DS 10:
Critical Phenomena in the van der Waals Gas

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Recall that a van der Waals gas is described in terms of two parameters a and b, and satisfies the equation of state

$$p = \frac{NRT}{V - Nb} - \frac{aN^2}{V^2}, \tag{1}$$

where N is the number of moles, and p, V, and T the pressure, volume, and temperature respectively.

1 Criticality

(a) Start by writing the van der Waals gas in terms of the pressure and volume *per particle* $v = V/N$. Show that

$$p = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{2}$$

(b) Let us try to write this equation in a simpler form. First, rewrite the above equation as a cubic equation in v, showing that

$$pv^3 - (RT + bp)v^2 + av - ab = 0. \tag{3}$$

(c) We are now going to find the *critical points* in terms of the parameters a and b. Argue that at the critical point

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 \qquad \text{and} \qquad \left(\frac{\partial [}{\partial 2}\right)_{]} pVT = 0. \tag{4}$$

(d) We could in principle perform the above differentiation, but it turns out there's a neat way to do it. First, argue that since the van der Waals equation is a *cubic* equation, near the critical point it can be written as

$$(v - v_c)^3 = 0. \tag{5}$$

Expand the above equation and compare term-by-term with the van der Waals equation given above to get values of p_c, v_c, and T_c.

(e) Using these values, rewrite the van der Waals equation in terms of $\tilde{p} = p/p_c$, $\tilde{v} = v/v_c$, and $\tilde{T} = T/T_c$, to get

$$\left(\tilde{p} + \frac{3}{\tilde{v}^2}\right)(3\tilde{v} - 1) = 8\tilde{T}. \tag{6}$$

2 Maxwell's construction

(a) Find the free energy for a van der Waals gas.

(b) Argue that to find the points of phase coexistence, we need to find two points that have the same value of the Gibbs free energy.

(c) Argue that this means that at the two points A and B,

$$F_B - F_A = - - p_A(V_B - v_A), \tag{7}$$

since the pressure is constant.

(d) Using the fact that

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V, \tag{8}$$

show that

$$F_B - F_A = -\int_A^B p\mathrm{d}V, \qquad \Longrightarrow \qquad \int_A^B p\mathrm{d}V = p_A(V_B - V_A). \tag{9}$$

(e) Interpret this result *graphically*.