

Stability of the bcc phase of ^4He close to the melting curve: A molecular dynamics study

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We have investigated whether the Aziz *et al.* [*J. Chem. Phys.* **70**, 4330 (1979)] model for ^4He renders the body-centered cubic phase more stable than the face-centered cubic phase in the proximity of the melting curve. Using molecular dynamics, we have simulated these solid phases in equilibrium with the liquid at a number of densities. In contrast to previous free energy molecular dynamics calculations, the model stabilizes the body-centered cubic phase. The stability field is just 5° wide below the melting curve at pressures around 140 Kbar and about 70° wide at pressures around 750 Kbar. Considering that the body-centered cubic phase is dynamically unstable at low temperature, this result bears striking similarities to transition metal phase diagrams.

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The submelting phase is of general interest because this defines the properties of a solid subjected to a high temperature (T). Many materials undergo a solid-solid (SS) transition on heating at ambient pressure (P). One might expect that such a transition would be observed at high P as well. The case when the new solid phase is stable at ambient T and high P is rather simple both for experimental and theoretical investigation (e.g., the B1-B2 transition in NaCl.¹) The situation changes drastically when such a phase is dynamically unstable at ambient T (e.g., bcc Fe,²⁻⁵ fcc Mo,⁶ and Ta,⁷ and bcc Xe⁸⁻¹² at high P). A number of studies provide contradicting results. This is also the case with the ^4He high pressure phase diagram. However, while in the case of Fe, Mo, and Xe one needs to perform experiments at thousands of K and kilobars, the case of ^4He seems to be comparably modest in terms of required pressure and temperature.

Evidence of an SS transition in ^4He was reported by Loubeyre *et al.*¹³ They observed a well-defined cusp point on the melting curve at 299 K and 11.65 Kbar. Theoretical support for the fcc-bcc transition in ^4He was provided.¹⁴⁻¹⁶ It was noted that the ^4He bcc phase cannot be treated in the same manner as the fcc phase because of soft phonons.¹⁴ It was also demonstrated by the correlated-cell-model calculation that the bcc phase becomes stable if the correlated motion of atoms in 110 plane is taken into account.¹⁶ This effect was noted by Holian *et al.*¹⁷ Using the most advanced method at that time of calculating free energies of the involved phases (the so-called λ method¹⁸) D. Frenkel¹⁹ found that at $T = 327.04$ K and around this temperature the model potential used by Loubeyre *et al.*^{14-16,20} does not yield a stable bcc phase. Later,²¹ the ^4He melting curve (MC) was measured by quasi-isochoric scanning. The authors performed experiments in the range from 200 to 460 K and from 70 to 240 kbar. The melting line was shown to be a smooth curve that lies close to extrapolations from much lower pressure. In addition, no anomalies were observed near room temperature, and thus there was no evidence for a fcc-bcc transition in the solid phase. On the basis of the experiments, it was concluded that the fcc-bcc-fluid triple point reported by previous investigators does not exist. Apparently, the situation required experiments with x-ray measurements of ^4He structure and these experiments

have been performed²² using single-crystal x-ray diffraction on solid ^4He from 1 to 58 GPa over the temperature range 46–400 K. The high-density properties of helium were pinned down: The hcp structure was found stable apart from an fcc loop along melting in between 15 K and around 285 K. It is interesting that stabilization of the hcp phase and its further transformation to the bcc phase on heating at higher PT was predicted by Loubeyre.²³

There is a contradiction between theoretical papers, one suggesting stabilization of the bcc phase around room temperature¹⁶ and another one¹⁹ suggesting no stabilization of the bcc phase at around room temperature. We note that the theoretical study by Frenkel¹⁹ was performed for a small cell and, therefore, could underestimate the free energy associated with long wavelength oscillations in bcc phase due to the correlated thermal motion.^{16,17} These oscillations have recently been shown important for the stabilization of the Fe bcc phase at high PT .²⁴

This issue was at rest until it was demonstrated that the experimental data on Xe MC⁸ could be due to stabilization of the bcc Xe phase.^{9,10} This finding for Xe was contradicted by Saija and Prestipino,¹² using the free energy Monte Carlo calculations approach, quite similar to that performed for ^4He . However, careful three-phase direct molecular dynamics (MD) simulations demonstrated¹¹ that Saija and Prestipino¹² free energy calculations are imprecise. Could it be that the similar calculations by Frenkel are also imprecise and the ^4He high- T phase does stabilize, at least according to theory? Previous simulations using comparably small samples with large T step²⁵ confirmed the finding of Frenkel.¹⁹ In the Xe study, very large samples (up to 4 million atoms) have been simulated in order to position the fcc-bcc-liquid point in the PT phase diagram. Therefore, we decided to undertake large-scale direct MD simulations to answer the question.

As a model of the interaction we used the pairwise interaction²⁰ that was used previously for ^4He .^{15,19,25} This model includes repulsion as a term $A\exp(-Br)$, where A and B are parameters and r is the distance between atoms. The magnitude of B defines the stiffness of interaction. For Xe $B = 13.0$ and for ^4He it is close to 13.3. Therefore, there is only a slight difference and one may expect to find

a high- T bcc ^4He phase as was found in Xe. Besides, an effective pair potential for ^4He makes the high- T bcc stable before melting.²⁵ Using the MD method with the Aziz²⁰ model, we first simulated the liquid at three pressures, namely 150, 400, and 800 Kbar. The temperature was first set very high to ensure melting and then the temperature was decreased to be somewhat higher than the MC of ^4He .^{21,25} The liquid consisted of 500 000 atoms placed in a cubic box with periodic boundary conditions (PBC). PBC have been applied in all of our simulations. Then, we simulated comparably small (32 000 and 31 250) samples of the fcc and bcc phases in the NPT (N , number of atoms) ensemble at the same pressures as in the liquid. These samples were introduced in the center of the boxes with liquid and coexistence simulations in the NVE (V , volume; E , total energy) ensemble have been run until the equilibrium between solid and liquid was reached. The initial temperature in the coexistence simulations was chosen below the melting temperature, so the solid sample could grow and the temperature would rise because of the positive heat of formation of the solid phase. By comparing the temperatures of equilibrium (Fig. 1) one can conclude which phase is more stable. Apparently, if phase A is in equilibrium with the liquid at a higher temperature than phase B and at about the same pressure, phase A is more stable. This means that below the temperature of equilibrium between A and the liquid phase, A is more stable than the liquid, on the other hand the liquid is more stable than phase B. Thus, phase A is more stable than phase B. In these simulations one has to be careful in checking the structure of the solid phase—it could be that fcc spontaneously changed to the bcc structure, as also was observed previously.¹⁵ For example, at about 750 Kbar (pressure changes somewhat when we introduce

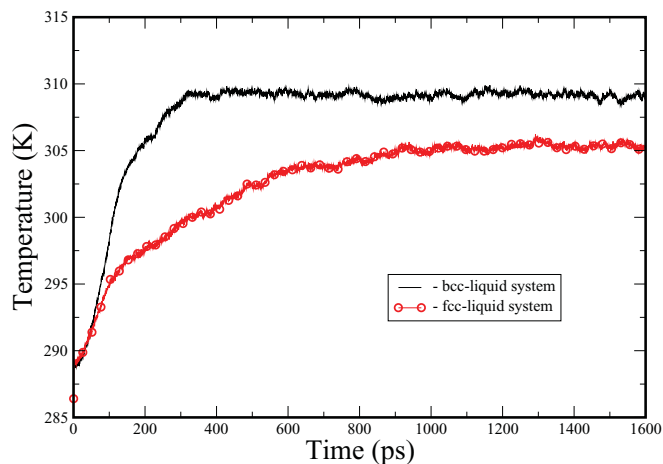


FIG. 1. (Color online) Temperature time dependence in coexistence simulations at low density. Temperature increases due to the growth of the embedded solid phase until it reaches the temperature of equilibrium between solid and liquid. The PT conditions of the bcc-liquid coexistence (solid curve) are 140.2 Kbar and 309.6 K and of the fcc-liquid coexistence (solid curve with circles) are 140.6 Kbar and 305.1 K. The statistical error is much smaller than the temperature difference as can be seen from the fluctuations of the curves. Similar results are obtained for higher density (corresponding pressures about 380.0 and 750.0 Kbar). This is evidence of a higher stability of the bcc phase as compared to the fcc phase.

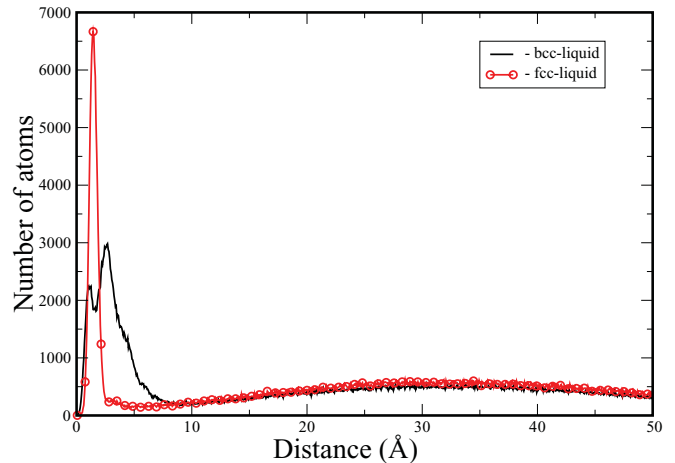


FIG. 2. (Color online) Mobility of atoms in the two-phase systems at the conditions of Fig. 1. The mobility is calculated as the distance atoms moved during the last 800 ps of simulations [when most of the crystallization was completed (Fig. 1)]. The number of atoms is calculated within bins of $\frac{1}{16}$ Å. There are two sorts of atoms: One sort demonstrates very restricted mobility within the solid lattice and the other one a broad distribution with a maximum around 30 Å. The fcc atoms give rise to a sharp peak corresponding to the nearest-neighbor distance whereas the bcc atoms give rise to two peaks—because there are two kind of nearest neighbors in the bcc lattice.

the solid in the center of the box with liquid and change the starting temperature) fcc spontaneously transformed into bcc in some simulations providing the impression that the melting temperatures of both phases are equal. All parameters were carefully checked for their impact on the results. Since our simulations are long, we checked whether there was any leakage of energy that could result in the temperature drift. The time step was 0.5 and 1 fs at the high and low pressures, respectively. Varying initial temperature we accepted only those simulations where both solid and liquid phases are present (Fig. 2) at the end of simulation and the temperatures are not changing due to growth/melting of the solid phases (Fig. 3). The bcc phase in our simulations becomes more stable than the fcc phase at T somewhat below 300 K. This is consistent with the Xe case where the bcc phase becomes more stable at T^* about 16 ($T^* = \frac{T}{\epsilon/k_B}$, where T^* is the dimensionless temperature, ϵ is the minimum of the interaction potential, and k_B is the Boltzmann constant). For the Aziz model, 300 K is equivalent to T^* about 27. It is higher than for Xe because the Aziz model is somewhat stiffer than the Buckingham model. The stability range is very narrow and becomes about 70° at the highest pressure explored (at about 750 Kbar; Fig. 4). The validity of presented results was carefully checked by numerous additional simulations not shown in Fig. 1. The structure was monitored by calculating the radial distribution function (RDF) in spherical layers of different radius (Fig. 3). From single phase solid simulations we know exactly what a particular phase RDF looks like, therefore, it is not difficult to distinguish the phase identity. The melting temperatures of both phases are shown in Fig. 4 and compared to experimental data.

The most comprehensive experimental study with control of the structure was performed in 1993.²² Only fcc and hcp

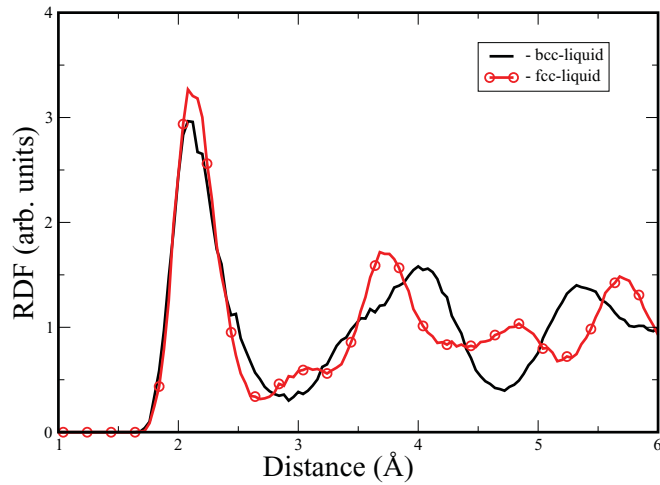


FIG. 3. (Color online) Radial distribution functions of the two-phase bcc-liquid and fcc-liquid systems. The radial distribution functions (RDFs) are computed for a single configuration at the end of the MD simulation. The RDFs are computed for the atoms belonging to a spherical layer of 3-Å thickness at the distance 40 Å from the center of the box (the box is a cube with edge length of 153.6 Å). The RDFs are typical of the bcc (solid curve) and fcc (solid curve with circles) phases; this can be confirmed by comparison of these RDFs with RDFs obtained for single solid phases.

phases have been observed. Note that the melting curve was not determined in this work. That means that it is not quite clear how close to melting the experimental PT points are located. The hardware did not allow one to measure the structure of small crystals, yet it is important when such crystals start to grow from the liquid.

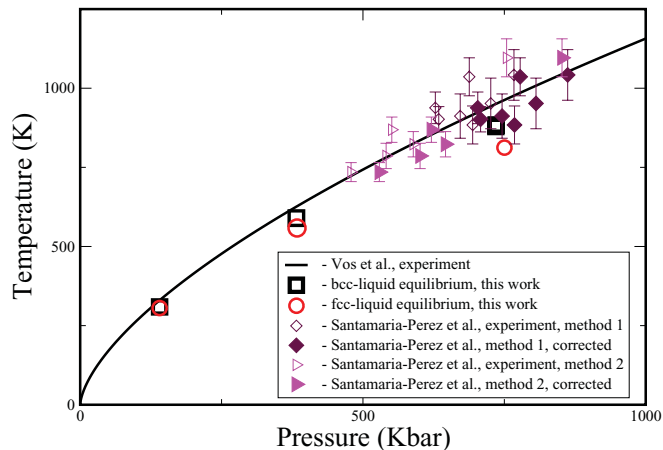


FIG. 4. (Color online) Data on melting of ^4He . (Experimental data) Solid curve, isochoric scanning;²¹ open diamonds and triangles with error bars, DAC data with laser heating. Temperatures were measured by two different methods.²⁶ The experimental points were corrected by computing thermal pressure for the measured temperatures (without considering error bars). The main result of this work are computed points of equilibrium between bcc and liquid (open square) and fcc and liquid (open circle). The difference at 140 Kbar is only 5 K while at 750 Kbar it becomes close to 70 K. The corrected experimental points look separated in two groups, where one corresponds to an SS transition and another to a melting transition.

Finally, recent experiments²⁶ reported melting points above the MC measured in 1990.²¹ If we consider thermal pressure and add that to the measured pressure, we get much better agreement with the earlier determined MC (Fig. 4). The experiments were performed without measuring the structure of helium. Therefore, it is possible²⁷ that some PT points are due to an SS transition and some are due to the melting transition. Indeed, it looks like the experimental points can be separated in two sets with the splitting width of about the difference between the bcc and fcc melting T (Fig. 4). Thus, our interpretation of experiments, when we are aware of the nature of the emerging phase and reasonably well can estimate the impact of the new phase, is different from the original interpretation.

The calculations of free energies^{12,19} have led to erroneous conclusions regarding the phase diagram of the studied model. We note that in both cases one feature is common—both Xe and ^4He interaction potentials produce a dynamically unstable bcc phase at low T . In both studies comparably small solid supercells were used and that could lead to underestimation of the correlated long wavelength motion known to stabilize a dynamically unstable bcc. Another reason could be that at these T , defects play a significant role. The defects have not been accounted for, neither by Frenkel¹⁹ nor by Saija and Prestipino,¹² partly because their samples were small (250, 256, and 512 atoms) and partly because they started from ideal crystals. Note that in our 500 000-atom samples defects are taken into account naturally due to the growth of the solid phases from liquid. In addition, it could be simply because we used much larger samples and, therefore, the accuracy of our calculation is much higher. Finally, the procedure of direct simulation is not subjected to errors as much as the procedure of free energy calculations where errors accumulate due to many intermediate steps involved in such calculations. Thus, the conclusions drawn from free energy calculations on small computational cells for dynamically unstable phases (such as bcc Fe or fcc Mo and Ta), for example, should be treated with caution.

It has been argued that free energy calculations are superior to coexistence simulations because the free energy calculations do not include the interface. Following this argument, one should dismiss experimental observations of a phase equilibrium if they contradict thermodynamic calculations because real experiments include the interface. The size of our samples is so large that any impact of the interface is negligible. In addition, there is no reason to believe that the impact of an interface would benefit any of the solid phases.

It is perhaps also worth noting that coexistence simulations should be performed for very large samples to distinguish between the phases where their free energy curves cross at almost zero angle. Even though the number of particles in our simulation was large, we needed to perform many runs starting from different initial T , varying length of simulation and time step to make sure that the results are reliable.

The Aziz potential is a pair potential and to get agreement with the experimental equation of state one needs either to account for three-body interaction (e.g., Ref. 23) or apply an effective potential, as we did earlier.²⁵ Now, irrespective of a pair potential or an effective potential applied, the bcc

^4He phase becomes stable below melting curve starting from about 300 K. We did not consider stability of the hcp phase that was demonstrated to be stable in the close vicinity of the melting curve.²² Therefore, it is possible that onset of the stability of the bcc phase is shifted to a higher T where bcc entropy eventually takes over. If so, the phase diagram becomes similar to the one calculated previously by Loubeyre.²³ However, the free energy calculations ruling out the bcc phase at 327.04 K and around that temperature can be safely dismissed.

Concluding, we demonstrated that the Aziz model gives rise to stability of the bcc ^4He phase. This is in contrast with free energies calculations performed for small samples. Our direct MD simulations are superior to the free energy calculations for the reasons outlined above. Free energy calculations of dynamically unstable phases with small cells need to be

revised. The bcc ^4He phase now appears to be stable according to both the Aziz and effective Buckingham²⁵ models, the latter being in very good agreement with *ab initio* data. A comprehensive experimental study of the ^4He phase diagram, especially at temperatures higher than 400 K, is urgently needed. This will allow one to resolve not only the ^4He phase diagram but also to shed light on the phase diagrams of transition metals, where a similar phenomenon has been suggested.

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