

Molecular dynamics investigation of the pressure induced B1 to B2 phase transitions of RbBr

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Abstract

The pressure induced transformation of rubidium bromide from the NaCl (B1) to the CsCl (B2) type structure is elucidated by means of molecular dynamics simulations. Two different approaches were followed. The “conventional” procedure of applying pressures, which are increased successively, leads to a phase transformation at a critical pressure of 80–85 kbar. This is 16–17 times the experimental value. On the other hand, the phase transition is studied by path sampling molecular dynamics simulations. This approach allows investigating the process at 5 kbar, i.e. it does not require over-driving. At this pressure the system takes pathways related to the route proposed by Bürger, exclusively. In the runs in which an over-pressurization of 80 kbar is applied, we instead observe both the Bürger mechanism and the route proposed by Watanabe et al.

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1. Introduction

Reconstructive phase transitions are fundamental physical phenomena, and the investigation of their atomistic mechanisms is a major experimental and theoretical challenge. Landau theory offers a comprehensive phenomenological account for continuous phase transitions and allows for the formulation of an order parameter [1]. However, this only applies if the space groups of the structures delimiting the phase transition are in the relation of a group and a direct subgroup. While this is the case for second order phase transitions, reconstructive (first order) phase transitions are not continuous and no order parameter can be defined.

In principle, constant pressure molecular dynamics simulations appear to be perfectly suited for the mechanistic study of phase transitions. Unfortunately the limited time scale of molecular dynamics simulations usually complicates the direct observation. A frequently chosen approach is to enhance the kinetics by applying pressures, which are considerably larger than the actual critical pressure required for the phase transition to occur. In the pioneering study of Ruff et al. this strategy was

used to investigate the pressure induced phase transition of RbBr [2]. Therein the authors observed a very large hysteresis effect. The high-pressure modification (B2) was obtained at a transition pressure of 230 kbar, which is about 46 times the experimental value and the reverse B2 to B1 transition could not be observed [2].

Very recently we presented a powerful molecular dynamics approach, allowing for the investigation of phase transitions at the critical pressure as obtained from experiment [3, 4]. Therein geometric models are applied for generating putative intermediate structures [5]. The manifold of possible transition paths is then explored by path sampling molecular dynamics simulations [6,7].

It is the aim of the present paper to relate the path sampling method to the “conventional” over-pressurization approach at the example of the pressure-induced phase transition of RbBr. From this we also explore the effect of external driving forces on the mechanisms of pressure-induced phase transitions.

2. Theory and simulation details

For reasons of comparability, the simulation system was chosen identical to one of the setups of Ruff et al.

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[2]. The model consists of 216 pairs of both, rubidium and bromide ions. The related Born-Mayer-Huggins parameters were taken from the literature [2]. Periodic boundary conditions are applied and Ewald summation is used for the electrostatics. Constant pressure and temperature were applied with the anisotropic Melchionna/Nose-Hoover thermostat barostat combination [7]. The temperature was kept constant at 623 K. All molecular dynamics simulations were carried out with the DLPOLY package [8]. A relatively small time-step of 0.2 fs was chosen in order to provide good time-reversibility, which is of considerable importance for the path-sampling scheme.

The path sampling approach of Chandler et al. [5,6] starts from an initial trajectory of the desired event. New trajectories are then generated in an iterative way by selecting a configuration from the preceding trajectory and slightly modifying the atomic momenta. Velocity changes are incorporated in a manner conserving the total energy, momentum and angular momentum, respectively. For this we chose random pairs of ions i , j and apply momentum changes Δp as follows:

$$\begin{aligned}\vec{p}_i^{\text{modified}} &= \vec{p}_i^{\text{old}} + \Delta p(\vec{r}_j - \vec{r}_i)/(|\vec{r}_j - \vec{r}_i|), \\ \vec{p}_j^{\text{modified}} &= \vec{p}_j^{\text{old}} - \Delta p(\vec{r}_j - \vec{r}_i)/(|\vec{r}_j - \vec{r}_i|).\end{aligned}\quad (1)$$

While Eq. (1) provides conservation of both the momentum and the angular momentum, the total kinetic energy of the new configuration is typically not conserved after this first inset of modifications. We hence rescale all ionic momenta by a factor of:

$$\sqrt{\frac{E_{\text{kin}}^{\text{old}}}{\sum_i |\vec{p}_i^{\text{modified}}|^2 / 2m_i}}.\quad (2)$$

As the total momentum and total angular momentum are equal to zero, this factorization does not affect their respective conservation.

The modified configuration is then propagated in both directions of time and the resulting trajectory is checked for the process of interest. In case the phase transition takes place, the trajectory is used for generating new ones, repeating the above procedure. As a quantitative measure of progress of the B1 \rightarrow B2 phase transition we chose the average coordination number in the crystal. This number is only taken as a descriptor of the process and not as the reaction coordinate. Path sampling does not involve the pre-definition of reaction coordinates, which makes it a very suitable method for mechanistic studies.

Because of the iterative nature of the path-sampling scheme, subsequent trajectories may not be considered as independent. Their correlation depends on the magnitude of the momentum changes applied each iteration. For good exploration of the trajectory phase

space, strong momentum modifications appear desirable. However the more drastic these changes are, the more likely the time propagation of the system yields in an unsuccessful attempt of the phase transition. Low acceptance probabilities during the path-sampling scheme imply a large number of ‘useless’ trajectory calculations. In order to find a balance between large trajectory modification and low acceptance rate, we set up an automated scheme. Therein the random momentum changes on the ions i are generated according to a Gaussian distribution. The half-width is given by

$$\Delta = \alpha \cdot p_i^0; \quad k_B T = \frac{p_i^0}{m_i},\quad (3)$$

whereas the ‘shooting parameter’ α controls the intensity of the momentum modifications.

We used a set of two different shooting parameters, α_{B1} and α_{B2} , corresponding to variation of configurations related to the B1 and the B2 phases, respectively. Once a path sampling iteration is started from a configuration of let’s say the B1 phase, the system is propagated for a maximum simulation time of 50 ps. In case the B2 phase is not observed from this run, the parameter α_{B1} is reduced by a factor of 1.1 and a new attempt is made. If, however the system is transformed into the B2 phase, α_{B1} is increased by 1.1 and the molecular dynamics run is stopped. The final configuration is then used for the next path sampling iteration. In the course of the sampling procedure, the shooting parameters α_{B1} and α_{B2} converge in such way that the probability of each iteration to yield a B1 \rightarrow B2 (or B2 \rightarrow B1) transition path is $\frac{1}{2}$.

The difference in free energy of the crystal in the B1 and the B2 phase, respectively, may in principle be calculated from a large set of molecular dynamics runs. For this, one could randomly generate configurations related to the B1 (B2) phase and investigate the probability $p_{B1 \rightarrow B2}$ ($p_{B2 \rightarrow B1}$) of observing a transformation to the B2 (B1) phase within a given time. The difference in free energy of both states is then obtained from $k_B T \ln(p_{B1 \rightarrow B2}/p_{B2 \rightarrow B1})$. However, in case the transition requires crossing of a large energy barrier, both probabilities are quite small and an extremely large number of molecular dynamics runs are needed to provide reliable statistics. This problem may be circumvented by applying the path-sampling scheme in combination with the automated adapting of the shooting parameters as described above. Once the iterations are converged, the parameters α_{B1} and α_{B2} contain information about the probabilities $p_{B1 \rightarrow B2}$ and $p_{B2 \rightarrow B1}$, respectively. Large shooting parameters imply large configuration modifications and hence indicate the existence of a large number of possible starting points for the phase transition. This may directly be associated to a high probability of observing the phase transition when starting a molecular dynamics run from a

randomly generated configuration. While the functional form $p_{B1 \rightarrow B2}(\alpha_{B1})$ is unknown, $\alpha_{B1} = \alpha_{B2}$ implies $p_{B1 \rightarrow B2} = p_{B2 \rightarrow B1}$ and hence the free energy difference between B1 and B2 is zero. The latter is the condition for the critical pressure of the $B1 \leftrightarrow B2$ phase transition. As a consequence, the shooting parameters may be used to verify if the pressure applied in the path sampling runs actually corresponds to the critical pressure of the simulation model.

3. Results

The most straightforward approach for studying pressure-induced phase transitions from molecular dynamics simulations is to simply apply over-critical pressure and wait for the desired process to happen. Since the critical pressure value of the model system is usually not known, it appears reasonable to start the simulations at low pressure and gradually increase the pressure until the phase transition is observed. As early as 1989 Ruff et al. used this technique for studying the $B1 \rightarrow B2$ phase transition of RbBr [2]. Therein the change of pressure was implemented at a rate of $8300 \text{ kbar ns}^{-1}$. In a molecular dynamics run of a few tens of picoseconds the $B1 \rightarrow B2$ transition was observed at a pressure of 230 kbar, which corresponds to about 46 times the experimental value [2]. One of the possible explanations for this large discrepancy could be related to the inaccuracy of the underlying model of RbBr. While surely being a source of some error, it appears quite unlikely that this can account for such drastic difference in the critical pressure values.

On the other hand, the limited time scales in molecular dynamics simulations may be expected to have a much stronger effect on this issue. The $B1 \rightarrow B2$ phase transition is related to the crossing of a barrier separating the two stable states. If this barrier is larger than $k_B T$, the phase transformation has to be thought of as a rare event. In molecular dynamics simulations this implies long ‘waiting times’, before the actual transition process can be observed. For many processes these periods exceed the scope of the simulation runs by several orders of magnitude. As a consequence, the phase transformation may typically not be observed from direct molecular dynamics simulations, if applying the critical pressure as obtained from experiment. This has motivated the use of over-critical pressure to enhance the phase transition kinetics. When gradually increasing the simulation pressure, at some point the driving of the process becomes sufficiently large to make the transition occur within the short time scale of the simulation runs. This phenomenon can be illustrated by using different rates of pressure increment. Three independent sets of molecular dynamics simulations were performed using the same model of RbBr as Ruff

et al. [2]. However, a significantly lower rate of 10 kbar ns^{-1} was chosen for elevating the simulation pressure. From these simulations, the $B1 \rightarrow B2$ transformation was observed at a pressure of 80–85 kbar. Though considerably lower than the estimate for the critical pressure of Ruff et al., this is still 16–17 times the experimental value. Accordingly, the accuracy in predicting the critical pressure could—at least to some extent—be improved. Nevertheless, the degree of over-driving is still dramatic.

Unfortunately, when using the simulation scheme described above, limited computational resources prevent sufficiently low rates of pressure increment in order to observe the $B1 \rightarrow B2$ phase transformation of RbBr at realistic conditions. Moreover, the over-driving may also be expected to effect the transition pathways connecting the two phases. Thus, for investigating the mechanism of the phase transition, it would be desirable to avoid over-pressurization at all. The path sampling approach of Chandler et al. allows molecular dynamics simulation of phase transitions applying the critical pressure as obtained from experiment [3,4]. As a prerequisite to the path sampling iterations, an initial trajectory of a phase transition event is needed. This may easily be obtained from simulation runs in which the over-pressurization is chosen sufficiently large to make the process occur spontaneously. Snapshots from the related transition path were taken and propagated in both directions of time applying a pressure of 5 kbar. From this a dynamical pathway connecting the B1 and B2 phases was obtained. Though the initial trajectory might not be a very likely one, it still serves well as a starting point for the path sampling iterations. Path sampling can be interpreted in terms of a Monte-Carlo sampling of the ensemble of trajectories corresponding to a specific process [3,4]. Thus, in the course of the iterations, the pathways relax towards more favorable regions of the ensemble of transition trajectories.

Indeed, the initial pathway is modified considerably. At 80 kbar the transformation occurs in a highly collective manner, entirely skipping nucleation and growth of the B2 phase. The pathways obtained from path sampling at 5 kbar clearly exhibit a heterogeneous character. In Fig. 1, snapshots taken from a representative trajectory are shown. For better visibility, the pictures include only the bromide ions (hence the connecting lines do not represent bonds and are only drawn as a help for the eye). For each of the bromide ions the coordination number was calculated individually by counting all rubidium ions within a cut-off distance of 3.5 Å. The highlighted balls represent Br^- ions, for which an 8-fold coordination by Rb^+ —as corresponding to the B2 phase—is observed (see also Fig. 2). In the upper right of Fig. 1 the B2 phase involves a few ions only. In the course of the phase transition,

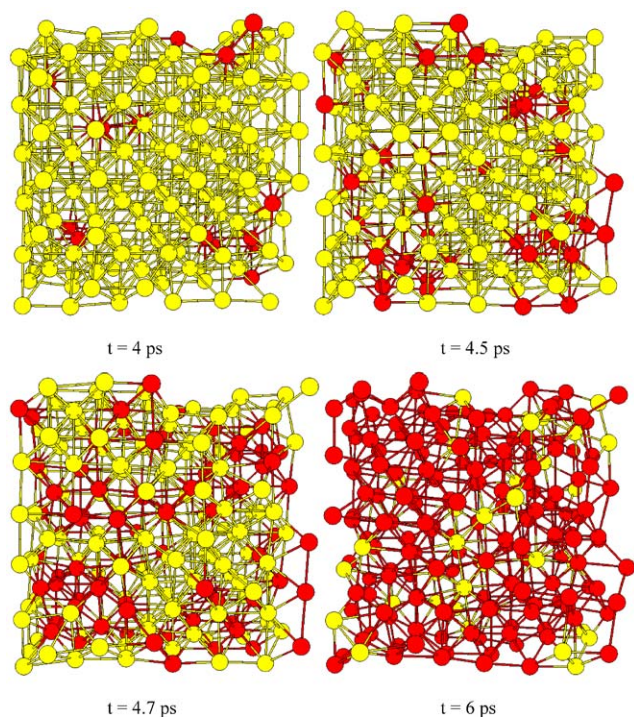


Fig. 1. Snapshot taken from a representative trajectory showing the arrangement of bromide ions, only. The highlighted balls represent Br⁻ ions, for which an 8-fold coordination by Rb⁺ is observed.

this phase grows and finally extends over the whole simulation box.

In the discussion of the possible pathways for B1 → B2 transitions currently two mechanisms are the most favored. Figs. 2a and b illustrate the routes proposed by Bürger [9] and Watanabe et al. [10], respectively. In both pathways the coordination number changes from 6 (B1) to 8 (B2). However the two mechanisms differ in the ionic displacements observed in the course of the phase transformation (Fig. 2).

In two of the trajectories obtained from molecular dynamics simulation at elevated pressure (80–85 kbar) the transformation was observed to follow the mechanistic route of Watanabe, while the third trajectory corresponds to the Bürger mechanism. These findings however are derived from only 3 ‘experiments’ and do not provide good statistics. The molecular dynamics simulations in which the pressure is gradually increased are computationally quite expensive and we thus did not produce further runs of this kind. Instead we explored the transition trajectories at 80 kbar using the path sampling scheme. Out of a total number of 200 transition paths in 55% the Bürger mechanism could be identified. Transition routes corresponding to the Watanabe mechanism were found at a slightly lower occurrence of 45%. So eventually both mechanisms appear to be possible when applying an over-pressurization of factor 16.

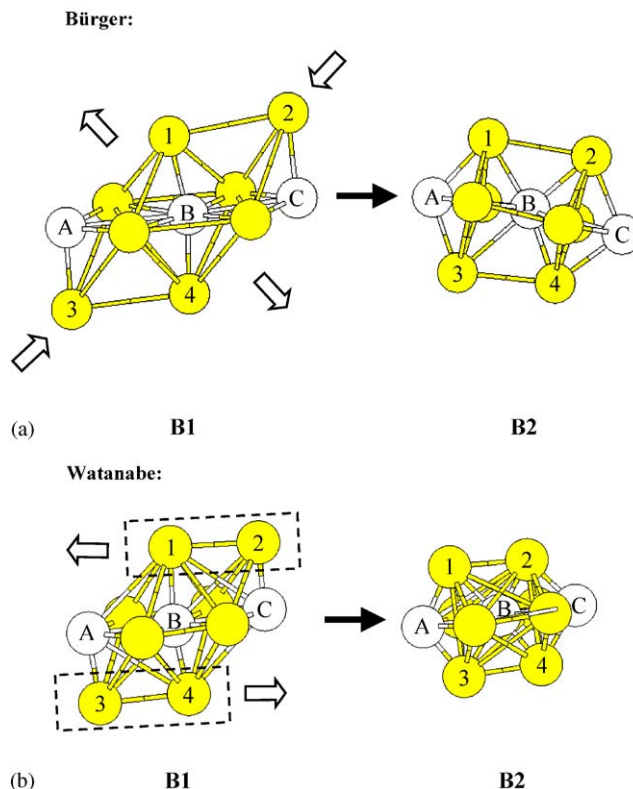


Fig. 2. (a) Illustration of the B1 → B2 transformation according to the mechanism of Bürger. The Br⁻ and (some of) the Rb⁺ ions are labelled as A–C and 1–4. In the B1 phase, the central bromide ion B is coordinated by 6 rubidium ions. Transformation to the B2 phase is related to compression along the unit cell diagonal (axis through 2 and 3) and expansion in the perpendicular directions. In the B2 phase the coordination numbers change to 8. (b) Same crystal fragment as in Fig. 1a, but the snapshots are shown for a trajectory following the mechanistic route proposed by Watanabe. The B1 → B2 transformation occurs via antiparallel shuffling of layers (indicated by dashed boxes). Note the different orientation of the unit cell of the B2 crystal structures shown in Figs. 2a and b.

This picture is dramatically changed when investigating the phase transition at the critical pressure (5 kbar). The related path sampling simulations were started from a trajectory of a B1 → B2 transition corresponding to the mechanism proposed by Watanabe. After only a few iterations, we obtained pathways related to the route proposed by Bürger, exclusively. This clearly demonstrates a strong preference of the later mechanism.

In both sets of path sampling runs, we monitored the evolution of the shooting parameters in the course of 200 sampling iterations. At 5 kbar, α_{B1} and α_{B2} were found to be roughly equal; $\ln(\alpha_{B1}/\alpha_{B2}) = 0 \pm 0.3$. This indicates that the critical pressure of the simulation model used is close to the value observed from experiment [2]. In contrast to this, the 80 kbar runs exhibited no convergence in α_{B1} and α_{B2} . While the parameter α_{B1} dramatically increased, α_{B2} decreased

considerably. After 200 iterations both parameters already differed by 5 orders of magnitude.

4. Conclusion

We presented molecular dynamics simulations of the pressure-induced transformation of rubidium bromide from the B1 to the B2 type structure. The “conventional” procedure of gradually increasing the pressure and attempting to observe the phase transition from direct simulation is related to a path sampling approach. The use of the first simulation scheme implies a considerable degree of over-pressurization. In three independent runs a pressure of 80–85 kbar was found to be required for observing the phase transformation. This is about 16–17 times the experimental value.

In contrast to this, the path sampling molecular dynamics simulation technique allows investigating the process at 5 kbar, i.e. the critical pressure as known from experiment. The resulting transition trajectories vary considerably from those observed at over-critical pressure. While at 80 kbar eventually both the Bürger and the Watanabe mechanism are possible, at 5 kbar only Bürger’s mechanism was found to be active. Moreover, at 80 kbar the transformation occurs in a highly collective manner, while at 5 kbar nucleation and growth of the B2 phase may be observed. At the

example of the B1 to B2 phase transition of RbBr, this illustrates the limited predictive power of the mechanistic studies based on extensive over-pressurization.

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References

- [1] L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Addison-Wesley Reading, MA, 1958.
- [2] I. Ruff, A. Baranyai, E. Spohr, K. Heinzinger, *J. Chem. Phys.* 91 (1989) 3148.
- [3] S. Leoni, D. Zahn, *Z. Kristallogr.* 219 (2004) 339.
- [4] D. Zahn, S. Leoni, *Phys. Rev. Lett.* 92 (2004) 250201.
- [5] C. Dellago, P. Bolhuis, F.S. Csajka, D. Chandler, *J. Chem. Phys.* 108 (1998) 1964.
- [6] P. Bolhuis, C. Dellago, D. Chandler, *Faraday Discuss.* 110 (1998) 421.
- [7] S. Melchionna, G. Ciccotti, B.L. Holian, *Mol. Phys.* 78 (1993) 533.
- [8] W. Smith, T. Forester, *J. Mol. Graph.* 14 (1996) 136.
- [9] M.J. Bürger, in: R. Smoluchowski, J.E. Mayer, W.A. Weyl (Eds.), *Phase Transformations in Solids*, Wiley, New York, 1951.
- [10] M. Watanabe, M. Tokonami, N. Morimoto, *Acta Crystallogr. A* 33 (1977) 294.