



A metadynamics study of the *fcc*–*bcc* phase transition in Xenon at high pressure and temperature



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ABSTRACT

To theoretically find a stable solid phase is not a trivial task even at 0 K. The difficulties multiply at high temperature (T) because even more elaborate crystal structure prediction methods fail in the vicinity of the melting transition. Moreover, if the submelting phase is dynamically unstable at low T some methods cannot be applied at all. The method of metadynamics allows finding local minima of Gibbs free energy without additional simplifications. However, so far this method has been mainly used for study of pressure-induced solid–solid phase transitions and not in searching for T -induced ones. Here we study the applicability of the technique to the latter class of problems as well as to the approximate determination of the transition temperature. We apply the metadynamics method to study the solid–solid phase transition in Xe described by the Buckingham potential at high temperature and observe the *fcc*–*bcc* phase transition in a pressure–temperature range consistent with earlier results.

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1. Introduction

A temperature induced solid–solid phase transition at high pressure is difficult to find in a diamond anvil cell (DAC) experiment [1]. Moreover, at high pressures and temperatures it is difficult to discriminate a solid–solid phase transition from melting [2,3].

A “flat” melting curve, that disagrees with melting predicted by the Lindemann criterion [4], was reported for Cu, Ni, and Fe [5], Mo, Ta [6], Ar, Kr and Xe [7] in the DAC measurements. The “flat” melting curve can be seen in Fig. 2(a) in Ref. [7]. It was attempted to explain this behavior by a temperature induced solid–solid transition (Fe [8], Mo [9], Ta [10], Xe [11]). The stable phase of Xe at normal conditions is the face centered cubic (*fcc*) lattice. The existence of a temperature induced stable body centered cubic (*bcc*) phase in Xe described by the Buckingham potential was proven experimentally [11]. This result was later confirmed by *ab initio* calculations [12]. Further, the triple-point *fcc*–*bcc*–liquid was determined [13].

Direct computer simulations using variable-cell molecular dynamics often fail to find a new phase due to free-energy barriers that separate the phases. One of the methods that can be used to determine the PT conditions at which such a phase transition occurs is metadynamics. This method is based on the work of

Rahman and Parrinello [14] and Laio and Parrinello [15] and originally was applied to the studies of structural phase transitions in crystals by Martoňák, Laio and Parrinello [16,17]. The main idea of this method consists in modification of the free energy surface by adding a history dependent term in such a way that the system is effectively pushed out of the free-energy well. The important advantage is that there is no requirement to know the possible structures *a priori*. This method allows to search for minima of the Gibbs free energy surface and, thus, for stable and metastable crystal structures. Metadynamics was successfully applied for searching new crystal structures obtained at high pressure and possible pathways of the pertinent phase transitions [18–20].

In this paper, we apply metadynamics to explore a solid–solid phase transition in Xe modelled with the Buckingham potential for which the T -induced phase is known to exist [11], and confirmed by a recent study using the adiabatic free energy dynamics (AFED) approach [21]. The aim of this study is to determine the range of applicability of the metadynamics approach. This might allow to apply it to other materials, e.g. transition metals such as Mo, Fe, Cu, for which the existence of T -induced phases is controversial [22–26].

2. Method

Metadynamics is a method for exploring the free energy surface (FES) expressed as function of selected collective coordinates \mathbf{h} [15].

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At given pressure and temperature a system in thermodynamical equilibrium is always in a global or local minimum of the Gibbs free energy $G(\mathbf{h}) = F(\mathbf{h}) + PV(\mathbf{h})$, where F is the Helmholtz free energy. The approach of metadynamics is based on escaping the free-energy minima by systematically adding a history-dependent potential constructed as a sum of Gaussians centered along the trajectory of collective variables [15].

For simulation of structural phase transitions in crystals the primitive unit cell \mathbf{u} could in principle be naturally used as order parameter. It is, however, more convenient to instead use a supercell since this setup naturally provides the possibility of a final structure with the number of atoms in the unit cell different from that in the original one. In case of a relatively small simulation box, where the creation of defects is too costly, the simulation box edges $\mathbf{a}, \mathbf{b}, \mathbf{c}$ could be taken as collective coordinates which can provide a coarse-grained description of the system. The matrix $\mathbf{H} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$, formed by three column vectors \mathbf{a} , \mathbf{b} and \mathbf{c} , is related to the unit cell via the relation $\mathbf{H} = \mathbf{u}\mathbf{m}$, where \mathbf{m} is an integer matrix [14,16]. In order to freeze the irrelevant rotational degrees of freedom, we can rewrite this matrix

$$\mathbf{H} = \begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix}$$

as upper-triangular, i.e. one could set the matrix components below the diagonal to zero and choose the 6D vector $\mathbf{h} = (h_{11}, h_{22}, h_{33}, h_{12}, h_{13}, h_{23})^T$ as a collective coordinate. Close to the equilibrium crystal structure \mathbf{h}^0 , the Gibbs free energy could be written as

$$G(\mathbf{h}) \approx G(\mathbf{h}^0) + \frac{1}{2}(\mathbf{h} - \mathbf{h}^0)^T \mathbf{A}(\mathbf{h} - \mathbf{h}^0),$$

where the Hessian matrix

$$A_{ij} = \partial^2 G(\mathbf{h}) / \partial h_i \partial h_j |_{\mathbf{h}^0}$$

can be calculated from finite differences of the pressure tensor [17]. Normally the potential well has a highly anisotropic shape. To reduce this effect the collective variables are transformed to

$$s_i = \sqrt{\lambda^i} \sum_j O_{ji} (h_j - h_j^0),$$

where λ^i are eigenvalues of the Hessian matrix \mathbf{A} and \mathbf{O} is an orthogonal matrix which diagonalizes \mathbf{A} . Here

$$-\frac{\partial G}{\partial h_{ij}} = V[\mathbf{h}^{-1}(\mathbf{p} - P)]_{ji},$$

where the volume of the system $V = \det(\mathbf{a}, \mathbf{b}, \mathbf{c})$, \mathbf{p} is the averaged microscopic pressure tensor and P is the external hydrostatic pressure. The collective variables evolve by equation

$$s^{t+1} = s^t + \delta s \frac{\vec{\phi}^t}{|\vec{\phi}^t|}$$

with stepping parameter δs , and $\vec{\phi}^t$ is the driving force

$$\vec{\phi}^t = -\frac{\partial G^t}{\partial \mathbf{s}}$$

determined from the history-dependent Gibbs potential

$$G^t(\mathbf{s}) = G(\mathbf{s}) + \sum_{t' < t} W e^{-|s - s^{t'}|^2 / 2\delta s^2},$$

where Gaussians are placed at all visited points of the trajectory in order to push the system out of the local minimum.

The implementation of metadynamics consists of three steps. Two steps are preparative. The first is equilibration of the system at given pressure and temperature and calculating the equilibrium vector \mathbf{h}^0 . Second is calculating the Hessian. This is made from finite differences of the stress tensor components by altering each of the 6 components of the vector \mathbf{h}^0 by $\pm 1\%$. The third step is metadynamics itself. The metadynamics code can be implemented as a wrapper to a molecular dynamics (MD) simulation without the need to modify the MD code. As the model of interaction the Buckingham pairwise potential was chosen because there is a proven solid–solid phase transition at high temperatures [27]. The potential is defined by the pairwise function

$$u_{\text{Buck}}(r) = A \exp(-r/\rho) - \frac{C}{r^6},$$

where parameters $A = 740899.6$ kJ/mol, $\rho = 0.343846$ Å and $C = 28944.64$ Å⁶ kJ/mol were taken from the work of Ross and McMahan [28]. The cutoff radius was taken to be 8 Å for large boxes and 6 Å for boxes with less than 500 atoms. We performed MD equilibration and sampling using the DL POLY software [29].

For all MD simulations we used a timestep of 1 fs. During each metadynamics simulation we equilibrated the starting configuration for 20,000 steps (20 ps) with a Berendsen barostat. Then 50,000 steps (50 ps) were used in each run for calculating the Hessian matrix. For each metadynamics step we run 1000 steps for equilibration and 1000 steps for gathering statistics, 2 ps total.

We made simulations to search for the phase transition temperatures using a system of 13,500 atoms when starting with the *fcc* lattice and of 13,718 atoms when starting with the *bcc* lattice (the cubic box with approx. the same number of atoms). We performed simulations of 3000 metadynamics steps using a Gaussian width $\delta s = 4, 18, 20, 30, 35, 50, 70, 80$ (GPa Å³)^{1/2} with the corresponding Gaussian height $W = \delta s^2$.

The melting curve of Xe was obtained up to 2000 GPa, using the Z-method [30] and two-phase method [13]. In the Z-method, the simulations were conducted using 2000 atoms for a pressure range from 10 to 2000 GPa starting from the *fcc* lattice. The melting temperatures of *bcc* and *fcc* phases were obtained also using the two-phase method. The initial conditions for this simulation were prepared in the following way. The ideal lattice with 128,000 atoms was generated and then melted with a temperature 50% higher than the melting temperature for a given pressure. Next, the system was equilibrated with the pressure and temperature close to the melting conditions calculated by the Z-method. Then, atoms belonging to a spherical region with radius 27 Å were removed. Instead a pre-equilibrated solid sphere with radius 25 Å was inserted. A 2 Å gap was created to guarantee that inserted atoms are not too close to the liquid atoms (note the non-physical behavior of the Buckingham potential (Fig. 1) at short distances). The resulting configuration was a supercell containing two phases – a solid sphere (2975 atoms for *bcc* and 3043 atoms for *fcc*) and liquid (124,218 atoms) surrounding it. A relaxation procedure was applied to minimize the energy of the system. Then the simulations were conducted using the NVE ensemble starting from a temperature slightly below the melting line. After the simulation starts, liquid atoms start to crystallize around the solid sphere. The latent heat of this atoms is released as a kinetic energy, raising the temperature in the simulation box (Fig. 2). This process will continue until either equilibrium between solid and liquid is reached, or all the liquid solidify. Because of small undercooling and the small size of the initial solid, both phases (solid and liquid) were always present in the end of simulation. As was expected, the *bcc* melting temperature was higher than that of *fcc* starting from the pressure ~ 50 GPa, indicating that *bcc* is more stable at higher pressures near the melting temperatures.

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