Equilibrium Shapes for Crystalline Solids

J. A. Dantzig

Abstract

The determination of the shape of a solid crystal in equilibrium with its melt was first described by Wulff using a geometric construct. Mathematical descriptions were later developed. In this note, some of the various methods used to compute the Wulff shape are described. Particular attention is paid to the determination of forbidden orientations for crystals with large anisotropy, and the calculation of their Wulff shapes.

1 Wulff’s construction

Wulff proposed without proof that the equilibrium shape of a crystal suspended in its melt could be obtained using the following geometric construction. Begin with a polar plot of the surface energy $\gamma_{sl}(n)$, where $n$ is a unit vector in a direction defined in the crystal coordinate system.

$$ r = n \gamma_{sl}(n) $$

(1)

The Wulff shape is constructed by placing a plane perpendicular to $n$ at each point on the surface defined by $r$. The locus of all of the interior points of these tangent planes is the Wulff shape. It should be obvious that if $\gamma_{sl}$ is isotropic, then the Wulff shape is a sphere, coinciding with the polar plot.

Let us illustrate this with two examples in 2-D, for a crystal having four-fold symmetry. Suppose that the anisotropic surface energy $\gamma_{sl}$ is given by

$$ \gamma_{sl}(\theta) = \gamma_{sl}^0 [1 + \varepsilon_4 \cos(4\phi)] $$

(2)

where $\varepsilon_4$ is a measure of the strength of the four-fold anisotropy. Fig. 1 illustrates the Wulff construction for $\varepsilon_4 = 0.05$ and $0.12$.

Consider first the case $\varepsilon_4 = 0.05$, presented in Fig. 1(a). The polar plot of $\gamma_{sl}$, normalized by $\gamma_{sl}^0$, is plotted in red. In the upper half plane, the perpendicular planes (actually, lines in 2-D) are shown as dashed black lines for several points on the gamma plot in the upper half-plane. The Wulff shape is then shown in blue. Because the anisotropy for this case is just 5%, the deviation of the Wulff shape from the gamma plot is fairly small.

Fig. 1(b) shows the more interesting case $\varepsilon_4 = 0.12$. The larger value of anisotropy leads to much larger deviation of the Wulff shape from the gamma plot. One can also see at the intersection of the Wulff shape with the coordinate axes, the construct produces a shape where a radial line intersects the Wulff shape at multiple points. The triangular-shaped regions outside of the inner convex hull, sometimes called “ears,” correspond to orientations that cannot be part of the equilibrium shape, sometimes called “forbidden orientations.”
One could simply snip off the ears and be left with the proper Wulff shape, but this is more difficult to do in 3-D, and does not tell us which orientations are forbidden. A construct that performs the required task is illustrated in Fig. 2, which is a close-up view of the upper right quadrant of Fig. 1(b) where \( \varepsilon_4 = 0.12 \). Most of the tangent planes have been omitted, leaving only those that correspond to the ear straddling the horizontal axis. The orientations that produce these forbidden orientations are highlighted in gray. It is important to understand that these orientations do not correspond simply to the directions where the tangent planes form the ear.

Figure 2 further illustrates a method to determine the forbidden orientations. We show in indigo the inverse-gamma plot, i.e., a polar graph of \( \gamma_{st}/\gamma_{st}^0 \). Forbidden orientations correspond to the non-convex regions of the inverse-gamma plot. We can identify those regions by computing the convex hull of the inverse-gamma plot (imagine placing a shrink-wrap coating over it). The orientations that are omitted from this convex hull are the forbidden orientations.

This procedure can be extended readily into 3-D. The construction of the sequence of perpendicular planes is a somewhat cumbersome, however. The next section develops a mathematical representation that facilitates this process. We then return to the procedure for identifying and removing the forbidden orientations, in 3-D.

1.1 The capillary vector \( \xi \)

The Wulff construction was based on a vector field, derived from the polar plot and local tangent planes. Gibbs first introduced such a field [1], which was later extended by Cahn and Hoffman. [2, 3] The capillary vector \( \xi \) is defined as

\[
\xi = \nabla (r \gamma_{st}(n))
\]
We will now go through a short derivation to show that $\xi$ has the exact properties required for the Wulff construction.

Following Hoffman and Cahn, we first invoke the vector identity

$$d(r\gamma_{st}) = \nabla(r\gamma_{st}(n)) \cdot dr$$
$$= \xi \cdot (rdn + ndr) \quad (4)$$

We also have, from simple expansion, that

$$d(r\gamma_{st}) = rd\gamma_{st} + \gamma_{st}dr \quad (5)$$

Comparing terms in Eqs. (4) and (5), we see that

$$\xi \cdot n = \gamma_{st} \quad (6)$$
$$\xi \cdot dn = d\gamma_{st} \quad (7)$$

The total derivative of Eq. (6) is given by

$$d\xi \cdot n + \xi \cdot dn = d\gamma_{st} \quad (8)$$

Subtracting Eq. (8) from Eq. (7) gives

$$n \cdot d\xi = 0 \quad (9)$$

Eq. (9) shows that $d\xi$ is perpendicular to the orientation vector $n$. In spherical coordinates, with $\theta$ defined as the polar angle and $\phi$ the azimuthal angle, we have

$$\xi = \gamma_{st}\hat{r} + \frac{\partial\gamma_{st}}{\partial \theta} \hat{\theta} + \frac{1}{\sin \theta} \frac{\partial\gamma_{st}}{\partial \phi} \hat{\phi} \quad (10)$$
The properties of $\xi$ evident in Eq. (10) are exactly those needed for the Wulff construction. For any given orientation $n$, aligned with the radial direction $r$, the radial component $\xi \cdot r = \gamma_{s\ell}$, and the remaining two terms define a vector in the tangent plane. Therefore, constructing a surface in space by plotting $\xi$ in Eq. (10) will produce a shape that is homothetic (geometrically similar, monotonically scaled) to the Wulff shape.

Now that we have a method to compute the equilibrium shape, we can extend the procedure developed in the preceding section to identify the forbidden orientations and remove the multi-valued portions of the putative Wulff surface. The steps in the algorithm are best understood in the context of an example. The expression used for 4-fold symmetry in 2-D, Eq. (2), can be used directly in 3-D by writing

$$\gamma_{w\ell} n = 1 - 3\varepsilon_4 + 4\varepsilon_4 Q_4$$

where $Q_4 = n_x^4 + n_y^4 + n_z^4$. We first illustrate the procedure for constructing the Wulff shape using the expression in Eq. (11), with the aid of Fig. 3.

- Construct the gamma plot for all orientations (Fig. 3(a)).
- Compute the putative equilibrium shape, shown in Fig. 3(b). This shape was calculated using the $\xi$-vector construction, described in the following section. Notice the ears and ridges, corresponding to the forbidden orientations.
- Compute the inverse-gamma plot and its convex hull (Fig. 3(c) and (d)). The orientations that remain, i.e., are not forbidden, are shown in the gamma plot, Fig. 3(e).
- Restrict the orientations for the equilibrium shape to those that remain in the convex hull of the inverse-gamma plot. The result is shown in Fig. 3(f).

A more complete expression for cubic symmetry involves an expansion in the cubic harmonics $Q_4$ and $S_4 = n_x^2 n_y^2 + n_y^2 n_z^2$. If one includes the first two terms in this expansion, we have

$$\gamma_{s\ell} = \gamma_{s\ell}^0 [1 + a_1 (Q_4 - 3/5) + a_2 (3Q_4 + 66S_4 - 17/7)]$$

One can show that Eq. (12) reduces to Eq. (2) in 2-D for $a_1 = 25\varepsilon_4/22$ and $a_2 = 21\varepsilon_4/22$. We therefore choose $a_1 = 0.136$, $a_2 = 0.115$ to be consistent with the 2-D example where $\varepsilon_4 = 0.12$. The result of the procedure given above for construction of the Wulff shape, this time using the expression for anisotropy given in Eq. (12), is shown in Fig. 4. One can see clearly that the Wulff shapes obtained using the different expressions for the anisotropy are quite different, even though their 2-D representations are identical.

An experimental method that is commonly used to determine the anisotropy parameters is to hold a sample with small embedded droplets just above the solidus for a period of time deemed long enough to produce an equilibrium shape. Then, by taking sections through the sample after quenching, the anisotropy parameters can be deduced. Notice that if one were to look at the equilibrium shape only in the (001) plane, both of the anisotropy representations presented in Figs. 3(f) and 4(f) would produce exactly the same shape. This emphasizes the importance of extending the experimental techniques to construct the entire droplet, e.g., by serial sectioning or x-ray tomography.
Figure 3: Stages in construction of the Wulff shape for cubic symmetry as written in Eq. (11), with $\varepsilon_4 = 0.12$. (a) Gamma plot. (b) Putative Wulff shape, computed using the capillary vector $\xi$. (c) Inverse-gamma plot. Notice the non-convex regions. (d) Convex hull of the inverse-gamma plot. (e) Gamma plot restricted to the orientations remaining in the convex hull of the inverse-gamma plot. (f) Equilibrium shape, obtained by restricting $\xi$ to the reduced set of remaining orientations.
Figure 4: Stages in construction of the Wulff shape when there are forbidden orientations, in this case for cubic symmetry with $a_1 = 0.136$, $a_2 = 0.115$. (a) Gamma plot. (b) Putative Wulff shape, computed using the capillary vector $\xi$. (c) Inverse-gamma plot. Notice the non-convex regions. (d) Convex hull of the inverse-gamma plot. (e) Gamma plot restricted to the orientations remaining in the convex hull of the inverse-gamma plot. (f) Equilibrium shape, obtained by restricting $\xi$ plot to the reduced set of remaining orientations.
This procedure is effective, and relatively easily implemented in a program such as MATLAB\textsuperscript{TM}. One important piece of information that is missing, however, is the size of the solid crystal. To determine the shape precisely, we must consider the thermodynamic equilibrium of a solid particle in an undercooled melt. This is the subject of the following section.

2 Equilibrium of a solid particle in an undercooled melt

2.1 Primary results

In the preceding sections, we accepted without proof that the Wulff construction represents the equilibrium shape of a crystal. In this section, we combine the capillary vector with equilibrium thermodynamics to demonstrate that this is indeed the case. We will go further, to determine the size of the crystal, as well. We begin by stating the key results, and then present their derivation.

Consider an undercooled melt, containing a single crystalline solid, at a temperature $T < T_f$, where $T_f$ is the equilibrium freezing temperature. Our domain consists of solid and liquid volumes, $V_s$ and $V_\ell$, respectively. Introducing expressions for the molar free energies $G_{\alpha}^m$ of the two phases, we have

\begin{align*}
G_{\ell}^m(T_f) &= H_{\ell}^m(T_f) - T_f S_{\ell}^m(T_f) \\
G_s^m(T_f) &= H_s^m(T_f) - T_f S_s^m(T_f)
\end{align*}

where $H_{\alpha}^m$ is the molar enthalpy, and $S_{\alpha}^m$ is the molar entropy of phase $\alpha$. At equilibrium, by definition, $G_{\ell}^m(T_f) = G_s^m(T_f)$, so by subtracting Eq. (14) from Eq. (13), we obtain

$$
\Delta S_m^f = \frac{L_m^f}{T_f}
$$

where $L_m^f$ is the molar enthalpy of fusion, usually called the latent heat of fusion, and $\Delta S_m^f$ is the molar entropy of fusion. For small undercooling below $T_f$, the values of $L_m^f$ and $\Delta S_m^f$ can be considered constant, and the molar free energy difference between the two phases then becomes

$$
G_{\ell}^m(T) - G_s^m(T) = \Delta G^m(T) = -\Delta S_m^f \Delta T
$$

where $\Delta T = T_f - T$ is the undercooling.

We will show in the next section that the equilibrium surface satisfies the following equation

$$
\nabla_s \cdot \xi = \frac{\Delta S_m^f \Delta T}{V_s^m}
$$

where $\nabla_s$ is the surface divergence, defined in the next section on differential geometry, Eq. (31). We will also show that the solution to Eq. (17) defines the equilibrium shape of the solid in equilibrium with the liquid at temperature $T < T_f$ is given by the surface $r$

$$
r = \frac{2V_s^m}{\Delta S_m^f \Delta T} \xi
$$

This result extends the results presented earlier, in that in addition to showing that the surface described by the capillary vector $\xi$ is homothetic to the equilibrium shape, it also gives
the size of the crystal. To demonstrate this simply, consider the case where the surface energy is isotropic, e.g., for an amorphous solid. We then have \( \xi = \gamma_{sl} \hat{n} \), and Eq. (18) describes a sphere of radius \( R \), given by

\[
R = \frac{2V_s^m \gamma_{sl}}{\Delta S_f^m \Delta T}
\]  

(19)

Rearranging terms to solve for \( T \) yields the Gibbs-Thomson equation:

\[
T = T_f - \frac{2V_s^m \gamma_{sl}}{\Delta S_f^m} \frac{1}{R} = T_f - \frac{2\Gamma_{sl}}{R}
\]

(20)

where we have defined the Gibbs-Thomson coefficient \( \Gamma_{sl} = \frac{2V_s^m \gamma_{sl}}{\Delta S_f^m} \).

Whereas Eq. (18) defines the equilibrium shape, we can also develop a form that applies locally, at any given point on the crystal surface. We first represent the surface in Cartesian form

\[
x = u; \quad y = v; \quad z = w(u,v)
\]

(21)

At any given point on the surface, we orient the coordinate system such that the \( z \)-axis lies along the normal vector, and introduce the notation

\[
\theta_1 = \frac{\partial z}{\partial x}; \quad \theta_2 = \frac{\partial z}{\partial y}
\]

(22)

The local form of the equilibrium equation becomes

\[
\frac{\Delta S_f^m \Delta T}{V_s^m} = -\left( \gamma_{sl} + \frac{\partial^2 \gamma_{sl}}{\partial \theta_1^2} \right) \frac{\partial^2 z}{\partial x^2} - 2 \frac{\partial^2 \gamma_{sl}}{\partial \theta_1 \partial \theta_2} - \left( \gamma_{sl} + \frac{\partial^2 \gamma_{sl}}{\partial \theta_2^2} \right) \frac{\partial^2 z}{\partial y^2}
\]

(23)

Eq. (23) takes on a more familiar form if the \( x \) and \( y \) axes are oriented along the principal directions. In that case, the middle term on the right hand side is zero, and we have \( \partial^2 z/\partial x^2 = 1/R_1 \) and \( \partial^2 z/\partial y^2 = 1/R_2 \), where \( R_1 \) and \( R_2 \) are the principal radii of curvature. We then have Herring’s formula for the relationship between the undercooling and local curvatures at any point on the surface

\[
\frac{\Delta S_f^m \Delta T}{V_s^m} = -\left( \gamma_{sl} + \frac{\partial^2 \gamma_{sl}}{\partial \theta_1^2} \right) \frac{1}{R_1} - \left( \gamma_{sl} + \frac{\partial^2 \gamma_{sl}}{\partial \theta_2^2} \right) \frac{1}{R_2}
\]

(24)

We now present derivations for the results just presented. We begin with a brief introduction to differential geometry, the calculus of curved surfaces. Those results are then used to derive the equations presented above.

### 2.2 Differential geometry

A few results from differential geometry are needed to relate the capillary vector to thermodynamics. This section parallels the development by Sekerka, Appendix C. [5] Consider a surface that is parameterized by \( (u,v) \), such that the surface Cartesian coordinates are \( (x(u,v), y(u,v), z(u,v)) \), and we use the shorthand notation \( r = r(u,v) \). Since \( u \) and \( v \) lie in the surface, the following two vectors are independent, although not necessarily orthogonal, tangent vectors:

\[
r_{,u} = \frac{\partial r(u,v)}{\partial u}; \quad r_{,v} = \frac{\partial r(u,v)}{\partial v}
\]

(25)
The surface unit normal vector \( \hat{n} \) may be constructed from \( r_{,u} \) and \( r_{,v} \) via the cross product:

\[
\hat{n} = \frac{r_{,u} \times r_{,v}}{|r_{,u} \times r_{,v}|} = \frac{H}{H}
\]  

(26)

where we have defined \( H = |r_{,u} \times r_{,v}| \). We can now create an orthonormal pair of tangent vectors:

\[
\hat{t}_u = \frac{r_{,v} \times \hat{n}}{H}; \quad \hat{t}_v = \frac{r_{,u} \times \hat{n}}{H}
\]  

(27)

Relations that will prove useful a little later are obtained by taking dot products:

\[
r_{,u} \cdot \hat{t}_u = \frac{r_{,u} \times r_{,v}}{H}
\]  

(28)

Using the formula for vector triple products, \( a \cdot (b \times c) = c \cdot (a \times b) \), Eq. (28) becomes

\[
r_{,u} \cdot \hat{t}_u = \hat{n} \cdot \frac{r_{,u} \times r_{,v}}{H} = \hat{n} \cdot \hat{n} = 1
\]  

(29)

Similarly, we have

\[
r_{,v} \cdot \hat{t}_v = 1.
\]

The orthonormal triad \((\hat{t}_u, \hat{t}_v, \hat{n})\) can now be used to define the surface gradient and divergence operations. The surface gradient \( \nabla_s \) is defined as

\[
\nabla_s = \hat{t}_u \frac{\partial}{\partial u} + \hat{t}_v \frac{\partial}{\partial v}
\]  

(30)

Consider a general vector \( b = b_u r_{,u} + b_v r_{,v} + b_n \hat{n} \). The surface divergence of \( b \) is constructed in the usual way,

\[
\nabla_s \cdot b = \nabla_s \cdot (b_u r_{,u} + b_v r_{,v} + b_n \hat{n})
\]  

(31)

Note that since \( \hat{t}_u \cdot \hat{n} = 0 = \hat{t}_v \cdot \hat{n} \), there is no contribution from the derivatives of \( V_n \) to Eq. (31). The latter term is understood by noting that \( \nabla_s \cdot \hat{n} = 2\bar{\kappa} \), where \( \bar{\kappa} \) is the mean curvature of the surface. When the vector \( V \) represents the surface itself, \( r(u, v) \), then the surface divergence becomes

\[
\nabla_s \cdot r = \left[ \hat{t}_u \frac{\partial}{\partial u} + \hat{t}_v \frac{\partial}{\partial v} \right] \cdot r = \hat{t}_u \cdot r_{,u} + \hat{t}_v \cdot r_{,v}
\]

\[
\nabla_s \cdot r = 2
\]  

(32)

Below, we will consider below normal perturbations to the surface \( r_0(u, v) \) of the form

\[
\delta r = r - r_0 = \hat{n}_0 \eta(u, v)
\]  

(33)

where \( \eta(u, v) \) is infinitesimal, and \( \hat{n}_0 \) is the unit normal to the original surface. Expanding \( \delta H \) in terms of this perturbation, and performing some algebra gives

\[
\delta H = 2\bar{\kappa}_0 H_0 \eta - H_0 \nabla_s \eta
\]  

(34)

Finally, we will need the surface divergence theorem. For a vector \( b \) defined on the surface, integrated over an area \( A \), bounded by the curve \( C \) with line element \( d\ell \), we have

\[
\int_A \nabla_s \cdot b \, dA = \oint_C b_t \cdot \hat{\tau} \, d\ell + \int_A 2\bar{\kappa} b_n \, dA
\]  

(35)
where \( \tau = d\ell \times \mathbf{n} \) is the outwardly directed normal vector to \( C \), tangent to the surface. \( b_t = b_u \mathbf{r}_u + b_v \mathbf{r}_v \) is the tangential part of \( b \) and \( b_n \) is the component normal to the surface.

With these results in hand, we turn now to the equilibrium shape of a solid particle in an undercooled melt.

### 2.3 Derivation of the equilibrium shape

The development here closely parallels that of Sekerka, Section 14.5. [5] The total Gibbs free energy of the entire system \( G \) is given by

\[
G = \int_{V_s} V_s^m G_s^m \, dV + \int_{V_{\ell}} V_{\ell} G_{\ell}^m \, dV + \int_A \gamma_{s\ell}(\mathbf{n}) \, dA
\]

(36)

where \( V_s \) and \( V_{\ell} \) are the volumes of the solid and liquid phases, respectively, and \( A \) is the surface of the solid particle.

Using the notation of the preceding section, let us take the surface of the equilibrium shape of the particle to be parameterized by \((u,v)\), and represented by \( r_0(u,v) \). We then consider a perturbation of the equilibrium shape, such that

\[
r = r_0(u,v) + \delta r(u,v) = r_0(u,v) + \mathbf{n}_0(u,v) \eta(u,v)
\]

(37)

where \( \eta(u,v) \) represents an infinitesimal perturbation, with \( \eta(u,v) = 0 \) and \( \nabla_s \eta(u,v) = 0 \) on its boundary, but otherwise arbitrary. Since we have assumed that \( r_0 \) represents the equilibrium state, the variation \( \delta G \) of the total Gibbs free energy should be zero.

\[
\delta G = 0 = \delta \left( \int_{V_s} V_s^m G_s^m \, dV + \int_{V_{\ell}} V_{\ell} G_{\ell}^m \, dV + \int_A \xi \cdot \mathbf{n} \, dA \right)
\]

(38)

where we have replaced \( \gamma_{s\ell} \) by \( \xi \cdot \mathbf{n} \), using Eq. (6). Since \( G \) is unchanged in the bulk phases by the variation \( \delta r \) given in Eq. (37), the volume integrals reduce to integrals over the area. We take \( \mathbf{n} \) to be positive pointing out of the solid into the fluid, so that Eq. (38) becomes

\[
\delta G = 0 = \int_A \left( \frac{G_s^m}{V_s^m} - \frac{G_{\ell}^m}{V_{\ell}} \right) \eta(u,v) \, dA + \int_A \xi \cdot \mathbf{n} \, dA
\]

(39)

For convenience, we take \( V_s^m = V_{\ell}^m \), and then using Eq. (16), we have \( G_s^m / V_s^m - G_{\ell}^m / V_{\ell} = -\Delta S_m^m \Delta T / V_s^m \).

The last integral in Eq. (39) requires some further examination. We first transform to an integral in parametric space, using the notation of the preceding section on differential geometry

\[
\delta \int_A \xi \cdot \mathbf{n} \, dA = \delta \int_{A_{uv}} \xi \cdot H \, du \, dv
\]

(40)

Note that \( \mathbf{n} = H / H \) from Eq. (26), and the Jacobian of the transformation to parametric space is \( H \), which is why \( H \) does not appear on the right hand side. Since the integral on the right
hand side of Eq. (40) is over a fixed domain, the variation can be taken inside the integral,

$$\delta \int_{A_{uv}} \mathbf{H} \, du \, dv = \int_{A_{uv}} (\delta \mathbf{H} + \mathbf{H} \cdot \delta \mathbf{H}) \, du \, dv$$  \hspace{1cm} (41)$$

Eq. (9) tells us that $\delta \mathbf{H} \cdot \mathbf{H} = 0$. Substituting the expression for $\delta \mathbf{H}$ from Eq. (34), Eq. (41) becomes

$$\delta \int_{A_{uv}} \mathbf{H} \, du \, dv = \int_{A} [2\bar{\kappa} \gamma_s \mathbf{\eta} - \mathbf{\xi} \cdot \nabla_s \mathbf{\eta}] \, dA$$  \hspace{1cm} (42)$$

Putting the last term in more convenient form to use the surface divergence theorem, we have

$$\mathbf{\xi} \cdot \nabla_s \mathbf{\eta} = \nabla_s \cdot (\mathbf{\xi} \mathbf{\eta}) - \mathbf{\eta} \nabla_s \cdot \mathbf{\xi}$$  \hspace{1cm} (43)$$

We now invoke the surface divergence theorem for the vector $\mathbf{\xi} \mathbf{\eta}$, using the relation $\mathbf{\xi} \cdot \mathbf{n} = \gamma_s \ell$, to obtain

$$\int_{A} \nabla_s \cdot (\mathbf{\xi} \mathbf{\eta}) \, dA = \int_{A} 2\bar{\kappa} \gamma_s \mathbf{\eta} \, dA + \oint_{C} \mathbf{\xi} \mathbf{\tau} \mathbf{\eta} \, d\ell$$  \hspace{1cm} (44)$$

Because we chose $\eta(u, v) = 0$ on $C$, the second term on the right hand side is zero. Combining the results from Eqs. (43) and (44) with Eq. (43) gives

$$\delta \int_{A} \mathbf{\xi} \cdot \mathbf{n} \, dA = \int_{A} \eta \nabla_s \cdot \mathbf{\xi} \, dA$$  \hspace{1cm} (45)$$

Substituting this result into Eq. (39) gives

$$\delta G = 0 = \int_{A} \left( -\frac{\Delta S_{m}^{m} \Delta T}{V_{m}^{s}} + \nabla_s \cdot \mathbf{\xi} \right) \eta(u, v) \, dA$$  \hspace{1cm} (46)$$

Since this equation must hold for all possible $\eta(u, v)$, the expression in parentheses must vanish, which leaves

$$\nabla_s \cdot \mathbf{\xi} = \frac{\Delta S_{m}^{m} \Delta T}{V_{m}^{s}}$$  \hspace{1cm} (47)$$

This is a differential equation for $\mathbf{\xi}$ defining the surface of the equilibrium shape. Since $\nabla_s \cdot \mathbf{r} = 2$ from Eq. (32), the solution to Eq. (47) is

$$\mathbf{r} = \frac{2V_{m}^{s}}{\Delta S_{m}^{m} \Delta T} \mathbf{\xi}$$  \hspace{1cm} (48)$$

2.4 Lagrange multiplier approach

The equilibrium shape can also be derived as the solution to the problem: Find the surface of minimum energy for a given fixed volume $V_0$. To that end, we define the augmented function

$$\mathcal{F} = \int_{A} \gamma_s \mathbf{\ell} \, dA - \lambda \left( \int_{V} dV - V_0 \right)$$  \hspace{1cm} (49)$$
where $\lambda$ is a Lagrange multiplier to include the constraint on the volume. The minimum corresponds to

$$
\delta F = 0 = \delta \int_{A} \xi \cdot \hat{n} \, dA - \delta \int_{V} \lambda \, dV \quad (50)
$$

The reduction of these two integrals proceeds exactly as it did in the preceding section: First introduce the perturbation given in Eq. (37), and then manipulate the two integrals in Eq. (50) to obtain

$$
\delta F = 0 = \int_{A} (\nabla_s \cdot \xi - \lambda) \eta(u, v) \, dA \quad (51)
$$

As above, since Eq. (51) must hold for all possible $\eta(u, v)$, the expression in the parentheses must vanish, and we have

$$
\nabla_s \cdot \xi = \lambda \quad (52)
$$

Finally, since $\nabla_s \cdot r = 2$, the equilibrium shape is given by

$$
r = \frac{2}{\lambda} \xi \quad (53)
$$

Equation (53) tells us that the equilibrium shape is homothetic to $\xi$, but it does not tell us the size of the crystal. To obtain the size, we must include the thermodynamics of the solid-liquid mixture.

**References**


