Transition state analysis of solid-solid transformations in nanocrystals

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A systematic simulation methodology is introduced for the accurate determination of experimentally measurable quantities characterizing solid-solid phase transformations under pressure. The atomistic mechanisms of nucleation and growth in a structural transformation of pressurized CdSe nanocrystals are identified using transition path sampling computer simulation. A committor-based transition state analysis is applied to extract activation enthalpies and activation volumes from transformation pathways at experimental conditions. The qualitative dependence of activation enthalpies on nanocrystal size is in good agreement with experimental data and supports the observed nucleation mechanism, which is characterized by a critical nucleus of elongated shape located on the crystal surface. Based on committor distributions along typical transformation pathways, the coordination number is identified as a suitable reaction coordinate for the process.

I. INTRODUCTION

Identifying the atomistic mechanisms of structural phase transformations of solids on the nanoscale is an important step both for a deeper understanding of the physical process itself, as well as for the synthesis of new materials with tailored physical and chemical properties. Size-dependent behavior, typical for the nanoscale, can often be successfully described by simple thermodynamic considerations. For instance, the strong size dependence of the transition pressure that characterizes pressure-induced transformations can be rationalized by models based on surface free energies. However, the specific surface structure and shape of a transformed particle and thus its surface free energy strongly depend on available atomistic transition routes. In materials design, in turn, the facilitation or inhibition of such routes by precise control of surface configuration and shape of the nanoparticle can be a practical way of stabilizing structures that are unstable otherwise.

The thermodynamic and kinetic aspects of nanocrystal transformations have been studied in detail in pressure experiments. Most significantly, Alivisatos and co-workers demonstrated that it is possible to measure activation enthalpies and activation volumes for such processes. Based on this experimental evidence it is possible to speculate about the underlying transformation routes; for an unambiguous identification of the mechanism on the atomistic level, however, experimental time and space resolution currently remain insufficient.

The necessary atomistic perspective is conveniently provided by molecular dynamics (MD) computer simulation. Nevertheless, the significance of a transformation mechanism observed with a computer simulation often remains unclear for two reasons. First, at experimental conditions of temperature and pressure, solid-solid transformations typically involve high kinetic barriers associated with nucleation events. The resulting waiting times often exceed seconds or even hours—timescales vastly out of range for atomistic computer simulations. The usual solution to this problem is to simulate at elevated pressure and temperature, such that transformations readily occur on the accessible picosecond timescale. Under such conditions, however, observed mechanisms will in general not be comparable to mechanisms observed experimentally.

Second, a direct comparison between quantities that are observable both in experiments and simulation is not easily achieved. Activation enthalpies and activation volumes, as measured in experiments, in principle provide an excellent indicator of mechanism because the height of the kinetic barrier is a direct consequence of the specific atomistic pathways. Calculation of such quantities, however, requires the identification of the central part of the transformation, the transition state containing the critical nucleus of the high pressure phase. In particular, it is not sufficient to identify the transformation pattern with the lowest energy barrier on the level of a periodically replicated unit cell. The real nucleation and growth mechanism consists of a series of atomic displacements with possibly different barriers. The overall activation enthalpy, as illustrated in Fig. 1, is then determined by the exact sequence of such steps and depends sensitively on the structure and morphology of the critical nucleus. Moreover, in a nanocrystal certain transformation routes might not be accessible at all because they lead to particularly unfavorable surface configurations.

Here, we extend our previous work and present a systematic methodology that overcomes these problems and establishes direct contact with experiments through the calculation of activation enthalpies and activation volumes at...
conditions close to experiments. We demonstrate its usefulness by identifying the nucleation mechanism of a structural transformation in CdSe nanocrystals. The timescale problem is avoided by means of transition path sampling (TPS), a simulation method for the study of rare events in complex systems. Using the committor, a statistical measure for the progress of the transformation, we identify the critical nuclei of the high pressure phase and calculate the corresponding activation enthalpies and activation volumes. A comparison with experimental values yields good qualitative agreement and supports the mechanism observed in the simulation, which involves a nucleation event on the surface of the crystal and subsequent growth by sliding of parallel crystal planes. Finally, committor calculations are used to assess the quality of putative reaction coordinates, which capture the essentials of the transformations.

Briefly, the proposed methodology consists of the following steps.

1. Transition path sampling simulations of the transformation of interest are performed for various values of crystal size and pressure, identifying the favorable atomistic mechanism.

2. The committor is determined as a function of time for trajectories chosen randomly from all harvested trajectories for given pressure and crystal size. All transition states along the trajectories are identified.

3. Along the same trajectories, the enthalpy and volume of the crystal as a function of time are computed. The average enthalpy and volume of the crystal in the low-pressure structure at the beginning of the trajectory, as well as in the final configuration at the end, are also calculated, giving an estimate of the dependence of the thermodynamic transition pressure on crystal size.

4. For every transition state along a given trajectory, the activation enthalpy and activation volume are determined by comparing enthalpy and volume at the transition state with the respective values of the low-pressure structure. These values are then averaged over all transition states along the trajectory and over all trajectories for given crystal size and pressure. The size and pressure dependence of the activation enthalpy and activation volume can then be compared to experimental values.

5. An analysis of committor distributions along typical transformation pathways identifies a suitable reaction coordinate.

In the following, this procedure and its application to the case of CdSe nanocrystals are discussed in depth. Section II is concerned with the details of the model of CdSe nanocrystals and its applicability to the experimental situation. In Sec. III, we discuss the employed simulation techniques and implementation details; simulation results are presented in Sec. IV.

II. MODEL

We use the empirical pair potential developed by Rabani39 for bulk CdSe. As the potential is the only published model for CdSe we are aware of, its use for the modeling of CdSe nanoparticles is pragmatically justified. Nevertheless, the predictive power of our simulations depends to some degree on the potential’s faithful reproduction of CdSe surface properties. A comparison of select surface properties between the Rabani potential and density functional theory (DFT) is discussed in Appendix A.

The shape of CdSe nanocrystals used in pressure experiments has been determined with electron microscopy, revealing that the crystals have well-defined facets dominated by (001) and (100) surfaces40 and an aspect ratio of about 1.2 in the wurtzite structure. The crystals studied in this work are hexagonal prisms built according to these specifications. Straightforward MD simulations have demonstrated that the transformation mechanisms for this particular crystal geometry decompose into two steps.41 In the first step, (001) wurtzite layers are flattened out, taking the crystal to the five-coordinated $h$-MgO structure. In a second step, the rock-salt structure is reached by a sliding motion of (100) planes. In real crystals, the perfect prismatic shape of the crystal will be degraded by steps and other surface defects. Also, faults in the perfect wurtzite stacking of (001) planes were observed experimentally. Straightforward MD simulations indicate that in crystals, which incorporate such defects, the $h$-MgO structure is not observed as a stable intermediate.41 Nevertheless, we use the $h$-MgO to rocksalt transformation in pristine crystals as a model for the full wurtzite to rocksalt transformation. We do this because preliminary simulations show that in the presence of surface defects transformations can get stuck in metastable intermediate states, resulting in significantly longer trajectories and therewith increased computational effort. The simplified model used here is justified because of two reasons. First, the $h$-MgO to rocksalt transformation is the rate-limiting step, clearly occurring at higher pressures than the step from wurtzite to $h$-MgO. Second, also in simulations using other models,17,25 a significant compression along the $c$-axis of the hexagonal wurtzite lattice was observed with increasing pressure; at the time of the transformation, the crystal is essentially in the $h$-MgO structure. An a priori justification of our approach is provided by the good agreement with experimental data, as discussed in Sec. IV C.
III. SIMULATION TECHNIQUES

A. Ideal gas barostat

The simulation setup consists of a nanocrystal of $N_c$ atoms immersed in a pressure bath that adapts to the shape and size of the crystal and consists of a fluctuating number of noninteracting gas particles, denoted by $N$. These gas particles interact with crystal atoms via a purely repulsive potential that depends only on the particle distance $r$, 

$$u(r) = \begin{cases} 
\epsilon \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r_{cut}}{\sigma} \right)^{-12} & \text{if } r < r_{cut}, \\
0 & \text{if } r \geq r_{cut}.
\end{cases}$$

In our simulations, we use the parameters $\epsilon = 1$ kJ/mol, $\sigma = 3.0$ Å, and $r_{cut} = 6.0$ Å, choices that prevent gas particles from entering the crystal. The simulation box is divided into cubic cells with side length $l = r_{cut} + 0.1$ Å. (See Appendix C for a discussion of this particular choice.) Thus, all gas particles that could possibly interact with crystal atoms in a given cell will be found in the cell itself and its nearest neighbor cells. That given, we define the system volume to be a function of the coordinates of the crystal atoms. At any time, the accessible volume $V$ of the system consists of all cells that contain crystal atoms and all cells adjacent to those. The MD algorithm used to solve the equations of motion for this system can be found in Ref. 37; a Monte Carlo implementation is discussed in Appendix C.

B. Transition path sampling

In straightforward MD simulations, the pressures needed to induce the transformation from wurtzite to rocksalt lie between 5.5 and 10 GPa, depending on crystal size and shape. While these pressures are only moderately higher than those used experimentally, the timescales differ by orders of magnitude. To observe the transformation in a simulation, the pressure has to be increased close to the point where the low-pressure phase becomes unstable. The resulting transformations proceed rather violently, with simultaneous nucleation events at different sites of the crystal and the formation of grain boundaries. 32,23,41

Simulations under experimental conditions can be conducted with TPS, a method that uses a Monte Carlo procedure to sample the ensemble of trajectories that connect two well-defined regions, A and B, in phase space. 35 This restriction of the space of pathways is particularly useful when A and B are separated by a barrier that is large compared to typical thermal fluctuations and the simulation of barrier-crossing trajectories becomes increasingly time consuming with conventional methods. In a TPS simulation, a Markov chain of paths is constructed by means of a trajectory displacement move called shooting, 36 and individual trajectories are accepted or rejected as members of the chain according to a detailed balance condition that ensures correct sampling. While a strong bias is thus applied in trajectory space, the underlying dynamics along individual trajectories remain untouched and true dynamical pathways are observed. In particular, the frequency of occurrence of different mechanisms reflects the one observable in a hypothetical, extremely long conventional simulation run.

C. Committor analysis

After convergence of the mechanism has been achieved in the TPS simulations, we collect at least 10 000 trajectories; from these, we randomly select five for further analysis. A typical converged transformation pathway, displaying the mechanism of sliding (100) planes, is shown in Fig. 2. To identify the transition states, we calculate the committor $p_B$ for all of the 1000 stored configurations along the paths. The committor is a statistical measure for the progress of the transformation and is defined as the probability of a particular configuration of the crystal to relax into state B, the rocksalt structure, rather than into the hexagonal structure. Thus, as the transformation proceeds, the committor changes its value from 0 to 1 and a configuration for which $p_B = 1/2$ is identified as a transition state. 35

We estimate $p_B$ using the computational scheme described in detail in Ref. 35, which ensures a consistent level of statistical error. Starting from every configuration of the crystal along a given trajectory (1000 such snapshots are
stored for any given pathway), short MD trajectories are initiated, each with particle velocities drawn from the appropriate Maxwell–Boltzmann distribution and a freshly created ideal gas atmosphere. When a trajectory reaches either stable state, it is terminated; the fraction of those that reach the rocksalt structure is an estimate for $p_B$ with a Gaussian uncertainty of
\[
\sigma = \sqrt{p_B(1-p_B)/M},
\]
where $M$ is the number of initiated trajectories. To ensure good statistics, a minimum of ten trajectories are performed. Further trajectories are initiated until the configuration at hand can be excluded from the ensemble of transition states with a certainty of 95%, i.e., when the estimate for $p_B$ lies outside the interval $[1/2-2\sigma; 1/2+2\sigma]$. Configurations that live to see a maximum of 100 trajectories are assumed to be transition states. Figure 3 shows the time evolution of the committor for a barrier-crossing event in a typical trajectory. As the crystal crosses the barrier top, repeated recrossings of the $p_B=1/2$ line are frequently observed and up to 25 transition states are identified along a single trajectory.

D. Measuring enthalpy and volume

For the calculation of the crystal’s enthalpy, a measure of its volume is needed that can be consistently compared to experiment. Through the use of the ideal gas barostat, it seems quite natural to use the following definition, which also follows from a thermodynamic theory of small systems. In all our simulations, the volume of the crystal, $V_c$, is calculated as the difference between the total volume of the system, consisting of nanocrystal and pressure bath, and the volume occupied by the pressure bath only, computable from the ideal gas equation of state:
\[
V_c = V - N(\beta P)^{-1}.
\]
As a macroscopic analogy, consider a swimming pool completely filled with water. It follows from the above definition that the amount of water that is displaced by a dog jumping into the pool is a measure for the dog’s volume.

IV. RESULTS AND DISCUSSION

A. Transition states

A compilation of transition states, identified through the committor criterion, is shown in Fig. 4. The shape of the critical rocksalt nuclei is surprising. Regardless of pressure or crystal size, the nuclei always appear on the surface, extending along the hexagonal $c$-axis over the full side length.

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FIG. 3. Committor $p_B$ (black) and $p_A=1-p_B$ (red) along a transition path of a 5 nm nanocrystal, calculated with the scheme described in the text. The point around 13.9 ps where $p_B=p_A=0.5$ marks the transition state.

FIG. 4. Critical nuclei for the $h$-MgO to rocksalt transformation in CdSe nanocrystals, for a series of pressures and crystal sizes. Transparent gray atoms are in the hexagonal structure, blue ones in the rocksalt structure. Crystals have been rotated such that the nuclei appear on the same crystal facet. Note that separate TPS simulations were conducted for every crystal size and pressure; there is no dynamical connection of configurations at different pressures for fixed crystal size.
of the crystal. The transformations begin with the indentation of a (100) side facet, preferably in the facet’s center. The resulting quasi-one-dimensional linear arrangement of atoms, each forming an additional bond with an opposite atom of the next (001) plane, forms the critical rocksalt nucleus at high pressures. At lower pressures, the transition state is reached after the rocksalt slab has grown in one of two equivalent [100] directions and along the lateral surface. This increased size of the critical nucleus at lower pressures is consistent with classical nucleation theory. Close to the thermodynamic transition pressure, the rocksalt structure is favored only slightly over the hexagonal structure. As a consequence, a larger amount of rocksalt is needed to pay the price of the interface than at higher pressures, at which the rocksalt structure is clearly more stable.

The differences of the observed nucleation mechanism to equivalent transformations in the bulk material are evident. In the bulk, nucleation will preferably happen at lattice defects such as grain boundaries that locally facilitate the accommodation of an interface between the low and high pressure structures. In nanocrystals in the size range considered here lattice defects are easily annealed out during synthesis; nucleation from such sites thus is not a possibility. As a consequence, the surface serves as a low energy nucleation site. We speculate that the free energy penalty due to unfavorable strain energetics compared to a nucleus of more spherical shape located on the crystal’s inside.

B. Size dependent transition pressure

A typical phenomenon in phase transformations of small systems is the size dependence of the thermodynamic transition point. For CdSe nanocrystals, a significant increase in transition pressure has been observed with decreasing crystal size. This behavior can be rationalized with simple thermodynamic models, in which different surface free energies are assigned to the two structures. A higher surface free energy in the high-pressure phase, resulting from unfavorable configurations introduced during the transformation, stabilizes the low-pressure phase and pushes the transition pressure to higher values. In both experiment and simulation this behavior is not easily observed because transformations happen far from equilibrium and large kinetic effects obscure comparatively subtle changes in thermodynamics.

Here, we estimate the size dependence of the thermodynamic transition pressure by determining the pressures at which the two structures have equal enthalpy. Using the algorithm discussed above, we calculate the enthalpy-pressure curves of the crystals in the two stable structures in long Monte Carlo runs of 10⁵ cycles each and determine their intersection. As the morphology of the rocksalt crystal is not unique, we calculate enthalpy-pressure curves for all different rocksalt crystals observed with TPS and obtain different transition pressures for different isomorphs. (For 6 nm crystals no TPS simulations were performed; for this size, the calculations were carried out using rocksalt configurations obtained in high-pressure MD runs.) However, typical variations are small (≈0.05 Gpa) and we define the average of the obtained values as the transition pressure for the given crystal size; the resulting data are shown in Fig. 5. Although our simulations reproduce the trend with crystal size observed in experiments, the experimental transition pressures are larger by a factor of about 2. This difference might be partly due to deficiencies of the model used in our simulations. However, the experimental method of assigning the thermodynamic transition pressure to the midpoint of the hysteresis curve presumes that activation energies for the forward and backward transformations show a similar dependence on pressure, an assumption that is not necessarily true. Indeed, an extrapolation of the pressure dependence of the rate constants for both directions of the transformation yields a co-existence pressure of 2.3 GPa for a 2.5 nm nanocrystal.

C. Activation enthalpy and activation volume

To link our results to experiments, we quantify the properties of the observed rocksalt nuclei by calculating their activation enthalpy and activation volume. Using the Monte Carlo algorithm discussed in Appendix C, we calculate the enthalpy and volume as a function of time for all selected transition pathways. For every configuration of the crystal, we average over 1000 realizations of the pressure bath with crystal atoms held fixed. The resulting curves are exemplarily shown in Fig. 6 for the transformation of a 3 nm crystal at 2.5 GPa. To dispose of short-lived fluctuations, we perform the following smoothing operations. First, we average enthalpy and volume over time intervals of 0.5 ps. We then correct for fluctuations of the crystal kinetic temperature $T_{kin}$ around the bath temperature $T_0=300$ K. In a harmonic approximation, these fluctuations offset the potential energy $U^{(co)}$ of the crystal by $3/2N_kB(T_{kin}-T_0)$, which we subtract from $U^{(co)}$. Recent work strongly indicates that such a harmonic approximation is valid even in regimes of high pressure and temperature. We note, however, that the applied smoothing is not essential to the calculation and merely reduces the spread of activation enthalpies and activation volumes determined from different pathways.

Finally, the activation enthalpy (and similarly, activation volume) is obtained as the difference of the enthalpy at the transition state and the average enthalpy in the $h-MgO$ structure, as shown in Fig. 6. Values for different transition states along a given trajectory are averaged to give single-pathway
activation enthalpies, which in turn are averaged over all five analyzed pathways to obtain the activation enthalpy for a given crystal size and pressure.

In Fig. 7, activation enthalpies and activation volumes are compared with experiment. The size dependence of the experimental activation enthalpies, which were obtained from the temperature dependence of the rate constant at a pressure of 4.9 GPa, is in good agreement with data we obtained at 3 GPa. The discrepancy with regard to absolute values is not surprising and most likely due to deficiencies of the simple pair potential used in our simulations, which were designed to reproduce selected properties of bulk CdSe. On the other hand, the almost linear dependence of the enthalpic barrier on the crystal diameter is found in both experiment and simulation and is consistent with the particular shape of the critical nuclei shown in Fig. 4. With increasing crystal size, the critical rocksalt nuclei expand primarily in one direction. Previously it was speculated that nanocrystals in the size range considered here would transform not through local nucleation and growth but in a single step, through a concerted motion of all crystal atoms. Such a mechanism, however, would result in an activation enthalpy that scales with the volume of the crystal, a behavior not observed in this work.

The comparison of activation volumes is complicated by the fact that, experimentally, activation volumes were determined at slightly different conditions than activation enthalpies, namely, from changes in the rate constant as pressure was varied between 5 and 7 GPa, assuming a constant value of the activation volume in this pressure range. Our simulations, however, indicate that the activation volume depends sensitively on the applied pressure. Thus, agreement between experiment and simulation might be expected to occur at higher pressures compared to activation enthalpies; indeed, we find fair agreement at 4 GPa.

Clearly, the observed trends with crystal size of activation enthalpy and activation volume can not continue to the bulk limit, where transformations are characterized by a critical nucleus of finite size that preferentially forms at defect sites of the crystal lattice. The transition to this different regime can be expected to occur at crystal sizes at which the concentration of such defects is no longer negligible.

D. Reaction coordinates

To substantiate the nucleation and growth scenario emerging from the visual inspection of the transition states, we identify the reaction coordinate, a dynamically relevant measure for the progress of the transformation. In principle, the committor $p_B$ is the ideal reaction coordinate in the sense that it tells what is likely to happen next. However, due to its unspecific nature, the committor does not provide direct insight into the transition mechanism nor can it be controlled in an experiment. Thus, it is desirable to express the committor in terms of variables with a transparent physical significance. As such a coordinate we propose to use the number of six-coordinated atoms, $N_6$, which can be viewed as a measure for the size of the rocksalt nucleus forming in the hexagonal matrix.

In contrast to the simple discrete criterion discussed in Appendix B, $N_6$ is calculated using a continuous distance criterion. Every pair of atoms is assigned a “bond length” $d_{ij}$ according to

$$d_{ij} = \begin{cases} 
1 & \text{if } r_{ij} < a, \\
\frac{b - r_{ij}}{b - a} & \text{if } a < r_{ij} < b, \\
0 & \text{if } r_{ij} > b.
\end{cases}$$

(4)

Here, $r_{ij}$ is the particle distance, $a = 3.0$ Å and $b = 4.8$ Å. (These values delimit the broad first minimum of the radial distribution function of unlike atom species.) The coordination number of particle $i$ is defined by summation over all

![FIG. 6. Enthalpy (top) and volume (bottom) as a function of time for a sample transformation pathway of a 3 nm crystal at 2.5 GPa. The gray field marks the interval in which the committor $p_B$ changes from 0 to 1, the dotted line indicates the transition state at $p_B=0.5$, which coincides with the top of the enthalpic barrier. Red and blue lines indicate the values of enthalpy and volume in the metastable h-MgO and rocksalt structures, respectively. By comparing values of enthalpy and volume at the transition state with those in the hexagonal structure, the activation enthalpy $\Delta H$ and volume $\Delta V$ can be easily determined. Reprinted with permission from Ref. 32. Copyright 2009 American Chemical Society.](image1)

![FIG. 7. Size and pressure dependence of activation enthalpy (top) and volume (bottom). Black dots with error bars indicate experimental data (Ref. 14). Reprinted with permission from Ref. 32. Copyright 2009 American Chemical Society.](image2)
atoms of the other species, \( c_j = \sum d_{ij} \). Correspondingly, we define the number of \( z \)-coordinated atoms as \( N_z = \sum d_z(c_i) \), with the function

\[
f_z(c) = \begin{cases} 
1 - |c - z| & \text{if } z - 1 < c < z + 1, \\
0 & \text{else.} 
\end{cases}
\]

FIG. 8. A good reaction coordinate: Committor \( p_B \) as a function of the fraction of six-coordinated atoms, \( n_6 = N_6 / N_c \), for configurations collected from transition pathways of a 3 nm nanocrystal at a pressure of 2.5 GPa. The solid curve is a fit to the data and the dashed curves indicate the 3σ-confidence interval around the fit. Only 14.8% of the data points fall outside of this interval, which is consistent with the statistical uncertainty of our committor calculation.

Figure 8 shows the committor versus the fraction of six-coordinated atoms, \( n_6 = N_6 / N_c \), for 330 configurations taken from four different transition trajectories of a 3 nm nanocrystal at a pressure of 2.5 GPa. As can be inferred from the figure, a particular value of \( n_6 \) specifies the corresponding value of the committor with good accuracy, indicating that \( N_6 \) is a satisfactory representation of the nucleation mechanism. The remaining spread of the data points is consistent with the statistical uncertainty of the committor calculation. To support this argument, the function \( p(n_6) = \frac{1}{2} [1 + \text{tanh}(a(n_6 - b))] \) is used for fitting as a possible parametrization of the committor in Fig. 8. If this parametrization is perfectly valid, all deviations of the data points from \( p(n_6) \) must be due to statistical errors because of the finite number of trajectories, \( M = 100 \) in this case, that are used to determine the committor of each configuration. Assuming Gaussian statistics, the standard deviation of \( p_B \) is given by Eq. (2); the corresponding 3σ-confidence interval is indicated in Fig. 8 and includes most of the data points.

As an example of a rather poor reaction coordinate, Fig. 9 displays an analogous analysis for the crystal volume. Although the volume changes considerably during the transformation, it is not a satisfactory indicator of the progress of the transition because of large fluctuations in configurational degrees of freedom that are not relevant for the nucleation event. Only slightly better results are achieved for the simple discrete coordination criterion discussed in Appendix B, which is insensitive to small changes in bond angles and distances which play an important role during nucleation.

The success of \( N_6 \) as a reaction coordinate is a direct consequence of the small size of the crystals and the uniformity of the rocksalt nuclei. When crystal size is increased toward the bulk limit, nucleation from different sites becomes important and \( N_6 \) ceases to be a good reaction coordinate because many uncorrelated rocksalt nuclei of subcritical sizes may lead to \( N_6 \) values that are characteristic for the critical nucleus in the nanoscale crystal. Then, a cluster criterion identifying contiguous regions of six-coordination is required for the definition of a good reaction coordinate.

V. SUMMARY

In the study of phase transitions, a direct comparison between experiment and MD computer simulation is often difficult to achieve due to long experimental time scales and a lack of properties that are easily determined with both methods. For the case of structural transformations, we introduce a systematic simulation methodology, which allows to make direct contact with experiments through the calculation of activation volumes and enthalpies. Simulations under experimental conditions are performed with TPS, a technique based on a statistical description of pathways, which is able to identify the most important mechanistic route of the transformation. Pathways generated with this technique are subject to a committor analysis, which yields transition states containing the critical nuclei of the product phase and gives access to the desired quantitative properties.

As a case of special interest, we apply this methodology to the pressure-induced transformation in a model of CdSe nanocrystals suspended in an explicit pressure bath. Our results explain the size trend of activation enthalpies observed experimentally in terms of a critical nucleus of elongated shape located on the crystal surface and highlight the different nucleation mechanisms in bulk and nanocrystalline systems. Although applied here to the latter, the methodology is applicable also to the bulk case and also to other transformations of condensed matter systems frequently studied with computer simulations.

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APPENDIX A: SURFACE PROPERTIES OF CRYSTAL MODEL

The Rabani pair potential for CdSe consists of a short-ranged Lennard-Jones part and Coulombic interactions and was parametrized to reproduce the elastic and lattice constants of bulk CdSe. While the simple ionic character implicitly assumed in the model is confirmed for the bulk material by density functional calculations, the surface properties of crystals modeled with the potential have not been studied yet. Here we compare the energies needed to evaporate a CdSe pair from the (100), (001), and (001̅) surfaces of a nanocrystal with DFT calculations. We prepare the crystal with bulk lattice constants and relax it, using the Rabani model, at 0 K. We then remove a pair of Cd and Se atoms from the center of the respective surfaces. The evaporation energy is defined as the difference between the energy of the relaxed $\text{Cd}_{216}\text{Se}_{216}$ crystal and the energy of the resulting $\text{Cd}_{215}\text{Se}_{215}$ crystal plus the energy of an isolated, relaxed CdSe dimer. We calculate these numbers both with the Rabani model and $\text{VASP}$, using projector augmented wave potentials. As shown in Table I, we find good qualitative agreement.

APPENDIX B: DEFINITIONS OF INITIAL AND FINAL STATES

In a TPS simulation, the initial and final states A and B, here the $h$-MgO and rocksalt structures, need to be well-defined regions in configuration space (or, more generally, phase space). These definitions should be chosen with care, as they must provide both a clear distinction between A and B and incorporate most of the equilibrium fluctuations within the states as well as all possible isomers. Often, this can be achieved with a suitable order parameter. In our case, a natural choice for such a parameter is the number of atoms with six nearest neighbors. Atoms are assumed to be nearest neighbors if their distance is smaller than 3.4 Å, a value roughly equal to the location of the first minimum of the radial distribution function. For crystals with diameters of 2, 3, 4, and 5 nm we use increasing thresholds of 8%, 20%, 30%, and 40% six-coordinated atoms, reflecting the decreasing surface-to-volume ratio, to define the rocksalt structure. These values, as confirmed by committer analysis, lie safely beyond the values at the transition state but still allow the formation of all relevant isomers in the rocksalt structure. Preliminary simulations showed, however, that the use of the same order parameter for the definition of the $h$-MgO structure is problematic. Values that are too low do not include all equilibrium fluctuations within A, while with larger values at higher pressures critical rocksalt nuclei are frequently assumed to lie in A—correct sampling of trajectories is corrupted. We therefore use a bond angle criterion to define A. The angles between nearest neighbors atoms that have a value of 120° in the perfect $h$-MgO structure are monitored and the crystal is assumed to be in state A only when none of these angles exceeds the ideal value by more than 35°. While this definition excludes all other possible isomers of the crystal in the $h$-MgO structure, we confirmed that no trajectories are rejected because they lead to such incompatible morphologies. This indicates that the hexagonal prismatic shape, which is also observed experimentally, provides a strong basin of attraction for the sampled trajectories due to particularly favorable surface free energies.

APPENDIX C: A MONTE CARLO ALGORITHM FOR THE IDEAL GAS BAROSTAT

For the study of atomistic transformation mechanisms with computer simulation, MD is the natural choice. In previous work we have shown how a barostat of ideal gas particles can be implemented efficiently within a MD simulation such that it conserves the probability distribution of a system at constant pressure and temperature. However, for the calculation of static quantities like the average energy a Monte Carlo version of the barostat might be advantageous. In this section we present such a Monte Carlo algorithm and show that it obeys detailed balance.

The probability distribution of the compound system, consisting of crystal and pressure bath, is given by
\[ \rho(x) = e^{-\beta(U + PV - \mu N)} , \]  
(C1)
where $x$ denotes the state of the system, specified by the positions of all particles, $U = U^{(cc)} + U^{(cg)}$ is the total energy of the system with contributions $U^{(cc)}$ and $U^{(cg)}$ from crystal-crystal and crystal-gas interactions, respectively, $P$ is the pressure, $\mu$ is the chemical potential of the ideal gas, and $\beta = 1/k_B T$ is the reciprocal temperature. To ensure that this probability distribution is conserved in our simulation, it is sufficient that the Monte Carlo moves used to evolve the system from an "old" state $o$ to a "new" state $n$ obey the detailed balance condition,
\[ \frac{p(o \rightarrow n)}{p(n \rightarrow o)} = \frac{N_n!}{N_o!} e^{-\beta(U_o-U_n+PV_o-PV_n-\mu(N_o-N_n))} . \]  
(C2)
Here, $p(o \rightarrow n)$ is the transition probability to go from state $o$ to state $n$ and the subscripts indicate respective quantities in these states. As discussed in Ref. 37, the prefactor accounts for all possible computer representations of a given physical state.

To sample the distribution given by Eq. (C1), we consider two different Monte Carlo moves. The first one is a standard displacement move of a single crystal atom, with all other particles fixed. A crystal particle is chosen at random and displaced by a small vector, whose components are drawn from a distribution symmetric about zero. For such a move, $p(o \rightarrow n)$ is the product of the probability $\sigma(o \rightarrow n)$ to try the move and the probability $\alpha(o \rightarrow n)$ to accept it,
\[ p(o \to n) = \pi(o \to n) \alpha(o \to n). \]  
(C3)

As the system volume and number of gas particles are left unchanged, detailed balance is satisfied by the standard Metropolis acceptance probability, \( \frac{1}{\sqrt{2\pi kT}} \), which takes into account the total change in energy,

\[ \alpha(o \to n) = \min[1, e^{-\beta(E_n - E_o)}]. \]  
(C4)

The second move affects the ideal gas atmosphere. Instead of displacing single gas particles, we want to resample the whole atmosphere in one step. Such a global move greatly enhances the efficiency of the calculation of static averages because successive realizations of the ideal gas atmosphere are uncorrelated; in a MD simulation, decorrelation will be typically reached after a few picoseconds. To resample the gas atmosphere, we proceed in the following way:

1. remove all gas particles from the simulation,
2. determine the system volume \( V_n \), that is, the total volume of all cells that contain crystal atoms and their next-neighbor cells, and
3. fill the accessible volume with new gas particles. To this end, perform \( k \) trial insertion moves, where \( k \) is a number drawn from a Poisson distribution,

\[ \mathcal{P}(k) = \frac{k^k e^{-k}}{k!}, \]  
(C5)

with an average of

\[ \bar{k} = \beta PV_n. \]  
(C6)

One such insertion move consists of the following steps. Choose the position \( r \) of the gas particle uniformly distributed over the total available volume; compute the interaction energy \( E(r) \) of the inserted gas particle with all crystal atoms; accept the insertion move with probability \( e^{-\beta E(r)} \).

This procedure is on average performed every \( N_c \) crystal particle displacement moves.

We now show that the above algorithm satisfies detailed balance. Because of a possibly large interaction energy with crystal atoms, in general not all of the \( k \) inserted particles will “survive” the acceptance criterion. As a result, there are many possible realizations of the move \( o \to n \) leading to a final number of \( N_n \) accepted gas particles at positions corresponding to state \( n \). Thus, \( p(o \to n) \) is the sum of the probabilities of all such realizations,

\[ p(o \to n) = \sum_{k=N_n}^\infty \mathcal{P}(k) \left( \frac{k}{N_n} \right)^{e^{-\beta E(o)}} (1 - \Pi_o)^{N_n - N_n} \frac{V_n^{N_n}}{V_n}, \]  
(C7)

where \( 1/V_n^{N_n} \) is the probability to put \( N_n \) particles in the right places and \( e^{-\beta E(o)} \) is the probability to accept them there. The factor \( \Pi_o \) denotes the probability that any one insertion move will be accepted, which depends on the positions of the crystal atoms and on the available volume \( V_n \),

\[ \Pi_o = \frac{1}{V_n} \int \frac{d\mathbf{r} e^{-\beta E(r)}}{V_n} \]  
(C8)

The factor \( (1 - \Pi_o)^{k-N_n} \), therefore, gives the probability that \( k-N_n \) of the total \( k \) insertion moves will be rejected. Inserting Eqs. (C5) and (C6) into Eq. (C7) we have, after some manipulation,

\[ p(o \to n) = \frac{\beta PV_n}{N_n!} \left( \frac{N_n}{V_n} \right)^{e^{-\beta E(o)}} (1 - \Pi_o)^{N_n - N_n} \]  
(C9)

where in the last step we have identified the fugacity of the ideal gas, \( e^{\beta \mu} = \beta P \). The ratio of transition probabilities of the forward and backward moves now becomes

\[ \frac{p(o \to n)}{p(n \to o)} = \frac{N_n!}{N_n} \left( \frac{N_n}{V_n} \right)^{e^{-\beta E(o)}} (1 - \Pi_o)^{N_n - N_n} \]  
(C10)

As the move affects only gas particles, \( U^{(cg)}_n - U^{(cg)}_o = U_n - U_o \), and this expression is identical to the detailed balance condition of Eq. (C2), except for the volume terms. However, if no new cells have been added to or removed from the simulation in step 2 of the algorithm, \( V_n = V_o \) and \( \Pi_o = \Pi_o \), and detailed balance is obeyed. In case the system volume has to be changed because since the last update of the gas atmosphere crystal atoms have been moved into or out of cells that do not hold any other crystal atoms, the respective volume terms do not cancel out. In this case, we can make use of the fact that gas particles in the cells that are removed or added do not interact with crystal atoms. (This is true only if the side length of the cells is larger than the cutoff distance of the gas-crystal interaction, and the number of crystal atom displacements between successive updates of the gas atmosphere as well as the maximum size of the particle displacement is not too large.) Then,

\[ \Pi_o = \frac{1}{V_n} \left( \int_{V_o} d\mathbf{r} e^{-\beta E(r)} - \int_{V_n} d\mathbf{r} + \int_{V_n} d\mathbf{r} \right) \]  
(C11)

where we have introduced the symbols \( V^- \) and \( V^+ \) for volume that is removed and added, respectively. Using this relation, it follows that

\[ V_n \Pi_o - V_o \Pi_o = V^+ - V^- = V_n - V_o. \]  
(C12)

Also in this case, detailed balance is thus obeyed. The last two equations reflect the fact that although the volume of the total system may change, the volume of the crystal is constant during the move. Therefore, a possible change of the total volume is equaled by the change of the volume available to gas particles. Note the connection between VII and the definitions of crystal and gas volume introduced in Sec. III D. II is given by the average number of inserted gas
particles $N$ (with crystal atoms held fixed) divided by the average number of trial insertion moves $\beta PV$; thus $\mathbb{V} = (N\beta P)^{-1}$ is the volume available to gas particles.

44. T. L. Hill, Thermodynamics of Small Systems (Dover, New York, 1994).