# Polymer Properties
## Quiz 2
## January 25, 2017

Hsiao-Ping Hsu, Wolfgang Paul, and Kurt Binder [*Macromolecules* **43** 3094–3102 (2010)] simulated linear (Fig. 3) and bottle-brush (Fig. 5) polymers with Gaussian scaling (3&5b), $d_f = 2 = 1/\nu$, and under good solvent conditions (3&5a), $d_f = 5/3 = 1/\nu$. They found that the persistence length does not rapidly converge to a plateau value under good solvent conditions.
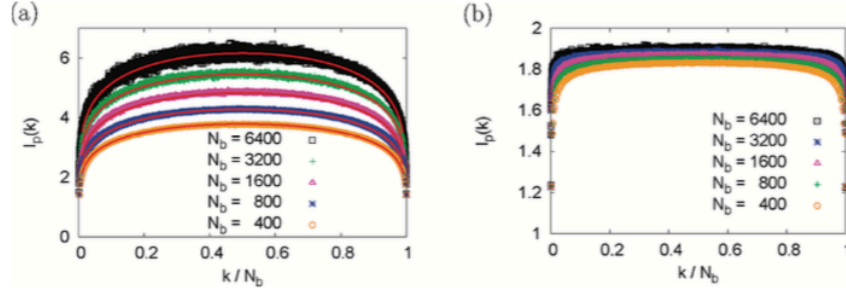


**Figure 3.** Flory's definition $l_p(k)$ for the local persistence length of a polymer chain (eq 6), plotted as a function of $k/N_b$ for $N_b = 400$ to $N_b = 6400$, as indicated in part a. Part a refers to the standard SAW model on the simple cubic lattice, and solid curves are best fits to eq 7, using $\alpha = 1.6888$ and $\nu = 0.5876$. Part b shows corresponding data for the same model at the $\Theta$ temperature (cf. Figure 2b).
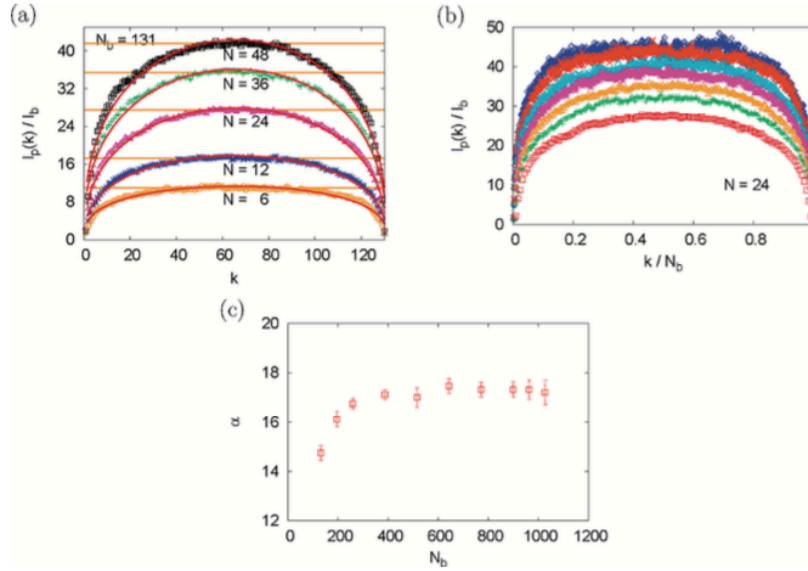


**Figure 5.** Local persistence length $l_p(k)$ plotted vs $k$ for $N_b = 131$ (a) side chain lengths $N = 6, 12, 24, 36,$ and 48 are shown (from bottom to top). In part a, dotted horizontal curves (plateau) indicate estimates $l_p^{(1)}$ of the persistence length (Table 1) and solid curves are fits to $l_p(k)/l_b = \alpha[k(N_b - k)/N_b]^{2\nu-1}$, cf. eq 7. The values of the parameters $\alpha$ and $\nu$ are listed in Table 2. Part b shows $l_p(k)$ plotted vs $k/N_b$ for fixed side chain length $N = 24$ and several choices of the backbone length, namely $N_b = 131, 195, 259, 387, 515, 771,$ and 1027 from bottom to top. Part c shows a plot of $\alpha$ vs $N_b$ when the simulation data are fitted to eq 7 in the range $0.3 < k/N_b < 0.7$.

a) Why do you think expanded coils might not show a plateau in persistence length while Gaussian chains show a clear plateau?

b) Hsu proposes to use an equation by Schäfer to model the behavior of persistence length in linear polymers with no side chains shown in Fig. 3a, $l_p/l_{bond}$ versus $k/N_b$,

$$\ell_p(k)/\ell_b \approx \alpha[k(N_b-k)/N_b]^{2\nu-1} \tag{7}$$

where k is the chain index and $N_b$ is the polymer chain length, $\alpha$ is a constant unique to each polymer. Consider the limits of equation 7 for $k = 0$ and $k = N_b$. Do these make sense? How about the limits of $N_b \Rightarrow 1$ and $N_b \Rightarrow \infty$? What about if $d_f = 1$?

c) In Figure 5a Hsu shows the behavior of bottle-brush polymers of variable arm length for chains with $N_b = 131$, N is the length of the side chains. Figure 5b shows the behavior as a function of $N_b$. Why does the arm length affect this behavior? Is k the correct parameter to use as the x-axis in Figure 3a? Would $k/l_p$ make more sense?

d) Figure 5c shows how the polymer specific constant, $\alpha$, depends on side chain length N. Discuss the observed behavior. What is $\alpha$?

e) There are two ways to simulate self-avoidance (good solvent behavior). A) Chains can be formed in an arbitrary condition and then allowed to equilibrate for a very long time with a repulsive potential in order to reach equilibrium behavior. B) A simpler method where chains are grown and if they cross themselves the growth is restarted so only chains that do not cross are retained. In this paper the PERM algorithm is used [Peter Grassberger PRE **56** 3682-93(1997)] that is a form of the latter chain rejection algorithm. How do you think these two simulation methods could impact the results in this study? In the first case what is the impact of not reaching equilibrium and in the second what is the impact of rejecting chains that do not conform to self-avoidance in terms of Figures 3 and 5.

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a)  There is no physical reason why persistence would be effected by long-range interactions since persistence length is controlled by local chain features like bond rotation angle. Local features shouldn't be affected by chain self-avoidance at long chain index differences.  Experimentally there is evidence that chains of the same length in good and theta solvents have the same persistence length.  This brings one to consider what possible flaws could exist in the simulations that could lead to this result.  Simulation of self-avoiding chains is not trivial and this may be an indication of the possible problems that could exist in these simulations.

b)  At the limits of k, the chain has a persistence length of 0.  This seems to contradict theory. When $N_b = 1$ $N_b - k = 0$ so the single chain unit has persistence of 0.  When $N_b = \infty$ the equation seems OK.  If $d_f = 1$ then $v = 1$ and the chain still behaves with a variable persistence length even though it is a rod.  This seems to be a major flaw in the equation.

c)  Arm length is expected to make the chains less flexible due to steric interaction.  So the behavior in Fig. 5a is expected.  $k/l_p$ would make more sense.  The chain is made up of Kuhn segments not bonds so k is not the proper parameter when persistence length varies.

d)  When $\alpha$ increases $l_p$ increases relative to the bond length.  However, there is no limit, such as $N_b = \infty$, where $l_p/l_b = \alpha$.  $\alpha = (l_p(N_b/2)/l_b) (N_b/2)^{2-4v}$.  So it is rather complex.

e)  Say that the starting condition of the chain for the equilibrium simulation is for all of the units to be crumpled into a compact object.  Then you would expect that the end groups would first relax and appear flexible while the center might take longer to reach a flexible state.  If equilibrium took much longer for a self-avoiding chain it would explain Figures 3 and 5.

In the second simulation method, that chosen by this group, the arbitrary rejection of self-avoiding chains would tend to reject chains that are bent since the chains would need to bend to cross themselves.  It would favor chains with higher persistence length. Comparing figures 3, a and b it is seen that the self-avoiding chains have a significantly higher persistence length consistent with this artifact.  This would seem to indicate that the sampling method has a strong impact on the observed persistence length.

Rejecting chains that cross at large index differences would favor rejection after a long growth time. So the accepted chains have an initial growth process similar to the Gaussian chain, then at long indexes are reject in favor of extended chains with a higher persistence.  This could lead to the observed behavior and is not related to the actual behavior of self-avoiding chains at equilibrium in solution in any way.   Overall, there is a large potential for errors in this simulation.