Nano-size scaling of alloy intra-particle vs. inter-particle separation transitions: prediction of distinctly interface-affected critical behaviour†

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Phase-separation second-order transitions in binary alloy particles consisting of ~1000 up to ~70 000 atoms (~1–10 nm) are modeled focusing on the unexplored issue of finite-size scaling in such systems, particularly on evaluation of correlation-length critical exponents. Our statistical-thermodynamic approach is based on mean-field analytical expression for the Ising model free energy that facilitates highly efficient computations furnishing comprehensive data for fcc rectangular nanoparticles (NPs). These are summed up in intra- and inter-particle scaling plots as well as in nanophase separation diagrams. Temperature-induced variations in the interface thickness in Janus-type intra-particle configurations and NP size-dependent shifts in the critical temperature of their transition to solid-solution reflect power-law behavior with the same critical exponent, \( n = 0.83 \). It is attributed to dominant interfacial effects that are absent in inter-particle transitions. Variations in \( n \) with nano-size, as revealed by a refined analysis, are linearly extrapolated in order to bridge the gap to larger particles within and well beyond the nanoscale, ultimately yielding \( n = 1.0 \). Besides these findings, the study indicates the key role of the surface-area to volume ratio as an effective linear size, revealing a universal, particle-shape independent, nanoscaling of the critical-temperature shifts.

Introduction

Alloy nanoscale particles (“nanoalloys”) exhibit distinct chemical and physical properties that lead to increasing numbers of technological applications in heterogeneous catalysis, magnetic and biomedical devices and others. Future developments obviously necessitate the foundation of basic research focusing on the relationship between structure at the atomic level and desired properties. Theoretical-computational modelling of alloy nanoparticles has become quite common in recent years,\(^2\) focusing on geometrical atomic-scale structures and chemical-order configurations at 0 K (using mainly DFT).\(^2\) The interest in possible temperature-induced nanophase transitions seems to be growing due to some predictions of unique features compared to the corresponding alloy bulk transitions. In spite of progress in experimental techniques, such as TEM, capable of sub-nano level imaging, information concerning nanoscale size-dependent critical phenomena in alloys is quite inaccessible by experiment. Among the three different prototypes, namely NP melting, order-disorder and separation transitions, the latter received somewhat lesser attention with very few reports of nanoalloy phase diagrams.\(^3,4\)

Finite-size scaling (FSS) is manifested in diverse phenomena in physics, chemistry, biology and in other fields of science and technology. However, compared to research on critical phenomena in magnetic particles and films as well as in polymeric systems, FSS in alloy nanoparticle second-order separation transitions has been scarcely explored, so its likelihood in such systems is one of the goals of this work. Related goals include bridging the gap between transition temperatures calculable for small–medium nanoparticles and larger particles (within and well beyond the nanoscale), as well as predicting the effects of alloy particle inner interface and shape. A major issue concerns intra-particle separation transitions vs. inter-particle ones. Theoretical-computational modelling of finite-size effects in non-alloy systems has been done mostly by Monte-Carlo (MC) simulations,\(^5\) but other approaches were also used, e.g., the mean-field analytical approximation.\(^6\) In the case of binary alloy NPs, a kind of finite-size power-law was predicted earlier for phase-separation in Ag–Cu using a phenomenological model,\(^7\) and more recently for order-disorder phase transitions using a quasi-chemical approach.\(^8\)

In view of the very limited and quite simplified theoretical treatments of finite-size effects on separation transitions in nanoalloys, a reasonably accurate and highly efficient new modelling is desirable in order to obtain a more comprehensive and realistic description of the phenomena. Thus, the present
study employs the statistical-thermodynamic analytical expression derived in the canonical ensemble by the “free energy concentration expansion method” (FCEM), which we developed before for Ising alloys. This mean-field approach can cope with the computationally demanding task that comprises finding separation transition temperatures in progressively larger alloy nanoparticles, as well as thermodynamic functions, in order to elucidate scaling behaviour including the determination of critical exponents. In particular, all temperature-dependent layer-by-layer average behaviour including the determination of critical exponents are independent of short-range interaction details (but do depend on the symmetry and spatial dimensionality of the system)\textsuperscript{15} differences in elemental bond energies and in atomic radii as well as surface bond energy variations\textsuperscript{16} are likely to be irrelevant and therefore are neglected in the present FCEM expression (besides \( V \), the reduced surface coordination is taken into account). The assumption of equal energies, \( w^{AA} = w^{BB} \), makes the computations less tedious, since the separation critical point (at the miscibility-gap apex) unambiguously corresponds to overall atomic concentration \( c_0 = 0.5 \) of a binary A-B alloy and is determined unequivocally once the NP becomes compositionally homogeneous, compared to finding it \textit{via} a particular thermodynamic function (specific heat, susceptibility, etc.).\textsuperscript{17} Moreover, by choosing geometrically simple rectangular shapes (mainly cubes, besides rods and platelets) the computations of larger NPs become even more feasible, including the study of the role played by the shape of the particle that can be conveniently changed.

It can be noted that the FCEM deals with a system of alloy NPs capable of exchanging constituent atoms. This facilitates studies of both intra-NP and inter-NP separation phenomena.\textsuperscript{11} Such separation occurs \textit{via} the surrounding media (irrespective of the specific kinetic mechanism of exchange) and the number of surrounding A and B atoms is assumed here to be negligible, as compared to the number of atoms in the NP assembly. Therefore, the overall number of constituent atoms is practically fixed, so that the canonical ensemble can be employed also in the case of inter-NP separation.

\section*{Finite-size-scaling (FSS): general}

Before introducing computation results some basic principles of the FSS theory of 2nd order phase transitions are outlined. Considering infinite systems, thermodynamic and correlation functions exhibit singularities at a critical point. Thus, the correlation length diverges according to \( \xi \propto t^{-\nu} \), where \( t \equiv T - T_C \) characterizes the relative deviation of temperature from the critical value, and \( \nu \) denotes a critical exponent. The situation changes considerably in finite-size systems, such as nanoparticles, when \( \xi \) approaches the NP size, \( L \), from below with increasing temperature,\textsuperscript{18} and the critical singularity is expected to be rounded due to cut-off of long-distance correlations (if \( L \gg \xi \) no appreciable effects are expected). Specifically, as a result of the constrained \( \xi \) a “pseudo”-critical-transition is expected at \( T_C \) (shifted below \( T_{C}^{\text{bulk}} \)), characterized by FSS power-law\textsuperscript{18} (corrections to scaling can be necessary)\textsuperscript{19}. Thus, the reduced shift, \( t_C \equiv \frac{T_{C}^{\text{bulk}} - T}{T_{C}^{\text{bulk}}} \), obeys \( t_C \propto L^{-1/\nu} \), where \( \nu \) can differ from the bulk value because of boundary effects.
Under “periodic boundary conditions” (PBC), all NP atoms have bulk-like atomic coordination, and therefore $\nu$ is expected to be close to the bulk value. On the other hand, the more realistic “free boundary conditions” (FBC), involving low-coordinated surface sites should reduce $T_C$ even further, so the corresponding increase in $t_C$ for a given $L$ leads to larger $\nu$. An “effective linear size” (ELS) is defined here in three ways based on (i) the volume-related total number of atoms $N$, $L_N \equiv \sqrt[3]{N}$, (ii) the number of surface atoms $N_{S\ell}$, $L_S \equiv \sqrt{N_{S\ell}}/6$, and (iii) their ratio, $L_{R} \equiv 6N/N_{S} = L_S^3/L_N^2$. Most of the results below are shown for $L \equiv L_N$ (unless otherwise noted).

Results and discussion

Intra-NP and inter-NP separation transitions

Concentration profile variations. FCEM/CGLM computations for intra-separation in $A_{0.5}B_{0.5}$ fcc nanocubes containing up to 66,326 atoms show at low temperatures an anti-symmetric concentration profile along the [100] separation axis resembling a step function (Janus-type intra-separated configuration, Fig. 1a). At somewhat higher temperatures, a more moderate interfacial profile develops that is close to hyperbolic tangent plot (consistent with a mean-field prediction\(^{20}\)) together with demixing-driven solute surface segregation. With a further increase in temperature the inner-interface and surface regions broaden and eventually form a pre-transition sinusoidal concentration profile with gradually decreasing amplitude, until the concentration gradient completely vanishes at a shifted $T_C$. In particular, the order parameter, $\eta$ (defined as the difference between the left and right side average concentrations), changes continuously (see Fig. 1a, inset) until a second-order phase transition occurs at $T_C$ when the concentration profile symmetry changes and the composition becomes homogeneously solid solution-like. Thus, the entropy driven changes involve two concurrent processes: (i) some mixing of the plateau regions, and (ii) widening of regions where more intensive surface and interface induced mixing occurs at the expense of the former plateau sub-peripheral layers. When the sinusoidal profile forms, the first process actually stops and layer concentrations start to change jointly. It can be noted that in the case of inter-NP separation of single-plateau monophase NPs (having no inner-interface), the surface segregation regions broaden with temperature, and eventually form a pre-transition half-sinusoidal concentration profile (not shown).

Critical exponent extracted from the interface thickness.

The concentration profile variations with temperature reflect a growing correlation length $\xi$ related to the thickness of the interface\(^{21}\) that can be defined as $w = (c_{\max} - c_{\min})/|dc/dz|_{\max}$. In the present modelling of equiatomic alloy NPs, $c_{\max}(c_{\min})$ is equal to the left (right) extremum of the concentration profile and $|dc/dz|_{\max}$ is its slope in the center (Fig. 1a). First, since in smaller NPs sinusoidal profiles form at lower temperatures, the interface reduced thickness, $w/L_{Z_2}$ is consistently larger (Fig. 1b). Secondly, it increases progressively with temperature until reaching a maximum in the sinusoidal profile just below $T_C$.

According to the above definition, the maximum of $w/L_{Z_2}$ can be readily shown to equal $1/\pi$ near $T_C$. The corresponding result $\xi \approx L_{Z_2}/\pi$ is consistent with the above-mentioned basic assumptions of the FSS theory. Furthermore, intra-NP variations of $\xi$ vs. $t$ obey the scaling relation $\ln \xi = -\nu \ln t + \text{const}$, as shown in the inset of Fig. 1b (the scaling plots are practically NP-size independent and coincide up to the respective $T_C$). While the slope gradually decreases at lower temperatures, it is quite constant closer to the transition (in the approximate range $-2.3 < \ln t < -3.1$), and the corresponding linear fitting gives $\nu_{\text{fit}} = 0.83 \pm 0.01$.

Scaling plots ($t_C$ vs. $L$). Their evaluation under both FBC and PBC reveals a clear power-low finite-size scaling behaviour. In particular, comprehensive scaling plots computed for intra, inter and bulk-like NPs are nearly linear (Fig. 2), with slight deviations noted for the smaller NPs. Under PBC, linear fitting
for $N > 1000$ gives a critical exponent that coincides with the known mean-field bulk value, $\nu_{\text{bulk}} = 0.50$. Under FBC, the critical exponent turns out to be larger, $\nu_{\text{intra}} = 0.835 \pm 0.006$, namely the same value as extracted above from interface thickness variations, and agrees with exponents obtained for entirely different systems, e.g., magnetic films. Similarly to the intra-NP transitions, inter-NP separation (see ESI, Fig. S2) exhibits FSS behaviour, but characterized by a somewhat upward displaced scaling plot having a smaller slope, corresponding to $\nu_{\text{inter}} = 0.942 \pm 0.006$, and the two transition plots tend to converge for large NPs (Fig. 2). In order to explore whether the intra/inter slope difference under FBC stems from inner-interface effects in the small-medium sized NPs, which would gradually vanish for larger NPs, a 2-point refined slope analysis has been undertaken (Fig. 2, inset). In the case of the intra-separation, the analysis does reveal a distinct dependence of the slope on the NP-size (consistent with scaling corrections considered in the FSS theory). In particular, it gradually decreases approaching the inter-NP separation slope (characterizing mono-phase particles without an inner interface), which is nearly size-independent and close to 1. Eventually, bridging the gap between NPs and the macroscopic limit by linear extrapolation gives critical exponents $\nu_{\text{FBC intra}} = 0.92 \pm 0.04$ and $\nu_{\text{FBC inter}} = 0.96 \pm 0.05$. Thus, the intra/inter slope differences in smaller NPs seem to reflect mainly inner interface effects. It can be noted that the critical exponent value close to 1 is consistent with predictions for surface constrained systems made using other theoretical tools, and with the simple consideration of surface effects on the reduced temperature, $t_C$, being proportional to the ratio of surface area to bulk volume. An exact solution for the 2D Ising lattice also yields $\nu = 1$. In order to further substantiate the above result concerning the extrapolated critical exponent value a logarithmic scaling correction was fitted to the data (instead of the 2-point slope procedure), namely $L \propto t_C^{3/2 \nu} \ln t_C$ giving again close values $\nu_{\text{intra}} = 1.01 \pm 0.03$ and $\nu_{\text{inter}} = 1.03 \pm 0.01$ (as well as $\nu$ values corresponding to some deviations from linearity particularly for smaller NPs).

**Specific heat.** Finite-size scaling behaviour is reflected also in configurational specific-heat variations, especially below and close to the critical transition temperature. Thus, starting at ~8000 and ~1000 atom NPs for intra and inter separation, respectively, the shifted peak is rounded and attenuated (Fig. 3a and b), all phenomena attributed to the cut-off of long-distance correlations. For larger NPs the peak sharpens, grows and approaches the typical mean-field “saw-tooth” bulk peak (with discontinuity in the specific heat at the critical point). Furthermore, since in the case of intra-NP separation each of the two nanophases corresponds to half of the NP edge, the roundness of the computed peak corresponds approximately to that of the twice smaller monophase NPs in the case of inter-separation transition (Fig. 3c).

**First-order transitions and nanophase diagrams.** To construct the full nanophase diagram, transition temperatures for non-equiaxial compositions were computed using the FCEM/CGLM method as done for the equiatomic case. Thus, for $c_0 \neq 0.5$ the concentration profiles are discontinuous at first-order transitions to solid-solution-like symmetric configurations with demixing-driven solute segregated surfaces (ESI† Fig. S1). Plotting the transition temperatures vs. composition for different nanocube sizes gives the corresponding diagrams (Fig. 4) including the apex second-order critical transition. For the latter, it can be noted that a finite-size limit exists, below which intra-NP phase separation is not possible (i.e., $T_C = 0$ K, Fig. 4, inset). While such limits agree with the predictions of ref. 7, the phenomenon is not confirmed by recent advanced modelling that takes into account stress relaxation and the possibility of non-crystalline structures, which become dominant for small sized NPs of certain alloy systems with large lattice mismatch.

With increased NP size the miscibility gap shifts to higher temperatures showing convergence of the nanophase diagrams towards the bulk one. These variations can be attributed to the increase in the fraction of inner atoms with NP size, or from another perspective in accordance with the FSS arguments given above, the variations in the apex region stem from the increase in the maximal correlation length. The computed inter-NP separation transitions (ESI† Fig. S2) occur at higher temperatures compared to intra-NP separation (Fig. 4), indicating separation destabilization by the inner interface, but the difference diminishes with increasing NP size as summarized for the apexes in the inset. The inter-NP and bulk diagrams are similar in shape, compared to somewhat reduced-range intra-NP miscibility gaps, again attributed to destabilizing interfacial effects.
NP shape effects

A major issue raised in this study is the feasibility of a generalized power law that is universally applicable to different NP shapes. A key factor concerns finding an appropriate definition of the effective linear size, ELS. Although its meaning is obvious for a cube (the edge length), it becomes somewhat ambiguous for less symmetric shapes. While, as noted above, ELS can be defined in different ways, in the present context of search for a universal power law, \( L_R \) seems to have a clear advantage over \( L_N \) and \( L_S \).

Specifically, for the NP shape close to a rectangle with “effective” dimensions \( L_{\text{max}} \times L_{\text{mid}} \times L_{\text{min}} \), \( N \propto L_{\text{min}}L_{\text{mid}}L_{\text{max}} \) and \( N_S \propto 2(L_{\text{mid}}L_{\text{min}} + L_{\text{mid}}L_{\text{max}} + L_{\text{min}}L_{\text{max}}) \). Accordingly, \( L_{R-1} \propto \left( L_{\text{min}}^{-1} + L_{\text{mid}}^{-1} + L_{\text{max}}^{-1}\right)^{-1/3} \), so the largest contribution corresponds to the smallest dimension limiting the correlation length growth. Namely, it reflects the expected dominant role of the smaller dimension, having surfaces close to the NP centre, in the \( T_C \) shift (\( L_R \) is appropriate even for nanowires and thin films, where contributions of infinite dimensions vanish).

Computations under FBC were made for rectangular nanoparticles, namely, cubes, as well as rods and platelets having aspect ratios 2, 4 and 6 (Fig. 5a, inset). The focus is on intra-separation perpendicular to the longest [100] axis that persists at higher temperatures because of a smaller interface area. Shape-specific finite-size scaling plots computed using the three definitions of the ELS are shown in Fig. 5. Surface effects related to the different NP shapes cause quite significant dispersion of the \( L_S \)-based plots, Fig. 5a (and to a lesser extent in the \( L_N \) plots, Fig. 5b). In particular, the scaling plots of NPs having a larger aspect ratio are shifted downwards. Likewise, for a given ratio, the platelet plot is shifted downwards vs. the rod plot. This is due to a larger fraction of surface sites \( N_S/N \) (ESI† Fig. S3) reducing the \( T_C \) value. On the other hand, the plots with respect to \( L_R \) exhibit markedly small dispersion and practically coincide in the scalable regime of larger NPs...
This shape-independent universal scaling plot can bridge via extrapolation the gap between $T_C$ in such NPs and $T_C^{\text{bulk}}$. The universality is thus manifested only when $L_R$ is chosen as ELS that adequately accounts for surface effects in different NP shapes, reflecting the role of the SA/V ratio in FSS.

**Conclusions**

This first study dedicated to finite-size scaling of nanoalloy phase separation second-order transitions employs a highly efficient computational method furnishing detailed FSS data for a broad range of NP sizes and several rectangular shapes. In spite of the approximations used (mean-field FCEM, CGLM, simple pair energetics), power-law scaling is manifested in all computations with distinctly consistent critical exponents obtained by different procedures, including directly fitted scaling plots and interface thickness analysis (Table 1). The refined (2-point) scaling analysis reveals a gradually decreasing role of the inner interface with NP size, so eventually the critical exponent for intra-NP separation coincides with that obtained for the interface-free inter-NP separation. The extrapolated critical exponent values ($\approx 1$) are in accordance with previous predictions for other systems, thus confirming the validity of the new modelling approach. Furthermore, the critical exponent extrapolation bridges the gap to larger particles within and well beyond the nanoscale. The predicted finite size scaling is accompanied by variations in transition-related peaks of the configurational specific-heat, including their shift, rounding and attenuation. In addition, this study by adopting the concept of “effective linear size”, associated with the surface area to volume ratio, reveals NP-shape independent universal scaling. This as well as the intriguing issue of the interface role and the extension of the introduced method to FSS in first-order separation transitions in alloy nanoparticles are likely candidates for future studies.

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**References**


