060421 Quiz 4 Polymer Properties

Scattering of electromagnetic radiation is usually considered in terms of binary interference effects (*re-radiation from 2 points*) because the power of scattered radiation is less than 1% of the incident radiation and the probability of a scattering event from multiple sites would follow a power series in this fraction; so while binary power might be 0.1 % of the incident intensity; ternary (3 points) would display 0.0001 % of the incident intensity.

a) Explain why the binary scattered intensity might be related to the pairwise (binary) correlation function, $g(\mathbf{r})$.

b) Give a mathematical expression for the pairwise correlation function. (Define the del operator, $\delta(x)$.)

c) If you needed to consider ternary interactions (3 particles) guess how you would need to modify this function.

d) By writing the Fourier transform of $g(\mathbf{r})$ in a series expansion of the exp(-i $\mathbf{q}\mathbf{\dot{r}}$) term and using a double summation for binary interactions in the polymer chain, we were able to obtain Guinier's Law. Was the Gaussian structure of the coil considered in this derivation? Explain where it was used or why you think it was not used.

e) Sketch a plot of the Debye function for polymer coils and Guinier's law for the same coil in a log intensity versus log scattering vector plot. Does this plot agree with your assessment in part "d"?

- 2) In class we considered 2 ways to obtain the RMS end-to-end distance, $\langle R^2 \rangle^{1/2}$ using the Gaussian distribution function.
 - a) Explain what these two approaches are.
 - b) Which approach gives a better value.

c) Sketch a plot of the Gaussian probability in 3D space versus end-to-end distance from $-Nl_k$ to $+Nl_k$, where N is the number of Kuhn units and l_k is the Kuhn length. What happens beyond Nl_k ?

d) Given the Boltzman probability function, $p_B(R) = \exp(-G(R)/k_BT)$, where G(R) is the free energy as a function of "R" and k_B is Boltzmann's constant, write an expression for the free energy of a Gaussian chain by comparison with the Gaussian probability function.

e) What can you say about the enthalpic part of the free energy for an isolated Gaussian chain from this comparison (remembering that G = H - TS).

3) In order to determine the effect of excluded volume on the chain end-to-end distance one of the methods of question "2" is modified following Flory and Krigbaum.

a) Explain which of the two methods of question "2a" can be used to obtain the end-toend distance for an exclude-volume chain and why the other method can not be used.

b) What is the probability of excluding a single chain unit's volume, V_c , from a polymer coil?

c) What is the probability for a polymer chain to be excluded from all of the chains excluded volume?

d) Show how this can be combined with the Gaussian probability function and write an expression for the free energy of an excluded volume chain.

e) What can you say about the enthalpic part of the free energy for an isolated chain with excluded volume through a comparison of this new expression with the Boltzmann expression (this is somewhat of a trick question).

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1) a) The binary correlation function considers the probability that two points or chain units will be separated by a distance "r". If two points are separated by "r" then they can contribute to the observed binary interference at $\mathbf{q} = 2\pi/\mathbf{r}$, where q is the scattering vector $\mathbf{q} = (4\pi/\lambda) \sin\theta$ and θ is the scattering angle.

b)

$$g(r) = \frac{1}{N} \sum_{n=1}^{N} g_n(r) = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle \delta \left(r - \left(R_m - R_n \right) \right) \right\rangle$$

where N is the number of steps in the chain and R_i are the chain step positions. The del operator equals 1 when the argument is 0 and equals 0 for all other situations.

c) For ternary interactions this function would become fairly complicated, needing basically 3 distances, g(q,r,s) and three del-operators,

$$g(q,r,s) = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} \sum_{o=1}^{N} \langle \partial (q - (R_m - R_n)) \rangle \langle \partial (r - (R_m - R_o)) \rangle \langle \partial (s - (R_n - R_o)) \rangle$$

There are other answers to this question.

d) It was not used since the Guinier function does not describe internal structure. The internal structure was not included since we did not use the Gaussian function to describe the position of the segments. This function would need to modify the summation of the position vectors using a Gaussian probability.

e) Yes it agrees.



2) a) The first approach is to integrate the probability function times R² and normalize by the integral of the probability function. The second approach is to set the first derivative of the probability function to 0 and solve for R* at the peak, the most probable value.
b) The integral gives the true value for the second moment.

c)



Beyond Nl_k the function should go to 0 since it is impossible to extend the chain beyond this point but the Gaussian continues with a finite probability.

d) $3R^2/(2Nl_k^2) = 3R^2/(2R_0^2) = G(R)/k_BT$ so $G(R) = 3k_BT R^2/(2R_0^2)$

e) The free energy from part "d" has only an entropic part TS and no enthalpic part so this is the free energy for a chain with no enthalpic interactions or excluded volume.

3) a) The derivative to obtain the most probable value is used since the integral for a modified Gaussian is not possible to solve using traditional methods.

b) $(1 - V_c/R^3)^{1/2}$ c) $(1 - V_c/R^3)^{N/(N-1)/2}$ d)

$$p(R) = \exp\left[\frac{1}{2}N(N-1)\ln\left(1-\frac{V_C}{R^3}\right)\right] = \exp\left(-\frac{N^2V_C}{2R^3}\right)$$

$$W(R)dR = W_0(R)p(R)dR = kR^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2V_C}{2R^3}\right)$$

 $G(R) = k_BT \{3R^2/(2R_0^2) + N^2V_c/(2R^3)\}$

e) This expression also lacks an enthalpic term. An enthalpic term must involve V_c being a function of 1/T.