Structural and dynamic features of liquid Si under high pressure above the melting line minimum

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Abstract

We report an \textit{ab initio} simulation study of changes in structural and dynamic properties of liquid Si at 7 pressures ranging from 10.2 GPa to 24.3 GPa along the isothermal line 1150 K, which is above the minimum of the melting line. The increase of pressure from 10.2 GPa to 16 GPa causes strong reduction in the tetrahedral ordering of the most close neighbors. The diffusion coefficient shows a linear decay vs drop in atomic volume, that agrees with theoretical prediction for simple liquid metals, thus not showing any feature at the pressures corresponding to the different crystal phase boundaries. The Fourier-spectra of velocity autocorrelation function shows two-peak structure at pressures 20 GPa and higher. These characteristic frequencies correspond well to the peak frequencies of the transverse current spectral function in the second pseudo-Brillouin zone. Two almost flat branches of short-wavelength transverse modes were observed for all the studied pressures. We discuss the pressure evolution of characteristic frequencies in the longitudinal and transverse branches of collective modes.

Keywords: liquid silicon, atomistic structure, collective excitations, high pressures, \textit{ab initio} simulations
INTRODUCTION

The behavior of condensed matter under high pressure is a fascinating field of studies which is important not only for fundamental knowledge of the material stability, but also for understanding the geophysical processes and for search for exotic structures and exotic properties, which can be manifested only at extreme conditions. As an example, a new exotic mechanism of metal-nonmetal transition at high pressures via localization of electrons in the interstitial areas, which was suggested in 2008 [1], triggered a number of experimental observations of this phenomenon, in particular in Li [2] and Na [3]. The obtained results changed absolutely the existing knowledge about the dependence of the conduction bandwidth of metals on the interatomic separation. Moreover, \textit{ab initio} atomistic simulations, performed for molten Li and Na, revealed an exotic tetrahedral ordering in liquid Lithium [4] and unusual electronic transitions in molten Na [5].

Liquid Si is one of the most interesting systems with partial covalent bonding, which can reveal liquid-liquid transitions in the supercooled state [6–10], which still is of great interest for simulation studies [11–13] for understanding different features of structural and dynamic properties as well as nucleation in liquid Si. Collective dynamics in liquid Si was much less studied. In 2006 Delisle et al. [14] performed an orbital-free \textit{ab initio} simulation study of liquid Si in the pressure range 4-23 GPa and for the temperatures 50 K above the melting line in order to compare their data to X-ray diffraction experiments by Funamori and Tsuji [15]. In [14] the authors reported dynamic structure of liquid Si, longitudinal and transverse current spectral functions as well as dispersion of collective excitations.

Collective dynamics of liquid metals especially on the spatial scales comparable to interatomic distances is not really clearly understood. In particular there were several reports on analysis of experimental dynamic structure factors obtained from inelastic X-ray scattering, in which the authors suggested nonzero contributions from transverse collective excitations to dynamic structure factors [16–18]. Later on in \textit{ab initio} molecular dynamics (AIMD) simulations of liquid Li [19] revealed that at high pressures the transverse current spectral functions showed a two-peak structure, which became more pronounced with increasing pressure. Later on similar findings were observed even at ambient pressure in liquid Tl [20].

The main task of this study is to find similar features in single-particle and collective dynamics of liquids Si along an isothermal line above the minimum of melting line. The
region around the minimum of melting line in liquid metals is of special interest because of possibility to observe there liquid-liquid transitions. The isothermal line on the phase diagram was chosen because of the need to have in simulations systems with the same mean thermal velocity of particles but with different pressures. We will calculate the static properties of liquid Si in the chosen region on the phase diagram and will study the single-particle and collective dynamics. The next section reports the details of our AIMDs. The third section contains the results and discussion and the last section contains conclusion of this study.

**AB INITIO SIMULATIONS**

We simulated liquid Si by the VASP package using a system of 300 particles in a cubic box subject to periodic boundary conditions. Seven pressures in the range 10.2 GPa-24.3 GPa at the temperature of 1150 K were studied in NVT ensemble. The isothermal line of 1150 K is above the minimum of the melting line in Si\(^{21, 22}\) (see Fig.1) and above the region of several crystal structures of Si. The initial system at the lowest pressure was obtained from classical simulations of liquid Si, while compressed liquid Si was sequentially obtained from the last configuration of lower density by rescaling the coordinates and the box size with subsequent equilibration over 4 ps. The time step was 2 fs, and the length of equilibrium production runs were not less than 20 000 configurations for each pressure.

For electron-ion interaction we took the PAW potentials\(^{23, 24}\), which allow to recover correct nodal structure of wave functions as well as correct distribution of electron density in the core region. The exchange-correlation functional was taken in GGA-PBE\(^{25}\) form. Because of the rather large size of the simulated system we took for the sampling of the electron density only the Gamma point in the Brillouin zone.

The smallest wave number in our simulations was in the range from 0.3815\(\text{Å}^{-1}\) for the lowest pressure and up to 0.3982\(\text{Å}^{-1}\) for the highest pressure. For calculations of the \(k\) -dependent quantities (static correlators and time correlation functions) we sampled all possible \(k\)-vectors with the same absolute value, and averaged the calculated \(k\)-dependent quantity over all possible directions of these \(k\)-vectors.
FIG. 1: Phase diagram of silicon with the thermodynamic points reported in this study (asterisks). The melting lines for Si were taken from Refs.[21,22].

RESULTS AND DISCUSSION

The standard analysis of atomic structure of the disordered systems can be performed via pair distribution functions (PDF), which are shown for the studied pressures along the isothermal line of 1150 K in Fig.2a. The main feature of the pressure dependence of PDFs in the range 10.2-24.3 GPa is the stable position of the first peak of PDF at 2.44 Å. Another interesting feature is almost flat region between 3.1 Å and 4.2 Å of the PDF at the lowest studied pressure, which reduces with increasing pressure and transforming into well-defined minimum of PDF at 3.29 Å for the pressure 24.3 GPa. The second maximum of PDF slightly changes its location from 4.99 Å at 10.2 GPa to 4.78 Å at 24.3 GPa. We compared in Fig.2b the calculated PDF at the pressure 14 GPa with the one obtained from X-ray diffraction experiments [15]. The amplitude of the first peak of calculated PDF is a bit larger, that is perhaps a consequence of the GGA-PBE, which usually overestimates the binding tendencies in liquid systems. However, the locations of the first and second maxima of PDF as well as the flat region between them are reasonably reproduced by the simulations.

We tried to decompose the region around the first maximum of PDF into different shells in order to understand why the location of the first maximum of PDF does not change with
the pressure increase that is usually observed for liquid metals under pressure. The shell decompositions of the region under the first maximum of PDF is shown in Fig.3 for the lowest and highest studied pressures. We identified seven shells of neighbors under the first maximum, and for as one can see from Fig.3 the main contribution comes from the three shells of the most bounded nearest neighbors within the distances up to 2.45 Å. These three shells have larger amplitudes than the further shells and do not change their amplitudes with pressure increase. Perhaps the stability of the location of first maximum of PDF under pressure is the consequence of remaining in the liquid system covalent bonds, which cause in solid state tetrahedral structure of the nearest neighbors.

Further analysis of the nearest neighbors in the liquid Si we performed with the bond-angle distribution functions $g_3(\cos \theta)$, calculated within a cut-off radius of 2.45 Å, that corresponds to the three shells of the most nearest neighbors. One can see in Fig.4 that the increase of the pressure results in reduction of triads of atoms with angles close to the tetrahedral one $\sim$109 degree with simultaneous increase of the triads with angles of the close-packed structure.

The single-particle dynamics in liquid Si under pressure was studied via normalized velocity autocorrelation functions

$$\psi(t) = \frac{\langle v_i(t)v_i(0) \rangle_{i,t_0}}{\langle v_i(0)v_i(0) \rangle_{i,t_0}} ,$$
FIG. 3: Decomposition of the first maximum of the pair distribution function into shells of nearest neighbors at the smallest and highest studied pressures.

FIG. 4: Pressure-induced change in three-body angular distribution functions $g_3(\cos \theta)$ for neighbors within the radius of 2.45Å, that corresponds to the three shells of the most nearest neighbors.

where the averages were taken over the ensemble of particles as well as over different origins $t_0$ of the time correlation functions. In Fig.5a one can see that for all the studied states the velocity autocorrelation functions show the cage effect, i.e. the negative values of $\psi(t)$ at small times which is caused by backscattering of particles due to collisions with nearest neighbors. The increase of pressure leads to a shift of this negative region towards smaller
FIG. 5: Velocity autocorrelation functions and their Fourier spectrum for liquid Si at T=1150K and three pressures.

times that is naturally for liquids getting denser. The Fourier spectrum \( \tilde{Z}(\omega) \) of the velocity autocorrelation function in the high-frequency region reflects the vibrational density of states in the system, while its value at zero frequency is defined by the diffusion coefficient \( D \). In Fig.5b one can see that up to the pressures 16.6 GPa due to the high diffusivity the Fourier spectrum of the velocity autocorrelation function contains only one high-frequency peak, while at the highest pressure due to the drop of the diffusivity we clearly observed the two-peak structure of \( \tilde{Z}(\omega) \), i.e. similar behavior as recently was observed for liquid Pb\(^{26}\) and liquid Al\(^{27}\) under pressure.

The diffusion coefficients, obtained from \( \tilde{Z}(\omega = 0) \), were verified by calculations of the long-time asymptotes of the mean square displacements \( \langle R^2(t) \rangle \) \(^{28}\). In Fig.6 we show the dependence of the two sets of data for diffusion coefficients of liquid Si along the isothermal line 1150 K on atomic volume. In \(^{29}\) Bylander and Kleinman predicted a linear dependence of diffusivity vs atomic volume if there is no change in the effective radius of particles. Since in our Fig.6 the diffusivity fits very well to a linear dependence one can conclude that there is no change in the effective radius of Si atoms in the studied pressure range, and this is an argument for the absence of liquid-liquid transformations which can be expected in the studied region above the minimum of the melting line. Note, that we observed the deviations from linear dependence of the diffusivity in liquid Rb at high pressures, where several other observations allowed to estimate the presence of structural transformation due to the change in effective radius of Rb atoms\(^{30}\). Also, a strong non-monotonic dependence
Collective dynamics in liquid Si was studied via time-Fourier spectra of longitudinal (L) and transverse (T) time correlation functions

\[ F^{L/T}(k, t) = \langle J_{L/T}(k, t)J_{L/T}(-k, 0) \rangle, \]

where we took the standard decomposition of the spatial Fourier components of total current into longitudinal and transverse components \[28\]. Note, that the local L-T cross-correlations (with the same wave number \(k\)) are zero as it should be due to symmetry rules. The AIMD-derived L and T current-current time correlation functions were used for calculations of their frequency spectra \(C^{L/T}(k, \omega)\), peaks of which were treated as manifestations of collective excitations. In Fig.7 we show the dispersions of L and T modes for four pressures, as they were obtained from peak positions of \(C^{L/T}(k, \omega)\). We obtained very similar evolution of the L and T collective modes with pressure as were recently observed for liquid Pb \[26\], liquid Al \[27\], liquid Na and In \[32\]: for wave numbers in the second pseudo-Brillouin zone there

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**FIG. 6:** Diffusivity as a function of atomic volume in the pressure range 10.2-24.3 GPa. The data obtained from the velocity autocorrelation functions (VACF) are shown by plus symbols with error bars, and the values from mean square displacements (MSD) - by cross symbols with error bars. The straight line is a prediction by Kleinman and Bylander \[29\].

of the diffusion coefficient was observed recently in fluid Hydrogen in the region of molecular-atomic transition \[31\].
exist two peaks on the transverse spectral function $C^T(k, \omega)$. The transverse peak positions are shown by cross symbols with error bars in Fig.7. In general, the transverse branches in the second pseudo-Brillouin zone look almost flat and their mean frequency increases with pressure, and that is why we took the as some characteristic frequencies $\omega_{T\text{low}}$ for the low-frequency T-band and $\omega_{T\text{high}}$ for the high-frequency T-band in the second pseudo-Brillouin zone, similarly as it was done in [32].

Similarly to the transverse case we took as some reference of the longitudinal dispersion the highest frequency of L-excitations $\omega_{L\text{max}}$, which they usually took at the first pseudo-Brillouin zone boundary, i.e. Debye-like frequency. In Fig.8 we show the pressure dependence of the three characteristic frequencies $\omega_{L\text{max}}$, $\omega_{T\text{low}}$ and $\omega_{T\text{high}}$ and their correlation with the observed peak positions of the Fourier-spectra of velocity autocorrelation functions. One can see that for the two highest pressures, when the $\tilde{Z}(\omega)$ contained two peaks, they both

FIG. 7: Evolution of dispersion of longitudinal (L) and transverse (T) collective excitations for liquid Si with pressure at $T=1150\text{K}$. 
FIG. 8: Correlation in peak locations of Fourier-spectra of velocity autocorrelation functions and highest frequency of longitudinal dispersion (Debye-like frequency) $\omega_{L}^{\text{max}}$ and flat regions of two transverse branches in the second pseudo-Brillouin zone $\omega_{T}^{\text{low}}$ and $\omega_{T}^{\text{high}}$ in the pressure range 10.2-24.3 GPa.

practically coincide with the frequencies $\omega_{T}^{\text{low}}$ and $\omega_{T}^{\text{high}}$ of the collective transverse current spectral functions. For the smaller pressures the $\omega_{T}^{\text{high}}$ follows the dependence of the high-frequency peak of $\tilde{Z}(\omega)$. By date it is not clear why the transverse current spectral functions show two-peak structure in the second pseudo-Brillouin zone. If this is due to the non-local L-T coupling (the local coupling is forbidden by the symmetry rules) then there should have been some similar features in the shape of longitudinal current spectral functions.

CONCLUSION

We presented our results of AIMD simulations for liquid Si along the isothermal line 1150 K which is above the minimum of the melting line of Si. Neither the studied structural quantities nor the pressure dependence of diffusion coefficient showed any feature for pressures above the minimum of the melting line, that makes evidence of the absence of liquid-liquid transformations in liquid Si in this region.
The Fourier spectra of single-particle velocity autocorrelation functions \( \tilde{Z}(\omega) \) and of collective transverse current-current correlation functions \( C^T(k, \omega) \) (for wave numbers \( k \) in the second pseudo-Brillouin zone) show very similar locations of their peaks. This is in line with the recent results for liquid Pb\[26\], liquid Al\[27\], liquid Na and In\[32\]. We cannot so far identify the origin of the high-frequency peak of \( C^T(k, \omega) \), which appears in the second pseudo-Brillouin zone. From the point of view of the manifestation of the L-modes in the spectra of transverse excitations due to broken spherical symmetry on the microscopic scale of nearest neighbors the local coupling (with the same wave number \( k \)) is prohibited for averages over all possible configurations, while the non-local mode coupling approach can be more useful in this case, however so far it was applied very rarely\[33\].

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