1 May 1999, Thermodynamics, Problem 2

1.1 (a)

We want the entropy of the chain when the ends are at x=0 and x=L. This is a combinatoric problem, because the energies of all the configurations are the same. Let n_f be the total number of steps forward and n_b the number of steps backward. Then we can write:

$$n_f a - n_b a = L$$

$$n_f + n_b = N$$

$$\rightarrow n_f = \frac{N + L/a}{2}$$

Then we need the number of ways to pick n_f forward steps out of a total N steps, that is:

$$W = \binom{N}{n_f} = \binom{N}{\frac{N+L/a}{2}} = \frac{N!}{\left(\frac{N+L/a}{2}\right)!\left(\frac{N-L/a}{2}\right)!}$$

$$S = k_B lnW = k_B ln\left[\frac{N!}{\left(\frac{N+L/a}{2}\right)!\left(\frac{N-L/a}{2}\right)!}\right] \quad (1)$$

1.2 (b)

We want the tension of the chain, for $L << Na$. Here I have two solutions:

1) (Pablo)

$$Z = \sum e^{-(Facos\theta)/kT} = e^{-Fa/kT} + e^{Fa/kT} = 2cosh(Fa/kT)$$

The average length of a single monomer is:

$$< l >= \frac{ae^{-Fa/kT} - ae^{Fa/kT}}{2coshFa/kT} = -a\,tanh(Fa/kT)$$

$$L = -Na\,tanh(Fa/kT)$$

$$tanh(Fa/kT) = -L/Na << 1$$

$$\rightarrow tanh(Fa/kT) \approx \frac{Fa}{kT} = -\frac{L}{Na}$$

$$F = -\frac{LkT}{Na^2} \quad (2)$$

2) (Vasily)

$$dU = TdS + FdL$$

$$T\left(\frac{\partial S}{\partial L}\right)_{N,U} = -F$$
$$F = \frac{2kTL}{Na^2}$$

Note that the two solutions differ, in absolute value, by a factor of 2. I don't really like the assumption of Vasily's solution that if you change L a little bit, U stays constant. Because when the problem says all configurational states are equally likely I understand it to mean "in the absence of external forces", or "for a given length".

1.3 (c)

It can be proven from the expression for the entropy that the configuration that maximizes entropy is the one with $L = 0$. So we take that to be the rest configuration. Then, using the force that we obtained in part b, we can obtain the required work by:

$$W = \int_0^L F(L')\,dL'$$

This gives two solutions, for my method and Vasily's, respectively:

$$W = -\frac{L^2kT}{2Na^2} \quad (Pablo) \tag{3}$$
$$W = \frac{L^2kT}{Na^2} \quad (Vasily) \tag{4}$$

There's something wrong about my work being negative: the thing would stretch with no external forces. But that probably just means that I used the wrong sign in computing the average length (I assumed the monomer to be in a state of higher energy if it was in the direction of the applied force, and lower if it was in the opposite direction, and it's likely that I got those wrong).

1.4 (d)

The heat is given by:

$$Q = \int TdS = T\Delta S$$

The entropy at zero length and at length L can be obtained from part a, and it is:

$$S(L = 0) = Nkln2$$
$$S(L) = Nkln2 - \frac{kL^2}{Na^2}$$
$$Q = -\frac{kTL^2}{Na^2} \tag{5}$$

So the polymer yields heat in the process.