

Physics 114 Statistical Mechanics Spring 2018  
Seminar 12

**Overview:**

This week, we study transitions between different equilibrium phases of matter. Knowing the chemical potential allows us to trace out coexistence curves on a phase diagram. We will use the important toy model of a van der Waals fluid, in order to study the liquid-gas phase transition. We'll derive that the enthalpy change, or "latent heat" of transition, determines the slope of the phase coexistence curve between any two phases on a P-T diagram.

We then focus on *critical phenomena* and so-called "second order" phase transitions. These are also known as "order-disorder" transitions. (The word "order" means two different things in these two sentences :-). We'll discover that there is something *universal* about their behavior in different physical systems like fluids and ferromagnets. We'll address one approach to understanding phase transitions: Mean field or Landau theory. (While it would be cool to study them via a second approach, Renormalization group, we don't have time ;-). We will discuss *scaling relations* leading to *critical exponents*.

Finally, since we are studying phase transitions, it is a great time to apply our understanding of boson statistics to a transition from a gas to a *Bose Einstein Condensate (BEC)*. As temperature drops below  $T_c$ , bosons make a transition to a very interesting phase, with an appreciable fraction of them sharing the ground state. This makes the bosons behave like a *superfluid*.

**Reading:**

G&T Sections

- 6.10
- 7.3, 7.4
- 9.1, 9.2

B&B Sections

- 26.1, 26.4
- 28.1 - 28.4 and 28.7
- 30.4

Schroeder

- Section 5.3
- Section 7.6

**Review reading:** Several sections were read in earlier seminars - no harm in looking back at them!

- G&T sections 7.1, 7.2 (chemical potential)
- G&T section 5.7 and problem 5.18 (Mean field theory for magnetic systems)
- B&B Appendices C.4 and C.5 (and new reading if you wish, Appendix A.13 of G&T) to remind yourself about the analytical way to talk about Bose Integrals (though Mathematica can surely do them :-)

### Concept checklist from readings:

- **Phase transitions and phase diagrams:** Ideal gasses have only one phase - gas. But a real substance can exist in different *phases*, which have distinct forms. Examples are the ordered packing of molecules in a solid vs. the disorder of a liquid, or the orientational ordering of molecules in a liquid crystalline phase. It is something of a miracle that this happens. Two molecules of a substance interact in a fixed way. So why, when you change  $P$  or  $T$  do you get a radically different form for the entire system? It's a *cooperative phenomenon*. As we read this week, it is all about which phase has a *lower free energy per molecule*. Throughout the topics this week, this is a recurring theme: *Lowest  $G$  means most thermodynamically stable system ... so the system will choose the phase with the lowest  $G(T,P,N)$ , given you fix  $T$ ,  $P$  and  $N$ .*
- The most basic kind of phase diagram is that of a pure substance when the pressure is not huge, as in left hand side of Figure 1 below. Axes are typically  $P$  vs  $T$ . Analogous magnetic systems, with  $B$  taking the place of  $P$ , are shown Figure 2 below, which is Schroeder Fig. 5.14. To read the diagram on the diagram, you might ask yourself "If I raise or lower  $P$  at constant  $T$ , what happens?" A big difference between  $H_2O$  and most other substance is that *raising*  $P$  in the solid phase takes you to a liquid. This makes intuitive sense because unlike most other substances  $\rho_{solid} < \rho_{liquid}$  for  $H_2O$ . See the Clausius-Clapeyron equation below for a more formal argument.

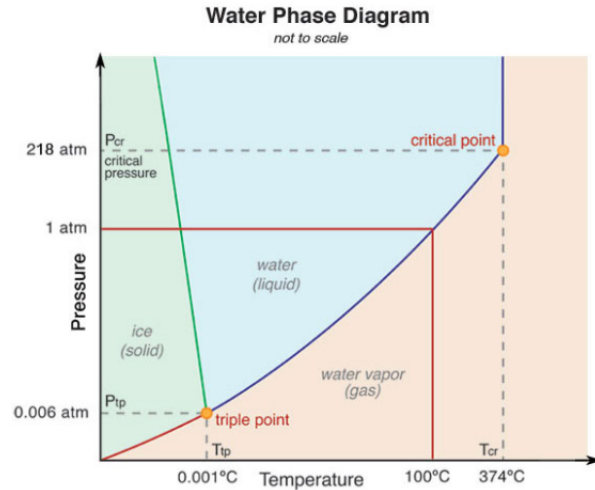


Figure 1: Phase diagram of  $H_2O$ , which can also be seen in all of the texts this week.

- Can you draw a phase diagram with other axes? How about  $P$  vs.  $\rho$  or equivalently  $P$  vs.  $V$ ? This is technically OK as in G&T Fig. 7.5 or Schroeder Fig. 5.23 reproduced below. But careful:  $V$  or  $\rho$  is not a control parameter. You might think it is but a system can do something beyond your control, like phase separate with two different densities:  $\rho_{liquid}$  and  $\rho_{gas}$  say.

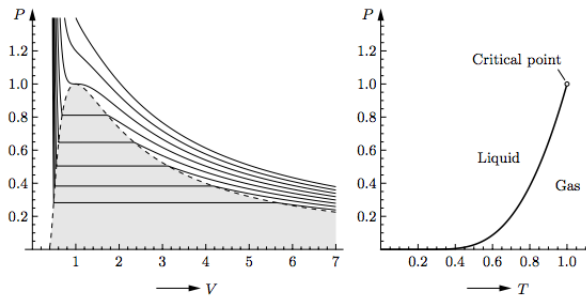
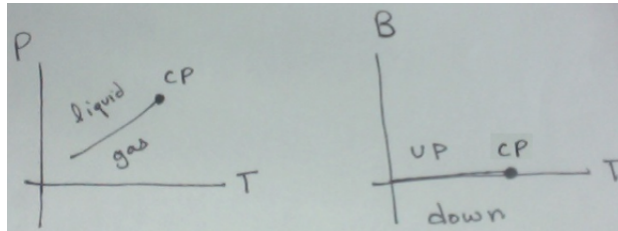


Figure 2: Phase diagrams of a van der Waals fluid.

- Some terminology you will learn this week:
  - phase: a state of matter characterized by macroscopic properties like density, symmetry, magnetic moment. These correspond to labelled areas on a phase diagram.
  - phase transition or phase transformation: the properties above change as a control parameter like temperature, pressure, external field is varied

- phase coexistence curve: curves on the phase diagram that separate one area from another. If there were more variables, these could be surfaces. This week we did not have time to talk about binary fluids, but they are a good example of a system where we have to be creative about how we plot, because the volume fraction  $x$  of one species is also a control parameter.
  - sublimation: the transition from solid to gas
  - melting/freezing: the transition between solid and liquid
  - vaporization: the transition from liquid to gas
  - vapour pressure: the pressure of gas above a solid - or above a liquid - if the two phases are in equilibrium.
  - latent heat: the heat, which is actually an enthalpy difference, between two phases. Usually symbolized by  $L$ .
  - Triple point: The special value of  $T$  and  $P$  where liquid, solid and gas all coexist. Not all systems have one ( $He^4$  doesn't.)
  - Critical point: The special value of  $T$  and  $P$  where liquid and gas coexist, but  $\rho_{liquid} = \rho_{gas}$  so there is no real distinction between them.
- One way to imagine the critical point: along the coexistence curve,  $\rho_{gas} < \rho_{liquid}$ , but the difference gets smaller as  $T$  gets higher. At  $T_c$ ,  $\rho_{gas} = \rho_{liquid}$  and beyond it, there is only a thing we call *fluid*. There are strong analogies between magnets and fluids.  $T_c$  is like the Curie temperature of a ferromagnet, and it is the critical temperature for our favorite “toy” model of a magnet, the Ising model.



- *Notation alert:* Different readings have different symbols conventions. One text uses  $G$  meaning per the total, Gibbs free energy mole, but another might mean  $G$  is per mole. Another text uses  $g$  meaning energy per molecule, and other texts use  $\mu$ , chemical potential, as a synonym for  $g$ . Also confusing, in one text  $L$  will mean latent heat per kg, or latent heat per mole. But in a different text, G&T for example, they switch to small letters so that  $l$  is the latent heat per mole. They also use small letters for entropy and volume, so  $s$  is entropy per mole, and  $v$  is volume per mole. B&B uses  $V_m$  per mole. Sigh!

- Areas of a single phase are separated by phase boundaries:  $P(T)$  curves where two phases coexist. What determines a phase boundary? At any point  $(T_b, P_b)$  on a phase boundary the Gibbs free energy per molecule will be numerically equal:  $\mu_A(T_b, P_b) = \mu_B(T_b, P_b)$ . It costs no free energy to interconvert from one phase to the other.
- B&B 28.7 talk about a few naming schemes for phase transitions:
  - First, vs. second, vs. third ... has to do with which derivative of  $G(T, P, N)$  shows the first discontinuity. E.g across the curves in a phase diagram, you have a first order transition. For a first-order transition, the latent heat is nonzero:  $L = T\Delta S \neq 0$ . Thus  $S$ , a first derivative of  $G$  with respect to  $T$  is discontinuous. Also,  $V$ , a first derivative of  $G$  with respect to  $P$ , is discontinuous.
  - Continuous vs. discontinuous: is a way to lump all orders beyond the first into one called "continuous". However, it makes good sense. First derivatives of  $G$  with respect to an external field like pressure or magnetic field are *order parameters*. For example, the magnetization  $M(T)$  is a derivative of energy with respect to magnetic field. It rises smoothly from zero as temperature drops below the Curie temperature.
  - Symmetry breaking: is what some transitions do. For example, a liquid is more statistically symmetric than a crystalline solid, which is not perfectly symmetric upon translation or rotation. On the other hand, a liquid and gas have equal amounts of symmetry.
- The *Gibbs-Duhem equation*:

$$dg = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT; \text{ or } d\mu = vdP - sdT$$

It looks like a weird flipping of the thermodynamic identity, where extensive are swapped with intensive variables. It plays a role in various arguments this week, including deriving the Clausius-Clapeyron relation (below) and the Maxwell construction as done in G&T section 7.4.

- **Clausius Clapeyron** Let's go with Schroder's notation that we have a mole of stuff that can be either in the  $A$  or  $B$  phase. Quantities below will all be considered to be measured per mole. The slope of the vapour pressure  $P(T)$  curve on the phase diagram is shown to obey:

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{L}{T\Delta V} .$$

Here,  $L$  is the *latent heat* or *enthalpy* of transition going from  $A$  to  $B$ . In other words,  $L = T\Delta S = \Delta H$  because when we straddle a line

between phases  $A$  and  $B$  in the phase diagram,  $G_A = H_A - TS_A = H_B - TS_B = G_B$ .

- When we cross a coexistence curve to move between, say, liquid and gas phases,  $L$  is not zero. (It is *positive* for liquid to gas, and *negative* for gas to liquid.) The density between a liquid and a gas jumps when you cross the curve. This is the big difference between liquids and gasses! The only exception is, as we mentioned above, at very end of the liquid-gas coexistence curve, the critical point.
- Good examples of how to use Clausius-Clapeyron are B&B 28.2, 28.3, 28.4 (the same as Example 7.4 in G&T). In these examples, we derive the shapes of  $P(T)$  for cases

- liquid  $\leftrightarrow$  gas assuming  $L$  is constant, and also taking into account the change of  $L(T)$  with temperature, which yields

$$P(T) = P_o \exp\left(-\frac{L_o}{RT} + \frac{(C_p \text{ gas} - C_p \text{ liquid}) \ln (T/T_o)}{R}\right)$$

Note: I think there is a missing  $T_o$  in Eq. B&B (28.31) because it needs to reduce to Eq. (28.23) at the starting temperature, which we might call  $T_o$ .

- liquid  $\leftrightarrow$  solid where we just assume  $L$  and the volume difference  $\Delta V$  between the phases is constant

$$P(T) = P_o + \frac{L}{\Delta V} \ln (T/T_o)$$

- A practical use for knowing  $P(T)$  is knowing how a change in pressure will change the freezing or boiling temperature of a substance. We have at least one problem on this application this week. There is much talk of this effect with respect to the "pressure melting" of water. G&T show that it cannot be true that this is what melts ice under a skater's skates (too little pressure), but Schroder points out that this *is* relevant to understand pressure-induced melting of glaciers.
- **Interesting in B&B but not required for you to know** Are *Troun's rule*, which gives a rough estimate of  $L$  for the gas/liquid phase transition. Also, *Kelvin's formula* which arises from a discussion of metastability ... why drops do not always coalesce ("nucleate") to form a liquid when this is the phase with a lower  $G$  ... but actually evaporate, leading to a metastable vapour phase.
- **The Van der waals equation of state** A gas whose equation of state is  $PV = NkT$  cannot undergo a phase transition. But the *van der Waals equation of state*

$$P = \frac{NkT}{V - Nb} - a \frac{N^2}{V^2} ; \text{ or in per mole language, } P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

models a substance which has realistic short range repulsion and long range attraction. It can make a transition between gas and liquid. Note that the constants  $a$  and  $b$  are different in these two formulations ... for example  $b$  is a *volume/molecule* on the left, and *volume/mole* on the right. The term proportional to  $b$  limits reduces the available volume for each molecule under the assumption that they cannot overlap.

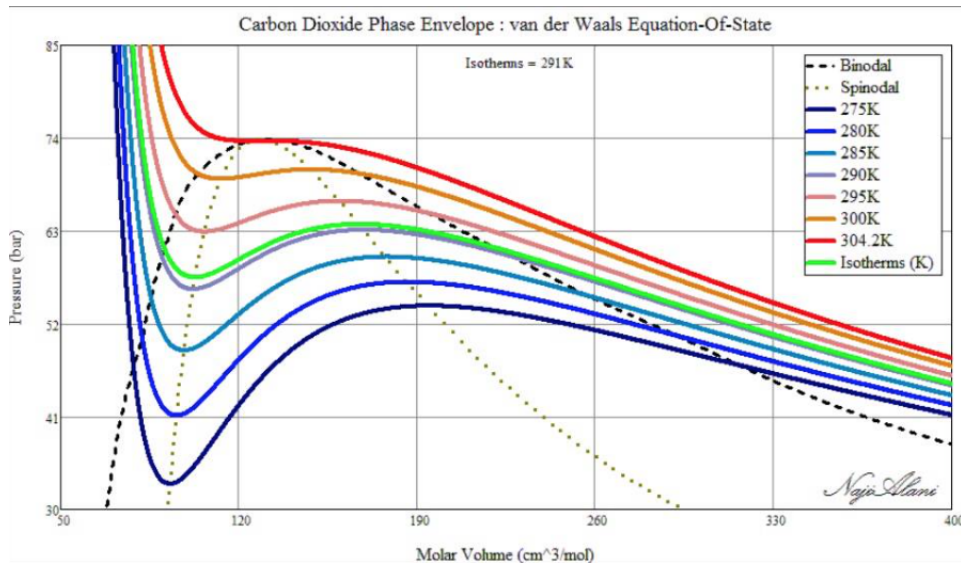
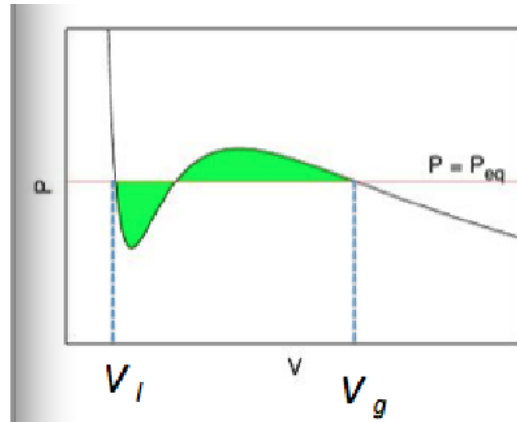
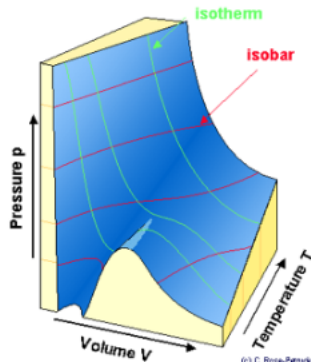
- The term proportional to  $a$  can be derived by assuming an attractive term in the energy  $U_{att} = -aN^2/V$  (or in the per/mole way of looking at things,  $U_{att} = -an_{moles}^2/V$ ). This is proportional to  $N^2$  (or  $n_{moles}^2$ ) since it has pairs of particles attracting one another. Then, either an argument like  $dU = -PdV$  or one constructing the partition function as in B&B p. 298 yields the vdW equation of state.
- There are issues with the phase diagram that the vdW gas produces. All three texts show  $P$  vs.  $V$  plots, where the isotherms do something crazy below a certain temperature,  $T_c$ . This critical isotherm is the one on which  $P(V)$  has a *point of inflection*, both first and second derivatives vanish. On isotherms for  $T < T_c$  the compressibility,  $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N}$  becomes negative in a range of  $V$  values. This is physically impossible! But it comes out of the math ... in particular I like B&B's argument in their Eq. (26.11) that  $P(V)$  is a cubic equation, and we shouldn't be surprised if it has an "S" shape. it will only do so for  $T < T_c$ .
- The readings make various arguments. Though B&B and Schroeder avoid doing this, G&T ends up writing  $g(T, \rho, N)$ , even though  $\rho$  is not  $g$ 's "natural variable".  $G(T, P, N)$  turns out to be multi-valued in a certain range of  $V$ . Looking at it another way (see figures below), when we are below  $T = T_c$ , viewing the phase diagram in  $P, V, T$  space, a curve of constant  $T$  opens up into an area. But this area is not a realm of thermal equilibrium.
- Interpretation: only the *boundary* of that area is physical and represents thermal equilibrium. The equilibrium system is confined to the black, dashed *binodal* line in the bottom figure below. The tan, dashed *spinodal* curve is the one inside which a system could never, ever go. This is where compressibility goes negative. However, a quickly cooled liquid could get inside the binodal ... it would be called "supercooled" and be considered *metastable*. This is the essence of Figure 7.7 of G&T, which shows the beginning of the "loop" in  $G(P)$  shown completely in Fig. 5.21 of Schroeder.
- Liquid and gas thus coexist at the two volumes on the boundary of the binodal,  $V_l$  and  $V_g$ . The *Maxwell equal area construction* tells us what these volumes are for given  $P$  and  $T$ . We draw a horizontal line

which insures that

$$\int_{P(V_l)}^{P(V_g)} V(P) dP = 0$$

- Doing this integral and setting it equal to zero is well and good, but how do we really find  $V_L(P)$  and  $V_G(P)$  for arbitrary  $P$ ? G&T take us through this partly-analytical, partly-numerical calculation on p. 400 that leads to their Figure 7.9.

### The ideal van der Waals fluid



### • Dimensionless variables and the vdW Critical Point

We get insight by writing the vdW equation of state in terms of dimensionless “reduced” variables  $\tilde{P} = P (27b^2/a)$ ,  $\tilde{T} = kT (27b/8a)$ ,  $\tilde{\rho} = \rho 3b$ , and  $\tilde{g} = (g/kT_c)(8/3)$ . This not only makes the vdW equation cleaner, but makes the critical point values  $T_c, P_c$  and  $\rho_c$  very pretty as well ... all equal to unity as one of our problems this week, G&T 7.10 shows.



- The *law of corresponding states* shows us that if we rescale  $P, V$  and  $T$  by their critical values, a remarkable number of pure substances fall on the *same* liquid-gas coexistence curve.
- We can also use the dimensionless vdW equation to derive *critical exponents*. A couple of problems treat these this week. There are cool analogies to the mean field Ising ferromagnet. For example,  $M \propto (T - T_c)^\beta$  is completely analogous to  $\rho_{liq} - \rho_{gas} \propto (T - T_c)^\beta$  ... with the same critical exponent for both. The vdW model *is* a *mean-field model of a real fluid*.

- **Order-disorder transitions and Critical phenomena**

So far in these notes, we spent most of our time on “first order” transitions that happen on curves in  $P - T$  space. Now we narrow our focus to *the vicinity of a single point, the critical point*. (So much effort to understand a single point?! We will try to make the case that this is interesting!) There is zero latent heat, and it the higher derivatives of free energy which are discontinuous or divergent. Despite the lack of a jump in the free energy due to a jump in the entropy, this kind of transition takes place *between an ordered and disordered phase*.

- G&T Ch. 9.1 has a review/extension of material from Ch. 5. In Ch. 5 *Mean field theory* gave us an approximate prediction of magnetization,  $m(T, H)$ . When you extend the theory to also talk about free energy,  $g(m, T, H)$ , you are doing what is called a *Landau theory*. G&T Problem 5.17 (which we didn’t do, but referred to) shows how this goes.
- Now the symbol for free energy per particle has become  $g(m)$ . More importantly, now we are being very general ...  $m$  does not have to be a magnetization and we don’t have to derive  $g$  from a specific partition function as in Ch. 5. The quantity  $m$  is the *order parameter*, which will be zero at  $T > T_c$  and rise smoothly from zero as  $T$  drops below  $T_c$ . We are meant to apply Eq. (9.1) quite broadly to create a Landau theory for any system. You will notice it is an analytic function, meaning a Taylor series in  $m$ . This is a hallmark of a mean field theory.

$$g(T, m) = a(T) + b(T)m^2/T + c(T)m^4/4 - Hm \quad \text{G\&T (9.1)}$$

- As many times in seminar, our guiding principle is that  $m$  will minimize  $g(m)$ . The key to finding a phase transition is to set  $b = b_0(T - T_c)$  (which was derived naturally in the ferromagnetic example in Ch. 5), with  $b_0, c > 0$ . From the minimization of  $m$  comes the emergence of three roots:  $m = 0, \pm m^*$  when  $T < T_c$ .
- In order to study critical phenomena, it is convenient to define dimensionless distance from the critical temperature as  $\epsilon = |T - T_c|/T_c$ . The result that  $m^* \propto \epsilon^{1/2}$  leads us to the *critical exponent*  $\beta = 1/2$ .

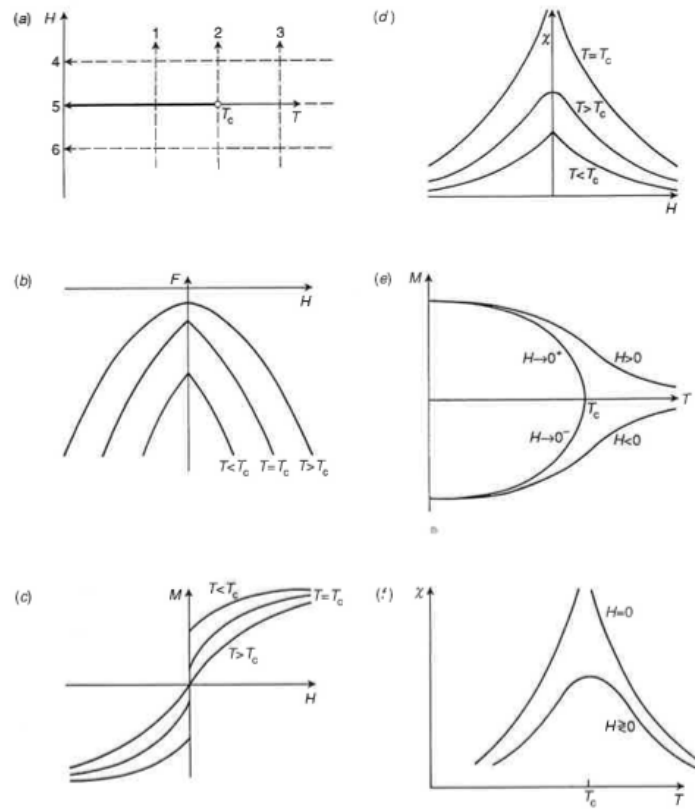


Fig. 2.1. (a) Phase diagram of a simple ferromagnet. There is a line of first-order transitions along  $H = 0$  which ends at a critical point at  $T = T_c$ . (b) Field dependence of the free energy. (c) Field dependence of the magnetization. (d) Field dependence of the susceptibility. (e) Temperature dependence of the magnetization. (f) Temperature dependence of the susceptibility.

Figure 3: Graphs of important quantities, using a ferromagnetic example (from Yeomans Ch. 2, found in our Resources folder.)

- Critical exponents are exciting, in part, because they are *universal*. They endow the same mathematical form, a *power law*, to quantities in vastly different systems (see Yeomans tables below). Also, any mean field treatment will yield the *same critical exponents*. Moreover, two systems can seem quite different but have a deep similarity - same spatial dimension and same kind of order parameter - and these will have the *same numerical values* for their critical exponents. Systems that share the same exponents are called members of a *universality class*. Finally, systems above a certain *upper critical dimension* will revert to their mean field critical exponents.

Table 2.3. Definitions of the most commonly used critical exponents for a magnetic system

Zero-field specific heat	$C_H \sim  t ^{-\alpha}$
Zero-field magnetization	$M \sim (-t)^\beta$
Zero-field isothermal susceptibility	$\chi_T \sim  t ^{-\gamma}$
Critical isotherm ( $t = 0$ )	$H \sim  M ^\delta \text{sgn}(M)$
Correlation length	$\xi \sim  t ^{-\nu}$
Pair correlation function at $T_c$	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

Table 2.4. Definitions of the most commonly used critical exponents for a fluid system

Specific heat at constant volume $V_c$	$C_V \sim  t ^{-\alpha}$
Liquid-gas density difference	$(\rho_l - \rho_g) \sim (-t)^\beta$
Isothermal compressibility	$\kappa_T \sim  t ^{-\gamma}$
Critical isotherm ( $t = 0$ )	$P - P_c \sim  \rho_l - \rho_g ^\delta \text{sgn}(\rho_l - \rho_g)$
Correlation length	$\xi \sim  t ^{-\nu}$
Pair correlation function at $T_c$	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

- Yet another intriguing thing about critical exponents is that they are not all independent, but obey certain *scaling relations*, as Table 9.1 of G&T shows. Most of these come from straightforward dimensional analysis, plus a bit of handwaving (e.g. that the only important length scale in the problem is  $\xi$ .)

- **Bose-Einstein condensation ...** is weird and wonderful. When a boson gas has its temperature reduced past  $T_c$ , a substantial number of particles begin to occupy the same state, the ground quantum state. They stop contributing to pressure or viscosity. To understand why this transition occurs, we first we might think about how the chemical potential changes with  $T$ . Fixing  $N$ , the total number of bosons, we can in principle find  $\mu$  via:

$$N = \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} - 1} g(\epsilon) d\epsilon$$

Calculated this way, using the classical density of states,  $g(\epsilon) \propto \epsilon^{1/2}$ , we find that the chemical potential rises to a value extremely close to zero as  $T$  gets very low. When  $\mu$  actually reaches zero (or  $\epsilon_0$ , the ground state energy ... which is close to zero in a real system, there will be one temperature  $T = T_c$  that satisfies this equation.

$$N = V \lambda_{th}^{-3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx \quad \text{with } \lambda_{th} = \frac{h^2}{\sqrt{2\pi m k T_c}}$$

- The dimensionless integral above has the value 2.315, so

$$N = 2.612 V \lambda_{th}^{-3} \equiv Li_{3/2}(z = 1) V \lambda_{th}^{-3} \equiv \zeta(3/2) V \lambda_{th}^{-3}$$

(These different ways of writing  $N$  are thanks to the polylogarithm treatment in B&B ... you can read about it in their Appendices C.4 and C.5, and you can remind yourself about Bose and Fermi integrals in G&T Appendix A.12.) This can only be true for one value of  $\lambda_{th}$ , hence one temperature, the *BEC transition temperature*. It will depend on the mass of particles and their density. From above:

$$kT_c = 0.527 \frac{h^2}{2\pi m} \left(\frac{N}{V}\right)^{2/3}$$

- Why can't we have bosons with lower temperatures than  $T_c$ ? We can, but we have to fix a problem in our formalism. We tried to find the temperature that gave us the known density  $N/V$ , by integrating energies from 0 to  $\infty$ . But below  $T_c$  we have *significant numbers of particles occupying the ground quantum state*. These are not accounted for in our integral weighted by  $g(\epsilon)$ , which happens to be zero at  $\epsilon = 0$ . We have to count low-lying quantum states using a sum, not an integral. The population of the ground state rises in a new way below  $T_c$ . A phase transition!
- The expressions for  $N$  above are correct, but only for the population of particles in the excited state. We thus write:

$$N_0 = N - N_{excited} = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]$$

The  $N_0$  particles that are “condensed” are in the ground energy state. So rather than thinking of them like a drop of water in a gas vapor, we should think of them as all slowed to their zero-point state of motion. In experiments, the atoms are localized in a magnetic trap. Here is a link to the Nobel prize lecture of Wolfgang Ketterle, who participated in the first experiment that found a BEC in ultra cold alkali halide atoms: <http://www.gangalib.org/ketterlelecture.php>. Here's an MIT video about creating the BEC: <https://www.youtube.com/watch?v=1RpLOKqTcSk>.

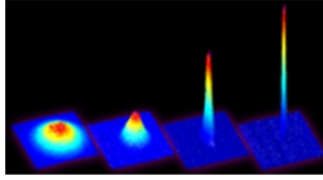


Figure 4: False color image of velocity space of Rubidium gas undergoing BEC -BaRbiE project, Univ. Ulm

- One can explore the thermodynamics of the  $N_{excited}$  particles, as one moves through the BEC phase transition. B&B Fig. 30.6 plots  $z$ ,  $U(T)$ , and  $C_V(T)$ , and problem 30.4 (not assigned) allows us to derive the inflection at  $C_V(T = T_c)$  which heralds the transition.

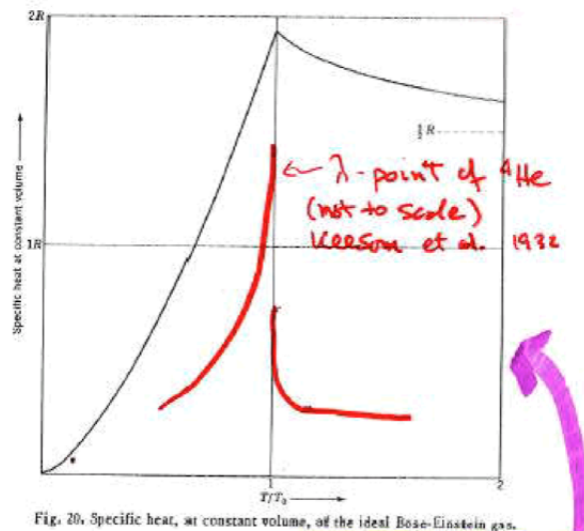


Fig. 20, Specific heat, at constant volume, of the ideal Bose-Einstein gas.

Figure 5: Specific heat of ideal bose gas, with superfluid helium specific heat cartooned in G. Baym lecture notes, Tokyo. 2004

- *Superfluidity* is a phenomenon related to BEC, though the differences are subtle. Superfluid bosons also share a quantum state, allowing them to escape through nanoscopic pores, move without viscosity, and follow each other in gravity-defying streams. Cool videos of superfluids exist: e.g. <https://www.youtube.com/watch?v=2Z6UJbwxBZI> . A Bose-Einstein condensate is not quite identical to a superfluid. Superfluids require interatomic interactions, whereas Bose-Einstein condensation is a result that emerges for noninteracting bosons.
- Bose-Einstein condensation is a *collective phenomenon*. A large number of bosons follow each other into the ground state. Were they distinguishable, there would be a very tiny fraction in the ground state, due to the many ways to distribute them among the many, many excited

states around energy  $kT$ . (This is the essence of the canonical distribution. Because  $E - TS$  is minimized, the large  $S$  of having particles in higher energy states fights with the low  $E$  of having them in lower energy states. The compromise for distinguishable, classical particles is that they hover around energy  $kT$ .) However, for bosons, there are far fewer excited state configurations available. The larger the number of bosons,  $N$ , the more important is the smallness of  $e^{-\epsilon N/kT} \approx e^{-N}$ , the probability of occupying a state of energy around  $kT$ . So the bosons lower their free energy by falling into the ground state. Like the degeneracy pressure of fermions, this is truly a result of bosons being identical! It is a demonstration that (as Schroeder says David Griffiths says) “even God cannot tell them apart”.

**Warmup Problems:** *Due by Tuesday afternoon on Moodle, or on paper in seminar*

**1: Clausius-Clapeyron and vapor pressure:** Schroeder Problem 5.35  
*Hint: This problem is actually done as an example in G&T Section 7.3 .*

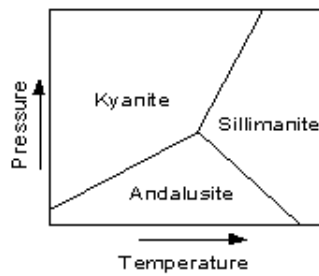
**2: Bose-Einstein Condensate: Putting in some numbers:** Schroeder Problem 7.66 parts a) - c)

**Regular problems:**

**1: Changes in boiling and freezing points** G&T problem 7.15

**2: Phase Diagrams:** Schroeder problem 5.24

**3: Phase diagrams:** Schroeder problem 5.29 parts (a),(b) and (c) .  
See the diagram below for a sense of the answers.



**4: More phase diagrams:** Schroeder Problem 5.34

**5: VdW phase transitions and the Law of Corresponding States:**  
G&T problem 7.10

**6: More about vdW phase transitions:**

i) Schroeder problem 5.52

ii) Plot  $G(t = 0.95, v)$  vs.  $v$ . Do you get something like G&T Fig. 7.6, with minima in the right places?

**7: VdW gas and critical exponents:**

i) G&T problem 7.18

ii) B&B problem 26.1 ... also, what does your answer give for the critical exponent  $\gamma$ ? How does this result compare to the mean field critical exponent  $\gamma$  for the Ising model of ferromagnetism?

**8: BEC Critical temperature:**

i) Schroeder problem 7.65

ii) G&T problem 6.39

**9: BEC behavior of pressure:** G&T problem 6.40