A Phase Transition in Ammonium Chloride

CHM 335

TA: David Robinson

Email: Drobinson@chm.uri.edu

Office Hour: Wednesday, 11 am

Purpose

- Determine the critical exponent for the order to disorder transition in ammonium chloride.
- Learn about critical phenomena in phase transitions.

Phase Transitions

- Transition between solid, liquid, gas
    - i.e boiling of water
- Exhibit discontinuities across phase boundary, such as in the molar volume
- Phase transitions are classified by order
- This is a first order phase transition

Order of Phase Transitions: First Order

- Order can be determined by derivatives of the chemical potential. Two systems of the same chemical composition have the same chemical potential at equilibrium:

$$d\mu_\alpha = d\mu_\beta$$

- For a pure sample, the chemical potential is equal to the molar Gibbs free energy, shown as the total differential:

$$d\mu = -S_m dT + V_m dP$$

- Which implies:

$$-S_{m,\alpha} dT + V_{m,\alpha} dP = -S_{m,\beta} dT + V_{m,\beta} dP$$

- In many phase transitions, the molar entropy and molar volume are not equal for the different phases (the liquid and gas phases of boiling water have very different volumes). Instead, the molar entropy and molar volumes are calculated from the first derivative of the chemical potential:

$$S_m = (\frac{\partial \mu}{\partial T})_V$$

$$V_m = (\frac{\partial \mu}{\partial P})_T$$

- First order phase transitions are discontinuous in the first derivative of the chemical potential.

Order of Phase Transitions: Second Order

- A Phase transition which is continuous in the first derivative, but discontinuous in the second derivative is considered second order. The discontinuities are observed in the following thermodynamic properties:

$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial S_m}{\partial T}\right)_P = \frac{C_{m,P}}{T}$$

$$\left(\frac{\partial^2 \mu}{\partial P^2}\right)_T = \left(\frac{\partial V_m}{\partial P}\right)_T = -V_m \kappa$$

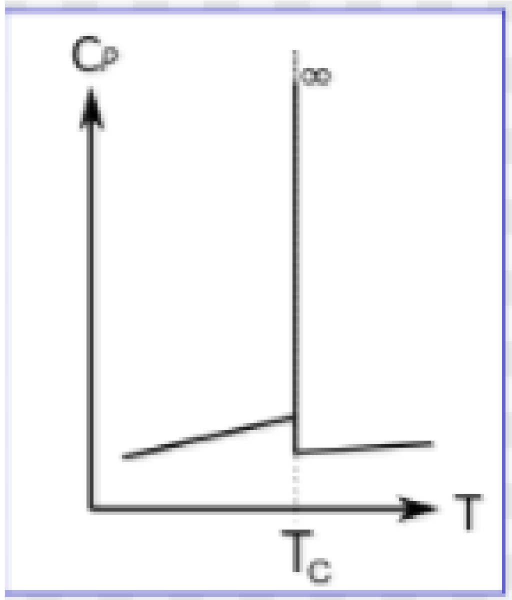
- Where κ is the isothermal compressibility

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial \mu}{\partial P}\right)_T\right)_P = \left(\frac{\partial V_m}{\partial T}\right)_P = V_m \beta_V$$

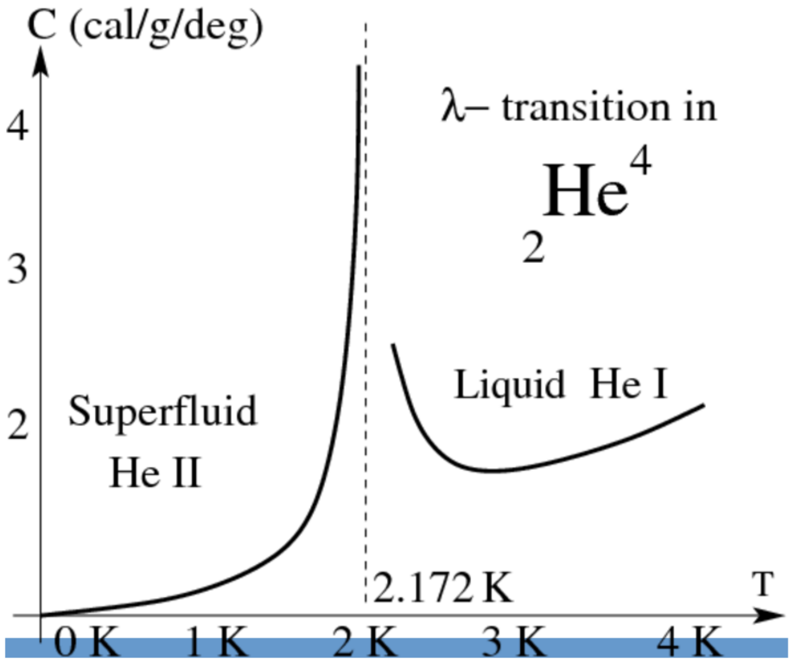
- Where β_V is the isobaric coefficient of thermal expansion.
- An example of second order phase transition may be the transition from normal to superconducting state of metals in the absence of a magnetic field. Such a transition shows continuity in density and latent heat, but has discontinuities in the heat capacity, isothermal compressibility, and isobaric coefficient of thermal expansion.

Order of Phase Transitions: Lambda Transitions

- Lambda transitions are neither first nor second order
- Lambda transitions exhibit continuous behavior while approaching from either side of a singularity
- Observed in many order to disorder transitions, as well as fluid behavior at critical points
- We will observe the order to disorder transition in ammonium chloride, an example of a lambda transition



https://commons.wikimedia.org/wiki/File:Phase_transition_first_and_second_order_de.svg



https://inspirehep.net/record/1283384/plots

The Van der Waals Fluid

- **Thermodynamic properties of fluids at *critical points* match the behavior of systems undergoing order-disorder transitions.* We will use the Van der Waals fluid to model behavior of transitions near critical points.**
- Approximate expansion upon the ideal gas law, which is only applicable to low pressures. The Van der Waals equation of state covers a wide breadth of pressures, and is therefore applicable to liquids.

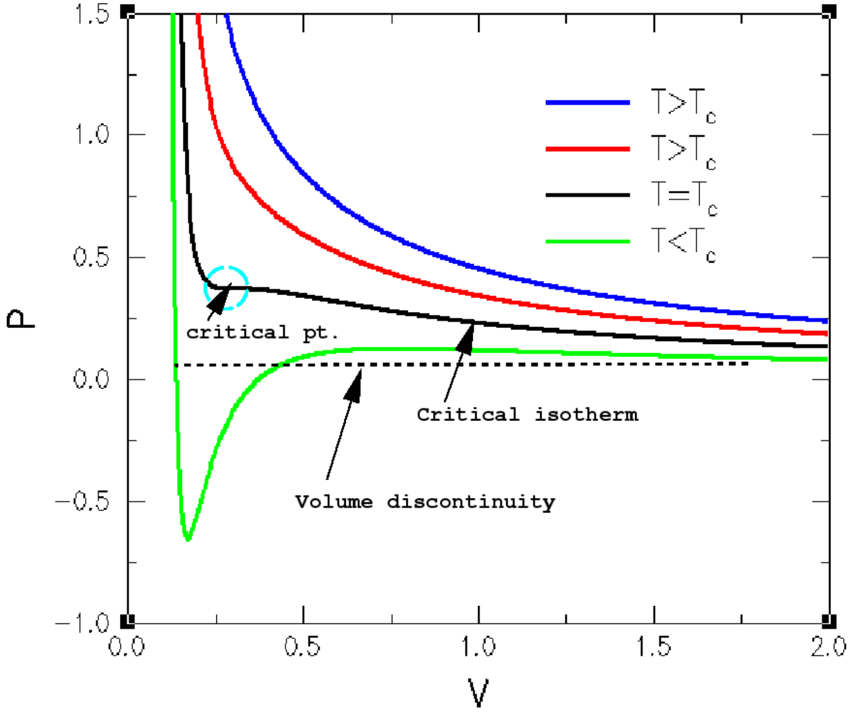
$$P = \frac{RT}{V_m - b} - \frac{a}{{V_m}^2}$$

- This includes parameters for intermolecular forces between atoms or molecules, a, and volume occupied by the atoms or molecules, b.

- Here is shown a set of Van der Waals Isotherms. In the lowest isotherm can be seen two regions, one highly compressible (gas) and one highly incompressible (liquid). Between the two phases is an impossible region. Why is this impossible?
- To remove this impossibility, the loop region in the Van der Waals isotherm is typically replaced by a horizontal line described by the Maxwell construction:

$$\Delta G_{m,vap} = \int_{V_{m,l}}^{V_{m,g}} dG = \int_{V_{m,l}}^{V_{m,g}} V_m dP$$

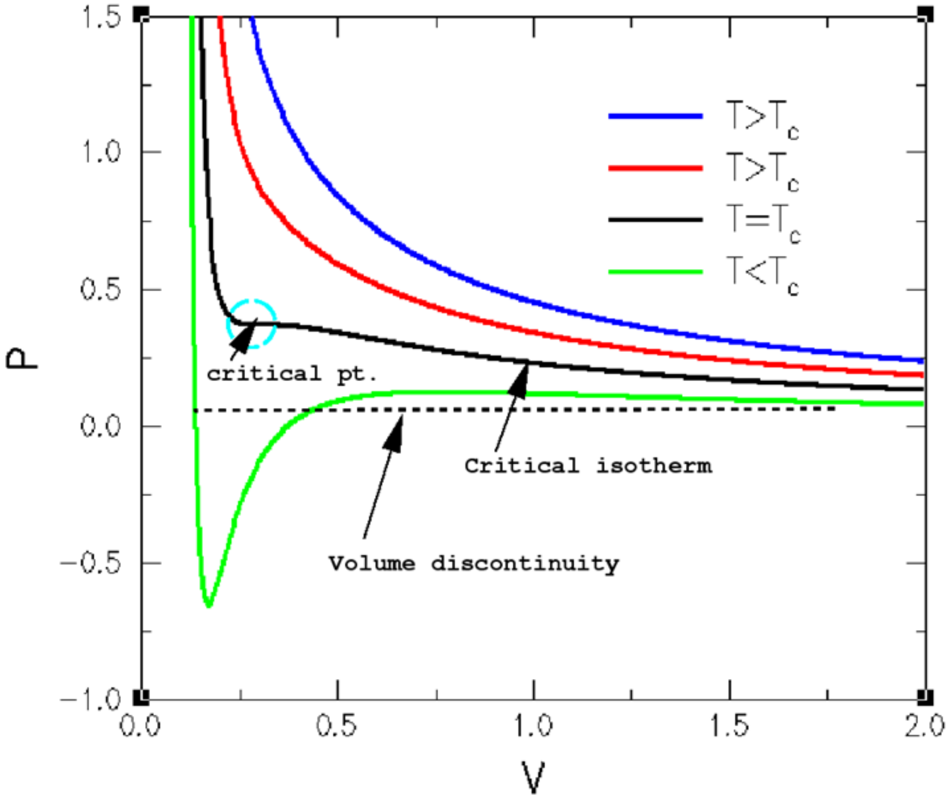
- that will be derived and described with integration by parts in your report.

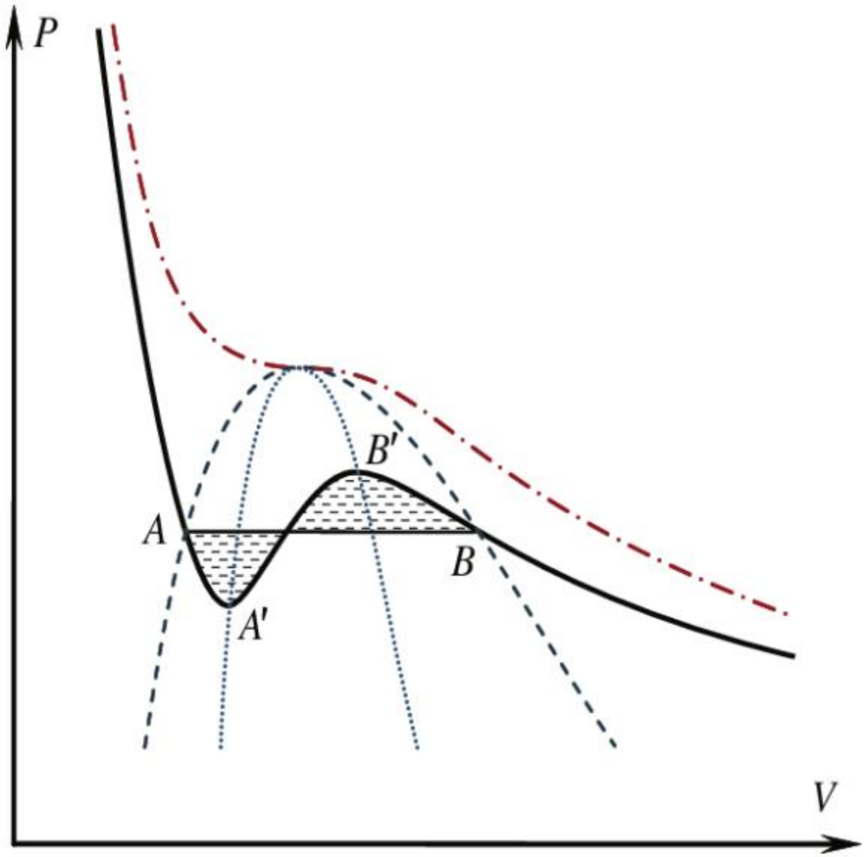


http://www.nyu.edu/classes/tuckerman/stat.mechII/lectures/lecture_8/node3.html

The Van der Waals Fluid

- The new isotherm more accurately describes real fluids. The unphysical loop regions are removed and replaced by the horizontal line in the figure. What does the horizontal line represent?
- The loop region disappears at a certain critical temperature (T_C), where the maximum and minimum of the loop regions coalesce into a single point.
- At the critical temperature, $\Delta V_{m,vap} = 0$.





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Critical Constants

- At the critical point of the critical isotherm for the Van der Waals fluid the upper and lower loop regions disappear, along with the horizontal line from the Maxwell construction, forming a point called the critical point.
- This point is a *point of inflection,* satisfied by the criterion:

$$(\frac{\partial P}{\partial V_m})_{Tc} = (\frac{\partial^2 P}{\partial V^2})_{Tc} = 0$$

- Therefore the second derivative of the Van der Waals equation of state yields three values, called critical constants:

$$V_c = 3b \qquad T_c = \frac{8a}{27Rb} \qquad P_c = \frac{a}{27b^2}$$

- These critical constants will be derived in your reports.

Derivation of a Power Law

- At the critical point, it is evident that an infinitesimal change in volume will not result in a pressure change:

$$(\frac{\partial P}{\partial V_m})_T = 0 \; at\ the\ critical\ point$$

- This implies that the isothermal compressibility diverges at the critical point:

$$\lim_{T \to T_C} \kappa = \lim_{T \to T_C} \left[-\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T \right] = \infty$$

- κ approaches infinity along the critical isochore (the plot of the behavior of a material at a certain constant critical volume), having behavior of the following "power law":

$$\lim_{T \to T_C} \kappa = A|T - T_C|^{-\gamma} \qquad (\gamma = 1)$$

- This power law is derived in the syllabus.

C_P Along the Critical Isochore

- Similar to that of κ, a power law can be derived for C_P along a critical isochore.
- The constant pressure heat capacity follows a similar power law to that of κ for the Van der Waals fluid:

$$\lim_{T\to T_C} C_P = B|T-T_C|^{-\gamma'}$$

- which will be derived in your report.
- In this case $\gamma' = 1$
- Note that the behavior of C_P as T approaches T_C is proportional to the behavior of κ as T approaches T_C, containing the same temperature dependence and critical exponent.

The Critical Exponent

- A power law is a description of a property that is dependent on another property raised to a power.
- Both the isothermal compressibility and constant pressure heat capacity depend on $|T - T_C|$ and are raised to the same critical exponent gamma.
- The critical exponent describes the divergence of a property as it approaches a critical point.
- Real fluids are not accurately described by the Van der Waals equation of state (or for that matter, the critical values which are extracted, as in the case of C_P). The critical exponent for κ and C_P along the critical isochore of real fluids have both been experimentally determined to be 1.23 – 1.25.
- The critical exponents for many diverging properties at critical points are identical. Those properties with identical critical exponents are said to belong to a universality class.
- Belonging to the same universality class as κ and C_P for real fluids along critical isochores is the order to disorder transition which we will observe in ammonium chloride.

Measuring Critical Exponents

- The accurate measurement of critical exponents has proven to be an exceedingly difficult task.
- Measurement of phenomena which result in singularities often have a non-singular background contribution.
- Typically in an experiment, both the critical value and the critical exponent are measured simultaneously, adding complexity to the experiment.
- *Critical slowing down* occurs as a variable approaches the critical value. The time necessary to equilibrate the system increases as $A - A_C$ approaches zero.
- For these reasons, do not be disheartened if your measured critical exponent is not exactly (or near) 1.23 – 1.25. Any value between 0.1 and 2 will be acceptable.

The Order to Disorder Transition in Ammonium Chloride

- The ammonium chloride lattice consists of an ammonium ion surrounded by eight chloride ions at the vertices of a cube. Close by ammonium ions also sit at the vertices of a cube, with a chloride ion at the center, forming a simple cubic structure.
- In the lowest energy state (0 K), each ammonium ion is oriented with each of the four hydrogen atoms directed at a chloride ion. The ammonium ions also interact with each other such that the lowest energy state has all ammonium ions oriented the same way. In this way, any place in the crystal lattice looks identical.
- At non-zero temperatures, thermal fluctuations can “flip” some of the ammonium ions. The hydrogen atoms of these flipped ammonium ions then point at a different set of chloride ions.
- As temperature increases, so does the number of flipped ammonium ions. At the critical temperature there is an equal number in both orientations. Above this temperature, orientations are random.
- We will observe this transition from order to disorder in ammonium chloride using a differential scanning calorimeter (DSC)

Procedure

- With gloved hands (for the whole procedure), use the tweezers to obtain a sample pan and place it on the balance.
- Tare the balance.
- Remove the sample pan from the balance with the tweezers and carefully place a few crystals of ammonium chloride into the pan.
- Place the pan back on the balance and record the mass. Use the mass and amount of crystals added to the pan to estimate 5 – 10 mg and add it to the pan.
- Place the pan back on the balance, record the mass, and move the pan to a stable surface.
- Use the tweezers to obtain a cover for the sample pan, and carefully place it on top of the pan.
- Transfer the pan to the crimping device, and crimp the pan as explained by your TA.
- If a blank is needed, crimp an empty pan (remember which is which!).
- At the DSC, remove the cover to the sample chamber. Carefully round cover with a gloved hand. Underneath there is another cover to be removed using the tweezers.
- Carefully place the blank on the left well, and the sample on the right well.
- Place the covers back on the instrument.
- Remove your gloves, open the DSC software, and follow your TA's instructions for generating an appropriate method file.
- Start the experiment, being sure to save your data file in an appropriate location.

Calculations

- Locate the peak in power. The corresponding temperature is your critical temperature (T_C). You can consider the power as C_P.
- Use the spreadsheet to convert the temperature to K. If you are unsure how to use spreadsheets to do lots on calculations unbelievably quickly, see your TA.
- Use the spreadsheet to calculate $\ln|T-T_C|$ for 20 datapoints above and below the critical temperature.
- Use the spreadsheet to calculate $\ln|C_P|$ for those same data points.
- Plot $\ln|C_P|$ as a function of $\ln|T-T_C|$ for the data points above the critical temperature. Adjust the included data points to resemble something linear, with as many data points as possible.
- Fit a trend line and determine the slope (your critical exponent) using the spread sheet.
- Repeat this process with the data points below the critical temperature.

Notes

- Since we are using google sheets, it will be easy to share your spreadsheets with me. Be sure to move your spreadsheets into a shared folder which I will create.
- If you have never used spread sheets, or are uncomfortable with them, please see your TA. This is a valuable tool that you should learn, as you will undoubtedly use them in the future.
- There is no error analysis for this lab, so be sure to understand concepts exceptionally well, since the majority of the points will be in the theory section.
- Used sample pans go into the solid waste container.
- Please be sure to show the equation of the trend line on the plot in your report.

Lab Report

- Cover page: Will contain a descriptive title, the date the lab was performed, and clearly differentiated writer and lab partners
- Abstract: Summarize the experiment: how you did it, and what you found. This should be a quick way for people to determine the general content of the paper. Write this last.
- Introduction: Will present background info. You may want to introduce phase transitions, working your way up to lambda transitions. This would also be a good time to introduce order to disorder transitions and the Van der Waals fluid.
- Theory: Detail the concepts of critical points using the Van der Waals fluid. Also you will be required to derive the equations 98, 99, and 118, as they appear in the syllabus. Be sure to give extra attention to this section.
- Procedure: Include a copy of your procedure, with my signature.
- Data: Provide a copy of your data, with my signature.
- Calculations: This will be your spread sheet and associate plot. Be sure the plot has a title, and axes are labeled.
- Discussion: Present your results and interpret them. Questions to think about are "do the critical exponents on either side of T_C match? What does this tell you about the accuracy of this experiment? How close are the experimental γ's to the literature values? "