Problem Set 6
2.772/BE.011
Dill & Bromberg: 10.1, 10.3, 10.6, 10.11

10.1
a)

$$q = \sum_l W(l) e^{-E_l/kT}$$
$$= 1 + e^{-\varepsilon_0/kT} + \gamma e^{-2\varepsilon_0/kT}$$

b) In order to get the average energy $\langle \varepsilon \rangle = \sum_l \varepsilon_l p_l$, we need the probabilities first.

$$p_1 = \frac{1}{q}, p_2 = \frac{e^{-\varepsilon_0/kT}}{q}, p_3 = \frac{\gamma e^{-2\varepsilon_0/kT}}{q}$$
$$\langle \varepsilon \rangle = (0)\frac{1}{q} + (\varepsilon_0)\frac{e^{-\varepsilon_0/kT}}{q} + (2\varepsilon_0)\frac{e^{-2\varepsilon_0/kT}}{q}$$
$$= \frac{\varepsilon_0 e^{-\varepsilon_0/kT}}{q}\left(1 + 2\gamma \frac{e^{-\varepsilon_0/kT}}{q}\right)$$

c) The probabilities are given by:

$$p_1^* = \frac{1}{1+e^{-1}+e^{-2}} = 0.665$$
$$p_2^* = \frac{e^{-1}}{1+e^{-1}+e^{-2}} = 0.245$$
$$p_3^* = \frac{e^{-2}}{1+e^{-1}+e^{-2}} = 0.090$$

d) To get the temperature of interest, just equate the probabilities.

$$p_1 = p_3$$
$$\frac{1}{q} = \frac{\gamma e^{-2\varepsilon_0/kT_0}}{q}$$
$$\gamma e^{-2\varepsilon_0/kT_0} = 1$$
$$-2\varepsilon_0/kT_0 = \ln 1/\gamma$$
$$T_0 = \frac{2\varepsilon_0}{k \ln \gamma} = \frac{2\left(2\ {kcal}/{mol}\right)}{\left(2\ {cal}/{mol \cdot K}\right)\ln 1000} = 289.5K$$

e)

$$\frac{\varepsilon_0}{kT} = \frac{2000\, {}^{cal}\!/_{mol}}{\left(2\, {}^{cal}\!/_{mol}\cdot K\right)\left(289.5K\right)} = 3.454$$

$$q = 1 + e^{-\varepsilon_0/kT} + \gamma e^{-2\varepsilon_0/kT} = 1 + e^{-3.454} + 1000e^{-6.908} = 2.032$$

$$p_1^* = \frac{1}{q} = \frac{1}{2.032} = 0.492$$

$$p_2^* = \frac{e^{-\varepsilon_0/kT}}{q} = \frac{e^{-3.454}}{2.032} = 0.016$$

$$p_3^* = \frac{\gamma e^{-2\varepsilon_0/kT}}{q} = 1000\frac{e^{-6.908}}{2.032} = 0.492$$

10.3

a) In order to determine the partition function and the probabilities, it is important to remember to adjust the energies so the lowest energy state is *0*. If you forget to do this, the partition function does not tell you the number of attainable states, though the probabilities all work out correctly.

$$q = 1 + e^{-(\varepsilon_1 - \varepsilon_0)/kT} = 1 + e^{\frac{-1200\, {}^{cal}\!/_{mol}}{\left(2\, {}^{cal}\!/_{mol\cdot K}\right)(300K)}} = 1 + e^{-2} = 1.135$$

b) Again, to determine the probabilities, we need to use the adjusted energy values.

$$p_0 = \frac{1}{q} = 0.88$$

$$p_1 = \frac{e^{-2}}{q} = 0.12$$

Now we're trying to calculate the average energy, so we need to use the actual energy values.

$$\begin{aligned}\langle \varepsilon \rangle &= p_0\varepsilon_0 + p_1\varepsilon_1 \\ &= (0.88)\left(600\, {}^{cal}\!/_{mol}\right) + (0.12)\left(1800\, {}^{cal}\!/_{mol}\right) \\ &= 744\, {}^{cal}\!/_{mol}\end{aligned}$$

10.6

In this question, we're given that our system has energy levels uniformly separated by ε_0. The question is perhaps unclear, but we are meant to assume that we have an infinite number of energy levels $\varepsilon_i=\{0, \varepsilon_0, 2\varepsilon_0 \ldots\}$. We need to calculate $p_0 = \frac{1}{q}$. So what is q?

$$q = \sum e^{-\varepsilon_i/kT} = \sum e^{-i\varepsilon/kT} = \sum \left(e^{-\varepsilon/kT}\right)^i$$

If we substitute $x = \left(e^{-\varepsilon/kT}\right)$, we can see that $q = \sum x^i$ is just the sum of an infinite geometric series.

$$\begin{aligned} q &= \sum x^i \\ &= \frac{1}{1-x} \\ &= \frac{1}{1-e^{-\varepsilon/kT}} \\ p &= 1-e^{-\varepsilon/kT} \\ &= 1-e^{\frac{-3.2\times10^{-20}\,J}{\left(1.3807\times10^{-23}\,J/K\right)(300\,K)}} \\ &= 0.9996 \end{aligned}$$

So more than 99.9% of all particles are in the lowest energy state.

10.11

For this problem we have 3 different macrostates that we need to consider: collapsed *W(c)=1*, partially extended *W(pe)=3*, and extended *W(e)=1*. From example 10.3 we know that $q = 1 + 4e^{-\varepsilon_0/kT}$ (both partially extended and extended have the same energy ε_0). Now we can compute the probabilities of each of the three states.

$$\begin{aligned} p_c &= \frac{1}{q} \\ p_{pe} &= \frac{3e^{-\varepsilon_0/kT}}{q} \\ p_e &= \frac{e^{-\varepsilon_0/kT}}{q} \end{aligned}$$

So the average end to end distance is given by:

$$\begin{aligned} \langle d \rangle &= p_c d_c + p_{pe} d_{pe} + p_e d_e \\ &= \frac{1+3\sqrt{5}e^{-\varepsilon_0/kT} + 3e^{-\varepsilon_0/kT}}{1+4e^{-\varepsilon_0/kT}} \end{aligned}$$

Plotting this for *ε=1 kcat/mol* and *ε=3 kcat/mol* we get: