Quiz 9
Polymer Properties
March 22, 2017

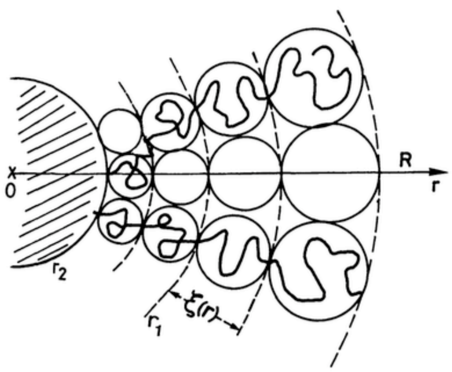

Fig. 1. — A representation of our model : every branch is made of a succession of blobs with a size ξ increasing from the centre of the star to the outside.

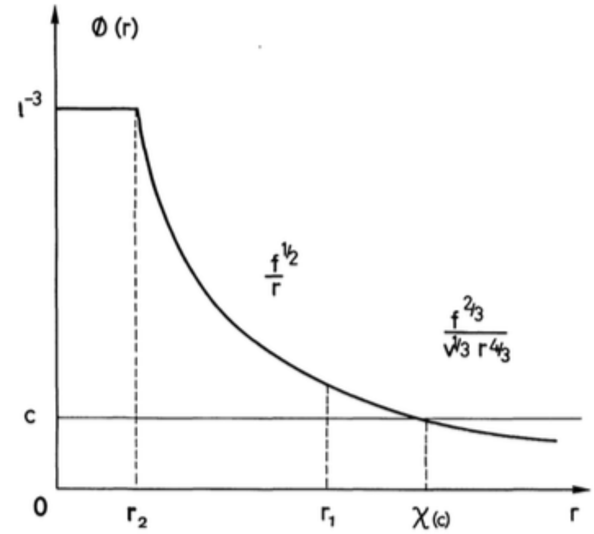

Fig. 2. — The density profile. Three regions appear. In the core ($r < r_2 \sim \sqrt{f}\, l$) the density is constant. In this region the structure is completely stretched. In the intermediate region ($r_2 < r < r_1 \sim f^{1/2} v^{-1} l$), because the concentration is high the blobs are ideal : $\varphi(r) \sim r^{-1} f^{1/2}$. In the outside region the excluded volume effects are present inside the blobs. The length $\chi(c)$ is discussed in section 3.

M Daoud, JP Cotton, *J. Physique* **43** 531 (1982).

The Daoud-Cotton (DC) model is a blob model for star polymers which has been widely used to predict properties of symmetrically branched polymeric structures such as dendrimers (tree-like polymers or arborial polymers) and highly branched star polymers. These topologies are used as viscosity enhancers and are a component of synthetic automotive oil. The DC model considers a radial depletion in chain concentration. By applying the concentration blob and tensile blob models to this concentration gradient, a gradient structure is predicted as shown in Figure 1. In this case the blob size changes with the radial position, r.

a) Sketch log of the scattered intensity/concentration versus log of q for the concentration blob model. Show a good solvent chain indicating the I(0)/c and $1/l_k$. Add to the plot curves for increasing concentration until a Gaussian chain is reached.
b) Obtain an expression for concentration blob size, ξ, as a function of concentration in the concentration blob regime.
c) Obtain an expression for coil size, *R*, as a function of concentration in the concentration blob regime.
d) For sizes less than r_2 in Figure 2, at the core of the star, the DC model indicates that the star arms are extended. Obtain an expression for the coil size, *R*, as a function of the effective force, *F*, applied to the chain in this stretched regime.

e) The regime from r_2 to r_1 in Figure 2 is the concentrated regime. Give an expression for R as a function of N in this regime.
f) Above $\chi(c)$ in Figure 2 the coils are fully expanded. Given an expression for R as a function of N in this regime.
g) What happens between r_1 and $\chi(c)$.
h) For a four arm star at the theta condition the structure is identical to a Gaussian chain since the coil units do not interact. This means that $d_f = 2$ but d_{min} increases and c decreases leading to extension of the chains. A similar behavior can be demonstrated for a good solvent coil where d_f is fixed at 3/5 due to equilibrium conditions in the Flory-Krigbaum theory. Is this scaling theory compatible with the DC model? Explain this and use it as a critique of the DC model.
i) Sketch a three-arm star with a random conformation. Consider a single arm of the three-arm star. Is there any reason to expect that the chains will be dispersed radially as shown in the Daoud Cotton model (consider the alternative model as a uniform fractal model).
j) If the temperature were dropped to the theta condition what changes would you expect in the structure shown in Figure 1? Raising the temperature from the theta condition would you expect the structure in Figure 1 to develop?

ANSWERS: Quiz
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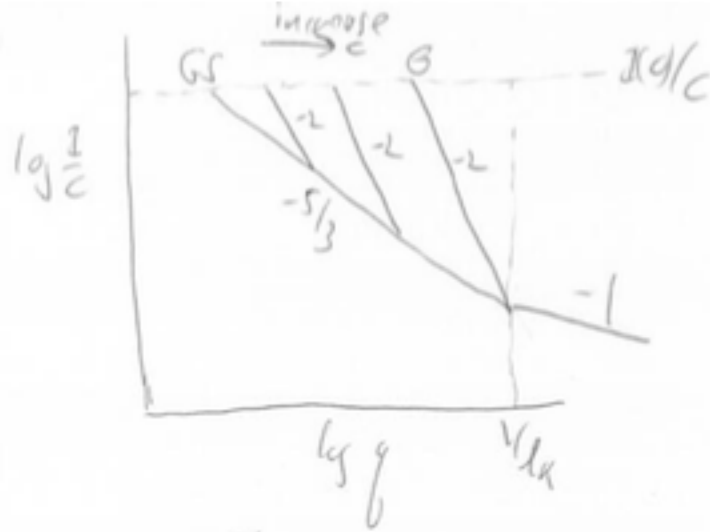
a)



b) $\xi \sim \left(\frac{c}{c^*}\right)^{-3/4}$

Blob is GS really $\left(\frac{\xi}{l_K}\right)^{5/3} = n_\xi$ # of Kuhn units in a blob

$R \sim R_0 \left(\frac{c}{c^*}\right)^{p} \sim (c)^{0} \rightarrow$ R is not a function of "c"

$R_0 \rightarrow N^{3/5}$, $c^* \sim N^{-4/5}$, $\frac{3}{5} + \frac{4p}{5} = 0 \therefore p = -3/4$

c)

$$R \sim \left(\frac{c}{c^*}\right)^{-1/8}$$

$$R \sim N_\xi^{1/2}\,\xi$$

$$N_\xi = \frac{N}{n_\xi} = \frac{N}{(\xi/l_k)^{5/3}}$$

$$R \sim \xi^{5/6}\,\xi^{-5/6}$$

$$R \sim \left(\left(\frac{c}{c^*}\right)^{-3/4}\right)^{1/6} = \left(\frac{c}{c^*}\right)^{-3/24} = \left(\frac{c}{c^*}\right)^{-1/8}$$

d) $R \sim F$

$$\xi \sim \frac{3kT}{F}$$

$$R \sim N_\xi\,\xi$$

$$N_\xi = \frac{N}{n_\xi} \qquad n_\xi \sim \left(\frac{\xi}{l_k}\right)^2 \qquad N_\xi \sim N\left(\frac{\xi}{l_k}\right)^{-2}$$

$$R \sim N\left(\frac{\xi}{l_k}\right)^{-2}\xi \sim \frac{N l_k}{\xi} \sim \frac{N l_k F}{3kT}$$

$$R \sim F$$

e) $R \sim N^{1/2} l_k$

Gaussian Scaling

f) $R \sim N^{3/5} l_k$

Flory-Krigbaum Result

Good Solvent Scaling

g) Concentration Blob Regime

$$R \sim \left(\frac{c}{c^*}\right)^{-1/8}$$

h) Chains are fractal objects and are not confined to a cone as shown in the model. The chain/arm meanders through the structure so the depiction is misleading. The scaling theory is not compatible with the DC Model.

i) See h

3 arms about a core with no cone restriction

j) At Θ there is no chain interaction. Arms move randomly as shown above. Having the fringes it is difficult to imagine the structure of Fig. 1 developing.