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William A. Tiller
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Introduction

1.1 Coupling equations

Crystallization is a many-variable, many-parameter interaction event in Nature and in technology and scientific understanding of this area feeds the very large application field illustrated in Fig. 1.1. For the territory lying within the scientific understanding box, it is necessary to treat the crystallization event as a dynamic system with many interacting parts or subsystems. These are illustrated in Fig. 1.2 for a typical case. The unique morphology and special phenomena associated with the crystallization event arise out of the conjunction of these subsystems interacting with each other in pairs, triplets, etc.

It is in the far-field domain of a growing crystal where the macroscopic or global thermodynamic state variables, $(C, T, P, \phi) \equiv (C_\infty, T_\infty, P_\infty, \phi_\infty)$ are fixed or changed dynamically according to some particular program $(\dot{C}_\infty, \dot{T}_\infty, \dot{P}_\infty, \dot{\phi}_\infty)$. However, it is mainly at the interface of the growing crystal that all the morphological, chemical segregation and embryonic physical defect phenomena arise in the crystallization event. Thus, scientific understanding of the overall process requires a description in terms of the thermodynamic state variables and their gradients at the growing interface; i.e., (C_i, T_i, P_i, ϕ_i) and $(\nabla_i C, \nabla_i T, \nabla_i P, \nabla_i \phi)$. The connection between the interface conditions and the far-field conditions occurs via a set of partial differential equations and their boundary value constraints. In the most general case, these are:

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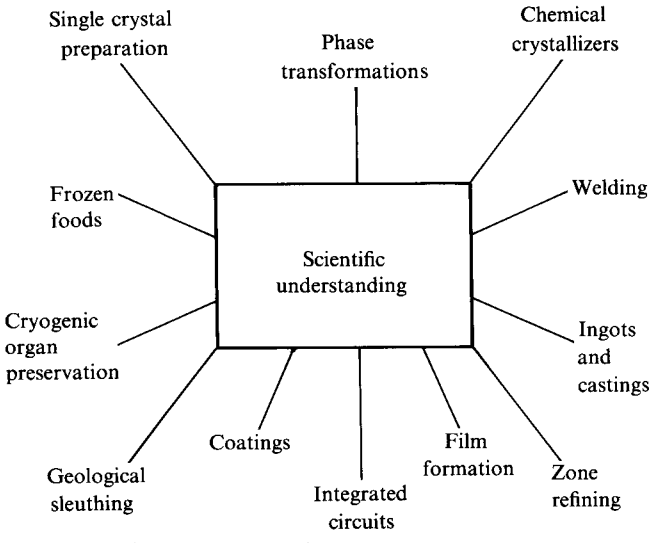

Fig. 1.1. A wide variety of application areas nourished by scientific understanding of crystallization.

(1) the transport of heat equation,
(2) the hydrodynamic flow equations,
(3) the transport of matter equation,
(4) the electrical potential equation,
(5) the stress and strain equations and
(6) the perturbation response of the interface equations.

The overall thermodynamic potential, ΔG_∞, driving a crystallization event is consumed, in part, in setting up these various fields, ΔG_{sv}, (since they all store energy) and, in part, at the interface itself, ΔG_i, where the latter energy is consumed in driving both the interface reaction leading to a change of state, ΔG_K, and the energy storage reactions in (i) new surface creation, ΔG_γ, (ii) strain field generation, ΔG_σ, (iii) physical defect formation, ΔG_d, (iv) metastable phase formation, ΔG_p, and non-equilibrium point defect formation, ΔG_{PD}. The free energy conservation equation for this process is

$$\Delta G_\infty = \Delta G_{sv} + \Delta G_i \tag{1.1a}$$

$$= \Delta G_{sv} + \Delta G_K + \Delta G_E \tag{1.1b}$$

$$= \Delta G_{sv} + \Delta G_K + \Delta G_\gamma + \Delta G_\sigma + \Delta G_d + \Delta G_p + \Delta G_{PD} \tag{1.1c}$$

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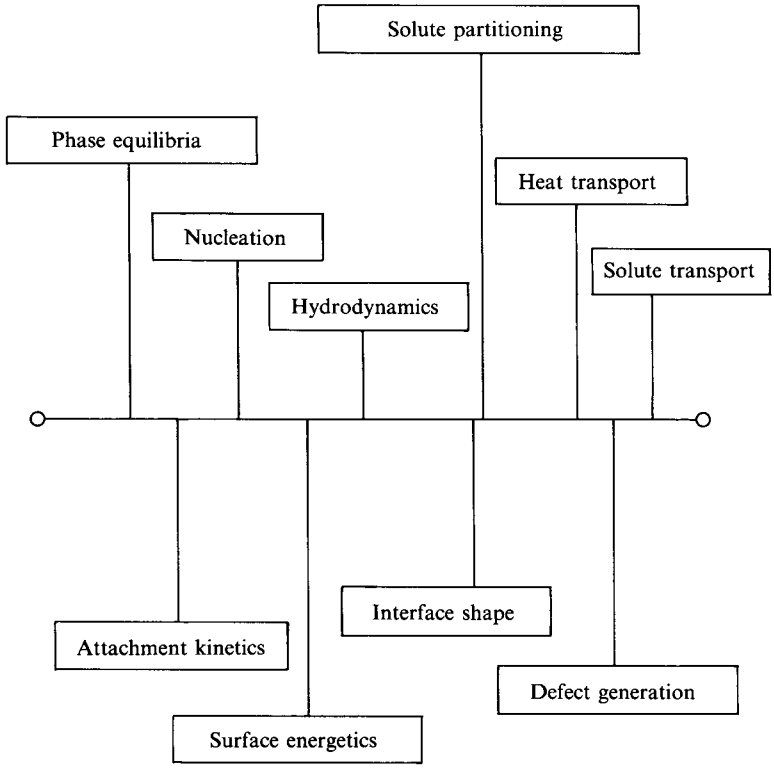

Fig. 1.2. System of interacting scientific considerations involved in a typical crystallization event.

In many crystal growth situations, it is not necessary to use the ΔG-coupling equation and, for simplicity, surrogate driving force equations may be used; i.e.,

$$\Delta T_\infty = \Delta T_C + \Delta T_T + \Delta T_E + \Delta T_K \tag{1.2a}$$

or

$$\Delta C_\infty = \Delta C_C + \Delta C_T + \Delta C_E + \Delta C_K \tag{1.2b}$$

or

$$\Delta P_\infty = \Delta P_C + \Delta P_T + \Delta P_E + \Delta P_K \tag{1.2c}$$

where the subscripts C and T refer to matter (concentration) and heat (temperature), respectively. The partitioning associated with Eqs. (1.2*a*) and (1.2*b*) is illustrated using the phase diagrams of Fig. 1.3 for the two different modes of phase change:

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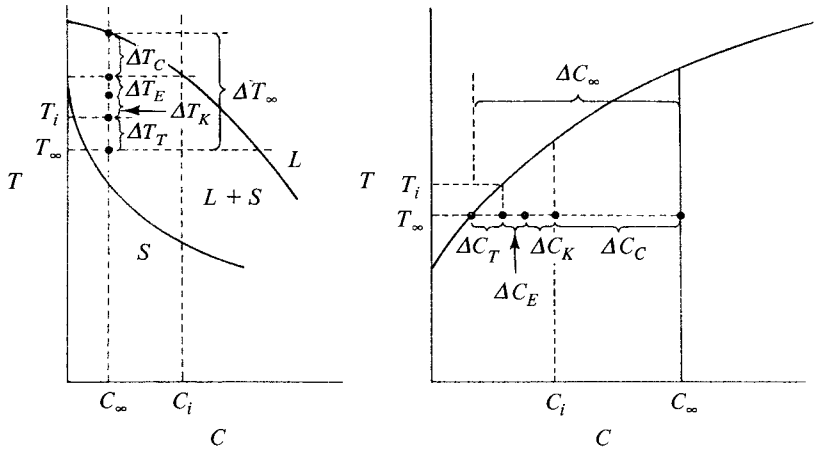

Fig. 1.3. Typical phase diagram illustrations of the coupling equations for ΔT and ΔC.

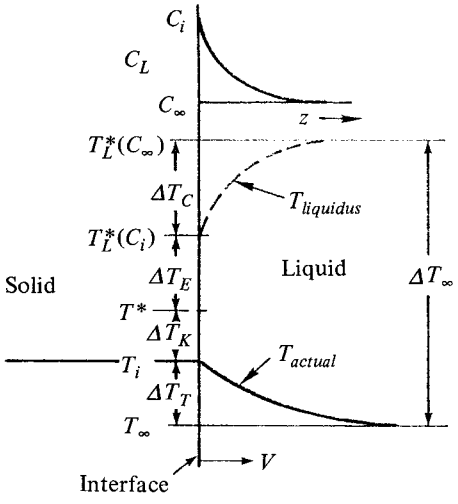

Fig. 1.4. Solute and temperature distributions plus key temperatures for unconstrained crystallization.

(1) *unconstrained crystallization*, where the surrogate far-field driving force in the nutrient phase, ΔT_∞, is greater than the interface surrogate driving force, ΔT_i, (see Fig. 1.4) and

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(2) *constrained crystallization*, where the surrogate far-field driving force in the nutrient phase, ΔT_∞, is less than the interface surrogate driving force, ΔT_i.

Although in the past, the tendency has often been to consider only one of these driving forces to be dominant and to neglect the rest, it can be readily shown that all of the primary quantities enter every crystallization event and each may dominate the growth process at different times. This is perhaps best illustrated by considering the unconstrained growth of a crystal in its nutrient from the onset of nucleation to the fully grown state. For this case, the velocity of crystallization, V, is as given in Fig. 1.5(a). At time $t = 0$, all of the driving force goes into forming the surface needed to comprise the nucleation event so that $V = 0$ and $\Delta G_\infty = \Delta G_E$ at $t = 0$. At long times, all of the driving force is consumed in the transport of matter and heat and in the storage of excess energy (for solid state transformation) so that $\Delta G_\infty = \Delta G_C + \Delta G_T + \Delta G_E$. At early to intermediate times, all processes simultaneously consume free energy. The variation of subprocess free energy with crystal size, R, is shown in Fig. 1.5(b) for the case of a crystal growing from a pure melt ($\Delta G_\sigma = \Delta G_d = \Delta G_p = \Delta G_{PD} = 0$). A number of specific subprocess dominance examples have been treated in Chapter 1 of the companion book.[1]

1.2 Interface attachment kinetics

For any system, the ΔG_j contribution of ΔG_E and the ΔG_K contribution are intimately coupled. For almost all cases of our experience, we are dealing with a terrace/ledge/kink (TLK) model of the interface on an atomistic level so that the free energy of the interface per unit area, γ, can be given in terms of the face (terrace) energy, γ_f, and the ledge energy, γ_ℓ, plus the density of each. Structural roughening of the ledges to generate kinks increases the enthalpy of the ledges but it increases the configurational entropy of the ledges even more so that γ_ℓ decreases as ledge roughening increases up to some optimum level which depends upon the enthalpy per bond between the crystal and the nutrient phase. These values of γ_f and γ_ℓ are generally also strongly decreased by atomic bond reconstruction on the terrace and ledge so that a marked interaction between these atomic displacement changes on the terrace, as well as kink formation changes on both the ledge and terrace, occurs.[1] Using the oversimplified nearest-neighbor-only dangling bond model, Fig. 1.6 gives a plot of the computed equilibrium

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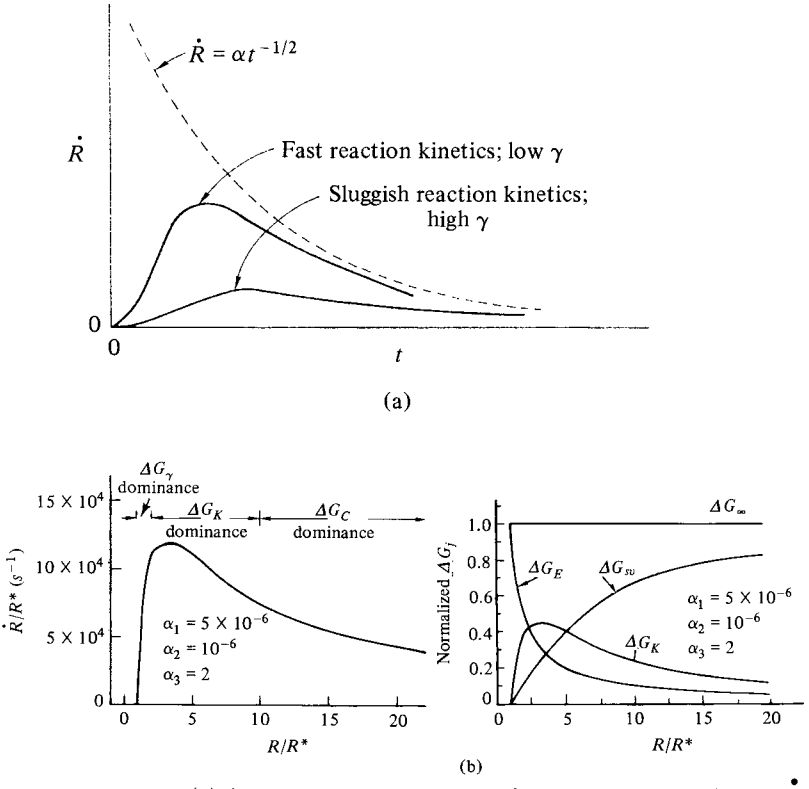

Fig. 1.5. (a) Schematic representation of particle growth velocity, $\dot{R}$, versus time, t, illustrating the effect of interface reaction kinetics plus the asymptotic approach to the transport dominance regime, and (b) relative spherical crystal velocity, $\dot{R}/R^*$, and the normalized driving force for the various subprocesses as a function of the relative crystal size, R/R^* (R^* = nucleus radius whereas α_1, α_2 and α_3 are a particular set of parameters defined in the mathematical description of the overall growth process[1]).

fraction of roughened states, X^*, on the (100) face of a simple cubic crystal as a function of the important bonding parameter $\varepsilon_1/\kappa T$, where ε_1 is the nearest-neighbor bond energy across the interface. Because of the many approximations involved in such a calculation, the error bars are expected to be quite large and only qualitative significance should be placed on such a plot.[1]

The kinetics of crystallization depends strongly on the density of kinks as well as on the interface driving force. At very small driving

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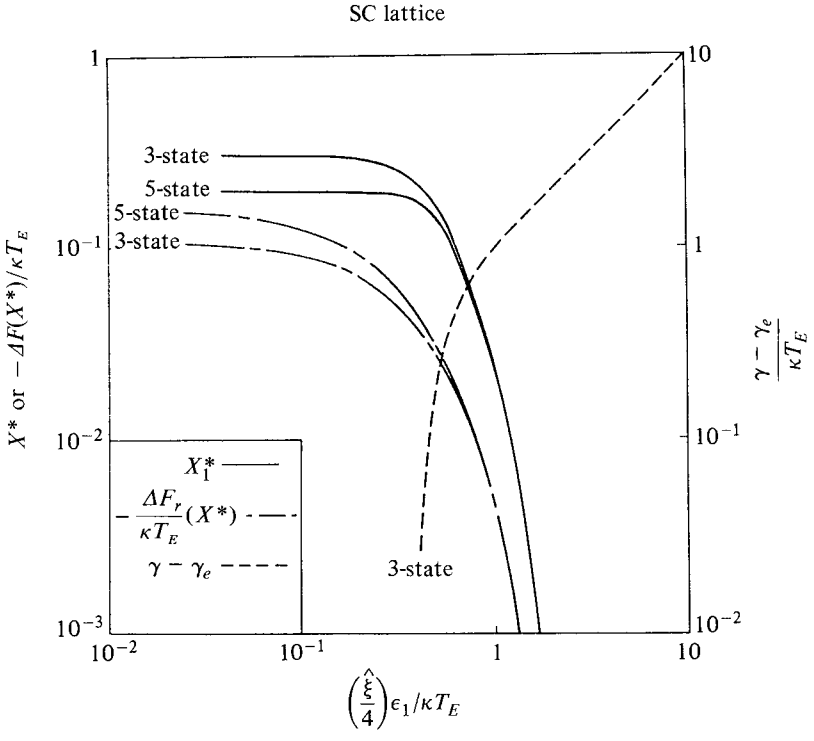

Fig. 1.6. Plot of roughening factors for a simple cubic lattice as a function of the key parameter $\vec{v}_1/\kappa T_E$ ($\hat{\xi}$ is a universal factor): (i) equilibrium population of +1 states for a 3- and 5-state model, (ii) decrease in free energy, $\Delta F(X^*)$, due to roughening for these two models and (iii) the interfacial energy, γ, for the 3-state model.

forces, ($\Delta G_K < (\mathrm{d}\gamma_\ell/\mathrm{d}x)_{max}$) phase change can only occur at kink sites on the ledges so the interface moves forward by the movement of kinks on ledges and the lateral passage of ledges over the surface. At intermediate driving forces ($(\mathrm{d}\gamma_\ell/\mathrm{d}x)_{max} < \Delta G_K < (\mathrm{d}\gamma_f/\mathrm{d}z)_{max}$), the ledges become more diffuse (higher kink density over more levels) because kinks can now form spontaneously on the ledge. At very large driving forces ($\Delta G_K > (\mathrm{d}\gamma_f/\mathrm{d}z)_{max}$), kinks can also form spontaneously on the terrace so that phase change can occur anywhere on the interface. Qualitatively, the smaller is $\varepsilon_1/\kappa T$, the greater is the kink density, the smaller are γ_ℓ and γ_f, the smaller is the anisotropy in γ_ℓ or γ_f and the greater is the crystallization rate for a given value of ΔG_K.

For those cases where a continuous supply of ledges occurs easily, the

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velocity of crystallization is proportional to both the density, ρ_ℓ, and height, h_ℓ, of these ledges on the interface and the rate of movement of these ledges; i.e.,

$$V = h_\ell \rho_\ell V_\ell = \beta_K \Delta G_K \tag{1.3a}$$

where

$$\beta_K = 2h_\ell a \beta_0 / \lambda_\ell \lambda_k \tag{1.3b}$$

and

$$\lambda_k = a'/X'^* \tag{1.3c}$$

at small driving forces. Here, a and a' represent atomic spacings while λ_ℓ and λ_k are the distances between ledges and between kinks, respectively. This formula applies in the domain where $\Delta G_K/\mathcal{R}T \ll 1$. When $\Delta G_K/\mathcal{R}T \tilde{>} 1$, we must use

$$V = \left(\frac{2h_\ell a a' B}{\lambda_\ell \lambda_k}\right) \exp\left(\frac{-\Delta G_A}{\mathcal{R}T}\right) \left[1 - \exp\left(\frac{-\Delta G_K}{\mathcal{R}T}\right)\right] \tag{1.3d}$$

From Eq. (1.3*d*), one can readily see how the kink density (λ_k^{-1}) enters the expression for V.

For the case where the velocity of crystallization is limited by the supply of ledges, via either two-dimensional nucleation or screw-dislocations, we find that

(a) two-dimensional nucleation:

$$V = V_0 \exp[-(\pi a'' \gamma_\ell^2 / \mathcal{R}T \Delta G_i)] \tag{1.4a}$$

where

$$V_0 = a'' A I_0 \tag{1.4b}$$

(b) screw dislocations:

$$V = \beta'_K |\Delta G_K| \Delta G_K \tag{1.4c}$$

where

$$\beta'_K = h_\ell a \beta_0 / 2\pi \gamma_\ell \lambda_k \tag{1.4d}$$

this formula applies only for the $\Delta G_K/\mathcal{R}T \ll 1$ domain. For the general case where both two-dimensional nucleation of layers and the lateral spreading of layers are equally important to the interface attachment kinetics, we find that[(1)]

$$V = \alpha_1 \exp[-\alpha_2/\kappa T][1 - \exp(-\overline{\Delta G}_K/\mathcal{R}T)]^{2/3} \tag{1.5a}$$

where

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$$\alpha_1 = \pi^{1/3} a'' I_0^{1/3} (2aa' B/\lambda_k)^{2/3} \exp(-2\Delta G_A/3\mathcal{R}T) \qquad (1.5b)$$

$$\alpha_2 = \pi a'' \gamma_\ell^2 / 3\overline{\Delta G}_i \qquad (1.5c)$$

The topography of such a surface is determined by the relative rates of the two processes defined by α_1 and α_2. When the nucleation rate is low (α_2 small) and the lateral spreading rate is high (α_1 large), the surface remains flat. When the nucleation rate is small to intermediate and the lateral spreading rate is very slow, the surface develops large undulations even though ΔG_K is constant. If impurities are also present and solute partitioning occurs at such undulations, ΔG_K varies from the center to the ledge of the undulation so that the undulations can be significantly increased in amplitude.

For the unconstrained growth of a crystal, we recognize that, from a simple dangling bond viewpoint, different ledges will require different driving forces at which uniform ledge attachment occurs ($\Delta G_K^{(hk\ell)} > (\mathrm{d}\gamma_\ell^{(hk\ell)}/\mathrm{d}x)_{max}$) so that the attachment kinetics in a particular crystallographic direction may take sudden "spurts" depending upon the overall magnitude of the local ΔG_K. From a more realistic viewpoint, where surface and ledge reconstruction are factored into the process, the kink density is not expected to follow such a simple relationship and some ledges with high γ_ℓ may roughen more readily than ledges with lower γ_ℓ because the former beneficially allow terrace reconstruction to proceed while the latter do not.[1] Finally, one will also find that, if the crystal is extrinsically conducting at the growth temperature, the population of charged kinks is greatly increased just as are the population of charged point defects in the volume of a crystal and the population of charged jogs on dislocation lines in the crystal. Such an extrinsic conduction factor could be partially or completely offset by impurity adsorption to poison kink sites. At this point in time, few specific experimental data are available to quantify either the surface and ledge reconstruction factor or the extrinsic conduction factor with respect to kink formation in specific crystal systems or specific orientations in these systems. This is territory for new research and is most likely to be extremely important in the area of thin film formation (where $\varepsilon_1/\kappa T$ is large, generally).

Returning to the overly simplistic viewpoint before ending this section, we note the baseline fact that kink formation is easiest when γ_ℓ is small so that rapid attachment kinetics should correspond with low surface energetics. This often makes it extremely difficult to decide upon the key factors determining a crystal's morphology.

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1.3 Surface energetics

For a static surface, it is well known that γ is a function of the crystallographic angles (θ, ϕ) of the surface normal relative to the closest packed crystallographic plane in the crystal. It is also well known that a particular surface (θ_1, ϕ_1) is thermodynamically predicted to decompose into two or more lower energy surfaces at (θ_2, ϕ_2) and (θ_3, ϕ_3), etc., when the γ-plot energetics are such that

$$\left\{\gamma + \left[\left(\frac{\partial^2\gamma}{\partial\theta^2}\right) + \left(\frac{\partial^2\gamma}{\partial\phi^2}\right)\right]\right\}_{\theta_1,\phi_1} < 0 \tag{1.6}$$

What is not so well appreciated is that, because of surface reconstruction effects, $\gamma(\theta, \phi)$ is also a function of ledge height (or terrace length) even for a static surface so we should begin to think in terms of $\gamma(\theta, \phi, h_\ell)$. Further, since terrace reconstruction is a thermally activated process and ledge movement requires terrace unreconstruction at the bottom of the ledge as well as terrace reconstruction at the top of the ledge, it is important to recognize that

$$\gamma \equiv \gamma(\theta, \phi, h_\ell, V_\ell) \tag{1.7a}$$

so that faceting and crystal form development also depend upon h_ℓ and V_ℓ. This also applies to layer formation via two-dimensional nucleation or screw dislocations. Finally, since the kink population on ledges in the intermediate driving force range will also depend upon ΔG_K and since γ_ℓ is a function of the ledge kink population, we extend Eq. (1.7*a*) to become

$$\gamma \equiv \gamma(\theta, \phi, h_\ell, V_\ell, \Delta G_K) \tag{1.7b}$$

Certainly facet formation and crystal form development will follow Eq. (1.6) utilizing Eq. (1.7*b*) as the proper basis for describing γ. However, this approach uses equilibrium thermodynamic reasoning for shape change but a dynamic description of γ for implementation. Since we are concerned here with dynamic faceting and surface morphology adjustments during crystal growth, it would be preferable to be more inclusive in our thermodynamic reasoning and include the departure from equilibrium at the growing crystal faces as part of an "effective" surface energy, γ_{eff}, i.e.,

$$\gamma_{eff} = \gamma(\theta, \phi, h_\ell, V_\ell, \Delta G_K) + \Delta G_K(\theta, \phi, h_\ell, V_\ell, \Delta G_K) \tag{1.8a}$$

Now, the criterion for dynamic facet formation and morphology adjustments during crystal growth becomes, from Eq. (1.6),

$$\gamma_{eff} + \left[\frac{\partial^2\gamma_{eff}}{\partial\theta^2} + \frac{\partial^2\gamma_{eff}}{\partial\phi^2}\right] < 0 \tag{1.8b}$$

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