Quiz 2 Polymer Properties September 6, 2013 (Take Home Due on September 9)

1) The figure below shows several models for semi-flexible polymers.

   a) In Figure "d" the chain structure resembles that of nanoparticle aggregates (top micrograph). Such aggregates do not display a measurable persistence length. Consider the difference between Figures b and d and give a general hypothesis for why this is the case. What are the minimum and maximum values possible for l_k?

   b) Consider the chain in Figure "b". The persistence length can be estimated by $<t_i \bullet t_j> = e^{-1} = \cos(68.4°)$. Estimate the persistence length using this approximation and compare it with l_k from the figure.

   c) The glass microfiber shown in the middle micrograph does not display a measurable persistence length while the worm like micelle in the bottom micrograph does display a measurable persistence length. Both display chain scaling similar to that of polymer chains in solution. Explain this behavior.

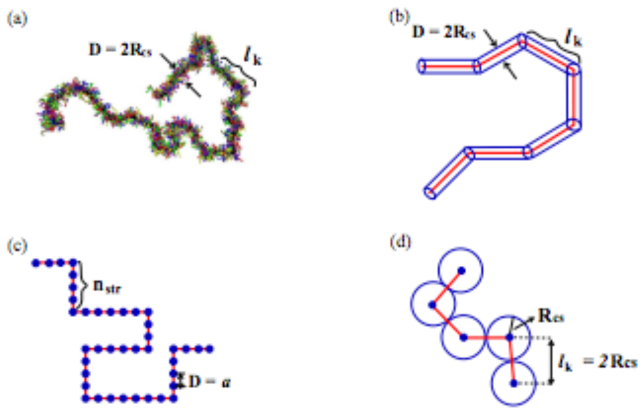
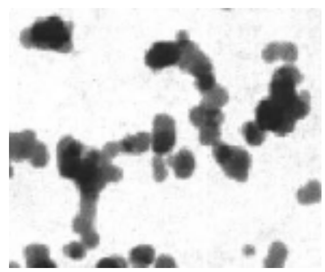
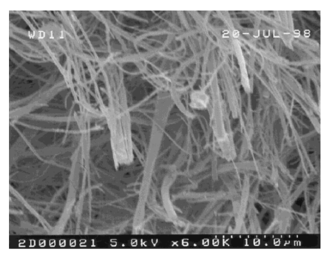


FIG. 4. Various models of semiflexible polymers, as discussed in the context of simulations. Case (a) shows the snapshot picture of a typical conformation of a simulated bottle-brush polymer using a backbone chain length $N_b = 1027$, side chain length $N_s = 24$, projected into the xy-plane (this model is discussed in more detail in Sec. 3). Case (b) shows a model of freely jointed cylindrical rods of Kuhn step length ℓ_K and diameter $D = 2R_{cs}$, with R_{cs} the cross-sectional radius (if $R_{cs} = 0$ this leads to a simple off-lattice random walk configuration, while excluded volume interaction is introduced if overlap of the cylinders is forbidden). Case (c) shows the SAW model on the square lattice with lattice spacing a ($D = a$ in this case), where 90° bends cost an energy $\varepsilon_b \gg k_B T$, so the chain consists of straight pieces where n_{str} steps go in the same lattice direction, with $n_{str} \gg 1$. Case (d) shows a model of tangent hard spheres with radius R_{cs} (and $\ell_k = 2R_{cs}$).





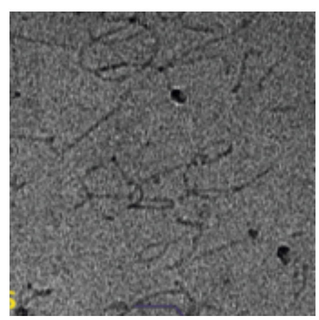


Figure 1. Left, from "Estimation of Persistence Lengths of Semiflexible Polymers: Insight from Simulations." HP Hsu, W Paul, K Binder, Polymer Science Series C (2013) Cornell University Press. Micrographs: TOP, Silica Nanoparticles Chain Aggregates (primary particles ~2nm) J. Appl. Phys. 97 054309 (2005); MIDDLE, Glass micro-fibers J. Polym. Sci. Polym. Phys. 36 3147 (1998); BOTTOM, Worm-like micelles, unpublished micrograph.

d) For the model of Figure 1d the bending force constant is defined by $F_{bend} = k_{bend} |\Delta\theta|$, where F_{bend} is the bending force and $\Delta\theta$ is the change in angle for three beads. It was proposed that $k_{bend} = k_B T l_p/(2R)$. If $l_{Kuhn} = 2l_p$ what is the value for the bending force constant in figure 1d? What does this imply concerning the flexibility of the model shown in Figure 1d?
Biopolymers 20 1481 (1981); Biopolymers 13 217 (1974).

e) Explain the three regimes of Figure 2a, below. (Swollen coils occur when chains are long enough to bend back and touch themselves.)

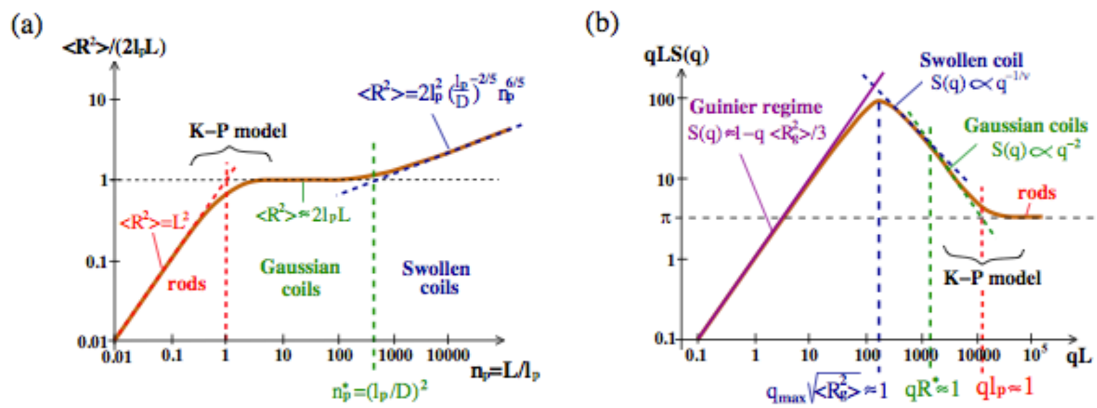


FIG. 5. (a) Schematic plot of the normalized mean square radius $\langle R^2\rangle/(2\ell_p L)$ versus $n_p = L/\ell_p$ (apart from a factor of 2 this is the number of Kuhn segments), on log-log scales. The Kratky-Porod (K-P) model describes the crossover from rods ($\langle R^2\rangle = L^2$) to Gaussian coils ($\langle R^2\rangle = 2\ell_p L$). At $n_p^* = (\ell_p/D)^2$, according to the Flory theory a crossover to swollen coils occurs, where $\langle R^2\rangle \propto n_p^{2\nu}$ with $\nu = 3/5$ (according to the Flory theory). (b) Schematic Kratky plot of the structure factor of a semiflexible polymer, $qLS(q)$ plotted vs. qL, on log-log scales. Four regimes occur: in the Guinier-regime, $S(q) \approx 1 - q^2\langle R^2\rangle/3$; it ends at the maximum of the Kratky plot, which occurs roughly at $q_{\max}\sqrt{\langle R^2\rangle} \approx 1$ (constants of order unity being ignored throughout). For very large L then a regime of swollen coils with $S(q) \propto q^{-1/\nu}$ is observed, until near $qR^* \approx 1$ a crossover to Gaussian coil behavior occurs ($R^* \approx \ell_p^2/D$). In the Gaussian coil regime $S(q) \propto q^{-2}$, until at $q\ell_p$ of order unity the crossover to the rod-like regime occurs ($qLS(q) = \pi$). Only the latter two regimes are captured by the Kratky-Porod model.

Figure 2 from HP Hsu, W Paul, K Binder, Polymer Science Series C (2013) Cornell University Press.

2) The probability for a random polymer chain to have an end-to-end distance $\langle R^2\rangle^{1/2}$ follows a Gaussian distribution if the chain has no excluded volume, that is, if the chain follows a diffusive pathway with no constraints. This Gaussian function has the same exponential form as the Boltzmann distribution allowing for an expression for the energy of an isolated chain as a function of $\langle R^2\rangle^{1/2}$.

a) Give the Boltzmann distribution and the Gaussian distribution for end-to-end distance $\langle R^2\rangle^{1/2}$.

b) What are the problems with using the Gaussian distribution for a polymer chain (truncation error, self-avoidance, other problems).

c) Obtain the spring constant for a Gaussian coil.

d) What are the limits of this spring constant? (Consider what happens in compression, large extension, and under other conditions.)

e) Would the expression for the energy of an isolated coil work for a cyclic polymer chain?

ANSWERS: Quiz 2 Polymer Properties September 6, 2013 (Take Home Due on September 9)

1) a) l_K is too small to observe, i.e. it is smaller than the diameter of the structure. The Minimum size for l_k is somewhat larger than the diameter (say 2.5 times the diameter to be observed by scattering) and the maximum size is L, the contour length.

b) by drawing tangents to the curve a persistence length (where the tangents are offset by about 68°) of about twice the sketched l_k is observed. This means that l_k is actually four times what is shown.

c) The persistence length for the GMF must be smaller than the diameter of the fibers. Some of the fibers show high curvature if you look closely, and using the 68° rule it is conceivable that the persistence length is smaller than the diameter.

d) From the figure l_K is 2R, so l_p is R and the spring constant is kT/2. The structure is highly flexible since the thermal energy is twice the energy needed to flex the structure.

e) For short chains the structure is below the persistence length so it appears as a rod. At larger lengths the structure is convoluted and shows Gaussian structure. Above a certain length it an fold back on itself and display excluded volume behavior.

2) a)

Boltzman Probability
For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

b) The chain is of finite contour length, $L = N_k\, l_k$, while the Gaussian function has no size limits. The chain generally displays excluded volume which is not accounted for in the Gaussian distribution.

c)

$$F = \frac{dE}{dR} = \frac{3kT}{nl_K^2} R = k_{spr} R$$

d) The function is useful only at small extensions, it is not good for compression, the chain must be in thermal equilibrium (no quiescent stress or strain) chain can not experience confinement forces such as at a surface etc.

e) It might work but strictly it would not since the cyclic has no ends so there is no end to end vector, and no Gaussian probability. You might be able to work around this.