Soft Matter Theory
Homework 3
Due: 14 June 2022

1. In this problem we will develop a scaling theory for the free energy of a polymer adsorbed to a surface. For a polymer adsorbed to a surface, each monomer is weakly attracted to the surface with energy $-\delta\, k_B T$ where $0 < \delta < 1$. The chain would like to increase the number of monomers at the surface, but it sacrifices conformational entropy by confining itself to the surface to do so.
    a. The chain has an adsorption blob of size ξ_{ads}, which is a small segment of the chain that has a cumulative energy of $k_B T$ due to surface-monomer interactions. Assuming a real (swollen) chain, <u>calculate the adsorption blob size</u>. Do this by (i) calculating the volume fraction of an adsorption blob in terms of ξ_{ads} and (ii) then calculate the number of monomers at the surface in terms of ξ_{ads}. You can then use the adsorption energy and the total energy of the thermal blob to obtain ξ_{ads}. *Hint: The answer is* $\xi_{ads} = b/\delta^{3/2}$.
    b. Using scaling methods similar to our examples in class, calculate F_{ads}, the adsorption free energy.
2. Consider the excluded volume potential between spherical particles (radius R) with the effective pairwise interaction potential

$$U(r) = \begin{cases} \infty, & r \le 2R \\ -k\, T_0\, (2 - \dfrac{r}{2R}), & 2R \le r \le 4R \\ 0, & r > 4R \end{cases}$$

where T_0 is the strength of the attractive potential with $T_0 = 100\text{K}$.
    a. Plot the potential as a function of r.
    b. Calculate (numerically is fine) the excluded volume of these particles as a function of T. Plot $v_{ex}(T)/R^3$ from 100 K to 1000 K and determine the θ-temperature.
3. Consider a linear polymer chain with $N = 400$ Kuhn monomers with length $b = 0.4$ nm in a solvent with θ temperature of 27 C. The mean-field approximation of the interaction part of the free energy for a chain of size R is:

$$F_{int} = k_B T\, R^3 \left[B\, \left(\frac{N}{R^3}\right)^2 + C \left(\frac{N}{R^3}\right)^3 + \cdots \right]$$

Where $B(T) = \left(1 - \frac{\theta}{T}\right) b^3$ and $C\ = b^6$.
    a. Use Flory theory to estimate the size of the chain at the Theta temperature. Give both the symbolic expression and the numerical value of the chain size in nm.
    b. Use Flory theory to estimate the size of the swollen chain at 60 C due to excluded volume repulsion (ignore 3 body repulsion, give result both symbolically and in nm).
    c. What is the number of Kuhn monomers in the largest chain that stays ideal at 60 C. (*Hint: At what N do two-body interactions become important?)*
4. Use the posted code (Rosenbluth Monte Carlo) to calculate the rms end-to-end distance of a self-avoiding FJC of length $N \in [1, 100]$. Note that this Rosenbluth MC code generates chains with non-Boltzmann statistics, so the ensemble average requires a statistical weight. You can an ensemble average using the formula,

$$\langle R \rangle = \frac{\sum_n W_n R_n}{\sum_n W_n}$$

where W_n is the statistical weight and R_n is the rms end-to-end distance of chain n. Use this formula to make a plot of $\frac{\ln(\langle R\rangle/b)}{\ln N}$ versus $\ln N$. What is the scaling exponent you obtain in the limit of large N?