Stabilization and transformation of asymmetric configurations in small-mismatch alloy nanoparticles: the role of coordination dependent energetics

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Chemical order in platinum–iridium truncated-octahedron nanoparticles as a model system was studied using coordination-dependent bond-energy variations (CBEV) and the statistical-mechanical free-energy concentration expansion method (FCEM) adapted for handling axially symmetric structures. Pt–Ir side-separated (“Quasi-Janus”, QJ) configurations are found to be stabilized at low temperatures mainly due to CBEV-related preferential strengthening of Pt-surface–Ir-subsurface bonds, and the greatly reduced number of hetero-atomic bonds. In comparison, the roles of local strain (by only ~2% atomic mismatch), short-range-order and vibrational entropy are minor. At higher temperatures, the QJ configuration is transformed into a partially disordered central-symmetric onion-like structure, and the sharp transition is accompanied by extensive pre-transition atomic exchange processes, reflected in a lambda-type heat capacity curve. The nanoparticle composition and size dependent transition temperatures, which are well below the bulk miscibility gap, furnish the first Pt–Ir nanophase diagram, which is likely to represent a distinct class of asymmetrically phase-separated nanoalloys having negligible mismatch but large preferential bond strengthening at the near-surface region.

1. Introduction

In the extensive theoretical and experimental research devoted to alloy nanoparticles (NPs), attention has been given recently to bi-metallic phase-separated (demixed) systems. Such binary NPs have been used in heterogeneous catalysis, and can find applications in other fields of technology, e.g., in biomedical drug delivery using core–shell configurations. Pt–Ir nanoparticles are used as catalysts in organic molecule hydrogenation, in oxygen reduction reactions, etc. One general route of research involves efforts to induce via kinetic effects mixed chemical order for catalytic reactions. A different route, which is employed in the present study, deals with the nature of equilibrium demixed configurations using mainly theoretical model computations. Thus, systematic studies of stable configurations with asymmetric off-centre elemental cores (aggregates) in the so-called “Janus particle” were reported most recently by Bochicchio and Ferrando using the second-moment approximation to the tight-binding model (SMA-TB potential) in conjunction with global optimization procedures. In particular, it was claimed that the formation of such side-separated inner aggregates, referred to as “morphological instabilities” with respect to the centred-core shell NPs, is quite a general phenomenon pertinent to poorly miscible NP systems of different shapes. Thus, in the case of considerable size mismatch (>10%) between the atoms of two alloying elements, such as Cu, Ni or Co alloyed with Ag, the main driving force is attributed to local strain energy effects. In the corresponding fcc NPs (e.g. truncated octahedra), subsurface sites are preferentially populated by the minority smaller atoms (first found for onion-like symmetric configurations), which initiate the growth of the Janus-type configurations. Having lower surface energy the other element (Ag) segregates to the external surface layer surrounding the bi-aggregate, forming a “quasi-Janus” (QJ) particle. Some experimental evidence for a transition from core–shell to Janus-type configuration by increasing the Ag content in Ag–Cu NPs was obtained recently by EFTEM. Effects of NP size on phase separation temperature in the same system were treated in an early study using Monte-Carlo (MC) simulations and a simple continuum model.

The above studies challenged us to explore the possibility of equilibrium phase separated chemical order in NP alloys having a relatively small atomic-size mismatch and a somewhat higher miscibility than the above-mentioned silver alloys. The key issue is whether low temperature Janus-type configurations can be stabilized even when strain effects are (nearly) absent. The present first case involves Pt–Ir truncated octahedra (TO) as...
a model system, and since the atomic mismatch is only 2% the driving force for possible stabilization of such configurations is likely to be altered. In particular, we wondered if the tendency of Ir atoms to segregate at the subsurface atomic layer, induced by preferential strengthening of its bonds with surface atoms (as predicted also in our previous study of 923 Pt–Ir cuboctahedra\textsuperscript{10}) can become a dominant driving-force and initiate the formation of an off-centre Ir aggregate as one side of a Qf NP. This question was not asked in that study mainly because of the imposed central symmetry constraint. The answer to it turns out to be definitely positive, as presented in Section 3. Additional goal concerns effects of temperature on the nanophase-separated chemical order in view of the well-known phase transformation of the Pt–Ir separated bulk to solid solution at high temperatures. Most of the study involved 201 atom TO, but in order to explore size effects some computations were done for 586 atom NPs, including nanophase transformations.

The role of the new driving force is studied here by an improved version of our previous modelling approach, which is capable of handling asymmetric Janus-type configurations (Section 2). The work focused on quantitative evaluation of all site-specific concentrations, leading to the construction of the first nanophase diagram for the almost unexplored Pt–Ir nanoparticle system. Beyond this specific case, the revealed role of coordination-dependent energetics in the stabilization of asymmetric configurations and their temperature-induced transformation is quite general, and should be pertinent to chemical and physical properties of other small-mismatch nanoalloys.

2. Methodology

Our previously introduced approach to the alloy NP energetics and statistical mechanics has been chosen in the present work because of its high transparency and efficiency. In particular, the coordination dependence of surface–surface and surface–subsurface elemental pair-bond energy variations (CBEV),\textsuperscript{10} in the form of polynomial functions, was extracted from DFT derived pure Ir and Pt surface-energy anisotropies.\textsuperscript{11} The reasonable accuracy of this two-layer model was revealed before by comparison with direct DFT computations of Pt–Pd NPs,\textsuperscript{12,13} as well as with near surface compositional profiles measured for Pt\textsubscript{0.25}Rh\textsubscript{0.75}(111).\textsuperscript{12,14} The CBEV data constitute a part of the input energetics to the free-energy concentration expansion statistical-mechanical method (FCEM),\textsuperscript{15} furnishing all temperature dependent site concentrations of NPs comprising up to ~1000 atoms. While the FCEM version used so far takes into account both short-range order and configurational entropy, three modifications have been done in the present study: (i) adaptation of the method for handling Janus-type asymmetric configurations by easing the restriction of central symmetry in favour of axial symmetry (Fig. 1). In particular, the number of geometrically inequivalent sites increases (e.g., from 24 to 120 in 586 TO) when dividing central-symmetric shells to smaller groups, each characterized by its specific location with respect to (and along) the symmetry axis chosen to be normal to the TO (111) face since it corresponds to maximal CBEV effects in Pt–Ir fcc NPs (described below; quite similar results were obtained for the [100] axis). Some FCEM/CBEV comparative computations were done under the restriction of central symmetry, and some others were repeated while omitting the CBEV or the short-range order (SRO) terms from the free-energy expression; (ii) incorporation of vibrational entropy in the free-energy due to its possible effects on transition temperatures\textsuperscript{16} in bulk or NP alloys; and (iii) incorporation of previously neglected coordination-dependent variations in the effective pair-interaction, V.

Total energies at 0 K were evaluated starting with Ir-dilute NPs (Ir = 1, 2 and 3 atoms) in order to find the energetically most favourable configurations. Otherwise, site-concentrations were obtained by minimization of the free energy using the “fmincon” function in the MATLAB computation package. To accurately localize the position of a possible phase transition, 10 K temperature steps were used, and a given temperature was approached by both heating and cooling. Substituting concentrations in the FCEM expression for the free energy provides thermodynamic properties, such as the NP configurational heat capacity variations with temperature.

Energetics

According to the CBEV model, the energy of a near-surface nearest-neighbor (NN) m–n bond equals the sum of the bulk energy\textsuperscript{10,17} (w\textsubscript{b}\textsuperscript{Pt–Pt} = 1.21 eV, w\textsubscript{b}\textsuperscript{Ir–Ir} = 1.32 eV) and its coordination-related variation, w\textsubscript{mn} = w\textsubscript{b} + δw\textsubscript{mn}. Both intra-surface and surface–subsurface (“inter”) bond-energies exhibit the expected general tendency to strengthen for lower coordinations.\textsuperscript{10} All the intra bond variations of Pt are larger than for Ir, thus amplifying the surface segregation tendency of Pt\textsubscript{b}\textsuperscript{18–22} whereas most of its inter variations are smaller. (Ir–Ir inter bond preferential strengthening is apparently related to dominant sp electronic contributions, as indicated by TB modeling.\textsuperscript{23}) The bulk value, V\textsubscript{b} = (w\textsubscript{b}\textsuperscript{Pt–Pt} - 2w\textsubscript{b}\textsuperscript{Pt–Ir} - w\textsubscript{b}\textsuperscript{Ir–Ir})/2 ≈ –23 meV, was derived from DFT-computed low-temperature formation enthalpy,\textsuperscript{24} and it is assumed that the coordination-dependent hetero-atomic bond energy relative variation (δw\textsubscript{mn}^\textsubscript{Pt–Ir}/w\textsubscript{b}^\textsubscript{Ir–Ir}) follows the arithmetic
average of the corresponding homo-atomic bond energy relative variations. Since for most of the surface–subsurface (inter) bonds, $|\delta w_{\text{Ir-Ir}}| > |\delta w_{\text{Pt-Pt}}|$, the in-between $|\delta w_{\text{Ir-Ir}}|$ value should be also larger than $|\delta w_{\text{Pt-Pt}}|$, so that replacing the Pt–Pt inter-bond by the Pt-surface–Ir-subsurface bond is energetically advantageous. Hence, it is instructive to evaluate quantitatively the NP bond energy gain due to the presence of a single Ir impurity at the subsurface site $m$,

$$\Delta E_m = 12(w_{\text{Ir-Ir}} - w_{\text{Pt-Pt}}) + \sum_s (\delta w_{\text{Ir-Ir}} - \delta w_{\text{Pt-Pt}}),$$

\(s \in \text{surf}, \ m \in \text{subsurf}\)  

(1)

### 3. Results and discussion

#### Low $T$

Going from low to higher Ir content, we start from a single Ir impurity in 201 Pt TO NPs at low temperatures. As noted above, surface sites are strongly unfavourable for Ir (Fig. 2a), as compared to inner core sites, and according to the balance of bond contributions including the CBEV, the energy increase ranges from 322 meV for (111) sites to 879 meV for the vertex. As a result, Pt atoms practically do not desegregate from the surface (<1%) even at ~1200 K, and therefore we focus below on the NP core alone. On the other hand, being usually larger for Ir, the inter-variations are expected to send this atom to the fully coordinated subsurface sites. The data shown in Table 1 demonstrate quantitatively the preferential strengthening of Pt surface–Ir subsurface bonds vs. Pt–Pt bonds (except for the vertex–subvertex opposite case), signifying that over quite a wide range of temperatures Ir impurity is not expected to leave the subsurface. Specifically, since Ir bonding with (111) surface Pt is the most preferable energetically (41.3 meV each), and the subedge has the largest number of such bonds (4) (in addition to strengthening of one edge–subedge bond by 14.5 meV), this site should be populated by the impurity first (Fig. 2b and c). For comparison, Ir impurity at the (111) subsurface has only 3 bonds with the (111) surface and no other bonding to surface sites, making this site less energetically favorable by 55.8 meV. While subsurface edge sites are energetically preferable also for two Ir impurity atoms (the closest ones are shown in Fig. 2c), a third Ir atom goes to a (111) site bridging the two edge Ir atoms (Fig. 2d) because of the separation tendency in this alloy, and in spite of subedge and subvertex CBEV stabilizing effects (Table 1).

With increase of the Ir content to 6 atoms, subsurface 2D clusters are formed by populating a triangle of edge and face sites (Fig. 2e), and additional 6 Ir atoms populate the adjacent vertices (Fig. 2f). Starting from Pt$_{177}$Ir$_{24}$, 3D Ir aggregates, forming Quasi-Janus configurations, become progressively bulkier (Fig. 2g–i).

#### Higher $T$

Exploring the QJ thermal stability, we found that these NPs quite remarkably exhibit a transformation to a central-symmetric multi-shell (MS) partially disordered onion-like configuration at a composition-dependent characteristic temperature (Fig. 3a). In particular, applying the FCEM/CBEV method from 1 K to 1200 K reveals some features common to all NP compositions (Fig. 3b). Thus, Ir atoms start to leave the least stable inner and interface sites of QJ NPs (e.g. #5 in Fig. 3b-left) at lower temperatures and then more stable sites until Ir leaves the most stable subedge site #3 (see Table 1) at the highest temperatures. Concurrently, sites of the original Pt side of the QJ NPs are populated by Ir, and eventually concentrations of the same shells all coincide at a quite sharp transition temperature ($T_{\text{trs}}$). The resultant MS properties

### Table 1

<table>
<thead>
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<th>Surf. site (s)</th>
<th>NP energy with single Ir impurity $^a$</th>
<th>m</th>
<th>(111)</th>
<th>(100)</th>
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<td>1</td>
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<td>+55.8</td>
</tr>
<tr>
<td>Inner</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
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</table>

$^a$ Preferential strengthening (–) or weakening (+) of Pt–Ir bonds relative to Pt–Pt. $^a$ Relative to Ir impurity at the subsurface edge, $\Delta E_{m} - \Delta E_{\text{edges}}$, computed according to eqn (1).
The configuration of the NP core has only 6 non-equivalent sites (shells), compared to 18 sites in the more ordered and less symmetric low-T QJ configuration. The transition together with the pre-transition intra and inter shell mixing processes described above obviously raise the NP entropy. These variations and the new MS configuration differ between the two NP compositions, namely the onion-like being more uniform, almost approaching a core–shell structure in the Ir-richer Pt$_{159}$Ir$_{42}$. Starting from the $T_{tr}$, it exhibits two distinct groups of shell concentrations, compared to a more dispersed distribution (five groups) in Pt$_{157}$Ir$_{24}$ (Fig. 3b). Furthermore, in the former case, the transition occurs at a significantly higher temperature for these almost equal size, more stable QJ Pt/Ir aggregates (Fig. 3a, top-right).

The roles of the CBEV and of SRO in the QJ to MS transition were studied by arbitrarily reducing the magnitude of the originally derived bond-energy variations, and by eliminating completely the SRO term from the FCEM expression (i.e., employing the Bragg-Williams approximation), respectively. Pt$_{146}$Ir$_{55}$ TO with QJ configuration (Fig. 4a, left) transforming to a nearly core–shell structure (Fig. 4a, right) have been chosen for modelling. (The transition from the Pt inner aggregate in the QJ core to six subvertex clusters comprising four Pt each, is compatible with the interplay of the CBEV and the separation tendency, and somewhat resembles the one predicted in our previous work$^{10}$ regarding Pt–Ir MS cuboctahedron.) For clarity of presentation only one pair of sites, whose variations mark the final transition temperature, has been chosen. In particular, Fig. 4b shows the temperature dependence of the Ir concentration of the most stable site of QJ (subedge, #3) together with that of the corresponding Pt populated subedge #4 (belonging to the same shell). The dependence obtained under presumed central-symmetry, marked MS in Fig. 4b, reflects significantly reduced thermal stability compared to QJ (full CBEV), but all three lines ultimately coincide together at $T_{tr}$ = 600 K. Under 40% reduction in all bond-energy variations $T_{tr}$ goes down by about 200 K, and the trend is quite linear (Fig. 4b and inset). This highlights the decisive role of the CBEV effect in stabilizing the Janus configurations in this system. Namely, preferential strengthening of Pt-surface–Ir-subsurface bonds over elemental Pt bonds, which “anchor” the Ir aggregate of the QJ structure to the NP subsurface, is at the origin of the stabilization. As to the SRO effect, which as expected is maximal around the transition, (Fig. 4b), it is smaller and in an opposite direction compared to

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**Fig. 3** Transitions of Pt$_{177}$Ir$_{24}$ and Pt$_{159}$Ir$_{42}$ TO NPs from quasi-Janus (QJ) to multi-shell (MS) configurations. (a) Cross sections of the four configurations. Intensities of red and blue colours are proportional to Pt and Ir concentrations, respectively. (b) Variations with temperature of the subsurface and inner core site compositions (selected sites are marked in (a) top left).
the CBEV effect, namely SRO lowers $T_{\text{trs}}$ by stabilizing somewhat the partially disordered high-$T$ nanophase. Further computations show that depending on the NP composition the SRO-induced downward shift can reach as much as 110 K.

Regarding estimation of vibrational entropy effects on the predicted transitions, we used the so-called “bond proportion model” (BPM), assigning fixed stiffness to bonds.\footnote{16} On the average, the stronger and hence stiffer bonds in the quite ordered QJ structure compared to the more disordered MS structure, have smaller vibrational entropy and hence should reduce the transition temperature.\footnote{16} Atomic frequency ratios were obtained using atomic masses (which are rather close in the case of Pt and Ir) and force constants extracted from SMA-TB potentials.\footnote{25} The predicted decrease in the transition temperature ($\sim 10$ K) occurs to be smaller than the decrease due to SRO.

Under imposed central-symmetry the temperature dependence of the 201-atom TO MS structure (Fig. 4) exhibits only gradual atomic intermixing, unlike the QJ–MS distinct nano-phase transition. (Using the same symmetry restriction, quite sharp intra-core phase transitions are expected to occur only in much larger NPs.\footnote{10}) The difference between the quite distinct and gradual transitions in such small NPs can be attributed to the clear symmetry change involved in the QJ–MS case, while in the pure MS case intermixing does not change the imposed symmetry.

In order to further inspect the role of CBEV in stabilizing the QJ vs. the MS structure the energy variation across the entire relevant temperature range has been computed for Pt$_{159}$Ir$_{42}$ using the FCEM with and without CBEV contributions (Fig. 5). The large energy decrease under CBEV reflects the near surface remarkable bond strengthening. But the main focus here concerns the relative stability of the QJ configurations under the two energetics models. Thus, compared to the small energy gap between the QJ and MS configurations ($\leq 0.15$ eV) in the $\delta w = 0$ case, the gap under CBEV amounts to $\sim 1$ eV, signifying the enhanced relative stability of the QJ NPs. To elucidate the origin of these energy gap differences the respective numbers of hetero-atomic bonds have to be compared (at 0 K). The CBEV causes preferential population of subsurface sites by Ir atoms, resulting under central symmetry in the MS onion-like

**Fig. 4** The effect of CBEV and SRO on the transition of Pt$_{159}$Ir$_{42}$ from QJ to MS configuration: (a) 3D schematics of the NP cores (subsurface) and cross sections. Intensities of red and blue colours are proportional to Pt and Ir concentrations, respectively, obtained using the full CBEV/FCEM. (b) Variations with temperature in concentrations of selected sites: full CBEV/FCEM – solid lines; 60% of CBEV magnitude – dashed lines; presumed central-symmetry – dotted line; without SRO – dashed-dotted lines. (inset: variations in the transition temperature vs. CBEV magnitude).

**Fig. 5** Demonstration of the remarkable role of CBEV in stabilization of quasi-Janus configurations: energy variations with temperature of QJ and MS Pt$_{159}$Ir$_{42}$ TO NPs computed without CBEV contributions (a), and with CBEV (b). Zero energy corresponds to QJ (CBEV) at 0 K. The temperature-dependent configurational heat capacity is shown by dotted lines.
(metastable) structure (Fig. 5b), which has energetically unfavorable extensive Pt–Ir interfaces. On the other hand, removing the central symmetry restriction results in QJ structures having significantly lower energy due to a smaller interface area. For example, we counted 228 Pt–Ir bonds in the QJ Pt159Ir42 structure that are 93 bonds less than in the onion-like structure. Thus, the stability of the ultimate structure of QJ NPs is governed by the optimal balance of CBEV and the reduced number of hetero-atomic bonds. However, in the hypothetical no-CBEV energetics, the quite globular QJ (Fig. 5a) has only 8 fewer Pt–Ir bonds compared to the similar MS core–shell structure in this case (both having a much smaller interface area than the CBEV-induced onion-like structure). Therefore, the energy gap between the MS and QJ structures (Fig. 5a) turned out to be much smaller than in the CBEV case (Fig. 5b), leading to a significant destabilization of the former QJ. Likewise, the no-CBEV energies of QJ and MS structures are very close in the case of other compositions.

The QJ–MS transition (under CBEV, Fig. 5b) is reflected also in a sharp energy-slope change at the transition temperature as compared to the gradual change in the MS energy. The corresponding configurational heat-capacity curve exhibits an extensive χ-peak\(^{26}\) that reflects the pre-transition concentration variations (mixing of Pt and Ir, Fig. 3b). As noted above, they start from the least stable QJ inner and interface sites significantly below the transition temperature, at which more abrupt atomic exchange processes involving the stable subsurface sites occur, and all site lines of the same shell coincide. A much weaker jump in the heat-capacity curve is obtained for the more smoothly-varying no-CBEV energies.

All transition temperatures computed for magic-number compositions in the two NP sizes furnish together a QJ–MS Pt–Ir nanophase (partial) diagram (Fig. 6) having in the 201 atom case a maximum close to the equiatomic composition and supposedly CBEV-related asymmetric shape. For the 586 atom NPs the corresponding \(T_{\text{tr}}\)s are higher, indicating the expected increase of the QJ–MS transition temperatures with NP size. Moreover, the maximum shifts to higher Ir concentration, and the curve resembles somewhat a semi-empirical bulk miscibility gap (dotted line, ref. 27), but as might be expected is still below it as well as below the bulk gap we obtained in a regular thermodynamic procedure by using the FCEM formula without CBEV. (There are still significant uncertainties concerning the actual critical temperature, \(T_{\text{tr}}\), and the shape of the Pt–Ir bulk gap.\(^{28,29}\)) A similar, but rather smooth transition from QJ to an onion-like configuration was reported for single-sized (586 atom) Au–Pt TO NPs using MC with embedded atom potential that was parameterized to match the bulk phase diagram.\(^{30}\) In the corresponding phase diagram introduced in that work, at a certain concentration range the \(T_{\text{tr}}\)s of NPs exceeds the bulk experimental value, unlike the present and previous cases. Regarding driving forces pertinent to QJ formation, strain energy release was tentatively mentioned\(^{30}\) although the atomic mismatch is quite small in Au–Pt. Hence, it can be argued that CBEV-related effects might be operative through inexplicit involvement in the embedded atom potentials, providing a dominant driving force for QJ formation in these two systems too. Obviously, it is desirable to confirm this assumption by direct FCEM/CBEV computations.

### 4. Conclusions

This article presents our first attempt to model asymmetric chemical order in small-mismatch phase separating alloy nanoparticles by means of an adapted version of the statistical-mechanical free-energy concentration expansion method (FCEM) together with DFT-based coordination-dependent bond-energy variations (CBEV) as the input. Being capable of handling axially symmetric configurations this procedure facilitates studies of Janus (or quasi-Janus) structures, and is both transparent and efficient. Applying it to Pt–Ir truncated-octahedron NPs for deriving all site-specific concentrations demonstrate the remarkable role of CBEV in stabilizing off-centre asymmetric configurations (2D subsurface clusters and 3D quasi-Janus at low and higher Ir content, respectively) via preferential strengthening of surface–subsurface Pt–Ir bonds. This driving force for the formation of Janus-type configurations is different from previously reported strain effects related to atomic mismatch, which amounts to only 2% in the case of Pt–Ir. A rough estimate of Pt(Ir) bulk strain energy based on a simple linear elasticity formula\(^{31}\) gives only few meV per Ir solute impurity, which is more than an order of magnitude smaller compared to CBEV effects in this system. Another finding of this work concerns the prediction at elevated temperatures of distinct transformations from the axial-symmetric phase-separated QJ to central-symmetric multi-shell configurations. The derived transition temperatures vs. composition and size furnish the first Pt–Ir nanophase (partial) diagram, which is well below the bulk miscibility gap. Although a nearly pure Pt surface persists for both configurations in a
wide range of temperatures and overall compositions, these results seem to be relevant to catalytic properties, which can be affected also by the subsurface composition.

The revised methodology introduced here together with its first implementation is part of a comprehensive plan to elucidate asymmetric configurations and their transformation to symmetric ones in other useful binary (and even ternary) nanoalloys with small size mismatch. Further tasks include comparison of the FCEM/CBEV results to those obtainable by other methodologies (e.g., DFT, SMA-TB/MD/MC simulations), as well as to experiments that can be quite problematic using current techniques for such small nanoparticles. Moreover, extending the modelling to larger, more practical nanoparticles has also a theoretical interest, being of key relevance regarding fluctuations and finite-size scaling when getting closer to the (bulk) critical temperature.

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Notes and references