Pressure effects on the transitions between disordered phases in supercooled liquid silicon

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We investigate the pressure effects on the transitions between the disordered phases in supercooled liquid silicon through Monte Carlo simulations and efficient methods to compute free energies. Our calculations, using an environment dependent interatomic potential for Si, indicate that at zero pressure the liquid-liquid phase transition, between the high density liquid and the low density liquid, occurs at a temperature 325K below melting. We found that the liquid-liquid transition temperature decreases with increasing pressure, following the liquid-solid coexistence curve. As pressure increases, the liquid-liquid coexistence curve approaches the region where the glass transition between the low density liquid and the low density amorphous takes place. Above 5 GPa, our calculations show that the liquid-liquid transition is suppressed by the glassy dynamics of the system. We also found that above 5 GPa, the glass transition temperature is lower than that at lower pressures, suggesting that under these conditions the glass transition occurs between the high density liquid and the high density amorphous. © 2011 American Institute of Physics. [doi:10.1063/1.3663387]

I. INTRODUCTION

Silicon is certainly one of the most studied materials due to its enormous technological importance. Nonetheless, the understanding of some of its properties still remains elusive and controversial. Silicon belongs to a group of substances, such as water, Ga, Ge, etc., that exhibit negative initial melting slopes, i.e., their melting temperatures decrease with applied pressure. In order to explain this anomalous behavior, as well as that of substances that display maxima in their melting lines, Rapoport,¹ over 40 years ago, proposed the so-called two-state or two-species model. According to this model, the liquid phase of these substances would be constituted by domains of the same chemical identity, however, of distinct structure and density. For a liquid in equilibrium, each species would contribute individually to the macroscopic density of the substance. However, depending on temperature and pressure, the relative contribution of each individual species can change, and eventually the density of the liquid could become larger than that of the crystal. Thus, explaining the anomalous behavior of the melting line.

The two-state model also predicts that, for given temperature and pressure, a spontaneous "unmixing" or separation of the two species can occur. This phase separation would constitute a first-order liquid-liquid phase transition (LLPT) at constant chemical composition between a high density liquid (HDL) and a low density liquid (LDL).² Due to experimental limitations, so far LLPT has been experimentally observed only in phosphorus³ and in the mixture of oxides $Al_2O_3-Y_2O_3$.^{4,5} In the case of phosphorus, the LLPT takes place when the liquid is at equilibrium, while in $Al_2O_3-Y_2O_3$ it occurs in the supercooled metastable regime. Recently, Zhang *et al.*⁶ employed neutron scattering experiments to measure the density of supercooled heavy water confined in a nanoporous silica matrix. They observed hysteresis in the measured density profiles between heating and cooling processes above 1000 bar. Although these findings are not conclusive, they provide support to a liquid-liquid first-order transition in supercooled water. In the case of Si, the main experimental limitation is to reach the required degree of supercooling, since the system is prone to crystallize. Two experiments^{7,8} using levitation techniques⁹ observed a decrease in the coordination number as temperature is lowered, however, there was no evidence of LLPT. Computer simulations have been heavily used in search, for examples, of LLPT. Evidence of LLPT has been observed, for instance, in computer simulations of water,^{10,11} Si,¹²⁻¹⁶ and Ga.¹⁷ In the case of Si, classical¹²⁻¹⁴ and the first-principles¹⁶ simulations have been used, as well as a combination of both approaches,¹⁵ in all cases the LLPT was observed in the deeply supercooled regime.

Another feature shared by the substances that present negative initial melting slope is their inability to form glasses when quenched from melt in normal conditions. Recently, however, Bhat et al.¹⁸ achieved the vitrification of Ge by quenching the melt under pressure. It has been proposed that these substances are poor glass formers because of the occurrence of the LLPT,¹⁹ which would promote nucleation and preclude glass transition. Nevertheless, amorphous phases of these substances can be obtained, for example, through the technique of vapor-condensation on a cold substrate.²⁰ If these amorphous phases can be considered glasses is still a subject of debate. In the case of amorphous Si, new experimental evidence suggests that the system indeed behaves like a glass.²¹ In order to investigate the amorphous-liquid transition in Si, experiments conducted in the 1980s²²⁻²⁴ suggested that low density amorphous (LDA) Si produced by

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ion implantation would melt directly into a HDL through a first-order transition, instead of undergoing a glass transition. This enigma persisted for 20 years, until Hedler et al.²⁵ performed an experiment at fast timescales (10^{-11} s) using the ion hammering technique that showed that amorphous Si undergoes a glass transition at about 1000 K. It is considered, however, that at longer timescales, the glass transition temperature should be lower, between 500 and 900 K.²⁶ Analogous to the liquid, the existence of LDA and high density amorphous (HDA) phases have been experimentally verified. The phase transition between these two forms of amorphous can be attained in the laboratory by initially preparing the HDA at high pressure and subsequently decompressing the system in order to obtain the LDA. This is a first-order transition that has been experimentally observed in water,²⁷ Si,²⁸ and Ge.¹⁸ In the last 10 years, the HDA-LDA phase transition in Si has been extensively investigated through the use of x-ray and Raman scattering combined with optical and electrical measurements, as well as molecular dynamics simulations.^{29–31} The observation of this amorphous-amorphous phase transition is viewed as a continuation of the liquid-liquid coexistence line into the amorphous region of the phase diagram.

In this work we study, through computer simulations, the effects of pressure on the transitions between metastable phases of supercooled liquid Si. The interval of pressures investigated ranges from 0 up to 10 GPa. Few examples of simulations of liquid and amorphous phases of Si under pressure are available in the literature.^{29–33} Recently, Vasisht et al.³⁴ reported the results of molecular dynamics simulations of supercooled liquid Si using the Stillinger-Weber interatomic potential to investigate the existence of a second critical point at the end of the LLPT line. Their investigation focused mainly on the tensile (negative pressure) regime, where the second critical point is believed to be located. To our knowledge, a systematic study of the transitions between the disordered (liquid and amorphous) phases of Si in the supercooled regime, under positive pressure and using a realistic model for Si, is still lacking. We have also studied the pressure-temperature melting line given by the model. This paper is organized as follows. In Sec. II, we present and discuss the technical aspects of the methodology employed in our simulations. The results are presented and discussed in Sec. III. Finally, in Sec. IV we draw our conclusions.

II. METHODOLOGY

The computer simulations performed in this work were carried out using the Monte Carlo (MC) method, which was implemented using the Metropolis algorithm.³⁵ The simulations were performed in the canonical ensemble (NVT) and in the isobaric-isothermal ensemble (NPT). In the NVT simulations, one Monte Carlo step or sweep consists in performing N attempts to move one atom of the system, where N is the number of atoms in the simulation cell, according to the Metropolis algorithm. In each attempt, the atom to be moved is randomly chosen, that means that in average in one Monte Carlo sweep one attempt to move each atom of the system is made. In the NPT simulations, aside from the attempts to move the atoms, one attempt to change the volume of the sim-

ulation cell is performed. We used a cubic 1000-atom cell in the simulations. Periodic boundary conditions were employed to avoid surface effects.

We used in the simulations the environment dependent interatomic potential (EDIP) (Ref. 36) to model the atomic interactions in Si. This empirical interatomic potential is based on a large database of Si properties, which includes bulk properties, cohesive energy, and lattice constant, of crystalline Si in the diamond cubic structure and the formation energy of a variety of point and extended defects obtained from *ab initio* calculations; aside from that the database also contains the experimental values of the elastic constants. This rich database provides a good transferability to the potential, which can give a good description of the liquid and the LDA, although the properties of these phases were not explicitly included in the database.

The calculation of the phase diagram of a substance requires the computation of the free energy of the various phases of the substance. To this end, we used a very efficient methodology, which results from the combination of the adiabatic switching (AS) method 37,38 and the reversible scaling (RS) method.^{39,40} Both methods are called non-equilibrium methods in the sense that the free energy is computed by determining the work performed to change the potential energy of the system very slowly, in such a way that dissipation is negligible. In the AS method, the potential energy is a mixture of the potential energy of the system of interest with the potential energy of a system of reference, of which the free energy is known. The mixture is controlled by a switching parameter that gives the relative contribution of each potential energy to the mixture. Then, by changing the switching parameter one can switch the potential energy from that of the system of interest to that of the system of reference, or vice versa. Therefore, by computing the work performed to go from one system to the other, we can determine the absolute free energy of the system of interest, since we know the free energy of the reference system. It should be pointed out that we are assuming here that both systems give the same kinetic energy contribution to the internal energy, so we can only be concerned about the potential energy contribution. The AS method gives the free energy for only a given temperature, therefore, if one needs to know the free energy in a wide range of temperatures, many simulations are required. This task can be efficiently done by the RS method, that allows the calculation of the free energy for a wide range of temperatures, requiring only the knowledge of the free energy for just a single temperature, which can be provided by the AS method. The RS method is based on the idea that one can map the free energy of a system in a range of temperatures onto the free energy of another system at a single temperature, provided that the potential energy of the latter system is the potential energy of the former one conveniently scaled. The free energy of the scaled system can be easily determined by the AS method. Therefore, one can, at least in principle, determine the free energy in a wide range of temperatures from only a single simulation, whose length is similar to those used to obtain thermodynamical quantities that are simple averages in phase space, such as volume, energy, enthalpy, etc. We have used an Einstein crystal (collection of harmonic oscillators)

as a reference system for crystalline silicon (c-Si) phase and an inverse 12th-power fluid for the liquid phase. The angular frequency of the harmonic was chosen to be that of the main vibration mode of the crystal, $\omega_{Si} = 84.44 \times 10^{12}$ rad/s. The parameters in the inverse 12th-power fluid were chosen to reproduce the first peak of the radial distribution function given by the EDIP model at zero pressure and temperature of 2000 K.

III. RESULTS AND DISCUSSION

In order to study the transitions between the disordered phases of Si, it is necessary to compute the free energy of the system at different external pressures. Initially, to obtain the reference free energies we performed AS simulations of the liquid at 2000 K for pressures ranging from 0 to 10 GPa. The AS method was used, with the inverse 12th-power fluid as the reference system and the length of the simulations was of 2.5 \times 10⁴ MC sweeps. Next, RS simulations were employed to determine the free energy for temperatures going from 2000 K to 400 K. In the RS simulations using the MC method, scaling the potential energy is formally identical to change the temperature of the system during the simulation.⁴¹ Therefore, aside from the free energy calculation, one can also monitor any other property of the system available from MC simulations. We also performed RS simulations in the opposite direction, starting at 400 K and going back to 2000 K, in order to ascertain effects of hysteresis and dissipation. The length of these simulations, either cooling down or heating up the system, was typically 4×10^6 MC sweeps. The Saviztky-Golay smoothing filter, performing a polynomial regression of second order on 1000 data points, was used for noise reduction in the results of atomic volume and excess entropy.

Figure 1 displays the atomic volume as a function of temperature for two values of the external pressure, 0 and 3 GPa. The graph for zero pressure in Fig. 1 shows that in the cooling curve the atomic volume initially decreases with temperature as it is expected, however, at about 1200 K there is a sharp increase of about 0.4 $Å^3$ in the specific volume. The heating curve, on the other hand, does not retrace back the cooling curve, the sudden drop in the atomic volume occurs at a higher temperature, showing that there is a hysteresis in the cooling and heating processes. The abrupt changes in the atomic volume together with the hysteresis loop are a clear indication of a first-order transition. This result is consistent with the findings of a previous study¹⁴ that found a first-order LLPT at 1135 K. The other graph displays the same processes of cooling and heating, but now at a pressure of 3 GPa. The noticeable differences between the two figures are: the reduction of the volume due to the applied external pressure and, most importantly, the hysteresis loop is shifted towards lower temperatures by about 150 K and becomes more prominent. That means that pressure lowers the LLPT temperature. This is expected, since the higher temperature liquid is the HDL; this is similar to the lowering of the melting point of Si by pressure. It is interesting to note that this behavior of the hysteresis loop as pressure increases is quite similar to that observed in heavy water confined in a nanoporous silica matrix.⁶ It is also noteworthy to mention that in the case of water the



FIG. 1. Atomic volume as a function of temperature for cooling and heating processes at 0 and 3 GPa.

second critical point is considered to be located at positive pressures, whereas in the case of silicon the second critical point is regarded to be located at negative pressures.³⁴ Because of that, Zhang *et al.*⁶ observed the hysteresis loop only above 1000 bar, while in our calculations the hysteresis loop is observed even at zero pressure. In a previous study,¹⁴ it was found that a liquid-amorphous transition in the EDIP model for Si takes place at 843 K. We will address the effects of pressure on this transition later. Both panels in Fig. 1 show that the LDA exhibits a negative thermal expansion coefficient. This unusual behavior of the model has been discussed before in the literature.⁴² However, we should emphasize that this behavior plays no role in the conclusions of this work.

Let us now analyze what happens in the system from the microscopic point of view. In Fig. 2, we show the atomic coordination as the system is cooled down. The coordination of each atom in the system is obtained by rounding the effective coordination Z in the EDIP model³⁶ to the nearest integer. The upper graph of Fig. 2 shows the results for zero pressure. Below 1300 K, approximately in the same interval of temperature where the volume hysteresis loop is located, the amount of fourfold atoms starts to increase rapidly, whereas the number of fivefold coordinated atoms decreases at the same rate. The amounts of fourfold and fivefold coordinated atoms stabilize only at about 900 K. The lower graph in Fig. 2 depicts the atomic coordination for the system under an external pressure of 3 GPa during the cooling process. In this case, one can see



FIG. 2. Atomic coordination as a function of temperature at 0 and 3 GPa during the cooling process.

a similar behavior to that at zero pressure, but now the abrupt changes in the amount of fourfold and fivefold coordinated atoms start happening at a lower temperature, at 1100 K, and stabilizing between 700 K and 800 K. The occurrence of the LLPT is evidenced in both figures by the rapid increase in the difference between the number of fourfold and fivefold coordinated atoms. However, the most important difference between the two panels is that, for the zero pressure case, at low temperatures about 95% of the atoms are fourfold coordinated and about 5% of fivefold coordinated atoms, while for 3 GPa the proportion between fourfold and fivefold coordinate atoms is 82% and 18%, respectively. Therefore, aside from shifting the LLPT, pressure also has an important role to determine the structure of the LDL. The results for intermediate temperatures (not shown) at 1 GPa and 2 GPa are similar to that for 3 GPa, except that the LLPT for those pressures takes place at higher temperatures.

In Fig. 3 we show the behavior of the volume of the system under the pressure of 4 GPa and 5 GPa. These figures show a very distinct behavior from that observed in Fig. 1. At 4 GPa, during the cooling process, the atomic volume begins to raise at 1000 K and stops increasing at about 700 K. However, during the raise of the volume one can observe large oscillations. The heating curve also shows large oscillations and an even larger increase in the volume than that observed in the cooling curve. The heating curve starts to retrace the cooling



FIG. 3. Atomic volume as a function of temperature for cooling and heating processes at 4 and 5 GPa.

one at about 1000 K. In contrast to the sudden changes in volume displayed in Fig. 1, the changes at the pressure of 4 GPa are smaller. Although hysteresis is present, the hysteresis loop is not well defined in this case. In the 5 GPa case, there is no indication of the LLPT. The volume decreases monotonously during cooling, initially showing oscillations that can be regarded as thermal fluctuations. However, below 900 K the amplitude of these oscillations increase substantially. The amplitude of the oscillations seems to decrease below 700 K. In average the volume in the cooling process resembles that of a simple liquid undergoing a glass transition as it is cooled down, with the volume decreasing monotonically with temperature until near the glass transition, where the slope of the curve changes. The heating curve in average retraces back the cooling curve.

Figure 4 displays our results for the atomic coordination for 4 GPa and 5 GPa. The graphs show a very distinct behavior, at 4 GPa we can see that below 1000 K the amount of fourfold coordinated atoms begins to increase rapidly, while the amount of fivefold coordinated atoms decreases proportionally, which is similar to the behavior depicted in Fig. 2. Although in this case, at the end of the cooling process, the relative amount of fourfold and fivefold coordinated atoms is 65% and 35%, respectively. At 5 GPa, on the other hand, the behavior is quite different, the amounts of fourfold and fivefold coordinated atoms fluctuate, but there is no sharp increase in the amount of fourfold coordinated atoms as the



FIG. 4. Atomic coordination as a function of temperature at 4 and 5 GPa during the cooling process.

temperature is lowered. Finally, at low temperatures the concentration of atoms with coordination 4 and 5 is approximately the same.

Our results indicate that as pressure increases, the LLPT temperature is pushed down towards the glass transition. Close to the glass transition, the dynamics of the liquid becomes very slow, the so-called glassy dynamics. The LLPT is a first-order transition, which occurs through nucleation, which in its turn requires atomic rearrangements that are significantly affected by the slow dynamics within the timescale of the simulation. At 4 GPa, the LLPT still can be observed, but it is significantly disrupted by the glassy dynamics. At 5 GPa, the dynamics is so slow that the LLPT is practically suppressed. The oscillations observed in the range from 700 K to 900 K are frustrated attempts of the nucleation of the LDL phase. Similar oscillations, in that range of temperatures, can also be seen in the atomic coordination. We can verify our conclusion by observing that for a higher pressure of 7.5 GPa, the oscillations observed in the volume during the cooling process at 5 GPa, decrease substantially, as can be seen in Fig. 5. At 7.5 GPa, the first-order transition temperature is below the glass transition temperature and, therefore, the transition is not observable, since in this case nucleation is also precluded. Furthermore, in Fig. 5 one can notice that at 7.5 GPa a change in the slope of the volume as function of temperature occurs about 650 K, that indicates the glass tran-



FIG. 5. Atomic volume for a cooling process as a function of temperature at 5 and 7.5 GPa.

sition for this pressure, which will be confirmed below by our excess entropy calculations.

In order to determine more precisely the LLPT and glass transition temperatures, we now turn to the free energy calculations. Aside from the free energy of the liquid, we also calculate the free energy of the crystalline phase in the diamond cubic structure. In this case, the Einstein crystal was used as a reference system in the AS method simulations. The simulations with the length of 2.5×10^4 MC sweeps provided the reference free energy at 300 K. The RS method was used to obtain the free energy of the crystal in the range of temperatures from 300 K to 2000 K. The length of the RS simulations in this case were also of 4×10^6 MC sweeps. The entropies of liquid and crystal can be readily obtained from the numerical derivative of the free energy, $S = -\partial F / \partial T$. In Fig. 6, we display the excess entropy of the liquid with respect to the crystal, $\Delta S = S_l - S_c$ as a function of temperature during the cooling process, for two values of pressure, 0 and 5 GPa. The excess entropy initially decreases monotonically with temperature in both cases, but at a given temperature (\approx 900 K upper graph and ≈ 650 K lower graph) it stops decreasing and then it becomes practically constant. We take the glass transition temperature to be that of the onset of the change in the behavior of the excess entropy of the liquid. As temperature is lowered, the entropy of liquid decreases at a higher rate than that of the crystal. However, at a certain temperature the liquid undergoes glass transition and the system begins behaving like



FIG. 6. Excess entropy as a function of temperature at 0 and 5 GPa during the cooling process.

a solid; diffusion ceases, within the timescale of the simulation, and the atoms just vibrate around equilibrium positions. The entropy of the amorphous is composed by two contributions, vibrational and configurational. The vibrational part decreases with temperature approximately at the same rate than that of the crystal. The configurational entropy, on the other hand, which is the configurational entropy of the liquid at the moment of the glass transition, remains frozen in the structure of the amorphous. This configurational entropy of the amorphous is also called residual entropy. These are the reasons for the excess entropy to be approximately constant with temperature after the glass transition. It is interesting to note that the excess entropies of the amorphous for both values of pressure are similar. The important point to understand why these two excess entropies are practically the same is that the liquid at zero pressure undergoes LLPT, while the liquid at 5 GPa does not. At 1600 K, the excess entropy of the liquid at zero pressure is higher than that of the liquid at 5 GPa. However, the drop in the excess entropy from 1600 K to 400 K for the liquid at zero pressure is 1.75 k_B /atom, while for the liquid at 5 GPa the decrease in excess entropy is 1.40 k_B /atom. The difference between these two drops in excess entropy is 0.35 k_{B} /atom, which is equivalent to the entropy associated with the latent heat released by the liquid at zero pressure during the LLPT (see below).

The transition temperature of a first-order phase transition can be obtained from the calculation of the Gibbs free energy of the two phases involved in the transition. The metastability of these phases allows us to ascertain the transition temperature from the crossing of the free energy curves of the two phases. From the results we have presented so far, we are able to estimate appropriate reference temperature for the calculation of the free energy of the LDL. This temperature should be below the temperature range where the hysteresis loop takes place, but it should be above the glass transition temperature. Because of the slow dynamics of the liquid in this range of temperatures, free energy calculations in this case ought to be done with greater care. In the calculation of the reference free energy, the length of the AS simulations was of 1.0×10^6 MC sweeps. The switching function, that connect the system of interest and the reference system, in this case was the function $\lambda(\tau) = (1 - \tau)^5$, instead of the usual linear function that was used in the other calculations. The advantage of using such a function is that for $\tau \approx 0$, when the main contribution is given by the inverse 12th-power fluid, the function varies more rapidly, while for $\tau \approx 1$, when the main contribution comes from the EDIP model, the function varies very slowly to take care of the slow dynamics. The RS simulations in this case comprised 2×10^6 MC sweeps. However, it should be pointed out that the interval of temperatures covered is half of that used in the previous calculations. In Fig. 7, we show the crossing between the two curves indicate a LLPT transition temperature of 1203 ± 10 K at zero pressure. The latent heat associated with the transition is given by $L_{l-l} = -T_{l-l}[(\partial F/\partial T)_{HDL} - (\partial F/\partial T)_{LDL}]$, yielding a latent heat of 0.037 eV/atom, which corresponds at 1203 K to an entropy of 0.36 k_B /atom. These results for the transition temperature and latent agree with previous calculations,¹⁴ the relatively small discrepancies are due to methodological differences in the two calculations.

Finally, we summarize our results in Fig. 8 in the form of a pressure-temperature phase diagram. Figure 8 also displays our results for the melting line obtained from simulations using the EDIP model together with experimental data for that magnitude. It is noteworthy that the negative slope



FIG. 7. Free energy as function of temperature for the HDL and LDL at zero pressure.



FIG. 8. Phase diagram of supercooled liquid silicon. Square symbols indicate the calculated liquid-crystal coexistence (melting), stars indicate the experimental liquid-crystal coexistence, circles the HDL-LDL coexistence, triangles the calculated glass transition, and the diamond is the experimental glass transition.²⁵ The error bars in the simulation results for the liquidcrystal coexistence and HDL-LDL coexistence are either equal to or smaller than the symbols. The lines passing through the simulation data are guides for the eye. The dotted line passing through the experimental melting points is a polynomial fit to three data points at the following pressures: 1 atm, 10.5 GPa,⁴³ and -2.5 GPa (Refs. 44 and 45) (the latter is not shown in the figure). The shaded areas indicate the location of the glass transition.

of the melting line obtained using the EDIP model increases towards larger negative values as pressure is raised, which is in agreement with the experimental observations by Voronin et al.⁴³ The LLPT line also exhibits a similar behavior with a negative slope. Since the determination of the glass transition is affected by some uncertainty, the shaded areas indicate the location of the glass transition. The LLPT line in Fig. 8 stops before entering the shaded areas, because at higher pressures the first-order transition is precluded by the glassy dynamics of the system. Our calculations indicate that above 5 GPa the glass transition occurs systematically at temperatures lower than those for pressures below 5 GPa. This is in agreement with the conjecture that the glass transition temperature of the HDL should be lower than that of LDL.² Our results are consistent with the findings by Bhat et al.¹⁸ that obtained HDA of Ge by quenching the liquid under a pressure of 7.5 GPa. Furthermore, our phase diagram is consistent with the estimates by Deb et al.²⁸ for the phase diagram of the metastable phases of supercooled liquid Si.

IV. CONCLUSIONS

We have investigated via computer simulations the pressure effects on the transitions between the disordered phases of supercooled liquid Si. We employed an efficient methodology to compute free energy and entropy combined with MC simulations. The occurrence of the LLPT in our simulations is clearly indicated by the hysteresis loop in the results for the volume in heating and cooling processes. As pressure is raised from 0 to 3 GPa, the hysteresis loop becomes more prominent and is shifted towards lower temperatures, displaying a very similar behavior to that observed in neutron scattering experiments of heavy water confined in a nanoporous silica matrix.⁶ Our results indicate that pressure causes a substantial decrease of the LLPT temperature, dropping from 1203 K at zero pressure to about 900 K for a pressure of 4 GPa. For an applied pressure of 5 GPa, the liquid is approaching the glass transition and its glassy dynamics precludes the LLPT. When the system is under a pressure of 7.5 GPa, the results show that the first-order transition temperature is already below the glass transition temperature. These results are consistent with estimates for the phase diagram of supercooled liquid Si based on an experiment that studied the transition HDA-LDA between the amorphous phases of Si.²⁸ Our results are also consistent with a recent experiment that obtained a HDA of Ge by quenching the liquid under a pressure of 7.5 GPa.¹⁸ The calculations indicate that for a pressure between 0 and 4 GPa, the glass transition temperature lies in an interval from 900 K to 750 K, however, for pressures ranging from 5 GPa up to 10 GPa the glass transition drops to about 600 K. Therefore, our calculations confirm the hypothesis that the glass transition temperature of the LDL is higher than that of the HDL.²

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