Transient Polymorphism in NaCl

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Ⓢ Supporting Information

ABSTRACT: We introduce a new collective variable (CV) that can be used to increase the frequency with which nucleation events are observed in biased atomistic simulations. This CV forces the ions to aggregate into clusters but does not force the ions to order themselves in a particular pattern. We perform metadynamics simulations using this CV in order to examine nucleation in a solution of sodium chloride and find that for small cluster sizes the usual bulk rocksalt structure is less stable than a structure that resembles wurtzite.
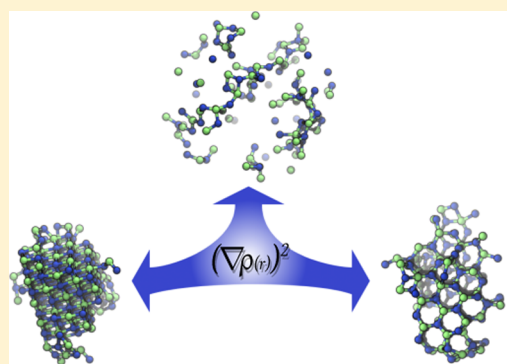
1. INTRODUCTION

Generating crystalline forms of chemical substances is critical in modern industrial chemistry. The crystalline form of a compound affects its processability and in some case its performance. There is thus an enormous amount of interest in understanding, and eventually controlling, the way that atomic order emerges as substances crystallize from solution or melt.[1] This process is composed of two stages: an initial nucleation followed by subsequent growth of the crystal to macroscopic size. The nucleation stage is usually the rate determining step for crystallization and is particularly difficult to understand. Obviously, during nucleation the first aggregates of particles must form together with a surface that separates the solution phase from the nascent crystal. These aggregates are typically very small, which makes it difficult to probe their structures. Furthermore, in many experiments, seed crystals are added so as to bypass the slow nucleation stage entirely.

Classical nucleation theory (CNT) is well-established and has been widely used to rationalize the results from simulations of crystallization in the melt.[2−4] However, it fails to explain a number of phenomena that have been observed in experiments on crystallization. For instance, during the early stages of crystallization, unstable polymorphs often form and subsequently convert into the more stable one. In addition, small, long-lived, prenucleation clusters can be found in solutions of inorganic compounds such as calcium carbonate.[5] Probing these phenomena with simulations is difficult because the time and length scales that are accessible in molecular dynamics (MD) simulations are considerably shorter than the time scales on which these complex processes occur. Consequently, in many simulations where nucleation-like events were observed the concentrations were increased well beyond the saturation threshold in order to increase the rate of nucleation.[6,7] This is problematic because other simulations have shown that the nucleation mechanism changes when the thermodynamic driving force is large.[4] Hence, dramatically increasing the supersaturation could affect the nucleation mechanism.

An alternative way of increasing the rate of nucleation is to use an enhanced sampling technique such as metadynamics.[8] These methods introduce a bias potential that acts along a few, user-selected collective variables (CVs) that describe the interesting chemical processes. This form of biasing has been used to examine the association of small numbers of ions in solution and to increase the frequency with which the nucleation events occur in studies on crystallization from the melt.[3,4,8−11] Recently, Trout and Santiso[12] used one of these methods to examine the nucleation of organic crystals in the melt and from solution. In their work, they used CVs that describe the local structure in the crystalline phase they wanted to form. This forces the crystal to form in the particular phase requested, which could present a problem if the initial crystalline nucleus has a structure that differs from that of the final bulk phase. An alternative has thus been to generate nuclei by adding one atom at a time.[13] However, when nuclei are generated in this way, a number of difficult to justify approximations about the nucleation mechanism have to be made.

The choice of CV is less critical when methods such as transition path sampling are used to understand nucleation, and a number of interesting studies of this process have been done using this technique.[14] Even in these studies, however, collective variables that distinguish the nucleated state from the solution state are still required. In this work, we propose just such a CV and use it to drive the nucleation of NaCl from solution. Our CV does not force a particular phase of NaCl to form and does not make strong assumptions as to the nucleation mechanism. We are thus able to observe all the species that form during the early stages of nucleation.

2. RESULTS AND DISCUSSION

Our new CV distinguishes between configurations in which the solute particles are distributed uniformly across the solution from those in which there are small aggregates. In developing this CV we took inspiration from the Ginzburg−Landau[15] theory of phase transitions, which uses a Taylor series expansion as a function of a defined order parameter:

$$S = \frac{1}{2} \int d\mathbf{r} (\nabla \rho(\mathbf{r}))^2 \tag{1}$$

to express the free energy of the system. When $\rho(r)$ is the solute density in the simulation box, this quantity distinguishes configurations in which the solute is distributed uniformly from inhomogeneous arrangements that contain crystal−liquid interfaces. To simulate the formation of solid nuclei in the melt, $\rho(r)$ in the above could be replaced by a spatially averaged value for the Steinhardt parameter Q_6.[16] This function would distinguish between regions where the particles were arranged as they are in a solid from those where the structure is liquid-like.

As in the original Landau theory, we use coarse graining to calculate $\rho(r)$. We take our cue from classical Density Functional Theory (DFT) and use a weighted density.[17]

$$\rho(r) = \sum_{i=1}^{N} \frac{1}{\sigma^3 (2\pi)^{3/2}} \exp\left(-\frac{(\mathbf{r} - \mathbf{R}_i)^2}{2\sigma^2}\right) \tag{2}$$

where the $\mathbf{R}_i$ are the atomic positions and σ is a smoothing length. To calculate the gradient in eq 1, we subdivide each axis into M slabs and compute the number of solute particles in slab j using

$$n_j^x = \int_{L/M(j)}^{L/M(j+1)} dx \int_0^L dy \int_0^L dz\, \rho(\mathbf{r}) \tag{3}$$

where L is the box length. The gradient operator can then be approximated as

$$s = \sum_{j=1}^{M} \left[(n_j^x - n_{j+1}^x)^2 + (n_j^y - n_{j+1}^y)^2 + (n_j^z - n_{j+1}^z)^2 \right] \tag{4}$$

Periodic boundary conditions are taken into account by imposing $n_{M+1}^x = n_1^x$ for x, y, and z. Expressing the density using Gaussian functions instead of delta functions in eq 2 reduces the fluctuations and allows us to write analytical derivatives for s. Furthermore, classical density functional theory suggests that the σ parameter in eq 2 should be set equal to L/M.

The fact that we can write analytical derivatives is important as it ensures that we can use biasing methods such as metadynamics. In these methods, an additional bias potential is

written as a function of a collective variable that describes the process of interest. For metadynamics, this potential is history dependent and is given by

$$V_G(s, t) = \sum_{t'} h \exp\left(-\frac{(s(t) - s(t'))^2}{2w^2}\right) \tag{5}$$

In this work, $s(t)$ is the value of the gradient CV at time t, and h and w are parameters. The bias is thus a sum over repulsive Gaussians that are centered on the values of the gradient that were visited during previous time steps. Clearly, these repulsive Gaussians force the system to move to configurations with relatively large gradients so the frequency of nucleation-like events is dramatically enhanced.

To test this new CV, we ran a metadynamics simulation on a 6.15 M (0% supersaturation) solution of sodium chloride composed of 360 NaCl formula units distributed randomly in a cubic box of sides 4.56 nm containing 2531 water molecules. This calculation was run using gromacs-4.5.5[18−21] patched with a modified version of PLUMED-1.2.2.[22] To model the interactions, we used the gromos53a6[23] force field for the ions and SPC/E[24] for the water—a combination that reproduces the free enthalpy of hydration of the ions.[23] Electrostatic interactions were calculated using the particle mesh Ewald sum, while nonbonded terms were cut off at 1.0 nm. In all calculations, the simulation time step was 2 fs. The solution was first equilibrated for 4 ns at a temperature of 300 K and a pressure of 1 bar using a Parrinello−Rahman barostat that only allowed tetragonal distortions[25] and that had a relaxation time of 1 ps. A 50 ns production metadynamics calculation was then run in which the volume was fixed and the temperature was maintained using a velocity rescaling thermostat[26] with a relaxation time of 0.1 ps. To calculate the CV defined in eq 3, we divided each box axis into six equal-volume slabs and set $\sigma = 0.4$ nm. For the metadynamics, Gaussian hills with h equal to 1.5 kJ mol^{-1} and w equal to 3 were added every picosecond. The evolution of the gradient CV during this simulation is shown in Figure 1. This figure clearly shows that the bias potential encourages the system to form aggregates of sodium and chloride ions by driving the gradient toward relatively high values. When we examine the trajectory, we find that the clusters that form when the gradient is large are for the most part amorphous and strongly hydrated. These structures
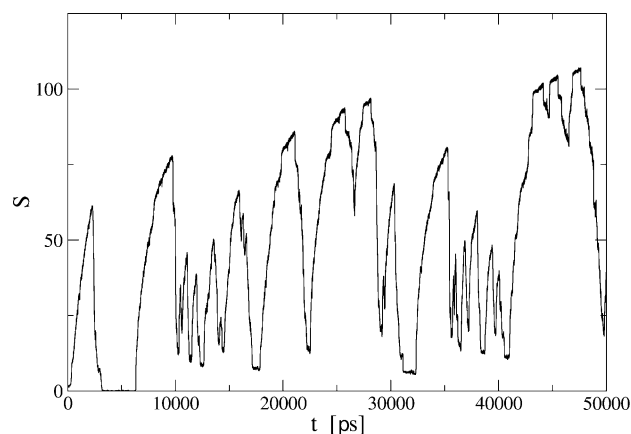

Figure 1. The evolution of the CV during the simulation. When the CV is large, aggregates of ions are present; when it is small, the ions are distributed uniformly through the solvent.

are not stable— in unbiased MD they tend to redissolve in about 1−2 ns. On occasion, we also find ordered structures, examples of which are shown in Figure 2. These ordered nuclei
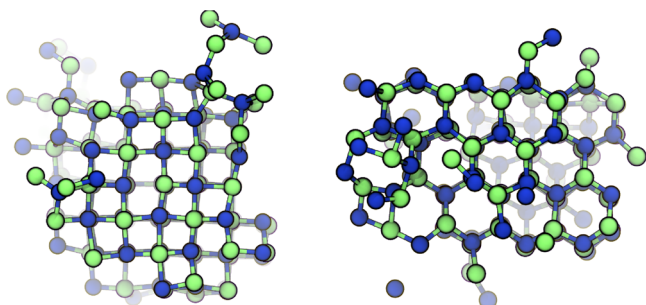

Figure 2. Snapshots of two of the ordered nuclei that form during our metadynamics simulation. The left panel shows the rocksalt nuclei, while the right panel shows the novel wurtzite-like structure.

have one of two possible structures. In the first structure, which is shown in the left panel of Figure 2, the sodium and chloride ions form the familiar rocksalt structure. Rather surprisingly, the second structure is a wurtzite structure, an unusual arrangement for a purely ionic system which would normally form more highly coordinated structures like rocksalt because of the strong Coulombic forces. Both of the structures shown in Figure 2 have a considerably longer lifetime than the amorphous aggregates. When we remove them from the solution and place them in water, we find that it takes on the order of 25−30 ns of unbiassed MD for them to redissolve. Furthermore, in a number of these simulations, we find that the rocksalt structure converts spontaneously to the wurtzite structure before redissolving. To further test the stability of this structure, we ran a 30 ns simulation of a 3 nm wurtzite nucleus in a saturated solution. The nucleus changed shape during this simulation but did not redissolve or undergo a phase transition to rocksalt.

To test that the wurtzite structure is not simply an artifact of our classical potential, we performed a geometry optimization, using density functional theory, on the bulk structure. This optimization was performed using CP2K,[27] the BLYP[28,29] exchange correlation functional, a TZVP basis function, and Goedecker−Teter−Hutter pseudopotentials.[30] Negligible structural changes are observed during the optimization, and there is a clear minimum in the energy versus volume curve. It is thus clear that the wurtzite structure corresponds to a true physical, metastable minimum in the potential energy landscape for bulk sodium chloride. Furthermore, this structure has an energy that is only 11.3 kJ mol^{-1} higher than that of rocksalt.

The evidence from the DFT and metadynamics calculations presented thus far suggests that the wurtzite structure is stable and that it may in fact participate in the NaCl nucleation. To test this assertion we would need to calculate the relative free energies of similarly sized rocksalt and wurtzite nuclei, which would be very difficult. If, however, we are willing to assume that the nuclei are spherical, we can use classical nucleation theory to approximate the difference, $\Delta\Delta G(r)$, between the free energies of formation of wurtzite and rocksalt nuclei of radius r as

$$\Delta\Delta G(r) = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \Delta\gamma \qquad (6)$$

where ΔG_v is the per volume difference in free energy between the two bulk phases and $\Delta\gamma$ is the difference between the

surface tensions of the two phases. The value of ΔG_v can be calculated by running short MD simulations on the two bulk phases. Supercells of 512 atoms for each of the structures were equilibrated during 3 ns NPT simulations before production calculations of 10 ns in the NVT ensemble at 300 K. From these production runs, the average total energies were calculated. Entropies were calculated using the quasi-harmonic approximation as implemented in gromacs-4.5.5.[18−21] The free energy of the rocksalt was found to be approximately 20% lower than that of the wurtzite structure (see Table 1).

Table 1. Per Volume Enthalpies, Per Volume Entropies, and Surface Tensions for the Rocksalt and Wurtzite Structures[a]

	H_γ [kJ mol^{-1} nm^{-3}]	S_v [kJ mol^{-1} nm^{-3} K^{-1}]	γ [mN m^{-1}]
rocksalt (6.15 M)	35.17	0.016	162. ± 2.0
wurtzite (6.15 M)	29.12	0.013	145. ± 4.0
rocksalt (0 M)	35.17	0.016	309. ± 3.0
wurtzite (0 M)	29.12	0.013	54. ± 6.0

[a]The errors for the bulk enthalpies are insignificant (10^{-4} kJ mol^{-1} nm^{-3}). Entropies are calculated using the quasi-harmonic approximation and are exact under that approximation.

Values for the surface tensions in eq 6 were calculated using the Kirkwood equation, which relates the surface tension to the stress tensor of the cell.[31] For wurtzite, an NVT simulation of the interface between the $(10\bar{1}0)$ surface and a saturated solution was performed, while for rocksalt the (100) surface was used. These particular surfaces were selected because they were the ones we most frequently observed in our metadynamics simulation. In our calculations of the surface tensions, the solution was twice the thickness of the NaCl slab. These calculations showed that the surface tension of the wurtzite structure is approximately is 10% lower than that of the rocksalt (see Table 1). Furthermore, as shown in Figure 3, an analysis of the structure of the water layers in contact with the sodium chloride surface explains why. When the NaCl ions in the crystal are arranged like the water molecules in ice (as they are in wurtzite), the water layers immediately above the surface are able to form a structure in which the surface is fully solvated, and the network of hydrogen bonds in the liquid is not greatly disrupted. When the NaCl ions are arranged in the rocksalt structure, this is not the case. To hydrate the rocksalt surface, molecules must be pulled out of the solution's hydrogen bonding network and down onto the solid surface. This fact is confirmed by the bottom panel of Figure 3, which shows the distribution of the number of hydrogen bonds per water molecule in our simulations. The number of hydrogen bonds near the rocksalt surface is clearly markedly lower than the number near the wurtzite surface as there is a marked difference in the average number of hydrogen bonds in the solution. In addition, the effect of the water becomes more marked if interfaces between the solid phases and pure water are simulated. In this case the difference in the surface tensions for the two structures increases to 70% (see Table 1). Figure 4 shows a plot of the difference between the free energy of wurtzite and rocksalt nuclei as a function of size. This curve was calculated using eq 6 and the values of $\Delta\gamma$ and ΔG_v obtained from the calculations described in the previous paragraphs and reported in Table 1. For small nuclei, the wurtzite is clearly more stable than rocksalt because of its smaller surface tension. It is therefore possible that sodium chloride nucleates via this
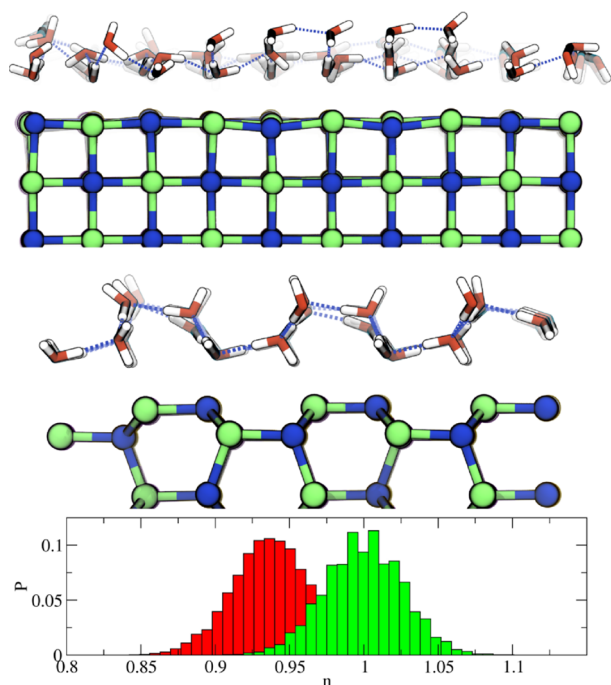
Figure 3. Two top panels: the structure of the water layers above the rocksalt and the wurtzite surfaces. The water molecules above wurtzite can hydrate the surface while retaining the hydrogen bond network. The water molecules above the rocksalt cannot do both these things simultaneously, and thus the surface tension of this structure is higher. This observation is confirmed in the bottom panel where we report probability distributions for the number of hydrogen bonds per water molecule in the simulations of the interface between these structures and the saturated solution. The green histogram corresponds to wurtzite, while the red is for rocksalt. It is clear that water molecules in the vicinity of the wurtzite surface form markedly more hydrogen bonds than molecules near the rocksalt surface.
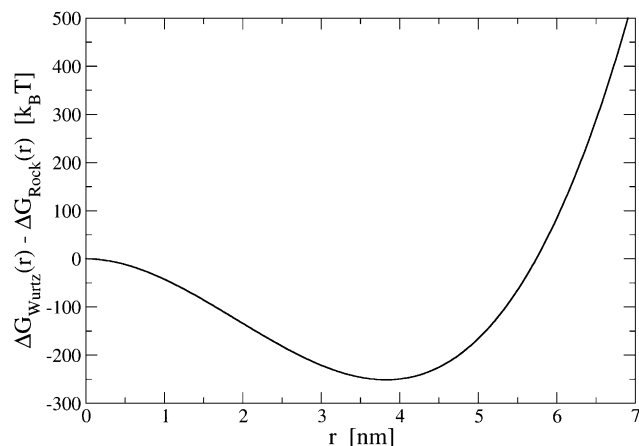

Figure 4. The difference in the CNT free energy of formation for wurtzite and rocksalt nuclei as a function of size. The figure shows the result obtained when the surface tensions between the crystals and the saturated solutions are used. As such, in eq 6 $\Delta\gamma$ is set equal to -17 mN m^{-1}, and ΔG_v equals -5.35 kJ mol^{-1} nm^{-3}. Wurtzite has a lower surface tension and thus is more stable than the rocksalt for nuclei of up to about 5.7 nm in radius.

wurtzite structure and only later converts to rocksalt. This is a rather surprising manifestation of the Ostwald step rule,[32] which states that in general it is not the most stable but the least stable polymorph that crystallizes first. Our results also show that water is not just a spectator. Water imprints its structure onto the NaCl nuclei and causes the wurtzite structure to appear.

3. CONCLUSION

Nucleation is a very difficult phenomenon to simulate because it involves a wide range of length scales and very long time scales. Nevertheless, the work presented in this letter demonstrates that metadynamics simulations can shed light on this phenomenon. Our metadynamics simulations of sodium chloride suggest that small clusters of this material can have a structure that is different from that of bulk rocksalt. When clusters initially aggregate, there is a competition between hydrated amorphous material, rocksalt nuclei, and nuclei of the new wurtzite-like phase. This is a qualitative result that is difficult to confirm quantitatively because of the difficulties associated with simulating dense phases within the μVT ensemble. However, the easier to calculate classical nucleation theory result suggests that at these small length scales the wurtzite structure is the most stable because of the interactions with the water molecules. In these CNT calculations, infinite periodic surfaces were considered so we cannot say quantitatively what effect edges and corners have on the free energy of the clusters. However, we see both fcc and wurtzite clusters in our metadynamics simulations, which suggests that the free energies for realistic clusters with both structures are similar. The effect the kinetics has on the formation of the structures is also unclear. This could be investigated quantiatively using forward flux sampling or transition path sampling. It is important to note, however, that in our metadynamics simulations the small aggregates that form have a great deal of conformational flexibility and that the bias only forces ions to aggregate. It does not force the ions to adopt a particular arrangement. In other words, for small clusters sizes the structures will rapidly interconvert. It is therefore likely that clusters with all three structures are present during the earliest stages of NaCl nucleation. We are confident that this hypothesis can be experimentally tested. Wurtzite nuclei could be stabilized in experiments by either exposing the NaCl solution to the surface of a suitable chosen crystal with the wurtzite structure or by confining the nucleus in an appropriately shaped cavity.[33,34]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Input files for the CP2K geometry optimization. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Torbeev, V.; Shavit, E.; Weissbuch, I.; Leiserowitz, L.; Lahav, M. *Cryst. Growth Des.* **2005**, *5*, 2190−2196.

(2) Anwar, J.; Boateng, P. *J. Am. Chem. Soc.* **1998**, *120*, 9600−9604.

(3) Auer, S.; Frenkel, D. *Nature* **2001**, *409*, 1020−1023.

(4) Trudu, F.; Donadio, D.; Parrinello, M. *Phys. Rev. Lett.* **2006**, *97*, 105701.

(5) Gebauer, D.; Coelfen, H. *Nano Today* **2011**, *6*, 564−584.

(6) Tribello, G. A.; Bruneval, F.; Liew, C.; Parrinello, M. *J. Phys. Chem. B* **2009**, *113*, 11680−11687.

(7) Demichelis, R.; Raiteri, P.; Gale, J. D.; Quigley, D.; Gebauer, D. *Nat. Commun.* **2011**, *2*, 590.

(8) Laio, A.; Parrinello, M. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 12562−12566.

(9) Quigley, D.; Rodger, P. M. *J. Chem. Phys.* **2008**, *128*, 221101.

(10) Angioletti-Uberti, S.; Ceriotti, M.; Lee, P. D.; Finnis, M. W. *Phys. Rev. B* **2010**, *81*, 125416.

(11) Bruneval, F.; Donadio, D.; Parrinello, M. *J. Phys. Chem. B* **2007**, *111*, 12219−12227.

(12) Santiso, E. E.; Trout, B. L. *J. Chem. Phys.* **2011**, *134*, 064109−064109.

(13) Kawska1, A.; Brickmann, J.; Kniep, R.; Hochrein, O.; D., Z. *J. Chem. Phys.* **2006**, *124*, 024513−024520.

(14) Zahn, D. *Phys. Rev. Lett.* **2004**, *92*, 0408011−0408014.

(15) Ginzburg, V.; Landau, L. *Zh. Eksp. Teor. Fiz.* **1950**, *20*, 1064−1082.

(16) Steinhardt, P. J.; Nelson, D. R.; Ronchetti, M. *Phys. Rev. B* **1983**, *28*, 784−805.

(17) Lutsko, J. F.; Nicolis, G. *Phys. Rev. Lett.* **2006**, *96*, 46102.

(18) Van der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A.; Berendsen, H. *J. Comput. Chem.* **2005**, *26*, 1701−1718.

(19) Berendsen, H.; Van der Spoel, D.; Vandrunen, R. *Comput. Phys. Commun.* **1995**, *91*, 43−56.

(20) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *J. Chem. Theory Comput.* **2008**, *4*, 435−447.

(21) Lindahl, E.; Hess, B.; van der Spoel, D. *J. Mol. Model.* **2001**, *7*, 306−317.

(22) Bonomi, M.; Branduardi, D.; Bussi, G.; Camilloni, C.; Provasi, D.; Raiteri, P.; Donadio, D.; Marinelli, F.; Pietrucci, F.; Broglia, R. A.; Parrinello, M. *Comput. Phys. Commun.* **2009**, *180*, 1961−1972.

(23) Oostenbrink, C.; Villa, A.; Mark, A.; Van Gunsteren, W. *J. Comput. Chem.* **2004**, *25*, 1656−1676.

(24) Berendsen, H.; Grigera, J.; Straatsma, T. *J. Phys. Chem.* **1987**, *91*, 6269−6271.

(25) Parrinello, M.; Rahman, A. *J. App. Phys.* **1981**, *52*, 7182−7190.

(26) Bussi, G.; Zykova-Timan, T.; Parrinello, M. *J. Chem. Phys.* **2009**, *130*, 014101.

(27) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. *Comput. Phys. Commun.* **2005**, *167*, 103−128.

(28) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(30) Goedecker, S.; Teter, M.; Hutter, J. *Phys. Rev. B* **1996**, *54*, 1703−1710.

(31) Kirkwood, J.; Buff, F. *J. Chem. Phys.* **1949**, *17*, 338−343.

(32) Ostwald, W. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **1897**, *22*, 289−330.

(33) Stephens, C. J.; Mouhamad, Y.; Meldrum, F. C.; Christenson, H. K. *Cryst. Growth Des.* **2010**, *10*, 734−738.

(34) Mitchell, C. A.; Yu, L.; Ward, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 10830−10839.