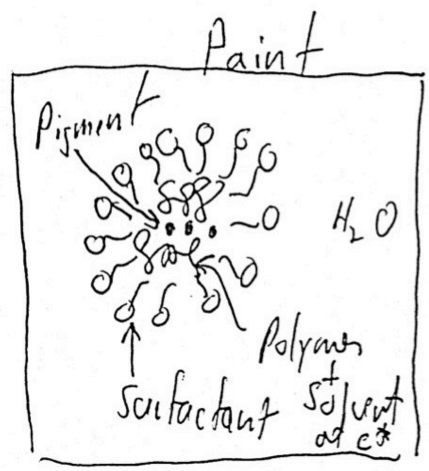
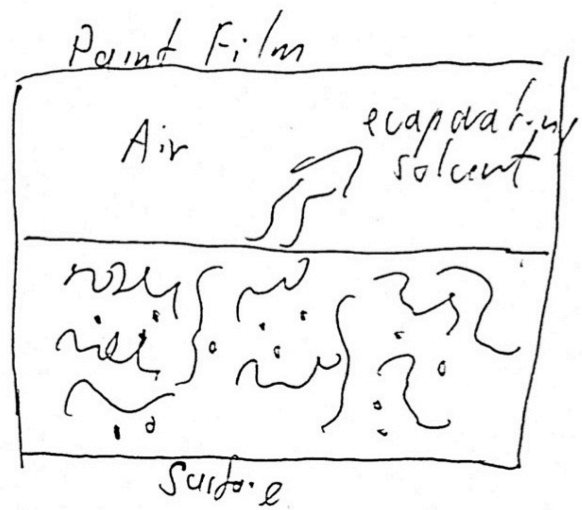
Quiz 12 Polymer Properties November 14, 2014

Latex or emulsion paints are composed of a water emulsion of polymer/pigment and solvent, with the polymer/solvent droplets encased by surfactants (soap) into 20 micron-size spherical micelles. The latex paint has a low viscosity when applied because it has the solution viscosity of a suspension of solid spheres. When the water dries the micelles break open and the polymer/co-solvent/pigment droplets coalesce into a polymer/solvent film containing the pigment. Finally, the co-solvent evaporates and a tough coating of pigment/polymer is produced.





a) What is the viscosity of a suspension of latex particles with 70% latex particles by volume relative to the solvent viscosity, η_0? (How does this compare with the viscosity of a polymer solution of 70% polymer (consider c*)? You will need to make some assumptions.)

b) The polymer is in a semi-dilute condition after the latex particles break. How would you expect the chain size (R/R_0) to change with time if the polymer concentration followed $c \sim (1 - \exp(-kt))$ and it began at c* before the micelles broke apart?

c) Consider that the chains in these drying droplets had reactive groups that allowed three crosslink sites per chain (f=4) so that a network of N/3 chain units between crosslinks was made. Explain what would happen to the structure of a chain between crosslinks of length N/3 if the droplet dried from c* (for chains of length N) to pure polymer. You need to make some assumptions but the chain length between crosslinks can be estimated.

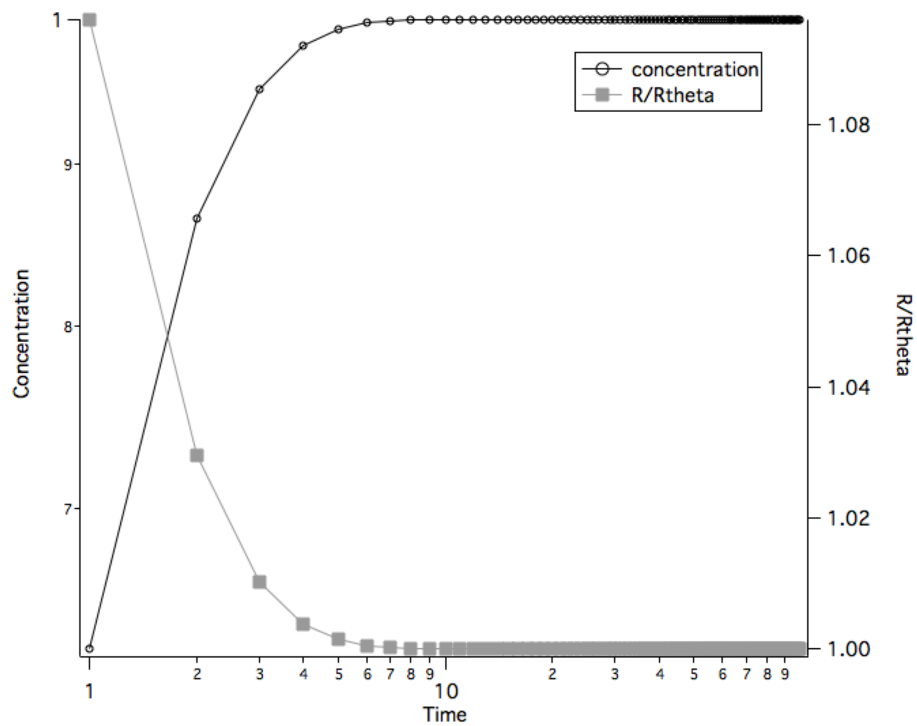
d) Consider that the paint is applied on a cold day (like today). How would this effect the process if the phase separation point for the polymer was 25°C and it displayed UCST behavior?

e) Polymers can display LCST or UCST behavior. How does thermal blob behavior differ for these two cases? (You may want to plot log I versus log q for dilute solutions and show an expression for the blob size as a function of temperature for the two cases.

ANSWERS: **Quiz 12 Polymer Properties November 14, 2014**

1) a) The Einstein equation describes the viscosity of a solution of spheres,
$\eta/\eta_0 = 1+2.5\phi = 2.75$
For a polymer solution far above the overlap concentration the viscosity would be much higher following an equation like $\eta/\eta_0 \sim (c/c^*)^3$ ~70^3 = 3.4e5.

b) $R = \xi\, n_\xi^{1/2} = R_{F0}\,(c/c^*)^{-3/4}\,(c/c^*)^{5/8} = R_{F0}\,(c/c^*)^{-1/8}$
so $R/R_0 = (1-\exp(-kt))^{-1/8}$



c) The chain would be reduced in length by $R_\theta/R_0 = (N/3)^{-1/5}$. This stretching would induce tensile blobs in the chain with $R_{tensile} = R_\theta(N/3)^{1/5} = N_\xi \xi$
We have that $N_\xi = N/n_\xi$, and $\xi = n_\xi^{1/2} l_k$, so $N_\xi = N(\xi/l_k)^{-2}$. Then
$R_\theta(N/3)^{1/5} = N(\xi/l_k)^{-2}\xi = N l_K^2/\xi$. So,
$\xi = N^{4/5}(3)^{1/5}\, l_K^2/R_\theta = N^{4/5}(3)^{1/5}\, l_K^2/(N^{1/2} l_K) = N^{3/10}(3)^{1/5}\, l_K$. And
$N_\xi = R_{tensile}/\xi = R_\theta(N/3)^{1/5}/(N^{4/5}(3)^{1/5}\, l_K^2/R_\theta) = R_\theta^2/(3^{2/5} N^{3/5}\, l_K^2) = (N/3)^{2/5}$

d) For UCST at 25°C, $\chi = B/298°K = ½ = 150/T$. A thermal blob would be induced in the polymer chain, $\xi = l_k/(1 - 300/T)$. The chain size would be $N_\xi = N l_k^2/\xi^2 = N(1 - 300/T)$.

e) LCST is phase separation on heating and $\chi = A - B/T$ so that when temperature rises χ increases towards ½. UCST is phase separation on cooling and $\chi = B/T$ so that as temperature drops χ increases towards ½. For LCST the thermal blob increases in size with temperature following $l_k/(1-2\chi) = l_k/(1 - 2A + 2B/T)$. For UCST the thermal blob increases in size with decrease in temperature following $l_k/(1-2\chi) = l_k/(1 - 2B/T)$.