Prediction of compositional ordering and separation in alloy nanoclusters

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Abstract

The statistical–mechanical free-energy concentration expansion method (FCEM) in conjunction with semi-empirical coordination-dependent energetic parameters was used for atomistic modeling of Ni–Cu–Al, Ni–Cu–Rh and the corresponding binary Ni–Cu, Ni–Al and Rh–Cu nanocluster systems, containing from 13 to 923 atoms with icosahedral and cuboctahedral shapes. The high efficiency of FCEM enables computations of such relatively large binary or ternary alloy clusters. Remarkable differences, governed by the opposite Ni–Cu and Ni–Al heteroatomic interactions, were noted in the surface segregated “magic-number” ordered compositional patterns of the two ternary clusters. Due to the strong Ni–Al interactions, the compositional ordering extends into the cluster core, and at elevated temperatures a sharp order–disorder transition occurs, depending on the cluster size, shape and composition. The computed site-specific atomic concentrations form the basis for evaluating pertinent thermodynamic functions. For all the alloy clusters a Schottky-type heat capacity anomaly is predicted and attributed to gradual desegregation excitation processes. In addition, inter-cluster compositional separation is computed for Rh–Cu clusters, and transition temperatures estimated from the disappearance of convexity in the free-energy vs. composition curves.

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1. Introduction

Due to their unique properties, small particles, such as alloy nanoclusters, are attracting growing interest in recent years. In view of limitations in current experimental tools, valuable information about site-specific surface compositional structures has been obtained only by theoretical computations. When such data are obtained as function of temperature, for example, it facilitates the study of phase transitions, which raises intriguing
questions concerning their distinctive features in single vs. system of alloy nanoclusters. As shown here, in contrast to transitions in a single small particle, which typically spread over a range of temperatures [1], alloy cluster macroscopic systems can exhibit (similarly to bulk systems) phase transition points, related to intra- or to inter-cluster compositional–structural transitions. We use the free-energy concentration expansion method (FCEM), originally derived for the theoretical prediction of surface segregation in the presence of short-range order (inter-atomic correlations) in binary alloys [2,3], and has proven to be an attractive tool for elucidating compositional structural transitions in cases of dilute clusters or ordered clusters with \( c'_I \approx 0 \) or 1 (at some “magic-number” composition), and at relatively high temperatures, when \( V_{pq}^{IJ} \) is small compared to the thermal energy \( kT \). It can also be derived [8] from an approximate formula for the correlation parameters \( \epsilon_{pq}^{IJ} = c'_p c'_q c'^J_{pq} c'^I_{pq} \), where \( X_{pq}^{IJ} = 1 - \exp \left( -\frac{V_{pq}^{IJ}}{kT} \right) \). At low temperatures \( X_{pq}^{IJ} \) approaches 1 for \( V_{pq}^{IJ} > 0 \), but diverges exponentially for \( V_{pq}^{IJ} < 0 \) (at high temperatures \( X_{pq}^{IJ} \) is an odd function of \( \frac{V_{pq}^{IJ}}{kT} \)). Thus, in order to avoid the divergence problem, the free-energy formula has to be slightly modified. In accordance with the Ising model, where hyperbolic tangent appears in pair correlation functions and is used as an expansion parameter [9], \( X_{pq}^{IJ} \) is approximated here by \( \tanh \left( \frac{V_{pq}^{IJ}}{kT} \right) \) (\( b = 0.6 \) is obtained by best fit of FCEM predictions to Monte Carlo simulations of (100) surface segregation in fcc solid solution [2]). The revised free-energy expression reads,

\[
F = kT \sum_p \left( N_p \sum c'_p \ln c'_p \right) + \sum_{p < q} N_{pq} \left( \frac{1}{2} \sum w_{pq}^{IJ} \left( c'_p + c'_q \right) - \sum_{\{IJ\}} \left( V_{pq}^{IJ} c'_I c'_J + c'_p c'_q \right) + kT c'_p c'_q c'^J_{pq} c'^I_{pq} \right). 
\]

Estimations of the homoatomic interactions (Table 1) are based [4,5] on coordination-dependent site energies [6,10,11], using experimental cohesion and surface tension data, and assuming uniform distribution of the site energy among its NN bonds [12–15]. Heteroatomic effective interactions were obtained from the heat of mixing [6,16] by the FCEM formula [8].

2. Theory

FCEM applied to cuboctahedron (CO) and icosahedron (ICO) clusters consisting of atoms located at central-symmetric concentric “shells”, yields all \( I \)-constituent \( p \)-shell concentrations, \( c'_p \). The energetic parameters entering FCEM computations comprise the nearest-neighbor (NN) interaction energy, \( w_{pq}^{IJ} \), based [4,5] on coordination-dependent semi-empirical site energies [6], and the effective interactions, \( V_{pq}^{IJ} \), between constituents \( I \) and \( J \) (\( V_{pq}^{IJ} = \frac{1}{2} \left( w_{pq}^{II} + w_{pq}^{JJ} - 2 w_{pq}^{IJ} \right) \)). Geometric input parameters include the number of atoms in each shell, \( N_p \), and the number of NN pairs belonging to \( p \)- and \( q \)-shells, \( N_{pq} \) [4]. The FCEM correction to BW, obtained by expanding relevant thermodynamic functions in terms of \( c'_I c'_J [2,3,7,8] \), is reasonably accurate (and small) in cases of dilute clusters or ordered clusters with \( c'_I \approx 0 \) or 1 (at some “magic-number” composition), and at relatively high temperatures, when \( V_{pq}^{IJ} \) is small compared to the thermal energy \( kT \).

3. Compositional structural transitions

Previous FCEM computations accomplished for Ni–Cu–Pd and Ni–Cu–Rh nanocluster systems
predicted surface segregation of Cu/Pd and Cu/Ni, respectively, with resultant core separation of almost pure Ni and of Rh [4,5]. Due to opposite heteroatomic interactions (attractive vs. repulsive), different surface segregated compositional patterns were noted for certain “magic-number” compositions: “mixed” Cu/Pd ordering for Ni–Cu–Pd, and Ni/Cu “demixed” order for Ni–Cu–Rh. The computations of compositional structures in the present study focus mainly on the Ni–Al and Ni–Cu–Al cluster systems. The corresponding semi-infinite solids, exhibit prominent interplay of ordering and Al surface segregation [3], resulting in anomalous surface segregation phenomena [7,8] related to the very strong Ni–Al attraction ($V_{NiAl}$ ~ 136 meV). Likewise, for the clusters, strong Ni–Al core mixing, significant role of inter-atomic correlations, and correspondingly considerable differences between FCEM and BW predictions are anticipated. According to the results for magic-number compositions (Fig. 1), both core and surface of Ni$_{168}$Cu$_{84}$Al$_{57}$ exhibit inter-shell Ni–Al “mixed order” (compositional oscillations), compared to the above mentioned Ni$_{78}$Cu$_{84}$Rh$_{147}$ with separation between the Rh core and the surface, characterized by predominantly Ni/Cu “demixed order”.

Effects of temperature on compositional structures are introduced first for magic-number binary Ni–Al clusters (Fig. 2). It should be noted that for the core and surface a nearly perfect order persists

<table>
<thead>
<tr>
<th>Coord. #, site</th>
<th>12, bulk</th>
<th>9, (111) face</th>
<th>8, (100) face</th>
<th>7, edge</th>
<th>5, vertex</th>
</tr>
</thead>
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<tr>
<td>Al</td>
<td>−3360</td>
<td>−2980 (380)</td>
<td>−2880 (480)</td>
<td>−2620 (740)</td>
<td>−1980 (1380)</td>
</tr>
<tr>
<td>Cu</td>
<td>−3490</td>
<td>−2770 (720)</td>
<td>−2550 (940)</td>
<td>−2330 (1160)</td>
<td>−1890 (1600)</td>
</tr>
<tr>
<td>Ni</td>
<td>−4440</td>
<td>−3609 (831)</td>
<td>−3289 (1151)</td>
<td>−2970 (1470)</td>
<td>−2329 (2111)</td>
</tr>
<tr>
<td>Rh</td>
<td>−5750</td>
<td>−4600 (1150)</td>
<td>−4210 (1540)</td>
<td>−3820 (1930)</td>
<td>−3020 (2730)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$w_{AlAl}$</th>
<th>$w_{CuCu}$</th>
<th>$w_{NiNi}$</th>
<th>$V_{NiAl}$</th>
<th>$V_{CuAl}$</th>
<th>$V_{NiCu}$</th>
<th>$V_{CuRh}$</th>
<th>$V_{NiRh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>560</td>
<td>582</td>
<td>740</td>
<td>958</td>
<td>136</td>
<td>31</td>
<td>7</td>
<td>23</td>
</tr>
</tbody>
</table>

Fig. 1. Shell concentrations in “magic-number” Ni–Cu–Rh and Ni–Cu–Al CO-309 atom clusters (100 K) computed by FCEM with energetic parameters from Table 1. Insets: schematics of the corresponding surface ordered compositional structures. The numbers mark sites of surface shells: 9, 10, 11—(100) face, 12—(111) face, 13, 14—edge, 15—vertex (shells 0–8 constitute the cluster core).
in the Ni_{36}Al_{19} CO-55 cluster up to a disordering temperature \( T_c = 1030 \) K, while for Ni_{205}Al_{104} CO-309 cluster \( T_c = 1450 \) K, both lower than \( T_c = 1580 \) K predicted by FCEM for the Ni_{3}Al bulk alloy. (Core order in the magic-number binary and ternary structures resembles the \( \text{L}1_2 \) bulk structure of Ni_{3}Al with melting temperature \( \sim 1660 \) K [17].) In the ternary Ni–Cu–Al clusters the mixed Ni–Al order at the (100) faces is combined with demixed Cu, that depending on concentration sequentially segregates to vertexes, edge sites and then to the (1 1 1) face (Fig. 3). The calculations indicate the same transition temperature for core and surface sites, reflecting rather strong coupling (in bulk alloys, on the other hand, the surface can have a different critical temperature [18]). However, as can be seen in Figs. 3 and 4, although a nearly perfect core order persists up to the transition temperature, Cu addition causes clear pre-disordering of the surface (surface-induced disorder, SID [3]). The important role of inter-atomic correlations is reflected by significant differences in the predictions of FCEM vs. BW approximations (Fig. 4). FCEM predicts sharp transition, whereas according to BW gradual disordering at unrealistically high temperatures is obtained.

The temperature evolution of the compositional structures, including possible pre-disordering and sharp transitions followed by gradual atomic mixing, should be reflected in thermodynamic functions. Thus, according to the computation results, the abrupt order–disorder transition in Ni_{36}Al_{19} CO-55 (Fig. 4) involves an appreciable latent heat of \( \sim 3 \) kJ/mol (Fig. 5a) and a corresponding heat capacity sharp peak followed by a relatively broad hump, characteristic of Schottky anomaly [19] (Fig. 5b). The latter contribution to the heat capacity was most recently predicted by us for the first time for cases of gradual desegregation/mixing thermal excitation processes in Rh–Cu and Ni–Cu nanocluster systems [20]. The \( C–T \) curve is characterized by heat-capacity onset \( (T_0) \) and maximum \( (T_{\text{max}}) \) temperatures, largely determined by the desegregation (segregation) energetics of the particular alloy cluster. The universality of the heat-capacity curves as a Schottky-type anomaly, is evident when reduced

![Fig. 2. Top: ordered compositional structures (100 K), and bottom: constituent shell concentrations vs. temperature in magic-number Ni–Al CO-55 and CO-309 clusters.](image-url)
coordinates, $T/T_{\text{max}}$ and $C/C_{\text{max}}$, are used (Fig. 6). Among all the subtle variations, it is instructive to compare FCEM computation results with an analytical solution [19] applied here to 13-atom clusters with fixed individual (magic) composition, $1/13$ (and no inter-cluster atomic exchange, i.e. a single cluster) and two-level energetics. In the latter, the non-degenerated lower energy level corresponds to the position of a single solute atom in the cluster center, and the 12-degenerated higher level to its position in one of the 12 surface vertexes. According to this single cluster approach the anomaly peak is narrower (Fig. 6), since in the FCEM computations compositional fluctuations make the energy spectrum and its derivative significantly wider.

Systematic computations of Schottky contributions to the heat capacity vs. temperature provided the characteristic temperature parameters for the two shapes and various sizes (up to 923 atoms) of the two binary alloy clusters, all of which are summarized in Fig. 7. In addition to the consistent shape effect, it can be noted that since $T_0$, corresponding to the onset of desegregation between surface and core sites, is controlled by the maximal surface coordination, it is nearly independent of the cluster size and shape for clusters comprising more than 55 atoms. Then, $T_0$ corresponds to exchange between the dense (111) face and the core (Fig. 7), whereas the absence of (111) faces in the smaller 13- and 55-atom clusters, leads to initial desegregation involving the less coordinated vertex, edge or (100) face sites, and thus resulting in somewhat higher excitation-energy related $T_0$ values. Unlike $T_0$, $T_{\text{max}}$ depends not only on the low-lying energy of the (111)-core desegregation, but on the whole spectrum of excitation (segregation) energies from faces, edges and vertexes, and therefore should be related to some average surface coordination.

Fig. 3. Top: effects of Cu content on surface ordered compositional structures (100 K), and bottom: constituent shell concentrations vs. temperature in Ni-Cu-Al CO-309 clusters.
FCEM, applied above to a system of clusters capable of atomic exchange, is suitable also for elucidation of inter-cluster separation phenomena. Thus, sets of shell concentrations obtained by minimization of the free energy can be considered as true equilibrium values only after inspecting the shape of the free-energy vs. overall concentration curve. Fig. 8 presents the mixing free energy of Rh–Cu 13-atom CO cluster, \( F_{\text{mix}} \), defined in Ref. [4] as the difference between the alloy free energy and the individual CO free energy.
and the pure element free energies, and computed with the derived concentrations. While the negative $F^{\text{mix}}$ values indicate no tendency to separate into the two elemental clusters, at low temperatures it does reveal a region of convexity (“miscibility gap”) between pure Rh and a marked minimum corresponding to a stable (“magic”) compositional structure, RhCu$_{12}$, having Rh central atom and Cu at the surface vertexes. Hence, for intermediate overall compositions in the convex region, the system is unstable with respect to separation into RhCu$_{12}$ and pure Rh clusters. It should be emphasized that, as mentioned above, while bulk systems are characterized by phase transition points (e.g., melting, compositional separation), transitions in a single small particle typically spread over a range of temperatures [1]. However, the large system of CO-13 clusters, capable of exchanging atoms, does exhibit inter-cluster separation, characterized by a distinct transition temperature marked by the disappearance of the convexity (Fig. 8). It signifies the onset of formation of “single phase” clusters having an intermediate composition. In particular, a transition temperature of $\sim$440 K was estimated for RhCu$_{12}$/Rh$_{13}$, that is considerably lower than the bulk value ($\sim$1423 K at $\sim$60 at.% of Rh [17]). This trend is in accordance with the depression of certain transition temperatures in small particles due to the reduced coordination [4,21]. It can be noted that due to the less dense surface, a CO cluster (system) has at intermediate concentrations a smaller number of unfavorable heteroatomic bonds compared to ICO clusters, and correspondingly somewhat lower transition temperature of inter-cluster separation (440 K vs. 580 K for ICOs [20]).

In conclusion, using the free-energy concentration expansion method, ordered “magic-number” compositional structures were predicted for several Ni–Cu–Al and Ni–Al nanoclusters, which disorder sharply at elevated temperatures. A Ni–Cu–Rh cluster system (and its binaries) are expected, on the other hand, to separate at certain temperatures into magic-number distinct clusters. For all cluster systems a Schottky-type heat capacity anomaly is predicted, and attributed to desegregation thermal excitation processes. Its measurement can in principle elucidate indirectly the cluster surface segregation energetics. Such FCEM computations...
for alloy clusters can be helpful in selecting conditions for fabricating particular desirable compositional structures. Moreover, the predicted phenomena are expected to have implications for the performance of alloy nanoclusters used in present and future technologies. Comparative FCEM computations, based on DFT calculated surface energies [22] (and without input cohesive energies), are in progress.

References