

Nucleation Barrier for Volume-Conserving Shape Changes of Faceted Crystals

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This paper considers volume-conserving shape changes of small faceted particles or cavities; these changes are driven by surface-energy reduction. If these changes require normal motion of the facets (singular surfaces), and if the perimeter free energy σ_p (per unit area) of a nucleus of a new facet layer is comparable to a typical surface free energy ($\sigma \approx 1 \text{ J/m}^2$), the energy barrier is prohibitively large for facets larger than a limiting size of approximately a nanometer unless they are intersected by dislocations that provide a source of steps. In the absence of such dislocations, particles that contain these facets are immobilized in their initial shapes. If $\sigma_p < \sigma$, the limiting facet size is increased by a factor of approximately σ/σ_p .

I. Introduction

SINGULAR or nonrough surfaces, which correspond to cusps in the plot of the surface free energy as a function of orientation, advance and retreat via the lateral motion of steps that add or subtract atomic layers. If a singular surface has no steps or step sources, its motion is limited by two-dimensional nucleation.^{1,2} The so-called “growth resistance” that is derived from the two-dimensional nucleation barrier was a controversial topic in the first half of the twentieth century, as researchers attempted to understand how singular surfaces could advance at supersaturations 10–100 times smaller than those predicted by nucleation theory.² This issue was settled by Frank,³ who convincingly argued that screw-dislocation/surface intersections provide the source of the steps necessary for a singular facet to advance or retreat under the low-supersaturation conditions that are observed in growth experiments. In this communication, a singular surface (or facet) without steps is termed an ideal singular surface. When the problem of two-dimensional nucleation on an ideal singular facet was revisited by Hirth,⁴ using a refined theory, the conclusions of the earlier investigations² were substantiated.

Although Frank’s model³ is most widely known for its explanation of crystal-growth phenomena, Herring^{5,6} noted that the two-dimensional nucleation barrier also would prevent the surface-free-energy-motivated motion of ideal singular facets during sintering. Searcy⁷ elaborated on this point and argued that, for a fully faceted particle with no dislocations to evolve to a new fully faceted shape closer to equilibrium, it would have to transform through an unfavorable configuration, and the probability of this happening decreases as the size of the particle increases.

The objective of this paper is to quantify the barrier that exists for a small crystal particle (or cavity in a crystal) with ideal

singular surfaces to undergo a volume-conserving morphological change toward equilibrium. Our central conclusion is that changes in particle shape that require normal motion of ideal singular facets are prohibited for facets larger than a certain limiting size, which is typically on the order of a nanometer. The barrier that prohibits shape changes is present because, as material is transferred from one facet (or from a continuously curved surface) to another facet, the advancing facet must, at some point, be covered by a partial layer. This intermediate state has a relatively higher energy⁷ that is approximately equal to the energy that is required to form a two-dimensional nucleus with an equivalent radial dimension that is comparable to the facet size ρ . In Section III, it is shown that, when ρ is greater than a limiting value (which is on the order of a nanometer), the corresponding nucleation rate is negligible. In other words, the equivalent supersaturation generated by particles larger than a few nanometers is insufficient to drive significant nucleation on a facet. The implication of this conclusion is that crystals with facets larger than the limiting size can reach an equilibrium shape only if their bounding singular surfaces are intersected by dislocations with a screw component. Models that are dependent on sources and sinks of matter on faceted surfaces require step-providing defects.⁸ In the absence of such defects, nucleation must be considered.

II. Nucleation Barriers for Shape Changes

The nucleation barriers for shape changes of crystals with the equilibrium shapes of a truncated sphere and a cube are calculated in this section, from a continuum standpoint. In both cases, the discussion is focused on the nucleation barrier to fluctuations around the equilibrium shape; the barrier will be approximately the same for shape changes of a near-equilibrium shape toward equilibrium. An estimate also is given of the barrier for a more-general non-equilibrium initial shape.

A sphere that has been truncated by two equal circular facets at opposite ends is illustrated schematically in Fig. 1. If the free energies of the singular and curved (isotropic) surfaces are σ_s and σ_c , respectively, then, according to the Wulff construction,⁶ $\sigma_s/\sigma_c = h/R$. Recognizing that $h = R \cos \theta$, we find that

$$\sigma_s = \sigma_c \cos \theta \quad (1)$$

Equation (1) also may be regarded as a local force balance in the radial direction at the edge of the facet.

First, we calculate the free energy ($\epsilon_0(r)$) necessary to create a circular partial layer of macroscopic height b and radius r on the circular facet of radius ρ (see Figs. 1(b) and 1(c)), using material taken from a bulk reservoir ($\mu = 0$). Following Herring,⁹ we find $\epsilon_0(r)$ to be given by the change in the surface energy:

$$\epsilon_0(r) = 2\pi br \left(\frac{-\sigma_s}{\tan \theta} + \frac{\sigma_c}{\sin \theta} \right) = 2\pi br \sigma_c \sin \theta \quad (2)$$

We now assume Eq. (2) to be valid when $b = a$, where a is the height of an atomic layer; we call this condition the macroscopic

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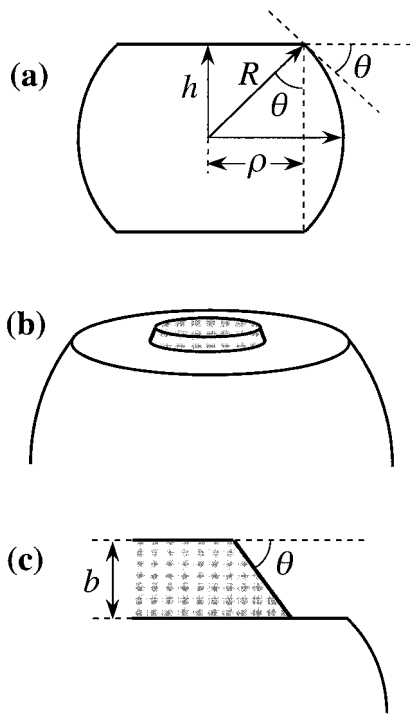


Fig. 1. (a) Schematic projection of the truncated sphere, viewed parallel to the ideal singular facet; (b) oblique projection showing a partial layer on the singular facet; and (c) geometry of the partial layer.

perimeter (MP) assumption. According to this assumption, Eq. (2) shows that the free energy per unit area of the perimeter is given by

$$\sigma_p = \sigma_c \sin \theta \quad (3)$$

To analyze fluctuations about the equilibrium shape, we consider the transfer of a fixed volume (πr^2) of material from the curved surface of chemical potential $2\sigma_c/R$ to the ideal singular surface to form the partial layer (hereafter called the nucleus) that has been described previously. The total required free energy is

$$\begin{aligned} \varepsilon_t(r) &= 2\pi a r \sigma_c \sin \theta - \pi a r^2 \left(\frac{2\sigma_c}{R} \right) \\ &= (2\pi a \sigma_c \sin \theta) \left(r - \frac{r^2}{\rho} \right) \quad (\text{for } 0 \leq r \leq \rho) \end{aligned} \quad (4)$$

where $\rho = R \sin \theta$ is used in the last step. This expression also gives the energy required for a reverse transfer of all but a nucleus of radius r from the facet to the curved surface (i.e., $-\varepsilon_t(r - \rho) = \varepsilon_t(r)$). Note that the nucleus has a positive free energy for all values of $0 \leq r \leq \rho$ and, as required by equilibrium, there is no net change in free energy to transfer a complete facet layer in either direction (see Fig. 2). The maximum of Eq. (4) occurs at $r = r^* = \rho/2$, which corresponds to a barrier height E_b of

$$E_b = \pi a r^* \sigma_p = \frac{1}{2} \pi a \rho \sigma_c \sin \theta = \frac{1}{2} \pi a R \sigma_c \sin^2 \theta \quad (5)$$

We note three points regarding Eq. (5). First, the barrier is symmetric, with respect to addition or removal of a complete facet layer (see Fig. 2(a)), which is consistent with the requirement that the two processes have equal probabilities in equilibrium. Second, the barrier energy is linear in the particle or facet size (for a given θ). Third, the barrier vanishes as θ approaches zero, showing that the model continuously reduces to that of an isotropic sphere. In this limit, the perimeter (step) energy given by Eq. (3) vanishes, which corresponds to the roughening transition of the vanishing facet.¹⁰

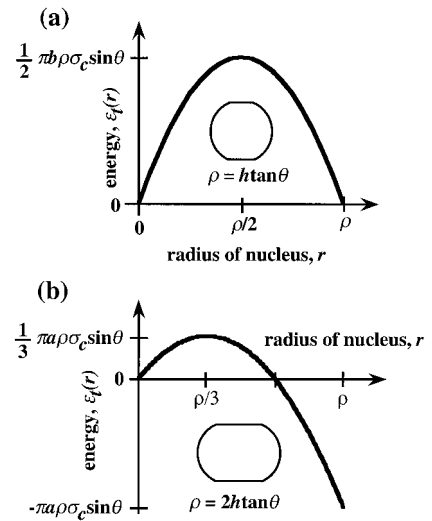


Fig. 2. Energy barrier for (a) the nucleation or removal of a new layer on a crystal with an equilibrium shape, based on Eq. (4) (or Eq. (6) with $\eta = 1$) and (b) the nucleation of a new layer on the foreshortened crystal, based on Eq. (6) with $\eta = 1/2$.

Equation (5) gives E_b for fluctuations around the equilibrium shape. To examine the barriers for particles with initial non-equilibrium shapes, we define the aspect ratio $\alpha = h/\rho$ and note that the equilibrium value of α is $\alpha_e = 1/\tan \theta$. We consider oblate shapes of revolution for which $\eta = (\alpha/\alpha_e) < 1$. We assume that the cross section of the curved surface is the arc of a circle, with θ still given by Eq. (1), and use the expression $\kappa = [(\cos \theta)/h] + [(\sin \theta)/\rho]$ to approximate the mean curvature of the surface; the expression is exact for the equilibrium shape and in the limit as α approaches zero. With these assumptions, it can be shown that the energy is given by

$$\varepsilon_t(r) = (\pi a \sigma_c \sin \theta) \left[2r - \left(\frac{1 + \eta}{\eta} \right) \frac{r^2}{\rho} \right] \quad (6)$$

Note that Eq. (6) is identical to Eq. (4) when $\eta = 1$, and the maximum of $\varepsilon_t(r)$ occurs at $r^* = \rho\eta/(1 + \eta)$. The barrier for fluctuations toward equilibrium is $E_{b+} \approx (\pi a \rho \sigma_c \sin \theta)[\eta/(1 + \eta)]$, whereas the barrier for fluctuations away from equilibrium is $E_{b-} \approx (\pi a \rho \sigma_c \sin \theta)\{1/[\eta(1 + \eta)]\}$, giving the ratio $E_{b+}/E_{b-} \approx \eta^2$. This asymmetry is clarified in Fig. 2(b), which is a plot of Eq. (6) for $\eta = 1/2$. The preceding results show that the barrier reduces to that given by Eq. (5) for $\eta = 1$ and the barrier does not change radically for η near unity; for $\eta = 1/2$, as assumed in Fig. 2(b), $E_{b+}(\eta = 1/2)/E_{b+}(\eta = 1) = 2/3$.

Finally, we consider a crystal whose equilibrium shape is that of a cube. Based on a qualitative argument, Searcy⁷ concluded that there is a barrier for such a particle to evolve toward equilibrium. This conclusion may be quantified by noting that the critical state for shape fluctuations of a cube of side S is that which consists of two equal partial layers on adjacent faces, which corresponds to the transfer of half a layer from one face to another. According to the MP assumption, these layers will be equal squares of sides $S/\sqrt{2}$ (for matter conservation). Therefore, the energy barrier is

$$E_b = 4a\sigma \left(\frac{S}{\sqrt{2}} + \frac{S}{\sqrt{2}} - S \right) = 4(\sqrt{2} - 1)a\sigma S \approx 1.66a\sigma S \quad (7)$$

which is comparable to that for the truncated sphere (Eq. (5)) for $\sigma \approx \sigma_c$, $\rho \approx S$, and $\sin \theta \approx 1$.

III. Nucleation Rates for Shape Changes

To estimate the nucleation rate I per unit area that corresponds to the barriers calculated in Section II, we use the classical

expression^{4,11} for the steady-state nucleation rate of a circular nucleus of critical radius r^* on an infinite singular facet:

$$I = Z\omega_c n_0 \exp\left(\frac{-E_b}{kT}\right) = A \exp\left(\frac{-E_b}{kT}\right) \quad (8)$$

where n_0 is the number of facet lattice sites per unit area, $Z = [\sigma_p a^5 / (4\pi^2 (r^*)^3 kT)]^{1/2}$ the Zeldovich or Farkas non-equilibrium factor,¹¹ $\omega_c = 8\pi r^* n_0 D_s / a$ the rate at which critical nuclei become supercritical (in which D_s is the surface diffusion coefficient), k the Boltzmann's constant, and T the absolute temperature. The pre-exponential factor A may be treated as an approximate constant if the variations in r^* and T are not too large and if we use a fixed value for D_s , which we take to be the upper-limit value ($D_s = 10^{-7}$ m²/s), which approximately corresponds to a jump frequency that is equal to the vibration frequency; this will give an upper estimate of A and, hence, I . With this value and the values $r^* = 10^{-9}$ m, $a = 3 \times 10^{-10}$ m, $n_0 = 1.1 \times 10^{19}$, $Z = 10^{-2}$ (typical value), and $kT = 10^{-20}$ J, we get for an upper estimate of the prefactor: $A = 1.0 \times 10^{31}$ (m²·s)⁻¹.

If we define nucleation rates of $I \leq 10^{-4}$ (nm²·s)⁻¹ (which is equivalent to a rate of less than one atomic layer per hour on a facet 1 nm² in size) and use the estimated value of A , the nucleation on the facet can be considered to be negligible for

$$E_b \geq 40kT \quad (9)$$

approximately. A more-exact criterion can be obtained by including the dependence of A on σ_p , r^* , and T (principally through D_s) and requiring the nucleation rate to be small for the facet area rather than for the fixed value of 1 nm²; however, Eq. (9) suffices as an approximate upper estimate of the value of E_b at and above which the nucleation rate is negligible; numerical estimates follow.

For shape changes of the cube near equilibrium with $kT = 10^{-20}$ J, we combine Eqs. (7) and (9) to obtain the upper estimate $S_L \approx 0.8$ nm (henceforth, limiting values are denoted by the subscript "L"), above which the rates of nucleation and shape changes are negligible. For shape changes (fluctuations) of the truncated sphere at (or near) equilibrium, the values of the limiting sizes of r^* , ρ , and R are dependent on the assumed value of θ , which also may be expressed in terms of $\sigma_p/\sigma_c = \sin \theta$. Combining Eqs. (5) and (9), we obtain $\rho_L = 2.5, 4.8$, and 9.7 nm for $\theta = 20^\circ, 10^\circ$, and 5° , respectively. The corresponding particle diameters are $R_L = 7.3, 28.1$, and 112 nm, respectively. Finally, for the non-equilibrium initial shape $\eta = 1/2$, we evaluate the results for $\theta = 20^\circ$ to find $\rho_L = 3.7$ nm.

IV. Discussion

The MP assumption is perhaps the most questionable of those used in the estimation of barrier height. The concept of a contact angle between the singular surface and the edge of the partial layer, which is implied by Eq. (1), certainly breaks down when the partial layer has an atomic-scale thickness. If the MP assumption underestimates the perimeter energy, then the nucleation barrier also is underestimated, which would make the limiting sizes even smaller than previously estimated. The perimeter energy is not expected to be significantly overestimated by the MP assumption, because this would imply an energy increase if steps were collected to form a macroscopic surface, which would contradict the assumed equilibrium shape. Thus, the MP assumption probably gives a lower limit for the perimeter energy and predicts the highest-feasible nucleation rate.

The barrier heights that are estimated here apply to cases where the sample is neither shrinking (evaporating) nor growing at a significant rate, and this situation is most closely approximated in experiments that involve internal cavities. In fact, step-producing defects have been used to rationalize the experimentally observed rates at which faceted cavities change shape and migrate.^{12–16} Recently, Kitayama and Glaeser¹⁶ measured the shape-change kinetics of pancake-shaped pores in sapphire. Pores with a variety

of orientations were measured, and only those principally bounded by (1010) surfaces, which are not on the equilibrium shape of sapphire, obeyed diffusion-limited kinetics. The remaining pores, whose principal faces are on the Wulff shape, evolved more slowly and showed a greater degree of variability. One compelling observation from the Kitayama and Glaeser¹⁶ work is that some of the pores changed shape dramatically during annealing while others, a few pore diameters away, seemed unchanged. Our present analysis is consistent with the suggestion that the pores that changed shape intersected dislocations whereas those that did not were bound by perfect singular surfaces.¹⁶ Finally, we note that models that recently have been developed to explain observations of unstable neck formation in faceted particles also are consistent with the theory that, for sufficiently large particles, step-producing defects are critical for volume-conserving shape changes.^{17,18}

V. Conclusion

Volume-conserving shape changes of small faceted defect-free particles or cavities, which are driven by surface-energy reduction and require normal motion of the facets (singular surfaces), are prohibited by the magnitude of the nucleation barrier for facet sizes larger than a certain limit, typically on the order of a nanometer. If the nucleus perimeter free energy σ_p is less than a typical surface value ($\sigma = 1$ J/m²), the limiting facet size increases by a factor of $\sim \sigma/\sigma_p$. The facet can move only when a step-producing defect (such as a dislocation with screw character) intersects a facet surface. In the absence of such a defect, the facets are immobile and nonequilibrium shapes are kinetically stabilized.

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References

- ¹W. K. Burton and N. Cabrera, "Crystal Growth and Surface Structure. Part I," *Discuss. Faraday Soc.*, **5**, 33–39 (1949).
- ²N. Cabrera and W. K. Burton, "Crystal Growth and Surface Structure. Part II," *Discuss. Faraday Soc.*, **5**, 40–48 (1949).
- ³F. C. Frank, "The Influence of Dislocations on Crystal Growth," *Discuss. Faraday Soc.*, **5**, 48–54 (1949).
- ⁴J. P. Hirth, "On Two Dimensional Nucleation," *Acta Metall.*, **7** [11] 755–56 (1959).
- ⁵C. Herring, "The Effect of Change of Scale on Sintering Phenomena," *J. Appl. Phys.*, **21** [4] 301–303 (1950).
- ⁶C. Herring, *Structure and Properties of Solid Surfaces*; pp. 5–81. Edited by R. Gomer and C. S. Smith. The University of Chicago Press, Chicago, IL, 1952.
- ⁷A. Searcy, "Driving Force for Sintering of Particles with Anisotropic Surface Energies," *J. Am. Ceram. Soc.*, **68** [10] C-267–C-268 (1985).
- ⁸W. C. Carter, A. R. Roosen, J. W. Cahn, and J. E. Taylor, "Shape Evolution by Surface Diffusion and Surface Attachment Limited Kinetics on Completely Faceted Surfaces," *Acta Metall. Mater.*, **43** [12] 4309–23 (1995).
- ⁹C. Herring, *The Physics of Powder Metallurgy*; pp. 143–79. Edited by W. E. Kingston. McGraw-Hill, New York, 1951.
- ¹⁰E. E. Gruber and W. W. Mullins, "On the Theory of Anisotropy of Crystalline Surface Tension," *J. Phys. Chem. Solids*, **28** [5] 875–87 (1967).
- ¹¹J. Feder, K. C. Russell, J. Lothe, and G. M. Pound, "Homogeneous Nucleation and Growth of Droplets in Vapours," *Adv. Phys.*, **15** [57] 111–78 (1966).
- ¹²R. S. Nelson, D. J. Mazey, and R. S. Barnes, "The Thermal Equilibrium Shape and Sizes of Holes in Solids," *Philos. Mag.*, **11** [109] 91–111 (1965).
- ¹³P. J. Lemaire and H. K. Bowen, "Migration of Small Pores in Potassium Chloride Due to a Temperature Gradient," *J. Am. Ceram. Soc.*, **65** [1] 49–52 (1982).
- ¹⁴D. R. Olander, A. J. Machiels, M. Balooch, and S. K. Yagnik, "Thermal Migration of Brine Inclusions in Synthetic Alkali Halide Single Crystals," *J. Appl. Phys.*, **53** [1] 669–81 (1982).
- ¹⁵J.-H. Choi, D.-Y. Kim, B. J. Hockey, S. M. Wiederhorn, C. A. Handwerker, J. E. Blendell, W. C. Carter, and A. R. Roosen, "Equilibrium Shape of Internal Cavities in Sapphire," *J. Am. Ceram. Soc.*, **80** [1] 62–68 (1997).
- ¹⁶M. Kitayama and A. M. Glaeser, "The Energetics and Kinetics of Pore Shape Evolution in Alumina," *Key Eng. Mater.*, **159–160**, 193–204 (1998).
- ¹⁷J. Rankin and B. W. Sheldon, "Surface Roughening and Unstable Neck Formation in Faceted Particles: I, Experimental Results and Mechanisms," *J. Am. Ceram. Soc.*, **82** [7] 1868–72 (1999).
- ¹⁸J. Rankin and B. W. Sheldon, "Surface Roughening and Unstable Neck Formation in Faceted Particles: II, Mathematical Modeling," *J. Am. Ceram. Soc.*, **82** [7] 1873–81 (1999). □