

Structural properties of supercooled liquid silicon by molecular dynamics

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Structural properties of supercooled liquid silicon have been investigated by large-scale molecular dynamics (MD) simulation with $N=1728$ particles using the empirical Stillinger-Weber (SW) potential. The latter has been modified by taking into account measurements of the density in the stable liquid near the melting point. The description of the ionic arrangement is in excellent agreement with the recent experiments of Ansell *et al.* [J. Phys.: Condens. Matter **10**, L73 (1998)]. On the other hand, the bond-angle distribution function compares quite well the *ab initio* MD, indicating clearly the superimposition of reminiscent covalent bonding configurations on the liquid-metallic phase. By the light of these experiments, our theoretical study indicates that (i) the SW potential remains a realistic empirical model for the prediction of disordered phases of silicon and (ii) the change in the structure upon supercooling is related to an increase of the density.

Silicon has been the subject of a large amount of experimental and theoretical studies over the three last decades.¹ It still remains of interest for researchers due to the lack of complete understanding of its physical properties in the condensed phases. While the crystalline (*c*-Si) and amorphous (*a*-Si) phases attract much attention due to technological aspects, the liquid state is less well studied, even though it is well known that *c*-Si and *a*-Si can be generated, respectively, from the stable liquid by the Czochralsky growth process and from the melt slightly supercooled. However, the high melting temperature $T_f=1683$ K is a serious impediment for the precise experimental study of liquid Si (*l*-Si) as shown by the recent results reported in the literature.²⁻⁵ The latter reveal unusual and contradictory behaviors of the macroscopic properties such as the density, the viscosity and the resistivity as a function of the temperature, for the stable and the supercooled liquids, which indicate possible structural changes—if not polymorphic phase transitions⁶—around the melting temperature. Therefore, the determination of the structural properties of silicon remains a challenge, especially in the supercooled liquid since little is known about how these features evolve.

Molecular dynamics (MD) is one of the most powerful technique, if not the only one, to study the structural properties of Si in the liquid state and to test directly the interatomic interactions. *Ab initio* MD, that have been carried out to obtain the structural, dynamical, and electronic properties of *l*-Si,⁷⁻⁹ provides reference results for other approximate theories. Nevertheless, this method is limited to few tens of atoms as it is too computationally expensive to perform extensive studies with large simulations, even with new order- N methods. First-principle approaches have also been put forward to take the covalent bonding into account in the

interactions. For example Jank and Hafner¹⁰ proposed to derive the interatomic forces within the second-order pseudo-potential theory, while Wang *et al.*¹¹ used a tight binding Hamiltonian.¹² In addition, several empirical many-body potential energy functions have been proposed in the literature during the last decade,¹³ which are very convenient for computational purposes. It appears that the potential propounded by Stillinger and Weber¹⁴ (SW) gives the best overall qualitative description of liquid silicon (see Balamane *et al.*,¹ and references therein). Especially, the SW model gives an excellent estimate of the melting temperature,¹⁵ which is particularly important for studying real supercooled states.

The aim of this paper is to report theoretical investigations of the structural properties for supercooled states based on the empirical SW potential. For this purpose, we define a different procedure of fitting of its parameters in order to predict the pair correlation function, the coordination number and the bond-angle distribution function by means of molecular dynamics simulations. Our results compare well with the experimental data of Ansell *et al.*,¹⁶ who have recently measured the structure of liquid Si by a levitation technique and observed significant structural changes upon supercooling. It must already be stressed that our results are consistent with the anomalous increase of the density of molten silicon pointed out by Sazaki *et al.*,³ at temperatures close to the melting point.

The potential energy function of a system containing N interacting particles is usually expanded as a sum over all particles of many-body contributions. Since *c*-Si consists of atoms maintained in place by strong and directional bonds, Stillinger and Weber¹⁴ proposed the following combination of pair and triplet potentials, namely,

$$u_2(r_{ij}) = \begin{cases} A \varepsilon [B(\sigma/r_{ij})^p - (\sigma/r_{ij})^q \exp[\sigma/(r_{ij} - a\sigma)]] & \text{if } r_{ij} < a\sigma, \\ 0 & \text{if } r_{ij} \geq a\sigma, \end{cases} \quad (1)$$

where $A = 7.049556277$, $B = 0.6022245584$, $p = 4$, and $q = 0$, whereas the three-body term, which is designed to stabilize the tetrahedral arrangement of the atoms in the solid state, reads

$$u_3(r_{ij}, r_{ik}, r_{jk}) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \quad (2)$$

with

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} \lambda \varepsilon \exp[\gamma\sigma/(r_{ij}-a\sigma)] \exp[\gamma\sigma/(r_{ik}-a\sigma)] [\cos(\theta_{jik}) + \frac{1}{3}]^2 & \text{if } r_{ij} < a\sigma \text{ and } r_{ik} < a\sigma, \\ 0 & \text{otherwise,} \end{cases} \quad (3)$$

where $\lambda=21$ and $\gamma=1.2$. The angles θ_{jik} , θ_{ijk} , and θ_{ikj} denote, respectively, the angles at vertex i, j , and k of the triangle (i, j, k) with sides $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, $r_{ik}=|\mathbf{r}_k-\mathbf{r}_i|$, and $r_{jk}=|\mathbf{r}_k-\mathbf{r}_j|$. In both two- and three-body interactions the well depth $\varepsilon=50$ kcal/mol and the cutoff radius $a=1.8$. Initially, a length scale $\sigma=2.0951$ Å was chosen so that the density of c -Si corresponds to the observed lattice spacing at $T=0$ K.

Taking the measurements of the density^{2,3} into account in the present work, we choose the value of σ to reproduce the experimental density $\rho=2.57$ g/cm³ at temperature $T=1829$ K, corresponding to the experimental conditions at which the structure factor in the stable liquid has been measured.^{16,17} To do it, we carry out MD simulations with the SW potential in the isobaric-isoenthalpic ensemble, as Broughton and Li,¹⁸ in order to obtain the thermodynamic state of interest, which is reached with the value of $\sigma=2.0618$ Å. As it will be seen later, this new value is consistent with the one proposed by Stillinger and Weber, albeit slightly lower, and allows us to reproduce correctly the position of the first peak of the experimental pair-correlation function. It is important to mention that this can be done without any modification of the melting temperature of the model. As a matter of fact, the reduced temperature of the model $T^*=k_B T/\varepsilon$ used in the simulations does not depend on the scaling factor σ . This would have not been the case if we had modified the depth ε of the potential.

Large-scale MD simulations are thus performed using a parallel algorithm.¹⁹ In order to calculate the structural properties of silicon for the stable and the supercooled states, 1728 atoms are set in a cubic box subject to the standard periodic boundary conditions. Such a large number of atoms is used to minimize finite size effects. A spatial decomposition of the simulation box is applied and the simulation is distributed among eight processors of the parallel machine. Verlet's algorithm in the velocity form is used to produce a discrete phase-space trajectory in the microcanonical ensemble (NVE) with a time step $\Delta t=2 \times 10^{-2} \tau$, where $\tau=\sigma(m/\varepsilon)^{1/2}=7.5270 \times 10^{-14}$ s. For each state investigated, the system is equilibrated during 10 000 time steps before the production period of 40 000 time steps is achieved, essential to gather statistics over a great number of independent configurations.

Supercooled states can be produced by performing different types of computer experiments as described by Abraham.²⁰ Beginning from the liquid state at $T=1829$ K and $\rho=2.57$ g/cm³, we have chosen to investigate the situation in which the system is crunched stepwise by diminishing the temperature and increasing the density simultaneously. The quenching rate corresponds to 3.2×10^{12} K/s, and the increase of density is obtained by reducing the size

of the box at each temperature step, to get the final values $\rho=2.71$ g/cm³ at $T=1603$ K and $\rho=2.75$ g/cm³ at $T=1542$ K, which correspond to the experimental temperatures investigated by Ansell *et al.*¹⁶ A consequence of the crunch is a rise of the pressure P of the system. Although the latter is zero at $T=1829$ K, corresponding to the desired experimental conditions, it reaches a value $P\sigma^3/\varepsilon=0.13 \pm 0.009$ at $T=1603$ K and $P\sigma^3/\varepsilon=0.16 \pm 0.008$ at $T=1542$ K.

To be sure that the system is still liquid when it is crunched under the melting point, we check the mean-square displacement (MSD), which has been plotted against time in Fig. 1. As expected, the MSD has an asymptotic linear behavior for the states studied, guaranteeing that the simulated system is supercooled at $T=1603$ K and $T=1542$ K, but not amorphous. It is seen that the number of time steps used, corresponding to 60 ps, is sufficient to extract the self-diffusion constant D from the slope of the MSD curves at long times. We find $D=0.8566 \times 10^{-4}$ cm²/s at $T=1829$ K which is close to the value of Broughton and Li¹⁸ ($D=0.98 \times 10^{-4}$ cm²/s at $T=2010$ K) and is compatible with those of the majority of liquids. For the supercooled states, the self-diffusion constant is smaller by nearly a factor 2 with respect to the value in the stable liquid, i.e., $D=0.5539 \times 10^{-4}$ cm²/s at $T=1603$ K and $D=0.5313 \times 10^{-4}$ cm²/s at $T=1542$ K.

In Fig. 2, we display the pair-correlation function $g(r)$ obtained with the SW potential in comparison with the recent experimental data of Ansell *et al.*¹⁶ For the stable liquid at 1829 K, the experimental $g(r)$ shows a subsidiary peak situated at around 3.5 Å, which is a characteristic feature of covalent liquids. Although the first peak of the calculated $g(r)$ is slightly narrower, its position and its magnitude are in very good agreement with the experiment, as the consequence of our fitting procedure of the σ value in the SW potential. In order to see the influence of the parameter σ , we

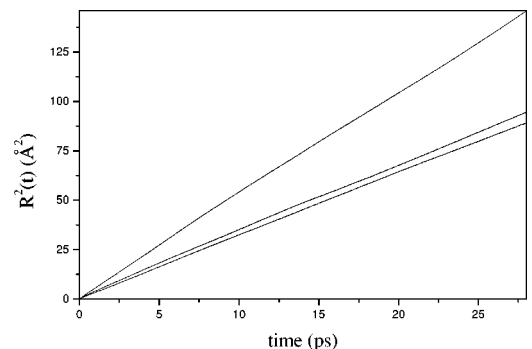


FIG. 1. Mean square displacement $R^2(t)$ as a function of time. The curves correspond to $T=1829$ K, $T=1603$ K, and $T=1542$ K from the top to the bottom.

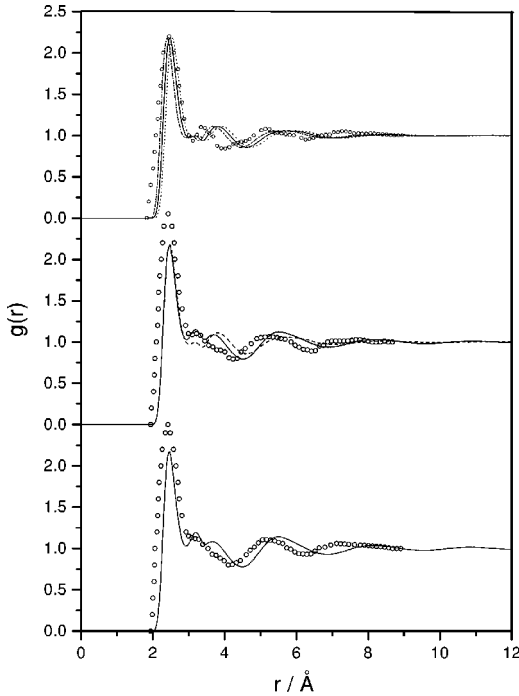


FIG. 2. Pair-correlation function for the stable liquid at $T = 1829$ K (upper curves) and the supercooled states at $T = 1603$ K (intermediate curves) and $T = 1542$ K (bottom curves). The solid line denotes the molecular dynamics results with the SW potential, while the open circles correspond to the experimental data of Ansell *et al.*¹⁶ At $T = 1829$ K the dash-dotted and dotted curves correspond, respectively, to pair-correlation functions calculated with a σ value smaller and greater than that of the fitted one. At $T = 1603$ K, the dashed curve corresponds to $g(r)$ obtained by a quench at constant volume from the stable liquid at $T = 1829$ K.

have plotted $g(r)$ using values of σ that depart on either side from the fit by 2%. The larger value, which shifts the curve of $g(r)$ towards large r , corresponds almost to that proposed by Stillinger and Weber. In addition, we can notice the hump located between the first peak and the subsidiary peak, which is not present in the experiments. This peculiarity has also been reported by Luedtke and Landman²¹ and Cook and Clancy¹⁵ in their studies with the SW potential.

In order to obtain the supercooled states ($T = 1603$ K and $T = 1542$ K) corresponding to those explored by Ansell *et al.*,¹⁶ the liquid is crunched below the melting point by using the MD procedure described previously. It is important to point out that these are genuine supercooled states for the SW potential. As we already said, changing the value of σ does not change its melting temperature, which is situated

between 1662 and 1704 K, a range including the experimental melting temperature $T_m = 1683$ K as shown recently by simulations of a solid-liquid interface.¹⁵ Therefore, the SW potential yields realistic results for the supercooled liquid that it should not be the case for Tersoff's potential²² studied recently by Ishimaru *et al.*,²³ since according to the authors the melting temperature of the model is almost twice the experimental value. The hump in $g(r)$, already present in the stable liquid, grows drastically and the second peak shifts toward small r while its height diminishes to form a double shoulder. A good agreement is found with the experiment for both temperatures, especially with regard to the prediction of the double shoulder that appears between 3 and 4 Å. It is worth mentioning that if the system is quenched under the melting point at constant volume, the double shoulder is not detected, as it can be seen on the dashed curve shown in Fig. 2 at $T = 1603$ K. In their *ab initio* MD calculations at constant volume, Stich *et al.*⁷ neither did observe this peculiarity for the supercooled state at $T = 1250$ K. This clearly indicates that it must be attributed to a strong increase of the melt density up to 2.71 g/cm³ at $T = 1603$ K and 2.75 g/cm³ at $T = 1542$ K. Our simulations corroborate the recent density measurements of Sazaki *et al.*,^{2,3} which reveal a sharp increase of the density in the liquid state upon cooling and whose extrapolated values coincide with ours.

In order to analyze the structural changes upon supercooling in more details, we consider the running coordination number

$$n(r_c) = 4\pi\rho \int_0^{r_c} r^2 g(r) r^2 dr, \quad (4)$$

which gives the mean number of atoms situated within a sphere of radius r_c . In Table I, $n(r_c)$ is tabulated for values of r_c corresponding to the successive minima of the calculated pair-correlation function. If Eq. (4) is integrated up to the first minimum, a small reduction of $n(r_c)$ is observed when the temperature diminishes. In the stable liquid, the coordination number is underestimated compared with the value of 6.4 commonly found in most experiments, whereas for the supercooled states the values are in close agreement with those of Ansell *et al.*¹⁶ If Eq. (4) is integrated up to the second minimum, $n(r_c)$ increases when T decreases, and takes the values of about 8 for the stable liquid and 10 for the supercooled states. Interestingly, with the radius corresponding to the third minimum of $g(r)$, the coordination number is almost the same for the three temperatures. So, when the system is undercooled, the variation of $n(r_c)$ indicates that two atoms in average are transferred from the third shell to

TABLE I. Running coordination number for three different radii corresponding to the minima of the pair-correlation function $g(r)$.

Shell	$T = 1542$ K		$T = 1603$ K		$T = 1829$ K	
	r_c (Å)	$n(r_c)$	r_c (Å)	$n(r_c)$	r_c (Å)	$n(r_c)$
1	2.90	5.23 ± 0.20 5.50 ± 0.50^a	2.93	5.37 ± 0.20 5.50 ± 0.50^a	2.99	5.54 ± 0.19 6.40 ± 0.50^a
2	3.46	9.86 ± 0.30	3.49	10.01 ± 0.29	3.33	7.83 ± 0.22
3	4.50	20.48 ± 0.37	4.47	20.78 ± 0.35	4.44	19.82 ± 0.38

^aExperimental values of the coordination number after Ansell *et al.* (Ref. 16).

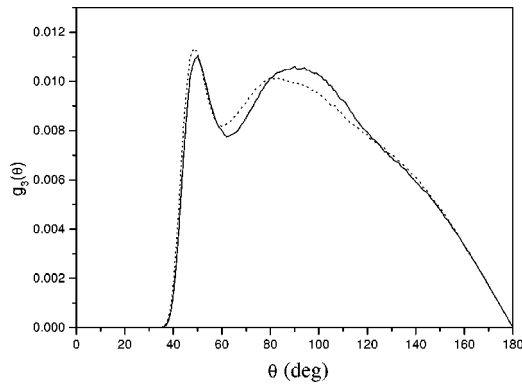


FIG. 3. Bond-angle distribution function for the stable liquid at $T=1829$ K (solid line) and the supercooled liquid at $T=1542$ K (dashed line).

the second one, that is consistent with the anomalous behavior of the density observed at temperature close to the melting point.^{2,3}

We now complete our analysis on the angular nature of the structural properties in considering the triplet correlation function $g_3(\theta, r_c)$, which measures the probability of finding two neighbors j and k , of a particle i taken as the origin, with an angle θ between the pairs $i-j$ and $i-k$, provided that both j and k are situated within a sphere of radius r_c . In Fig. 3, the function $g_3(\theta, r_c)$ is displayed with r_c equals 3.33 Å for $T=1829$ K and 3.46 Å for $T=1542$ K. These values of r_c , which correspond to the second minimum of $g(r)$, are consistent with those used by Stich *et al.*⁷ and Fabricius *et al.*⁹ in their respective *ab initio* MD, as well as by Ishimaru *et al.*²³ with Tersoff's potential. For both temperatures, our curves of $g_3(\theta, r_c)$, similar to theirs, consist in a prominent peak near 50° followed by a broad distribution with a single maximum containing a bump at around 150° . This distribution, which differs slightly from the original SW potential, demonstrates the tendency to accentuate the ideal tetrahedral order^{18,21} with a single maximum close to the tetrahedral bond angle of 109° . This remark is not supported by the *ab initio* simulations of Kresse and Hafner²⁴ on *l*-Ge, since the distribution of the bond angles is almost random in the stable *l*-Ge whereas the tetrahedral angle distribution is dominant in supercooled states.

Studying the variation of the bond-angle distribution with various coordination numbers, Ishimaru *et al.*²⁵ found that the peak at 50° starts to grow when n exceeds 5. Such a behavior could reveal the existence of reminiscent covalent bondings close to that of the β -Sn structure composed of four nearest neighbors and two next nearest neighbors, as suggested by Gaspard *et al.*,²⁶ because of the bond angles associated at 94.0° and 149.3° . Nevertheless, if our results indicate a slight preference for this reminiscent configuration, the signature of the nearly free electron character of the metallic-liquid phase cannot be ignored. When the temperature changes from 1829 to 1542 K, it is interesting to remark that the height of the main peak of $g_3(\theta, r_c)$ decreases and its position shifts from 90° to 80° . In the same time, the peak at 50° increases and slightly shifts toward small angles. This angular displacement of the distribution is consistent with an increase of the density. Therefore, the competition between the two kinds of structures and the fluctuations induced in the local atomic arrangement upon supercooling could be at the origin of the anomalous behavior of the density of *l*-Si near the melting point.

Despite the fact that the SW is an empirical model, we would like to underline the good agreement found for the ionic structure and coordination number of liquid and supercooled Si with the new experimental results of Ansell *et al.*¹⁶ provided that the length scale σ is fitted on the thermodynamic state of the stable liquid silicon. Therefore, it is suggested that the SW potential could now be used with the new value of σ for the analysis of the dynamical properties of liquid, supercooled and amorphous silicon. Studying the structure of Si in the supercooled states, we have predicted the double shoulder on the pair-correlation function, which is observed in the experiments.¹⁶ It is shown that its emergence is strongly related to the increase of the density imposed by our crunching process, in agreement with the new measurements of density^{2,3} near the melting point. The large-scale molecular dynamics simulations reveal a rearrangement of atoms within the two first coordination shells and a change in the three-body distribution function that combines covalent bonding configurations and liquid metallic phase.

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