

Chapter 5

Surfaces

The energy of a surface and its dependence on crystallographic orientation can determine the equilibrium shape of the crystal. However, even more important to crystal growth is the effect of surface structure on atom attachment kinetics. To explore these important properties of surfaces, we first examine surface energetics, and the thermodynamics of surface defects. We next examine the implications for crystal growth.

5.1 Surface Energy

The surface energy is defined in terms of the free energy change when a solid is separated into two pieces at a large distance (Fig. 5.1). If we define ΔG as:

$$\Delta G = G_{II} - G_I$$

where G_{II} is the free energy of the two piece solid, and G_I is the free energy of the same system in one piece, then the surface free energy γ is defined as:

$$\Delta G = 2A\gamma$$

where A is the cross sectional area and the factor of two is because we have created two surfaces. This will usually be a positive quantity, reflecting the energy cost of the broken bonds in configuration II .

The surface energy is often referred to as a surface tension, a term which an image of force per length, or surface stress. For a liquid surface stress, tension and energy are the same thing, but for a solid, the surface stress differs from surface energy. Imagine that we stretch a surface of length L

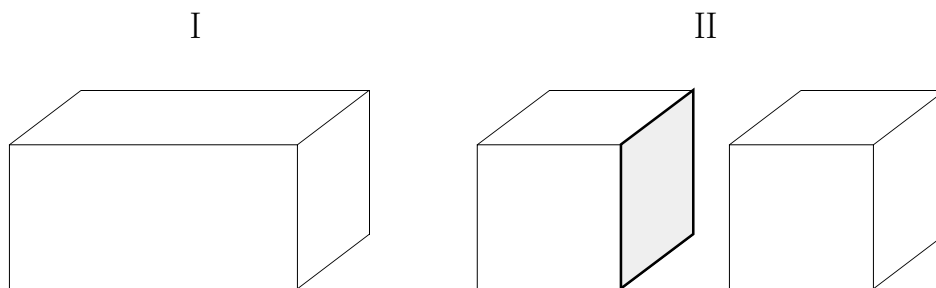


Figure 5.1: Schematic of two configurations of a solid used in defining surface energy.

and initial width z with a force F (Fig. 5.2). The free energy change $d\Delta G$ associated with this stretching is equal to the reversible work done¹:

$$d\Delta G = \gamma dA + Ad\gamma = F dx = \frac{F}{L} dA$$

So the surface stress, which is the force per unit length, is given by:

$$\frac{F}{L} = \gamma + A \frac{d\gamma}{dA}$$

Since liquids have sufficient atomic mobility to maintain the equilibrium surface atomic density in the presence of a strain,

$$\frac{d\gamma}{dA} = 0$$

so the surface energy and surface stress are the same. For solids, a strain will change the surface atomic spacing and hence change γ so that in general:

$$\frac{d\gamma}{dA} \neq 0$$

and the surface stress and surface energy differ.

¹Here we take $\Delta G = \gamma A$ since we are only dealing with one surface

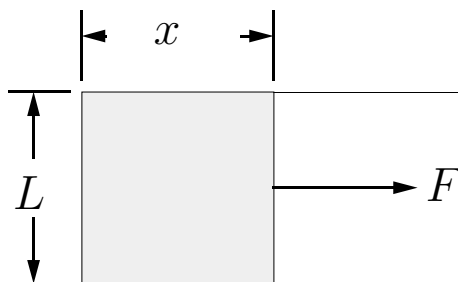


Figure 5.2: Schematic of experiment to determine the relationship between surface energy and surface stress by pulling with force F on edge of a surface.

5.1.1 Surface Stress

Surface stress is different from surface energy, although the terms are often mistakenly used interchangeably². The surface stress is related to the force a surface can exert. To see this, consider the various steps in Fig. 5.3, which shows schematic steps for deforming and splitting a block to form two new (stretched) surfaces. In step I, we split the block forming two new surfaces. This has energy cost $2\gamma A$, where γ is the surface free energy and $A = lx$ is the original surface area. In step II, we stretch the split block from its equilibrium length by an amount δx . This has deformation energy cost given by:

$$(F_B + 2lf_s) \delta x$$

where F_B is the force exerted by the bulk of the block³, and f_s is the surface stress, or the force per unit length exerted by the two new surfaces. Contrast this to the deformation energy in step III, which does not have the effect of the two new surfaces, and so is given by:

$$F_B \delta x$$

In step IV, we create two new stretched surfaces. This has energy cost $2\gamma' A'$ where γ' and A' are the surface energy and area of the stretched surfaces respectively.

²In fact, for a liquid, the surface stress and surface energy are the same thing.

³Note that the quantity F_B also includes the effect of the original surfaces on the un-split block.

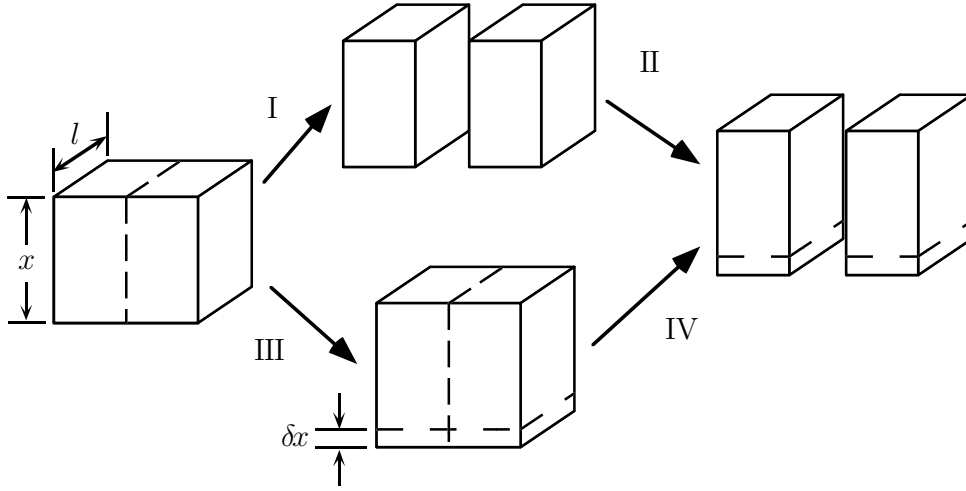


Figure 5.3: Schematic of different deformation and surface-forming paths.

The path with steps I and II must have the same total energy cost as the path with steps III and IV, since they have the same initial and final configurations. Hence we find:

$$2\gamma A + (F_B + 2lf_s)\delta x = F_B\delta x + 2\gamma' A'$$

Solving for f_s yields

$$f_s = \frac{\gamma' A' - \gamma A}{l\delta x} \quad (5.1)$$

For small deformations we can expand γ' in a Taylor's series and find:

$$\gamma' \approx \gamma + \frac{d\gamma}{d\epsilon} \frac{\delta x}{x}$$

where ϵ is the strain. Similarly we find for A'

$$A' = l(x + \delta x) = A \left(1 + \frac{\delta x}{x}\right)$$

Inserting these into equation 5.1 we find

$$f_s = \frac{1}{l\delta x} \left\{ \left(\gamma + \frac{d\gamma}{d\epsilon} \frac{\delta x}{x} \right) \left[A \left(1 + \frac{\delta x}{x}\right) \right] - \gamma A \right\}$$

$$\begin{aligned}
&\approx \frac{1}{l\delta x} \left(\gamma + \frac{d\gamma}{d\epsilon} \right) A \frac{\delta x}{x} \\
&= \gamma + \frac{d\gamma}{d\epsilon}
\end{aligned}$$

where we have discarded terms second order in δx . Hence for solids, where the surface energy γ might depend on the strain state, the surface stress and surface energy can differ.

5.1.2 Enthalpy

The surface energy we have described so far is a free energy and has both enthalpy ΔH^s and entropy $T\Delta S^s$ contributions. That is:

$$\gamma = \Delta H^s - T\Delta S^s$$

To examine the surface enthalpy we consider a simple model of a solid where the cohesive energy comes entirely from nearest neighbor bonds. This model is more illustrative than accurate, and much more sophisticated approaches are needed to calculate actual surface enthalpies. Consider first the liquid-solid interfaces. For a liquid-solid transition the enthalpy difference per volume is ΔH_F , the enthalpy of fusion or melting. We define ϵ_F to be the difference in bond enthalpy between solid and liquid atomic bonds. Counting only nearest neighbor bonds the enthalpy per volume and the bond enthalpy are related through:

$$\Delta H_F = \frac{z \epsilon_F}{2 V_A}$$

where z is the number of nearest neighbors and V_A is the atomic volume. Our treatment can be generalized to include surfaces between a solid and vacuum by using ΔH_T rather than ΔH_F , where ΔH_T is the enthalpy of transformation, which for a solid-vacuum interface is the enthalpy of sublimation.

To calculate the surface enthalpy within this model, we can just write:

$$\Delta H^s = \mathcal{F}_{BB}(\Delta H_F V_A)\sigma$$

where \mathcal{F}_{BB} is the fraction of bonds broken per surface atom, or the fraction of enthalpy per atom, the product $\Delta H_F V_A$ represents the total enthalpy per atom, and σ is the surface atomic density (#atoms/area). This expression

gives the enthalpy per unit area. Another measure of surface enthalpy might be the enthalpy per surface atom which is given by:

$$\Delta H_A^s = \mathcal{F}_{BB}(\Delta H_F V_A)$$

The fraction of broken nearest neighbor bonds per surface atom can be found from:

$$\mathcal{F}_{BB} = \frac{1}{z} \left(\frac{z - \# \text{ in-plane nearest neighbors}}{2} \right)$$

The surface atomic density σ is just:

$$\sigma = cd$$

where c is the atomic density, given by $1/V_A$, and d is the spacing between adjacent planes.

As an example, we consider the (111) surface in an fcc metal. Here each surface atom is missing three of its nearest neighbors, so $\mathcal{F}_{BB} = 3/12$. For FCC (111) planes, $d = a/\sqrt{3}$, where a is the lattice parameter. Hence we find for the surface enthalpy:

$$\Delta H^s = \frac{3}{12} \Delta H_F V_A \sigma = \frac{1}{4} \Delta H_F d = 0.14 a \Delta H_F$$

The highest density planes are frequently the lowest energy since they have the smallest number of broken bonds.

5.1.3 Surface Energies from Bulk Parameters

In our treatment of surface energies, we found that the surface enthalpy of a solid-vacuum interface could be approximated by:

$$\Delta H^s = \mathcal{F}_{BB} \Delta h_{\text{vap}} \sigma \quad (5.2)$$

where \mathcal{F}_{BB} is the fraction of broken bonds for an atom on the surface, Δh_{vap} is the enthalpy of vaporization per atom, and σ is the density of atoms on the surface. The question arises of how well this estimate does. To compare this relationship with experimentally determined values we consider an average surface, so that we do not concern ourselves with variations in \mathcal{F}_{BB} , but consider an averaged surface energy for a solid which has an average number

of broken bonds $\langle \mathcal{F}_{BB} \rangle$. Furthermore we say that the average surface atom density is given by:

$$\sigma = \frac{1}{V_A^{2/3}}$$

where V_A is the atomic volume. Hence we can arrive at the relationship:

$$\Delta H^s = \frac{\langle \mathcal{F}_{BB} \rangle \Delta h_{\text{vap}}}{V_A^{2/3}}$$

One way of ascertaining the accuracy of this expression is to use tabulated data for surface and vaporization enthalpies to calculate the effective number of broken bonds $\langle \mathcal{F}_{BB} \rangle$. If we find a reasonable and consistent number for this quantity we can say that our expression is reasonably accurate.

For convenience we work with molar quantities of vaporization enthalpy per mole $N\Delta h_{\text{vap}}$ and surface area per mole $(NV_A)^{2/3}$, where N is Avogadro's number. We find:

$$\begin{aligned} \langle \mathcal{F}_{BB} \rangle &= \frac{\Delta H^s V_A^{2/3}}{\Delta h_{\text{vap}}} \\ &= N^{1/3} \frac{\Delta H^s (NV_A)^{2/3}}{N\Delta h_{\text{vap}}} \end{aligned}$$

To test this relationship we list the relevant quantities and the quantity $\langle \mathcal{F}_{BB} \rangle$ in table 5.1. We see that for the transition metals, where the surface enthalpies, molar areas, and vaporization enthalpies vary greatly, (standard deviations are 26%, 16% and 27% respectively), the value we find for $\langle \mathcal{F}_{BB} \rangle$ is nearly a constant (standard deviation is less than 6%). We find the average fraction of broken bonds is 0.17, which corresponds to one out of 5.9 bonds. Hence we conclude that Eqn. 5.2 is a reasonable approximation for the magnitude of the surface energy.

The success of this approximation means that the average surface enthalpy per atom is just some fraction ($\sim 1/6$) of the enthalpy of vaporization per atom. Note that this relationship is independent of the broken nearest neighbor bond model for the enthalpy of a solid. However, the calculation of the surface enthalpy for various orientations of surfaces from equation 5.2 relies on assigning the enthalpy of transformation to the formation of nearest neighbor bonds. This assumption has not been verified by the comparison in table 5.1 and so calculation of accurate variations in surface energies for different orientations is more uncertain.

Element	ΔH^s ($\mu\text{J}/\text{cm}^2$)	$(NV_A)^{2/3}$ (cm^2)	$N\Delta h_{\text{vap}}$ (kJ/mole)	$\langle \mathcal{F}_{BB} \rangle$
Sc	120	6.1	376	0.16
Ti	205	4.8	464	0.18
V	260	4.1	511	0.18
Cr	240	3.7	395	0.19
Mn	160	3.8	283	0.18
Fe	255	3.7	413	0.19
Co	255	3.5	427	0.18
Ni	245	3.5	428	0.17
Cu	185	3.7	336	0.17
Y	110	7.3	424	0.16
Zr	195	5.8	607	0.16
Nb	270	4.9	718	0.16
Mo	295	4.4	657	0.17
Tc	305	4.2	(660)	0.16
Ru	305	4.1	650	0.16
Rh	275	4.1	551	0.17
Pd	210	4.3	376	0.20
Ag	125	4.7	283	0.18
La	90	8.0	432	0.14
Hf	220	5.6	619	0.17
Ta	305	4.9	781	0.16
W	330	4.5	848	0.15
Re	365	4.3	774	0.17
Os	350	4.2	788	0.16
Ir	310	4.2	669	0.16
Pt	255	4.4	564	0.17
Au	155	4.7	368	0.17

Table 5.1: Comparison of zero temperature surface energies and enthalpy of formation for several solid elements. Data from A.R. Miedema *Z. Metallkde* **69**, 287, (1978) and references therein.

Angular Dependence

A surface inclined at some angle relative to a crystallographic plane will often have a higher surface enthalpy. To illustrate the origin of this effect, we calculate the fraction of broken bonds for atoms in a simple cubic solid on a plane inclined at an angle θ relative to the (001) plane as illustrated in Fig. 5.4. This fraction includes missing neighbors in directions perpendicular and parallel to the surface. We find:

$$\mathcal{F}_{BB}\sigma_A = \left(\lambda_{\parallel} \mathcal{F}_{BB\parallel} |\cos \theta| + \lambda_{\perp} \mathcal{F}_{BB\perp} |\sin \theta| \right) \lambda_{\parallel}$$

where λ_{\parallel} and λ_{\perp} are the linear atomic densities parallel and perpendicular to the nominal surface, and $\mathcal{F}_{BB\parallel}$ and $\mathcal{F}_{BB\perp}$ are the fraction of the missing nearest neighbors for surfaces which occur in the parallel and perpendicular directions respectively.

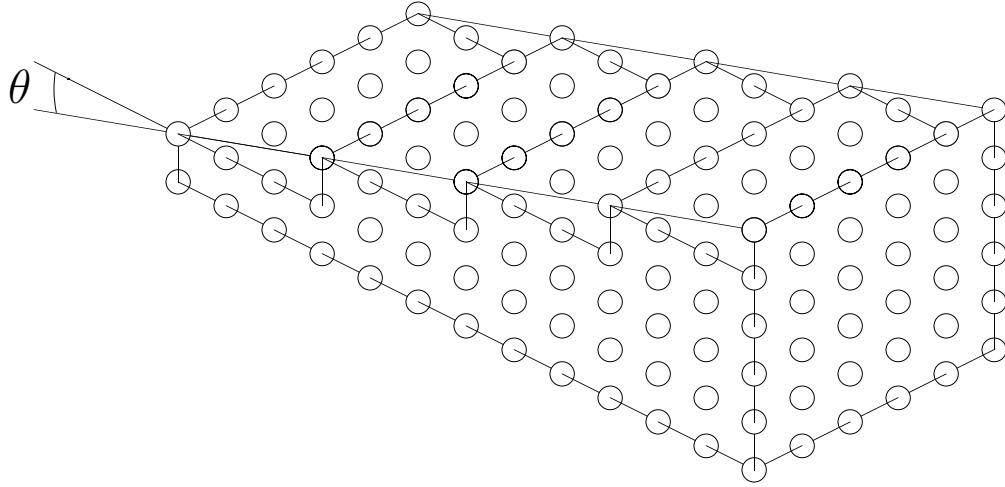


Figure 5.4: Illustration of a surface at an angle θ relative to the (001) surface in a simple cubic solid.

For the (001) surface, we have $\lambda_{\parallel} = \lambda_{\perp} = 1/a$ where a is the lattice parameter, and $\mathcal{F}_{BB\parallel} = \mathcal{F}_{BB\perp} = 1/z = 1/6$. Hence we find for the surface enthalpy:

$$\Delta H^s = \mathcal{F}_{BB}\sigma \Delta H_F V_A = \frac{1}{6a^2} (|\cos \theta| + |\sin \theta|) \Delta H_F V_A$$

This is shown plotted as a function of angle θ in Fig. 5.5. The surface enthalpy has a minimum cusp at $\theta = 0$, reflecting that there is the smallest number of broken bonds at this orientation.

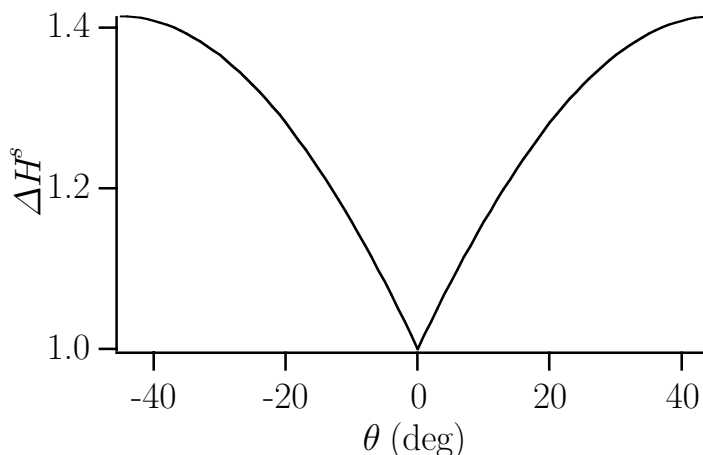


Figure 5.5: Plot of surface energy as a function of angle of surface, showing cusp at the point of the smallest number of broken bonds.

The angular dependence of the surface energy can be represented in a γ -plot. In this plot, a surface is constructed so that the distance of the γ -plot surface from the origin is proportional to the surface energy of a plane which is perpendicular to a vector from the origin to the γ -plot surface. A section of a γ -plot is shown for the simple cubic example is shown in Fig. 5.6. The equilibrium crystal shape can be determined from such a plot by constructing planes perpendicular to the line between the origin and the surface for every point on the γ -plot surface. The innermost polyhedra is the lowest energy configuration.

5.1.4 Entropy

There are two main contributions to the entropy per surface atom. Firstly, the surface atoms have more thermal freedom due to the reduction of geometric constraints. Secondly, there are extra configurational entropy contributions associated with defects which are characteristic of a surface. These include surface vacancies, kinks, steps, and islands. Hence $\Delta S^s > 0$ so that

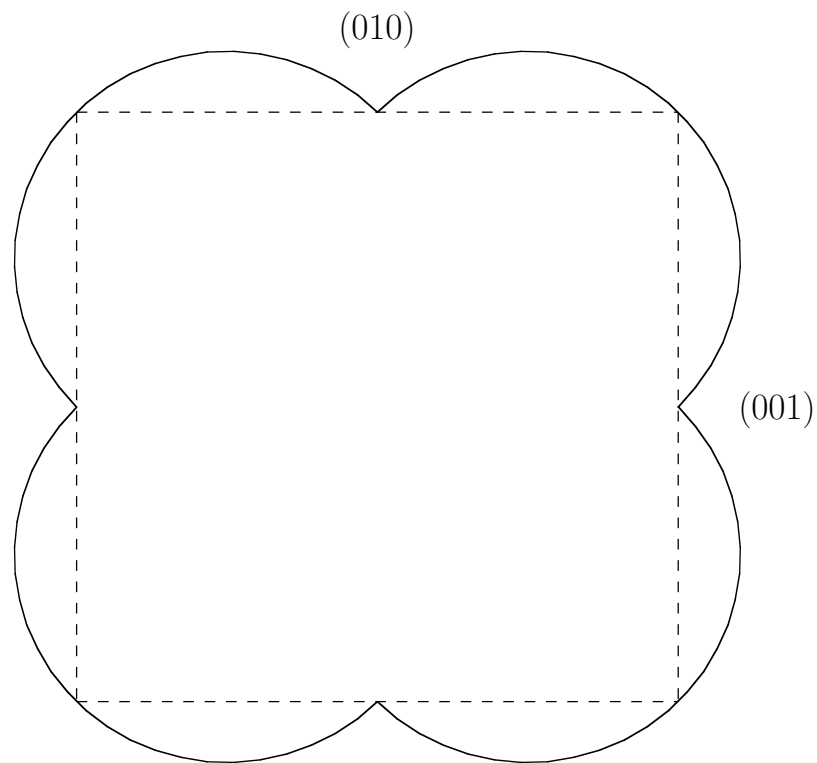


Figure 5.6: γ -plot for a simple cubic solid considering only nearest-neighbor bonds. The dotted line shows the equilibrium crystal shape, which in this case is a cube with (001) type faces.

the surface free energy $\gamma < \Delta H^s$ and is temperature dependent. The sharp plots in surface energy plots tend to be rounded by including the effects of entropy.

5.2 Thermodynamics of Surface Defects

The presence of surface defects can greatly affect atom attachment and growth. A surface with many defects has many sites for an arriving atom to inhabit. For example, consider the surface defects shown in Fig. 5.7. Notice that an arriving atom which locates itself on a kink site, has not changed the total surface area and hence has not changed the energy of the surface. However, an arriving atom which lands on the adatom site will increase the surface area and surface energy and will thus be in a much less stable site. If a surface has very few defects such as kink sites, atoms landing on the surface must occupy higher energy sites, and hence their probability of staying on the surface and contributing to growth is lower. A surface which has a high equilibrium concentration of defects will be more likely to experience uniform growth, that is attachment of atoms over the entire surface resulting in growth rate proportional to the driving force. The description of the various growth modes is covered in more detail in subsequent chapters.

Surfaces have a broader range of defects than is allowed in the bulk. Some of these are shown in Fig. 5.7. In order to examine the number of a given type of defect we model their formation enthalpy with the nearest-neighbor bond model, by counting the nearest neighbor bonds which must be broken to form a given defect. We again relate the bond enthalpy, ϵ_b , to the enthalpy Δh_T per atom associated with the transformation. For example, if we are considering a liquid-solid surface, Δh_T becomes Δh_F the latent heat of fusion per atom. If we are considering a solid-vapor surface, Δh_T becomes Δh_s , the heat of sublimation per atom. For a solid of N atoms with z nearest neighbors, there are $Nz/2$ nearest neighbor bonds which must be broken for a complete transformation. Assigning half of the bond enthalpy ϵ_b ⁴ to each atom involved in the bond, we see that:

$$\Delta h_T = \frac{z}{2} \epsilon_b$$

⁴Here we use ϵ_b to represent the bond enthalpy difference across the surface. For a vacuum-solid interface, ϵ_b would be the total bond enthalpy.

We next must classify the various defects which might exist in a surface, and count the number of broken bonds required to form each defect type. Referring to Fig. 5.7, Table 5.2 lists the enthalpy of each of the defect types for a simple cubic structure.

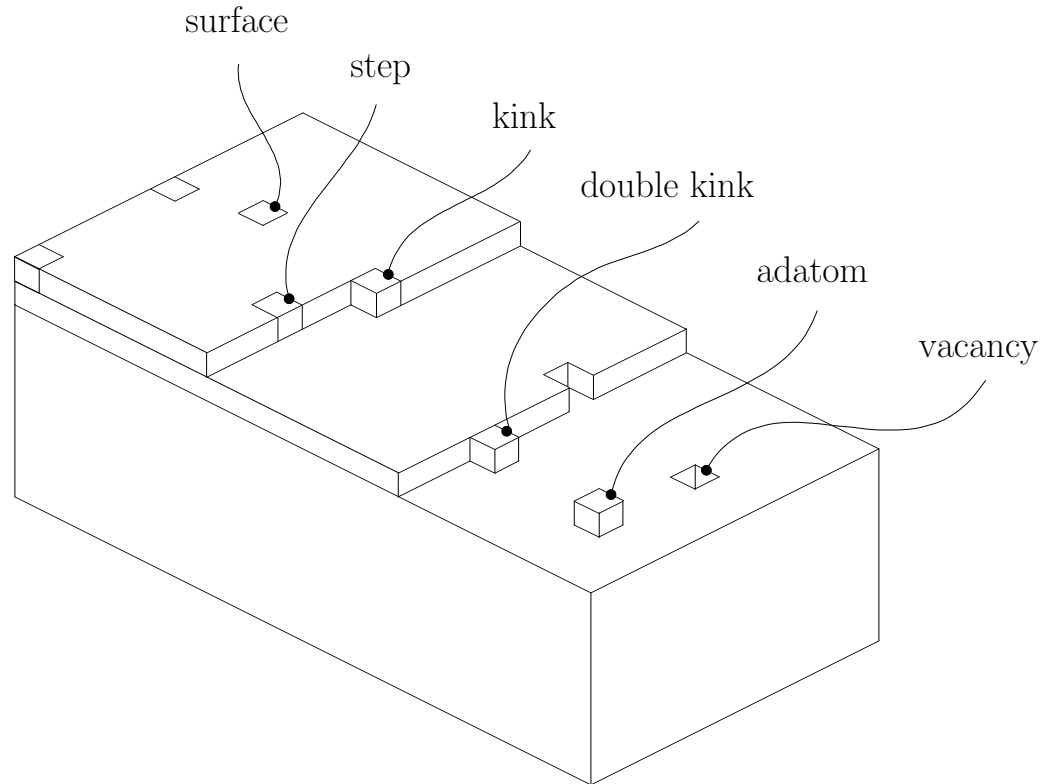


Figure 5.7: Schematic of surface showing the various types of defects.

Of course, enthalpy is not the entire story, if it were, the equilibrium concentration of these defects would be zero. However, the configurational entropy associated with these defects will assure, that at equilibrium at finite temperatures, there will be some nonzero concentration of each of these defect types. We first consider the concentration of surface vacancies and adatoms. We employ a three level model, where the surface can be at one of three different levels, corresponding to the vacancy, surface and adatom sites, denoted as -1 , 0 , and $+1$ respectively. If we only consider these three

Site	Enthalpy Relative to Bulk Atom	
Surface Atom	$\Delta h_T/6$	$\epsilon_b/2$
Step Atom	$\Delta h_T/3$	ϵ_b
Kink Atom	$\Delta h_T/2$	$3\epsilon_b/2$
Double Kink Atom	$2\Delta h_T/3$	$2\epsilon_b$
Surface Vacancy or Adatom	$5\Delta h_T/6$	$5\epsilon_b/2$

Table 5.2: Enthalpy increase of various surface defects for simple cubic nearest-neighbor, bond-breaking model.

levels, then the fractions x_i of the atoms on each level must add up to unity:

$$x_{-1} + x_0 + x_{+1} = 1$$

We consider the situation where formation of a -1 site is accompanied by formation of a $+1$ site so that $x_{-1} = x_{+1} \equiv x$. The enthalpy of isolated ± 1 sites is greater than that of a regular surface (0) site by an amount (again, for a simple cubic structure):

$$\frac{5\Delta h_T}{6} - \frac{\Delta h_T}{6} = \frac{2\Delta h_T}{3} = 2\epsilon_b$$

This enthalpy of formation is analogous to the enthalpy of vacancy formation. However, unlike vacancies, the concentration of these ± 1 sites can be fairly large so we must modify the formation enthalpy to allow for neighboring defects. If two $+1$ sites or two -1 sites are neighbors, the number of broken bonds is reduced by one. The probability that a given site will have a defect as one of its nearest neighbors is $4x$, so that pairs occur with probability $4x^2$. We can then write the change in enthalpy over that of a perfect crystal as:

$$\Delta H = 2 \left(2\epsilon_b x - 4x^2 \frac{\epsilon_b}{2} \right) = 4\epsilon_b x(1 - x)$$

where the factor 2 out front comes from the fact that we form both $+1$ and -1 sites simultaneously when we take an atom out of an otherwise smooth surface and place it on a $+1$ site.

We find the entropy from the familiar equation:

$$\Delta S = k_B \ln \Omega$$

where Ω is the number of ways to arrange the defects on the surface. The number of ways to arrange m different types of a total of N objects is:

$$\frac{N!}{\prod_{j=1}^m N_j!}$$

where N_j is the number of objects of type j . For the calculations of the equilibrium concentration of vacancies, (Section 2.5, Eqn. 2.7) we had $m = 2$, a lattice site was occupied by either a vacancy or an atom. Here we have $m = 3$ and we find:

$$\Omega = \frac{N!}{(xN)!(xN)![(1-2x)N]!}$$

where N is the number of surface atoms, xN is the number of +1 sites and the number of -1 sites, and $[(1-2x)N]$ is the number of 0 sites.

The free energy change associated with formation of these sites to roughen the surface will then be:

$$\Delta G = 4\epsilon_b x(1-x) - T\Delta S$$

We find the equilibrium concentration, x^0 , of these defects by setting:

$$\left. \frac{\partial \Delta G}{\partial x} \right|_{x=x^0} = 0$$

This yields:

$$\begin{aligned} \frac{x^0}{1-2x^0} &= \exp \left[\frac{-2\epsilon_b(1-2x^0)}{k_B T} \right] \\ &= \exp \left[\frac{-2\Delta h_T(1-2x^0)}{3k_B T} \right] \end{aligned}$$

We can generalize this expression to take into account other types of surface defects and other structures. We define f to be the fraction of broken nearest neighbor bonds relative to the reference site. For example, in the above case, the +1 site has 4 more broken nearest neighbor bonds than the surface (0) site, so that $f = 4/6$. We can then write:

$$\frac{x^0}{1-2x^0} = \exp \left[\frac{-f\Delta h_T(1-2x^0)}{k_B T} \right] \quad (5.3)$$

For a given situation, Eqn. 5.3 can be numerically solved for x^0 .

As an example consider a Cu (111) surface near the melting point in equilibrium with its vapor. A surface atom has 3 nearest neighbor bonds broken, while 6 more nearest neighbor bonds are broken in forming ± 1 site. Hence, $f = 9/12 - 3/12 = 1/2$. The transformation enthalpy, Δh_T , is the heat of sublimation, which we estimate to be the sum of the heats of fusion and vaporization. We find, $\Delta h_T = 313$ kJ/mole. With such a large Δh_T we can take the small x^0 limit of Eqn. 5.3 and find:

$$\begin{aligned} \frac{x^0}{1 - 2x^0} \approx x^0 &= \exp \left[\frac{-\Delta h_T}{2k_B T_m} (1 - 2x^0) \right] \\ &\approx \exp(-13.9) \\ &= 9.4 \times 10^{-7} \end{aligned}$$

Hence, the equilibrium shape of the surface of a metal near its melting point, in contact with its vapor or a vacuum, will be very smooth.

In contrast, we consider for our next example the situation of a metal near its melting point in contact with its liquid. Now Δh_T is just the heat of fusion. The ratio:

$$\frac{\Delta h_F}{k_B T_m}$$

is about 1.1 for most metals (See Table 5.3).

Metal	$\Delta h_F/k_B T_m$
Cu	1.15
Mg	1.19
Al	1.38
Mo	1.00

Table 5.3: Table of heats of fusion for several metals.

For the close packed surface of a metal with 12 nearest neighbors, we have:

$$f \frac{\Delta h_F}{k_B T_m} = 0.55$$

We now must solve Eqn. 5.3 numerically, and we find:

$$x^0 = 0.30$$

Hence, near the melting point, in contact with their liquid, most metals are very rough.

Non-metals tend to be smoother, as can be seen by examining the case of the Si (100) surface. Here our nearest-neighbor model breaks down, since there are no nearest neighbor bonds in the plane. Thus next-nearest-neighbors are important. For simplicity, we just take the value for f found for the simple cubic case, $f = 2/3$. The heat of fusion for Si is $\Delta h_F = 11.7$ kCal/mole. Hence,

$$\frac{\Delta h_F}{k_B T_m} = 3.47$$

Solving Eqn. 5.3 we find:

$$x^0 = 0.10$$

Thus a Si surface in contact with its melt is considerably smoother than that of a metal.

As a final example we apply our formalism to roughness of a step on the surface of a metal in contact with its vapor. Steps which are rough have a large concentration of kinks and double kinks as in Fig. 5.7. We first consider the formation of double kinks on a step along the $[1\bar{1}0]$ direction in a Cu (111) surface. We break two bonds in moving a step atom out to form double kink pair, so that $f = 1/6$. Solving Eqn. 5.3 numerically gives:

$$x^0 = 0.01$$

so that there is a kink atom every 100 atoms along the step. For formation of a kink in the step, $f = 1/12$ and we find that:

$$x^0 = 0.13$$

Therefore even in the case of a metal in contact with its vapor, we find that the step surfaces are quite rough.