Solutions to problem set 5

Problem 2

Estimates of molecular forces.

a) C-O bond:
E = 84 kcal/mol = 84 kcal/mol · 4.184 kJ/kcal · 1000 J/kJ / (6 ·10^{23}/mol) = 5.9 ·10^{-19} J
$F = E / \Delta x = 5.9 \cdot 10^{-19}$ J / (10^{-10} m) = $5.9 \cdot 10^{-9}$ N = 5.9 nN

S-S bond:
$E = 3.6 \cdot 10^{-19}$ J
F = 3.6 nN
i.e. the rupture forces for covalent bond are in the nN range. For more information, see Michel Crandbois, Martin Beyer, Matthias Hauke Clausen-Schaumann, Hermann E. Gaub, *How Strong Is a Covalent Bond?*, *Science* (1999)

b) Non-covalent bonds in biological systems have to be stronger than E = 4 pN·nm = 10^{-21} J and have to withstand forces larger than ≈ 4 pN·nm/1 nm = 4 pN, otherwise thermal fluctuations would constantly break them. At the same time, they are considerably weaker than covalent bonds with energies in the range of $E \approx 10^{-19}$ J and forces ≈ 1 nN. Therefore, typical rupture forces for non-covalent bonds are 10-100 pN and typical energies 10-100 pN·nm ≈ 2-20 times $k_B T$.

Problem 3

Force-extension relationship for the 1D freely-jointed chain. We consider the 1D FJC model, with a two-state variable σ that takes on the value $\sigma_i = +1$ for each segment that points "forward" in the z-direction, along the external applied force, or $\sigma_i = -1$ for segments that point "backwards", against the external force. The total extension is then given by

$$z = b \cdot \sum_{i=1}^{N} \sigma_i \tag{1}$$

To derive an expression for the average extension $\langle z \rangle$, we take the ensemble average, averaging over "states of the world" j, weighting the value that z takes on in each state, z_j by the probability of the state to occur p_j:

$$\langle z \rangle = \sum_j p_j \cdot z_j = \sum_{\sigma_1=\pm 1} ... \sum_{\sigma_N=\pm 1} p(\sigma_1, ..., \sigma_N) \cdot z \tag{2}$$

The probability for a state with energy E_j to occur is given by its Boltzmann factor, properly normalized:

$$p_j = p(\sigma_1, ..., \sigma_N) = \frac{e^{-E_j/(k_B T)}}{Z} = \frac{e^{-(-f \cdot z)/(k_B T)}}{Z} = \frac{e^{(f \cdot b \cdot \sum_{i=1}^{N} \sigma_i)/(k_B T)}}{Z} \tag{3}$$

where the normalization Z is the partition function (i.e. the sum over all Boltzmann factors) and we have used the expression for the extension z from Equation 1.
Inserting the expression for the probabilities and for the length z into Equation 2, we get

$$\langle z \rangle = \sum_{\sigma_1=\pm 1} \ldots \sum_{\sigma_N=\pm 1} \left(\frac{e^{(f \cdot b \cdot \sum_{i=1}^{N} \sigma_i)/(k_B T)}}{Z} \right) \cdot \left(b \cdot \sum_{i=1}^{N} \sigma_i \right) \tag{4}$$

which can be written short hand by using the "logarithm trick" (you can verify this by simply doing the derivative):

$$\langle z \rangle = k_B T \frac{\partial}{\partial f} \ln \left(\sum_{\sigma_1=\pm 1} \ldots \sum_{\sigma_N=\pm 1} e^{(f \cdot b \cdot \sum_{i=1}^{N} \sigma_i)/(k_B T)} \right) \tag{5}$$

We notice that the argument of the logarithm is just the product of N independent and identical factors:

$$\langle z \rangle = k_B T \frac{\partial}{\partial f} \ln \left(\left(\sum_{\sigma_1=\pm 1} e^{(f \cdot b \cdot \sigma_1)/(k_B T)} \right) \cdot \ldots \cdot \left(\sum_{\sigma_N=\pm 1} e^{(f \cdot b \cdot \sigma_N)/(k_B T)} \right) \right) \tag{6}$$

This allows us to write it as a simply product and "pull down" the factor N:

$$\langle z \rangle = k_B T \frac{\partial}{\partial f} \ln \left(e^{(f \cdot b)/(k_B T)} + e^{(-f \cdot b)/(k_B T)} \right)^N = k_B TN \frac{\partial}{\partial f} \ln \left(e^{(f \cdot b)/(k_B T)} + e^{(-f \cdot b)/(k_B T)} \right) \tag{7}$$

Finally, we carry out the derivative with respect to f; to make the results look "pretty", we can additionally use a trigonometric identity:

$$\langle z \rangle = N \cdot b \frac{e^{(f \cdot b)/(k_B T)} - e^{(-f \cdot b)/(k_B T)}}{e^{(f \cdot b)/(k_B T)} + e^{(-f \cdot b)/(k_B T)}} = N \cdot b \cdot \tanh(f \cdot b / k_B T) \tag{8}$$