1 Phase Transitions

1.1 Introductory Phenomenology

Consider a single-component system in thermodynamic equilibrium. Let us describe the system with the set of (independent) variables T, p, and N. The appropriate 'free energy' is the Gibbs Free Energy $G(T, p, N)$. Recall that $G = \mu N$ where $\mu(T, p)$ is the chemical potential per particle. It is sometimes convenient to use the Gibbs Free Energy per mole g defined by $G = \nu g$ where ν is the number of moles in the system. One could equally well work with intensive quantities that are defined per particle,

It is also useful to recall the thermodynamic relations (in terms of intensive variables)

$$s = -\left(\frac{\partial g}{\partial T}\right)_p \quad \text{and} \quad v = \left(\frac{\partial g}{\partial p}\right)_T \tag{1}$$

where s is the entropy per mole and $v = V/\nu$ is the volume per mole. The system is described by an equation of state that is a functional relation between p, T, and v, *e.g.,* the ideal gas law is $pv = RT$, valid at high temperatures and low densities.

Specifying two of the fields T and p specifies the state of the system. They control the densities entropy and the volume respectively. The other field μ that controls the number is a function of T and p. The state of the system can be represented by points in the $p - T$ plane and one expects each point to correspond to a precise volume v that can be obtained from the equation of state. The 'phase diagram' of a generic one-component substance is shown in Fig. 1.

Different regions of the figure correspond to different phases, Solid, Liquid, and Gas as denoted in the figure. The state of the system corresponds to a single, spatially homogeneous phase in almost all of the plane except on lines and at points. The lines represent equilibrium states along which two different phases with different number densities molar volumes *coexist.* This means that the mass density ρ undergoes a discontinuous jump across the transition line. The discontinuity in the density is well-known: steam and water have very different densities. Only at the boundaries does phase coexistence occur; only at an isolated triple point (T_t, p_t) can three phases coexist.

Shown in the next figure is the schematic phase diagram of a one-component fluid near the critical region. The pressure is plotted along the ordinate and the density along the abscissa. The isotherms and tie lines in the two phase region are displayed. Note that across the coexistence line the density (or the molar volume) jumps discontinuously from its value in the gas phase to the value in the liquid phase whether one varies the temperature or the pressure. (For water at $100C$, this jump would occur

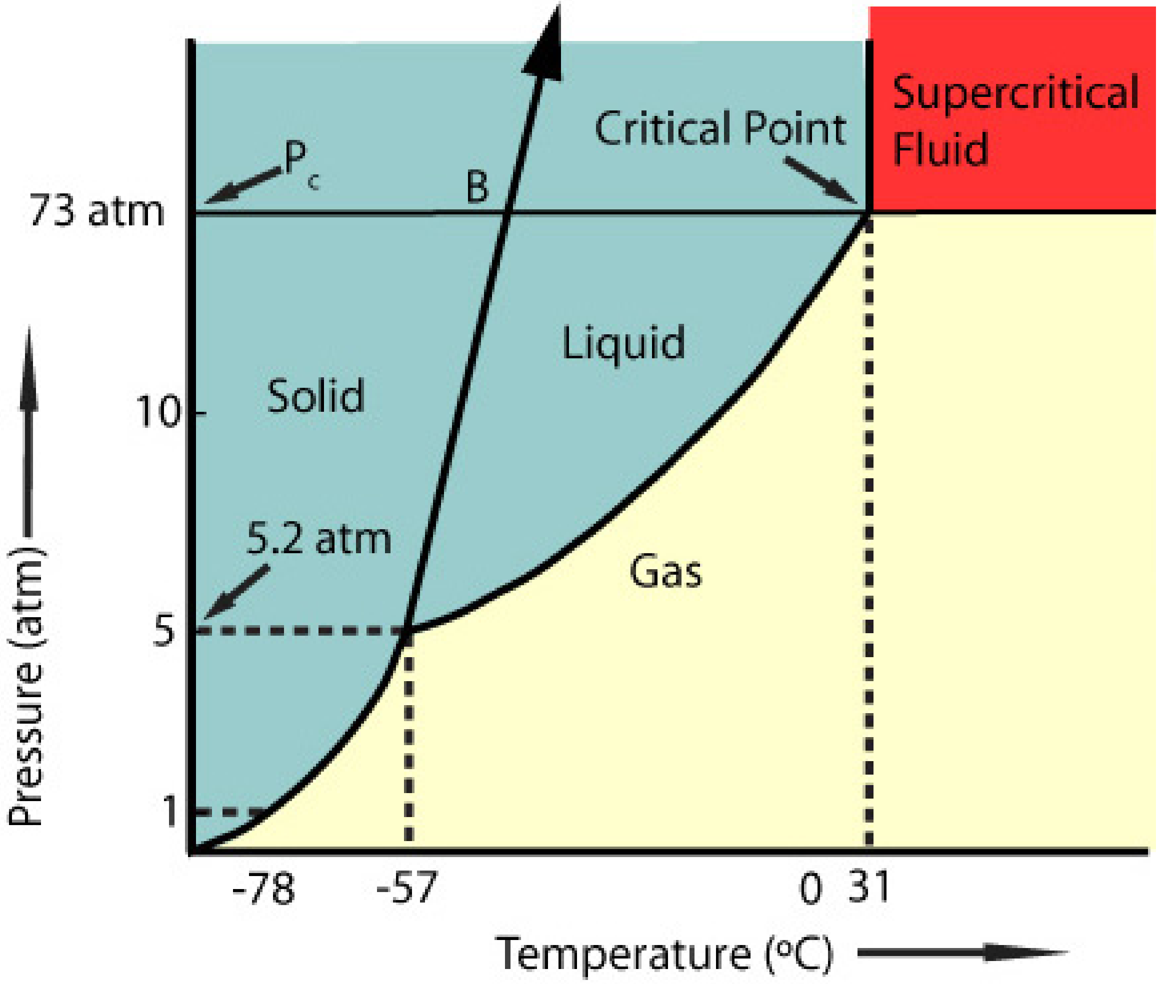
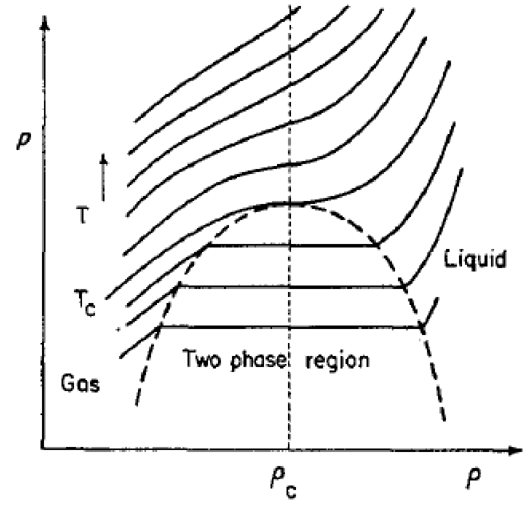


Figure 1: The phase diagram for carbon dioxide. Note that sublimation occurs at atmospheric pressure as you know for dry ice. The region denoted by supercritical fluid is not as well-defined as this figure I downloaded from the web makes it appear.


p
T
T_c
Gas
Two phase region
Liquid
ρ_c
ρ

at a pressure of approximately 1 atmosphere and in convenient units the density is $1677\, cm^3/gm$ for steam and $1.043\, cm^3/gm$ for water.)

There are, similarly, jumps in the density across the coexistence line between the Liquid and Solid phases (this is the *melting* or *fusion* curve) and Gas and Solid phases (this is called the *sublimation* curve). The process of freeze-drying takes advantage of the sublimation curve! Freeze drying involves the removal of water or other solvent from a frozen product by sublimation.

Note that the molar volume is the first derivative of the Gibbs Free Energy with respect to the pressure. See Equation 1. The Gibbs Free Energy is a smooth (analytic) function of its variables at all the points in Fig. 1 (this is being asserted !) except at these lines where the *first* derivative is discontinuous. These are, therefore, called *first-order* transitions. Transitions in which one or more first derivatives of the relevant thermodynamic potentials change discontinuously as a function of their variables may be called **first-order** transitions.

The other first derivative of μ with respect to T is also discontinuous yielding jump in the entropy which signals the fact that one phase is more ordered than the other. Typically, the liquid is more ordered than the gas and the solid more than the liquid. How does the difference in entropy manifest itself ? Consider water below its boiling point. When heat is added to the system its temperature increases. However, exactly at the boiling point the addition of heat does not increase the the temperature but merely serves to convert water into steam. This quantity of heat is familiar to you as *latent heat.* This quantity of heat $L = \Delta Q$ is given by $L = \Delta Q = T\Delta S$ where T is the temperature at which the liquid boils at that pressure and ΔS is the change in entropy.

The latent heat of vaporization of water is $2.26 \times 10^6\ J/kg$ at normal atmospheric pressure at $100°C$ and the latent heat of fusion of ice is $3.34 \times 10^5 J/kg$.

There are a few other features about the phase diagram that demand our attention. One point in the phase diagram to be noted is the one with coordinates (T_t, p_t) called, for obvious reasons, a *triple point* where all three phases coexist. This may appear peculiar because it is not common. For H_2O this point occurs at $273.16K$ but at a pressure of $0.0061 \times 10^5 Pa$ that is roughly 160 times smaller than atmospheric pressure.

The point denoted C is the critical point that is identified as follows: As one follows the vaporization curve up, the discontinuity in the density decreases until at C it vanishes altogether. Beyond T_c varying the pressure does not lead to a jump in the density nor is there the phenomenon of phase separation. In general, the critical point is the terminus of a locus of first-order transition points. The termination of the liquid-gas coexistence curve means that one can go from a liquid phase 'continuously' to a gas phase without encountering a non-analyticity such as an abrupt change in the density. The critical point for water occurs at $647.4K \approx 374C$ and a pressure of $221.2 \times 10^5 Pa \approx 218 atm$. This is unfamiliar territory in terms of the parameters.

Transitions in which the first derivatives of the thermodynamic potential remain continuous while only higher-order derivatives such as the compressibility, the specific heat or the susceptibility are divergent or change discontinuously at the transition point are referred to as continuous transitions.

The dominant characteristic is the large increase of the microscopic fluctuations in the vicinity of a critical point: fluctuations of density, energy, magnetization, become macroscopic and, correspondingly, the related second thermodynamic derivatives (specific heats, susceptibilities) and the intensities for the scattering of waves off the system become very large or even tend to infinity at certain wavelengths.

Note that experimentally the liquid-solid transition does not terminate. (More about this later!)

Having noted this phenomenology it is worth considering the phase diagram in the $p - v$ (or $p - \rho$) plane in more detail focussing on the Liquid-Gas part for simplicity. See Fig. 2. At the first-order-transition there are two coexisting densities say ρ_1 and ρ_2; what about the values of the densities in between. In a fit of perversity if we maintained a system at an intermediate density precisely at (p, T) corresponding to a first-order transition what will the system do ? The system *phase separates* into two fractions one consisting of one phase at density ρ_1 and the other at ρ_2. The intermediate densities correspond to phase coexistence. The ruled area corresponds to this region; the straight lines connecting the points representing the pure phases are called *tie-lines* and correspond to a fixed pressure and temperature. Experimentally, consider CO_2 in a sealed tube at a density of approximately 0.5 gm/cc at a pressure of 72 atmospheres. At $T = 29C$, one sees a meniscus between the liquid and the vapor. As one heats up to $30C$ significant changes in the densities occur and at $31C$ there is enhanced scattering of visible light, a phenomenon termed *critical opalescence.* At a higher temperature there is a single homogeneous phase and the meniscus has disappeared. See the site with the video that I have given on the site.

The mole fractions f_1 of phase 1 and f_2 of phase 2 that coexist are easily determined by the ‘lever’ rule. We know that the sum adds up to zero and the density of the system is determined by the fractions and the densities of the coexisting phases.

Critical Opalescence: (fourth link; I liked the second video)
http://www.msm.cam.ac.uk/doitpoms/tlplib/solid-solutions/demo.php

Intensive versus extensive: Clearly pressure and density are intensive and the entropy or energy S and U are extensive but then entropy per mole or energy per mole denoted by s and u are intensive. We shall use the term ”density” for such a variable, which though intensive plays quite a different role in thermodynamic equations than temperature and pressure$p$, which we shall refer to as ”fields. ”' Other examples of fields are the chemical potentials of different components in fluid mixtures, and magnetic and electric fields in paramagnets and dielectrics, respectively. The fields (in contrast with densities) have the property that they take on identical values in two phases which are in thermodynamic equilibrium with each other.

Phase coexistence chemically and physically homogeneous, bounded by a distinct interface with other phases and physically separable.

Clausius-Clapeyron Equation:Consider four points on the phase coexistence curve two on either side but infinitesimally separated along the coexistence curve. If points A_1 and A_2 are across from each other in the two phases 1 and 2 we have $\boxed{\mu_{A_1} = \mu_{A_2}}$. Points B_1 and B_2 are across from each other separated by infinitesimal Δp and ΔT we also have $\boxed{\mu_{B_1} = \mu_{B_2}}$. Therefore, we find

$$\mu_{B_1} - \mu_{A_1} = \mu_{B_2} - \mu_{A_2} \,. \tag{2}$$

From the fundamental thermodynamic identity we have the Gibbs-Duhem relation $\boxed{\mu_{B_1} - \mu_{A_1} = -s_1\, dT + v_1\, dP}$ since we are in phase 1 and similarly we also have $\boxed{\mu_{B_2} - \mu_{A_2} = -s_2\, dT + v_2\, dP}$. Therefore, we obtain the slope of the coesistence curve $\boxed{\dfrac{dP}{dT} = \dfrac{s_2 - s_1}{v_2 - v_1} = \dfrac{\ell}{T\,\Delta v}}$.The anomalous density dependence of water makes the slope of the melting curve negative in contrast to most substances. Na up to $100 GPa$ shows a negative slope. There is actually a minimum at $118 GPa$ and then it increases![1]

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[1] Gregoryanz et al. , *Science* **320** (5879) 1054-1057.

The enthalpy of vaporization can be viewed as the energy required to overcome the intermolecular interactions in the liquid (or solid, in the case of sublimation). Hence helium has a particularly low enthalpy of vaporization, $0.0845 kJ/mol$, as the van der Waals forces between helium atoms are particularly weak. On the other hand, the molecules in liquid water are held together by relatively strong hydrogen bonds, and its enthalpy of vaporization, $40.65 kJ/mol$ (Since $1J = 0.239C$ and this corresponds to $18 grams$ this is $540C/gm$), is more than five times the energy required to heat the same quantity of water from $0C$ to $100C$ ($c_p = 75.3 JK^{-1} mol^{-1}.$).

Discuss Pressure cookers

Gibbs Phase Rule: If there are C components we determine P the maximum number of phases that can coexist. The system is described by giving the pressure and temperature that are the same in all phases. In addition, each phase is specified by specifying the fractional concentration of each component in each phase: there are $C - 1$ fractional concentrations (since the sum is unity) in each of the P phases and thus $P\,(C-1) + 2$ independent variables. The conditions to be satisfied are

$$\begin{aligned} \mu_1^{\alpha_1} &= \mu_1^{\alpha_2} = \cdots \mu_1^{\alpha_P} \\ \mu_2^{\alpha_1} &= \mu_2^{\alpha_2} = \cdots \mu_2^{\alpha_P} \\ &\cdots\cdots\cdots\cdots \\ \mu_C^{\alpha_1} &= \mu_C^{\alpha_2} = \cdots \mu_C^{\alpha_P} \end{aligned}$$

There are $P-1$ equations for each component and since there are C components we have $C\,(P-1)$ equations to be satisfied. and the number of independent variables is $2 + P\,(C-1)$; therefore,

$$C\,(P - 1) \leq 2 + P\,(C-1)$$

Therefore, $\boxed{P \leq C + 2}$.

Note an important qualification. In the phase diagram of a ferromagnetic metal there is a (critical) transition line across which a ferromagnetic phase occurs in a region of the (p, T) phase. In this region two magnetic phases (up and down) coexist assuming Ising symmetry. Does this signal a breakdown of the Gibbs phase rule ? No ! One must enlarge the phase diagram to include the symmetry-breaking field H. So the Gibbs phase rule is valid only when all the thermodynamic fields are included.

nonsense: *the saturation vapor pressure, also known as equilibrium vapor pressure, is an upper limit of the quantity of vapor that the atmosphere can hold*

1.2 van der Waals Equation

An approximate equation of state derived by Johannes van der Waals in his Leiden thesis of 1873 provides us with considerable insight into the liquid -gas phase transition. Physical interpretation of the van der Waals equation: historically, van der Waals suggested his equatio of state on the basis of experimental results for the equation of state of various gases, toward the end of the nineteenth century. At that time the microscopic interactions between gas particles were not known, and van der Waals postulated the necessity of an attractive interaction between gas atoms based on the observed decreases in pressure. It was only later on that such interactions were observed directly, and then attributed to the induced dipole-dipole forces by London.

The equation for the pressure p and the volume per mole as v with $V = \nu \mathsf{v} = Nv/N_A$ where N_A is the Avogadro number is given by

$$\left(p + \frac{\tilde{a}}{\mathsf{v}^2}\right)(\mathsf{v} - \tilde{b}) = RT \tag{3}$$

where the gas constant $R = N_A k_B$. Note that $\tilde{a}$ is intensive and has units of $J \cdot m^3$ and $\tilde{b}$ is also intensive and has units m^3.

It is also common to write the equation the volume per particle $v \equiv \frac{V}{N}$ and write van der Waals equation in the form

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T\,. \tag{4}$$

This is essentially the form in the text. The logic is explained in K&K. Briefly the effective volume per particle is reduced from v by an excluded volume, a microscopic volume denoted by b. From our perspective this is the effect of Coulomb repulsion and the Pauli exclusion principle that provide a spherical hard core to a simple atom like Argon or Xenon. In addition, van der Waals postulated an attractive interaction that reduced the pressure from $\frac{k_B T}{(v-b)}$ by $a\,n^2$ where as usual $n \equiv \frac{1}{v}$. The attractive interaction between atoms at distances beyond the inner repulsive core can be obtained using quantum mechanics from a second-order time-independent perturbation theory calculation. It has a $-\frac{1}{R^6}$ decay where R is the distance between the nuclei for spherically symmetric atoms; the calculation is usually performed for two hydrogen atoms in their ground state. The contribution to the pressure may be viewed as follows: a gas molecule far from the walls has equal densities of atoms in all directions. The atoms that are close to the wall and traveling toward the hard wall (it is the collision and the consequent momentum transfer that yields a force) have atoms only on one side and their attraction reduces the speed and hence, the pressure exerted on the wall is decreased. On the average (this is the mean-field assumption neglecting fluctuations in densities) the interaction depends on the product of the number densities.

This approximate equation of state was derived by Johannes van der Waals in his Leiden thesis of 1873 and provides us with considerable insight into the liquid -gas phase transition.

We first note that this yields a *cubic* equation for v:

$$pv^3 - (k_B T + bp)v^2 + av - ab = 0\,. \tag{5}$$

This means that if we try to draw an isotherm (*i.e.,* fix T) in the $p - v$ plane it is possible to find three values of v for a given p because there could be three real roots, values of v. One can argue that at high temperatures there is a unique v *i.e.,* there is a unique phase but as the temperature is lowered below the critical temperature T_c the isotherms develop a 'wiggle' (to use a technical term). (See Figure on the next page)

From our description of the phenomenology we would like *two* solutions corresponding to the liquid and gas phases at a given $T < T_c$ and p but we also expect the isotherm to have a constant pressure in the coexistence region. However, we find three solutions and what is worse, there is a region where $(\partial v/\partial p) > 0$ which leads to a negative compressibility. If you look at the graph, when you increase the pressure the volume increases. This is thermodynamically unstable. Can you make this explicit. This breakdown of van der Waals' theory was given an *ad hoc* fix by James Clerk Maxwell called the Maxwell equal-area construction.

We replace the wiggly part of the isotherm by a horizontal line at a fixed pressure; but for a given isotherm where does one draw it ? Maxwell's simple prescription is to draw it such that the areas A_1 and A_2 between the constant pressure line and the isotherm are equal (See Figure above) This makes the molar Gibbs free energy the same for the two phases at L and G in the Figure. We establish this below. Denote the fixed pressure by p^*. Since the chemical potentials are equal and we know that

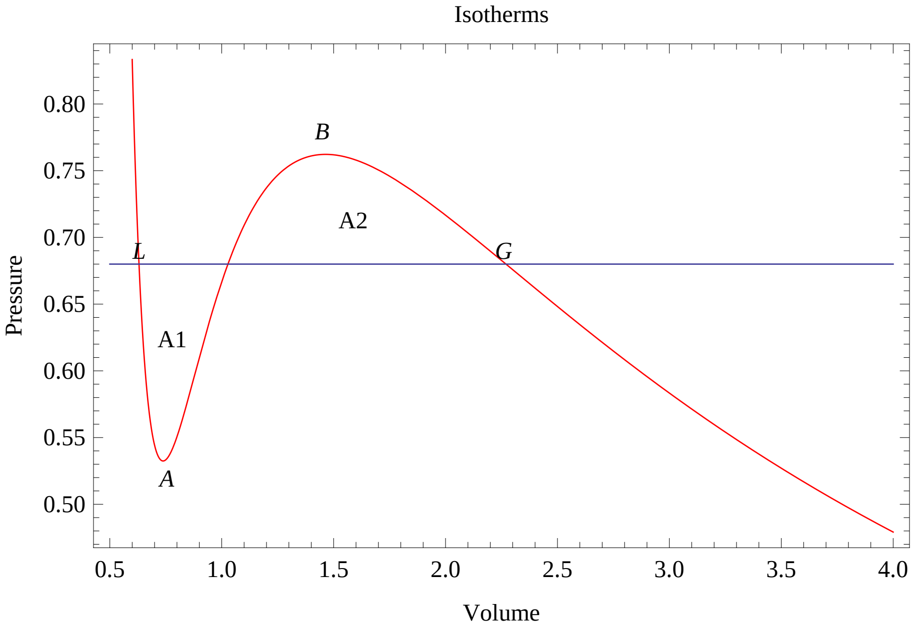

Figure 3: The isotherm at $\frac{T}{T_c} = \frac{11}{12}$. Between A and B the compressibility is negative. The horizontal line is chosen using Maxwell's construction. As an aside we point out uch lower temperatures lead to negative pressures.

$v = \left(\frac{\partial\mu}{\partial p}\right)_T$ we have

$$\int_L^G d\mu = \int_L^G dp\, v = \int_L^G \left[d(pv) - p\, dv\right] . \tag{6}$$

The first term yields $\mu_G - \mu_L$ which vanishes at coexistence. The last expression has two terms; the first term yields $(pv)_L - (pv)_G$ and we have

$$p^* v_L - p^* v_G - \int_L^G p(v)\, dv = 0 . \tag{7}$$

The first term is the area under the horizontal line between v_L and v_G. The second term is the area under the isotherm. Since these are equal the areas A_1 and A_2 must be the same as stated.

Thus Maxwell's construction yields the correct constant pressure term for any isotherm below T_c (i.e., there are wiggles) by the equal area construction. The extreme intersections of this horizontal with the isotherm yield the values of the coexisting volumes. The constant pressure corresponds to the tie lines drawn in the phenomenological description of phase coexistence.

So the approximate equation of van der Waals and Maxwell's construction yield a description of the liquid-gas phase transition. It is certainly not a rigorous or a logically complete picture but is still an important ingredient in our understanding of first-order transitions.

1.2.1 The critical point in van der Waals theory

We now proceed to examine the critical point in a bit more detail. The point at which the three roots coalesce into one corresponds to the critical point. The isotherm that corresponds to the critical point is characterized by a horizontal tangent and is in fact an 'inflection point' . Therefore, at the critical point the following conditions are satisfied:[2]

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0. \tag{8}$$

Denote the critical point values of the volume per particle, temperature, and pressure by v_c, T_c and p_c respectively. They can be obtained by solving the above equations explicitly. Since

$$p = \frac{k_B T}{(v-b)} - \frac{a}{v^2} \tag{9}$$

the two conditions yield

$$\frac{k_B T_c}{(v_c-b)^2} = \frac{2a}{v_c^3} \tag{10}$$

$$\frac{2k_B T_c}{(v_c-b)^3} = \frac{6a}{v_c^4} \tag{11}$$

Dividing one equation by the other we have $(v_c - b) = 2v_c/3$; solving for the critical volume per particle we obtain $\boxed{v_c = 3b}$. The critical temperature is obtained from Equation (10)) as $\boxed{k_B T_c = 8a/27b}$. The critical pressure can now be obtained from the equation of state: $\boxed{p_c = a/27b^2}$.

It is convenient to define scaled variables $\hat{p} = p/p_c$, $\hat{t} = T/T_c$, and $\hat{v} = v/v_c$. We now re-write the van der Waals equation of state in terms of the scaled variables:

$$\left(\hat{p} + \frac{3}{\hat{v}^2}\right)\left(\hat{v} - \frac{1}{3}\right) = \frac{8\hat{t}}{3}. \tag{12}$$

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[2] At the critical point van der Waals equation can be written as $p\,(v - v_c)^3 = 0$ since all three roots coincide and we can use this to obtain the same results.

This is an amazing result ! The equation states that if the pressure, temperature, and molar volume are re-expressed in units of the critical values p_c, T_c, and v_c respectively, the equation of state is the *same* for all substances. Note that only constants appear in the above equation. This is referred to as *the law of corresponding states.* This is the notion of *universality.* Even though the van der Waals equation is not obeyed by all substances this notion of universality has survived in the modern description of the behavior near the critical point. See handout of the data for a variety of materials near the liquid-gas critical point.

The fact that the critical isotherm is horizontal in the $p-v$ diagram means that the isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial p)$ is infinite. Now we will investigate how the isothermal compressibility diverges as one approaches the critical point along the critical isochore, *i.e.,* at $v = v_c = 3b$. Using

$$\frac{\partial p}{\partial v} = \frac{2a}{v^3} - \frac{RT}{(v-b)^2} \tag{13}$$

we have

$$\frac{1}{\kappa_T} = -\frac{2a}{v^2} + \frac{RTv}{(v-b)^2}. \tag{14}$$

Now let $v = 3b$ and study how $\kappa_T \to \infty$ as $T \to T_c$.

$$\begin{aligned} \frac{1}{\kappa_T} &= -\frac{2a}{9b^2} + \frac{3RT}{4b} && (15) \\ &= \frac{3b}{4}(RT - \frac{8a}{27b^2} && (16) \\ &\propto (T - T_c) && (17) \end{aligned}$$

where we have used Eq. (13). This allows us to introduce the first of a menagerie of "critical exponents" that are used to describe the non-analyticity (*e.g.,* divergence) of different physical quantities as one approaches a critical point. You do not have to remember which one is which but appreciate the fact that they exist! Define the critical exponent γ by

$$\kappa_T \propto \left(\frac{T - T_c}{T_c}\right)^{-\gamma}. \tag{18}$$

From the preceding analysis of the compressibility in the van der Waals theory we have shown that $\gamma = 1$. We will compare this behavior with the divergence of the susceptibility near a critical point in a ferromagnet.

One can show that the jump in the density of the specific volume vanishes as $(-t)^{\beta}$ with the mean-field value of $\beta = 1/2$ as we approach the critical point along the coexiatence curve. This is easier to derive for a ferromagnet.

Discuss the specific heat.

The free energy of the fluid within the van der Waals approximation is derived formally in the Appendix at the end. A more heuristic discussion is in the text. See Equation 38 on page 288.

$$F(T, V, N) \,=\, -N\,k_B T\,\left[-\log(e\,\lambda_T^3) \,+\, \log\left(\frac{V}{N} \,-\, b\right) \,+\, \beta\,a\frac{N}{V}\right] \tag{19}$$

where $b \equiv \Omega/2$ (Ω is the volume of the hard core) and $a = u_0\,\Omega_1/2$ where u_0 is the magnitude of the attractive potential and Ω_1 is the volume over which the attractive interaction acts.

Curie-Weiss molecular field theory Consider magnetic moments for the case[3] when the angular momentum $J = \frac{1}{2}$. Let $\mu_m = g\mu_B\, J$ be the magnitude of the magnetic moment and g is the Landé g-factor. If you do not know this it does not matter for this course; all we need is the magnitude of the moment. For $J = 1/2$ and $g = 2$ we have $\mu_m = \mu_B$. As an aside we recall that the magnetic moment points opposite to the spin direction for electrons. Clearly, the magnetic moment assumes values $\pm\mu_m$ and so we introduce an Ising spin $\sigma = \pm 1$ as a discrete degree of freedom that we have to sum over. There is an interaction between pairs of spins that are situated on the sites of a regular lattice and we will deal mostly with near-neighbor pairs. The interaction of two spins can be written as $\mathscr{H} = -A\,\mu_m^2\,\sigma_i\sigma_j \equiv -J\,\sigma_i\sigma_j$ where σ's assume values ± 1. Recall that J (units of energy) arises from Heisenberg exchange typically.[4] *We have used J both for the angular momentum and the exchange interaction (not my fault) but we will rarely go back to the quantum mechanics of angular momentum and so J will be the spin-spin interaction energy.* The magnetic field interaction is $-\mu_m\, H\,\sigma_i$. The real problem is to evaluate

$$Z = \sum_{\{\sigma_i = \pm 1\}} e^{-\beta\mathscr{H}} \quad \text{where} \quad \mathscr{H} = -J\sum_{<ij>} \sigma_i\sigma_j - \mu_m H \sum_i \sigma_i \tag{20}$$

where the sum on i is over all the sites of say a square or cubic lattice in the thermodynamic limit and the sum on $< ij >$ is a sum over all near-neighbor pairs. This is a fomidable problem and we follow the mean-field route first.

Focus on the part of the Hamiltonian that involves a given spin σ_i.

$$\mathscr{H}_i = -J\,\sigma_i \sum_{j\in NN} \sigma_j - \mu_m H\sigma_i \tag{21}$$

where the sum is over all the near neighbors (NN) of the spin i. We will denote the number of neighbors (called the coordination number sometimes) by z; note that $z = 6$ for a cubic lattice. One can interpret the energy as that of a dimensionless spin σ_i in an effective field $H_{eff} = J\sum_{j\in NN}\sigma_j + \mu_m H$ with dimensions of energy. The effective field is fluctuating in the sense that its value is different in different configurations of the neighboring spins. The idea of mean-field theory for a ferromagnet is

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[3] One can get only two states even for higher angular momentum J when there is uniaxial anisotropy, for example, a term like $-\alpha\, J_z^2$ in the Hamiltonian where $\alpha > 0$. (How can such a term arise in the quantum theory of atoms?) Then states with $J_z = \pm J$ have the lowest energy.

[4] For those who will work on magnetism there are other interactions such as super-exchange or double exchange.

to replace the value of the fluctuating spin σ_j by its (statistical mechanical) average value $\langle\sigma_j\rangle \rightarrow m$ assumed to be uniform.[5] Thus we have

$$\mathscr{H}_i = -[z\,J\,m + \mu_m H]\,\sigma_i\,. \tag{22}$$

We can evaluate the partition function and expectation value of σ_i for a single spin easily. We find

$$\langle\sigma_i\rangle = \tanh\left[\beta(zJm + \mu_m H)\right]\,. \tag{23}$$

We now let $\langle\sigma_i\rangle \rightarrow m$ since the mean value is the same at all sites. This is imposing self-consistency, in that we obtain the same uniform magnetization at site i due to the magnetization on the near neighbors. Observe that we have obtained the equation of state of a ferromagnet within mean-field theory,

$$m = \tanh\left[\beta(zJm + \mu_m H)\right]\,. \tag{24}$$

This is the analog of the van der Waals equation for a fluid.

Now the analysis consists in finding the solutions of $\boxed{m = \tanh(\beta z\,J\,m)}$ **in zero field**. Plot the left-hand side and the right-hand side on the same graph and note that the slope at $m = 0$ is 1 and $\frac{zJ}{k_B T}$ respectively. Clearly, one finds a single solution ($m = 0$) for $k_B T \geq zJ$ and three solutions for $T < \frac{zJ}{k_B} \equiv T_c$. We have determined the critical temperature and find non-zero values of m below the Curie or critical temperature. For T near T_c we have since m is small

$$\frac{zJ}{k_B T}\,m = \tanh^{-1} m \approx m + \frac{m^3}{3} \tag{25}$$

and the solutions are either $m = 0$ or $m = \pm\sqrt{3\left(\frac{T_c}{T} - 1\right)}$. We will show later that the $m = 0$ solution is unstable below the Curie temperature. Note that zero-field equation of state (set $H = 0$ in Equation (23)) is symmetric under the (global) transformation $m \rightarrow -m$ as is the Hamiltonian under $\sigma_i \rightarrow -\sigma_i$. The solution for $T < T_c$ spontaneously breaks the symmetry.

We also see that $\boxed{m \sim (-t)^\beta}$ where $t \equiv \frac{T - T_c}{T_c} << 1$ and the exponent $\beta = \frac{1}{2}$ within mean-field theory. If we do not set $H = 0$ we have $m(T, H)$ that allows us to find the susceptibility.

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[5] Although we use the notation m the average moment is actually $\mu_m\,m$.

Appendix: *A crude derivation based on statistical mechanics*[6]

The partition function for a classical gas of N atoms interacting via a potential $\mathscr{V}(\vec{r})$ is given by

$$Z_N(T,\,V) \;=\; \frac{1}{N!}\prod_{i=1}^{N}\left(\int d^3r_i\int d^3p_i\right)\,e^{-\beta\sum_j\frac{\vec{p}_j\cdot\vec{p}_j}{2m}}\,e^{-\beta\sum_{i<j}\mathscr{V}(\vec{r}_i-\vec{r}_j)}\,. \tag{26}$$

The momentum integral is simple and yields $1/\lambda_T^{3N}$ as in the case of an ideal gas. Please refresh your memory. The coordinate integral can only be evaluated approximately. Divide the potential energy into two parts and do them separately. Imagine

$$\mathscr{V}(r) = \begin{cases}\infty & \text{for } r\,\le\,R_1;\\ -u_0 & \text{if } R_1\,< r\,\le\,R_2;\\ 0 & \text{if } r\,>\,R_2.\end{cases} \tag{27}$$

This is *not* a systematic approximation[7] and can be written as follows:

$$Z_N(T,\,V) \;=\; \frac{1}{N!}\,\frac{1}{\lambda_T^3}\,e^{-\beta\overline{U}}\prod_{j=1}^{N}\left(V\,-\,(j-1)\,\Omega\right) \tag{28}$$

The repulsive part can be thought of as being an infinitely repulsive sphere of volume $\Omega\,=\,\frac{4\pi}{3}\,R_1^3$ and the last term represents this excluded volume. The attractive part is approximated by $\overline{U}$ as an averaged attractive potential energy. This can be done as follows:

$$\begin{aligned}\overline{U} \;&=\; \frac{1}{2}\sum_{i\neq j}\mathscr{V}(\vec{r}_i-\vec{r}_j)\;\to\;\frac{1}{2}\int d^3r\int d^3r'\,n(\vec{r})\,n(\vec{r}\,')\,\mathscr{V}(\vec{r}-\vec{r}\,')\\ &\approx\;\frac{n^2}{2}\,V\int d^3r\,\mathscr{V}(\vec{r})\;=\;-\frac{n^2}{2}\,V\,u_0\,\Omega_1\;=\;-\frac{N^2}{2V}\,\Omega_1\,u_0\end{aligned} \tag{29}$$

where $u_0\,>\,0$ is the magnitude of the attractive part of the potential energy. The integral is replaced by the value of the potential times the volume over which it acts denoted by Ω_1.

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[6] This was not done in class; if you want to be a theorist you should look through it.

[7] In principle, one can do a Virial expansion but we will not do this. Many textbooks can guide you through this

The product can be simplified as follows for low density (i.e., $N\Omega << V$) by considering its logarithm:

$$\sum_{j=1}^{N}\left[\log V + \log\left(1 - \frac{(j-1)\Omega}{V}\right)\right] \approx N\log V - \frac{\Omega}{V}\sum_{j=1}^{N}(j-1) \approx N\log V - \frac{N^2\Omega}{2V}. \tag{30}$$

Re-exponentiating we have[8]

$$V^N e^{-N\frac{N\Omega}{2V}} \approx V^N\left(1 - \frac{N\Omega_1}{2V}\right)^N = \left(V - \frac{N\Omega}{2}\right)^N. \tag{31}$$

So the free energy is given by

$$F(T,V,N) = -k_BT\left[-\log(N!\lambda_T^3) + N\log\left(V - \frac{N\Omega}{2}\right) + \beta u_0\Omega_1\frac{N^2}{2V}\right] \tag{32}$$

We simplify this using Stirling-de Moivre's formula and write

$$F(T,V,N) = -N\,k_BT\left[-\log(e\,\lambda_T^3) + \log\left(\frac{V}{N} - \frac{\Omega}{2}\right) + \beta u_0\Omega_1\frac{N}{2V}\right] \tag{33}$$

Please compare this with the expression in K&K. So we have using $p = -(\partial F/\partial V)_{N,T}$

$$p = \frac{Nk_BT}{V - \frac{N\Omega}{2}} - u_0\Omega\frac{N^2}{V^2} \tag{34}$$

and we obtain van der Waals equation.

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[8] It may be surprising that what is subtracted from V on the average is $N\Omega/2$ and *not* $N\Omega$.