Part II : Interfaces
Module 3 : A bond-breaking model

3 A bond-breaking model

3.1 Motivation

In a crystal, the interfacial energy (especially at low temperatures) is by definition anisotropic. How can we calculate the anisotropic interfacial energy?

3.2 A bond-breaking model for surface energies of solids

In this section, we develop a simple bond-breaking model to calculate the surface energy of a solid; we assume that the solid is in contact with its own vapour; we also assume that the temepratures are low enough that the primary contribution to the surface energy comes from the broken bonds.

Consider a simple cubic lattice with a lattice parameter of a. Let us consider a surface that makes an angle of θ with one of the principal axes of the crystal. The crystalline surface (of unit length) is shown schematically in Figure. 7. The open circle marked 1 represents an atom in the bulk; it has formed four bonds in the plane of the figure; if we consider the crystal to be infinite in the direction perpendicular to the plane of the figure, it has also formed two bonds in the perpendicular direction: one above the plane and another below. The filled circle, which represents a surface atom has formed only two bonds out of the four that it can form in the plane of the figure. These dangling bonds are the ones that contribute to the enthalpy (in this case, internal energy) of the interfacial free energy.

From the given geometry, it is clear that the number of broken bonds along the principal axes in the plane of the figure are $\cos(\theta)/a$ and $\sin(|\theta|)/a$. Accounting for the third dimension, the total number of broken bonds per unit area of such a surface is $[\cos(\theta) + \sin(|\theta|)]/a^2$. If the bond strength is ϵ, since each bond is shared between two atoms, the internal energy due to the broken bonds per unit length of the surface plane (E_{sv}) is given by the expression

$$E_{sv} = \frac{\epsilon}{2a^2} \left[\cos\theta + \sin|\theta|\right] \tag{5}$$

A schematic plot of the expression 5 is shown in Figure 8. The key point to note is that the interfacial energy has a cusp at $\theta = 0$; this means that any surface with any angle other than $\theta = 0$ is energetically costlier for the

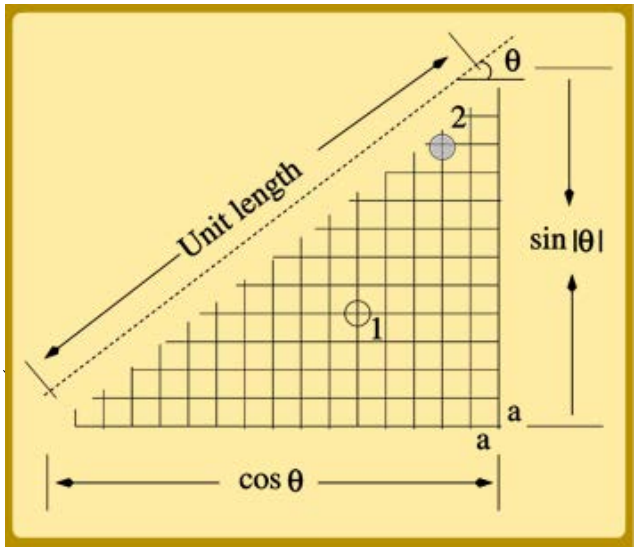

Figure 7: A cubic crystal of lattice parameter a with a surface of unit length that makes an angle of θ with one of the principal axes of the crystal; we have assumed that the crystal is infinite in the third dimension (the axis perpendicular to the plane of the figure).

sytem.

3.3 Tutorial problems and questions

1. Calculate the number of broken bonds per unit area in a Nickel crystal on the (111), (110) and (100) planes.

2. Calcualte the number of atoms per unit area in an Iron crystal on the (111), (110) and (100) planes.

3.4 Solutions to the tutorial

1. Calculate the number of broken bonds per unit area in a Nickel crystal on the (111), (110) and (100) planes.

   Ni is fcc and the lattice parameter of Ni is 3.52 Å. There are two atoms on a (100) plane. Hence the density of atoms per unit area of a (100) plane of a Ni crystal is 1.61 $\times 10^{19}$. For preparing the (100) surface, for

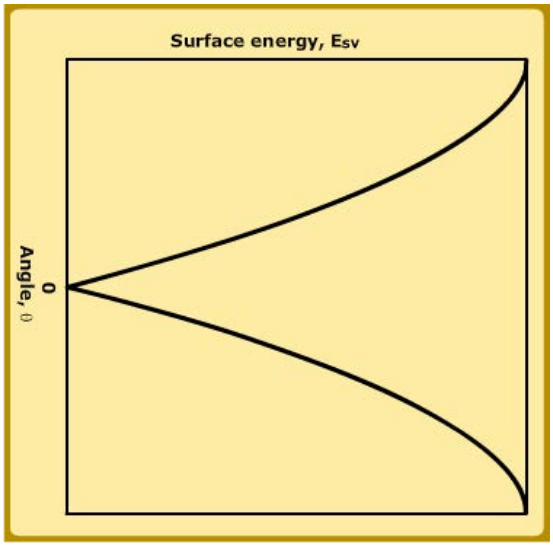

Figure 8: The plot of the expression 5 giving the interfacial energy as a function of θ, the angle of the surface plane.

each atom 4 bonds are broken; however, since each bond is common to two atoms, the total number of bonds broken per atom is 2. Hence, total number of broken bonds are 3.22 $\times 10^{19}$.

Similarly, number of atoms per unit area on the (110) plane is 1.142 $\times 10^{19}$ and the number of atoms per unit area on the (111) plane is 1.864 $\times 10^{19}$. On (110) plane, the number of broken bonds per atom is 2.5 and on the (111) plane the number of broken bonds are 1.5. Hence, the total number of broken bonds can be calculated by multiplying these numbers with the atomic densities.

2. Calcualte the number of atoms per unit area in an Iron crystal on the (111), (110) and (100) planes.

   Fe is bcc and the lattice parameter of Fe is 2.87 Å. Hence, the number of atoms per unit area of the (100), (110) and (111) planes of Fe are 7 $\times 10^{18}$, 1.72 $\times 10^{19}$ and 1.21 $\times 10^{19}$.

3.5 Supplementary information

In a simple bond breaking model, we only consider the chemical part of the free energy. In a solid, at the free surface, the atoms can also have elastic relaxation. Such contributions to the free energy can be accounted for using molecular dynamics simulations.

The grain boundary grooving is a phenomenon in which a grain boundary in contact with a vapour tends to develop a groove to achieve equilibrium of forces acting at the triple junction of vapour phase and the two grains. Using the groove angle, it is possible to determine the anisotropy in grain boundary energy. Further, as we show in the next section, the equilibrium shapes of crystals can be non-spherical and facetted. The relative surface areas of different facets in such crystals also indicate the relative surface energies (and hence help determine the anisotropy).