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First-principles coexistence simulations of supercooled liquid silicon

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ABSTRACT

We perform first-principles coexistence simulations of the low-density and the high-density phases of supercooled liquid silicon and find a negative slope for the coexisting line in the temperature-pressure plane. Electron density maps and electron-localization function plots of the two phases of silicon show marked differences. The calculated differences suggest more localized electrons in the low-density liquid compared to the high-density liquid, coming from an increased population of covalent bonds, which further explain the calculated negative slope in the two phase coexistence regime. This is consistent with the presence of a pseudo-gap in low-density liquid silicon, absent in the high-density liquid which shows a metallic behavior.

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1. Introduction

Non-crystalline forms of silicon are technologically important materials and several experiments and simulations, both classical and quantum mechanical, have studied its amorphous [1–7], liquid [8,9] and supercooled liquid [10–15] forms in recent years. Its close analogy to water [16–19] makes it even more fundamentally interesting. The vast literature presently agrees to the presence of at least two types of amorphous silicon, a high-density and a low-density phase, and perhaps even more new phases under higher pressures [7]. Large hysteresis is observed across the amorphous phase-boundaries, suggesting that they are well separated by a line of first-order phase-transition [2]. While the high-density forms are metallic, the low-density forms are semiconducting, similar to crystalline silicon.

The evolution of the atomic and electronic structure with temperature has been a long-standing challenge in condensed matter theory. Several theories to explain this have been put forth [18–21]. In a recent first-principles computer simulation [14] we identified the presence of two types of liquids separated by a line of first-order transition and a critical point in the supercooled regime,

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0022-3093/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jnoncrysol.2010.06.067 in good agreement to previous predictions using Stillinger-Weber type classical potentials [13]. The two phases were identified by a van der Waals-like loop in the pressure-volume plane, and differed in their density, local atomic structure and in their electronic structure. The low-density liquid (LDL) had a more open network compared to the high-density liquid (HDL). The simulations also showed that the electronic density of states in LDL has a pseudo-gap unlike in HDL which is more free-electron-like. This is consistent with previous electronic-structure studies [10] of Stillinger-Weber silicon, which also find an order of magnitude difference in the resistivity between the two phases possibly arising from their difference in the liquid structure. Our study suggested that while the high-density phase was a metastable extension of the equilibrium liquid to lower temperatures, the low-density phase was a new phase more closely related to the low-density amorphous phase and to crystalline silicon.

Here we report results from our phase coexistence simulations of LDL and HDL in the supercooled regime. The idea is to directly confirm that the two phases are indeed separated by a first-order line, as indicated in our recent work. We also compute and study the electron density and electron-localization function [22] in the two phases which directly shows that the increased open network structure of the LDL compared to HDL gives rise to increased electron-localization between bonded silicon atoms thereby depleting the number of electronic states near the Fermi level [10,14].

2. Method

All simulations were performed using the Vienna *ab initio* simulations package (VASP) [23,24] together with Projector Augmented Wave[25,26] potentials in the Generalized Gradient Approximation. Electronic structure calculations of energies, pressures [27] and forces used the Γ *k* point only and were conducted at the default energy cutoff of 245 eV. Molecular-dynamics (MD) of coexistence studies utilized a 1 fs time step while other simulations used a 2 fs time step. Velocities were rescaled at every time step to maintain constant temperature. All simulations were performed for a system size of 200 atoms.

We initially started with HDL and LDL configurations from a well equilibrated constant volume runs for N = 100 atoms for a duration of ~8 ps with similar average pressures for T=982 K, 1032 K and 1082 K (These runs were a subset of tempering runs [28,29] over a temperature range of T = 982 K-1332 K for densities from $\rho = 0.047 - 0.058$ atoms/Å³). At each temperature the HDL simulation box was sheared at constant volume so as to match the 'x' and 'y' lattice parameters of the LDL simulation box, joining them along the 'z' direction creating an interface. Due to periodic boundary conditions we actually have two interfaces perpendicular to the z-axis. The final densities at each of the above temperatures were $\rho = 0.054$, 0.053 and 0.0523 atoms/Å³ respectively. From our P–V isotherms in Ref. [14], it is easy to note that the chosen densities are in a region of negative thermal compressibility (i.e. $\kappa_{\rm T} = -(1/V)(\partial V/\partial P)_{\rm T} < 0)$. This puts us in a thermodynamically unstable regime corresponding to two phase coexistence, which is expected in a finite-size simulation box due to the free energy cost of forming an interface separating the two liquid phases. Due to the sudden change in the shape of the sheared HDL side of the box, the HDL atoms have to be equilibrated. The interface was thus annealed at each temperature by first performing MD of the HDL atoms with the LDL atoms fixed for ~0.5-1 ps, and then subsequently performing MD of the LDL atoms with the HDL atoms kept fixed ~0.5-1 ps. Finally all constraints were removed and the free interface was allowed to reach equilibrium in about 1-2 ps. Data was then collected from equilibration runs of 8-10 ps at the three different temperatures.

In our previous simulations [14] we had employed tempering over temperature to our molecular-dynamics simulations to improve

T=0982K

equilibration at supercooled temperatures. We had also performed lengthy simulations of ~7–10 ps without tempering at several temperatures and densities. The P–V isotherms from the latter agree very well with the published results using tempering. As such we believe that 8–10 ps runs, as reported here, are sufficient to adequately sample the configurational space in our coexistence simulations.

3. Results and discussion

Fig. 1 shows overlay of snapshots from the full duration (equilibrium runs only) of our coexistence simulations for two of our lowest three simulated temperatures. They are projected onto the x-z plane. The red atoms were initially in LDL while the green atoms were in HDL. The trajectories of the atoms indicate which of the two phases they belong to over time. LDL atoms have low diffusion identified by a highly confined trajectory, while an atom that prefers to be in HDL phase is expected to have a more wide-spread trajectory due to its high diffusivity. This also identifies the location of the interface. In all our temperatures we find a stable interface. Indeed as seen in Fig. 1, some of the atoms which were initially in LDL (red color) transform to HDL atoms (high diffusivity) over time, but then the interface remains fairly confined in space and is stable over time. Presence of a stable interface shows coexistence of the two phases and is a direct proof to the existence of a first-order transition between LDL and HDL in supercooled silicon. We also verified the persistence of a mean density variation in the z direction with a wavelength equal to the system size, quantitatively confirming what is visually evident in the figures shown.

Our simulations naturally give us the coexistence pressure as a function of temperature. Fig. 2a shows the coexistence line in the T–P plane. The calculation of pressure is described in Ref [14]. Error bars are computed by dividing the data into three parts and computing their rms error. At our highest temperature (T = 1082 K) the coexistence pressure is small, consistent with a negative critical pressure \sim -12 kB obtained in previous studies [14]. As the temperature is lowered the pressure increases. The calculated values of the coexistence pressure are within the ballpark of what one would expect from isotherms calculated in Ref. [14]. From the Clausius–Clapeyron equation, the slope i.e. dT/dP is equal to (v_{LDL} – v_{HDL})/(s_{LDL} – s_{HDL}). By definition

"Free"liquid-liquid interface

T=1032K



HDL

z-

Fig. 1. Overlapping snapshots of coexistence simulations projected onto the x-z plane.



Fig. 2. Temperature vs coexistence pressure of supercooled silicon from coexistence simulations.

 $v_{\rm LDL}\!>\!v_{\rm HDL}.$ As such a negative slope in the T–P plane suggests that LDL (which has a larger volume) has lower entropy than HDL, presumably due to the increased orientational order found in its open network arrangement. An increased orientational order dictates an underlying change in the electronic structure which we discuss later in this section. A negative slope is also consistent with the slope of the experimentally measured phase boundary between low-density



amorphous and high-density amorphous phases [1,2] at very low temperatures and high-pressures, suggesting that the low-density and the high-density amorphous phases are indeed further metastable extensions of LDL and HDL, respectively, to lower temperatures and high pressures.

To investigate the origin of increased orientational order in LDL and subsequent formation of a pseudo-gap in the electronic density of states [14], we computed the electronic-charge density as well as the electron-localization function (ELF) [22] of representative structures at a supercooled temperature of T = 1182 K in the two coexisting phases (HDL (ρ = 0.053 atoms/Å³) and LDL (ρ = 0.049 atoms/Å³)) from simulations described in Ref. [14]. ELF is a measure of electron pair-correlation in the system relative to a uniform electron-gas with the same average electron density. It is mapped onto a range of [0, 1]. An ELF of '1' corresponds to a perfect correlation leading to a strong localization and an ELF of 1/2 corresponds to a uniform electron-gas. Fig. 3a shows the corresponding histograms. At ELF = 1/2, both LDL and HDL have



Fig. 3. a. Histogram of the electron-localization function calculated for representative structures in the HDL and LDL phases coexisting at T=1182 K corresponding to simulations described in Ref. [14]. b. Isosurfaces (red) of the electron-localization function at a value of 0.84 calculated for a representative structure in our current coexistence simulation of silicon (green) at T=982 K and ρ =0.54 atoms/Å³.

Fig. 4. Electron density isosurfaces for coexisting HDL and LDL phases at T = 1182 K for representative structures.

similar frequencies but show a marked increase above a value of 1/2. LDL shows a higher frequency close to the value of '1', especially from 0.8 to 1, suggesting an increased localization compared to HDL.

So in which regions of space one would find large values of ELF? Increased electron localization is expected between atoms if they are covalently bonded [22]. Fig. 3b shows isosurfaces of ELF at a value of 0.84 for a representative structure in our coexistence simulation at T = 0982 K. In LDL regions with large values of ELF are predominantly located between near-neighbor atom pairs, indicating that almost all bonds are covalent. But there are very few of such regions in the coexisting HDL phase. Fig. 4 further shows the electron charge-density isosurfaces of representative HDL and LDL configurations coexisting at T = 1182 K [14]. While most of the atoms in LDL are bonded to at least 4 atoms, indicated by strong electronic-charge density between the atoms, there are large patches of electron density (marked with circles) in HDL located in regions where no bonds are expected to form. Presence of these delocalized electrons is expected to further reduce the electron-localization away from '1' in HDL (Fig. 3a). These plots clearly indicate that at low-density where there is an increased phase-space volume, supercooled liquid silicon prefers the more open network structure where every silicon atom has nearly 4 silicon bonds required to give it a closed electron shell configuration. This open network structure is close to that of solid silicon which is the equilibrium phase at the supercooled temperatures. This leads to more covalent bonding than HDL thereby causing an increased orientational order in LDL which in turn lowers its entropy with respect to HDL causing the negative slope of the coexistence curve in the T-P plane. This increased localization is expected to lead to a reduced electron mobility giving rise to a reduced density of states at the Fermi level thereby creating a pseudo-gap as reported in the previous studies.

4. Conclusion

We have performed simulations of coexistence between LDL and HDL silicon in the supercooled regime and traced the coexistence curve in the T-P plane. The slope is negative, consistent with experimentally measured phase-boundaries between low-density amorphous and high-density amorphous phases, suggesting that the amorphous phases are metastable extensions of the supercooled liquid to lower temperatures and higher pressures. A negative slope further suggests that LDL has lower entropy than HDL, possibly due to its increased orientational order. Origin of this order is seen to arise from an increase in covalent bonding seen as an increase in electronlocalization around bonds in LDL compared to those in the coexisting HDL phase.

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