Title
THE EQUILIBRIUM SHAPES OF CRYSTALS AND OF CAVITIES IN CRYSTALS

Author
Searcy, A.W.

Publication Date
1982-07-01

LBL-14716 c.2
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to Surface Science

THE EQUILIBRIUM SHAPES OF CRYSTALS AND OF CAVITIES IN CRYSTALS

Alan W. Searcy

July 1982

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL-14716

The Equilibrium Shapes of Crystals and of Cavities in Crystals

Alan W. Searcy

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Materials Science and Mineral Engineering
University of California, Berkeley CA 94720

July 1982

Abstract: Surface free energies are assumed to be the sum of the excess free energies of bonding of molecules in or near the surface, and the stable form of a crystal or cavity is assumed to be the form that makes the sum of these excess free energies a minimum. When only plane surfaces are allowed, this model predicts the same shapes for crystals as an equation of Wulff, which is based on the macroscopic thermodynamic relation of Gibbs. The new model explains rounding of edges and corners which are not allowed by the Wulff relation, and predicts that surfaces of quasispherical equilibrium forms may have anisotropic surface free energies. The microscopic model is shown to provide a useful framework for analysis of whether unstable crystal or cavity shapes will evolve into stable or metastable forms. Some crystals and cavities that have been assumed to have equilibrium shapes may have metastable shapes, and others certainly do.

I. Introduction

Gibbs [1], and independently Curie [2], derived as the condition which determines equilibrium shapes of crystals

$$\Sigma_i \sigma_i A_i \text{ is a minimum,} \tag{1}$$

where σ_i is the specific surface free energy per unit area of crystal face i and A_i is its area. Wulff [3] first recognized that Eq. (1) implies that the facets of crystals or of cavities in crystals should obey the relation

$$\sigma_i/h_i = \sigma_j/h_j = \ldots \tag{2}$$

where, h_i is the distance from a common center drawn normal to crystal or cavity facet i.

Equation (1) describes the minimum work of surface formation derived from macroscopic thermodynamics and, therefore, (1) and (2) both appear almost self-evidently correct. But under conditions that favor equilibrium, cavities in metals are reported to be bounded by faceted, low-index surfaces [4,5]. In contrast, exterior surfaces of high-purity metal crystals often show little or no faceting [6,7].

The difference is usually regarded as reflecting experimental error in one or the other kind of experiment. It has been suggested, for example, that the faceting of cavities may not be an equilibrium property [8]. But annealing causes cavities formed by inert gas ion bombardment of metal foils to evolve from spherical to faceted shapes [6,7]. This evidence that these faceted cavities are more stable than rounded ones cannot be dismissed.

The fault for the apparent discrepancy between shapes of crystals and cavities may lie partly in the theory. Gibbs' proof was developed from macroscopic thermodynamics specifically for faceted crystals. It is shown in the next section of this paper that interpretations which have been given of rounded crystal surfaces in terms of Eq. (2) may not adequately explain particle properties. Then it is shown that if the free energy of a crystal surface is viewed as the sum of the excess free energies of those molecules of the crystal which are in or near the surface, the condition found for equilibrium is equivalent to Eq. (1) as long as rounding of surfaces is arbitrarily excluded. But the microscopic model shows that rounded surfaces need not obey Eq. (2).

In a discussion section, the microscopic model is shown to imply that metastable shapes are likely often to be produced and that some presumed equilibrium shapes of crystals and cavities probably are metastable forms. An accepted determination of the relative temperature dependences of surface tensions of different facets of cavity surfaces is shown to be questionable.

II. Theory

A defect in the macroscopic model is that it provides no means of describing separately the thermodynamic behavior of molecules which are at corners or edges of surface planes. Edge and corner atoms are less tightly bonded than molecules in other parts of a surface. In consequence, a rounding of edges and corners that is not predicted by Eq. (2) might be expected [9]. Herring [10] addressed this problem by assuming that, in the vicinity of an edge, the surface tension can be expressed as a series formed of constants multiplied by the radius of curvature to the 0, -1, -2, ... powers. He then sought values for the constants and radius of curvature that are plausible and that would be consistent with Gibbs' fundamental relation, Eq. (1).

From his analysis Herring concluded that when the Wulff construction predicts faceted crystals, rounding of "at most a few tens of atom spacings" can occur, and that when the Wulff construction predicts that all or part of the equilibrium shape will be smoothly rounded, "for a specimen of observable size the amount of rounding will correspond fairly closely to that demanded by the Wulff construction without any further refinements."

Herring applied these deductions to interpret the observation that metal tips which have been used in field emission studies approach smoothly rounded shapes with perhaps a few flat regions in the crystallographically simplest directions. He concluded that either anisotropy of surface tensions must be low enough to give a Wulff construction of the smoothly rounded type, or that the rounded shape of the field emission tips is not an equilibrium one.

Careful efforts made subsequent to Herring's analysis to establish equilibrium conditions in tips of field emitters continue to yield essentially hemispherical forms [11,12]. Drecksler and Nicholas [13] have calculated theoretical equilibrium shapes using Morse or Mie potentials that are in excellent agreement with experimental observation when constants are used that yield surface energies of only slight directional anisotropy. Consequently, most investigators would probably now accept Herring's first suggested interpretation--that the tip shapes reflect an equilibrium consistent with Wulff's analysis.

Direct observations of diffusion in the adsorption layers of field emitter tips, however, show substantial dependence on surface orientation [14] and suggest, therefore, that adsorption energies vary substantially with surface orientation; such variations imply that the bonding energies of atoms in the surface layer also vary substantially with orientation.

To develop a thermodynamic model that may be in better accord with molecular behavior in and on crystal surfaces, a single component or pseudo-single component crystal is here assumed to have a free energy of formation from its constituent molecules that is an additive function of the free energies of bonding of each molecule to other molecules, whether next- or more distant neighbors. The crystal is in its most stable form when its constituent molecules are arranged in whatever way makes its total surface free energy a minimum. A crystal or cavity that is bounded only by plane surfaces, i, j, ..., is considered first.

The excess free energy of molecules in the outermost layer of the i surface over molecules in the bulk crystal is G_{i1a}, G_{i1b}, ... and in the next outermost layer is G_{i2c}, G_{i2d}, ..., where a and b, for example, identify molecules of the layer with different excess free energies. The i surface is thus considered to include those subsurface layers in which, because of the presence of the surface, average molecular free energies are raised above the free energies of molecules in the bulk by some arbitrarily small fraction of kT, where k is the Boltzmann constant. Molecules at edges between crystal surfaces and molecules near edges have free energies G_{ij1e}, G_{ij1f}, G_{ij2g}, ..., where the first two subscripts identify the surface planes to which the edge molecules belong, the number identifies the layer, and the last subscript identifies possible different excess free energies for molecules of the same edge and layer.

An approximation in Eq. (1) is that the free energy of formation of edges or corners is simply the sum of the free energies of formation of an equivalent area of surfaces of the planes bounded by the edges or corners. When this approximation is adopted, G_{ijle}, for example, is equal to $G_{ila} + G_{jla}$; that is, the free energy of edge and corner mlolecules can be assigned to the surfaces which the edge and corner molecules terminate. Then when n_i is defined as the sum of all molecules with excess free energies because of the presence of surface i

$$\Sigma_i n_i G_i = \Sigma_i \sigma_i A_i, \tag{3}$$

and for crystals which are restricted to having only plane surfaces the microscopic model is equivalent to the macroscopic model.

The assumption that only planar crystal faces are allowed can be dropped, and the most stable form of a crystal or cavity in a crystal is then that for which

$$\Sigma_i n_i G_i \text{ is a minimum,} \tag{4}$$

where the summation is now understood to be over all molecules in which the free energy is raised over that of molecules in the bulk by the presence of exterior or cavity surfaces, whether planar or curved.

Equation (4) allows rounded corners and edges to be treated in the same framework as curved surfaces; within the overall limit set by Eq. (4) there is no restriction set on their radii of curvature, and a surface with essentially equal radii of curvature over two solid angles from a common center does not necessarily have the same specific surface free energy over those two solid angles.

Application of Eq. (4) can be illustrated by comparing theoretical relative stabilities at 0°K of a facetted face centered cubic (fcc) crystal to a spherical fcc crystal of the same volume. The expected facets are on 100 and 111 planes. For present purposes, the excess atomic enthalpy H_i for each atom can be assumed to be proportional to the difference between the number of neighbor atoms in the bulk crystal and the number of neighbors N_i for atom i, that is, $H_i = k(12 - N_i)$. This assumption makes the ratio of surface enthalpies in 100 surfaces to enthalpies in 111 surfaces, $H_{100}n_{100}/H_{111}n_{111} = (4 \cos 60°)/3 = 1.15$, where $n_{100} = n_{111} \cos 60°$ because of the lower packing density in 100 planes.

The Wulff relation makes 1.15 the ratio of lengths of the normals from a common center to the 100 and 111 faces of a cubo-octahedron. Equation (4) asserts that a sphere of the same volume will have an equal total surface free energy when

$$\frac{\sigma_{ave}}{r} = \frac{\sigma_{111}}{h_{111}} = \frac{\sigma_{100}}{h_{100}} \qquad (5)$$

where σ_{ave} is the average surface free energy per unit area over the sphere and r is its radius. For equal volumes, $r = 0.985\ h_{100}$, and therefore a quasispherical crystal could be more stable than the unrounded polyhedral form despite having sub-areas of surface with unit surface free energies more than 15% greater than areas formed of 111 surfaces. Equation (2) would be consistent with quasispherical forms only if σ values vary no more than a few percent [13].

Data of Van Hardeveld and Hartog [15] can be used to show that essentially spherical crystals with surfaces of varying local surface free energies can have low total free energies. As part of a statistical study of adsorption sites on metal crystals, they calculated the number of nearest neighbors for all the surface atoms of a number of polyhedral crystals and of a quasispherical crystal, all of which could be formed from 683 atoms packed in an fcc structure. The 683 atoms of the quasispherical crystal are placed on all lattice sites lying within a sphere with a radius equal to 4.9 times the atomic diameter and with its center at a lattice site. A so-called rearranged sphere of a larger number of nearest neighbors per atom is formed by movement of eight atoms of the quasispherical crystal to vacant lattice sites with five neighboring occupied sites. The polyhedral shapes included by Van Hardevelt and Hartog considered several truncated octahedra, for which the surfaces are 111 and 100 surfaces, but the faces are not formed at the distances required by the Wulff construction. Evidently a symmetrical cubo-octahedron cannot be formed of 683 atoms.

Crystals formed of 683 atoms are so small--if formed of gold atoms, only $\sim$3 nm in cross section--that a significant fraction of the atoms of the polyhedral crystals are in edge or corner sites, consequently it is not surprising to calculate that the unsymmetrical pair-bonded polyhedra have higher surface enthalpies than does the rearranged sphere. But the fact that the average number of neighbors per surface atom in the rearranged sphere is 8.1, compared to 9 in 111 surfaces and 8 in 100 surfaces suggests that spherical particles can be stable, despite markedly anisotropic bonding, for larger crystals as well.

III. Discussion

The microthermodynamic model that leads to Eq. (4) and the macrothermodynamic model that leads to Eq. (2) are both straightforward derivations based on the same initial assumption. The two approaches might have been expected to lead to identical results, but the microthermodynamic analysis suggests that particle equilibrium may be achieved by molecular packing arrangements that violate Eq. (2). In particular, Eq. (2) allows quasispherical crystals to be formed only if the specific surface free energies in each solid angle of the crystal are nearly identical, while the microthermodynamic model allows greater surface free energy variations and allows corners and edges to take forms not allowed by Eq. (2).

That crystal forms which do not obey the Wulff relation can be stable is demonstrable by model calculations of the kind illustrated by use of the Van Hardeveld and Hartog data. Experimental demonstrations that such forms are stable is more difficult. The experimental evidence for substantial anisotropy in surface free energies which was presented above is qualitative. It would be desirable to study the surface anisotropy of field emitter tips by excitation methods that provide measurements of individual bond energies.

Equation (2) cannot be used to describe metastable crystal or cavity shapes. The microthermodynamic model provides a useful framework for understanding their formation and persistence. The difference in stability between two forms of a crystal or cavity are given by $G_{tb} - G_{ta}$, where G_{tb} and G_{ta} are total surface free energies for the crystal or cavity in forms b and a. Provided the free energy change is negative, its magnitude plays no direct role in determining whether the transformation will actually take place. The driving force for shape changes are instead differences in free energies in sub-areas of the existing surface at any given time, say sub-area α and β.

Because shape changes are never directly driven by the free energy difference between initial and final forms, structure-sensitive kinetic factors can often play major roles in shape evolution. If, for example, an initially spherical particle or cavity is unstable relative to a symmetrical polyhedral form, it is almost certainly also unstable relative to a variety of other forms with the same facets, but with relative areas that violate both Eq. (2) and Eq. (4). It can be expected that dislocations usually provide the fastest path for matter transport between sub-areas of a crystal or cavity surface, as they do in crystal vapor phase transport [16], because vaporization and surface diffusion are closely related processes [17]. A statistical fluctuation in dislocation densities, which have been shown to be important in cavity migration [18], can cause unsymmetrical facet development.

When a particle or cavity has reached a shape that is bounded by surfaces that approximate those of the most stable form, further evolution may become too slow to observe in experimentally practicable times. Experimental observations should be evaluated with this expectation in mind. Perhaps, for example, while transfer of a monolayer from one surface to another would reduce the total free energy, transfer of one-half a monolayer would produce an intermediate form of higher total free energy. This kind of possibility could be tested by calculations of the kind made by Van Hardeveld and Hartog.

This analysis suggests that greater caution should be exercised in accepting persistent crystal forms as stable, or as consequences of impurities. For example, the observation [6] that initially spherical particles of gold, silver, and copper are transformed on annealing to partially rounded polyhedral shapes is definitive evidence that those latter shapes are more stable than the initial spheres. But, for gold particles annealed at 1000°C in dry H_2, contamination by the furnace atmosphere is unlikely, and observations of minor imperfections in "nearly all" profiles may not indicate nonuniform contamination, as suggested by Sundquist [6], but rather the development of metastable shapes that cannot further evolve.

The assumption [6] that the relative specific surface free energies of 100 and 111 surfaces can be deduced from relative areas of facets in partially faceted crystals may not be warranted, even if one accepts Eq. (2), because the relative areas may simply be those that evolve by the kinetically most favorable process.

Development of rounded crystals from the partially rounded polygonal crystals when silver is heated through 775°C and copper is heated somewhat above 1000°C must mean that the entropy of transition to the essentially spherical crystals is positive, as noted by Sundquist [7]. The positive entropy may not be a consequence of surface roughening as Sundquist suggested, however. It seems likely that the particles observed by Sundquist have atomically smooth surfaces like those of field emitter tips. If so, the positive entropy of rounding is not due to surface roughening of the kind considered in the model of Burton, Cabrera, and Frank [19].

Because polyganized cavities in magnesium, cadmium, and zinc evolve from initially spherical cavities [4,5], the polygonal forms must be more stable than spherical ones. Observations that the ratio of cavity dimensions along the c axis to dimensions along the a axis of the hexagonal cavities show wide statistical fluctuations--for zinc by a factor of two--constitute clear evidence that the cavities commonly approach metastable shapes. The assumption [20] that relative surface entropies can be calculated from the temperature dependence of the average axial ratios must be questioned; the average depends on unevaluated kinetic variations.

The thermodynamic properties of any system can always be described without any knowledge of the internal composition or structure. But to many scientists the attraction of chemical thermodynamics lies in using our understanding of structure and bonding to predict thermodynamic behavior under conditions that have not been directly studied. The most important conclusion from this study is that an analysis of the structure and bonding in surfaces can provide new insights in surface thermodynamics. Papers are in preparation on the utilization of this approach to analysis of particle-vapor equilibria and of multilayer adsorption equilibria.

Acknowledgments

Valuable advice on this manuscript was provided by John M. Prausnitz, David J. Meschi, and Dario Beruto. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. J.W. Gibbs, The Collected Works, Vol.1. Thermodynamics (Longmans, Green, & Co., New York 1931) p. 320.
2. P. Curie, Bull. Soc. Min. de France 8 (1885) 145.
3. G. Wulff, Z. Krist. 34 (1901) 449.
4. W.A. Miller, G.J.C. Carpenter, and G.A. Chadwick, Phil. Mag. 19 (1969) 305.
5. H.O.K. Kirchner and G.A. Chadwick, Phil. Mag. 20 (1969) 405.
6. B.E. Sundquist, Acta Metall. 12 (1964) 67.
7. B.E. Sundquist, Acta Metall. 12 (1964) 585.
8. J. Friedel, Ann. Phys. 1 (1976) 257.
9. C. Herring and M.H. Nichols, Rev. Mod. Phys. 21 (1949) 185.
10. C. Herring, Phys. Rev. 82 (1951) 87.
11. A. Muller and M. Drechsler, Surf. Sci. 13 (1969) 471.
12. E.W. Muller in Chemistry and Physics of Solid Surfaces, Vol. 1 (Eds. R. Vansalow and S.Y. Tong, CRC Press, Cleveland OH 1977) p.1.
13. M. Drechsler and J.F. Nicholas, J. Phys. Chem. Solids 28 (1967) 2609.
14. H.P. Bonzel in Chemistry and Physics of Solid Surfaces, Vol. 1 (Eds. R. Vanslow and S.Y. Tong, CRC Press, Cleveland OH 1977) p.87.
15. R. Van Hardeveld and F. Hartog, Surf. Sci. 15 (1969) 189.
16. G.M. Rosenblatt in Heterogeneous Kinetics at Elevated Surfaces, Eds. D.R. Belton and W.R. Worrell (Plenum Press, New York, 1970) p.38.
17. A.W. Searcy and D. Beruto, J. Phys. Chem. 78 (1974) 1298.
18. P.J. Lemaire and H.K. Bowen, J. Am. Ceram. Soc. 65 (1982) 49.

19. W.K. Burton, N. Cabrera, and F.C. Frank, Trans. Roy. Soc. (London) A243 (1951) 299.

20. H.O.K. Kirchner and G.A. Chadwick, Phil. Mag. 22 (1970) 449.