Physics 114 Statistical Mechanics Spring 2021

Week 12 Conceptual Overview

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.**.

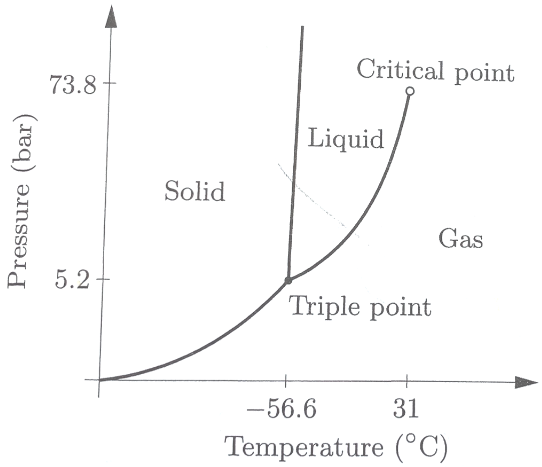


Figure 1: Phase diagram of a typical substance, CO_2.

- The most basic kind of phase diagram is that of a pure substance as in Figure 1 above. Axes are typically P vs T . (Analogous magnetic systems would have the external magnetic field taking the place of pressure, as seen in Schroeder Fig. 5.14.) To read diagrams like this, you might ask yourself "If I change P at constant T, will I cross the curve separating two different phases?" And vica-versa: "What about changing T at constant P?" Figure 2 below indicates a difference between H_2O and most other substances: Raising P when one begins in the solid phase (ice) eventually takes you to the liquid (water). This is because unlike most other substances $\rho_{solid} < \rho_{liquid}$ for H_2O. The Clausius-Clapeyron equation glossed below completes the formal argument.

- This phenomenon (raising pressure turns solid into liquid) also occurs in more exotic systems, like low temperature ^3He. There, we'd also use Clausius-Claperyon to see why. But in this case, solid has not a lower density, but a higher *entropy* than the liquid! (This weird fact arises because the liquid phase has an entropy dominated by the behavior of an ideal Fermi gas. The solid's entropy is dominated by a paramagnetic solid; the magnets being the ^3He nuclei.)

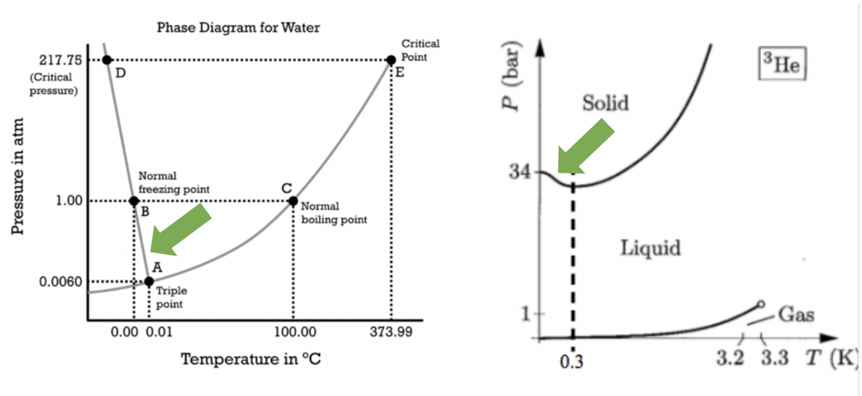


Figure 2: Phase diagrams for H_2O and ^3He. Green arrows show unusual negative slope for $P(T)$ along solid-liquid coexistence curve

- Can you draw a phase diagram with other axes? How about P vs. ρ or equivalently P vs. V? This is technically OK as in G&T Fig. 7.5 or Schroeder Fig. 5.23 which is Figure 3 below. But careful: V or ρ 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: ρ_{liquid} and ρ_{gas} say.

- 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

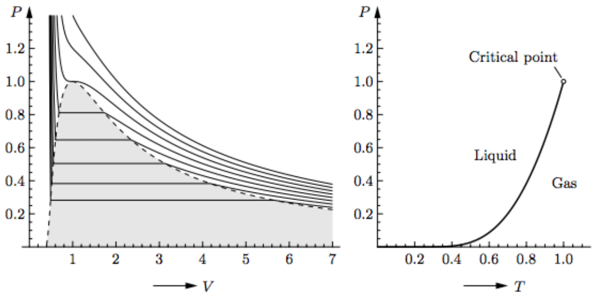
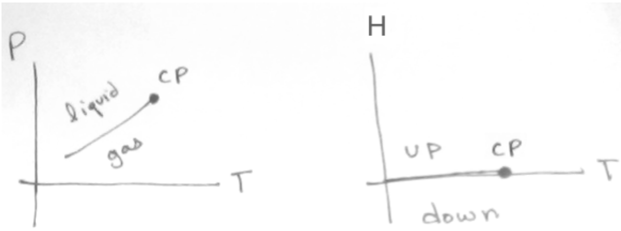


Figure 3: Phase diagrams of a van der Waals fluid.

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 μ, 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*:

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

  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 it is explained 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:

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

  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 Examples 28.2, 28.4 (identical to G&T Examples 7.3 and 7.4). We derive the shapes of $P(T)$ for cases:
  - liquid ↔ gas:

    $$P(T) = P_o \; exp(-L_o/RT)$$

  - liquid ↔ solid where we just assume L and the volume difference ΔV between the phases is constant:

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

  - You are not responsible for the case where L varies with T, treated in B&B Example 28.3.

- 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.

- **Something in B&B that I would like you to know:** B&B section 28.6 talks about *colligative properties*. That is, one can change a freezing or boiling point by adding solute to a pure substance. We do not have time this semester to talk about phases of systems that are mixtures of pure substances. There are all kinds of new possible phases in such cases. B&B Section 28.5 tells us about the *Gibbs phase rule* for example, which dictates the topology of the phase diagram. (You have a triple point ... can you have a quadruple point? Not with a pure substance but yes with a mixture :-) Bottom line: I would like you to understand and be able to apply this outgrowth of *Raoult's law*:

$$T - T^* = \frac{RT^{*2}\, x_B}{\Delta H} \quad \textit{change in transition temperature with added solute}$$

What was Roult's law? In B&B Ch. 22, it told us how the chemical potential changes when a small mole fraction x_B of solute is added to a solvent.

- **Interesting in B&B but not required for you to know** Are *Trouton'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*

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

  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.

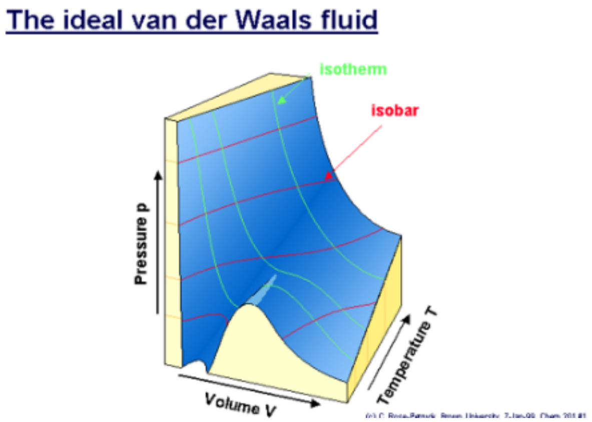
- There are issues with the phase diagram that the vdW gas produces. All three texts show P vs. V plots, where the isotherms do something crazy below a certain temperature, T_c. This critical isotherm is the one on which $P(V)$ has a *point of inflection*, both first and second derivatives vanish. On 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 $T < T_c$.

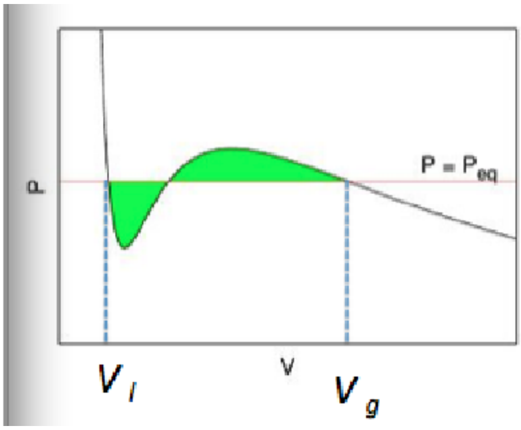
- The readings make various arguments. Though B&B and Schroeder avoid doing this, G&T ends up writing $g(T, \rho, N)$, even though ρ is not g's "natural variable". $G(T, P, N)$ turns out to be multi-valued in a certain range of V. Looking at it another way (see figures below), when we are below $T = T_c$, 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.

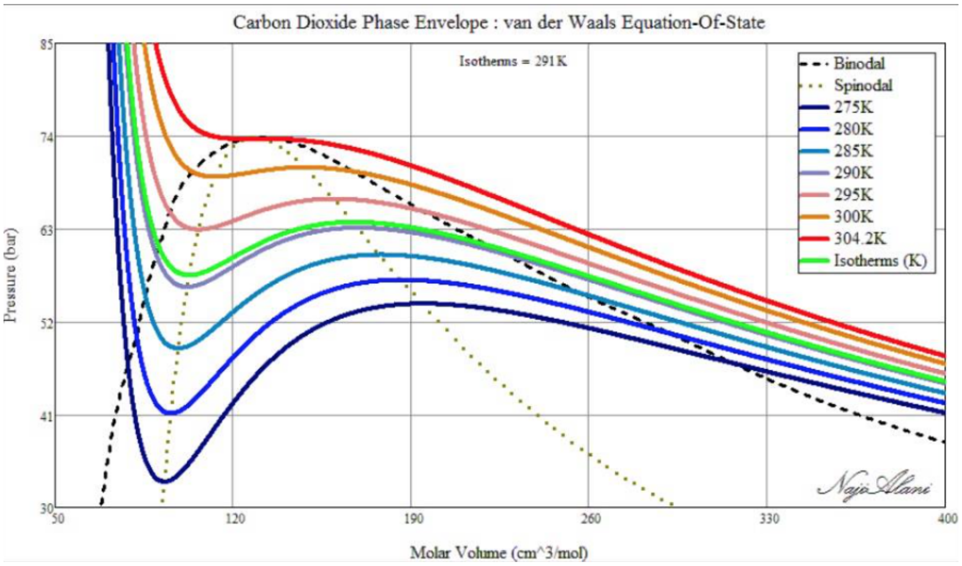
- Interpretation: only the *boundary* of that area is physical and represents thermal equilibrium. The equilibrium system is confined to the black, dashed *binodal* line in the bottom figure below. The tan, dashed *spinodal* curve is the one inside which a system could never, ever go. This is where compressibility 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 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.







- **Reduced 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 ρ_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.*

- **Virial coefficients** Suppose we have a classical gas that is dense enough for interparticle interactions to matter, but insufficiently dense or cold for transition to a liquid. Now pressure can be written as a *virial expansion.* B&B are fond of writing expressions *per mole* so framed this way, for one mole with molar volume V_m:

  $$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2}$$

  In G&T language, this would be

  $$P/kT = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + ...$$

- G&T and B&B go on to justfy this virial series in similar ways (though B&B is a lot shorter and just fine for our purposes). Recall the general form for the partition function:

  $$Z(T,V,N) = \frac{1}{N!\ h^{3N}} \int ... \int d\mathbf{r_1}, ..., d\mathbf{r_N}\ d\mathbf{p_1}, ..., d\mathbf{p_N}\ e^{-\beta U(\mathbf{r_1},...,\mathbf{r_N},\mathbf{p_1},...,\mathbf{p_N})}$$

  For much of seminar, we've been dealing with an ideal gas, so U was wholly kinetic: $U = U_K \equiv \Sigma_i p_i^2/2m$. In this case, the partition function was:

  $$Z(T,V,N) = Z_{ideal}(T,V,N) = \frac{1}{N!} V^N (\frac{\sqrt{2\pi mkT}}{h})^N$$

- Now we will assume there is potential energy as well as kinetic. So $U = U_K + U_P$. We find that we can write the partition function as a product $Z = Z_{KE} Z_{PE}$ where $Z_{KE} = Z_{ideal}$ and Z_{PE} is often seen written as Z_c. This is because Z_c is called the "configuration integral" - it depends on the spatial configuration $\mathbf{r_1}, ..., \mathbf{r_N}$. We thus have

  $$Z_{PE} = Z_c = \frac{1}{V^N} \int ... \int d\mathbf{r_1}...d\mathbf{r_N} e^{-\beta U_P(\mathbf{r_1}...,\mathbf{r_N})}$$

- *Notice* the V^N in the denominator! We need it! Otherwise, $U = 0$ would not lead to $Z = Z_{ideal}$.

- Two approximations: i) We use *pair potentials* - so two particles contribute to U_p via $u(\mathbf{r_i}, \mathbf{r_j})$, no matter where the other particles in the system are located. ii) It is only the *scalar distance between particles i and j* that determines their potential energy. Thus

  $$U_P = \Sigma_{i<j} u(|\mathbf{r_i} - \mathbf{r_j}|) \equiv \Sigma_{i<j} u(r_{ij})$$

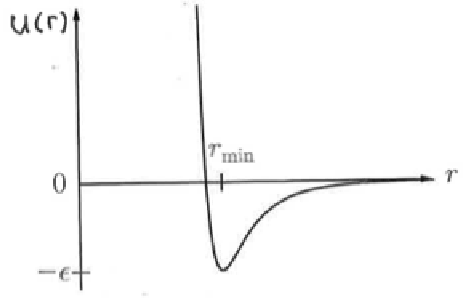
  where the sum is over all distinct pairs of particles. This leads to

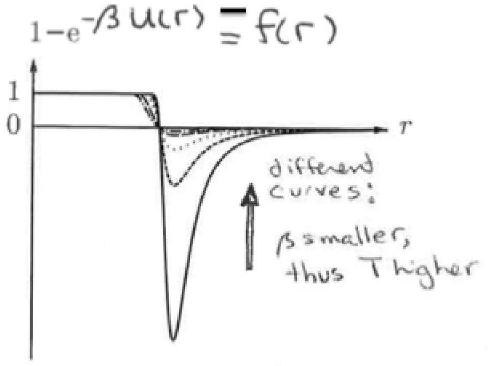
  $$Z_c = V^{-N} \int ... \int d\mathbf{r_1}...d\mathbf{r_N} \quad \Pi_{i<j} e^{-\beta u(r_{ij})}$$

- Now comes a notation that B&B doesn't use but G&T, and most other people do. We frame Z_c in terms of the *Mayer f functions* $f(r_{ij}) = e^{-\beta u(r_{ij})} - 1$. See the figure below ...

- The $f(r)$ functions go quickly to zero as soon as a pair of particles are separated by r greater than the range of their interactions. These are "molecule-sized" functions. By definition,

  $$Z_c = V^{-N} \int ... \int d\mathbf{r_1}...d\mathbf{r_N} \quad \Pi_{i<j}[1 + f(r_{ij})]$$





- From here, one expands out the infinite product. Note that $f(r)$ is small when βu is small ... i.e. when interactions between particles are not too important on a scale of kT. If we truly expect f to be small enough to ignore for all pairs of particles, we have $Z_c = 1$. This is an ideal gas.

- If we can't ignore these factors of f, we have the issue of calculating terms in the product.

$$Z_c = \frac{1}{V^N}\int ... \int d\mathbf{r_1}...d\mathbf{r_N}[1+\Sigma_{pairs\ i<j} f(r_{ij}) + \Sigma_{distinct\ pairs\ i<j,\ k<l}\, f(r_{ij})f(r_{kl})+...]$$

- It is at this point that we say that we are stopping only at the very first sum above ... only one power of $f(r)$. This is like saying that our gas is dilute enough that it is rare to have a triplet (or quadruplet or ...) of particles close to each other at any one time. We can make the usual N large approximation

$$Z_c = 1 + \frac{N^2}{2V}\int d\mathbf{r} f(r)$$

  We now integrate over angle space for the one remaining 3d coordinate, $\mathbf{r}$, to arrive at

$$Z_c = 1 - \frac{NB_2(T)}{V} \quad where \;\; B_2(T) = -2\pi\int_0^\infty r^2 f(r)dr$$

- Last steps ... use $F = -kTlnZ$ and $P = -(\frac{\partial F}{\partial V})_T$ to get our first term in the virial expansion for free energy and pressure:

$$F = F_{ideal} + \frac{N}{V}kT\ B_2(T)\ ; \quad \frac{PV}{NkT} = 1 + \frac{N}{V}B_2(T)$$

- **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. But sometimes we want to focus on the *the vicinity of a single point, the critical point.* A transition at the critical point involves 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.*

- When we studied the Ising model in Week 9, $(H = 0,\ T = T_c)$ was the critical point. *Mean field theory* gave us an approximate prediction of magnetization, $m(T, H)$. When one extends mean field theory to also talk about free energy, $f(m, T, H)$, it's called a "Landau theory". G&T Problem 5.17 (which we didn't do, though we used the resulting $f(m, T, H)$ in Problem 5.18) explained the steps. The quantity m was the *order parameter*, which was zero at $T > T_c$ and rose smoothly from zero to a nonzero value of $m_o(T)$ as T was reduced below T_c. Thus, $m_c = 0$ for the Ising model. In order to study critical phenomena, we learned that it was convenient to define dimensionless distance from the critical temperature. So say $\epsilon \equiv |T - T_c|/T_c$. The result that $m - m_c \propto \epsilon^{1/2}$ (where m_c happens to be 0) leads us to the *critical exponent* $\beta = 1/2$.

- I bring this up now because *the van der Waals equation of state comes from a mean field theory* for the free energy, $g(T, P, N)$. When we read G&T section 7.4.2 and do problems G&T 7.18 and B&B 26.1 this week, we see that the values for the critical exponents β, δ, and γ are precisely those that we'd get from the Landau free energy for a magnetic system. The analogy is that near the critical point, gas density (in reduced units) behaves like magnetization: $\tilde{\rho} - \rho_c \equiv m - m_c$. And pressure (again, reduced units) is like magnetic field: $\tilde{p} - p_c \equiv H - H_c$.

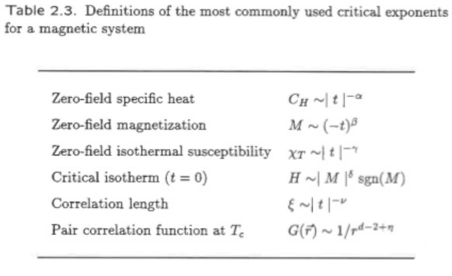


Table 2.3. Definitions of the most commonly used critical exponents for a magnetic system

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

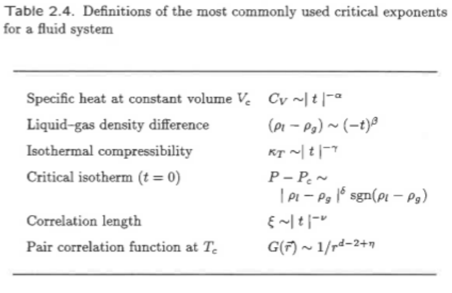


Table 2.4. Definitions of the most commonly used critical exponents for a fluid system

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