080305 Quiz 8 Polymer Properties

PNIPAM (poly-N-isopropyl acrylamide) is used as a drug release polymer because it displays an LSCT in water with a critical temperature at around 35º C close to the temperature of the human body. Through adjustment of the PNIPAM structure in aqueous gels a drug can be selectively released from the gel when it approaches diseased tissue that is hotter than the surrounding tissue.

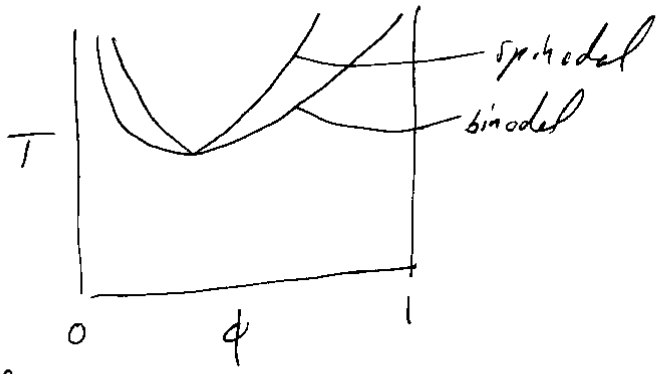
1) A researcher began studies of PNIPAM polymer in solution by making a series of solutions and measuring the cloud point to construct a phase diagram.
   a) Describe what a cloud point is and sketch an LSCT phase diagram.
   b) If the molecular weight of the PNIPAM is known how could the interaction parameter be determined using the cloud point? (You will need to take a derivative to obtain an equation for the cloud point using $d\ln\phi/d\phi = 1/\phi$ and $d\ln(1-\phi)/d\phi = -1/\phi$.)
   c) What functionality would you expect the chi parameter to have in temperature? Explain.

2) The researcher made gels of PNIPAM and then performed controlled quenches (rapid temperature jumps). He noticed that at certain compositions the phase separated PNIPAM gel displayed a web-like structure.
   a) Explain what caused the web-like structure in these gels.
   b) How could this structure be avoided?
   c) Would you expect this structure to form in an actual drug release condition in the body? Why?

3) a) Explain the terms critical slowing-down and critical point using the words fluctuation and free-energy space in the context of the Flory-Huggins equation.
   b) Give a generic expression for the critical interaction parameter and critical composition then show the values for a blend of gases, a polymer/solvent mixture and a symmetric polymer blend.
   c) It is often said that polymers do not mix. Use the Flory-Huggins equation to explain why this is the case. (Show what part of the Flory-Huggins equation drives miscibility and which part drives phase separation; explain why they favor or disfavor miscibility; and show the dependence of these terms on molecular weight.)

ANSWERS **080305** **Quiz 8 Polymer Properties**

1) a) for a mixture the cloud point is the temperature where the system first phase separates with rising (LCST) or dropping (UCST) temperatures. It reflects the binodal point.



b) The binodal occurs when $\frac{df}{d\phi} = 0$

We use the Flory Huggins Equation

$$f = \frac{\phi \ln\phi}{N} + (1-\phi)\ln(1-\phi) + \phi(1-\phi)\chi$$

$$\frac{df}{d\phi} = \frac{\ln\phi}{N} + \frac{1}{N} + \frac{1}{\phi} - \ln(1-\phi) + 1 + \chi - 2\phi\chi \equiv 0$$

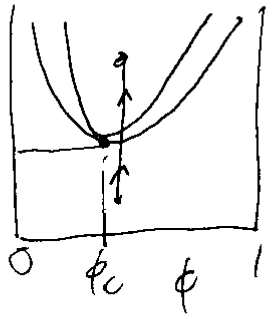
if you know ϕ & N you can solve for χ

c) $\chi = A - \frac{B}{T}$ because this is an LCST system.

As $T \uparrow$ χ is positive & layer than $\left(\frac{\phi \ln\phi}{N} + (1-\phi)\ln(1-\phi)\right)$

As $T \downarrow$ χ is less than this term due to "A"

(2)

a) 

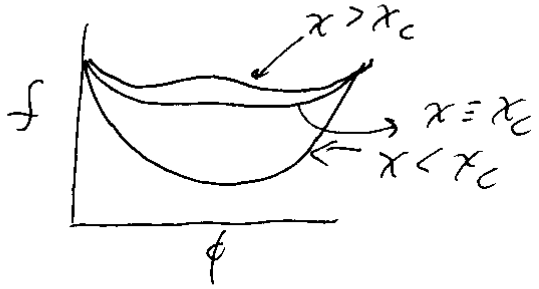
rapid T jump ⇒ spinodal structure

b) avoid by slow heating away from the critical composition

c) No it would not form in the body because heating is slow.

(3) a)

A plot of the Flory Huggins equation in free energy space



fluctuations in composition picks those curves where $+\delta\phi = -\delta\phi$ so $\langle\phi\rangle$ remains the same. At the critical x there is no difference in f for different ϕ so there is no preference for

which fluctuations are stable & fluctuations of all sizes & compositions are possible. There is no driving force to form fluctuations so the kinetics (Rate) of phase separation goes to 0. This is called "critical slowing-down"

(b)

	Generic	Gasses $N_A = N_B = 1$	Polymer Soln $N_A \neq N_B = 1$	Symmetric Polymer Blend $N_A = N_B = N$
ϕ_{A_c}	$\frac{\sqrt{N_B}}{\sqrt{N_B}+\sqrt{N_A}}$	$\frac{1}{2}$	$\frac{1}{1+\sqrt{N_A}} \sim \frac{1}{\sqrt{N_A}}$	$\frac{1}{2}$
χ_c	$\frac{1}{2}\left(\frac{1}{\sqrt{N_A}}+\frac{1}{\sqrt{N_B}}\right)^2$	2	$\frac{1}{2}\left(\frac{1}{\sqrt{N_A}}+1\right)^2 \sim \frac{1}{2}$	$\frac{2}{N}$

(c)

$$f = \frac{\phi \ln \phi}{N_A} + \frac{(1-\phi)\ln(1-\phi)}{N_B} + \phi(1-\phi)\chi$$

($\ln\phi$: Negative; $\ln(1-\phi)$: Negative; $\phi(1-\phi)\chi$: Positive)

Entropy	Enthalpy
Favors Miscibility	Favors Phase Separation
Negative Term	Positive Term
High Molecular Weight Makes This term <u>Small</u>	No Molecular Weight Dependence