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:

\[
\begin{align*}
  n_f a - n_b a &= L \\
  n_f + n_b &= N \\
  \rightarrow n_f &= \frac{N + L/a}{2}
\end{align*}
\]

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

\[
W = \binom{N}{n_f} = \binom{N}{N + L/a} = \frac{N!}{(N + L/a)! (N - L/a)!}
\]

\[
S = k_B \ln W = k_B \ln \left[ \frac{N!}{(N + L/a)! (N - L/a)!} \right]
\]

(1)

1.2 (b)

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

1) (Pablo)

\[
Z = \sum e^{-(F \cos \theta) / kT} = e^{-Fa/kT} + e^{Fa/kT} = 2 \cosh(Fa/kT)
\]

The average length of a single monomer is:

\[
< l > = \frac{ae^{-Fa/kT} - ae^{Fa/kT}}{2 \cosh Fa/kT} = -a \tanh(Fa/kT)
\]

\[
L = -Na \tanh(Fa/kT)
\]

\[
tanh(Fa/kT) = -L/Na << 1
\]

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

\[
F = -\frac{LkT}{Na^2}
\]

(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:

\[ W = -\frac{L^2 kT}{2Na^2} \quad (Pablo) \]

\[ W = \frac{L^2 kT}{Na^2} \quad (Vasily) \]

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:

\[ S(L = 0) = Nkln2 \]

\[ S(L) = Nkln2 - \frac{kL^2}{Na^2} \]

\[ Q = -\frac{kTL^2}{Na^2} \quad (5) \]

So the polymer yields heat in the process.