

## 9.1: Surfaces and Surface Energy

We have been ignoring the thermodynamics of surfaces and interfaces throughout this text. Were we justified in doing so? To evaluate, we will make what is called a “back of the envelope” calculation, which is a rough estimation of the magnitude of a physical quantity via a simple phenomenological model; this exercise is developed in example problem 9.1. The results demonstrate that the number of surface atoms is a very small percentage of the same in the bulk; so we can probably justify our previous dismissal of surface energy. However, if we repeated the calculation with a 20 nm NaCl particle, then ~13% of the atoms reside on the surface. What are the energetic consequences when a fair number of atoms are on the surface?

Let’s define the internal energy ( $U$ ) of the nanoparticle. To do so we will split the energy into two contributions, a bulk part plus surface energy which is just like an excess function that we examined in Chapter 7 with solutions. It is easy to calculate the energetic contribution from bulk atoms, we simply divide the per molar energy internal energy ( $U$ ) by Avogadro’s number ( $N_A$ ), and then multiply the result by the number of interior atoms ( $N$ ). Taking a similar approach for the surface energy prompts us to determine the internal energy per unit area and multiply it by the total area of the surface. The total internal energy is thus:

$$U = N \cdot \frac{U_m}{N_A} + A \cdot \gamma \quad (9.1.1)$$

where  $\gamma$  is the internal energy per unit area. Unfortunately, defining  $\gamma$  is problematic. For one, it isn’t clear how to define what constitutes a particle’s surface. To understand, we will use a specific example of a material, zinc sulfide (ZnS), which has an overall cubic unit cell as shown in Figure 9.1. Zinc sulfide’s “zinc blende” structure defined by the location of the zinc and sulfur atoms in the unit cell. The bulk structure is generated by translating the unit cell in a replicative manner (up, down, left, right etc.) as shown in the figure. We can already see that the large crystal has six flat surfaces, or we can create one by cutting through it. This is where understanding surfaces becomes more complex- the cut can be made at various angles, and the surface properties such as the number of atoms per unit surface area depends on how we make the cut. Furthermore, we may be able to make the surface composed of either one type of atom or another depending on where we slice it. We expect different surface energies if the surfaces are made of different atoms! Thus, we need a way to describe the type of surface we are calculating the energy of.

### 9.0.1 Miller Indices

There exists a system for classifying the type of surface that is being studied. We won’t discuss crystal unit cells further, other than to note that there are many types and shapes of unit cells that are replicated in space to generate the bulk material.

Earlier we discussed how surfaces can be made from cutting a perfect crystal. Shown in Figure 9.2 are some examples, such as a cut across the front face (Fig. 9.2 A). We could also cut through the diagonal or across the center of the crystal (Figs. 9.2 B, C) or cut off a corner (Fig. 9.2 D). All of these surfaces are distinct, and as such we need a method for distinguishing all of them apart. The way to do this was developed by William Hallows Miller, a Welsh mineralogist, in 1839. Each surface can be described by a plane which bisects the  $x$ ,  $y$ , and  $z$  coordinate axes at some point, even if that crossing point is  $\infty$  in the case of the plane being parallel to that axis. Shown at the top of the figures is the point at which the plane bisects the coordinates; the Miller index is simply the inverse of those points.

To demonstrate how surfaces with different Miller indices are different, shown in Figure 9.3 are ZnS  $\{100\}$  and  $\{111\}$  planes defined as above. Next, we rotated the cube such that the planes are directly facing up, facing you like a mirror in the bathroom. As can be seen, the surfaces appear very different, where the  $\{100\}$ -type appears as small squares and the  $\{111\}$  is composed of small triangles that form interlocking hexagons. Also shown are transmission electron microscope images of a particle with those surfaces pointed up. Again, we see how the appearance is not just something that the model looks like, it is in fact real.

### 9.1.2. Surface energy

Now that we can discuss specific surfaces, we now must define how they differ energetically. To do so let us consider what is surface energy? Given that we have been discussing preparing surface via cleaving a crystal, one definition is the reversible work necessary to create the surface. Also recall from Chapter 5 that the changes in Helmholtz and Gibbs energies are equal to reversible work. Another way to view surface energy is to realize that surface atoms are missing bonds as shown in Figure 9.4 Here one can see that a, given the structure of the unit cell, that a bulk atom has 4 nearest neighbors and 12 next-nearest neighbors (4 in plane and 8 more “up” and “down”). However, at a  $\{100\}$  surface there are 3 nearest neighbor and 8 next-nearest neighbor atoms. Clearly this isn’t “good” for the atom, which means that surface energy is inherently energetically raising. For the  $\{111\}$  surface the situation is worse- there are two missing nearest neighbors and 4 missing next-nearest neighboring atoms. Clearly this surface

must have even higher energy! In fact, it is a trend that the surface energy correlates with higher Miller indices as can be seen in Table 9.1 for the [GrindEQ\_\_1\_A200\_A200\_] vs. [GrindEQ\_\_1\_A201\_A201\_] surfaces of ZnS and NaCl.

### 9.1.3 Nanoparticles and surfactants

The nature of surface energy is hopefully clear given that surface atoms are missing bonds and bonding partners. There is an additional, somewhat complicating dynamic that also affects surface energy, which is reconstruction. Surface atoms may “compress” to the nearest neighbors that they have to try to regain electron density. This is especially observable in nanoparticles that have high surface to volume ratios. As shown in Figure 9.5, small nanoparticles of semiconducting CdSe...

### 9.1.4. Surface tension

Surface energy,  $\gamma$ , is exactly as described above. As for surface tension,  $\sigma$ , you are already familiar with this because surface tension is why bubbles are round and why you were able to see bugs can walk across the water of a stream.

Material, surface, termination	Surface Energy ( $\gamma$ J/m <sup>2</sup> )
ZnS [GrindEQ__100_], Zn	1.12 <sup>a</sup>
ZnS [GrindEQ__100_], S	1.30 <sup>a</sup>
ZnS [GrindEQ__111_], Zn	0.87 <sup>a</sup>
ZnS [GrindEQ__111_], S	1.01 <sup>a</sup>
NaCl [GrindEQ__100_]	0.30
NaCl [GrindEQ__110_]	0.40

Table 9.1 Surface energies and tension for various solids and liquids.

Liquid	$\sigma$ , Surface Tension (mN/m)
Water (25 °C)	71.97
Mercury	487

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