020501 Quiz 6 Polymer Properties

1) Sketch the free energy versus composition for a symmetric polymer-polymer blend

   -for χN> 2,
   −χN = 2 and
   −χN<2.
   -**Show** the critical point, critical composition, spinodal point and binodal point on these plots.
   -Explain how the critical value of χN can be determined from an expression for the free energy (in words).
   -**What is** "critical slowing down"? Show on one of the plots drawn of free energy versus composition.
   For a binary blend that is phase separated
   -**how can** the composition of the two phases and the relative volume fraction of the phases be determined from a plot of the free energy versus composition.

   If you looked at a phase separated polymer blend that displayed a web like structure in an optical microscope
   -what could you say concerning the value of χN for this sample?

2) On a free energy versus composition sketch

   -**explain how** composition fluctuations might be involved in determining miscibility for the single phase, bimodal and spinodal regimes.
   If φ is the value for an instantaneous composition fluctuation (deviation from the mean),
   -**what is** $<\varphi>$ for a thermally equilibrated system?
   -Explain how a random composition fluctuation, $\varphi(r)$, could be decomposed into Fourier components, $\varphi(k)$ where k has units of inverse distance.
   According to Einstein's theorem for the equipartitioning of energy
   -can one perform thermodynamics on a single Fourier component, $\varphi(k)$?
   -**How is** the wavenumber, k, related to a scattering measurement? (k has the units 1/length).

Answers: 020501 Quiz 6 Polymer Properties

1)

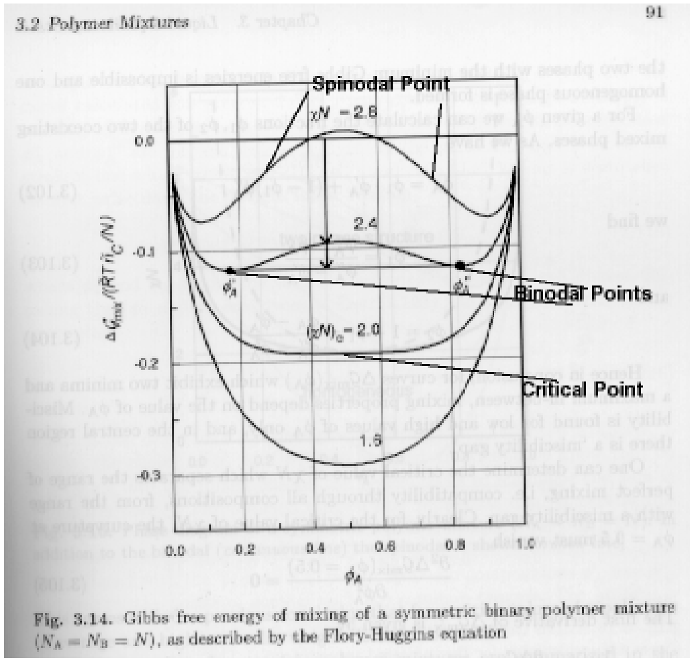

Fig. 3.14. Gibbs free energy of mixing of a symmetric binary polymer mixture ($N_A = N_B = N$), as described by the Flory-Huggins equation

$\chi N = 2$ is critical, $\chi N > 2$ is phase separated and $\chi N < 2$. is single phase.

Critical slowing down involves the flat curve. When composition fluctuations probe free energy the system is insensitive to large fluctuations so perturbation theory doesn't work and the kinetics are slow since the differences between different composition fluctuations are small.
A tie line decides the volume fractions as discussed in class and the bimodal points decide the compositions.
Spinodal is for a deep quench so $\chi N <<< 2$

2) As discussed in class, the system probes the free energy curve by thermal fluctuations in composition. If the net change in free energy is negative the system phase separates. This should be discussed for single phase, binodal and spinodal regimes.
$\langle \varphi \rangle = 0$ since they are random fluctuations.
Any noise pattern can be decomposed into a series of cosine waves of different amplitudes. A plot of amplitude versus wave number (1/wavelength) for these cosine waves is the spectral density for the system. (If the distribution is due to a spectroscopic effect such as IR absorption this is the IR absorption spectrum). If energy is partitioned to all wave vectors without external bias then each wave vector can be considered independently. (This is the same reasoning behind the use of an IR spectrum peak to describe a single vibration in a molecule for instance.) This is a theorem, i.e. it is an accepted feature of thermally equilibrated systems that seems to be held up by experimental observations.
The wave number k is the Fourier equivalent of the spatial distribution of composition fluctuations, r. $k = q/2\pi$, so in terms of scaling k is q. $q = 2\pi/\lambda(\sin\theta/2)$, where θ is the scattering angle.