Van der Waals equation, Maxwell construction, and Legendre transforms

Markus Deserno
Department of Physics, Carnegie Mellon University, Pittsburgh, PA 51213, USA
(Dated: March 4, 2013)

The van der Waals equation is the best known example of an equation of state that exhibits a first-order phase transition with a critical end point. Since clearly the pressure remains a monotonic function of the volume in experiment, the van der Waals equation is amended by a Maxwell construction, in which the famous "equal area" cut of the van der Waals loop replaces that loop. This equal area construction is equivalent to replacing the corresponding van der Waals Helmholtz free energy by its convex envelope. In fact, the relation between these two, as well as the associated Gibbs free energy, is also the perfect example and opportunity to understand how typical features of phase transitions appear in thermodynamic potentials and their Legendre transforms.

I. SCALED SPECIFIC FREE ENERGY

The Helmholtz free energy of the van der Waals gas can be written as follows:

$$F(T,V,N) = -Nk_{\mathrm{B}}T\left[1+\log\frac{(V-Nb')T^{3/2}}{Nc'}\right] - \frac{a'N^2}{V}\ , \tag{1}$$

where a', b', and c' are constants (i.e., independent of T, V, and N). We will first re-express this equation in the following way:

1. Volume and free energy are divided by N, thus making them intensive. In other words, we revert to specific volume and a specific free energy:

$$V \to v \ = \ V/N\ , \tag{2a}$$
$$F \to f \ = \ F/N\ . \tag{2b}$$

2. We know that the van der Waals equation has a critical point. We will measure temperature in units of the critical temperature T_{c}, specific free energy in units of $k_{\mathrm{B}}T_{\mathrm{c}}$, and specific volume in units of the critical specific volume v_{c}:

$$T \to \tilde{T} \ = \ T/T_{\mathrm{c}}\ , \tag{3a}$$
$$f \to \tilde{f} \ = \ f/k_{\mathrm{B}}T_{\mathrm{c}}\ , \tag{3b}$$
$$v \to \tilde{v} \ = \ v/v_{\mathrm{c}}\ . \tag{3c}$$

   To accomplish these replacements, we also need to know (or check for ourselves—see below) that $V_{\mathrm{c}} = 3b'$ and $k_{\mathrm{B}}T_{\mathrm{c}} = 8a'/27b'$.

after these replacements we find

$$\tilde{f}(\tilde{T},\tilde{v}) = -\tilde{T}\left[1+\log\frac{(\tilde{v}-\frac{1}{3})\tilde{T}^{3/2}}{c''}\right] - \frac{9}{8\tilde{v}}\ , \tag{4}$$

with a new (dimensionless) constant c''. Changing its numerical value adds a term proportional to $\tilde{T}$ to the specific free energy, and hence proportional to $\tilde{T}N$ to the free energy. Since in the following we will only be interested in derivatives with respect to volume, we can set $c'' \equiv 1$ without any effects.

The scaled pressure $\tilde{p} := p/p_{\mathrm{c}} := 8pv_{\mathrm{c}}/3k_{\mathrm{B}}T_{\mathrm{c}}$ is now

$$\tilde{p} = -\frac{8}{3}\left(\frac{\partial\tilde{f}}{\partial\tilde{v}}\right)_{\tilde{T}} = \frac{8\,\tilde{T}}{3\tilde{v}-1} - \frac{3}{\tilde{v}^2} \tag{5}$$

To check whether we got the critical point right, let us calculate

$$\frac{\partial\tilde{p}}{\partial\tilde{v}} = -\frac{24\tilde{T}}{(1-3\tilde{v})^2} + \frac{6}{\tilde{v}^3}\ , \tag{6a}$$
$$\frac{\partial^2\tilde{p}}{\partial\tilde{v}^2} = -\frac{144\tilde{T}}{(1-3\tilde{v})^3} - \frac{18}{\tilde{v}^4}\ . \tag{6b}$$

At the critical point we must have $\frac{\partial\tilde{p}}{\partial\tilde{v}} = \frac{\partial^2\tilde{p}}{\partial\tilde{v}^2} = 0$, which immediately gives $\tilde{v}_{\mathrm{c}} = \tilde{t}_{\mathrm{c}} = 1$, as we have arranged. This also shows that at the critical point we have $\tilde{p}_{\mathrm{c}} = \tilde{p}(1,1) = 1$, thus explaining the extra factor $\frac{8}{3}$ we introduced above in the definition of the scaled pressure.

II. SCALED GIBBS FREE ENERGY

The specific Gibbs free energy follows from the specific Helmholtz free energy via a Legendre transformation:

$$\tilde{g}(\tilde{T},\tilde{p}) = \min_{\tilde{v}}\left\{\tilde{f}(\tilde{T},\tilde{v}) + \tilde{p}\tilde{v}\right\}\ . \tag{7}$$

This always works, even when for $\tilde{T} < \tilde{T}_{\mathrm{c}} = 1$ the Helmholtz free energy ceases to be a convex function of the specific volume by developing a local concave "bump". It is precisely this bump which gives rise to the van der Waals loop in the pressure, and replacing $\tilde{f}$ by its convex envelope is equivalent to the well-known equal-area Maxwell construction—as can be seen as follows: If the Maxwell loop starts at $\tilde{v}_1$ and ends at $\tilde{v}_2$, $\tilde{p} = -\partial\tilde{f}/\partial\tilde{v}$ implies

$$0 = \int_{\tilde{v}_1}^{\tilde{v}_2}\mathrm{d}\tilde{v}\ \left[\tilde{p}(\tilde{v}) - \tilde{p}_{\mathrm{eq}}\right] \ \Rightarrow\ -\tilde{p}_{\mathrm{eq}} = \frac{\tilde{f}(\tilde{v}_2)-\tilde{f}(\tilde{v}_1)}{\tilde{v}_2-\tilde{v}_1}\ . \tag{8}$$

Since $\tilde{p}_{\mathrm{eq}} = \tilde{p}(\tilde{v}_{1,2}) = -\partial\tilde{f}/\partial\tilde{v}|_{1,2}$, this condition shows that the equal-area construction on $\tilde{p}(\tilde{v})$ is equivalent to a double tangent construction on $\tilde{f}(\tilde{v})$, i.e., making $\tilde{f}(\tilde{v})$ convex.

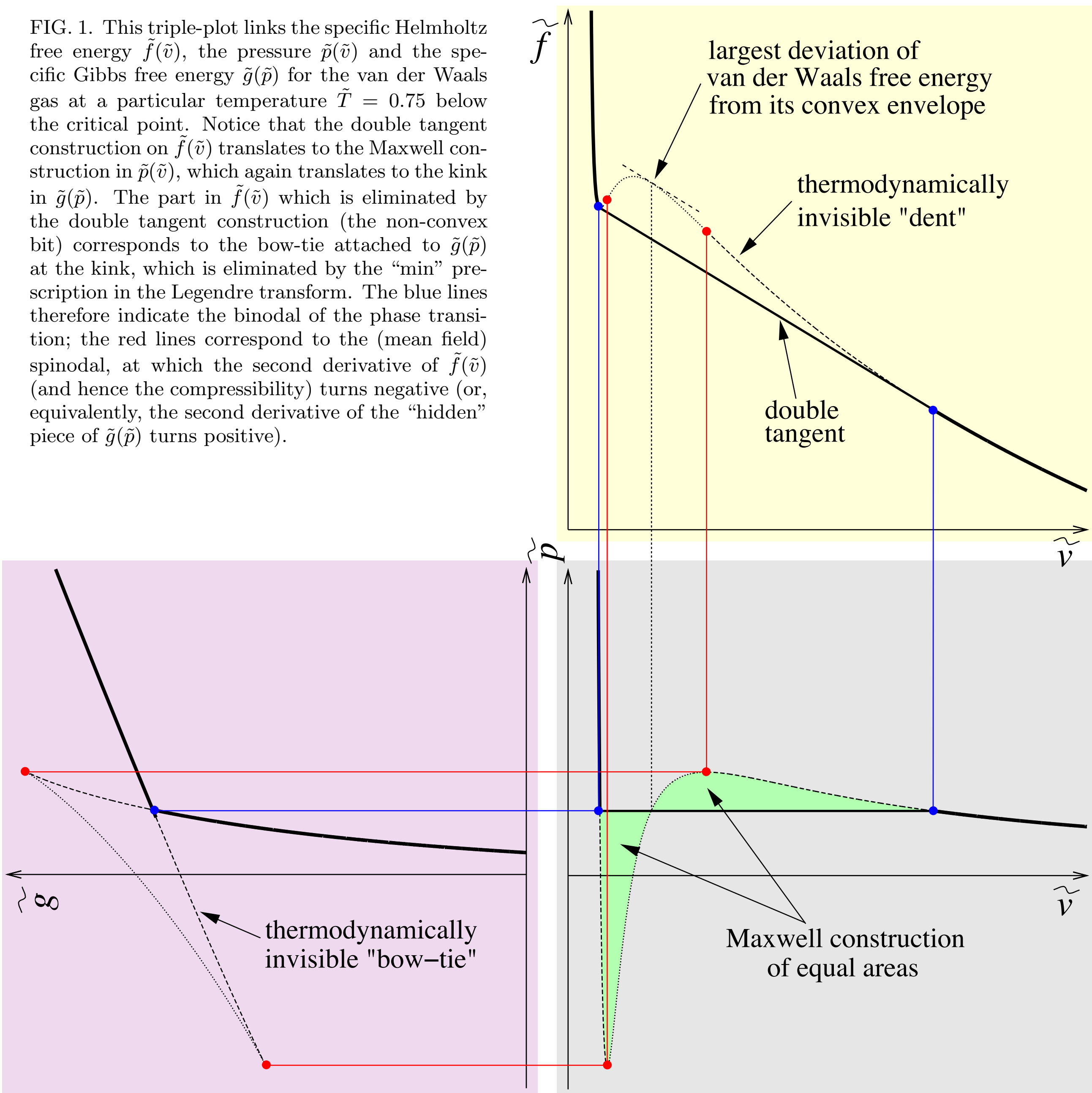

FIG. 1. This triple-plot links the specific Helmholtz free energy $\tilde{f}(\tilde{v})$, the pressure $\tilde{p}(\tilde{v})$ and the specific Gibbs free energy $\tilde{g}(\tilde{p})$ for the van der Waals gas at a particular temperature $\tilde{T} = 0.75$ below the critical point. Notice that the double tangent construction on $\tilde{f}(\tilde{v})$ translates to the Maxwell construction in $\tilde{p}(\tilde{v})$, which again translates to the kink in $\tilde{g}(\tilde{p})$. The part in $\tilde{f}(\tilde{v})$ which is eliminated by the double tangent construction (the non-convex bit) corresponds to the bow-tie attached to $\tilde{g}(\tilde{p})$ at the kink, which is eliminated by the "min" prescription in the Legendre transform. The blue lines therefore indicate the binodal of the phase transition; the red lines correspond to the (mean field) spinodal, at which the second derivative of $\tilde{f}(\tilde{v})$ (and hence the compressibility) turns negative (or, equivalently, the second derivative of the "hidden" piece of $\tilde{g}(\tilde{p})$ turns positive).

We know that the Legendre transform $\tilde{g}(\tilde{p})$ will be concave *even* if the function we started with does not necessarily have a positive second derivative everywhere. In fact, we know that if we were to replace $\tilde{f}(\tilde{v})$ by its *convex envelope* we would get the same Legendre transform. Moreover, the Legendre transform of a *linear region* transforms into a *kink* (and *vice versa*!), and all the non-convexity vanishes from the description. Where does it go? It is eliminated by the "min" procedure leading to the definition of $\tilde{g}$, and hence we *do* lose information if we Legendre transform functions that are not fully convex (or fully concave). However, we can illustrate where it is "hiding": take the definition of the Legendre transform and write it *parametrically* in the following way: Each pair $\{\tilde{p}\,,\ \tilde{g}(\tilde{p})\}$ can evidently be written as $\{-\frac{\partial \tilde{f}}{\partial \tilde{v}}\ ,\ \tilde{f}(\tilde{v}) - \frac{\partial \tilde{f}}{\partial \tilde{v}}\,\tilde{v}\}$, which can be viewed as a *parametric representation* of the graph of $\tilde{g}(\tilde{p})$ with $\tilde{v}$ as the parameter. Plotting this, we see that—without insisting on taking the minimum value—the locally non-convex pieces in $\tilde{f}(\tilde{v})$ reappear as a curiously shaped "bow-tie" attached to the graph of the proper Legendre transform. The two pieces where $\tilde{f}(\tilde{v})$ already deviates from its convex envelop but still has a positive derivative simply continue the two branches of the graph of $\tilde{g}(\tilde{p})$ on both sides of the kink. The piece in $\tilde{f}(\tilde{v})$ where even the second derivative is negative connects these two extensions via two cusps. All of this is jointly illustrated in Fig. 1.