

# Part II : Interfaces

## Module 2 : Interfacial free energy

### 2.1 Motivation

What is interfacial energy? How do we measure it?

### 2.2 Interfacial free energy

By interfacial energy we always mean the interfacial free energy. Interfacial free energy is the excess free energy associated with an interface. This excess free energy is the energy cost associated with the introduction of that interface.

For example, consider two differently oriented crystallites as shown in Fig. 5; let them be put together to form a grain boundary. Let  $G_1$  be the bulk free energy (per unit volume) of the crystallite 1 and  $G_2$  be the bulk free energy (per unit volume) of the crystallite 2. When they are put together (a volume  $V_1$  of the crystallite 1 and a volume  $V_2$  of the crystallite 2), the resultant system with the grain boundary has an energy  $G$  which can be written as

$$G = G_1V_1 + G_2V_2 + G_{xs} \quad (1)$$

$G_{xs}$  is the excess free energy; it is always positive. Grain boundary energy is the excess free energy per unit area of the grain boundary; that is,  $G_{xs} = \gamma_{gb}A_{gb}$ . From this expression, it is also clear that the units of  $\gamma_{gb}$  is  $\text{J/m}^2$ .

In Table. 1, we give a list of some of the interfaces in materials and the typical order of magnitude of the interfacial free energies of these interfaces.

### 2.3 Solids: interfacial free energy is not surface tension

In a typical fluid-vapour interface, the interfacial excess free energy is the surface tension: the force that tries to minimize the surface area. If one of the phases across the interface is a solid, then, the surface tension and the interfacial free energy are not the same.

Consider a soap film in a wire frame as shown in Fig. 6; let the surface tension of the film be  $\gamma \text{ J/m}^2$ . Let  $A$  be the area of the film. Suppose we increase

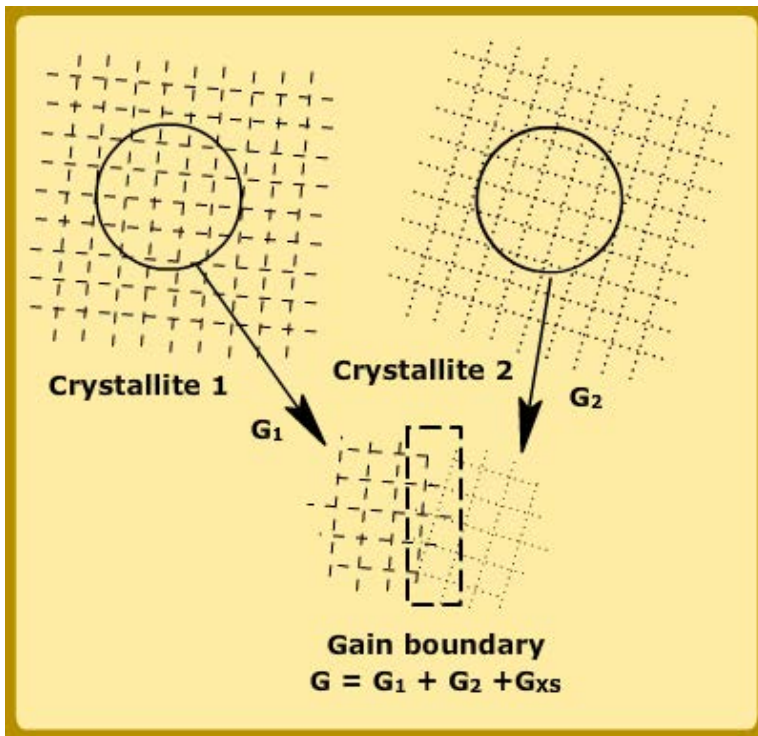
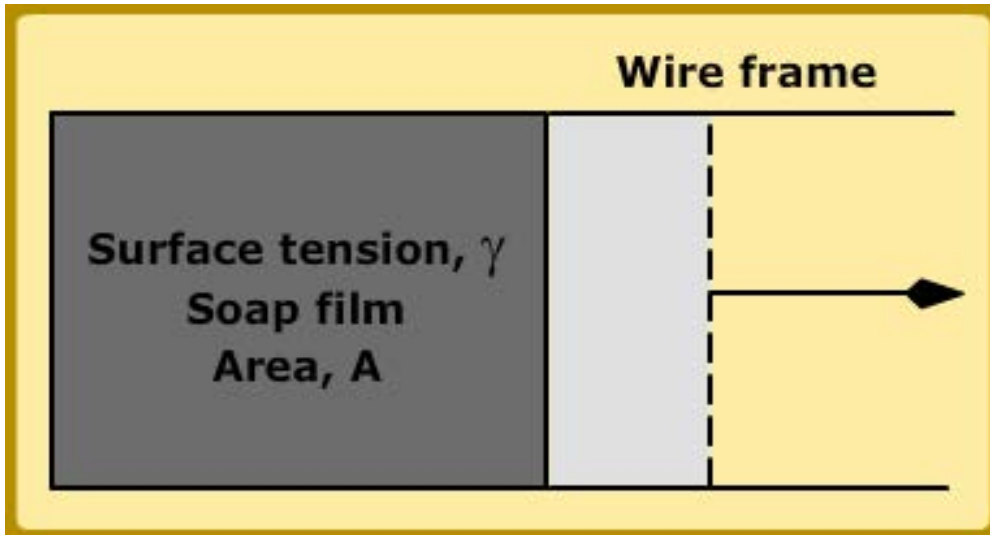


Figure 5: Formation of grain boundary and origin of grain boundary energy.

<b>Boundary</b>	<b>Typical energy (order of), J/m<sup>2</sup></b>
Grain boundary: Separates two crystallites of different orientations	$10^{-1}$
Twin boundary: Separates two crystallites of different orientations	$10^{-2}$
Coincident Site Lattice (CSL) boundary: Separates two crystallites of different orientations	$10^{-2}$
Free surface (of metals): Separates a crystallite from vapour	$10^0$
Anti-phase boundary: Separates two ordered domains	$10^{-2}$
Precipitate-Matrix interface: Separates a second phase from the matrix	$10^{-1}$ (coherent, semi-coherent) to $10^0$ (incoherent)
Solidification front: Separates a solid from its melt or a solution	$10^{-1}$

Table 1: Some typical interfaces in materials and their energies



the area of the film by  $dA$ . The total work done in stretching the film by  $dA$  is given by  $\gamma dA$ .

Consider the free energy of a solid system with a free energy of  $G$ ; there are two contributions to  $G$ ; the first is the bulk free energy  $G_0$ ; the second is the contribution from the interfaces, which is given by  $\gamma A$ , where  $\gamma$  is the interfacial energy per unit area and  $A$  is the area of the interface. Now, there are two ways in which the interfacial free energy can be changed in this system. One is to keep  $\gamma$  a constant and change  $A$ ; the other is to keep  $A$  constant but change  $\gamma$  itself. The second option is possible only in the case of solids since liquids and vapours cannot support any shear stresses. In other words,

$$G = G_0 + \gamma A \quad (2)$$

and

$$dG = \gamma dA + A d\gamma \quad (3)$$

Thus, we see that if  $d\gamma = 0$ , the change in free energy is equal to the work done in increasing the interface area; and, hence, the interfacial free energy is the same as surface tension; this happens only for liquids and vapour. On the other hand, in general, in solids, the surface tension is not the same as the interfacial free energy.

## 2.4 Interfacial energy anisotropy in solids

Interfacial energy is the interfacial excess free energy. Hence, it can be written in terms of enthalpy and entropy as follows:

$$\gamma = H_b - TS_b \quad (4)$$

where,  $H_b$  and  $S_b$  are the enthalpy and entropy associated with the boundary. Further, if one considers a solid-vapour interface in which a solid is in contact with its vapour, the enthalpy  $H_b$  can be replaced by internal energy associated with the boundary,  $E_b$ .

Consider a temperature that is low enough that the entropy contribution to the excess free energy can be neglected. In such a solid-vapour interface, almost all the interfacial energy contribution comes from the internal energy of the boundary. One can estimate the internal energy contribution using a simple bond-breaking model in such a system as follows.

Let us consider a crystalline solid. In the bulk, each atom has a certain number neighbour with which it bonds. For example, an atom in the bulk fcc structure bonds with 12 of its neighbours; an atom in the bulk bcc structure bonds with 8 of its neighbours; an atom in a simple cubic structure bonds with 6 of its neighbours and so on. However, if an atom is on the surface, certain number of its neighbours are missing; hence, the bonds are not satisfied; such dangling bonds are the ones which contribute to the internal energy of the system.

In a crystalline solid, obviously, surface formed with different planes will have different energies because the number of broken bonds per unit areas are different on different planes. Hence, the interfacial energy is also anisotropic in crystalline solids. This anisotropy is more prominent at lower temperatures. As temperatures rise, the entropy contribution becomes dominant and makes the interfacial energy less anisotropic.

## 2.5 Tutorial problems and questions

1. Consider a gold wire of radius 160 microns. It is held at about 1060°C and it loaded in tension by a suspended weight. For the wire to undergo zero creep (that is neither extension nor contraction due to the suspended weight), a load of 1.48 mN has to be applied (including

the weight of the wire). What is the surface tension of gold at this temperature?

## 2.6 Solutions to the tutorial

1. The circumference of the gold wire is  $2\pi r$  where  $r$  is the radius of the wire. The surface tension acting on this length balances the given weight. Hence, we get  $2\pi r\gamma = mg$ ; that is,  $\gamma = \frac{mg}{2\pi r}$ . This gives the surface tension as 1.473 N/m.

## 2.7 Supplementary information

There are many models that describe the interfaces and their structure. We discuss the bond breaking model for the solid-vapour interface in the next section. For small angle grain boundaries, there are models based on dislocations. In this model, a small angle grain boundary is assumed to be made up of a wall of dislocations. In the case of a small angle tilt boundary, one can show that the energy of the grain boundary increases linearly with the misorientation using what is known as the Read-Shockley equation; see [7].