1 May 2001, Thermodynamics, Problem 2

1.1 (a)

Each monomer can be treated independently, for there are no interactions between them. Each one can be of length a or b:

$$Z_1 = e^{-\beta(E_a+Pa)} + e^{-\beta(E_b+Pb)}$$

where P is the tension. The partition function for the whole system is:

$$Z = Z_1^N = [e^{-\beta(E_a+Pa)} + e^{-\beta(E_b+Pb)}]^N \tag{1}$$

Now, the average length of each monomer will be given by:

$$< l >= a\frac{e^{-\beta(E_a+Pa)}}{Z} + be^{-\beta(E_b+Pb)}Z$$

so the average length of the whole chain will be:

$$L = \frac{N[ae^{-\beta(E_a+Pa)} + be^{-\beta(E_b+Pb)}]}{e^{-\beta(E_a+Pa)} + e^{-\beta(E_b+Pb)}} \tag{2}$$

Alternatively, we can find the potential:

$$\Phi = -kTlnZ = -NkTln[e^{-\beta(E_a+Pa)} + e^{-\beta(E_b+Pb)}]$$

Since P is analogous to the pressure and Φ is a function of pressure, number of particles and temperature, it's analogous to the Gibbs free energy, and therefore:

$$d\Phi = -SdT + LdP + \mu dN$$
$$L = \left(\frac{\partial \Phi}{\partial P}\right)_{T,N}$$

and the same answer comes out.