

Nucleation Energy Barriers for Volume-Conserving Shape Changes of Crystals with Nonequilibrium Morphologies

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This paper quantifies the nucleation energy barrier that must be overcome if a faceted, defect-free particle with a nonequilibrium morphology is to change shape by intraparticle transport. Two types of crystals are considered: those whose equilibrium form is a truncated sphere and those whose equilibrium form is a cube. Numerical estimates show that, for a particle near equilibrium, the barrier becomes insurmountable for a facet larger than a few tens of nanometers. For nonequilibrium shapes where material must be transferred from faceted surfaces to uniformly curved surfaces to reach the equilibrium shape, the facets enlarge without a nucleation barrier (at a rate limited by diffusion or surface attachment kinetics) until they reach a fraction of their equilibrium size that is typically between 0.5 and 0.75. At this point, a significant barrier is encountered that, in the absence of step producing defects, prevents the particle from continuing toward equilibrium. For nonequilibrium shapes where material must be transferred to faceted surfaces from other parts of the crystal for it to reach the equilibrium shape, significant energy barriers for the nucleation of new layers persist even when the shape is far from equilibrium. Predictions from our model are compared to experimental observations reported by other researchers.

I. Introduction

FOR A crystalline particle with facets to change shape, it is generally necessary for a facet to move in a direction normal to its plane. This, in turn, requires a step to propagate across the face of the facet, adding or removing a layer of atoms. If the facet contains no preexisting steps, then a nucleation event is required to provide a propagating step. Hence, in general, there is a nucleation (free) energy barrier (NEB) for shape changes of defect-free particles containing facets.

The NEB present during the growth of a faceted crystal is well known.¹ In the growth situation, it is possible to overcome the NEB by increasing the supersaturation in the growth medium. Here, we consider isolated crystals undergoing volume conserving shape changes. In this case, the equivalent supersaturation that can be generated is limited by the crystal's size and shape. The NEB for shape changes of an isolated equilibrium crystal whose shape is a sphere truncated at two opposite ends by facets (see Fig. 1) has recently been estimated.² The results show that the equivalent supersaturation generated by crystals larger than a few tens of nanometers is insufficient to drive significant nucleation on a facet.

Manuscript No. 188104. Received December 5, 2000; approved March 20, 2001. Supported primarily by NASA under Grant No. 8-1674 and partially by the MRSEC program of the National Science Foundation under Award No. DMR-0079996. This implies the NEB prevents a defect-free crystal above the critical size from reaching the equilibrium shape.

The main purpose of this paper is to extend the calculations of NEBs to crystals with nonequilibrium shapes. The resulting knowledge of the shape dependence of the barriers allows a better understanding of the approach of a crystal toward the equilibrium shape, including the point at which the crystal becomes kinetically immobilized. The calculations are based on two model equilibrium shapes: the truncated sphere just mentioned and the fully faceted shape of a cube. The NEBs are calculated for prolate (elongated) and oblate (foreshortened) shapes. Emphasis is placed on the barriers for changes of these shapes toward (rather than away from) equilibrium.

A secondary purpose of the paper is to show the generality of NEBs for a crystal at equilibrium by extending the barrier calculations beyond those for our model equilibrium shapes to any facet on a general equilibrium shape. This includes, for example, finite facets with smooth edges which are not included in the truncated sphere or cube models. These calculations, presented in Section II, do not deal with nonequilibrium shapes, but the magnitude of the NEBs for the equilibrium shape give some indication of the kinetics of approach to that shape.

The assumptions underlying the calculations, adopted in the previous paper² and here, are the following: (*i*) the crystal is approximated as a continuum; (*ii*) the crystal is isolated so that only intraparticle material transport is possible; (*iii*) the crystal is free of any step producing defects emerging on the facets; (*iv*) the free energy of the perimeter of a partial layer (or nucleus) on a facet is assumed to be given by Eq. (2), which is consistent with what was called the macroscopic perimeter assumption in the



Fig. 1. Schematic diagram depicting an axial section of the truncated sphere, defining the geometric parameters used in the text.

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previous paper;² and (v) the surface stresses and volume changes upon transfer of material are neglected.

We determine the barrier, $E_{\rm b}(+)$, for (atomic) layer addition on a facet and the barrier, $E_{\rm b}(-)$, for layer removal from a facet. For volume conserving transformations, the former results in facet shrinkage (lateral dimensions) and the latter in facet growth. The net nucleation rate, *I*, leading to layer addition is given by

$$I = A_{+} \exp\left[\frac{-E_{\rm b}(+)}{kT}\right] - A_{-} \exp\left[\frac{-E_{\rm b}(-)}{kT}\right]$$
(1)

where $A_+, A_- > 0$ are prefactors, k Boltzman constant, and T the absolute temperature. In equilibrium, $E_{\rm b}(+) = E_{\rm b}(-)$ and $A_+ = A_- = A$. In the previous paper,² we made an upper estimate of A from which we concluded that the nucleation rate becomes negligible for either process when $E_{\rm b}(kT) \ge 40$. We will continue to use this value, recognizing that our estimate of the prefactor would have to be low by ~17 orders of magnitude to raise the critical value of $E_{\rm b}(kT)$ from 40 to 80; the latter value would double the critical size, but not change our major conclusions in any essential way.

In Section II, we calculate the NEB for any facet on a general equilibrium shape. In Section III, general expressions are derived for the NEBs of nonequilibrium shapes of the truncated sphere model in terms of the facet radius and the mean curvature of the continuous surface. In Section IV, the results of numerical calculations of the NEBs are presented for prolate and oblate shapes evolving toward the equilibrium truncated sphere shape. In Section V, the maximum NEBs toward equilibrium are calculated for elongated and foreshortened cube shapes. In Section VI, a discussion is given of experimental and theoretical evidence in the literature supporting our calculations and conclusions. Special attention is given to the relevance of our results to the interpretation of experiments in which prolonged annealing of a small crystal or cavity is assumed to yield the equilibrium shape. Section VII offers a summary.

II. NEB for a General Facet on an Equilibrium Crystal

The previous calculation of NEBs was based on crystals with the specific idealized equilibrium shapes of a truncated sphere or a cube.² For these shapes, there is a discontinuity of slope at the facet edges representing missing orientations (the corresponding Wulff planes may, however, pass through the facet edges). In this section, to show that NEBs are a general feature of any facet on an equilibrium shape, we extend the analysis to include facets with no slope discontinuity at the edges. We assume that the periphery of a nucleus on the facet may be approximated as a step of variable orientation. A nucleus of a given area then has the lowest free energy when its peripheral step has the same shape as the step defining the facet edge, since both are essentially determined by a two-dimensional Wulff construction on the orientation dependent step free energy. Hence, the perimeter free energy of the nucleus is

$$\varepsilon_{\rm p} = \omega a \oint \sigma_{\rm p} \, \mathrm{d}l \tag{2}$$

where the integral is conducted over the perimeter of the nucleus (l) when coincident with the facet edge, σ_p is the nucleus perimeter or step free energy per unit area, *a* the height of the nucleus, and ω a linear scale factor representing the size of the nucleus relative to the size of the facet ($0 \le \omega \le 1$). The area of the nucleus is $\omega^2 A_F$ where A_F is the area of the facet. Therefore, the free energy required to form the nucleus of size ω is

$$\varepsilon = \omega a \oint \sigma_{\rm p} \, \mathrm{d}l - \omega^2 a A_{\rm F} \mu_{\rm e} \tag{3}$$

Equation (3) represents the free energy required to take a volume $\omega^2 a A_F$ of material from the reservoir at chemical potential μ_e and form a nucleus of perimeter free energy given by the first term.

Because the free energy of the crystal is a minimum at equilibrium, there is no change of free energy when a complete layer of atoms is transferred to or from a facet. In other words, ε must vanish for $\omega = 1$. Use of this condition in Eq. (3) gives

$$\mu_{\rm e} = \left(\frac{1}{A_{\rm F}}\right) \oint \sigma_{\rm p} \, \mathrm{d}l \tag{4}$$

and substitution of this relation for μ_e into Eq. (3) gives

$$\varepsilon = a \oint \sigma_{\rm p} \, \mathrm{d}l(\omega - \omega^2) \tag{5}$$

Equation (5) has a maximum at $\omega = 1/2$ which represents the NEB and is given by

$$E_{\rm b}^{\rm e} = a \oint \sigma_{\rm p} \frac{dl}{4} = a \mu_{\rm e} \frac{A_{\rm F}}{4} = a \sigma_{\rm F} \frac{A_{\rm F}}{2d_{\rm F}}$$
(6)

where we have used the general relation $\mu_e = 2\sigma_F/d_F$ in which σ_F and d_F are the free energy and the perpendicular distance of the facet from the crystal center, respectively. Equation (6) also gives the barrier for the removal of a layer from the facet at equilibrium, by time reversal arguments, and hence represents the barrier to shape fluctuations about equilibrium. In other words, even though steps are present at the periphery of the facet, the vanishing layer must pass through a high-energy configuration ($\omega = 1/2$) that is identical to that reached by the growing layer. For a crystal of a given size (and a corresponding fixed μ_e), Eq. (6) shows that E_b^e is proportional to the area of the facet; for equilibrium crystals of the same shape (and hence of the same σ_f) but of different sizes, E_b^e varies linearly with the size.

Equation (6) is valid for facets whose neighboring orientations are either present as assumed in the discussion or, if missing, have Wulff planes that pass through the facet edge (degeneratively present). Otherwise, Eq. (6) may be shown to give a lower bound for the barrier energy.³

To estimate the magnitude of $E_{\rm b}^{\rm c}$, consider a circular facet on the equilibrium form of radius ρ for which $A_{\rm F} = \pi \rho^2$ and $\rho/d = \tan \alpha$, where α is the angle subtended by the facet. Equation (6) can then be rewritten in the following way:

$$E_{\rm b}^{\rm e} = \frac{1}{2} \left(a \sigma_{\rm F} \pi d_{\rm F} \tan^2 \alpha \right) \tag{7}$$

With $a = 3 \times 10^{-10}$ m, $\sigma_{\rm F} = 1$ J/m² and $\alpha = 20^{\circ}$, we have $E_{\rm b}^{\rm e} = 6.24 \times 10^{-11} d_{\rm F}$ J. Therefore, to obtain a value of $E_{\rm b}^{\rm e} < 40kT$, where $kT = 1.75 \times 10^{-20}$ J (1000°C), $d_{\rm F}$ is <11.3 nm.

III. NEBs for Nonequilibrium Shapes of the Truncated Sphere Model; Analytic Expressions

In this section, we determine analytic expressions for the NEBs as a function of parameters defining nonequilibrium shapes of crystals whose equilibrium shapes are truncated spheres. In Section IV, we use these expressions for a numerical evaluation of the NEBs. For the equilibrium truncated sphere of radius *R*, shown in Fig. 1, the equilibrium values of the facet radius ($\rho_e = R \sin \theta$) (θ , termed the contact angle) and the distance of the facet from the center of the crystal ($d_e = R \cos \theta$) are fixed by the angle between the facet and the continuous surface. The surface free energies of the continuous surface, σ_c , and the facet, σ_F , are related through the Wulff theorem by $\sigma_F/\sigma_c = d_e/R = \cos \theta$. Finally, the equilibrium chemical potential is given by $\mu_e = 2\sigma_c/R$, which together with Eq. (4) and the preceding relations yields, for the step free energy,

$$\sigma_{\rm p} = \sigma_{\rm c} \sin \theta \tag{8}$$

$$E_{\rm b}^{\rm e} = \frac{1}{2} \left(\pi a \sigma_{\rm c} R \sin^2 \theta \right) \tag{9}$$

Equation (9) is a special case of Eq. (7) for $\alpha = \theta$. The nonequilibrium shapes we consider are specified by $d/d_e > 1$ (prolate) or $d/d_e < 1$ (oblate). We assume these shapes all enclose the same volume V and all have the same contact angle θ , which represents a condition of local equilibrium. The key to calculating the shapes is the assumption that the circular facets are immobile (fixed *d*) and that the continuous surface adjusts to achieve the minimum area under the given constraints. The corresponding surfaces of revolution are called unduloids and are characterized by a constant mean curvature, κ .⁴ In the next section, we calculate κ as a function of d/d_e at fixed V and θ . The value of κ then determines the chemical potential $\mu = \sigma_c \kappa$ of the reservoir with which material is exchanged to add or remove a layer of atoms on the facet.

The assumption of immobile facets is valid at equilibrium for particles above the critical size as already discussed. As d/d_e departs from unity, we continue to use the assumption as long as it is supported by the resulting barrier size. Since the nucleation rate is an exponential function of the barrier size, the range of d/d_e for which the assumption is valid is quite well defined.

For layer addition, material is taken from the continuous surface to form the nucleus on the facet. The required free energy is given by Eq. (3), adapted to the present case with a circular nucleus of radius *r* and a general μ :

$$\varepsilon = 2\pi a \sigma_{\rm p} r - \pi a \mu r^2 \tag{10}$$

With $\mu = \sigma_c \kappa$ and $\sigma_p / \sigma_c = \rho_c / R = \sin \theta$, we may write the value of *r* at which the maximum of Eq. (10) occurs as $r^* = \rho_c / R \kappa$ and the value of the maximum, representing the barrier $E_b(+)$ for layer addition, as

$$\frac{E_{\rm b}(+)}{E_{\rm b}^{\rm e}} = \frac{2}{R\kappa} \tag{11}$$

where $E_{\rm b}^{\rm e}$ is defined in Eq. (9). Equation (11) is valid provided $r^* < \rho$ or $1/(R\kappa) < \rho/\rho_{\rm e}$.

For layer removal, the lowest free energy path is obtained by taking material from the outer annular sector of the facet and placing it on the continuous surface. The free-energy change is thus

$$\varepsilon = 2\pi a \sigma_{\rm p} (r - \rho) + \pi a (\rho^2 - r^2) \sigma_{\rm c} \kappa \tag{12}$$

The maximum of Eq. (12) occurs at the same value of r as before, $r^* = \sigma_p / \sigma_c \kappa = \rho_e / R \kappa$, and the value of the maximum, representing the barrier for layer removal, $E_b(-)$, may be written as

$$\frac{E_{\rm b}(-)}{E_{\rm b}^{\rm e}} = \frac{2}{R\kappa} \left(R\kappa \frac{\rho}{\rho_{\rm e}} - 1 \right)^2 \tag{13}$$

This equation is valid provided $1/(R\kappa) < \rho/\rho_e$. For $\rho < \rho_e/R\kappa$, the barrier for layer removal vanishes. Equations (11) and (13) are independent of scale.

IV. Numerical Calculation of the NEB for the Truncated Sphere Model

Prolate and oblate nonequilibrium shapes with the same volume are considered under the constraints that the continuously curved surface maintains a uniform curvature and the contact angle between the flat facet and continuously curved surface is preserved for all aspect ratios. To determine how the NEB changes with particle shape, it was necessary to find the curvatures on the lateral sides of crystals with the same volume as the equilibrium crystal, but different aspect ratios. The equilibrium particle volume is defined by the contact angle between the facet and the continuously curved surface. We begin by choosing a fixed nonequilibrium ρ and a trial curvature. These initial values are smaller than the equilibrium values for prolate shapes and larger for oblate shapes. With reference to the coordinate system in Fig. 1, the initial point of the curved surface is defined by the assumed facet radius ($\rho = y(0)$). The slope of the curve at the initial point is determined by the contact angle ($y_x(0) = 1/\tan \theta$), and the second derivative (y_{xx}) is determined from the curvature and slope by the following equation:

$$\kappa = -\frac{y_{xx}}{(1+y_x^2)^{3/2}} + \frac{1}{y(1+y_x^2)^{1/2}}$$
(14)

Next, a Taylor expansion is used to find y(dx/2) and y(dx). The next value along the curve is taken to be y(dx/2), the slope at this position is calculated using a difference quotient ((y(dx) - y(0))/dx), and the second derivative is calculated according to Eq. (14), using the new value of the slope. Points on the curve are found by repeating this process until the slope diminishes to zero $(y_x(d) = 0)$. Recognizing the symmetry of the particle, the volume is calculated and compared to the equilibrium volume. Using the false position method,⁵ the choice of $dx = 5 \times 10^{-5} \rho_e$ allows a value of κ to be obtained which produces a crystal shape with the equilibrium volume to within 0.001%. By sequentially selecting new values of ρ and seeking curvatures that produce shapes with the correct volume, a range of particles with different aspect ratios is defined.

For each shape, the NEB for the removal or addition of new layers is calculated according to Eqs. (11) and (13), respectively. For a particle with a contact angle of 35°, the addition and removal barriers are illustrated in Fig. 2. For the prolate shape to evolve toward equilibrium, the facet must move toward the center of the crystal by transferring material from the facet to the curved surface. This process increases the curvature toward the equilibrium value of 2/R. The barrier for this process is represented by the dashed line. We see that when d/d_e is >1.3, the NEB vanishes. Therefore, longer thinner particles can quickly evolve to this shape at a rate dictated by diffusion or surface attachment limited kinetics. However, below this ratio, the NEB quickly rises. Assuming a particle with a 1 µm radius and the physical constants already cited at the end of Section II, 40kT corresponds to 0.004 on the vertical scale. In other words, the evolution toward the equilibrium shape will be arrested at the point where the NEB rises above the horizontal axis.

For the oblate shapes to evolve toward equilibrium, material must be transferred from the equatorial region of the particle to the facet, moving the facet further from the center of the crystal and reducing the curvature. The NEB remains significant, even when



Fig. 2. (—) Layer addition and (- - -) removal barriers for crystals with $\theta = 35^{\circ}$. Inset in the figure are axial sections of the oblate shape, for which $d/d_e = 0.43$ (left), the equilibrium shape, for which $d/d_e = 1$ (middle), and the prolate shape, for which $d/d_e = 1.32$ (This is the shape for which $1/R\kappa = \rho/\rho_e$).

the crystal is far from its equilibrium shape. In the prolate case, the NEB diminishes as the facet dimension approaches a size comparable to the critical nucleus; for small aspect ratios in the oblate case, the facet is much larger than the critical nucleus. The fact that the facet is large in comparison to the critical nucleus is offset somewhat by the increase in the curvature of the lateral surfaces and this causes the NEB to diminish slowly as the shape departs from equilibrium.

The NEB is calculated as a function of aspect ratio and contact angle and the results are summarized in Fig. 3. In this analysis, we can take the contact angle to be a measure of the anisotropy ratio of the surface energy. Two trends are noteworthy. First, the NEB for oblate shapes evolving toward equilibrium is not significantly affected by the contact angle. Second, as the contact angle diminishes and the particle becomes more nearly isotropic, prolate particles can very nearly reach equilibrium before a significant NEB is encountered. However, for particles with a more significantly anisotropic surface energy, the inward motion of the facet is arrested by the NEB long before the equilibrium shape is reached.

The results in Fig. 3 are generally applicable to particles of any size. To determine if any particular particle is immobilized, we have to consider the absolute values for the NEB. The barrier for layer addition or removal at equilibrium is graphed as a function of particle size in Fig. 4 for particles with a range of contact angles. For reference, a line representing 40kT at 1000°C is added to the plot. For example, one can see that for a crystal with an equilibrium radius of 1 μ m and $\theta = 15^{\circ}$, the NEB becomes insurmountable when $E_{\rm b}/E_{\rm b}^{\circ} = 0.02$ and $d/d_{\rm eq} = 1.06$.

Another way to look at these data is to consider how large the facet grows before it encounters a significant NEB. The facet can always grow to one half of its equilibrium size without encountering a NEB. After this point, the facet continues to grow until the NEB becomes insurmountable. Considering again the particle with $R = 1 \ \mu m$, $\sigma_c = 1 \ J/m^2$, and $a = 3 \times 10^{-10}$ m, the growth of a facet with $\theta = 5^\circ$ is arrested when $\rho/\rho_{eq} = 0.72$. For a particle with $\theta = 35^\circ$, growth stops when $\rho/\rho_{eq} = 0.56$. In summary, we expect the growth of the facet to be arrested when it is between one half and three quarters of its equilibrium size; the greater the anisotropy ratio, the further from equilibrium the shape is immobilized.

V. Calculation of the NEB for the Cube Model

We consider a crystal with the equilibrium shape of a cube with edges of length L along xyz axes. The nonequilibrium shapes we discuss are those for which the z face is square (L_2 by L_2), but for which the length L_1 along the z direction either satisfies $L_1 > L$ (prolate) or $L_1 < L$ (oblate); volume conservation requires $L_1(L_2)^2 = L^3$. We confine the calculation of the NEB to the barriers for changes toward equilibrium, which means layer removal on the z face for the prolate case and layer addition on the



Fig. 3. Layer addition and removal barriers for crystals with $\theta = 5^{\circ}$, 15°, 25°, and 35°. For the oblate shapes, the layer-addition barriers overlap at the resolution of this graph.



Fig. 4. Values of E_b° for crystals with $\theta = 5^{\circ}$, 15°, 25°, and 35° as a function of *R*. These values were calculated assuming $\sigma_c = 1 \text{ J/m}^2$ and $a = 3 \times 10^{-10}$ m; the horizontal line is added to indicate the energy of 40 kT at 1000°C.

z face for the oblate case. The barriers are the free energies of the critical state representing the maximum free energy of the lowest free-energy path for material transfer. The calculation of the NEB for fully faceted particles is complicated by the fact that addition or removal of a complete layer on one face usually results in only a partial layer on the other participating face. A subsequent transfer will encounter a different barrier, in general, because of the different degree of coverage of the participating face. We confine the calculation to the maximum of the sequence of barrier free energies. If this is prohibitive, changes do not occur. If it is not prohibitive, the other barriers are not prohibitive either.

Consider first the prolate case. It is clear that the critical state of maximum free energy is the unstable equilibrium in which the material removed from the *z* face leaves a square nucleus ($s \times s$) and also forms a square nucleus of the same size on one of the side faces. Mass balance requires $2s^2 = L_2^2$. The free-energy change ε to form the configuration and, hence, the barrier magnitude is

$$\varepsilon_{\rm b}(-) = 8a\sigma s - 4a\sigma L_2 = 4(2^{1/2} - 1)a\sigma L_2 \tag{15}$$

But the barrier $\varepsilon_{\rm b}$ to fluctuations about equilibrium is the same expression with L_2 replaced with *L*. Hence $\varepsilon_{\rm b}(-)/\varepsilon_{\rm b} = L_2/L$. Finally, using the constant-volume condition, and letting $\lambda = (L_1/L)$, we obtain

$$\varepsilon_{\rm b}(-)/\varepsilon_{\rm b} = (1/\lambda)^{1/2} \tag{16}$$

as λ increases, the barrier slowly decreases.

Consider next the oblate shape. The lowest free-energy path for transfer of material from a side face (say the x face) to the z face requires the largest free-energy reduction per material removed from the x face. This occurs by first removing a strip of material of length u in the y direction until a square $L_1 \times L_1$ remains and then removing material symmetrically to shrink this square. There are two cases.

Case I: A critical state of two equal squares of sides $s < L_1$ can be formed, one on the *z* face and one remaining on the *x* face. This requires $L_1 < L_2 < 2L_1$ and the mass balance is $2s^2 = L_1L_2$. The free energy barrier is

$$\varepsilon_{\rm b}(+) = [8s - 2(L_1 + L_2)]a\sigma \tag{17}$$

Combining this equation with the mass balance, the volume conservation and the equilibrium barrier, we obtain

$$\frac{\varepsilon_{\rm b}(+)}{\varepsilon_{\rm b}} = \frac{1}{4(2^{1/2} - 1)} \left[8^{1/2} (\lambda)^{1/4} - (\lambda) - \left(\frac{1}{\lambda}\right)^{1/2} \right]$$
(18)

for $(1/4)^{1/3} < \lambda < 1$. This is a decreasing function of λ in the indicated interval.

Case II: $L_2 > 2L_1$. The critical state now consists of a square on the *z* face but a remaining rectangle on the *x* face. To find the critical state we use the mass balance condition $L_1u = s^2$ and the free energy change for a general *u*

$$\varepsilon = -2ua\sigma + 4sa\sigma = (-2u + 4(L_1u)^{1/2})a\sigma \tag{19}$$

Differentiating Eq. (19) with respect to u, we find the value of u that maximizes $\varepsilon(u^*)$ to occur at $u = u^* = L_1$, corresponding to a square removed from the x face. The corresponding free-energy barrier may be written as

$$\frac{\varepsilon_{\rm b}(+)}{\varepsilon_{\rm b}} = \frac{1}{2(2^{1/2} - 1)}\,\lambda\tag{20}$$

Eq. (20) is valid for $\lambda < (1/4)^{1/3};$ again this is a decreasing function of $\lambda.$

The energy barriers in Eqs. (16), (18), and (20) are presented in Fig. 5 as a function of λ , which can be taken as a measure of the aspect ratio. Assuming the same physical parameters as before for a 1 μ m crystal, unity on the vertical axis corresponds to 5 × 10⁻¹⁶ J. Considering the fact that 40*kT* at 1000°C is 7 × 10⁻¹⁹ J, we see that the barrier remains significant even for highly anisotropic particles.

VI. Experimental and Theoretical Evidence for the Nucleation Energy Barrier

The nucleation energy barrier and its ramifications have been recognized for some time. For example, Herring^{6,7} and Searcy⁸ noted that the NEB should affect the rates at which faceted particles coarsen and sinter. The present paper represents an effort to quantify the barrier in a general and widely applicable manner. In this section, we briefly review evidence from the literature which supports the idea that this barrier exists and that it can be large enough to prevent the motion of crystal facets.

(1) Nelson *et al.*⁹ reported on the shapes of faceted bubbles in metals with radii that were several tens of nanometers. When on grain boundaries, the bubbles reached a stationary shape faster than those in the bulk of the metal. If the triple junction formed where the grain boundary intersects the bubble can act as a step source that eliminates the need to nucleate new steps, then the relatively slower morphological evolution of the bulk bubbles can be explained by the presence of a NEB.



Fig. 5. Nucleation-energy barriers for fully faceted shapes. Only the barriers for evolution toward equilibrium ($\lambda = 1$) are depicted. Shapes with $\lambda = 1/4$ (lower left), $\lambda = 1$ (top left), and $\lambda = 4$ (top right) are inset as examples. In all three cases, L_1 is the vertical dimension of the crystal, and L_2 is the lateral dimension.

(2) Willertz and Shewmon¹⁰ reported that, when heated between 873° and 977° C, helium bubbles in gold with submicrometer radii migrate 10^{4} – 10^{5} times slower than would be expected based on the surface diffusion coefficient. In this case, migration involves removing gold atoms from one facet and adding them to another. These results were explained by assuming that the rate of motion of a faceted bubble is determined by the frequency with which steps can be nucleated on a flat facet and that there was a NEB for this process.

(3) The rates at which inclusions migrate in alkali halides have been linked to the presence of threading dislocations.^{11,12} Inclusions with sizes less than a micrometer, which are unlikely to be continuously threaded by a dislocation, moved slowly and erratically. Larger inclusions, which were much more likely to be threaded by a dislocation, showed steady, larger mobilities under a comparable thermal gradient driving force. The presence of a NEB in the absence of a threading dislocation was proposed to explain these observations.

(4) Metois and Heyraud¹³ compared the kinetics of the shape transformation of lead spheres and plates supported on graphite. The lead crystals used in this study had radii between 0.5 and 5 μ m. They reported that small molten spheres of lead supported on graphite, when crystallized, reached an apparent (nearly spherical) equilibrium form in ~4 h at 250°C. However, when tabular crystals were annealed at the same temperature for up to 160 h, only a subset of the crystals reached the same apparent equilibrium state; the remainder maintained oblate shapes. We surmise that this is because of the asymmetry of the NEB for the two cases. For a tabular crystal to convert to a more spherical one, the large facet must shrink and the NEB for this process remains significant even at large deviations from equilibrium. However, as facets grow on the spherical crystal, the NEB becomes significant only when the particle closely approximates its equilibrium shape.

(5) Transmission electron microscopy (TEM) micrographs of voids (with radii between 10 and 100 nm) formed near the tips of indentation induced cracks in Al_2O_3 after high temperature annealing (1600°C for 50 h) showed that those with threading dislocations had shapes that were different from those that did not.¹⁴ While the authors ascribed this to the strain associated with the dislocation, it is also possible that absence of a NEB led to the difference.

(6) Faceted particles of ZrO_2^{15} and MgO^{16} with radii on the order of 50 nm have been observed during *in situ* TEM annealing. Isolated particles of ZrO_2 without dislocations maintain stationary states during annealing at 850°C or 2 h. This observation, together with the formation of unstable necks between pairs of faceted MgO particles,¹⁷ was explained by the presence of a NEB on the faceted parts of the surface.

(7) Kitayama *et al.*¹⁸ reported on the evolution of highly oblate cavities (20 μ m × 20 μ m × 0.5 μ m) in Al₂O₃ during annealing at 1900°C for up to 16 h. While some of the cavities evolved to a reproducible equilibrium shape, others maintained a stationary oblate morphology. The authors suggested that the immobilized shapes were defect free, while those that evolved to equilibrium contained step producing defects.

(8) Recent observations of liquid lead inclusions in aluminum have also been explained in terms of a NEB.¹⁹ Liquid filled inclusions exhibit thermal history and size dependent metastable shapes. The observation that smaller inclusions (<70 nm in diameter) reach equilibrium more easily and that the equilibrium is more easily reached by cooling from a more spherical shape than heating from a faceted shape is consistent with our predictions for the size and shape dependence of the NEB.

(9) Recent observations of facets on micrometer-sized, isolated, defect free lead crystals by *in situ* ultrahigh-vacuum scanning tunneling microscopy have demonstrated that during cooling, facet enlargement occurs by the sequential removal of individual atomic layers.²⁰ The observation that facets formed at relatively low temperatures do not shrink when the temperature is increased indicates that there is a NEB for the addition of new layers from the curved part of the crystal.

One of the principal means of evaluating the anisotropy of the surface energy is to observe the shapes of small particles supported on an inert substrate that have been annealed until they reach a stationary state. This technique has been applied to gold,^{21,22} lead,²³ indium,²⁴ NaCl,²⁵ and selected alloys.²⁶ The procedure involves melting a film of the metal so that it dewets to form separate and nearly spherical liquid drops, which are then solidified and annealed until they reach a stationary state. At the end of the experiment, the self-similarity of the crystals and the fact that longer annealing times do not cause shape changes is taken as an indication that an equilibrium state has been reached. However, neither of these conditions are inconsistent with a set of particles that are kinetically trapped in a nonequilibrium state by the presence of a NEB.

An important question is, if the particles do get trapped in a nonequilibrium state, how far off are the estimates of the surface energy anisotropy? We consider the case of gold, which was studied on a graphite substrate by Heyraud and Metois²¹ and on a SiC substrate by Wang and Wynblatt.²² In both cases, the energy anisotropy was determined by measuring the distance from the facet to the center of the crystal. For gold on graphite, the anisotropy ratio ($\gamma_{100}/\gamma_{111}$) was observed to be about 2%; for gold on SiC, the anisotropy ratio was observed to be $\sim 4\%$. It was also reported that the contact angle θ between the facets and the continuous surfaces was 5° and 19° for the {100} and {111} surfaces, respectively.²² Assuming that the facets on the cube behave as those on our model truncated sphere, then we conclude that the $\{100\}$ and $\{111\}$ facets were 1% and 9% further from the center than they would have been in equilibrium, respectively. If we place the facets in their presumed equilibrium positions, the actual anisotropy ratio of gold would be 12%. In other words, the effect of the NEB is to make stationary shapes that evolve from spheres appear to be more isotropic than they really are. Winterbottom and Gjostein²⁷ evaluated the anisotropy ratio for gold using a thermal groove technique. Assuming that the groove root acts as step producing defect, the NEB should not affect this measurement. It is therefore interesting to note that the anisotropy ratio derived from this experiment (7%) is higher than that derived from either of the Wulff shape experiments.

VII. Summary

Based on evidence in the literature, it seems clear that the NEB influences the morphological evolution of faceted, defect free crystals. In this paper, we have shown that at equilibrium, the NEB is proportional to the area of the facet and, we have quantified the barrier for certain nonequilibrium shapes. We find that when material must be transferred to a facet from other parts of the crystal, the NEB remains significant even at large deviations from the equilibrium shape. Crystals with facets and uniformly curved surfaces were also considered. For oblate shapes containing large facets that must move away from the center of the crystal, significant energy barriers for the nucleation of new layers persist even when the shape is far from equilibrium. For nonequilibrium shapes where facets must grow to reach the equilibrium shape, the facets enlarge without a nucleation barrier until they reach about half of the equilibrium size. The principal conclusion from this work is that defect free crystals larger than a few tens of nanometers can become immobilized in stationary states before reaching their equilibrium form.

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