

# PHYS 427 - Thermal and Statistical Physics - Discussion 11 Solutions

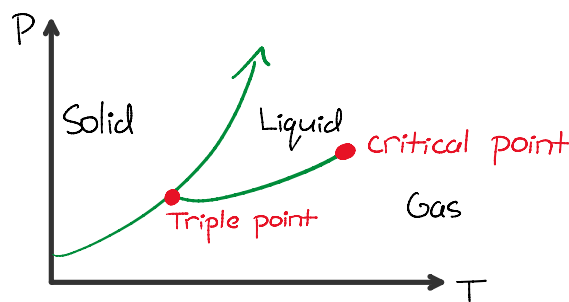
Last week we started exploring the topic of phase transitions. Moving forward, it is probably a good idea to have a clear notion of what we mean when we talk about *phases*.

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 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**.

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

$$pV = Nk_B T \quad (1)$$

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,

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

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<sup>1</sup> 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

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

Show that

$$p_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad k_B T_c = \frac{8a}{27b}. \quad (4)$$

*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

$$\hat{p} \equiv p/p_c \quad \hat{V} \equiv V/V_c \quad \hat{T} = T/T_c. \quad (5)$$

Show that the van der Waals equation becomes

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

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.

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<sup>1</sup>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  $T \rightarrow T_c$  from below, this transition happens at  $p \rightarrow p_c$  and  $V \rightarrow V_c$ . 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

$$\pi = 4\tau - 6\tau\nu + 9\tau\nu^2 - \frac{3}{2}\nu^3 + \dots, \quad (7)$$

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  $(1 + \epsilon)^\alpha = 1 + \alpha\epsilon + (\alpha(\alpha - 1)/2!)\epsilon^2 + (\alpha(\alpha - 1)(\alpha - 2)/3!)\epsilon^3 + \dots$*

- (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  $\kappa_T \equiv -\frac{1}{V}(\partial V/\partial p)_T$  scales as

$$\kappa_T \propto |T - T_c|^{-\gamma} \quad \text{at } V = V_c. \quad (8)$$

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

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

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

### SOLUTION:

(a) This is a homework problem, and I don't want to spoil your fun... But I'd suggest following the hint given above, in the problem statement. It makes the algebra a bit easier. The idea is to implicitly differentiate the VdW equation twice with respect to  $V$  (at constant  $T$ ). This gives two equations (one from taking just one derivative, the other from when you take two derivatives). These two equations, together with the VdW equation itself, allow you to solve for the three unknowns  $p$ ,  $V$  and  $T$ .

(b) This is also a homework problem. It's a matter of inserting the definitions. Solve the VdW equation for  $p$ , then insert  $p = p_c\hat{p}$ ,  $T = T_c\hat{T}$ , etc.

(c) Also a homework problem! The hint is a good way to organize your work. The first part of the hint (the "without approximation" part) is straightforward. Just take (6) and insert  $\hat{p} = \pi + 1$ ,  $\hat{T} = \tau + 1$ , etc.

The Taylor approximation in the second part is known as the binomial theorem. Do your future self a favor and memorize it now if you haven't already—it shows up all the time in calculations. A good way to commit it to memory is to derive it for yourself by taking successive derivatives of  $f(x) = (1 + x)^\alpha$  and inserting them into Taylor's theorem,  $f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n f}{dx^n} \Big|_{x=0}$ .

The geometric series is the special case where  $\alpha = -1$ . And actually, the only other case we need is  $\alpha = -2$ , which can be obtained by differentiating the geometric series:

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + x^4 + \dots \quad (10)$$

$$\implies \frac{1}{(1+x)^2} = 0 - 1 + 2x - 3x^2 + 4x^3 + \dots \quad (11)$$

Still it's good to memorize the binomial theorem, because you can't obtain the series for e.g.  $(1+x)^{-1/2}$  by differentiating the geometric series.

(d) Also also a homework problem! The easiest isotherm to draw is the critical isotherm, which is the one where  $T = T_c$ , i.e.  $\tau = 0$ . Then from (7), we have  $\pi = -\frac{3}{2}\nu^3$ , which is easy to draw on the  $\pi$ - $\nu$  plane (equivalently, the  $p$ - $V$  plane). The isotherms where  $\tau > 0$  and  $\tau < 0$  are a little trickier, but still doable without a computer. To get started, think about the behavior of  $\pi$  very close to  $\nu = 0$ , where most of the terms can be ignored.

(e) When  $V = V_c$ , we have

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (12)$$

$$= -\frac{1}{V_c} \left( \frac{\partial V}{\partial p} \right)_T \quad (13)$$

$$= -\frac{V_c}{V_c p_c} \left( \frac{\partial \hat{V}}{\partial \hat{p}} \right)_\tau \quad (14)$$

$$= -\frac{1}{p_c} \left( \frac{\partial \nu}{\partial \pi} \right)_\tau \quad (15)$$

Now we just have to evaluate the derivative at  $V = V_c$ , i.e. at  $\nu = 0$ . From (7),

$$\left( \frac{\partial \pi}{\partial \nu} \right)_\tau = -6\tau, \quad (16)$$

so

$$\kappa_T = \frac{1}{6p_c} \frac{1}{\tau} \quad (17)$$

$$= \frac{T_c}{6p_c} (T - T_c)^{-1}, \quad (18)$$

where I inserted  $\tau = \hat{T} - 1 = T/T_c - 1$ . We identify  $\gamma = 1$  by comparing to (8).

(f) You may object that it wasn't necessary to do part (e) in terms of  $\tau$  and  $\nu$  and  $\pi$  if we're just going to switch back to  $T$  and  $V$  and  $p$  at the end. Why didn't we just leave (7) in terms of  $T$ ,  $V$  and  $p$ ? One answer is that it emphasizes the universality mentioned in part (b). Another practical answer is that it actually clears away a lot of the clutter, once you are used to it. Now that you have seen how (e) goes, I think you will be ok with the following. I glance at (7) and immediately write down

$$\pi = -\frac{3}{2}\nu^3 \text{ when } \tau = 0 \implies p - p_c \propto (V - V_c)^3, \quad (19)$$

so  $\delta = 3$ . In general, writing things in terms of appropriately shifted and rescaled *dimensionless variables* like  $\pi$ ,  $\nu$  and  $\tau$  is the way to go in any physics problem. It emphasizes the structure, and often what we are interested in is structure rather than specific values. In this problem, we didn't care about the specific values of the proportionality constants in  $\kappa_T \propto (T - T_c)^{-\gamma}$ , etc. We were more interested in the *structure*, i.e. the manner in which  $\kappa_T$  depends on  $T - T_c$ .

By the way, as I mentioned during the discussion, here's the main reason to be interested in critical exponents: it turns out that many physical systems which differ in their details nevertheless share the same critical exponents. This phenomenon is called universality.

Universality divides the set of conceivable physical systems into “universality classes” such that the members of a given universality class all have precisely the same behavior near the critical point.

It turns out that all mean field theories lie in the same universality class. We have two examples of mean field theories in this course: the VdW model and the mean field theory of the ferromagnet. Both have the same critical exponents (after appropriately mapping the variables from one to the other).