060407 Quiz 2 Polymer Properties

1) Polymers are best described by statistical features since they are disordered structures. For a system described by a large number of random events the Gaussian distribution is often used to approximate the average features.

   a) Write the Gaussian distribution function for 1d and sketch the distribution curve (probability versus x or R).
   b) We mentioned in class that a Gaussian chain displays a mass-fractal dimension of 2 making it a 2d object. Is there a part of the Gaussian distribution function that indicates this dimensionality? If no explain why; if yes indicate which part.
   c) Would the Gaussian distribution be appropriate for a self-avoiding walk? Explain how or why.
   d) Would the Gaussian distribution be appropriate for a chain whose connectivity dimension, c, was 1.5 and whose minimum dimension, d_min was 1.33? Explain what c and d_min are.

2) In class we mentioned renormalization of the Gaussian structure.

   a) What does normalization mean? Think of a normalized distribution function and generalize the concept.
   b) In your own words explain (or guess) what renormalization means.
   c) In class we used the concept of renormalization to allow for an arbitrary (non-physical) value for the primary step length. Give an example of a situation where it would be useful to use a step length other than the physical persistence length.
   d) Give an expression for the effect of z, the lattice coordination number on the persistence length.
   e) Explain how the bond rotational-energy-map (energy versus rotation angle ψ) from last week's quiz could be related to "z".

3) This week's graduate seminar speaker, V. Davis, mentioned that carbon nano-tubes can display a type of persistence length that is similar to persistence in polymers.

   a) Is a carbon nano-tube's long-range conformation subject to thermal equilibrium if the chain is longer than a micron? Explain.
   b) Is a CNT's short-range conformation subject to thermal equilibrium given the structure of a rolled graphitic sheet with basically a single planar bond conformation.
   c) Give some problems you might expect from the application of the concept of a thermally equilibrated persistence length to CNT's.
   d) V. Davis cooks her tubes with lithium to functionalize and compatibilize the tubes with polymers and solvents. Would you expect such treatment to affect the observed persistence length? How or why?
   e) Polymers are commonly found at 100% concentration (a melt) while CNT's will form a useless clump at high concentrations. Explain this observation as best you can. (The word "entropy" may or may not be of use here.)
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1) 

\[ p(x, \mu, \sigma) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2} \]

\[ p(R, n, \beta) = \frac{\delta r}{(2\pi \sigma^2)^{1/4}} e^{-\frac{1}{2} \left( \frac{R}{\sigma} \right)^2} \]

b) The standard deviation defines the second moment of size as \( nb^2 \). This defines a 2d object.
c) No, a SAW is not a random structure. There is no simple distribution function to describe a SAW.
d) While the fractal dimension of such a chain is 2 (because \( 1.33 \times 1.5 = 2 \) the chain does not follow the Gaussian probability function for the same reason that a disk \( (c=2, d_{\text{min}}=1) \) would not follow Gaussian statistics. A disk is not built from a random walk, nor is the chain of \( c = 1.5 \) and \( d_{\text{min}} = 1.33 \).
e) \( c \) is the connectivity dimension. \( c \) has a value of 1 for a linear chain and \( d_f \) for a regular object. \( c \) relates the minimum path, \( p \), to the molecular weight \( z \) so \( p^c = z \). \( d_{\text{min}} \) is the mass fractal dimension for a primitive path \( p \) in the structure so that \( p = R^{d_{\text{min}}} \).

2) 
a) Normalization of a probability function means that you integrate the probability function from + to - infinity and divide the function by this value so that the integral is set to 1. This means that the function represents the actual probability of an event happening rather than this probability times some constant. Normalization does not effect the shape or nature of a distribution function (unimodal, bimodal etc.), it only effects the absolute value of the function.
b) Renormalization means to change the base value of a structure, that is to use an arbitrary step length such as the statistical segment length. This is possible for a fractal structure where structural scaling is uniform across size scales (displaying self-similarity).
c) If we know the number of chemical units, \( N_{\text{chem}} \), in a polymer (from synthesis) but do not know the number of persistence units, it is possible to measure the chain size, \( R \), and to calculate an arbitrary statistical segment length, \( l_{\text{ssl}} \), that is defined by \( l_{\text{ssl}} = R / \sqrt{N_{\text{chem}}} \). This value can be used to calculate chain size, \( R \), from \( N_{\text{chem}} \) for other similar polymers without knowledge of the persistence length or \( N_{\text{per}} \).
d) \( l_{p,\text{eff}} = l_p (z/(z-2))^{1/2} \)
e) More restrictions on bond rotation effectively decrease \( z \). If the bonds were freely jointed \( z \) would be infinite. \( z \) is lower for a fixed bond angle and free rotation and lowest for constrained rotation about a fixed bond angle.
3) a) No. A micron scale object is not subject to thermal motion in the way that a polymer chain is. There is a fundamental difference between molecules (which hold kT energy) and macroscopic objects that do not. A CNT of such large size is not a molecule in this sense.

b) No. There is little or no local flexibility in this structure. The persistence length observed for these structures is due to the modulus of an almost macroscopic object. The persistence is not derived from an energy map such as seen for bond rotation in polymers.

c) One problem is Davis' somewhat naïve attempt to observe a "phase-diagram" for this system. Since the objects are not subject to thermal equilibration there is no reason to expect to observed thermodynamic behavior. The lack of thermal dependence to miscibility in this system indicates that is not a thermodynamic system but a macroscopic system. (There are many answers to this question.)

d) The chemical modification of this system perturbs the conjugation of the carbon bonds and dramatically alters all properties of the tubes. The persistence length would probably decrease since the structure becomes much less rigid. Alternatively, steric interference of the alkyl side groups that are added could possibly increase persistence but this seems unlikely. Persistence would change and would probably decrease.

e) A polymer chain explores the available conformational space and this exploration allows for a number of different states and a higher entropy. The nano-tubes do not display entropy since, they are too large to be subject to thermal equilibration and because they are so rigid that they display essentially only one state. This means that individual nanotubes, as macroscopic objects, do not display useful properties we associate with a single phase material.