

Surface Science

An Introduction

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The Surface Tension of Solids

Consider now a detailed description of the surface tension of solid surfaces, or solid–fluid interfaces. We have already shown that in order to have mechanical equilibrium in a system containing both solid and fluid phases, we must assume that the solid–fluid interface behaves as though it had a surface tension associated with it.

Looking at the question of solid surface tension in detail, however, we see that there is a fundamental difference in behavior between solid and liquid surfaces. This difference manifests itself when we consider the process of changing the area of an existing surface. In the case of a liquid, for example, the surface of a liquid in a vessel as shown in Figure 3.7, the surface area may be increased simply by tilting the vessel, as shown in the figure. In this case, the incremental surface area is formed by material flowing from the bulk of the liquid to form additional surface having identical properties to the preexisting surface. That is, the state of the surface is not changed as its extent is changed.

The situation in a solid is quite different. Because the solid has a finite resistance to shear, one must stress the solid in order to cause an increase in its surface area. In the stressing process, bond angles and bond distances are changed. The state of the surface is no longer that associated with the unstressed surface.

We can describe the changes in the state of the surface associated with extending the surface area of a solid in terms of a parameter called the surface stress. This is a parameter that is related to, but not in general equal to, the surface tension. To understand the differences between the two parameters, and to develop the relations between them, consider the work done in the two following processes:

1. Take a unit cube of a solid material, as shown in Figure 3.8a, and stretch it along the x -direction, at constant y and unconstrained z . The work done in this case is

$$W_0 = \int f dx = f_{\text{bulk}} dx, \quad 3.20$$

where f_{bulk} is the force required to strain the bulk material of the cube.

2. Take the same unit cube, split it along the x - y plane as shown in Figure 3.8b, and then stretch the two halves along the x -direction as before, at constant y and unconstrained z . In this case, the work done is

$$W_1 = \int f dx = f_{\text{bulk}} dx + 2f_{\text{st}} dx, \quad 3.21$$

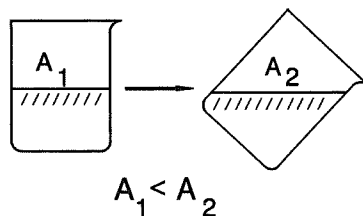


Figure 3.7 Illustration of the process of changing the surface area of a liquid.

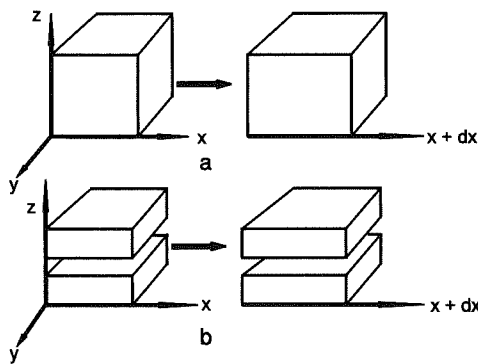


Figure 3.8 Operations carried out to define the surface stress in a solid, showing (a) stretch unit cube along x at constant y ; and (b) cut cube along x - y plane, then stretch along x at constant y .

in which f_{xx} is the surface stress in the x -direction. From Equations 3.20 and 3.21

$$f_{xx} = \frac{W_1 - W_0}{2dx} = \frac{W_1 - W_0}{2\epsilon_{xx}}, \quad 3.22$$

where ϵ_{xx} is the strain along the x -axis. That is, $(W_1 - W_0)$ is the work required to deform the surface along the x -direction and f_{xx} is the force (or stress) required to do the work that results in a strain ϵ_{xx} .

We could carry out similar experiments in which the unit cube was stretched in the y -direction at constant x , or in which the cube was sheared in the x - y plane. These exercises would yield

$$f_{yy} = \frac{W'_1 - W'_0}{2\epsilon_{yy}}$$

and

$$f_{xy} = \frac{W''_1 - W''_0}{2\epsilon_{xy}}. \quad 3.23$$

What we have developed in this exercise are the parameters f_{xx} , f_{yy} , and f_{xy} , which are the components of a second-order tensor describing the state of stress in the surface. This demonstrates one initial significant difference between surface stress and surface tension: surface stress is a tensor, surface tension is a scalar.

Let us go on to develop the relation between the surface stress components and the surface tension. To do this, we will consider the work done in performing a given overall process following two different paths.

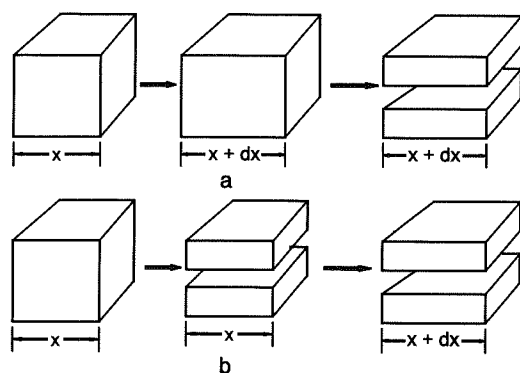


Figure 3.9 Operations carried out to show the relation of surface tension to surface stress, showing (a) stretch unit cube along x , then split, and (b) split unit cube, then stretch along x .

Starting again with a unit cube of a solid material, first stretch the cube along the x direction, then split the cube along the x - y plane, as shown in Figure 3.9a. The work done in this process is

$$W_I = W_0 + 2(\gamma + \Delta\gamma)(1 + \epsilon_{xx}) \approx W_0 + 2\gamma + 2\Delta\gamma + 2\gamma\epsilon_{xx}, \quad 3.24$$

neglecting the second-order term $2\Delta\epsilon_{xx}$. As an alternative, first split the cube along the x - y plane, then stretch the two halves along the x direction, as shown in Figure 3.9b. For this case the work done is:

$$W_{II} = 2\gamma + W_I. \quad 3.25$$

Note that in both cases the terms containing γ are associated with the work done in forming the new surfaces.

Since both of the above processes are assumed to have been carried out reversibly, and with no heat transfer from the surroundings,

$$W_I = W_{II} \quad 3.26$$

$$W_0 + 2\gamma + 2\Delta\gamma + 2\gamma\epsilon_{xx} = W_I + 2\gamma, \quad 3.27$$

or

$$\frac{W_I - W_0}{2\epsilon_{xx}} = \gamma + \frac{\Delta\gamma}{\epsilon_{xx}} \approx \gamma + \frac{d\gamma}{d\epsilon_{xx}}, \quad 3.28$$

or

$$f_{xx} = \gamma + \frac{d\gamma}{d\epsilon_{xx}}. \quad 3.29$$

By a similar set of steps we could deduce that

$$f_{yy} = \gamma + \frac{d\gamma}{d\epsilon_{yy}}, \quad f_{xy} = \frac{d\gamma}{d\epsilon_{xy}} \tag{3.30}$$

Thus, we can define the components of the surface stress tensor in terms of the surface tension and the changes in the surface tension with the respective strain terms.

The relations just developed will be applied to two practical cases, in order to see the explicit relationship between the stress components and the surface tension. Consider first the case of a cube of liquid. In this case, as discussed previously, the change in surface tension associated with stretching the surface will be zero, as material can flow from the bulk to the surface as extension proceeds. Since γ is unchanged, $d\gamma/d\epsilon = 0$ and we have

$$f_{xx} = \gamma, \quad f_{yy} = \gamma, \quad f_{xy} = 0. \tag{3.31}$$

That is, the surface stress in a liquid surface is isotropic and numerically equal to the surface tension.

Alternatively, one may look at the relation between surface stress and surface tension in a simple solid. To do this, one must develop a model of the solid and postulate its response to stress. This will be done by assuming a simple cubic crystal structure and describing the bonding in the crystal by a nearest neighbor model. That is, the binding energy of the crystal is simply the sum of the energies of all of the nearest neighbor bonding interactions.

In such a solid, the surface tension will be just the sum of the energies associated with the nearest neighbor bonds that are broken in the process of creating the surface by splitting the crystal along the desired crystallographic plane. That is,

$$\gamma = \frac{\Phi v}{2}, \tag{3.32}$$

where Φ is the energy per nearest neighbor bond, v is the number of bonds per unit area, and the factor of 2 accounts for the fact that two surfaces are formed in the splitting process.

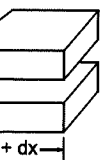
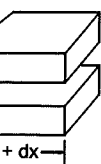
For the case of the (100) surface of a simple cubic crystal, as shown in Figure 3.10,

$$\Phi = \frac{\Delta H_s}{3}, \quad v = \frac{nm}{nma^2} = \frac{1}{a^2},$$

or

$$\gamma = \frac{\Phi}{2a^2} = \frac{\Delta H_s}{6a^2}. \tag{3.33}$$

For the case of a surface vicinal to this (100) surface, with a misorientation angle θ , as shown in Figure 3.11,



surface tension to surface stress, unit cube, then stretch along x .

first stretch the cube along the direction shown in Figure 3.9a. The work

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then, first split the cube along the x -direction, as shown in Figure 3.9b.

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$$\frac{d\gamma}{d\epsilon_{xx}}, \tag{3.28}$$

$$\frac{d\gamma}{d\epsilon_{xx}}. \tag{3.29}$$

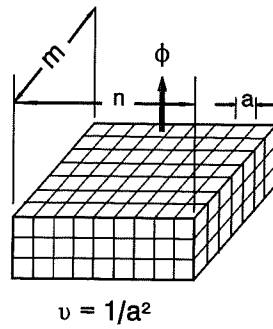


Figure 3.10 Nearest neighbor model for determining the surface tension of a solid for the case of a singular surface.

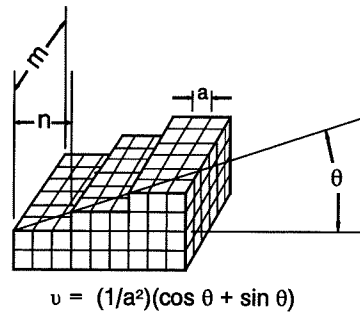


Figure 3.11 Nearest neighbor model for determining the surface tension of a solid for the case of a vicinal surface.

$$\Phi = \frac{\Delta H_s}{3}, \quad v = \frac{1 + \tan \theta}{a^2 / \cos \theta},$$

or

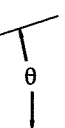
$$\begin{aligned} \gamma &= \left(\frac{\Phi}{2a^2} \right) (\cos \theta + \sin \theta) \\ &= \left(\frac{\Delta H_s}{6a^2} \right) (\cos \theta + \sin \theta). \end{aligned} \quad 3.34$$

Note that since $(\cos \theta + \sin \theta)$ is always greater than unity, the γ of the vicinal surface will always exceed that of the corresponding singular surface.

What, then, is the surface stress for such a surface? The nearest neighbor bond distance in the crystal at equilibrium is set by the condition that this equilibrium length



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minimizes the energy of the system. Consequently, any change in position of the surface atoms relative to their positions in the bulk of the crystal will cause an unfavorable increase in system energy. Thus, the surface as formed will be unstrained. Moreover, since the surface tension is associated only with bonds broken perpendicular to the surface (in this simple cubic model), the contribution to the surface energy per bond is unchanged when the surface is extended. However, the surface tension per unit area (the conventional way of measuring surface tension) will decrease as stretching proceeds, as the number of bonds per unit area will decrease. The change in surface tension with strain will be given by

$$\begin{aligned} \gamma + \Delta\gamma &= \left(\frac{\Phi v}{2}\right) \left(\frac{1}{1 + \epsilon_{xx}}\right) \\ &\approx \left(\frac{\Phi v}{2}\right) (1 - \epsilon_{xx}). \end{aligned} \tag{3.35}$$

Thus,

$$\begin{aligned} \frac{\Delta\gamma}{\epsilon_{xx}} &\approx \frac{d\gamma}{d\epsilon_{xx}} \\ &= -\frac{\Phi v}{2} = -\gamma, \end{aligned} \tag{3.36}$$

and, from Equation 3.29,

$$f_{xx} = \gamma + \frac{d\gamma}{d\epsilon_{xx}} = \gamma - \gamma \tag{3.37}$$

or

$$f_{xx} = 0. \tag{3.38}$$

Thus, no surface stress is present, even though the surface tension is finite. In any real solid, the surface stress components would not in general be equal to zero, but neither would they be equal to the surface tension.

The critical point of the foregoing discussion is that the relation between the surface stress components and the surface tension is determined by whether or not the nature of the surface is changed in the process of extending the surface. In a liquid, with no resistance to shear, the surface tension is unchanged by an extension process. The new surface formed is identical to the old, and surface stress is equal to surface tension (assuming only that the extension process is slow enough to permit adsorptive equilibrium to be maintained). In a solid, except at very high temperatures (a case which we will consider later in this chapter, in the section on measurement of solid surface tensions), because of the limits on atomic mobility, the state of the surface does change in the extension process and the surface stress is no longer identical to the surface tension.

The γ Plot

The orientation dependence of the surface tension of a solid surface can be described graphically using a construction known as the γ plot. In this construction, the surface tension of a crystal face of orientation S is described in terms of σ , a unit vector normal to the orientation S , and the magnitude of γ associated with this orientation, $\gamma(\sigma)$. A polar plot is then constructed in which the radius vector is

$$\mathbf{R} = \gamma(\sigma)(\sigma) . \quad 3.39$$

The surface generated by the tip of \mathbf{R} is the γ plot and is in general a closed surface of some arbitrary shape.

Consider the shape of the γ plot for a few simple cases. The simplest case is that of a liquid, for which γ is independent of orientation. For this case, \mathbf{R} will have the same magnitude for all directions of σ , and the γ plot will be a sphere.

As a second case, consider the model discussed above, that of a simple cubic crystal held together with nearest neighbor bonds. For this case, we determined that, for faces vicinal to (100),

$$\gamma(\theta) = (\Phi/2a^2)(\cos \theta + \sin \theta) . \quad 3.40$$

The two-dimensional γ plot for this case is shown in Figure 3.12. Note that the plot is made up of the outer envelope of four circles, each having a diameter $\Phi/\sqrt{2}a^2$, all tangent to the origin of the plot.

This plot represents a simple model, but it illustrates a number of features that are common to all such plots. The presence of cusps at low index faces is a common feature of all plots based on pair bonding models. The nearest neighbor model shows cusps only at singular orientations; more sophisticated models would show additional cusps. Extension of the model to three dimensions, for the same model assumptions discussed previously, would lead to a γ plot that was the outer envelope of eight spheres, each having a radius $\sqrt{3}\Phi/2a^2$, all tangent to the origin of the plot and centered on the corners of a cube. This feature that the γ plot is made up of segments of spheres

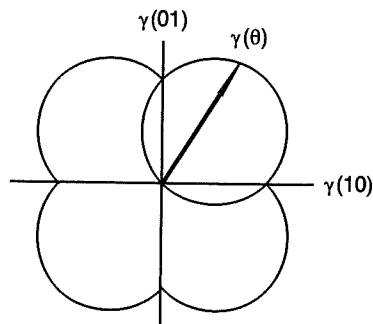


Figure 3.12 γ plot for a two-dimensional simple cubic solid, assuming nearest neighbor bonding.

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passing through the origin is a general feature of all plots based on pair bonding models. Consideration of second nearest and farther neighbors merely complicates the plot by adding more spheres to the construction and, consequently, more cusps to the plot. The general expression for γ in the two-dimensional case of a many neighbor model is

$$\begin{aligned} \gamma(\theta) &= \frac{\gamma_0 + \left(\frac{\epsilon}{a}\right) \tan \theta}{1/\cos \theta} \\ &= \gamma_0 \cos \theta + \left(\frac{\epsilon}{a}\right) \tan \theta, \end{aligned} \tag{3.41}$$

where $\epsilon = f(\theta)$. For the case of nearest neighbors only, $\epsilon/a = \gamma_0$, and we revert to Equation 3.40.

Finally, it must be noted that an assumption in these calculations is that the surface is defect free. Thermally induced adatom-vacancy pairs, or other defect pairs that would be present in finite concentrations at finite temperatures, will modify the treatment above, as γ is associated with the change in Helmholtz free energy involved in the formation of new surface. Since $F = E - TS$, any process that changes E (e.g., vacancy formation energy) or S (e.g., mixing defect sites with perfect sites) will change γ and hence the γ plot. The major effect of these changes is to blunt the cusps of the γ plot, so that $d\gamma/d\theta$ will not be discontinuous at singular orientations. The trend in all cases is toward a more nearly spherical γ plot as the melting temperature is approached.

Measurement of Surface Tension of Liquids

The two final sections of this chapter will consider practical methods for measuring the surface tension, first for the case of liquid surfaces and then for solids. A number of techniques have been developed for the measurement of liquid surface tension. Of the two most common, one makes use of the application of LaPlace's equation to liquid in a capillary tube, and the other uses the balance between surface tension and gravitational forces.

The so-called capillary rise method of surface tension measurement can be explained with reference to Figure 3.13. Here we have a small diameter capillary tube, immersed in a large body of liquid. If the liquid wets the walls of the capillary tube, (that is, if the contact angle is zero), then the initial situation, when the tube is first immersed in the liquid, will be as shown in Figure 3.13a. If we consider the balance of forces in the vertical direction in the tube, just below the surface of the meniscus, we see that p^α is less than p^β by the amount

$$(p^\beta - p^\alpha) = \frac{2\gamma}{r}, \tag{3.42}$$

from LaPlace's equation. To restore the balance of forces, liquid must rise up the capillary until the weight of the liquid column balances this difference in pressure.

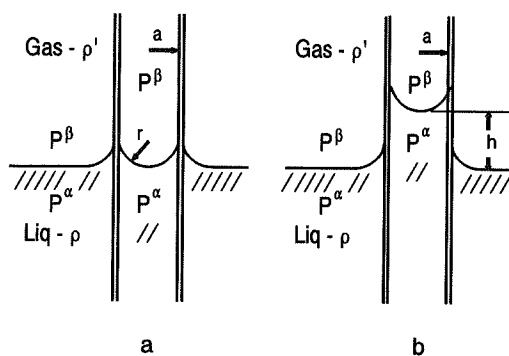


Figure 3.13 Capillary rise method of measuring the surface tension of a liquid, showing (a) initial state, and (b) final equilibrium state.

Figure 3.13b shows this situation. The weight change associated with the rise of the liquid column is

$$hg(\rho - \rho'), \quad 3.43$$

in which ρ is the density of the liquid and ρ' the density of the gas phase. Thus, at equilibrium

$$p^\beta = p^\alpha + hg(\rho - \rho') \quad 3.44$$

or

$$(p^\beta - p^\alpha) = \frac{2\gamma}{r} = hg(\rho - \rho'). \quad 3.45$$

If a small enough tube is used that the radius of curvature of the liquid surface, r , is equal to the radius of the tube, a , and assuming that $\rho' \approx 0$, Equation 3.45 reduces to

$$\gamma = \frac{1}{2} hg \rho a, \quad 3.46$$

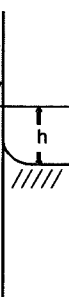
thus expressing γ in terms of the gravitational constant, g , and the experimentally observable variables h , ρ , and a . In general, if the contact angle θ is not zero, a term $r = a/\cos \theta$ will appear in the expression, yielding

$$\gamma = \frac{1}{2} hg \rho (a/\cos \theta). \quad 3.47$$

This relation gives γ in terms of constants and observables.

A similar argument holds for systems in which the liquid does not wet the tube. Figure 3.14 shows the situation in this case. Because the liquid surface is convex, the meniscus must be depressed to reach equilibrium.

The second method of determining γ is a little less obvious than the first one, but has been used often to measure the surface tension of liquid metals. This technique depends on the combined effects of gravity and surface tension on the shape of a drop hanging from a tip (pendant drop) or resting on a flat surface (sessile drop). The situation is shown in Figure 3.15.



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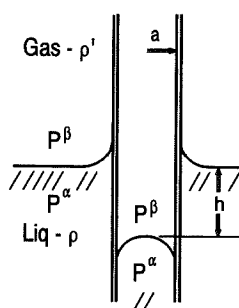


Figure 3.14 Capillary depression in a system in which the liquid does not wet the solid.

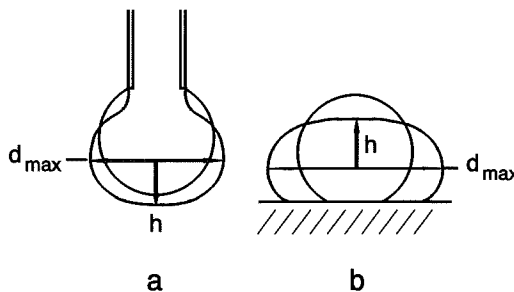


Figure 3.15 Drop shape methods of measuring the surface tension of a liquid for (a) pendant drop and (b) sessile drop.

In the absence of gravitational forces, the drop would be a sphere. Gravitational forces distort the drop to a shape that is complex but that can be rigorously defined. These shapes have been calculated to high precision in terms of γ and the gravitational constant, g . These shapes can be characterized in terms of the maximum diameter of the drop and the height of the maximum diameter above the bottom of the drop, for the case of the pendant drop, or in terms of the height of the top of the drop above the maximum diameter and maximum diameter for the case of the sessile drop. That is, by measurement of these parameters (usually from a photograph of the drop or using a telescope to look at a drop in an oven), one can determine the surface tension from published tables and a knowledge of the density of liquid.

Measurement of Solid Surface Tensions

Although, as we have discussed previously, there are fundamental differences between the concept of surface tensions in solids and those in liquids, it is possible in some circumstances to make a direct measurement of the surface tension of a solid material. The classic measurement of this kind is based on a technique developed by Udin, Shaler, and Wulff [1952], which allows determination of the surface tension of a solid from a purely mechanical test.

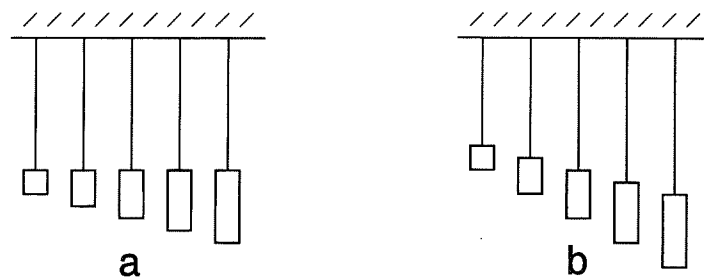


Figure 3.16 Measurement of the surface tension of solid wires by the zero creep method of Udin, Shaler and Wulff. Part (a) shows wire lengths before heating and part (b) shows wire lengths after creep has occurred at high temperature.

The basis of this measurement lies in the difference between the work of formation of a surface, and the stretching of a solid surface. The stresses associate with stretching arise because the solid cannot, in general, respond to the stretching force by atom movements at a rate fast enough to relieve the applied stress, as a liquid can. If the force is small enough, however, and is applied to the surface of a solid at a high enough temperature that diffusion is rapid, and in a configuration which supplies large numbers of the defects required for diffusive transport, then this limitation can be circumvented.

In practice, one begins with fine polycrystalline wires, loads them with a range of small loads, and holds them at temperatures close to the melting point for long periods of time. The initial and final conditions observed in such a study are shown in Figure 3.16. It can be seen from the figure that wires with small loads contract, while those with large loads extend.

Mechanical considerations dictate that in a situation such as this, net diffusive transport will go on unless and until the pressure tensor within the solid is isotropic. Thus, for the no-motion case, the at equilibrium

$$p_{xx} = p_{yy} = p_{zz} = p^\beta. \quad 3.48$$

If one looks at a cross-section of the wire subjected to the load P that corresponds to the no-motion case, as shown in Figure 3.17, the result for the balance of forces in the vertical direction is

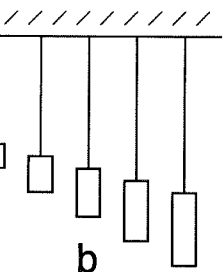
$$2\pi r\gamma - \pi r^2 p^\beta = P - \pi r^2 p^\alpha, \quad 3.49$$

in which $p^\beta \neq p^\alpha$ because of the considerations which led to LaPlace's equation. Application of LaPlace's equation to this case leads to

$$(p^\beta - p^\alpha) = \frac{\gamma}{r} \quad 3.50$$

(Note that the result is γ/r , rather than $2\gamma/r$ because the curved surface is cylindrical rather than spherical.) Substitution of this expression into the force balance equation yields

$$2\pi r\gamma - \pi r^2 p^\alpha - \pi r\gamma = P - \pi r^2 p^\alpha, \quad 3.51$$



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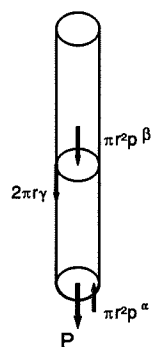


Figure 3.17 Force balance in the zero-creep method for a single crystal wire.

or

$$P = \pi r \gamma, \quad 3.52$$

allowing the surface tension to be calculated from the applied load for zero motion and the wire diameter.

In practice, one must also allow for the presence of grain boundaries in the wire. Generally the specimens used in this type of experiment have the configuration shown in Figure 3.18. Consideration of the grain boundary surfaces and the surface tension associated with them modifies the above equation for γ of the solid to

$$P = \pi r \gamma_{surf} - \left(\frac{n}{\ell} \right) (\pi r \gamma_{gb}), \quad 3.53$$

where n/ℓ is the number of grain boundaries per unit length of wire and γ_{gb} is the interfacial tension of the grain boundary.

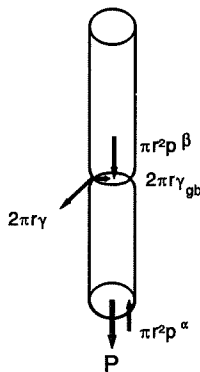


Figure 3.18 Force balance in the zero-creep method for a polycrystal wire.