DS 11:
Phase Transitions

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1 Phase coexistence

(a) In the previous DS we showed that at equilibrium, the chemical potentials of the liquid and gas phases had to be equal, i.e. that

$$\mu_{\text{liquid}} = \mu_{\text{gas}}. \tag{1}$$

Come up with an argument of why this must be so at thermodynamic equilibrium. (*Hint:* What type of equilibrium does the above equation describe?)

(b) Show that the equality of the chemical potentials is equivalent to saying that the Gibbs free energy per particle must be equal in the two phases, i.e.

$$g_{\text{liquid}} = g_{\text{gas}}. \tag{2}$$

Do this in two ways: use the Euler relation, and use the minimisation of the Gibb's free energy.

(c) Use this equation to show that as we move across the line of phase transitions (in the PT plane, for example), the Gibb's Free Energy G is continuous.

(d) Now, imagine that you are actually sitting *on* the line of phase transitions. How does g change *along* this line? To show this, start by writing $\mathrm{d}G$ in terms of its natural variables, both for the liquid and the gas.

(e) Show that

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_{\text{gas}} - s_{\text{liquid}}}{v_{\text{gas}} - v_{\text{liquid}}} \tag{3}$$

(f) Appropriately defining a *specific latent heat* L, show that we can write (Why is it *heat*?)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(v_{\text{gas}} - v_{\text{liquid}})}. \tag{4}$$

The above equation is known as the *Clausius-Clapeyron* equation. It relates the *slope* of the coexistence curve $p(T)$ to a function of the specific latent heat L, the temperature T, and the change in the specific volume v.

(g) **An approximate solution**: We can try to find an approximate solution to the above equation for an ideal gas. Argue that since $v_{\text{gas}} \gg v_{\text{liquid}}$, you can write

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{Lp}{k_B T^2}. \tag{5}$$

The above equation is sometimes *also* called the Clausius-Claperyon equation. Solve this equation and find $p(T)$.

(h) While we have spoken about liquid-gas transitions, this equation is true for all first order transitions. In particular, let us apply this to the melting of ice. The latent heat (of fusion) is $L = 3.35 \times 10^5 J/\text{kg}$, and the specific volumes in the solid and liquid phases are $v_{\text{solid}} = 1.09070 \times 10^{-3} m^3/\text{kg}$ and $v_{\text{solid}} = 1.00013 \times 10^{-3} m^3/\text{kg}$. Find how much pressure is needed to lower the melting temperature of ice by 1°.

2 Critical exponents

Let us now focus our attention to the physics close to the critical point. It is not very clear what the appropriate questions to ask are, but it turns out they are:

- How does $v_{\text{gas}} - v_{\text{liquid}}$ change as we approach the critical point along a coexistence curve?
- How does the volume change with pressure as we move along the critical isotherm?
- How does the compressibility κ change as we approach $T \to T_c$? (Recall $\kappa = -(1/v)\left(\frac{\partial v}{\partial p}\right)_T$.)

We will try to answer these questions for the van der Waals gas.

(a) In the last DS we saw that we could write the van der Waals equation in terms of pressures, volumes, and temperatures scaled by their corresponding critical values as

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

When $T < T_c$ (i.e. $\tilde{T} < 1$) there must be two stable solutions, one for the liquid phase and one for the gas phase. Show that this means that

$$\tilde{T} = \frac{(3\tilde{v}_{\text{liquid}} - 1)(3\tilde{v}_{\text{gas}} - 1)(\tilde{v}_{\text{liquid}} + \tilde{v}_{\text{gas}})}{8\tilde{v}^2_{\text{liquid}}\tilde{v}^2_{\text{gas}}} \tag{7}$$

(b) We would now want to expand the above equation for small $\epsilon = \tilde{v}_{\text{gas}} - \tilde{v}_{\text{liquid}}$. This looks like it's a very difficult task, but is greatly simplified if you realise that the above equation is symmetric in both the $\tilde{v}$s. Consequently, as $\tilde{T} \to 1$, $\tilde{v}_{\text{liquid}}, \tilde{v}_{\text{gas}} \to 1$, we can write

$$\tilde{v}_{\text{liquid}} = 1 - \frac{\epsilon}{2} \qquad \text{and} \qquad \tilde{v}_{\text{gas}} = 1 + \frac{\epsilon}{2}. \tag{8}$$

Substitute this into the above equation, and keeping only the leading order term show that

$$\tilde{T} \approx 1 - \frac{1}{16}\left(\tilde{v}_{\text{gas}} - \tilde{v}_{\text{liquid}}\right)^2, \qquad \Longrightarrow \qquad (\tilde{v}_{\text{gas}} - \tilde{v}_{\text{liquid}}) \sim (T_c - T)^{\beta}, \quad \text{where} \quad \beta = 1/2. \tag{9}$$

(c) For the second question, the answer can be obtained with no extra calculations. Remember that the critical point is a saddle point, and so the first and second derivatives of the pressure with respect to volume must be zero, i.e.

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0. \tag{10}$$

Argue that this means that around the critical point

$$p - p_c \sim (v - v_c)^3, \qquad \Longrightarrow \qquad (v - v_c) \sim (p - p_c)^{1/\delta}, \quad \text{where} \quad \delta = 3. \tag{11}$$

(d) Show that

$$\kappa \sim (T_c - T)^{-\gamma}, \quad \text{where} \quad \gamma = 1. \tag{12}$$