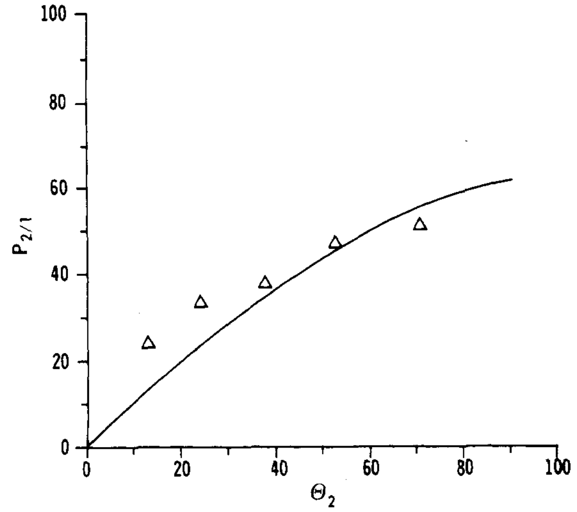

Figure 13. Comparison of the theoretically calculated (solid line) and experimentally determined (△) $P_{2/1}$ values plotted against θ_2 for PVPh–PPL blends.

retical results for the PVPh–PCL and PVPh–PPL blends, respectively. The results, while not as obviously pleasing as those of the PVPh blends with PVAc and EVA[70], are in satisfactory agreement. Again, we would emphasize the overall shape of the curves rather than the absolute values, which are subject to significant error.

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Registry No. PVPh (homopolymer), 24979-70-2; PVAc (homopolymer), 9003-20-7; EVA (copolymer), 24937-78-8; PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; PPL (homopolymer), 25037-58-5; PPL (SRU), 24938-43-0.

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Polymers at a Liquid–Liquid Interface

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ABSTRACT: We study the behavior of homopolymers at the liquid–liquid interface of a biphasic regular binary solution. We find that the polymers are attracted to the interface, with the polymer concentration profile having a maximum near the interface, on the side of the better solvent. Expressions for interfacial width and the surface tension are derived.

I. Introduction

Comparatively little attention has been paid to the behavior of polymers at liquid–liquid interfaces. Most of the research in this area has been confined to binary systems (phase-separated solution of a single solvent and a monodisperse polymer.[1-4] In the following we will address the theory of the behavior of homopolymers at the liquid–liquid interface of a biphasic regular binary solution (i.e., a system consisting of a monodisperse polymer and two simple solvents). Surprisingly, we find that homopolymers may be attracted to the interface, even though they are not assumed to be amphiphilic. This predicted facet of homopolymer behavior may be relevant to wetting behavior, emulsion stabilization, etc.

Understanding of these systems may be developed by considering the various interactions between the polymer monomeric units (M) and the two types of solvent molecules (1 and 2): (i) the interaction energy between solvent 1 and the monomer (M–1) as compared with the interaction energy between solvent 2 and the monomer (M–2) (when the energy associated with the M–1 interaction is lower than the energy associated with the M–2 interaction, we will say that "solvent 1 is the preferred solvent"); (ii) the interaction energy between solvent 1 molecule and solvent 2 molecule (1–2) relative to the energy associated with the configuration where the two different solvent

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molecules (1 and 2) are separated by a monomer (1–M–2) (when the interaction energy associated with the 1–M–2 configuration is lower we will refer to the effect of the monomer as "screening"). Two extreme cases are screening without a preferred solvent and preferential solvent without screening. The polymer concentration gradient in the first case (screening, no preferred solvent) should be symmetric with respect to the interface with an extremum at the interface. In the case of two good solvents we expect a maximum at the interface, which will lower the overall energy of the system as a result of the screening. In the second case where we have a preferred solvent but no screening, there is nothing to attract the polymer to the interface. We may expect then a monotonic polymer concentration gradient, increasing from the poor solvent toward the better one.

In intermediate cases, where both screening and preferred solvent effects are present, we expect to find a maximum in the polymer concentration profile, but its position will shift to accommodate the preferred solvent.

The theory may be formulated in the framework of the van der Waals–Cahn[5,6] theory of the liquid–liquid interfaces as adapted to polymer problems by de Gennes.[7,8] This is a mean field theory whose validity close to T_c is only qualitative. On the other hand, the theory assumes weak concentration gradients that may be realized only in the vicinity of T_c. Our results are therefore strictly applicable only to a narrow temperature range in the neighborhood of T_c. We believe, though, that the results are qualitatively correct over a broad temperature range.

II. Formulation of the van der Waals–Cahn–de Gennes Theory

Consider a ternary system consisting of a monodisperse polymer (DP = N) and two solvents. We will designate the volume fraction of the polymer by ϕ and the volume fraction of the solvents by ϕ_1 and ϕ_2. Inscribe this system on a Flory–Huggins lattice (lattice constant a). When incompressibility is assumed, the free energy density of mixing for the system is given by

$$F = (kT/a^3)(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + (\phi/N) \ln \phi + \chi_1\phi_1\phi + \chi_2\phi_2\phi + \chi_{12}\phi_1\phi_2) \qquad \text{(II-1)}$$

Here χ_i is the interaction parameter for the monomer–solvent i pair, while χ_{12} is the interaction parameter for the solvent 1–solvent 2 pair.

For a sufficiently dilute polymer solution ($\phi \ll 1$), the demixing critical temperature (T_c) of the binary system is displaced only slightly. For such a case, and in the vicinity of T_c, F may be written as a virial expansion in ϕ and in the order parameter $\eta \equiv \phi_1 - \phi_2$. Taking the limit $N \rightarrow \infty$ and discarding constant and linear terms we obtain

$$F = \frac{kT}{a^3}\left(\frac{1}{2}v_p\phi^2 - \frac{1}{2}v_s\eta^2 + \frac{1}{12}\eta^4 + \Delta\phi\eta + \frac{1}{2}\phi\eta^2\right) + \text{higher order terms} \qquad \text{(II-2)}$$

where

$$\Delta \equiv (1/2)(\chi_1 - \chi_2) \qquad v_s \equiv \chi_{12}/2 - 1$$
$$v_p \equiv 1 - \chi_1 - \chi_2 + (1/2)\chi_{12} \qquad \text{(II-3)}$$

Notice that F contains two coupling terms: $\Delta\phi\eta$ and $(1/2)\phi\eta^2$. The first reflects the preferred solvent interaction. The second term will turn out to be responsible for the screening. We may discard the higher order terms as $\eta << 1$ in the vicinity of T_c and we have taken the polymer solution to be dilute.

Let us comment on some of our assumptions. In taking the limit $N \rightarrow \infty$ we have neglected the translational entropy of the polymer. The configurational entropy of the polymer will be taken into account separately. The assumed incompressibility makes our system have two independent variables that we take to be ϕ and η. We will generally confine ourselves to the good solvent case; i.e., $\chi_1 << 1$ and $\chi_2 << 1$.

In the following, we will analyze this system and consider in detail two limiting cases. In these cases we will require the coexistence curve in the vicinity of T_c. Rather than obtaining it from the equality of the three chemical potentials we will use the following equivalent conditions:

$$\mu_\eta^{(\alpha)} = \mu_\eta^{(\beta)} \qquad \mu_\phi^{(\alpha)} = \mu_\phi^{(\beta)} \qquad \Pi^{(\alpha)} = \Pi^{(\beta)} \qquad \text{(II-4)}$$

Here α and β designate the two phases, μ_η and μ_ϕ are the so-called exchange potentials given respectively by $\partial F/\partial\eta$ and $\partial F/\partial\phi$, and Π is the "osmotic pressure" given by $\Pi = F - \phi\mu_\phi - \eta\mu_\eta$.

Our interest is in the properties of the biphasic liquid–liquid interface near T_c. Microscopic characterization of the interface for a semidilute polymer solution is provided by the three concentration gradients. With the incompressibility assumption, the interface is specified completely by two spatially varying concentrations: $\eta = \eta(x)$ and $\phi = \phi(x)$. Macroscopically, the interface property of interest is the surface free energy per unit area γ (which is the surface tension for a planar surface). This may be obtained in terms of the Cahn–van der Waals theory of interface.

For a semidilute polymer solution we may express γ as

$$\gamma = \int_{-\infty}^{+\infty} I \, dx \qquad \text{(II-5)}$$

where the energy density functional I includes contributions associated with spatial variations of the concentrations.

$$I = W + \frac{kT}{a^3}\left[\frac{1}{2}m_\eta^2 a^2\left(\frac{d\eta}{dx}\right)^2 + \frac{1}{2}m_\phi^2 a^2 \frac{1}{\phi}\left(\frac{d\phi}{dx}\right)^2\right] \qquad \text{(II-6)}$$

m_η and m_ϕ are dimensionless constants characterizing the η and ϕ gradients. W is given by

$$W = F - \phi\mu_\phi^{(eq)} - \eta\mu_3^{(eq)} + \Pi^{(eq)} \qquad \text{(II-7)}$$

and represents the free energy difference needed to create unit volume at composition ϕ and η from a reservoir of osmotic pressure $\Pi^{(eq)}$ and chemical potentials $\mu_\phi^{(eq)}$ and $\mu_\eta^{(eq)}$ in the absence of an interface. The presence of the interface is accounted for by augmenting W with the two "square gradient" terms, which allows for slow spatial variations. Let us remark that the connectivity of the polymer is accounted for through the presence of the ϕ^{-1} factor in front of the $(d\phi/dx)^2$ term.[7] For sufficiently large values of N it is possible to have a semidilute solution that satisfies the condition $\phi << 1$.

Minimization of the surface tension yields the Euler–Lagrange equations (denoting $d\eta/dx$ by η_x, etc.)

$$\frac{\partial I}{\partial \eta} - \frac{d}{dx}\frac{\partial I}{\partial \eta_x} = 0$$
$$\frac{\partial I}{\partial \phi} - \frac{d}{dx}\frac{\partial I}{\partial \phi_x} = 0 \qquad \text{(II-8)}$$

resulting in two coupled second-order differential equations of the form

$$d^2\eta/dx^2 = g(\phi,\eta) \qquad d^2\phi/dx^2 = f(\phi,\eta) \qquad \text{(II-9)}$$

The use of W in I ensures that $d^2\eta/dx^2$ and $d^2\phi/dx^2$ will vanish in the bulk in accord with thermodynamic equilibrium.

In the general case, the Euler–Lagrange equations are complicated. In order to gain insight into the problem, we discuss two simplified cases in which F contains a single coupling term only. In the absence of coupling terms, the polymer concentration is strictly uniform and is completely independent of the solvent demixing. The first case, to which we will refer as the "symmetrical case", is defined by $\Delta = 0$ and

$$F_{\mathrm{s}} = \frac{kT}{a^3}\left(\frac{1}{2}v_{\mathrm{p}}\phi^2 - \frac{1}{2}v_{\mathrm{s}}\eta^2 + \frac{1}{12}\eta^4 + \frac{1}{2}\phi\eta^2\right) \quad \text{(II-10)}$$

This implies that solvents 1 and 2 are equally good solvents for the polymer. The second case, the "asymmetric case", is defined by

$$F_{\mathrm{a}} = \frac{kT}{a^3}\left(\frac{1}{2}v_{\mathrm{p}}\phi^2 - \frac{1}{2}v_{\mathrm{s}}\eta^2 + \frac{1}{12}\eta^4 + \Delta\phi\eta\right) \quad \text{(II-11)}$$

It describes a situation where the two solvents are sufficiently dissimilar ($\Delta \gg (1/2)\eta$), so that we can neglect the $(1/2)\phi\eta^2$ term.

In general, three correlation lengths are needed to characterize the interface. One correlation length is typical to each of the concentration gradients, and a third length is required to specify their relative position. It turns out that for the two extreme cases under consideration, the third length is not required (i.e., it is zero). This is obvious from the symmetry consideration in the symmetric case. In the asymmetric case, we expect the polymer concentration to reflect the quality of the solvent, i.e., the polymer concentration gradient to be proportional to the solvent concentration gradient. There is no reason to expect one concentration gradient to be displaced with respect to the other.

It is natural to compare the two correlation lengths to their "bare" counterparts, i.e., the lengths characteristic of the decoupled system in which the interface and the polymer concentration fluctuations are not constrained to occur in the same region.

The bare correlation length associated with the polymer for bulk polymer solutions is given by

$$\xi_\phi = m_\phi a/\phi_0^{1/2}$$

where ϕ_0 is the volume fraction of the bulk polymer. The bare length associated with the interface of a demixed binary solution is given by

$$\xi_\eta = m_\eta a/\eta_0$$

where η_0 is the bulk value of η.

Each of the two special cases can be solved explicitly for two limits: the diffuse interface limit defined by $\xi_\eta >> \xi_\phi$, and the sharp interface limit defined by $\xi_\phi >> \xi_\eta$. The diffuse interface limit is realized near T_{c}, while the sharp interface limit is realized away from T_{c}. [In mean field theory $\eta_0 \sim (|T - T_{\mathrm{c}}|)^{1/2}$].

In the diffuse interface limit we will take $\mathrm{d}^2\phi/\mathrm{d}x^2$ to be negligible for both the symmetric and asymmetric cases. The polymer gradient is driven by the η gradient and is therefore of second order of smallness. By setting $f(\phi,\eta) = 0$, we can solve

$$\mathrm{d}^2\eta/\mathrm{d}x^2 = g(\phi,\eta)$$

for η and thus calculate γ.

In the sharp interface limit we will solve the Euler–Lagrange equations for $|x| > \xi_\eta$. In this domain we can take $\mathrm{d}^2\eta/\mathrm{d}x^2$ to be zero and solve $g(\phi,\eta) = 0$ for η, thus enabling us to solve

$$\mathrm{d}^2\phi/\mathrm{d}x^2 = f(\phi,\eta)$$

The solution obtained is not valid for $|x| < \xi_\eta$; furthermore, it is important to notice that the van der Waals–Cahn theory is not applicable to the sharp interface due to the exclusion of terms higher than the square gradient term. Still, we believe the results to be correct qualitatively.

Where an explicit solution is obtained, we find that it is characterized by a single length, which is related to but not identical with the longer of the two "bare" correlation lengths, ξ_η and ξ_ϕ. The dependence of this characteristic length on the coupling of the two gradients is one of the main conclusions of this study.

By defining the general case in the same limit, we will be able to demonstrate (without explicit solution) that its behavior is intermediate to the two simplified cases. This gives us some justification to claim that our conclusions apply to this case, too.

Sections III and IV deal with the symmetric and asymmetric situations, respectively. Section V deals with the general case.

III. Symmetric Case

Because by symmetry the polymer is portioned equally between the two phases, the coexistence curve derived from (II-4) is given by

$$\eta_\alpha = -\eta_\beta = \eta_0$$

$$\eta_0^{\mathrm{critical}} = 0$$

$$\phi_\alpha = \phi_\beta = \phi_0 \quad \text{(III-1)}$$

while v_{s} is given by

$$v_{\mathrm{s}} = \phi_0 + (1/3)\eta_0^2 \quad \text{(III-2)}$$

Defining

$$\eta = \eta_0\theta$$

$$\phi = \phi_0\psi^2$$

$$\lambda^2 = \phi_0/\eta_0^2 \qquad \xi_\phi = m_\phi a/(\phi_0)^{1/2}$$

$$\xi_\eta = m_\eta a/\eta_0 \quad \text{(III-3)}$$

we obtain

$$I = \frac{kT}{a^3}\eta_0^4\left[\frac{1}{2}v_{\mathrm{p}}\lambda^4(\psi^2 - 1) + \frac{1}{2}\lambda^2(\psi^2 - 1) \times (\theta^2 - 1) + \frac{1}{12}(\theta^2 - 1)^2 + \frac{1}{2}\xi_\eta^2\left(\frac{\mathrm{d}\theta}{\mathrm{d}x}\right)^2 + \frac{1}{2}\xi_\phi^2\lambda^4\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2\right] \quad \text{(III-4)}$$

and the corresponding Euler–Lagrange equations

$$\xi_\eta^2\ \mathrm{d}^2\theta/\mathrm{d}x^2 = (1/3)(\theta^2 - 1)\theta + \lambda^2\theta(\psi^2 - 1) \quad \text{(III-5)}$$

$$\xi_\phi^2\ \mathrm{d}^2\psi/\mathrm{d}x^2 = 2v_{\mathrm{p}}\lambda^2(\psi^2 - 1)\psi + \psi(\theta^2 - 1) \quad \text{(III-6)}$$

We will begin by considering the diffuse limit. As it corresponds to a near-critical state we have $\lambda^2 >> 1$. Neglecting $\mathrm{d}^2\psi/\mathrm{d}x^2$, we find

$$\psi^2 - 1 = (1/2v_{\mathrm{p}}\lambda^2)(1 - \theta^2) \quad \text{(III-7)}$$

A rough sketch of $\psi^2(x)$ can be obtained by investigating (III-7) and its derivative, assuming θ to be a monotonic function such that $\theta(0) = 0$ and $\mathrm{d}\theta/\mathrm{d}x \to 0$ as $x \to \pm\infty$. We find

$$\frac{\mathrm{d}\psi^2}{\mathrm{d}x} = -\frac{1}{2v_{\mathrm{p}}\lambda^2}\theta\frac{\mathrm{d}\theta}{\mathrm{d}x}$$

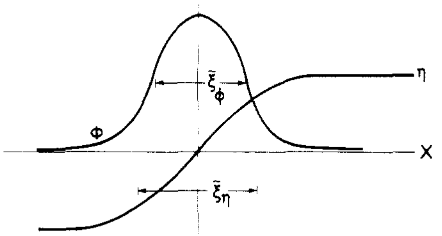

Figure 1. Sketch of the concentration profiles for the symmetric case.

which, according to our assumptions on θ, would equal zero at $x = 0$ and at $x = \pm\infty$. As

$$\frac{d^2\psi^2(0)}{dx^2} = \frac{1}{2\upsilon_p\lambda^2}\left(\frac{d\theta}{dx}\right)^2_{x=0}$$

We conclude that ψ^2 has a maximum at $x = 0$ for $\upsilon_p > 0$ (Figure 1).

An explicit solution for $\psi^2(x)$, $\eta(x)$, and γ is obtainable by integrating (III-5), making use of (III-7), the assumed properties of θ, and the requirement of γ to be positive. We find

$$\frac{d\theta}{dx} = \pm\frac{1}{\xi_\eta}\left(\frac{1}{6} - \frac{1}{4\upsilon_p}\right)^{1/2}(\theta^2 - 1) \qquad \text{(III-8)}$$

and as $\theta^2 \leq 1$ we obtain

$$\eta = \eta_0 \tanh (x/\tilde{\xi}_\eta) \qquad \text{(III-9)}$$

where

$$\tilde{\xi}_\eta = \xi_\eta\left(\frac{1}{6} - \frac{1}{4\upsilon_p}\right)^{-1/2} \qquad \text{(III-10)}$$

Notice that for $\upsilon_p > 3/2$, $\tilde{\xi}_\eta > \xi_\eta$, but furthermore $\tilde{\xi}_\eta$ diverges and $d\theta/dx$ vanishes while υ_p approaches zero. A similar phenomenon will be found in the sharp interface limit.

By substituting (III-9) into (III-7), we find

$$\theta = \theta_0 + \frac{\theta_0}{2\upsilon_p\lambda^2}\cosh^{-2}\left(\frac{x}{\tilde{\xi}_\eta}\right) \qquad \text{(III-11)}$$

Using (III-8), (III-7), (III-4), and (II-5) and taking $(d\psi/dx^2)$ to be at the same order of smallness as $d^2\psi/dx^2$ and thus negligible, we obtain

$$\gamma = \frac{kT}{a^3}\eta_0{}^4\tilde{\xi}_\eta\left(\frac{2}{9} - \frac{1}{3\upsilon_p}\right) \qquad \text{(III-12)}$$

We will now consider the opposite limit, at a sharp interface. As this limit corresponds to a noncritical state and as $\theta_0 << 1$ we have $\lambda^2 << 1$. For $|x| > \xi_\eta$ we have in this case $d^2\theta/dx^2 = 0$ and so

$$1 - \theta^2 = 3\lambda^2(\psi - 1) \qquad \text{(III-13)}$$

Preliminary investigation of (III-13) along the same lines as before shows $\psi^2(x)$ to have an extremum at $x = 0$ that is always a maximum.

Explicit solution is obtainable by integrating (III-6) with (III-13) and demanding in addition to the condition previously discussed that

$$\psi^2 \rightarrow 1 \quad \text{as } x \rightarrow \pm\infty \qquad \text{(III-14a)}$$

$$\psi_x \rightarrow 0 \quad \text{as } x \rightarrow \pm\infty \qquad \text{(III-14b)}$$

We obtain

$$\frac{d\psi}{dx} = \pm\frac{1}{\xi_\phi}\left(\upsilon_p - \frac{3}{2}\right)^{1/2}(\psi^2 - 1) \qquad \text{(III-15)}$$

Assuming $0 \leq \psi \leq 1$ leads to a discontinuous solution for θ, which we reject. For $\psi^2 >> 1$ we obtain

$$\psi^2 = \coth\left(\frac{|x|}{\tilde{\xi}_\phi} + 3^{1/2}\lambda\right) \qquad \text{(III-16)}$$

where

$$\tilde{\xi}_\phi = \xi_\phi\left(\upsilon_p - \frac{3}{2}\right)^{-1/2} \qquad \text{(III-17)}$$

For $1.5 \leq \upsilon_p \leq 2.5$ we thus find $\tilde{\xi}_\phi \geq \xi_\phi$, while for $\upsilon_p \geq 2.5$ we have $\tilde{\xi}_\phi \leq \xi_\phi$. As in the diffuse interface limit $\tilde{\xi}_\phi$ diverges while $d\psi/dx$ vanishes as υ_p approaches 1.5.

By making use of (III-15) and (III-13), we find

$$\theta = \pm\left[1 - 3\lambda^2 \sinh^{-2}\left(\frac{x}{\tilde{\xi}_\phi} + 3^{1/2}\lambda\right)\right]^{1/2} \qquad \text{(III-18)}$$

Note that θ is discontinuous at $x = 0$. This is an artifact due to our assumption that $\xi_\eta << \xi_\phi$, i.e., that the interface is a step function on the scale of interest.

Using (III-15), (III-13), (III-4), and (II-5) and taking $(d\theta/dx)^2$ to be negligible as $d^2\phi/dx^2$, we obtain

$$\gamma = \frac{4}{3}\frac{kT}{a^3}\phi_0{}^2\tilde{\xi}_\phi\left(\upsilon_p - \frac{3}{2}\right) \qquad \text{(III-19)}$$

In the symmetric case, for good solvents, we find that the interface attracts polymer molecules. In both limits we obtain a symmetric maximum of the polymer concentration curve that is centered at the interface.

In order to understand this effect, we have to remember that the translational entropy of polymer molecules is negligible; i.e., there is entropic penalty involved with the shift of polymer molecules from the bulk to the interface region. Configurational entropy is important in determining the shape of the concentration gradient, but the existence of the maximum can be understood in terms of energetics alone. In the symmetric case there is no preferred solvent. The interaction energy associated with the pairs M–1 and M–2 is identical. On the other hand, for good solvents, the configuration 1–M–2 is associated with a lower energy than the configuration 1–2 (1–2–M, M–1–2, 1–1–2, etc.). We refer to the lowering of the interaction energy due to the separation of the 1–2 pair by a monomer as "screening" and this is the driving force responsible for the predicted attraction of polymer molecules to the interface.

When the quality of the solvents becomes poorer, we find that the renormalized length associated with the interface (be it $\tilde{\xi}_\phi$ or $\tilde{\xi}_\eta$, depending on the limit considered) diverges, while the associated gradient approaches zero. These seems to indicate the occurrence of a three-phase coexistence.[9] The third phase is polymer-rich and is located at the interface. This transition occurs in the good solvent region ($\chi_1 = \chi_2 = \chi = 1/4$). The screening effect would seem to be the driving force for the transition.

IV. Asymmetric Case

Here, the coexistence curve is given by

$$\eta_\alpha = -\eta_\beta = \eta_0$$

$$\eta^{\text{critical}} = 0$$

$$\phi_\alpha = \phi_0 - (\eta/\upsilon_p)(3\tilde{\upsilon}_s)^{1/2} \qquad \text{(IV-1)}$$

$$\phi_\beta = \phi_0 + (\Delta/\upsilon_p)(3\tilde{\upsilon}_s)^{1/2}$$

where

$$\tilde{v}_s = v_s + \Delta^2/v_p$$

ϕ_0 is the overall monomer volume fraction and we have assumed the overall volume fraction of the two solvents to be equal. Define

$$g = (\Delta/v_p)(\eta_0/x_0) \tag{IV-2}$$

Note that ϕ_0 in (IV-2) as well as in ξ_ϕ, ξ_η, and λ^2 is not identical with the ϕ_0 in (III-3). We find

$$I = \frac{kT}{a^3}\eta_0{}^4\left[\frac{1}{2}v_p\lambda^2(\psi^2 - 1 - g\theta)^2 + \frac{1}{12}(\theta^2 - 1)^2 + \frac{1}{2}\xi_\eta{}^2\left(\frac{\mathrm{d}\theta}{\mathrm{d}x}\right)^2 + \frac{1}{2}\xi_\phi{}^2\lambda^2\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2\right] \tag{IV-3}$$

The corresponding Euler–Lagrange equations are

$$\xi_\eta{}^2\frac{\mathrm{d}^2\theta}{\mathrm{d}x^2} = \frac{1}{3}(\theta^2 - 1)\theta - gv_p\lambda^4(\psi^2 - 1 - g\theta) \tag{IV-4}$$

$$\xi_\phi{}^2\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = 2v_p(\psi^2 - 1 - g\theta)\psi \tag{IV-5}$$

In the diffuse limit, where $\mathrm{d}^2\psi/\mathrm{d}x^2 \simeq 0$ we have

$$\psi^2 = 1 + g\theta \tag{IV-6}$$

from which we see immediately that $\psi^2(x)$, too, is a monotonic function with no extremum at $x = 0$ where $\psi^2(0) = 1$ (Figure 2).

Integrating (IV-5) by making use of (IV-6), we obtain

$$\eta = \eta_0 \tanh\,(x/\tilde{\xi}_\eta) \tag{IV-7}$$

where

$$\tilde{\xi}_\eta = 6^{1/2}\xi_\eta \tag{IV-8}$$

and

$$\phi = \phi_0 + \eta_0(\Delta/v_p)\tanh\,(x/\tilde{\xi}_\eta) \tag{IV-9}$$

while γ is given by

$$\gamma = \frac{4}{3(6)^{1/2}}\frac{kT}{a^3}\eta_0{}^4\xi_\eta \tag{IV-10}$$

In the second limit—the sharp interface—where $\mathrm{d}^2\theta/\mathrm{d}x^2 \simeq 0$ for $|x| > \xi_\eta$ we find

$$\psi^2 - 1 - g\theta = \frac{1}{3fv_p\lambda^4}(\theta^2 - 1)\theta \tag{IV-11}$$

From which we learn that

$$\psi^2 - 1 - g\theta \rightarrow 0 \quad \text{as } x \rightarrow \pm\infty \tag{IV-12}$$

a result that will serve as a boundary condition later on.

The preliminary analysis in this case produces

$$\frac{\mathrm{d}\psi^2}{\mathrm{d}x} = \left(g - \frac{1}{3gv_p\lambda^4} + \frac{1}{gv_p\lambda^4}\theta^2\right)\frac{\mathrm{d}\theta}{\mathrm{d}x} \tag{IV-13}$$

We see that $\mathrm{d}\psi^2/\mathrm{d}x$ is proportional to $\mathrm{d}\theta/\mathrm{d}x$ around $\theta = 0$, indicating that if there are extrema in $\psi^2(x)$, they must be displaced from the binary interface into one of the bulk regions. On the other hand, the two bulk regions are indistinguishable in (IV-13). As the two bulk phases are known to differ in their solvation quality, we conclude that $\psi^2(x)$ is a monotonous sigmoid-like function. Once we know the general form of $\psi^2(x)$, we can obtain an explicit solution by solving (IV-5) for $|x| > \xi_\eta$, which means solving

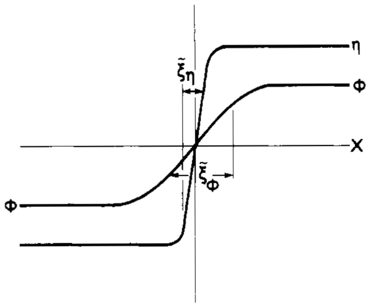

Figure 2. Sketch of the concentration profiles for the asymmetric case.

$$\xi_\phi{}^2\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = 2v_p\psi^2 - (1 \pm g)\psi \tag{IV-14}$$

where the plus sign corresponds to $x > \xi_\eta$ and the minus sign to $x < -\xi_\eta$. Making use of the results of the preliminary analysis, we obtain

$$\phi = \left(\phi_0 - \eta_0\frac{\Delta}{v_p}\right)\coth^2\left(\frac{x}{\tilde{\xi}_\phi{}^{(-)}} + \alpha_-\right) \qquad x \leq 0$$

$$\phi = \left(\phi_0 + \eta_0\frac{\Delta}{v_p}\right)\tanh^2\left(\frac{x}{\xi_\phi{}^{(+)}} + \alpha_+\right) \qquad x \geq 0 \tag{IV-15}$$

where

$$\xi_\theta{}^{(\pm)} = [v_p(1 \pm g)]^{-1/2}\xi_\theta$$

$$\alpha_+ = \operatorname{arctanh}\,(1 + g)^{1/2}$$

$$\alpha_- = \operatorname{arccoth}\,(1 - g)^{1/2} \tag{IV-16}$$

Note that this solution is valid for $g < 1$ and given the condition that $\tilde{\xi}_\phi{}^{(+)} < \tilde{\xi}_\phi < \tilde{\xi}_\phi{}^{(-)}$.

$\eta(x)$ for $|x| > \xi_\eta$ is easily found by using (IV-12). As this part of $\eta(x)$ is just the "tail" at the interface, it is of comparatively little interest other than the fact that it is characterized by $\tilde{\xi}_\phi{}^{(\mp)}$.

γ for this case is given by

$$\gamma = \frac{2kT}{a^3}\theta_0\eta_0\frac{\Delta}{v_p{}^{1/2}} \tag{IV-17}$$

The polymer concentration curve in the asymmetric case was found to be sigmoid in shape for both limits. This concentration profile reflects the monotonic change of the solvent quality between the two bulk phases. In the absence of screening interaction the interface is not attractive to polymer molecules; neither is there any indication of a possible Cahn type prewetting transition.

V. General Case

Though we did not obtain an explicit solution in this case, we were able to find out the rough shape of the polymer concentration profile in the diffuse limit.

As usual we will start with the coexistence curve. In calculating the coexistence curve in this case we made use of the lever rule and the assumption that the overall volume fraction of the two solvents is equal. It is given by

$$\eta_\alpha + \eta_\beta = \frac{2\Delta}{(2/3)\upsilon_p - 1}$$

$$\eta_\alpha = \eta_\beta = 3(\phi_0 - \tilde{\upsilon}_s) - \frac{2\Delta}{3\upsilon_p}(\eta_\alpha + \eta_\beta)$$

$$\eta^{\text{critical}} = \frac{\Delta}{(2/3)\upsilon_p - 1}$$

$$\phi_\alpha + \phi_\beta = 2\phi_0$$

$$\phi_\alpha - \phi_\beta = -(1/3)(\eta_\alpha + \eta_\beta)(\eta_\alpha - \eta_\beta) \qquad \text{(V-1)}$$

Defining

$$\phi = \phi_\alpha \psi^2 \qquad \phi_\beta/\phi_\alpha \le \psi^2 \le 1$$

$$\eta = \eta^2\theta \qquad \eta_\beta/\eta_\alpha \le \theta \le 1$$

$$\begin{aligned} &\phi_\alpha/{\eta_\alpha}^2 = \lambda^2 \qquad \upsilon_s/{\eta_\alpha}^2 = \hat{\upsilon}_s \qquad \Delta/\eta_\alpha = \hat{\Delta} \\ &\xi_\phi = m_\phi a/{\phi_\alpha}^{1/2} \qquad \xi_\eta = m_\eta a/\eta_\alpha \end{aligned} \qquad \text{(V-2)}$$

we obtain

$$\begin{aligned} I = \frac{kT}{a^3}{\eta_\alpha}^4 \Bigg[& \frac{1}{2}\upsilon_p\lambda^4(\psi^2 - 1)^2 - \frac{1}{2}\hat{\upsilon}_s(\theta - 1)^2 + \hat{\Delta}\lambda^2(\psi^2 - 1) \times \\ & (\theta - 1) + \frac{1}{12}(\theta^2 - 1)^2 + \frac{1}{6}(\theta - 1)^2 + \frac{1}{2}\lambda(\psi^2 - 1)(\theta^2 - 1) + \\ & \frac{1}{2}{\xi_\phi}^2\lambda^4\left(\frac{d\psi}{dx}\right)^2 + \frac{1}{2}{\xi_\eta}^2\left(\frac{d\theta}{dx}\right)^2 \Bigg] \end{aligned} \qquad \text{(V-3)}$$

and the corresponding Euler–Lagrange equation

$$\begin{aligned} {\xi_\eta}^2\frac{d^2\theta}{dx^2} = -\hat{\upsilon}_s(\theta - 1) + \hat{\Delta}\lambda^2(\psi^2 - 1) + \frac{1}{3}(\theta^3 - 1) + \\ \lambda^2(\psi^2 - 1)\theta + \lambda^2(\theta - 1) \end{aligned} \qquad \text{(V-4)}$$

$${\xi_\phi}^2\lambda^2\frac{d^2\psi}{dx^2} = \psi[2\upsilon_p\lambda^2(\psi^2 - 1) + 2\hat{\Delta}(\theta - 1) + (\theta^2 - 1)] \qquad \text{(V-5)}$$

In the diffuse limit, corresponding to $\lambda^2 >> 1$ and $d^2\psi/dx^2 \simeq 0$, we have

$$\psi^2 = 1 - \frac{\hat{\Delta}}{\upsilon_p\lambda^2}(\theta - 1) - \frac{1}{2\upsilon_p\lambda^2}(\theta^2 - 1) \qquad \text{(V-6)}$$

and so

$$\frac{d\psi^2}{dx} = -\frac{1}{\upsilon_p\lambda^2}(\hat{\Delta} + \theta)\frac{d\theta}{dx} \qquad \text{(V-7)}$$

which indicates a possible extremum at $\theta = -\Delta/\eta_\alpha$. This possible extremum may have a physical meaning only in $\eta_\beta/\eta_\alpha \le \Delta/\eta_a \le 1$, i.e., if $\Delta << 1$. This condition would locate the extremum near the interface. Substituting $\theta = -\Delta/\eta_\alpha$ into (V-7) gives

$${\psi_{\text{ext}}}^2 = 1 + \frac{1}{2\upsilon_p\lambda^2}(\hat{\Delta}^2 + 2\hat{\Delta} + 1) \qquad \text{(V-8)}$$

Notice that both the position and the amplitude at the extremum reduce to their proper values for $\Delta = 0$.

In the sharp interface limit, this type of analysis does not produce conclusive results.

Conclusions

Homopolymers may be attracted to the interface of a biphasic binary solution. The polymer concentration profile at the interface can be analyzed in terms of the gradual change in solvent quality and of screening. The screening—lowering of the free energy due to the presence of a monomer between solvent molecules of different kinds—is responsible for the attraction. In the general case, where both screening and change in solvent quality occur, the polymer concentration profile is expected to show a maximum, which is slightly displaced toward the bulk of the phase of better solvent. Similar results were obtained earlier by Leibler[10] for copolymers in biphasic melts.

Due to the coupling between the two concentration gradients, a single length characterizes both of them on a certain scale. This is a renormalized version of the longer of the two bare correlation lengths.

When solvent quality of both phases becomes poorer there are indications for the occurrence of a three-phase coexistence. The third phase is polymer-rich and is located between the two "older" phases. This phase transition is driven by the screening interaction rather than by the change in solvent quality (it occurs while both phases are in the good solvent regime).

The attraction of polymers to interfaces may affect transport through the interface.[11] Such an effect may supply an indirect means to check the concentration profile at the interface. More direct means include scattering techniques.

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