

Wed. 1/28 Fri. 1/30	3.3 Entropy and Paramagnetism 3.4-6 Mechanical and Diffusive Equilibrium	HW9: 18,20,24,25 (except f) HW10: 32, 36, 37	
Mon. 2/2 Wed. 2/4 Fri. 2/6	Review Exam 1 (C 12.0-12.2.5) 4.1-2 Engines & Fridges	HW11: 1,10,15	HW 8,9,10

3.1 Entropy and Heat

3.1.1 Predicting Heat Capacities

- Recall the definition of the heat capacity: $C_V = \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T} \right)_{V,N}$ the latter says, if you don't do work (change volume, and you're not doing other types of work either) or change the particle count, then a heat flow equates a change in internal energy. That just follows from the First Law of Thermodynamics (change in internal energy equals heat flow in and work done on).
 - Why bother?** Heat Capacities are of practical use because you can often determine experimentally: measure both the energy that's transferred into the system (perhaps by knowing the energy leaving another system to go into it), and the system's temperature. So, this is a handy touch-point between theory and experiment.

- Einstein Solid**

- High T, q >> N**

- $C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \left(\frac{\partial NkT}{\partial T} \right)_{V,N} = N_{osc}k = 3N_{atom}k$ in accordance

with the equipartition theorem: energy is equally distributed between the two degrees of freedom (potential and kinetic of vibration) for each oscillator.

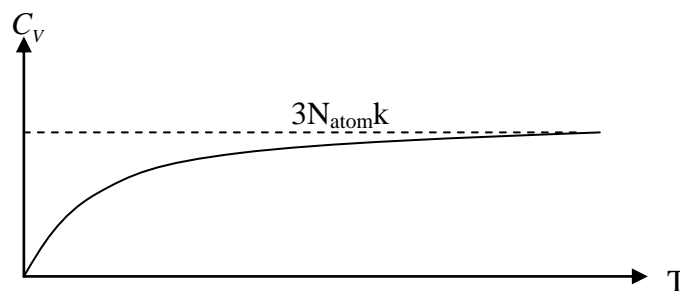
- Low T, q << N**

Problem 3.8 Starting with the energy that we'd found for this, $U = N_{osc} \epsilon e^{-\frac{\epsilon}{kT}}$, find the expression for the heat capacity.

- $C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \left(\frac{\partial}{\partial T} N \epsilon e^{-\frac{\epsilon}{kT}} \right)_{V,N} = N \epsilon e^{-\frac{\epsilon}{kT}} \left(\frac{\partial}{\partial T} \left(-\frac{\epsilon}{kT} \right) \right)_{V,N} = N \epsilon \frac{\epsilon}{kT^2} e^{-\frac{\epsilon}{kT}}$

- $C_V = 3N_{atom}k \left(\frac{\epsilon}{kT} \right)^2 e^{-\frac{\epsilon}{kT}}$

using $\frac{d}{dx} e^{f(x)} = e^{f(x)} \frac{d}{dx} f(x)$



To see that this function does indeed go to 0 as T goes to 0, look at it as follows:

$$C_v = 3N_{\text{atm}} k \left(\frac{\epsilon}{kT} \right)^2 e^{-\frac{\epsilon}{kT}} = 3N_{\text{atm}} k \frac{1}{\left(\frac{kT}{\epsilon} \right)^2 e^{\frac{\epsilon}{kT}}}$$

Then we need the denominator to go to

infinity as T goes to 0. Looking at the denominator and expanding the Taylor series of the exponential we can see

$$\left(\frac{kT}{\epsilon} \right)^2 e^{\frac{\epsilon}{kT}} = \left(\frac{kT}{\epsilon} \right)^2 \left(1 + \frac{\epsilon}{kT} + \frac{1}{2} \left(\frac{\epsilon}{kT} \right)^2 + \frac{1}{3!} \left(\frac{\epsilon}{kT} \right)^3 + \dots \right) = \left(\left(\frac{kT}{\epsilon} \right)^2 + \frac{kT}{\epsilon} + \frac{1}{2} + \frac{1}{3!} \left(\frac{\epsilon}{kT} \right) + \dots \right)$$

in the limit that $T \rightarrow 0$, the first two terms vanish, the third term sticks around, the fourth term and all higher order terms blow up. So it's clear that $\lim_{T \rightarrow 0} \left(\frac{kT}{\epsilon} \right)^2 e^{\frac{\epsilon}{kT}} = \infty$ and

$$\text{so } \lim_{T \rightarrow 0} C_v = \lim_{T \rightarrow 0} 3N_{\text{atm}} k \frac{1}{\left(\frac{kT}{\epsilon} \right)^2 e^{\frac{\epsilon}{kT}}} = \frac{1}{\infty} = 0.$$

• **Recipe**

- Use quantum and combinatorics to find $\Omega(U, V, N, \dots)$
- $S = k \ln \Omega$
- $\frac{1}{T} = \frac{\partial S}{\partial U_{V, N, \dots}}$
- Solve for U and then $C_v = \frac{\partial U}{\partial T_{V, N, \dots}}$
- **Q:** Someone asked about the negative heat capacity of star clusters – how can that be *negative*?
 - It's the potential energy. Recall that specific heat is defined as $C = \frac{\partial Q}{\partial T}$ and $\Delta U = Q + W \Rightarrow Q = \Delta U - W$
 - Well, $\Delta U = \Delta K.E + \Delta P.E.$
 - So, $C = \frac{\partial K.E.}{\partial T} + \frac{\partial P.E.}{\partial T} + \frac{\partial W}{\partial T}$
 - Let's think about the first two terms in a gravitational system. As you might expect, the kinetic energy tends to increase with increased temperature; however, increasing an orbit's kinetic energy means decreasing its radius – decreasing the potential energy. So, the second term can be negative. In some situations, it can be negative enough to make C negative.
 - For more info: Google “heat capacity of star” and read “Gravitational Million-Body Problem”.

3.1.2 Measuring Entropies

- We went down the *theoretical* path and started from multiplicity, got to entropy, and from that got to temperature – energy relationship. *Experimentally*, information tends to move the other way – from measuring the temperature and energy changes, you can determine the entropy. Turning the definition of temperature around gives us
 - $dS = \frac{dU}{T}$ _{v,N,...}
 - of course, since we're holding V, N, ... constant, the only way the energy can change is through heating, Q.
 - $dS = \frac{Q}{T}$ This is often offered as the definition of entropy.
 - **Constant T.** In the case of a phase change, T is constant, so this form can be used directly (neglecting corresponding volume change).
 - Then again, under the constant volume condition, even if the temperature does change, $Q = C_v dT$
 - $dS = \frac{C_v dT}{T}$ _{v,N,...}
 - $\Delta S = \int_i^f \frac{C_v dT}{T}$ _{v,N,...} ← Used in Pr. 3.14
 - **Why bother?** Again, heat capacity is experimentally determinable.

- **H 21-2 Change in Entropy**
 - **Non-quasistatic processes.**
 - Halliday and Resnick point out that in practice, the system can change in non-quasistatic ways; for example, if you puncture a balloon and all the air leaks out, in the process, there's a pressure difference between at one end of the balloon and at the other, so you can't imagine it to have a single, well defined pressure at any given instant.
 - **State Variable to the rescue.**
 - However, it further points out that entropy is a state variable, that is, a change in entropy describes specifically the initial state of order and the final state of order. In this way it is similar to, say, gravitational potential energy of a rock, it reflects how high the rock is finally and how high it is initially. In both cases, the change in state properties ultimately only cares what the initial and final states are, *not the path between them*.
 - This means that, while in theory, the path taken between two states can be ugly, and not easily characterized in terms of thermodynamic variables, in practice, we don't care! We are free to integrate over *any* path between the two points. So we naturally

choose a quasi-static one, i.e. one over which the thermodynamic variables are well defined the whole way.

- **State Variable for Ideal Gas and non-constant volume.**
 - Without the statistical view of entropy, one can't in principle prove that it is a state variable, but with it, one can very easily appeal to the definition.
 - $dU = Q + W$
 - In an ideal gas, $dU = C_v dT$
 - (specifically, $C_v = f/2 Nk$, which is T independent)
 - If we're talking differentially small steps, and only mechanical work, then $W = -PdV$ so
 - $Q = C_v dT + PdV$ and
 - $$\Delta S = \int_i^f dS = \int_i^f \frac{Q}{T} = \int_i^f C_v \frac{dT}{T} + \int_i^f \frac{P}{T} dV = C_v \ln \frac{T_f}{T_i} + Nk \ln \frac{V_f}{V_i}$$

- **Third Law of Thermodynamics (I)**
 - This relation only gives you *differences* in entropy, not individual values. But the value at $T = 0$ is generally known.
 - At $T = 0$, all the particles are in the lowest possible state. There's only one way for that to be. $\Omega=1, S = k \ln(1) = 0$. This is the 3rd Law of Thermodynamics.



- **Residual Entropy**
 - It often takes energy to loose energy. For example, Think of a bolder perched on a cliff. It has lots of potential energy which it can't loose unless someone gives it a push, then it has kinetic energy which it can impart to other particles and ultimately have less energy. If a system is cooled on a time scale much shorter than the relaxation time, disorder can be *frozen-in*. In this way entropy is frozen in, so that lowest energy state is inaccessible and S isn't 0.
 - Think of a bowl of trail mix – big nuts and little m&m's all mixed up – lots of disorder, lots of entropy. But if I shake it gently (give it a little energy) the little m&m's will sink to the bottom. This reduces the disorder reduces the entropy. Note however, that it took energy input to achieve this lower state. Without that input, my bowl has some disorder "frozen in", i.e., it has some residual entropy.
 - Ex. The lowest energy state in a ferromagnet is all dipoles aligned. If you heat one up, many get unaligned, if you suddenly cool it, then they're stuck that way.
 - **Note:** Book comments that Eq'ns 3.15 and 3.16 for ideal gas and Einstein solid don't go to 0 as T goes to 0. For the Ideal Gas one, the poor behavior is no surprise, that model wasn't *intended* for use around $T = 0$, by which time almost all gasses condense into liquids or solids, and in any case, we have to think a little more quantum mechanically still. For the Einstein solid, the result they use comes form *assuming* $q \gg N$, but that's the wrong assumption for $T = 0$. The $q \ll N$ limit gives a much better result.

Questions on this



- **Third Law (II)**

- For $\Delta S = \int_i^f \frac{C_V dT}{T}$ V, N, \dots not to blow up at $T = 0$ (where we say S would ideally be 0), we need $\lim_{T \rightarrow 0} C_V = 0$. This is another statement of the Third Law. Note that this is satisfied by the example done above.

3.1.3 The Macroscopic View of Entropy

Ex. Like 10 (Halliday 21.9) In an experiment, 200 g of aluminum (with a specific heat of 900 J/kg K) at 100°C is mixed with 50.0 g of water at 20.0°C, with the mixture thermally isolated. (a) What is the equilibrium temperature? What are the entropy changes of (b) the aluminum, (c) the water, and (d) the aluminum-water system?

A)

$$Q_{Al \rightarrow W} + Q_{W \rightarrow Al} = 0$$

$$m_{Al} c_{Al} \Delta T_{Al} + m_W c_W \Delta T_W = 0$$

$$m_{Al} c_{Al} (T_f - T_{i,Al}) + m_W c_W (T_f - T_{i,W}) = 0$$

$$T_f = \frac{m_{Al} c_{Al} T_{i,Al} + m_W c_W T_{i,W}}{m_{Al} c_{Al} + m_W c_W} = \frac{0.200 \text{ kg} \cdot 900 \text{ J/kgK} \cdot 100^\circ\text{C} + 0.050 \text{ kg} \cdot 4186 \text{ J/kgK} \cdot 20.0^\circ\text{C}}{0.200 \text{ kg} \cdot 900 \text{ J/kgK} + 0.050 \text{ kg} \cdot 4186 \text{ J/kgK}}$$

$$= \frac{18,000 \text{ J/K} \cdot ^\circ\text{C} + 4186 \text{ J/K} \cdot ^\circ\text{C}}{389.3 \text{ J/K}} = 57.0^\circ\text{C}$$

B)

$$\Delta S_{Al} = \int_i^f \frac{C_{V,Al} dT}{T} = \int_i^f \frac{m_{Al} c_{Al} dT}{T} = m_{Al} c_{Al} \int_i^f \frac{dT}{T} = m_{Al} c_{Al} \ln \frac{T_f}{T_{i,Al}}$$

C)

$$\Delta S_W = \int_i^f \frac{C_{V,W} dT}{T} = \int_i^f \frac{m_W c_W dT}{T} = m_W c_W \int_i^f \frac{dT}{T} = m_W c_W \ln \frac{T_f}{T_{i,W}}$$

$$D) \Delta S_{Al,W} = \Delta S_{Al} + \Delta S_W = m_{Al} c_{Al} \ln \frac{T_f}{T_{i,Al}} + m_W c_W \ln \frac{T_f}{T_{i,W}}$$

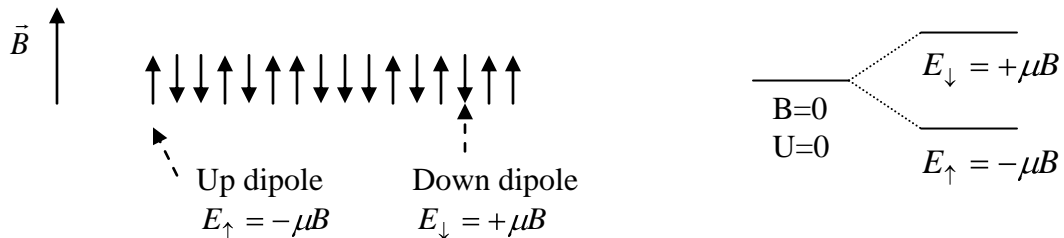
3.3 Paramagnetism (for more on the E&M of it, see Griffiths, end of Ch 5 and on into Ch 6)

- **Two-State Paramagnet**
- You'll recall that we came up with the multiplicity for this system back in Ch 2. Part of our motivation was simply that it was a simple system. Now we can build on that and come up with energy-temperature relationships as well as specific heat. While our model is extremely simple, it has a few other merits that make it worth looking at:

- It displays some fairly exotic behavior that challenges a simplistic understanding of temperature and such
- It works extremely well (matches experiment). That's a key criteria for a good model / theory.
- Also, though we won't do it, our model can be extended to multi-state paramagnets and it works great there too.
- Para magnetism is generated by unpaired atomic-electrons aligning their spins or orbits anti-parallel to external magnetic fields, or nuclei doing the same; given the negative charge of the electron, this means aligning their magnetic moments parallel to the fields. It is necessary that the electrons be unpaired since, if they had mates, their mates would point in the opposite direction, thus canceling any net effect.

3.3.1 Notation and Microscopic Physics

- **Dipoles:** Charges circulate with in the solid, perhaps the atomic electrons. That circulation crates a magnetic field / serves as a magnetic dipole. It's handy to characterize this in terms of a magnetic dipole moment, (classically that's the current times the area it encircles). We'll focus on this aspect and not worry about exactly what charges are responsible.
- **Quantized:** Electron spin is either (mostly) parallel or anti-parallel to a given axis – 2 choices. We'll treat this simple case. (For more discussion and the more general case, see Kittel's Intro to Solid State Ch 14.)
 - It is energetically favorable for the dipole to be aligned with the magnetic field, i.e., for the charge circulation to produce a field parallel to the applied field, so this is the lower energy state.
 - We imagine the dipoles to interact much more strongly with the strong external field than the weak field produced by their neighbors.



- $U = N_{\uparrow}E_{\uparrow} + N_{\downarrow}E_{\downarrow} = N_{\uparrow}(-\mu B) + N_{\downarrow}(\mu B) = \mu B(N_{\downarrow} - N_{\uparrow})$
 - or since $N = N_{\uparrow} + N_{\downarrow} \Rightarrow N_{\downarrow} = N - N_{\uparrow}$
- $U = \mu B(N - N_{\uparrow} - N_{\uparrow}) = \mu B(N - 2N_{\uparrow})$

- **Magnetization:** This is the net magnetic moment of the whole system (note, Griffiths defines it as net magnetic moment *per unit volume*).
 - $M = \mu N_{\uparrow} - \mu N_{\downarrow} = -\mu(N - 2N_{\uparrow})$
 - Comparing with the expression for energy, $M = -\frac{U}{B}$

- **Multiplicity:** This is simply a two state system $\Omega = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!}$

3.3.2 Numerical Solution / Qualitative Discussion

You will be asked to do similar things for an Einstein solid.

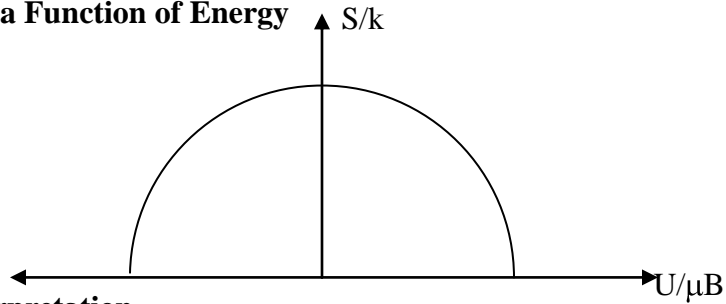


- As we did in chapter 2, we can simply evaluate (or ask Excel to evaluate) the multiplicity: Ω
- We can add a request for evaluating entropy: $\frac{S}{k} = \ln \Omega$
- Total energy (per magneton and field): $\frac{U}{\mu B} = N - 2N_{\uparrow}$
- Temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial (\ln \Omega)}{\partial (\mu B (N - 2N_{\uparrow}))} = \frac{k}{\mu B} \frac{\partial (\ln \Omega)}{\partial N_{\uparrow}} \approx \frac{k}{-2\mu B} \frac{\Delta (\ln \Omega)}{\Delta N_{\uparrow}} \Rightarrow T \left(\frac{\mu B}{k} \right) \approx -2 \frac{\Delta N_{\uparrow}}{\Delta \ln(\Omega)}$$

Results

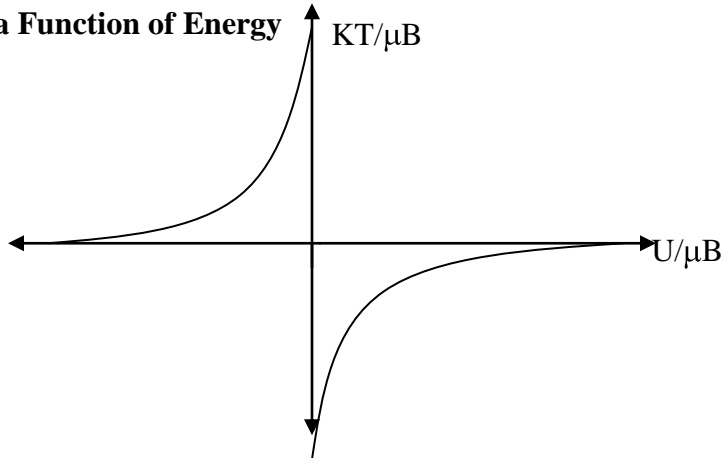
- **Entropy as a Function of Energy**



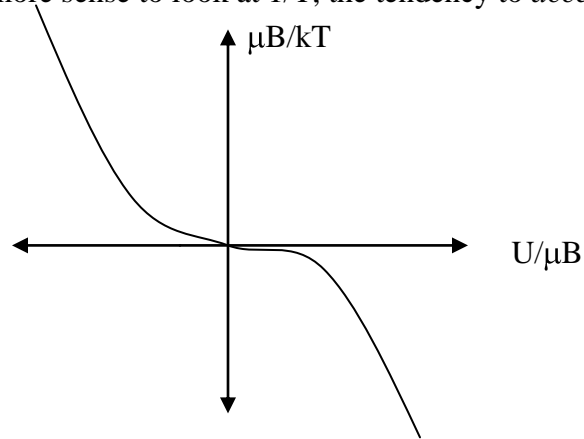
Interpretation

- Entropy is maximum when energy is 0. That's when half the dipoles are up and half are down. Well, that is the macrostate with the most microstates: how many ways to order things 1/2 up and 1/2 down. If we did not restrict energy, this would be the state the system would settle in.
- Entropy is minimum when energy is maximumly positive or negative. This is when all the dipoles are up or all the dipoles are down. Of course, there's only one way to have them all up or to have them all down.

- **Temperature as a Function of Energy**



- **Interpretation**
- Temperature is the energy vs. entropy slope / the tendency to *give up* energy.
- It may make more sense to look at $1/T$, the tendency to *accept* energy.



- For positive energy, entropy is increased by giving up energy! That's a *negative* temperature. That's like our enlightened people getting happier giving away money. That the temperature goes infinitely negative for 0 energy or that its inverse goes to 0 means that eventually giving even a huge amount of energy away infinitesimally increases entropy, so it must give away a lot of energy to achieve a significant change.
- For negative energy, entropy is increased by gaining energy. Again, near 0 energy, the temperature goes infinite, the inverse goes to 0. Even a large gain has little change in entropy.
- **Practical note:** Say you start with a paramagnet in a negative energy situation and you decrease its temperature so it settles into the lowest energy state. Then you flip the direction of the magnetic field; all of a sudden, the poles are in the highest energy state, a negative temperature situation for entropy will be increased by giving up energy.

○ **Negative temperatures.**

- These are characteristic of systems with maximum energies. Just as entropy is decreased as the lowest energy state becomes full, so does it decrease as the highest energy state becomes full. For negative energy, entropy is increased by gaining energy. That's positive temperature. However, that it goes infinitely positive means that it's going to end up giving up energy to most any other system, since most other system still have smaller temperatures.
- That we have negative temperatures is a consequence of our adopting a broader definition of temperature. Rather than it's simply being that thing that increases with thermal expansion (i.e. what thermometers measure) we say it's now the 'generosity' of a system with its energy, or $1/T$ is its 'greed' for energy. This new intuition should replace the old one.

Questions here

3.3.3 Analytic Solution

You will be asked to do similar things for an Einstein solid.

Do problem 3.25 for this system.

$$S = k \ln \Omega = k \ln \left(\frac{N!}{N_{\uparrow}! (N - N_{\uparrow})!} \right) \approx k \ln \left(\frac{N^N}{N_{\uparrow}^{N_{\uparrow}} (N - N_{\uparrow})^{N - N_{\uparrow}}} \right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U_{V,N}}$$

$$U = \mu B (N - 2N_{\uparrow}) \Rightarrow \partial U = -2\mu B \partial N_{\uparrow} \text{ or } \frac{\partial N_{\uparrow}}{\partial U} = -\frac{1}{2\mu B}$$

$$\frac{1}{T} = \frac{\partial N_{\uparrow}}{\partial U} \frac{\partial S}{\partial N_{\uparrow V,N}} = -\frac{1}{2\mu B} \frac{\partial S}{\partial N_{\uparrow}}$$

Cleaning up our S in preparation for this:

$$S = k \ln \left(\frac{N^N}{N_{\uparrow}^{N_{\uparrow}} (N - N_{\uparrow})^{N - N_{\uparrow}}} \right) = k \ln N^N - k N_{\uparrow} \ln N_{\uparrow} - k (N - N_{\uparrow}) \ln (N - N_{\uparrow})$$

$$\text{So, } \frac{\partial S}{\partial N_{\uparrow}} = -k \ln N_{\uparrow} - k(1 - +k) + k \ln (N - N_{\uparrow}) = k \ln \left(\frac{N - N_{\uparrow}}{N_{\uparrow}} \right)$$

To rephrase this in terms of energy, we use $\frac{N}{2} - \frac{U}{2\mu B} = N_{\uparrow}$

$$\frac{\partial S}{\partial N_{\uparrow}} = k \ln \left(\frac{N - \left(\frac{N}{2} - \frac{U}{2\mu B} \right)}{\frac{N}{2} - \frac{U}{2\mu B}} \right) = k \ln \left(\frac{\frac{N}{2} + \frac{U}{2\mu B}}{\frac{N}{2} - \frac{U}{2\mu B}} \right) = k \ln \left(\frac{1 + \frac{U}{N\mu B}}{1 - \frac{U}{N\mu B}} \right)$$

$$\frac{1}{T} = \frac{\partial N_{\uparrow}}{\partial U} \frac{\partial S}{\partial N_{\uparrow V,N}} = -\frac{1}{2\mu B} k \ln \left(\frac{1 + \frac{U}{N\mu B}}{1 - \frac{U}{N\mu B}} \right) = \frac{k}{2\mu B} \ln \left(\frac{1 - \frac{U}{N\mu B}}{1 + \frac{U}{N\mu B}} \right)$$

$$\text{Solving for U in terms of T gives } U = N\mu B \left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}} \right) = -N\mu B \tanh \frac{\mu B}{kT}$$

$$\text{Magnetization then is simply } M = -\frac{U}{B} = N\mu \tanh \frac{\mu B}{kT}$$

The specific heat, holding magnetic field constant is

$$C_B = \frac{\partial U}{\partial T}_{N,B} = -N\mu B \frac{\partial}{\partial T} \left(\tanh \frac{\mu B}{kT} \right) = -N\mu B \frac{1}{\cosh^2 \frac{\mu B}{kT}} \frac{\partial}{\partial T} \left(\frac{\mu B}{kT} \right) = Nk \left(\frac{\mu B / kT}{\cosh \mu B / kT} \right)^2$$

- Bohr magneton
- Curie's law: High T or Low B behavior $\frac{\mu B}{kT} \ll 1$

- Magnetization

- High T means low $1/T$, so we can look at the leading term in the Taylor series.

- $$M = N\mu \tanh \frac{\mu B}{kT} = N\mu \left(\frac{\mu B}{kT} - \frac{1}{3} \left(\frac{\mu B}{kT} \right)^3 + \frac{2}{15} \left(\frac{\mu B}{kT} \right)^5 - \dots \right) \approx N \frac{\mu^2 B}{kT}$$