

Figure 1: The chemical potential of a solid liquid and gas. The lowest chemical potential is the equilibrium phase. Where the chemical potentials cross is the phase transition.

9 Phase transitions

Last time, we learned that the phase with the lowest chemical potential (or free energy per particle) is the equilibrium phase. Let's explore that idea a little more.

$$G = U - TS + pV = \mu N \quad (1)$$

That means that

$$\mu(p, T) = \frac{U(p, T, N)}{N} - T \frac{S(p, T, N)}{N} + p \frac{V(p, T, N)}{N}. \quad (2)$$

In other words, the chemical potential is determined by the internal energy per particle, the entropy per particle, and the volume per particle (which is the inverse of the particle density). By changing T and p , the relative importance of the entropy per particle and volume per particle changes.

9.1 Higher temperature \rightarrow higher entropy

Let's consider the case where we start at a $T = 0$ K, keep the pressure constant, and increase the temperature T . According to Eqn 2,

$$\mu = \frac{U}{N} - T \frac{S}{N} + p \frac{V}{N}, \quad (3)$$

where we have left off the functional dependence. In general we know that as T increases, U increases roughly linearly (like equipartition), S increases logarithmically (if the heat capacity is roughly constant), and V increases roughly linearly for a gas, and less for a solid or a liquid. A detailed analysis of this is certainly possible, but let's simplify thing by assuming that U, S, V do not change as a function of temperature. This is a good approximation in any small enough region; we'll mostly be interested in the regions around the phase transitions. To simplify our equations a little bit, let's define some lower-case variables: $u = U/N$, $s = S/N$, and $v = V/N$, which are the internal energy, entropy, and volume *per particle*. These are useful quantities because they don't depend on how many particles there are in the system.

In the constant U, S, V approximation, we can determine at what temperature a phase transition occurs fairly simply. Let's consider a solid and liquid. Then for the liquid

$$\mu_\ell = u_\ell - Ts_\ell + pv_\ell \quad (4)$$

and for the solid

$$\mu_s = u_s - Ts_s + pv_s. \quad (5)$$

To find the temperature of the phase transition (the melting temperature), we set the difference in chemical potentials equal to zero:

$$\mu_\ell - \mu_s = (u_\ell - u_s) - T_{melt}(s_\ell - s_s) + p(v_\ell - v_s) = 0. \quad (6)$$

As you can see, only the difference in internal energies, entropies, and volumes per particle matters. For a liquid and solid, we expect:

$$u_\ell - u_s > 0 \quad (7)$$

$$s_\ell - s_s > 0 \quad (8)$$

$$v_\ell - v_s \simeq 0. \quad (9)$$

(while we all know that ice has a larger volume than liquid water, that will not matter too much here). Given those approximations,

$$T_{melt} \simeq \frac{u_\ell - u_s}{s_\ell - s_s}. \quad (10)$$

As you can see, the phase transition occurs when the internal energy cost and the entropy gain upon melting are in balance with each other.

You can probably already see that increasing the temperature tends to favor phases with higher entropy, since that will lower the chemical potential. This is generally the case. As temperature increases, the phases that appear are higher in entropy. Note that as the system crosses the phase transition between solid and liquid, its internal energy will increase; in fact it is drawing heat from its surroundings spontaneously in order to make the transition. This effect is used to make ice cream – ice melting into water draws quite a lot of heat from the ice cream for fast cooling.

9.2 Higher pressure → higher density

We can perform a very similar analysis as temperature for the pressure of phase transitions. Starting from the same equation, keeping T constant and changing just the pressure:

$$\mu_\ell - \mu_s = (u_\ell - u_s) - T(s_\ell - s_s) + p_{melt}(v_\ell - v_s) = 0. \quad (11)$$

Here, if the volume difference is zero then pressure cannot create a phase transition; it can only do so if the volumes are different between phases. In general you can solve this for p_{melt} just like T_{melt} if you know that volume difference.

9.3 Latent heat, enthalpy, and entropy

Now let's consider the heat that the system uses to undergo a phase transition. Let's consider the case in which we are melting ice. What we observe is that the temperature and pressure do not change, but some amount of heat must be transferred to melt all the ice before the temperature can rise again. This means that the heat capacity during the phase transition is infinite, so we must take some care in treating this situation. The total amount of heat it takes to cross the phase transition is called the latent heat L .

Recall the fundamental relation:

$$dS = \frac{dQ}{T}. \quad (12)$$

Since the temperature is constant during the phase transition, then we can integrate simply and determine that the latent heat is quite closely related to the change in entropy

$$L = T\Delta S = T(S_\ell - S_s), \quad (13)$$

where we have specialized to the liquid and solid. Alternatively, we can write this in terms of the quantities per particle

$$\frac{L}{N} = T(s_\ell - s_s) \quad (14)$$

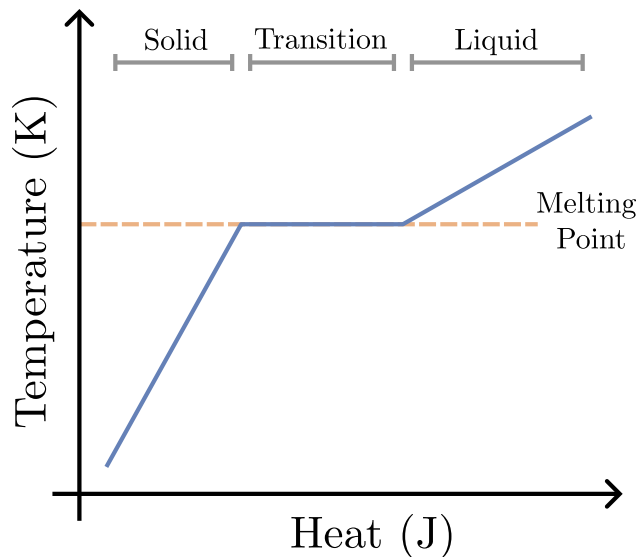


Figure 2: Temperature as a function of adding heat to a system, melting it. In the first rise of temperature, the system is a solid, and the inverse of the slope is the heat capacity dQ/dT . In the flat part, the system is melting, and the horizontal distance traveled is the latent heat. Finally, the third rise is the system in the liquid phase, with a different heat capacity.

We also know that at the phase transition,

$$\mu_\ell - \mu_s = (u_\ell - u_s) - T(s_\ell - s_s) + p(v_\ell - v_s) = 0. \quad (15)$$

Substituting for $T(s_\ell - s_s)$,

$$(u_\ell - u_s) + p(v_\ell - v_s) = \frac{L}{N}, \quad (16)$$

then multiplying by N ,

$$(U_\ell - U_s) + p(V_\ell - V_s) = L. \quad (17)$$

All these equations can be useful; it's often the case that the latent heat per kg is known, which can be converted to the latent heat per particle.

The quantity $U + pV$ is so useful that it gets a new name: **enthalpy**, which is often referred to as H . The latent heat is then

$$L = \Delta H = T\Delta S. \quad (18)$$

It's interesting to think about this last relationship and what it means. On the enthalpy side, we are determining how much energy it takes to increase the internal energy from solid to liquid (in a solid the molecules are in a lower potential energy configuration than the liquid so the internal energy is lower), and to make space in the environment for the liquid phase (the $p\Delta V$ term). In other words, it's how much energy it takes to change the solid into the liquid in that environment. The right hand side $T\Delta S$ is exactly equal to how much heat flows out of the environment into the system, due to the fundamental relation. So this equation is really just following from energy conservation. All these effects happen spontaneously because they minimize the free energy and thus maximize the total entropy.