090404 Quiz 2 Polymer Properties

Chain persistence is on strong footing since it can be verified analytically (calculation), theoretically and experimentally by several techniques. Chain persistence is important to calculation of chain conformational thermodynamics and kinetics (diffusion).

a) Explain the importance of chain persistence to our understanding of polymers.

b) Show how chain persistence can be theoretically demonstrated for a chain with a simple short range interaction. Give an expression for $\langle r_i \cdot r_j \rangle$ where r_i is the chain step vector, and use this expression to calculate $\langle R^2 \rangle$, and b_{eff}, where b_{eff} is the length of persistence for the chain with a simple short range interaction.

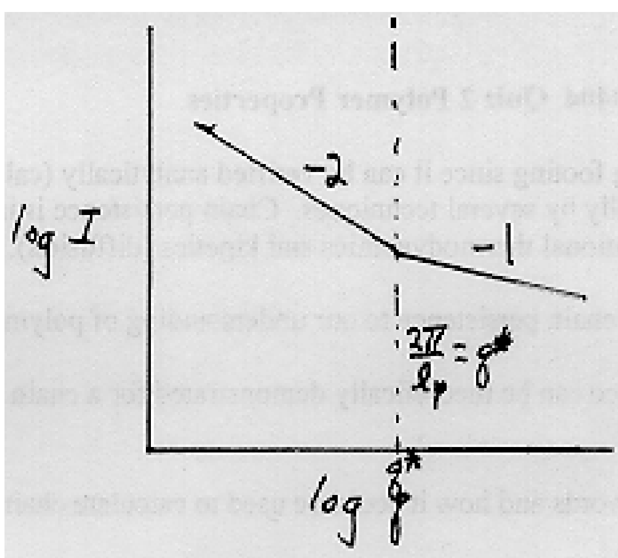
c) How does "b)" also verify the retention of chain scaling for persistent chains?

d) Explain what RISM is in words and how it could be used to calculate chain persistence. Your description should mention the partition function, Z.

e) Persistence is evidenced in neutron scattering from a polymer coil as a transition in mass-fractal dimension from 2 for a Gaussian chain to 1 for the persistence unit (rod). In scattering, the scattered intensity, I(q), can scale with the inverse size, $q = 2\pi/d$, through a power-law relationship,

$$I(q) = B\, q^{-df} \qquad (1)$$

where B is a constant for a given scaling regime, see figure below. Show how a linear equation can be obtained in a log-log plot (below) by taking the log of equation (1) to yield a linear equation and then explain the transition shown in the figure keeping in mind that low-q reflects larger size-scales.



ANSWERS 090404 Quiz 2 Polymer Properties

a) Isolated polymer chains display two main features, a local persistence and a global scaling, fractal regime. Our understanding of polymers and our ability to predict their properties relies on a definition of these two fundamental components. For example, to calculate the conformational entropy of a coil it is necessary to have a measure of the number of zero conformational-entropy units, persistence units, in the chain. Similarly, calculation of kinetic features such as the viscosity, rely on a physical definition of the persistence unit or Kuhn step, $l_K = 2l_p$. For example, in the Rouse model the chain friction factor is calculated by a linear sum of the friction factors for the Kuhn units in the chain.

b) In class we considered a chain that was identical to a Gaussian chain except that a backward step was not allowed. For such a chain the average dot product of two step vectors is given by,

$$\langle r_i \cdot r_j \rangle = \frac{b^2}{(z-1)^{|i-j|}} \tag{1}$$

where z is the coordination number for a step and b is the length of a step. Then the average square end-to-end distance is given by,

$$\langle R^2 \rangle = \sum_{i=1}^{n}\sum_{j=1}^{n} \langle r_i \cdot r_j \rangle \quad \sum_{i=1}^{n}\sum_{k=0}^{\infty} \frac{b^2}{(z-1)^k} = nb^2 \frac{z}{z-2} = nb_{eff}^2 \tag{2}$$

where b_{eff} is an effective length of persistence for this simple short range interaction.

c) (2) shows that despite the presence of short range interactions the end-to-end distance and coil size still retain Gaussian scaling since the relationship between coil size and number of persistence units indicates a mass-fractal dimension of 2.

d) RISM is a mathematical method using a linear Ising Model that accounts for rotational isomeric states in a polymer chain to calculate the distribution of rotational angles for bonds and the free energy of the chain at a given temperature. Knowing the distribution of rotational angles it is possible to calculate the mean length of persistence. The partition function is calculated from the energy associated with a given isomeric state of the chain using,

$$Z = \sum_{\{\psi_i\}} \exp\left(\frac{-u\{\psi_i\}}{kT}\right) \tag{3}$$

where the summation is over the possible rotational states. The partition function is then used to calculate the free energy of the chain using,

$$f_p = -kT \ln Z \tag{4}$$

e) $\log(I) = \log(B) - d_f \log(q)$
gives a line that decays with a slope $-d_f$.

The graph shows two regimes of power-law scaling. At high-q the curve shows 1-d scaling and reflects the persistent unit. At low-q the curve shows 2-d scaling and reflects Gaussian coil structure. The transition point is related to the persistence length.