6294 *Macromolecules* **1996,** *29,* 6294−6300

Interfacial Tension in Binary Polymer Mixtures

A. V. Ermoshkin[†] **and A. N. Semenov***[,†,‡]

Physics Department, Moscow State University, Moscow 117234, Russia, and Department of Applied Mathematics, University of Leeds, Leeds LS2 9JT, U.K.

Received October 31, 1995; Revised Manuscript Received May 21, 1996[⊗]

ABSTRACT: An advanced theoretical model for the structure of the interface between two immiscible homopolymers is presented. The theory is based on a combination of the Flory−Huggins model and the square-gradient approach. We first analyze the effect of molecular weights of the components on the interfacial tension in the limit of high molecular weight ($\chi N \gg 1$). A general approximate expression for the interfacial free energy of the system is derived, the expression being valid for both limits of narrow and broad interfaces. The interfacial tension for a system of two immiscible homopolymers is calculated as a function of the homopolymer molecular weights and the Flory χ-parameter. The results are compared with the predictions of other theories and also with experimental data.

1. Introduction

Interfacial properties of binary polymer mixtures are of great interest from fundamental point of view and for many applications. The simplest example is an incompressible mixture of two immiscible homopolymers (A and B). The structure of the interface in this system had been first considered by Helfand and Tagami[1−3] within the framework of the mean-field approximation, which is known to be accurate for concentrated polymer systems.[4] They derived an expression for the interfacial tension in the case of symmetric polymers and the limit of infinite molecular weight of the chains:

$$\gamma_\infty = T\frac{b}{v}\left(\frac{\chi}{6}\right)^{1/2} \tag{1}$$

where T is the temperature, b is the statistical segment (the mean-squared end-to-end distance is Nb^2), N is the number of monomers per chain, v is the specific monomer volume, and χ is the Flory−Huggins parameter of interaction.[1−3] The thickness of the interface is

$$\Delta = \frac{2b}{\sqrt{6}}\chi^{-1/2}$$

The corresponding profile of the volume concentration of an A-component is

$$\phi_A(z) = 0.5[1 + \tanh(2z/\Delta)] \tag{2}$$

where the axis z is assumed to be chosen normal to the interface. Later, Helfand and Sapse[5] generalized the result, taking into account geometric asymmetry of the polymers

$$\gamma_\infty = T\left[\frac{\beta_A + \beta_B}{2} + \frac{1}{6}\frac{(\beta_A - \beta_B)^2}{\beta_A + \beta_B}\right]\left(\frac{\chi}{6}\right)^{1/2} \tag{3}$$

with $\beta_i = b_i/v_i$ for species i equal to A and B. However, numerous experimental data on the interfacial tension for a variety of the mixtures show that the tension depends not only on the parameters of polymer links but also on the molecular weights.[12] The effect of finite molecular weight has been studied theoretically in a number of papers.[6−8] In all these studies, a correction to the interfacial tension of order of $1/N$ is obtained.

In the next section, we reconsider the problem in the limit $\chi N \gg 1$ (note that this regime is often called the narrow interface limit since in this case the interfacial thickness is much smaller than the chain size: $\Delta \ll R = N^{1/2}b$) and derive an asymptotically exact expression for the correction to γ.

In the third section of this paper, we show how the theory can be extended to include also intermediate regimes where χN is not large.

The calculated molecular weight dependencies of the interfacial tension are then compared with asymptotic theories and with experimental data.

2. Interfacial Tension in the Limit $\chi N \gg 1$

Let us consider an incompressible mixture of two immiscible homopolymers, and assume the symmetric case: $b_A = b_B = b$, $v_A = v_B = v$. A generalization of the theory for an asymmetric case is trivial. Let $\phi(\mathbf{r}) \equiv \phi_A(\mathbf{r})$ be the local volume fraction of the A-component at the point $\mathbf{r}$. We assume that the plane $z = 0$ corresponds to the interface, so that the region $z > 0$ corresponds to the A-phase and $z < 0$ to the B-phase. The incompressibility condition implies that

$$\phi_A(z) + \phi_B(z) = 1$$

In the limit $\chi N \gg 1$ the coexisting phases are almost pure A and pure B, so that

$$\phi(\infty) = 1, \qquad \phi(-\infty) = 0 \tag{4}$$

The free energy F of the system can be considered as a functional of the monomer density profile $\phi(\mathbf{r})$ and can be represented as

$$F[\phi] = F_{conf}[\phi_A] + F_{conf}[\phi_B] + F_{int} \tag{5}$$

where

$$F_{int} = \frac{\chi T}{v}\int \phi_A\phi_B \, d^3r \tag{6}$$

is the excess energy of interaction between A and B monomers in the Flory-Huggins form [4]. The terms $F_{conf}[\phi_A]$ and $F_{conf}[\phi_B]$ represent the conformation free energy corresponding to inhomogeneous distribution of A and B monomers, respectively. In the limit of the narrow interface ($\Delta \ll R$), the square gradient form for

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[†] Moscow State University.

[‡] University of Leeds.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

S0024-9297(95)01636-6 CCC: $12.00

the conformation free energy is accurate:[4,9]

$$F_{conf}[\phi] = F_0[\phi] \equiv \frac{Ta^2}{4v}\int\frac{(\nabla\phi)^2}{\phi}\,\mathrm{d}^3r \tag{7}$$

where $a \equiv b/\sqrt{6}$.[19]

A minimization of the free energy (5)−(7) with additional condition (4) gives rise to the well-known result for the interfacial tension, eq 1, which is independent of molecular weight (this is true since the right-hand sides of both eq 6 and eq 7 do not depend on N). Obviously, corrections to the above equations might lead to a molecular weight dependence of γ (even in the region $\chi N \gg 1$). Let us consider these corrections.

The Flory−Huggins model, eq 6, implies a quadratic form for the density of excluded-volume interactions. It is known[8,10] that higher order terms (ϕ^3, ϕ^4, etc.) might give important contribution to F_{int}. However, these corrections do not imply an explicit molecular weight dependence of the interfacial tension. A physical reason for this dependence is that the monomers which are close to chain ends might interact in a slightly different way than other monomers. Obviously, these end effects should lead to a relative correction of order $1/N$. On the other hand, a correction to the conformation part of the free energy is proportional to $1/(\chi N)$ (see below); that is, this correction is larger by a factor $\sim 1/\chi$, which is large since normally $\chi \ll 1$. Below we consider this correction to the conformation free energy assuming that the energy of interactions still can be described by eq 6.

Equation 7 is exact in the limit $N \to \infty$ (and also for a continuous model of polymer chain, $a \to 0$), where it can be derived using the so-called ground state dominance.[4,9,13] Below we outline the general way to derive the conformation free energy including a correction of order $O(1/N)$ to the dominant term, eq 7, following the lines first proposed by Lifshitz.[14]

We note first that the conformation free energy of, say, the A-component, $F_{conf}[\phi_A]$, is actually equal to the free energy of an ideal system of A-chains in a nonequilibrium state characterized by a nonuniform concentration profile, $\phi(\mathbf{r}) = \phi_A(\mathbf{r})$. It is useful to consider the ideal system under external field, $U(\mathbf{r})$, which induces the given nonuniform monomer density profile (with the field we return to an equilibrium situation). Within the mean-field approximation (which is adopted throughout the paper) the average density profile corresponding to a given external field can be found by minimization of the corresponding thermodynamic potential:[20]

$$\tilde{F}[U] = \min_{\phi}\{F_{conf}[\phi] + \int U\phi\,\mathrm{d}^3r\} \tag{8}$$

Note that the last equation implies that $\phi = \delta\tilde{F}/\delta U$. Therefore we can rewrite the relation between the thermodynamic potentials as

$$F_{conf}[\phi] = \tilde{F}[U] - \int\frac{\delta\tilde{F}}{\delta U}U\,\mathrm{d}^3r \tag{9}$$

We are now in a position to calculate the thermodynamic potential of the ideal system under external field, $\tilde{F}[U] = -\ln\tilde{Z}$. Since the chains do not interact, the partition function can be represented as

$$\tilde{Z} = Z_1^{\mathcal{N}}/\mathcal{N}! \tag{10}$$

where

$$\mathcal{N} = \frac{1}{N}\int\phi(\mathbf{r})\,\mathrm{d}^3r \tag{11}$$

is the total number of (A) chains in the system, and Z_1 is the partition function of a single chain under the field U.

In order to proceed, we need to specify the particular structure of a polymer chain. It is well known that large-scale properties of polymer systems (corresponding to scales larger than the link size a) are insensitive to the microscopic chain structure.[9] It is thus reasonable to model a polymer chain as a sequence of beads $\{\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N\}$ connected by phantom bonds (standard Gaussian model[9,13]). The statistical weight of a polymer chain is then

$$W(\mathbf{r}_1,\mathbf{r}_2,...) = \prod_{i=1}^{N-1} g(\mathbf{r}_{i+1}-\mathbf{r}_i)\prod_{i=1}^{N}\exp[-U(\mathbf{r}_i)] \tag{12}$$

where $g(\mathbf{r}_{i+1}-\mathbf{r}_i)$ is the statistical weight of the ith bond. The single-chain partition function Z_1 can be calculated by integration of W over all variables. It is convenient to perform this integration in two steps: First we integrate over positions of all internal beads $\mathbf{r}_2$, ..., $\mathbf{r}_{N-1}$ to obtain the so-called Green function:

$$G_N(\mathbf{r}_1|\mathbf{r}_N) = \int W\,\mathrm{d}^3r_2...\mathrm{d}^3r_{N-1} \tag{13}$$

where $G_N(\mathbf{r}|\mathbf{r}')$ is the statistical weight of a chain with two ends fixed at the points $\mathbf{r}$ and $\mathbf{r}'$. Then

$$Z_1 = \int G_N(\mathbf{r}|\mathbf{r}')\,\mathrm{d}^3r\,\mathrm{d}^3r' \tag{14}$$

It is easy to check that the Green function obeys the following recurrent equation

$$G_{N+1}(\mathbf{r}|\mathbf{r}') = \int Q(\mathbf{r},\mathbf{r}'')G_N(\mathbf{r}''|\mathbf{r}')\,\mathrm{d}^3r'' \tag{15}$$

where $Q(\mathbf{r},\mathbf{r}'') = \exp(-U(\mathbf{r}))g(\mathbf{r}-\mathbf{r}'')$. Note that the operator $\hat{Q}$ defined by $\hat{Q}\psi = \int Q(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\,\mathrm{d}^3r'$ becomes Hermitian (symmetric) if the scalar product of two functions ψ and φ is defined as $(\psi,\varphi) = \int\exp(U(\mathbf{r}))\psi(\mathbf{r})\varphi(\mathbf{r})\,\mathrm{d}^3r$. The recurrent equation can be thus solved using standard methods. Taking into account an obvious initial condition

$$G_1(\mathbf{r}|\mathbf{r}') = \exp(-U(\mathbf{r}))\delta(\mathbf{r}-\mathbf{r}')$$

we get

$$G_N(\mathbf{r}|\mathbf{r}') = \sum_s \Lambda_s^{N-1}\psi_s(\mathbf{r})\psi_s(\mathbf{r}') \tag{16}$$

where ψ_s and Λ_s are the normalized eigenfunctions and the corresponding eigenvalues of the operator $\hat{Q}$, $\hat{Q}\psi_s = \Lambda_s\psi_s$, and we assume that the spectrum of the operator is discrete, $s = 0, 1, ...$

Let Λ_0 be the largest eigenvalue corresponding to the ground state $\psi_0(\mathbf{r})$. At this point, we introduce the basic assumption: we assume that the gap between Λ_0 and the next (nearest) eigenvalue Λ_1 is large enough: $(\ln\Lambda_0 - \ln\Lambda_1)N \gg 1$. Note that this assumption is always valid for long enough chains. With this assumption, the sum in eq 16 is dominated by the first term with $s = 0$, all other terms being exponentially small relative to the first one (the so-called ground state dominance):

$$G_N(\mathbf{r}|\mathbf{r}') \simeq \Lambda_0^{N-1}\psi_0(\mathbf{r})\psi_0(\mathbf{r}')$$

Using eq 14, we get $Z_1 \simeq [\int\psi_0(\mathbf{r})\,\mathrm{d}^3r]^2\Lambda_0^{N-1}$. Now using eq 10, we get the free energy $\tilde{F} = -\ln \tilde{Z}$:

$$\tilde{F}[U] \simeq -\mathsf{N}N \ln \Lambda_0 + \mathsf{N}\left\{\ln \frac{\mathsf{N}}{e} + \ln\left(\int \psi_0 \hat{g} \psi_0 \, \mathrm{d}^3 r\right) - 2 \ln\left(\int \psi_0 \, \mathrm{d}^3 r\right)\right\} \quad (17)$$

where $\hat{g}\psi = \int g(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}') \, \mathrm{d}^3 r$. Note that the first term on the right-hand side of eq 17 dominates for large enough N, whereas the second term provides a correction; the ratio of the correction to the dominant first term is proportional to $1/N$. Omitting the second term in eq 17 and then using eq 9, we get the well-known result[9,13,14]

$$F_{conf}[\phi] = \int \phi(\mathbf{r}) \ln\left(\frac{\hat{g}\psi}{\psi}\right) \mathrm{d}^3 r$$

where the function $\psi(\mathbf{r}) \equiv \text{const}\ \psi_0(\mathbf{r})$ is related to the given monomer distribution:

$$\phi(\mathbf{r}) = \psi(\mathbf{r}) \hat{g} \psi \quad (18)$$

Obviously, the second term in eq 17 must induce a correction to F_{conf}. According to the theorem on small increments,[18] this correction is exactly the same as the correction to $\tilde{F}$ (apart from higher order terms, i.e., the terms of relative order higher than $O(1/N)$). Thus we get

$$F_{conf}[\phi] = \int \phi(\mathbf{r}) \ln\left(\frac{\hat{g}\psi}{\psi}\right) \mathrm{d}^3 r + \mathsf{N}\left\{\ln \frac{\mathsf{N}}{e} + \ln\left(\int \psi \hat{g} \psi \, \mathrm{d}^3 r\right) - 2 \ln\left(\int \psi \, \mathrm{d}^3 r\right)\right\} \quad (19)$$

where N is defined in eq 11 and $\psi(\mathbf{r})$ in eq 18.

Equation 19 is the general result valid in the region of ground state dominance. Now we assume that the characteristic scale of inhomogeneity, Δ, is larger than the link size: $\Delta \gg a$. In this case, $U \ll 1$ and we can substitute operator $\hat{g}$ by $1 - a^2\nabla^2$ in the first term of the right-hand side of eq 19 and just by 1 in all other terms (for more details, see ref 13). The equation $\hat{Q}\psi = \Lambda\psi$ in this limit reduces to the well-known Edwards equation

$$-a^2 \nabla^2 \psi + U\psi = E\psi \quad (20)$$

where $E = -\ln \Lambda$. Thus in this continuous limit, we get instead of eqs 18 and 19

$$F_{conf}[\phi] = F_0[\phi] + \mathsf{N}\left\{\ln \frac{\mathsf{N}}{e} + 2 \ln \mathsf{N} - 2 \ln\left(\int \phi^{1/2}(\mathbf{r}) \, \mathrm{d}^3 r\right)\right\} \quad (21)$$

where $F_0[\phi]$ is defined in eq 7.

Let us turn to the original interfacial problem. Taking into account that the system is essentially one-dimensional, $\phi = \phi(z)$, we consider now all extensive quantities per unit area of the interface (i.e. in x,y plane), and thus rewrite the last equation as

$$F_{conf}[\phi] = \frac{a^2}{4} \int \phi^{-1} \left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)^2 \mathrm{d}z + \mathsf{N}\left\{\ln \frac{\mathsf{N}}{e} + 2 \ln \mathsf{N} - 2 \ln\left(\int \phi^{1/2}(z) \, \mathrm{d}z\right)\right\} \quad (22)$$

where $\mathsf{N} = \int \phi(z) \, \mathrm{d}z$. Next we note that the A-system is infinite, so that the total (conformational) free energy is also infinite. Obviously, it is the difference $F_{conf} - F_{ref}$ that is of interest, where F_{ref} is the ideal-gas free energy of the bulk A-phase: $F_{ref} = \mathsf{N} \ln(\phi_{bulk}/eN)$, where ϕ_{bulk}/N is the concentration of chains, and $\phi_{bulk} = \lim_{z\to\infty} \phi(z) = 1$.

Note that with infinite A-phase the spectrum of eq 20 is actually continuous. At this point, we will use the following trick: Let us put two boundaries at $z = -L$ and $z = L$ with additional boundary conditions $\mathrm{d}\psi/\mathrm{d}z = 0$ at $z = \pm L$. Obviously, the limit $L \to \infty$ corresponds to the original system. The zero-order solution (see eq 2), $\phi(z) = \psi^2(z) = 0.5[1 + \tanh(2z/\Delta)]$, implies that $\mathrm{d}\psi/\mathrm{d}z$ is exponentially small if $|z| \gg \Delta$. Therefore the imposed boundary conditions at $z = \pm L$ imply an exponentially small correction to the zero-order free energy if $L \gg \Delta$. As we verify below, the first-order correction to the conformational free energy is also insensitive to L as soon as $L \gg \Delta$. Therefore we can choose any L satisfying the condition $L \gg \Delta$. It is convenient to set L in between Δ and $R = N^{1/2}a$ so that $\Delta \ll L \ll R$. With this choice, the system (A-phase) is a layer of thickness L, so that the spectrum of eq 11 is discrete, and the gap between the lowest and the next eigenvalues, $\ln \Lambda_0 - \ln \Lambda_1 = E_1 - E_0 \simeq \pi^2 a^2/L^2$, is much wider than $1/N$. Therefore the ground state does dominate. Using eq 22, we get

$$F_{conf} - F_{ref} = \frac{a^2}{4} \int \phi^{-1} \left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)^2 \mathrm{d}z - 2\,\mathsf{N} \ln\left(1 + \frac{B}{N\mathsf{N}}\right)$$

where $B \equiv \int (\sqrt{\phi} - \phi) \, \mathrm{d}z$. Note that $B \sim \Delta$ and $N\mathsf{N} \equiv \int \phi(z) \, \mathrm{d}z \sim L$. Therefore $B/(N\mathsf{N})$ is small and the correction term can be represented as

$$-2\,\mathsf{N} \ln\left(1 + \frac{B}{N\mathsf{N}}\right) = -2\frac{B}{N}\left\{1 + O\left(\frac{\Delta}{L}\right)\right\}$$

Therefore the correction is nearly independent of L in the limit $L \gg \Delta$, as was stated above, and we get finally

$$F_{conf} - F_{ref} = \frac{a^2}{4} \int \phi^{-1} \left(\frac{\mathrm{d}\phi}{\mathrm{d}z}\right)^2 \mathrm{d}z - \frac{2}{N} \int (\sqrt{\phi} - \phi) \, \mathrm{d}z \quad (23)$$

The second term on the right-hand side of eq 23 represents a correction due to finite length N of polymer chains. Note that the correction is proportional to the small parameter $1/N$; it is also asymptotically exact since during the derivation we did not employ any approximations apart from omitting higher order terms (smaller than those of order higher than $1/N$).

An end correction analogous to that considered above was calculated before for orientation free energy of an anisotropic system of semiflexible macromolecules;[16] the same ideas as outlined above were also used in ref 17.

The result, eq 23, can be compared with the analogous free energy term used in ref 7, where the conformation free energy was approximated by (in our notations)

$$F_{conf} \simeq F_0[\phi] + \frac{1}{N} \int \phi \ln \phi \, \mathrm{d}z \quad (24)$$

Although both correction terms are qualitatively similar (note that both corrections are negative since $\phi \le 1$), they obviously differ quantitatively.

It is interesting to apply the general result, eq 23, to the case of weakly inhomogeneous system, $\phi(z) = 1 + \delta\phi(z)$, $\int \delta\phi(z) \, \mathrm{d}z = 0$, for which the free energy is known exactly in the form of series over $\delta\phi$.[4] Up to the second order, the exact expansion gives (cf. with eqs 36–37)

$$F_{conf} = F - F_{ref} = \frac{1}{2N} \int \frac{1}{f_D(Na^2q^2)} \delta\phi_q \delta\phi_{-q} \frac{\mathrm{d}q}{2\pi} \quad (25)$$

where f_D is the Debye function

$$f_D(u) = \frac{2}{u^2}(u + e^{-u} - 1) \tag{26}$$

and $\delta\phi_q$ is the Fourier image of the function $\delta\phi(z)$. Taking into account that the characteristic wavenumber $q \ll 1/R$ (that is, the characteristic scale of inhomogeneity is much smaller than R; this condition is necessary for eq 23 to be applicable) and retaining only the terms up to the first order in $1/N$, we rewrite the last equation as

$$F_{conf} \simeq \frac{1}{4}\int\left(q^2a^2 + \frac{1}{N}\right)\delta\phi_q\delta\phi_{-q}\frac{dq}{2\pi}$$

A similar expansion of the right-hand side of eq 23 for small $\delta\phi$ produces exactly the same expression for F_{conf}. Note that the first term in brackets corresponds to the term F_0 in eq 23, and the second term is the finite molecular weight correction. On the other hand, it is easy to find that expression (24) overestimates the correction by a factor of 2 (for small $\delta\phi$).

Using eqs 5, 6, and 23, we get the interfacial free energy (per unit area) of the original mixture $F_{intf} = F - F_{ref}$ (here F_{ref} is the total reference free energy of both pahses without any interface):

$$F_{intf} = \frac{a^2}{4}\int\frac{(\nabla\phi)^2}{\phi(1-\phi)}\,dz + \chi\int\phi(1-\phi)\,dz - \frac{2}{N_A}\int(\sqrt{\phi} - \phi)\,dz - \frac{2}{N_B}\int(\sqrt{1-\phi} - 1 + \phi)\,dz \tag{27}$$

The interfacial tension, γ, can be now obtained by minimization of F_{intf}:

$$\gamma = \min_{\phi} F_{intf}[\phi] = \gamma_\infty\left(1 - K\left(\frac{1}{\chi N_A} + \frac{1}{\chi N_B}\right)\right) \tag{28}$$

where $\gamma_\infty = a\sqrt{\chi}/v$ and $K = 2 \ln 2$.

The molecular weight dependence of the interfacial tension was considered previously in refs 6–8, where similar results were obtained: the predicted dependencies $\gamma(N_A,N_B)$ can be represented in exactly the same form with different prefactors, $K = \ln 2$,[6] $K = \pi^2/12$,[7] and $K = 3[1 - (1/6)^{1/3}] \simeq 1.35$.[8] Note that the numerical difference between the result of ref 8 and the asymptotically exact result $K = 2 \ln 2 \simeq 1.39$ is small. The difference between the results is due to approximations used in refs 7 and 8. The origin of the difference between the asymptotically exact result, eq 28, and the result of ref 6, which was also intended to be asymptotically exact, is explained below.

Let us start with a point of agreement between two approaches: the first-order ($1/N$) correction to γ_0 is solely due to the placement entropy, and thus is proportional to the correction to the single-chain partition function (the contribution of one component only, say A, is considered below):

$$\Delta\gamma \propto \frac{1}{N}\int_{-\infty}^{\infty}[q(z,N) - H(z)]\,dz \tag{29}$$

where $q(z)$ is the partition function of a chain with one end fixed at point z (thus $q(z)$ is given by integration of $G_N(z,z')$ over z'), and $H(z)$ is the Heaviside function. Equation 29 can be directly derived from the placement entropy term (the last term) in eq 2.9 of ref 6 using eq 2.10 of that paper. The function $q(z,N)$ can be represented as[6] $q(z,N) = q_0(z) + q'(z,N)$, where $q_0(z) = \psi(z) = \sqrt{\phi(z)}$ is the infinite chain partition function, and q' is a correction. It was recognized[6] that the correction is small for large N, $q' \propto 1/\sqrt{N}$, and so it was omitted. An important point however is that although q' is small, the corresponding scale is large, $z \sim aN^{1/2}$, in comparison with the scale over which $q_0(z) - H(z)$ is nonnegligible, $z \sim \Delta \propto N^0$. Therefore the omitted term, $\int q'(z,N)\,dz$, is of the same order as the term, $\int[q_0(z) - H(z)]\,dz$, which was kept in ref 6: both terms are proportional to N^0. Hence the dependence $\Delta\gamma \propto 1/N$ obtained in ref 6 is correct; however, the calculated prefactor in this relation is not exact.

3. End Effects in the General Case

Let us first consider a homogeneous mixture of two homopolymers A and B, $\phi(\mathbf{r}) = \phi_0$, where $\phi(\mathbf{r})$ is the local volume fraction of the component A. The free energy of the system according to the Flory–Huggins[4,13] model can be written as

$$F = F_0^0 = \frac{TV}{v}\left(\frac{1}{N_A}\phi_0 \ln \phi_0 + \frac{1}{N_B}(1 - \phi_0)\ln(1 - \phi_0) + \chi\phi_0(1 - \phi_0)\right) \tag{30}$$

where V is the volume of the system. The first two terms in this expression describe the translational entropy of polymer chains of type A and B, respectively, and the third term takes into account the interaction between monomers. For the case of an inhomogeneous system, the free energy in the Cahn–Hilliard approximation is[4,13]

$$F_{CH} = F_0 + F_1 \tag{31}$$

where

$$F_0 = \frac{T}{v}\int\left(\frac{1}{N_A}\phi \ln \phi + \frac{1}{N_B}(1 - \phi)\ln(1 - \phi) + \chi\phi(1 - \phi)\right)d^3r \tag{32}$$

and

$$F_1 = \frac{T}{v}\int\frac{1}{4}\left(\frac{a_A^2}{\phi} + \frac{a_B^2}{1 - \phi}\right)\left(\frac{d\phi}{dr}\right)^2 d^3r \tag{33}$$

corresponds to a decrease of the conformation entropy of the chains due to concentration variations (see eq 7).

Equations 31–33 are correct for the narrow interface regime:

$$N_i a_i^2 \gg \Delta \tag{34}$$

where $i = A,B$. The inequality (34) holds if

$$\chi N_i \gg 1 \tag{35}$$

Our aim is to calculate the interfacial tension for the intermediate regime $\chi N_i \sim 1$.

Let us first assume that the system is weakly inhomogeneous, $\phi = \phi_0 + \delta\phi(z)$, $\phi\delta \ll 1$. This case is well described by the linear response theory within the framework of the random phase approximation[4]

$$F \simeq F_{RPA} = F_0^0 + \frac{T}{2v}\int\gamma(q)\delta\phi_q\delta\phi_{-q}\frac{dq}{(2\pi)} \tag{36}$$

where $\delta\phi_q$ is the Fourier component of $\delta\phi(z)$, F_0^0 is defined by eq 30,[21] and

$$\gamma(q) = \frac{1}{\phi_0 N_A f_D(u_A)} + \frac{1}{(1-\phi_0)N_B f_D(u_B)} - 2\chi \quad (37)$$

where $f_D(u)$ is the Debye function, defined in eq 26, and

$$u_i = N_i a_i^2 q^2 \quad (38)$$

We notice that the Cahn–Hilliard free energy defined by eqs 31–33 for small $\delta\phi$ can be represented as

$$F_{CH} \simeq F_0^0 + \frac{T}{2v}\int \tilde{\gamma}(q)\delta\phi_q\delta\phi_{-q}\frac{\mathrm{d}q}{(2\pi)} \quad (39)$$

where

$$\tilde{\gamma}(q) = \frac{1}{\phi_0 N_A}\left(1+\frac{u_A}{2}\right) + \frac{1}{(1-\phi_0)N_B}\left(1+\frac{u_B}{2}\right) - 2\chi \quad (40)$$

Therefore we can rewrite eq 36 as

$$F = F_{CH} + F_2 \quad (41)$$

where F_{CH} is defined in eqs 31–33 and

$$F_2 \simeq \frac{T}{2v}\int\int K(z_1 - z_2)\delta\phi(z_1)\delta\phi(z_2)\,\mathrm{d}z_1\,\mathrm{d}z_2 - \frac{T}{4v}\left(\frac{1}{\phi_0 N_A} + \frac{1}{(1-\phi_0)N_B}\right)\int(\delta\phi(z))^2\,\mathrm{d}z \quad (42)$$

with

$$K(z) \equiv \int K(q)\exp(qz)\frac{\mathrm{d}q}{(2\pi)}$$

$$K(q) \equiv \gamma(q) - \tilde{\gamma}(q) + \frac{1}{2}\left(\frac{1}{\phi_0 N_A} + \frac{1}{(1-\phi_0)N_B}\right) \quad (43)$$

Equations 41 and 42 specify the general approximate expression for the free energy which is used below. The term F_2 is the correction to the Cahn–Hilliard free energy. Note that eq 42 is exact if $\delta\phi(z) \ll 1$, i.e. in the vicinity of the critical point of the mixture where the interface is broad. On the other hand, in the limit of narrow interface ($\Delta \ll R$), the approximation involved in eq 42 is not important since F_2 in this limit is small compared to the main term F_{CH} (note that $K(q) \to 0$ as $q \to \infty$). We thus expect that eqs 41 and 42 provide a reasonably good approximation also in the general case.

4. Numerical Solution

Let us consider a system that is separated into two macroscopic phases with volume fractions of A component equal to ϕ_1 and ϕ_2 in the bulk of these phases (far from the interface). Note that here we study the general case $\chi N \gtrsim 1$ (rather than $\chi N \gg 1$), so that ϕ_1 and ϕ_2 might not be very close to 0 and 1 correspondingly. In order to calculate the interfacial tension, we should minimize the following functional

$$F_{intf} = F - F_{ref} = F[\phi(z)] + \int(\alpha\phi + \beta)\,\mathrm{d}z \quad (44)$$

where $F[\phi(z)]$ is defined in eqs 41–43, and α and β are defined by the conditions

$$F_{intf}[\phi_1] = F_{intf}[\phi_2] = 0 \quad (45)$$

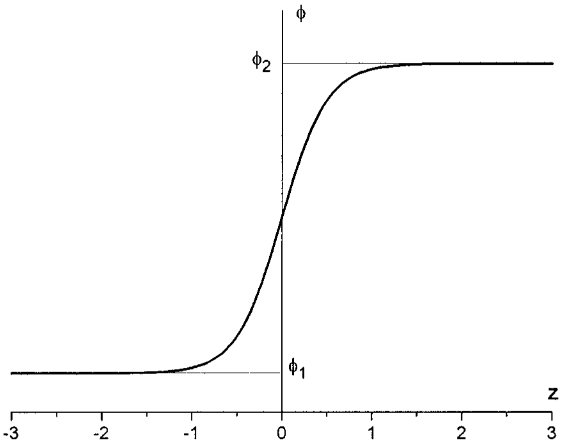

Figure 1. Typical profile of volume concentration as a function of the reduced distance from the interface $z = x/\Delta$.

In order to minimize the functional (44), we use the following iterative numerical procedure: we start with a probe concentration profile of the form[11]

$$\phi(z) = \frac{\phi_1+\phi_2}{2} + \frac{\phi_1-\phi_2}{2}\tanh\left(\frac{2z}{\Delta}\right) \quad (46)$$

with the interfacial thickness[3] $\Delta = (a_A + a_B)/\sqrt{\chi}$ (see Figure 1).

We then change the profile according to the master equation

$$\frac{\partial\phi}{\partial t} = -p\frac{\delta F_{intf}}{\delta\phi} \quad (47)$$

where t is the "time", which is proportional to the number of iteration steps, and $p > 0$. Note that eq 47 implies that F_{intf} is decreasing with time,

$$\frac{\mathrm{d}F_{intf}}{\mathrm{d}t} = \int\frac{\delta F_{intf}}{\delta\phi}\frac{\partial\phi}{\partial t}\,\mathrm{d}z < 0 \quad (48)$$

Therefore the profile $\phi(z)$ must tend to the equilibrium one as $t \to \infty$.

5. Results and Discussion

The results of the numerical minimization procedure for the functional (44) are compared below with numerical results of the Cahn–Hilliard theory, eqs 31–33, and with previous analytical predictions, eq 28.

Figure 2 shows that in the region $\chi N \sim 5$ the difference between interfacial tension obtained with the Cahn–Hilliard approach and with our approach, eqs 41–44, is about 10%, and it is negligible for $\chi N \gtrsim 500$.

In Figure 3 the numerical results are compared with the analytical predictions, eq 28, valid in the limit of narrow interfaces. Note that the theory presented in section 2 ($K = 2 \ln 2$) and the theory of ref 8 ($K \simeq 1.35$) are both in good agreement with numerical results for large $\chi N \gtrsim 10$, while other theories considerably overestimate the tension.

In order to compare the numerical predictions with experimental data, we should map the experimentally measured parameters of the system to the theoretical parameters. Every component i is characterized by M_{ni}, the average molecular weight of the chains, by the density ρ_i, and by β_i, the effective statistical length,

$$R_i = \beta_i\sqrt{M_{ni}} \quad (49)$$

(here $R_i = b_i\sqrt{N_i}$ is the rms end-to-end distance).

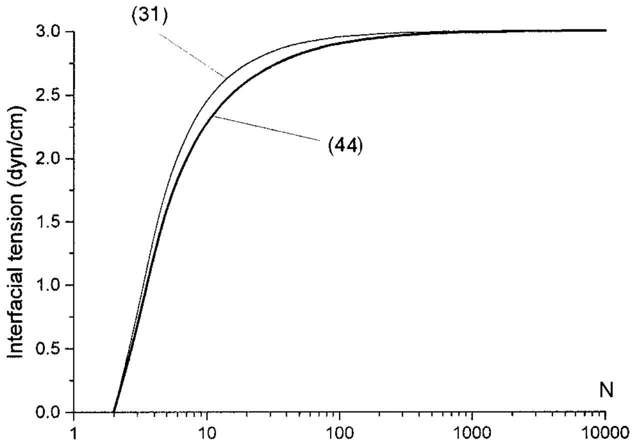

Figure 2. Comparison of the numerical results for the interfacial tension, eq 44, with the Cahn–Hilliard theory, eq 31. The parameters used are $N_A = N_B = N$, $a_A = a_B = 1$ Å, $\chi = 1$, $v = 1.38 \times 10^{-22}$ cm^3, and $T = 300$ K.

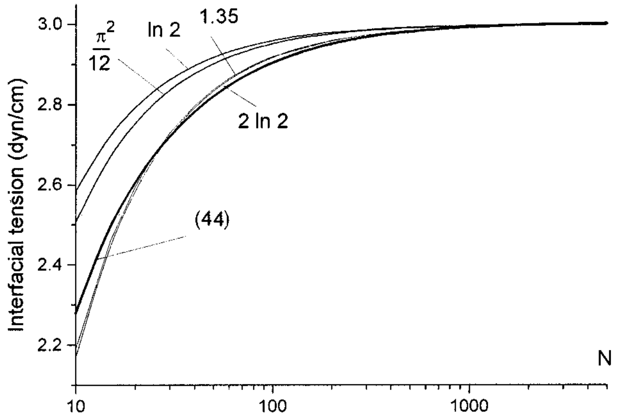

Figure 3. Comparison of the numerical results for the interfacial tension, eq 44, with the analytical predictions, eq 28, with different constants K. The parameters used are $N_A = N_B = N$, $a_A = a_B = 1$ Å, $\chi = 1$, $v = 1.3 \times 10^{-22}$ cm^3, and $T = 300$ K.

The effective monomer volume is

$$v_i = m_i/\rho_i \tag{50}$$

where m_i is the monomer molecular weight. Note that an effective monomer can be defined in an arbitrary way, so that it does not necessarily coincide with a true chemical link. It is convenient to define the effective A and B links so that their volumes be equal:

$$v_A = v_B = v \tag{51}$$

That means that m_A and m_B are related:

$$m_B = \frac{\rho_B}{\rho_A} m_A \tag{52}$$

We also set $m_A = 100$ for convenience.

Other parameters used in the theory are connected with the experimentally accessible quantities as

$$N_i = \frac{M_i}{m_i}, \qquad a_i = \beta_i \sqrt{m_i/6}$$

Interactions between monomers of type A and B can be characterized by the interaction parameter α:

$$F_{int} = T\alpha \int \phi(\mathbf{r})(1 - \phi(\mathbf{r}))\, d^3r \tag{53}$$

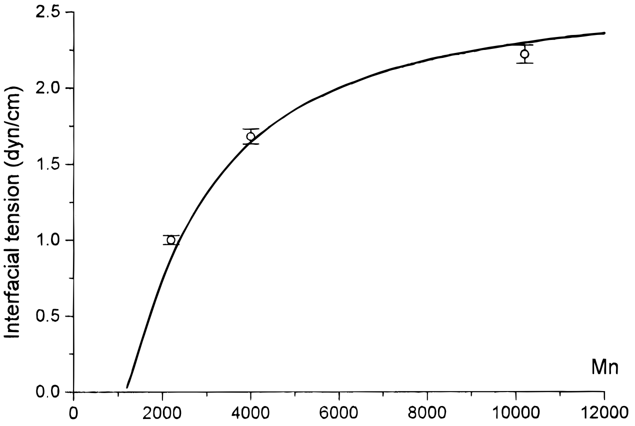

Figure 4. Interfacial tension between PS and PBDH 4080 as a function of PS M_n at 184 °C.

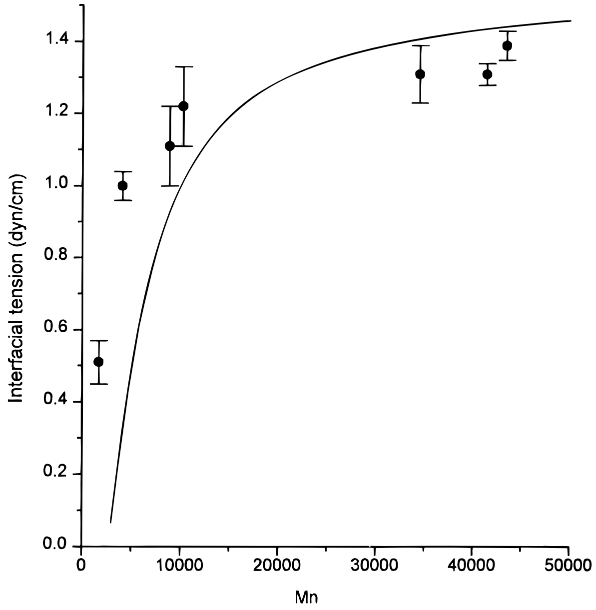

Figure 5. Interfacial tension between PS and PMMA 10000 as a function of PS M_n at 199 °C.

Table 1. Characteristics of the Materials

material	β, Å	ρ, g/cm^3
PDMS	0.66	0.95
PBD	0.79	0.87
PBDH	0.10	0.79
PS	0.67	0.96
PMMA	0.64	1.1

where F_{int} is the interaction free energy term. The parameter α is obviously related to the Flory–Huggins parameter χ (see eq 6):

$$\chi = \alpha v = \alpha \frac{m_A}{\rho_A} \tag{54}$$

We stress that α is a universal characteristic of a polymer mixture and it does not depend on the definition of the effective monomer. The available data on the α parameters are appreciably scattered; that is why we use it as a fitting parameter.

Table 1 shows the experimental values of β and ρ for the polymers considered.

Figures 4–6 show the experimental data for interfacial tension between different polymer pairs[12] and the numerical predictions. Table 2 presents the values of the interaction parameter α obtained by fitting for different polymer pairs. In Figure 6 we see a good

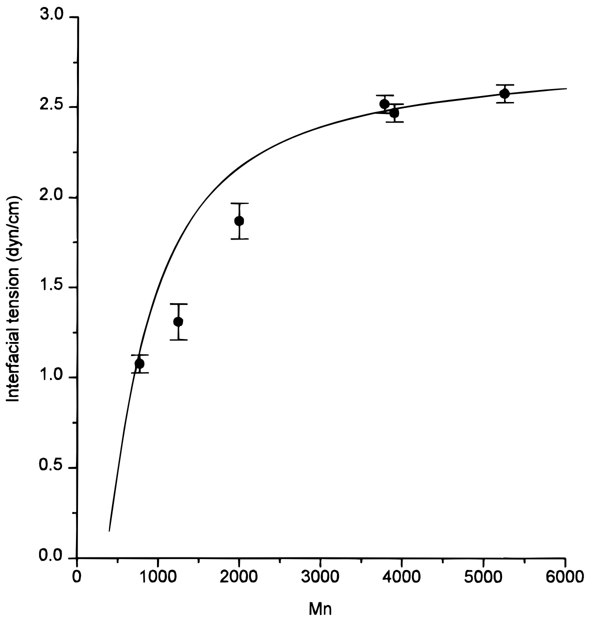

Figure 6. Interfacial tension between PDMS and PBD 1000 as a function of PDMS M_n at 25 °C.

Table 2. Interaction Parameters

pair	α, 10^{-3} mol/cm^3
PBD/PDMS (25 °C)	3.35
PS/PBDH (184 °C)	0.93
PS/PMMA (199 °C)	0.45

coincidence of our theory with experimental data for the PDMS/PBD system. The agreement is also good for PS/PBDH pair (see Figure 4). Note that the fitted interaction parameter $\alpha = 0.93 \times 10^{-3}$ mol/cm^3 (see Table 2) differs significantly from that calculated using the relationship

$$\alpha = (-1.61 + 894/T) \times 10^{-3}\ \text{mol/cm}^3 \qquad (55)$$

reported in ref 12: at 184 °C $\alpha = 0.34 \times 10^{-3}$ mol/cm^3. We comment that eq 55 was obtained in ref 12 using the data on the interfacial tension and the Helfand–Tagami theory,[3] valid for infinite molecular weights of polymers. We thus conclude that the molecular weight dependence of the interfacial tension is very important for this case: with end effects taken into account, we get the apparent α, which is larger by a factor of 2.5 than that obtained using the theory neglecting these end effects.

For the PS/PMMA system, the agreement between the theory and experimental data is less impressive (see Figure 5). Actually, if we change the fitting parameter α in order to fit the experimental data at low molecular weights, we would get a marked disagreement in the region of high molecular weights: the theory would overestimate the interfacial tension by a factor of 2 in this region.

6. Conclusion

In this paper, we consider the molecular weight dependence of the interfacial tension γ in systems of two immiscible homopolymers both analytically and numerically. In the analytical part (section 2), we find that the effect of finite molecular weight of polymers results in a negative correction to γ of order of $1/\chi N$. The exact value of the corresponding prefactor $K = 2 \ln 2$ (see eq 28) is calculated; the value agrees well with the results of ref 8 and with numerical results reported in the present paper; however, it differs appreciably from (otherwise similar) predictions of refs 6 and 7.

We also derive an approximate analytical expression for the free energy of an inhomogeneous blend of two homopolymers valid for both high and moderate values of χN. The dependence of the interfacial tension on the homopolymer molecular weights is then calculated numerically.[22]

The numerical results are compared with experimental data.[12] The agreement is good for the PBD/PDMS and PS/PBDH systems and is poor for the PS/PMMA blend. For the latter system, the disagreement is far beyond possible errors due to approximations of the theory. This discrepancy (if it is not due to experimental uncertainties) might indicate that the model based on the Flory–Huggins interaction term (eq 6) is inadequate for the PS/PMMA system: it is possible that higher order terms (proportional to ϕ^3 and ϕ^4) in the density of the excess free energy of interaction are important for this blend.

Acknowledgment. The authors are grateful to I. A. Nyrkova for useful comments. Partial support from the Russian Foundation of Fundamental Research (RFFI) is acknowledged. This work was also supported in part by NATO's Scientific Affairs Division in the framework of the Science for Stability Programme.

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(19) Equation 7 is strictly exact for a system of Gaussian chains in the limit $N \to \infty$, which should be taken for a *fixed* concentration distribution $\phi(\mathbf{r})$. Although the square gradient expression does not describe correctly the free energy *density* on large scales $z \sim N^{1/2}a$,[15] the contribution to the *total* free energy, coming from this large-scale region, does vanish in the limit mentioned above.
(20) Here and until the end of the section, we assume that monomer volume v and the temperature T are taken as unity.
(21) Here and below, we again take into account that the system is homogeneous in the x,y plane and consider all energetic quantities per unit area in this plane.
(22) The theory presented in the paper, being of the mean-field type, does not describe correctly the critical vanishing of the interfacial tension in the vicinity of the critical point. Note however that the critical region, where the theory does not work, is very narrow if both N_A and N_B are large.[4]

MA951636R