

9.2: Surface Expansion Work

This textbook has thus far exclusively examined the thermodynamics of volume-type work, where energy is realized by multiplying volume by its conjugate pressure. Although difficult to conceptualize, work is also performed by expanding a surface: $\partial w = F \partial A$, where A is the area and F is the energy per unit area, otherwise known as surface tension. Already we note that there is a very important difference compared to a gas's pressure-volume work: $\partial w = -P_{ext} \partial V$; basically where is the minus sign? First, let us study the internal energy of a system performing reversible, isothermal pressure-volume work: $\partial U = 0 \quad J = T \partial S - P \partial V$

which requires $\partial S = \frac{P}{T} \partial V = \frac{nR}{V} \partial V$. When integrated, we find that: $\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$, a familiar equation from Chapter 4. As a result, it is fundamentally true that an increase in volume results in greater entropy. This makes sense when we think of a compression as imparting order; after all, if you compress a gas completely, it may collapse into a perfect crystal with no entropy at all!

Now we ask why the expansion of surface area is positive work. Let's remove the possibility of pressure-volume work and insert in its place the energy for a surface:

$$\partial U = T \partial S + \gamma \partial A$$

assuming a reversible, isothermal surface expansion requires: $\partial U = 0 \quad J = T \partial S + \gamma \partial \sigma$ and as such:

$$\partial S = -\frac{\gamma}{T} \partial A$$

which integrates to: $\Delta S = -\frac{\gamma}{T} \Delta A$. As a result, increasing surface area results in a decrease in entropy of the system, which at first appears counter-intuitive as one naturally would like to make surface expansion work analogous to volume expansion. To resolve, we need to think about what types of system realistically can experience a surface area change, for which we immediately realize- rubber bands.

Shown in Figure 9.6 is a representation of the interwoven polymer strands that comprise a rubber band, which is a ~ 2 -dimensional material and thus makes a good model for a surface. For the rubber band to be stretched the polymers must be fairly orderly, which is a low entropy state. When compressed the polymer strands are all tangled all over, which clearly indicate that surface entropy is increased when the surface area is extended.

For a theory to be proven true there must be an experiment that validates it. To do so, we got a 4 ft. rubber band and tied the end to a hammer as shown in Figure 9.7 Next, the rubber band was heated over its length with a heat gun. Now, let's predict the outcome- heating will cause disorder as shown in Figure 6.1B. The resulting increase in entropy must be realized by randomization of the elastic band's polymer strands, which will then shorten its overall length. As shown in the figure, the hammer raises by ~ 1 in. Therefore, heating shortens the rubber band, and while the effect is fairly slight, the shortening of the which is highly counterintuitive.

9.2.1 Surface related phenomenon: pressures of small droplets

We think of work as force times a change of distance, which we saw in Chapter 2 is the same as pressure times a change of volume. Let's apply the same analysis to a droplet. Considering the work to expand a surface, here the curved surface of a sphere, we find that:

$$\partial w = \gamma \partial A$$

where the surface tension γ has units of N/m and $\partial \sigma$ is in m^2 . Consider the change in surface area of a sphere with radius r as it grows by ∂r . A sphere has a surface area $4\pi r^2$, and a sphere with a radius $r + \partial r$ has a surface area of:

$$4\pi(r + \partial r)^2 = 4\pi r^2 + 8\pi r \cdot \partial r + 4\pi(\partial r)^2$$

If we assume that $4\pi(\partial r)^2$ is very small compared to $8\pi r \partial r$ and can thus be ignored, then the change of surface area is:

$$\partial A = 4\pi r^2 + 8\pi r \cdot \partial r - 4\pi r^2 = 8\pi r \cdot \partial r$$

Now when we insert this into the equation for work we find:

$$\partial w = \gamma \partial A = 8\pi\gamma r \cdot \partial r$$

As work is force times a change of distance and ∂r is that change of distance, then $8\pi\gamma r$ is the force that a spherical surface imparts on the interior. Force over area is pressure, and as a result, the surface tension pressurizes the interior of a droplet by:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{8\pi\gamma r}{4\pi r^2} = \frac{2\gamma}{r}$$

where again we use the fact that the area of a sphere is $4\pi r^2$.

The pressure inside a sphere must equal the exterior pressure if a droplet is to retain a stable, rounded shape. The exterior pressure includes the above resulting from surface tension in addition to the normal pressure (we assume it is P). As a result, the interior pressure of a droplet is:

$$P_{int} = P + \frac{2\gamma}{r}$$

This means that small droplets have higher interior pressures compared to larger ones.

As it applies to soap bubbles, we have to make a small change to the expression above: $P_{int} = P + \frac{4\gamma}{r}$, because a soap bubble technically has pressure arising from both the interior and exterior of the round soap film. The fact that a smaller bubble is under higher pressure is likely intuitive to you as most of us liked to blow soap bubbles as children. Ever see two fuse together? As shown in Figure 9.8, when that happens you may recall that the smaller one seems to get “sucked into” the bigger bubble. That’s because it’s under higher pressure, thus it collapses when the interior is exposed to the lower pressure inside the larger one which appears to grow.

9.2.2 Phase diagram: The Gibbs–Thomson equation

In the previous section we demonstrated how surface tension causes the interior pressure of a small particle to be higher than the bulk material. This has an important effect when a solid crystal is beginning to form in a freezing liquid. Initially, the particle must have nano-sized dimensions, and thus it will have a higher internal pressure. This in turn increases the chemical potential such that the small solid particle is not thermodynamically stable. Thus, one can ask how do things ever freeze? It turns out that if the temperature is lower than the freezing (fusion) point, then the nucleating solid particles are stabilized.

In this section we study the thermodynamics of nanoparticle stability using the example of solid particle nucleating in a freezing liquid as shown in Figure 9.X. Initially we will assume that the chemical potentials are equal:

$$\mu_{liq} = \mu_{solid}$$

However, we know that the solid nanoparticle has a higher internal pressure (P) compared to the bulk (P°) which raises its chemical potential: $\mu_{solid} + \int_{P^\circ}^P V_m^{solid} dP$. Thus, the temperature (T) must be lower than the bulk freezing temperature (T_{fus}) to offset this. The chemical potential thus has two corrections, one for pressure and temperature:

$$\mu_{solid} + \int_{T_{fus}}^T -S_m^{solid} dT + \int_{P^\circ}^P V_m^{solid} dP$$

where $P > P^\circ$ and $T < T_{fus}$. Concerning the surrounding liquid, it must experience the same decrease in temperature which also affects its chemical potential:

$$\mu_{liq} + \int_{T_{fus}}^T -S_m^{liq} dT = \mu_{liq} + \int_{T_{fus}}^T -S_m^{liq} dT$$

The temperature (T) can be found where chemical potentials of the solid nucleating nanoparticle and surrounding liquid remain equal:

$$\mu_{liq} + \int_{T_{fus}}^T -S_m^{liq} dT = \mu_{solid} + \int_{T_{fus}}^T -S_m^{solid} dT + \int_{P^\circ}^P V_m^{solid} dP$$

There is no pressure-volume modulation of the liquid’s chemical potential as it is in the bulk state. The solid isn’t so lucky, and its chemical potential is raised by internal pressure as:

$$\int_{P^*}^P V_m^{solid} \partial P = V_m^{solid} \cdot \Delta P = V_m^{solid} \cdot \frac{2\gamma}{r}$$

using the relationship $P_{int} = P + \frac{2\gamma}{r}$ from section 9.1.1.

As for the effect of temperature, we combine the temperature integrals on the left side:

$$\mu_{liq} - \mu_{solid} + \int_{T_1}^{T_2} -S_m^{liq} \partial T + \int_{T_{bulk}}^T S_m^{solid} \partial T = V_m^{solid} \cdot \frac{2\gamma}{r}$$

and then combine them because they have the same limits:

$$\int_{T_{fus}}^T -S_m^{liq} \partial T + \int_{T_{fus}}^T S_m^{solid} \partial T = \int_{T_{fus}}^T (S_m^{solid} - S_m^{liq}) \partial T = \int_{T_{fus}}^T -\Delta S_{fus,m} \partial T = -\Delta S_{fus,m} (T - T_{fus})$$

Since we have already established that: $\mu_{liquid} - \mu_{solid} = 0 \text{ J/mol}$ we are left with:

$$-\Delta S_{fus,m} (T - T_{fus}) = V_m^{solid} \cdot \frac{2\gamma}{r}$$

which can be rearranged as:

$$T = T_{fus} - \frac{V_m^{solid}}{\Delta S_{fus,m}} \cdot \frac{2\gamma}{r}$$

where the entropy change of fusion is defined by the entropy per mole of the liquid state minus the solid state. As in section , we can use the enthalpy of fusion divided by the fusion temperature to represent the change in entropy, $\Delta S_{fus,m} = \frac{\Delta H_{fus,m}}{T_{fus}}$:

$$T = T_{fus} - \frac{T_{fus} \cdot V_m^{solid}}{\Delta H_{fus}} \cdot \frac{2\gamma}{r}$$

The Gibbs-Thomson equation describes some well-known effects, such as the aging of ice cream. It gets crunchier, doesn't it? That's because the smaller ice crystals are melting in the freezer if it isn't cold enough, which makes the bigger ones even bigger. Thus, over time you feel like your biting down on a mouthful of ice cubes! A few other examples are shown in Figure 9.9, such as DSC calorimetry on porous glass soaked in benzene that shows freezing of the liquid in smaller pores occurring at lower temperature than the bulk liquid. Also aluminum metal particles show size-dependent melting points once they are on a nanometer-size scale. Although the temperature drop isn't very large, you can imagine that engineers need to take these data into account when designing microelectronic components because heat becomes a bigger problem once the circuits themselves become smaller and smaller.

9.2.3 Phase diagram: The Kelvin and Ostwald-Freulich equations

Now let's move from solid-liquid to liquid-gas equilibrium as a function of size. consider the concept of equal chemical potentials of a vapor originating off a water droplet surface and the interior liquid. In this case:

$$V_m^{liq} \cdot \partial P^{liq} + S_m^{liq} \cdot \partial T = V_m^{vap} \cdot \partial P + S_m^{vap} \cdot \partial T$$

where the changes in pressure of the liquid ∂P^{liq} is not the same as the gas ∂P because of the effect of the addition of pressure due to the surface tension. For the purposes of this demonstration, let us consider the temperature constant, and thus $\partial T = 0 \text{ K}$. We are left with:

$$V_m^{liq} \partial P^{liq} = V_m^{vap} \partial P$$

Now consider how the relationship would change as a function of changing radius. Since the liquid phase is in the interior of the droplet:

$$\partial P^{liq} = \partial \left(P + \frac{2\gamma}{r} \right) = \partial P + 2\gamma \cdot \partial \left(\frac{1}{r} \right)$$

Plugging this into $V_m^{liq} \partial P^{liq} = V_m^{vap} \partial P$ from above along with some simplification: $\partial P + 2\gamma \cdot \partial \left(\frac{1}{r} \right) = \frac{V_m^{vap}}{V_m^{liq}} \partial P$

Now we will bring ∂P over to one side and $2\gamma \cdot \partial \left(\frac{1}{r}\right)$ to the other:

$$\partial P - \frac{V_m^{vap}}{V_m^{liq}} \partial P = \left(\frac{V_m^{liq}}{V_m^{liq}} - \frac{V_m^{vap}}{V_m^{liq}} \right) \partial P = - \left(\frac{V_m^{vap} - V_m^{liq}}{V_m^{liq}} \right) \partial P = -2\gamma \cdot \partial \left(\frac{1}{r} \right)$$

Thus:

$$\frac{V_m^{vap} - V_m^{liq}}{V_m^{liq}} \partial P = 2\gamma \cdot \partial \left(\frac{1}{r} \right)$$

Now we assume that the volume of the vapor is much higher than the liquid $V_m^{vap} - V_m^{liq} \approx V_m^{vap}$, and we will turn to our old friend the perfect gas law: $V_m^{vap} \approx \frac{RT}{P}$. Thus:

$$2\gamma \cdot \partial \left(\frac{1}{r} \right) = \frac{RT}{V_m^{liq}} \frac{\partial P}{P}$$

Integration of both sides yields: $\int_{\frac{1}{m^{-1}}}^{\frac{1}{r}} 2\gamma \cdot \partial \left(\frac{1}{r} \right) = \int_{P^*}^P \frac{RT}{V_m^{liq}} \frac{\partial P}{P}$

where P° is the pure partial pressure. The left side is: $\int_{\frac{1}{m^{-1}}}^{\frac{1}{r}} 2\gamma \cdot \partial \left(\frac{1}{r} \right) = 2\gamma \cdot \frac{1}{r}$ and the right is: $\frac{RT}{V_m^{liq}} \ln \left(\frac{P}{P^*} \right)$. Equating the two: $\frac{RT}{V_m^{liq}} \ln \left(\frac{P}{P^*} \right) = 2\gamma \cdot \frac{1}{r}$ yields the Kelvin equation:

$$\ln \left(\frac{P}{P^*} \right) = \frac{2\gamma V_m^{liq}}{RT} \cdot \frac{1}{r}$$

And thus $P = P^* \cdot \exp \left(\frac{2\gamma V_m^{liq}}{RT} \cdot \frac{1}{r} \right)$. As a result, we see that the partial pressure of a vapor originating off a liquid droplet is higher than from a bulk source. Eventually, a droplet can be so small that it has a higher partial pressure than the surrounding atmosphere, whereupon it disintegrates.

There is another interesting aspect of the above relationship which is revealed by a units analysis:

$$\frac{2\gamma V_m^{liq}}{RT} = \frac{J/m^2 \cdot m^3/mol}{J/K/mol \cdot K} = \text{meters}$$

Furthermore, if one inserts typical values into the above for molar volumes and surface energies as in the example problem, then this lengthscale is on the order of a few nanometers. Consequently, the factor $\frac{2\gamma V_m^{liq}}{RT}$ is often described as a critical radius R_{crit} , which allows us to demonstrate the Ostwald-Freulich equation:

$$P = P^* \cdot e^{\frac{R_{crit}}{r}}$$

Here we can see that if a water droplet is smaller than its critical radius, then its vapor pressure rises dramatically. The droplet is unlikely stable, and will evaporate allowing the water molecules to adhere to the surfaces of larger droplets making them even larger. This process is called Ostwald ripening, a behavior that is observed in many different systems aside from water mist. The example of ice cream becoming crunchier over time is one. Another is in geology, where “phenocrystals” are often observed in rocks. In chemistry, we like to make nanoparticles.

9.2.4 Nanoparticle Synthesis: The Lamer Model

The synthesis of small inorganic nanoparticles, such as the gold colloids that give color to stained glass windows, allows us to summarize all the size-dependent phenomena that has been discussed thusfar. Metal and semiconductor nanoparticles are at the forefront of materials science research due to the increase in surface area which is beneficial for catalysis and the ability to tune many physical properties with size. Such nanoparticles need to be synthesized which is a whole field of science in chemistry. The “burst nucleation theory” of LaMer provides a framework for understanding the thermodynamic basis for many of the existing methods.

As we have discussed, nature abhors a surface because creating surface area decreases entropy (or, equivalently there is a positive change in Gibbs energy at constant pressure and temperature). Counter to this is the fact that forming bonds is generally

energetically downhill, and scales with volume because more bonds take up more volume. Consequently, we can write a phenomenological model for the Gibbs energy of formation of small particles:

$$\Delta G = 4\pi \cdot \gamma \cdot r^2 - \frac{4}{3}\pi \cdot r^3 \cdot |\Delta_f G_V|$$

where γ is the surface energy and $|\Delta_f G_V|$ is the absolute value of the Gibbs energy of formation per unit volume. The fundamental revelation with the above is that the energy rises as r^2 and decreases as r^3 . As a result, for $r \ll 1$ the area term is dominant while the opposite is true when $r \gg 1$. Consequently, we see that small particles are not stable but if they can just get big enough they just might keep growing.

If small particles are unstable, then how is it that anyone is able to synthesize nanoparticles to begin with? In the 1950's Victor LaMer developed a standard model to describe how such small using the preparation of colloidal sulfur in a water/acetone solution as shown in Figure 9.10.

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