120215 Quiz 4 Morphology of Complex Materials

1) A Gaussian polymer has a probability for an end-to-end distance R proportional to exp(-$3R^2/(2nl^2)$). This is compared to the Boltzmann probability to obtain an expression for the energy of this chain under the assumption that the chain conformation is thermally equilibrated.
   Surfactant bilayer membranes are flexible, thermally equilibrated structures at room temperature (M Nagao *Phys. Rev. E* **80** 031606 (2009)) that should follow a 2d Gaussian probability function of exp($-R^2/(nl^2)$) for membranes of sufficient lateral size where the membrane contains n^2 subunits of size l, and R is the lateral edge-to-edge distance of the bilayer membrane.

   a) Calculate the spring constant for such a membrane by writing an expression for the energy of the membrane as a function of R and taking the first derivative to obtain the force, $F = k_{spring} R$ and the tensile blob size for this membrane.
   b) When the membrane is confined to a spherical structure, such as in a micelle, a certain tension is associated with the curvature of the micelle. From the Laplace equation we could write $F \sim \frac{2\gamma}{L}$ where γ is the surface tension, and L is the radius of the micelle (this equation is not dimensionally correct). Use this equation to calculate the characteristic tensile-blob size for a bilayer membrane in a micelle as a function of L.
   c) What transition occurs at this blob size?
   d) For a typical micelle γ/kT has a value of about 1.08 (K. Shinoda, M. Hato and T. Hayashi, *J. Phys. Chem.* **76** 909-14 (1972)). How does this compare with your expectations associated with your answer to question "b"?
   e) Graphene is a conjugated carbon sheet. Conjugated carbon bonds must exist in a planar conformation due to the presence of sp^2 hybrid orbitals. When the sheet meets a defect such as an oxidized carbon, a kink is introduced into the sheet with a relatively large angle with respect to the sheet plane (on the order of 109.5°). So this is similar to a crumpled piece of stiff paper. Compare the micelle bilayer, which is flexible, with the graphene sheet in the context of the different local chain models that were mentioned in class. (Which would follow Kuhn's model and which the persistent chain model?)

2) Polymer chains have a fixed concentration within the coil in solution c* ~ 1/[η].
   a) Why is this concentration called the overlap concentration?
   b) Polymer solutions have been categorized into dilute, semi-dilute and concentrated regimes relative to c*. Explain the chain structure in these three regimes.
   c) In the semi-dilute regime the concentration blob size, ξ_c, can not depend on molecular weight, n of the chain. Why is this the case?
   d) As the concentration increases does ξ_c become larger or smaller? Why?
   e) In both the tensile blob and the concentration blob thermally random structures adapt to imposed constraints through the introduction of a new size scale where a scaling transition occurs. Describe the persistence length as a type of blob that follows this same model.

Answers: 120215 Quiz 4 Morphology of Complex Materials

1) a) From comparison with the Boltzmann probability, $E = \frac{kTR^2}{nl^2}$ $\frac{dE}{dR} = F = \frac{2kT}{nl^2} R = k_{spr} R$

if we set $\xi_{Tensile} = n^{1/2} l = R$ we have $\xi_{Tensile} = \frac{2kT}{F}$

b) $\xi_{Tensile} = \frac{kT}{\gamma} L$

c) This blob size reflects the transition from a randomly weaving membrane to a flat sheet.

d) The value of 1.08 seems small since the blob size would be most of the micelle. I would expect a values on the order of 0.1 to 0.3 for this to make sense.

e) The graphene sheet will follow straight paths with discrete bend points similar to a Kuhn chain with the flat parts representing Kuhn steps. The membrane bilayer is similar to a persistent chain with a continuous curvature to the sheet. The graphene sheet has highly restricted fold points so it is not a freely jointed chain, it is more like a freely rotating or in this case a restricted folded sheet or some similar terminology.

2) a) c* is called the overlap concentration because it is the concentration where chains begin to touch each other on average.

b) In the dilute regime the chains are self avoiding walks with a dimension of 5/3. In the semi dilute regime the chain is composed of concentration blobs. The blobs have a dimension of 5/3 and the blobs form chains of dimension 2. In the concentrated regime the chains have Gaussian scaling and the dimension is 2. As concentration increases the blob size decreases.

c) The concentration blob size can not depend on the molecular weight of the chain since the blob is smaller than the chain and the chains can not be individually seen in the semi-dilute regime due to chain overlap.

d) The concentration blob size decreases with concentration since the chains overlap to a greated extent as concentration increases. It is a natural consequence of the constraints on the system as shown in the derivation presented in class.

e) We can consider that the chain would naturally adopt a convoluted conformation due to thermal motion. This is opposed by the bond restrictions of the chemical structure. So the persistence length is introduced as a size scale where the force created by bond restrictions, steric constraints, charges and other energetic effects just oppose the thermally driven entropy of the chain. We could write an energy expression equating the enthalpy of bond restrictions and the enthalpy associated with sub units of n chain units and solve for n where these energies balance. This should yield something close to the persistence length. There are other ways to calculate the persistence length as a scaling transition introduced by local/internal chain restrictions.

It should be noted that there is a parallel between the concentration blob and the thermal blob in that the scaling regimes are reversed in size. Similarly, there is a parallel between the tensile blob and the persistence length. In both cases the parallel involves the difference between an internally imposed constraint (persistence and temperature) versus an externally imposed constraint (force or concentration).