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Electronic Supplementary Information

Nano-size scaling of alloy intra-particle vs inter-particle separation transitions: Prediction of distinctly interface-affected critical behavior

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First-order intra-NP transitions

In case of overall atomic concentration $c_0 \neq 0.5$ the concentration profile is discontinuous at a first-order transition temperature.

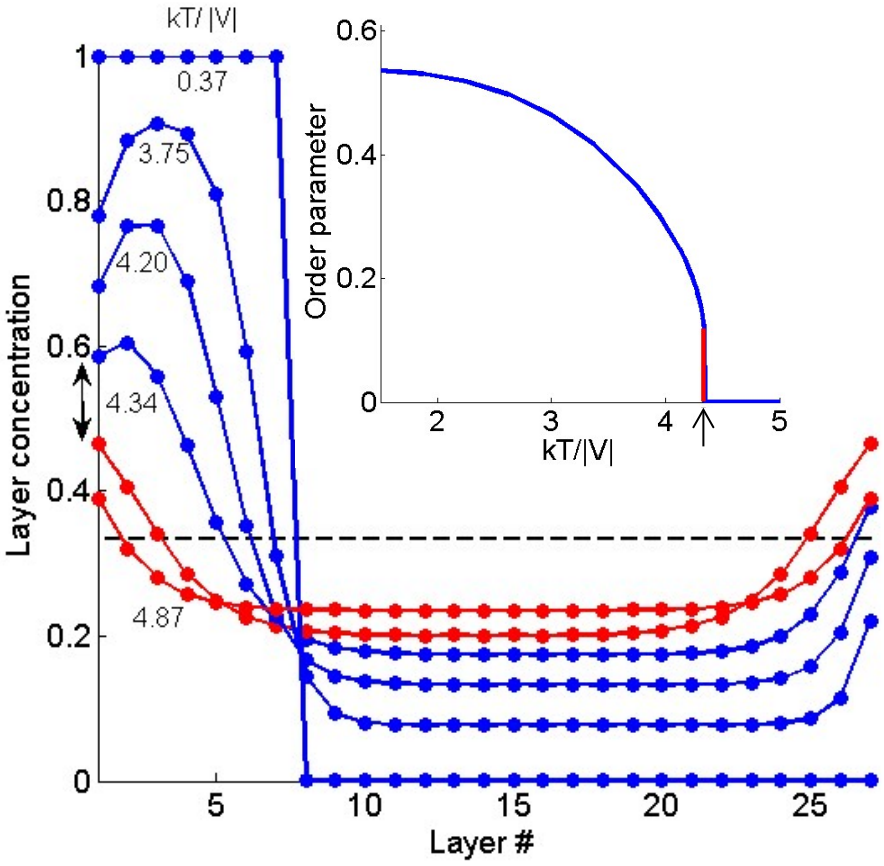

Fig. S1. Layer concentration profiles in $A_{0.26}B_{0.74}$ 9842-atom fcc-based nanocubes below (blue) and above (red) a first-order transition temperature. Inset: order parameter (defined as the difference between left and right side average concentrations) vs. reduced temperature. The abrupt transition is indicated by arrows.

Free energy computations for the construction of inter-NP phase separation diagram

At high temperatures the computed free energy indicates no tendency for separation into A and B-enriched NPs, whereas at low temperatures it does reveal a region of convexity between two minima corresponding to stable compositional structures (tangent constructions are indicated). Thus, the nanosystem exhibits a bulk-like "miscibility gap" (Fig. 4).

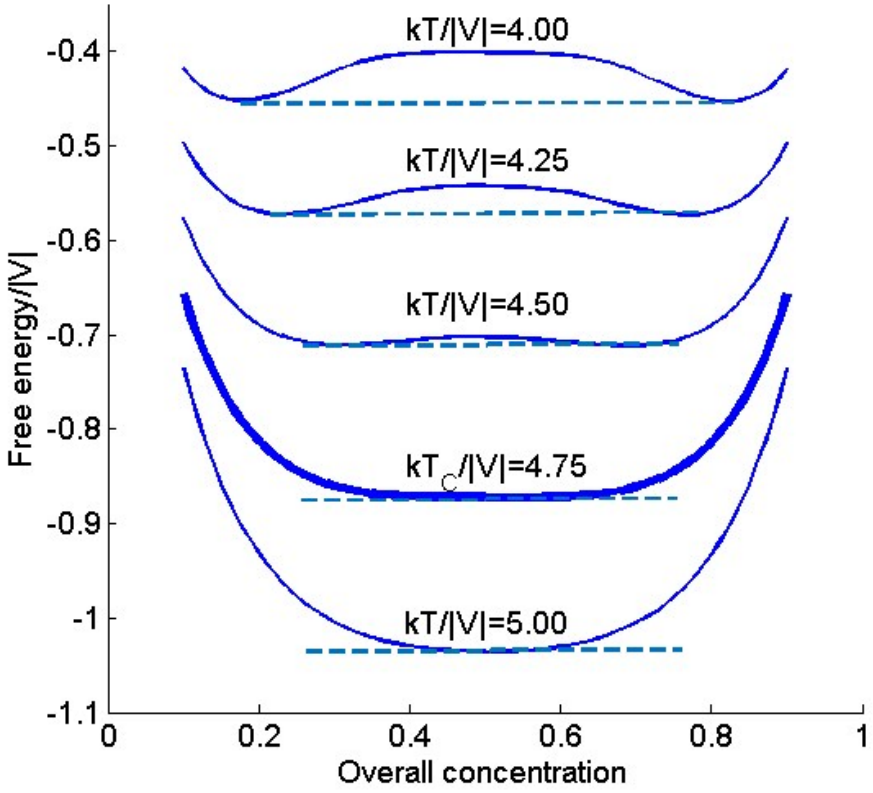

Fig. S2. Reduced free energy vs. concentration for an assembly of nanocubes consisting of 1099-atom each (reduced temperatures are indicated).

Geometric characteristics of rectangular nanoparticles with different shapes

A clear (inverse) correlation exists between the relative positions of surface fraction lines and the corresponding scaling plots (Fig. 5b).

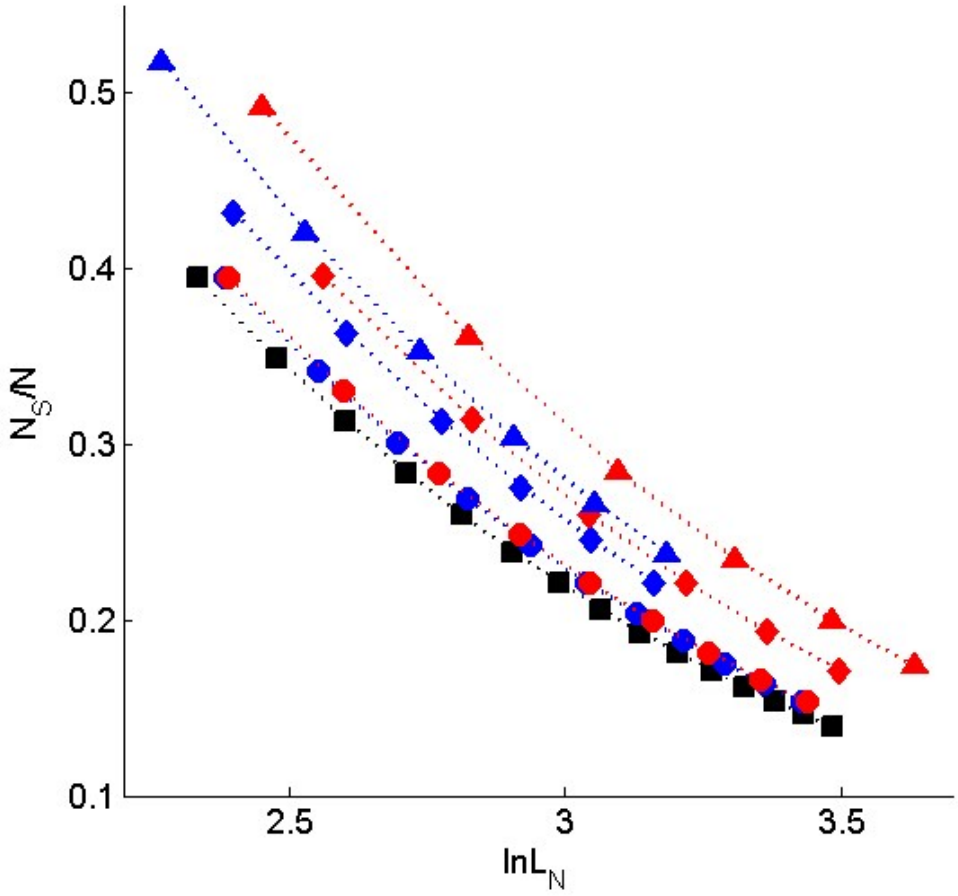

Fig. S3. Fraction of surface sites vs. ”effective linear size” based on the NP volume plotted for different shapes. Cubes – black squares, rods – blue, platelets – red. Aspect ratios: circles -2, diamonds - 4, triangles - 6.