Zinc Nano-cluster investigated by Molecular Dynamic Simulations

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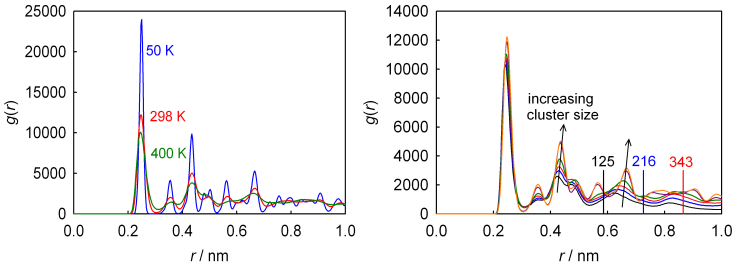
Introduction:

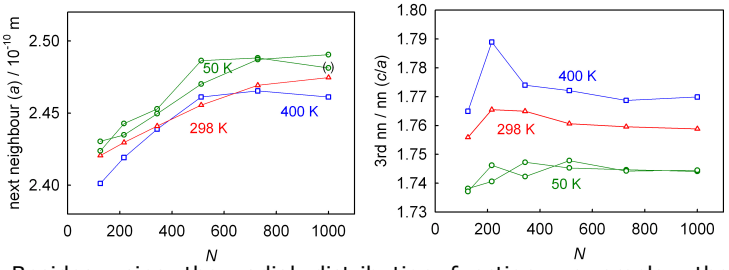
Molecular dynamics simulations where performed with a new parameterisation of the embedded atom method (EAM)[1] in order to investigate nano-clusters of the hcp metal zinc. This model is capable of describing the hcp structure of zinc in the bulk phase as well as in small clusters. The clusters investigated here are obtained in particle formation simulations from supersaturated vapour. For removing the latent heat during particle formation we added argon as carrier gas. The interaction between the argon atoms and Ar-Zn is modelled with the Lennard-Jones potential. The clusters are detected by the Stillinger criterion[2] with a distance value of 1.025 σ. Zn:Ar ratio is 1:2

Structure:

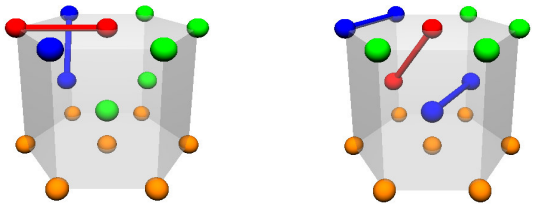
We plot the pair correlation function *g(r)* of the equilibrated cluster averaged over one nano-second for a 1000 zic atom cluster below. One can see that small clusters tend to liquid-like structure while large clusters tend to crystalline structure. The valid range of the calculated *g(r)* is limited by cluster size, so the cluster radius for small clusters are marked in the figure below.



Next neighbour distances were obtained from the first and third maximum of the *g(r)* (see below). In case of a solid-like cluster these distances correspond to the lattice constants *a* and *c*. The average value of the resulting *c/a* ratio is 1.76 which lies between the ideal value of 1.63 and the bulk-zinc value of 1.86. One can see a trend of increasing *c/a* ratio with increasing temperature.

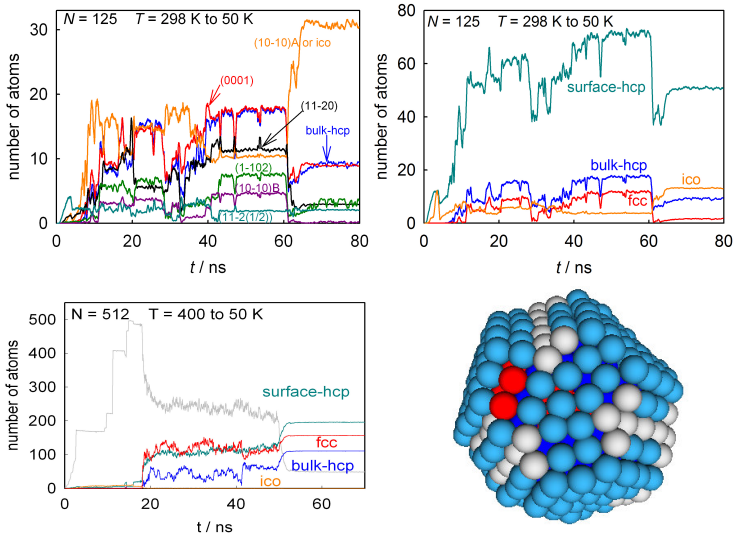


Besides using the radial distribution function we employ the common neighbour analysis (CNA) to determine details of the structural composition. CNA signatures were developed for hcp-surfaces. Examples are shown for the (0001) hcp-plane with the signature 311 (left) and 421(right).



Lit.:

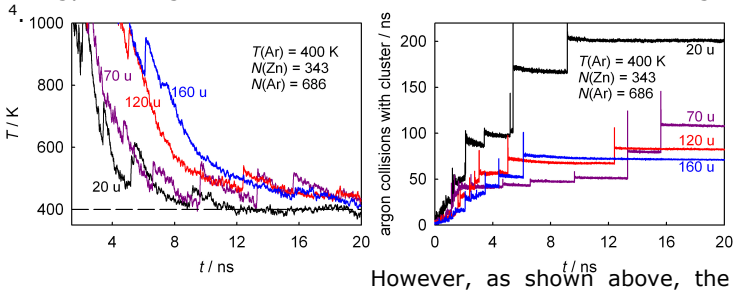
[1] F. Römer, S. Braun, T. Kraska, PCCP submitted
[2] F. H. Stillinger, J. Chem. Phys. 38, 1486 (1963).
[3] N. Lümmen, T. Kraska, Comp. Mat. Sci., 2006, **35**, 210.
[4] J. Westergren, H. Grönbeck, J. Chem. Phys., 1997, 107, 3071.
[5] A. Steinfeld, Int. J. Hydrogen Energy, 2002, **27**, 611.

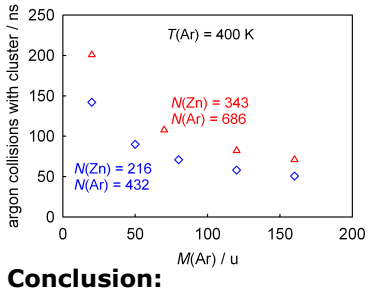


The CNA includes icosahedral (ico), octahedral, fcc and hcp structures for the bulk as well as surfaces and edges. For further analysis of the structure formation we plot the contributions to the hcp structure separately (shown above for 125 zinc atoms). These are bulk-hcp and various surface-hcp structures.

Variation of carrier gas mass:

The amount of carrier gas in the simulation has a significant effect on the nucleation and particle formation[3]. Instead of increasing the amount of carrier gas, we analysed the effect of the molar mass of the carrier gas using pseudo-argon with different molar masses but same Lennard-Jones parameters. It has been shown that the energy exchange increases with the molar mass of the carrier gas[4].





However, as shown above, the most effective gas turns out to be the lightest with a molar mass of 20 u. The reason is the dependence of the argon atom velocity on the molar mass. The higher the mass the slower are the atoms and less collisions with the cluster can take place in given period of time.

Conclusion:

Comparison of the simulations show that during cluster growth icosahedral structure is preferred, whereas after solidification the hcp-structure becomes dominant. For small clusters the icosahedral structure remains stable. Also the structure formation in the surface exhibits clear differences depending on the cluster size. While for small clusters hcp-surface structures appear, which are equivalent to icosahedral surface structures, for large clusters we find hcp-surface structures equivalent to fcc-surface structures. The formation of zinc clusters is of interest in a solar process for hydrogen formation[5]. The understanding of the zinc particle formation and their structures can help to optimize the process.