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Edge energies: Atomistic calculations of a continuum quantity

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Controlling the properties of self-assembled nanostructures requires controlling their shape. Size-dependent shape transitions, frequently observed at nanolength scales, are commonly attributed to edge energy effects. To rigorously test such theories against experiment, quantitative atomistic calculations of edge energies are essential, yet none exist. I describe a fundamental ambiguity in the atomistic definition of edge energies, propose a definition based on equimolar dividing surfaces, and present an atomistic calculation of edge energies for Pd clusters.

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I. INTRODUCTION

A major goal of nanoscience is to control the properties of functional nanostructures, including, for example, catalyst particles, quantum dots on surfaces, and inclusions in alloys. Synthesis at the nanoscale is most commonly achieved by controlled self-assembly; understanding the energetic factors governing self-assembly is a critical goal. At the nanoscale, edge energy is commonly invoked as an important driver for self-assembly. For example, edge energies are included in theories for the shapes of snow crystals,[1] discussions of surface faceting,[2] theories for the shapes of strained Ge pyramids grown on a surface,[3] and discussions of Pb inclusions in bulk Al.[4] Generally edge energies are discussed as an important contributor to the total energy at the nanoscale, yet there appear to be no first-principles or semiempirical calculations of edge energies.[2] There are two papers which discuss edge energies in terms of broken bond models.[5,6] Other papers treat edge energies as an independent variable, and discuss nanoshapes as a function of the edge energy.[3,7]

Experiments often show changes in the shape of nanoobjects as a function of their size. This has been an area of considerable recent interest resulting in a number of experimental[8,9] and theoretical investigations.[10–12] Shape transitions are commonly attributed to edge energy effects. Testing these theories requires calculation of quantitative edge energies from an atomistic model to serve as an input for continuum calculations of shape transitions. While one might suppose that atomistic calculation of edge energies would be routine, I show that there is an ambiguity in the atomistic definition of edge energies, and discuss a resolution of this ambiguity.

The problem in defining edge energies is related to the problem of defining the exact position of an atomic surface in the direction normal to the surface. This problem is addressed by the well-known concept of the Gibbs dividing surface. As Gibbs points out, “It will be observed that the position of this surface is as yet to a certain extent arbitrary.”[13] Depending on the exact position choosen for the Gibbs dividing surface, the surface contribution to extensive properties of the solid will vary. For a single component system, a common choice of dividing surface is the equimolar surface.[14] The equimolar surface is defined so that the surface contribution to the molar amount of the solid is zero. Finally, we note that Gibbs has mentioned the possibility of calculating line properties such as tension at the linear intersection between two or more dividing surfaces. To quote Gibbs, “We may here remark that a nearer approximation in the theory of equilibrium and stability might be attained by taking special account, …, of the lines in which surfaces of discontinuity meet. … We might recognize linear densities of energy, of entropy, and of the several substances which occur about the line.”[15] In this paper I describe the application of such an approach to determine the linear density of energy at an edge formed by the intersection of two dividing surfaces.

In this paper we will assume that the clusters we are dealing with can be represented by flat surfaces (facets) that intersect forming straight edges. Given this assumption, the total energy of a polyhedral cluster, with the shape independent of edge length, can be written in the form

$$E_{\mathrm{total}} = As^3 + Bs^2 + Cs + D, \qquad (1)$$

where s is the edge length and A, B, C, and D are coefficients related to the bulk, surface, edge, and vertex energy, respectively. Theories for equilibrium shape, including the Wulff construction, are based on this assumption of flat facets with an orientation dependent surface energy.

II. MOTIVATION: MAGNITUDE OF POSSIBLE ERRORS

The purpose of this section is to demonstrate the extremely large uncertainties that can result from the failure to rigorously define edge length. We include this section because implicit assumptions are often made in the definition of edge energies. Hopefully the reader will be convinced that this is more than a minor semantic problem, and will be inoculated against erroneous assumptions which may occur in more abstract discussions of the subject. The reader may chose to read this section quickly, continue to Sec. III which proposes a precise definition of edge length based on equimolar dividing surfaces, and return to this section as desired.

We illustrate the problem by considering quantitative calculations for a cuboctahedral cluster. Consider such a cluster having n atoms along each edge as shown in Fig. 1. First we calculate the total energy, $E_{\mathrm{total}}(n)$, of the cluster using an embedded atom method (EAM) calculation. Table I gives

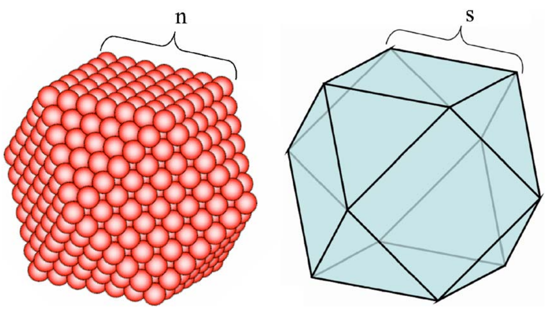

FIG. 1. (Color online) A cuboctahedral cluster of Pd atoms having $n=7$ atoms along each edge is shown on the left. A geometrical cuboctahedron having edge lengths, s, is shown on the right. Theories such as the Wulff construction, which predict shapes as a function of surface and edge energies, implicitly assume that the surfaces are flat, and that the edges are straight intersections of these surfaces. The major point of this paper is that defining and calculating edge energies require a precise definition of s as a function of n. In Sec. III this function is derived based on the choice of the geometrical surfaces as equimolar Gibbs dividing surfaces.

$E_{\mathrm{total}}(n)$ and the total number of atoms, N, for Pd clusters with $5 \leqslant n \leqslant 9$. The next step is to expand the total energy in powers of the edge length, s, as in Eq. (1) above. From the coefficients A, B, C, and D, the bulk, surface, edge, and vertex energies, respectively, can be calculated. The problem is that to determine these coefficients, a precise definition for the edge length, s, measured in Å, as a function of n is essential. The correct way to do this is not obvious, although it seems reasonable that the correct value would lie somewhere in the range

$$(n-1)d \leqslant s \leqslant nd, \tag{2}$$

where a is the fcc lattice constant and $d=a/\sqrt{2}$ is the nearest-neighbor distance. In order to see how critically important this is, we will consider three possible choices for s, namely, $s=(n-1)d$, $s \approx (n-1/2)d$, and $s=nd$. [The exact definition of the intermediate choice will be given by Eq. (5) appearing later in this paper]. Figure 2(a) shows a plot of $E_{\mathrm{total}}(s)$ for these three definitions of s. For all three definitions least square fitting gives the same bulk energy coefficient, $A=-0.626\,21\ \mathrm{eV}/\text{Å}^3$. The total interface energy is calculated as

$$E_{\mathrm{interface}} = Bs^2 + Cs + D = E_{\mathrm{total}} - As^3. \tag{3}$$

TABLE I. Results of embedded atom method calculation of energies of Pd cuboctahedral clusters. The number n is the number of atoms on the edge of the cuboctahedral cluster (see Fig. 1). The number N is the total number of atoms in the cluster. E_{total} is the total energy of the Pd cluster from an EAM calculation. Since the atomic positions were relaxed in the total energy calculation, changes of the total energy due to relaxation of surface and edge atom positions are included in the total energy. The last column shows the total energy after subtracting the bulk energy, NE_{coh}.

n number of atoms on edge	N total number of atoms	E_{total} (eV)	E_{total}-NE_{coh} (eV)
5	309	−1086.234	121.956
6	561	−2012.793	180.717
7	923	−3357.798	251.132
8	1415	−5199.442	333.208
9	2057	−7615.919	426.951

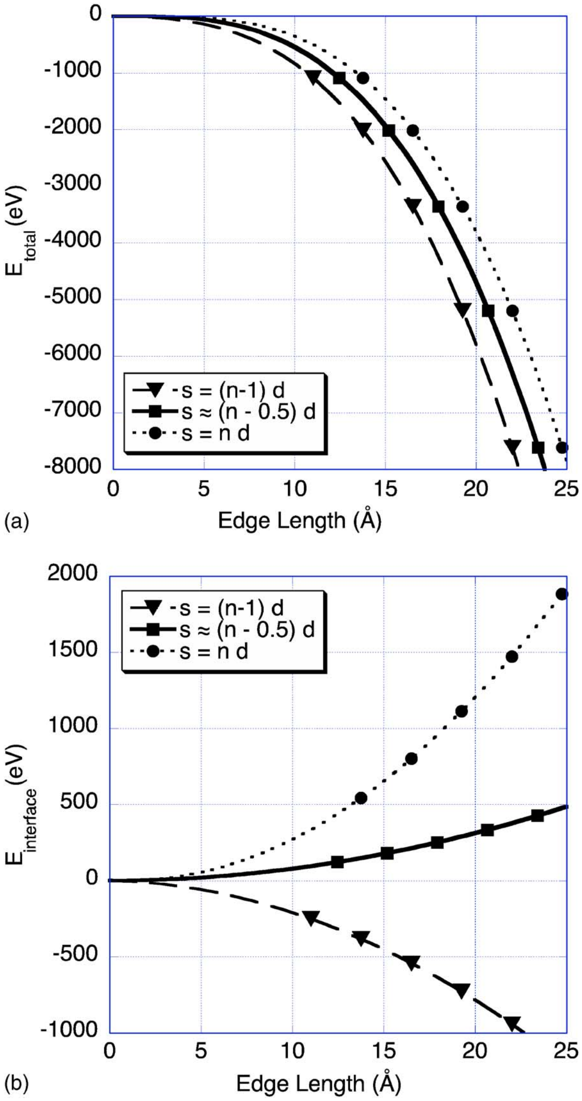

FIG. 2. (Color online) This figure shows the importance of a precise definition of the edge length, $s=f(n)$, as a function of the number of atoms, n, along an edge. The first graph (a) plots the calculated total energy as a function of the edge length for three different definitions of s. The curves labeled "$s=(n-1)d$" and "$s=nd$" represent the limiting definitions [d is the nearest neighbor distance, see Eq. (2) of the text]. The curve labeled "$s \approx (n-0.5)d$" is actually plotted using Eq. (5) of the text to define edge length. Least squares fitting to a cubic polynomial [Eq. (1)] gives a term As^3, the bulk contribution to the total energy. The second graph (b) plots the interface energy, defined as $E_{\mathrm{total}}-As^3$, for the three definitions of s. We will show in Sec. IV that the value of the interface energy is reasonable for "$s \approx (n-0.5)d$". The other definitions give interface energies which are much too large and/or incorrect in sign.

Figure 2(b) shows a plot of $E_{\text{interface}}(s)$ for the three different definitions of s. Only one of these curves gives a surface energy anywhere near the correct value. As we shall latter verify, the correct value is given by the curve labeled $s \approx (n-1/2)d$. The curve for $s=nd$ gives surface energies that are approximately four times the correct value! The curve for $s=(n-1)d$ gives surface energies that are approximately two times the correct value and have the wrong sign! This shows that the problem of defining the edge length will be crucial to the definition and calculation of edge energies.

An alternate approach is to begin by subtracting the total bulk cohesive energy, NE_{coh}, from E_{total} to isolate the interface terms. Here N is the total number of atoms in the cluster and E_{coh} is the bulk cohesive energy per atom. This approach is standard in slab calculations for surface energies. We show here that it does not solve the problem of defining the edge length or allowing calculation of edge energies.

We start with the calculation of E_{total} using the embedded atom method and subtract the bulk energy, NE_{coh}, from the total energy. Table I gives numerical values for $E_{\text{total}}\text{-}NE_{\text{coh}}$ for cuboctahedral clusters having 5–9 atoms on an edge. Since $E_{\text{total}}\text{-}NE_{\text{coh}}$ is the sum of the surface, edge, and vertex energies, it can be written as a quadratic polynomial of the edge length, s,

$$E_{\text{total}}\text{-}NE_{\text{coh}} = Bs^2 + Cs + D. \tag{4}$$

As before, we must define s before we can fit a polynomial. We consider the same definitions of s used previously, $s=(n-1)d$, $s \approx (n-1/2)d$, and $s=nd$. Figure 3(a) shows a plot of $E_{\text{total}}\text{-}NE_{\text{coh}}$ plotted using these three definitions for s. These functions are fit by a quadratic polynomial as in Eq. (4). For these three definitions of s, the fitting coefficient B is equal to 0.770 61. From the cubic fit we can also plot the sum of the edge and vertex, $E_{\text{edge}}+E_{\text{vertex}}=Cs+D$, as shown in Fig. 3(b). The edge energy would be $\varepsilon = C/24$ and would be proportional to the slope seen in the plot. Since the slope of the three lines is very different depending on the definition of s, the edge energy cannot be calculated without a precise definition for the edge length.

III. DEFINITION OF EDGE LENGTHS BASED ON EQUIMOLAR SURFACES

The problem of defining edge lengths is related to the problem of defining the exact position of the surface of a solid. The well known concept of the Gibbs dividing surface is a rigorous solution to the problem. We can place the Gibbs dividing surface where we like (within reason), but the value of surface excess quantities will depend on the position of the dividing surface. In order to define the edge lengths, we consider a faceted cluster as being built from intersecting dividing surfaces, one surface for each facet. The edges are formed by the intersection of two dividing surfaces and the vertices are formed by the intersection of three dividing surfaces. For the case of a cuboctahedron, Fig. 1 shows the atomic cluster on the left and the geometrical shape formed from the assemblage of dividing surfaces on the right. Defining the edge length, s, is thus seen to be a problem in choosing the position of the dividing surfaces.

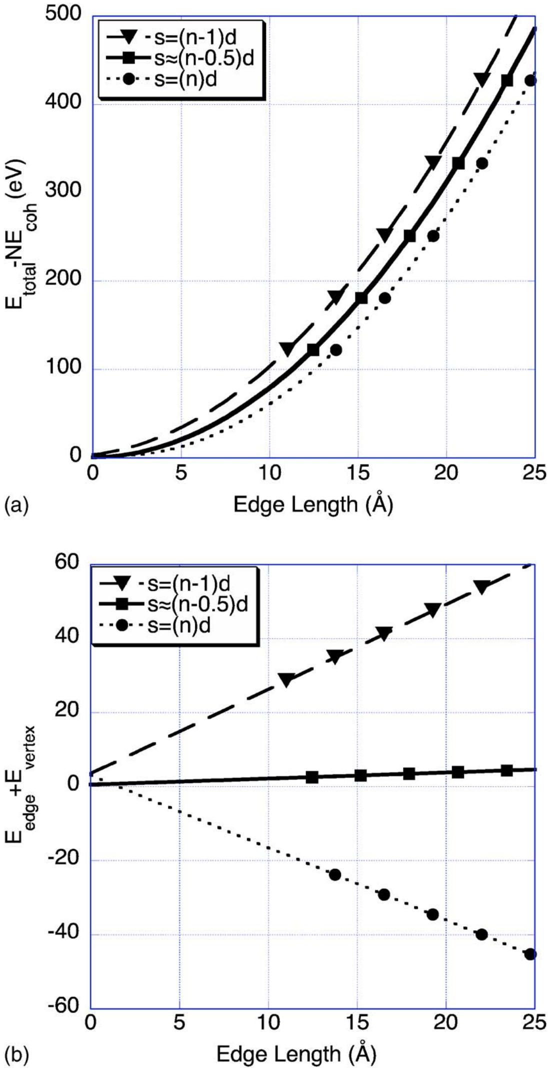

FIG. 3. (Color online) (a) plots the quantity, $E_{\text{total}}\text{-}NE_{\text{coh}}$, for three plausible definitions of the edge length, s, defined in the text and in the caption for Fig. 2. Least squares fitting to a quadratic polynomial [Eq. (4)] gives a term Bs^2, the surface contribution to the total energy. The second graph (b) plots the sum of the edge and vertex energy, defined as $E_{\text{total}}\text{-}NE_{\text{coh}}\text{-}Bs^2$, for the three definitions of s. The calculated edge energy would be proportional to the slope of the lines. The three different definitions of s give vastly different results for the edge energy. This demonstrates again that a rigorous and precise definition of the edge length, s, is essential in order to define and/or calculate the edge energy.

While the position of a dividing surface is generally arbitrary, we will find that the problems described in the previous section are resolved in a consistent manner by defining the edge length using equimolar dividing surfaces. To see this, we refer to Eq. (1). We know that the total bulk energy, As^3, should equal NE_{coh}, where E_{coh} is the bulk cohesive energy per atom and N is the total number of atoms. For a cuboctahedron formed by dividing surfaces, the definition of a dividing surface implies that the total bulk energy is equal to the constant energy density of bulk palladium, $\rho = 4E_{\text{coh}}/a^3$, integrated over the volume of the cuboctahedron formed by the dividing surfaces, $V=(5\sqrt{2}/3)s^3$. The bulk energy of the cuboctahedron formed by the dividing surfaces is $V\rho$. The total number of atoms in a cuboctahedral cluster is $N=(10n^3/3)-5n^2+(11n/3)-1$. Substituting these equations for N, V, and ρ in the equation $NE_{\mathrm{coh}}=V\rho$ and solving for s we find

$$s = \left[\sqrt[3]{n^3 - \frac{3n^2}{2} + \frac{11n}{10} - \frac{3}{10}}\right]\left(\frac{a}{\sqrt{2}}\right). \tag{5}$$

This gives us a precise definition of s, as needed to separate bulk, surface, edge, and vertex energies. It is will also be convenient to have a series expansion for s. Expanding Eq. (5) in a Taylor series gives

$$s = \left[n - \frac{1}{2} + \frac{7}{60n} + O\left[\frac{1}{n^2}\right]\right]\left(\frac{a}{\sqrt{2}}\right). \tag{6}$$

Since we are ultimately interested in calculating energies, this derivation was based on energy density. A derivation using number density would be nearly identical, and the final definition of s would be the same. This means that the dividing surfaces we will use to define s are equimolar surfaces.

IV. CALCULATION OF EDGE AND VERTEX ENERGIES FOR A CUBOCTAHEDRON

With this definition for s, we can return to the problem of calculating surface, edge, and vertex energies for the cuboctahedron. We plot $E_{\mathrm{total}}(s)$ with s defined by Eq. (5). This is the curve labeled "$s \approx (n-1/2)d$" in Fig. 2.

From a cubic fit [Eq. (1)] we get the coefficients A, B, C, and D which relate directly to the bulk (cohesive) energy, the surface energy, the edge energy, and the vertex energy. The log-log plot shown in Fig. 4, plots $-As^3$, Bs^2, Cs, and D. We will now consider each term in order to verify that the bulk and surface energies agree with standard EAM calculations, and to obtain numerical values for the edge and vertex energies.

We consider first the bulk energy term. The cluster least square fit gives $A=-0.626\,21$ eV/Å^3. The volume of the cuboctahedron is $V=(5\sqrt{2}/3)s^3$ and the energy density of bulk Pd is $\rho=4E_{\mathrm{coh}}/a^3$. The EAM functions used were fitted to give $E_{\mathrm{coh}}=3.91$ eV and $a=3.89$ Å. Thus the predicted value of A is $-(V\rho/s^3)=-0.626\,26$ eV/Å^3 in good agreement with the EAM cluster least squares fit.

Next we consider the surface energy term. The least squares fit gives $B=0.768\,18$ eV/Å^2. The (111) surface area of the cuboctahedron is $A_{111}=(2\sqrt{3})s^2$ and the (100) surface area of the cuboctahedron is $A_{100}=6s^2$. The EAM functions used here give surface energies of $\gamma_{111}=75.82$ meV/Å^2 and $\gamma_{100}=85.15$ meV/Å^2 from bulk slab calculations. Thus the predicted value of B is $(A_{100}\gamma_{100}+A_{111}\gamma_{111})/s^2 =0.7735$ eV/Å^2 in good agreement with the EAM cluster least squares fit.

Finally we are ready to calculate the edge energy of a cuboctahedron. Because all of the edges are formed by the intersection of a (111) surface and a (100) surface, we will use the notation, $\varepsilon_{111\text{-}100}$ to denote the edge energy. The cluster least squares fit gives $C=0.207\,06$ eV/Å. The total edge length of the cuboctahedron is $24s$. Consequently we calculate $\varepsilon_{111\text{-}100}=C/24=8.63$ meV/Å. This calculated value for the edge energy is included in Table II.

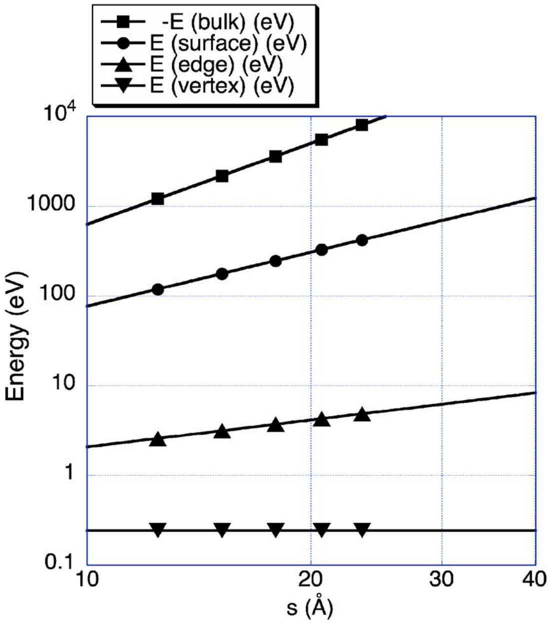

FIG. 4. (Color online) This figure shows the values of the bulk, surface, edge, and vertex energies from EAM calculations for Pd cuboctahedral clusters having $5 \leqslant n \leqslant 9$ atoms on an edge. The edge length, s, was defined by the equimolar surfaces [see Eq. (5) of the text]. The total energy was fit by a cubic polynomial [see Eq. (1) of the text]. The bulk, surface, edge, and vertex contributions are plotted here as $-As^3$, Bs^2, Cs, and D respectively. The negative of the bulk energy is plotted so that all four energies can be compared on a single log-log plot.

The last step is to calculate the vertex energy of the cuboctahedron. The cuboctahedron has 12 vertices at which two (111) facets meet two (100) facets. The cluster least squares fit gives $D=0.244\,41$ eV. Dividing by 12 we get the vertex energy, $\alpha_{\mathrm{cuboct}}=20.3$ meV.

V. CALCULATION OF EDGE AND VERTEX ENERGIES FOR AN OCTAHEDRON

The definition of edge length, s, for an octahedron follows the procedure described for a cuboctahedron in Sec. III. Here it will suffice to give the equations which define the edge length based on equimolar dividing surfaces. We find

$$s = \left[\sqrt[3]{n^3 + \frac{n}{2}}\right]\frac{a}{\sqrt{2}} \tag{7}$$

and

TABLE II. This table gives the edge energies calculated from EAM calculations and from a bond-breaking model described in the Appendix.

	$\varepsilon_{111\text{-}111}$	$\varepsilon_{111\text{-}100}$
EAM	4.6 meV/Å	8.6 meV/Å
Bond breaking	0.0 meV/Å	0.0 meV/Å

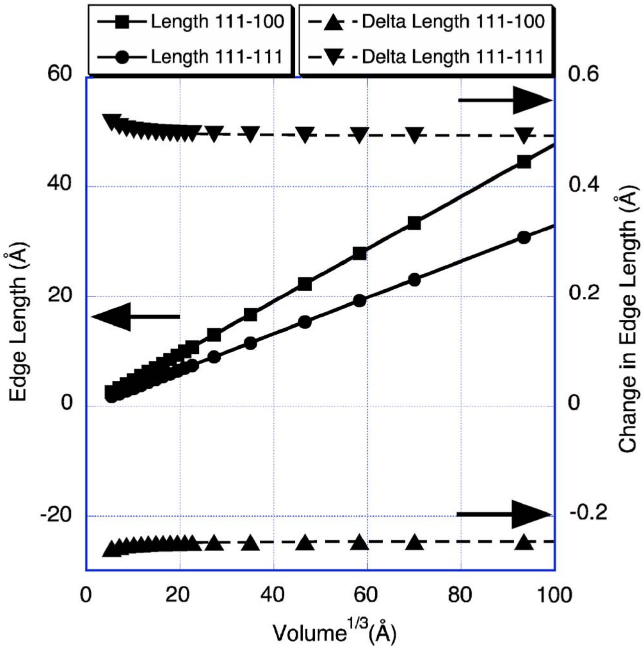

FIG. 5. (Color online) This plot shows the results of a Wulff construction (minimizing the surface energy of an atomic cluster, subject to the constraint of constant volume). The values for surface energy are taken from the calculations in the text. The left vertical axis shows the edge lengths predicted by the Wulff construction as a function of the cube root of the cluster volume. The plot also shows the changes in the edge lengths predicted by including the edge energies given in Table II to the total energy [see Eq. (9) of the text]. Since the changes in edge length are <0.6 Å for all cluster sizes, and edge lengths are constrained by discrete atomic distances, the edge energies will have essentially no effect on the shape of Pd clusters at any length scale.

$$s = \left[n + \frac{1}{6n} + O\left[\frac{1}{n^3}\right] \right] \frac{a}{\sqrt{2}}. \tag{8}$$

For an octahedron the edge length defined by Eq. (7) is approximately nd, whereas for a cuboctahedron the edge length defined by Eq. (5) is approximately $(n-1/2)d$. The fact that the definition of s is so different for these two cases emphasizes the importance of a rigorous and precise definition. The process for fitting the total energy of the octahedron with a bulk, surface, edge, and vertex term is done much as for the cuboctahedron. The bulk and surface energies from the series expansion for the total energy of the octahedron are in good agreement with values from conventional EAM calculations. The edges of the octahedron are formed at the intersection of two (111) facets. Thus we will use the notation $\varepsilon_{111\text{-}111}$ for the edge energy. We calculate $\varepsilon_{111\text{-}111}=4.60$ meV/Å and $\alpha_{\text{oct}}=127$ meV. Table II of this paper summarizes the values of the edge energies found from these EAM calculations and gives the values of the edge energies from a bond-breaking model described in the Appendix.

VI. EFFECT OF EDGE ENERGIES ON CLUSTER SHAPE

One of the major motivations for calculating edge energies (see Sec. I) was to examine the possible role of edge energies in causing shape transitions for nanoparticles. For larger clusters the equilibrium shape of a particle is governed primarily by the surface energies and the lowest energy shape is determined by the Wulff construction. As an example, consider a truncated octahedral particle. We will assume here that the surface energy of surfaces other than (100) and (111) are sufficiently large, and thus that they are not part of the equilibrium shape. The Wulff shape is determined by minimizing the interface energy, $E_{\text{interface}} = 6A_{111}\gamma_{111} + 8A_{100}\gamma_{100}$, subject to the constraint of constant volume. Here A_{111} is the area of a (111) facet and A_{100} is the area of a (100) facet. We will use the notation $L_{111\text{-}111}$ for the edge length at the intersection of two (111) facets and $L_{111\text{-}100}$ for the edge length at the intersection of a (100) and a (111) facet. Figure 5 shows these two edge lengths as a function of the cube root of the particle volume, and is a convenient measure of particle size.

By adding edge energies to the interface energy we can determine their effect on cluster shape. The interface energy becomes

$$E_{\text{interface}} = 6A_{111}\gamma_{111} + 8A_{100}\gamma_{100} + 12L_{111\text{-}111}\varepsilon_{111\text{-}111} + 24L_{111\text{-}100}\varepsilon_{111\text{-}100}. \tag{9}$$

By minimizing the interface energy subject to the constraint of constant volume the edge lengths can be determined. Since $\varepsilon_{111\text{-}111}$ is smaller than $\varepsilon_{111\text{-}100}$ the effect of the edge energies will be to lengthen $L_{111\text{-}111}$ and shorten $L_{111\text{-}100}$, while keeping the total volume constant. Figure 5 shows the changes in the edge lengths which result from including edge energies. $L_{111\text{-}111}$ is increased by about 0.5 Å and $L_{111\text{-}100}$ is decreased by about 0.25 Å over the whole range of cluster size. Since these changes are much less than the nearest-neighbor distance, the actual cluster shape will rarely be changed by the edge energies for any cluster size.

The basic result of this paper is that edge energies cannot be defined or calculated without careful and precise definitions for edge lengths and facet areas. A precise definition is suggested based on the concept of intersecting equimolar surfaces. Using this definition, the edge and vertex energies have been calculated for Pd clusters. Finally, I show that the calculated edge energies will have essentially no effect on the equilibrium crystal shape for Pd nanoclusters. The issues raised here will be crucial for future work on the role of edge energy in the self-assembly of nanostructures. They also demonstrate the challenges to be encountered in applying continuum concepts at the nanoscale.

ACKNOWLEDGMENTS

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APPENDIX: BOND-BREAKING MODEL OF EDGE ENERGY

Previous discussions of edge-energies have commonly used bond-breaking models.[5,6] At the atomic level, every atom can easily be classified as a bulk, surface, edge, or vertex atom. Even though every atom can be classified, the correct definition of edge length and surface area remains ambiguous. From the atomic point of view, the ambiguity is that "edge atoms" could equally well be considered as being part of the areas of the two surfaces meeting to form the edge.

In order to make contact with the previous work, it is appropriate to revisit the bond-breaking model and to calculate the edge and vertex energies for fcc clusters using the definition of surface area and edge length based on intersecting equimolar dividing surfaces. In this Appendix only, the length unit used is the nearest neighbor distance and the energy unit used is one-half of the energy required to break a nearest neighbor bond. In these units, the bulk cohesive energy is 12, and the surface energies (for an infinite planar surface) are $\gamma_{111}=2\sqrt{3}$ and $\gamma_{100}=4$. In order to distinguish between the octahedron and the cuboctahedron, we will use subscripts. For example, the number of atoms on an edge will be written n_{oct} for the octahedron and n_{cuboct} for the cuboctahedron.

The calculation parallels the EAM calculations described in the body of this paper. However, because we can readily calculate the total interface energy by counting broken bonds, there is no need to include bulk terms in the derivation. Thus the total interface energy is written in powers of the edge length, as $E_{\text{interface}}=Bs^2+Cs+D$.

In order to calculate the interface energy for an octahedron, with n_{oct} atoms on an edge, it is necessary to count the total number of broken bonds. For an octahedral cluster there are $4(n_{\text{oct}}-3)(n_{\text{oct}}-2)$ surface atoms each having three broken bonds, $12(n_{\text{oct}}-2)$ edge atoms each having five broken bonds, and six vertex atoms each having eight broken bonds. Summing all these contributions, the total number of broken bonds at the surface, edge and vertex atoms is $E_{\text{interface}}=12n_{\text{oct}}^2$.

At this point we equate the two expressions for the interface energy and write

$$Bs_{\text{oct}}^2+Cs_{\text{oct}}+D=12n_{\text{oct}}^2. \tag{A1}$$

Next we use the definition for the edge length, s_{oct}, given by Eq. (8). We substitute $s_{\text{oct}}=n_{\text{oct}}+1/6n_{\text{oct}}$ in Eq. (A1), collect equal powers in n_{oct}, and discard all terms with negative powers of n_{oct}. By equating coefficients of terms having the same power in n_{oct}, we find $B=12$, $C=0$, and $D=-4$. Since $Bs_{\text{oct}}^2=\text{Area}_{\text{oct}}\gamma_{111}$ and $\text{Area}_{\text{oct}}=2\sqrt{3}s_{\text{oct}}^2$ we find $\gamma_{111}=2\sqrt{3}$ from our cluster calculation in perfect agreement with the infinite plane value.

Since $C=12\varepsilon_{111\text{-}111}$ we find that the edge energy, $\varepsilon_{111\text{-}111}$, for the octahedron is identically zero in a broken bond model. Since $D=6\alpha_{\text{vertex}}$, we find the vertex energy for the octahedron to be $\alpha_{\text{vertex}}=-2/3$ for the octahedral cluster.

The calculation for a cuboctahedron is similar. For a cuboctahedron there are $4(n_{\text{cuboct}}-3)(n_{\text{cuboct}}-2)$ (111) surface atoms each having three broken bonds, there are $6(n_{\text{cuboct}}-2)^2$ (100) surface atoms each having four broken bonds, there are $24(n_{\text{cuboct}}-2)$ edge atoms each having five broken bonds, and there are 12 vertex atoms each having eight broken bonds. Summing all these contributions, the total number of broken bonds for the cluster is $E_{\text{interface}}=36n_{\text{cuboct}}^2-36n_{\text{cuboct}}+12$.

As before, we equate the two expressions for the interface energy and write

$$Bs_{\text{cuboct}}^2+Cs_{\text{cuboct}}+D=36n_{\text{cuboct}}^2-36n_{\text{cuboct}}+12. \tag{A2}$$

We substitute the definition for s_{cuboct} given by Eq. (6) into Eq. (A2), collect equal powers of n_{cuboct}, and discard all terms with negative powers of n_{cuboct}.

By equating coefficients to the same order in n_{cuboct}, we find $B=36$, $C=0$, and $D=-5.4$. The value for B corresponds to exactly to the value expected based on the areas and surface energies of the two types of facets. We also find $\varepsilon_{111\text{-}100}=0$ and $\alpha_{\text{vertex}}=-0.45$.

The important conclusion from the bond-breaking model is that if edge length and surface area of clusters are defined using equimolar dividing surfaces, the calculated surface energies are equal to their value from infinite slab calculations and the edge energies of the two types of edges are precisely zero. In Ref. 6, using bond-counting methods, the authors comment: "The main result of our calculations is the surprising agreement of the microscopic results … with the predictions of the macroscopic Wulff's rule, even for particles as small as those with 2000 or 3000 atoms" (in spite of the fact that ~7% of atoms are edge or vertex atoms). The calculations presented in this Appendix show that edge energies are zero for a simple bond-breaking model, thus explaining the previous "surprising" results of Ref. 6.

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