Problem Set 7
2.772/BE.011
Dill & Bromberg: 10.7, 10.8, 11.2, 11.5, 11.11(a)

10.7) The populations of spins in a magnetic field.
We have two states in our system of spins: spin up and spin down. And we know the difference in energy between the two states: $\Delta\varepsilon$. Therefore we can define the lower state as having $\varepsilon=0$ and the excited state as having $\varepsilon = \varepsilon_o$ (from plugging in their values for a 300MHz NMR machine etc.)

(a) We want the relative population difference: $\dfrac{N_+}{N_+ + N_-} - \dfrac{N_-}{N_+ + N_-} = \dfrac{N_+ - N_-}{N_+ + N_-}$

$$\frac{N_+}{N_-} = \exp\left(\frac{\varepsilon}{kT}\right) \; --> \; N_+ = N_- \exp\left(\frac{\varepsilon}{kT}\right)$$

$$N_+ + N_- = N_-\left(1 + \exp\left(\frac{\varepsilon}{kT}\right)\right)$$

$$N_+ - N_- = N_-\left(\exp\left(\frac{\varepsilon}{kT}\right) - 1\right)$$

$$\frac{N_+ - N_-}{N_+ + N_-} = \frac{1 - \exp\left(\dfrac{\varepsilon_0}{kT}\right)}{1 + \exp\left(\dfrac{\varepsilon_0}{kT}\right)}$$ this is the answer, but we can simplify this even further:

for small $\dfrac{\varepsilon}{kT}, 1 - \exp\left(\dfrac{\varepsilon}{kT}\right) \approx \dfrac{\varepsilon_0}{kT}$ so,

$$= \frac{(2.79)(5.05x10^{-24}\,J/Tesla)(7Tesla)}{2(300K)(1.38x10^{-23}\,J/K)} = 1.19x10^{-2}$$. This is the fractional population difference.

(b) The population difference changes with temperature: as T increases, the population difference decreases (populations become equal). As T→ 0, all of the population goes to the lower energy state.

(c) The partition function $q = 1 + \exp\left(\dfrac{\varepsilon_0}{kT}\right)$ (note that the lower energy state is taken as the ground state, with respect to which the other energy is measured).

10.8) Energy and entropy for indistinguishable particles.
We have equations for <e> and S for distinguishable particles, which we derived using the Q we derived for distinguishable particles: $Q = q^N$. We also derived Q for

indistinguishable particles: $Q = \dfrac{q^N}{N!} \approx \dfrac{q^N}{\left(\dfrac{N}{e}\right)^N}$ using Sterling's approximation so that it

will be easier to take derivatives. So we can do these derivations again using this new Q! (Note that you should be able to compute energies like U and F as well as <e> and S from pretty much any Q or q.)

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right) \approx -\frac{\partial}{\partial \beta}(N \ln q - N(\ln N - \ln e)) = -\frac{\partial}{\partial \beta}(N \ln q - N \ln N + N) =$$

$$-N\frac{\partial}{\partial \beta}(\ln q - \ln N + 1) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)$$

So, $<\varepsilon> = \dfrac{U}{N} = -\left(\dfrac{\partial \ln q}{\partial \beta}\right)$, so <ε> does not depend on distinguishability!

Now $S = k \ln Q + \dfrac{U}{T} = Nk(\ln q - \ln N + 1) - \dfrac{N}{T}\left(\dfrac{\partial \ln q}{\partial \beta}\right)$

11.2) The statistical mechanics of oxygen gas.
We have one mole of oxygen at a given temperature and volume.

(a) The translational partition function $q_{translation} = \left(\dfrac{2\pi mkT}{h^2}\right)^{3/2} V$

And m = about 32 g/mol = 5.31×10^{-26} kg/molecule
k = 1.38×10^{-23} JK-1, T = 273.15K, h = 6.626×10^{-34} Js

$$q_{translation} = \left(\frac{2(3.14)(5.31 \times 10^{-26} kg)(3.77 \times 10^{-21} J)}{(6.63 \times 10^{-34} Js)^2}\right)^{3/2} (22.4 \times 10^{-3} m^3)$$

$$= 3.43 \times 10^{30} \frac{accessible\_states}{molecule} ----\left(note: \frac{kgm^2}{s^2} = J\right)$$

(b) The translational component of the internal energy per mole is calculated the same as in the book (bottom of p. 207 to top of p. 208). Remember the equation though, $U = NkT^2\left(\dfrac{\partial \ln q}{\partial T}\right)$, because q might not be the same the next time you have to do this.

$$U_{translation} = \frac{3}{2}RT(per\_mole) = 3.4\frac{kJ}{mol}$$

(c) The constant-volume heat capacity

$$Cv(per\ mole) = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R = 12.47\frac{J}{Kmol}$$

11.5) The translational partition function in two dimensions.
We can derive the 2D translational partition function based on the 1D derivation we already did:

For each dimension: $q_{translation,1D} = \left(\dfrac{2\pi mkT}{h^2}\right)^{1/2} L$ and $q_{translation,2D} = q_{translation,1D}^2$

So, if A = area = L^2, then $q_{translation,2D} = \left(\dfrac{2\pi mkT}{h^2}\right)A$

11.11) Heat capacities of liquids.

(a) We are given Cv for liquid argon at T=100K.

We can approximate liquid argon as spherical (so there are no rotations and no vibrations… we can make this assumption for single atoms like this since there is no obvious way that we could detect rotations, and there needs to be 2 things before we get vibration, otherwise 'vibration' just looks like translation). So, argon has only translational freedom. So:

$Cv = \dfrac{3}{2}nR = n\left(\dfrac{3}{2}\right)\left(8.314\dfrac{J}{Kmol}\right) = 12.47\dfrac{J}{Kmol}$ can be rationalized. The rest of the

heat capacity must be due to intermolecular interactions.