Chemistry C3102-2006: Polymers Section

HOMEWORK #4

Due Tuesday, May 30

1. The free energy of a chain in good solvent is estimated in the Flory argument as

$$F \sim k_B T\Big(\beta\frac{N^2}{R^3} + \frac{3R^2}{2Na^2}\Big)$$

(a) Explain physically what the first and second terms on the RHS represent and how these terms contribute to the swelling of the chain in good solvent

The free energy is comprised of two contributions: the internal energy and the entropy: $F = U - T$. The first term on the RHS of the given free energy expression is the internal energy. Castng the internal energy as a virial expansion:

$$U = Vk_BT(\beta\eta^2 + \gamma\eta^3 + \ldots)$$

where η is the density of monomers: $\eta \equiv N/V$ and β is the second virial coeffcient. The Flory argument considers only the lowest order term in this expansion, that is, the two-body or pairwise or monomer-monomer interaction contributes to U as:

$$U \sim Vk_BT\beta\Big(\frac{N}{V}\Big)^2 = k_BT\beta\Big(\frac{N^2}{V}\Big) = k_BT\beta\Big(\frac{N^2}{R^3}\Big).$$

In good solvent, the monomer-monomer interactions are repulsive, causing the chain to swell. Indeed, interactions alone would favour very large R so as to decrease the distance between monomer pairs and increase solvent-monomer interactions. Thus, a large R will decrease the internal energy contribution, $k_BT\beta\frac{N^2}{R^3}$ where $\beta > 0$, and decrease the contribution o the internal energy contribution to F. Thus, internal energy favours large R.

The second term of the RHS is the entropy of the chain, assumed to be the entropy of an ideal chain:

$$-TS(R) = -T(k_B \ln(p(\mathbf{R})) = -T(\phi - \Big(\frac{3\mathbf{R}\cdot\mathbf{R}}{2Na^2}\Big)$$

where ϕ is a constant, independent of $\mathbf{R}$. This reduces to

$$-TS(R) = k_BT\frac{3R^2}{2Na^2}.$$

As this term depends upon R^2, larger R decreases the chain's entropy (and increases the entropic contribution to F) and therefore, entropy disfavours large chains.

Thus the internal energy and entropy are in opposition or compete and the balance is determined β which is, itself, temperature dependent.

(b) The chain will adopt a size, R, that minimises the free energy. This indicates that you can find the equilibrium chain size by finding an expression for R for which $dF/dR = 0$, and ensuring that the extremum is a minimum, $d^2F/dR^2 > 0$. Demonstrate that the equilibrium R that you obtain by that exercise is equivalent to the expression obtained by equating competing energy terms in the Flory expression for F.

i. **Finding R that minimises the free energy, F.**

$$\begin{aligned} F &\sim k_B T\Big(\beta\frac{N^2}{R^3} + \frac{3R^2}{2Na^2}\Big) \\ \frac{dF}{dR} &\sim k_B T\Big(-\frac{3\beta N^2}{R^4} + \frac{3R}{Na^2}\Big) \end{aligned}$$

In order that $dF/dR = 0$, then the bracketted derivative terms must be equal to 0 or:

$$\frac{3\beta N^2}{R^4} = \frac{3R}{Na^2}$$

Before we go further, it is useful to compare the units on both sides of the above equation. On the LHS, the units are 1/length as R is in units of length, a^2 is length squared and N is dimensionless. On the RHS, β is in units of volume or length cubed so that the RHS is also 1/length. We can however cast β as $\beta' a^3$ where β' is a dimensionless second virial coefficient. Then

$$\begin{aligned} \frac{3\beta' N^2 a^3}{R^4} &= \frac{3R}{Na^2} \\ \beta' N^3 a^5 &= R^5 \\ R &\sim N^{3/5} a, \end{aligned}$$

where the last expression is the Flory radius of a solvated chain.

ii. **Equating energy terms that are in opposition.** As the first term favours large R and the entropic term disfavours large R, we can achieve the same scaling behaviour by simply equating the competing energy terms:

$$\begin{aligned} \frac{\beta' N^2 a^3}{R^3} &= \frac{3R^2}{2Na^2} \\ \beta' N^3 a^5 &= \frac{3}{2} R^5 \\ R &\sim N^{3/5} a \end{aligned}$$

(c) You are a reviewer of a manuscript that proposes a "correction term" to the Flory argument. This correction term is claimed to be necessary to more accurately reflect the entropy of a self-avoiding random walk. The propose, amended Flory argument is:

$$F \sim k_B T\Big(\beta\frac{N^2}{R^3} + \frac{3R^2}{2Na^2} R^b\Big)$$

The authors make a controversial statement which the editor is asking you to comment on directly:

> The value of b is small but can be both positive or negative $-1 < b < 1$, depending upon the chemical composition of the solvent.

What do you write to the editor?

The authors are suggesting that the entropy of a good solvent chain differ from that of an ideal chain by a factor of R^{-b} where $-1 < b < 1$. Let's explore what this means in terms of the size of the chain. The proposed size of the chain will be

$$R \sim N^{3/5-b} a.$$

This is obtained by minimising the free energy.

If $b < 0$, then for the range $-1 < b < 0$, $N^{8/5}a < R < N^{3/5}a$. That is the size of the chain scales more strongly with N than the ideal case. However, the limiting case of $b = -1$ does not make sense: $R \sim N^{8/5}a$. How can a chain size scale more strongly than the number of monomers. Clearly, the largest size of a chain is the number of monomers times the monomer size, Na. The authors suggested range of values of b include the physical impossibility that the average end-to-end distance is larger than the contour length of the chain.

if $b > 0$, then for the range $0 < b < 1$, $N^{3/5}a < R < N^{-2/5}$. that is, the size of the chain scales less strongly with N than the ideal case. However, the limiting case of $b = 1$ does not make physical sense: $R \sim N^{-2/5}a$, that is the size decreases with N. This makes no sense in both good and poor solvent!

2. Contrast the stretching-force law (force, f, versus end-to-end-distance, R) of a chain in good solvent, ideal solvent, and poor solvent.

   (a) **In poor solvent.** In poor solvent the force required to pull the a strand of chain, monomer-by-monomer, out of a collapsed (solvent excluding globule) is a constant as the work that you do to pull the chain out is dictated by the surface tension of the globule.

   $$f \sim \text{constant and independent of extension}$$

   (b) **In ideal solvent.** In theta solvent, the force required to extend the ends of the chain a distance R, is entirely entropic and

   $$f = -kR$$

   where k is a spring constant $k \sim k_B T/(Na^2)$.

   (c) **In good solvent.** In good solvent the force required to extend the ends of the chain will be similar to that of the ideal chain at large values of R where the monomers of the stretched chain are far apart so that monomer-monomer repulsion does not contribute; but at smaller R where monomers can be in close distance, monomer-monomer interactions can contribute. To quantify this contribution, we can write down the Flory argument:

   $$f = -\frac{dF}{dR} = k_B T\Big(\frac{3N^2a^3}{R^4} - \frac{3R}{Na^2}\Big).$$

   As you see, for large R, the first term is proportional to R^{-4} will be small in comparison to the entropic term, and consequently you can expect that the stretching at high extensions is Hookean. To quantify that we can recast the above force law by gathering up N terms, making terms as dimensionless as possible:

   $$\begin{aligned} f &\sim 3k_B T\Big(\beta'\frac{N^2a^3}{R^4} - \frac{R}{Na^2}\Big) \\ \frac{fa}{k_B T} &\sim \beta'\Big(\frac{R_0}{R}\Big)^4 - \frac{Ra}{R_0^2} \end{aligned}$$

where I have let R_0 represent the size of the chain under ideal conditions. Now clearly, to stretch a chain, $R > R_0$ as the Flory radius is larger than R_0. So we need to consider plotting the equation

$$\frac{fa}{k_B T} \sim \beta'\Big(\alpha^{-4} - \frac{\alpha}{\sqrt{N}}\Big)$$

That is, we plot the dimensionless force, $fa/(k_B T)$ versus α for $\alpha = R/R_0 > 1$ with given values of β' and N. You see that as you stretch more, that is, as α gets larger, you recover the purely entropic stretching term.

3. Qualitatively describe what the force of squashing of a chain in poor solvent over dimensions ranging from $H \sim N^{3/5}a$ to $H \sim a$.

   In poor solvent, the chain will collapse onto the surface into a monomer-filling, solvent-excluding globule. Depending upon whether the polymer wets the surface or not (as quantified by the contact angle), the size of the globule can be between $R \sim N^{1/3}a$ for a non-wetting surface, or $R \sim a$ for polymer-attractive surface where the polymer forms a pancake. Thus, there will be no polymer squashing until the slit distance is reduced to R. As we are looking only at slit distances larger than a, we will consider only the non-wetting surface where the globule size is

   $$R \sim N^{1/3}a.$$

   The spherical globule is unchanged until $H \sim N^{1/3}a$. For slit widths smaller than this, the globule will be squashed. The work that goes into squashing does not change the entropy of the chain much, but is expended in creating a solvent/globule surface whose area increases from the minimal surface area of the original spherical globule. So the force is identified with the change in surface energy with compression. To quantify this somewhat, let's assume when it is squashed, the chain forms a cylinder of diameter D. The volume of the cylinder is taken up by the monomers

   $$\pi D^2 H = Na^3,$$

   so that D of the cylinder is determined by the slit distance using $D \sim \sqrt{Na^3/H}$. Now the energy associated with the surface of the cylinder comes in 2 parts: Let γ_H present the energy per area of the globule-compressing surfaces and γ_S the energy per area of the globule-solvent contact so that

   $$E = 2\gamma_H \pi D^2 + \gamma_S 2\pi DH$$

   As D depends upon H, we rewrite using

   $$E = 2\gamma_H \pi \frac{Na^3}{H} + \gamma_S 2\pi \sqrt{\frac{Na^3}{H}}H.$$

   Then the force is $f = -dE/dH$ (and not worrying about constants...), or

   $$f = -\gamma_H \frac{Na^3}{H^2} + \gamma_S \sqrt{\frac{Na^3}{H}}$$

   surface that is in contact with solvent and not the squashing surfaces