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Addressing the discrepancy of finding equilibrium melting point of silicon using MD simulations

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Abstract

We have performed MD simulations to study the equilibrium melting point of silicon using (i) solid-liquid coexistence method (ii) Gibbs free energy technique, and compared our novel results with the previously published results obtained from Monte Carlo (MC) void-nucleated melting method based on the Tersoff-ARK interatomic potential [*PRB 72 (2006) 125206*]. Considerable discrepancy was observed (~20%) between the former two methods and the MC void-nucleated melting results, leading us to question the applicability of the empirical MC void-nucleated melting method to study a wide range of atomic and molecular systems. A wider impact of the study though is that it highlights the bottleneck of the Tersoff-ARK potential in correctly estimating the melting point of silicon.

Keywords: Melting point; Silicon; Molecular dynamics; Tersoff-ARK; Tersoff potential

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1. Introduction

Near melting phenomena are rather complex and detailed explanations of the thermodynamic mechanisms involved in the melting process are rather unclear in the literature and so are the methods employed to estimate the melting temperature [1]. In the past, various numerical techniques including the molecular dynamics (MD) method have been employed to estimate the equilibrium melting point of various materials. According to Zhang and Maginn [2], the methods for the calculation of the melting point can be categorized into:

i) Direct methods, including one-phase [3, 4], hysteresis [5], void-nucleated [6-12] and solid-liquid coexistence [13-17] methods.

ii) Gibbs free energy-based methods (thermodynamic integration method [18-24]) such as Hoover and Ree's single-occupancy cell [25, 26], Frenkel and Ladd's Einstein crystal [27] and pseudo-supercritical path [28].

Among direct methods, the solid-liquid coexistence method is a reliable choice in which the melting point could be bracketed within a desired interval; however, it requires a relatively large simulation cell and multiple simulation runs, and is thus a time-consuming method. In the free energy method, the Gibbs free energy of the solid and liquid phases is computed at different temperatures, and then melting point is assumed to be the temperature at which both phases exhibit the same Gibbs free energies. Calculation of the melting temperature through introduction of voids in a perfect crystal for the sake of avoiding overestimation of melting point is another approach known as the void-nucleated method. As per this method, an increase in the size of the void causes the melting temperature versus void size curve to first exhibit a decrease and then attains a plateau region where the melting point becomes independent of the number of voids. The temperature of this plateau region is taken, empirically, as the thermodynamic melting point of the material. Agrawal *et al.* [6-8] in their exploratory works noted that the theoretical basis and in-depth thermodynamic

considerations for this method are not established, making this method empirical in nature. In this work, we present a MD simulation case study by comparing the simulated equilibrium melting point of silicon using (i) the solid-liquid coexistence method (ii) the Gibbs free energy method and (iii) published results obtained using the void-nucleated method. Our simulations were informed by the Tersoff-ARK potential [6] which was categorically developed with the motivation to accurately describe the melting point and density of the liquid phase of silicon.

2. Computational details and results

We employed an open-source code LAMMPS [29] for studying the solid-liquid coexistence method to obtain the phase instability temperature (T_{ins}) of silicon crystal using the one-phase method. A 15×15×15 supercell of silicon containing 27,000 atoms was heated in the canonical ensemble (NVT). To avoid the so-called hysteresis phenomenon, a low heating rate of 9×10^{9} K/s was used to permit the solid atoms to gently attain thermodynamic equilibrium. Also, reflective boundaries were used to avoid the spurious effects of superheating of the cell while using periodic boundary conditions (PBCs). As shown in Figure 1, T_{ins} was obtained as 1397 K. At this critical value of T_{ins} the value of Lindemann index [30] experiences an upward jump due to destabilised cluster of atoms caused by thermal excitation [31]. This critical value of temperature is referred as the first-order melting transition. It is believed that the solid-liquid transition starts with nucleation in order to overcome the Gibbs free energy barrier to the formation of a nucleus of the daughter phase (viz, via thermal fluctuation) [5]. The bulk molten temperature (T_{em}) was found to be 1616 K. The structural changes during melting (from covalent to metallic) causes an atomic volume shrinkage (calculated using Voronoi tessellation [32]) of ~9.2%, which is consistent with the reported experimental

values [33, 34]. Aside from the solid-liquid coexistence method, the hysteresis method [5] with PBCs was also employed, however, the supercooling temperature (T^-) was not realized. In general, aside from some special cases, T^- is immensely tough to obtain since crystal nucleation is a rare event [2].

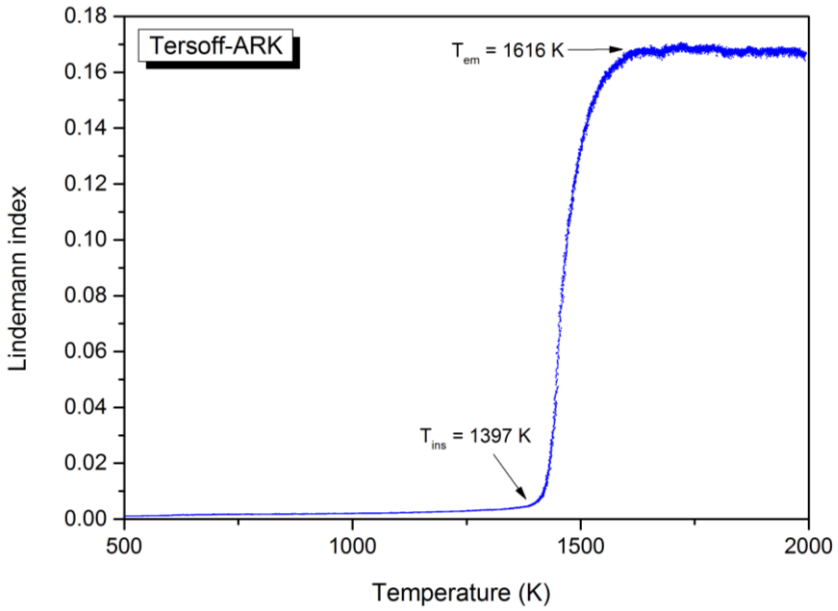


Figure 1: Variation of the Lindemann index upon gradual heating. T_{ins} corresponds to the phase instability temperature (or first-order melting transition temperature) while T_{em} corresponds to the bulk molten temperature of silicon.

The phase instability temperature obtained by the one-phase method can be used as an initial estimate for the solid-liquid coexistence simulation to bracket the melting point. For this purpose, a simulation box comprising of $m \times n \times l$ periodic solid cell was employed in a way that the longer direction (<001>) lies normal to the solid-liquid interface. The system was then equilibrated near the initial guess of melting temperature in the isobaric-isothermal ensemble (NPT). To preserve the hydrostatic pressure conditions, an anisotropic barostat was employed. To prepare the solid-liquid coexisting system, the central half of the system was

heated and melted at a fairly high temperature under the NVT ensemble whereas the other half of the cell was kept fixed. The melted half of the system was then further equilibrated in the NPT ensemble at the initially estimated melting temperature and zero pressure. During equilibration of the melted half, the other half was kept fixed and the length of the system in the <001> direction was permitted to relax. Then, the solid and liquid halves were brought into contact and the system was equilibrated in the NPT ensemble at the same temperature to zero the <001> direction pressure. To abate the impact of non-hydrostatic stresses on the melting temperature, the simulation cell was further relaxed in the NPT ensemble with the anisotropic barostat. The entire simulation was repeated at different temperatures till the melting temperature converged. One may question here that the melting temperature is presumed to be size-dependent owing to the increased fraction of loosely bounded surface atoms at reduced dimension [35]. To answer this question, a convergence check was performed to determine the dependence of the estimated melting point on the size of the simulation box. Figure 2 compares the evolution of the average potential energy per atom of the solid-liquid coexistence for two different system sizes at different temperatures simulated for a relatively longer simulation time (10 ns). Figure 2(a) shows that for a 320-atom simulation cell, when the temperature is below 1410 K, the average potential energy of the solid-liquid coexistence system decreases with time, indicating that the crystal phase tends to grow and the system solidifies. Contrary to this, at temperatures above 1415 K, the potential energy increases, suggesting that the simulation cell undergoes melting transition. Accordingly, the equilibrium melting temperature of silicon for a 320-atom simulation cell was obtained as 1412.5±2.5 K. Likewise, as depicted in Figure 2(b), the equilibrium melting temperature of silicon for a 108000-atom simulation box was determined as 1365±5 K. Figure 3(a) presents the calculated melting point versus the number of atoms in MD simulations, where the calculated melting point converges for a simulation cell containing

~20800 atoms. We infer that the calculation of melting point using simulation cells containing less than 320 atoms was non-trivial owing to the high levels of energy fluctuations. In all, according to Figure 3(a), the equilibrium melting temperature of silicon using the solid-liquid coexistence method is 1365±5 K.

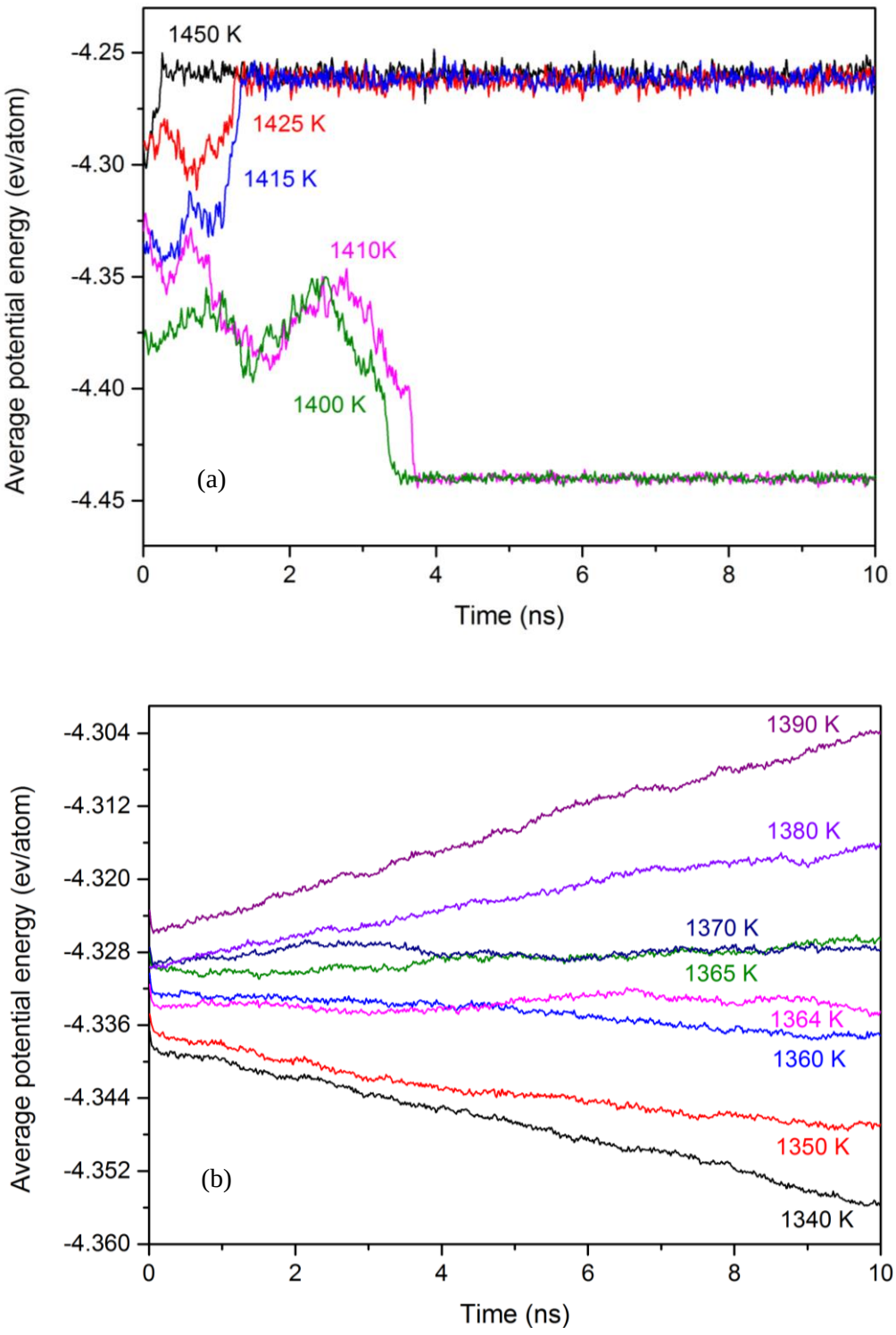


Figure 2: Evolution of the average potential energy of the solid-liquid coexistence cell versus the simulation time at various temperatures for (a) a 320-atom simulation cell and (b) a 108000-atom simulation cell.

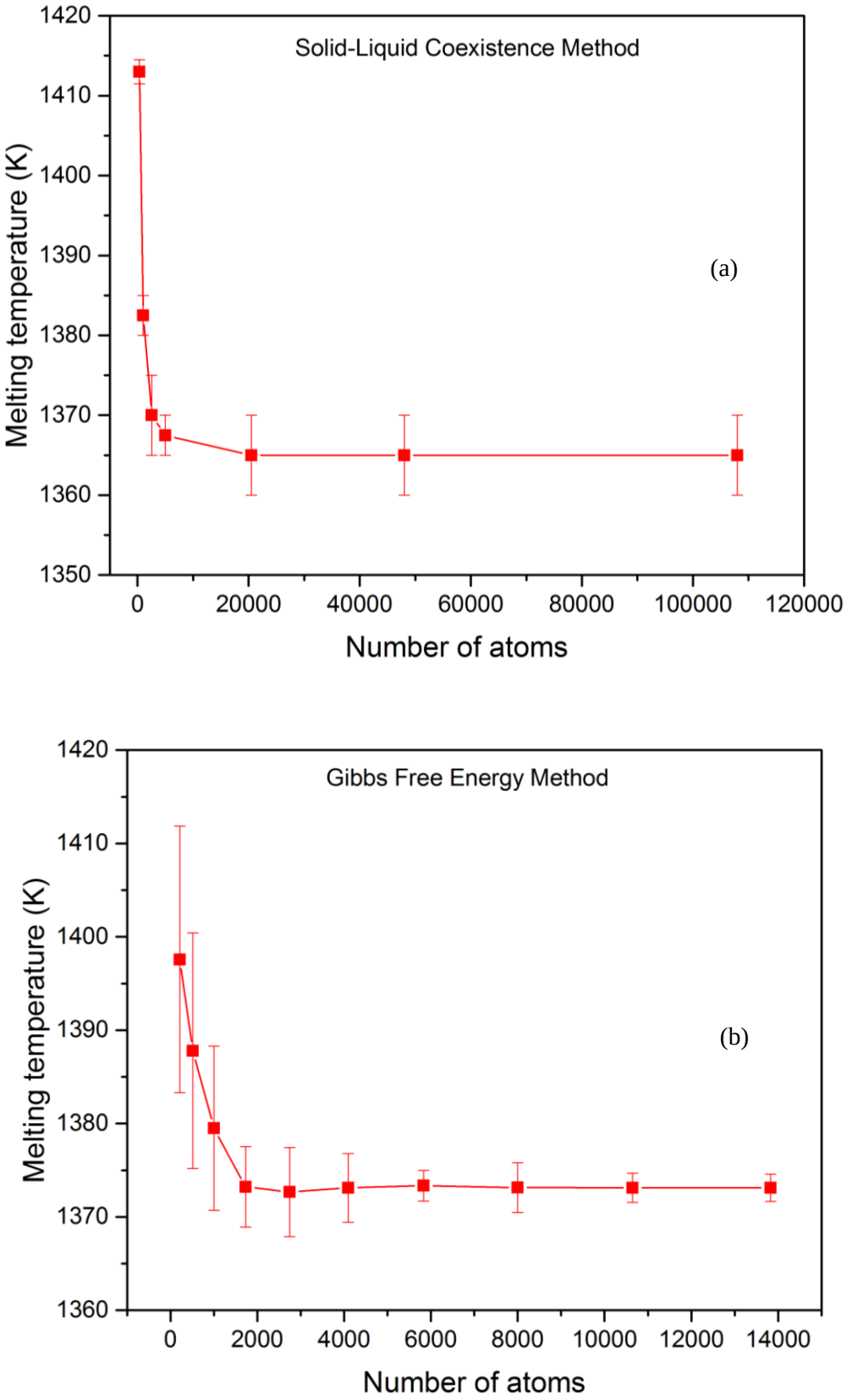


Figure 3: The calculated melting point versus the number of atoms in the MD simulation cell using (a) the solid-liquid coexistence method and (b) the Gibbs free energy method.

We also employed the Gibbs free energy technique to calculate the melting point of silicon using the same potential function but using a different MD simulation toolbox "MD++" [36]. Simulation cells with different number of atoms were constructed using periodic boundaries along all the three directions. At zero pressure, the Helmholtz free energy of the solid phase F_S at 1300 K was calculated by adiabatic switching from the solid phase described by the actual potential model to the harmonic approximation of the same potential function [37]. Since the equilibrium volume was achieved during this process, F_S can be inferred as the Gibbs free energy at zero pressure. Then, the Gibbs free energy for the solid phase G_S as a function of temperature in the range of 1300 K < T < 1500 K (in the increments of 0.02 K) was calculated using the reversible scaling method [38]. For the liquid phase, the Helmholtz free energy (also the Gibbs free energy) at zero pressure and 1500 K was calculated by adiabatic switching from the liquid to a purely repulsive potential and then to the ideal gas limit. Again, the Gibbs free energy for the liquid phase G_L as a function of temperature between 1200 K and 1500 K was calculated using the reversible scaling method [38]. In the end, both G_S and G_L were plotted as a function of temperature T on the same scale and the melting temperature was determined as the intersection of the two curves [39, 40]. Figure 4 shows the Gibbs free energy per atom of both the solid phase and liquid phase for two different supercells. The results of convergence study are shown in Figure 3(b), where the equilibrium melting point is determined as 1373±1.5 K. Overall, Figure 3 also suggests that the Gibbs free energy method converges much faster for a less number of atoms (~2000 silicon atoms) as opposed to the solid-liquid coexistence method requiring about 20,000 silicon atoms to converge.

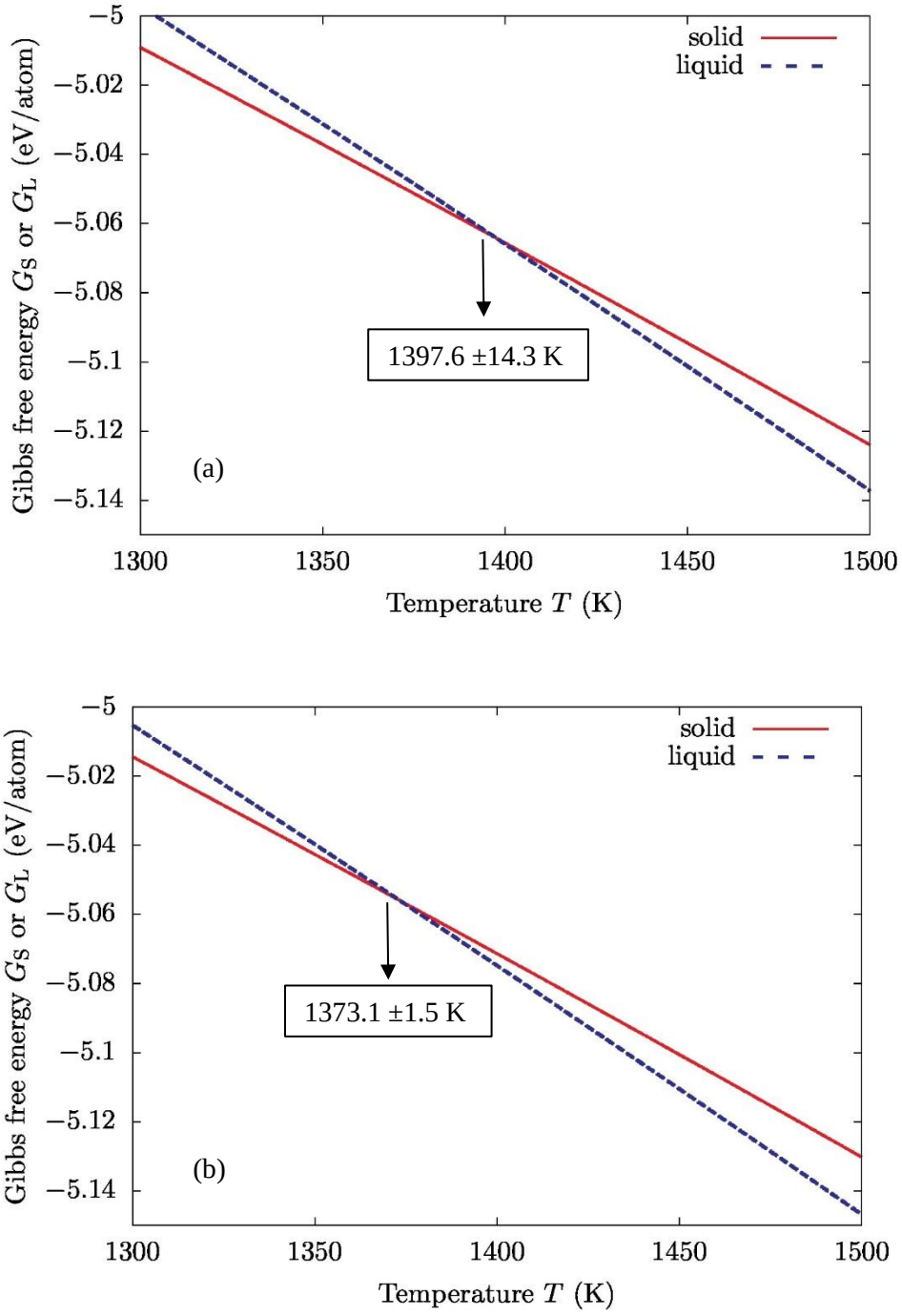


Figure 4: Gibbs free energy per atom for both the solid phase and liquid phase for (a) a 216-atom simulation cell and (b) a 13824-atom simulation cell.

We did not perform the void-nucleated calculations and have taken this data readily from the developers of the Tersoff-ARK potential. Agrawal *et al.* [6] deployed the MC simulations of

void-nucleated melting method and reported the melting point of silicon as 1711 K, which is approximately 20% higher than what has been obtained by us from the solid-liquid coexistence method (1365±5 K) and the Gibbs free energy method (1373.1±1.5 K) using the same Tersoff-ARK potential. It is imperative to note that the simulation size used by the developers of the Tersoff-ARK potential is very small (216 silicon atoms), and it is not clear how the size effect has influenced the calculated melting temperature in the presence of voids. Of interest is that the MC void-nucleated melting method was utilized to estimate the melting point of silicon given by the original Tersoff potential [41, 42], and the value obtained was around 2509 K [6], which is in fair accordance with the results of solid-liquid coexistence method (2584 K [43]), therefore system size (216 atoms) seems to be a less influential factor in the reported erroneous value of the melting point of silicon obtained by the developers of the Tersoff-ARK potential. The authors posit that either introduction of voids in such a small simulation box or the improper postulation of considering the transition temperature in the plateau region as the melting point may have led to incorrect estimations of the melting point in the Tersoff-ARK paper.

On the other hand, the work of Koning *et al.* [44] suggests that the source of such discrepancy can be the hysteresis occurring in the void-nucleated method. They reported that the melting point of Argon given by the MD void-nucleated method [11] is 5% higher than that of the thermodynamic results. In another study carried out by Agrawal *et al.* [8], the MD void-nucleated melting method overestimated the melting point of nitromethane up to 4% as opposed to the solid-liquid coexistence method. Zhang and Maginn [2] conducted an interesting work showing that at least three “plateau” temperatures (~500 K, ~450 K, and ~350 K) being recognisable for a complex atomistic model of the ionic liquid, 1-n-butyl-3-methylimidazolium chloride [BMIM][Cl] while using the MD void-nucleated method, posing a key question as to which plateau temperature corresponds to the true melting temperature.

Considering the results obtained from the two rigorous and accurate techniques employed in this study and the fact that the experimental value of the melting point of silicon is about ~1687 K [45], we respectfully question the accuracy of the Tersoff-ARK potential.

3. Concluding remarks

In this work, we have calculated and compared the equilibrium melting point of silicon using three techniques namely, the MD solid-liquid coexistence, the MD Gibbs free energy, and the MC void-nucleation techniques. The two former methods provide a close approximation whilst the latter method revealed a 20% discrepancy with respect to the former two methods. Our results cast doubt on the validity of the empirical assumption used in the MC void-nucleated method that the melting temperature in the plateau region near the critical void size is the true melting point. These results led us to identify the bottleneck of the Tersoff-ARK potential in correctly estimating the melting point of silicon and a bigger implication of this would mean revisiting all the studies which are subsequently based on this potential.

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