121108 Quiz 9 Polymer Properties

1) The Gaussian random walk chain and diffusion have some mathematical similarities. The situation becomes somewhat confusing when we model the diffusion of polymer coils at $qR_g<<1$ such as for dynamic light scattering.

a) Write an equation describing the Gaussian shape of the number (or density) of diffusion walks of length x, $\rho(t,x)$, as a function of the diffusion coefficient, D, and the time, t.

b) Write a similar Gaussian function for the probability of a certain end to end distance, R, of a random polymer chain, $P(R, nl^2)$.

c) What diffusive motion does the equation of part "a" correspond to?

d) Describe how the first moment of the scattering autocorrelation function is determined, $g^1(q, \tau)$.

e) In the expression for the cluminate, $\Gamma = q^2D$, why is q raised to the power 2? If the particles were charged and in an electric field what value would this exponent have?

2) a) A polymer chain displays Gaussian scaling in small angle scattering, $I(q) \sim q^{-2}$. Rods display $I(q) \sim q^{-1}$. Explain the origin of the power -1 for rods.

b) In what way does your derivation in part "a" depend on a kind of blob model and renormalization of the chain structure?

c) Explain what a tensile blob is. How might this be important to stretching a tethered chain using an AFM probe?

d) Describe the difference between a dilute solution, semi-dilute solution and a concentrated polymer in terms of the chain structural scaling.

e) Derive the behavior of thermal blob size, ξ_T, as a function of the interaction parameter and the persistence length.

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1) a)

$$\rho(x,t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-x^2/2(2Dt)}$$

$$\langle x^2 \rangle = \sigma^2 = 2Dt$$

b) $P(R, nl^2) \sim \exp\left(\frac{-3R^2}{2nl^2}\right)$

c) Diffusive motion of the entire chain as a spot since $qR^g << 1$.

d) Otain g^2 from the intensity as a function of time:

$$g^2(q;\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

then calculate g^1.

$$g^2(q;\tau) = 1 + \beta\left[g^1(q;\tau)\right]^2$$

e) For random diffusion $\langle x^2 \rangle = 2Dt$ so time is related to distance squared for a 2-d walk. Since q reflects the inverse distance we expect to see q^2 in the expression for Γ. If the polymers were charged and in an electic field we would expect to see ballistic motion $\langle x^2 \rangle \sim t^2$, and $\Gamma \sim qD$.

2 a) If the coil can be viewed as being composed of blobs of size ξ_c, with n_c persistence units then the chain is made up of $N_c = N/n_c$, blobs. The scattered intensity is proportional to $N_c n_c^2$. For scattering for $1 < qR_g < ql_p$, with the Bragg size $r \sim 1/q$ we have that $n_c \sim (r/l_p)^{df}$ and $N_c \sim (R/r)^{df}$ so $I(q) \sim N_c n_c^2 \sim (R/r)^{df} (r/l_p)^{2df} \sim \sim (R/l_p^2)^{df} r^{df} \Rightarrow (R/l_p^2)^{df} q^{-df}$. For a rod $d_f = 1$ and $I(q) \sim q^{-1}$.

b) In "a" the chain is renormalized to subunits of size "r". This structure of size "r" is essentially a blob. So this approach uses renormalization and a blob model more or less, similar to how the Rouse approach uses a blob model. For a true blob model there is a transition in scaling at the blob size, in this case there is not transition in scaling and we are considering external restrictions for the blob size, similar to the Rouse approach.

c) When a force is applied to a polymer chain in the Gaussian state the chain is drawn out. At large scales (n is large) the spring constant for the chain is low so it easily is drawn, $k_{spr} = 3kT/(nl^2)$ and $F = k_{spr} R$ is low. At small scales n is small so the spring constant and force

are much higher. At some point the applied force balances with the variable spring constant with n so that for sizes larger than that scale the chain is fully straightened, linear or rod like, and for small sizes the chain is random. This transition size is called the tensile blob size and the chain is envisioned as being composed of N_t of these blobs, each of which have n_t persistence units so that the total chain number of persistence units, $N = n_t N_t$. The blob size occurs at a point where the energy of the applied force, $F\xi_t = 3kT$ (force times distance on which it is applied equals energy), so $\xi_t = 3kT/F = n_t^{1/2} l_p$, so $n_t = (3kT/(Fl_p))^2$.
The coil size $R = N_t\xi_t = (N/n_t)(3kT/F) = (N/(3kT/(Fl_p))^2)(3kT/F) = N l_p^2 F/(3kT)$
$R = R_0 (F/(3kT))$.
When a chain is stretched by an AFM tip and is attached to a surface at one end then we expect the length of the chain to follow this equation in force. We should notice a reduction in chain length with temperature.

d) In dilute solution the chain displays good solvent scaling in most cases, $d_f = 5/3$. When the concentration is increased above the overlap concentration, c*, a concentration blob, ξ_c, is introduced between R_g and l_p. For sizes larger than the blob size, screening of interactions leads to Gaussian scaling, $d_f = 2$. For sizes smaller than the screening length of blob size, the chains are not screened and good solvent scaling is observed. The blob size follows $\xi \sim R\left(\frac{c}{c^*}\right)^{-3/4}$ until a concentration where $\xi = l_p$. At that concentrations above c**, $c^{**} \sim c^*\left(\frac{R}{l_p}\right)^{4/3}$, the chain is in a concentrated condition and all interactions are screened so that the chain has a Gaussian configuration, $d_f = 2$.

e)

$$R = N_T^{3/5}\xi_T = \left(N/n_T\right)^{3/5}\xi_T = \left(N/\left(\xi_T/l\right)^2\right)^{3/5}\xi_T = N^{3/5}\xi_T^{-1/5}l^{6/5}$$

Flory-Krigbaum Theory yields: $R = V_c^{1/5}(1-2\chi)^{1/5}N^{3/5}l^{2/5}$

By equating these:

$$\xi_T = \frac{l}{(1-2\chi)}$$