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Some Theorems on the Free Energies of Crystal Surfaces

CONYERS HERRING
Bell Telephone Laboratories, Murray Hill, New Jersey

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Although the interpretation of experiments in such fields as the shapes of small particles and the thermal etching of surfaces usually involves problems of kinetics rather than mere equilibrium considerations, it is suggested that a knowledge of the relative free energies of different shapes or surface configurations may provide a useful perspective. This paper presents some theorems on these relative free energies which follow from the Wulff construction for the equilibrium shape of a small particle, and some relations between atomic models of crystal surfaces and the surface free energy function used in this construction. Equilibrium shapes of crystals and of noncrystalline anisotropic media are classified, and it is pointed out that the possibilities for crystals include smoothly rounded as well as sharp-cornered forms. The condition is formulated for thermodynamic stability of a flat crystal face with respect to formation of a hill-and-valley structure. A discussion is presented of the limitations on the applicability of the results imposed by the dependence of surface free energy on curvature; and it is concluded that these limitations are not likely to be serious for most real substances, though they are serious for certain idealized theoretical models.

I. INTRODUCTION

MANY fields of physics, chemistry, and metallurgy encounter the need for an understanding of the surface structures of crystals which have been subjected to various kinds of heat treatment. Examples of such fields include thermionic emission, sintering, and many problems in adsorption and catalysis. A complete understanding of surface structures will not be easy to achieve, however; the many experimental studies which have been conducted on "thermal etching" and related phenomena indicate that the processes involved are quite varied and complex.[1,2] In fact, it has long been recognized that the shapes of growing crystals, the structures of heated surfaces, etc., are in most cases determined by a competition between the rates of various mechanisms of transport, such as condensation, diffusion, chemical reaction rates, and that a complete understanding of such structures usually requires a detailed knowledge of these kinetic factors.[3] Nevertheless, one can expect in many cases to gain a valuable perspective on problems of crystal form and surface structure by investigating the surface free energies of the various possible configurations of the surface of a crystal. The cases in which surface free energy is important are, of course, those in which the dimensions of the crystal grains, or of the surface irregularities, are sufficiently small. In such cases the tendency of the crystal to lower its surface free energy is often the principal motivation for changes in surface structure which take place—as seems to be the case in sintering, for example—and under proper conditions one may even approach an equilibrium configuration of minimum free energy. The present paper will be concerned merely with this rather limited problem of the relative free energies of various shapes and surface structures of a crystal, with inclusion of a few results applicable to noncrystalline anisotropic phases, such as liquid crystals and tactoids.

The most obvious problem in this field is that of determining what shape a small crystal must assume if its surface free energy is to be a minimum for a given volume. The solution to this problem was stated by Wulff[4] almost half a century ago; and as Wulff's theorem will serve as a foundation for some of the arguments to be presented here, a brief description of it is in order. The surface free energy of any body is an integral of the form

$$\int \gamma(\mathbf{n})dS \tag{1}$$

extended over the surface of the body, where the specific surface free energy γ is, for anisotropic bodies, a function of the orientation of the unit outward normal $\mathbf{n}$ at each surface point. Let γ be plotted radially as a function of the direction of $\mathbf{n}$; for a crystalline body a two-dimensional cross section of this plot will look something like the outer curve in Fig. 1, with cusped minima in certain directions corresponding to surfaces of particularly simple structure. At each point of this polar plot construct a plane perpendicular to the radius vector at that point. Then the volume which can be reached from the origin without crossing any of the

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[1] For a brief survey of the problem of surface structure of metals with special emphasis on topics important to the field of thermionic emission, see C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949), Sect. II, 1 and II, 2 and especially Appendix III.

[2] A brief review of experimental work in this field has been given by R. Shuttleworth, Metallurgia **38**, 125 (1948).

[3] See, for example, K. Spangenberg, "Wachstum und Auflösung der Kristalle," in *Handwörterbuch der Naturwissenschaften* (Verlag Gustav Fischer, Jena, 1934), second edition, Vol. X.

[4] G. Wulff, Z. Krist. 34, 449 (1901). The first rigorous proof of Wulff's result seems to have been given by H. Liebmann, Z. Krist. **53**, 171 (1914); see also M. v. Laue, Z. Krist. **105**, 124 (1943). These proofs, although they leave no doubt that the result is true in general, are a little unsatisfying logically in that they prove merely that no polyhedron can be an equilibrium shape unless it is geometrically similar to the polyhedron obtained from application of the Wulff construction to the set of normal directions occurring for the sides of the polyhedron. However, A. Dinghas, Z. Krist. **105**, 304 (1944), has shown how an inequality due to Brunn and Minkowski can be used to prove directly that any shape differing from that given by the Wulff construction has a higher surface free energy than the latter. Although Dinghas considers only a special class of polyhedral shapes, his method is easily extended to arbitrary shapes, since the Brunn-Minkowski inequality is true for convex bodies in general.

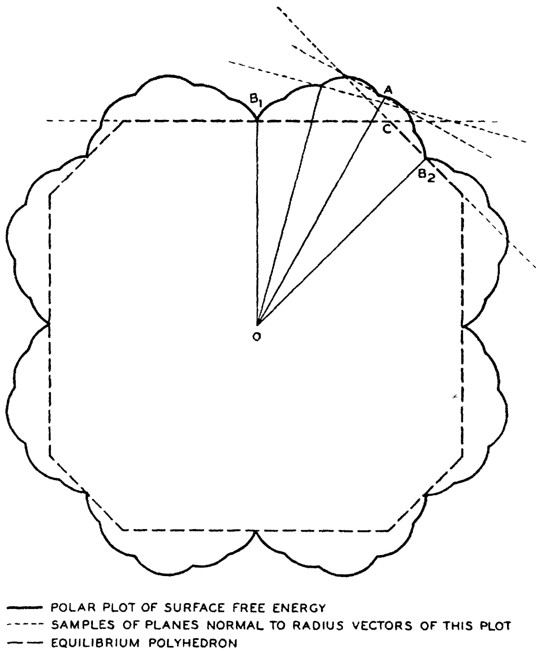

FIG. 1. Typical polar plot of surface free energy for a crystal and the Wulff construction based on it.

planes is, according to Wulff, geometrically similar to the ultimate equilibrium shape for the crystal; i.e., the shape which minimizes Eq. (1) for fixed volume. This construction is shown by the dashed line in the figure. The proofs of this theorem which have been given[4] have been formulated only for the case in which the equilibrium shape is a polyhedron, but they are easily generalized to apply to cases in which part or all of the equilibrium shape is bounded by smoothly curved surfaces.

This equilibrium shape is of direct practical interest only for very small crystals, since for a large crystal a significant alteration in shape can be achieved only by transporting a large number of atoms through a large distance, and the effort involved in doing this becomes very large in comparison with the decrease in Eq. (1) which rewards it. For large crystals it is of greater interest, therefore, to inquire how the free energies of neighboring configurations compare, even though none of these is at all close to the shape given by the Wulff construction. In Sec. II we therefore consider the question: when can the free energy of a plane surface be lowered by rearranging the atoms into hills and valleys of a size large compared with atomic dimensions but still small from the macroscopic standpoint?

Section III will be devoted to an investigation of the conditions under which the equilibrium shape can be bounded in part by continuously curved regions, or more generally, the conditions under which a continuously curved surface can be thermodynamically stable with respect to small distortions or roughenings.

In Sec. IV it will be shown that the often-used assumption that the atoms of a crystal interact attractively in pairs leads to a Wulff construction which has certain degenerate properties, so that conclusions based on this assumption may be qualitatively as well as quantitatively altered by slightly modifying the assumption. This will be illustrated in Sec. V by a discussion of the amount of rounding of edges and corners which is to be expected for surface structures in local thermodynamic equilibrium.

II. THERMODYNAMIC STABILITY OF A HILL-AND-VALLEY SURFACE STRUCTURE

To see under what circumstances it is possible to decrease the free energy of an initially flat surface by rearranging the atoms into hills and valleys, consider a polar plot of surface free energy such as that in Fig. 1. Let OA be the direction normal to the crystal surface in question. Consider any three other directions OB_1, OB_2, OB_3 (only the first two are shown in the plane of the drawing), having positive projections on OA. The planes normal to these three directions could form the sides of a hill-and-valley structure on a macroscopic surface normal to OA. The surface free energy of such a hill-and-valley structure would be, per unit area of the macroscopic surface,

$$\gamma_h = \gamma_1 f_1 + \gamma_2 f_2 + \gamma_3 f_3, \tag{2}$$

where γ_1, γ_2, γ_3 are the surface tensions of the three boundary planes just mentioned, and f_1, f_2, f_3 are the areas of surfaces of these three types in the hill-and-valley structure per unit projected area in the plane of the macroscopic surface. If we let $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$, $\boldsymbol{\sigma}_3$ be the unit normal vectors for the three boundary planes, the equations determining f_1, f_2, f_3 are

$$f_1\boldsymbol{\sigma}_1 + f_2\boldsymbol{\sigma}_2 + f_3\boldsymbol{\sigma}_3 = \boldsymbol{\sigma}, \tag{3}$$

where $\boldsymbol{\sigma}$ is the unit vector in the direction OA. Now if we let $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, $\boldsymbol{\tau}_3$ be the system reciprocal to $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$, $\boldsymbol{\sigma}_3$, i.e.,

$$\boldsymbol{\tau}_1\cdot\boldsymbol{\sigma}_1 = \boldsymbol{\tau}_2\cdot\boldsymbol{\sigma}_2 = \boldsymbol{\tau}_3\cdot\boldsymbol{\sigma}_3 = 1, \quad \boldsymbol{\tau}_i\cdot\boldsymbol{\tau}_j = 0 \quad (i \neq j),$$

Eq. (2) can be written

$$\gamma_h = (\gamma_1\boldsymbol{\tau}_1 + \gamma_2\boldsymbol{\tau}_2 + \gamma_3\boldsymbol{\tau}_3)\cdot\boldsymbol{\sigma}. \tag{4}$$

The vector in parentheses is, however, identical with the vector $\mathbf{c}$ which joints the origin to the corner C defined as the intersection of the three planes drawn normal to OB_1, OB_2, OB_3, respectively, at the points where these directions intersect the polar plot of γ. For

$$\mathbf{c}\cdot\boldsymbol{\sigma}_1 = \gamma_1, \quad \mathbf{c}\cdot\boldsymbol{\sigma}_2 = \gamma_2, \quad \mathbf{c}\cdot\boldsymbol{\sigma}_3 = \gamma_3,$$

and the vector in parentheses satisfies these equations. Thus, finally

$$\gamma_h = \mathbf{c}\cdot\boldsymbol{\sigma}, \tag{5}$$

i.e., the surface free energy of the hill-and-valley structure is represented by the length OM from the origin to the foot M of a perpendicular drawn from C to OA.

Thus, if there exists any set of directions OB_1, OB_2, OB_3 with positive projections on OA, such that M lies inside the polar plot of γ, an ideal crystal surface normal to OA will be thermodynamically unstable with respect to formation of some sort of hill-and-valley structure. The converse is also true: if no such set of directions exists, the ideal surface normal to OA will be stable. The possibility of more than three types of surface for the sides of the hill-and-valley structure does not impair this conclusion, since the free energy of any hypothetical structure with more than three types of hill side can always be lowered by eliminating all but the three most favorable types. Now the condition that M be inside the polar plot of γ is the same as the condition that C be inside the plane drawn normal to OA at the point of its intersection with the γ-plot. If there exists a set OB_1, OB_2, OB_3 for which this is the case, the plane normal to OA cannot occur as a boundary plane in the Wulff construction for the equilibrium shape, i.e., it can neither form a flat portion of the boundary nor be tangent to a continuously curved portion; conversely, if OA is included among the normals of the equilibrium shape, some such set OB_1, OB_2, OB_3 must exist. We therefore have the result: *If a given macroscopic surface of a crystal does not coincide in orientation with some portion of the boundary of the equilibrium shape, there will always exist a hill-and-valley structure which has a lower free energy than a flat surface, while if the given surface does occur in the equilibrium shape, no hill-and-valley structure can be more stable.*

The implications of this result depend very much on the nature of the equilibrium shape. If the equilibrium shape is a polyhedron, as has usually been assumed to be the case for crystals, then a crystal surface chosen with a random macroscopic orientation will almost always prefer to have a hill-and-valley structure. At the other extreme, if the equilibrium shape has no sharp corners at all, then surfaces of every orientation will prefer to remain smooth.

III. QUALITATIVE CHARACTERISTICS OF THE γ-PLOT AND THE EQUILIBRIUM SHAPE

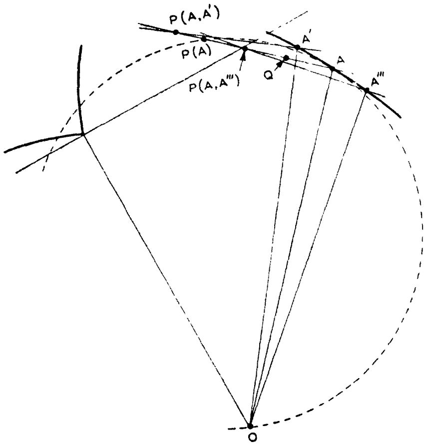

FIG. 2. Use of the tangent sphere to predict properties of the Wulff construction. The heavy curve shows two portions of the polar plot of surface free energy, and the dashed circle is a cross section of the sphere tangent to this plot at A and passing through the origin O.

Let us now consider under what conditions a given direction will occur among the surface normals of the equilibrium shape. In Fig. 2, let O be the origin of the Wulff diagram and OA a normal direction to be investigated. Let A' be another point of the γ-plot infinitesimally distant from A. The plane normal to OA at A and that normal to OA' at A' will intersect along a line through P; a third such plane, constructed on a line OA'' lying outside the plane of the drawing (not shown, of course) would intersect the other two planes at some point P_s. The figure has been drawn for the case in which P_s and P coincide; but we shall use different symbols for them, since P_s does not in general lie in the plane OAA' of the drawing. Now if A is a point in whose neighborhood the slope of the γ-plot varies continuously with direction, $P_s(A, A', A'')$ will approach a limiting position $P_s(A)$ as A' and A'' approach A. A sphere drawn with the origin and $P_s(A)$ as opposite ends of a diameter will be tangent to the γ-plot at A. If any point of the γ-plot, either in the neighborhood of A or in some more distant region, lies inside this sphere, $P_s(A)$ will lie outside the surface of the Wulff construction for the equilibrium shape; if the γ-plot is entirely outside the sphere, $P_s(A)$ will be on the periphery of the equilibrium shape. Since we are assuming the slope of the γ-plot to be continuous near A, no other point Q of the plane $AP(A)$ can be on the periphery of the equilibrium shape, for there can always be found an A''' in the neighborhood of A whose plane will pass inside Q. We therefore have the result: *If OA is a radius vector of the γ-plot in whose neighborhood the derivatives of γ are continuous, then a necessary and sufficient condition for the direction OA to occur among the normals of the equilibrium shape is that the γ-plot nowhere pass inside the sphere drawn through the origin and tangent to the γ-plot at A. When the γ-plot is outside this sphere at all points except A, all orientations in the neighborhood of OA will occur among the normals of the equilibrium shape; i.e., the latter will be continuously curved in the region where its normal has the direction OA.*

Combination of this result with that of the preceding Section gives the further conclusion: *A continuously curved surface with normals in the neighborhood of OA will be stable with respect to formation of a hill-and-valley structure if, and only if, the γ-plot nowhere passes inside the sphere through the origin and tangent at A.*

We consider next the conditions under which a plane region of finite area can occur as part of the boundary of the equilibrium shape. Since the position of the point $P_s(A)$, defined previously varies continuously with A (Fig. 2), except at points of the γ-plot where the derivatives of γ are discontinuous, it is clear that in order for the boundary of the equilibrium shape to consist in part of a finite area of a plane such as $AP(A)$ in Fig. 2, it is necessary that A be a cusp of the γ-plot. Extending this reasoning gives the result: *In order that the surface of the equilibrium shape have a flat portion of finite extent and with an orientation normal to a given vector OA of the γ-plot, it is necessary and sufficient that the γ-plot have a pointed cusp at A and simultaneously that there be some sphere through A and the origin which lies entirely inside the γ-plot. In order that the surface have a finite cylindrical portion with surface normals corresponding to a certain plane sector of the γ-plot, it is necessary and sufficient that the γ-plot have a knife-edge cusp for all directions in this sector, and simultaneously that for each point A of the cusp in this sector it be possible to draw a sphere through the origin, tangent to the knife-edge cusp at A, and lying entirely inside the γ-plot.*

These results provide a convenient tool for exploring the possible types of equilibrium shapes for various types of γ-plots. We shall consider first the case where γ and its derivatives are continuous for all directions. As we shall show presently, this case cannot occur for crystals, for which γ may be expected to have cusped minima in crystallographically simple directions; however, it may occur for liquid crystals and for the anisotropic colloid phases known as tactoids.[5] For this case there are clearly two possibilities:

(a) All directions occur among the normals to the equilibrium shape, so that there are no sharp edges or corners. This will occur if the sphere tangent at any point of the γ-plot always lies inside it, a condition which will obviously be fulfilled if the γ-plot is sufficiently close to a sphere.

(b) The equilibrium shape is bounded by a number of smoothly curved (not flat) surfaces which intersect in sharp edges. This includes all cases not falling under (a); photographs of tactoids[5] usually show shapes of this type.

As has just been mentioned, the γ-plot for a crystal may be expected to have cusps; and it can, in fact, be argued that at sufficiently low temperatures point cusps occur for all orientations whose Miller indices are rational, and knife-edge cusps for orientations any two of whose Miller indices are rational. The argument is similar to that used by Read and Shockley[6] to deduce the corresponding result for grain boundary energies, and it will be sketched only briefly here. We assume that when the Miller indices are rational, the surface structure of lowest energy will consist of atomic steps arranged in some sort of two-dimensional lattice structure. If the unit normal describing the orientation of the surface is changed infinitesimally, say from $\mathbf{n}$ to $(\mathbf{n}+\delta\mathbf{n})$, the arrangement of minimum energy will be the same two-dimensional lattice of steps as before, but with widely spaced lines along which the interval between steps is slightly greater or slightly less than in the original lattice. The density of these lines will be proportional to $\delta\mathbf{n}$; and when this density is low, the modification of the energy will be proportional to the density of lines, hence to $\delta\mathbf{n}$. A similar proportionality to $\delta\mathbf{n}$ will hold for the energy change when the normal is changed to $(\mathbf{n}-\delta\mathbf{n})$; but the coefficient will, in general, be different. The average of the specific surface energies for $(\mathbf{n}+\delta\mathbf{n})$ and $(\mathbf{n}-\delta\mathbf{n})$ will thus, in general, differ from that for $\mathbf{n}$ by an amount of order $\delta\mathbf{n}$, so that the γ-plot has a cusp for orientation $\mathbf{n}$. This cusp must point toward rather than away from the origin, since otherwise the step array assumed for orientation $\mathbf{n}$ would not be the arrangement of minimum energy.

This conclusion needs to be modified somewhat at the high temperatures at which most of the phenomena involving surface tension of crystals occur. For when the spacing between steps is large, as for say a (20, 1, 0) surface of a cubic crystal, thermal fluctuations in the positions of the steps may be sufficient to prevent their having any long-range order; in other words, the two-dimensional lattice of steps may "melt."[7] When this occurs, no cusp in the γ-plot is to be expected. When the spacing of steps is small—for example, a (210) surface—they may be expected to have a long-range order, and the considerations of the preceding paragraph should apply. The most reasonable form to assume for the γ-plot of a crystal at elevated temperature is, therefore, a plot which is smooth except in directions in which two or all of the Miller indices have the ratio of sufficiently small integers; in these directions cusps of the type mentioned in the preceding paragraph should occur.

Assuming the γ-plots of crystals to be of this form, we may use the italicized results above to classify the possibilities for crystals as follows:

(c) The equilibrium shape consists of a number of flat surfaces joined by rounded regions, with no sharp edges or corners. This will occur if the cusps are so mild that none of the tangent spheres passes outside the γ-plot.

(d) The equilibrium shape consists of flat surfaces and curved regions, with sharp edges.

(e) The equilibrium shape is a polyhedron. This will occur if the cusps are so pronounced that no tangent sphere can be drawn inside all the cusps.

Of the five cases we have enumerated, all except case (e) have been practically ignored in the literature.

IV. SPECIAL CASES WHICH LEAD TO A γ-PLOT COMPOUNDED OF PORTIONS OF SPHERES

It is clear from the results of the preceding section that a cusped γ-plot whose smooth regions are portions of spheres through the origin represents a transitional case

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[5] H. Zocher, Z. anorg. u. allgem. Chem. **147**, 91 (1925); J. Jochims, Kolloid-Z. **41**, 215 (1927); H. Zocher and K. Jacobsohn, Kolloid-Z. **41**, 220 (1927), Kolloid-Beihefte **28**, 167 (1929); W. Heller and W. Wojtewicz, Phys. Rev. (A) **75**, 343 (1949).

[6] W. T. Read and W. Shockley, Phys. Rev. **78**, 275 (1950).

[7] This "melting" is closely related to the existence of a critical temperature for surface fluctuations, a phenomenon which has been studied quantitatively by W. K. Burton and N. Cabrera, Disc. Faraday Soc. **5**, 33 (1949).

between case (e) (polyhedral equilibrium shape) and case (c) (smooth shape). For such a γ-plot all of the perpendicular planes erected on radius vectors of any one of the spherical regions pass through a common point. The principal object of this Section is to prove that a theoretical γ-plot of this sort is predicted by any model of a crystal based on the assumptions that the atoms interact attractively in pairs by means of forces of finite range and that the surface and interior lattice spacings are the same.

Let us assume the energy of a crystal relative to separated atoms to be

$$E=-\tfrac{1}{2}\sum_{i\neq j}\epsilon_{ij}=-\sum_{b}\nu_b\epsilon_b, \qquad (6)$$

where $\epsilon_{ij}=\epsilon_b$ is the negative interaction energy of atoms i and j, a function of the vector $\mathbf{b}$ connecting them, and ν_b is the number of pairs of atoms separated by the vector $\mathbf{b}$. For simplicity we assume, in the present treatment, that all atoms are alike; however, the analysis can be generalized to include at least some types of non-monatomic crystals. If the surface and interior lattice spacings are assumed to be the same, an ideal surface of the crystal normal to any unit vector $\mathbf{n}$ will have the same atomic arrangement as if one passed a plane normal to $\mathbf{n}$ through the middle of the lattice and removed the material on one side. If f_b is the number of interatomic vectors of type $\mathbf{b}$ per unit area of a plane normal to $\mathbf{b}$, the surface energy, as determined from the number of bonds cut, is

$$\gamma_n=\Sigma_b\,\epsilon_b f_b|\mathbf{n}\cdot\mathbf{b}|/b. \qquad (7)$$

If the interatomic forces have finite range, there will be a only finite number of $\mathbf{b}$'s for which $\epsilon_b\neq 0$, and the possible directions for $\mathbf{n}$ can be divided into pyramids within each of which none of the quantities $\mathbf{n}\cdot\mathbf{b}$ changes sign. Within any such pyramid p, therefore,

$$\gamma_n=\mathbf{n}\cdot\mathbf{s}_p, \qquad (8)$$

the vector $\mathbf{s}_p$ changing as we go from one pyramid to another. Thus, under the assumptions used, the locus of the end of the vector $\gamma_n\mathbf{n}$ is, within each pyramid, the surface of a sphere passing through the origin; the spheres change as we go from one pyramid to another.

Consider now a path on the surface of the γ-plot, passing from one of the pyramidal regions of solid angle, say p_1, to another p_2. As we follow this path, either the sphere going with p_2 will cut inside that going with p_1, as in (a) of Fig. 3, or it will cut outside as in (b). The former is impossible if all the ϵ_b are of the same sign (>0). For then all the terms in Eq. (7) are positive, so that the $\mathbf{s}_p$ in whose pyramid $\mathbf{n}$ lies gives a larger value of $\mathbf{n}\cdot\mathbf{s}_p$ than any other pyramid p'. Since for case (a) of Fig. 3 a vector $\mathbf{n}$ lying in p_1 has $\mathbf{n}\cdot\mathbf{s}_1<\mathbf{n}\cdot\mathbf{s}_2$, only cusps of the type shown in (b) can occur when all ϵ_b are >0. When some of the ϵ_b are <0, as for an ionic crystal, Eq. (8) may lead either to case (a) or to case (b). If it leads to case (a), the ideal crystal surface formed by cutting through the volume of the crystal along a plane cannot be stable, since, as was shown in the preceding section, the γ-plot cannot have outward-pointing cusps.

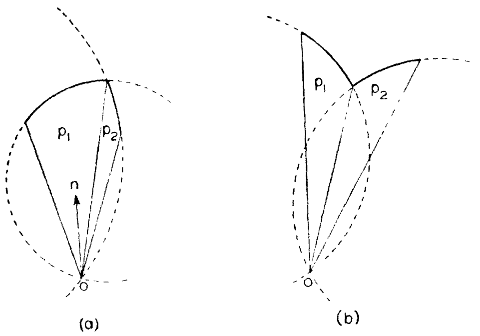

FIG. 3. Portions of the polar plot of the surface energy of an ideal crystal plane for a crystal model obeying Eq. (6). The heavy curves are portions of the polar plot, while the dashed curves are the continuations of the circles to which they belong.

The results just proved can be generalized a little. Consider a surface whose orientation differs from that of one of the simple crystallographic planes (*hkl*) by a fairly small angle θ, so that fairly widely spaced steps result. Instead of assuming that the atoms interact in pairs, we may assume merely that the energy of the surface in question is proportional to the projection of its area onto (*hkl*) plus a term proportional to the density of steps, i.e., that steps whose spacing exceeds a certain distance do not interact. This assumption, as is easily seen, leads to the prediction of the spherical form of Fig. 3 (b) for the γ-plot over the range of orientations to which the assumption applies.

Stranski and his collaborators[8,9] have carried out extensive investigations on the dependence of equilibrium forms and other properties of crystals on the range of the interatomic forces, using the assumption of attractive pair-wise interactions. From what has been said earlier in this Section, it is clear that this model, though useful as an aid in visualizing the physical mechanisms responsible for the surface structures of crystals, has rather special properties which real crystals, especially metallic ones, will not, in general, possess. One illustration of this fact is provided by the comparison of the energies of an atomically smooth surface and a hill-and-valley surface, the problem we have treated for the general case in Sec. II. Our Eq. (5), which has the same form as Eq. (8), implies that if a surface with macroscopic normal OA (Fig. 1) is made up of hills with sides normal to vectors OB_1, OB_2, OB_3 of the γ-plot, the macroscopic surface tension γ_h will,

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[8] This work has been published in a large number of papers of which we shall cite only a few: I. N. Stranski, Z. physik. Chem. **B11**, 342 (1931); I. N. Stranski and R. Kaischew, Z. Krist. **78**, 373 (1931), Z. physik. Chem. **B26**, 312 (1934); Ann. Physik **23**, 330 (1935); I. N. Stranski, Z. physik. Chem. **B38**, 451 (1938); I. N. Stranski and R. Suhrmann, Z. Krist. **105**, 481 (1944), Ann. Physik **1**, 153 (1947); I. N. Stranski, Disc. Faraday Soc. **5**, 13 (1949). See also the brief summary in reference 9.

[9] I. N. Stranski, Ber. deut. chem. Ges. **A72**, 141 (1939).

if plotted radially as a function of the direction of OA, lie on a portion of the sphere passing through the origin, B_1, B_2, and B_3. But if the assumptions of pair-wise interaction and uniform lattice spacing hold, and if B_1, B_2, and B_3 are so chosen that the γ-plot for atomically smooth surfaces has no cusps in the pyramid $OB_1B_2B_3$, then by Eq. (8) the γ-plot for smooth surfaces in this region will also be a sphere going through these four points. In other words, for any OA the smooth surface and the hill-and-valley surface will have the same energy. This equality will not, in general, hold if less restrictive assumptions regarding the interatomic forces are used. In the next Section, we shall discuss another problem with respect to which this model likewise behaves in an exceptional manner.

V. APPLICATION TO THE ROUNDING OF EDGES

In this Section, we shall consider the question of the sharpness of the edges and corners of an equilibrium polyhedron, or of a hill-and-valley surface formed by thermal etching. The present discussion will be limited to cases in which the Wulff construction predicts ideally sharp edges, i.e., cases (b), (d), and (e) of Sec. III. Moreover, since this paper is concerned with the phenomenological rather than the atomistic approach to crystal surfaces, we shall be able to treat only those cases (if such exist) in which the radius of curvature of the edges and corners is fairly large compared with atomic dimensions; these are, of course, the cases for which the departure from ideal sharpness is most likely to be detectable experimentally.

When the minimum radius of curvature is large, it is tempting to retain the expression (1) for the surface free energy of the crystal, taking account of the curved edges by allowing γ to depend on the radius of curvature ρ of the surface, e.g., by setting

$$\gamma(\mathbf{n},\rho)=\gamma_0(\mathbf{n})+[\gamma_1(\mathbf{n})/\rho]+[\gamma_2(\mathbf{n})/\rho^2]\cdots. \tag{9}$$

For simplicity we shall consider only an edge where the surface contour is cylindrical, so that only one radius of curvature need be considered. To make an equation of the form of Eq. (9) significant it is, of course, necessary that the position of the mathematical surface, by which the crystal surface is idealized, be defined accurately at each point. For a crystal a definition of sufficient accuracy is that of Gibbs,[10] which places the surface in such a position that, for any cylinder bounded by an element of the surface, the normals erected around its boundary, and a closing surface in the deep interior, the mass within the cylinder equals its volume times the interior density. This definition locates a plane surface precisely and locates a curved surface to within an uncertainty in the normal direction of the order of a^2/ρ, where a is the lattice constant; this accuracy is sufficient for our purpose.

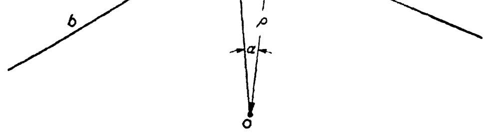

FIG. 4. Cross section of the surface of a crystal near where two flat faces a and b meet in a rounded edge.

Consider the rounded edge, shown in Fig. 4, connecting two flat surfaces a and b which make an angle θ with each other. Although this edge will not, in general, have a circular cross section, for simplicity we shall consider it constrained to be circular, so that ρ is constant over it. We wish to compare the free energies of the various possible surfaces of this form which one can obtain by choosing different values for ρ. When $\rho=0$, the surface is the sharp-edged one ACB which minimizes $\int\gamma_0 dS$ but makes the higher terms of Eq. (9) infinite; when ρ is very large, the higher terms of Eq. (9) are negligible and $\int\gamma_0 dS$ increases with increasing ρ. The explicit expression for $\int\gamma dS$ is easily written down if faces a and b have an extension $\gg\rho$, since, for this case, only a negligible outward displacement of faces a and b is required to keep the volume of the crystal constant when ρ is changed. Supposing planes a and b fixed, we have, for a length L normal to the plane of the figure,

$$(1/L)\int\gamma_0 dS$$
$$=\text{const}-(\gamma_{0a}+\gamma_{0b})\rho\tan(\theta/2)+\langle\gamma_0\rangle_{\text{Av}}\rho\theta, \tag{10}$$

$$(1/L)\int[(\gamma_1/\rho)+(\gamma_2/\rho^2)]dS=\langle\gamma_1\rangle_{\text{Av}}\theta+\langle\gamma_2\rangle_{\text{Av}}\theta/\rho, \tag{11}$$

where $\langle\gamma_0\rangle_{\text{Av}}$, $\langle\gamma_1\rangle_{\text{Av}}$, $\langle\gamma_2\rangle_{\text{Av}}$ are averages over the range $-\theta/2$ to $\theta/2$ of the angle α of Fig. 4. The sum of Eqs. (10) and (11) is a minimum with respect to ρ when

$$\rho^2=\langle\gamma_2\rangle_{\text{Av}}\theta/[\langle\gamma_0\rangle_{\text{Av}}\theta-(\gamma_{0a}+\gamma_{0b})\tan(\theta/2)]. \tag{12}$$

Whenever this equation gives a $\rho\gg$ the lattice constant, it should describe fairly correctly the amount of rounding which an edge of the equilibrium shape will have.

The denominator of Eq. (12) has a simple geometrical interpretation in terms of the polar plot of surface free energy, an interpretation which, though valid for any γ_{0a} and γ_{0b}, is most easily demonstrated for the case where $\gamma_{0a}=\gamma_{0b}$. This denominator can be written

$$\int_{-\theta/2}^{\theta/2}[\gamma_0-\tfrac{1}{2}(\gamma_{0a}+\gamma_{0b})\sec(\theta/2)\cos\alpha]d\alpha. \tag{13}$$

When $\gamma_{0a}=\gamma_{0b}$, the coefficient of $\cos\alpha$ in the integrand is just the distance from the origin to the edge C of the Wulff construction in Fig. 5. The whole integrand is, therefore, the distance NM, where $ON=\gamma_0(\alpha)$, and M

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[10] J. W. Gibbs, *Collected Works* (Longmans, Green, and Company, New York, 1928), p. 314.

is the intersection of ON with the sphere having OC as a diameter. The integral Eq. (13), which is the denominator of Eq. (12), is, therefore, essentially proportional to the area of the shaded region, being an integral over this region in which each element of area is given a weight inversely proportional to its distance from the origin. Thus, the more nearly this portion of the γ-plot approaches the dotted sphere, the larger will be the equilibrium radius of curvature ρ of the edge of the crystal. The theoretical model considered in the preceding Section, which assumes pair-wise attractive interactions and uniform lattice spacing, therefore predicts a very large value of ρ for the edges of the equilibrium form, this value being limited only by the fact that the size of the specimen is finite rather than infinite as we have assumed in deriving Eq. (12). Stranski,[9] using an atomistic argument based on this model, has already pointed out that ρ becomes infinite as the size of the specimen is increased; the new feature of the calculation of Eq. (12) is that it allows us to estimate ρ when the assumptions of this model are not fulfilled.

At the present time, numerical estimates must, of course, be very crude, since we can only guess at $\langle\gamma_2\rangle_{\mathrm{Av}}$. A reasonable guess would be $\langle\gamma_2\rangle_{\mathrm{Av}}\sim f\langle\gamma_0\rangle_{\mathrm{Av}}a^2$, where a is the lattice constant, and f is a quantity of the order of a fraction of unity. Equation (12) then gives

$$\rho/a\sim(2fA/\Delta A)^{\frac{1}{2}}, \tag{14}$$

where A is the area of the section of the γ-plot of Fig. 5 between the normals to a and b, and ΔA is the shaded area. It is clear from this that the γ-plot must be very close indeed to the sphere before ρ becomes larger than 10 or 20 atom spacings. It does not seem likely that the special models, referred to in the preceding paragraph and in Sec. IV, can be sufficiently nearly valid for any metals for this to occur; and we accordingly conclude that, for metals for which case (e) of Sec. III holds, the edges and corners of the equilibrium shape will be sharp to within at most a few tens of atom spacings. When case (d) or case (c) obtains, part or all of the equilibrium shape will be smoothly rounded, and reasoning similar to that just given suggests that for specimens of observable size the amount of rounding will correspond fairly closely to that demanded by the Wulff construction without any further refinements.

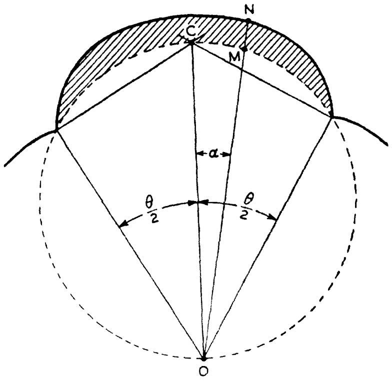

FIG. 5. Geometrical significance of the denominator of Eq. (12). The heavy curve is the polar plot of surface free energy with origin at O, and the dashed curve is a section of a sphere.

An example to which these conclusions can be applied is provided by the sharp points of tungsten and other metals which have been used in field emission studies.[11] These points, of the order of a micron or less in diameter, appear to revert to a particular standard shape when heated to temperatures of the order of half the melting temperature, this shape being a smoothly rounded one with, perhaps, a few flat regions in the crystallographically simplest directions. For tungsten, at least, there is other evidence, summarized in reference 1, which suggests that the equilibrium shape for a larger specimen is polyhedral or almost so. Since the arguments just given are unfavorable to the hypothesis that the observed rounding is due to the dependence of surface tension on curvature, we must conclude either that the equilibrium shape determined by the Wulff construction is not polyhedral after all but of the smoothly rounded type (c), or else that the standard shape of the field emission points is not an equilibrium shape but a quasi-steady configuration determined by some continuing transport process.

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[11] A review has been given by R. O. Jenkins, Repts. Prog. Phys. **9**, 177 (1943). See also E. W. Müller, Z. Physik **120**, 270 (1943); **126**, 642 (1949).