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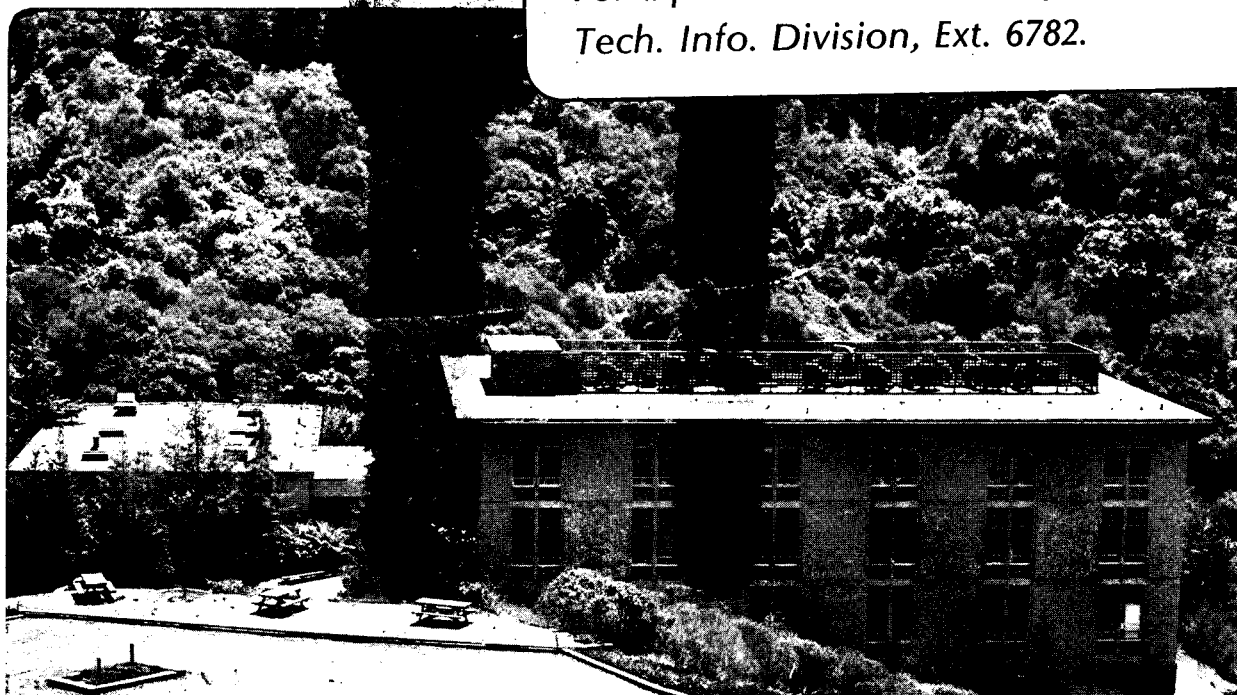## UNIVERSITY OF CALIFORNIA

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THE INFLUENCE OF MOLECULAR MOTIONS ON THE
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The Influence of Molecular Motions on the Stabilities
and Shapes of Solid Particles

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## Abstract

A conjecture of Gibbs, that the relative weakness of bonds at crystal
edges and corners would cause rounding which is not predicted by his
thermodynamic expression for stable crystal shapes, is evaluated in two
ways.  First, the vacancy distribution necessary for dynamic equilibrium
between adjacent crystal rows or layers of different bond energies is
derived.  Then it is shown that minimization of the total free energy of
two parts of a crystal with respect to their total vacancy concentration
leads to the same vacancy distribution.  Generalization of these results
shows that the stabilities of particles which have a fixed number of
sites are greatest when vacancies are so distributed as to equalize
molecular fluxes between every pair of regions of different bonding
energies.  Rounding will occur when the mole fractions of vacancies
required at corners and edges to maintain the molecular flux balance
approach unity.

The equilibrium shapes of particles or of cavities in particles were shown independently by Gibbs[1] and by Curie[2] to be the shapes given by the requirement that

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

where $\sigma_i$ is defined by Gibbs in this context as the work of formation of surface i and $A_i$ is the corresponding surface area. But in a footnote Gibbs pointed out that the predictions of Eq. (1) are probably inexact. He wrote:

"Since the molecules at the corners and edges of a perfect crystal would be less firmly held in their places than those in the middle of a side, we may suppose that when the condition of theoretical equilibrium (665) is satisfied several of the outermost layers of molecules on each side of the crystal are incomplete toward the edges."[1]

This problem of edge and corner rounding was discussed by Stranske and his coworkers.[3] Herring[4] attacked it by evaluating the rounding that would result if the specific surface free energies near edges over an assumed uniform radius of curvature at the edge is a plausible function of the specific surface free energies of the surfaces that meet at the edge. From this model, Herring concluded that, when the Wulff construction[5]--which is a direct consequence of relation (1)--predicts faceted crystals, for metals 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 specimens of observable size, the amount of rounding will correspond fairly closely to that demanded by the Wulff construction without any further refinements."

In the present paper a thermodynamic relation is derived that provides a quantitative description of the influence of molecular motions on the stabilities of crystalline particles. The condition for internal particle equilibrium is first derived from kinetic expressions for the fluxes between adjacent regions of the crystal. The same condition is again derived by minimizing the total particle free energy with respect to the distribution of vacancies among subregions of the crystal.

## Theory

At constant temperature, pressure, and number of molecules of the single component of the particle, relation (1) is equivalent to the requirement that the total Gibbs free energy of formation of the surface from a condensed phase of fixed free energy content per molecule $G_b$ be a minimum.[6,7] When free energies of the particle are viewed as the sum of the free energies of its molecules, relation (1) can be replaced by

$$\Sigma \, n_i (G_i - G_b) \text{ is a minimum,} \qquad (2)$$

where $n_i$ is the number of molecules in any collection of the same molecular free energy $G_i$ and $\Sigma \, n_i$ is the total number of molecules in the particle. The free energies of the molecules in corners, edges, and

the outermost molecular layer of each surface differ from each other, and successive molecular layers near the surface may have free energies enough greater than $G_b$ to require separate terms in the summation. Equation (2) has been evaluated at 0 K for face-centered cubic crystals of a variety of shapes using a 6-12 Leonard Jones potential.[7]

Above 0 K, each collection of molecules in a crystal will have vacant lattice sites. If the collections are each equilibrated independently, the free energy of $n_i$ molecules distributed with $n_{vi}$ vacancies on $n_i + n_{vi}$ sites is

$$\Sigma n_i G_i = \Sigma (n_i G^t_i + n_i kT \ell n X_i + n_{vi} G^t_{vi} + n_{vi} kT \ell n X_{vi}), \quad (3)$$

where the superscript t's indicate thermal free energies, $X_i$ is the mole fraction of the i sites occupied by molecules, and $X_{vi}$ is the mole fraction of vacant i sites.[8] The sum of the last two terms is zero when the collections are separately equilibrated and Eq. (2) becomes a summation over i of the first two terms of Eq. (3). But we can show that the vacancy concentrations implied by Eq. (3) are inconsistent with the vacancy concentrations required if, for example, at equilibrium the molecular flux from i to j must be equal to the flux from j to i.

Consider the fluxes that pass between the collection $n'_i$ and $n'_j$, where the primes identify subsets of molecules that form adjacent planes parallel to a surface or adjacent rows parallel to an edge. We can adapt standard expressions for molecular movement in solids[9] to take into account the influence of different bonding environments in the $n'_i$ and $n'_j$ collections and derive the conditions for dynamic equilibrium.

The probability that any particular molecule of the $n'_i$ collection will have an adjacent j-site vacant is the product of the mole fraction of i-sites that are occupied, $X_i$, and the mole fraction of j-sites that are vacant, $X_{vj}$. To be converted to a j-molecule and i-vacancy pair, the initial molecule-vacancy pair must acquire a thermal free energy $G^*-G^t_i-G^t_{vj}$, where $G^*$ is the maximum free energy on the path traversed in phase space by the pair, $G^t_i$ is the thermal free energy of the i-molecule, and $G^t_{vj}$ is that of the j-vacancy. At equilibrium, the detailed form of the free energy barrier and the magnitude of $G^*$ will not influence the equilibrium; it is only necessary that some reaction path, or paths, have a low enough barrier so that dynamic equilibrum is established. Then the total flux from the $n'_i$ subset to the j collection is

$$J'_{ij} = n'_i \nu_{ij} g'_{ij} \exp[-(G^*-G^t_i-G^t_{vj})/kT]X_i X_{vj} , \qquad (4)$$

where $\nu_{ij}$ is the frequency with which a pair is excited to the free energy $G^*$, and $g'_{ij}$ is a geometrical factor to be evaluated below. The molecular flux from $n'_j$ to $n'_i$ is given by a similar expression

$$J'_{ji} = n'_j \nu_{ji} g'_{ji} \exp[-(G^*-G^t_j-G^t_{vi})/kT]X_j X_{vi} . \qquad (5)$$

The geometrical factor $g'_{ij}$ is the probability that the molecule of an i-molecule and j-vacancy pair will move in the direction in physical space that transfers the molecule and vacancy across the free energy barrier $G^*$. To determine the relative values of the products

$\nu_{ij}g'_{ij}$ and $\nu_{ji}g'_{ji}$ we consider collections for which $n_i \neq n_j$, but for which the bonding in the sets i and j are equal so that $G^t_i = G^t_j$, $G^t_{vi} = G^t_{vj}$, and $X_{vi} = X_{vj}$. For dynamic equilibrium, $J'_{ij} = J'_{ji}$; therefore

$$\nu_{ij}g'_{ij}/\nu_{ji}g'_{ji} = n'_j/n'_i \; . \tag{6}$$

And by the principle of microscopic reversibility,[8] $\nu_{ij} = \nu_{ji}$, so $g'_{ij}/g'_{ji} = n'_j/n'_i$. The frequencies remain equal when the thermal free energies of the collections i and j are not equal, and the geometric factor should not depend on the free energies. Therefore, Eq. (6) should be valid for any adjacent rows or layers.

Now adopting the assumption of dynamic equilibrium for the more general case, we can set Eq. (4) equal to Eq. (5) and introduce the equality, Eq. (6), to obtain

$$\exp[-(G*-G^t_i-G^t_{vj})/kT]X^d_i X^d_{vj}$$

$$= \exp[-(G*-G^t_j-G^t_{vi})/kT]X^d_j X^d_{vi} \; , \tag{7}$$

where the superscripts d have been introduced to identify the particular values of the mole fractions that make the net flux characteristic of the dynamic equilibrium become zero. This equation reduces to

$$G^t_i-G^t_{vi} - kT\ln X^d_{vi}/X^d_i = G^t_j-G^t_{vj} - kT\ln X^d_{vj}/X^d_j \tag{8}$$

By the definitions chosen, the molecules and vacancies of the $n'_i$ sites adjacent to the $n'_j$ sites are indistinguishable in energy from those on $n_i$ sites not adjacent to the j-collection. (If $n'_i$ and other $n_i$ sites were distinguishable, $n'_i$ could be treated as a separate collection and flux exchanges between $n'_i$ sites and adjacent $n_i$ sites would obey Eq. (8).) Fluxes between two adjacent subsets of the i-collection can only be equal if both have the same mole fractions of molecules and vacancies. Consequently, at equilibrium $X^d_{vi}$ and $X^d_i$ are the mole fractions of vacancies and molecules characteristic of all the $n_i$ sites, not just those adjacent to the j-collection.

Because $X^d_{vi}/X^d_i$, for example, is equal to $n^d_{vi}/n^d_i$, where the d's designate the numbers of vacancies and molecules in the i-collection when dynamic equilibrium is established, Eq. (8) can be put in the equivalent form

$$G^t_i - G^t_{vi} - kT\ell n\; n^d_{vi}/n^d_i = G^t_j - G^t_{vj} - kT\ell n\; n^d_{vj}/n^d_j \quad (8')$$

We will assume for the present that the total number of each kind of sites, $n_i + n_{vi} = n_{it}$ and $n_j + n_{vj} = n_{jt}$, is fixed. Then if Eq. (8) is to be obeyed, when only two collections, i and j, are considered, some number of molecules $\Delta n_i$ must be transferred from the j-collection to the i-collection and an equal number of vacancies must be transferred from the i- to the j-collection. The exchange between the two collections changes their total free energy from that given by Eq. (3) to

$$(n_i + \Delta n_i)G^t_i + (n_i + \Delta n_i)kT\ell n \ (n_i + \Delta n_i)/n_{it}$$

$$+ \ (n_{vi} - \Delta n_i)G^t_{vi} + (n_{vi} - \Delta n_{vi})kT\ell n \ (n_{vi} - \Delta n_i)/n_{it} \qquad (9)$$

$$+ \ (n_j - \Delta n_i)G^t_j + (n_j - \Delta n_i)kT\ell n \ (n_j - \Delta n_i)/n_{jt}$$

$$+ \ (n_{vj} + \Delta n_i)G^t_{vj} + (n_{vj} + \Delta n_i)kT\ell n \ (n_{vj} + \Delta n_i)/n_{jt}$$

When Eq. (9) is differentiated with respect to $\Delta n_i$, Eq. (8') is recovered.

That Eq. (8) corresponds to a minimum in free energy rather than a maximum can be demonstrated by taking the second derivative of Eq. (9) with respect to $\Delta n_i$; all terms in the second derivative are positive:

$$d^2G/d\Delta n^2_i = kt[1/(n_i + \Delta n_i) + 1/(n_{vi} - \Delta n_i)$$
$$+ \ 1/(n_j - \Delta n_i) + 1/(n_{vj} + \Delta n_i)] \qquad (10)$$

The free energy is lowered by the redistribution described by Eq. (8) because vacancies have been exchanged from the collection of relatively low molecular free energy and high vacancy free energy for molecules from the collection of higher molecular free energy and lower vacancy free energy.

In a particle with more than two different molecular environments, dynamic equilibrium requires that Eq. (8) characterize the vacancy distribution between each separate pair. Then any change of vacancy distribution between any of the pairs must, as shown by Eq. 10,

increase the particle free energy. Consequently, when the particle is at overall equilibrium,

$$\Sigma[G^t_i - G^t_{vi} - kT\ell n(X_{vi}/X_i)] \text{ is a minimum} \tag{11}$$

for the particle as long as the number of sites in each collection is fixed.

## Discussion

In the analysis that led to Eq. (11), the number of each kind of site was always held constant. Above 0 K, a given particle may develop many different site and vacancy distributions which satisfy Eq. (11). Of these, the site and vacancy distribution that has the lowest minimum gives the stable shape in the sense considered by Gibbs and Curie. Other shapes that satisfy Eq. (11) are metastable, but may persist for very long times.

For example, a crystal can be metastable if its surfaces are the same ones present when Eq. (11) takes its absolute minimum value and if those surfaces have relative areas different from those required for the absolute minimum. To transform a ledge-free metastable crystal into the most stable shape would require passing through intermediate shapes in which ledges are present. Because the ledges raise the total surface free energy, it can be expected that for a 1 $\mu$m metal crystal more than $10^3$ atoms would have to move from one face to another before continued growth of the new shape would be thermodynamically favored over rebuilding the initial metastable shape. Experimental observations suggest that metastable shapes are common.[6,10]

Eq. (11) confirms Gibbs' prediction that Eq. (1) is an inexact description of particle internal equilibrium, and therefore of equilibrium particle shapes at finite temperatures. At finite temperatures, because the difference between the free energy of vacant and filled sites can be expected to increase in the order corner < edge < surface < bulk, vacancy concentrations will be higher in edges than in surfaces. When the mole fraction of vacancies required in edges by Eq. (11) approaches 1, the edges must become rounded.

Quantitative application of Eq. (11) will be the subject of a paper by Y. Wu, L.M. Falicov, and the author. Implications of dynamic equilibrium to solute distributions between crystalline particles and their surfaces and to particle-vapor equilibrium are under study.

## Acknowledgments

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