Chemical physics of polymer solutions

Exercise 1

27 October 2003

1. Consider a one-dimensional Gaussian chain made of N monomers of length a each. One end of the chain is fixed at the origin. The other end is pulled with force f to the right ($+x$). The chain is in contact with a thermal bath of temperature T. Assume that $fa \ll k_{\mathrm{B}}T$.

   (a) Find the distribution of the end-to-end distance, $p(x, N)$.

   (b) What is the mean end-to-end distance, $\langle x \rangle$? Go back to the free energy of a force-free chain derived in the class and find the force required to hold the "entropic spring" at a given end-to-end distance. Compare the results.

   (c) What is the mean-square fluctuation (variance) of the end-to-end distance, $\langle x^2 \rangle - \langle x \rangle^2$?

   You may find the following steps helpful:

   - Write down the contribution from the force to the chain energy and identify the contribution from a single monomer.
   - Calculate the probabilities of right and left steps in the presence of force, using the Boltzmann relation in the limit $fa \ll k_{\mathrm{B}}T$.
   - Derive the corresponding continuous equation for $p(x, N)$ and solve it.

2. Consider a particle undergoing one-dimensional random walk with step size a and step duration τ. The particle experiences an external potential $\phi(x)$. The potential changes moderately at the length scale of a, such that we can assume $a\partial_x\phi \ll k_{\mathrm{B}}T$. Derive the continuous equation for the distribution of the end-to-end distance at time t, $p(x, t)$.

3. Consider a one-dimensional flexible chain made of N monomers of length a. The monomers experience an external potential $\phi(x)$. The potential is weak and changes moderately at the length scale of a, such that we can assume $a\partial_x\phi \ll \phi \ll k_{\mathrm{B}}T$. Derive the continuous equation for the distribution of the end-to-end distance, $p(x, N)$. (Note that, unlike Question 2, there is an energy associated with just introducing each monomer.) Compare the equation you get with the one you got in Question 2. Does it remind you of another equation from a different area?

4. Consider a three-dimensional flexible chain made of N monomers of length a. The monomers are located on the sites of a cubic lattice (of lattice parameter a).

   (a) Derive the continuous equation for the distribution of the end-to-end vector $\mathbf{r} = (x, y, z)$, $p(\mathbf{r}, N)$.

   (b) Solve the equation.

   (c) Find the mean-square end-to-end distance $\langle r^2 \rangle$ and compare to the one-dimensional case. What is the exponent ν? What is the dimensionality of the chain, D?