Polymer Physics (RPK-B, week 2)

1. Exercise 5.1 (R&C)
   Note that v is negative so we are dealing with a partially collapsing chain here. Partial, because $|v|$ is still a lot smaller than $b^3 = 125$ Å. We therefore need the picture developed in section 3.3. Chains that are smaller than the thermal blob size will be ideal and, those that are longer will take the form of a dense globule of thermal blobs, for which we derived

$$R_{\text{gl}} \approx \frac{b^2}{|v|^{1/3}} N^{1/3} \ .$$

   The number of monomers in a thermal blob is $b^6/v^2 = 100$, so that, not surprisingly, the middle option is exactly at the boundary between the two behaviors

   (i) This chain is below the thermal blob size and therefore ideal, $R \approx b\sqrt{N} \approx 35$ Å.

   (ii) Here we can choose which equation we use, as we are on the boundary between the two behaviors. Both formulas give $R \approx 50$ Å.

   (iii) Now we need the dense globule of thermal blobs, and get $R \approx 108$ Å.

2. Exercise 5.10 (R&C)

   (i) $r \approx bn^{1/2}$

   (ii) $r \approx bn^{1/2}$

   (iii) $r \approx bn^{1/2}$ for $n < g_{\text{T}}$, but $r \approx \frac{b^2}{|v|^{1/3}} n^{1/3}$ for $n > g_{\text{T}}$.

   (iv) Chains in the supernatant (low ϕ) behave like in item (iii), but chains in the precipitate (high ϕ) will be ideal (see discussion on page 176).

   (v) All chains are ideal. $r \approx bn^{1/2}$.

   (vi) Self-avoiding walk of thermal blobs: $r \approx b \left(\frac{v}{b^3}\right)^{2\nu-1} n^{\nu}$.

   (vii) $r \approx b \left(\frac{v}{b^3\phi}\right)^{(\nu-1/2)/(3\nu-1)} n^{1/2}$.

   (viii) All chains are ideal. $r \approx bn^{1/2}$.

3. Exercise 5.12 (R&C)

   (i) The chain can be modeled as a sequence of Pincus blobs (tension blobs). Inside such a blob, the chains essentially do not feel the stretching force and they behave as unperturbed chains in semidilute solution do, i.e.,

$$\xi_{\text{P}} \approx b \left(\frac{v}{b^3\phi}\right)^{\frac{\nu-1/2}{3\nu-1}} g_{\text{P}}^{1/2} \ . \tag{1}$$

   The pulling makes for a roughly linear chain of N/g_{P} Pincus blobs of size ξ_{P}, so that the ends are $R_f = \xi_{\text{P}} N/g_{\text{P}}$ apart. Using Eq. (1) to eliminate g_{P} from this, we get

$$R_f = \frac{b^2 N}{\xi_{\text{P}}} \left(\frac{v}{b^3\phi}\right)^{\frac{2\nu-1}{3\nu-1}} = \frac{R_0^2}{\xi_{\text{P}}} \ ,$$

   where we used Eq. (1) evaluated at $g_{\text{P}} = N$ to get the mean square end-to-end distance of the unperturbed chain R_0. This gives $\xi_{\text{P}} =$

R_0^2/R_f and hence the number of Pincus blobs is $R_f/\xi_{\mathrm{P}} = (R_f/R_0)^2$. Estimating the stretching free energy as $k_{\mathrm{B}}T$ per Pincus blob, we get

$$F = k_{\mathrm{B}}T \left(\frac{R_f}{R_0}\right)^2 .$$

This result is valid until R_f gets so large that the Pincus blob size has shrunk to the correlation length. Demanding that $\xi_{\mathrm{P}} = R_0^2/R_f$ is larger than or equal to ξ from Eq. (5.23) in the book results (after shuffling a bit with the exponent of ϕ) in

$$R_f \leq \frac{R_0^2 \phi}{b} \left(\frac{v}{b^3\phi}\right)^{\frac{2\nu-1}{3\nu-1}} .$$

(ii) Now the Pincus blobs are smaller than the correlation length so we need to use Eq. (3.77) in the book to describe what happens inside them, giving

$$\xi_{\mathrm{P}} \approx b \left(\frac{v}{b^3}\right)^{2\nu-1} g_{\mathrm{P}}^{\nu} .$$

The calculation now follows the same arguments as the previous one. It is convenient to use the size R_{F} the swollen chain would have had if there were no correlation effects to simplify the resulting expressions. The number of Pincus blobs turns out to still be given by $\left(\frac{R_f}{R_{\mathrm{F}}}\right)^{1/(1-\nu)}$, as we also found in Eq. (3.36) in the book. The fact that in this semidilute solution R_{F} does not represent the unperturbed size only affects the prefactor of the free energy, not its scaling with R_f. We therefore still have the free energy

$$F(R_f) \approx k_{\mathrm{B}}T \left(\frac{R_f}{R_{\mathrm{F}}}\right)^{1/(1-\nu)} .$$

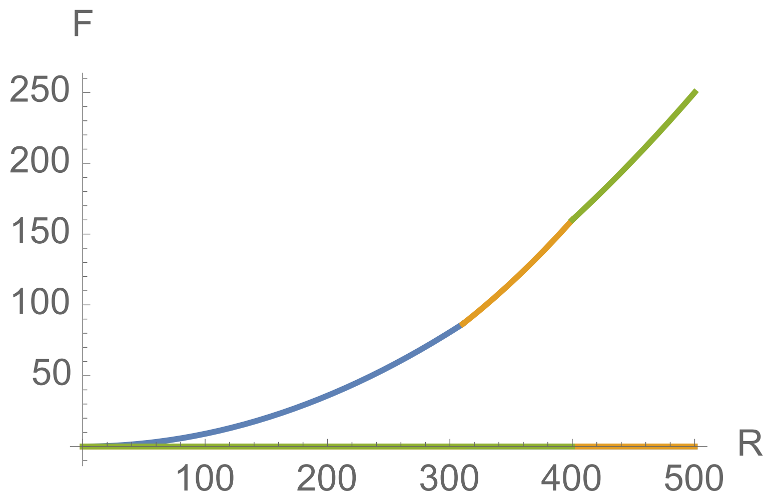
This result is valid for R_f that are larger than the limit of the previous section but smaller than the R_f at which the Pincus blob coincides with the thermal blob. The latter happens when the number of Pincus blobs is equal to the number of thermal blobs $N/g_{\mathrm{T}} = Nv^2/b^6$, so that

$$\frac{R_f}{R_{\mathrm{F}}} \leq \left(\frac{Nv^2}{b^6}\right)^{1-\nu} .$$

(iii) In this case the chain conformations are ideal inside the Pincus blobs so the result derived in Eq. (3.35) in the book applies without any modifications. It is valid when R_f is larger than the upper bound derived for the intermediate regime in the previous item.

(iv) The answer to this question has been merged in to the previous three items.

Finally, a plot of the full solution to this exercise, showing the three regimes for the case $b = 1,\ v = 0.4,\ \phi = 0.25,\ N = 1000$.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