PHYS 427 - Thermal and Statistical Physics - Discussion 11

Last week we started exploring the topic of phase transitions. Moving forward, it is probably a good idea to have a clear notion of what we mean when we talk about *phases*.

First, we know the partition function, and hence the free energy, of a system is a function of many variables: temperature, chemical potential, volume, external fields, and so on. If we draw an axis for each of these variables, the resulting space is where we label the **phase diagram** of the system.

- **Phase of matter**: A region in the phase diagram where the free energy is analytic (i.e. can be expressed with a Taylor series).
- **Phase transition**: A region in the phase diagram where the free energy is non-analytic (i.e. cannot be expressed with a Taylor series).

We organize phase transitions into two classes:

- (1) **First order phase transitions**: At least one derivative of the free energy is discontinuous across the phase boundary.
- (2) **Continuous phase transitions**: All first derivatives of the free energy are continuous across the phase boundary. Some higher order derivatives of the free energy energy are discontinuous.

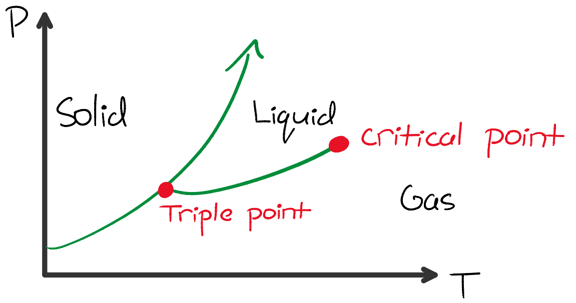

Figure 1: Caricature of a common phase diagram in the P-T plane.

As an example, Fig. 1 shows a phase diagram in the P-T plane. The green lines represent phase boundaries. Notice there's a clear distinction between the solid phase and liquid/gaseous phases; however, depending on your location in the plane, the distinction between the liquid and gas phase is not always clear. This is because it is possible to go from one of these regions to another without ever undergoing a phase transition — hence it is common to refer to a liquid/gas simply as a "fluid".

Today, we're going to focus on the liquid-gas **critical point**.

1. **Van der Waals equation of state**: Recall the equation of state of an ideal gas is

$$pV = Nk_BT \tag{1}$$

The ideal gas model of a fluid works well for high temperatures and low pressures, but it is too simplistic to describe the liquid-gas phase transition. The problem is the ideal gas completely ignores the interactions between particles.

If we include particle-particle interactions, it becomes very difficult to find the equation of state. However, if we resign to treating interactions only in a certain "averaged" sense, we can obtain a so-called mean-field description of the fluid. As shown in the lecture, this leads to the **van der Waals** equation of state,

$$\left(p + \frac{N^2a}{V^2}\right)(V - Nb) = Nk_BT, \tag{2}$$

where $a, b > 0$ are parameters that are different for different gases. (They could be measured by fitting the van der Waals equation to experimental data.)

In this problem, we will use the van der Waals equation of state to make predictions about the behavior of the fluid in the vicinity of the liquid-gas critical point.

(a) The critical point[1] of the van der Waals equation is the point (p_c, V_c, T_c) at which the isotherms develop an inflection point, i.e. where

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0. \tag{3}$$

Show that

$$p_c = \frac{a}{27b^2}, \qquad V_c = 3Nb, \qquad k_BT_c = \frac{8a}{27b}. \tag{4}$$

Hint: apply $(\partial/\partial V)_T$ to the van der Waals equation. Then do it again.

(b) Define a fractional pressure, temperature and volume by

$$\hat{p} \equiv p/p_c \qquad \hat{V} \equiv V/V_c \qquad \hat{T} = T/T_c. \tag{5}$$

Show that the van der Waals equation becomes

$$\hat{p} = \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}. \tag{6}$$

This is called the law of corresponding states. It shows that fluid behavior is *universal*, at least insofar as fluids can be described by the van der Waals equation. In other words, if you made plots of $\hat{p}$, $\hat{V}$ and $\hat{T}$ for different fluids (having different values of a and b), all graphs would coincide.

[1] Why are (3) the conditions for the critical point? Because isotherms with $T < T_c$ exhibit a liquid-gas phase transition as a function of pressure (after being properly interpreted via Maxwell's construction), while isotherms with $T > T_c$ do not. Moreover, as $T \to T_c$ from below, this transition happens at $p \to p_c$ and $V \to V_c$. You can see this from your graph in part (c).

(c) Expand Eq. 6 about $\hat{V} = 1$ and $\hat{T} = 1$ to third order in $\tau \equiv (\hat{T} - 1)$ and $\nu \equiv (\hat{V} - 1)$ to obtain

$$\pi = 4\tau - 6\tau\nu + 9\tau\nu^2 - \frac{3}{2}\nu^3 + \ldots, \tag{7}$$

where $\pi \equiv \hat{p} - 1$. *Hint: first show (without approximation) that* $\pi = -1 + 4(\tau + 1)(1 + 3\nu/2)^{-1} - 3(1 + \nu)^{-2}$. *Then use the Taylor approximation* $(1 + \epsilon)^\alpha = 1 + \alpha\epsilon + (\alpha(\alpha - 1)/2!)\epsilon^2 + (\alpha(\alpha - 1)(\alpha - 2)/3!)\epsilon^3 + \ldots$

(d) Using (7), sketch the van der Waals isotherms in the p-V plane in the vicinity of the critical point. You may recognize your sketch from class!

(e) In actual fluids, near the liquid-gas critical point it is observed that the isothermal compressibility $\kappa_T \equiv -\frac{1}{V}\left(\partial V/\partial p\right)_T$ scales as

$$\kappa_T \propto |T - T_c|^{-\gamma} \qquad \text{at } V = V_c. \tag{8}$$

Using 7, show that $\gamma = 1$ for the van der Waals model.

(f) In actual fluids, near the liquid-gas critical point it is observed that the pressure scales as

$$|p - p_c| \propto |V - V_c|^\delta \qquad \text{at } T = T_c. \tag{9}$$

Using 7, show that $\delta = 3$ for the van der Waals model.