Introduction to the Properties of

CRYSTAL SURFACES

J. M. BLAKELY

Professor of Materials Science and Engineering
Cornell University

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CHAPTER 1

THERMODYNAMICS OF SURFACES

1.1. INTRODUCTION

Equilibrium thermodynamics is a subject based on three basic postulates, or laws, in which one derives relationships among the various state functions such as internal energy E, entropy S, enthalpy H, Helmholtz free energy F, Gibbs free energy G, etc., and the state parameters temperature T, pressure P, volume V, mole fraction x_i of component i, etc. One can derive a number of useful relationships which apply to surfaces.

The extensive thermodynamic properties of a solid will include contributions which depend on the area (and perhaps the shape) of its surface. These are normally (and justifiably) neglected in treating properties of the bulk solid but are of considerable interest for our present purpose. There are different ways in which the thermodynamic properties of surfaces can be defined. For example, if we consider an interface separating two otherwise homogeneous phases α and β, the surface thermodynamic functions may be defined in terms of a *surface phase* or by introducing the concept of a *dividing surface*. In the first method the system is considered to be one in which there are three phases present—the two bulk phases and a surface phase: the boundaries of the surface phase are somewhat arbitrary and are usually chosen to be at locations at which the properties are no longer varying significantly with position. The surface phase then has a finite volume and may be assigned thermodynamic properties in the normal way. With the method involving a single dividing surface, the surface contributions to the thermodynamic functions are defined as the excesses over the values that would obtain if the bulk phases retained their properties constant up to an imaginary surface separating the two phases. We adopt the latter procedure here and in the present chapter we consider only one-component crystals.

In discussions of thermodynamic properties of any system, the free energy functions generally play an important role since they can be used for developing convenient criteria for equilibrium. Surface tension plays a similar role in thermodynamic treatments of surface properties, and we shall devote most of the present chapter to a discussion of surface tension in solids. Much of the development follows that for the case of simple liquids but with important modifications arising from the dependence of solid surface properties on crystallographic orientation and from the relatively low mobility of atoms in the solid state. The first of these is important in determining the equilibrium shapes of small crystals and the stability of planar surfaces with normals along particular crystallographic directions. The second leads to a possible distinction between surface stress and surface tension, whereas for liquids the two quantities are always numerically equal. In this chapter we discuss also the equilibrium configuration at the intersection of interfaces and the effects of curvature of crystalline surfaces.

1.2. ONE-COMPONENT SYSTEMS

Consider an interface between two phases α and β (solid–vapor, solid–liquid, solid–solid, etc.) in a one-component system. We will suppose the phases α and β to extend sufficiently far from the interface that we may characterize them by their bulk concentrations C^α, C^β (moles/unit volume) as indicated in Fig. 1.1. For the purpose of defining surface quantities we imagine a surface (*DS*, Fig. 1.1) to be constructed separating the two phases and coinciding approximately with the transition region between α and β. We can then define any extensive property *P* of the surface or interface by an equation of the type

$$P_{\text{total}} = P^\alpha + P^\beta + P^s, \tag{1.1}$$

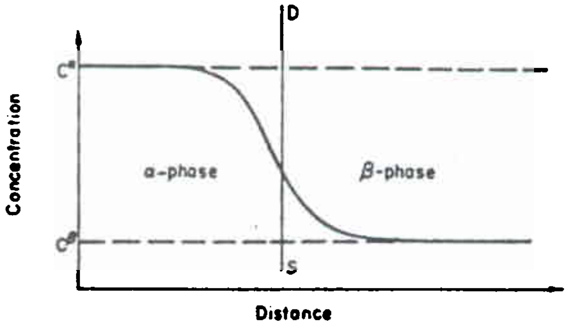

FIG. 1.1. Variation of the concentration of a particular component across the interface between two phases α and β. C^α and C^β are the concentrations of that component in the two phases at large distances from the interface. *DS* is the dividing surface.

where P^α and P^β are the values of the extensive quantity for the α and β phases respectively if they continued *homogeneous* up to the dividing surface. P_{total} is the value of the quantity for the entire system and P^s the value of P to be associated with the surface. Defined in this way it is clear that P^s is to be regarded as the *excess* value of P for the real system compared to that of the imaginary system consisting of two homogeneous phases with an ideally discontinuous change in properties at a particular mathematical surface. As examples we may write

$$\begin{aligned} S^s &= S_{\text{total}}-(S^\alpha+S^\beta), \\ E^s &= E_{\text{total}}-(E^\alpha+E^\beta), \\ F^s &= F_{\text{total}}-(F^\alpha+F^\beta) \end{aligned} \tag{1.2}$$

for the surface excess entropy, internal energy, and Helmholtz free energy respectively. Also a quantity which is of interest in connection with adsorption and segregation phenomena is the excess amount of material or excess number of moles n^s to be associated with the interface. This is defined as

$$\begin{aligned} n^s &= n_{\text{total}}-(n^\alpha+n^\beta) \\ &= n_{\text{total}}-(C^\alpha V^\alpha+C^\beta V^\beta), \end{aligned} \tag{1.3}$$

where n_{total} is the total number of moles in the entire system and n^α and n^β refer to the α and β phases respectively; V^α and V^β are the volumes of the two phases measured to the dividing surface and C^α and C^β the concentrations (moles per unit volume) in the homogeneous phases. For simplicity we may specialize to planar interfaces with no variations in properties parallel to the interface. (We should expect the results derived here to remain valid for nonplanar interfaces provided the radius of curvature is significantly greater than the width of the transition region.) The quantities in eqns. (1.1)–(1.3) are then defined[†] with respect to a cylinder of unit cross-sectional area perpendicular to the interface and extending into the phases α and β. The excess number of moles per unit area is generally denoted by Γ and often referred to simply as the surface excess.

It is obvious that the value of any surface property defined by the above equations will depend upon the choice of the location for the dividing surface. We will consider below a particularly convenient choice.

The *surface tension* γ may be defined as the reversible work involved in creating unit area of *new* surface at constant temperature, volume, and total number of moles,

$$\gamma = \lim_{dA \to 0} \frac{dw}{dA}, \tag{1.4}$$

where dw is the amount of work associated with the increment dA in area.

Since at constant temperature and volume the work done is equal to the change in Helmholtz free energy of the whole system

$$\begin{aligned} \gamma\, dA = dF_{\text{total}} &= d(F^\alpha + F^\beta) + dF^s \\ &= \mu\, d(n^\alpha + n^\beta) + dF^s \\ &= -\Gamma\mu\, dA + f^s\, dA \end{aligned}$$

or

$$\gamma = f^s - \Gamma\mu, \tag{1.5}$$

[†] To denote the values of thermodynamic functions per unit area of surface we use lower-case letters, e.g. e^s, s^s, f^s represent the internal energy, entropy, and Helmholtz free energy per unit area.

where μ is the chemical potential and f^s is the value of F^s per unit area or, in other words, the *specific surface free energy*. We may note from (1.5) that γ is the surface density of the quantity $(F-G)$ (usually referred to as the Ω potential), a relationship which was used by Gibbs for the definition of γ. We shall use this definition in Chapter 2 in connection with the composition variation near the surface of a binary solid.

Since Γ and f^s were defined with respect to an arbitrary dividing surface their individual values will depend on the choice of this surface. However, γ as defined by eqn. (1.4) is clearly independent of the choice so that the surface tension has a unique value for any particular interface. Thus in general the surface tension and specific surface free energy are not equal. This fact is of more importance in connection with multicomponent systems since for a one-component system it will in general be possible to choose the dividing surface such that $\Gamma = 0$. This is, in fact, the conventional choice for a single-component system, and thus the surface tension and specific free energy may be identified in this case.

Surface tension is a quantity which is directly measurable (see Chapter 3), and evidently by measuring its temperature dependence we may extract values of the surface (internal) energy and entropy, quantities which will reflect the differences in binding and vibrational motion of the surface atoms. Since

$$f^s = e^s - Ts^s, \quad \text{where} \quad s^s = -\left(\frac{\partial f^s}{\partial T}\right)_{v,\Gamma},$$

we obtain (for one component)

$$e^s = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_v. \tag{1.6}$$

The experimental data on liquids indicate in general that $(\partial\gamma/\partial T)$ is negative which in turn implies a positive excess surface entropy. The temperature coefficient of γ for solids also seems to be negative although the data on γ as a function of T for solids are still rather sparse. Such information would, however, be extremely valuable for testing calculations, based on microscopic models, of the internal energy and entropy contributions to the surface tension. The empirical relationship

$$\gamma = \beta(T - T_c) \tag{1.7}$$

for the variation of γ with T known as the Eötvös law is found to hold quite well for many simple liquids. Here T_c is the critical temperature and β a constant characteristic of the material. In the absence of a better model the surface tension of solids is usually also taken to vary linearly with temperature. Some experimental data for copper through the equilibrium melting temperature T_m are shown in Fig. 1.2. The scatter is clearly too great to allow a comparison of the internal energy and entropy contribution to the surface tensions of the phases, but the discontinuity of about 25% in γ at the melting point

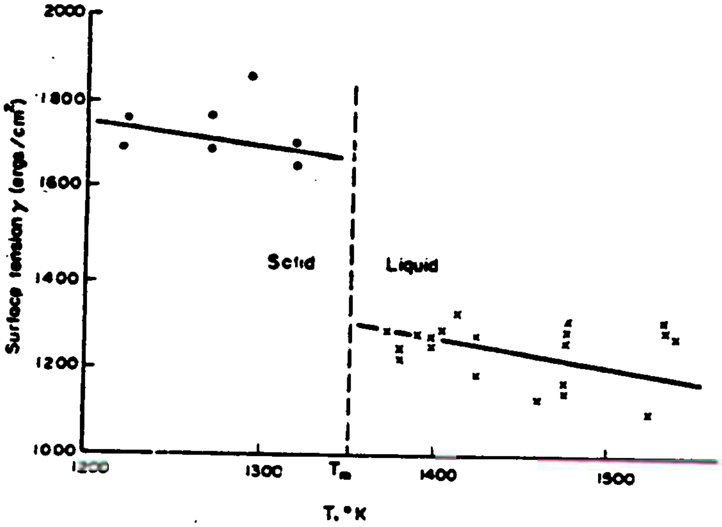

FIG. 1.2. Variation of surface tension of copper with temperature through the melting point T_m. Although there is considerable scatter in the data, the discontinuity in γ at the melting point is quite clear. (Data for the solid from H. Udin, A. J. Shaler, and J. Wulff, *Trans. AIME* **185**, 186 (1949). (Data for the liquid from tabulations in P. Kozakevitch, in *Liquids: Structure, Properties, Solid Interaction*, ed. T. J. Hughel, Elsevier, 1965, and in D. A. Belforti and M. P. Lopie, *Trans. AIME* **227**, 20 (1963).)

seems to be quite well established. In general the ratio of the surface tension of the solid to that of the liquid at the melting point appears to be about 1.1–1.3 from the available data on metals and because of the greater availability of experimental surface tensions for liquids the value for the solid is often extrapolated from the liquid data; an estimate of the solid surface tension at a temperature below T_m may be obtained by assuming

$$\frac{1}{\gamma(T_m)}\frac{\partial\gamma}{\partial T} \simeq -0.2\times 10^{-4}/^{\circ}\mathrm{K}$$

for the common metals.

Some numerical values of surface tension for nominally pure solids are given in Table 3.2 (p. 64). Although some of these results may have been influenced by small amounts of impurities, the data suggest that for common metals such as copper, nickel, etc., the value of γ is about 1–2×10³ ergs/cm² or approximately 0.4–1.0 eV for each atom in an atomic plane parallel to the dividing surface.

1.3. SURFACE TENSION AND SURFACE STRESS

There exists considerable confusion in the literature on solid surfaces about the meaning of the quantities surface tension and surface stress. The difficulty arises partly from the use of different terminology by different authors, but in many cases it is associated with the fact that most of the earlier work on surfaces was concerned with liquid–vapor interfaces for which the distinction is unimportant, and in fact the two quantities are numerically equal in that case. In general, surface stress is a tensor quantity, whereas surface tension as defined by eqn. (1.4) or (1.5) is evidently a scalar. (In section 1.4 we shall in fact see that γ varies with the surface orientation and is therefore a scalar function of the unit vector along the surface normal.) Perhaps the best discussion of the meaning of surface tension and stress in crystalline solids is that given in a now well known series of publications by Herring, and we shall outline here the main features.

Surface tension corresponds to the work to create unit area of new surface whereas surface stress is involved in computing the work involved in deforming a surface. As we shall see, the two quantities will be numerically equal when atomic mobilities are sufficiently high to preserve the microscopic configuration of the surface following the deformation. More quantitatively, consider an arbitrary change dA in the area A of the surface; this may be expressed in terms of a change of the strain tensor ε_{ij} describing the surface plane by $\Delta\varepsilon_{ij}$ defined by

$$dA = A\sum \Delta\varepsilon_{ij}\,\delta_{ij} \qquad (i, j, = 1, 2). \tag{1.8}$$

The amount of work required for such a deformation may be written (to first order) by defining a surface stress tensor g_{ij} such that

$$dw = A\sum g_{ij}\,\Delta\varepsilon_{ij} \qquad (i, j = 1, 2). \tag{1.9}$$

The amount of work required is also equal to the change in the quantity γA, so that

$$\begin{aligned} dw &= d(\gamma A) = \gamma\, dA + A\, d\gamma \\ &= \gamma A \sum_{i,j} \Delta\varepsilon_{ij}\ \delta_{ij} + A\sum_{i,j}\left(\frac{\partial\gamma}{\partial\varepsilon_{ij}}\right)\Delta\varepsilon_{ij}. \end{aligned} \tag{1.10}$$

Hence equating the right hand sides of eqns. (1.9) and (1.10) and noting that the resulting equality is true for any arbitrary additional strain component $\Delta\varepsilon_{ij}$,

$$g_{ij} = \gamma\ \delta_{ij} + \left(\frac{\partial\gamma}{\partial\varepsilon_{ij}}\right) \tag{1.11}$$

as the desired relationship between surface stress g_{ij} and surface tension γ. Thus we see that, in general, surface stress and surface tension will be numerically equal only if γ is unaffected by the deformation. This is evidently true in the case of a liquid where atomic mobilities are high and there is no long range correlation in atomic positions. The surface stress will be isotropic with zero shear components (i.e.

$g_{11} = g_{22}$, and $g_{12} = g_{21} = 0$), so that it may be characterized by a single quantity g where

$$g = \gamma. \tag{1.12}$$

For a solid, due to the long range correlation in atomic positions and low atomic mobilities, it may not be possible, in any reasonable experimental time, to keep constant the local configuration around any particular atom in the surface region where the deformation of the surface area is performed. Hence in this case γ will be altered, i.e. $(\partial\gamma/\partial\varepsilon_{ij}) \neq 0$ in general for a crystalline surface. Since γ is almost invariably[†] positive as evidenced by the fact that the surface areas of condensed phases do not spontaneously expand, the surface stress of liquids is always positive or tensile. This produces, e.g. in a small liquid droplet, a tendency to contract, resulting in an increase in density or a decrease in mean atomic volume. On the other hand, the surface stress of crystalline solids can be either tensile (positive) or compressive (negative) depending on the magnitude and sign of $(\partial\gamma/\partial\varepsilon_{ij})$. Thus small crystalline particles of some materials may be expected to show some increase of atomic volume relative to bulk material, whereas those of other materials will have decreased mean atomic volume.

We should note in passing that the existence of a surface stress does not in itself imply that the arrangement of atoms in the surface region is different from that in the interior of the crystal. The condition for the existence of such rearrangements in a crystal at equilibrium is that they correspond to a minimization of the total free energy or of the total internal energy at $T = 0°K$. It is also worth commenting that in a solid even at high temperatures we would generally not expect the surface stress tensor to be zero although this is obviously a possibility. Mechanisms whereby the surface stress state of a solid can be altered can be devised, but it is considerably more difficult to predict whether they will be energetically favorable. Figure 1.3

[†] The surface tension associated with the interface between normal and superconducting regions in type II superconductors may effectively be negative.

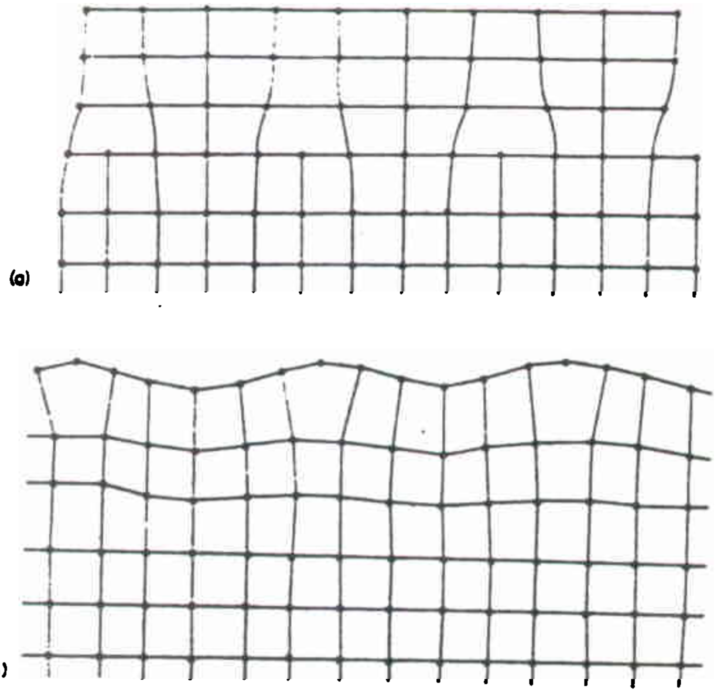

FIG. 1.3. Illustration of how the state of compression or tension in the surface layers can be altered by suitable arrays of dislocations. In (a) the array of dislocations allows the mean spacing in the surface layers to be greater than that in the bulk; (b) illustrates a possible "rumpling" effect which effectively decreases the surface spacing.

indicates examples of possible surface configurations, involving arrays of dislocations, which would lead to changes in the surface stress from that characteristic of an ideal plane.

1.4. VARIATION OF SURFACE TENSION WITH ORIENTATION

A study of the arrangements of atoms in different planes of a crystal will immediately suggest that most properties associated with solid surfaces will vary with the crystallographic orientation of the surface plane.[†] This is confirmed by experimental studies of such diverse phenomena as chemical reactions between surfaces and solutions, electron emission, and surface atomic diffusion. Surface tension is also expected to vary with orientation since the binding energies and vibrational modes of the surface atoms will depend on the local atomic arrangement. If this variation of γ with orientation is sufficiently marked, the equilibrium shapes of crystals will be polyhedral and planar surfaces of certain orientations may be unstable with respect to a spontaneous decomposition into a surface composed of segments of two or more other orientations even although this process involves a net increase in the real surface area. We will consider here the connection between crystal morphology and the variation of γ with orientation. This problem is of considerable interest in heterogeneous catalysis by small metallic particles since catalytic efficiency may be a strong function of surface orientation. In a later section we return to a discussion of experimental techniques of determining γ.

Consider a one-component system (for which we may use the terms surface tension and specific surface free energy interchangeably) in

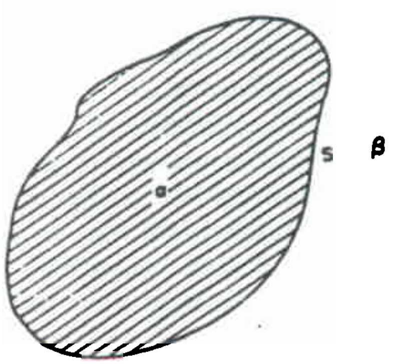

FIG. 1.4. Particle of α-phase separated from the β-phase by an interface (or dividing surface) S, e.g. a crystalline particle in contact with its vapor. The equilibrium shape of S is that given by the inner envelope of the γ-plot of Fig. 1.5.

[†] An excellent and extensive array of ball models of crystalline surfaces is given in the book by J. F. Nicholas, *An Atlas of Models of Crystal Surfaces*, Gordon & Breach, 1965. See also Chapter 4.

which there are two phases α and β separated by an interface (Fig. 1.4). The problem we wish to focus on is that of determining the equilibrium shape of the interface. At fixed temperature and total volume the condition of equilibrium is one of minimum Helmholtz free energy. We will suppose the phases α and β to have their equilibrium volumes and will consider changes only with respect to alterations in the boundary shape. With these restrictions the equilibrium condition is that

$$\int_S \gamma(\hat{\mathbf{n}})\, dA = \text{minimum}, \tag{1.13}$$

when $\gamma(\hat{\mathbf{n}})$ means the surface tension of a surface whose orientation is denoted by the unit vector $\hat{\mathbf{n}}$ along the normal and the integral is taken over the interface S. We are, of course, neglecting all external gravitational, electrical, or magnetic fields although the external gravitational field in particular may be of importance in real situations.[†]

For interfaces between simple liquids and gases where γ is independent of orientation, it is clear that the condition of equilibrium is simply one of minimum surface area so that the equilibrium interface shape is spherical. There is some experimental evidence that in certain crystalline substances the crystal–vapor interface approaches this condition at elevated temperatures. However, when there is appreciable variation of γ with orientation the resulting equilibrium shape will be polyhedral with surfaces of low γ being preferentially exposed. There is, of course, no way in which $\gamma(\hat{\mathbf{n}})$ can be deduced from thermodynamics; it must be either measured or computed from a microscopic model. We will suppose for our present purpose that $\gamma(\hat{\mathbf{n}})$ has been so determined and ask, Given $\gamma(\hat{\mathbf{n}})$ what is the equilibrium shape?

The variation of γ is most conveniently represented by a polar diagram, called the ***Wulff plot***, in which the radius vector represents the orientation of the surface (i.e. the direction of the surface normal $\hat{\mathbf{n}}$) and the magnitude of the surface tension, i.e. it is the plot $\mathbf{r} = \gamma(\hat{\mathbf{n}})\hat{\mathbf{n}}$. A two-dimensional section perpendicular to a [100] direction

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[†] The distortion of small droplets produced by the gravitational field can in fact be used in determining the surface tension of liquids as, for example, in the sessile drop method (see, for example, A. W. Adamson, *Physical Chemistry of Surfaces*, Interscience, 1967).

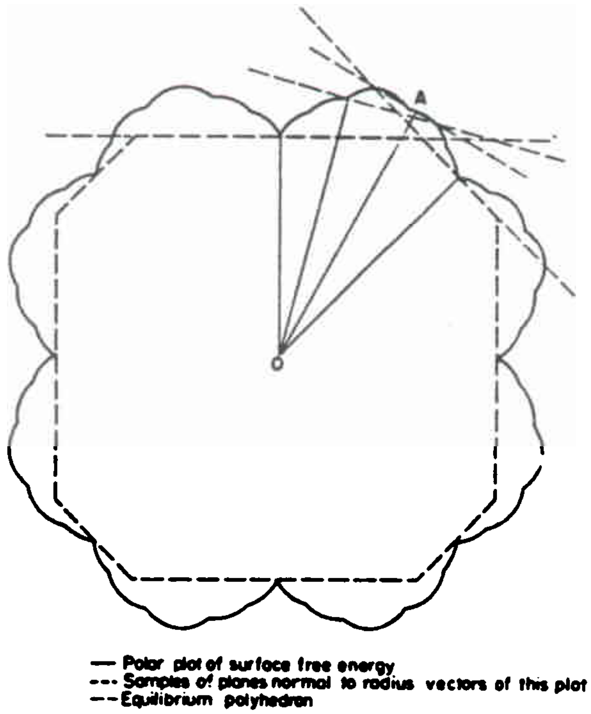

FIG. 1.5. Two-dimensional section of a polar plot of surface tension (Wulff plot) for a cubic crystal in which the vector from the origin to any point on the plot represents the direction of the normal to a particular plane and the magnitude of the surface tension for that particular plane. The equilibrium shape of a crystal can be derived from its Wulff plot; it is the inner envelope of Wulff planes. Surfaces with orientations such as *A*, which are not present in the equilibrium or Wulff shape, may be metastable with respect to faceting (see text). (After C. Herring in *Structure and Properties of Solid Surfaces*, ed. R. Gomer and C. S. Smith, University of Chicago Press, 1953, Chapter 1.)

of the Wulff plot of a cubic crystal is shown schematically in Fig. 1.5. The Wulff plot will have symmetry properties which are the same as those of the crystal and for a cubic crystal: for example, the entire plot may be specified by considering only one octant of the diagram. Thus the γ-plot may then alternatively be represented by lines of constant surface tension in the stereographic triangle as indicated in Fig. 1.6, and

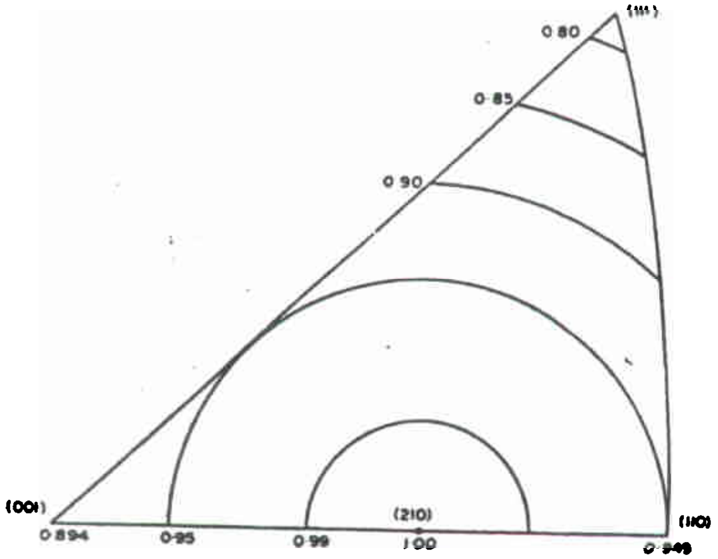

FIG. 1.6. Representation of the γ-plot of a cubic crystal in the stereographic triangle. The lines are contours of constant surface tension and are normalized with respect to the value for the (210) surface. This particular plot is a calculated one for a face-centered cubic crystal and is based on nearest neighbor interactions (see section 5.3). (Courtesy W. Winterbottom and N. A. Gjostein.)

this is generally the most convenient method for presenting experimental data. Figures 1.5 and 1.6 have been drawn to indicate that certain orientations may correspond to local minima in surface tension. These minima have generally been referred to in the literature as *cusps* although they will not, in general, strictly satisfy the mathematical definition of a cusp which would require the slope of the γ-plot to become infinite. The surfaces corresponding to the cusp orientations are termed *singular*.

If we consider any point P on the diagram the plane through P perpendicular to the radius vector OP is referred to as a *Wulff plane* and is obviously parallel to the crystal surface to which the point P refers. The equilibrium shape of the crystal is determined from the γ-plot by a procedure known as the *Wulff construction* which consists of finding the inner envelope of the Wulff planes for all possible directions. This is shown schematically in Fig. 1.5. Clearly the Wulff construction gives the correct result for a liquid. The proof of the correctness of this procedure for crystalline materials has been given by a number of authors with different degrees of generality.[†] We may note that although it is possible by this construction to go uniquely from the Wulff plot to the equilibrium shape, the reverse procedure is clearly not possible although the ratios of the surface tension for various pairs of orientations which are present in the final shape could be determined from the equilibrium shape.

At elevated temperatures where atomic transport rates become appreciable, a phenomenon known as *faceting* frequently occurs. This consists of the break-up of an initially flat surface into a hill and valley structure which is made up of portions of two or more other orientations one of which is generally a low index plane (see Figs. 1.8 and 1.9). The exposed flat areas of this low index plane are called *facets*. Since the effect may have a significant influence on many surface properties such as average electronic work function, catalytic activity, or oxidation rate, etc., it is worth while to consider it in some detail and in particular to investigate the criteria for the stability of planar surfaces of a given orientation. These criteria can most readily be developed with the aid of the Wulff plot and, in fact, we can assert immediately that a flat surface which is of an orientation present in the equilibrium shape will be stable with respect to faceting; surfaces of other orientations will exhibit faceting. Thus if an experimental Wulff plot were available for the temperature range and environment of interest it would be possible to predict whether or not a particular surface would be stable and also to determine the new surfaces which would be exposed if faceting should occur. Extensive data on Wulff plots are not yet available, and for this reason stability criteria have been developed which involve only a small segment of the polar plot of γ. If the surface with which we are dealing has an

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[†] See, for example, the article The kinetic and thermodynamic properties of surfaces, by J. P. Hirth in *Energetics in Metallurgical Phenomena* (ed. W. M. Mueller), Gordon & Breach, 1965.

orientation close to that of some low index plane *S* we may be interested in the stability of our surface with respect to exposing segments of *S*. This question can most readily be answered using the so-called "Herring tangent sphere criterion". If we consider a section of the γ-plot passing through some singular orientation *S* and the surface of interest *A* (Fig. 1.7), the condition for stability of *A* with respect to formation of portions of *S* is that the sphere drawn through *A* and through *O*, the γ-plot origin, should lie inside the γ-plot between

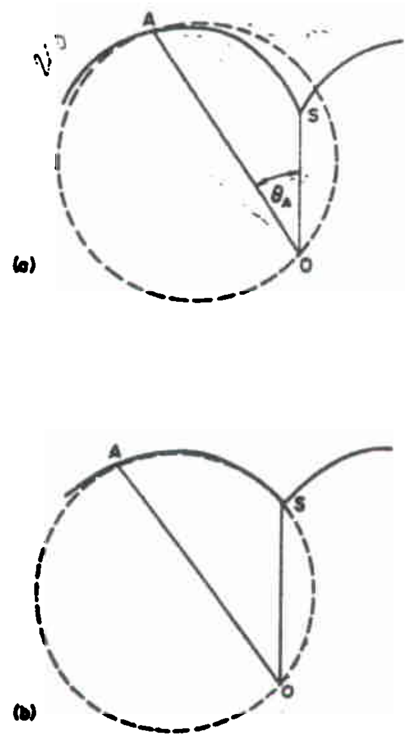

FIG. 1.7. Tangent sphere criterion for stability of a particular surface with respect to faceting. *OA* represents the surface tension and orientation of a surface *A* close to some surface *S* at which a γ-plot cusp occurs. *A* is unstable with respect to faceting if the sphere through the origin and tangent to the γ-plot at *A* is pierced by the γ-plot as shown in (a); (b) represents the limiting condition for stability of a surface with respect to forming facets of *S*. The sphere tangent at *A* passes through *S*.

A and S. The limiting conditions will be when the γ-plot point representing S lies on the sphere and the γ-plot and the sphere have a common tangent at S. These two conditions may be expressed by the equations for the stability of A:

$$\left(\frac{\partial\gamma}{\partial\theta}\right)_S \geqslant \gamma_A \sin\theta_A + \left(\frac{\partial\gamma}{\partial\theta}\right)_A \cos\theta_A,$$
$$\gamma_S \geqslant \gamma_A \cos\theta_A - \left(\frac{\partial\gamma}{\partial\theta}\right)_A \sin\theta_A. \qquad (1.14)$$

The equality applies when A and S coexist, a situation which would be obtained by the break-up of a surface of orientation between A and S (Fig. 1.7). When such faceting is observed (Figs. 1.8 and 1.9),

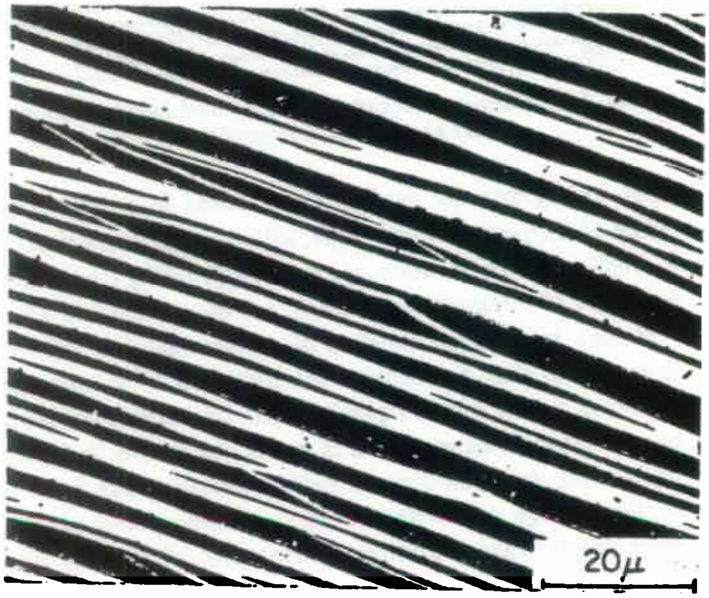

FIG. 1.8. Example of a silver crystal exhibiting linear faceting. The mean surface is inclined at about 10° to the (111) plane. The light bands of the optical micrograph are portions of (111) plane, while the dark regions are portions of "complex" surface. The crystal had been heated in air at 900°C for 10 days. (Courtesy A. J. W. Moore.)

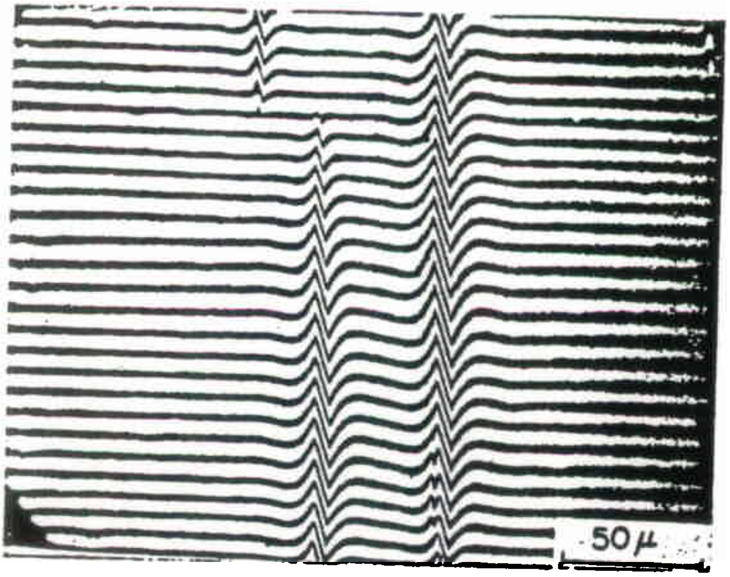

FIG. 1.9. Interferometric pattern from isolated facets on an otherwise flat surface of copper. (Courtesy of W. D. Robertson.)

eqns. (1.14) may be used to derive some information on the local shape of the γ-plot. For example, with the approximation that $(\partial\gamma/\partial\theta)_A$ is small we may obtain γ_A/γ_S and $1/\gamma_S(\partial\gamma/\partial\theta)_S$ from measurement of the angle of intersection S with A, i.e. the orientation of A.

Before leaving the question of surface stability (for the moment) it is appropriate to mention the influence of kinetic effects on the observations. It may be possible that irreversible evaporation of the crystal takes place at such a rate that the system is far from equilibrium, with the result that the surface configuration is determined not by free energy minimization but by kinetic parameters. Thus it has been argued that a number of examples of faceting are essentially unrelated to the Wulff plot and that the topography is due to the variation of evaporation rate with orientation. This point of view is well represented in the review article by Moore cited in the bibliography. Another interesting situation arises if the process of faceting is one which involves a nucleation barrier. Thus if faceting occurs by a continuous rotation of the surface normal of a portion of the surface, then an orientation such as *A* (Fig. 1.5) will be metastable. Alternatively, a nucleation barrier could arise simply from the extra free energy associated with edges of facet planes. The nonuniform nature of faceting and the occasional appearance of isolated facets on otherwise flat surfaces (Fig. 1.9) may be taken as evidence for a nucleation barrier to faceting.

1.5. INTERSECTION OF INTERFACES

Polycrystalline solids contain a variety of interfaces which include grain boundaries, stacking faults, and twin boundaries as well as free surfaces of various orientations. The problem of determining the overall arrangement of these interfaces which is the stable one is very complex, but the local equilibrium configuration at the intersection of interfaces is considerably simpler to predict and is also of some fundamental interest in connection with the determination of the relative surface tensions of the different interfaces. We consider three planar interfaces (Fig. 1.10) intersecting along a line through *O* and perpendicular to the plane of the paper and examine the region in the immediate vicinity of the intersection to obtain the configuration stable with respect to *small* displacements. Our derivation of the equilibrium configuration again follows the classic work of Herring. As we shall see later, a useful method for determining the γ-plot is based on these considerations.

Consider a small displacement of the line of intersection parallel to the boundary 1 so that boundary 1 is represented by *bP*, boundary 2 by *aBP*, and boundary 3 by *cCP*. Considering unit length perpendicular to the plane of the paper the change in surface tension or surface free energy is, to first order,

$$\delta F^s = \gamma_1(OP)+\gamma_2(BP-BO)+\gamma_3(CP-CO)$$

$$+BP\,\frac{\partial\gamma_2}{\partial\alpha_2}\,\delta\alpha_2+CP\,\frac{\partial\gamma_3}{\partial\alpha_3}\,\delta\alpha_3. \qquad (1.15)$$

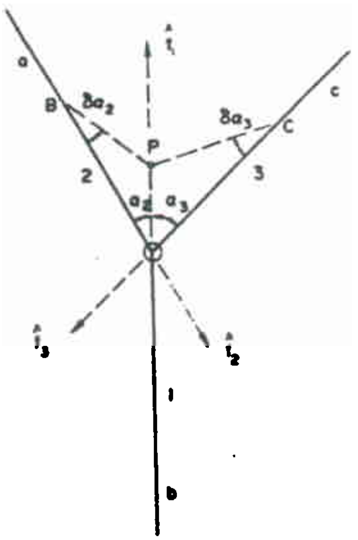

FIG. 1.10. Intersection of three planar boundaries along a line through O and perpendicular to the plane of the paper. To establish the equilibrium configuration we imagine the line of intersection to be displaced to P and examine the stability of the system with respect to such small displacements.

Evaluating the lengths in terms of the angles and using the condition for the initial configuration to be the equilibrium one, i.e. $\delta F' = 0$, gives

$$\gamma_1-\gamma_2\cos\alpha_2-\gamma_3\cos\alpha_3+\sin\alpha_2\left(\frac{\partial\gamma_2}{\partial\alpha_2}\right)+\sin\alpha_3\left(\frac{\partial\gamma_3}{\partial\alpha_3}\right)=0. \quad (1.16)$$

If $\hat{t}_i$ is a unit vector lying in the plane of the diagram and in the plane of the boundary i as shown in Fig. 1.10, we may rewrite eqn. (1.16) as

$$\left(\gamma_1\hat{t}_1+\gamma_2\hat{t}_2+\gamma_3\hat{t}_3+\frac{\partial\gamma_1}{\partial\hat{t}_1}+\frac{\partial\gamma_2}{\partial\hat{t}_2}+\frac{\partial\gamma_3}{\partial\hat{t}_3}\right)\cdot\hat{t}_1=0. \quad (1.17)$$

Similarly, by considering displacements of the line of intersection along $\hat{t}_2$ and $\hat{t}_3$ we may generate two other equations analogous to (1.17). Since $\hat{t}_1$, $\hat{t}_2$, and $\hat{t}_3$ are nonparallel co-planar vectors the vector quantity in the square brackets must be identically zero. Thus the equilibrium configuration at the intersection of three planar interfaces may be written as

$$\sum_{i=1}^{3}\left(\gamma_i\hat{t}_i+\frac{\partial\gamma_i}{\partial\hat{t}_i}\right)=0. \qquad (1.18)$$

The vector quantities $\partial\gamma_i/\partial\hat{t}_i$ have the mathematical form of a torque, i.e. the change in a free energy per unit of angular rotation, and are generally referred to in the literature as the *torque terms*. They may alternatively be viewed as a force per unit area acting normal to the interface.[†] The following are two special cases in which the torque terms are especially important in influencing interface morphologies.

(a) *Twin boundaries*

Twin boundaries are rather specialized internal interfaces in solids in that although the two crystals on either side of the boundary are related to each other by large orientation differences they have extremely small values of surface tension associated with them. For example, in copper the twin boundary tension is of the order of 30 ergs/cm^2 as compared to ~ 500 ergs/cm^2 for a normal high angle grain boundary. The reason for the low value of γ in this case is that one crystal can be obtained from the other by performing a reflection operation about the twin plane (of type $\{111\}$ in face-centered cubic metals) and nearest neighbor coordination is not disturbed by the presence of the boundary. Small perturbations in the orientation of the boundary relative to the two crystals would thus be expected to lead to relatively large increases in tension. Thus we expect $\partial\gamma_i/\partial\hat{t}_i$ to be very large for a twin and in such a direction as to maintain the boundary coincident with the twinning plane. This is the main reason that twin boundaries invariably produce straight traces on the surface of face-centered cubic metals (Fig. 1.11).

[†] Note that eqns. (1.18) are equivalent to (1.16) for the special case of the intersection of two interfaces.

[illegible]

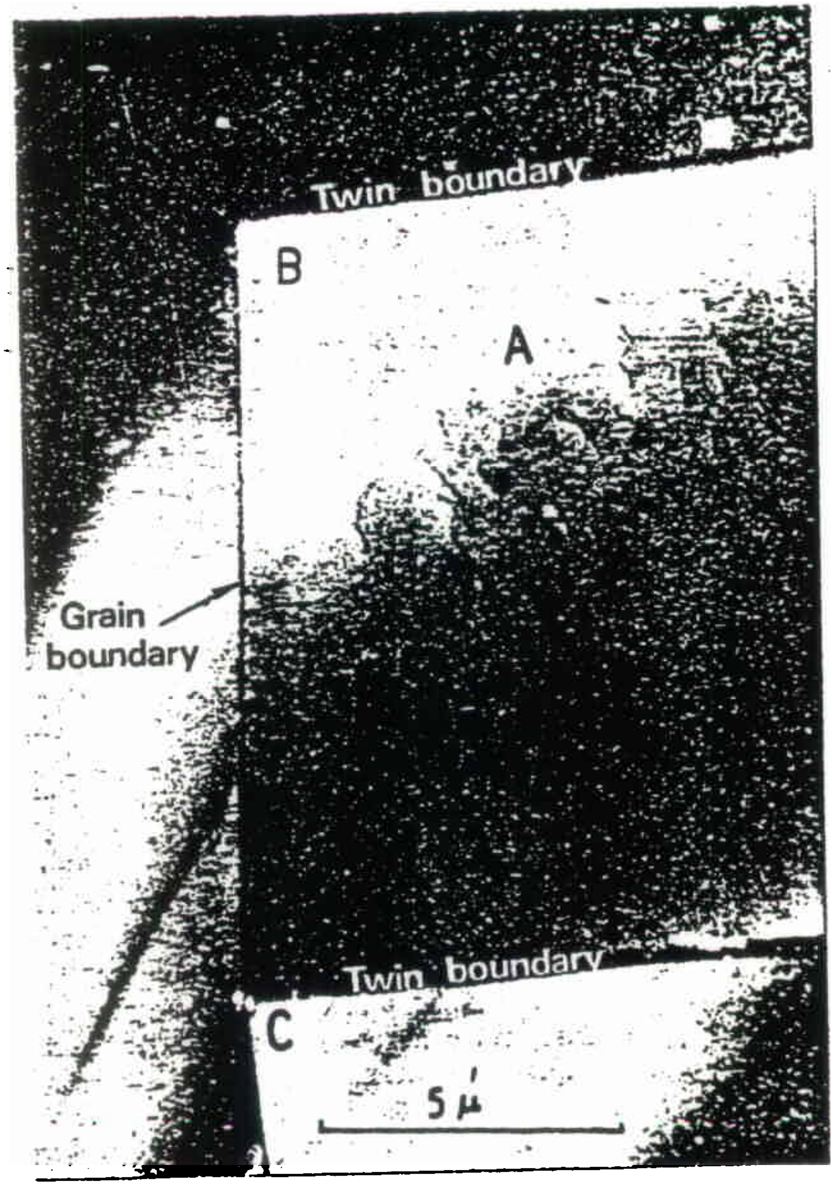

FIG. 1.11. Electron micrograph showing the intersection of a pair of twin boundaries with a grain boundary in a copper-1 wt.% antimony alloy. At *C* all three boundaries lie in the same 180°. (From M. C. Inman and H. R. Tipler, *Metallurgical Reviews* 8, 105 (1963).)

(b) *Three intersecting boundaries all in the same 180°* (Figs. 1.11 and 1.12)

For fluid interfaces for which the quantities $\partial\gamma_i/\partial\hat{t}_i$ are zero it is obvious that the configuration at the intersection of three such bound-

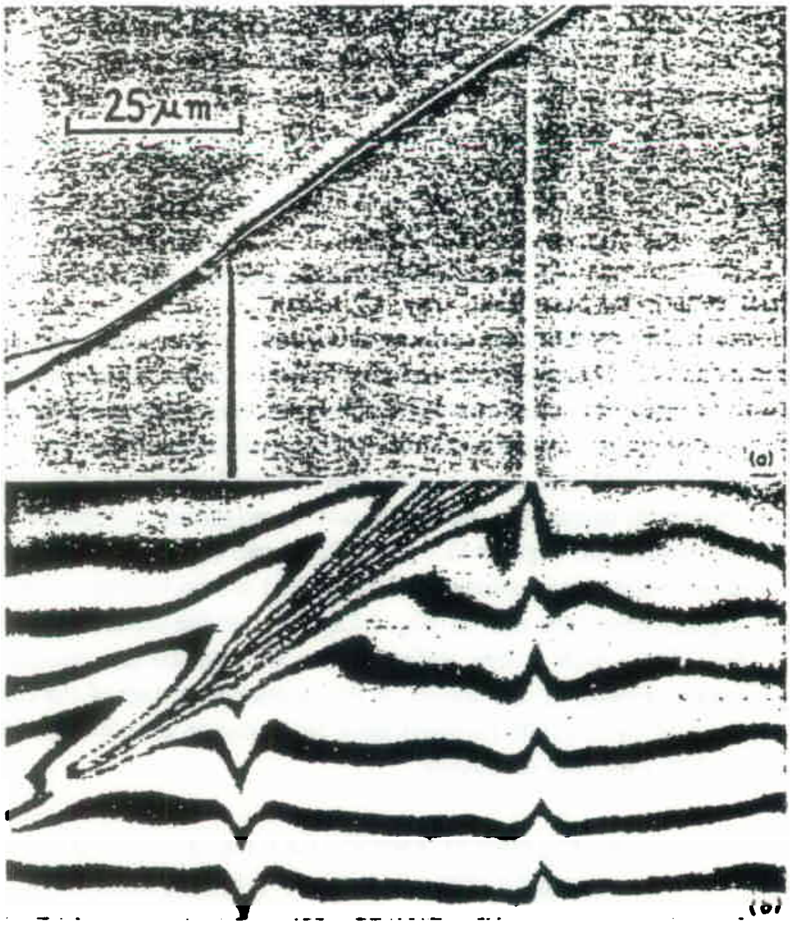

Fig. 1.12. (a) Intersection of a pair of twin boundaries with a free surface. (b) A two-beam interference microscope photograph showing the topography of the surface in (a). That all three boundaries can lie in the same 180° at their intersection is due to the influence of the variation of surface tension with surface orientation. (Courtesy of H. Mykura.)

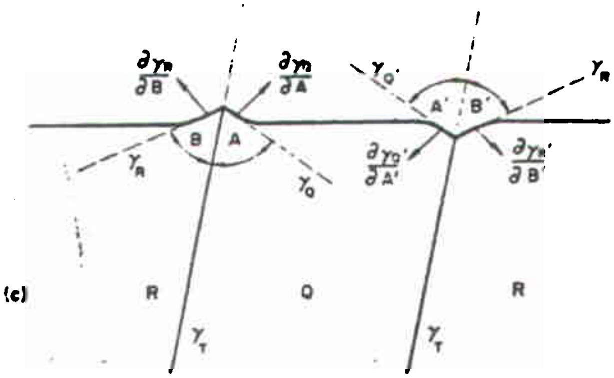

FIG. 1.12. (c) Definition of quantities used in eqn. (3.9).

aries cannot be such that they all lie in the same semicircle. However, for crystalline interfaces this situation becomes possible and a number of examples can be found in the literature. They usually involve a twin boundary or a low angle boundary which has a sufficiently small free energy such that the derivatives of the γ's with respect to orientation are significant in magnitude compared to the γ's themselves. Figures 11.1 and 1.12(a) and (b) show examples with three intersecting boundaries. In Fig. 1.11 a twin boundary intersects a grain boundary and in Fig. 1.12(b) we see the intersection of twin boundaries with a free surface. Later we shall see how quantitative measurements of the angles at the intersections and of the orientations of the crystals involved have been used to determine the Wulff plot of a number of crystals.

1.6. CURVED INTERFACES AND THE GIBBS–THOMPSON RELATION

Curved interfaces are involved in numerous practical situations with bubbles, droplets, and precipitate particles, and in a number of techniques for determining the surface tensions of both liquids and solids. There are two relationships which are of special interest in connection with curved surfaces. These are contained in the equation of Young and Laplace and in the Kelvin or Gibbs–Thompson relation. The first of these equations has to do with the excess pressure inside a spherical droplet and the second is concerned with the relationship between equilibrium vapor pressure and radius; they are not independent and, indeed, the second may be simply derived from the first. The Young and Laplace equation can be obtained for a liquid droplet by considering the condition of mechanical equilibrium in the presence of an isotropic surface stress g. At equilibrium the pressure inside the drop exceeds that outside by an amount ΔP given by

$$\Delta P = \frac{2g}{R}, \tag{1.19a}$$

$$= \frac{2\gamma}{R}, \tag{1.19b}$$

where R is the liquid drop radius. The second equation applies to an isotropic fluid for which surface stress and tension are identical. The increase in chemical potential caused by the pressure increase of eqn. (1.19) is to first order

$$\Delta\mu \simeq \Omega_0 \Delta P = \frac{2g}{R}\Omega_0, \tag{1.20}$$

where Ω_0 is the atomic volume. If we treat the vapor as an ideal gas for which the chemical potential is equal to $(kT \ln p + \text{constant})$ the vapor pressure p that is in equilibrium with the spherical particle is related to that over a flat surface p_0 by

$$kT \ln\left(\frac{p}{p_0}\right) = \Delta\mu \tag{1.21a}$$

or

$$kT \ln\left(\frac{p}{p_0}\right) = \frac{2\gamma}{R}\Omega_0. \tag{1.21b}$$

Equation (1.21b) is the usual form of the Gibbs–Thompson equation. This equation shows that the higher the curvature the greater the vapor pressure so that in a system containing a distribution of drop sizes the small ones should be expected to disappear by transfer to the larger particles, as is indeed observed.

For interfaces involving solids we might expect that relationships similar to eqns. (1.19) and (1.21) would exist. However, in such cases one has to be more careful about the distinction between surface stress and tension and also to recognize the orientational and directional dependence of these quantities. Thus the Young and Laplace equation should be replaced for a solid–vapor interface by a relationship between the stress distribution in the particle and the surface stress. However, the approximation that the surface stress is isotropic is often made in connection with solid surfaces. For example, for small crystalline particles the surface stress is assumed also to be given by eqn. (1.19a) which should give rise to an average fractional decrease in atomic volume given by

$$\frac{\Delta\Omega}{\Omega_0} = \beta\frac{2g}{R}$$

or for a cubic crystal, a fractional change in lattice parameter

$$\frac{\Delta a}{a} = \frac{1}{3}\beta\frac{2g}{R}, \tag{1.22}$$

where β is the isothermal bulk compressibility. A number of investigators have in fact reported deviations in the lattice parameters of small crystalline particles We shall quote some of these measurements later but it is worth noting at this point that the resulting values of g obtained by using eqn. (1.22) are significantly different in magnitude in most cases from the corresponding surface tensions. Negative values of g corresponding to surfaces in compression have in fact been obtained in a few cases, whereas values of γ are invariably positive.

For interfaces between a solid and a liquid or a solid and a vapor, the Gibbs–Thompson relation is more complicated than eqn. (1.21) for the reasons noted above. However, for some purposes the directional effects are ignored and a reasonably satisfactory (if not quantitative) description of phenomena involving curved solid interfaces can often be given using the form of eqn. (1.21). A more general form of the Gibbs–Thompson equation has, however, been derived for the case where there is sufficiently high atomic mobility that the surface stress and tension may be identified but where the dependence of γ on orientation is included. We shall derive the form of the Gibbs–Thompson relationship, corresponding to eqn. (1.20), following arguments similar to those given by Herring.

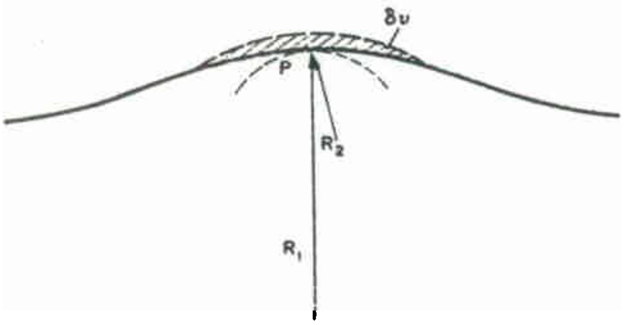

FIG. 1.13. Portion of a curved surface of a crystalline solid with principal radii of curvature R_1 and R_2. To examine the value of the chemical potential in the vicinity of any point P we imagine a small hump of volume δv to be created and apply the criterion for (local) equilibrium that the system should be stable against such perturbations. (After C. Herring, in *The Physics of Powder Metallurgy*, ed. W. E. Kingston, McGraw-Hill, 1951.)

Consider a portion of a surface having principal radii of curvature R_1 and R_2 (Fig. 1.13) and imagine the creation of a small hump of volume δv by the introduction of $\delta v/\Omega_0$ vacancies into the crystal at this portion. Ω_0 is the atomic volume. Then if μ_v is the local value of the vacancy chemical potential and p the mean hydrostatic pressure locally in the crystal, the change in the volume contribution to the Helmholtz free energy may be written as $-p\,\delta v+\mu_v(\delta v/\Omega_0)$. The increase in surface free energy is $\delta(\int \gamma\, dS)$. For equilibrium we require the net change in free energy to be zero, i.e.

$$\left(-p\,\delta v+\mu_v\frac{\delta v}{\Omega_0}\right)+\delta\left(\int \gamma\, dS\right)=0$$

or

$$\mu_v = p\Omega_0 - \frac{\Omega_0}{\delta v}\delta\left(\int \dot{\gamma}\, dS\right). \tag{1.23}$$

The second term on the right hand side may be evaluated as shown by Herring in terms of the local radii of curvature, surface tension, and its derivatives with respect to orientation. We obtain

$$\mu_v = p\Omega_0 - \Omega_0\gamma\left\{\left(\frac{1}{R_1}+\frac{1}{R_2}\right)+\frac{1}{\gamma}\left(\frac{\partial^2\gamma}{\partial n_x^2}\,\frac{1}{R_1}+\frac{\partial^2\gamma}{\partial n_y^2}\,\frac{1}{R_2}\right)\right\}. \tag{1.24}$$

The derivatives with respect to n_x and n_y measure changes in surface tension γ with changes in the orientation of the surface normal in the direction of the two principal curvatures. The chemical potential of atoms relative to its value μ_0 beneath a flat surface where the pressure is taken as zero is given by

$$\mu = \mu_0 + p\Omega_0 \tag{1.25}$$

if we neglect small terms of order $x_v kT$, where x_v is the fractional vacancy concentration.

Combining eqns. (1.24) and (1.25),

$$\mu - \mu_v = \mu_0 + \Omega_0\gamma\left\{\left(\frac{1}{R_1}+\frac{1}{R_2}\right)+\frac{1}{\gamma}\left(\frac{\partial^2\gamma}{\partial n_x^2}\,\frac{1}{R_1}+\frac{\partial^2\gamma}{\partial n_y^2}\,\frac{1}{R_2}\right)\right\}. \tag{1.26}$$

If vacancies are always in local equilibrium so that we may set $\mu_v = 0$ everywhere we obtain, corresponding to eqn. (1.20),

$$\Delta\mu = \Omega_0\gamma\left\{\left(\frac{1}{R_1}+\frac{1}{R_2}\right)+\frac{1}{\gamma}\left(\frac{\partial^2\gamma}{\partial n_x^2}\,\frac{1}{R_1}+\frac{\partial^2\gamma}{\partial n_y^2}\,\frac{1}{R_2}\right)\right\}. \tag{1.27}$$

It is clear that this generalized Gibbs–Thompson relationship reduces to that of a liquid when γ may be regarded as isotropic. We shall use eqn. (1.27) in discussing mass transport near the surfaces of crystals in section 7.3. For the moment we note that gradients in chemical potential can be generated by gradients in surface curvature and that these will produce atomic fluxes. The magnitudes of the deviations in chemical potential are quite small for all but the smallest radii of curvature. For example, for a radius of curvature of 1 micron (10^{-6} m), $\Delta\mu/kT \approx 10^{-3}$ at 1000°K for a typical metal. The measurement of the rate at which these differences in chemical potential are eliminated in crystals provides information on parameters such as volume or surface diffusivities.

So far in our discussion of one-component systems we have not considered the question of the equilibrium structure of the interface. This question cannot, of course, be answered completely for any particular case within the framework of thermodynamics since a specific model of atomic interactions must be adopted at some point in the development. However, the general framework for the description of the transition or inhomogeneous region between two phases and the general concept of diffuse interfaces are of considerable interest. We shall take up this topic in Chapter 2 in connection with interfaces in multicomponent systems. For the moment we may note that an interface between two phases should not be regarded as a mathematical plane at which there is a discontinuous change in properties from those characteristic of one bulk phase to those characteristic of the other bulk phase. Rather the transition should be regarded as occurring over a region of finite width (as indicated schematically in Fig. 1.1). This effect will be most marked for liquid–vapor interfaces or liquid–liquid interfaces near critical points where the interface essentially becomes infinitely diffuse as the two phases become identical.

In dealing with curved interfaces in section 1.6 we have implicitly assumed that the value of the surface tension was independent of the local radius of curvature of the surface. There are actually a number of published papers dealing with the question of the dependence of γ on curvature for liquid systems. It appears to be generally agreed that γ will not depart from its value characteristic of a macroscopic flat surface until the particle radius becomes comparable to atomic dimensions. This is intuitively reasonable since deviations from the macroscopic value should be significant only when the curvature is sufficiently large that the surface coordination is changed or that there is a distortion of the transition region. The exact way in which γ varies with curvature will depend on the type of atomic interactions that are involved. The usefulness of macroscopic thermodynamic quantities such as surface tension is questionable in any event when the system contains only a small number of atoms.

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