The common tangent and Maxwell contructions

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Abstract

Some brief notes about phase coexistence, the common tangent, and the Maxwell construction.

1 Thermodynamics

A quick review.

First Law, single component homogeneous system, for the internal energy $U = U(V, S, N)$

$$dU = -p\,dV + T\,dS + \mu\,dN. \tag{1}$$

Hence,

$$p = -\left(\frac{\partial U}{\partial V}\right)_{T,N} \qquad T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{V,T}$$

Euler theorem for n-order homogeneous functions $f = f(x, y, \ldots)$ reads

$$f = f(\lambda x, \lambda y, \ldots) = \lambda^n f \implies x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + \ldots = nf. \tag{2}$$

The internal energy U is homogeneous, of first order, for all its three arguments (they are all extensive variables: if the system size is by increased λ, all three will increase in the same way, and so will U.) Therefore,

$$U = -pV + TS + \mu N. \tag{3}$$

Helmoltz's free energy is defined

$$A(V, T, N) = U - TS. \tag{4}$$

This means:

$$A = -pV + \mu N. \tag{5}$$

which also may be explained by F being homogeneous, first order, but only for V and N.

Taking differentials,

$$dA = -p\,dV + S\,dT + \mu\,dN. \tag{6}$$

Hence,

$$S = \left(\frac{\partial F}{\partial T}\right)_{V,N}.$$

Gibbs' free energy is defined

$$G(p, T, N) = U - TS + pV. \tag{7}$$

This means:
$$G = \mu N. \tag{8}$$

In other words, Gibbs' free energy per molecule is just the chemical potential.

Finally, the grand potential is defined

$$\Omega(p, V, \mu) = U - TS - \mu N. \tag{9}$$

This means:
$$\Omega = -pV. \tag{10}$$

In other words, $\omega = \Omega/V = -p$.

2 The common tangent

In many theories, a Helmholz free energy results that may contain a concave region when plotted as a function of the density. See Fig. 1.

This region is not physical: the free energy must always be concave-up. A simple way to fix is is to apply a common tangent, patching up the concave region (a procedure to form what is called a convex hull.) This is the right procedure: the densities at which the tangent is drawn are the equilibrium densities of two phases (e.g. liquid and vapor.)

To see why this the right procedure, from Eq. (5)

$$a = \frac{A}{V} = \mu\rho - p,$$

so that

$$\frac{\partial a}{\partial \rho} = \mu.$$

That derivative is the slope of the tangent, which is the same at both ends.

Indeed, the chemical potential of two phases in equilibrium must be the same. This expresses the fact that the transfer of molecules between both phases is balanced (in the sense that the molecular fluxes are equal, they do not have to be zero.) It is clear that the densities should then correspond to points on the $a(\rho)$ curve with the same slope the fact that the tangent should be common is
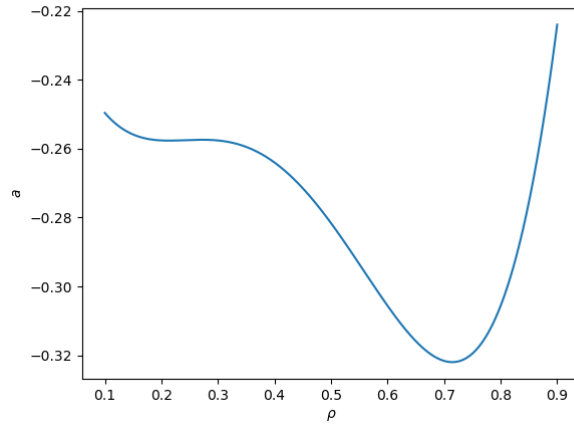
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Figure 1: A possible isotherm of free energy density vs. density showing a concave region. Function $a = -0.2 - 0.2\rho + 0.1\rho^2 - 0.7(\rho - 0.4)^2 + 4(\rho - 0.4)^4$.
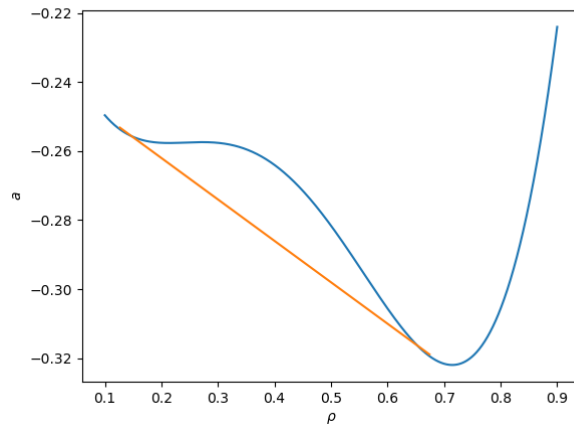

Figure 2: Helmholtz free energy density as a function of density. The common tangent "convexifies" the function and actually yields the right coexisting densities.
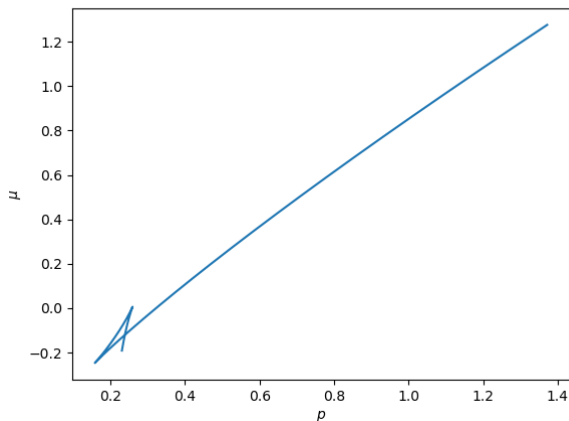
Figure 3: Graph of μ as an implitic function of p. The point at which the curve intersects itself gives the equilibrium values of both quantities. In this example, $p = 0.238$ and $\mu = -0.12$. The two kinks are the boundaries of the spinodal region, and the short segment between them, in which μ decreases as p increases, is unphysical and corresponds to the region inside the spinodal.

due to the fact that the pressure need also be the same for the two phases at equilibrium. Mathematically, the line tangent to $a(\rho_1)$, at density ρ_1, is

$$\bar{a}(\rho) = a_1 + \left.\frac{\partial a}{\partial \rho}\right|_{\rho_1} (\rho - \rho_1) = a_1 + \mu_1(\rho - \rho_1) = -p_1 + \mu_1 \rho$$

Since it reaches $a(\rho_2)$,

$$a_2 = -p_1 + \mu_1 \rho_2 \implies p_1 = \mu_1 \rho_2 - a_2 = p_2.$$

So, indeed, the pressure is equal.

Incidentally, the fastest way to Fig. 3.

3 The Maxwell construction for the chemical potential

If we plot the chemical potential as a function of density, we will find a loop. This is of course the derivative of $a(\rho)$. Equilibrium must correspond to a horizontal line, since the chemical potential is the same for the two phases. The other condition, equal pressure, is the equivalent of the common tangent in this case, and represents a Maxwell construction. Namely: the two areas between the horizontal line must be the same.
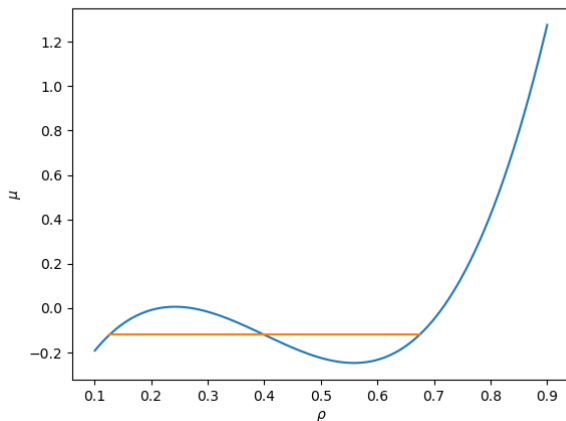
Figure 4: Maxwell construction for the chemical potential. The areas above and below the equilibrium chemical potential must be equal. Notice the Gibbs free energy may be alternatively plotted, since $G = \mu N$.

To demonstrate this, let us begin again from

$$p = \mu\rho - a.$$

Differentiating with respect to ρ,

$$\frac{\partial p}{\partial \rho} = \rho\frac{\partial \mu}{\partial \rho}, \tag{11}$$

since $\mu = \partial a/\partial \rho$. Integrating from one density to another,

$$\int_{\rho_1}^{\rho_2} \frac{\partial p}{\partial \rho} = \int_{\rho_1}^{\rho_2} \rho\frac{\partial \mu}{\partial \rho},$$

or

$$p_1 - p_2 = 0 = \int_{\rho_1}^{\rho_2} \rho\frac{\partial \mu}{\partial \rho}.$$

The latter integration corresponds in general to a vanishing area over the mean, as demonstrated by this little lemma.

Lemma 1. *If a function $f(x)$ satisfies $f(x_1) = f(x_2) := f_0$ and the following integral vanishes:*

$$\int_{x_1}^{x_2} x\frac{df}{dx}dx = 0,$$

then

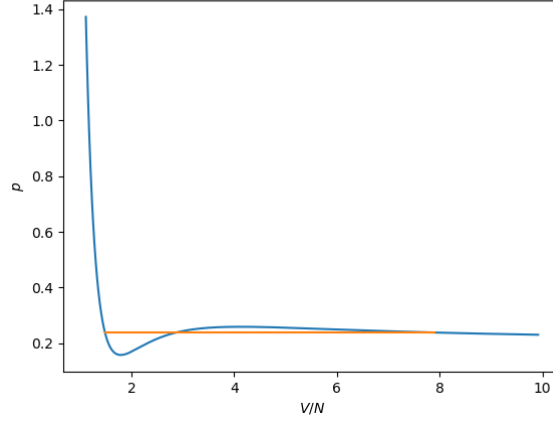$$\int_{x_1}^{x_2} (f - f_0)dx = 0,$$

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Figure 5: The usual Maxwell construction: pressure vs. volume. The areas below and under the equilibrium pressure are equal.

Proof. Integrating by parts:

$$\int_{x_1}^{x_2} x\frac{df}{dx}dx = [xf]_{x_1}^{x_2} - \int_{x_1}^{x_2} fdx.$$

As f is assumed to be the same at both ends,

$$\int_{x_1}^{x_2} x\frac{df}{dx}dx = f_0(x_2 - x_1) - \int_{x_1}^{x_2} fdx = \int_{x_1}^{x_2} (f_0 - f)dx.$$

Therefore, if the originating integral vanishes, so does this one, and

$$\int_{x_1}^{x_2} (f - f_0)dx = 0.$$

$\square$

4   The Maxwell construction for the pressure

If we now plot the pressure a function of density, another loop will be found. Again equilibrium must correspond to a horizontal line, since the pressure must be the same for the two phases. The other condition is now equal chemical potential. This is the better known Maxwell construction. Namely: the two areas between the horizontal line must be the same, but this time in a plot against the *volume* (not the density.)

We may rewrite Eq. (11) as

$$\frac{\partial \mu}{\partial \rho} = \frac{1}{\rho}\frac{\partial p}{\partial \rho}.$$

Integrating,

$$\int_{\rho_1}^{\rho_2} \frac{\partial \mu}{\partial \rho} d\rho = \int_{\rho_1}^{\rho_2} \frac{1}{\rho} \frac{\partial p}{\partial \rho} d\rho.$$

The integral on the left is zero, since it evaluates to $\mu(\rho_2) - \mu(\rho_1) = 0$. Therefore

$$\int_{\rho_1}^{\rho_2} \frac{1}{\rho} \frac{\partial p}{\partial \rho} d\rho = 0.$$

This integral does not comply with our previous lemma, but if we change variables from ρ to $v = 1/\rho$,

$$\frac{\partial p}{\partial \rho} d\rho = \frac{\partial p}{\partial v} dv.$$

The integral is now

$$\int_{v_1}^{v_2} v \frac{\partial p}{\partial v} dv = 0.$$

Our lemma now applies, hence the areas of $p(\rho)$ around the equilibrium pressure must be equal. In practice, it is often the total volume $V = Nv$ what is used in the x axis, which of course does not change the result. The difference is that, in this shape, those areas mean mechanical work, $W = \int p\,dV$, and an alternative argument can be put forward about why this construction must be valid. I think this was historically the first explanation.

5 A note about the forbidden region

The section of the free energy, pressure, and chemical potential that is fixed by this constructions does not correspond to an equilibrium situation. This does not mean it is entirely unphysical. Part of it corresponds to a valid physical system, but in a metastable state. This is the part is most clearly explained in the p vs ρ plot: regions where $p(\rho)$ is an increasing function. In practice, they correspond to situations where a fluid is compressed beyond its phase coexistence conditions, in such a way that a small disturbance may bring about the phase change. The case where the phase transition is driven by temperature is well-known: overheating and undercooling of fluids. (In a p vs V diagram, the pressure must decrease with V.)

The region where the pressure decreases with the density is completely unphysical. No system can be placed in that region, called the spinodal. Still, if a system is suddenly turned to those conditions, an interesting dynamical phenomena occurs, called spinodal decomposition (in the metastable zones, the dynamics is rather driven by nucleation.)

There is also a theory where the information in this region is used: the van der Waals theory for the molecular structure of the interface. In this theory, the density changes smoothly from a value ρ_1 to ρ_2, therefore necessarily passing through forbidden values.