Are Nanoparticle Corners Round?

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S Supporting Information

ABSTRACT: Experimental results for corner rounding in nanoparticles as a function of size are reported. We find that the rounding is independent of size, which appears to violate the conditions for both the thermodynamic and kinetic Wulff conditions. To understand this, we first verify that continuum concepts such as the weighted mean curvature and preferential nucleation at a twin boundary are valid at the nanoscale using density functional theory calculations. We then explain the rounding as a consequence of a nominal singularity in continuum models for sharp corners, showing that rounded or in some cases slightly truncated corners are a Lyapunov (steadystate) solution. We point out that in almost all cases the



corners of materials at the nanoscale will be rounded, and also that the rounding can be exploited to measure the chemical potential during the growth conditions.

INTRODUCTION

With the recent increase in interest in materials at the nanoscale there has been extensive development in methods for both synthesizing materials with nanometer precision as well as imaging them with picometer accuracy. In most cases the classic models for understanding the structure of these materials which date back to the 19th century have held up very well. For instance, the Wulff construction for the thermodynamic shape of an isolated particle¹⁻⁵ has been shown to apply for sizes from nanometers to millimeters, and can be modified to include substrates⁶ and twins, 7,8 and the kinetic version of this for both single crystals $^{9-15}$ and twins^{16,17} has been shown to hold for many cases where growth dominated. Both of these approaches have, in many cases, sharp corners and edges. For many applications such as plasmonics¹⁸ one wants to have very sharp corners, and even very small rounding can have large effects.^{19,20} As a second example in catalysis a very successful model for rationalizing many particle size effects is consideration of how many edge and corner atoms there are as a function of size, since these can have higher activity.²

A subtle question that appears to have largely escaped attention for nanoparticles is whether the corners and edges are really sharp. In fact, there is an important reason to raise this question. Within a continuum model the chemical potential of a sharp corner can be understood in terms of the weighted mean curvature (wmc),²² a limit that is similar to a functional derivative of the total surface energy $E_{\rm S}$ with respect to h_i the normal distance to the facet,

$$\operatorname{wmc}(h_i) = \lim_{\delta \to 0} \frac{\Delta E_{\rm S}(h_i + \delta h_i)}{\Delta V(h_i + \delta h_i)} = \frac{\mu^{\rm s}(h_i)}{\Omega_0} \tag{1}$$

where $\mu^{s}(h_{i})$ is the chemical potential associated with a given facet *i* as a function of h_{i} and Ω_{0} is the atomic volume. For a

simple corner, as illustrated in Figure 1, the chemical potential at the apex scales can be written as

$$\operatorname{wmc}(h_i) = \frac{\overline{\gamma_i}}{L_i - h_i} \tag{2}$$

with L_i the distance from the Wulff center to the apex as shown in Figure 1, and the facet disappears for $h_i \ge L_i$ with a weighted mean surface energy $\overline{\gamma}_i$. The wmc is nominally singular for a sharp corner. Is this an artifact of a continuum model, or are sharp



Figure 1. Illustration of truncation of a (001) facet for different numbers of planes (*N*) to take account of atomicity, with the Gibbs equimolar surface shown. Here L_i is the distance normal to the facet from the Wulff center to the apex, while h_i would be the distance from the Wulff center to the facet shown here for N = 2.

Received: July 20, 2015 Revised: August 19, 2015

The Journal of Physical Chemistry C

corners not present in many cases? There is a substantial literature where at larger scales these singularities are handled by a regularization via a curvature term (e.g., refs 23-31 and references therein), but whether this is valid at the atomic scale for a nanoparticle is not obvious.

In this note we provide experimental evidence and a theoretical analysis to demonstrate that in many cases corners and edges are not sharp at the nanoscale. Electron microscopy data for gold nanoparticles from a conventional polyol synthesis show that their corners are rounded, with a radius of curvature that is largely independent of size. To understand this, we first demonstrate via density functional theory calculations that the singularity of the chemical potential in a continuum model is nominally valid, provided that atomicity is taken into account and the units are carefully chosen to include the Gibbs equimolar partition.^{32,33} The intent is to show that continuum models for chemical potentials in nanoparticles and atomistic ones agree. We next show that there will be a steady-state, Lyapunov stable solution with finite, size-independent truncation of sharp corners. Finally, we provide an inductive proof that the stable shape will tend toward a rounded corner, without invoking any curvature regularization. This analysis does not disprove the conventional kinetic-Wulff solution; rather it indicates that it has to be modified at the nanoscale. While exceptions are always possible, both the experimental data and theoretical analysis indicate that most corners and edges are not sharp.

EXPERIMENTAL AND THEORETICAL METHODS

Synthesis of anisotropic Au nanoparticles with different shapes was performed via a modification of a one-pot polyol synthesis,³ using different concentrations of polyvinyl pyrolidone (PVP) to yield different size particles For larger particles (65–120 nm), 2 g of polyvinyl pyrolidone (PVP, $(C_6H_9NO)_n$; MW = 55 000 g/mol) was dissolved in 25 mL of diethylene glycol ($C_4H_{10}O_3$). To make smaller nanoparticles, the PVP concentration was altered. All of the solutions were refluxed at 255 °C for 10 min. An amount of 20 mg of HAuCl₄·3(H₂O) salt dissolved in 2 mL of diethylene glycol was then added rapidly, and the mixture was allowed to reflux for 10 more minutes. Reaction was stopped using a cold water bath, and the particles were washed with anhydrous ethanol (C₂H₅OH, EtOH) repeatedly. Particles were spun down via centrifugation at 6000 rpm for 30 min. Supernatant was removed, and more EtOH was added to replace the adsorbed diethylene glycol/PVP in the system. Removal of DEG was confirmed through UV-vis spectroscopy.

The morphology of the samples was characterized via conventional transmission electron microscopy in a JEOL2100F. Edge length and corner rounding of the particles were measured using Digital Micrograph and ImageJ software. The number of each different shape was counted manually using at least 100 nanoparticles per sample or until the data were statistically significant.

Density functional calculations to analyze the weighted mean curvature were performed using the all-electron APW+lo WIEN2K code³⁵ for a simple gold pyramid with *P*4/*mmm* symmetry as a function of truncation as shown in Figure 1, using the Wu and Cohen generalized gradient approximation functional.³⁶ Technical parameters were a maximum wavevector divided by the smallest muffin-tin radius (RKMAX) of 8.0, muffin-tin radii of 2.5 au sampled on a logarithmic mesh of 981 points, and a special k-point of (1/6, 1/3, 1/4). The cell size was 23.1691 Å × 23.1691 Å × 45.0533 Å. Additional reference calculations with the same parameters except for the Brillouin-zone sampling were calculated for a *P*4/*mmm* 21-layer Au(001) 1 × 1 periodic slab

surface (unreconstructed) with a 2.89614 Å \times 2.89614 Å \times 57.34064 Å unit cell and bulk gold, with $10 \times 10 \times 2$ and $10 \times 10 \times 10$ k-point sampling. All calculations where converged to approximately 2mRyd/au forces and used the DFT minimized lattice parameters for bulk gold.

While these calculations were reasonably accurate, because of the large cell size, they are not perfect but adequate to demonstrate that the classical chemical potential of a facet via a weighted-mean curvature approach is consistent with atomistic calculations to 5% or better as discussed later.

RESULTS

We focus here upon the decahedral multiply twinned nanoparticles (Dh) and truncated bitetrahedra (BTd) with a twin plane (or more than one) normal to the viewing direction; several examples of these are shown in the images in Figure 2. Note that in both cases there is a twin boundary at the corner, with the vector normal to the boundary perpendicular to the viewing direction for the Dh and parallel for the BTd. Depending upon how much PVP was present, the particle sizes changed, being smaller for higher concentrations. Figure 3a shows results for the corner-rounding as a function of edge length for 2 g of PVP (MW \approx 55 000 g/mol) for both the Dh and BTd, and Figure 3b for the Dh over a wider size range using three different concentrations as shown in the figure. While there is a slight change at the smaller sizes and more scatter in the data at larger sizes, over the total range the rounding is very close to constant.

We will now build up the explanation of the experimental results primarily via a continuum model, which will be a sequence of steps. For each, we will point out how the continuum model corresponds to atomistic modeling results which already exist in the literature or are described here. This enables us to demonstrate that the continuum model is general.

As mentioned above, the corners of the Dh and BTd are both at twin boundaries viewed from two orthogonal directions. The thermodynamic minimum energy shape at a twin has a re-entrant surface,^{7,8} and the overall shape is concave. However, there is faster growth at the twin boundary due to faster nucleation of an atomic layer, as known for some time in the literature (e.g., refs 37-41). A specific formulation of the rate was given recently by Gamalski et al.,⁴¹ who assumed nucleation on both sides of the twin which leads for the shapes here to a kinetic-Wulff shape without the re-entrant feature.^{16,17} At least for gold the mechanism appears to be slightly different, and a little clarification is appropriate as a slight digression. As discussed in more detail in the Supporting Information, DFT calculations indicate that there is an effective zero excess energy associated with nucleation bounded by the twin boundary, so nucleation and faster growth will occur via a half circle monatomic terrace. The reason the excess energy is almost zero is because the atoms in a twin termination are able to bond to the atoms on the other side of the twin in the surface underneath; see Figure S1d.

Having established the basics of the kinetic enhancement at a twin boundary at the atomic scale and hence for the small scales herein, we need to investigate whether the singularity at a corner is an artifact of a continuum model or valid in atomistic calculations. It is well-known that atomicity can lead to terms not found in continuum models; for instance, as early as the 1930s Stranski and Kaichew⁴² (see also ref 2 and references therein) worried about what happened when surface areas were too small to accommodate vicinal facets. Beyond this, it is sometimes considered that continuum models are not valid for surface energies at small sizes. The available evidence dating back to the important



Figure 2. Transmission electron microscope images of different Dh (top) and BTd (bottom), with scale bars of 50 nm.

work of Cleveland and Landman³² indicates that they are valid so long as the Gibbs equimolar volume is used to define surface areas. While this suggests that the wmc approach to chemical potential should be valid provided that atomicity is included, it does not prove it. As shown in Figure 4, for a simple pyramidal test case the expected inverse scaling is obeyed exceedingly well. We therefore conclude that we can apply the continuum wmc formulation without any concerns about its validity for small sizes.

With the relevant continuum terms verified, we leave the atomistic formulation behind and turn to a continuum analysis, avoiding a regularization approach, for the moment with only the simple truncation of Figure 1. The nanoparticles in the polyol synthesis are kinetic shapes, and the shape of a nanoparticle in this limit is given by

$$h_i = \lambda v_i \tag{3}$$

which can also be written in more compact form as the set of points $S_{\rm K}$

$$S_{\rm K} = \{x: x \cdot \hat{n} \le \lambda \nu(\hat{n}) \text{ for all unit vectors } \hat{n}\}$$
(4)

where h_i is the distance of facet "*i*" from the origin, v_i is the growth velocity of that face, and λ is a constant with different values for different sized nanoparticles. For these growth conditions (in contrast to others such as diffusion control) for a large facet the velocity is controlled by the time taken to nucleate a single atomic height ledge as mentioned above which depends upon the chemical potential of the external medium and that of the flat surface, plus the time for this to grow to cover the facet by atom attachment at the step.

This equation has two well-known steady state solutions for a given facet. One is when all the facet is part of the inner envelope; i.e., it grows slowly and is present in the nanoparticle. The second is when the facet is outside the inner envelope; i.e., it grows fast and is not present in the particle. There is a third possibility when the facet size is comparable to that of a critical single atomic height nucleus and in particular if the chemical potential of the facet (via the wmc) is larger than that of the surrounding solution. In such a case the single-layer nucleus will never be stable. This third case leads to a steady-state solution where $\mu_{\text{ext}} = \mu_i = \Omega_0 \overline{\gamma}_i / (L_i - h_i)$. This is a Lyapunov stable solution, since if $(L_i - h_i)$ increases because of growth rate fluctuations, the growth velocity dh_i/dt will increase, as there is a larger driving force to add atoms to the facet. Similarly if $(L_i - h_i)$ decreases, the growth velocity will decrease and atoms would tend to be etched back into the solution from the facet. Note that for the steady state solution, $(L_i - h_i)$ is independent of the particle size.

As the final step, we need to extend beyond the simple truncation model with a flat facet. This answer is too simple for two reasons:

- (a) The kinetic-Wulff condition assumes that growth occurs via nucleation of a small two-dimensional island followed by step-flow growth across the facet, but if the surface is rough with existing steps, there is no nucleation barrier.
- (b) A flat facet also has corners, and one can apply the same arguments to these, truncating them in turn ad infinitum.

By induction, since a flat facet violates the conditions, we should consider a rough one where there is no nucleation barrier and no corners. While we will not exclude slightly more complex local shapes (a topic for future work), the simplest approximation is to consider a sphere for truncation of corners of a cylinder for edges. In this case the stable solution changes to $\mu_{ext} = \mu_i = C\Omega_0 \gamma_R / R$ where *R* will be the radius of the corner, *C* depends upon the angles for the corner, and γ_R is the effective surface free energy of the rounded corner. A representative calculation of *C* is given in the Supporting Information for the case of a circular cone. This is



Figure 3. (a) Measurements for 2 g of PVP of Dh and BTd. (b) Measurements for Dh in different concentrations of PVP.



Figure 4. Plot of the chemical potential in eV/atom for a (001) facet versus 1 over the truncation N.

consistent with the experimental results. We note that here the radius R is also proportional to the homogeneous critical nucleation radius that would be used within a spherical model. (Note that this is *not* the critical radius for the initial nucleation of the nanoparticles; rather it is that for the growth conditions which will normally be much larger.) By use of h_R and R as vectors defined in Figure 5, this solution can be written in compact form as

 $S_{\rm K} = \{x: x \cdot \hat{n} \le \min(|h_{\rm R} + R|, \lambda \nu(\hat{n})) \text{ for all unit vectors } \hat{n}\}$ (5)

with $h_{\rm R}$ constrained to yield a continuous external surface.

As a final point of the analysis, we return to the scatter in the experimental measurements of the corner curvature. The



Figure 5. Plot of the conditions for a steady-state solution with rounded (rough) corners.

solution given above is the Lyapunov-stable steady-state solution, but in actual growth the shape will oscillate about this solution only asymptotically converging to it. The scatter in the experimental data is "real" and shows the magnitude of the deviations from this solution during growth.

DISCUSSION

All generalizations are dangerous, and in principle one can conceive of special circumstances where it may be possible to fabricate corners or edges that are truly sharp by using high

The Journal of Physical Chemistry C

chemical potentials. We believe that this will be the exception rather than the rule. If one looks at experimental electron microscope or scanning probe images of nanoparticles from solution, evaporative growth or other means that are in the literature with kinetic control of the shape all that we are aware of show rounded corners and edges. We note that an obvious opportunity exists to mine existing data to determine the chemical potential of the solution by analyzing the rounding as a function of synthesis condition. The scatter of the rounding can also be exploited to look at the homogeneity of the growth conditions. For completeness we note that a similar result could be obtained by using a more continuum based curvature regularization strategy as cited earlier (e.g., refs 23-31 and references therein), but proving that this is a valid approximation at the atomic level appropriate for nanoparticles is not simple. Here we avoid this, as the corners in effect self-regularize by dissolving back into the solution.

It is worth mentioning that in many cases the shape of a nanoparticle in equilibrium with its vapor phase or some concentration of atoms in a solution may also contain rounding at the corners and edges by the same argument as we have used here, or they may be sharp. Whether or not this occurs will be strongly influenced by the rate of exchange with the external medium, and it may take almost infinitely long for equilibrium to be achieved. This would be an interesting topic for further study, albeit it would be challenging experimentally to ensure that equilibrium is achieved.

CONCLUSION

The kinetic shapes of corners and edges will in most cases violate the classical models and not be sharp but atomically rounded, provided that atomicity is included. This does not invalidate solutions such as the well-known Wulff construction in kinetic or thermodynamic forms but instead requires a slightly more complicated but still essentially classical analysis of the processes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b07021.

DFT calculations to clarify twin nucleation and derivation of a three-dimensional form of the corner angle-dependent constant *C* (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thanks Peter Voorhees for useful comments. This work was supported by Materials Research Center (MRSEC) at Northwestern University, on Grant MRSEC-1121262. MRSEC is funded through National Science Foundation.

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