Quiz 11 Polymer Properties November 8, 2013

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 number (or density) of diffusion walks of length x, $\rho(t,x)$, as a function of the diffusion coefficient, D, and the time, t. (This is a Gaussian function.)

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) Hao Li and Tom Witten, in deriving an expression for persistence in polyelectrolytes, describe the tensile blob model for polyelectrolytes in the following two paragraphs.

We start by considering a polyelectrolyte consisting of N segments, with segment length a. The charges are A segments apart, with strength q_0. Following refs 9 and 11, we shall not explicitly consider counterions. Instead, we consider counterions as providing a screening, so that the charges on the chain will interact via a screened Coulomb potential,

$$U_{ij} = l_B \frac{\exp(-\kappa r_{ij})}{r_{ij}} \qquad (2.1)$$

Here $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two charged monomers, κ is the inverse screening length, and $l_B \equiv q_0^2/(\epsilon k_B T)$ is the Bjerrum length, with ϵ the dielectric constant of the solvent. Hereafter, we shall use the reduced charge $q \equiv q_0/\epsilon^{1/2}$ and measure energy in units of $k_B T$. We assume that the chain has a bare persis-

tence length l_0. For flexible polymers, $l_0 \approx a$. To focus on the effect of long-range interaction, we shall also neglect the self-avoidance of the monomers. Thus in the absence of the charge interaction, the chain would form a random coil with radius of gyration $R_G \simeq aN^{1/2}$.

Now consider the chain conformation with charge interactions turned on. It is known that for unscreened interaction, the chain consists of linearly stretched blobs of characteristic size ξ;[1,2] within each blob the random walk configuration is not strongly affected. This leads to a radius of gyration proportional to the molecular weight, $R_G \simeq \xi N/N_b$, where N_b is the number of monomers in a blob. When screening is introduced, one expects that this picture of linearly stretched blobs should remain valid within a screening length if $\kappa^{-1} \gg \xi$. More precisely, it should be so within a persistence length l_p with $l_p \gg \xi$. In a simple scaling argument, one obtains blob size by assuming that the electrostatic interaction within a blob is roughly k_BT, giving $\xi \approx \xi_0 = a(l_B/a)^{-1/3}A^{2/3}$.

Li H, Witten TA, *Macro.* **28** 5921 (1995).

a) Make a sketch showing a, N, A, ξ, and q_0 for this model in the absence of charge and a similar sketch showing the change that occurs when charge is "turned on". Indicate the power scaling of A and N with length.

b) Explain why the scaling of R_g with mass changes from $N^{1/2}$ to N^1 after charges are "turned on".

c) Make a plot of log I versue log q for scattering from these polyelectrolyte chains when charges are turned off and when charges are turned on. Assume it is the same chain so that I(q=>0) is the same for the two curves and at high-q the two curves are the same.

d) Consider that a net force due to the electrostatic charge, F, is applied to the chain. Write an expression for the blob size using this force F and kT.

e) Compare the expression given by Li and Witten for the blob size with your expression from part "d" to obtain an expression for this force, F. (Explain your expression for F especially the temperature dependence.)

ANSWERS: **Quiz 11 Polymer Properties November 8, 2013**

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:

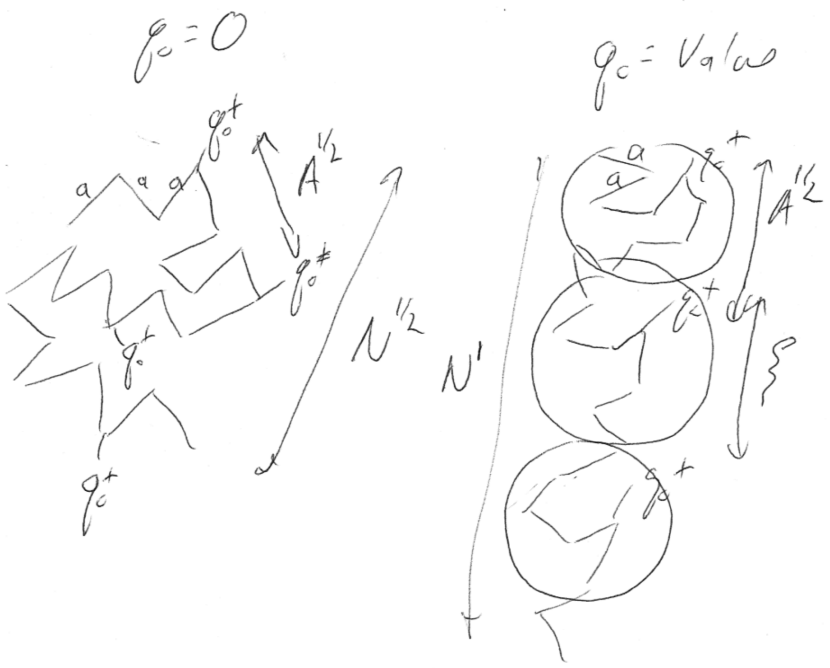
$$g^2(q;\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

then calculate g^1.

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

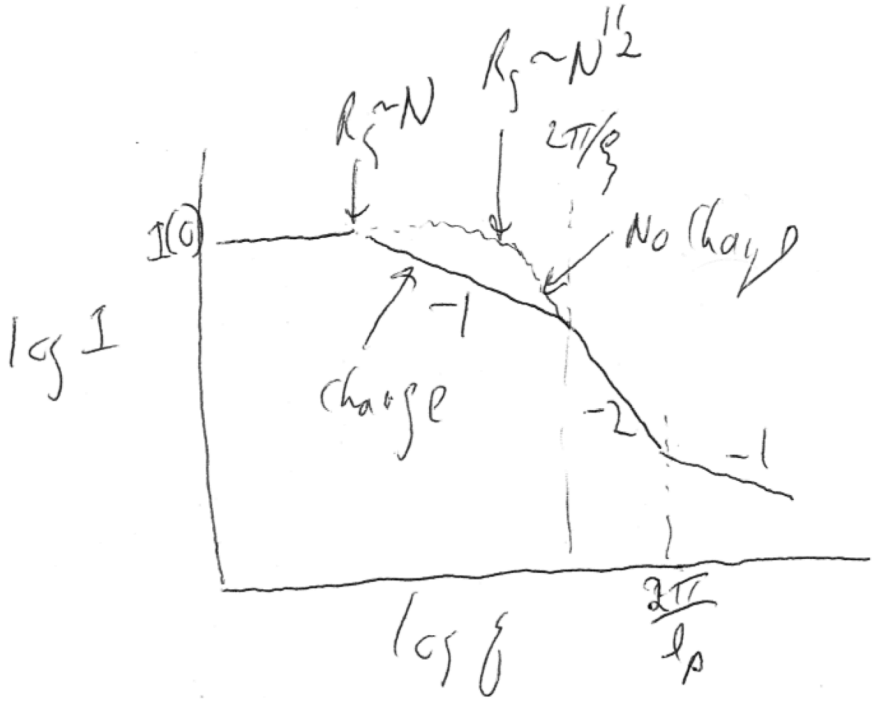
e) For random diffusion $\langle x^2 \rangle = 2Dt$ so time is related to distance squared for a 2-d walk. Since q reflects the inverse distance we expect to see q^2 in the expression for Γ. If the polymers were charged and in an electic field we would expect to see ballistic motion $\langle x^2 \rangle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

2 a)



b) There is an effective force that draws out the chain into a linear structure caused by charge repulsion. This straightens out the chain on a large scale and is opposed by the entropy of the chain (kT).

c)



d) $\xi = k_B T/F$

e)

$$\xi = a\left(\frac{l_B}{a}\right)^{-1/3} A^{2/3}$$

$$l_B = q_0^2 / \varepsilon k_B T$$

$$\xi = a^{2/3} q_0^{-2/3}$$

$$\xi = \frac{A^{2/3} a^{2/3} \varepsilon^{1/3} (kT)^{1/3}}{q_0^{2/3}}$$

$$\xi = \frac{kT}{F}$$

$$\text{So} \quad F = \frac{q_0^{2/3}}{kT^{2/3} A^{2/3} a^{2/3}}$$

The force depends on charge ξ
It becomes weaker at high temp
It becomes weak @ layer spacing "A"
It becomes weaker with large chain stiffness "a"