

Polymer Blend:

The Gibbs free energy of mixing for a polymer blend is given by Strobl p. 88 eqn. 3.86:

$$G_{\text{mix}} = RTn_c \left(\left(\frac{n_a}{N_a} \ln \frac{n_a}{N_a} + \frac{n_b}{N_b} \ln \frac{n_b}{N_b} + \frac{n_a n_b}{N} \right) \right)$$

where the number of moles of polymer a is given by $n_a = V/v_a$ and v_a is the molar volume of polymer a, V is the system volume. The degree of polymerization of polymer a is given by $N_a = v_a/v_c$ where v_c is the molar volume of a reference unit. For a symmetric system where $N_a = N_b$ this can be written,

$$G_{\text{mix}} = RT(n_a + n_b) \left(\frac{n_a}{N} \ln \frac{n_a}{N} + \frac{n_b}{N} \ln \frac{n_b}{N} + \frac{n_a n_b}{N} \right)$$

the term $\left(\frac{n_a n_b}{N} \right)$ is the governing term for miscibility. The critical point is where $\left(\frac{n_a n_b}{N} \right) = 2$ for a binary blend of polymers. This is obtained by setting the second derivative with respect to molar fraction to 0 (spinodal equation) and then setting the composition to 0.5 (the critical point). It can also be obtained by setting the third derivative to 0.

The binodal (miscibility limit) is determined by setting the first derivative.

Appendix 4:

A concentration fluctuation at wave vector k is associated with a change in the Gibbs free energy that is described by equations of the type given above. For a finite fluctuation a generic expression in terms of linear response theory is:

$$G = a_k \frac{\delta c_k^2}{2}$$

where a_k is a modulus, i.e. the magnitude of the free energy response to a fluctuation of size δc_k . Positive and negative fluctuations have the same effect.

A field h_k can be associated with this fluctuation, i.e. if the fluctuation is viewed as being driven by a field such as a thermal gradient field.

$$\delta c_k = a_k^{-1} h_k$$

This can also be expressed as,

$$\delta c_k = \chi_k \delta \phi_k$$

where χ_k is the susceptibility of the concentration to a potential, χ_k is also called the response coefficient. It is directly related to the scattered intensity, $S(q) = kT \chi_q$. We also have that $\chi_k = 1/a_k$.

The differential expression for the change in free energy is given by,

$$dG = \sum_k \delta c_k = a_k \delta \phi_k$$

Fluctuations are driven by thermal energy and the distribution in space is random and follows Boltzmann statistics,

$$p(\phi_k) \sim \exp(-a_k \phi_k^2 / 2kT)$$

so the mean square fluctuations are given by the variance of the distribution,

$$\langle \phi_k^2 \rangle = kT/a_k = \chi_k kT$$

The scattered intensity from a homogeneous system is governed by the mean square fluctuations,

$$v_c S_c(q = k) = \langle \phi_k^2 \rangle = \chi_k kT$$