Equilibrium shapes of facetted 3D metal nanoclusters intercalated near the surface of layered materials

King Lai  
*Iowa State University and Ames Laboratory*

Ann Lii-Rosales  
*Iowa State University and Ames Laboratory*

James W. Evans  
*Iowa State University, jevans@ameslab.gov*

Follow this and additional works at:  [https://lib.dr.iastate.edu/ameslab_manuscripts](https://lib.dr.iastate.edu/ameslab_manuscripts)

Part of the Condensed Matter Physics Commons, Materials Chemistry Commons, and the Nanoscience and Nanotechnology Commons

**Recommended Citation**  
Lai, King; Lii-Rosales, Ann; and Evans, James W., "Equilibrium shapes of facetted 3D metal nanoclusters intercalated near the surface of layered materials" (2020). *Ames Laboratory Accepted Manuscripts*. 731.  
[https://lib.dr.iastate.edu/ameslab_manuscripts/731](https://lib.dr.iastate.edu/ameslab_manuscripts/731)

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Equilibrium shapes of facetted 3D metal nanoclusters intercalated near the surface of layered materials

Abstract
Experimental studies indicate that 3D crystalline metal nanoclusters (NCs) intercalated under the surface of graphite have flat-topped equilibrated shapes. We characterize the shapes of these facetted NCs sandwiched between a blanketing graphene layer and the underlying graphite substrate. Specifically, we focus on the cases of fcc Cu and hcp Fe NCs. The analysis involves numerical minimization of the system energy for a specified NC volume and NC height, the latter corresponding to the separation between parallel top and bottom facets. Our numerical analysis quantifies how the distance of the side facet planes from center of the nanocluster varies linearly with a natural characteristic linear dimension of the nanocluster. Calculated shapes of fcc Cu and hcp Fe NCs are consistent with the hexagonal footprints observed in scanning tunneling microscopy studies.

Disciplines
Condensed Matter Physics | Materials Chemistry | Nanoscience and Nanotechnology
Equilibrium Shapes of Facetted 3D Metal Nanoclusters Intercalated near the Surface of Layered Materials

King C. Lai,1,2 Ann Lii-Rosales,1,3,* and James W. Evans1,2

1Ames Laboratory – USDOE, Iowa State University, Ames, Iowa, 50011
2Department of Physics & Astronomy, Iowa State University, Ames, Iowa, 50011
3Department of Chemistry, Iowa State University, Ames, Iowa 50011

Abstract

Experimental studies indicate that 3D crystalline metal nanoclusters (NCs) intercalated under the surface of graphite have flat-topped equilibrated shapes. We characterize the shapes of these facetted NCs sandwiched between a blanketing graphene layer and the underlying graphite substrate. Specifically, we focus on the cases of fcc Cu and hcp Fe NCs. The analysis involves numerical minimization of the system energy for a specified NC volume and NC height, the latter corresponding to the separation between parallel top and bottom facets. Our numerical analysis quantifies how the distance of the side facet planes from center of the nanocluster varies linearly with a natural characteristic linear dimension of the nanocluster. Calculated shapes of fcc Cu and hcp Fe NCs are consistent with the hexagonal footprints observed in STM studies.

*Current Address: Department of Chemistry, University of Colorado Boulder, Boulder, Colorado, 80309

1. Introduction

Recent experimental scanning tunneling microscopy (STM) studies have demonstrated the possibility to form 3D crystalline nanoclusters or nanocrystals (NCs) of various metals [1-6] which are intercalated or encapsulated under the top graphene layer(s) of highly-oriented pyrolytic graphite (HOPG). The synthesis process requires both preliminary sputtering of the HOPG surface to generate defects or portals through which metal atoms can enter the underlying gallery, and then subsequent deposition of metal atoms at high temperature. Such encapsulated NCs have potential for applications in micro- or nano-electronics including heat sinks and electrical contacts [3,5]. Other potential applications are related to the protection of catalytic metal nanoclusters against oxidation and coarsening (cf. Ref.[7]). Intercalation of metals is realized in other layered systems such as supported graphene, although formation of 3D clusters is not observed [8-10]. Efforts continue to realize near-surface metal intercalation in other layered materials [11-13].

Of particular interest here are 3D fcc Cu NCs encapsulated in HOPG formed by deposition of about 100 atoms/nm² of Cu at 800 K on a HOPG surface bombarded with Ar⁺ ions for 30 sec. These NCs have diameters in the range d ≈ 35 – 600 nm and heights h ≈ 2 – 45 nm with an average d/h ≈ 17 (and somewhat lower values of d/h for the largest sizes) [3,4]. Also of interest are 3D hcp Fe NCs in HOPG formed by deposition of about 10 monolayers of Fe at 900 K.
on a HOPG surface bombarded with Ar⁺ ions for 60 sec. These NCs have an average diameter of \( d \approx 50 \text{ nm} \) and width of \( h \approx 2.5 \text{ nm} \), so that \( d/h \approx 20 \) [5,6]. The feature that these Fe nanostructures have hcp (versus bulk bcc) crystalline structure was proposed in previous studies [5,6]. Of particular significance for the current contribution is the observation based upon STM studies of these systems combined with appropriate theoretical analysis that the larger 3D NCs appear to have equilibrated shapes, at least with respect to the height versus width aspect ratio [4,6]. Furthermore, although STM cannot directly image the metal NC shape, as it is hidden beneath a graphene blanket, it is clear that most NCs for both Cu or Fe have flat tops. For Cu, this corresponds to a fcc(111) facet, and for Fe, it was proposed to correspond to a hcp(0001) facet. The STM imaging also provides information on the shape of the footprint of the metal NC.

Complete analysis of equilibrium NC shape in these systems must consider both the 3D metal NC and the covering blanket of stretched graphene layer(s). Specifically, one minimizes the total energy associated with this composite nanostructure which includes a strain contribution from the stretched graphene sheet, surface and interfacial energies contributions for this metal-graphene system, as well as a delamination energy associated with separating the top graphene blanket layers from rest of the HOPG constituting the substrate underneath the NC [4,6]. The non-trivial strain component of this problem can only be solved analytically using a simple cylindrical geometry model for the metal NC shape, and after also making additional approximations [4,6].

Our approach in this work is different with a focus on providing an accurate theoretical determination of the faceted 3D equilibrium shape of metal NCs in such systems. We adopt the view that experimental STM data allows a reasonable estimate of the total volume of each encapsulated metal NC, as well as a precise estimate of the height \( a \) from line profile analysis. Again, although STM cannot directly image the metal NC, it does reveal that top of the NC corresponds to a flat facet. We reasonably assume that bottom of the NC is also a flat facet supported on the underlying graphite. Thus, to determine the NC shape for prescribed volume and height, it suffices to solve the energy minimization problem for an NC with this volume sandwiched between two parallel surfaces or “plates” with prescribed separation. In this case, the total system energy which must be minimized just includes contributions from metal surface energy, and from the adhesion of the metal NC to the upper and lower “plates” (which physically are the covering graphene blanket and the supporting graphite substrate, respectively). In other words, given the prescribed NC height (as well as volume), it is not necessary to analyze a strain problem.

Traditional theories and formalisms determine the equilibrium shape of 3D NCs under different conditions: unsupported NCs [14]; supported NCs on a flat substrate [15,16]; supported NCs at a corner between flat substrates [17]. Particular emphasis has been placed on the case of faceted NCs. However, for the system involving a NC sandwiched between two parallel surfaces or plates, analysis has only considered a 2D system [18], or a 3D system for the case of weak anisotropy without faceting [19]. The latter is appropriate for liquid crystal systems where there is particular
interest in the shape of the meniscus. The problem of determining equilibrium shapes of sandwiched facetted 3D NCs, which of relevance here, has not been addressed previously.

In Sec.2, we will first briefly review the traditional continuum treatments for equilibrium crystal shape for various unsupported and supported scenarios. Next, in Sec.3, we present the formalism for analysis of intercalated NCs which enables numerical calculations. Then, in Sec.4, we report the results of numerical calculations for the shape of 3D Cu NCs [4] and 3D Fe NCs [5] encapsulated or intercalated in graphite as our targeted systems. In Sec. 5, we discuss the extensions of our approach and the implications of our data.

2. Traditional theory of unsupported and supported equilibrium NC shape

For an isolated free-standing 3D (or 2D) NC, the equilibrium shape is determined by the classic Wulff construction [14]. Minimization of the surface free energy of the NC is transformed into a geometrical construction based upon the polar plot of the surface energy, \( \gamma(\hat{n}) \), as a function of the surface normal, \( \hat{n} \). For a faceted NC, effectively \( \gamma_i \) is finite only for a discrete set of orientations \( i = 1, 2, 3 \ldots \). The Wulff construction then reduces to the simple relation

\[
\frac{\gamma_i}{\gamma_j} = \frac{h_i}{h_j},
\]

where \( h_i \) denotes the (perpendicular) distance of the facet plane \( i \) from the center of the NC. Thus, the ratio of distances, \( h_i \), to different facets is given by the ratio of surface energies, \( \gamma_i \). A 2D schematic of the Wulff construction is shown Fig. 1a. Recently, this construction has found extensive application in the area of solution-phase synthesis of unsupported metal nanocrystals [20].

Another class of systems involves 3D NCs supported on a 2D substrate [21-24]. Such systems are particularly important in the context of catalytic metal nanoclusters on oxide or other non-metallic supports. In this case, Kaischew’s theorem [15], also known as the Winterbottom construction [16], describes equilibrium shape. For this construction, one can regard the surface
energy of the contacting facet as being effectively reduced by the adhesion energy $\beta$ between NC and substrate. This leads to a modified relation

$$\frac{h_s}{h_i} = \frac{\gamma_s - \beta}{\gamma_i} = \frac{h_j}{h_i} = \frac{\gamma_j}{\gamma_i},$$

(2)

where subscript $s$ indicates the surface in contact with the substrate. This equilibrium shape simply corresponds to that of the Wulff construction with a truncated portion as shown in Fig.1b. In (2), distances are measured from the center of the non-truncated Wulff shape. Note that the stronger the NC-substrate adhesion, the larger $\beta$, and the greater the extent of the truncation of the Wulff shape. Above a critical value of $\beta$, the NC adopts a 2D form completely wetting the substrate.

For a NC at the corner formed by two non-parallel intersecting substrates, the appropriate extension of Kaischew’s theorem has been described as the Summertop construction [17]. For all of the Wulff, Kaischew or Winterbottom, and Summertop constructions, there is a unique equilibrium shape independent of size or volume for the same set of $\gamma_i$ (and $\beta$). Thus, for NCs with different volumes $V$, this equilibrium shape has the feature that all linear dimensions of the facets scale like $V^{1/3}$. However, for a NC sandwiched between two parallel surfaces or “plates”, the equilibrium shape clearly loses this rescalability. For each choice of parameters and prescribed NC height or “plate separation” $h_{\text{total}}$, there exists only one volume $V_0$ such that the dimensions satisfy (2). However, the need here is to determine the equilibrium shape of the sandwiched NC for a general prescribed volume, $V$. For 2D sandwiched NCs [18], one can first follow a Summertop type construction to determine the shape of the NC side facets and then translate theses side facets either together or apart to fit the required volume. For 3D sandwiched NCs, although there exists a previous study for weak anisotropy [19], there does not exist a formulation for facetted NCs providing a compact expression for NC shape analogous to Wulff construction or Kaischew’s theorem. Thus, for the two specific systems of interest in this paper, in the next section we determine the equilibrium shape of the sandwiched NCs by numerical analysis of the relevant energy minimization problem.

3. Formulation for NCs intercalated between parallel surfaces

We consider faceted 3D NCs with anisotropic surface energies $\gamma_i=1,2,3,\ldots$ specified for a discrete set of facets with orientations $\hat{n}_i=1,2,3,\ldots$. There are two parallel surfaces in contact with the upper and lower surfaces or plates separated by $h_{\text{total}}$ with orientations $\hat{n}_1$ and $\hat{n}_2 = -\hat{n}_1$ for top and bottom directions, respectively. The adhesion energies describing contact of the metal with these top and bottom surfaces are denoted by $\beta_1$ and $\beta_2$, respectively. We assume $h_{\text{total}}$ is small enough, or equivalently the prescribed NC volume $V$ is large enough, such that the equilibrated NC is in contact with both surfaces. This is the case for the metal NC intercalation systems of interest here. A 2D schematic of the system under consideration here is shown in Fig.1c.
For the total free energy of the systems considered here, the contribution associated with delamination of the covering graphene layers from the remainder of the graphite is regarded as constant, as is that from the bulk volume term for the metal NC (given the fixed volume). Thus, these contributions do not affect the shape of the NC. The other contributions to the free energy of the system $E$ have the form

$$E = \sum_{i=1,2} (\gamma_i - \beta_i) A_i$$

where $A_i$ is the area of facet with normal vector $\hat{n}_i$. Minimization of $E$ with a fixed volume $V$ follows from a Lagrange multiplier approach

$$\delta E - \lambda \delta V = 0,$$

where $\lambda$ is the Lagrange multiplier. Solution of this minimization problem leads to a set of $h_i$ which determines the equilibrium shape.

Note that there is some freedom in selection of the origin of the coordinate system within the NC from which distances to facets are measured. We prescribe the height of the origin so that $h_1/h_2 = (\gamma_1 - \beta_1)/\gamma_2 - \beta_2$. This natural choice for the distance between the origin and the substrate-NC interfaces is motivated by Kaischew’s theorem (2). The lateral position of the origin is at the unique (lateral) center of the NC. The volume of the NC is then given by

$$V = \sum_i A_i h_i/3.$$  \hfill (5)

Let the position of vertices $r_{i,j}$ of the facet $i$ with $j$ being the label of vertices ordered in an anti-clockwise manner. The area $A_i$ can be generally written as a sum of areas of the constituent triangles. An example of a hexagon is shown in Fig. 2. Thus, one has

$$A_i = \sum_{j>2} \sqrt{s_{i,j}(s_{i,j} - |r_{i,1} - r_{i,j}|)(s_{i,j} - |r_{i,1} - r_{i,j-1}|)(s_{i,j} - |r_{i,j} - r_{i,j-1}|)},$$

with $s_{i,j}$ being the semi-perimeter of the triangle formed by vertices $r_{i,1}, r_{i,j}, r_{i,j-1}$,

$$s_{i,j} = \frac{|r_{i,1} - r_{i,j}| + |r_{i,1} - r_{i,j-1}| + |r_{i,j} - r_{i,j-1}|}{2}.$$  \hfill (7)

Fig. 2 Schematic illustrating the approach to computing the area of a hexagonal facet where the facet is divided into constituent triangles.
The procedure for determining the equilibrium NC shape can be then divided into two parts. First, expressions are obtained for the positions of vertices \( r_{i,j} \) in terms of \( h_i \). Then, by varying all the \( h_{i>2} \), these dimensions are determined from (3)-(7) through the Lagrange multiplier method for a chosen \( V \). However, a significant challenge is to select an appropriate initial NC geometry given that, apriori, one cannot in general guess the complex arrangement and number of facets and vertices in the equilibrium structure, as this depends on the relative strengths of \( \beta_1, \beta_2 \) and \( \gamma_i \). For that reason, we start with the special choice of NC volume \( V = V_0(h_{\text{total}}) \), where all \( h_i \) obey (2). Examples of this special shape will be provided in the next section for the specific systems of interest. Such a NC shape is this special case of a standard Wulff or Kaschiew construction. It is thus well explored and software is available [25] to facilitate its construction which we exploit. For this NC shape, one can identify the position of vertices in terms of \( h_i \) by

\[
\mathbf{r}_{i,j} \cdot \hat{n}_k = h_k,
\]

where \( k \) is the indices of three facets next to the vertex at \( r_{i,j} \). With this set of \( h_i \) for \( V = V_0(h_{\text{total}}) \), we then proceed to incrementally change the volume to \( V = V_0(h_{\text{total}}) + dV \) and obtain the corresponding new set of \( h_i \). Note that during this processes, pairs of vacancies can collide or merge and then separate so that different facets are neighbors (sharing an edge) before and after collision. Such possible topological changes naturally complicate tracking NC geometry evolution, and are discussed further in the Supplementary Materials. We repeat this procedure until the size reaches the targeted value observed in an experiment. This procedure yields a series of equilibrium shapes at different volumes with a fixed height \( h_{\text{total}} \).

Given the form of (3)-(7), for a given set of all \( \gamma_i \) and \( \beta \), one can transfer the results for one \( h_{\text{total}} \) to a different \( h_{\text{total}} \) by rescaling all length \( h_i \) by ratio of new and old \( h_{\text{total}} \) (so the volume \( V \) is rescaled by the cube of this ratio).

4. Examples: Cu and Fe NCs intercalated in graphite

As a first example, we consider 3D fcc Cu NC intercalated near the surface of graphite, i.e., the Cu NC is sandwiched between a parallel graphene monolayer sheet (GML) at the top and a graphite substrate at its bottom. This system was characterized in STM experiments [3, 4]. We incorporate into our modeling of the Cu NC the seven favorable surface facets of fcc Cu: (111), (100), (221), (331), (310), (311), (210), with surface energies reported by Tran et al. [26] based on DFT analysis using the PBE functional. For the adhesion of Cu (111) to GML and graphite, we utilize results for the adhesion energies, \( \beta_1 = \beta_{\text{GML-Cu(111)}} \) and \( \beta_2 = \beta_{\text{Graphite-Cu(111)}} \), which were reported in Ref. [27]. This analysis assumes that the top and bottom facets of the 3D NC have a hexagonal close-packed (111) structure. Previous experimental observations and theoretical analysis of metal-graphene or graphite interfacial structure and energetics provide strong evidence for this view [3]. Model parameters are summarized in Table 1, and discussed further in the Supplementary Materials.
Miller indices: \((eV/nm^2)\)

<table>
<thead>
<tr>
<th>Surface energy (\gamma)</th>
<th>Miller indices</th>
<th>((eV/nm^2))</th>
<th>Miller indices</th>
<th>((eV/nm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>8.364</td>
<td>(311)</td>
<td>9.613</td>
<td></td>
</tr>
<tr>
<td>(100)</td>
<td>9.176</td>
<td>(310)</td>
<td>9.925</td>
<td></td>
</tr>
<tr>
<td>(221)</td>
<td>9.238</td>
<td>(210)</td>
<td>9.987</td>
<td></td>
</tr>
<tr>
<td>(331)</td>
<td>9.488</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adhesion (\beta)</th>
<th>(\beta_{\text{GML-Cu(111)}})</th>
<th>(\beta_{\text{Graphite-Cu(111)}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta_{\text{GML-Cu(111)}})</td>
<td>2.200</td>
<td>2.265</td>
</tr>
</tbody>
</table>

Table 1 Dominant surface energies of fcc Cu NC [26] and adhesion of its (111) facets with a graphene sheet and graphite substrate [27].

We set the Cu NC height to \(h_{\text{total}} = 7.83\) nm corresponding to the experimental example shown Fig. 4 and taken from [4]. Following the procedure discussed in Sec.3 to find the equilibrium shape, the starting configuration corresponds to the unique volume \(V = V_0(h_{\text{total}})\) where the relations (2) apply. This special shape is shown in Fig. 3. However, \(V_0\) does not correspond to the much larger experimental volume (and diameter) of the nanocluster with \(h_{\text{total}} = 7.83\) nm. This much flatter equilibrium shape for the NC with the appropriate experimental diameter of about \(d = 34.3\) nm is shown in Fig. 4. Thus, to obtain the results shown in Fig. 4, the volume is adjusted incrementally towards the experimental value, and the \(h_i\) recalculated as described in Sec.3. The output of these calculations for various volumes \(V\) is represented as a video in Supplementary Materials. A complete set of dimensions, \(h_i\), for the final Cu NC from our numerical analysis shown in Fig. 4a-b (as well as values for special case \(V = V_0\)) are summarized in Table 2.

---

Fig. 3 Equilibrium shape of fcc Cu NC in contact with GML and graphite for the special volume \(V = V_0(h_{\text{total}})\) where the relations (2) from Kaischew’s theorem apply. The analysis is performed with the energetic parameters in Table 1.

We should note, however, that the above continuum analysis is geared to macroscopic nanocrystals size. In this regime, even facets with the smallest linear dimensions (e.g., the minority facets which appears along the edges between lower index facets), these dimensions are very large when measured in units of lattice constants. However, in the actual nanoscale fcc Cu NC systems of interest, these smallest linear dimensions could only be a few atoms, potentially...
smaller than the unit cell dimensions associated with the minority higher index facets. Consequently, those facets would be absent in the nanoscale system. As an aside, a refined but substantially more complex analysis geared to the nanoscale could write the energy associated with the NC as a sum of bulk, surface or interface, edge, and vertex energies [28] (where edge and vertex energies would need to be determined, e.g., from DFT analysis). Then, the equilibrium NC shape would again be determined from energy minimization.

Fig. 4 The equilibrium shape of the sandwiched fcc Cu NC with the experimental height $h_{\text{total}} = 7.83$ nm and diameter $d \approx 34.3$ nm obtained from numerical energy minimization. Views are shown: (a) orthogonal to the substrate, and perpendicular to (111) top and bottom facets; and (b) from a horizontal direction. Corresponding derivative-mode experimental image with the same height and diameter (averaged of three corner-corner distances $d = 34.3$ nm) from [4] is shown in (c). The topographic version of the image is shown as the inset. The small features on the surface around the NC are small clusters of Cu atoms nucleated at surface defects.

The hexagonal shape of the top (111) facet is consistent with the experimental observation from Ref. [4] where the top facet corresponds to the central part of the nanostructure image in Fig.4c. The outer part corresponds to the unsupported covering graphene blanket which adheres to the underlying graphite about 25 nm further out than the edge of the metal NC. Here, we should note that experiment observations also find some NCs where the top facet is a distorted hexagon. However, these presumably reflect partially equilibrated growth shapes.
All $V$

<table>
<thead>
<tr>
<th>$V = V_0 = 748.5\text{nm}^3$</th>
<th>$h_{(111)}$</th>
<th>$h_{(311)}$</th>
<th>$h_{(310)}$</th>
<th>$h_{(210)}$</th>
<th>$h_{(331)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_1$</td>
<td>3.937</td>
<td>5.3851</td>
<td>5.9076</td>
<td>5.9478</td>
<td>6.1085</td>
</tr>
<tr>
<td>$h_2$</td>
<td>3.893</td>
<td>6.1889</td>
<td>6.3898</td>
<td>6.4300</td>
<td>6.7949</td>
</tr>
</tbody>
</table>

$V = 6877.5\text{nm}^3$

<table>
<thead>
<tr>
<th>$h_{(111)}$</th>
<th>$h_{(311)}$</th>
<th>$h_{(310)}$</th>
<th>$h_{(210)}$</th>
<th>$h_{(331)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_1$</td>
<td>15.426</td>
<td>6.1682</td>
<td>16.256</td>
<td>17.283</td>
</tr>
<tr>
<td>$h_2$</td>
<td>14.667</td>
<td>17.256</td>
<td>17.883</td>
<td></td>
</tr>
<tr>
<td>$h_3$</td>
<td>17.794</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. $h_i$ of different surface facets with $h_{\text{total}} = 7.83\text{nm}$. For all $V$, $h_1 = h_{\text{total}}(\gamma_{(111)} - \beta_1)/(2\gamma_{(111)} - \beta_1 - \beta_2)$ and $h_2 = h_{\text{total}}(\gamma_{(111)} - \beta_2)/(2\gamma_{(111)} - \beta_1 - \beta_2)$.

As a second example, we consider 3D hcp Fe NC intercalated near the surface of graphite. This system was also characterized in STM experiments [3, 4]. Here, we incorporate into our modeling of the Fe NC the six most favorable surface facets of hcp Fe: (0001), (2130), (1010), (2021), (1012), (2112), with surface energies reported by Tran et al. [26]. Adhesion of hcp Fe to graphene and graphite, $\beta_1 = \beta_{\text{GML-Fe(0001)}}$ and $\beta_2 = \beta_{\text{Graphite-Fe(0001)}}$, respectively, were determined by DFT analysis [6] assuming that the top and bottom of the 3D Fe NC correspond to (0001) facets. Model parameters are summarized in Table 3, and discussed further in the Supplementary Materials.

<table>
<thead>
<tr>
<th>Surface energy $\gamma$</th>
<th>Miller indices</th>
<th>(eV/nm$^2$)</th>
<th>Miller indices</th>
<th>(eV/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>18.04</td>
<td>(2130)</td>
<td>19.91</td>
<td>(1012)</td>
</tr>
<tr>
<td>(1010)</td>
<td>20.35</td>
<td>(2112)</td>
<td>22.03</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adhesion</th>
<th>Miller indices</th>
<th>(eV/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{\text{GML-Fe(0001)}}$</td>
<td>2.406</td>
<td></td>
</tr>
<tr>
<td>$\beta_{\text{Graphite-Fe(0001)}}$</td>
<td>2.633</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Dominant surface energies of hcp Fe NC [26] and adhesion of its (0001) facets with a graphene sheet (GML), graphite substrate [6].

We set the Fe NC height as $h_{\text{total}} = 1.89\text{nm}$ corresponding to the experimental example shown in Fig. 7b from Ref. [5]. The starting configuration with special volume $V_0$ for our procedure to determine the equilibrium shape described in Sec. 3 is shown in Fig. 5. Again, the volume is adjusted towards the much larger experimental value, and the $h_i$ recalculated as described in Sec.3. See the video in Supplementary Materials for a representation of this analysis. The equilibrium shape of the hcp Fe NC with the above height and a diameter $d = 69.8\text{nm}$ matching experiment is shown in Fig. 4c. Details of the dimensions of the Fe NC from our numerical analysis shown in Fig.4a-b (as well as values for special case $V = V_0$) are summarized in Table 2. The shape of the top (0001) facet agrees with the rounded hexagonal footprint observed in experiment.
Again, in the actual nanoscale hcp Fe NC system, some minority facets predicted by this macroscale continuum analysis are likely to be absent. See the comments for Cu nanoclusters.

Fig. 5 Equilibrium shape of hcp Fe NC in contact with GML and graphite for the special volume $V = V_0 (h_{total})$ where the relations (2) from Kaischew’s theorem apply. The analysis is performed with the energetic parameters in Table 3.

Fig. 6 The equilibrium shape of the sandwiched hcp Fe NC with the experimental height $h_{total} = 1.89 \text{ nm}$ and diameter $d \approx 69.8 \text{ nm}$ obtained from numerical energy minimization. Views are shown: (a) orthogonal to the substrate, and perpendicular to (0001) top and bottom facets; and (b) from a horizontal direction. Corresponding derivative-mode experimental image with the same height and diameter (average of three corner-corner distances $d = 69.8 \text{ nm}$) from [5] is shown in (c). The small features on the surface around the NC are small clusters of Cu atoms nucleated at surface defects.
Table 4 \( h_i \) of different surface facets with \( h_{\text{total}} = 1.89 \) nm. For all \( V \), \( h_1 = h_{\text{total}}(\gamma_{(0001)} - \beta_1)/(2\gamma_{(0001)} - \beta_1 - \beta_2) \) and \( h_2 = h_{\text{total}}(\gamma_{(0001)} - \beta_2)/(2\gamma_{(0001)} - \beta_1 - \beta_2) \).

<table>
<thead>
<tr>
<th>( V = V_0 = 8.2117 ) nm(^3)</th>
<th>( h_{(2130)} )</th>
<th>( h_{(10\overline{1}2)} )</th>
<th>( h_{(10\overline{1}0)} )</th>
<th>( h_{(2\overline{1}1)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>All ( V )</td>
<td>0.9519</td>
<td>1.2124</td>
<td>1.2390</td>
<td>1.2732</td>
</tr>
<tr>
<td>( V = 6968.0 ) nm(^3)</td>
<td>34.695</td>
<td>24.684</td>
<td>33.369</td>
<td>32.545</td>
</tr>
</tbody>
</table>

5. DISCUSSION

As noted above, unlike the Wulff construction for unsupported NCs and Kaischew’s theorem for simply supported NCs, for NCs sandwiched between parallel surfaces, there is no unique equilibrium shape. Furthermore, there is no available simple recipe for predicting the shape from the set of \( h_{\text{total}}, \gamma_i \) (and \( \beta \)). However, it is instructive to explore relationships between various linear dimensions \( h_i \) of the NC for this case where the height is fixed. To this end, we introduce a characteristic length scale of the NC,

\[
h' = \sqrt{V/h_{\text{total}}}. \tag{9}\]

Then, the correlation between \( h_i \) and \( h' \) is shown in Fig. 7 from the data for the Cu and Fe NC systems analyzed in the last section.

Fig. 7. \( h_i/h_{i0} \) versus \( h'/h'_0 \) for sandwiched (a) fcc Cu analyzed and (b) hcp Fe NC in Sec. 4. The subscript 0 corresponds to value at the special Kaischew’s theorem \( V = V_0 \). Linear fits to the slopes are also indicated.

In both cases, all \( h_i \) vary linearly with \( h' \) which implies that each \( h_i \) varies linearly with respect to any other \( h_i \). No doubt, the same linear relation would apply generally for sandwiched NC
systems. Note that when $V = V_0$, it follows that $h_{i0}/\gamma_i = h_{i0}/\gamma_i$ is independent of plane subscript according to (2). Thus, combining this result with the linear relations between various $h$’s, the hypothesized relation between $h_i$ and $h_j$ can be written as

$$\frac{h_i}{\gamma_i} = \alpha_{ij} \frac{h_j}{\gamma_j} + (1 - \alpha_{ij}) \frac{h_{i0}}{\gamma_j},$$

(10)

where $\alpha_{ij}$ are coefficients relating $h_i$ and $h_j$.

Next, we will discuss some natural extensions of the analysis in this paper. In the above, the equilibrium shape of intercalated islands sandwiched between parallel surfaces is constructed by starting with NCs of a substantially smaller volume $V = V_0$. Then, $V$ is incrementally increased recalculating the equilibrium shape at each step until the experimental value is reached. However, instead one can incrementally reduce the volume and recalculate the equilibrium shape. Following this process, one finds the existence of a threshold volume at which the NC detaches from confining surface with the weaker adhesion $\beta$. Below this threshold volume, the energy of the NC configuration in contact with both substrates exceeds that of the detached configuration with the same volume. After detachment, determination of equilibrium shape is reduced to a simple Kaischew’s theorem problem.

Finally, we comment in a more general context on the lack of size scaling (or of a unique equilibrium shape) for intercalated NCs with fixed height. Beyond the case of an NC sandwiched between parallel surfaces with fixed separation, it is clear that in any situation where the confining geometry imposes a characteristic length scale that size scaling is lost. This is not the case for a NC at a corner in 2D or 3D, the Summertop scenario. However, it is the case for a NC supported on a grooved surface, incorporated into a channel (e.g., etched vertically into a surface), or for NCs imbibed or impaled in arrays of nanopillars [29,30]. Lastly, it is appropriate to compare our analysis of the equilibrium shape of intercalated NCs of fixed height with that for the full intercalation problem treating as variable the geometry of the strained graphene blanket, and thus where the NC height is no longer fixed. In this case, at least in a simplified treatment of strain neglecting the bending contribution to the strain energy, one does have size scaling [4,6].

6. CONCLUSION

A detailed analysis has been provided for the equilibrium shapes of faceted 3D NCs sandwiched between a pair of parallel surfaces of fixed separation, $h_{\text{total}}$, where analysis was based upon numerical minimization of the system energy. Motivation for this analysis was provided by recent experiments revealing the intercalation of 3D NCs of various metals under the surface of HOPG [1-6]. We specifically determined NC equilibrium shapes for the cases of fcc Cu (with $h_{\text{total}} = 7.83\text{nm}$ and diameter $d = 34.3\text{nm}$) and hcp Fe (with $h_{\text{total}} = 1.89\text{nm}$ and diameter $d = 69.8\text{nm}$). The calculated shapes of the top facets are consistent with observations in STM experiments [4,5] Our approach is not restricted within these two metals or crystal structures,
but instead applicable to generally all mono-metallic 3D facetted NCs sandwiched between a pair of surfaces. This study advances previous work on intercalated 3D metal NCs where simpler models for 3D metal NC geometry had been utilized.

Acknowledgements

We thank Patricia A. Thiel for useful discussions. KCL and JWE were supported for the theoretical analysis work by the U.S. Department of Energy (USDOE) Office of Science, Basic Energy Sciences Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory Chemical Physics program. ALR was supported for experimental studies by the USDOE Division of Materials Sciences. The work was performed at Ames Laboratory which is operated for the USDOE by Iowa State University (ISU) under Contract No. DE-AC02-07CH11358.

References


