Nucleation and Growth in Pressure-Induced Phase Transitions from Molecular Dynamics Simulations: Mechanism of the Reconstructive Transformation of NaCl to the CsCl-Type Structure

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We perform path sampling molecular dynamics on the pressure-induced reconstructive phase transition from NaCl to CsCl type structure. Unlike the molecular dynamics simulations prior to this work our approach does not drive the process by applying elevated pressure. As a consequence, we are able to observe nucleation events that initiate the successive transformation of the crystal. The competing phases are separated by an interface exhibiting a well-defined structure that propagates through the crystal during phase transition.

Reconstructive (first order) phase transitions abound in nature, and are of fundamental importance. Yet the elucidation of their mechanisms remains a major challenge. The lacking of a group-subgroup relationship between the two crystalline phases means, in terms of standard Landau theory [1], that reconstructive transitions do not proceed in a concerted manner. The orientation relation of the crytstallographic directions is also *a priori* not given, and many mechanistic approaches to the transition rely on a symmetry path [2,3], which allows for a mapping of the positions from one structure to the other. Such geometric interpolation however, may not be interpreted in terms of a dynamical pathway. The corresponding transition route is inherently concerted, involving a collective movement of the atoms. The direct observation of nucleation and growth is elusive to such models. Nevertheless, continuous models are of great use for the prediction of putative intermediate phases.

In this Letter we implement a powerful strategy to elucidate the mechanistic details of reconstructive phase transitions. Therein constant-pressure molecular dynamics simulations are performed at the experimental transition pressure and temperature. We escape the limitations imposed by the transition event being rare by applying the path sampling algorithm developed by Chandler *et al.* [4,5]. Though a small, periodic simulation box is used, our approach in principle does not obscure nucleation processes. We illustrate this by the example of sodium chloride.

NaCl undergoes a high-pressure transition from NaCl type or $B1$ (space group $Fm\bar{3}m$) to CsCl type or $B2$ (space group $Pm\bar{3}m$) at $p = 26.8$ GPa and $T = 300$ K [6]. Two main mechanisms for this reconstructive phase transition have been proposed over the years. In the so-called Bürger mechanism [7] the distortion occurs as a compression of the unit cell of NaCl along the cell diagonal and an expansion in the perpendicular direction. The second, pointed out by Hyde and O'Keeffe [8], involves an interplanar movement and an antiparallel displace-ment of atoms in adjacent (100) NaCl layers. While experimentally difficult to assess, mainly due to the large volume change of the crystal, the mechanisms have been studied in a considerable number of theoretical approaches. Among them, first principles studies [9,10] on kinetic aspects of the transition showed the closeness of activation energy for the Bürger mechanism and those of Hyde and O'Keeffe. A similar result was obtained in another recent work [2], in which also other mechanisms are enumerated. Constant-pressure molecular dynamics approaches so far support either the first or the second mechanism, depending on the algorithm used [11].

In principle, constant pressure and temperature molecular dynamics simulations appear as being particularly suited to study phase transitions. A major difficulty is that such processes usually occur on time scales much larger than the few ns of a molecular dynamics simulation. A common practice to circumvent this limitation is the use of elevated pressure (and sometimes also temperature). While this can enhance the kinetics to almost any desired extent, too strong driving may affect the mechanism of the process. Thus, over-pressurization should be avoided as much as possible.

We investigate the phase transition of NaCl to the CsCl structure type in molecular dynamics simulations applying the critical pressure and temperature from experiment. The key to being able to do without over pressurization is the use of the path sampling technique, which allows for the study of rare events without driving forces. Starting from a trajectory in which the process of interest is observed, new trajectories are obtained in an iterative way. This is accomplished by selecting a configuration from the preceding trajectory and slightly modifying the atomic momenta. Velocity changes are incorporated in a manner that the total energy, momentum, and torque are conserved. The modified configuration is propagated in both directions of time.

The resulting trajectory is then checked for the process of interest, monitoring the coordination numbers as a

discriminating order parameter. In case the desired event takes place, the trajectory is used for generating a new trajectory, repeating the above procedure. Because of the iterative nature of the path sampling method, subsequent trajectories may not be considered as independent. However, in the present work four iterations were found to be sufficient to ensure decorrelation.

A further consequence of the iterative nature of the path sampling method is the need of a first trajectory as a starting point. Without driving the system by over pressurization the time needed for observing just a single trajectory exibiting a phase transition event exceeds the scope of molecular dynamics simulations.

In a previous study, a geometrical model [12,13] of the transition between the two phases was applied for systematically searching an intermediate state [14]. The putative intermediate state is topologically in between the two crystalline phases, and should evolve dynamically towards different crystalline structures depending on the direction of time propagation. Two initial trajectories were generated using different geometrical models of the phase transition. One of these corresponds to the mechanism proposed by Bürger, while the other one is described in Ref. [14]. For each of the two initial trajec-

tories an independent set of path sampling iterations was run. Thus we chose to model a putative intermediate state and obtain a first trajectory from propagation in both directions of time. Each configuration obtained from the geometrical models is based on the interpolation of the $B1$ and $B2$ structures of NaCl. Therein all atoms are treated in the same manner, hence in the modeled intermediates the ionic arrangement is highly symmetric.

Molecular dynamics simulations of periodic boxes were carried out using a modified version of the DLPOLY program [15,16]. The simulation system included, depending on the underlying path sampling set, 270 and 216 pairs of sodium and chloride ions. The model parameters were taken from the literature [17]. Ewald summation was applied to the electrostatics. In order to ensure good time-reversibility a relatively small time step of 0.2 fs was chosen. Constant pressure and temperature were applied with the anisotropic Melchionna–Nose-Hoover thermostat barostat combination [18]. We wish to point out the importance of using a barostat, which allows box shape variations, in order to avoid biasing the mechanistic analysis of the phase transition.

The initial transition trajectories involve a highly ordered collective movement. However, after only a few
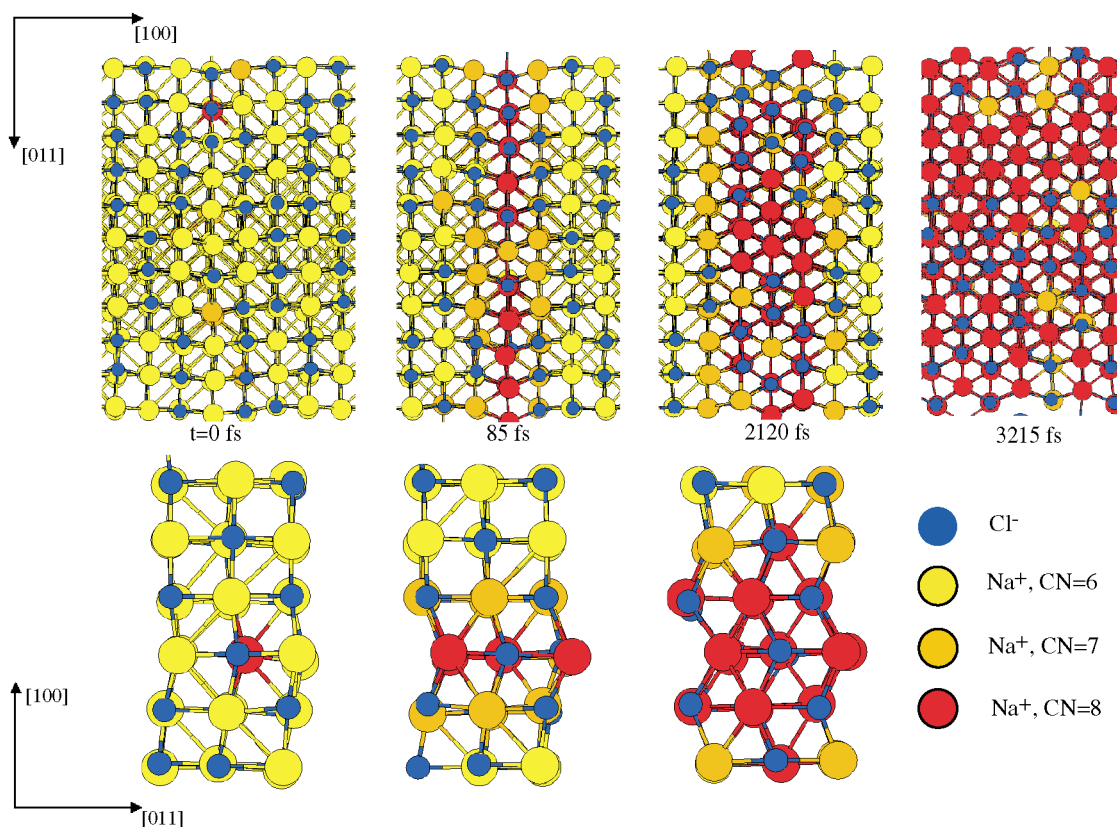

FIG. 1 (color).   Snapshots from a typical trajectory of the NaCl-type to CsCl-type phase transition. The transition is observed to start with a single sodium ion as a nucleation center ($t = 0$ fs). In its neighborhood ions are likely to move in the direction of the first ion displacement. This results in a fast two-dimensional propagation of a CsCl type structure ($t = 85$ fs). Propagation in the perpendicular direction is related to the displacement of planes along the direction of the initial ion displacement ($t = 2120$ fs).

iterations this character is no longer observed and the phase transition occurs via nucleation and growth rather than a concerted transformation of the whole simulation box. Moreover, memory of the underlying mechanism of the initial trajectory was lost and both sampling runs converged to the same type of pathways.

An important feature of the path sampling method is that it may be interpreted in terms of a Monte Carlo sampling of trajectories of a desired process. Thus the relevance of a mechanism may be related to the probability of finding corresponding dynamical pathways. Both of the initial trajectories correspond to concerted phase transitions. The quick convergence of trajectory sampling towards nucleation and growth demonstrates its strong preference over collective pathways.

A representative transition trajectory as obtained from path sampling is illustrated in Fig. 1. The changes in the coordination number of Na^+ ions, from 6 in NaCl-type to 8 in CsCl-type over an intermediate state with coordination 7, are monitored by a color code. The picture is symmetric for Cl^- ions.

Beginning with the displacement of a single atom in the [011] direction with respect to the NaCl unit cell, the motion propagates rapidly to the neighbor atoms in the same (100) layer. After 85 fs the layer has shifted by approximately 1/4 of the face diagonal of the cubic cell. The two closest (100) layers then shift in an antiparallel way with respect to the initial motion, whereby a first inset of CsCl structure type phase appears, which extends over three layers (2120 fs). The outer layers follow, until the transformation to the CsCl structure is accomplished (3215 fs). The orientation of the NaCl- and CsCl-type unit cells with respect to each other corresponds to the one of the model of Hyde and O'Keeffe.

The antiparallel shuffle of (100) layers occurs as a subsequent series of local events, rather than as a concerted movement of all ions in the simulation box. As a consequence we observe an interface between the two regions of pure NaCl or CsCl type structure (Fig. 2). In a very recent paper [19] Toledano *et al.,* in the framework of generalized Landau theory, described a displacive model involving a transformation of the NaCl type to the CsCl type via the α-TlI type ($B33$) structure [20]. This intermediate can be confirmed from our simulations. It is observed only locally as an interfacial (100) layer between the $B1$ and $B2$ phases. In this layer, the coordination number of Na^+ and Cl^- is 7 (Fig. 2). In order to illustrate the dynamics of the interface, we monitored the coordination number of single ions as a function of time. A typical curve is shown in Fig. 3. Coordination numbers of 6, 7, and 8 correspond to the $B1$-, $B33$-, and $B2$-type structures, respectively. In the course of the phase transition, the $B33$ interface propagates along the [100] direction. Hence, the ions remain only temporarily within the B33-type structure. This period varies from 1 to 3 ps. The fluctuations observed in Fig. 3 may be interpreted in
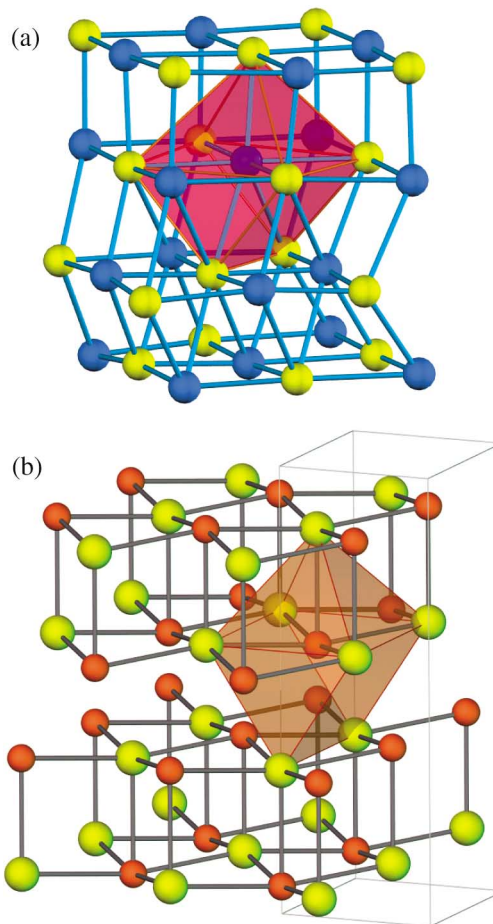

FIG. 2 (color). (a) In the interface region between NaCl- and CsCl-type a structure with coordination number of 7 is formed. Locally, the structure corresponds to α-TlI type structure (b).

terms of attempts in growing of the $B1$ (change in coordination number to 6) and the $B2$ (change in coordination number to 8) phase regions, respectively. Typically we observed 5–15 of such fluctuations, before the ion under consideration is finally consumed by the $B2$ phase. In the molecular dynamics studies prior to this work, elevated pressure and temperature was used to enhance process kinetics [11]. In contrast to the present work, these authors observed concerted transformations corresponding to the Bürger and the Hyde and O'Keeffe pathways [7,8]. We expect this to be a consequence of over-driving the phase transition. This is supported by the fact that in the simulations of Nga and Ong [11] the phase transition occurs on a much faster time scale, entirely skipping nucleation and growth.

It is reasonable to expect the limited box size and the periodicity of the model system to affect our results. The periodic boundary conditions imply an additional coupling of the ions in the simulation box. This tends to favor such transitions, in which the whole model system undergoes the phase transition as a collective movement of all ions. However, even for the small simulation box used, we
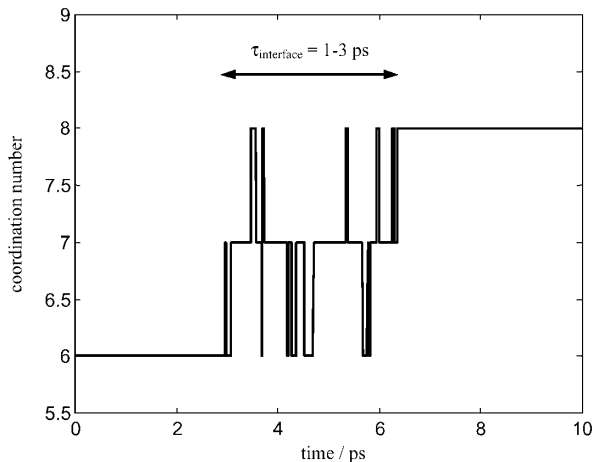
FIG. 3.   Typical evolution of the coordination number of a single ion (Na^+) in the course of the phase transition.

observe nucleation and growth to be strongly preferred. Reducing the finite size effect by choosing larger model systems is expected to even increase the dominance of the nucleation and growth mechanism. It should be stated, that once a new phase is formed, it experiences coupling to its periodic images. This is similar to a situation in which several nuclei are present at low distance and enhance the growth rate of each other. However, we wish to emphasize that this is a finite-size effect. A profound investigation of the validity of classical nucleation theory versus the existence of several correlated nuclei implies much larger model systems.

The effect of the periodic boundary conditions also needs to be considered when discussing the critical nucleus of the phase transition. While a proper analysis of the size of the critical nucleus surely requires much larger simulation systems, we believe our observations concerning its shape to be transferable. During the $B1$ to $B2$ transition, the $B2$ phase was found to grow quickly in the [010] and the [001] direction and at a lower rate in the [100] direction. Accordingly, the shape of the $B2$ region is more similar to a tetragonal prisma, rather than spherical as typically assumed by classical nucleation theory.

In conclusion, we presented a path sampling molecular dynamics study of the pressure-induced phase transition of sodium chloride from the NaCl type to the CsCl type structure. Therein the critical pressure and temperature as taken from experiment are applied. The analysis is based on a manifold of transition pathways. Therein, the relevance of a certain mechanism is related to the probability of finding trajectories corresponding to this mechanism. While initially starting from trajectories based on different transition routes, the path sampling simulations dem-onstrated a clear preference of nucleation and growth rather than a concerted transformation of the whole simulation box.

Our simulations exhibit the formation of an interface with a well-defined structure, which propagates in space during the phase transition. This could not be accessed in the studies prior to this work. Its observation is a benefit of the underlying simulation strategy, enabling the process to be observed from molecular dynamics simulation without applying over-pressurization.

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