

Notes

Analytic Interface Profile Approximation for Ternary Polymer Blends

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Recently, Lifschitz, Freed, and Tang (LFT) proposed an analytic interface profile for compressible binary blends.¹ They employ a simple hyperbolic tangent interface profile using the width parameters in the profile as the only adjustable parameters to be determined by minimizing the interfacial tension. In this hyperbolic tangent variational approximation, the segregation of the vacancies along the interfaces, however, is not considered. It is known that compressible binary blends are special types of incompressible ternary systems where the third component, the vacancy, adsorbs at the interfaces. The adsorption of a third minority component in the interfaces is quite general. In compressible binary blends, the adsorption of the vacancies at the interfaces is small and as LFT showed it can indeed be neglected. In incompressible ternary blends, however, a considerable amount of the third minority component segregates along the interfaces.^{2,3} In this note, we modify the analytic interface profile, proposed by LFT to account for the adsorption of the third minority component along the interfaces.

We have recently studied the interfaces between the α and β phases rich in A and B components, respectively, when a third minority homopolymer C is added to A and B polymer blends.⁴ We analyzed the interfacial properties, such as the interfacial tension, the interfacial thickness, and the adsorption of C per interfacial thickness, in terms of the interaction parameter between components I and J, χ_{IJ} , and $\bar{\varphi}_C < \bar{\varphi}_A = \bar{\varphi}_B$, where $\bar{\varphi}_I$ is the mean volume fraction of component I. We considered symmetric systems with polymers A, B, and C each having degrees of polymerization equal to $N(N_A = N_B = N_C = N)$ when C is nonselective, $\chi_{AC} = \chi_{BC} = \eta\chi_{AB} = \eta\chi$, where η is a parameter varying from 0. As η increases, the interactions between the minority component C and the majority components A and B increase. The interfacial properties were calculated extending the perturbative variational approximation (PVA) developed by Lifschitz and Freed to study the interface profile of compressible binary blends.⁵ The interface profile was in excellent agreement with the steady-state solution of the nonlinear decomposition equations.^{2,3} Though this method is appropriate to determine the interfacial properties of ternary blends, it requires complex numerical techniques and cannot therefore give a simple solution for the interface profile.

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In this note, we develop a much simpler approach, hereafter referred to as the modified hyperbolic tangent variational approximation (MHTVA), to study the interfacial properties of ternary incompressible polymer blends.

We only study here ternary systems with a nonselective C component, $\bar{\varphi}_C < \bar{\varphi}_A = \bar{\varphi}_B$, decomposed into α and β phases with equilibrium compositions $\bar{\varphi}_I^\alpha$ and $\bar{\varphi}_I^\beta$, respectively, $I = A, B$. Since we need to determine the interfacial thicknesses of the composition profiles of $\varphi_A(x) - \varphi_B(x)$ and of $\varphi_C(x)$ and the adsorption, three parameters are required to describe the interface (as opposed to the LFT case of symmetric compressible binary blends, where only one parameter was used). We propose to model the composition profiles $\varphi_I(x)$, $I = A, B$, and C, by

$$\varphi_A(x) = a + b \tanh(\lambda_1 x) - \frac{\delta}{2 \cosh(\lambda_2 x)} \quad (1a)$$

$$\varphi_B(x) = a - b \tanh(\lambda_1 x) - \frac{\delta}{2 \cosh(\lambda_2 x)} \quad (1b)$$

$$\varphi_C(x) = 1 - \varphi_A(x) - \varphi_B(x) = \bar{\varphi}_C + \frac{\delta}{\cosh(\lambda_2 x)} \quad (1c)$$

where $a = (\bar{\varphi}_{A(B)}^\alpha + \bar{\varphi}_{A(B)}^\beta)/2 = (1 - \bar{\varphi}_C)/2$ and $b = (\bar{\varphi}_A^\beta - \bar{\varphi}_A^\alpha)/2 = (\bar{\varphi}_B^\alpha - \bar{\varphi}_B^\beta)/2$.

The parameters λ_1 and λ_2 are associated with the interfacial thicknesses of the composition profiles of $\varphi_A(x) - \varphi_B(x)$ and $\varphi_C(x)$, respectively,

$$L_1 = \frac{2.0(\bar{\varphi}_A^\alpha - \bar{\varphi}_A^\beta)}{\left| \frac{d(\varphi_A(x) - \varphi_B(x))}{dx} \right|_{x=0}} = \frac{2}{\lambda_1} \quad (2a)$$

$$L_2 = \frac{2.0(\varphi_C(0) - \bar{\varphi}_C)}{\left| \frac{d\varphi_C}{dx} \right|_{\max}} = \frac{4}{\lambda_2} \quad (2b)$$

where $|d\varphi_C/dx|_{\max}$ is the maximum of the absolute value of $d\varphi_C/dx$. The parameter δ is proportional to the adsorption of C per interfacial thickness, Γ_C , which is defined in nonselective C systems as

$$\Gamma_C = \frac{1}{L} \int_{-\infty}^{\infty} (\varphi_C(x) - \bar{\varphi}_C^e) dx = \frac{\delta\pi}{4} \quad (3)$$

where $\bar{\varphi}_C^e = \bar{\varphi}_C^{\alpha(\beta)} = \bar{\varphi}_C$ and L is the interfacial thickness, which we take equal to L_2 in eq 2b.

We obtain λ_1 , λ_2 , and δ by minimizing the interfacial tension σ with respect to variations of λ_1 , λ_2 , and δ , i.e., $\partial\sigma/\partial\nu = 0$, $\nu = \lambda_1, \lambda_2, \delta$. We start with an initial guess obtained from the PVA in ref 4 and then use the Newton–Raphson method to refine the guess.

Table 1. Comparison between the Interfacial Properties, σ , L_1 , L_2 , and Γ_C , in the Modified Hyperbolic Tangent Variational Approximation (MHTVA) and the Perturbative Variational Approximation (PVA) for Nonselective C Systems ($\chi_{AC} = \chi_{BC} = \eta\chi_{AB} = \eta\chi$)^a

$\bar{\varphi}_C$	η	χN	σ		L_1		L_2		Γ_C	
			MHTVA	PVA	MHTVA	PVA	MHTVA	PVA	MHTVA	PVA
0.1	1.0	2.4	0.0326	0.0327	8.1599	8.0628	10.9136	11.4625	0.0131	0.0141
0.1	1.0	2.7	0.1213	0.1216	5.2539	5.0537	6.9944	8.2618	0.0419	0.0342
0.1	0.0	2.7	0.1333	0.1332	4.6542	4.5137	6.5031	6.8113	0.0200	0.0194
0.1	0.0	3.0	0.2448	0.2445	3.6627	3.4872	5.3216	5.6180	0.0316	0.0295
0.2	0.0	3.0	0.0998	0.1003	5.2900	5.1302	7.4142	7.5508	0.0388	0.0324

^a The interfacial tension σ and the interfacial thicknesses L_1 and L_2 have the units $k_B T(3N^{1/2}a^2)$ and $(N^{1/2}a)/3$, respectively.

Consider a ternary system described by the free energy functional per site,

$$\Delta f = \Delta f_0 + \sum_{I=A,B,C} \bar{\kappa}_{II} (\nabla \varphi_I)^2 \quad (4)$$

where Δf_0 is the free energy per site of a homogeneous system, and $\bar{\kappa}_{II}$ is the gradient energy term coefficient. When the homogeneous system is unstable, such that equilibrium is established if two phases coexist, the compositional gradient terms are required to determine the equilibrium interface profile. For a flat interface between α and β phases, the interfacial tension σ is given by the difference per unit area of interface between the actual free energy and that which it will have if the properties of the two phases were continuous,⁶

$$\sigma = N_V \int_{-\infty}^{\infty} \left(\Delta f_0^m + \sum_{I=A,B,C} \bar{\kappa}_{II} \left(\frac{d\varphi_I}{dx} \right)^2 \right) dx \quad (5)$$

where N_V is the number of monomers per unit volume and

$$\Delta f_0^m = \Delta f_0(\{\varphi_I(x)\}) - \Delta f_0(\{\bar{\varphi}_I^{\alpha}\}) \quad (6)$$

We use for simplicity the Flory–Huggins mean field free energy per lattice site given by⁷

$$\frac{\Delta f_0}{k_B T} = \frac{\varphi_A \ln \varphi_A}{N_B} + \frac{\varphi_B \ln \varphi_B}{N_B} + \frac{\varphi_C \ln \varphi_C}{N_C} + \chi_{AB} \varphi_A \varphi_B + \chi_{BC} \varphi_B \varphi_C + \chi_{AC} \varphi_A \varphi_C \quad (7a)$$

The gradient energy terms are functions of the local compositions,^{8,9}

$$\bar{\kappa}_{II} = \frac{k_B T a^2}{36 \varphi_I(x)} \quad I = A, B, C \quad (7b)$$

where a is the monomer length.

With the MHTVA, we analyze the interfacial properties as a function of $\bar{\varphi}_C$ and χN for $\eta = 0$ and $\eta = 1$. We obtain the same scaling results as in ref 4 for small $\bar{\varphi}_C$ and/or for systems close to a critical point, $(\chi N(1 - \bar{\varphi}_C))^{\text{crit}} = 2$. The adsorption of C per interfacial thickness, Γ_C , is proportional to $\bar{\varphi}_C(1 - \bar{\varphi}_C)([\chi N(1 - \bar{\varphi}_C)]/2 - 1)$, the interfacial tension, σ , is proportional to $(1 - \bar{\varphi}_C)([\chi N(1 - \bar{\varphi}_C)]/2 - 1)^{3/2}$, and

$$L_J \sim R_g(1 - \bar{\varphi}_C)^{-\mu}([\chi N(1 - \bar{\varphi}_C)]/2 - 1)^{-1/2}, \quad J = 1, 2$$

where R_g is the chain radius of gyration ($\sim N^{1/2}a$), and the power μ is determined numerically and found to be dependent on η . In parts a and b of Figure 1, we plot

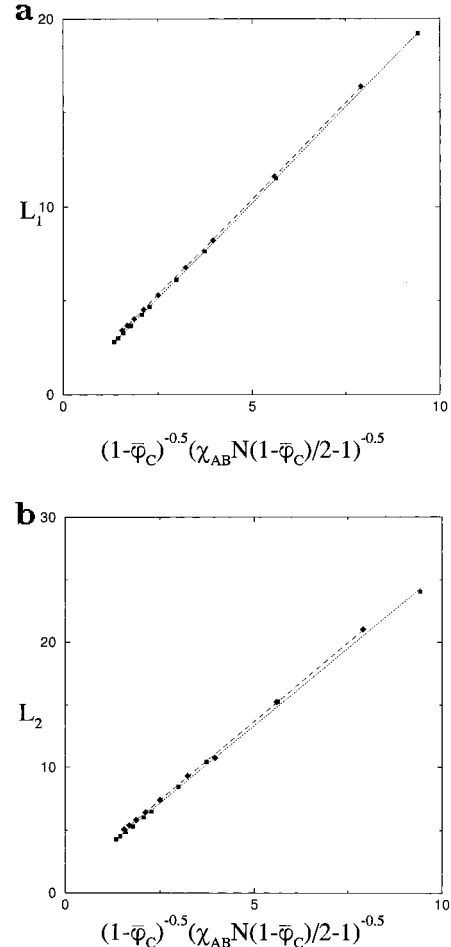


Figure 1. Plots of (a) L_1 and (b) L_2 versus $(1 - \bar{\varphi}_C)^{-\mu}([\chi_{AB}N(1 - \bar{\varphi}_C)]/2 - 1)^{-0.5}$ for $\eta = 0$, where $\mu(\eta=0) = 1/2$. The symbols (■··■) and (◆··◆) correspond to $\bar{\varphi}_C = 0.1$ and 0.2 , respectively. The computed values of L_1 and L_2 are presented in terms of the unit $(N^{1/2}a)/3$.

L_1 and L_2 versus $(1 - \bar{\varphi}_C)^{-\mu}([\chi N(1 - \bar{\varphi}_C)]/2 - 1)^{-1/2}$, respectively, for $\eta = 0$ in which case $\mu = 1/2$. In Figure 2, we plot Γ_C versus $\bar{\varphi}_C$ for $\eta = 0$ and $\eta = 1$ at $\chi N = 2.7$. The adsorption of the minority component C follows two types of behavior: (1) the system has a critical point increasing $\bar{\varphi}_C$, $\bar{\varphi}_C^{\text{crit}}$, in which case there is a maximum in the adsorption of C per interfacial thickness, Γ_C , at a certain $\bar{\varphi}_C < \bar{\varphi}_C^{\text{crit}}$, and (2) there is a three-phase region increasing $\bar{\varphi}_C$ (for η sufficiently large, such as when $\eta = 1$), in which case we previously found that there is adsorption of component K in the interface between the I- and J-rich phases.² In Table 1, we compare interfacial properties determined from the MHTVA and from the PVA for deep and shallow quenches. The MHTVA breaks down for η large and/or $(\chi N(1 - \bar{\varphi}_C)) \gg 2$.

We conclude that the modified hyperbolic tangent variational approximation properly describes the inter-

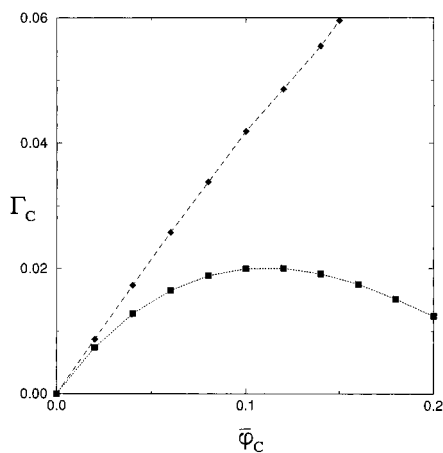


Figure 2. Plot of Γ_C versus $\bar{\phi}_C$ at $\chi N = 2.7$ for $\eta = 0$ (■···■) and $\eta = 1$ (◆- -◆).

face profile for low degrees of adsorption of C. A low degree of adsorption is seen in ternary polymer blends. In ternary small-molecule mixtures and/or alloys, however, since large adsorptions are found along the

interfaces, the MHTVA cannot describe such interfaces.¹⁰

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