Homework 6 (due October 24, 2019)

(1) Polymer Conformations I   **(15 pts)**

The conformation of an *ideal* polymer chain of $(N+1)$ identical monomers (bond length l) follows a random walk with N steps. From random walk theory, the RMS end-to-end distance scales with N as $R_e = \sqrt{\langle R_N \rangle^2} = N^{1/2}$.

In distinction for *real* polymer chains, there are correlations between their chain segments which lead to deviations in the random walk statistics. These correlations may originate from excluded volume repulsions or from van-der-Waals attraction between the chain segments. The relative strengths of these interactions depend on the quality of the solvent in which the polymer "lives": In a *good solvent*, excluded volume effects dominate, whereas in a *poor solvent*, the van-der-Waals attraction dominates. Both solvent conditions affect the *long-range* correlations between the polymer segments, and therefore alter the scaling law for the random walk.

(a) Explain how (and why!) the scaling exponents, $v_{good\ solvent}$ and $v_{poor\ solvent}$, should deviate from that for an ideal polymer, $v_{id} = 1/2$.

(b) In a *theta solvent*, repulsive and attractive interactions cancel exactly. How does the chain size $\langle R_N^2 \rangle^{1/2}$ depend on N in that solvent, and why?

(c) In log-log plot, draw R_e against N *to scale* for a polymer in a theta solvent, for the same polymer in a good solvent ($v = 0.6$) and in a poor solvent ($v = 1/3$).

(d) The dependence of the radii of polymer coils on solvent quality can be quantitatively determined in diffusion measurements, for example by light scattering. The diffusion constant D depends on the hydrodynamic radius of the chain as $D = (k_B T / 6\pi\eta R)$, where $R \equiv R_G = R_e / \sqrt{6}$ is the radius of gyration of the polymer coil and η is solvent viscosity.

If a short polymer chain (MW = 1,000) has a diffusion constant of D = 100 μm^2/s, in a good, a poor and a theta solvent (at low MW, long-range correlations are negligible, therefore D is approximately the same in all cases), estimate the values of D for polymers of MW = 1,000,000 in the three cases under the assumption that η is the same for all three solvents.
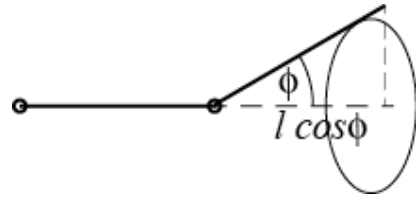
(2) Polymer Conformations II (15 pts)

(a) From the definition of the persistence length,

$$l_p = \lim_{N\to\infty} \sum_i \langle \hat{r}_1 \cdot \vec{r}_i \rangle = \frac{1}{l} \lim_{N\to\infty} \sum_i \langle \vec{r}_1 \cdot \vec{r}_i \rangle,$$

determine l_p for a freely rotating chain of bond length l and bond angle ϕ.

(b) Consider double-stranded DNA as a stiff polymer with an effective bond length, $l_{eff} = 300$ Å in 200 mM salt. Its actual "bond length" (distance between nucleotide repeats) is $l = 3.4$ Å.

(i) Which rms end-to-end distance, R_e, do you expect for a free DNA segment that consists of 10^6 repeats (*i.e.*, 2×10^6 nucleotides)?

(ii) What is the "concentration" of loops, *i.e.* the probability per unit volume to find one end of the DNA chain at the location of the other end?