Energy Barriers for the Morphological Evolution and Coarsening of Faceted Crystals

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Abstract. Crystals completely bounded by flat facets change shape, grow, or shrink only through the lateral motion of steps across the facets. If the crystal is free of step producing defects such as screw dislocations, then such steps must be created by a two dimensional nucleation process. Here, we quantify the energy barrier for the nucleation of steps during the morphological evolution and coarsening of faceted crystals. Our analysis indicates that for defect free, faceted crystals larger than a few nanometers, the nucleation energy barrier will prevent crystals from attaining their equilibrium shape. Furthermore, this energy barrier also limits the growth and dissolution of crystals during coarsening.

1. Introduction

The nucleation (free) energy barrier (NEB) present during the growth of a faceted crystal is well known [1]. We have recently considered how the NEB influences the morphological evolution of isolated, defect free crystals with equilibrium and non-equilibrium shapes [2,3]. The principal results were that if the facets are larger than a few nm, fluctuations around the equilibrium shape will not occur. Furthermore, the NEB will prevent defect free crystals larger than a few nm from evolving to their equilibrium shape [3]. In the present paper, we review these calculations for the specific case of a crystal whose equilibrium shape is a cube. We calculate the NEB for fluctuations about, and morphological changes toward, the equilibrium shape. Using the same approach, we then consider the role of the NEB on the coarsening of faceted crystals by examining its influence on growth and dissolution when the crystal can exchange matter with a reservoir at a fixed chemical potential.

2. NEB for Intraparticle Transport on a Cube Shaped Crystal

We begin by considering an isolated crystal with its equilibrium cube shape, an edge length of L, and a surface energy of σ. We wish to calculate the NEB that must be overcome to transport material from one facet to another. As illustrated in Fig. 1, material is removed from the top facet to form a square island with area s_2^2 on the side facet. Since atoms will be removed from the periphery, a square island with area s_1^2 is left behind on the top facet. To conserve matter, it must be true that $L^2 = s_1^2 + s_2^2$. Obviously, the only energy change in this process is associated with the change in the edge energy. Assuming that the step edges have the same energy per area as the facets (σ), then the energy for the transfer is:

$$\varepsilon_b^e = 4a\sigma s_1 + 4a\sigma s_2 - 4a\sigma L \tag{1}$$

In Eq. 1, the first two terms on the right hand side represent the added perimeter energy while the last one represents the energy eliminated. It is clear from Eq. 1 that there is no net energy change to transfer a layer in either direction and this point is illustrated graphically in Fig. 1. Figure 1 also demonstrates that to transfer the layer, the crystal must pass through an intermediate state with a higher energy. The maximum is reached when the area of the partial layer on each facet is the equal (s_1=s_2= L/√2). If we return these numbers to Eq. 1, we see that the barrier to the transfer of a layer from one facet to another is 1.66 $a\sigma L$.

We have previously shown nucleation on a facet can be considered negligible if

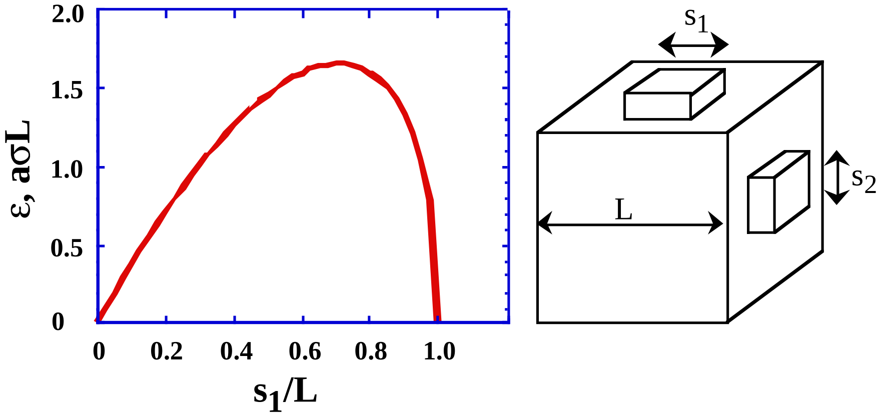

Fig. 1. The NEB for transferring a layer from the top facet of a cube to side (Eq. 1) and a schematic of the process.

the barrier energy is ≥ 40kT [2]. This estimate is based on a classical expression for the steady-state nucleation rate on an infinite singular facet and defines nucleation rates ≤ 10^{-4}nm^{-2}s^{-1}, equivalent to a rate of less than one atomic layer per hour on a facet of 1 nm^2, as negligible [4]. If we take a to be 2.5 Å, σ to be 1 J/m^2, and T= 1000 °C, then the barrier will only be surmounted for particles where $L <$ 1.7 nm. In other words, for defect free particles of sizes greater than about 2 nm, the NEB will prevent fluctuations about the equilibrium shape.

3. NEB for Intraparticle Transport on a Crystal with a Nonequilibrium Shape

We now consider non-equilibrium shapes with volumes $L_1(L_2)^2=L^3$, square facets perpendicular to z (L_2 by L_2), and length along z, L_1, such that $L_1>L$. Here, we consider only the NEB as the crystal evolves toward its equilibrium shape. The barriers are the free energies of the critical state representing the maximum free energy of the lowest free energy path for material transfer. In calculating the NEB for this shape, we note that the removal of a complete layer from the face perpendicular to z 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 will not occur. If it is not prohibitive, neither will the other barriers be prohibitive.

For the long, thin crystal (prolate shape) to evolve toward equilibrium, the facets perpendicular to z must move toward the center. In this case, the critical state of maximum free energy is the unstable equilibrium in which the material removed from the z face leaves a square nucleus (sxs) 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 to form the configuration and hence the NEB is

$$\varepsilon_b(-) = 8a\sigma s - 4a\sigma L_2 = 4(\sqrt{2}-1)a\sigma L_2. \qquad (2)$$

Since Eq. 1 and 2 are identical when $s_1=s_2=s$ and $L_2=L$, we see that $\varepsilon_b(-)/\varepsilon^e_b = L_2/L$. Using the constant volume condition, we obtain

$$\varepsilon_b(-)/\varepsilon^e_b=(L/L_1)^{1/2}; \qquad (3)$$

as L_1/L increases, the barrier slowly decreases. It is interesting to note that even when the crystal is far from equilibrium, the barrier can be significant. For example, consider a crystal for which L = 10 nm. Using the values for the physical parameters cited in section 2, the barrier for a 5 nm x 5 nm x 40 nm crystal to move material from a small face to a large one is about 2 x 10^{-18}J or more than 100 kT at 1000°C. In other words, if the crystal had no step generating defects, it would be kinetically frozen in a stationary configuration far from its equilibrium shape. Elsewhere, we have shown that there are similar barriers for oblate ($L_1<L$) shapes [3]. The influence of the NEB on morphological changes has been observed experimentally. The erratic morphological evolution of cavities in sapphire annealed for up to 16 h at 1900°C [5] and the stationary states of 50 nm zirconia crystals annealed on a hot stage in the TEM for several hours at 850 °C [6] were both explained in terms of the NEB.

4. Effect of the NEB on Coarsening

We now consider the NEB for the addition or subtraction of layers when the cube is able to exchange matter with a reservoir at a fixed chemical potential. This is intended to represent the processes that must occur during the coarsening of faceted particles. As before, the crystal has its equilibrium shape and an edge length of L. We assume that the crystal is situated in a medium in which it is slightly soluble so that it can exchange material with a reservoir of the same substance, at a fixed chemical potential of μ_∞. We can imagine this reservoir to be a large number of identical cubes of the same material where the distance from the center of each cube to any of its six facets is R^* so that $\mu_\infty=2\sigma/R^*$. Now consider the transfer of material from the reservoir to the crystal. To do so, a square nucleus of area s^2 and height a must be placed on the facet. The energy for this transfer is:

$$\varepsilon(s) = 4as\sigma - as^2\,\frac{2\sigma}{R^*}\,, \tag{4}$$

for $0 \le s \le L$. In Eq. 4, the first term on the right hand side is the energy of the perimeter of the nucleus and the second term is the change in the free energy on moving a volume of material (as^2) from the reservoir to the flat surface. Note that if the crystal is in equilibrium with a reservoir of identical particles ($R^*=L/2$), then there should be no energy change when a single layer of atoms is transferred from the reservoir. Equation 4 shows that this is the case when $s=L$ and $R^*=L/2$. However, to add even a single layer, the crystal must past through a relatively higher energy state that contains a partial layer. By differentiation of Eq. 4, we see that the maximum occurs at $s = R^*$ and that the barrier to addition, ε_+, is:

$$\varepsilon_+ = 2a\sigma R^* \tag{5}$$

where R* is between 0 and L. In this case, the NEB is independent of the crystal size and depends only of R^*, which characterizes the size of the particles in the reservoir. If we assume the same physical quantities as before, then the crystals will grow only when R^* is less than a critical value of about 1.4 nm. In other words, only crystals with $L < 3$ nm can provide supersaturation that is high enough to drive nucleation on a flat facet. If we take R^* as a representation of a mean crystal size in a distribution, then as soon as R^* rises above the critical value, the NEB will halt growth.

The energy to remove a layer from the crystal and place it in the reservoir is:

$$\varepsilon(s) = 4as\sigma - 4aL\sigma + (aL^2 - as^2)\frac{2\sigma}{R^*} \tag{6}$$

Where the first two terms on the right hand side represent the energy difference between a complete layer and a partial layer; this is ≤ 0 for all valid values of s. The final term on the right hand side is the energy increase associated with moving a volume of material from the flat surface to the reservoir. The maximum of Eq. 6 is at $s = R^*$ and the barrier to removing a layer, ε_-, is:

$$\varepsilon_- = 2a\sigma\left[R^* + L\left(\frac{L}{R^*} - 2\right)\right] \tag{7}$$

where R* is between L/2 and L. Note that for a crystal in contact with a reservoir of identical particles ($R^* = L/2$), $\varepsilon_+ = \varepsilon_- = 2a\sigma R^*$, as we would expect for the equilibrium case. The barrier to remove a layer is smaller if the reservoir is made up of crystals that are somewhat larger ($L/2 < R^* <$ L) and vanishes completely if the particles in the reservoir are twice as large as the crystal ($R^* \geq L$).

According to these results, illustrated in Fig. 2, the coarsening of defect free faceted crystals will be limited by the NEB; when the mean field chemical potential (μ_∞) decreases to the point where corresponding values of R^* are beyond a few nm, growth will stop. The results are in sharp contrast to conventional coarsening theory, in which atoms are driven to or away from surfaces by chemical potential gradients where they attach or detach without a nucleation barrier [7,8]. In real populations of crystals, some will contain defects that produced steps and these crystals will continue to grow after the perfect crystals become immobilized. We believe that this might explain abnormal coarsening in systems of faceted crystals.

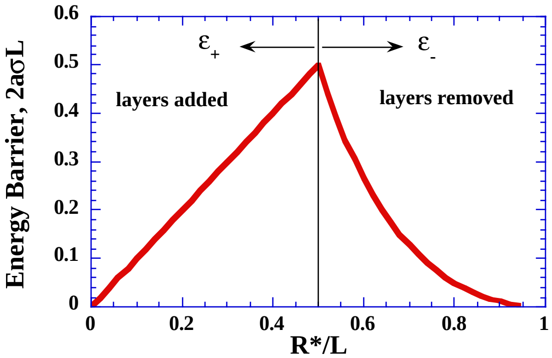

Fig.2. The barriers for addition of layers to the crystal (from a reservoir containing smaller crystals) and removal of layers (from a reservoir containing larger crystals).

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