Morphological transformations and fusion of PbSe nanocrystals studied using atomistic simulations

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Classical force fields interaction potentials

Atoms of the nanocrystal (NC) and of the molecules interact via the Coulomb and Lennard-Jones (LJ) potentials:

$$U_{ij}(r_{ij}) = U_{Coulomb}(r_{ij}) + U_{LJ}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \tag{1}$$

Cross-coefficients are obtained from the interaction parameters through the Lorentz-Berthelot mixing rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. The parameters for the intra- and intermolecular interactions for NC2 are taken from the united atom TraPPE force field.[1] The LJ potential is truncated and shifted at 10 Å. Note that the model in the present work does not account for polarizability or charge transfer. The five interaction parameters for PbSe (four LJ coefficients and the partial charges) were fitted to the available elastic and lattice constants using the GULP code.[2-4] The result is summarized in Table S1 below, together with the parameters for ethylamine from the TraPPE force field. The effective charge of the ions obtained from our fit ($|q| = 1.29e$) is slightly larger than the partial charge in the similar model for CdSe ($|q_{Cd,Se}| = 1.18e$).[5] Despite the fact that the electronegativity of Pb is larger than that of Cd (1.9 and 1.7, respectively), the effective charge in PbSe is larger than in CdSe because the Pb 6s electrons contribute to the chemical bonding in PbSe (they are not localized).[6] The values of ε_{LJ} for Pb and Se are rather small, in line with the ionic nature of this material.

Table S1. Non-bonded interaction parameters for PbSe and ethylamine (NC2). The parameters for Pb and Se are derived in the present work; the ones for NC2 are taken from Ref. [1]. The LJ interactions are truncated and shifted at 10 Å.

		Pb	Se	N	H	CH$_2$	CH$_3$
q	[e]	1.29	-1.29	-0.892	0.356	0.18	0.0
σ_{LJ}	[Å]	3.29	4.36	3.34	0.0	3.95	3.75
ε_{LJ}/k_B [K]		30.0	45.3	111.0	0.0	46.0	98.0

We have computed the pressure-enthalpy diagram for bulk PbSe in various crystal structures at 300 K using Monte Carlo simulations in the isobaric-isothermal ensemble; see Fig. S1. Note that free-energy calculations would be computationally much more expensive, while the entropic contribution to the free energy in ionic solids is typically small.[7] At ambient conditions, rocksalt is by far the most stable structure, in agreement with experiment.
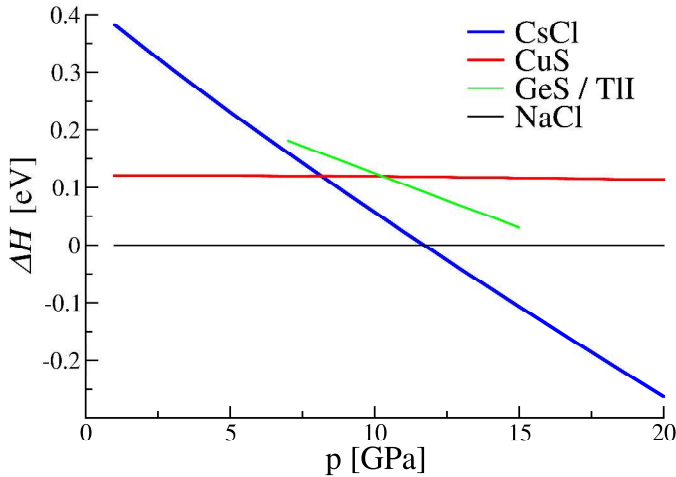

Figure S1: Pressure-enthalpy diagram for bulk PbSe in different crystal structures at 300 K computed using isobaric-isothermal Monte Carlo simulations (10,000 cycles, whereby the number of MC steps per cycle equals the number of atoms). The enthalpy difference (per ion pair) with respect to the NaCl phase is plotted. The seven-fold coordinated orthorhombic GeS and TlI structures yield equal enthalpies. Outside the plotted range (7-15 GPa), they undergo a transformation either into a NaCl or into a CsCl phase during the simulation. The four-fold coordinated ZnS structures (zincblende, wurtzite) are unstable over the entire pressure range.

The denser CsCl structure has a lower enthalpy for pressures above 12 GPa. The exact transition pressure has not been determined experimentally yet.[8] It is known, however, that for pressures above 16 GPa, PbSe adopts the CsCl structure.[8,9] Investigation of the transition mechanism and of intermediate structures will be subject of future simulation studies.[10]

Simulation of the capping molecules

The binding energy for a single amine molecule to CdSe NCs was found to be 0.9 eV using a combination of the Rabani model[5] for CdSe with the TraPPe force field.[11] This value is in excellent agreement with quantum chemical calculations and experimental data. We expect the binding energy to be slightly higher for PbSe due to the larger partial charge on Pb compared to Cd. The capping molecules adsorb to the NC via two mechanisms, which have been discussed in detail for CdSe.[11] The first mechanism, the direct adsorption, corresponds to the situation when the nitrogen atom of an amine headgroup binds to a surface cation. The second mechanism, the indirect adsorption, accounts for the amine molecules adsorbed via a hydrogen bond to a directly adsorbed amine ligand. Due to the presence of the second mechanism, a maximum coverage of small NCs with amine ligands is not well-defined. It is important to note that both the bare NC and the capped NC presented in this section are subject to surface strain due to the missing bonds on the surface.

Molecular dynamics simulations

In molecular dynamics (MD) simulations, the equations of motion were integrated using the velocity Verlet algorithm with a time step of 2 fs. The velocities were initialized such that both the total linear momentum and the angular momentum are zero. The velocities were rescaled to the desired temperature T during the equilibration time. Afterward, T was kept constant using the momentum-conserving Lowe-Andersen thermostat.[12] The MD simulations are carried out in a cubic box with a side length of 20 nm representing (capped) NCs in vacuum. Electrostatic interactions are cut at half the box length. As the box length is very large, long-range corrections do not need to be considered.

Monte Carlo simulations

Monte Carlo (MC) simulations of bulk PbSe were carried out in the isobaric-isothermal ensemble (NPT). The simulation box contained at least 1024 atoms, and it was allowed to expand or contract in each direction according to the imposed pressure. The long ranged part of the electrostatic interactions was calculated using the force-shifted-and-damped implementation of the Wolf method[13] with the cut-off radius of 14 Å and damping parameter α of 0.24 Å^{-1}. For the systems of interest, we had verified that this choice of parameters gives the same energies as the computationally more expensive Ewald summation.

For the preparation of capped NCs, we use the grand-canonical MC simulations. In these simulations, ligand molecules are inserted or removed according to their chemical potential (or, equivalently, fugacity). The translational and conformational degrees of freedom are realized using various Monte Carlo trial moves (displacement, rotation, pivot-rotation, configurational-bias MC). The fugacity is chosen large but well below the saturated vapor pressure of ethylamine to prevent formation of a liquid phase around the NC.

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Supporting Movie captions

Supporting Movie 1

Spontaneous crystal fusion of two 3.4 nm PbSe NCs that are mutually aligned. A bridge is formed first at the left-hand side of the gap between the surfaces, followed by closing of the gap at the right-hand side, after which the gap closes also at the left-hand side. Interface relaxations then enable full crystal fusion. The length of the movie corresponds to a simulation time of 20 ns. Corresponding snapshots are displayed in Fig. 3 (top)

Supporting Movie 2

Spontaneous crystal fusion of two 3.4 nm PbSe NCs. The two crystal lattices are mutually misaligned over two axes with tilt angles of 27° and 11°. After rotations to achieve attachment, subsequent rotations align the two crystal lattices and simultaneously close the gap, after which full fusion is obtained. The length of the movie corresponds to a simulation time of 20 ns. Corresponding snapshots are displayed in Fig. 3 (bottom).

Supporting Movie 3

Real-time TEM recording of a crystalline PbSe bridge, connecting two PbSe nanocrystals, at room temperature. The bridge is continuously changing in width and position, and is disrupted by the lateral motion of the connecting NCs. The movie was recorded at 5 frames per second, and is displayed at 10 frames per second.