080220 Quiz 6 Polymer Properties

1) Self-similarity in the study of turbulent flow involves considering disordered flow as being composed of eddies of a continuous spectrum of sizes from L to η. Where L is the maximum size of eddies where energy is input and η is a characteristic minimum size where energy is dissipated as heat. Energy is transferred from larger to smaller eddies with no viscous dissipation. At each size, r, or wave vector, k ~ 1/r, the eddies are space filling, that is larger eddies are entirely composed of smaller eddies. This is the standard model used to describe a hurricane for example. Energy transfer form large to small eddies occurs with no viscous dissipation and most of the systems energy exists at the largest sizes governed by the energy transfer rate, ε.

a) Compare self-similarity in turbulent flow with self-similarity in a polymer chain by drawing a sketch of eddies of different size and a chain.

b) In turbulence eddies of a given size are at times referred to as "blobs". How does this definition of a blob differ from the definition of a *tensile blob* in a polymer chain?

c) In turbulence it is of interest to describe the distribution of energy or energy spectrum, E(k), in the system as a function of wave vector k ~ 1/r. Generally a power-law is obeyed for systems where viscous dissipation can be ignored for intermediate wave vectors, $E(k) \sim k^{-5/3}$. By comparing with a self-avoiding walk explain what such a power-law spectrum might mean in terms of assumptions concerning the turbulent system. (List the SAW assumptions and give analogous assumptions for the turbulent system.)

2) a) Write an expression for the energy of an isolated chain as a function of temperature using the chi-parameter.

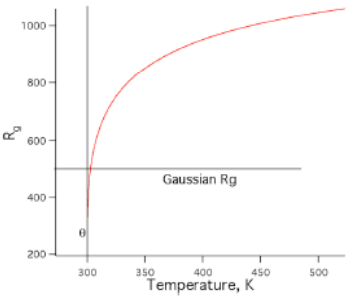
b) Use this expression for a SAW chain and the expression for a Gaussian chain to calculate the spring constant, k_{spr}, for these two chains, $F = k_{spr} R$.

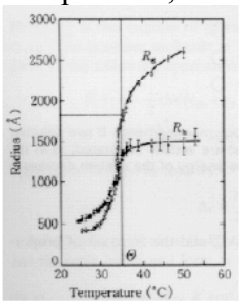
c) Does the non-linearity of the spring constant for the SAW become larger or smaller with higher deformation, R? Does it become larger or smaller as T drops? Explain these.

3) The Flory-Krigbaum analysis results in an expression for the coil size with temperature,

$$R_F = N^{3/5} l_K^{2/5} \left(V_0(1-2\chi)\right)^{1/5} = N^{3/5} l_K \left(1 - \frac{2z\Delta\varepsilon}{kT}\right)^{1/5}$$

which is plotted to the right, next to experimental data.





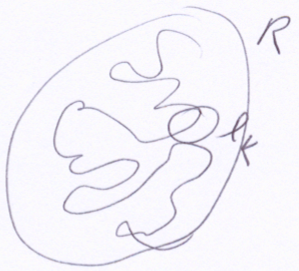
a) Explain the paradox between the prediction of two states (SAW and Gaussian) and the F-K thermal dependence of R_F.

b) Calculate the temperature (χ) dependence of the thermal blob size by calculating the dependence of R_F for a thermal blob model and comparing with the F-K result.

c) Sketch the scattering patterns of log I(q) vs log q describing thermal blob theory (show a SAW chain, a Gaussian chain and two chains at intermediate temperatures).

Answers: **080220 Quiz 6 Polymer Properties**

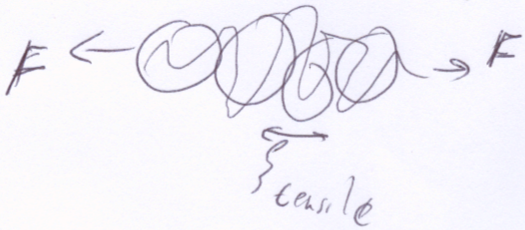
1) a)



At different size scales (magnification) between L & ξ the system appears identical

Similarly the chain can be decomposed into subsegments of different size that appear the same at different magnifications

b) A tensile blob is of fixed size for a fixed force applied to the chain



The blob described for tensile force is of fixed size.

$$\xi_{tensile} = \frac{3kT}{F}$$

c) Turbulence $E(k) \sim k^{-5/3}$ SAW $I(q) \sim q^{-5/3}$

Assumption

{ Chain is self avoiding at minimum size V_0
Excluded Volume exists
Chain is otherwise random

At size eddies are identical and are not super imposed ←

Eddies fill space ←

2) a) $E = KT\left(\frac{3R^2}{2n\ell^2} + \frac{N^2}{2}\frac{V_0}{R^3}(1-2x)\right)$

$x = \frac{2\Delta\varepsilon}{KT}$

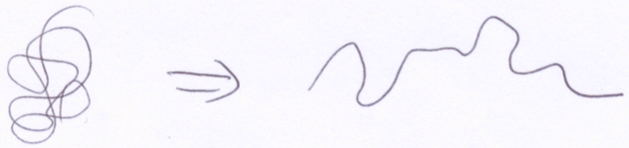
b) $F = \frac{dE}{dR} = \left(\frac{3kT}{n\ell^2}\right)R$ For Gaussian

$K_{spr}{}_{gaussian} = \left(\frac{3kT}{n\ell^2}\right)$

SAW

$F = \frac{dE}{dR} = KT\left(\frac{2}{n\ell^2} - \frac{3N^2}{2}\frac{V_0(1-2x)}{R^5}\right)R$

c) Smaller with larger R & smaller as T drops,
as R increases self-overlap becomes less likely



so the excluded volume term becomes less important.

Similarly, as T drops $(\tau - 2x) \Rightarrow 0$

& the chain appears to loose self-avoidance & excluded volume.

3) a) Paradox: The chain scaling in molar mass has only two functional terms for thermally equilibrated polymers:

Gaussian $R \sim N^{1/2}$

SAW $R \sim N^{3/5}$

So only two states are possible, expanded & Gaussian.

However, F-K theory + experimental evidence shows a continuous change in R_s with temperature. This paradox is resolved with the Thermal Blob structural model.

b) $$R_F \sim N_T^{3/5} \xi_T \quad (1)$$

$$\xi_T \sim n_T^{1/2} l_K \quad (2)$$

$$N = N_T n_T \quad (3)$$

(1) & (3) $$R_F \cong N^{3/5} n_T^{-3/5} \xi_T$$

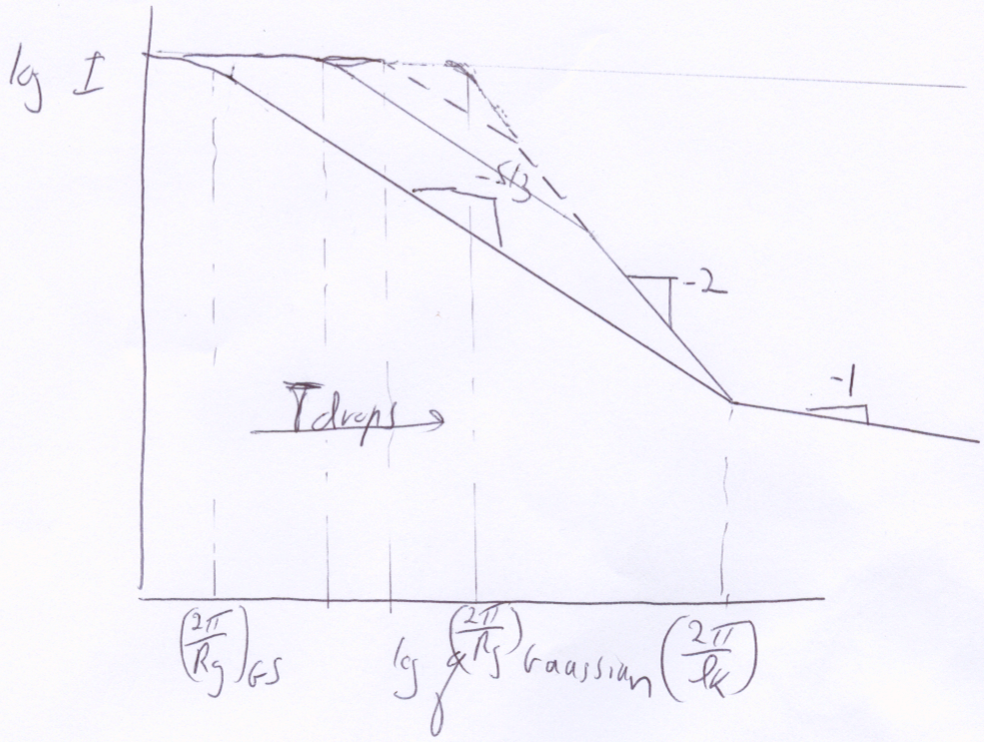
(2) $$R_F \sim N^{3/5} \left(\frac{\xi_T}{l_K}\right)^{-6/5} \xi_T = N^{3/5} \xi_T^{-1/5} l_K^{6/5} \quad (4)$$

From F-K

$$R_F = N^{3/5} l_K (1-2x)^{1/5} \quad (5)$$

equate (4) & (5)

$$\frac{l_K^{1/5}}{(1-2x)^{1/5}} = \xi_T^{1/5} \quad \text{so} \quad \xi_T = \frac{l_K}{(1-2x)} \quad (6)$$


log I
-4/3
-2
-1
I drops
$\left(\frac{2\pi}{R_g}\right)_{GS}$
log $\left(\frac{2\pi}{R_g}\right)_{Gaussian}$
$\left(\frac{2\pi}{R_K}\right)$