

Comment on 'Structure of supercooled liquid silicon' by Ansell *et al*

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COMMENT

**Comment on ‘Structure of supercooled liquid silicon’ by
Ansell *et al***

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Abstract. We correct a statement made in a recent paper (Angell *S et al* 1998 *J. Phys.: Condens. Matter* **10** L73–8) that computer simulations on supercooled liquid silicon were not available. We further point out that the simulations that have been made provide an important confirmation of the findings of Angell *et al*, from the x-ray diffraction studies, that the Si coordination number rapidly decreases in the supercooling range. Of particular interest is the observation that, at the limit of the 340 K supercooling reported in Angell *et al*, the laboratory liquid has the same coordination number that the simulated system reaches at the temperature of its first order liquid–liquid transition. This implies that the crystallization is promoted by the liquid–liquid transition, as is also seen in the simulation. We point out other systems in which such provocative behaviour should be found.

In a recent and provocative x-ray diffraction study of the structure of liquid silicon, Ansell *et al* [1] showed that it was possible to obtain data down to 143 K below the normal melting point. With this capability they showed that the coordination number of the supercooling liquid decreased sharply with decreasing temperature from 6.2 at 115 K above the melting point of 1685 K to 5.6 at 143 K below. In the course of the discussion of the results, the authors state that ‘There are no MD simulations reported for silicon in the supercooled state’. The purpose of this comment is to correct the latter statement and to show that the changes in coordination number reported by Ansell *et al* are comparable with those reported for the simulated liquid in the same temperature range. This is of special interest because of the support given by the new experimental results for the existence of a first order transition from the metallic liquid to a tetrahedrally coordinated amorphous semiconducting phase during sufficiently rapid cooling, and for a direct relation between this transition and the limit of supercooling.

Simulations of the supercooled liquid state of silicon have been carried out by two groups [2, 3] using the Stillinger–Weber (SW) potential [4] and a third group using a modified version of this potential [5]. The SW potential was shown by its originators to reproduce the melting point of the real substance rather well ($T_m(\text{SW}) = 1690$ K) but to somewhat underestimate the heat of fusion. Lüdke and Landman [2] showed that there was a hysteresis near 1000 K in the energy of the simulated structure obtained during rapid cooling and subsequent heating, and interpreted it in terms of the occurrence of a first order phase change from higher to lower coordinated states. The more detailed studies by Grabow and co-workers [3] confirmed the first order character of the transition and showed that it occurred with a small change in coordination number (see figure 1(a)) at a temperature somewhat below that of a water-like maximum in the density which was observed at ~ 1350 K (see figure 1(b)). The transition to the low density phase was accompanied by a change in energy (amounting to only 15% of the fusion energy) and small (6%) decrease in density (figure 1).

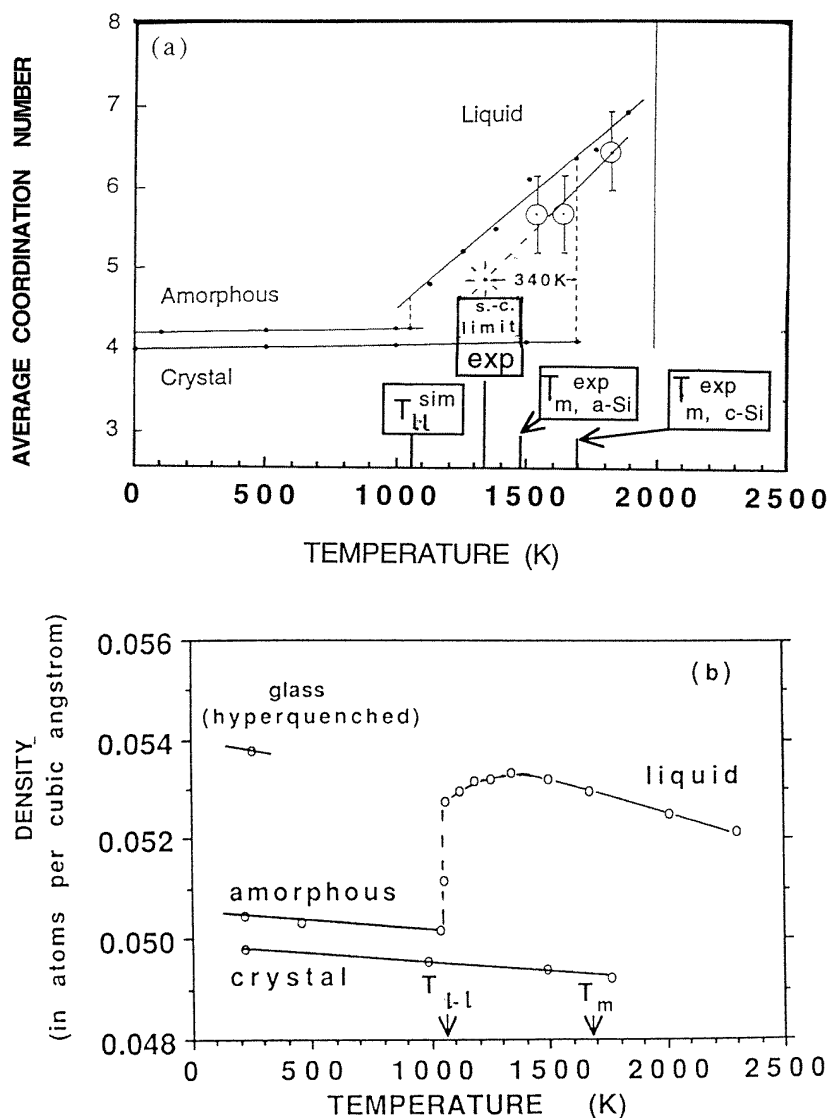


Figure 1. (a) Coordination numbers of Si in liquid Si as a function of temperature by simulation using the Stillinger–Weber potential, from Angell *et al* (1996b) [3], compared with experimental values obtained from x-ray diffraction measurements on levitated liquid samples in [1]. The temperature at which the density maximum in simulated liquid Si occurs, and the experimental ‘melting point’ of a-Si is observed [6], are indicated by arrows. Experimental and simulated equilibrium melting points, which are the same within simulation uncertainty, are also indicated. (adapted from Angell *et al* (1996b) [3] by permission). (b) Density dependence of normal and supercooled liquid silicon simulated with the S-W potential, showing the water-like density maximum at 1350 K and the first order transition to the tetrahedral a-Si phase at 1060 K (from Angell *et al* (1996a) [3], by permission).

The variation in the coordination number of liquid SW silicon with temperature is reproduced from Angell *et al* (1996b) [3] in figure 1. The results tabulated by Ansell *et al* [1] are included as open circles. The general agreement with the temperature dependence of

the simulated liquid coordination number is evident, but there is a consistent disposition in the simulations to higher coordination numbers. The differences are barely outside the stated uncertainty of the experimental numbers [1]. The experimental rate of coordination change seems to be a little larger than its simulated equivalent.

According to Ansell *et al* [1], their levitated liquid sample technique permits supercooling to some 340 K below the normal melting point. If we extend their coordination number plot linearly to this degree of supercooling, we observe that the coordination number reaches a value close to that at which the simulated system undergoes its phase transition. This experimental supercooling limit, 1345 K, is somewhat below the temperature 1485 ± 50 K (short arrow in figure 1(a)) at which the laser heating measurements of Thompson *et al* [6] and Donovan *et al* [7] indicated a first order melting of a-Si though this measurement was conducted under extremely fast heating conditions in order to avoid preemptive crystallization. An overestimate of the transition temperature would be understandable.

Donovan *et al* argued that the transition they observed at 1345 K must be reversible. It is important, then, to consider the state of silicon which is produced by the reverse (cooling) process. The diffusivity of crystalline silicon at 1345 K is $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ [8]. The diffusivity of the amorphous silicon at this temperature would surely be at least as high as that of the crystal, so the state produced by the phase transitions on cooling should be considered a liquid [9]. This is because the typical diffusivity at the liquid-to-glass transition (e.g. Si in SiO_2 glass [10] is $10^{-18} \text{ cm}^2 \text{ s}^{-1}$). Thus the transition would be described best as a liquid-liquid transition, consistent with theories that exist for such transitions in tetrahedrally inclined systems [11–16]. We therefore designate the temperature of this transition T_{ll} , and assign it the value 1345 K.

As further evidence for the assignment of 1345 K as T_{ll} , we note that in the simulation of [3], crystallization of the supercooled liquid was never observed at $T > T_{ll}$. Once the transition to the tetrahedral phase had occurred, however, crystallization followed rapidly, despite the much lower diffusivity of Si in this phase. The crystals nucleated at the surface of the tetrahedral phase droplets where, evidently, the barrier to nucleation is low. The important point is that such rapid crystal growth would be possible in a viscous liquid phase, but not in a glass, which supports the idea of a transition to a second liquid phase. It seems reasonable, then, to suppose that the experimental supercooling limit is imposed by the occurrence of the same transition. It is notable that a similar sharply defined lower limit to the supercooling of liquid germanium has been reported by Filliponi and Diccico [17], 260 K below the melting point, and that this is the temperature predicted by the two-liquid model of Ponyatovsky and Barkalov [11] for a liquid-liquid phase transition for this substance at zero pressure.

A clear suggestion of these latter observations is that levitation studies of the limits of supercooling should be made for a wide range of 4:4, 3:5 and 2:6 compounds with zinc blende and related crystal structures (e.g. SiC, InSb and ZnTe) and their mixtures so as to reveal a pattern in their supercooling limits. The object here would be to identify the existence of cases in which the liquid-liquid transition occurs on more leisurely time scales such that quenching procedures would permit the trapping and detailed study of this interesting phase separation process for comparison with the only case of 'trapped' isocompositional isotropic liquid-to-isotropic liquid transition so far reported, that of quenched $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ solutions [18].

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