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# Anomalous diffusivity in supercooled liquid silicon under pressure

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We perform isothermal-isobaric first-principles molecular-dynamics simulations to investigate the dynamics of liquid silicon (*l*-Si) under pressure. We find that the self-diffusion coefficient increases with increasing pressure in the deeply supercooled state. This anomalous diffusivity is attributed to the formation of locally tetrahedral configurations which on average reduces the diffusivity at low pressures. Densification hinders the formation of the tetrahedral configurations, thus the diffusivity increases with increasing pressure. The tetrahedral configurations frequently formed at low pressures may be viewed as fragments of the low-density form of *l*-Si. It is therefore conceivable that transformations between two distinct liquids, low- and high-density liquids, locally occur in deeply supercooled *l*-Si. The present findings indicate the profound generality of the dynamics in liquids with a tetrahedral network such as water.

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The effect of pressure on transport properties has been investigated in a variety of liquids, particularly in water and silicate melts [1–6]. Measurements of the self-diffusion coefficients in such liquids show that the diffusivity increases with increasing pressure at low temperatures. This "anomalous" diffusivity is considered to come from the destruction of a network structure, e.g., tetrahedral framework in water, by densification. Intensive studies to clarify microscopic mechanisms of the anomalous diffusivity have been conducted in water and silicate melts [1–6]. However, in contrast, no attempt has been made to probe such an anomalous diffusion in liquid silicon despite its crystalline form having a perfect tetrahedral network.

Recently, striking similarities between water and silicon (Si) have been revealed with respect to their disordered phases, liquid and amorphous states [7–9], as well as crystalline phases. Of particular interest is that both Si and water exhibit similar polyamorphic transformations between two distinct amorphous states, low-density amorphous (LDA) and high-density amorphous (HDA) states [7,8]. Computer simulations have also shown that transformations between low-density liquid (LDL) and high-density liquid (HDL), viz. *liquid-liquid transformation*, should occur in water and Si in the supercooled condition [9,10]. It is therefore expected that the diffusion characteristics of water such as the anomalous pressure dependence are also exhibited in liquid Si (*l*-Si).

In this paper, we investigate the pressure dependence of diffusivity in *l*-Si by first-principles molecular-dynamics (FPMD) simulations. We find that the calculated diffusion coefficient definitely increases as pressure increases in the deeply supercooled state, whereas it decreases with increasing pressure at a temperature slightly below the melting point. The present calculations demonstrate that the anomalous diffusivity in supercooled *l*-Si can be attributed to the extremely low diffusivity at low pressures which results from the frequent formation of locally tetrahedral configurations. We also address the formation of the tetrahedral configurations in connection with a *local* liquid-liquid (LDL-HDL) transformation that may induce various anomalies as those in water [11].

Isothermal-isobaric FPMD simulations based on the Car-Parrinello [12] and Parrinello-Rahman-Nosé-Hoover techniques [13,14] were performed with a 64-atom supercell of *l*-Si at various pressures. The electronic state calculation was based on density functional theory within the local density approximation [15]. Details of the computations are the same as those in Ref. [8]. It is well known that relatively lengthy runs are necessary to obtain dynamic properties in liquids. We thus performed a series of MD runs, each for 45–90 ps, at pressures ranging from 0 to ~20 GPa. In the present study, the pressure dependence of the diffusivity has been investigated at 1100 and 1500 K: the former corresponds to the deeply supercooled state and the latter is slightly below the melting temperature of Si (1685 K). Note that *l*-Si at ~1700 K has a coordination number of ~6.5 and the tetrahedral network is considerably collapsed compared to that of crystalline Si at atmospheric pressure [16] (i.e., "normal" *l*-Si corresponds to HDL [9]).

Figure 1 shows the power spectrum $\hat{Z}(\omega)$ of the velocity auto-correlation function, $Z(t)=\langle v_i(t)v_i(0)\rangle/\langle v_i(0)v_i(0)\rangle$, for *l*-Si at 1100 K. We observe a TA-like vibrational mode of crystalline Si at ~100 cm$^{-1}$ at all pressures up to 18 GPa. This is a remnant of the tetrahedral bonding [17] and is more clearly seen at lower pressures. We also find that the zero-frequency value of $\hat{Z}(\omega)$, $\hat{Z}(0)$, increases as pressure increases up to ~10 GPa. $\hat{Z}(0)$ is proportional to the self-diffusion coefficient, so that an anomalous diffusivity is expected at 1100 K. In contrast, no distinct vibrational peak is found in $\hat{Z}(\omega)$ at 1500 K which monotonically decreases with $\omega$, as in previous FPMD calculations on *l*-Si above ~1700 K [16].

The self-diffusion coefficient $D$ as a function of pressure for 1100 and 1500 K is shown in Fig. 2. We calculated $D$

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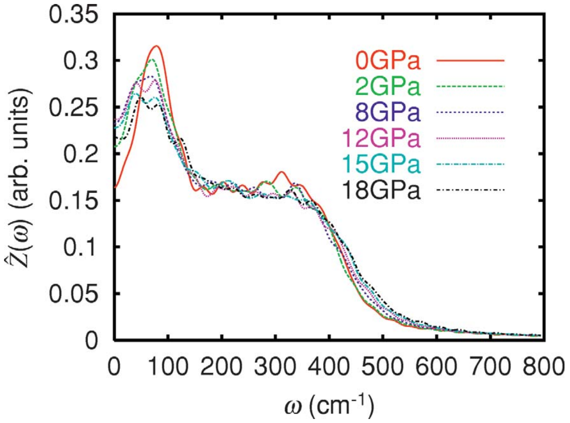

FIG. 1. (Color) Power spectrum $\hat{Z}(\omega)$ of the velocity autocorrelation function $Z(t)$ for $l$-Si at 1100 K.

from both the atomic mean-square displacement and the Green-Kubo relation, $D=kT\hat{Z}(0)/M$, where $M$ is the atomic mass. The calculated values by the two methods are in good agreement with each other [18]. $D$ shows a broad maximum in the range of 7–15 GPa at 1100 K, while it gradually decreases at 1500 K, showing conspicuous dependence of $D$ upon the temperature. It has been considered that the anomalous diffusivity observed in water results from the competition of the following two mechanisms [2,3]: (1) the breakdown of the tetrahedral network leading to the increase of atomic mobility; and (2) the packing effect by densification leading to the decrease of atomic mobility. In supercooled $l$-Si, as indicated in Fig. 1, tetrahedral configurations are well preserved at low pressures but they are gradually collapsed by densification. It is thus considered that the above two mechanisms for water diffusivity also work in supercooled $l$-Si. The present findings reveal the profound generality of the anomalous diffusivity in tetrahedrally coordinated substances such as Si and water.

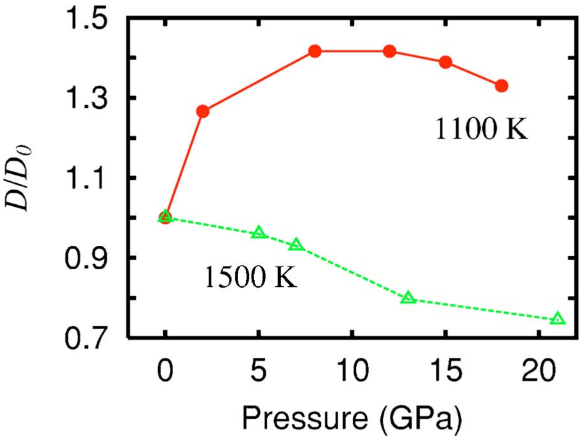

FIG. 2. (Color online) Pressure dependence of the self-diffusion coefficient $D$ (scaled by the 0 GPa value, $D_0$) for $l$-Si at 1100 K (red filled circles) and 1500 K (green open triangles) with a maximum error of ~7%: $D_0 \sim 5.3\times10^{-5}$ cm$^2$/s at 1100 K and $D_0 \sim 1.8\times10^{-4}$ cm$^2$/s at 1500 K.

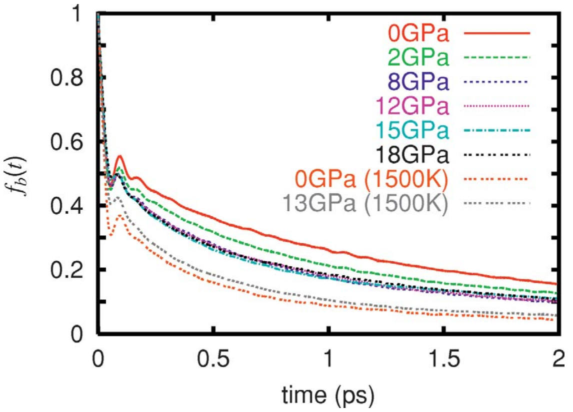

FIG. 3. (Color) Time-correlation function $f_b(t)$ for $l$-Si at 1100 K (0–18 GPa) and 1500 K (0 and 13 GPa).

Figure 3 shows the time-correlation function $f_b(t)$ defined as

$$f_b(t) = \frac{\langle p_{ij}(t)p_{ij}(0)\rangle}{\langle p_{ij}(0)p_{ij}(0)\rangle}, \tag{1}$$

where $p_{ij}(t)=\theta(r_c-r_{ij}(t))$ and $r_{ij}(t)=|r_i(t)-r_j(t)|$ [19]. $\theta(r)$ is the Heaviside function, $r_i(t)$ is the position of the atom $i$ at time $t$, and $\langle\ \rangle$ denotes an average over time origins. $f_b(t)$ is the probability of finding two atoms separated by $r_c$ or less at time $t$ under the condition that so they are at $t=0$. Thus it approximately gives the lifetime of the atomic bonds whose length is $r_c$ or less [19,20]. Previous simulations on $l$-Si have shown that atoms separated by ~2.486 Å (4.7 a.u.) or less are connected by a strong covalentlike bond [16]. We therefore take $r_c$ as 2.486 Å to estimate the lifetime of the covalentlike bond. In Fig. 3, we see that $f_b$ rapidly drops and then monotonically decreases at all pressures and temperatures. At 1100 K and low pressures, the bond lifetime $\tau$ is drastically shortened by pressurization. This indicates that the atomic mobility is enhanced by pressurization and is consistent with the increase of $D$ at pressures up to ~10 GPa. However no significant change is found above ~10 GPa; pressurization, in contrast, appears to slightly extend the bond lifetime [20]. This reflects the reduction of the atomic mobility at higher pressures and is again consistent with the decrease of $D$ above ~10 GPa. $f_b(t)$ at 1500 K also indicates the reduction of diffusivity by pressurization. It is therefore considered that the competition between the above two mechanisms for diffusivity is manifest at 1100 K, whereas the second mechanism (the packing effect) plays a more fundamental role in the diffusivity at 1500 K due to the considerable reduction of the tetrahedrality even at 0 GPa. If one assumes that the covalentlike bonds break once interatomic distance exceeds $r_c$, the bond lifetime $\tau$ is calculated as only ~70 fs at 0 GPa and 1100 K. However the broken bonds are frequently recovered for the same pairs during the MD runs. The bond lifetime therefore is effectively much longer than ~70 fs as indicated by $f_b(t)$. We roughly estimated $\tau$ as ~1 ps at 0 GPa and 1100 K [20].

To get more insight into the anomalous diffusivity, we focus on structural properties of $l$-Si. As suggested by $\hat{Z}(\omega)$ and $f_b(t)$, and also by previous studies on water and silicate melts [1–6], the tetrahedral framework should play a key role

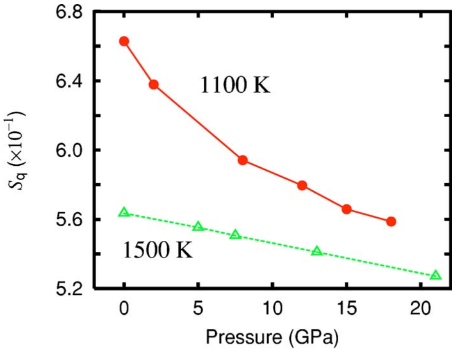

FIG. 4. (Color online) Pressure dependence of $S_q$ for *l*-Si at 1100 K (red filled circles) and 1500 K (green open triangles).

in the diffusivity of *l*-Si. Therefore, to elucidate the pressure dependence of the tetrahedrality, we calculated the order parameter $S_q$ that measures the extent to which the arrangement of an atom and its four nearest neighbors is tetrahedral [21]. The pressure dependence of $S_q$ is displayed in Fig. 4. It is easily seen that the tetrahedrality is lowered by pressurization at both temperatures: $S_q$ is 1 in a perfect tetrahedral network, whereas it is 0 in an ideal gas [4]. Although $S_q$ is drastically reduced by pressurization at 1100 K, the persistence of the tetrahedrality is remarkable at lower pressures. The 1500 K values of $S_q$ are all below 0.58, whereas the 1100 K values at pressures $\leqslant \sim 10$ GPa are higher than 0.58. Considering that $D$ at 1100 K begins to decrease above $\sim$10 GPa, $S_q$ of 0.58 appears to be the threshold above (or below) which the diffusive mechanism is more dominated by the destruction of the tetrahedral framework (or by the packing effect). The similar analysis has also been given in SPC/E water and a diffusive anomaly is found with $S_q \geqslant 0.615$ [4].

Figure 5 demonstrates a direct correlation between $S_q$ and the potential energy $E^*$ during the course of the MD run at 0 GPa and 1100 K ($E^*$ is scaled and shifted for comparison as $E^* = E \times 0.625 + 158.4$, where $E$ is the original potential energy in a.u.). When $S_q$ takes high values, $E^*$ is substantially low, and vice versa. This means that highly tetrahedral configurations are energetically favorable in supercooled *l*-Si. Also shown in Fig. 5 is the time variation of an atomic displacement (in Å) during time interval $dt$, $|\delta r(t;dt)| = |r_i(t+dt/2) - r_i(t-dt/2)|$, where $dt$ is taken to be $\sim$180 fs. Remarkable correlations between $|\delta r(t;dt)|$ and $S_q$ or $E^*$ are also evident indicating that high tetrahedrality tends to reduce atomic mobility due to the rigid network structure. We note that fluctuations in $S_q$ at 0 GPa and 1100 K are much larger than those above $\sim$10 GPa. The large fluctuations reflect the considerable structural changes underscored by the frequent formation and breakdown of the locally tetrahedral configurations.

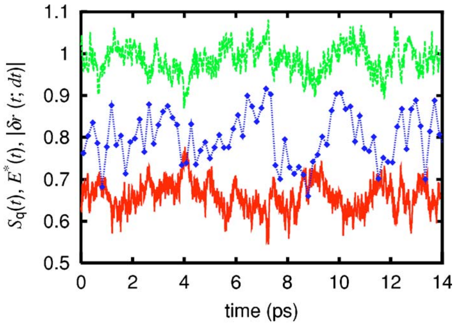

FIG. 5. (Color online) Time evolution of *instantaneous* $S_q$ (red solid lines: bottom), potential energy $E^*$ (green dashed lines: top), and the short-time atomic displacement $|\delta r(t;dt)|$ (blue dotted lines: middle) for *l*-Si at 0 GPa and 1100 K (see text for $E^*$).

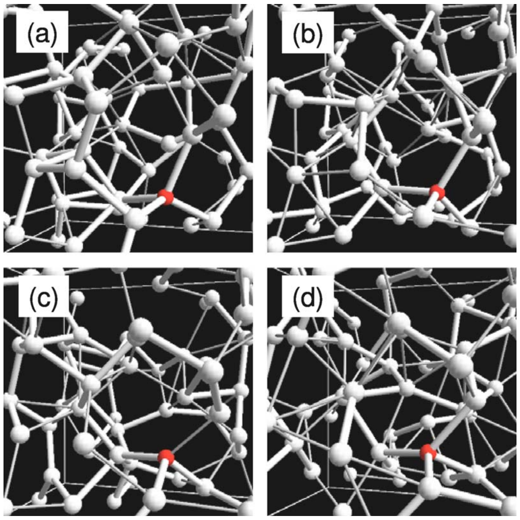

FIG. 6. (Color online) Time evolution of a tetrahedral configuration at intervals of $\sim$0.1 ps at 0 GPa and 1100 K. The highlighted atom (red: lower right) is four-coordinated by the covalentlike bonds (thick white lines) throughout the time span of $\sim$0.3 ps. Atoms separated by 2.962 Å or less are linked by thin white lines.

A visual inspection reveals that a tetrahedral configuration can persist for over 0.3 ps at 0 GPa and 1100 K. In Fig. 6, the time evolution of a tetrahedral configuration at intervals of $\sim$0.1 ps is displayed. This sequence is observed around $t = 6$ ps in Fig. 5. We clearly see that the highlighted atom is encompassed by only four neighboring atoms and most of them are covalently bonded (the bond length is $r_c$ or less) throughout the time span of $\sim$0.3 ps. Although one bond happens to be elongated [Fig. 6(c)], it is shortly recovered indicating the strong persistence of the tetrahedron [Fig. 6(d)]. We also recognize that the formation of the tetrahedral configuration concurrent with open spaces hinders the highlighted atom from moving about. These snapshots thus confirm that the formation of the locally tetrahedral framework reduces the diffusivity, which results in the anomalous diffusivity in supercooled *l*-Si.

The present simulations have demonstrated that the anomalous pressure dependence of diffusivity actually arises in supercooled *l*-Si. The low diffusivity at low pressures can be attributed to the frequent formation of the locally tetrahedral (high $S_q$) configurations, which is hampered by densification at high pressures. Consequently, the diffusivity increases with increasing pressure until the tetrahedrality is considerably lowered. Further densification enables the packing effect to achieve a dominant position in the diffusivity, thus yielding the decrease of $D$ at pressures $\geqslant \sim 10$ GPa. Recently, the close relationship between diffusivity and the configurational entropy [22] has been revealed in the SPC/E water model [3]. Such a relationship should also arise in *l*-Si because the formation of relatively rigid tetrahedral structures tends to reduce the configuration space explored by the system: That is, the low diffusivity in *l*-Si is closely related to the low configurational entropy. In the present calculations, the formation and breakdown of the tetrahedral configurations are clearly reflected in the marked fluctuations in $S_{\mathrm{q}}$ at 0 GPa and 1100 K.

It is of further interest to note that the locally tetrahedral configurations may be considered as *local* LDL forms or LDL fragments. In other words, liquid-liquid (LDL-HDL) transformations may *locally* occur in the deeply supercooled state. This is consistent with the structure and dynamics in deeply supercooled *l*-Si being much more heterogeneous than those in "normal" *l*-Si (Fig. 5, for example, demonstrates the heterogeneity in time). However HDL should still be dominant over LDL because the *local* LDL forms can survive for only a short period (~0.3 ps as in Fig. 6). Despite the frequent formation of the LDL fragments at low pressures, *full* LDL, in contrast, is hardly observed as extreme supercooling is required. Sastry and Angell have recently observed *full* "HDL to LDL" transformations of Si in their MD calculations at ~1060 K [9]. However it is still uncertain that *full* LDL is actually stable liquid and is observable in laboratory experiments [23]. The stability of *full* LDL Si definitely deserves further investigations, which should lend us a clear picture of polyamorphic transformations in tetrahedrally coordinated substances, such as Si and water.

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[20] The bond lifetime $\tau$ can be estimated by $\tau = \lim_{t\to\infty} \int_0^t f_b(t')dt'$.

[21] $S_{\mathrm{q}}$ is the orientational order parameter defined as $S_{\mathrm{q}} = 1 - \frac{3}{8}\Sigma_{i=1}^{3}\Sigma_{j=i+1}^{4}(\cos\theta_{ij} + \frac{1}{3})^2$, where $\theta_{ij}$ is the angle between the vectors that join a central atom with its *i*th and *j*th nearest neighbors. See Ref. [4] for details. Note that Fig. 5 displays the time variation of *instantaneous* $S_{\mathrm{q}}$ values, while its time averages at various pressures and temperatures are plotted in Fig. 4.

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