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## Scaling of interfacial properties in ternary polymer blends

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**Abstract.** – We analyze interfaces between A-rich and B-rich phases in symmetric ternary polymer blends with a non-selective C minority component. The interfacial tension  $\sigma$  and the interfacial thicknesses of the composition profiles of  $\varphi_A(x) - \varphi_B(x)$ , and  $\varphi_C(x)$ ,  $L_1$  and  $L_2$ , respectively, are calculated by solving the linearized equation resulting from minimizing  $\sigma$  as a function of the average composition of C,  $\bar{\varphi}_C = 1 - \bar{\varphi}$ , with  $\bar{\varphi}/2 = \bar{\varphi}_A = \bar{\varphi}_B$ , and the net interaction per thermal energy between components A and B,  $\chi_{AB} = \chi$  ( $\chi_{AC} = \chi_{BC} = \eta\chi$ ). As  $\bar{\varphi}_C$  increases the interfacial thickness increases and the interfacial tension decreases. Our results are in excellent agreement with the steady-state solution of the non-linear spinodal decomposition equations.

Most polymer blends are strongly incompatible and will phase separate upon mixing [1]. The mechanical properties of these multiple-phase materials are determined to a large extent by the interfacial properties, such as the interfacial tension and the interfacial thickness. We have recently analyzed interfaces of immiscible A and B homopolymers in the presence of a minority homopolymer C [2]. We found considerable segregation of the C component along the interfaces between  $\alpha$  and  $\beta$  phases rich in A and B, respectively, even if C is not an A-B copolymer [3], [4]. We studied the degree of the adsorption of C in the  $\alpha$ - $\beta$  interfaces. The segregation of C along the interfaces can in principle enhance the stability of polymeric phases by lowering the interfacial tension and increasing the interfacial thickness. In this paper we study the interfacial properties when a third homopolymer C is added to A and B polymer blends.

The adsorption of C at the interfaces between  $\alpha$  and  $\beta$  phases is a function of the net interaction per thermal energy ( $k_B T$ ) between components I and J,  $\chi_{IJ}$ . It has been analyzed as a function of  $\bar{\varphi}_C < \bar{\varphi}_A = \bar{\varphi}_B$ , where  $\bar{\varphi}_I$  is the mean composition of I, and thermal energy in symmetric systems with A, B, and C degrees of polymerization equal to  $N$  ( $N_A = N_B = N_C = N$ ) solving numerically the non-linear spinodal decomposition equations (NLSDE) in the steady state [2]. Here we develop the scaling analysis of the interfacial properties in non-selective C

systems, where  $\chi_{AC} = \chi_{BC} = \eta\chi_{AB}$ , in terms of  $\bar{\varphi}_C$ ,  $\chi_{AB}$ , and  $\eta$  minimizing the interfacial tension. We compare these results with those obtained by solving the NLSD in the steady state.

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

$$\Delta f = \Delta f_0 + \sum_{I=A,B,C} \bar{\kappa}_{II} (\nabla \varphi_I)^2, \quad (1)$$

where  $\Delta f_0$  is the free energy per site of a homogeneous system, and  $\bar{\kappa}_{II}$  is the gradient energy term coefficient. When  $\Delta f_0$  is unstable, such that equilibrium is established if two phases coexist, the compositional gradient terms are required to determine the equilibrium interface profile. The interface profile is obtained by finding the lowest minimum of the interfacial tension. In a flat interface between  $\alpha$  and  $\beta$  phases of compositions  $\bar{\varphi}_I^\alpha$  and  $\bar{\varphi}_I^\beta$ , respectively, the interfacial tension  $\sigma$  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 [5],

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

where  $N_V$  is the number of monomers per unit volume and

$$\Delta f_0^m = \Delta f_0(\{\varphi_I(x)\}) - \sum_I \frac{\varphi_I(x)}{N_I} \mu_{0,I}^{\alpha(\beta)}, \quad (3)$$

where  $\mu_{0,I}^{\alpha(\beta)}$  is the chemical potential in the equilibrium phases. The composition of C is eliminated through the incompressibility constraint. An extremum of  $\sigma$  is obtained by solving simultaneously the resulting two Euler-Lagrange equations [6]. In symmetric systems with a non-selective C component ( $\varphi_A(x) = \varphi_B(-x)$ ), using the boundary conditions  $\Delta f_0^m = 0$  and  $\frac{d\varphi_A}{dx} = \frac{d\varphi_B}{dx} = 0$  as  $x \rightarrow \pm\infty$ , these two Euler-Lagrange equations reduce to

$$\Delta f_0^m = \kappa_{AA} \left( \frac{d\varphi_A}{dx} \right)^2 + 2\kappa_{AB} \frac{d\varphi_A}{dx} \times \frac{d\varphi_B}{dx} + \kappa_{BB} \left( \frac{d\varphi_B}{dx} \right)^2 \quad (4)$$

with  $\kappa_{II} = \bar{\kappa}_{II} + \bar{\kappa}_{CC}$ ,  $I = A, B$ , and  $\kappa_{AB} = \bar{\kappa}_{CC}$ . There are many solutions for eq. (4). Only the lowest minimum  $\sigma$  will give the actual interface. Though the actual interface profile cannot be solved analytically, it can be obtained numerically by solving the linearized solution for eq. (4) [7], [8]. In this paper, the perturbative variational approximation (PVA), developed by Lifschitz and Freed [7] to study interfaces in symmetric compressible binary blends, is extended to study interfaces in symmetric incompressible ternary blends (*i.e.* eq. (4)).

We construct the ternary-blends phase diagrams using the Flory-Huggins mean-field free energy per lattice (the regular solution model), as in [2]. The gradient energy terms are functions of the local compositions [9],  $\bar{\kappa}_{II} = \kappa_B T a^2 / 36 \varphi_I(x)$ ,  $I = A, B, C$ , where  $a$  is the monomer size. Two types of phase diagrams result for non-selective C blends with  $\bar{\varphi}_A = \bar{\varphi}_B$ : i) when  $\eta = 0$  and/or  $\eta\chi_{AB}N$  is sufficiently small, a critical point appears at  $(\chi_{AB}N(1 - \bar{\varphi}_C))^{\text{crit}} = 2$  increasing  $\bar{\varphi}_C$  and/or  $\chi_{AB}N$ , ii) when  $\eta\chi_{AB}N$  is sufficiently large, a three-phase region  $\alpha, \beta$ , and  $\gamma$  appears increasing  $\bar{\varphi}_C$  (or  $\chi_{AB}N$ ), where  $\gamma$  is a new phase rich in the minority C component.

In the non-selective C cases where in general the symmetry  $\varphi_A(x) = \varphi_B(-x)$  holds, it is convenient to let  $\varphi_A(x) = r^2(x) \cos^2 \vartheta(x)$  and  $\varphi_B(x) = r^2(x) \sin^2 \vartheta(x)$  [7]. Equation (4) thus becomes

$$\Delta f_0^m = 4 \times \frac{\kappa_B T a^2}{36} \times r_0^2 \left[ \frac{1}{1-r^2} \left( \frac{dh}{d\vartheta} \right)^2 + (1+h)^2 \right] \left( \frac{d\vartheta}{dx} \right)^2 \quad (5)$$

with  $r[\vartheta(x)] = r_0(1 + h[\vartheta(x)])$ ,  $r_0^2 = \bar{\varphi}_A^{\alpha(\beta)} + \bar{\varphi}_B^{\alpha(\beta)}$ , and  $h[\vartheta(\pm\infty)] = 0$ . Assuming  $h[\vartheta(x)] = \sum_1^{n_0} \epsilon_{2n-1} \sin(\lambda_{2n-1}\vartheta(x) + \omega_{2n-1}) \ll 1$  [7] with  $\lambda_{2n-1} = (2n-1)\pi/(\vartheta(+\infty) - \vartheta(-\infty))$  and  $\omega_{2n-1} = -\lambda_{2n-1}\vartheta(-\infty)$ ,  $\Delta f_0^m$  can be expanded around  $(r_0, \vartheta)$ . Therefore, any extremum of  $\sigma$  has the form

$$\sigma = 2N_V \times \left( \frac{1}{2} \sum_{n,m=1}^{n_0} v_{2n-1,2m-1} \epsilon_{2n-1} \epsilon_{2m-1} + \sum_{n=1}^{n_0} \gamma_{2n-1} \epsilon_{2n-1} + \int_{\vartheta(-\infty)}^{\vartheta(+\infty)} E(\vartheta) d\vartheta \right) \quad (6)$$

with

$$\begin{aligned} v_{2n-1,2m-1} = & \int_{\vartheta(-\infty)}^{\vartheta(+\infty)} A(\vartheta) \lambda_{2n-1} \lambda_{2m-1} \cos(\lambda_{2n-1}\vartheta + \omega_{2n-1}) \cos(\lambda_{2m-1}\vartheta + \omega_{2m-1}) d\vartheta + \\ & + \int_{\vartheta(-\infty)}^{\vartheta(+\infty)} B(\vartheta) \sin(\lambda_{2n-1}\vartheta + \omega_{2n-1}) \sin(\lambda_{2m-1}\vartheta + \omega_{2m-1}) d\vartheta, \end{aligned} \quad (7a)$$

$$\gamma_{2n-1} = \int_{\vartheta(-\infty)}^{\vartheta(+\infty)} C(\vartheta) \sin(\lambda_{2n-1}\vartheta + \omega_{2n-1}) d\vartheta \quad (7b)$$

with  $(1 - r_0^2)A(\vartheta) = (k_B T a^2 r_0^2 \Delta f_0^m / 9)^{1/2} = X$ ,  $B(\vartheta) = X r_0 (r_0 \Delta f_0^{m(2)} / 2 + \Delta f_0^{m(1)} (1 - D/4)) / \Delta f_0^m$ , and  $C(\vartheta) = X(1 + D/2)$ , where  $D = r_0 \Delta f_0^{m(1)} / \Delta f_0^m$  and  $\Delta f_0^{m(1)} = \partial^1 \Delta f_0^m / \partial r^1$ . The solutions of  $\{\epsilon_{2n-1}\}$  are obtained by minimizing the interfacial tension  $\sigma$  in eq. (6) with respect to the variations of  $\{\epsilon_{2n-1}\}$ , which can be expressed in the matrix form,  $[\epsilon_{2n-1}] = -[v_{2n-1,2m-1}]^{-1} \times [\gamma_{2n-1}]$ . Once  $\{\epsilon_{2n-1}\}$  are found,  $\vartheta(x)$  is obtained numerically by integrating eq. (5), generating  $r[\vartheta(x)]$  and the compositions  $\varphi_I(x)$ ,  $I = A, B, C$ .

It should be noted that although the global incompressibility constraint,  $\int \Delta \varphi_I(x) = 0$ , where  $\Delta \varphi_I(x) = \varphi_I(x) - \bar{\varphi}_I$ , is included in  $\sigma$  (eq. (2)), we do not recover it when we approximate  $\sigma$  up to second-order terms in  $\epsilon$  (eq. (6)). Global incompressibility can be obeyed in different ways. For example, if we solved the NLSD in the steady state with periodic boundary conditions as in ref. [2], we obtained that the  $\alpha$  and  $\beta$  phases have compositions  $(\bar{\varphi}_A^{\alpha(\beta)} + \frac{\delta}{2}, \bar{\varphi}_B^{\alpha(\beta)} + \frac{\delta}{2}, \bar{\varphi}_C - \delta)$ , and  $\delta \rightarrow 0$  when the bulk size is very very large. However, if we solved the NLSD in the steady state with the equilibrium boundary conditions, since  $\delta = 0$ ,  $\Delta \varphi_C(x)$  becomes negative just before entering the interface region and then positive in the interface region. If the Euler-Lagrange equations could be solved exactly, we believe we will obtain the same results of the NLSD with the equilibrium boundary conditions. Though the regions of negative values of  $\Delta \varphi_C(x)$  are not obtained with the second-order PVA approach, the values of  $\Delta \varphi_C(0)$  with the PVA approach are nearly equal to the steady-state solution of the NLSD with equilibrium boundary conditions.

For  $\eta = 0$  the interfacial tension at a fixed  $\chi_{AB}N$  value is a maximum when  $\bar{\varphi}_C = 0$ . When the interaction between A and C and B and C ( $\eta$ ) increases, since the amount of C segregating in the interfaces increases, the interfacial tension is even more reduced. In systems with a critical point ( $\eta \chi_{AB}N \ll 1$ ), as  $\bar{\varphi}_C$  increases,  $\sigma$  decreases up to  $\sigma = 0$  when  $\bar{\varphi}_C$  reaches  $\bar{\varphi}_C^{\text{crit}}$ . In fig. 1 we plot  $\sigma$  vs.  $Y$ , where  $Y = (1 - \bar{\varphi}_C)(\frac{1}{2}\chi_{AB}N(1 - \bar{\varphi}_C) - 1)^{3/2}$  at various  $\chi_{AB}N$  values for  $\eta = 0$ . We find that  $\sigma$  is linear with  $Y$  when  $Y$  is large (*i.e.* when  $\bar{\varphi}_C \ll \bar{\varphi}_A = \bar{\varphi}_B$ ) with a slope strongly dependent on  $\chi_{AB}N$ . When  $Y \approx 0$  (around the critical point), on the other hand, one can show, following Cahn and Hilliard [5], that  $\sigma = (2k_B T / 3\sqrt{N}a^2)Y$ , which from fig. 1 we see only holds for  $Y$  infinitesimally near 0.

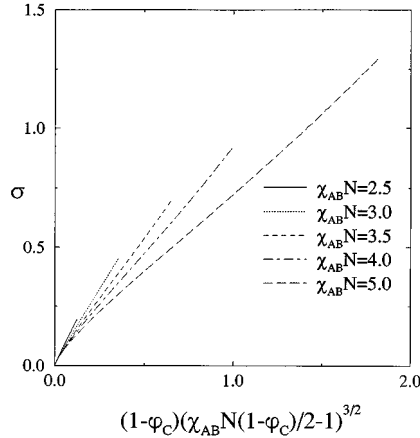


Fig. 1. – Plots of  $\sigma$  vs.  $(1 - \bar{\varphi}_C)(\frac{1}{2}\chi_{AB}N(1 - \bar{\varphi}_C) - 1)^{3/2}$  in non-selective C systems ( $\chi_{AC} = \chi_{BC} = \eta\chi_{AB} = \eta\chi$ ) for  $\eta = 0$  at various  $\chi_{AB}N$  values. The values of  $\sigma$  are in the unit of  $k_B T / 3\sqrt{N}a^2$ .

Since the symmetry  $\varphi_A(x) = \varphi_B(-x)$  holds in non-selective C systems, it is natural to determine the interfacial thicknesses from the composition profiles of  $\varphi_A(x) - \varphi_B(x)$  and  $\varphi_C(x)$ ,

$$L_1 = \frac{2.0 \times (\bar{\varphi}_A^\alpha - \bar{\varphi}_A^\beta)}{\left| \frac{d(\varphi_A(x) - \varphi_B(x))}{dx} \right|_{x=0}}, \quad (8a)$$

$$L_2 = \frac{2.0 \times (\varphi_C(0) - \bar{\varphi}_C)}{\left| \frac{d\varphi_C}{dx} \right|_{\max}}, \quad (8b)$$

respectively, where  $\left| \frac{d\varphi_C}{dx} \right|_{\max}$  is the maximum of the absolute value of  $d\varphi_C/dx$ .

If the adsorption of C at the interfaces is neglected, one can show analytically that, near the critical point,

$$L_1 = \frac{\alpha\sqrt{N}a}{3}(1 - \bar{\varphi}_C)^{-\mu} \left( \frac{\chi N(1 - \bar{\varphi}_C)}{2} - 1 \right)^{-1/2} \quad (9)$$

with  $\alpha = 2$  and  $\mu = 0$ . Numerically, where there is adsorption of C we find that  $\mu(\eta = 0) = 1/2$  and  $\mu(\eta = 1) = 3/2$  even when the system is far away from the critical point. Also numerically we find that  $L_2$  has the same scaling results as  $L_1$  with  $\alpha \cong 2.45$ , as shown in fig. 2a) and b) for  $\eta = 0$  and  $\eta = 1$ , respectively. For  $\eta = 1$  at  $2.57 < \chi N < 2.74$ , however, when the system is close to the three-phase region, the interface is broader than predicted by eq. (9).

The adsorption of C at the interfaces was found to be in excellent agreement with those computed by solving the NLSD in the steady state. The scaling with  $\eta$ ,  $\chi N$ , and  $\bar{\varphi}_C$  is given elsewhere [2].

In summary, with the addition of a third minority C component in immiscible A and B blends the interfacial tension decreases and the interfacial thickness increases. In symmetric ternary blends with a non-selective C component, the segregation of C in the interfaces between the A-rich and B-rich phases increases as  $\eta$  increases. Therefore, the interfacial thickness increases and the interfacial tension decreases as  $\eta$  increases. We conclude that the perturbative variational approximation gives basically the same results as the steady-state solution of the

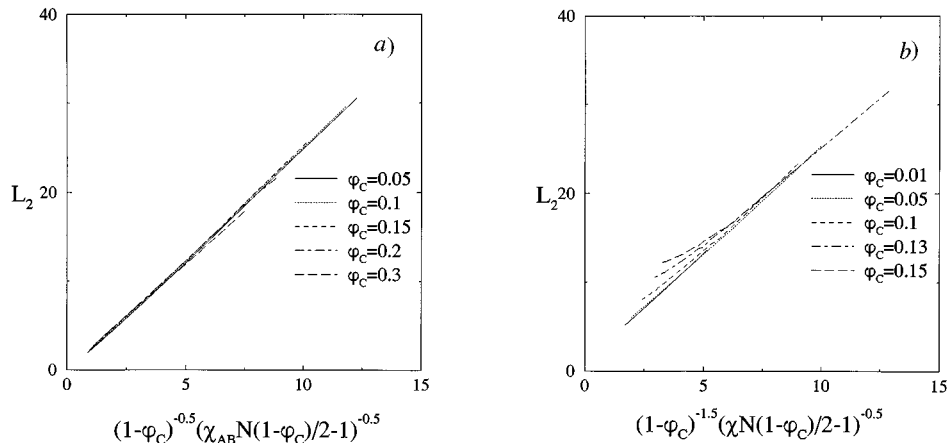


Fig. 2. – The interfacial thickness  $L_2$  in eq. (8b) as a function of  $\bar{\varphi}_C$  and  $\chi N$  for a)  $\eta = 0$  and b)  $\eta = 1$ , respectively. The values of  $L_2$  are in the unit of  $\frac{\sqrt{Na}}{3}$ .

non-linear spinodal decomposition equations in ternary polymer blends. For systems having smaller gradient energy term coefficients, such as ternary alloys and small molecules, this approach breaks down due to the large degree of adsorption along the interfaces [10].

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