

## Molecular Dynamics Simulations of Pressure-Induced Phase Transitions: From Unit Cells to 'Real' Materials

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Phase transitions are fundamental phenomena of nature. A proper description of the nucleation and growth of new structures in response to external stress is of fundamental interest in physics, chemistry and materials sciences. Understanding the underlying mechanisms at the atomic level of detail still constitutes a major challenge to both experiment and theory. For continuous, second-order phase transitions the atomic displacements are typically small. Within classical Landau theory an order parameter can easily be formulated due to the relationship of a group and a (direct) subgroup of space groups of the structures surrounding the phase transition. Reconstructive first-order phase transformations on the other hand involve a dramatic reorganization of the bonds, with large atomic movements, pronounced discontinuities in the physical quantities, and the presence of a hysteresis. Since the symmetries of the limiting structures are not in the relation of a group and a direct sub-

group, there are no a priori preferable ways of mapping the positions from one structure to the other and a large variety of different mechanistic routes may account for the phase transition.

Reconstructive phase transformations are very common in allotropic transitions among the elements, in alloys and covalent compounds, and involve fundamental structure types. Nevertheless, due to the lack of an obvious symmetry relationship and their discontinuous character, involving nucleation and growth of new phases, reconstructive phase transitions have always been considered as the extra-terrestrial among critical phenomena. As a consequence, no unifying approach has been attempted, until now.

Many theoretical approaches to the investigation of structural transformations are based on static models, in which the atomic configurations are interpolated from a limiting symmetry to the other, based on a choice of the reciprocal orientation of

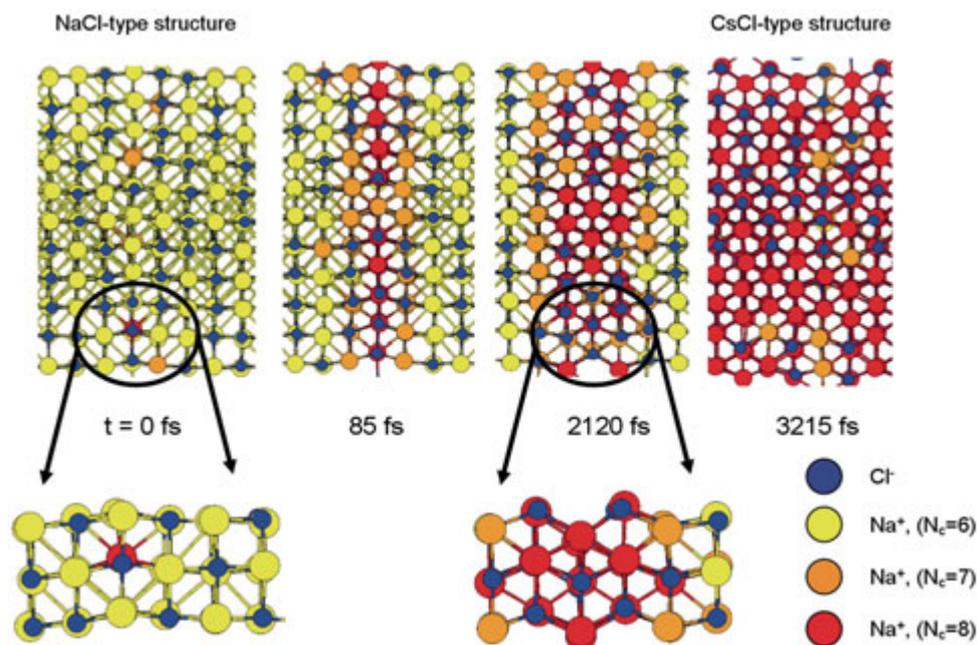


Fig. 1: Snapshots from a typical trajectory of the transformation of NaCl from the rocksalt to the high-pressure modification of CsCl-type structure. The transition starts with a single sodium ion (highlighted in red) as a nucleation center ( $t = 0$  fs). In its neighborhood ions are likely to move in the direction of the first ion displacement. This results in fast two-dimensional growth ( $t = 85$  fs). Growth in the perpendicular direction is related to the dislocation of planes along the direction of the initial ion displacement ( $t = 2120$  fs).

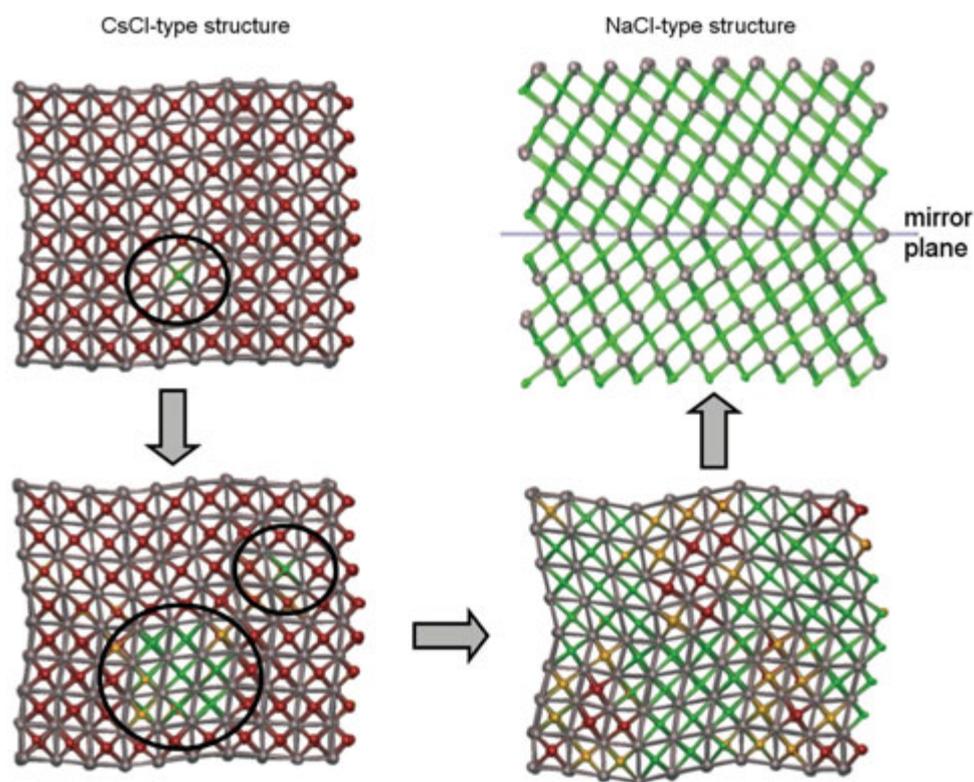


Fig. 2: Left: Formation of independent nucleation centers and temporarily coexisting domains in the simulation box, viewed along the  $[001]$  direction of the CsCl-type structure of KF. The coordination number ( $N_c$ ) of F with respect to  $K^+$  is coded in color using red, yellow and green for  $N_c = 8, 7$  and  $6$ , respectively. Potassium ions are shown in gray. Right: Phase growth from the two nucleation centers eventually results in two domains of the NaCl-type structure exhibiting different orientations. The grain boundaries correspond to mirror planes.

the crystals, that may be argued from experiments. While such approaches allow the investigation of the mechanisms describing the overall displacement of the atoms, the underlying models imply a concerted movement involving all atoms. Not very realistic and of very difficult experimental access, is the insistence on the formulation of an intermediate, albeit metastable structure. The direct observation of heterogeneous processes like nucleation and growth remains elusive.

In principle, constant pressure molecular dynamics simulations appear perfectly suited for a detailed mechanistic study of pressure-induced phase transitions. However, because of the large activation barrier separating the two phases the observation of a spontaneous transition in the short time sketches accessible to standard molecular dynamics simulations is usually very unlikely. In a recent work [1] we have shown that this limitation may be overcome using a simulation strategy based on the transition path sampling algorithm developed by Chandler et al. (see also “*Extending the Scope of ‘In Silico Experiments’: Theoretical Ap-*

*proaches for the Investigation of Reaction Mechanisms, Nucleation Events and Phase Transitions*”). This method does not involve the predefinition of a reaction coordinate and is thus particularly suited for the investigation of reconstructive processes. Instead, the reaction coordinate results naturally from the simulation strategy. Moreover, path sampling does not require enhancing the process kinetics by applying overcritical pressure, which may be of great importance for not biasing the mechanistic analysis [2]. The simulations can be performed at the experimental temperature and pressure (Fig. 1).

In absence of artificial driving forces, we are the first to be able to observe local nucleation events, followed by subsequent phase growth [1-4]. In most of our studies of pressure induced phase transitions so far, only a single nucleation center could be identified. However, in macroscopic crystals phase transitions are known to start from several nuclei. Phase growth from multiple centers is an important phenomenon, since it finally results in grain boundaries or even twinned crystals. The

observation of only a single nucleation center in molecular dynamics simulations is surely a consequence of using finite model systems (and periodic boundary conditions). Provided large enough simulation cells, the observation of several nuclei in a single molecular dynamics run should be possible. While in principle this holds for every crystal, we were able to identify a compound of a particularly high density of nucleation centers. From this we demonstrated the investigation of multi-centered solid-solid phase transitions and the formation of grain boundaries within molecular dynamics simulations of systems counting only a modest number of atoms (potassium fluoride, model of 640 ion pairs, Fig. 2) [3].

The simulation strategy and the numerical setup developed so far can easily be transferred to classes of compounds as different as ionic and covalent

solids, metals, elements and alloys, as well as to finite systems. The realistic parameters and the unique simulation setup make an extensive analysis of the phenomenon of nucleation and grain formation in the solid state for the first time possible.

### References

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