

Growth driven phase transitions in Zinc Oxide nanoparticles through machine-learning assisted simulations

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A. PLIP+Q VALIDATION ON GROWTH CONDITIONS

In order to assess the reliability of the PLIP+Q model under growth conditions, we performed single point DFT calculations using structures extracted from the PLIP+Q MD simulations. Specifically, we focused on the WRZ-310 and BCT-324 cases and selected configurations at 2 ps, 3 ps and 4 ps after the successive depositions of Zn and O atoms [See Fig. SI-1.a]. In total, we have considered 75 configurations spanning different deposition positions. Figure SI-1.b compares the atomic forces obtained from DFT with those predicted by PLIP+Q. The just deposited atoms are highlighted in color, while atoms already present in the nanoparticle are shown in black. The plot reveals no significant difference between the two atom sets, indicating a consistent force prediction by PLIP+Q, regardless of atom origin. The computed root-mean-square error is $0.22 \text{ eV}/\text{\AA}$, which is not as small as the most recent MLIP models. This can be attributed to (1) the employed high temperature, (2) the out-of-equilibrium nature of the growth process and (3) the hybrid nature of PLIP+Q which is positioned in between purely ML and classical IP.

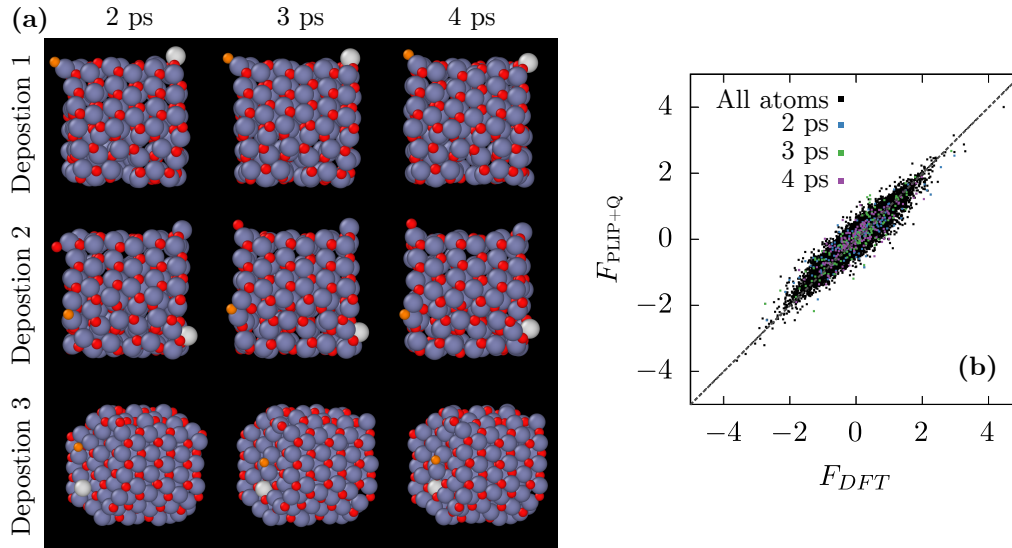


Figure SI-1. (a) Typical atomic configurations at 2 ps, 3 ps and 4 ps after the successive depositions of Zn and O atoms in the BCT-324 case. We used grey, red, white and oranges to color respectively original Zn and Ox atoms and deposited Zn and Ox atoms. (b) Comparison of atomic forces obtained from DFT with those predicted by PLIP+Q. Forces on just deposited atoms are highlighted in color, while those on atoms already present in the nanoparticle are shown in black.

B. INFLUENCE OF THE DEPOSITION RATE

To confirm our results, we carried out additional simulations with the deposition rate reduced by a factor of five which means a deposition every 50 ps. Fig. SI-2 shows typical crystallization and Zn excess curves obtained for the WRZ-310 and the BCT-324 systems. Results using this slower deposition rate are very similar both qualitatively and quantitatively to the previous results.

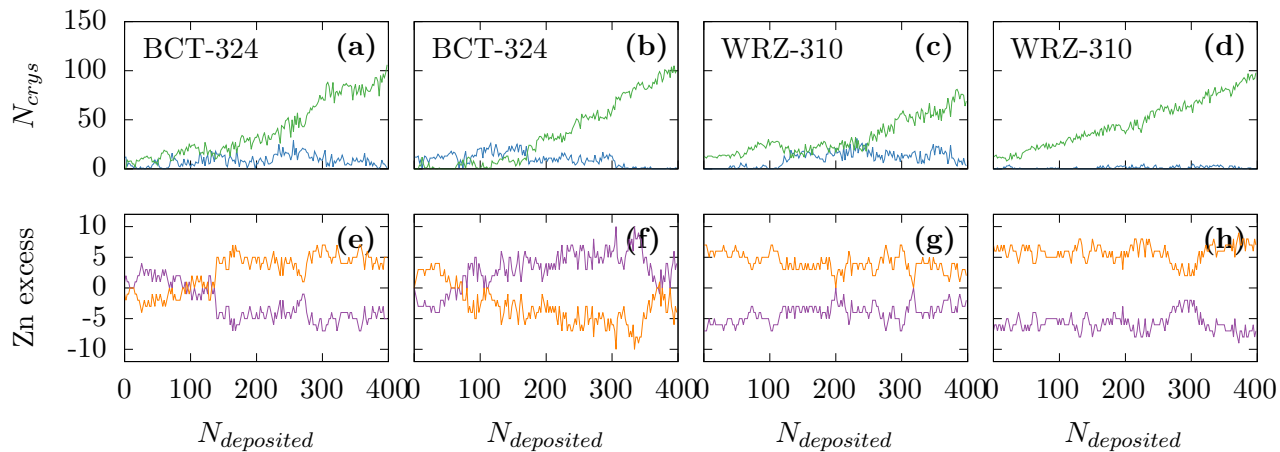


Figure SI-2. Results obtained at a slower deposition rate. (a) to (d): Examples of the evolution of the number of atoms of the BCT (blue) and WRZ (green) type inside the crystalline nucleus as a function of the number of deposited atoms obtained for BCT-324 and WRZ-310 initial seeds at 500 K. (e) to (h): Corresponding excess of Zn atoms at opposite ends of the nanoparticle, in orange and purple, respectively.

C. SURFACE MOBILITY OF DEPOSITED ATOMS

A common challenge in growth modeling is that certain simulation parameters may not allow for sufficient mobility of the deposited atoms, potentially causing the system to remain trapped in irregular morphologies. To assess whether this occurred in our simulations, we computed the mean square displacements using two different deposition rates and compared these results with simulations performed without any deposition. As shown in Fig.SI-3, we find that (1) the deposition process generally enhances atomic mobility, (2) slower deposition rate leads to lower mobility, and (3) the deposition induces additional displacements even for atoms belonging to the original seed.

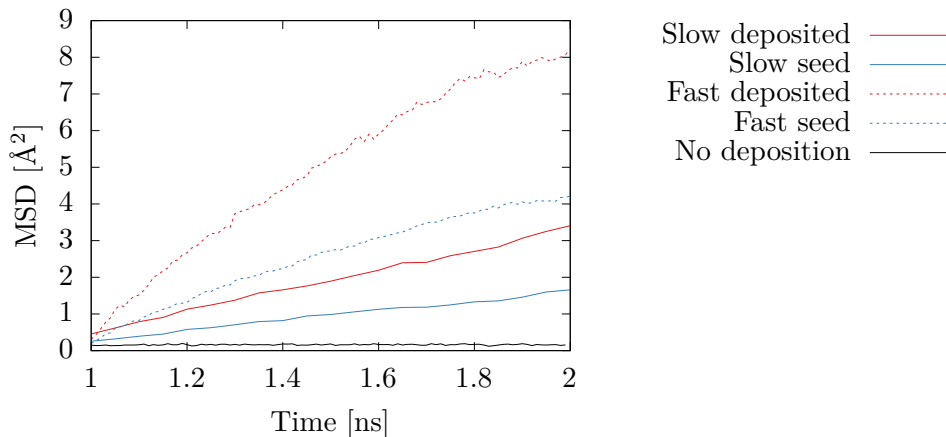


Figure SI-3. Mean square displacement averaged over all simulations for the BCT-162 seed at two different deposition rates: one ZnO pair deposited every 50 ps (solid lines) and every 10 ps (dashed lines).

D. CONVERGENCE OF THE MEAN

To analyze if 10 simulations are sufficient, we performed the convergence of the mean which is a more thorough stability analysis. In particular, for values of $N_{samples}$ going from 1 to 9, we randomly selected subsets of $N_{samples}$ of our 10 measurements and measured the corresponding average. By doing this randomization 20 times, we can obtain a mean and a standard deviation of the average when using only $N_{samples}$ instead of the 10 measurements. For each value of the temperature and the initial seed size, Fig. SI-4 shows that both mean and the standard deviation of the average starts by largely fluctuating when using only 1 to 5 samples but then it reaches a plateau starting from 7 until 10 samples. Quantitatively, this results at most to an error of 9% when using 9 instead of 10 simulations. This confirms that 10 simulations should be sufficient to provide a quantitative measurement of the number of deposited atoms required to reach the BCT→WRZ transition.

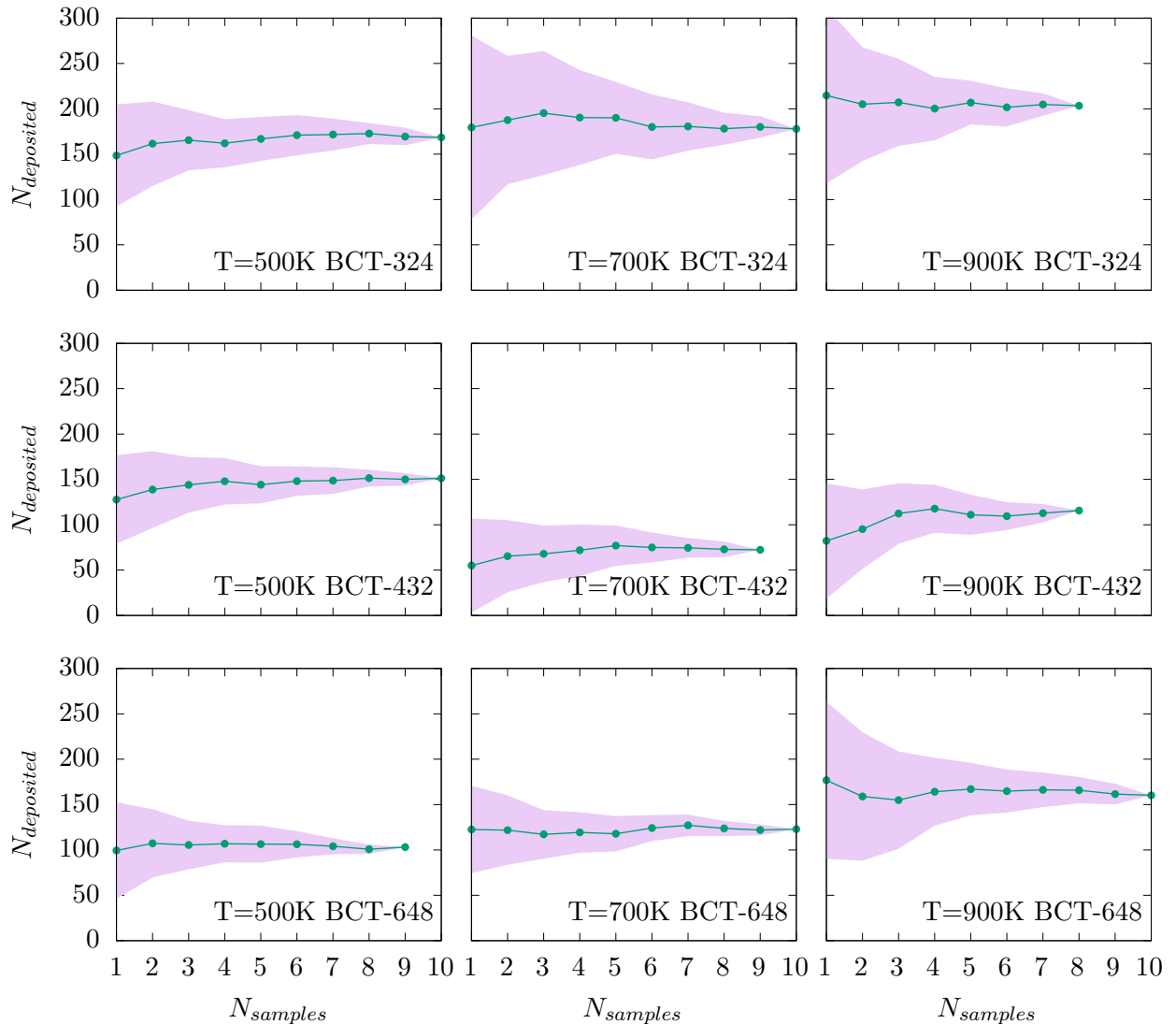


Figure SI-4. Convergence of the mean results with in green the obtained subsampled mean and in violet the corresponding standard deviation. We note that since the BCT→WRZ transition does not occur in all the cases, some convergence of the mean calculations were done with less than 10 samples.

E. DELAYED WRZ GROWTH

Fig. SI-5 shows the few cases where we observe a delayed growth of WRZ when starting from WRZ seed. In all cases, we observe a concomitant quench of the Zn excess.

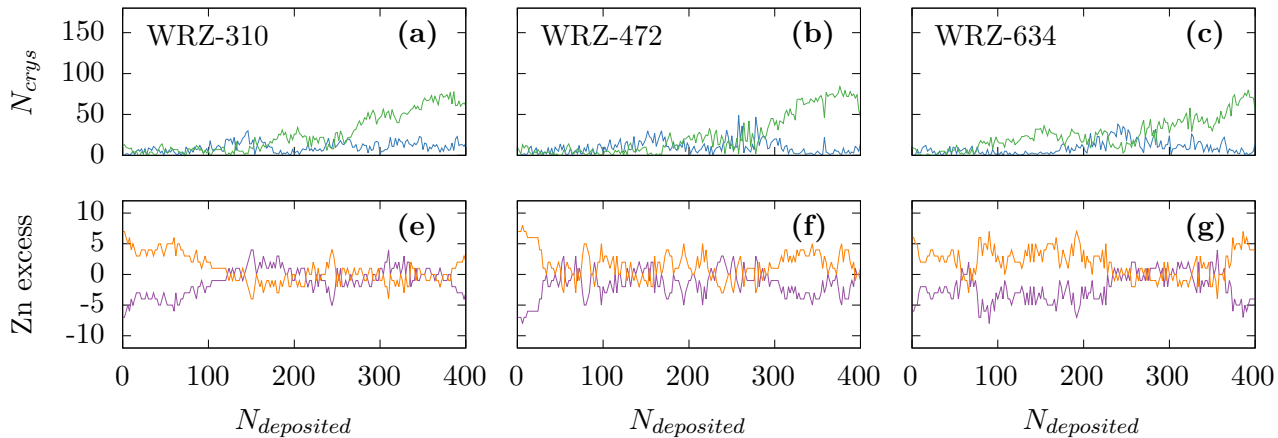


Figure SI-5. Results for the cases in which growth of WRZ phase is substantially delayed. (a) to (c): Evolution of the number of atoms of the BCT (blue) and WRZ (green) type inside the crystalline nucleus as a function of the number of deposited atoms obtained for WRZ-310, WRZ-472 and WRZ-634 initial seeds. (d) to (g): Corresponding excess of Zn atoms at opposite ends of the nanoparticle, in orange and purple, respectively.