

Structural Changes on Supercooling Liquid Silicon

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Introduction

Despite the promise of advanced materials, silicon (Si) still dominates semiconductor technology. Since crystalline silicon is normally generated from the melt by the Czochralski process, and since future techniques for producing Si chips may involve the imprinting of a thin molten layer [1], the properties of normal and supercooled liquids acquire significant importance. In fact, however, there is relatively little information in the literature about these liquids, and the data that do exist are often characterized by serious discrepancies, even with regard to properties as basic as density, viscosity, and conductivity. The difficulties appear to arise partly from their rather high melting point and partly from their corrosive nature; thus, many of the results published actually relate to solutions of the container material in the bulk liquid. Measurements made with containerless techniques [2, 3] seem to largely avoid these problems. Measurements of conductivity by contactless techniques have been pioneered recently [3].

The structure factor $S(q)$ has been measured by x-ray diffraction (XRD) several times in recent years [4-8]. While all the experimental data are in good agreement above the melting point, different behaviors have been observed as a function of temperature below the melting point. For instance, Ansell et al. [6] reported that there was a decrease in the coordination number with decreasing temperature, while Kimura et al. [7] found an increase, so this question remains open.

From a theoretical point of view, it has been shown that a lowering of the coordination number with temperature in the supercooled liquid occurs even under compression [9]. This was interpreted recently as being due to the possible existence of a second low coordinated liquid phase associated with a liquid-liquid phase transition [10, 11]. There appear to be strong grounds for regarding this as a reversible first-order transition. Experimental estimates of the transition temperature range from 1345K (the observed supercooling limit [6]) to 1340-1420K (from calorimetric studies [12]) and to 1480 ± 50 K (from

transient conductance measurements with laser heating [13]). If the transition temperature is 1345K or higher, Angell and co-workers [10, 11] argue that the tetrahedral disordered phase is liquid below it, so that this becomes a polymorphic liquid transition of the type proposed to occur generally in tetrahedrally coordinated liquids [14]. Nevertheless, this work was based on an empirical potential, whereas *ab initio* molecular dynamics (AIMD) simulations, which handle changes in the electronic structure consistently with those in the atomic structure, should provide a more powerful and realistic tool for investigating changes in both of these with temperature and density.

Methods and Materials

We addressed these deficiencies in previous work by using a joint experimental and theoretical approach to study one aspect of normal and supercooled liquids that is, in some sense, fundamental to all their properties: namely, atomic structure. On the experimental side, we used the conical nozzle levitation (CNL) method [15] and 25-keV photons at undulator beamline station 12-ID-B at the APS to provide high-quality XRD data out to large wave vectors. The use of two lasers, one heating the sample from above as in previous work and the other heating it from below through an opening in the nozzle, makes it possible to minimize gradients (less than 4K over the region irradiated by the x-ray beam) and extend the supercooling regime (230K below the melting point of 1685K). On the theoretical side, we used the SIESTA code [16] for the AIMD computer simulation. It treats the electronic and atomic properties on the same footing. We set up a parametrization similar to that used successfully by Fabricius et al [17]. The simulations were performed on a cubic cell containing $N = 64$ atoms with a typical duration of 3 ps for equilibration followed by 5 ps for the production of the physical properties. The self-diffusion constants extracted from the simulations are $1.32 \text{ \AA}^2/\text{ps}$ at 1767K, $0.91 \text{ \AA}^2/\text{ps}$ at 1667K, $0.87 \text{ \AA}^2/\text{ps}$ at 1543K, and $0.68 \text{ \AA}^2/\text{ps}$ at 1458K.

Results

Figure 1 shows the experimental and simulation structure factors $S(q)$ at four temperatures. The experimental $S(q)$'s possess characteristic features found in previous experiments [4-7]: a main peak situated at q of $\approx 2.6 \text{ \AA}^{-1}$, with a shoulder on its high- q side. As the temperature in the supercooled regime decreases, the intensity of the first peak grows, and the shoulder becomes resolved into a second peak, but their positions remain essentially unchanged. The AIMD results have been extracted from the simulated configurations by using the direct formulation of $S(q)$. The main features of the experimental data are reproduced, although the height of the first peak is underestimated, and the second peak is better resolved and slightly shifted toward a higher q . With decreasing temperature, the first two peaks both sharpen up, as they do in the experimental results.

The corresponding pair-correlation functions $g(r)$ displayed in Fig. 2 give a picture of the orientationally average atomic arrangements in real space. The experimental $g(r)$'s were obtained from the $S(q)$ results by direct Fourier transform with a Lorch modification function to reduce truncation effects [18] and the densities taken from Egry [2]. The curves show the specific characteristics of liquid Si, with a main peak located at 2.5 \AA and subsidiary peaks around 3.8 \AA and 5.6 \AA , with subsequent shallow oscillations. As the temperature decreases, the first peak sharpens without a significant change in position, while the second peak shows a change in profile, with the suggestion of a splitting at 1458K (also observed in our previous work [6]). The AIMD results of $g(r)$ are in reasonable agreement, although the first peak is always slightly narrower and higher than the experimental one, and the subsidiary peaks are shifted toward a lower r . With decreasing temperature, the first peak sharpens up for the experimental and simulation data.

Coordination numbers N_c , obtained from both the experiment and simulation by integrating the radial distribution function $n(r) = 4\pi r^2 \rho g(r)$, where ρ is the number density, up to the first minimum of $g(r)$, are shown in Fig. 3. The two sets of numbers are in good agreement and show a significant decrease in the coordination number with temperature. The values obtained by fitting Gaussian functions to the experimental $T(r) = 4\pi r g(r)$ showed the same trend but were consistently lower by 0.2 to 0.3. This behavior in the supercooled regime is in agreement with our previous measurements [6] and not with the results of Kimura et al. [7], who found the opposite trend.

Additional evidence for the reestablishment of the tetrahedral order on supercooling is provided by the three-body correlation function $g^{(3)}(\theta)$. The inset in Fig. 2 shows $g^{(3)}(\theta)$ derived from the AIMD results. In the normal liquid at 1767K , it consists of a broad distribution

with two peaks, a smaller one near 60° , and a larger one centered at 90° closer to the tetrahedral angle of 109° . In the supercooled regime at 1458K , the latter becomes more pronounced, while the former is considerably reduced, indicating that the tetrahedral ordering is reinforced. As a matter of fact, a bond angle distribution function calculated with a smaller cutoff of 2.5 \AA , close to the covalent bond length (thin lines), shows a single peak close to the tetrahedral angle. The fraction of atoms forming such covalent bonds is calculated to be 22% at 1767K , 24% at 1667K , 28% at 1543K , and 30% at 1458K .

Discussion

In conclusion, joint XRD measurements and AIMD simulations of liquid Si provide strong support for a reinforcement of the tetrahedral ordering as the temperature is reduced in the supercooled liquid, as evidenced by the following three trends: (1) A decrease in coordination number. (This finding confirms our previous results [6] as well as those from recent conventional MD with the Stillinger-Weber potential [9, 10]). (2) Enhancement of the shoulder following the first peak of the structure factor into a clearly resolved peak. (This peak is the highest one in amorphous Si [19] and can be taken as a characteristic of the tetrahedral structure.) (3) An increase in the amplitude of the maximum in the bond-angle distribution close to the tetrahedral angle.

Both the XRD and AIMD results in the present work show a reduction in the coordination number upon supercooling — a major result with implications for the liquid-liquid transition [10].

Acknowledgments

This work was supported by the CNRS and by the National Aeronautics and Space Administration (NASA) Microgravity Sciences and Applications Division under Grant No. NAS8-00122, and the U.S. Department of Energy (DOE). Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Computer time made available by the Ecole Normale Supérieure de Lyon is gratefully acknowledged. The authors thank M. Beno and J. Linton of BESSRC at the APS for experimental help and guidance, J. Rix for assistance with the equipment, and P. Nordine for useful discussions.

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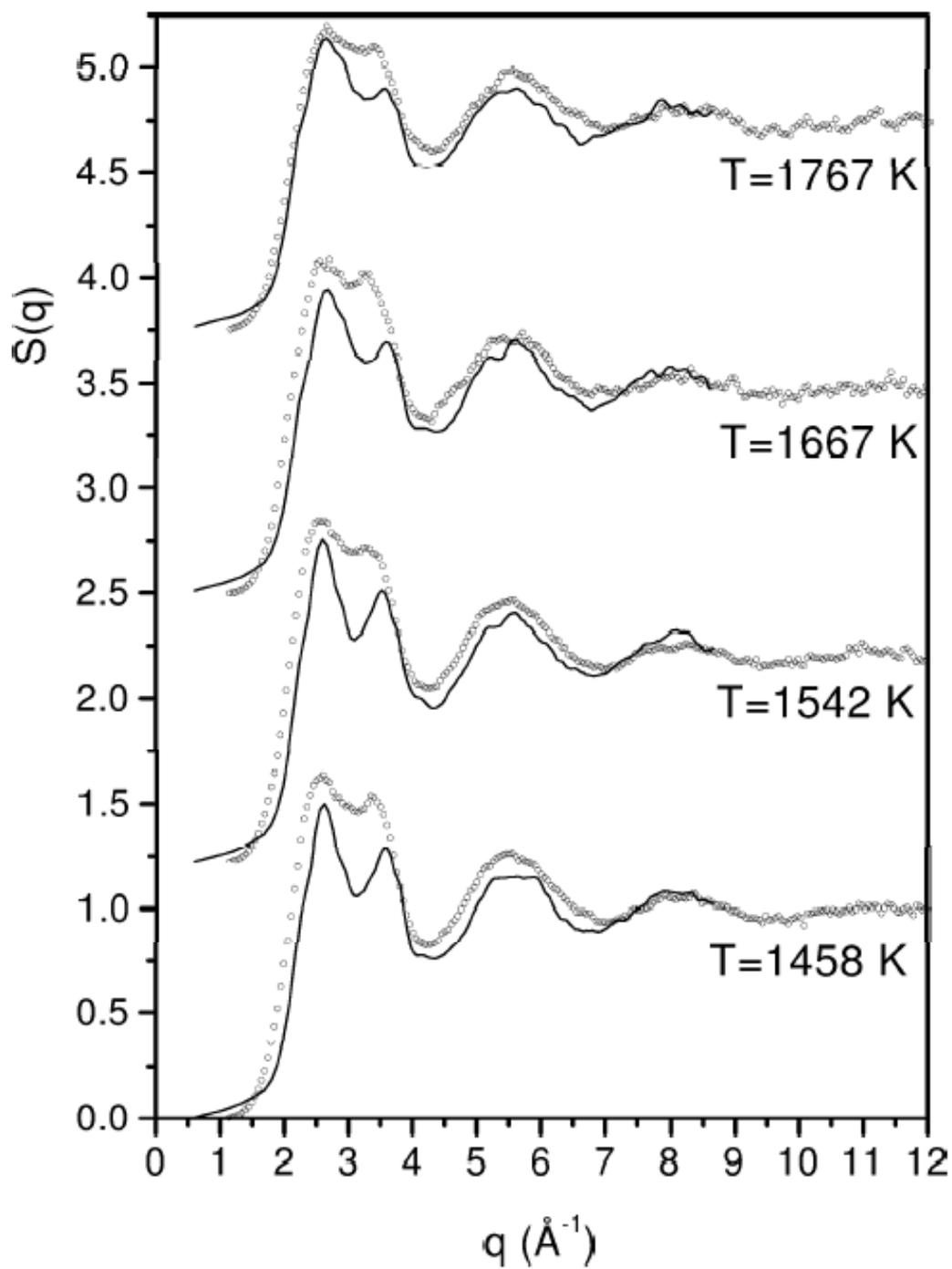


FIG. 1. Structure factor $S(q)$ for liquid silicon (the curves for $T = 1542$, 1667 , and 1767 K are shifted upward by 1.25 , 2.5 , and 3.75 , respectively). The open circles correspond to the experimental data, and the solid lines are the simulation results. The equilibrium melting point is 1685 K.

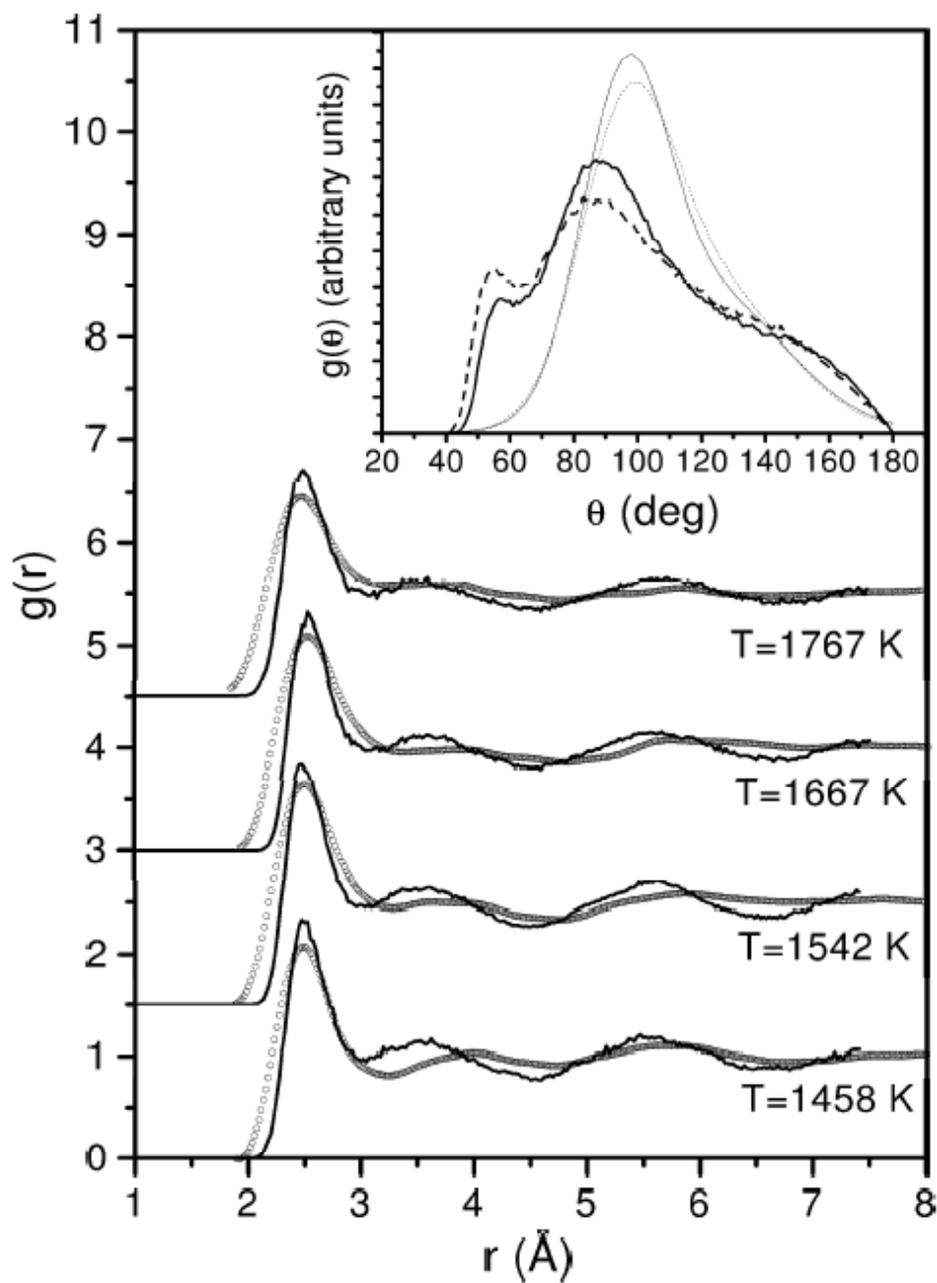


FIG. 2. Pair-correlation function $g(r)$ for liquid silicon (the curves for $T = 1542$, 1667 , and 1767 K are shifted upward by 1.5 , 3 , and 4.5 , respectively). Notation is the same as in Fig. 1. The inset represents the bond-angle distributions $g^{(3)}(\theta)$ at $T = 1458$ K (solid line) and $T = 1767$ K (dashed line). The thin lines represent the corresponding tetrahedral component of $g^{(3)}(\theta)$ calculated with a smaller cutoff, close to the covalent bond length.

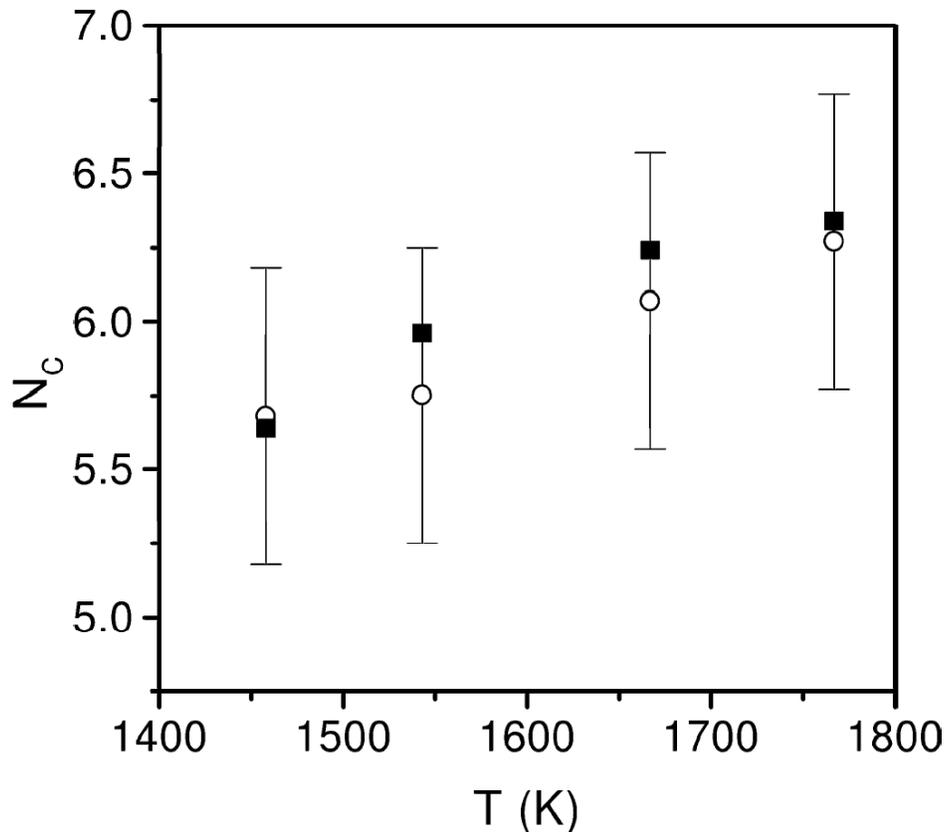


FIG. 3. Coordination number as a function of temperature. The open circles with error bars correspond to the experimental data, and the solid squares are the simulation results. The error bars represent the uncertainty in the absolute values of the experimental points. The uncertainty in the changes with temperature is much lower.

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