Exploring the nature of the liquid-liquid transition in silicon: A non-activated transformation

(Supplementary Information)

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1. Identification of large-volume atoms

We identify the LDL silicon in terms of the characteristic of low density. A direct path is identifying the large-volume atoms using the Voronoi polyhedron method. However, the Voronoi volume, \( V_i \) (\( i \) denotes atom \( i \)), cannot effectively distinguish the large-volume atoms belonging to LDL from the HDL environment. Figures 1a and b show the probability distributions of the Voronoi volume for the normal liquid and the crystalline Si-I as well as for the normal liquid and the LDL phase. The overlaps between them are serious, thus, it is difficult to distinguish the low-density region using the Voronoi polyhedron method.

The average atomic volume defined in equation (1) involves the volume information of the neighboring atoms, and is expected to diminish the effect of the volume fluctuation. Figures S1c and d show the results for the cases presented in Figs. S1a and b. It can be seen that the overlaps are considerably reduced. We define the atoms with \( V_i > 19.6 \, \text{Å}^3 \) as large-volume atoms, which ensure that most atoms in the low-density region are identified.
To confirm that the LDL silicon obtained in our simulations is identical to that reported in the previous studies, we check the thermodynamic, structural and dynamic appearance.

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2.1 Density change

The low-density silicon is obtained via quenching liquid silicon from 2000 K to 1300 K at a cooling rate of 100 K per 1.2 ns, and then continues to 900 K at a rate of 20 K per 1.2 ns. The configuration is recorded every 2000 MD steps and a total of 600 configurations are sampled at each temperature. The density is produced by averaging the 600 configurations. The quenching is carried out in the negative pressure range from 0 to -1.6 GPa. Figure S1a shows the density as a function of temperature at the five example pressures. The transitions from HDL to LDL are observed. The density of LDL silicon shows a decrease with increasing tensile stress. The systems are quenched at four different cooling rates: 10 K per 0.1, 0.8, 1.2 and 2.0 ns from 1300 K. The density of LDL silicon depends on cooling rate: a higher cooling rates lead to a larger density of LDL. When the cooling rate is decreased to 10 K per 2.0 ns, the crystallization of Si-I occurs instead of the HDL-LDL transition ($P=0$ GPa), as shown in Fig. S2b.
density changes across the transition are identical with the published results [Beaucage, P. & Mousseau, N. *J. Phys.: Condens. Matter* **17**, 2269 (2005)].

**2.2 Radial distribution function and structure factor**

A common description of the global structure is provided by the radial distribution functions (RDF), which measures the averaged particle density as a function of distance from a central atom and is given by

\[ g(r) = \frac{n(r)}{4\pi r^2 \rho \Delta r} \]  

(S1)

where \( n(r) \) is the atom number between \( r \) and \( r + \Delta r \), \( \rho \) is the number density of the system. Figure S3a shows the RDFs of HDL, LDL and crystalline Si-I. The RDF of LDL is consistent with the reported results [Sastry, S & Angell, C. A. *Nature Mater.* **2**, 739 (2003); Ganesh, P. & Widom, M. *Phys. Rev. Lett.* **102**, 075701 (2009); Jakse, N. & Pasturel, A. *Phys. Rev. Lett.* **99**, 205702 (2007)]. Using the RDF, the structure factor is given by

\[ S(q) = 1 + \frac{4\pi \rho}{q} \int_0^\infty [g(r) - 1] \sin(qr) dr \]  

(S2)

where \( q \) is the wave vector. Figure S3b shows \( S(q) \) of HDL, LDL and the system in the transition to LDL. For the sake of comparison, \( S(q) \) of Si-I is calculated. The characteristic features of the \( S(q) \) curves are identical to the results provided by the first-principle simulations [Ganesh, P. & Widom, M. *Phys. Rev. Lett.* **102**, 075701 (2009)].
2.3 Coordination number

The coordination number is calculated by counting the atom number within the nearest-neighbor distance, $r_c$ that is determined by the RDF. Figure S4 shows the coordination number as a function of temperature at zero pressure for both LDL and Si-I. The coordination number of LDL and Si-I is 4.2 and 4.0, respectively, which is in good agreement with the previous simulations [Vasisht, V. V., Saw, S. & Sastry, S. *Nature Phys.* 7, 549 (2011)].
2.4 Diffusion coefficients

The diffusion coefficients of silicon are calculated by the long-time limit of the mean-squared displacement (MSD),

\[
D = \frac{1}{6N} \lim_{t \to \infty} \frac{1}{t} \sum_{i=1}^{N} \left\langle \left\{ r_i(t) - r_i(0) \right\}^2 \right \rangle
\]

where \( r_i(t) \) and \( r_i(0) \) are the positions of atom \( i \) at time \( t \) and 0 respectively, \( N \) is the atom number. In the simulations, the atomic configuration is recorded every 2 ps (2000 MD steps), and MSD is averaged for 100 measurements with the time interval of 200 ps. Then the self-diffusion coefficient is achieved from the convergence of Eq. S3 to asymptotic behavior. Figure S5 shows the diffusion coefficients as a function of the inverse of temperature. Across the transition, the diffusion coefficients of LDL silicon are in the order of magnitude of \( 10^{-8} \) \( \text{cm}^2\text{s}^{-1} \), featuring a viscous liquid, which is comparable to the other results in the order of magnitude. The diffusion tends to be slowed down with increasing tensile stress, as shown in Fig. S5. The pressure dependence of diffusion coefficients shows that the transition occurs at higher temperature as the tensile stress increases.

![Diffusion coefficient](image)

**Fig. S5.** Diffusion coefficient. The diffusion coefficients are plotted as a function of the inverse of temperature at \( P = 0 \) and -0.4 GPa. The diffusion coefficients of LDL phase are in the order of \( 10^{-8} \) \( \text{cm}^2\text{s}^{-1} \), and one order of magnitude larger than the values of crystalline Si-I. The negative pressure tends to decrease the diffusion coefficient, leading to the occurrence of HDL-LDL transition at higher temperature.

2.5 Intermediate scattering function

The intermediate scattering function is defined by

\[
F(q,t) = \frac{1}{N} \left\langle \rho(q,t)\rho(-q,0) \right\rangle
\]

where \( \rho(q,t) = \sum_j \exp(-iq \cdot r_j(t)) \). The intermediate scattering function is related to the structure factor by
Figure S6 shows the intermediate scattering function of HDL and LDL. The curve of LDL displays a distinct \(\beta\)-relaxation process, suggesting a fragile-to-strong transition of supercooled silicon accompanying the LDL transition.

**Fig. S6.** Intermediate scattering function. The intermediate scattering function, \(F_i(q,t)\) is simulated at \(T=1800, 1100\) and \(1050\) K, respectively and \(q\) is the wave-vectors. The curve for the LDL phase (red) shows the \(\beta\)-relaxation. The dashed line is a fitting to the Kohlrausch-Williams-Watts (KKW) relaxation function, \(F_i(q,t) = A\exp\left[-(t/\tau)^\beta\right]\), \(\beta\) and \(\tau\) are the stretched exponent and the structural relaxation time, respectively.

### 3. Calculating the fractal dimension

The box fractal dimension of the LDL network is calculated by the following method. Define a parameter, \(\delta_i\) as

\[
\delta_i = \frac{X_{\max} - X_{\min}}{i} \quad (i = 1, 2, \ldots, n)
\]

where \(X_{\max}=\max(r_x, r_y, r_z)\) and \(X_{\min}=\min(r_x, r_y, r_z)\). Then, we place a set of box with the side length of \(\delta_i\) to the simulation cell with the common origin and count the atom number in the \(i\)th box, \(N(\delta_i)\). The box fractal dimension, \(D_f\) is given by

\[
D_f = \frac{\sum_{i=0}^{n-1} \left[\log N_i(\delta_i) \cdot \log \delta_i\right]}{\sum_{i=0}^{n-1} \log \delta_i^2}
\]

Figure S7 shows the box fractal dimension as a function of temperature.
4. Nucleation rate and nucleation barrier

For the sake of comparison, we evaluate the MFPT of the nucleation process, by which we calculate the nucleation rate and the free energy barrier (nucleation barrier). Table S1 list the parameters associated with nucleation of Si.

Table S1. The size of critical nuclei \( n^* \), the fitting parameter \( c \) in Eq. 5, the system volume \( V \), the nucleation rate per unit time and volume \( J_V \), and the nucleation barrier \( \Delta G \) for \( N=1000, 2744 \) and 4096.

<table>
<thead>
<tr>
<th>( N )</th>
<th>( n^* )</th>
<th>( c )</th>
<th>( V ) ((\times10^4 \text{ Å}^3))</th>
<th>( J_V ) ((\times10^{33} \text{ s}^{-1} \text{ m}^{-3}))</th>
<th>( \Delta G ) ((k_B T))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>63</td>
<td>0.01149</td>
<td>2.021</td>
<td>7.061</td>
<td>3.89</td>
</tr>
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</tr>
<tr>
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<td>0.01527</td>
<td>7.702</td>
<td>2.885</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Fig. S7. Fractal dimension of LDL framework. The box fractal dimension continuously increases to 2.6 through the HDL-LDL transition, indicating the LDL framework has a three-dimensional configuration.