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Molecular Weight and Polydispersity Effects at Polymer-Polymer Interfaces

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ABSTRACT: We study the interfacial properties of immiscible polymers, going beyond the usual approximation of infinite molecular weight, complete immiscibility. For finite molecular weights, the interfaces are broader and the interfacial tensions smaller than predicted by this approximation. These corrections are entropic effects and are significant for typical experimental situations: they are in fact inversely proportional to the incompatibility $\chi_{AB}N$, where χ_{AB} is the Flory interaction parameter between unlike (A and B) monomers and N the number of monomers per chain. In polydisperse systems, small chains accumulate slightly at the interface, lowering the interfacial tension. Our analysis seems consistent with recent interfacial tension measurements.

I. Introduction

An understanding of the physics of polymer-polymer interfaces is essential for many practical applications, such as adhesion or coextrusion. Most polymer pairs are in fact immiscible at ambient temperatures and form multiphase systems whose bulk physicochemical behavior depends strongly on the properties of the interfaces between the different phases.^{1,2}

The most accessible interfacial quantity in a two-phase system is the interfacial tension, which can be experimentally determined from the profile of a drop of one phase immersed in the other phase.³ Measurements of this kind are performed specifically to gain insight into interactions at the molecular level. With the help of an adequate theory, they allow one to infer a measure of

the incompatibility between unlike monomers.⁴

There are various theories that relate the interfacial properties of two immiscible polymers, e.g., A and B, to the microscopic interactions described by the (Flory) interaction parameter χ_{AB} between the corresponding monomers. In the early 1970s, Helfand and co-workers constructed a self-consistent field theory of polymer-polymer interfaces.^{4,5} They found, in the limit of infinite molecular weight, very simple expressions relating the interfacial tension, γ_∞ , and the interfacial thickness, D_∞ , to the interaction parameter:

$$\gamma_\infty = \frac{kT}{a^2}(\chi_{AB}/6)^{1/2} \quad (\text{I.1})$$

$$D_\infty = 2a/(6\chi_{AB})^{1/2} \quad (\text{I.2})$$

where a is the statistical segment (monomer) length. These results were eventually extended to asymmetric poly-

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mers (i.e., with different monomer sizes).⁶ As shown by de Gennes and as discussed below, eq I.1 and I.2 may also be derived by the random phase approximation.⁷

The Helfand theory has been found to describe the essential features of high molecular weight polymer-polymer interfaces (the typical χ_{AB} being 10^{-2} and the typical monomer length 5–7 Å); low interfacial tensions (about 1 dyn/cm) and large polymer-polymer interpenetration at the interface, i.e., wide interfaces (a few monomers, or a few tens of angstroms). The theory is in qualitative agreement with experiments.⁸

However, the assumption of infinite chain length is not an accurate approximation for many situations: recent measurements suggest in fact that there are important corrections to the results (I.1) and (I.2) for polymers of finite length. In a series of experiments, Anastasiadis and co-workers^{8,9} found strong molecular weight effects for chains with molecular weights up to 10^5 . In particular, the interfacial tension was shown to increase with increasing molecular weight of chains.

Real polymer samples are composed of finite chains and are *polydisperse*. It is therefore of interest to investigate the effect of polydispersity on interfacial properties. Intuitively, we expect chains with different molecular weights to behave in different ways at the interface. In particular, there should be an excess of small chains at the interface because this is capable of lowering the interfacial tension.

Anastasiadis and co-workers⁹ investigated the effect of finite chain length on the interfacial tension of immiscible polymer blends through a modified Cahn-Hilliard approach.¹⁹ By a numerical evaluation of the theoretical expression for the interfacial tension, they were able to obtain reasonable agreement with experiment. In the present paper we extend the work of ref 9 by providing analytical expressions for the finite molecular weight corrections to the interfacial thickness and tension and by investigating the effects of polydispersity.

We utilize a mean-field procedure commonly employed for the study of interfaces involving polymers.⁹⁻¹⁸ The Cahn-Hilliard approximation¹⁹ will be made: as the interface is broad (compared to a monomer size), the inhomogeneities in concentrations can be accounted for in the free energy density by squared gradients of these concentrations. The coefficients of these squared gradient terms may be calculated through the random-phase approximation.

In the next section (section II), we study the interface between monodisperse A and B polymers with different, but comparable, chain lengths N_A and N_B . We evaluate the leading order corrections to the infinite molecular weight results for the interfacial properties. For typical incompatibility degrees ($w_A = \chi_{AB}N_A$ and $w_B = \chi_{AB}N_B$ between 5 and 10, say), it turns out that these corrections are significant: the complete segregation approximation (w_i or $N_i \rightarrow \infty$), although valid for the bulk equilibrium properties, is not in general a good approximation for the interface properties.

The interface between polydisperse polymers is analyzed in section III. We consider a very special type of polydispersity in which the A and B chains have the same bimodal molecular weight distribution. In spite of this simplicity, we expect it to exhibit the same features that would be found in more general polydisperse systems. As expected, our calculations show that small chains preferentially locate at the interface, thus lowering the interfacial tension. However, this polydispersity effect disappears when the chains become very long.

The last section (section IV) is devoted to the discussion of experiments.

II. Interfaces between Monodisperse Polymers

We consider two strongly segregated A and B homopolymers with comparable (high) incompatibility degrees $w_A = \chi_{AB}N_A$ and $w_B = \chi_{AB}N_B$. Each phase is nearly pure in one of the two polymer species.

The interface between the A-rich and the B-rich phases (phases α and β) is assumed to be flat. The monomer volume fractions $\phi_A(z)$ and $\phi_B(z) = 1 - \phi_A(z)$ vary smoothly along the z -axis between the equilibrium values ϕ_A^β and ϕ_B^β at $z = -\infty$ and ϕ_A^α and ϕ_B^α at $z = +\infty$. The plane $z = 0$, where $\phi_A = \phi_B = 1/2$, divides the A-rich phase ($z > 0$) and the B-rich phase ($z < 0$).

II.1. Interface Energy Functional. The interfacial tension and the concentration profile throughout the interface are obtained by minimizing a certain interface energy functional. This interface energy functional is defined, for a given concentration profile $\phi_A(z) = 1 - \phi_B(z)$, as the difference between the total free energy of the system and that which it would have if there was no interface:

$$\gamma a^2 = \int_{-\infty}^{+\infty} d\left(\frac{z}{a}\right) \left[F(z) - \frac{\phi_A(z)}{N_A} \mu_A(e) - \frac{\phi_B(z)}{N_B} \mu_B(e) \right] \quad (\text{II.1})$$

$F(z)$ is the free energy per monomer in the plane of coordinate z , and $\mu_A(e) = \mu_A^\alpha = \mu_A^\beta$ and $\mu_B(e) = \mu_B^\alpha = \mu_B^\beta$ are the chain chemical potentials in the two phases at equilibrium. It is convenient to express these chemical potentials in term of the exchange chemical potential $\mu = \partial F / \partial \phi_A$:

$$\mu_A = N_A(F + \phi_B \mu) \quad (\text{II.2a})$$

$$\mu_B = N_B(F - \phi_A \mu) \quad (\text{II.2b})$$

The free energy per monomer of the inhomogeneous system $F(z)$ is calculated within the mean-field Cahn-Hilliard and random-phase approximations in Appendix A. Our expression is essentially the same as that employed in ref 9 and 17.

Using eq II.1 and II.2 and eq A.1 and A.5, and changing the space variable $z \rightarrow z' = z(6\chi_{AB})^{1/2}/a = z/D_\infty$, we get for the interface energy functional the very simple form

$$\gamma = \gamma_\infty \int_{-\infty}^{+\infty} L(\phi_A(z'), \dot{\phi}_A(z')) dz' \quad (\text{II.3})$$

where γ_∞ is given by eq I.1 and the energy density L is a functional of the A monomer volume fraction ϕ_A and its derivative $\dot{\phi}_A = d\phi_A/dz'$

$$L(\phi_A, \dot{\phi}_A) = K(\phi_A, \dot{\phi}_A) - W(\phi_A) \quad (\text{II.4})$$

K being the "kinetic" part, quadratic in $\dot{\phi}_A$

$$K(\phi_A, \dot{\phi}_A) = \dot{\phi}_A^2 / 4\phi_A(1 - \phi_A) \quad (\text{II.5})$$

and W the "potential" part, depending only on ϕ_A

$$-W(\phi_A) = f_{FH}(\phi_A) - f_{FH}(\phi_A^\alpha) - (\phi_A - \phi_A^\alpha)\mu_0(e) \quad (\text{II.6})$$

In eq II.6, f_{FH} is the reduced Flory-Huggins free energy (see eq A.1) and $\mu_0(e) = \mu(e)/kT\chi_{AB}$ is the reduced exchange chemical potential at equilibrium.

Equations II.3–II.5 possess an analogy²⁰ with a particle trajectory problem in Lagrangian mechanics: under the action of the potential $W(\phi_A)$, the "particle position" ϕ_A evolves between the equilibrium positions ϕ_A^β at "time" $z = -\infty$ and ϕ_A^α at "time" $z = +\infty$. The only peculiar

aspect of this analogy is that the coefficient of ϕ_A^2 (the "mass") is not constant and depends on ϕ_A . It may be verified, however, that the law of conservation of energy

$$K(\phi_A, \dot{\phi}_A) + W(\phi_A) = \text{constant} = 0 \quad (\text{II.7})$$

remains valid for the trajectory that minimizes the functional (II.3).

The existence of such a first integral greatly simplifies the problem: the concentration profile $\phi_A(z)$ is obtained through a simple quadrature instead of the usual second-order Euler-Lagrange differential equation, and the interfacial tension may be calculated without any knowledge of the concentration profile. We first analyze the situation far from the interface ($z \rightarrow \pm\infty$).

II.2. Equilibrium Properties. The equalities between the chain chemical potentials in both phases are equivalent to the equalities (see eq II.2) between the exchange chemical potentials

$$\mu(\phi_A^\alpha) = \mu(\phi_A^\beta) \quad (\text{II.8a})$$

and the "osmotic pressures":

$$F_{\text{FH}}(\phi_A^\alpha) - \phi_A^\alpha \mu(\phi_A^\alpha) = F_{\text{FH}}(\phi_A^\beta) - \phi_A^\beta \mu(\phi_A^\beta) \quad (\text{II.9a})$$

From eq A.1, ϕ_A^α and ϕ_A^β are solutions of the following set of equations:

$$\frac{1}{w_A} \ln \left[\frac{\phi_A^\alpha}{\phi_A^\beta} \right] - \frac{1}{w_B} \ln \left[\frac{1 - \phi_A^\alpha}{1 - \phi_A^\beta} \right] - 2(\phi_A^\alpha - \phi_A^\beta) = 0 \quad (\text{II.8b})$$

$$\frac{1}{w_B} \ln \left[\frac{1 - \phi_A^\alpha}{1 - \phi_A^\beta} \right] + \left(\frac{1}{w_B} - \frac{1}{w_A} \right) (\phi_A^\alpha - \phi_A^\beta) + [(\phi_A^\alpha)^2 - (\phi_A^\beta)^2] = 0 \quad (\text{II.9b})$$

In the strong segregation regime, there is a very simple approximate solution: writing $\phi_A^\alpha = 1 - \epsilon_\alpha$ and $\phi_A^\beta = \epsilon_\beta$, with ϵ_α and ϵ_β small compared to 1, we get from the previous equations $\epsilon_\alpha = e^{-w_B}$ and $\epsilon_\beta = e^{-w_A}$. Thus

$$\phi_A^\alpha = 1 - \phi_B^\alpha \approx 1 - e^{-w_B} \quad (\text{II.10a})$$

$$\phi_A^\beta = 1 - \phi_B^\beta \approx e^{-w_A} \quad (\text{II.10b})$$

This first-order perturbation solution is a very good approximation for high incompatibility degrees; more specifically, the solution (II.10) is within 15% of the exact solution when $w_A, w_B > 4$, i.e., for chains with incompatibility degrees two or more times higher than the value $w_k = 2$, corresponding to the critical point for demixing. It is interesting to note that the equilibrium concentrations converge very rapidly (exponentially) toward the complete segregation limits when the incompatibility increases.

II.3. Concentration Profile through the Interface. Interfacial Thickness. The profile ϕ_A is the solution of the first integral (eq II.7):

$$\frac{\dot{\phi}_A^2}{4\phi_A(1 - \phi_A)} = f_{\text{FH}}(\phi_A) - f_{\text{FH}}(\phi_A^\alpha) - (\phi_A - \phi_A^\alpha)\mu_0(e) \quad (\text{II.11})$$

with boundary conditions corresponding to the equilibrium concentrations $\phi_A^\alpha = \phi_A(z=+\infty)$ and $\phi_A^\beta = \phi_A(z=-\infty)$ calculated before. In the infinite molecular weight limit, this differential equation has an analytical solution, the familiar hyperbolic tangential profile:

$$\phi_A^\infty(z) = \frac{1}{2}[1 + \tanh(z')] = \frac{1}{2}[1 + \tanh(z/D_\infty)] \quad (\text{II.12})$$

D_∞ , given by eq I.2, is thus the interfacial thickness.

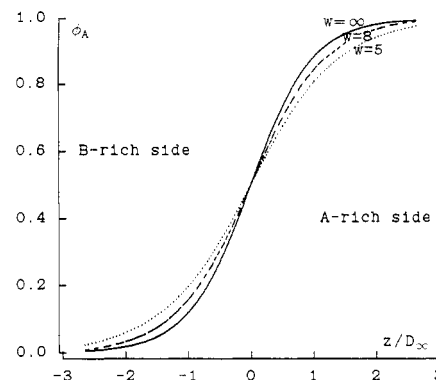


Figure 1. Composition profiles for different incompatibilities $w = w_A = w_B$ as a function of the reduced distance from the interface z/D_∞ . Dotted line corresponds to $w = 5$, dashed line to $w = 8$. The full line represents the hyperbolic tangential profile, corresponding to an infinite incompatibility degree (eq II.12).

In the general case, eq II.11 has to be integrated numerically. In Figure 1, we show the composition profiles corresponding to different incompatibilities. The manner in which the solution converges toward the infinite incompatibility limit (eq II.12) as the incompatibility is increased is interesting. Close to the interface, we get, using eq II.11, II.10, and A.1, to first order in z

$$\phi_A(z \approx 0) \approx \frac{1}{2} + z' \dot{\phi}_A(0) \approx \frac{1}{2} \left[1 + \frac{z}{D_\infty} \left[1 - 2 \ln 2 \left(\frac{1}{w_A} + \frac{1}{w_B} \right) \right]^{1/2} \right] \quad (\text{II.13})$$

where small terms (compared to $1/w_A + 1/w_B$) have been neglected in $\phi_A(0)$. Thus, in the interfacial region ($z \approx 0$), ϕ_A converges slowly (approximately as the inverse of the incompatibility degrees) toward $\phi_A^\infty (\approx 1/2 + z/D_\infty)$. This is a very important result that we will discuss further.

From the previous equation, we determine the interfacial thickness, defined by $D = (\phi_A^\alpha - \phi_A^\beta) / (d\phi_A/dz)(z=0)$:

$$D = D_\infty \left[1 - 2 \ln 2 \left(\frac{1}{w_A} + \frac{1}{w_B} \right) \right]^{-1/2} \approx D_\infty \left[1 + \ln 2 \left(\frac{1}{w_A} + \frac{1}{w_B} \right) \right] \quad (\text{II.14})$$

This quantity decreases slowly toward its asymptotic limit D_∞ . For typical values of the incompatibility degrees (say $w \approx 5$), there will be important corrections to this asymptotic value. The origin of these corrections is purely entropic. We comment on the importance of these corrections at the end of this section.

At large distances from the interface, eq II.11 has a very different behavior. By extracting the asymptotic behavior for $z \rightarrow \infty$ from the integrated form of the equation, we find

$$\phi_A(z) = \phi_A^\alpha \left[1 - \frac{3}{2} e^{-w_B} e^{-2^{1/2} z/R_B} \right] \quad (\text{II.15})$$

where $R_B = N_B^{1/2} a / 6^{1/2}$ is the radius of gyration of the B homopolymer.

The asymptotic approach to ϕ_A^α is exponential, but the decay length is proportional to $R_B = D_\infty w_B^{1/2}$, much larger than the interfacial thickness, which is the only scale in the infinite molecular weight profile, eq II.12. At finite molecular weight there are thus three relevant lengths that enter the composition profile: D , characterizing the

behavior near the interface; R_B , describing the approach to equilibrium in the A-rich phase; and R_A , describing the corresponding region in the B-rich phase. The emergence of multiple scales suggests that a perturbation expansion of the Euler-Lagrange equation about the profile eq II.12 is a singular one and requires special methods. Note, however, that in the present monodisperse problem a perturbative solution can be avoided because a first integral exists, eq II.11. As a result, we can calculate the interfacial thickness and tension (see below) without first solving for the profile. This will not prove to be possible in the polydisperse case to be addressed in section III.

The asymptotic profile in eq II.15 is actually not relevant to the interfacial tension or thickness for large incompatibility degrees. Although R_B is very large and the decay very slow in this case, the e^{-w_B} prefactor makes all contributions to D or γ from the asymptotic profile exponentially small. In contrast, the "inner" region of the profile gives w^{-1} contributions to these quantities (cf. eq II.14).

II.4. Interfacial Tension. The interfacial tension γ may be calculated from the first integral²⁰ (eq II.7):

$$\gamma/\gamma_\infty = \int_{-\infty}^{+\infty} (K - W) dz = \int_{-\infty}^{+\infty} 2K dz = \int_{\phi_A^\beta}^{\phi_A^\alpha} [-W(\phi_A)/\phi_A(1-\phi_A)]^{1/2} d\phi_A \quad (\text{II.16})$$

Expanding the integrand for large incompatibilities, we get

$$[-W(\phi_A)/\phi_A(1-\phi_A)]^{1/2} = 1 + \frac{1}{2w_A} \frac{\ln \phi_A}{1-\phi_A} + \frac{1}{2w_B} \frac{\ln(1-\phi_A)}{\phi_A} - \frac{1}{2\phi_A(1-\phi_A)} [f_{FH}(\phi_A^\alpha) - (\phi_A - \phi_A^\alpha)\mu_0(e)] \quad (\text{II.17})$$

and, after integration, we obtain for the interfacial tension the leading order corrections to the asymptotic limit γ_∞ :

$$\gamma = \gamma_\infty \left[1 - \frac{\pi^2}{12} \left(\frac{1}{w_A} + \frac{1}{w_B} \right) + \dots \right] \quad (\text{II.18})$$

In eq II.17 and II.18, we have neglected small terms compared to $1/w$: in particular, we used the fact that ϕ_A^α and ϕ_A^β are exponentially close to 1 and 0, respectively. From eq II.18, we see that the interfacial tension increases slowly with increasing molecular weight or incompatibility toward its asymptotic limit γ_∞ . As for the interfacial thickness, these corrections are entropic in nature: they come from the entropic part of the (Flory-Huggins) free energy. Equation II.18 is presumably the asymptotic behavior of the theory constructed by Anastasiadis and co-workers.⁹ However, in their numerical calculations this regime was apparently not explored.

II.5. Discussion. Our results indicate that the interfacial properties should exhibit some molecular weight dependence for typical experimental situations with polymers of finite molecular weight. Typical incompatibility degrees,²¹ w , lie between 5 and 15. From eq II.14 and II.18, it may be seen that the corrections are then on the order of 10–30%. In contrast, the equilibrium values are very close to their infinite molecular weight limits ($\phi_B^\alpha = 1 - \phi_A^\alpha < 10^{-2}$ for $w > 5$).

We expect our results to be valid provided that the interface is smaller than the radius of gyration R_g of a chain. In particular, our analysis does not hold for slightly incompatible systems where the interface becomes of order

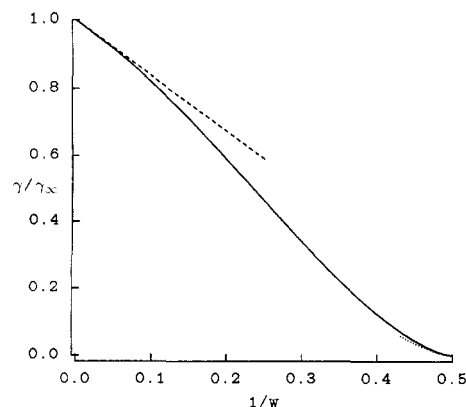


Figure 2. Reduced interfacial tension γ/γ_∞ as a function of the inverse incompatibility $1/w$ (full line). The dashed line is the asymptotic linear behavior (eq II.17) valid for large incompatibilities. Near the critical point ($1/w \approx 0.5$), the dotted line represents the more exact solution of Joanny and Leibler¹⁰ (see also Figure 10 of ref 9).

R_g or larger. Near the critical demixing point where the interface is much larger than R_g , we have for the square gradient coefficient, using the $qR_g^2 < 1$ regime of the structure factors (see Appendix A): $\Gamma = \Gamma_{cr} = 1/6\phi_A(1 - \phi_A)$.¹⁰ This is slightly different from the value in the strong segregation limit $\Gamma = 1/4\phi_A(1 - \phi_A)$. For intermediate incompatibilities, this coefficient should lie between these two limits, with a crossover occurring when the interface width is on the order of R_g .²² Since the limiting values of the coefficients differ only slightly, we believe that our approximation is very good for typical segregated polymer-polymer systems (the molecular weight corrections to the value $1/4\phi_A(1 - \phi_A)$ should in fact be very small).

Figure 2 shows the calculated (from eq II.16 and II.6) interfacial tension plotted as a function of the inverse incompatibility $1/w$. Note that the asymptotic behavior (eq II.18) is a good approximation for a wide range of incompatibilities, say w greater than 5 ($1/w < 0.2$). The increase of interfacial tension with molecular weight is, however, slower for smaller molecular weight. This apparent behavior was pointed out in ref 9.

III. Interfaces between Polydisperse Polymers

We consider the simplest molten polydisperse system: the polymer A and polymer B melts are both binary mixtures with the same bimodal distribution of molecular weights. We call N_1 the length of the small chains, N_2 the length of the long chains ($N_1 < N_2$), and x_0 the volume fraction of monomers belonging to small chains.

This system is a quaternary mixture. However, because of incompressibility, there are three independent volume fractions, e.g., the total monomer A volume fraction ϕ_A and the two volume fractions of monomers belonging to small chains ϕ_{A1} and ϕ_{B1} . Symmetry dictates that $\phi_{A1}(-z) = \phi_{B1}(z)$, $\phi_{A2}(-z) = \phi_{B2}(z)$, and $\phi_A(-z) = \phi_B(z)$. It is thus sufficient to know the concentration profiles in the half space ($z > 0$), i.e., in the A-rich phase.

We will follow the same procedure as in the monodisperse case, studying first the equilibrium properties.

III.1. Equilibrium Properties. The equilibrium concentrations ϕ_i^α and ϕ_i^β may be found by equating the chain chemical potentials in the two coexisting phases:

$$\mu_i(\phi_A^\alpha, \phi_{A1}^\alpha, \phi_{B1}^\alpha) = \mu_i(\phi_A^\beta, \phi_{A1}^\beta, \phi_{B1}^\beta) \quad (\text{III.1})$$

where i stands for the polymer species A1, A2, B1, or B2 and α and β denote the A-rich and the B-rich phases,

respectively. Because of the symmetry, there are only two independent equations:

$$\mu_{A1}^\alpha = \mu_{A1}^\beta \quad (\text{III.2a})$$

$$\mu_{A2}^\alpha = \mu_{A2}^\beta \quad (\text{III.2b})$$

The third equation is a consequence of the symmetry:

$$\phi_{A1}^\alpha + \phi_{B1}^\alpha = \phi_{A1}^\beta + \phi_{B1}^\beta = x_0 \quad (\text{III.3})$$

It may be checked that the equalities between the chain chemical potentials are equivalent to the equalities between the exchange chemical potentials μ_{A1} and μ_{B1} (see eq III.10). The free energy per monomer has the simple Flory-Huggins form:

$$F_{\text{FH}}/kT = \frac{\phi_{A1}}{N_1} \ln \phi_{A1} + \frac{\phi_{A2}}{N_2} \ln \phi_{A2} + \frac{\phi_{B1}}{N_1} \ln \phi_{B1} + \frac{\phi_{B2}}{N_2} \ln \phi_{B2} + \chi_{AB} \phi_A \phi_B \quad (\text{III.4})$$

From eq III.2, we get the following equations for the equilibrium concentrations:

$$\frac{1}{w_1} \ln \left[\frac{\phi_{A1}^\alpha}{\phi_{B1}^\alpha} \right] + 2\phi_A^\alpha - 1 = 0 \quad (\text{III.5a})$$

$$\frac{1}{w_2} \ln \left[\frac{\phi_{A2}^\alpha}{\phi_{B2}^\alpha} \right] + 2\phi_A^\alpha - 1 = 0 \quad (\text{III.5b})$$

In the strong segregation regime (i.e., for large $w_i = \chi_{AB} N_i$), there is an accurate approximate solution to eq III.5. In the A-rich phase, the proportion of small A chains remains close to x_0 (see eq III.3), and then from eq III.5a

$$\phi_{B1}^\alpha \approx x_0 e^{-w_1} \quad (\text{III.6})$$

and from eq III.5b

$$\phi_{B2}^\alpha \approx (1 - x_0) e^{-w_2} \quad (\text{III.7})$$

An interesting quantity is the fraction of "minority" monomers belonging to small chains (e.g., the B monomers in the phase α):

$$y = \frac{\phi_{B1}^\alpha}{\phi_{B1}^\alpha + \phi_{B2}^\alpha} \approx \frac{x_0 e^{-w_1}}{x_0 e^{-w_1} + (1 - x_0) e^{-w_2}} \quad (\text{III.8a})$$

It is interesting that this quantity increases very rapidly with the chain asymmetry $w_2 - w_1$: for example, $y \approx 0.9$ for a system containing an equal amount (i.e., $x_0 = 0.5$) of monomers in short and in long chains with $w_2 - w_1 = 2$. For large asymmetries $w_2 - w_1$, we have

$$y \approx 1 - \frac{1 - x_0}{x_0} e^{-(w_2 - w_1)} \quad (\text{III.8b})$$

The previous results (eq III.6-III.8) may be straightforwardly extended to more general polydisperse systems. In segregated polymer systems, the molecular weight distribution of the "minority" polymers within the bulk phase is strongly skewed toward the low molecular weights. The "minority" monomers, however, are present in a very small amount. As will be seen below, the behavior of polydisperse blends in the vicinity of the interface is also quite interesting.

III.2. Interface Energy Functional. The interface energy functional that must be minimized is the following:

$$\gamma a^2 = \int_{-\infty}^{+\infty} \frac{dz}{a} \left[F[\phi_A(z), \phi_{A1}(z), \phi_{B1}(z)] - \sum_{i=A,B} \frac{\phi_{ij}(z)}{N_j} \mu_{ij}(e) \right] \quad (\text{III.9})$$

where F is the free energy (per monomer) of the inhomogeneous phase.

The chain chemical potentials may be written in terms of the exchange chemical potentials $\mu = \partial F / \partial \phi_A$, $\mu_{A1} = \partial F / \partial \phi_{A1}$, and $\mu_{B1} = \partial F / \partial \phi_{B1}$:

$$\mu_{A1} = N_1[(1 - \phi_A)\mu + (1 - \phi_{A1})\mu_{A1} - \phi_{B1}\mu_{B1} + F] \quad (\text{III.10a})$$

$$\mu_{A2} = N_2[(1 - \phi_A)\mu - \phi_{A1}\mu_{A1} - \phi_{B1}\mu_{B1} + F] \quad (\text{III.10b})$$

$$\mu_{B1} = N_1[-\phi_A\mu - \phi_{A1}\mu_{A1} + (1 - \phi_{B1})\mu_{B1} + F] \quad (\text{III.10c})$$

$$\mu_{B2} = N_2[-\phi_A\mu - \phi_{A1}\mu_{A1} - \phi_{B1}\mu_{B1} + F] \quad (\text{III.10d})$$

The functional γ then takes the very simple form:

$$\gamma a^2 = \int_{-\infty}^{+\infty} \frac{dz}{a} [F(z) - F(e) - (\phi_{A1} - \phi_{A1}^\alpha)\mu_{A1}(e) - (\phi_{B1} - \phi_{B1}^\alpha)\mu_{B1}(e)] \quad (\text{III.11})$$

Because of the symmetry, $\mu_{A1}(e) = \mu_{B1}(e) = \mu_1(e)$. Then, using eq III.3 and changing the space variable z to $z' = z(6\chi_{AB})^{1/2}/a = z/D_\infty$, we get for the functional γ :

$$\gamma = \gamma_\infty \int_{-\infty}^{+\infty} dz' L(z') \quad (\text{III.12})$$

with

$$L(z') = f(z') - f(e) - [\phi_{A1}(z') + \phi_{B1}(z') - x_0]\mu_{10}(e) \quad (\text{III.13})$$

where $f = F/kT\chi_{AB}$ and $\mu_{10} = \mu_1/kT\chi_{AB}$ are reduced forms of the free energy (per monomer) and of the exchange chemical potential μ_1 .

It is useful to chose as concentration variables the fraction of monomers belonging to small chains, relative to the total fraction of monomers, i.e., dropping primes on z :

$$x(z) = \phi_{A1}(z)/\phi_A(z) \quad (\text{III.14})$$

and

$$y(z) = \phi_{B1}(z)/\phi_B(z) \quad (\text{III.15})$$

The functional $L = K - W$ may be expressed as a function of ϕ_A , x , y , and their derivatives. The kinetic part K is, from Appendix B

$$K = \frac{1}{4} \left[\frac{\dot{\phi}_A^2}{\phi_A(1 - \phi_A)} + \frac{\phi_A \dot{x}^2}{x(1 - x)} + \frac{(1 - \phi_A) \dot{y}^2}{y(1 - y)} \right] \quad (\text{III.16})$$

The first term on the r.h.s of this equation is the same as for the monodisperse case (see eq II.5). The two last terms are due to the variations in polydispersity across the interface. The potential part depends only on ϕ_A , x , and y :

$$-W = f_{\text{FH}} - f_{\text{FH}}(e) - [x(z)\phi_A(z) + y(z)(1 - \phi_A(z)) - x_0]\mu_{10}(e) \quad (\text{III.17})$$

where f_{FH} is the reduced Flory-Huggins free energy.

III.3. Composition Profiles. The present variational problem is not integrable (there are three independent concentration variables and only one first integral:

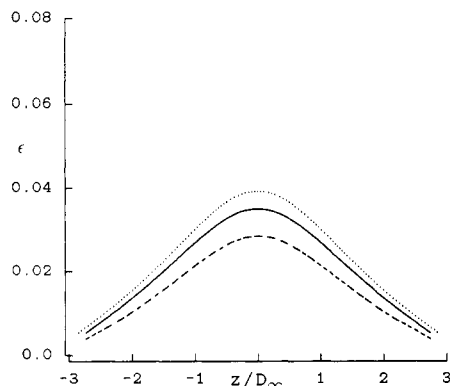


Figure 3. Small-chain excess at the interface for a system with an incompatibility degree ratio $r = w_2/w_1$ of 1.4 and $w_1 = 5$. The curves correspond to different fractions of monomers in small chains $x_0 = 1/2$ (dotted), $x_0 = 2/3$ (full), and $x_0 = 1/4$ (dashed).

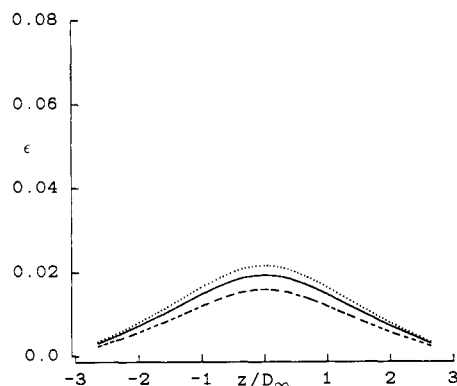


Figure 4. Same w_1 and x_0 as Figure 3, with a ratio $r = 1.2$.

$W + K = 0$). Alternatively, there are three Euler-Lagrange differential equations that must be solved:

$$\frac{\partial L}{\partial \phi_A} - \frac{\partial}{\partial z} \frac{\partial L}{\partial \dot{\phi}_A} = 0 \quad (\text{III.18a})$$

$$\frac{\partial L}{\partial x} - \frac{\partial}{\partial z} \frac{\partial L}{\partial \dot{x}} = 0 \quad (\text{III.18b})$$

$$\frac{\partial L}{\partial y} - \frac{\partial}{\partial z} \frac{\partial L}{\partial \dot{y}} = 0 \quad (\text{III.18c})$$

where $L = K - W$ is given by eq III.16 and III.17.

The boundary conditions are those of bulk equilibrium (see section III.1):

$$\phi_A(z=+\infty) = 1 - \phi_A(z=-\infty) = \phi_A^\alpha \quad (\text{III.19a})$$

$$x(z=+\infty) = y(z=-\infty) = \phi_{A1}^\alpha / \phi_A^\alpha \quad (\text{III.19b})$$

$$y(z=+\infty) = x(z=-\infty) = \phi_{B1}^\alpha / \phi_B^\alpha \quad (\text{III.19c})$$

We have solved numerically this set of second-order coupled differential equations for different values of the incompatibilities and of the fraction x_0 of monomers in small chains. The method used is a relaxation method.²³

One interesting quantity is the volume fraction of small chains, $\phi_{A1} + \phi_{B1}$. We have represented on Figures 3–5 the small-chain excess

$$\epsilon(z) = \phi_{A1}(z) + \phi_{B1}(z) - \phi_{A1}^\alpha - \phi_{B1}^\alpha \quad (\text{III.20})$$

as a function of the distance z to the interface for different polydisperse systems. Our calculations indicate that ϵ is a positive function with a maximum at the interface ($z = 0$) that is small for typical polydispersities: for example $\epsilon \approx 0.04$ at the interface for a system with an equal amount of small ($w_1 = 5$) and long ($w_2 = 7$) chains (see

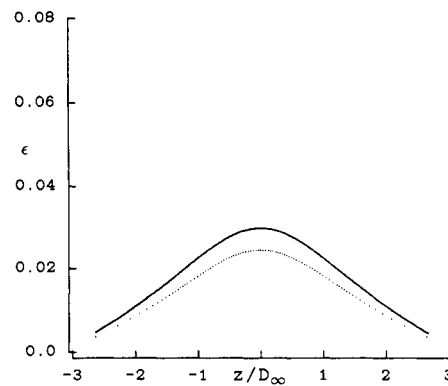


Figure 5. Small chain excess at the interface for two systems with same r ($r = 1.29$) but different w_1 , $w_1 = 5$ (full line) and $w_1 = 7$ (dotted line). The fraction of monomers in small chains and long chains is equal ($x_0 = 0.5$).

Figure 3). Thus, at the interface, 48% of the monomers belong to long chains and 52% to small chains, and the proportions are identical far from the interface. There is in fact a slight accumulation of small chains at the interface.

One would expect indeed more significant effects for smaller chains and/or larger incompatibility differences.

More precisely, the numerical calculations indicate that the small-chain excess at the interface (i) decreases when the chain length ratio $r = w_2/w_1$ decreases to 1 (one of the chain lengths, say w_1 , remaining constant) (compare Figures 3 and 4); (ii) decreases when both chain lengths simultaneously increase (the ratio r remaining constant) (Figure 5). Indeed, when both chains become very long, the difference in chain lengths does not play any role.

The physical reason may be understood from the analysis of monodisperse systems (section II): having more small chains at the interface has the effect of lowering the interfacial tension.

III.4. Interfacial Tension. We may find an approximate expression for the interfacial tension between polydisperse blends when the incompatibilities w_i are large and the difference Δw is small. Namely, if one assumes that x and y remain close to their average value x_0 across the interface, the interface energy functional (eq III.13) simplifies to:

$$L(z) = \frac{\phi_A(z)}{w_n} \ln \phi_A(z) + \frac{\phi_B(z)}{w_n} \ln \phi_B(z) + \phi_A(z)\phi_B(z) + \phi_A^2/4\phi_A(1-\phi_A) \quad (\text{III.21})$$

where $w_n = 1/(x_0/w_1 + (1-x_0)/w_2)$ is the number-averaged incompatibility degree. Terms on the order of $x - x_0$, $y - y_0$ and their derivatives have been neglected in eq III.21. Then, using the results of section II.4, we get for the interfacial tension:

$$\gamma \approx \gamma_\infty \left[1 - \frac{\pi^2}{6w_n} + \dots \right] \quad (\text{III.22})$$

Since the number-average molecular weight is most heavily weighted by the smallest molecular weights, eq III.22 shows that the interfacial tension is lowered by the presence of small chains. Small chains in fact play a surfactant role.

IV. Conclusion

The present study has shown the importance of molecular weight and polydispersity effects on the properties of polymer-polymer interfaces. The origin of these effects

is purely entropic. The loss of translational entropy due to the confinement of the chains into one-half space is more severe for small chains. As a result the interface is broader for small chains, and for a polydisperse system, it is more advantageous (energetically) to expel large chains from the interface. These effects are significant for typical experimental situations, contrary to the effects on the bulk equilibrium properties.

The behavior of chain ends has not been studied in this paper. Such a study would in fact require other methods, such as the one of ref 4–6. This has been done in ref 24, where it is shown that chain ends adsorb, to $O(1/w)$, to the interface. A slightly different change in the concentration profile is found. As in the present paper, the $O(1/w)$ change in interfacial tension comes from the $O(1/w)$ entropy of mixing part of the free energy, not from the change of concentration profile. A result for γ analogous to eq II.18 is found, except that the factor $\pi^2/12 = 0.82$ is replaced by $\log 2 = 0.69$, because of a slightly different treatment of the entropy of mixing.

To our knowledge, there are very few systematic experimental studies of molecular weight and polydispersity effects in polymer–polymer interfaces. In a recent study, Anastasiadis et al.,⁹ using a pendant drop technique and digital image processing of the data, measured the interfacial tension for three immiscible polymer blends with different molecular weights and polydispersities. They found indeed that interfacial tension increases as the molecular weight is raised. The rate of increase, however, seems slightly slower than our M_n^{-1} prediction. Fitting their data with a $C_1 + C_2 M_n^{-z}$ power law, Anastasiadis and co-workers found an exponent $z = 0.54$ for a PBD 1000/PDMS 770 to 3780 system at 25 °C, $z = 0.68$ for a PBDH 4080/PS 2200 to 10 200 system at 171 °C, and $z = 0.9$ for a PMMA 10 000/PS 2200 to 43 700 system at 199 °C [PBD, polybutadiene; PDMS, poly(dimethylsiloxane); PBDH, hydrogenated 1,2-polybutadiene; PS, polystyrene; PMMA, poly(methyl methacrylate); the numbers stand for number-average molecular weights M_n]. These values have to be taken with caution because of experimental errors, but as pointed out by in ref 9, it is interesting to note that the smallest value for z ($z = 0.54$) is observed for the most polydisperse and lowest molecular weight system ($M_w/M_n = 2$ for the PDMS samples), whereas the largest value for z ($z = 0.9$) is observed for the system with the highest molecular weights. This suggests that the asymptotic regime (the M_n^{-1} behavior of eq III.22) is not yet reached for this range of molecular weights.

For monodisperse blends, we find a finite molecular weight correction to the interfacial tension that varies as $(\chi_{AB}N)^{-1}$. This suggests that measurements of the interfacial tension for different (large) molecular weights could provide another means of determining the Flory interaction parameter χ_{AB} for immiscible blends.

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Appendix A: Free Energy of a Segregated Polymer A–Polymer B Monodisperse System in the Cahn–Hilliard and Random-Phase Approximations^{9,17}

In the Cahn–Hilliard approximation, the free energy per monomer at position z is equal to the free energy of

a homogeneous phase, which we assume to have the simple Flory–Huggins form

$$F_{FH} = \chi_{AB} kT \left[\frac{\phi_A(z)}{w_A} \ln \phi_A(z) + \frac{\phi_B(z)}{w_B} \ln \phi_B(z) + \phi_A(z)\phi_B(z) \right] = \chi_{AB} kT f_{FH} \quad (\text{A.1})$$

supplemented by a square gradient term accounting for slow concentration variations:

$$F_{sq} = \frac{1}{2} kT \Gamma (\nabla \phi_A)^2 = \frac{1}{2} kT \Gamma (d\phi_A/dz)^2 \quad (\text{A.2})$$

Γ can be obtained as the coefficient of the q^2 term in a small q (scattering vector) development of the inverse structure factor $S^{-1}(q)$ of the polymer mixture. In the random phase approximation⁷

$$S^{-1}(q) = S_A^{-1}(q) + S_B^{-1}(q) - 2\chi_{AB} \quad (\text{A.3})$$

$S_A(q)$ and $S_B(q)$ being the structure factors of noninteracting (Gaussian) A and B chains: $S_i(q) = \phi_i N_i g_D(q^2 R_g^2)$, with g_D the Debye function.⁷ Since the interface is expected to be much smaller than the radius of gyration of a chain, R_g , Γ corresponds to the intermediate regime ($a < q^{-1} < R_g$) of these structure factors:

$$\Gamma = \frac{a^2}{12} \left(\frac{1}{\phi_A} + \frac{1}{\phi_B} \right) \quad (\text{A.4})$$

It follows that

$$F_{sq} = \frac{a^2 kT}{24} \left[\frac{1}{\phi_A} \left(\frac{d\phi_A}{dz} \right)^2 + \frac{1}{\phi_B} \left(\frac{d\phi_B}{dz} \right)^2 \right] = \frac{a^2 kT}{24\phi_A(1-\phi_A)} \left(\frac{d\phi_A}{dz} \right)^2 \quad (\text{A.5})$$

Appendix B: Free Energy of a Segregated Polymer A–Polymer B Polydisperse System in the Cahn–Hilliard and Random-Phase Approximations

The polydisperse system of interest is the quaternary mixture of A1 and B1 (small) chains and A2 and B2 (long) chains considered in section III.

The free energy per monomer contains two parts. The free energy of the homogeneous phase is the Flory–Huggins free energy:

$$F_{FH}/kT = \frac{\phi_{A1}}{N_1} \ln \phi_{A1} + \frac{\phi_{A2}}{N_2} \ln \phi_{A2} + \frac{\phi_{B1}}{N_1} \ln \phi_{B1} + \frac{\phi_{B2}}{N_2} \ln \phi_{B2} + \chi_{AB} \phi_A \phi_B \quad (\text{B.1})$$

The square gradient terms may be obtained by generalizing the approach of Appendix A. They correspond to the coefficients of the q^2 term in a small scattering vector (q) expansion of the inverse structure factor $S^{-1}(q)$. The structure factor is the Fourier transform of the correlations of the concentration fluctuations: $S_{ij}(q) = \langle \delta \rho_i(q) \delta \rho_j(-q) \rangle$. It turns out that this 3×3 matrix is diagonal for the concentration variables $\rho_i = \phi_A, x, y$, defined by eq III.14 and III.15.

In the random-phase approximation, the concentration fluctuations are linearly coupled to the “fields” acting on the monomers. Applying small fields U_i on the monomers of type i induces the changes in concentration:

$$\delta \phi_i(q) = -S_i(q) [U_i(q) + U(q) + \chi_{AB} \delta p_i(q)] \quad (\text{B.2})$$

with $\delta p_i = \delta \phi_A$ if $i = B1$ or $B2$ and $\delta p_i = \delta \phi_B$ if $i = A1$ or $A2$. U is a potential ensuring incompressibility ($\sum \delta \phi_i(q)$

= 0). $S_i(q)$ is the structure factor of noninteracting (Gaussian) chains of type i ; i.e., $S_i(q) = \phi_i N_i g_D(q^2 R_{gi}^2)$ with g_D the Debye function. We define new fluctuations by

$$\begin{aligned}\delta\phi_A &= \delta\phi_{A1} + \delta\phi_{A2} \\ \delta\phi_B &= \delta\phi_{B1} + \delta\phi_{B2} \\ \delta\phi &= \frac{S_{A2}}{S_A^2} \delta\phi_{A1} - \frac{S_{A1}}{S_A^2} \delta\phi_{A2} \\ \delta\psi &= \frac{S_{B2}}{S_B^2} \delta\phi_{B1} - \frac{S_{B1}}{S_B^2} \delta\phi_{B2}\end{aligned}$$

where $S_A = S_{A1} + S_{A2}$ and $S_B = S_{B1} + S_{B2}$. In the regime of interest ($q^2 R_g^2 > 1$), it is easy to verify that $\delta\phi$ and $\delta\psi$ correspond to the fluctuations in x and y : $\delta\phi = \delta x$ and $\delta\psi = \delta y$.

The conjugated fields U_A , U_B , U_x , and U_y are such that

$$\begin{aligned}U_A &= \delta F / \delta\phi_{A1} = U_A + \frac{S_{A2}}{S_A^2} U_x \\ U_{A2} &= \delta F / \delta\phi_{A2} = U_A - \frac{S_{A1}}{S_A^2} U_x \\ U_{B1} &= \delta F / \delta\phi_{B1} = U_B + \frac{S_{B2}}{S_B^2} U_y \\ U_{B2} &= \delta F / \delta\phi_{B2} = U_B - \frac{S_{B1}}{S_B^2} U_y\end{aligned}$$

From eq B.2, we obtain for $q^2 R_g^2 > 1$:

$$\begin{aligned}U_A &= -(S_A^{-1} + S_B^{-1} - 2\chi_{AB})\delta\phi_A = -\frac{(qa)^2}{24\phi_A(1-\phi_A)}\delta\phi_A + \dots \\ U_x &= -\frac{S_A^3}{S_{A1}S_{A2}}\delta x = -\frac{\phi_A(qa)^2}{24x(1-x)}\delta x + \dots \\ U_y &= -\frac{S_B^3}{S_{B1}S_{B2}}\delta y = -\frac{\phi_B(qa)^2}{24y(1-y)}\delta y + \dots\end{aligned}$$

The contribution to the free energy due to concentration inhomogeneities is thus

$$\begin{aligned}\frac{F_{sq}}{kT} &= \frac{a^2}{24\phi_A(1-\phi_A)} \left[\frac{d\phi_A}{dz} \right]^2 + \frac{a^2\phi_A}{24x(1-x)} \left[\frac{dx}{dz} \right]^2 + \\ &\quad \frac{a^2\phi_B}{24y(1-y)} \left[\frac{dy}{dz} \right]^2 \quad (\text{B.3})\end{aligned}$$

This expression is equivalent to

$$\frac{F_{sq}}{kT} = \frac{a^2}{24} \left[\frac{1}{\phi_{A1}} \left(\frac{d\phi_{A1}}{dz} \right)^2 + \frac{1}{\phi_{A2}} \left(\frac{d\phi_{A2}}{dz} \right)^2 + \frac{1}{\phi_{B1}} \left(\frac{d\phi_{B1}}{dz} \right)^2 + \frac{1}{\phi_{B2}} \left(\frac{d\phi_{B2}}{dz} \right)^2 \right] \quad (\text{B.4})$$

a generalization of eq A.5.¹

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