

Chapter 2

Development of Theory for Bulk Polymer Blend Systems

I follow the development of theory for solutions and blends of polymers. I take a minimal historical approach by focussing on the primary literature in which the theory was developed, and show how the work culminated ultimately in the Flory-Huggins-de Gennes free energy of mixing, which is the base theory for the study of spinodal decomposition in polymer blends.

2.1 Introduction

The aim of this chapter is to provide an overview of the development of theory for bulk *polymer*¹ systems, which came from a drive to understand the behaviour of *solutions*² and *blends*³ of polymers, which differed significantly from the behaviour of non-polymer systems. I take a minimal historical approach to this, using what I regard to be the most important literature in which the theory was developed, to give a narrative to the development of the theory. This chapter can be summarised in the following. The behaviour of polymers in solution prompted the development of an entropy of mixing valid for long chain molecules. To fit the theory to data required an empirical term to account for the heat of mixing, the form of which was quickly grounded theoretically. The entropy of mixing and heat of mixing can be combined, along with a term accounting for energy contributions from compositional gradients, to give the Flory-Huggins-de Gennes free energy of mixing, which can be used to understand and study spinodal decomposition of polymer blends.

It is useful at this point to introduce the Gibbs free energy, which is appropriate when considering incompressible systems (although the assumption of constant

¹Polymer: a molecule consisting of repeated units, like a string of beads or a chain. These repeat units are called *monomers*. A chain *segment* usually refers to a single monomer.

²Solution: a liquid mixture of solvent (e.g. water, toluene) and solute (e.g. sugar, polymer), in which the solute is dispersed in the solvent.

³Blend: a liquid mixture of two components (e.g. a blend of two polymers).

volume is of course not general). Since the subject matter of this chapter is mainly changes upon mixing, we can consider the Gibbs free energy change, given by

$$\Delta G = \Delta H - T \Delta S, \quad (2.1)$$

where ΔH is the Heat (Enthalpy) of Mixing, ΔS is the Entropy of Mixing, and T is the Temperature. I will refrain from elaboration of standard thermodynamics terminology throughout.

Terminology

I will briefly introduce terms as they appear, but more detailed definitions of Terminology are given on page 167. There are several terms that are used in passing while discussing literature in this section, and those that are not specifically important to this thesis will not be explicitly defined; definitions can be found elsewhere and in the corresponding citations.

2.2 Entropy of Mixing

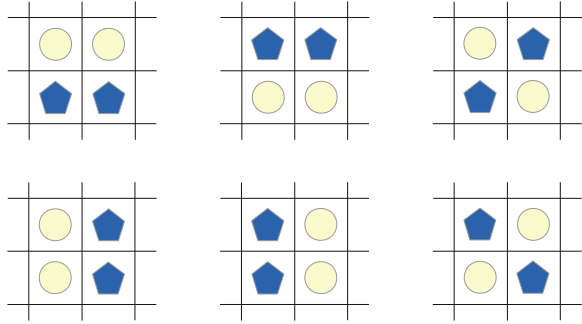
By 1940 there was a substantial body of evidence showing that polymer solutions deviated significantly from Raoult's law [Eq. (2.8)], which describes how the vapour pressure of an ideal solution (zero heat of mixing $\Delta H = 0$) depends on the vapour pressure of the pure components of the solution and the molar fraction of those components in the solution. These deviations were initially, and almost exclusively, put down to enthalpic effects: it was assumed that a non-zero heat of mixing was causing the deviations from Raoult's Law. However, careful experiments showed that deviations from Raoult's Law were significant even when the heat of mixing really was zero. The first successful efforts to explain these deviations were undertaken by Huggins [1, 2] and Flory [3], who derived a form for the entropy of mixing suitable for polymers.

2.2.1 Entropy of Ideal Solutions

Consider a mixture AB of fluids A and B , consisting of equal sized *simple molecules*.⁴ An *ideal solution* has zero heat of mixing, which means that there is no difference in the enthalpic interactions U between molecules of the pure components (A - A and B - B interactions) and between molecules of different components (A - B interactions) i.e. $2U_{AB} = U_{AA} + U_{BB}$. This means that the molecules will

⁴Simple Molecules: molecules that can be treated as spheres, because they consist of a few atoms at most and their internal structure need not be explicitly considered.

Fig. 2.1 A blend AB on a quasi-solid lattice. There are $n = 4$ simple molecules, $n_A = 2$ and $n_B = 2$, hence the number of distinguishable configurations is $\Omega = 4!/2!2! = n!/n_A!n_B! = 6$. All six distinguishable configurations are shown



randomly mix to maximise entropy, since there are no particularly favourable or unfavourable interactions that would prevent an entirely random mixing.

The entropy of the mixture is given by the Boltzmann equation

$$S = k_B \ln \Omega, \quad (2.2)$$

where Ω is the number of distinguishable configurations of the mixture. To calculate Ω , we can place each molecule on a quasi-solid lattice. If the molecules of fluids A and B are the same size, then the number of configurations available to $n = n_A + n_B$ molecules is $n!$, but the number of distinguishable configurations is

$$\Omega = (n_A + n_B)!/n_A!n_B!. \quad (2.3)$$

A schematic of a set of available configurations is shown in Fig. 2.1.

Using Eq. (2.2), we can find the change of entropy upon mixing as the difference in entropy between the mixture and the pure components, $\Delta S_{mix} = S_{AB} - S_A - S_B$, giving the entropy of mixing per molecule as

$$\Delta S_{mix} = -k_B [x_A \ln x_A + x_B \ln x_B], \quad (2.4)$$

where $x_A = n_A/n$ and $x_B = n_B/n$ are molar fractions of A and B respectively. The entropy change ΔS_{mix} is a configurational entropy, because it only accounts for entropy changes due to the change of available configurations upon mixing. Strictly speaking this expression only applies to mixtures in which the molecules of both species are interchangeable, i.e., equal sizes and interaction energies; this means a molecule of A can be swapped with a molecule of B with no penalty.

A *regular solution* is one in which the entropy of mixing is given by Eq. (2.4), as for an ideal solution, but with $\Delta H \neq 0$. That polymer solutions do not obey Raoult's Law even when there was zero heat of mixing meant that polymer solutions are *non-regular* solutions.

($n_s = 27$) and n_p polymer molecules ($n_p = 3$), we require $n_s + xn_p$ lattice cells ($n_s + xn_p = 27 + (3 \times 6) = 45$). We then place, at random, the end segment of a single polymer chain on a lattice cell, hence there are $n_s + xn_p$ possible configurations for this move. The next segment from the same chain has much less freedom, of course, because it is connected to the first segment. Given this restriction, this segment has z sites to choose from, where z is the coordination number. This gives the second segment z sites to choose from (in this case, perhaps $z = 5$, since there are five neighbouring sites to choose from; this drops out of the resulting expression). However, this second segment doesn't really have this much choice, since if the polymer chain were part of a filled lattice, there might already be segments from another chain next to the first segment of the chain we are considering. Using assumptions (iii) and (iv), we assume that we may put the number of configurations for the second segment to be $z(1 - f_p)$ where f_p is the probability that a cell is already occupied (f_p also drops out of the final expression). Once all polymer chains have been placed on the lattice, the remaining sites are filled with solvent molecules. Counting up all the configurations available, and subtracting the entropy of the pure states of both polymer and solvent, we arrive at

$$\begin{aligned}\Delta S_{mix} &= -k_B \left[n_s \ln \frac{n_s}{n_s + xn_p} + n_p \ln \frac{xn_p}{n_s + xn_p} \right] \\ &= -k_B [n_s \ln(\phi) + n_p \ln(1 - \phi)],\end{aligned}\quad (2.5)$$

where ϕ is the volume fraction of solvent, therefore $1 - \phi$ is the volume fraction of polymer.

Although in (i), we defined a segment as being equal in size to a solvent molecule, it may be necessary that a segment in the polymer chain is necessarily the size of several solvent molecules, since a segment must be at least so big as to allow the chain complete flexibility around these segments. In this case, we should define the lattice cell to be the size of the segment, and have several solvent molecules to one cell. Flory addressed this [3], arguing that this can be accounted for by the rescaling $n_s \rightarrow n_s/\beta$, $x \rightarrow x/\beta$ where β is the number of solvent molecules that will fill a cell the volume of a single polymer segment. This simply re-enforces the requirement to correctly measure the polymer chains in terms of segment lengths/lattice spacing (so a polymer chain may consist of 15 repeat units/monomers, but a segment may consist of 3 monomers, hence the chain is 5 segments long).

It is more natural to express this equation per 'molecule', where the number of molecules equals the number of lattice cells $n_s + xn_p$. We arrive at

$$\Delta S_{mix} = -k_B \left[\phi \ln(\phi) + \frac{(1 - \phi)}{x} \ln(1 - \phi) \right], \quad (2.6)$$

where ΔS_{mix} has been redefined as the entropy of mixing per molecule. This equation can be generalised to polymer-polymer mixtures. If the solvent is replaced by polymer species A with y number of segments, then the factor of ϕ can be replaced by ϕ/y

in the first term. It is more natural to replace y with N_A and x with N_B , where N_i represents the number of segments in species i (the segment size of both species being chosen to be equal in the definitions of N_i). This gives

$$\Delta S_{mix} = -k_B \left[\frac{\phi}{N_A} \ln(\phi) + \frac{(1-\phi)}{N_B} \ln(1-\phi) \right]. \quad (2.7)$$

Equation (2.7) is known as the Flory-Huggins Entropy of Mixing. Notice that unlike Eq. (2.4), the logarithm terms contain volume fractions. If $N_A = N_B = 1$ then Eq. (2.7) reduces to Eq. (2.4) for ideal solutions.

Although any lattice parameters do not strictly appear in (2.7), it is worth noting again that the ‘length’ of a polymer species should be counted in units of lattice size. So if species A and B have the same number of monomer units and are both flexible around these units, then if the size of A -monomers are twice the size of B -monomers, we have $N_A = 2N_B$ (assuming the lattice cells are the size of the A -monomers, which is required to allow the A -chains to be flexible). Working in volume fractions ϕ accounts for the other mathematical difference due to B -chains having half the volume of A -chains.

2.3 Heat of Mixing

Although deviations from Raoult’s law could be shown to derive from the entropy of mixing given by Eq. (2.5), fits to the activities data still require a term that took the heat of mixing into account [5]. Of course, generally a heat of mixing term for polymers will be required, because the heat of mixing is rarely zero.

2.3.1 Activities Data

Raoult’s law relates the vapour pressure of an ideal solution to the vapour pressure of each solution-component and the mole fraction of that component. Huggins used an expression essentially equivalent to Raoult’s Law, writing the chemical potential μ_i of species i in a solution as [5]

$$\mu_i = \mu_i^o + RT \ln a_i, \quad (2.8)$$

where the reference state with chemical potential μ_i^o may refer to the pure component, for simplicity. The ‘activity’ is defined as $a_i = p_i/p_o$, where p_i and p_o are the vapour pressures of component i in the solution and as pure component, respectively. An expression for the difference in chemical potential can be found from the entropy of mixing:

$$\Delta\mu_p = -\frac{\partial(T\Delta S)}{\partial n_p^*}, \quad (2.9)$$

where n_p^* is now the number of moles of polymer, and $\Delta\mu_p = \mu_p - \mu_p^o$. The entropy of mixing (2.5) in terms of the number of moles of solvent and polymer is then

$$\Delta S_{mix} = -R \left[n_s^* \ln \frac{n_s^*}{n_s^* + x n_p^*} + n_p^* \ln \frac{x n_p^*}{n_s^* + x n_p^*} \right]. \quad (2.10)$$

Using Eq. (2.9) and converting back into volume fractions, we arrive at

$$\frac{\Delta\mu_p}{RT} = \ln a_p = \ln \phi_p + (1 - x)\phi_s. \quad (2.11)$$

From the way the number of segments x in the polymer molecules is defined, x can be written in terms of a ratio of volumes of the polymer and solvent molecules $x = \bar{V}_p / \bar{V}_s$. Generalising to polymer-polymer systems (since we can always choose $N = 1$ for either polymer for it to be a simple solvent), there are two expressions for a binary mixture

$$\begin{aligned} \ln a_A &= \ln \phi_A + \left(1 - \frac{\bar{V}_A}{\bar{V}_B}\right) \phi_B, \\ \ln a_B &= \ln \phi_B + \left(1 - \frac{\bar{V}_B}{\bar{V}_A}\right) \phi_A, \end{aligned} \quad (2.12)$$

where either A or B could be a polymeric solute or a solvent.

The osmotic pressure of the solvent can be related to the activity by

$$\frac{\Pi}{c_s} = -\frac{RT}{c_s^2} \ln a_s, \quad (2.13)$$

where c_s is the concentration of polymer solute or equivalently (given different units) the partial molar volume. In order to account for how, in polymer solutions, Π/c_s increases with c_s Huggins needed to include an empirical term in Eq. (2.12) which “takes care of the heat of mixing, deviations from complete randomness of mixing, and other factors” [5]:

$$\begin{aligned} \ln a_A &= \ln \phi_A + \left(1 - \frac{\bar{V}_A}{\bar{V}_B}\right) \phi_B + \mu_A \phi_B^2, \\ \ln a_B &= \ln \phi_B + \left(1 - \frac{\bar{V}_B}{\bar{V}_A}\right) \phi_A + \mu_B \phi_A^2. \end{aligned} \quad (2.14)$$

Using Eqs. (2.13) and (2.14) Huggins showed that the expression for the entropy, Eq. (2.7), fit data on polymer solutions, providing the empirical constants μ_A and μ_B

are chosen suitably for a particular solution (with the condition that $\mu_A \bar{V}_A = \mu_B \bar{V}_B$, which is natural since the heat of mixing is a mutual interaction between opposing species and must be balanced). In hindsight, the need for the empirical constants to be included in Eq. (2.14) can be seen to arise from the definition of the chemical potential (2.9), since the full expression should be $\Delta\mu_p = \partial(\Delta G)/\partial n_p^*$. However, the form of ΔH was not yet known.

2.3.2 A van Laar Form for the Heat of Mixing

Flory provided a simple derivation for an appropriate form for the heat of mixing [4]. The result is the van Laar expression for the heat of mixing of simple molecules, which has a simple lattice-based explanation [6], which follows. If a fluid *A* and fluid *B*, both consisting of simple molecules, occupy molar volumes *v* and *V* respectively, then for a solution of *n* moles of *A* and *N* moles of *B*, the internal energy per mole of solution can be written as

$$U_{AB} = \frac{\epsilon_{AA}(vn)^2 + 2\epsilon_{AB}(vnVN) + \epsilon_{BB}(VN)^2}{vn + VN}. \quad (2.15)$$

Subtracting the energy of (the same quantity of) the pure fluids $U_A = \epsilon_{AA}vn$, $U_B = \epsilon_{BB}VN$, and gathering terms, gives

$$\Delta U = \Delta\epsilon \frac{vVNn}{nv + NV}, \quad (2.16)$$

$$\Delta\epsilon = 2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}. \quad (2.17)$$

For polymer systems, the argument can be made that the form of interactions between polymer segments and solvent molecules should be the same as those between simple molecules. Assuming no volume change upon mixing, $\Delta H = \Delta U$, so the partial molal heat of *A*, given by $\Delta\bar{H}_A = \partial\Delta H/\partial n$, is then

$$\Delta\bar{H}_A = \Delta\epsilon\phi_B^2, \quad (2.18)$$

which is exactly the same form as the heat of mixing term in Eq. (2.14). However, Flory was quick to point out that the use of this term provides satisfactory agreement with experiment, but that it clearly must contain “contributions from other factors the origins of which are not yet clear” [4]. This could include, of course, entropy effects due to the heat of mixing and configurational entropy modifications to Eq. (2.7) from the fact that, given a finite heat of mixing, systems of polymers and solvents will not be entirely uniform.

2.3.3 The Flory-Huggins Interaction Parameter

A heat of mixing consistent with Eq. (2.16) can be derived from a general lattice model with coordination number z , as in Flory's textbook [7]. However, I found the latter derivation slightly difficult to follow, so I have opted to derive the heat of mixing in line with a more modern approach [8].

A *mean-field*⁵ assumption can be applied to a binary polymer mixture AB on a quasi solid lattice. Assume that the probability that a lattice cell picked at random will contain a segment of A or B is given by the volume fraction of A or B , denoted by ϕ_A or ϕ_B respectively. Also, given this chosen site, the probability that any neighbouring site contains a segment of A or B is also given by ϕ_A or ϕ_B respectively. If the interaction energy between two A segments is ϵ_{AA} , then given the probability of choosing an A -segment when choosing the first site is ϕ_A , and given that the probability of a neighbouring site containing an A -segment is ϕ_A , then the contribution to the average site energy from A - A interactions will be $\epsilon_{AA}\phi_A^2$. The average energy of a site can then be given by the general formula

$$U_{site} = z \sum_{i=A,B} \sum_{j=A,B} \epsilon_{ij} \phi_i \phi_j, \quad (2.19)$$

whereas the total energy of the pure states of A and B is given by

$$U_{pure} = z \sum_{i=A,B} \epsilon_{ii} \phi_i. \quad (2.20)$$

Performing $U_{site} - U_{pure}$ gives the change in internal energy upon mixing per site. Assuming no volume change, this is the same as the enthalpy of mixing.

$$\begin{aligned} \Delta H_{mix} &= k_B T \chi \phi_A \phi_B, \\ \chi &= z \Delta \epsilon / k_B T, \\ \Delta \epsilon &= 2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}. \end{aligned} \quad (2.21)$$

Equation (2.21) is almost exclusively used to represent the heat of mixing. The dimensionless parameter χ is called the Flory-Huggins interaction parameter. It can be measured in experiments, and is usually considered to be an experimental parameter to describe the heat of mixing without reference to any microscopic effects or lattice theory model. However, in this particular lattice theory model from which χ has been explained, χ is purely enthalpic in origin. An entropic contribution is generally necessary.

⁵Mean-field: average interactions are used in place of counting up individual interactions, such that the local behaviour can be written in terms of macroscopic average properties.

Non-combinatorial Entropy

The entropy of mixing (2.7) represents the combinatorial entropy of mixing, resulting only from the change in available configurations for *non-interacting* chains (in other words, it arises from the increased volume in which the polymer molecules can distribute themselves, which allows them access to more configurations [9]). In general, we should expect χ to have an entropic part too, usually referred to as a non-combinatorial entropy, and may arise from the non-uniformity of a solution caused by preferential attraction between like components, or from a change in the accessibility of energy levels or restriction of certain rotational configurations due to interactions.

The entropy of mixing can be obtained from Eq. (2.1) as

$$\Delta S = -\frac{\partial \Delta G}{\partial T}, \quad (2.22)$$

and the enthalpy/heat of mixing as

$$\Delta H = \Delta G + T \Delta S. \quad (2.23)$$

Substituting in the entropy of mixing (2.7) and the heat of mixing (2.21), and assuming that it is possible that χ depends on temperature, gives

$$\Delta S = -k_B \left[\frac{\phi}{N_A} \ln(\phi) + \frac{(1-\phi)}{N_B} \ln(1-\phi) + \phi(1-\phi) \frac{\partial(\chi T)}{\partial T} \right]. \quad (2.24)$$

From this follows that

$$\Delta H = \Delta G + T \Delta S = k_B T \phi_A \phi_B \left(\chi - \frac{\partial(\chi T)}{\partial T} \right). \quad (2.25)$$

Comparing this with the heat of mixing (2.21) we see that, in general, the Flory-Huggins interaction parameter χ has both an enthalpic and entropic part [7, 10], such that $\chi = \chi_H + \chi_S$, where

$$\chi_H = \chi - \frac{\partial(\chi T)}{\partial T} = -T \frac{\partial \chi}{\partial T}, \quad (2.26)$$

$$\chi_S = \frac{\partial(\chi T)}{\partial T}. \quad (2.27)$$

Thus in order for the interaction parameter to be purely enthalpic, it must have temperature dependence $\chi \propto 1/T$.

Anomalous contributions to the entropy of mixing were often put down to changes in volume which the lattice model used to derive Eq. (2.7) cannot include. Whilst changes in volume will of course alter the entropy, numerous experiments under fixed volume still show that there is a contribution to the entropy upon mixing that cannot

be accounted for by Eq. (2.7) and thus a non-combinatorial entropy contribution must exist [9]. This idea is now a standard part of the literature [11].

Dependence of Heat of Mixing on Volume Fraction

In Flory's first paper on the subject [3] it was suggested that the agreement between theory and experiment would be better if the enthalpy term equivalent to $\Delta\epsilon$ in Eq. (2.18), which acts as an analogue of χ , was given an appropriate dependence on concentration. For the rubber-toluene solution measurements in question, the theory was rather accurate for high concentrations of rubber solute, but matched the data at low rubber concentrations only with an empirical fit for the heat of mixing. In [4], Flory returned to this matter, mentioning that the fit that Huggins had made to a benzene-rubber solution (which required no concentration dependence for the empirical terms containing μ_i) was correct, but that the matter was actually more complicated. Other measurements that separately measured the heat of mixing and entropy of mixing in this system confirmed that both departed significantly from the theory, but "when these two somewhat erroneous equations are combined, however, a satisfactory free energy function is obtained, as Huggins has shown". Flory suggested that a finite heat of mixing might be responsible, since this would necessarily lead to non-uniform mixing (clusters of solute in pure solvent).

This idea was explicitly addressed by Flory in a paper soon after [12], in which Flory investigated the case of highly diluted polymer solutions. Experiments showed that the heat of dilution was dependent on the concentration of polymer solute, and there was a marked difference between dilute and concentrated solutions. The heat of mixing as given by the van Laar form in Eq. (2.14) could be reconciled with the data provided that μ is reformulated as

$$\mu = \beta + \alpha/RT, \quad (2.28)$$

in which both α and β depend on the concentration. Flory states that the benzene-rubber system analysed by Huggins is essentially a special case in which the free energy function does not require μ to depend on concentration, even though the entropy and heat of dilution equations when considered separately do not match the data. Flory points out that the value of μ needed for the fit is actually much lower than theory would predict, which indicates that μ is really just an empirical constant, and that "in spite of the approximate constancy of μ for rubber in benzene at all concentrations, it is unlikely that this condition applies to high polymer solutions in general". Flory showed that a different μ was required for solutions of high concentration than low concentration, and the constant α must change and, generally, it is "likewise necessary to throw the burden of μ on β in dilute solutions" [12]. Equation (2.28) is essentially equivalent to the modern common expression for the Flory-Huggins parameter:

$$\chi = A + \frac{B}{T}. \quad (2.29)$$

2.4 Flory-Huggins Free Energy of Mixing

Substituting the Entropy of Mixing (2.7) and the Heat of Mixing (2.21) for polymer systems into the expression for the Gibbs free energy (2.1), we obtain the Flory-Huggins Free Energy of Mixing $f_{FH} \equiv \Delta F_{mix} = \Delta H_{mix} - T \Delta S_{mix}$. In units of $k_B T$, we can write

$$f_{FH}(\phi) = \frac{\phi}{N_A} \ln(\phi) + \frac{(1-\phi)}{N_B} \ln(1-\phi) + \chi\phi(1-\phi). \quad (2.30)$$

The expression $f_{FH}(\phi)$ is the ‘bulk’ free energy for a polymer blend, giving the free energy per lattice site in the Flory-Huggins lattice with spacing a .

Phase Diagram from the Flory-Huggins Free Energy

Equation (2.30) can be used to compute a *phase diagram*⁶ for the blend which separates the one-phase region (the components of the polymer blend remains mixed together, entropy overcoming enthalpy) from the two-phase region (the polymer blend de-mixes into two phases, each rich in one component of the polymer blend) in the plane of composition and temperature. Figure 2.3 is a phase diagram for the polymer blend $N = N_A = N_B$, containing a coexistence curve and spinodal line, explained below.

The limits of stability of a polymer blend can be calculated by consideration of the first and second derivatives of the free energy (2.30) with respect to composition, $dF/d\phi$ and $d^2F/d\phi^2$ respectively. To demonstrate, I will consider a blend in which the two polymers A and B have the same chain lengths (degree of polymerisation) $N_A = N_B = N$, since this is the simplest example. The first derivative is

$$\frac{\partial F}{\partial \phi} = \frac{1}{N} \ln\left(\frac{\phi}{1-\phi}\right) + \chi(1-2\phi). \quad (2.31)$$

$dF/d\phi = 0$ corresponds to minima in the free energy, and we can rearrange the resulting expression so that we can plot a locus of points for which $dF/d\phi = 0$, giving us the ‘coexistence curve’

$$\chi_{\text{coex}} = \frac{1}{N} \frac{1}{2\phi-1} \ln\left(\frac{\phi}{1-\phi}\right). \quad (2.32)$$

(If the blend is not symmetric, then calculating the coexistence curve is more complicated, requiring equating the chemical potentials of both species). The second derivative is

⁶Phase Diagram: a diagram, drawn in a space of variables such as composition and temperature, that separates regions corresponding to different stable *phases* with lines, which correspond to the limits of stability of these phases. e.g. for water, a phase diagram in the temperature-pressure plane separates regions of vapour, liquid and solid.

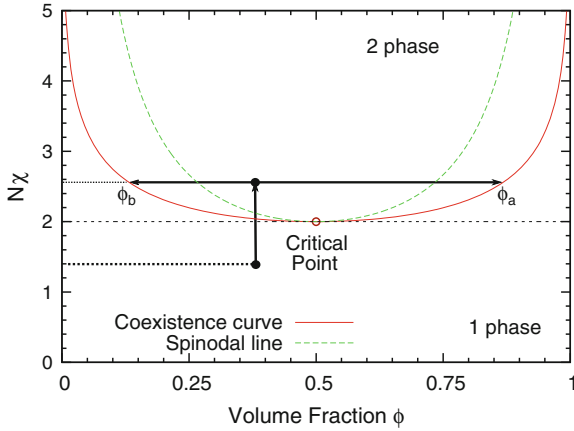


Fig. 2.3 Phase diagram in the ϕ - χ plane (essentially equivalent to composition-temperature) for a polymer blend $N = N_A = N_B$. Below the coexistence curve, it is favourable for the polymer blend to remain mixed, hence 1-phase is stable. Above the coexistence curve, it is favourable for the polymer blend to de-mix, hence 2-phases are stable. Between the coexistence curve and the spinodal line, 1-phase has more energy than 2-phases, but 1-phase is metastable, and so 1-phase may still exist in this region. So the spinodal line represents the limit of stability for the blend remaining in the 1-phase state i.e. above the spinodal, 1-phase is unstable. The critical point (ϕ_C, χ_C), located at critical volume fraction ϕ_C and critical temperature χ_C , corresponds to where the coexistence curve and spinodal line coincide. It is the first point at which the blend becomes unstable upon increasing χ (assuming $\chi = A + BT^{-1}$, then the critical point marks the highest temperature for which a blend in the 1-phase region is unstable)

$$\frac{\partial^2 F}{\partial \phi^2} = \frac{1}{N} \frac{1}{\phi(1-\phi)} - 2\chi, \quad (2.33)$$

$d^2 F/d\phi^2 = 0$ corresponds to minima in the free energy for which the curvature of the free energy is also zero, and this expression can be rearranged to obtain the locus of points called the ‘spinodal line’

$$\chi_s = \frac{1}{2N} \frac{1}{\phi(1-\phi)}. \quad (2.34)$$

Quenching a polymer blend, such that the temperature changes and the blend passes from the 1-phase region to the 2-phase region, results in ‘spinodal decomposition’ i.e. phase separation induced by crossing the spinodal line. This will be discussed more in Sect. 2.6.

2.5 Flory-Huggins-de Gennes Free Energy

In order to study how a polymer blend undergoes *phase separation*, in which a 1-phase mixture de-mixes into a 2-phase mixture, we need to take into account energy costs from different phases being in contact with each other e.g. a phase rich in polymer *A* being in contact with a phase rich in polymer *B*. The interface between these phases will have a finite width, so this interface is essentially a composition gradient across which the composition goes from *A*-rich to *B*-rich. We need to account for free energy contributions from composition gradients.

2.5.1 Free Energy of Non-uniform Systems

Cahn and Hilliard [13–16] are probably owed the most credit to development of theory to describe non-uniform systems. Cahn was primarily interested in binary alloys and mechanisms of phase separation and the interfaces in the resulting structures. Although the original treatment by Cahn and Hilliard was in the context of a binary mixture of simple fluids or quasi-solids, the theory is very general, requiring only a small change to describe polymer systems.

In the first of a series of three papers, all published under the leading title “Free energy of a non-uniform system” [13–15], Cahn and Hilliard presented “a general equation for the free energy of a system having a spatial variation in one of its intensive scalar properties” [13], which for simplicity was chosen to be a binary solution. Cahn and Hilliard’s original treatment of the problem was based on expressing the local free energy f^* “as the sum of two contributions which are functions of the local composition and the local composition derivatives” [13, 15]. For an isotropic system which has no directionality, it was then supposed that the local free energy f^* could be expressed as

$$f^*(c, \nabla c, \nabla^2 c, \dots) = f(c) + \kappa_1 \nabla^2 c + \kappa_2 (\nabla c)^2 + \dots \quad (2.35)$$

where f is the energy of a uniform system, the derivatives terms represent local composition gradients and κ_i are coefficients that may possibly depend on the local composition. It is noted no assumptions are made about the nature of κ_i , which of course could depend on local concentration [15]. The form of Eq. (2.35) is intuitive for an isotropic system, because only even powers of the gradient term may appear if direction is not important.

The energy f^* refers to the local energy of a volume dV , hence the total free energy in a system of volume V is given by

$$F = \int_V f^* dV. \quad (2.36)$$

This result, which describes an inhomogeneous system, has two contributions to the free energy: a local contribution $f(c)$ from the system being held at composition c ; and the energy contribution from a local composition gradient in the system. After a little re-arranging, we can express this as

$$\begin{aligned} F &= \int_V f^*(c, \nabla c, \nabla^2 c, \dots) dV, \\ &= \int_V \left[f(c) + \kappa(\nabla c)^2 + \dots \right] dV, \end{aligned} \quad (2.37)$$

$$\kappa = -d\kappa_1/dc + \kappa_2. \quad (2.38)$$

So in general we see that κ may indeed depend on the concentration. Equation (2.37) is limited to a regime in which the composition gradients are not too steep, or to be more exact where “the ratio of the maximum in this free energy function to the gradient energy coefficient κ must be small relative to the square of the intermolecular distance” [13]. If this is not the case, then higher even powers of the derivatives of local concentration need to be included in Eq. (2.35).

Cahn and Hilliard used Eq. (2.37) to investigate the properties of the interface between two coexisting phases, and applied it to regular solutions of simple molecules [13]. The surface and interfacial energies predicted by manipulations of Eq. (2.37) agreed extremely well with experimental data and were in agreement with two empirical expressions for the latter known to generally apply. Furthermore, the theory produced extremely good agreement with data on the interfacial energy close to the critical temperature T_C (χ_C ; see Fig. 2.3), which is significant as it validated the dependence of the surface energy on the distance from the critical temperature that the theory predicted [13]. As explicitly explained by Cahn, the advantage of this representation of a non-uniform system is “the splitting of the thermodynamic quantities into their corresponding values in the absence of a gradient and an added term due to the gradient” [14].

2.5.2 Random Phase Approximation for Polymer Chains

The Random Phase Approximation is a self-consistent field calculation for (dense) polymer systems, attributed to de Gennes [17–20]. Using the RPA it is possible to find the form of $\kappa(\phi)$, the coefficient of the gradient term in Eq. (2.37), suitable for describing polymer systems. I will briefly follow the outline of the derivation for $\kappa(\phi)$, leaving the full derivation for the citations below.

Self-consistent Field Calculations

The idea behind a self-consistent field calculation (a type of mean-field treatment) for polymer systems is as follows [17]. We choose a form of interaction between polymer segments, and then derive a potential based on this interaction and the local

concentration of segments. We then take an *ideal/non-interacting* chain and place it in this potential, and derive the resulting concentration profile. We ask if our profile for the concentration is consistent with this potential, given the interactions producing the potential, i.e., we've placed our ideal chains, now if we make them non-ideal (interacting), will the interactions between segments produce the potential? Almost certainly not, so we update the concentration profile so that it's appropriate for our potential. However, since the potential is also dependent on the concentration, we then update the potential, and then update the concentration again etc. This is an iterative procedure, and following de Gennes we can describe it as

$$U(\mathbf{r}) = Tv\phi(\mathbf{r}), \quad (2.39)$$

where T is temperature and v is the excluded volume occupied by a segment. Given an ideal polymer chain in a potential $U(\mathbf{r})$ we can calculate a new concentration profile $\phi'(\mathbf{r})$, and then calculate a new potential $U'(\mathbf{r})$ etc. We hope that the potential and concentration profile converge on a stable fixed solution upon enough iterations.

De Gennes points out that the first application of a self-consistent field treatment to polymers was by Edwards [21], and I found the explanation given in Edward's work to be extremely enlightening. Edwards explains that the probability of finding a segment at distance L along the chain and distance r from the origin is not simply a random walk, due to the excluded volume principle—a segment cannot occupy a certain volume that is excluded by the presence of another segment. Thus the probability distribution is broadened and Edwards shows that “it will turn out that p (the probability distribution) will play the role of a potential”. Note that the potential arises from the excluded volume principle, so we need only know that there is an interaction which achieves an excluded volume effect.

The Random Phase Approximation

The motivation behind the Random Phase Approximation (RPA) is: we want to compute a response function that tells us how a weak perturbation at point r will effect the concentration at a point r' . We will allow our chains to sit in an overall potential that is the sum of this weak perturbing potential and a self-consistent potential that is due to all of the surrounding chains. We wish to find this self-consistent potential, and this is quite a difficult problem. I will briefly describe the principles behind the random phase approximation, avoiding the dense mathematics but following the description in de Gennes book [17].

The change in local concentration at point r due to a weakly perturbing potential $W(r')$ at point r' is

$$\delta\Phi_n(\mathbf{r}) = -\frac{1}{T} \sum_{\mathbf{r}'} \sum_m S_{nm}(\mathbf{r}\mathbf{r}') W_m(r'), \quad (2.40)$$

where the index m represents segment m such that W_m is the perturbing potential acting on segment m , and S_{nm} is a response function that relates how the perturbation

on segment m at r' affects segment n at r . Thus we see that all perturbations on all segments have been included. Since we are considering an isotropic system, the response function may only depend on the separation $r - r'$, so we switch to Fourier space to simplify the treatment

$$\delta\Phi_n(\mathbf{q}) = -\frac{1}{T} \sum_m S_{nm}(\mathbf{q}) W_m(q). \quad (2.41)$$

After some difficult maths, the central result of RPA emerges as

$$\begin{aligned} S_{nm}(\mathbf{q}) &= S_{nm}^0(\mathbf{q}) - \frac{S_n^0(\mathbf{q}) S_m^0(\mathbf{q})}{\sum_{nm} S_{nm}^0(\mathbf{q})}, \\ &= S_{nm}^0(\mathbf{q}) - \frac{S_n^0(\mathbf{q}) S_m^0(\mathbf{q})}{N g_D(\mathbf{q})}, \end{aligned} \quad (2.42)$$

where $S_{nm}^0(\mathbf{q})$ is the non-interacting response function (which is known, hence allowing the substitution of the Debye scattering g_D function for the sum over these response functions) and $S_n^0(\mathbf{q}) = \sum_m S_{nm}^0(\mathbf{q})$.

What exactly does Eq. (2.42) mean? The derivation of this result does not involve introducing specific interactions as such, other than the implied repulsive interaction that is responsible for excluded volume, so the result really represents the distribution of polymer segments caused by there being other polymer segments around. For a detailed derivation, the reader should consult de Gennes book [17]. The main point here is that we can calculate the response function S_{nm} from quantities that we already know. We can measure S_{nm} using neutron scattering experiments, using chains partially labelled with deuterium [19, 20]. The results of these experiments will tell us the distribution of labelled segments and therefore of the polymer chains, assuming that the labelling of segments doesn't introduce additional interactions.

2.5.3 The Flory-Huggins-de Gennes Free Energy

We still need to calculate a coefficient κ of the gradient term in Eq. (2.37) suitable for polymer systems. A derivation can be found in modern textbooks [8, 10]. We ask how the local composition changes with respect to a change in the local chemical potential. When the volume we consider is very large compared to the chain size, such that this volume as a whole will not contain fluctuations of concentration, we obtain from Eq. (2.30) with $\chi = 0$ (such that the polymer mixture is ideal) the chemical potential of species i as $\mu_i = \partial\Delta F/\partial\phi_i$:

$$\mu_i = \frac{kT}{N_i} \ln \phi_i + \text{const}, \quad (2.43)$$

providing we write $\phi \equiv \phi_i$ and $1 - \phi \equiv \phi_{j \neq i}$. We can then easily derive the response function that we desire

$$\frac{\partial \phi_i}{\partial \mu_i} = \phi_i \frac{N_i}{kT}. \quad (2.44)$$

Using the notation $\delta(\Delta\mu) = \delta\mu_A - \delta\mu_B$ and noting that for a binary mixture we must have $\phi_A + \phi_B = 1$, then we obtain with $\phi = \phi_A$

$$\frac{\partial \phi}{\partial(\Delta\mu)} = \frac{1}{kT} \left(\frac{1}{\phi N_A} + \frac{1}{(1 - \phi) N_B} \right)^{-1}. \quad (2.45)$$

This won't be correct for small volumes where fluctuations are significant. Working in Fourier space, we can adapt the latter equation to

$$\begin{aligned} \frac{\partial \phi(\mathbf{q})}{\partial(\Delta\mu(\mathbf{q}))} &= \frac{1}{kT} \left(\frac{1}{\phi S_A(\mathbf{q})} + \frac{1}{(1 - \phi) S_B(\mathbf{q})} \right)^{-1}, \\ &= \frac{1}{kT} S_{ni}(\mathbf{q}), \end{aligned} \quad (2.46)$$

where S_{ni} is the response function for non-interacting chains.

To account for a potential, so as to consider interacting chains, we can then write

$$\frac{1}{S(\mathbf{q})} = \frac{1}{S_{ni}(\mathbf{q})} - V(\mathbf{q}), \quad (2.47)$$

and we note that for $q = 0$ this potential must equal 2χ , since by definition this is our interaction in the FH regime based solely upon the enthalpy between two monomers. For small q it must be true that

$$V(\mathbf{q}) = 2\chi \left(1 - \frac{1}{6} q^2 r_0^2 \right), \quad (2.48)$$

because this term arises from a first order expansion of a Gaussian distribution describing a bare response function for a non-interacting chain [17, 20] and r_0 , which is of the order of the segment size a (which is therefore equal to the lattice spacing in the Flory-Huggins lattice), measures the range of inter-segment forces [8]. Inserting the approximate potential V and the response functions S_A and S_B into Eq.(2.47) we obtain an expression for the scattering response function $S(\mathbf{q})$ that is consistent with a free energy (in units of $k_B T$) of the form [8]

$$F = \int \left[f_{FH}(\phi) + \kappa(\phi)(\nabla\phi)^2 \right] d\mathbf{r}, \quad (2.49)$$

$$\kappa(\phi) = \frac{\chi_0^2}{6} + \frac{a^2}{36\phi(1-\phi)} \approx \frac{a^2}{36\phi(1-\phi)}, \quad (2.50)$$

for which it is common practice to neglect the small first term in $\kappa(\phi)$. The result is the Flory-Huggins-de Gennes free energy for a binary polymer system:

$$F[\phi, \nabla\phi] = \int \left[f_{FH}(\phi) + \frac{a^2}{36\phi(1-\phi)} (\nabla\phi)^2 \right] d\mathbf{r}, \quad (2.51)$$

which is the starting point for studying the kinetics of, and morphology resulting from, phase separation of polymer blends.

2.6 Spinodal Decomposition

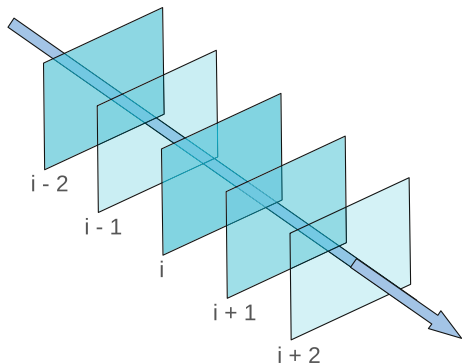
A mixture of two components may exist either as one phase (the entropy of mixing overcomes the heat of mixing) or as two phases (the heat of mixing overcomes the entropy of mixing). A phase diagram like Fig. 2.3 separates regions of stability of blends existing as one-phase and two-phases. Phase separation from one phase into two phases, caused by the thermodynamic instability of the mixture as it is brought across the spinodal line from the one-phase to the two phase region, is called Spinodal Decomposition. I will first discuss an early example involving a crystalline solid, not only because it is an important example in the development of theory, but because it is a good introduction to several concepts.

2.6.1 A Crystal with a 1D Inhomogeneity

Hillert considered a crystalline solid consisting of two components *A* and *B*, in which a variation in composition *x* (the volume fraction of *A*, $0 < x < 1$) was allowed in one direction along the crystal [22]. This system was modelled by consecutive parallel 2D planes $i-1, i, i+1, \dots$, every plane having some characteristic composition $x_{i-1}, x_i, x_{i+1}, \dots$. Figure 2.4 shows a schematic representation.

Hillert calculated the free energy of this system. For the interaction energy (heat/enthalpy), it was assumed that an atom in a particular plane *i* could interact with *Z* nearest neighbours in total, with *z* of these nearest neighbours being located in the *next* plane $i+1$. The system as a whole has average composition x_a , interaction strength *v*, and the total number of atoms within a single atomic plane is *m*. The energy of interaction for plane *i* interacting with next plane $i+1$ is then $\Delta U = vm \{Z(x_i - x_a)^2 - z(x_i - x_{i+1})^2\}$. The change in entropy arising from a single plane *i* being at a composition different from the average composition is given by regular solution theory $\Delta S = m \left\{ x_p \log \frac{x_p}{x_a} + (1 - x_p) \log \frac{1-x_p}{1-x_a} \right\}$. Hence, after summing across all planes in the system, the energy difference between the inhomogeneous and homogeneous states is

Fig. 2.4 Parallel 2D planes of a crystal, in which the composition of each plane $0 < x_i < 1$ is represented, in this schematic, by the degree of transparency of the planes. The arrow represents the direction of inhomogeneity in the crystal



geneous state and the homogeneous (note the direction of consideration of energy difference, which gives a minus sign) is

$$\begin{aligned} \Delta F = & -vm \sum_p \left\{ Z(x_p - x_a)^2 - z(x_p - x_{p+1})^2 \right\} \\ & + k_B T m \sum_p \left\{ x_p \log \frac{x_p}{x_a} + (1 - x_p) \log \frac{1 - x_p}{1 - x_a} \right\}. \end{aligned} \quad (2.52)$$

Nature of Stable Solutions

Hillert considered stable (mathematical) solutions to the problem, which requires calculation of the change in free energy “when atoms are exchanged between two neighbouring planes $p - 1$ and p ” i.e. what is the *functional derivative* of the free energy with respect to composition x_p of plane p . For equilibrium (stable solutions) we require $\delta \Delta F / \delta x_p = 0$. For small amplitude fluctuations around the average composition x_a , stable solutions were found to obey the relation

$$x_{p+1} = x_{p-2} - x_{p-1} + x_p - 2M(x_{p-1} - x_p), \quad (2.53)$$

where M is a constant given by a combination of parameters (including average composition x_a , the number of nearest neighbours Z and z , the temperature T , and the interaction energy v).

It turns out that $M = 1$ corresponds to the spinodal curve for a 1D system: (one-phase region) $|M| > 1$ corresponds to states outside the spinodal for which the only physically relevant solution (in which $0 < x_p < 1$) was $x_p = \text{const} = x_a$ i.e. a homogeneous state; (two-phase region) $|M| < 1$ corresponds to inside the spinodal, for which relevant solution for small amplitude fluctuations are of the form $x_p = x_a + C \sin p\phi$ where C is a constant. For shallow depths beyond the spinodal, the wavelength (of the composition variation) extends over many atomic planes, but as distance into the spinodal increases ($|M| \rightarrow 0$) the wavelength becomes of order

unity (on the order of a few atomic planes). Consideration of large compositional variations required numerics to be performed on a computer, but the results showed that again the equilibrium states within the spinodal were sinusoidal in nature.

Wavelengths

Hillert supposed that a kinetic treatment of the problem would give insight into what composition variation wavelengths might dominate by showing which wavelengths would grow the fastest. It was also noted that in order for the system to increase the wavelength of fluctuations (in order to lower energy) a re-arrangement of the system is necessary that should also be studied from a kinetic perspective. By deriving a diffusion equation for the system and applying random fluctuations (fluctuations with a spectrum of amplitudes and wavelengths), Hillert found that a spectrum of wavelengths first developed, followed by small wavelength fluctuations decreasing in amplitude, causing the average wavelength of the system grow with time. Consideration of the fastest growing wavelength is important in spinodal decomposition studies [22].

2.6.2 Stability of a Solution

Cahn considered the stability of a solid-solution with respect to compositional fluctuations [23], where ‘solution’ is meant in the sense of a binary mixture which may support composition gradients, and ‘solid’ is meant in the sense that there is an elastic energy contribution to the free energy (arising from strain in the material when an initially homogeneous region becomes inhomogeneous). I will leave out the elastic energy contribution in my discussion here.

Cahn considered the free energy of a two-component solution using Eq. (2.37). To consider fluctuations requires knowledge of how the free energy changes when a small amount of one-component is replaced with another, but “in the presence of a gradient, if we make a local change in composition we also change the local gradient”, so we must consider the functional derivative of the free energy with respect to composition. If a functional F is given by

$$F = \int g(r, c(r), \nabla c(r)) dV, \quad (2.54)$$

then the functional derivative of F with respect to $c(r)$ is given by

$$\frac{\delta F}{\delta c} = \frac{\partial g}{\partial c} - \nabla \cdot \frac{\partial g}{\partial (\nabla c)}, \quad (2.55)$$

as long as the integrand vanishes at the boundaries of integration. Applied to Eq. (2.37) [such that g is the integrand f^* of Eq. (2.37)] we obtain

$$\frac{\delta F}{\delta c} = \frac{\partial f}{\partial c} + \frac{\partial \kappa}{\partial c} (\nabla c)^2 - 2\kappa \nabla^2 c. \quad (2.56)$$

The functional derivative can be used to formulate a diffusion equation which may be used to study the morphology resulting from spinodal decomposition.

2.6.3 Diffusion Equation

The chemical potential μ can be related to the functional derivative via $\mu = \delta F / \delta c$. Cahn considered the matter current $J = -M \nabla \mu$, where M is a positive mobility coefficient, and the continuity equation $\partial c / \partial t = -\nabla \cdot J$. Disregarding all terms non-linear in c , so as to consider infinitesimal compositional fluctuations corresponding to the initial stages of spinodal decomposition, we have

$$\frac{\partial c}{\partial t} = M \frac{\partial^2 f}{\partial c^2} \nabla^2 c - 2M \kappa \nabla^4 c, \quad (2.57)$$

confirming Cahn's assertion that "the diffusion equation must contain a higher order term reflecting the thermodynamic contributions of the gradient energy term". The first term of Eq. (2.57) allows us to interpret $M f''$ as an interdiffusion coefficient. The second term accounts for gradients and interfaces.

Wavelengths

For small variations in c about the average c_0 , the solution to Eq. (2.57) is $c - c_0 = A(k, t) \cos k \cdot r$, where k is the wavevector of a compositional variation and $A(k, t)$ is an amplification factor depending on the wavelength, which yields

$$\frac{\partial A}{\partial t} = -M k^2 \left[\frac{\partial^2 f}{\partial c^2} + 2k^2 \kappa \right] A, \quad (2.58)$$

and therefore solutions are of the form

$$A(k, t) = A(k, 0) \exp [R(k)t], \quad (2.59)$$

$$R(k) = -M k^2 \left[\frac{\partial^2 f}{\partial c^2} + 2k^2 \kappa \right], \quad (2.60)$$

Cahn referred to $R(k)$ as a kinetic amplification factor, which if negative means that the solution is stable to fluctuations of wavevector k , and which if positive means the the solution is unstable to fluctuations of wavevector k . The critical wavelength by definition separates these two regimes, and corresponds to the smallest possible wavelength for which the mixture is unstable, $R(k_c) = 0$. Cahn noted that "surface tension prevents decomposition of the solution on too fine a scale." This important point is why equations like (2.37) and (2.51) are required to study phase separation,

because without a gradient energy term, the mixture could decompose on an infinitely fine scale. However, since this would yield an enormous amount of gradient energy, this is not actually energetically favourable, and so does not happen.

Cahn found that the fastest growing wavelength was related to the critical wavelength

$$k_{\max} = \sqrt{2}k_c, \quad (2.61)$$

Fluctuations of wavelength k_{\max} “will grow the fastest and will dominate. This principle of selective amplification depends on the initial presence of these wavelengths but does not critically depends on their exact amplitude relative to other wavelengths”. This is a very important idea in spinodal decomposition.

2.6.4 Morphology from Spinodal Decomposition

To investigate the structures that may result from spinodal decomposition, Cahn used the solution to Eq. (2.57) given by $c - c_0 = A(k, t) \cos k \cdot r$ [16]. Since all sums of all solutions are also possible solutions, due to superposition theory, the most general solution is

$$c - c_0 = \sum_{\text{all } k} \exp \{R(k)t\} [A(k) \cos(k \cdot r) + B(k) \sin(k \cdot r)]. \quad (2.62)$$

The problem of studying the temporal evolution is much simpler if only the wavelength with the fastest growing amplitude is considered i.e. k_{\max}

$$c - c_0 \approx \exp \{R(k_{\max})t\} \sum_{k_{\max}} [A(k) \cos(k \cdot r) + B(k) \sin(k \cdot r)]. \quad (2.63)$$

Hence “The predicted structure may be described in terms of a superpositioning of sinusoidal composition modulations of a fixed wavelength, but random in amplitude, orientation, and phase” and “at some time after phase separation starts, a description of the composition in the solution will be a superposition of sine waves of fixed wavelength, but random in orientation, phase, and amplitude”. The sum in Eq. (2.63) remains, even though only $k = k_{\max}$ is considered in the sum, because Cahn generated a predicted morphology by summing over waves with different directions and amplitudes.

The resulting morphology was a highly interconnected bi-continuous structure, which resembled that of phase separable glasses believed to have undergone spinodal decomposition. Cahn stated that “theory of spinodal decomposition has been shown to predict a two-phase structure”, although strictly speaking this result only applied to the initial stages of phase separation. Kinetic restrictions would of course mean that

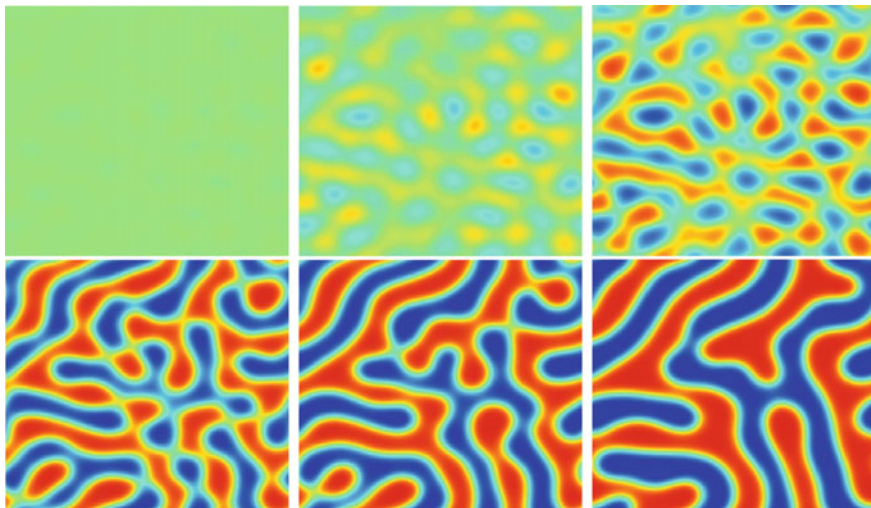


Fig. 2.5 Shown here only for visualisation purposes are simulation snapshots I produced of a phase separating symmetric polymer blend ($N_A = N_B = N$, average volume fraction $\bar{\phi} = 1/2$), created by solving the Cahn-Hilliard-Cook equation (2.65) for a polymer blend. The initially nearly-homogeneous blend phase separates and coarsens into a highly interconnected bicontinuous morphology, the latter of which is similar to that obtained by Cahn

this structure would indicate the qualitative features that would be expected from the late stages, since rearrangement of material at late stages is restricted by the structures formed at early stages. Figure 2.5 shows simulation snapshots of a phase separating polymer-blend, produced by solving the diffusion equation (2.65) for a polymer-blend (Eq. (2.65) is essentially Eq. (2.57), but with random thermal noise included and without limiting to small variations around c_0) shown for visualisation purposes: the final morphology, a bicontinuous structure, is very similar to that obtained by Cahn.

2.6.5 Random Noise and Spinodal Decomposition

Cahn’s theory of the early stages of spinodal decomposition [16] is known to break down at later stages, mainly as a result of neglecting higher order terms in the gradient energy that bring in other harmonics [24]. However, Cook noted that it was not understood why the theory could also break down for the initial stages of spinodal decomposition for which it was designed to study. Cook suggested that “the breakdown at the very early stages of the transformation which is caused by thermal fluctuations is not so widely appreciated” [24]. A strong example of the lack of understanding was the complete lack of spinodal decomposition in some glass mixtures, which were practically identical to other glass mixtures which did have

the features of spinodal decomposition. This could not be accounted for by a theory that suggested that only the initial amount of decomposition in the glass mixture (the spectra of composition fluctuations in the initial mixture) would result in different late-time features.

Supposing that “fluctuations in composition caused by thermal effects which were not included in the original theory” may have been responsible, Cook modified Cahn’s diffusion equation given in Eq. (2.57) to include thermal noise, which should give rise to Brownian motion of the fluid. This was justified by Cook because it is understood that “the equilibrium state is dynamic and that, for the case of a stable, single phase, binary solid solution, an appreciable flux of solute occurs at equilibrium.” To include this random thermal contribution, Cook modified the matter current equation $J = -M\nabla\mu$ to include a “quasi-random thermal contribution to the total flux”, denoted by j , resulting in a material current

$$\begin{aligned} J &= -M\nabla\mu + j \\ &= -M\nabla\frac{\delta F}{\delta c} + j. \end{aligned} \quad (2.64)$$

Cook’s important contribution to the rate equation for spinodal decomposition lead to the name “Cahn-Hilliard-Cook” theory for equations of the form

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[M\nabla\frac{\delta F}{\delta c} \right] - \nabla \cdot j(r, t) \quad (2.65)$$

$$\equiv \nabla \cdot \left[M\nabla\frac{\delta F}{\delta c} \right] + \eta(r, t). \quad (2.66)$$

The randomly fluctuating field $\eta(r, t)$ has certain properties, such that its average value is zero. Using averaging to treat the random term (the average properties are well defined), the rate of change equation given by Cahn in Eq. (2.58) gains an extra term, giving $dI(k, t)/dt = M(k)\{[f'' + 2\kappa k^2]I(k, t) - k_B T/\Omega c_0(1 - c_0)\}$, where Ω is the volume per atom. So the rate of change of intensity has two separate contributions: (a) a thermodynamic driving force “which is proportional to the free energy associated with the Fourier coefficient of wavevector k ”; and (b) a thermal driving force “which is proportional to the temperature and independent of the wave vector”.

The inclusion of thermal noise has several non-trivial implications for spinodal decomposition [24], especially in the early stages of spinodal decomposition when the free energy of the fluctuations is $\sim k_B T$ “and thus the influence of random fluctuations will be pronounced”: (i) the critical wavevector k_C is now determined by the condition that the thermal driving force (from the thermal noise) is equal to the thermodynamic driving force (arising from the free energy of the system); (ii) the rate of intensity will be greater given the thermal driving force, since “every movement in the fluctuation field... which increase the magnitude of a Fourier coefficient is amplified”; and (iii) the

“thermal driving force indicates early stages of decomposition outside the spinodal... in this ‘operational’ sense the spinodal, itself, becomes a diffuse boundary”.

2.6.6 Spinodal Decomposition of a Polymer Blend

I will briefly discuss, for completeness, the relaxation of a polymer melt, which is an important idea of spinodal decomposition, although the concept will not be discussed in the rest of this thesis. Relaxation concerns, to give a broad definition, how an unstable mixture ‘relaxes’ into a stable mixture in spinodal decomposition. Relaxation can be described by a relaxation time for different wavelengths (lengthscales) of the decomposition.

De Gennes extended the study of the dynamics of spinodal decomposition to polymer blends [18]. For polymer blends, there are a variety of length scales that are important, and so it may be important to have a dependence of the mobility on the wavelength of fluctuations in a polymer blend. This can be done by introducing a wavelength dependent Onsager coefficient $\Lambda(q)$ into the usual expression for the matter current $J = -M\nabla\mu$. This effectively allows a dependence of the constant M on the wavelength of each Fourier component. The result is a current for each Fourier component

$$J_q = -\frac{\Lambda(q)}{k_B T} (\nabla\mu)_q. \quad (2.67)$$

We can allow use of the following expression for the relaxation time for a mode of wavelength q :

$$\frac{1}{\tau_q} = -\frac{1}{\delta\phi_q} \frac{\partial(\delta\phi_q)}{\partial t}, \quad (2.68)$$

where $\delta\phi$ is a small fluctuation away from the homogeneous state ϕ_0 , such that we can express the composition using $\phi = \phi_0 + \delta\phi$. If wavelengths of fluctuations produce negative values for τ_q^{-1} , then compositional fluctuations of this wavelength grow with time.

De Gennes derived a relaxation formula for a symmetric binary polymer blend, assuming the form $\Lambda(q) \propto q^2$ for polymer blends (based on a scaling ansatz) [18]. The result for the relaxation time “differs from the standard Cahn-Hilliard equation for spinodal decomposition” for simple molecules, this difference arising from “the presence of long chains”. It was noted that “the characteristic length l is much smaller than the coil size... (thus) spinodal decomposition is an excellent probe for fluctuations of short wavelength.” The assumption $\Lambda(q) \propto q^2$ was later found to be false [25].

Pincus continued the work of de Gennes by taking into account new knowledge of the nature of the Onsager coefficient [25]. The nature of the relaxation of modes in a polymer melt leads to a significantly altered dependence of the Onsager coefficient on the wave vector q , namely that $\Lambda(q) \propto q^{-2}$. This gives a very different result for

the relaxation time [still of the form Eq. (2.68)]. Unlike the results of the earlier work by de Gennes which showed that spinodal decomposition should probe very short wavelengths “much smaller than the coil size” [18], it now appeared that “the unstable mode has a wavelength comparable to the ideal chain radius and therefore should vary as $N^{1/2}$ with only a weak concentration dependence”. Also, “the corresponding growth rate is proportional to the reptation diffusion coefficient in a melt and thus scales as N^{-2} and has a concentration dependence that reflects the shape of the spinodal line”. Concerning the latter point, this means that upon going from the one-phase to the two-phase region, the *rate* of spinodal decomposition depends on the concentration.

Mean-Field Treatments of Polymer Systems

Binder later did a similar calculation, but using the chemical potential as calculated via functional derivatives [26]. Binder notes that mean-field treatments of spinodal decomposition in fluids of simple molecules can fail due to fluctuation effects that are not included in mean-field treatments. However, “a simplifying feature due to the large size of the polymer chains is the mean-field character of the unmixing transition, fluctuation corrections to the mean-field description can be safely neglected.” On the linearisation approximation $\phi(r, t) \equiv \phi_0 + \delta\phi(r, t)$ used to calculate the relaxation time, Binder noted that “whilst it is well known that the linearisation approximation is not valid in the critical region of non-mean-field liquid... its validity in the present case should be much better justified.” The main result is that “the wavevector q_m of maximal growth in spinodal decomposition is typically of the order of $q_m \sim R^{-1}$ ” where R is the polymer coil radius.

2.7 Summary

In this chapter, I discussed the development of theory to describe bulk polymer blend systems, beginning with the development of an entropy of mixing valid for long chain molecules, followed by a heat of mixing, and an expression for the free energy cost of compositional gradients. Together, these expressions give the Flory-Huggins-de Gennes free energy of mixing. I discussed the coexistence curve and spinodal line for a binary blend system, as well as spinodal decomposition whereby a blend phase separates into phases rich in either component upon being quenched from the one-phase to the two-phase region. This chapter has covered the bulk theory required in this thesis, and the next chapter extends this theory to include surfaces, allowing films to be studied theoretically.

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