

1 Interfacial free energy and the γ -plot

1.1 The free energy of an interface

Whilst the interest in the atomic structure and electronic behaviour of surfaces has arisen relatively recently, the method of treating interfaces thermodynamically was introduced as long ago as the last century. Gibbs, in particular, published a considerable contribution to the field in 1878 and much of this work still forms the basis of a large part of the present understanding of interfacial phenomena.

Of particular interest is the concept of the free energy, per unit area, of an interface, and necessarily associated with this, the method of defining the interface position relative to the two phases which lie on either side of it. The concept of a free energy associated with an interface may easily be appreciated by considering the total free energy of some system consisting of two phases of volumes V_1 and V_2 in contact. The total Gibbs free energy, for instance, will be given by

$$G = G_1V_1 + G_2V_2 + \gamma_{12}A_{12} \quad (1.1)$$

where A_{12} is the area of the interface separating the phase and γ_{12} is the Gibbs free energy per unit area of the interface. An understanding of a surface energy may be achieved by considering the surface of a material whose energy may be described on a pairwise bonding model. Clearly, because of the different environment of atoms near the surface of the material, the energy of these atoms will be different from those in the bulk. For the sake of convenience this difference is associated with the dividing surface between the phases.

The Gibbs free energy per unit area of a surface may be decomposed, in the normal way, as

$$\gamma = \epsilon - T\eta + pv \quad (1.2)$$

where ϵ is the surface energy per unit area, η the surface entropy per unit area and v the surface volume per unit area. This final term, v , is associated with the change in atom density in a material near the interface; for instance, there may be a different spacing of the outermost planes near a free solid surface. This is an extremely small term and may be neglected in almost all cases of interest. Thus, in general, the Gibbs free energy per unit area is equivalent to the Helmholtz free energy

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per unit area which is also often defined as γ . A more complete treatment and derivation of the concept of surface free energy was given by Gibbs (1878) but the above discussion will suffice for our present needs. It is, however, of interest to point out that Gibbs accounted for adsorption at the interface by the addition of terms $\mu_i \Gamma_i$ to the surface free energy where μ_i is the chemical potential of the i th species of adsorbed atoms, and Γ_i is the surface density of these atoms. Also, in general, the *Gibbs dividing plane* or interface, is defined only as a plane passing through all points having a similar environment in the boundary region between the two phases. This surface has a degree of freedom in displacement perpendicular to the surface; this is removed for one-component systems by the necessity that the surface mass term shall be zero. Thus, if an equation of the general form of (1.1) is written with the total mass of the system on the left hand side and the G_1 , and G_2 replaced by the densities of the two bulk phases, the surface is positioned such that no surface term need appear in this equation. For multi-component systems, the problem of defining the position and thickness of the interface has been discussed in detail by Cahn & Hilliard (1958).

1.2 **Surface tension and its relation to surface free energy**

The definitions given above for the interfacial free energy per unit area (which will be referred to, for the sake of convenience, as the surface free energy) corresponds to the work involved in creating unit area of interface. In the rest of the discussion in this chapter it is this quantity which is of significance in determining the equilibrium in a two phase system (when the total Gibbs free energy is a minimum). However, as will be seen in the next chapter, the quantity measured experimentally is usually the surface tension of the interface. For an interface between two fluids the relationship between these two quantities is simple. In this case a consideration of the work done against the surface tension in expanding an interface to create new area of interface shows that this work is equal to the surface free energy of the same area of new interface. Thus the surface tension and surface free energy are numerically equal if expressed in similar units. However, this is not necessarily true for an interface which is bounded on at least one side by a solid (which for convenience will be referred to as a solid surface, though this may be a free solid surface, a solid-liquid interface or a solid-solid interface). As Gibbs pointed out, whilst the surface free energy corresponds to the work done in *forming* the surface, the surface tension depends on the work done in *stretching* the surface. The equivalence of these two

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processes requires the tacit assumption that there is no marked change in surface structure associated with the latter process and thus no work is spent in deforming the surface. In using experimental determinations of the surface tension to give a value of the surface free energy it is assumed, therefore, that the temperature at which the experiments are performed is sufficiently high for surface and bulk diffusion to correct the distortion effects and so permit the equality to be used.

1.3 **The γ -plot and the terrace-ledge-kink model of a surface**

In order to fully characterise an interface in terms of its surface free energy, γ must be known for all orientations of the interface and conventionally it is plotted on a polar diagram such that the length of the radius coordinate is proportional to the value of γ for a surface perpendicular to the direction of the radius vector. For a simple liquid interface there is no orientation dependence of γ and so the γ -plot (as this polar diagram is commonly known) is a sphere, and any section passing through the origin of the coordinate system (which therefore provides a more convenient two-dimensional γ -plot) is a circle.

For a solid surface, however, γ is clearly a function of crystallographic orientation and so the γ -plot will not be spherical. To determine the general features of the γ -plot for a solid surface it will be convenient to consider the free surface of a solid at the absolute zero of temperature so as to remove thermal disordering and entropy effects. Let us first consider surfaces having orientations close to that of a low index plane. These surfaces will appear as a series of terraces of the low index plane, the step density in this terraced structure being characteristic of the deviation of the surface normal from that of the low-index plane, θ . Thus for such a surface composed of steps, or ledges of height a , having a mean separation in the complex surface, l (see fig. 1.1(a)), it is clear that

$$\sin \theta = a/l. \quad (1.3)$$

Now according to the terrace-ledge-kink (TLK) model of a surface, the surface energy can be decomposed into terms giving the energy for the low index plane, γ_0 per unit area of the low index plane (the terraces), the ledge energy, β per unit length of ledge, and in the case of more complex orientations than that considered here there will be a further term due to the energy of kinks in the ledges (fig. 1.1(b) shows an example of such a surface). For any particular azimuth the kink density on the ledges will be constant, and only the separation of the ledges will change with θ , so the particular model used here of a low

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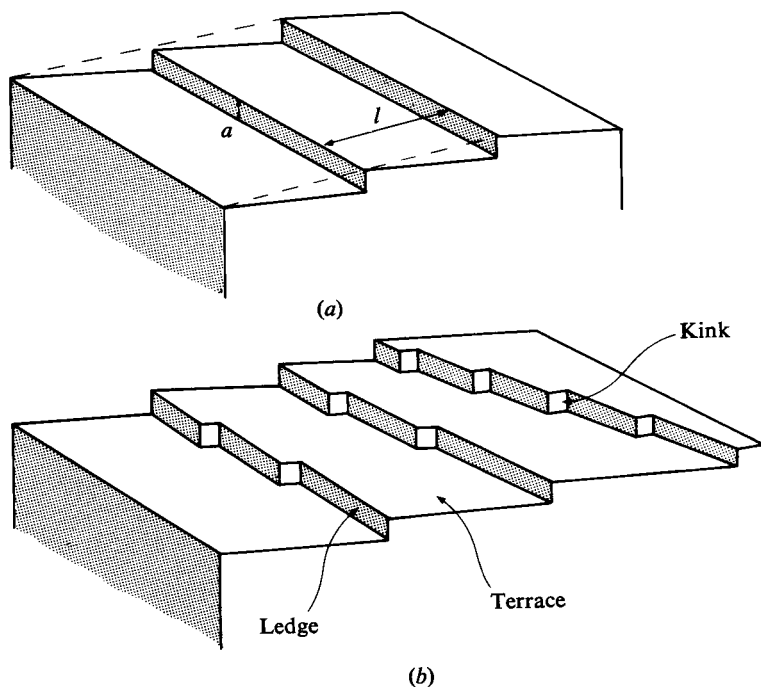


Fig. 1.1. (a) A simple stepped or ledged surface with low index terraces. (b) More complex surface including kinked ledges.

index azimuth involves no loss of generality providing that the absolute value of the ledge energy is not specified. For this surface, therefore, as shown in fig. 1.1, the surface energy per unit area is given by

$$\begin{aligned}\gamma_\theta &= \gamma_0 \cos |\theta| + \beta/l \\ &= \gamma_0 \cos |\theta| + \frac{\beta}{a} \sin |\theta|.\end{aligned}\quad (1.4)$$

Note that the $|\theta|$ terms have been introduced because γ_θ is independent of the sign of θ due to the symmetry of the situation. It is easy to show that (1.4) describes the relationship shown in fig. 1.2. The point of particular interest is that the graph shows that there will be a 'cusp' in the γ -plot at orientations corresponding to low index planes. This cusp is a sharp minimum in γ_θ but is a mathematical singularity rather than a simple minimum (i.e. $\partial\gamma_\theta/\partial\theta$ is discontinuous at this point). It is not, in fact, a point of self-tangency which is the more correct mathematical definition of a cusp in the normal way, but the term is in popular use and usefully describes the appearance of the curve.

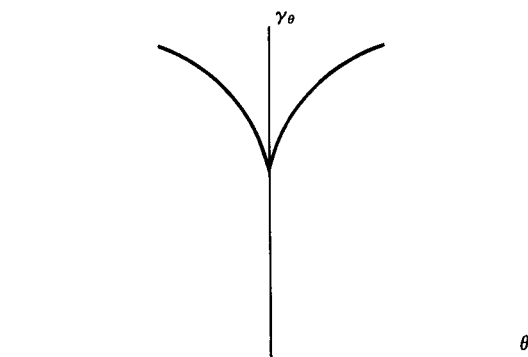


Fig. 1.2. The dependence of γ_θ on θ for the simple model depicted in fig. 1.1.

While this application of the TLK model of the surface is a very simple and therefore special case, it is possible, by suitable mental agility in describing a more complex surface on a TLK model, to show that cusps will appear in the γ -plot at all orientations corresponding to surfaces having rational Miller indices. Each of these singularities corresponds, as does a rational set of Miller indices, to a particular long range ordering described in the surface by particular sets of ledge and kink spacings. Evidently, in this model no account is being taken of thermal vibrations of the atoms which might destroy this long range order; this point will be discussed later in this chapter (§1.5).

It should, however, be pointed out that this treatment and the one which follows are designed to determine the *surface energy* which is only equivalent to the *free surface energy*, γ , at the absolute zero of temperature. However, this is the only temperature at which the above considerations are valid. Firstly, however, we shall use the other commonly applied method of determining surface energies, in its most general form to show more clearly the shape of the γ -plot for a solid surface.

1.4 **Pairwise bonding models**

This alternative model of a solid surface is derived from assuming that a crystal consists of atoms interacting attractively in pairs by means of forces of finite range. The surface energy of a surface may then be given by the sum of the energies of all bonds broken by the surface and passing through unit area of the surface. It is easy to see that this is the same as the sum of the energies of all bonds broken by the surface originating from the atoms situated below unit area of the surface.

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First, consider all interatomic bond vectors of the type \mathbf{u}_i having associated energy $E(u_i)$. Now, if \mathbf{n} is a unit normal to the surface under consideration, then all atoms having broken bonds of the type \mathbf{u}_i will lie between the surface and a plane parallel to the surface but a distance $\mathbf{n} \cdot \mathbf{u}_i$ below the surface. Thus, if Ω is the volume of crystal per atom then the number of atoms below unit area of the surface having broken bonds of the type \mathbf{u}_i will be $(\mathbf{n} \cdot \mathbf{u}_i)/\Omega$. Thus the surface energy of this surface is given by

$$\gamma_n = \sum \mathbf{n} \cdot \mathbf{u}_i \frac{E(u_i)}{\Omega} \quad (1.5)$$

where the summation is over all i for which $\mathbf{n} \cdot \mathbf{u}_i > 0$, or

$$\gamma_n = \mathbf{n} \cdot \sum_i \mathbf{u}_i \frac{E(u_i)}{\Omega}. \quad (1.6)$$

Notice that bonds for which $\mathbf{n} \cdot \mathbf{u}_i < 0$ are directed back into the crystal and are therefore not broken.

Now if the interatomic forces are of finite range, this summation has a finite number of terms and also there is a small range of orientations for which any set of i (for which $\mathbf{n} \cdot \mathbf{u}_i > 0$) is constant; these orientations lie in a pyramid, p , say. Within this pyramid we may write

$$s_p = \sum_i \mathbf{u}_i \frac{E(u_i)}{\Omega} \quad (1.7)$$

where s_p is a fixed vector in p , and so within p

$$\gamma_n = \mathbf{n} \cdot s_p. \quad (1.8)$$

Thus, we have from this relation, that the projection of s_p on \mathbf{n} has magnitude γ_n . That is, within the pyramid p , the locus of the end of the vector $\mathbf{n}\gamma_n$ is a sphere passing through the origin of the polar (γ -plot) coordinate system. This is shown in fig. 1.3. In general, therefore, providing that a pairwise bonding model is a suitable description of the crystal and its surface, the γ -plot will be composed entirely of portions of spheres which pass through the origin. Moreover, the intersections of these spheres (where cusps will be formed) occur where the set of \mathbf{u}_i for which $\mathbf{n} \cdot \mathbf{u}_i > 0$ changes; this occurs when one or more of the $\mathbf{n} \cdot \mathbf{u}_i = 0$, a condition which clearly corresponds to some rational index orientation. Thus the general picture of a solid surface γ -plot at absolute zero of temperature is of a surface composed entirely of portions of spheres (all of which will be convex outside as they pass through the origin), with cusps at the junctions of these spheres corresponding to all rational index orientations. This shape has been aptly described

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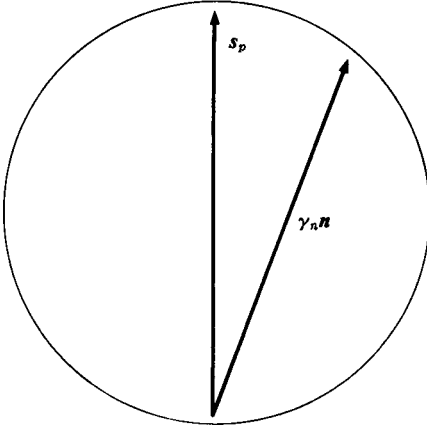


Fig. 1.3. Vector diagram for s_p and $n\gamma_n$ showing the section of the γ -plot generated in the pyramid p .

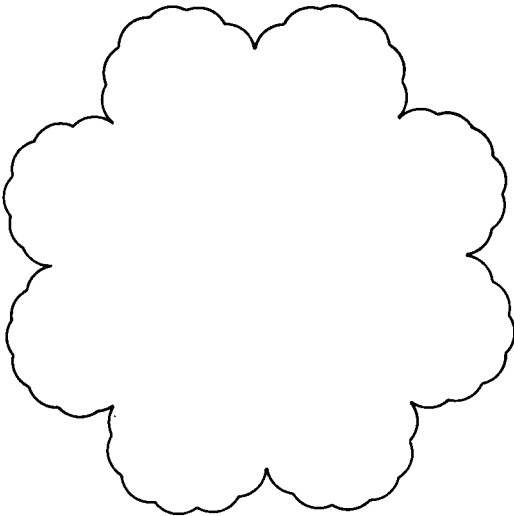


Fig. 1.4. A schematic γ -plot at 0°K.

by Frank as a ‘raspberry’ figure. A schematic γ -plot of this type is shown in fig. 1.4.

1.5 Effect of temperature on the γ -plot

At elevated temperature the shape of the γ -plot simplifies from that shape described above. This is because the increase in temperature

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results in a certain amount of surface disordering (for instance, in the form of the equilibrium concentration of kinks on ledges). This tends to destroy the long range order on the high index surfaces and so the singularities in the γ -plot corresponding to these surfaces may be expected to disappear and the associated cusps to be smoothed out. This problem has been treated in some detail for a free solid surface in the TLK model, particularly by Burton, Cabrera & Frank (1951). For a high index surface, the surface disorders gradually with increasing temperature as the density of opposite sign kinks on the surface ledges increases, until all long range order has disappeared. For a low index surface the picture is rather different. Disordering can occur by the generation of surface vacancies and adatoms but it is important to consider cooperative effects as the population of these increase. In analysing this situation the 'roughening' of the surface was considered on a two, three and five level model using Bethe's (1935) method for treating order-disorder phenomena. In this way they showed that the disordering of the surface occurs largely within quite a narrow temperature range after the fashion of a phase transition. For this reason the effect is known as 'surface melting'. Below the surface melting temperature the surface is well-ordered and smooth on an atomic scale. Frank (1958) has suggested that an interface of this type be called a 'singular' surface. Above the transition temperature, the surface atoms are in a completely disordered state and thus the singularity in the γ -plot corresponding to that orientation of surface will disappear, and the cusp will be rounded initially into a simple minimum. Burton, Cabrera and Frank also made some semi-quantitative predictions as to the value of the surface melting temperature for different surfaces, and found that for low index surfaces corresponding to planes of close packing in which the atoms are bound within the plane by bonds in two directions, the surface melting temperature is likely to be significantly higher than the bulk melting point. Thus surface melting will not be observed on these planes. For other orientations, however, surface melting is likely to occur below the bulk melting temperature. These results show that the complex γ -plot shape predicted in §1.4 for absolute zero temperature will be simplified by a rounding-off of many of the cusps at elevated temperatures. The extent to which this process has occurred depends on the temperature but in general there will always be some cusps remaining right up to the melting point of the solid. Fig. 1.5 depicts schematically the γ -plot of a solid surface at some elevated temperature.

Since the work of Burton, Cabrera and Frank other authors have shown that different models of the surface predict similar effects.

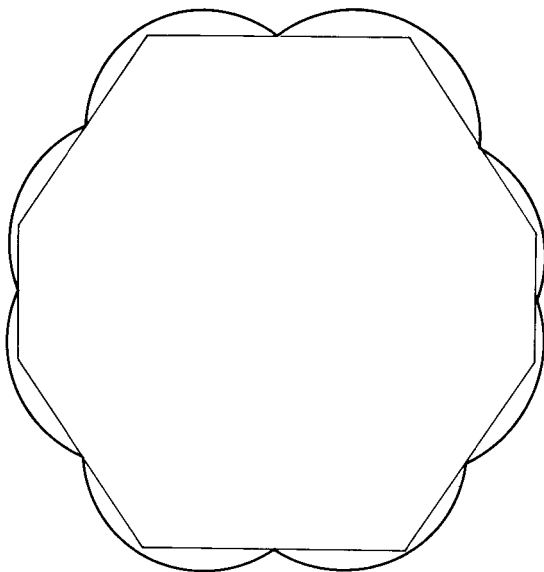


Fig. 1.5. A schematic γ -plot at elevated temperature. The Wulff construction for the equilibrium shape of a particle is also shown.

Mullins (1959) has shown that a very simple treatment using Bragg–Williams order–disorder theory predicts the surface melting type of behaviour. Gruber & Mullins (1967) have considered the disappearance of γ -plot cusps for low index plane surfaces, taking into account the configurational entropy of the surface, and similarly predict the occurrence of melting and confirm its lack of importance for the close-packed plane orientations below the melting point of the bulk solid.

1.6 **Equilibrium shape of a surface**

From a complete knowledge of the γ -plot for the interface between two phases it is possible to determine the equilibrium shape of the interface. The most general case is that of the equilibrium shape of a particle of one phase surrounded by the other phase. In the absence of external constraints the equilibrium shape will not be a function of which phase is the ‘particle’ and which is the surrounding phase. For instance, the equilibrium shape of a solid particle surrounded by its own vapour will be the same as that of a void in the solid. Experimentally, one might start with a very small spherical particle and observe the change in shape as the surface approaches equilibrium. In principle, any particles of any size will eventually achieve thermodynamic equilibrium and the same equilibrium shape, but in practice the time taken to achieve

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equilibrium is shortest for a small particle. Moreover, in a small particle the surface energy driving force will be large relative to other terms due to external constraints (such as gravity). Clearly, the total free surface energy of a particle, or any closed surface, is given as

$$G = \int \gamma(\mathbf{n}) \, dS, \quad (1.9)$$

where \mathbf{n} is the outward normal at some element of area on the surface dS , and equilibrium will finally be achieved when the shape corresponds to the minimum value of G . The construction which permits the equilibrium shape to be deduced from the γ -plot is originally due to Wulff (1901) and is normally referred to as Wulff's theorem or the Wulff construction. This states that if planes are drawn perpendicular to the radius vectors where they cut the γ -plot, then the inner envelope of these planes corresponds to the equilibrium shape. A construction of this type is shown superimposed on the γ -plot in fig. 1.5. Probably the most interesting feature of the equilibrium shape emerging from this is the presence of facets corresponding to some of the deepest cusps and therefore being of rather low index (close-packed plane) orientations. Thus a large number of orientations are not represented on the equilibrium surface as the portion of the γ -plot corresponding to these orientations falls outside the constructed equilibrium surface shape. Evidently, a crystal in equilibrium at absolute zero (could such a state be achieved) would have an entirely polygonal shape, being composed entirely of facets. At elevated temperatures this need not be true, however, because if the cusps which do produce facets are shallow, rounded regions may appear on the equilibrium shape. However, as long as some cusps remain in the γ -plot at least some facets will appear in the equilibrium shape. For the case of free solid surfaces, therefore, which were treated in the Burton, Cabrera and Frank analysis discussed in the previous section, some facets will be expected to remain on the equilibrium shape right up to the bulk melting point.

While equilibration over the overall shape of a particle, for the free solid surface at least, is an extremely slow process, the local equilibrium in a surface may be expected to occur in a much shorter time because of the smaller amount of mass transfer and shorter distances of transfer required to achieve the desired state. Further deductions can be made about the shape of such a surface from the γ -plot, for, if the surface has an orientation corresponding to a large surface free energy, it is evident that a breakdown into a hill-and-valley structure of lower free surface energy surfaces may be favourable, despite the higher surface area incurred by this change. It is this effect which leads to the so-called