Problem Set 11

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1. For each of the following irreversible processes, explain how you can tell that the total entropy of the universe has increased.
   (a) Stirring salt into a pot of soup.

   > **Solution:** Stirring itself raises entropy as heat energy is equalised for different parts of the soup.

   (b) Scrambling an egg.

   > **Solution:** Energy is converted to heat, which raises entropy at this temperature.

   (c) Humpty Dumpty having a great fall.

   > **Solution:** Potential energy is converted (eventually) to heat. When heat is distributed to the surroundings, there will be more energy equally distributed, which raises entropy.

   (d) A wave hitting a sand castle.

   > **Solution:** Temperature of sand castle tends to the temperature of seawater. Entropy increases as energy is spread more evenly.

   (e) Cutting down a tree.

   > **Solution:** Potential energy of the tree is converted to heat, spreading energy to the environment, which raises entropy.

   (f) Burning gasoline in an automobile.

   > **Solution:** Chemical energy is converted to heat, which can be easily transferred. This allows for more microstates, as energy is no longer chemically locked in gasoline. This raises entropy.

2. Show that the entropy of a two-state paramagnet, expressed as a function of temperature, is $S = Nk[\ln(2\cosh x) - \tanh x]$, where $x = \mu B/kT$. Check that this formula has the expected behavior as $T \to 0$ and $T \to \infty$.

> **Solution:** We can write $\frac{S}{k}$ in terms of N and $N_\uparrow$. We can then rewrite S if we can express those two terms in terms of x. Now
> $$N_\uparrow = \frac{1}{2}\left(N - \frac{U}{\mu B}\right)$$

We also know

$$U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

so

$$N_\uparrow = \frac{N}{2}(1 + \tanh x)$$

Substituting into the expression for $\frac{S}{k}$,

$$\begin{aligned}
\frac{S}{k} &\approx N\ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow)\ln(N - N - \uparrow) \\
&= N\ln N - \frac{N}{2}(1+\tanh x)\ln\left(\frac{N}{2}(1+\tanh x)\right) - \frac{N}{2}(1-\tanh x)\ln\left(\frac{N}{2}(1-\tanh x)\right) \\
\frac{S}{Nk} &\approx \ln N - \ln\frac{N}{2} - \frac{1}{2}\left(\frac{\sinh x + \cosh x}{\cosh x}\ln\frac{\sinh x + \cosh x}{\cosh x} + \frac{\cosh x - \sinh x}{\cosh x}\ln\frac{\cosh x - \sinh x}{\cosh x}\right) \\
&= \ln 2 - \frac{1}{2\cosh x}\left(e^x \ln\frac{e^x}{\cosh x} + e^{-x}\ln\frac{e^{-x}}{\cosh x}\right) \\
&= \ln 2 - \frac{1}{2\cosh x}(e^x - e^{-x}) + \ln\cosh x \\
&= \ln(2\cosh x) - \tanh x \\
S &= Nk[\ln(2\cosh x) - \tanh x]
\end{aligned}$$

As $T \to 0, x \to \infty$, so S goes to infinity, which is expected. As $T \to \infty, x \to 0$, so S goes to $Nk\ln 2$, which is also expected, with there only being 2 states.

3. What partial-derivative relation can you derive from the thermodynamic identity by considering a process that takes place at constant entropy? Does the resulting equation agree with what you already knew? Explain.

Solution: At constant entropy, $dS = 0$, so

$$dU = -PdV$$

When entropy is constant, we know the only change in internal energy comes from work done, PdV, agreeing with that is known.

4. Use the thermodynamic identity to derive the heat capacity formula

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

which is occasionally more convenient than the more familiar expression in terms of U. Then derive a similar formula for C_P, by first writing dH in terms of dS and dP.

Solution: At constant volume, $dU = TdS$. Then

$$\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\
&= T\left(\frac{\partial S}{\partial T}\right)_V
\end{aligned}$$

Then similarly,

$$dH = dU + PdV + VdP = TdS + VdP = TdS$$

where the last equality comes from constant pressure. Hence

$$\begin{aligned} C_P &= \left(\frac{\partial H}{\partial T}\right)_P \\ &= T\left(\frac{\partial S}{\partial T}\right)_P \end{aligned}$$

5. Polymers, like rubber, are made of very long molecules, usually tangled up in a configuration that has lots of entropy. As a very crude model of a rubber band, consider a chain of N links, each of length l (see Figure 3.17). Imagine that each link has only two possible states, pointing either left or right. The total length L of the rubber band is the net displacement from the beginning of the first link to the end of the last link.

   (a) Find an expression for the entropy of this system in terms of N and N_R, the number of links pointing to the right.

   Solution:

   $$\Omega = \binom{N}{N_R} \Rightarrow S = k\ln\binom{N}{N_R} \Rightarrow k(N\ln N - N_R\ln N_R - (N - N_R)\ln(N - N_R))$$

   (b) Write down a formula for L in terms of N and N_R.

   Solution:

   $$L = l|N_R - N_L| = l|N_R - (N - N_R)| = l|2N_R - N|$$

   (c) For a one-dimensional system such as this, the length L is analogous to the volume V of a three-dimensional system. Similarly, the pressure P is replaced by the tension force F. Taking F to be positive when the rubber band is pulling inward, write down and explain the appropriate thermodynamic identity for this system.

   Solution:

   $$dU = TdS + FdL$$

   Note the sign flip because P points outwards but F points inwards. This makes sense, as energy increases when dL is positive. Then dU has a TdS component and a work done component, similar to the thermodynamic identity.

   (d) Using the thermodynamic identity, you can now express the tension force F in terms of a partial derivative of the entropy. From this expression, compute the tension in terms of L, T, N, and l.

   Solution: We know

   $$P = T\left(\frac{\partial S}{\partial V}\right)_U$$

Using this analogy,

$$\begin{aligned}
F &= -T\left(\frac{\partial S}{\partial L}\right)_U \\
&= -T\left(\frac{\partial S}{\partial N_R}\frac{\partial N_R}{\partial L}\right)_U \\
&= kT(1+\ln N_R - 1 - \ln(N-N_R))\frac{1}{2l} \\
&= \frac{kT}{2l}\ln\frac{N_R}{N-N_R} \\
&= \frac{kT}{2l}\ln\left(1+\frac{2L}{Nl}\right)
\end{aligned}$$

(e) Show that when $L << Nl$, the tension force is directly proportional to L (Hooke's law).

Solution: In this case, $\frac{L}{Nl} \to 0$, so the logarithm tends to $\frac{2L}{Nl}$, and

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

(f) Discuss the dependence of the tension force on temperature. If you increase the temperature of a rubber band, does it tend to expand or contract? Does this behavior make sense?

Solution: Tension force is proportional to temperature. If you increase the temperature, tension increases, so it contracts. It does make sense, because at higher temperatures, N_R and N_L should be closer, causing L to decrease.

(g) Suppose that you hold a relaxed rubber band in both hands and suddenly stretch it. Would you expect its temperature to increase or decrease? Explain. Test your prediction with a real rubber band (preferably a fairly heavy one with lots of stretch), using your lips or forehead as a thermometer. (Hint: The entropy you computed in part (a) is not the total entropy of the rubber band. There is additional entropy associated with the vibrational energy of the molecules; this entropy depends on U but is approximately independent of L.)

Solution: Temperature should increase. Total entropy should be constant, but entropy according to part (a) decreases, as N_R increases. Then vibrational energy must increase to keep entropy constant, which results in an increase in temperature.

6. Consider a monatomic ideal gas that lives at a height z above sea level, so each molecule has potential energy mgz in addition to its kinetic energy.

(a) Show that the chemical potential is the same as if the gas were at sea level, plus an additional term mgz

Solution: The new potential energy is given by

$$U' = U + mgzN$$

Then

$$\mu' = \frac{dU'}{dN} = \frac{dU}{dN} + \frac{d}{dN} mgzN = \mu + mgz$$

(b) Suppose you have two chunks of helium gas, one at sea level and one at height z, each having the same temperature and volume. Assuming that they are in diffusive equilibrium, show that the number of molecules in the higher chunk is

$$N(z) = N(0)e^{-mgz/kT}$$

Solution:

$$-kT \ln[\frac{V}{N_0}\left(\frac{2\pi mkT}{h^2}\right)^3 /2] = -kT \ln[\frac{V}{N_B}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}] + mgz$$

$$-kT \ln \frac{1}{N_0} = -kT \ln \frac{1}{N_B} + mgz$$

$$\ln \frac{N_0}{N_B} = \frac{mgz}{kT}$$

$$N(z) = N_0 e^{-\frac{mgz}{kT}}$$