PARTICLE SIZE EFFECTS ON WULFF CONSTRUCTIONS

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The equilibrium structure of small particles is analysed by minimising the total surface energy of atomistic clusters. Large deviations from the bulk Wulff construction are identified for fairly large (~ 10 nm) particles due to sphere packing corrections. These act as additional edge terms which can be significantly larger than the true edge terms. For a simplified fcc model, it is shown that the fraction of (100) surface drops markedly as the particle size drops because of these packing effects. This can lead to very large particle size effects for a face sensitive catalytic reaction. It is also pointed out that these packing corrections link very small (< 100 atom) cluster to very large particles.

1. Introduction

The equilibrium structure of a particle has been a subject of interest for many years. When the particles are sufficiently large that a continuum model can be employed, the equilibrium morphology is determined by the Wulff construction. (For some recent reviews see refs. [1–3].) This approach can be extended to the case of non-single crystal particles, primarily those containing twin boundaries, this modified Wulff construction [4,5] proving capable of successfully explaining the typical wide spread of small (~ 20 nm) particle morphologies. At the opposite end of the spectrum of very small clusters (< 100 atoms), fairly detailed analyses have been performed using pair potentials (e.g. refs. [6–8]). Although there are questions as to the proper form of the potential to be used, primarily for metallic clusters when one would expect an oscillatory pseudopotential, substantial success has been achieved in understanding some of the early features of nucleation and growth.

With the two extremes of very small and very large particles fairly well understood, an immediate question is what determines the particle morphology in between these size ranges. Considerable attention has focussed on multiply twinned particles or MTPs (e.g. refs. [4,5,9–13]) as a possible bridge. However, although these particles occur extensively for silver and gold, the experimental evidence conclusively demonstrates that these non-crystallographic structures are often absent (e.g. refs. [12–16]). Therefore they cannot be the only possible bridging morphology between the very large and the very small.

In this paper we investigate this intermediary region, approaching the problem by analysing the deviation from the bulk Wulff construction as the particle size decreases. By expressing atomistically the total surface energy and the number of atoms in the cluster, large sphere packing effects are identified. These act as additional edge or vertex terms, and can be significantly larger than the effects due to true edge or vertex atoms. For the simple case of an fcc single crystal with only (111) and (100) facets, there is a marked decrease due to these packing effects in the proportion of (100) surface atoms as the particle size drops. It is pointed out that very significant catalytic particle size effects can be expected in this intermediary region between the essentially molecular clusters and the large continuum particles due to these morphological changes.

2. Analysis

We will start in this section with a very general approach, generating the sense of the major effects, and then illustrate the analysis with a simplified fcc model in the next section.

Consider an arbitrary particle whose shape is specified by the set of normal distances h_i to each "i" surface facet. In a generalised analysis, the total energy associated with the surface of the particle, S, can be written:

$$S = h_i h_j \left(A_{ij} + B_i/h_j + C/h_i h_j + \ldots \right),$$ (1)

and the total number of atoms N represented as

$$N = h_i h_j h_k \left(D_{ijk} + F_{ij}/h_k + G_i/h_j h_k + \ldots \right),$$ (2)

where summation is implied in both of these equations.

To generate local minima for the surface morphology of the particle, we look for minima of the Lagrangian

$$L = S - \lambda N,$$ (3)

which includes the constraint

$$N = N_0 \quad \text{a constant},$$ (4)

that is, minimize S for a fixed number of atoms.

Let us discuss in a little detail eqs. (1)–(4), since they contain all basic physics of this paper. We are interested in a form which converges to the continuum analysis for large h_i, i.e. S proportional to the surface area and N proportional to the total volume. This immediately implies the inverse power expansion. The non-continuum terms (B_i, C, F_{ij}, G_i) arise from two sources. Firstly there are the true edge and vertex atoms, and secondly packing corrections. The latter are particularly important, and merit further discussion. Let us consider a simple fcc octahedron with triangular (111) faces. If the edge

length of each face corresponds to n atoms, we can decompose the surface into

$4(n-2)(n-3)$	(111)	atoms,
$12(n-2)$	edge	atoms,
6	vertex	atoms.

Considering these terms, we have $12(n-2)$ true edge atoms and $-20n$ edge-like (111) atoms. We term these (111) atoms edge-like since they scale linearly with the particle size, and thus behave as if there were extra edges on the particle. Taking the energy associated with edge atoms to be comparable to the energy of an atom on a (111) face, we have the surprising result that the octahedron has effectively a *negative* number of edge atoms. The source of these edge-like terms is how spheres pack to produce a (111) face; there are less atoms present than the continuum measure of surface area would predict. In a similar fashion, we have corrections to the total number of atoms in the cluster, the leading of which scale as the particle size squared ($F_{ij}h_ih_j$ from eq. (2)). Since the Lagrangian constant λ has dimensions of an energy divided by the number of atoms the first volume correction ($\lambda F_{ij}h_ih_j$) is also edge-like. The next packing corrections will scale invariant with the particle size, and thus act as additional vertex terms.

From the very simple analysis described above, it follows that these edge-like terms are large, easily more important than the true edge atom energies in the cluster. The type of series in eqs. (1) and (2) are rather slowly convergent, so effects are possible even for quite large particles. The general equilibrium morphology for a large number of surface facets can be obtained by solving eqs. (1) and (2). This is somewhat messy, but is relatively straightforward numerically using current computers. Rather than attacking this general problem, we will consider a specific evaluation of some relatively simple models in the next section. From these we can generate important results on the effects of these edge-like packing effects, and connect to the cluster analyses described earlier.

3. Simple fcc models

To illustrate the effects of the packing corrections on the equilibrium particle shape, we will consider a simple model of an fcc crystal with only (111) and (100) facets as shown in fig. 1. The total number of atoms in the cluster and at the various different surface geometries are shown in table 1, defined in terms of the number of atoms n and m along the edges as shown in fig. 1. For a real cluster, n and m must be integers, but in order to facilitate the analysis we have considered them as continuous, non-integral, variables. (We have avoided the regions where n or m are less than 2 when some of the edge terms vanish.)
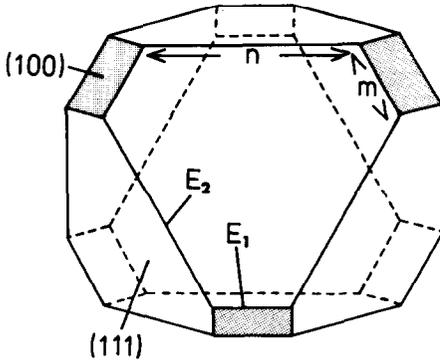
Fig. 1. Diagram of the simplified fcc particle used in the analysis, showing the definition of n, m and the edges E_1 and E_2. Note that n and m correspond to the number of atoms along the edges E_2 and E_1 respectively, which scale to the lengths.

Minimization of the total surface energy for specific numbers of atoms was performed for six different models which are summarized in table 2. These were chosen to illustrate the relative strength of the edge-like packing terms and the true edge terms. The various models are: an equal energy (EE) model were the energy per surface atom is independant of the local geometry, the main effects being from the packing terms; a simple broken bond (BB) model, which is a relatively crude representation of an fcc crystal; and four variants of the broken bond model termed A, B, C, D, each with slightly different edge energies in order to test the relative strength of the true edge and the edge-like terms.

There are surprisingly large number of interesting effects which are shown graphically in figs. 2–7. The most significant trend throughout, except for the extreme case of model A, is that the fraction of the surface (100) atoms drops as the particle size decreases. These curves (figs. 2 and 3 particularly) are similar to those based upon simple surface counting statistics without any morphological changes (e.g. refs. [17,18]). However, major effects such as the

Table 1
Total number of atoms and surface atoms for the simple fcc model, with $x = n + 2m - 2$, $y = m - 1$, and $z = n - 1$

	Number of atoms
Total (N)	$x(2x^2 + 1)/3 - y(2y^2 + 3y + 1)$
(111)	$8\{2yz + [y(y-3) + z(z-3)]/2 + 1\}$
(100)	$6y^2$
E_1	$24(y - 1)$
E_2	$12(z - 1)$
Vertex	24
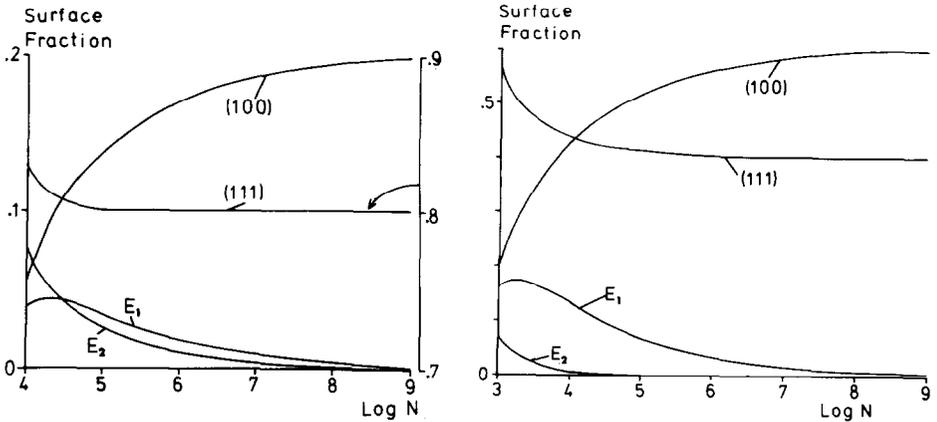
Fig. 2. Plot of the surface fraction of (111), (100) and edge atoms E_1 and E_2 as a function of N for an equilibriated broken bond (BB) model. The curve for the (111) atoms is drawn using the scale to the right. The strong drop in the fraction of (100) surface should be noted. We note that the sum of (100) and E_1 atoms is essentially a constant fraction.

Fig. 3. Plot of the surface fraction of different types of surface atoms against N for the equal energy (EE) model. The similarity to fig. 2 should be noted.

slow rise in surface (111) are absent in these earlier analyses. The surface variations are large as can be seen from figs. 2 and 3, certainly significant for less than 1E6 atoms in the cluster. These are surprisingly large clusters, being about 20 nm in size. It is useful to parametise these changes in term of the ratio n/m, as shown in figs. 4 and 5. From these figures it is apparent that n/m scales as $N^{-1/3}$ for the large particles, indicative of edge effects. For smaller clusters of less than about 5E4 atoms (10 nm), the curves deviate from $N^{-1/3}$ behavior, indicating that vertex effects are becoming important. The only vertex terms that can be entering here are the vertex-like corrections to the volume ($\lambda G_i h_i$ from eq. (2)). Although these terms scale with size like vertices, they are functions of h_i and therefore change with the particle shape. In contrast both the true vertex terms and the vertex-like corrections to S are

Table 2
Energies per surface atom for the different models used

	EE	BB	A	B	C	D
(111)	4	3	3	3	3	3
(100)	4	4	4	4	4	4
E_1	4	5	4	4	4.5	5.5
E_2	4	5	7	6	5.5	4.5
Vertex	4	6	6	6	6	6
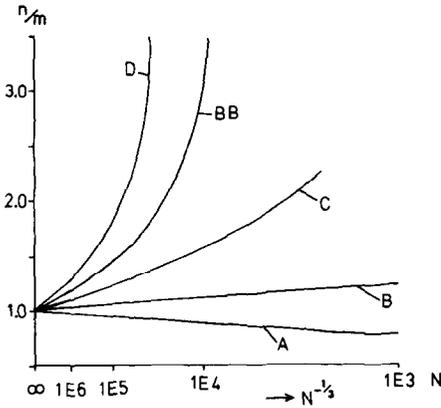
Fig. 4. Plots of n/m for the broken bond (BB) and variants A–D against $N^{-1/3}$, with specific values of N also shown.
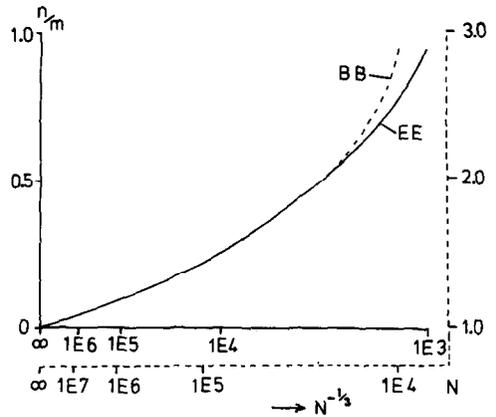
Fig. 5. Plot of n/m for the equal energy (EE) model against $N^{-1/3}$ – the solid curve and axes. For comparison, n/m against $(N/2)^{-1/3}$ for the broken bond (BB) model is shown by the dashed curve and axes. Except for small clusters, the two curves are identical.
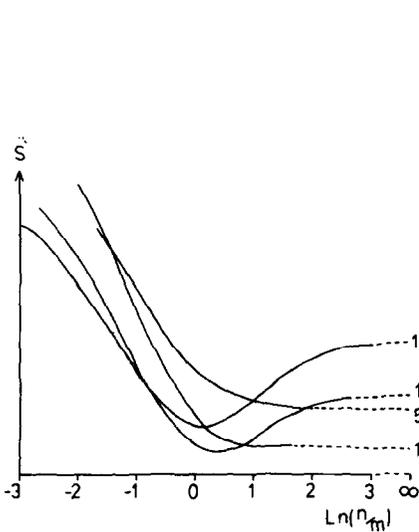
Fig. 6. Plots of S against $\ln(n/m)$ for fixed numbers of atoms in the clusters. The $y(S)$ axes have been shifted and have different scalings. The values for $\ln(n/m) = \infty$ correspond to fcc octahedra with only (111) facets.
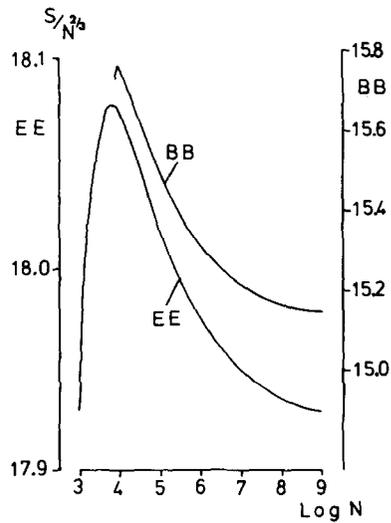
Fig. 7. Variation of $S/N^{2/3}$ against N for the broken bond (BB) model, axis shown to the right, and equal energy (EE) model for which the axis is shown on the left.

independent of the particle shape. We also note that the form of the curves are almost identical except for scaling, as shown in fig. 5.

Moving now to consider the effect of true edge atom terms, we first note one peculiarity of the simple (111) and (100) model used herein. When changing n and m, any change in (111) edge atoms is exactly compensated by a change in (100) edge atoms. Therefore there is no energy gain in trading (111) edge atoms for (100) edge atoms when the energy associated with these edges is identical (BB and EE models). In models A–D the edge energies have been varied in order to show the relative strength of the edge effects. Obviously they are important, but we note that it takes the extreme model A to offset the trend of n/m increasing with smaller particles. This implies that the true edge effects are less important in general than the packing terms.

The variation of the total surface energy as a function of the ratio n/m as shown in fig. 6 is also of interest. These surfaces of equal volume show definite minima for moderately large clusters (1E6 atoms), these minima shifting to higher value of the ratio as the size decreases. However, rather than just a simple shift, the surfaces also flatten on the high ratio side; as the size drops the minima soften towards complete elimination of the (100) faces. For instance, for 1E4 atoms there is a minimum for $n/m = 2.9$ in the broken bond model, separated by a very small maximum from a second minimum for no (100) atoms. Below a certain critical size, here about 9E3 atom (~ 4 nm particle size), the (100) facets become unstable and the particle switches over to only (111) faces. Therefore during growth we would expect a smooth transition from solely (111) facetted particles to those with both (111) and (100) faces, without any nucleation barrier for (100) facet formation. We note that with a more accurate calculation including the (currently unknown) surface energies at low temperatures, we would expect to find a somewhat smaller critical size, perhaps 5E3 atoms (~ 2 nm).

One final feature is the variation of $S/N^{2/3}$, which is a measure of the total surface energy of the particle. ($S/N^{2/3}$ is a constant in a continuum model for a particular particle morphology independant of size.) As shown in fig. 7, there is surprisingly little variation considering the magnitude of the facetting changes. However, the variations are sufficiently large that when different particle morphologies are being considered (e.g. MTPs and single crystals), correct evaluation of the minimum energy morphology will be critical.

4. Discussion

From the very simple analysis herein, it is apparent that very large morphological changes occur even in single crystal particles when the particle size drops. These changes occur even in rather large particles due to the slow convergence of the sphere packing series. Rather than MTPs being the sole link

between the very small and very large particles, it is instead the packing corrections that are the link. (The importance of sphere packing is inherent in the very small cluster analyses, e.g. refs. [1–3].) These corrections may lead to MTP structures such as icosahedra, but this does not have to be the case. (We note that an icosahedron is a very efficient sphere packing.) Obviously the model used herein is simplified and further effects may arise with, for instance, an allowance for interactions with more distant atoms (e.g. refs. [19]), but we would expect the general results to still hold.

The most immediate and perhaps important result that follows from the analysis is the identification of a very large catalytic particle size effect. If a reaction is face specific, for instance preferring (111) to (100) faces, the large variations shown in figs. 2 and 3 will be very important. This is a generalisation of surface statistical effects from the initial philosophy of edge and vertex atoms (e.g. refs. [17,18]) to include the possibility of face specific effects. At present the experimental data (e.g. refs. [4,5]) is not good enough to test these predictions, but in the fairly near future high resolution electron microscopy (e.g. refs. [20,21]) should permit direct experimental measurements of small cluster structure, and direct measurement of the surface statistics.

Acknowledgments

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