

## Theory of Polymeric Alloys

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### Summary

A theory of inhomogeneous multicomponent polymer systems developed earlier by the authors is used to study the phase diagrams of a mixture of block copolymers, homopolymers and solvents. We assume that the deviation of the local volume fraction of any component from its average value is small, and we expand the free energy of the system up to fourth order in the fluctuations. This approach enables us to determine the spinodal boundaries and to estimate the location of the binodals. Some new features of the resulting polymeric phase diagrams are the prediction of eutectic points, similar to those observed in metallurgy, and the phenomenon of homopolymer-induced mesophase formation.

### Introduction

Blends of block copolymers and homopolymers often exhibit microphase separation, and show a rich variety of different morphologies (HASHIMOTO et al., 1974; EASTMOND and PHILLIPS, 1979; RAMOS and COHEN, 1977; RIESS et al., 1971) which have been studied for practical applications relating to emulsifying agents and high-impact plastics as well as for scientific interest. Recently there has been considerable theoretical activity in this area (MEIER, 1977; LEIBLER, 1980; NOOLANDI and HONG, 1982). While the phenomenon of microphase formation in a pure block copolymer system is reasonably well understood (HELFAND and WASSERMAN, 1980; LEIBLER, 1980), the situation for blends is much less clear. In this paper we give preliminary results on the calculation of phase separation behavior expected for these systems compared to pure block copolymers.

### Theoretical Model

We study the reduced free energy per unit volume  $f = F/\rho_0 V k_B T$  of a mixture of small molecules, homopolymers and block copolymers.  $F$  is the total free energy of the system,  $V$  the total volume,  $\rho_0$  a reference number density,  $k_B$  Boltzmann's constant and  $T$  the absolute temperature. As shown in our earlier papers (HONG and NOOLANDI, 1981; NOOLANDI and HONG, 1982), the free energy of the inhomogeneous mixture may be written (relative to the Flory-Huggins free energy of the homogeneous state)

$$\Delta f = \frac{1}{2V} \sum_{\kappa\lambda} \int d^3x d^3y \chi_{\kappa\lambda} (\underline{x} - \underline{y}) \psi_{\kappa}(\underline{x}) \psi_{\lambda}(\underline{y}) - \frac{1}{V} \sum_{\kappa} \int d^3x \psi_{\kappa}(\underline{x}) \omega_{\kappa}(\underline{x}) - \sum_{\kappa} \frac{\phi_{\kappa}}{r_{\kappa}} \ln \left( \frac{Q_{\kappa}}{V} \right), \quad (1)$$

where  $\psi_{\kappa}(\underline{x}) = \phi_{\kappa}(\underline{x}) - \phi_{\kappa}$  is the deviation of the local volume fraction from its average value. The subscripts  $\kappa, \lambda$  label the various components of the system, and  $\omega_{\kappa}(\underline{x})$  is the self-consistent mean field potential acting on component  $\kappa$ . The quantity  $Q_{\kappa}$  is defined in terms of the distribution function  $Q_{\kappa}$  for the polymer or small molecule, which in turn is given by the solution of a diffusion equation involving the effective field  $\omega_{\kappa}(\underline{x})$ . The "c" over the summation sign indicates that a copolymer is treated as a single component, and  $r_{\kappa} = \rho_0 Z_{\kappa} / \rho_{0\kappa}$ , where  $Z_{\kappa}$  is the degree of polymerization. The Flory-Huggins parameter,  $\chi_{\kappa\lambda}$ , is simply the spatial integral of the corresponding non-local parameter,  $\chi_{\kappa\lambda}(\underline{x} - \underline{y})$ .

Our approach to determining the phase diagram of a multicomponent system involves assuming that the magnitude of the fluctuations is small, i.e.  $|\psi_{\kappa}(\underline{r})/\phi_{\kappa}| \ll 1$ , and expanding in powers of  $\psi_{\kappa}$ . This approach is strictly valid only near the spinodal line, and away from this region the accuracy of the calculation decreases. However, we expect that most of the qualitative features of the phase diagrams remain unchanged.

The mathematical details are considerably simplified by working with the Fourier transforms of the important quantities,

$$\tilde{\psi}_{\kappa}(\underline{k}) = \int d^3x \psi_{\kappa}(\underline{x}) e^{-i\underline{k} \cdot \underline{x}} \quad (2)$$

$$\tilde{Q}_{\kappa}(\underline{k}, t | \underline{k}_0) = \int d^3x d^3x_0 Q_{\kappa}(\underline{x}, t | \underline{x}_0) e^{-i(\underline{k} \cdot \underline{x} - \underline{k}_0 \cdot \underline{x}_0)}.$$

The diffusion equation for  $\tilde{Q}_{\kappa}$  can then be expanded in a straightforward way as a power series in  $\tilde{\omega}_{\kappa}(\underline{k})$ . This in turn enables us to expand the logarithm in Eq.(1), and finally the entire expression for  $\Delta f$  can be written as a series expansion in  $\tilde{\omega}_{\kappa}$ . We retain all terms up to fourth order in this expansion, and minimizing  $\Delta f$  with respect to  $\tilde{\omega}_{\kappa}$  allows us to express  $\tilde{\psi}_{\kappa}$  in terms of  $\tilde{\omega}_{\kappa}$ , and consequently to write  $\Delta f$  as an expansion up to fourth order in  $\tilde{\psi}_{\kappa}$ . Minimization of the  $\Delta f$  functional with respect to  $\tilde{\psi}_{\kappa}$  then gives the equilibrium concentration profiles of the various components.

Here we do not present the algebraic details of the calculation (HONG and NOOLANDI, to be published). In order to study the phase separation behaviour of a mixture of a diblock copolymer AB and another component S (either a homopolymer or a small molecule) we have assumed a lamellar structure (with  $f_A = r_A / (r_A + r_B) = f_B = 0.5$ ) with the composition fluctuations dominated by one wave vector  $\underline{k}^*$ . For a symmetric solvent ( $\chi_{AS} = \chi_{BS}$ ), the end result for  $\Delta f$  is particularly simple,

$$\Delta f = -0.27\chi_{AB} \left[ \phi_c - 10.5 / (r_c \chi_{AB}) \right]^2 \quad (3)$$

where  $\phi_c$  is the volume fraction of block copolymer, and  $r_c = r_A + r_B$ . Since  $\Delta f$  must be negative for an equilibrium non-homogeneous structure, we find immediately the requirement  $r_c \chi_{AB} \phi_c \geq 10.5$  for this to occur, in agreement with LEIBLER (1980) for  $\phi_c = 1.0$ . The periodicity of the microdomain structure is found to be  $D = 1.32 (Z_c)^{1/2} b$ , where  $b$  is the average Kuhn length for the block copolymer, and is independent of the solvent concentration in this calculation. This result gives an indication of the limitations of the present work, since our earlier detailed numerical calculations (which did not rely on a power series expansion in  $\tilde{\omega}_{\kappa}$  or  $\tilde{\psi}_{\kappa}$ ) showed a decrease in the periodicity with increasing solvent concentration (NOOLANDI and HONG, 1980) a result which has recently been verified experimentally by HASHIMOTO et al., (1982).

### Phase Diagrams

Taking into account the Flory-Huggins free energy in the homogeneous "reference" state, and using the above result for  $\Delta f$ , we may study the phase separation diagram for the system. Fig. 1 shows such a diagram for a poor, nonselective solvent. The solid lines are the boundaries of different regions indicated by HM (homogeneous-mesophase), M (mesophase), H (homogeneous), and HH (homogeneous-homogeneous). Depending on the governing parameters, the system may form a single mesophase, a single homogeneous phase, or may phase separate into a homogeneous solvent-rich phase and a mesophase, or a solvent phase and a homogeneous polymer solution. The temperature at which  $\chi_{AB} Z_C$  corresponds to the point E (17.9 in Fig. 1) may be thought of as a eutectic temperature for the polymeric alloy system, in the sense that it is the lowest temperature for which the homogeneous solution, besides the almost pure solvent, can exist. At this temperature

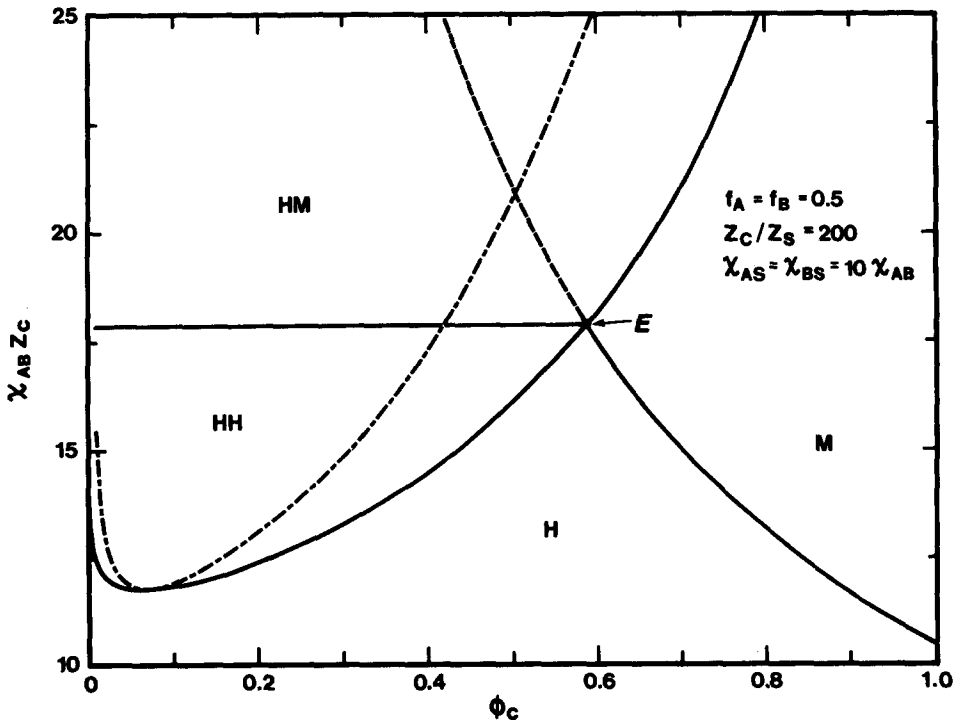
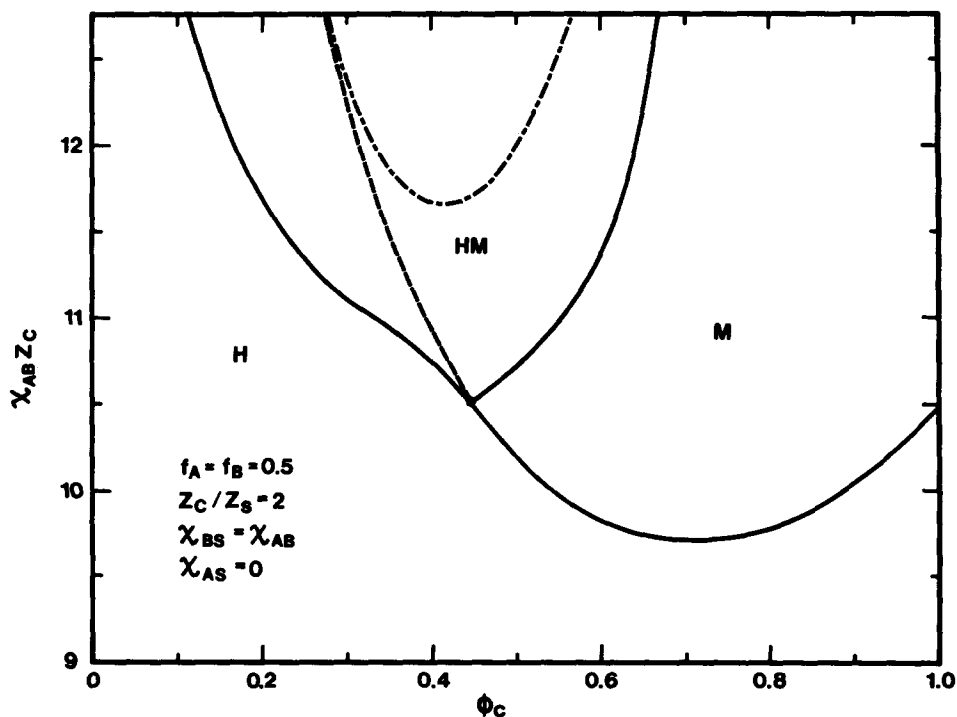


Fig. 1: Phase diagram of a diblock copolymer-solvent mixture. The volume fraction of copolymer is  $\phi_C$ , and  $Z_C$  is the degree of polymerization.  $Z_S=1$  for the solvent, and  $f_A, f_B$  denote the volume fractions of monomer A,B in the copolymer. The different regions are discussed in the text.

we can have three phases in equilibrium, the almost pure solvent, the homogeneous polymer solution at  $\phi_c = 0.59$ , and the mesophase at  $\phi_c = 0.59$ . In this case the latter two phases are indistinguishable, but in general this is not so. The continuation of the HM spinodal line beyond the point E is shown for illustration by the dashed line. The dot-dashed curve shows the spinodal for the HH region determined from Flory-Huggins theory, and the left and right boundaries of HH are the corresponding binodals.

Fig. 2 shows the phase diagram for a mixture of a block copolymer and a homopolymer corresponding to one of the blocks. Since the interaction parameters are now asymmetric ( $\chi_{AS} \neq \chi_{BS}$ ), a simple result such as given by Eq.(3) is not found, and the analysis is more involved. As in the previous figure, the dashed and dot-dashed lines indicate the spinodals, and the solid lines represent the binodals. The most interesting feature of this diagram is the prediction that a small amount of homopolymer added to the block copolymer system will induce mesophase formation. Normally the critical value of



**Fig. 2:** Phase diagram of a diblock copolymer-homopolymer mixture. The volume fraction of copolymer is  $\phi_c$ , and  $Z_C$ ,  $Z_S$  are the degrees of polymerization of the block copolymer and homopolymer, respectively. The homopolymer in this case corresponds to the A block of the copolymer.

$\chi_{AB}^Z$  for mesophase formation in a pure block copolymer system is 10.5 (LEIBLER, 1980). With about 25% weight fraction of the corresponding homopolymer in the mixture, the critical value of  $\chi_{AB}^Z$  is predicted to drop to about 9.7. A more detailed account of these phase diagrams and other new results will be published elsewhere.

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