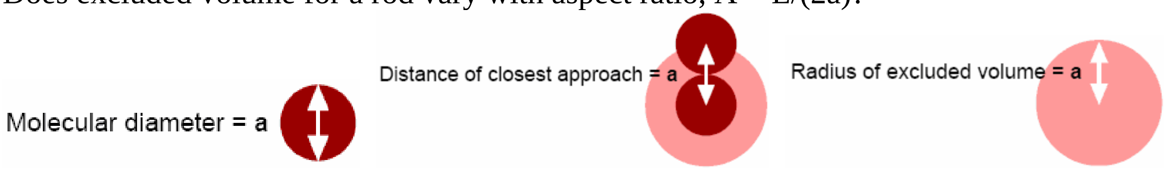
050429 Quiz 5 Polymer Properties

The concept of excluded volume began with an extremely simple physical model based on common sense. If we consider an ideal gas composed of non-interaction spheres the ideal gas law applies, $P/RT = n/V = \phi$, where the system concentration is given by ϕ. For a non-ideal gas with hard core interactions we consider the virial expansion in ϕ, $P/RT = \phi + A_2 \phi^2 + A_3 \phi^3 + \ldots$ A_2 has units of volume per number and represents binary interactions (squared ϕ). A_2 increases the observed pressure so effectively reduces the available volume. The lost volume is called the excluded volume.

a) Show that for spheres the excluded volume is given by $4V_0$ (V_0 is the atomic volume and divide by 2 for 2 atoms). Also, calculate the volume excluded for a rod of length L and radius a. Does excluded volume for a rod vary with aspect ratio, $A = L/(2a)$?



b) In polymers, P can be related to the osmotic pressure, π, and ϕ is related to the concentration. The second virial coefficient is given by $V_{excluded}/2$ where $V_{excluded}$ is the excluded volume for the entire chain of length N, summed for each mer unit. Give an expression, using the interaction parameter χ, for the excluded volume of a polymer chain. By equating this expression with that for a sphere, give the scaling of R_{sphere} with $N_{polymer}$.

c) Write an expression for the probability of an end to end distance R for a polymer chain that displays excluded volume using the interaction parameter χ. Where is the excluded volume fraction in this expression?

d) Sketch a plot of R_g and R_h versus temperature for a polymer coil near the θ temperature. Why does R_g differ from R_h? Give the Flory-Krigbaum expression for coil size. Does the Flory-Krigbaum expression for coil size agree with this plot?

e) In a plot of log intensity versus log q show a Gaussian chain with persistence noting R_g, l_p and the scaling regime; the same coil in a good solvent noting the same regions and regions that are intransigent (don't change) to solvent goodness; and a coil that displays thermal blobs (intermediate R_g). Explain how the thermal blob can structurally accommodate changes in χ with temperature.

ANSWERS QUIZ 5

Sphere

a) $V_0 = \frac{4}{3}\pi a^3$

$V_{ex} = \frac{\frac{4}{3}\pi (2a)^3 V_0}{2\,\frac{4}{3}\pi a^3} = 4V_0$

Rod is same as figure

$V_{ex} = AL = \frac{L\pi(2a)^2}{2} = 2V_0 = 4\pi a^3 A$

$V_0 = \pi a^2 L$

$= 2\pi a^3 A$

$V_{ex} \sim A$ for fixed "a"

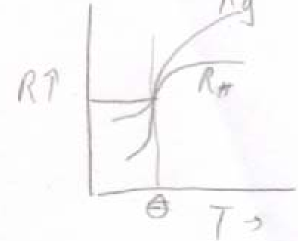
b) $N^2 V_0 \left(\frac{1}{2} - \chi\right)$

$N^2 V_0 \left(\frac{1}{2} - \chi\right) = \frac{16}{3}\pi a^3$

$a = \left(\frac{3}{16\pi}\right)^{1/3} N^{2/3} V_0^{1/3} \left(\frac{1}{2} - \chi\right)^{1/3}$

c) $P(R) = kR^2 \exp\left(\frac{-3}{2}\left(\frac{R}{R_g}\right)^2 - \underbrace{\left(\frac{N^2 V_0 \left(\frac{1}{2} - \chi\right)}{R^3}\right)}_{\text{Volume Fraction Excluded}}\right)$

d)



R_h is related to the smallest profile

$\left(\frac{R}{R_0}\right)^5 - \left(\frac{R}{R_0}\right)^3 = \frac{9\sqrt{6}}{16} \frac{V_0(1-2\chi)}{b^3} \sqrt{N}$ or $R \sim (1-2\chi) N^{3/5}$

Yes agrees

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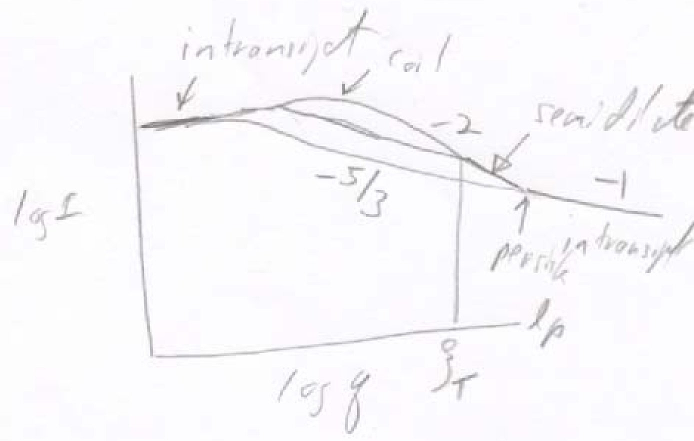
(2)

(c)



ξ_T gets smaller in size with increasing T between R_g & b