

How Does Tetrahedral Structure Grow in Liquid Silicon upon Supercooling?

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We present an extensive set of isothermal-isobaric first-principles molecular-dynamics simulations of liquid silicon over a temperature range of 950–1700 K. We find that the tetrahedral order gradually grows upon cooling to ~ 1200 K, but that the growth accelerates significantly below ~ 1200 K. This growth process gives rise to anomalous changes in density and liquid structure upon supercooling. In particular, we find that the atomic coordination number remains constant to ~ 1200 K and then begins to decrease below ~ 1200 K, which resolves the existing controversy regarding liquid structure in the supercooled regime [T. H. Kim *et al.*, Phys. Rev. Lett. **95**, 085501 (2005)].

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Liquid silicon (*l*-Si) has been a focus of interest for the past years because it exhibits unusual aspects such as low atomic coordination despite its metallic nature. These aspects are particularly enhanced upon supercooling. Recently, the possible existence of two distinct liquid forms, low-density liquid (LDL) and high-density liquid (HDL), in the supercooled regime has been a topic of intense research. Much work has aimed at exploring the transition between HDL (low tetrahedrality) and LDL (high tetrahedrality) in supercooled *l*-Si as well as in other liquids having tetrahedral coordination [1,2]. A molecular-dynamics (MD) study by Sastry and Angell demonstrated that the Stillinger-Weber potential [3] yields a first-order HDL (normal *l*-Si) to LDL transition (liquid-liquid transition) in the deeply supercooled regime, which is followed by vitrification to normal amorphous Si (*a*-Si) [4]. A subsequent MD study, however, has pointed out that the nature of the transition strongly depends on a model potential [5]. In our previous first-principles MD (FPMD) calculations [6], highly tetrahedral atomic configurations (LDL fragments) are frequently formed in deeply supercooled *l*-Si, but no clear indications of a liquid-liquid transition were detected, nor were they detected experimentally. While the transition between low-density amorphous (*a*-Si) and high-density amorphous Si has been clearly confirmed both in experiments and theoretical calculations [7–9], the existence of a liquid-liquid transition has been a matter of debate.

In contrast to theoretical calculations, the measurement of *l*-Si far below the melting temperature T_m (1687 K) is a major experimental challenge. Recently developed containerless techniques allow us to measure supercooled *l*-Si down to 200–300 K below T_m [10–13]. However, previous measurements have led to controversial conclusions regarding the temperature dependence of liquid properties such as density and structure factor [10–15]. Some previous measurements, for example, have reported a variation in the coordination number N_c upon cooling (increase [11] or decrease [10]), whereas other measure-

ments have shown that N_c remains constant down to ~ 1400 K [12,13] (note that currently *l*-Si below ~ 1400 K is experimentally inaccessible).

In order to resolve such conflicting findings, we have carried out isothermal-isobaric FPMD simulations of deeply supercooled *l*-Si. We have found that N_c remains constant upon cooling to ~ 1200 K and then begins to decrease below ~ 1200 K. The present finding is consistent with the experimental measurement by Kim *et al.* [12] and would aid in our further understanding of unusual aspects in the supercooled regime, including a liquid-liquid transition.

A series of isothermal-isobaric FPMD simulations [16,17], each for 23–130 ps, was carried out with a 64-atom supercell of *l*-Si over a temperature range of 950–1700 K [18]. The electronic state calculation was performed within the local density approximation [19] of density functional theory (DFT). The electronic wave functions were expanded in a plane wave basis with an energy cutoff of 21.5 Ry, and the norm-conserving pseudo-potential [20] was used to describe the electron-ion interaction [21]. In the present study, we aim to elucidate the temperature dependence of liquid properties under normal pressure. However, the experimental value of the density ρ at T_m ranges from 2.52 to 2.59 g/cm³ [15,25]. We thus examined the density dependence of liquid properties by running FPMD simulations at two pressures, p_0 and p_1 [26]; the former pressure p_0 gives ρ of 2.59 g/cm³, while the latter p_1 gives ρ of 2.52 g/cm³ at ~ 1700 K. We found that, although the stability of the supercooled state strongly depends on the external pressure below ~ 1100 K, both the pressures yield essentially the same results at temperatures ≥ 1100 K. Our attention in this Letter therefore will be focused on *l*-Si under the pressure p_0 .

Figure 1 shows the density ρ as a function of temperature. We see that ρ monotonically increases as the temperature decreases and reaches a broad maximum around 1200 K. It is well known that liquid water (*l*-water) exhibits a density maximum at 4 °C under normal pressure, but in

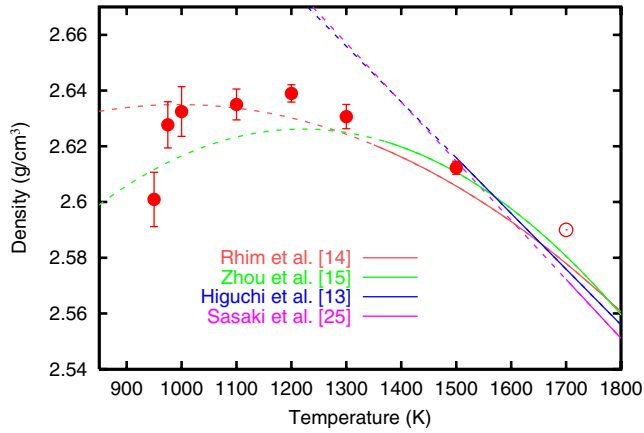


FIG. 1 (color online). Density ρ of *l*-Si as a function of temperature. Circles denote the present results (error bars at 1500 K are smaller than the corresponding symbol size). An open symbol (1700 K) indicates a *NVT* calculation ($\rho = 2.59 \text{ g/cm}^3$) performed to obtain the nominal pressure value of p_0 . Experimental data [13–15,25] that are fitted to quadratic or linear functions are also shown for comparison (solid lines). Note that broken lines denote extrapolated experimental data.

l-Si, no one has experimentally confirmed a density maximum. Our results demonstrate that *l*-Si under low pressure also exhibits a density maximum, although it is much broader compared to that of *l*-water. It should be remarked that the Stillinger-Weber potential, with ρ of 2.59 g/cm^3 at 1700 K, yields no density maximum above $\sim 1000 \text{ K}$. Large uncertainties in ρ below 1100 K results from the frequent formation of LDL fragments in HDL-Si. The formation of LDL fragments tends to reduce ρ and enhance its fluctuation and structural heterogeneity [6]. Details of such structural heterogeneity below 1100 K will be discussed elsewhere; we hereafter focus on *l*-Si at temperatures $\geq 1100 \text{ K}$.

The experimental results fitted to quadratic or linear functions are shown as solid lines in Fig. 1 (note that extrapolated data are also shown in broken lines). It is found that the data of Rhim *et al.* [14] and Zhou *et al.* [15] are consistent with our results. The others [13,25], however, fail to reproduce the density variation in our calculations below 1400 K, although they are still consistent with our data above 1400 K. It is clearly demonstrated that linear functions are inappropriate to describe the density variation in a wide temperature range below $\sim 1700 \text{ K}$.

Temperature-induced structural changes are manifest in the pair correlation function $g(r)$ and the structure factor $S(Q)$ in Fig. 2. With decreasing the temperature, the first peak of $g(r)$ becomes sharp and the second peak grows in intensity, both of which are particularly visible at 1100 K. These structural changes are apparently reflected in $S(Q)$. The first peak and a shoulder on the high- Q side of $S(Q)$ become resolved into two distinct peaks ($\sim 2.6 \text{ \AA}^{-1}$ and $\sim 3.5 \text{ \AA}^{-1}$) as the temperature decreases. Excellent agreement with the experimental data [13,27] is found above $\sim 1300 \text{ K}$.

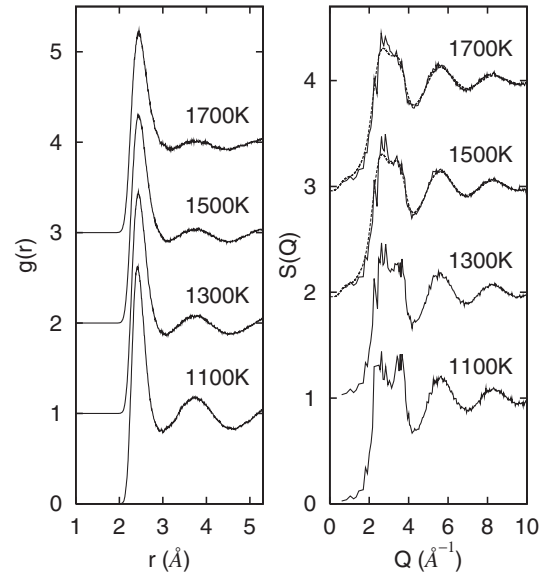


FIG. 2. Pair correlation functions $g(r)$ (left) and structure factors $S(Q)$ (right) for supercooled *l*-Si, compared with experimental data of $S(Q)$ at 1557 and 1710 K [13] (dashed lines).

The characteristic structural changes in $g(r)$ and $S(Q)$ are expected to be due to the increase of the number of tetrahedral configurations which are a basic unit of the crystalline structure (the diamond structure) of Si. We demonstrate the increase of the tetrahedrality by calculating the order parameter q_t that measures the degree of tetrahedrality in the arrangement of an atom and its four nearest neighbors (q_t is 1 in a perfect tetrahedral network) [28]. The distribution of q_t , $P(q_t)$, at four temperatures is displayed in Fig. 3. A main peak ($q_t \sim 0.5$) at temperatures $\geq 1300 \text{ K}$ gradually shifts toward higher q_t as the temperature decreases, indicating a gradual increase of the tetrahedrality. The peak however becomes much broader at 1100 K, and $P(q_t \geq 0.8)$ is significantly enhanced. The

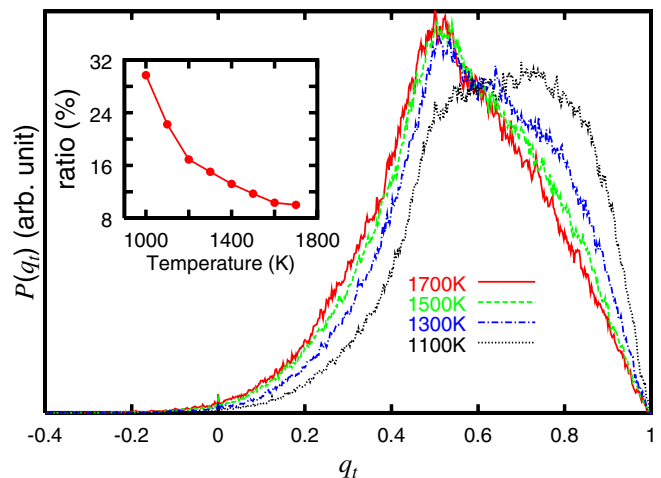


FIG. 3 (color online). Temperature dependence of the distribution of q_t , $P(q_t)$. Inset: the ratio of $P(0.8 \leq q_t \leq 1)$ to $P(q_t \leq 1)$ as a function of temperature.

inset of Fig. 3 shows the temperature dependence of the ratio, $\int_{0.8 \leq q_i \leq 1} P(q_i) dq_i / \int_{q_i \leq 1} P(q_i) dq_i$. This clearly shows that the tetrahedrality steadily increases down to ~ 1200 K, but that the increase is significantly accelerated below ~ 1200 K. It appears that this accelerated increase prompts the growth of the second peak of the $g(r)$ at 1100 K (Fig. 2). The position of the second peak is about 3.75 Å which is close to the expected position for the second peak (3.84 Å) of the diamond structure having a perfect tetrahedral network. It is therefore considered that the substantial structural changes at ~ 1100 K are induced by the rapid growth of the tetrahedral network.

The drastic increase of the tetrahedrality affects the temperature dependence of the coordination number N_c . In Fig. 4, N_c is plotted against temperature, along with previous experimental and FPMD results [29]. It is evident that N_c in the present calculations remains almost constant with decreasing the temperature down to ~ 1300 K ($N_c \approx 6.2$). However, N_c begins to decrease at ~ 1200 K and reaches a substantially low value (5.6) at 1100 K, reflecting the rapid growth of the tetrahedrality as expected. Experimentally, no conclusive results have been obtained thus far. Kim *et al.* [12] and Higuchi *et al.* [13] have reported that N_c is almost constant down to ~ 1400 K (N_c is 6 in Ref. [12] and ~ 5 in Ref. [13]). Kimura *et al.* however observed an increase of N_c , whereas Ansell *et al.* observed a decrease of N_c with temperature (Fig. 4) [10,11]. Our FPMD results thus support the experimental data reported by Kim *et al.* at temperatures ≥ 1400 K. Interestingly, previous FPMD calculations by Jakse *et al.* [27] have shown a decrease of N_c above ~ 1400 K. It appears that the growth of the tetrahedral order is accelerated at temperatures much higher than 1200 K. This tendency is also found in their $S(Q)$ [27]. It is likely that the covalent nature of atomic bonding, i.e., tetrahedrality,

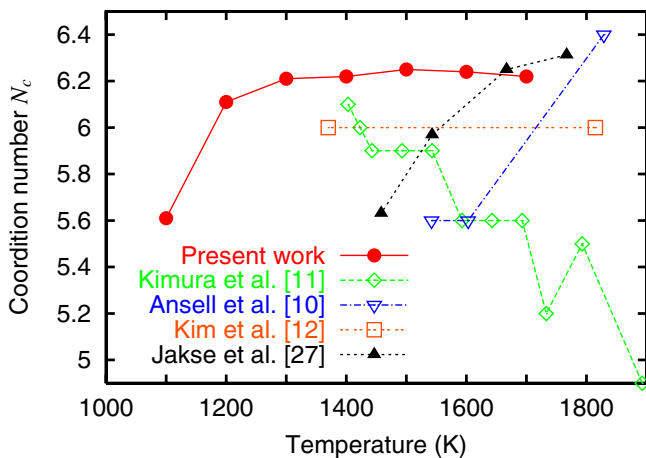


FIG. 4 (color online). Comparison of the temperature dependence of N_c with previous experimental [10–12] and FPMD results [27]. Note that Kim *et al.* reported a constant N_c of 6 in the temperature range between 1370 and 1815 K [12].

is more exaggerated in their calculations than in our calculations at the same temperatures.

Despite the continuous development of the tetrahedral order (Fig. 3), N_c shows no significant changes above ~ 1200 K. This can be explained by the temperature dependence of average distances of the first eight neighbors. We clearly see in Fig. 5 that the distances of the first four or five neighboring atoms gradually decrease with temperature, while those of the 6th–8th neighboring atoms remain unchanged except at 1100 K, which should increase to form a highly tetrahedral network. This unexpected behavior indicates that the gradual increase of the tetrahedrality down to ~ 1200 K is not sufficient, on average, for the establishment of the tetrahedral order beyond the first four neighbors; i.e., large LDL fragments are unlikely formed. Since r_c is beyond the first four neighbors (3–3.1 Å; Fig. 2) and the average distances of the 6th–8th neighbors remain unchanged, N_c is almost constant at temperatures $\geq \sim 1300$ K [29]. This is consistent with ρ that monotonically increases with decreasing the temperature to ~ 1200 K (Fig. 1). It is likely that the moderate increase of the tetrahedrality is not sufficient to expand the entire volume above ~ 1200 K. For temperatures $\leq \sim 1200$ K, in contrast, the tetrahedral order rapidly grows as shown in Fig. 3. This rapid growth leads to the formation of relatively large LDL fragments. The distances of the 6th–8th neighbors apparently increase, thus resulting in the decrease of N_c below ~ 1200 K. The decrease of ρ should also be induced by the rapid growth which is now sufficient to expand the entire volume. As discussed previously, the drastic growth of a tetrahedral network is clearly reflected in the $g(r)$ and $S(Q)$ at 1100 K. We therefore conclude that the establishment of the tetrahedral order beyond the first four neighbors is the key to characterizing the structural properties as well as the density below ~ 1200 K.

The present calculations have disclosed the growth process of the tetrahedral order in *l*-Si upon supercooling. The degree of the tetrahedral order steadily increases upon

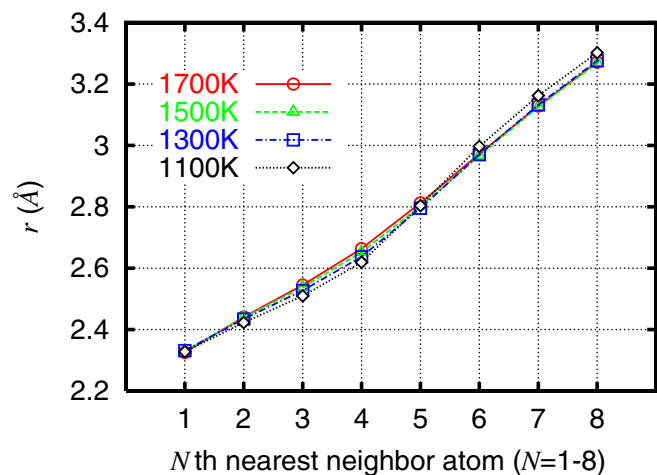


FIG. 5 (color online). Temperature dependence of average distances of the first eight neighbors.

cooling down to ~ 1200 K, but this gives no significant structural changes in the scale beyond the first four neighbors (e.g., constant N_c). However further cooling below ~ 1200 K triggers the rapid development of the low-density network structure, which results in the drastic changes of structural properties such as $g(r)$ and N_c .

Finally, it is worth noting that structural changes in $g(r)$ and $S(Q)$ upon cooling are similar to those of supercooled l -water on crossing the Widom line at which point thermodynamic response functions reach their maxima [30]. Since a Widom line emanates from a critical point, the present results may suggest the possible existence of a liquid-liquid critical point in Si, although no conclusive evidence supporting this is yet available. Further investigations of the temperature dependence of thermodynamic response functions, such as specific heat, of supercooled l -Si would be of crucial importance to examine the liquid-liquid critical point, and thus a low-density form of l -Si.

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