Question 1 (4p)

Which two free energy contributions are accounted for in the Flory radius scaling law? Why is it possible to "ignore" the contribution from energetic interactions with the solvent molecules?

The Flory radius takes into account conformational entropy and excluded volume entropy (self-avoidance). The solvent interactions can be ignored because in the end they give rise to the same scaling with end-to-end distance (as long as we are dealing with a good solvent).

Question 2 (5p)

100 mg of poly(ethylene glycol) ($-CH_2-CH_2-O-$) with molecular weight 20 kg/mol is dissolved in 1 mL water. Will the solution be in the diluted regime or will the coils start to "overlap" in solution? Use the Flory radius $R_F = [abv]^{1/5}N^{3/5}$ with $a = 0.3$ nm, $b = 0.7$ nm and $v = 0.07$ nm^3.

Calculate $R_F = 17$ nm (with $N = 20000/44$). The molecular concentration in the solution is 100 g/L, which translates to 5 mM (for this molecular weight). That concentration corresponds to 3×10^{24} molecules/m^3, which means that each molecule has a volume of 300 nm^3 available. This is much less that the volume occupied by each polymer ($\sim R_F^3$) so the solution is not in the diluted regime.

Question 3 (3p)

According to de Gennes the height of a polymer brush in a good solvent is:

$$H_{ext} \propto \Gamma^{1/3}N$$

We have a responsive polymer brush which can collapse onto the surface into a thickness H_{col}. Assume all solvent molecules are expelled from the brush when it collapses. How does the ratio H_{ext}/H_{col} scale with degree of polymerization and grafting density?

If there is no solvent in the collapsed brush it contains only polymer. The volume that each coil occupies is $H_{col}/\Gamma = Na^3$, where a^3 is the physical size of one chemical monomer (although this does not matter for the scaling in the end). We get that:

$$\frac{H_{ext}}{H_{col}} \propto \frac{\Gamma^{\frac{1}{3}}N}{\Gamma N} = \Gamma^{-2/3}$$

Question 4 (3p)

Describe at least two conditions for a polymer melt to exhibit viscoelastic behavior. Why is this relatively rare for most polymers?

Some examples are temperature above glass transition, temperature above melting point and reasonably long chains to get entanglement. It is rare mainly because most polymers are either glassy or at least semi-crystalline at room temperature.