

Structural and dynamical heterogeneity in deeply supercooled liquid silicon

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We report on a first-principles molecular-dynamics study of structural and dynamical heterogeneity in supercooled liquid silicon. We find that highly tetrahedral configurations are intermittently formed and that spatially heterogeneous dynamics is concurrently induced in the deeply supercooled state (1000 K). This heterogeneity is responsible for the anomalous structural relaxation characterized by the stretched-exponential function. The temporal structural fluctuation is found to give rise to the $1/f$ dependence in the corresponding power spectral density. In a moderately supercooled state (1600 K), the structural and dynamical heterogeneity is quite weak, in contrast to the deeply supercooled state. The applicability of the Stillinger-Weber potential to the deeply supercooled state is also discussed.

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The recent development of experimental and computational techniques has enabled us to gain a profound understanding of liquids in the supercooled state [1]. It has been revealed that dynamics in a supercooled liquid becomes much slower than that above its melting temperature T_m , being observed as, e.g., a non-Arrhenius temperature dependence and nonexponential relaxation of the correlation function [1–3]. These phenomena are considered to arise from the microscopic dynamics in supercooled liquids [2,3]. Many attempts have thus been made to elucidate the slow dynamics from an atomistic viewpoint.

Molecular-dynamics (MD) simulations are a powerful tool to obtain microscopic information on bulk liquids. Many of the recent MD studies on supercooled liquids have focused on structural and dynamical heterogeneity, which is believed to account for the slow dynamics. It has been shown in a Lennard-Jones (LJ) mixture that mobile particles tend to form stringlike clusters and that their motion is highly cooperative [4]. This dynamical heterogeneity has been discussed in conjunction with the potential energy landscape formalism, and attempts have been made to establish the connection between dynamical and structural heterogeneity [4–6].

In liquids with a tetrahedral network such as water, the heterogeneity has been related to the structural fluctuation between two possible distinct liquid forms, high-density liquid (HDL: low tetrahedrality) and low-density liquid (LDL: high tetrahedrality) [7], which were originally introduced to interpret a transition between high-density amorphous (HDA) and low-density amorphous (LDA) phases [8,9]. The idea of two distinct liquid forms has been invoked to explain various anomalies in tetrahedrally coordinated liquids [7,8,10–12]. Shiratani and Sasai have shown that TIP4P water exhibits considerable structural fluctuation between HDL-like and LDL-like fragments over a wide temperature range [7]. They also found that this structural heterogeneity is relevant to multiple-time-scale dynamics, which should be a key aspect of the slow dynamics under supercooling.

Liquid silicon (*l*-Si) has also been a focus of interest be-

cause it may have the same two liquid forms as water. Previous MD calculations have predicted the existence of a LDL phase [13] or LDL fragments [11,12] in the deeply supercooled regime (~ 1000 K). However, no research has been conducted on the heterogeneous nature associated with the two liquid fragments and its relevance to multiple-relaxation processes.

In this Rapid Communication, we present an extensive first-principles molecular-dynamics (FPMD) study of deeply supercooled *l*-Si. Because the validity of the Stillinger-Weber (SW) potential for the deeply supercooled state has recently been called into question [14], first-principles numerical simulations are highly desirable for investigating supercooled *l*-Si. Our calculations reveal that the structural heterogeneity associated with LDA (or LDL) fragments actually arises and that this structural heterogeneity induces dynamical heterogeneity, which is responsible for the nonexponential relaxation process at an atomistic level. The existence of the heterogeneity suggests that supercooled *l*-Si exhibits various anomalies as water, which are partly reported in Ref. [12].

Isothermal-isobaric FPMD simulations [15,16] were performed for a 64-atom supercell of *l*-Si with periodic boundary conditions. The electronic-state calculation was performed within the local density approximation of density functional theory (DFT). The electronic wave functions were expanded in a plane-wave basis with an energy cutoff of 21.5 Ry at the Γ point in the Brillouin zone. The norm-conserving pseudopotential was used to describe the electron-ion interaction. Details of the computational techniques are given in Ref. [16]. A 200 ps production run for *l*-Si at 1000 K was performed after an equilibration stage of ~ 8 ps under pressure P_0 , which yields a density ρ of 2.59 g/cm³ at T_m (1687 K) [17]. Another production run was performed for comparison to calculate the properties of moderately supercooled *l*-Si (1600 K) under the same pressure P_0 . We also performed MD simulations using the SW potential to examine the heterogeneity in SW *l*-Si at 1000 K [18]. Some of the SW-MD results will be compared with the FPMD results.

We demonstrate considerable structural fluctuations in su-

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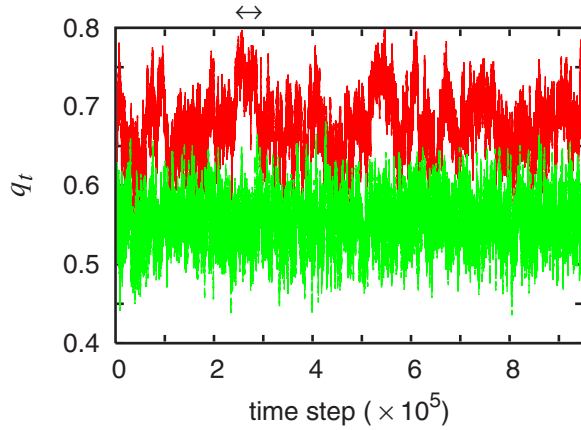


FIG. 1. (Color online) Time evolution of q_t , averaged over all atoms for 1000 K (upper red lines) and 1600 K (lower green lines). Arrows indicate the high- q_t period at 1000 K. A time step of 0.121 fs was used to integrate equations of motion.

percooled *l*-Si 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 tetrahedron) [21]. The time evolution of q_t , averaged over all atoms, for 1000 K and 1600 K, is shown in Fig. 1. The fluctuation of q_t is remarkable at 1000 K. Although its time average (q_{ave}) is ~ 0.68 , q_t intermittently remains very high (~ 0.75) during a few ps. Such a high- q_t state is, for instance, found at time step $\sim 2.7 \times 10^5$, which lasts for ~ 4 ps (high- q_t period; see Fig. 1). The temporal behavior of q_t indicates significant structural heterogeneity at 1000 K. In contrast, at 1600 K, q_t fluctuates around ~ 0.55 and its fluctuation is strongly suppressed. This indicates that *l*-Si at 1600 K is much more homogeneous than at 1000 K.

The strong correlation between structural and dynamical heterogeneity has been explored in a variety of supercooled liquids. In order to investigate this correlation in *l*-Si at 1000 K, we calculated the short-time atomic displacement (in Å) during the time interval dt , $\delta r = |r_i(t+dt) - r_i(t)|$, where dt is 0.36 ps unless specified [22]. Figure 2 shows the contour plot of the probability $P(\bar{q}_t, \delta r)$ that an atom takes \bar{q}_t and δr in the MD run. Here, \bar{q}_t is defined for each atom as a time average of q_t over dt . Figures 2(a) and 2(c) show $P(\bar{q}_t, \delta r)$ calculated from the 200-ps MD run using $dt=0.36$ and 0.18 ps, respectively. We see that the distribution is considerably broad, reflecting a highly heterogeneous nature. The key feature is that δr decreases as \bar{q}_t increases. High tetrahedrality therefore tends to reduce atomic mobility. Interestingly, while $P(0.5 \leq \bar{q}_t \leq 0.8, \delta r \geq 1.0)$ increases as dt increases from 0.18 to 0.36 ps, $P(\bar{q}_t \geq 0.9, \delta r \geq 0.8)$ remains quite low. This implies that atoms having such high- q_t values ($\bar{q}_t \sim 0.9$) almost freeze as in a glassy state during 0.36 ps. Figures 2(b) and 2(d) provide deeper insight into the dynamics of high- q_t atoms. Figure 2(b) displays $P(\bar{q}_t, \delta r)$ calculated from only the high- q_t period, $P_h(\bar{q}_t, \delta r)$. The primary peak shifts to higher \bar{q}_t and lower δr , and the overall profile is markedly different from that of $P(\bar{q}_t, \delta r)$ [Fig. 2(a)]. Figure 2(d) shows “partial” $P_h(\bar{q}_t, \delta r)$, which is calculated only for a select set of 11 atoms whose q_t remains especially high in the

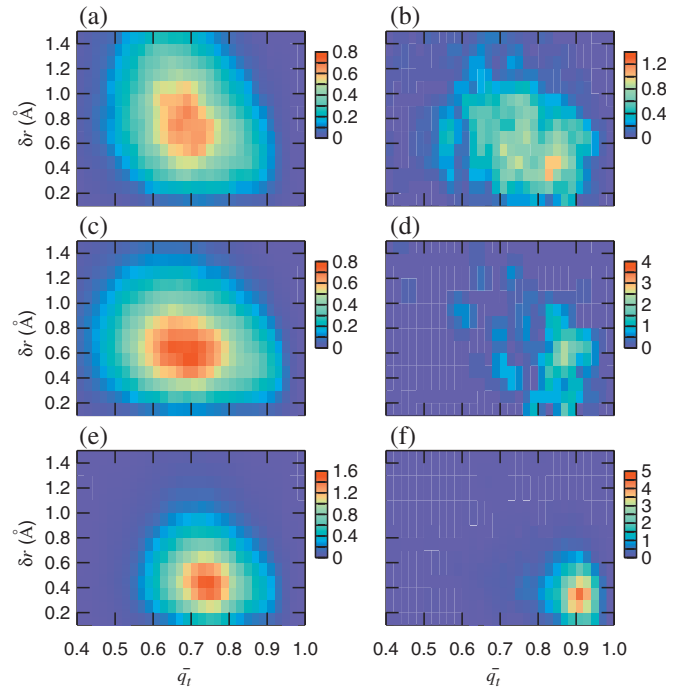


FIG. 2. (Color) Contour plots of $P(\bar{q}_t, \delta r)$ for 1000 K. Panels (a) and (c): $P(\bar{q}_t, \delta r)$ from a 200 ps MD run using $dt=0.36$ ps (a) and $dt=0.18$ ps (c). Panels (b) and (d): $P_h(\bar{q}_t, \delta r)$ for all atoms (b), and for the selected 11 atoms (d). Panels (e) and (f): $P(\bar{q}_t, \delta r)$ for SW *l*-Si (e) and for LDA Si under the pressure P_0 (f). Note that dt is taken to be 0.36 ps except for (c) and the color scale is in arbitrary units.

high- q_t period. The peak at $\bar{q}_t \sim 0.9$ is conspicuous, indicating the existence of “frozen” atoms during 0.36 ps. What is particularly notable is that the profile of the partial $P_h(\bar{q}_t, \delta r)$ is similar to that of $P(\bar{q}_t, \delta r)$ for LDA Si at 1000 K [Fig. 2(f)]. This similarity thus leads us to conclude that the formation of “LDA fragments” induces structural and dynamical heterogeneity in deeply supercooled *l*-Si.

$P(\bar{q}_t, \delta r)$ for SW *l*-Si is shown in Fig. 2(e) for comparison. The distribution is less broad than the FPMD result [Fig. 2(a)]. We easily see that the tetrahedrality is overestimated, and thus, the diffusivity is underestimated in SW *l*-Si.

The spatial correlations of high- q_t atoms and of low- q_t atoms are examined by the pair correlation function $g(r)$. Figure 3 shows $g(r)$ between the high- q_t atoms ($q_t \geq 0.8$), $g_h(r)$, and $g(r)$ between the low- q_t atoms ($q_t < 0.5$), $g_l(r)$. The difference between $g_h(r)$ and $g_l(r)$ is striking. The sharp first peak in $g_h(r)$ reflects a highly tetrahedral configuration, while the broader peak in $g_l(r)$ indicates weak atomic bonding compared with covalent (tetrahedral) bonding. The prominent second peak in $g_h(r)$ shows that the high- q_t atoms tend to form the tetrahedral order extending beyond the first-neighbor shell. The low- q_t atoms, in contrast, exhibit almost no correlation beyond ~ 3 Å: they are unlikely to form any peculiar structures. The coexistence of these different types of structures is a distinct feature of the deeply supercooled state.

Dynamical heterogeneity is manifest in the autocorrelation function $C(t)$ defined by

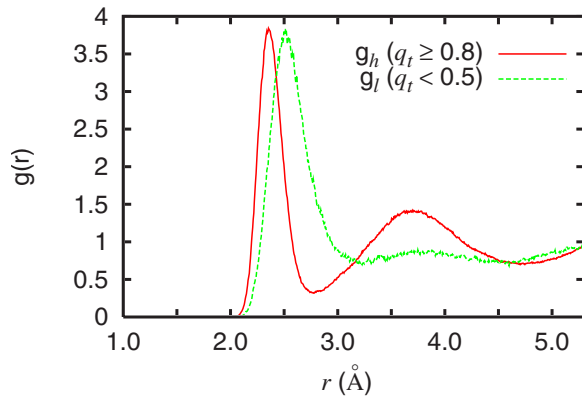


FIG. 3. (Color online) Pair correlation function between high- q_t atoms, $g_h(r)$, and that between low- q_t atoms, $g_l(r)$, for l -Si at 1000 K.

$$C(t) = \frac{\langle \delta q_t(t) \delta q_t(0) \rangle}{\langle \delta q_t(0) \delta q_t(0) \rangle},$$

where $\delta q_t(t) = q_t(t) - q_{ave}$ and $\langle \dots \rangle$ denotes an average over atoms and time. Figure 4 shows $C(t)$ calculated for various types of atoms: $C(t)$ for all atoms is labeled C_{all} , and $C(t)$ for atoms that are the high- q_t (low- q_t) atoms at $t=0$ is labeled C_{high} (C_{low}). We also calculated “partial” C_{high} , which is for the atoms whose first neighbor (C_{high-I}) or first and second neighbors ($C_{high-II}$) are also the high- q_t atoms at $t=0$ as well as the atoms themselves. It is seen in Fig. 4 that C_{high} decays more slowly than C_{all} , whereas C_{low} decays faster than C_{all} . We found that $C(t)$ can be well fitted by the stretched-exponential form $e^{-(t/\tau)^\beta}$: the relaxation time scale τ is ~ 0.06 ps for C_{low} and ~ 0.1 ps for C_{high} . The persistence of atomic configurations is therefore enhanced as q_t increases. This persistence is further enhanced when the neighboring atoms also possess high q_t at $t=0$. As shown in Fig. 4, C_{high-I} and $C_{high-II}$ have a considerably long relaxation time. In fact, τ for $C_{high-II}$ is calculated to be ~ 0.25 ps, which is 4 times larger than τ for C_{low} . It is therefore considered that the larger the tetrahedral order, the longer the structural relaxation time. This multiple-time-scale behavior is a manifestation of the dynamical heterogeneity in deeply supercooled

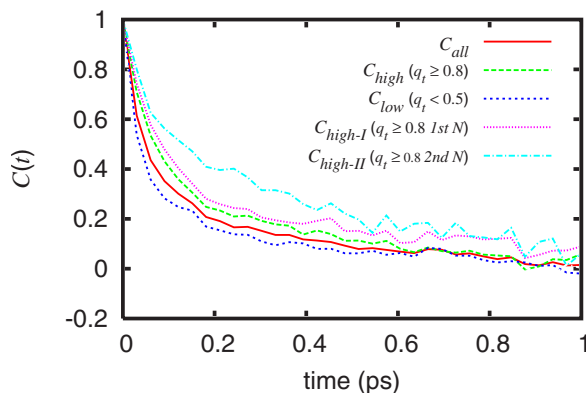


FIG. 4. (Color online) Time correlation function $C(t)$ for the various types of atoms (see text) at 1000 K.

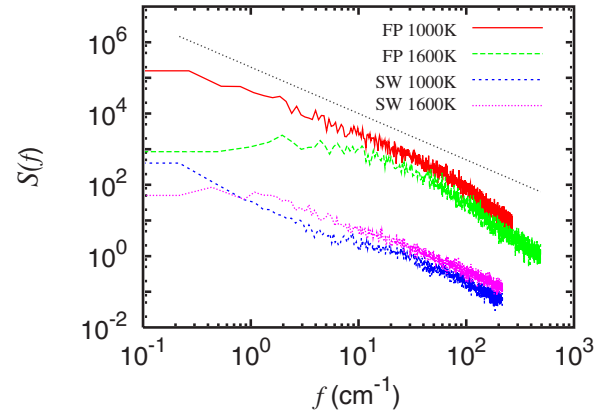


FIG. 5. (Color online) Power spectra of the q_t fluctuation (Fig. 1) for 1000 K and 1600 K. FPMD results denoted by “FP” are compared with SW-MD results denoted by “SW.” FPMD results for 1600 K are shifted downward by $|\log 0.4|$ for clarity. Dotted lines indicate $1/f^{1.3}$.

l -Si (1000 K). Note that the parameter β in $e^{-(t/\tau)^\beta}$ is 0.5–0.6 for all types of $C(t)$ at 1000 K, indicating less sensitivity to the tetrahedrality of each atom than τ .

The present finding casts some light on the mechanism of the nonexponential relaxation. Many of the previous studies have argued that the stretched-exponential relaxation results from the growth of independent domains that relax exponentially with different time scales [2,3,23]. We have, however, found no indication of domain separation or partial solidification in our system by visual inspection. This is further supported by the fact that $C(t)$ for arbitrarily chosen 20 atoms also exhibits the stretched-exponential relaxation with almost the same τ and β as those of C_{all} . These results suggest that the nonexponential relaxation may arise from the inherent atomic dynamics—i.e., intermittent structural fluctuations between the high- and low- q_t states—not from the superposition of exponential decays associated with long-lived distinct domains [24,25]. Detailed analyses on the entire mechanism are left for future work.

The multiple-time-scale behavior is also manifest as the $1/f$ -type dependence in the power spectral density $S(f)$ of the q_t fluctuation (Fig. 1). Figure 5 shows $S(f)$ for l -Si at 1000 K and 1600 K. It is seen that the spectrum for the FPMD l -Si at 1000 K (FP) indeed yields the $1/f^\alpha$ dependence with $\alpha \sim 1.3$ in a range 0.4–100 cm^{-1} . In contrast, the $1/f$ range is much narrower at 1600 K (FP). The spectrum is mostly a white noise below 10 cm^{-1} , indicating the lack of long-time correlation observed at 1000 K. It has been shown that water exhibits the $1/f$ -type dependence, which is attributed to the global rearrangement of the tetrahedral network on a time scale of several tens of ps [7,26]. The present result implies that global structural rearrangements also take place on a time scale of 100 ps or less in deeply supercooled l -Si.

The results for SW l -Si are also shown in Fig. 5. Interestingly, the $1/f$ dependence is still preserved in a relatively wide range (1–100 cm^{-1}) at 1600 K as well as at 1000 K. This again demonstrates that the formation of the tetrahedral network is overestimated in SW l -Si.

In summary, we have demonstrated the structural and dy-

namical heterogeneity in deeply supercooled *l*-Si. The formation and collapse of highly tetrahedral configurations (LDA fragments), which are moderate at 1600 K but are prominent at 1000 K, are found to be responsible for this heterogeneity. The present findings suggest that supercooled *l*-Si exhibits similar anomalies to those of water in thermodynamics response functions (e.g., the isobaric specific heat), which are closely related to the structural fluctuation. The

temperature dependence of such thermodynamic properties in *l*-Si should deserve further investigation.

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