Molecular Dynamics Study of Melting and fcc-bcc Transitions in Xe

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We have investigated the phase diagram of Xe over a wide pressure-temperature range by molecular dynamics. The calculated melting curve is in good agreement with earlier experimental data. At a pressure of around 25 GPa and a temperature of about 2700 K we find a triple fcc-bcc liquid point. The calculated fcc-bcc boundary is in nice agreement with the experimental points, which, however, were interpreted as melting. This finding suggests that the transition from close-packed to bcc structure might be more common at high pressure and high temperature than was previously anticipated.

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The present study was motivated by the recent diamond anvil cell (DAC) experiments [1] on Xe, where the authors claimed to observe a most peculiar behavior of the melting curve as a function of pressure [$T_m(P)$]. The melting temperature data generally agreed with the expected behavior up to a certain pressure. However, at this pressure the dT_m/dP slope of the experimental curve became drastically reduced. This change of slope was attributed to a boundary between a solid-liquid and a glass-liquid melting transition. A similar cusp was observed [2] when measuring the high-pressure melting curve of ^{4}He. In this case the cusp was attributed to a fcc-bcc transition [3]. Frenkel [4] has calculated that the fcc-bcc transition in ^{4}He occurs in a metastable range above T_m. However, in what follows we show that the experimental data [1] for Xe is likely to be a manifestation of the fcc-bcc transition. It occurs below T_m according to our calculations.

Previously, xenon has been very intensively studied [5,6] at low temperatures (T). These studies have shown that Xe crystallizes in the fcc structure at normal pressure. At pressures around a few gigapascals (GPa) Xe undergoes a martensitic transformation into an uncertain intermediate phase between the fcc and hcp structures without any volume change. At a pressure of about 70 GPa Xe transforms into the hcp structure and becomes metallic at a pressure above 1 Mbar [6]. The intermediate phase is believed to be a close-packed structure with a somewhat random stacking of layers. According to the present views [7], the intermediate structure would not appear if the conditions of the high-pressure experiments would be ideally hydrostatic. Since the thermodynamic properties of close-packed structures are extremely close [8] to each other, we do not consider the intermediate structure further in the present work.

Rare-gas materials have been a subject of molecular dynamics (MD) studies for decades. Actually, the first MD simulation of a realistic liquid was done by Rahman [9] for Ar. Among the many reasons for this is the relative simplicity of a reliable description of the interatomic interactions in rare-gas materials. Since then, rare-gas materials have been the subject of numerous studies, e.g., [10–13], which have clearly demonstrated that these materials can be reliably modeled using the rather simple Buckingham potential, namely,

$$\phi(r) = \varepsilon\left\{\frac{6}{\alpha - 6}\exp\left[\alpha\left(1 - \frac{r}{r^*}\right)\right] - \frac{\alpha}{\alpha - 6}\left(\frac{r^*}{r}\right)^6\right\}, \tag{1}$$

where $\phi(r)$ is the interaction potential between two atoms at a distance r. The quantities ε, r^*, and α are adjustable parameters. Properties such as the equation of state of the fluid and the solid phases, melting temperatures, shock wave adiabat, heat and entropy of melting, to name a few, were calculated to be in excellent agreement with experimental data. It was also noticed [10] that the parameter α [Eq. (1)] for Ar, Kr, and Xe is the same. Therefore, the phase diagrams for these substances can be scaled in dimensionless units and should be topologically equivalent. We used this potential [Eq. (1)] with the parameters suggested by Ross and McMahan [10] ($\varepsilon/k = 235$ K, $\alpha = 13.0$, and $r^* = 4.47$ Å, where k is the Boltzmann constant). These parameters were initially obtained by Ross and McMahan from corresponding state theory using parameters for Ar. The comparison of calculated and experimental data on equation of state [14] and Hugoniot adiabat [15] both in liquid and solid stability fields [10] showed that the potential is suitable for application up to at least 50 GPa in pressure and 6000 K in temperature. This is a wider pressure-temperature range than the range of the recent experiment [1] (up to 40 GPa and 3500 K). We calculated the Xe volumes at pressures up to 55 GPa at $T = 300$ K. The difference between calculated and measured [16] volumes is less than 1%, which is about experimental error [16]. The effective pair potential which we use includes isotropic average of three-body interaction [17]. Therefore, there is a sufficient ground to rely on this potential for calculating phase transitions in Xe.

Using this potential and the two-phase MD simulation method [18–20] we calculated the melting temperatures of Xe up to a pressure of 1 Mbar (Fig. 1). The results of MD simulations have been checked against all possible influences such as number of atoms, time step, run duration, parameters of Nose-Hoover thermobarostat, cutoff distance of the potential, etc. [13]. Because of long runs (up to 200 ps) and a large number of atoms (up to 16 000), statistical errors are negligible. The two-phase method, which we applied, is equivalent to a calculation of the Gibbs free energies of the solid and the liquid to determine the melting temperature [22]. In this method, liquid and solid presimulated supercells are put together, comprising a new supercell containing a solid-liquid interface. This allows us to remove the barrier which prevents melting/crystallization. This method has been tested earlier for a number of materials and was found to perform very well [18–20,22]. We calculated Xe melting temperatures at pressures from 0 to 0.7 GPa with a pressure step of 0.1 GPa. The difference between calculated and measured [23–26] melting temperatures is less than 10°. Therefore, it was surprising to find a large difference between theory and experiment (Fig. 1), in particular, despite the fact that we are applying a reliable method and a well tested model for the interatomic interactions. However, there are two factors which are important when comparing the calculated and experimental melting curves.

First, during these two-phase simulations we observed an interesting feature. At pressures and temperatures higher than 25 GPa and 2700 K, the size of the computational cell changed in an unexpected way during the simulation. Normally, below the melting temperature, the liquid part of the two-phase cell freezes into the fcc structure in the solid part of the cell. In this case sizes of the orthorhombic computational cell form a ratio $a{:}b{:}c = 1{:}1{:}2$ (the interface is in the ab plane). However, at the T and P above the dashed line, as indicated in Fig. 1, the ratio of $a{:}b{:}c$ was close to $\sqrt{2}{:}1{:}2\sqrt{2}$. This suggested that the initial fcc-liquid cell might be freezing into the bcc structure via the Bain path [27]. Indeed, from a closer examination, which involved simulations of the fcc and bcc Xe phases, analysis of structure, radial distribution functions and coordination numbers, as well as animations of melting/freezing, revealed that what we observe is a sign of the unexpected fcc-bcc transition. Such a transition, which was not taken into account when interpreting the results of the experiment [1], gives us the possibility of an alternative explanation.

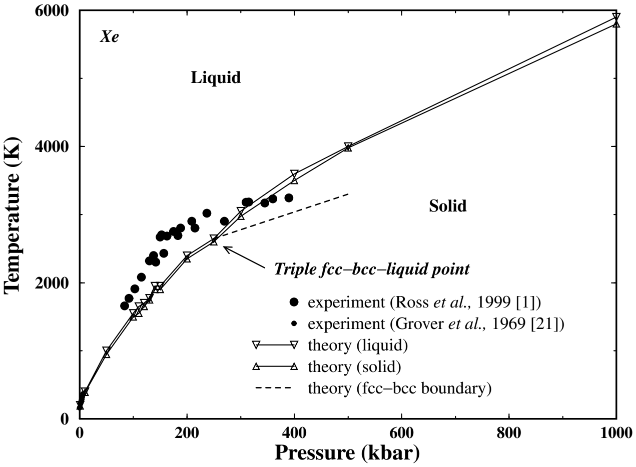

FIG. 1. The pressure (1 GPa = 10 kbar) dependence of the melting temperature of Xe as calculated (triangles) and measured (filled circles). The positions of the triangles indicate the lowest temperatures of the liquid and the highest temperatures of the solid stability. Note the kink at the pressure of 25 GPa, which is due to the fcc-bcc transition. The triangles are connected by lines for convenience. The fcc-bcc phase boundary (dashed line) is calculated as described in the text.

Second, one should realize that in laser heated DAC experiments the pressure is measured prior to the heating. It is possible that the pressure in the heating spot changes with increasing temperature. Since the volume of the whole sample is constant, the correct treatment is to compare the experimental and theoretical data in the volume-temperature (V-T) plane (Fig. 2). As can be seen from Fig. 2, the agreement immediately becomes good, despite the large temperature scatter of the experimental data. This suggests that the thermal pressure plays an important role and that the DAC heating experiments in some cases have to be treated at constant volume rather than at constant pressure; otherwise the comparison might be misleading. While some of the experimental points (Fig. 2) are situated within the solid-liquid region and are melting points, some of the points at the high pressure (low volume) are close to the calculated fcc-bcc transition in the V-T field. Therefore, we have good reasons to suggest

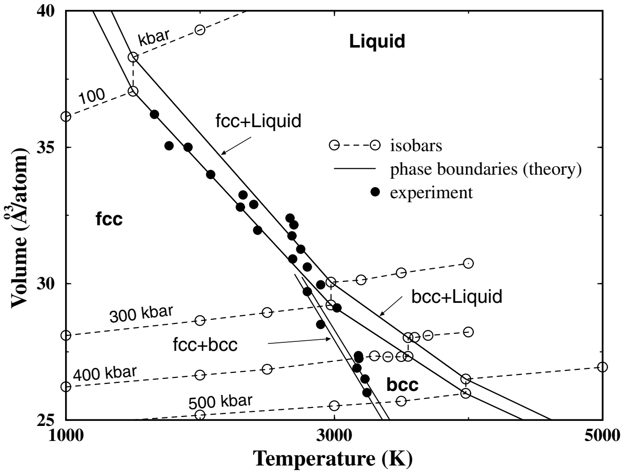

FIG. 2. Volume-temperature phase diagram of Xe as calculated (solid curves) and measured [1] (filled circles) in the pressure range from 10 to 50 GPa (1 GPa = 10 kbar). The calculated isobars are shown by dashed lines. Fields of stabilities are indicated in the figure by corresponding letters (e.g., bcc between 3500 and 4000 K points to the stability of the bcc phase in this range). The vicinity of the triple fcc-bcc-liquid point is shown schematically. The volume change at the fcc-bcc transition is not shown. The field of solid + liquid coexistence is calculated with the two-phase method and the field of the fcc + bcc is calculated as described in the text.

that it was the fcc-bcc transition which was observed, contrary to the original interpretation that it was melting.

The triple fcc-bcc-liquid point is located at 25 GPa as follows from our two-phase simulations. The V-T field of the fcc-bcc transition was determined at 40 and 50 GPa. We calculated enthalpies and volumes of the fcc and bcc phases at 40 and 50 GPa as a function of T and used the data in the following way. Phase equilibrium can be calculated from the condition that chemical potentials of two phases are equal at the P and T of the transition, i.e.,

$$\Delta G = \Delta U + P\Delta V - T\Delta S = 0, \qquad (2)$$

where G is the Gibbs energy; U—internal energy; S—entropy; and V—volume. The sign Δ designate their change at the phase transition. The P and T are conditions of our simulations; U and V are readily available from the same simulations. The only problem is to calculate ΔS. While there are a number of methods available to do that, for our purposes it is sufficient to estimate ΔS from experimental data (Fig. 1), using the Clausius-Clapeyron equation and our calculated ΔV. For example, at $P = 50$ GPa the ΔV is 0.068 $\mathrm{cm}^3/\mathrm{mole}$. The scatter of the experimental data is large and ΔS can be estimated to range from 1.9 to 4.2 $\mathrm{J\,mol^{-1}\,deg^{-1}}$. The enthalpy difference between the fcc and bcc phases is nearly independent on T at a given pressure (in the range of the dynamical stability of the bcc phase, i.e., as calculated, above the $T = 3000$ K) and is equal to 6400 J/mole at the pressure 50 GPa. Then, the temperature of the transition can be anywhere from about 1500 to 3400 K. Since the bcc phase is dynamically unstable when $T < 3000$ K, we are left with the narrow interval between 3000 and 3400 K. The fcc-bcc transition as shown in Figs. 1 and 2 was calculated using the lowest limit for the entropy change. While the exact PT coordinates for the fcc-bcc transition are unknown, the transition itself below the melting temperature can be unambiguously documented.

Figure 3 shows the structure of Xe at 30 GPa at a number of temperatures just below melting. One can see that while at temperatures up to 2700 K the initial fcc + liquid two-phase supercell freezes into the fcc structure, at higher temperatures it freezes into the bcc structure. A further temperature increase leads to melting. Since the simulations have been done in the NTP ensemble, the calculated phase corresponds to the minimum of the Gibbs energy, which might be local. Since the two-phase system (fcc + liquid) is given freedom to choose between either the fcc or the liquid phase, it is quite remarkable that the simulated phase ends in the bcc structure. This means that the bcc structure has lower Gibbs energy than either fcc or liquid. The simulations at 30 GPa and 2900 K, starting from three different initial structures, results in identical bcc structure (Fig. 3) below the T_m.

In summary, the arguments for the thermodynamic stability of the bcc phase are as follows: (i) thermodynamic calculations give stability of the bcc phase; (ii) the temperature of dynamical instability of the bcc phase is higher than that of the fcc above the pressure of the triple point; (iii) the bcc phase develops spontaneously from the initial two-phase fcc + liquid system. All these methods produce consistent results. The thermodynamic stability of the bcc phase is found below the melting temperature.

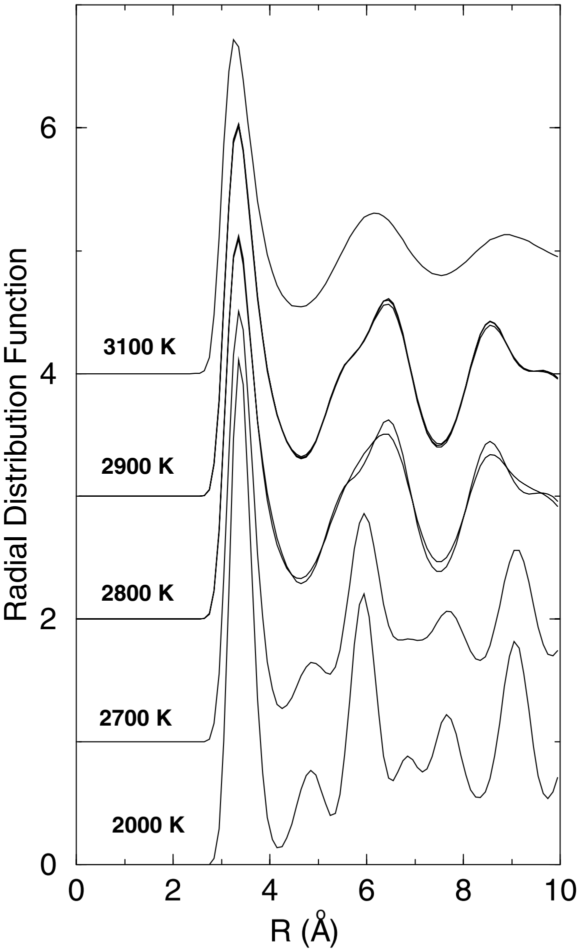

FIG. 3. Radial distribution functions (RDF) of Xe, calculated at the pressure of 30 GPa and the temperatures in the legend. The RDF are shifted by 1, 2, 3, and 4 at different T for convenience. The RDF are calculated using different starting configurations, namely, at 2000 and 2700 K: fcc + liquid; at 2800 K: fcc + liquid and bcc + liquid; at 2900 K: ideal bcc, fcc + liquid, and bcc + liquid; at 3100 K: fcc + liquid and bcc + liquid. The RDFs at the temperatures of 2000 and 2700 K are typical of the fcc structure, while the RDFs at 2800 and 2900 K are characteristic of the bcc structure. The 3100 K RDF is typical for liquid.

The statistical errors are sufficiently small to not affect our results in any sensible way. For example, error in pressure is less than 0.1 GPa in the simulations at 50 GPa. Some of the irregular behavior of melting temperatures (Fig. 1) is due to the nature of the two-phase method [18]. The study [4] dismissing the fcc-bcc transition in ^{4}He might be not sufficiently precise. In that study the properties of the bcc phase have been calculated with 250 atoms. Figure 4 shows that this number might be too small to correctly calculate stability of the bcc phase. While the 250 atoms system MD run results in the fcc structure, the

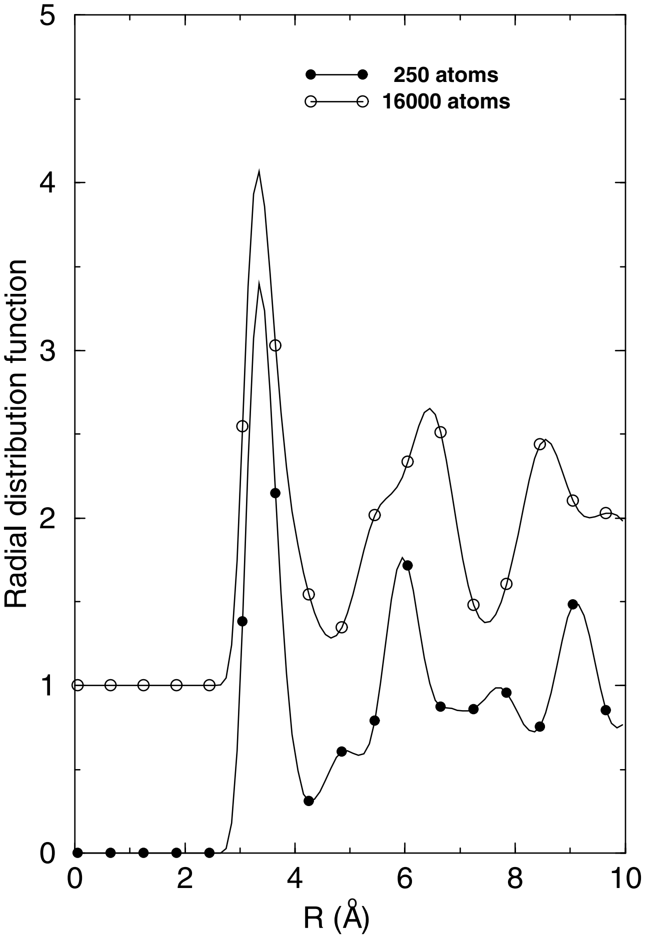

FIG. 4. Radial distribution functions of Xe, calculated at $P = 30$ GPa and $T = 2800$ K from the initial bcc structure with 250 and 16 000 atoms. The RDFs are calculated using runs of 100×10^3 time steps and averaged over the last 25×10^3 time steps. All parameters of MD runs, except the number of atoms, are identical. The RDF calculated with 16 000 atoms (shifted up by 1 for convenience) is typical of the bcc, while the RDF calculated with 250 atoms is typical of the fcc structure (compare with Fig. 3).

correct calculations with 16 000 atoms result in the bcc structure. The only difference in these simulations was the number of atoms.

Summarizing, we have identified a new fcc-bcc transition in Xe at high PT. The theoretical results are in good agreement with experimental data. The same transition is likely to be common for Ar and Kr. The results of melting experiments with visual observation of phase transitions have to be reassessed.

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[1] M. Ross, R. Boehler, D. B. Boercker, and P. Soderlind, in *Proceedings of the International Conference on High Pressure Science and Technology (AIRAPT-17), Honolulu, HI, 1999,* edited by Murli H. Manghnani, William J. Nellis, and Malcolm F. Nicol (Universities Press, Hyderabad, India, 2000), Abstract No. 195; R. Boehler, M. Ross, P. Soderlind, and D. B. Boercker, Phys. Rev. Lett. **86**, 5731 (2001).
[2] P. Loubeyre, J. M. Besson, J. P. Pinceaux, and J. P. Hansen, Phys. Rev. Lett. **49**, 1172 (1982).
[3] D. Levesque, J.-J. Weis, and M. L. Klein, Phys. Rev. Lett. **51**, 670 (1983).
[4] D. Frenkel, Phys. Rev. Lett. **56**, 858 (1986).
[5] A. P. Jephcoat *et al.,* Phys. Rev. Lett. **59**, 2670 (1987).
[6] M. I. Eremets, E. A. Gregoryanz, V. V. Struzhkin, H.-K. Mao, and R. J. Hemley, Phys. Rev. Lett. **85**, 2797 (2000).
[7] H. Cynn (private communication).
[8] D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3188 (1984).
[9] A. Rahman, Phys. Rev. **136A**, 405 (1964).
[10] M. Ross and A. K. McMahan, Phys. Rev. B **21**, 1658 (1980).
[11] A. B. Belonoshko, High Press. Res. **10**, 583 (1992).
[12] A. B. Belonoshko, Science **275**, 955 (1997).
[13] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, London, 1987).
[14] K. Syassen and W. B. Holzapfel, Phys. Rev. B **18**, 5826 (1978).
[15] R. N. Keeler, M. van Thiel, and B. J. Alder, Physica (Utrecht) **31**, 1437 (1965).
[16] A. N. Zisman, I. V. Aleksandrov, and S. M. Stishov, Phys. Rev. B **32**, 484 (1985).
[17] P. Loubeyre, Phys. Rev. B **37**, 5432 (1988).
[18] A. B. Belonoshko, R. Ahuja, and B. Johansson, Phys. Rev. Lett. **84**, 3638 (2000).
[19] A. B. Belonoshko, Geochim. Cosmochim. Acta **58**, 4039 (1994).
[20] A. B. Belonoshko, Phys. Chem. Miner. **25**, 138 (1998).
[21] R. Grover, R. N. Keeler, F. J. Rogers, and G. C. Kennedy, J. Phys. Chem. Solids **30**, 2091 (1969).
[22] J. R. Morris, C. Z. Wang, K. M. Ho, and C. T. Chan, Phys. Rev. B **49**, 3109 (1994).
[23] P. H. Lahr and W. G. Eversole, J. Chem. Eng. Data **7**, 42 (1962).
[24] A. Michels and C. Prins, Physica (Utrecht) **28**, 101 (1962).
[25] J. C. Stryland, J. E. Crawford, and M. A. Mastoor, Can. J. Phys. **38**, 1546 (1960).
[26] W. B. Streett, L. S. Sagan, and L. A. K. Staveley, J. Chem. Thermodyn. **5**, 633 (1973).
[27] E. C. Bain, Trans. Am. Inst. Min. Metall. Eng. **70**, 25 (1924).
[28] K. Refson, MOLDY, Release 2.13, 1998, a general-purpose molecular dynamics code. Available free at http://www.earth.ox.ac.uk/keith/moldy.html.