \Delta v \overline{S}. \tag{4}$$

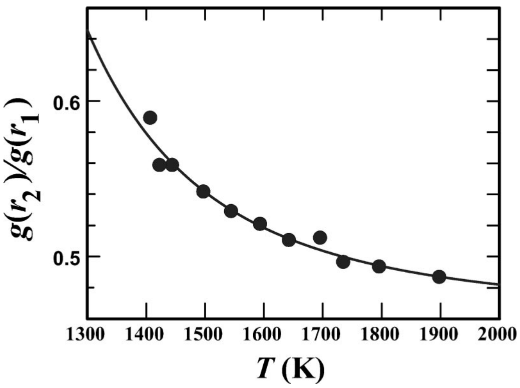

FIG. 2. Temperature dependence of $g(r_2)/g(r_1)$ of Si calculated from the experimentally measured $g(r)$ (Ref. 24). Solid line: $g(r_2)/g(r_1) = 0.46 + 3.6\times 10^{-4}\exp(8107/T)$. Its anomalous increase upon cooling is very well described by the Boltzmann factor, $\exp(8107/T)$ (solid line).

Here v_{sp}^B is the normal part of v_{sp}, which is governed by density ordering, and it monotonically decreases upon cooling. This yields the following expression of density anomaly:

$$\rho \cong \rho_B - \rho_B \frac{\Delta v}{v_{sp}^B}\overline{S}, \tag{5}$$

where ρ_B is the background (normal) part of the density. Thus, the anomalous part of density should be proportional to $\overline{S}$. We fit the following function to the data of the density of liquid Si,[25] using $\Delta E = 8107$ K, which is determined above, and assuming the linear temperature dependence of ρ_B:

$$\rho = c + dT - e\,\exp(8107/T). \tag{6}$$

Here c, d, and e are positive constants, which are used as the adjustable parameters in the fitting. The result is quite satisfactory, as shown in Fig. 3. Note that the behavior of the background part is reasonable.

For making the discussion more quantitative, the estimation of Δv is necessary. If the pressure dependence of ρ is available, we can estimate Δv with the a help of Eq. (2), as

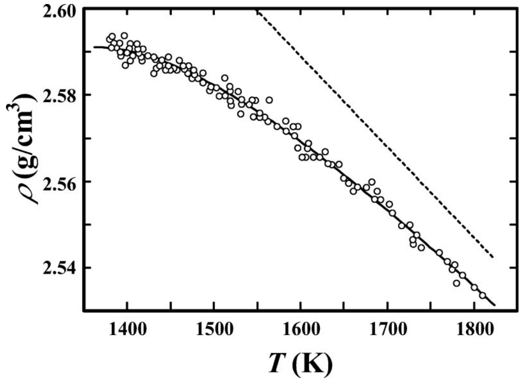

FIG. 3. Density anomaly of liquid Si. Solid line: $\rho = 2.926 - 2.105\times 10^{-4}T - 1.246\times 10^{-4}\exp(8107/T)$(g/cm^3); dashed line: the background part.

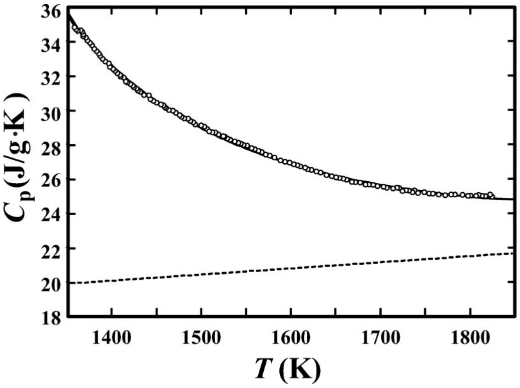

FIG. 4. Heat capacity at constant pressure of liquid Si. Solid line: $C_P = 15.07 + 3.576 \times 10^{-3} T + 3.182 \times 10^{-2} \exp(8107/T)$ (J/g K); dashed line: the background part.

in the case of water.[18] The relationship between short-range tetrahedral ordering and the associated low local density may also be clarified theoretically.[26] The experimental and theoretical efforts along the above directions are highly desirable to elucidate how the short-range bond ordering is related to the local density.

Next we consider the anomaly of heat capacity.[27] According to our model, the entropy σ increases upon heating, reflecting a decrease in $\overline{S}$:

$$\sigma = \sigma_B - \Delta\sigma\overline{S}, \tag{7}$$

where $\Delta\sigma = k_B \ln(g_\rho/g_S)$. Thus, $C_P = T(\partial\sigma/\partial T)_P$ should increase upon cooling as

$$C_P = T(\partial\sigma_B/\partial T)_P + [-T(\partial\Delta\sigma/\partial T)_P + \beta\Delta\sigma(\Delta E - P\Delta v)]\overline{S}. \tag{8}$$

Thus, the anomalous part of C_P should also be proportional to $\overline{S}$. We fit the following function to the data of C_P of liquid Si (Ref. 25) at ambient pressure with assuming the linear temperature dependence of the background part:[27]

$$C_P = f + gT - h\exp(8107/T). \tag{9}$$

Here *f*, *g*, and *h* are positive constants, which are used as the adjustable parameters in the fitting. The result is again quite satisfactory, as shown in Fig. 4. Note that the behavior of the background part is reasonable.

It should be stressed that the anomalies of ρ and C_P are both very well described by a common Boltzmann factor with the same energy ($\Delta E = 8107$ K) as that describing the temperature dependence of $g(r_2)/g(r_1)$. The anomalous parts of $g(r_2)/g(r_1)$, ρ and C_P, all of which are proportional to $\overline{S}$, should decrease with an increase in pressure P [see Eq. (2)]. At a very high pressure, all the anomalies should disappear. Thus both ρ and C_P should approach their background parts with an increase in P.[18] This prediction should be checked in the future.

Here it is worth mentioning the thermodynamic anomalies of other members of water-type atomic liquids. It is known that the density anomaly of Ge is much weaker than that of Si, but the heat capacity anomaly of Ge is significant.[28] This may be explained by smaller Δv for Ge than for Si (see the above expressions for ρ and C_p anomalies). Note that the density jump during melting, which should be related to Δv, is 11% for Si, while 5% for Ge. We also mention that similar heat capacity anomaly is observed in Ga,[29] too. Finally, we mention that we must include the effects of cooperative excitation of locally favored structures to describe the behaviors at a lower temperature.[19]

C. Correlation between the shape of the equilibrium phase diagram and the thermodynamic anomalies

Here we consider the physical origin of the correlation between the shape of the phase diagram and the thermodynamic anomalies. The water-type phase diagram (see Fig. 1) tells us that there are two competing orderings, both of which can attain long-range crystalline order. For water-type atomic liquids, the density order parameter represents the metallic-bond nature, which favors the isotropic symmetry and leads to crystallization into a body-center cubic (bcc) crystal. The bond order parameter, on the other hand, represents the covalent-bond nature, which favors the tetrahedral symmetry and leads to crystallization into a diamond-type crystal. Crystallization below the crossover pressure P_x can be regarded as long-range tetrahedral bond (S) ordering, while that above P_x as long-range density (ρ) ordering.[30] The former is characterized by the volume increase upon crystallization, while the latter is by the volume decrease upon crystallization. The relation $\partial T_m/\partial P < 0$ below P_x guarantees the existence of locally favored structures of $\Delta v > 0$. Our model suggests that this is a sufficient condition for waterlike anomalies. Thus, we predict that liquids with a water-type phase diagram should generally have waterlike anomalies. This prediction is confirmed at least for Si, Ge, and Ga.

We also predict that the viscosity of a water-type liquid might decrease with an increase in pressure at a low temperature as in the case of water, reflecting the decrease in the degree of short-range bond ordering [see Eq. (2)], although it should increase with a further increase in pressure. Please refer to Ref. 18 for the details of the mechanism.

IV. RELATION BETWEEN THE EASE OF VITRIFICATION AND THE PHASE DIAGRAM

A. Two-order-parameter model of liquid glass transition and its relation to other models based on frustration

1. Two-order-parameter model of liquid-glass transition

Before discussing the relation between the ease of vitrification and the equilibrium phase diagram, we briefly explain our two-order-parameter model of liquid-glass transition.[17] Our model focuses on the short-range bond ordering in liquids, which we regard as a quite generic feature of liquids. For liquids like SiO_2, water, and Si, for example, locally favored structures are tetrahedral structures, while for metallic glass formers they are icosahedral ones.[13,31] According to our two-order-parameter model,[17] vitrification is due to frustration effects of short-range bond order against crystallization, namely, competing ordering between long-range density

(ρ) ordering and short-range bond (S) ordering. Locally favored structures formed in an ordinary liquid, which are more stable than normal-liquid structures, play a similar role to random magnetic impurities in spin glass for crystallization. Thus, they suppress crystallization and help vitrification. According to our model, a liquid suffering from stronger disorder effects, or a liquid with larger $\overline{S}$, should be stronger, or less fragile.

2. Comparison of our model with other models based on frustration

Since our model focuses on frustration in liquids, our model may look similar to other frustration models.[22,32–38] Despite the apparent similarity, however, there is a crucial difference in the physical picture between them. Frustration in our model stems from the competition between the two order parameters with different symmetries. The frustration exists for most liquids except for water-type liquids (see below) and liquids such as Ar that have little short-range order. For ordinary glass-forming liquids, the density order parameter leads to long-range density ordering, namely, *real* crystallization into the equilibrium crystal, while the bond order parameter has short-range order. The latter acts as impurities against the crystallization because of the incompatibility of the symmetries between these two order parameters. Geometrical (symmetrical) frustration between crystalline order and short-range bond order is a key concept of our model, which leads to the prediction that the equilibrium phase behavior, more specifically, the sign of the volume change upon crystallization, is correlated with the fragility and the ease of vitrification, as will be shown below.

In other frustration models,[22,32–38], frustration stems from the internal frustration of the order parameter (e.g., Q_6) itself. In other words, short-range bond ordering tries to attain its long-range ordering (e.g., quasicrystalline order), but frustration prevents this (Q_6).[39] Thus, these models leave the symmetry of real equilibrium crystals out of consideration. Accordingly, the avoidance of crystallization into a real crystal, which is necessary for vitrification, is presupposed, or more precisely, frustration is not thought to be a physical factor directly controlling the glass formability in these models. In these models, which we call a one-order-parameter model with internal frustration, thus, there is almost no direct connection between frustration and crystallization, although this itself has nothing to do with the validity of models.

Some of these frustration models also predict that a stronger liquid suffers from stronger frustration (see, e.g., Refs. 37 and 38), as our model does.[17] However, this apparent similarity is worthy of careful consideration to clarify the difference in the basic physical picture between the two types of frustration models. It is known that the locally favored structures of liquids such as SiO_2, Si, and water all have the tetrahedral symmetry of Q_3. This symmetry can have a true long-range order; for example, the diamond-type crystal has this symmetry. Thus, internal frustration of the tetrahedral bond order parameter seems to be rather weak. In relation to this, the following questions are to be answered: (i) Why is SiO_2 a very strong liquid? (ii) Why is the glass-forming behavior so different between SiO_2 and liquids such as water and Si? The latter might be explained by the difference in other factors such as viscosity, but the former should be explained in the framework of the previous frustration models. At the first glance, it seems to be rather difficult to find a natural explanation for question (i), although this point should be considered more carefully.

Our model, on the other hand, explains these two problems as follows. (i) SiO_2 has a high number density of locally favored structures with the tetrahedral symmetry ($\Delta v > 0$) due to large ΔE. Thus, they cause strong frustration against crystallization into ρ crystal. Note that crystals such as cristobalite, tridymite, and quartz, into which SiO_2 tends to crystallize at ambient pressure, have higher densities than the liquid. Thus, the crystallization should be regarded as long-range density (ρ) ordering. These strong frustration effects, which are characterized by large $\overline{S}$, make SiO_2 a very strong liquid. (ii) For SiO_2, crystallization is long-range density ordering. For water and Si, on the other hand, it is long-range bond ordering at ambient pressure. Thus, the tetrahedral short-range order has strong frustration effects only for the former and does not for the latter.

However, which of the above two approaches based on frustration and others that do not focus on frustration is most relevant to the physical description of liquid-glass transition should carefully be studied in the future, since it is directly related to the fundamental physical question about why and how liquids vitrify.

3. Role of internal frustration of the bond order parameter in our model

Our model does not necessarily require the internal frustration of the bond order parameter. We stress that the internal frustration does not play a crucial role in vitrification itself in our model. For example, strong internal frustration exists for locally favored structures having a symmetry of Q_6, but does not for those having a symmetry of Q_3. The latter is the case for water-type liquids as well as SiO_2.

Even in our model, however, the degree of internal frustration has the important role in determining the degree of localization of locally favored structures. When locally favored structures do not suffer from strong internal frustration, for example, they are not so strongly localized compared to the case of icosahedral structures. Thus, locally favored structures can have medium-range order in such a liquid. For example, this is consistent with the known experimental results on liquid SiO_2, which suggests the existence of medium-range order. Our model further suggests that these locally favored structures of medium-range order are the origin of the first sharp diffraction peak (or prepeak) and the boson peak that are commonly observed in strong glass-forming liquids.[40]

B. Absence of frustration effects for water-type liquids below the crossover pressure P_x

Next we consider how the ease of vitrification is related to the shape of the phase diagram on the basis of our model.

Their relation can be explained by the compatibility between the locally preferred symmetry and the crystallographic symmetry. For liquids having locally favored structures of the icosahedral symmetry (Q_6) (e.g., metallic alloys), for example, the locally preferred symmetry is not consistent with the symmetry of the crystal, into which a liquid tends to crystallize. For this case, real crystallization is driven by the density order parameter, and not by the bond order parameter. Thus, the frustration between long-range density ordering and short-range bond ordering may cause slow dynamics and lead to vitrification,[17,41,42] if it is strong enough.

For water-type atomic liquids such as Si and Ge, on the other hand, the tetrahedral symmetry (Q_3) of the locally favored structures is consistent with the diamondlike structure of the equilibrium crystal at ambient pressure. Crystallization of Si and Ge below P_x can be regarded as the long-range ordering of S (or Q_3) itself. Thus, the locally favored structures have few frustration effects on crystallization into the S crystal and even help crystallization into the S crystal. Thus, these liquids should be poor glass formers and should not have slow dynamics associated with glass transition. On the other hand, they have strong frustration effects on crystallization into the ρ crystal at a high pressure (see Fig. 1) since the tetrahedral symmetry of locally favored structures is not compatible with the symmetry of the ρ crystal. Thus, the glass-forming ability should be much higher at a high pressure than at ambient pressure. In our model, it is the frustration between the two order parameters that makes the free-energy landscape of a liquid complex and leads to the slow dynamics in its supercooled state below T_m.[17]

Here we also consider how short-range bond ordering and the resulting frustration affect the kinetics of crystal nucleation. First the short-range bond ordering lowers the free-energy of liquid by $(\Delta E - T\Delta\sigma)\bar{S}$. Upon nucleation, furthermore, locally favored structures must be destroyed in the volume of a crystal nucleus if their symmetry is not consistent with that of the crystal. These effects suppress the nucleation frequency I as[17]

$$I = \frac{k}{\eta}\exp\left[-\frac{A\Delta H_f}{T[\Delta T_r - (\Delta G/\Delta H_f)\bar{S}]^2}\right], \tag{10}$$

where k and A are constants, η is the viscosity, ΔH_f is the heat of fusion, and $\Delta T_r = (T_m - T)/T_m$. Here ΔG is a free-energy barrier to break up a unit volume of locally favored structures and it is an increasing function of the degree of the frustration. Note that the expression of I for $\Delta G = 0$ reduces to that derived by Turnbull.[43] The above frustration-induced suppression of the nucleation frequency exists only when the symmetry of locally favored structures is not consistent with that of the crystal into which a system tends to crystallize. When the symmetry of locally favored structures is consistent with that of the crystal, locally favored structures even help nucleation and thus $\Delta G < 0$. This should be the case for water, Si, Ge, Sb, Bi, and Ga, as described above. The negative ΔG should significantly reduce the glass-forming ability of these liquids. This is consistent with the fact that these liquids just crystallize upon cooling and cannot be vitrified by a simple temperature quench.[41,44]

C. Switching of the relevant order parameter and its effects on the ease of vitrification

With an increase in pressure, the crystal into which a liquid crystallizes switches from S crystal to ρ crystal at the crossover pressure P_x. This tendency to crystallize into a ρ crystal can appear even below P_x when a liquid is quenched into the competing ordering region or into the ρ-crystal region (see Fig. 1). Such switching behavior below P_x is indeed observed in the competing ordering region for Sb, Bi, and Ga. For Bi emulsion samples, for example, a liquid crystallizes into both S-type and metastable ρ-type crystals by a deep quench, which is confirmed by the difference in their T_m.[45]

According to our model, this switching of crystal, into which a liquid tends to crystallize, from S-type to ρ-type should lead to the increase in frustration. This prediction is very consistent with the following experimental findings of Zhang and Wang:[14] Liquid Ge cannot be vitrified at ambient pressure by a temperature quench and just crystallizes into Ge-I crystal (S crystal). But it can be vitrified at high pressures ($\sim$3 GPa) by a temperature quench into the competing ordering region (see Fig. 1). More importantly, the amorphous phase coexists with the high-pressure form of Ge crystal, Ge-II (ρ-crystal) just after the quench,[46,47] although it seems to eventually transform into a Ge-I crystal (S crystal). This indicates that switching of the crystal form, into which a liquid tends to crystallize, from S crystal to ρ crystal is indeed related to the glass-forming ability. It should be noted that the similar behavior is also observed in water.[15] Thus, we propose that frustration between short-range bond ordering and long-range crystalline ordering is one of the key factors determining the glass-forming ability.

Finally, it may be worth mentioning the kinetic factor, which is primarily determined by the viscosity of a liquid. Usually, the viscosity of a liquid monotonically increases with an increase in pressure. Contrary to this common behavior, however, it is known that the viscosity of water decreases with an increase in pressure up to $\sim P_x$ and then increases with its further increase. This unusual behavior can also be explained by the decrease in the short-range bond order with an increase in P [see Eq. (2)].[18] If the same scenario works, thus, we cannot expect a drastic increase in the viscosity at the pressure applied in the above experiment for liquid Ge. At a higher pressure, however, frustration effects may change the situation. According to our model,[17] frustration is a necessary and sufficient condition for a liquid to have the complex free-energy landscape. Once frustration is set in above P_x, thus, it lead to slow dynamics of a system, reflecting the complex free-energy landscape, which helps vitrification. In a sufficiently high-pressure region, viscosity should increase with pressure, as in usual glass-forming liquids. Thus, frustration has both thermodynamic and kinetic effects that help vitrification there.

These considerations suggest that our explanation based on the frustration effects of short-range bond order on crystallization is plausible. Since there are other physical factors determining the glass-forming ability, however, further careful studies are necessary to unambiguously determine what the most relevant factor to the above phenomena is. In particular, the pressure dependence of viscosity should clearly tell us which of the thermodynamic and kinetic factors is more important for the above phenomena; for example, if the viscosity of liquid Ge around 3 GP is not so different from that at ambient pressure, we can ascribe the observed enhancement of glass-forming ability at high pressures to the above-mentioned thermodynamic factors.

V. SUMMARY

Our model tells us that *the equilibrium phase behavior (the P-T phase diagram) is closely related to both the thermodynamic anomalies and the ease of vitrification*. There exist at least five elements whose phase diagrams[1] have the feature characterized by Fig. 1: Si, Ge, Sb, Bi, and Ga.[16] The crossover pressure P_x is located approximately at 14, 10.5, 6, 2.4, 1, and 0.2 GPa, respectively, for Si, Ge, Sb, Bi, Ga, and water.[1,7,8] We classify these elements into ‘‘water-type atomic liquids.’’

Our model predicts that these liquids should share two common features: (i) thermodynamic and dynamic anomalies similar to those of water (known for Si, Ge, and Ga) and (ii) poor glass-forming ability at ambient pressure (known for water, Si, Ge, Bi, and Ga). Concerning feature (ii), our model also predicts that these liquids should be more easily vitrified at high pressures, where locally favored structures should have frustration effects against crystallization (long-range density ordering). This correlation between the volume increase upon crystallization and the poor glass-forming ability is a prediction unique to our model based on the competition between the two order parameters. Our model suggests that the compatibility of the symmetry of locally favored structures with that of the crystal, into which a liquid tends to crystallize, is one of the key physical factors that determine the ease of vitrification of liquid.

It may be worth noting here that there are some compounds that also have the water-type phase diagram (see Fig. 4). They are many of the binary equiatomic compounds formed between group-III and -V elements (e.g., InSb, GaSb, AlSb, InAs, GaAs, AlAs, InP, GaP, and AlP)[48] and those formed between group-II and -VI elements (e.g., HgTe, CdTe, and CdSe).[49] Our model predicts that these compounds should also share features common to liquid water and the above water-type atomic liquids. This prediction should be checked in the near future.

Our model may shed a new light on the physical understanding of the thermodynamic anomaly of liquids and the liquid-glass transition. Since our discussion is speculative, however, further careful studies on their physical origins are highly desirable. Particularly interesting are experimental studies on how the glass-forming ability changes as a function of pressure and how it is related to the type of crystallization in water-type liquids.

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