

The magnetization of the material is then

$$M(N, T, B) = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

5. The heat capacity C_V should be straightforward. What do you get?

The magnetization function in step (4) above is an interesting result. Experimentally, paramagnetic systems are known to obey *Curie's Law* at low values of magnetization. The temperature dependence of the magnetization when the external field B is small is given by:

$$M = C \frac{B}{T} \text{ (Curie's Law)}$$

where C is a material constant called the *Curie Constant*. Does our magnetization obey Curie's law? For small B at non-zero temperatures, we have $kT \gg \mu B$ and we can Taylor expand the tanh function:

$$\tanh x = x - \frac{x^3}{3} + \frac{2}{15}x^5 - \dots$$

. Therefore, when $kT \gg \mu B$, we have

$$M(N, T, B) \approx N\mu \left(\frac{\mu B}{kT}\right)$$

Apparently, the Curie Constant is $C = N\mu^2/k$. Our paramagnetic model reproduces Curie behavior at low B .

12.4 Pressure and Mechanical Equilibrium

Two systems, A and B brought to contact and allowed to equalize volumes (imagine that each box is a flexible membrane so that the two volumes can reach equilibrium) will come to *mechanical equilibrium*. This condition is synonymous with

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

. We let mechanical equilibrium define the pressure, and find

$$P(T, V, N) = T \left(\frac{\partial S}{\partial V} \right)_{U, N}$$

We can derive equations of state from this relation. For example, the ideal gas has a multiplicity function given by

$$\Omega(U, V, N) = f(N) V^N U^{3N/2}$$

The Sakur-Tetrode entropy is then

$$S(U, V, N) = k \log \Omega = k \left[\log f(N) + N \log V + \frac{3N}{2} \log U \right]$$

The pressure is then

$$\begin{aligned} P(T, V, N) &= T \left(\frac{\partial S}{\partial V} \right)_{U, N} = \frac{NkT}{V} \\ &\Rightarrow PV = NkT \end{aligned}$$

We've derived the Ideal Gas Law from the multiplicity function of the ideal gas. You can follow the same procedure to derive the equation of state for any system for which the pressure has a well defined meaning. As a final example, we can consider the protein folding problem alluded to in the text. First, we'll need a very important relation which I'll call the "Entropy Identity." If we let S be a function of U and V , then we can write the differential of S as

$$dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV$$

Using the definitions of temperature and pressure in terms of the entropy, we can write the entropy identity as

$$dS = \frac{dU}{T} + \frac{P}{T} dV \quad \text{Entropy Identity}$$

We'll consider several applications of this identity in the next few classes. This entropy identity turns out to be really useful in the homework!

Protein Folding Example: In class, we discussed the structure-function paradigm of molecular biology. The determination of the final shape of a folded protein is a very difficult and important problem in this field. In essence, the protein folding process is driven by electrostatic interactions and entropy. Let us consider the reason that proteins fold into complex shapes at all. While the details of the folding process are driven by the electrostatics (chemical bonding), the fact that proteins fold at all is purely the result of the higher entropy of the more disordered (folded) state as compared to the linear chain state of the unfolded protein.

As a toy model of a simple protein, consider a chain consisting of N monomers, each of length l_0 . The monomers are simple links that can either “point” right or left. Let the number of such monomers that point to the right be N_R , and the number of monomers that point to the left be N_L such that $N = N_R + N_L$. The equilibrium length of the folded structure will be $L = l_0(N_R - N_L)$ as shown in the figure. Each link has two

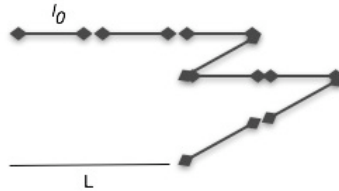


Figure 4: toy model of a one-dimensional protein. The end-to-end length is L , while the link-length is l_0 .

possible states (left and right), so we can immediately write down the multiplicity function:

$$\Omega = \binom{N}{N_R}$$

. The entropy is found by analogy to the coins or paramagnet example:

$$S(N, N_R) = k [N \log N - N_R \log N_R - (N - N_R) \log(N - N_R)]$$

. The goal of this calculation is to determine the entropy-driven restoring force F that tends to crumple the chain. This force will be a function of temperature. If we consider that we want $F > 0$ to represent a restoring force that shrinks the chain, then the force F is analogous to $-P$. We can rewrite the entropy identity accordingly:

$$dU = TdS + FdL$$

. The last term is the work done on the chain by quasistatically stretching it by an amount dL . Now, consider that we wish to consider the thermodynamics of our chain under constant temperature conditions - the protein chain is in a cell at constant T . For an isothermal process, we have $dU = 0$, and $TdS = -FdL$. Therefore, the analogy to the pressure definition above is

$$F = -T \left(\frac{\partial S}{\partial L} \right)_U$$

. For these notes, I'll spare you the algebra we worked in class to compute this force. The ingredients were

- $N_R = \frac{1}{2} \left(N + \frac{L}{l_0} \right)$

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$$\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \frac{\partial N_R}{\partial L} = \frac{1}{2l_0} \frac{\partial S}{\partial N_R}$$

- Assume $Nl_0 \gg L$

After some algebra and the three ingredients above, we find

$$F \approx \frac{kTL}{Nl_0^2}$$

Some interesting behaviors are now apparent:

- The restoring force is linear in L . The longer the chain, the larger is the tendency to crumple
- The tension in the chain is greater at higher temperatures. Therefore, increasing the temperature should cause the chain to fold up. This is the opposite behavior that we find in an ideal gas which wants to expand as the temperature is increased.
- We have assumed adiabatic stretching - the total entropy should be constant. But, as the chain contracts, the configurational entropy increases. Therefore, the vibrational entropy must decrease to compensate for the increase in configurational entropy. The reduction in the total number of vibrational states available to the chain corresponds to a decrease in the effective temperature of the chain.

The last point has some interesting physical consequences. Consider a rubber band which is pretty much a network of simple polymer chains like the one we've been modeling. As you stretch the rubber band, you are *decreasing* the configurational entropy (chain is straightening out). This must be compensated for (in the adiabatic approximation) by an *increase* in the vibrational entropy - an increase in the temperature of the rubber band! Conversely, as you allow the rubber band to shrink, the configurational entropy goes up, the vibrational entropy goes down, and the temperature of the rubber band goes down! You can check this by stretching and relaxing a rubber band that is just barely touching your lips. You can usually feel the temperature changes on those fat rubber bands. Not so much on the thin ones.