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Lifshitz points in blends of AB and BC diblock copolymers

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PACS. 83.70Hq – Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

PACS. 64.60Cn – Order-disorder transformations; statistical mechanics of model systems.

PACS. 83.80Es – Polymer blends.

Abstract. – We consider micro- and macro-phase separation in blends of AB and BC flexible diblock copolymers. We show that, depending on architecture, a number of phase diagram topologies are possible. Microphase separation or macrophase separation can occur, and there are a variety of possible Lifshitz points. Because of the rich parameter space, Lifshitz points of multiple order are possible. We demonstrate Lifshitz points of first and second order, and argue that, in principle, up to 5th-order Lifshitz points are possible.

Introduction. – The phase behaviour of block copolymer melts is remarkably rich. In a blend of homopolymers only macrophase separation (with wave number $q_* = 0$) occurs. Macrophase separation in a block copolymer melt is prevented by the chemical connectivity of the constituent blocks, which leads to microphase-separated structures with $q_* \neq 0$, typically corresponding to structural periods $L \simeq 10 - 100$ nm [1, 2]. In a blend containing a block copolymer melt and one or more molten homopolymers, microphase separation of the block copolymer can compete with macrophase separation of the homopolymers at low temperatures [1].

In a binary blend of a block copolymer and a homopolymer, the homopolymer swells the microphase-separated structure formed by the copolymer, if the homopolymer chain length is less than or equal to that of the corresponding block [1, 3]. On the other hand, macrophase separation can occur for homopolymer chains longer than the corresponding block. In a ternary blend, block copolymer added to a blend of homopolymers acts as a compatibilizer to prevent macrophase separation or reduce the lengthscale associated with the microphase-separated structure [1, 4]. A similar interplay between micro- and macro-phase separation has recently been explored experimentally for AB/AB diblock copolymer blends by Hashimoto

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and coworkers [5]. Recently, self-consistent field theory has been applied to examine the phase behavior of binary homopolymer/copolymer blends [6-8], blends of two homopolymers with block copolymer [9, 10] and binary blends of block copolymers [11, 12]. Particularly interesting critical phenomena have been predicted for certain blends of copolymer with one or two homopolymers. The latter case was first studied using Landau mean-field theory, employing the random phase approximation (RPA) [13, 14]. In addition to lines of critical points corresponding to macrophase separation or microphase separation, mean-field theory predicts that Lifshitz points can occur at the boundary between disordered, uniformly ordered and periodically ordered phases [13, 14]. The wave number for microphase separation approaches zero continuously as the Lifshitz point is approached [15]. The presence of a Lifshitz point in the phase diagram for blends of two polyolefin homopolymers and the corresponding diblock was first inferred experimentally via small-angle neutron scattering by Bates *et al.* [16], which indicated a growing correlation length extrapolating to an apparent Lifshitz point. However, subsequent work showed that composition fluctuations destroy the mean-field Lifshitz point and a microemulsion phase becomes stable [17]. Mean-field theory can then be used to locate the region of microemulsion stability via the virtual Lifshitz point.

In contrast to these studies of copolymer/homopolymer blends and blends of AB diblocks, we are unaware of any experimental work on blends of an AB diblock with a BC diblock. This letter presents some predictions for these systems, which should stimulate future experimental work. We consider only flexible polymers, and employ the RPA, first applied to AB diblocks by Leibler [18], to locate spinodal points for macro- or micro-phase separation, and to compute the wave numbers and eigenvectors of the unstable modes. We use this information to calculate the Lifshitz points in the phase diagrams, as functions of molecular architecture. This approach is expected to be valid for long, weakly segregated, chains. Generalization of the approach outlined here to allow for composition fluctuations and finite chain length should be straightforward, using methods developed for pure block copolymer melts [19, 20]. A theory for micelle formation in blends of strongly segregated AB and BC diblocks has recently appeared [21]; and microemulsion phases in ternary blends with triblock copolymers have been studied theoretically [22, 23] in weak segregation; but we are unaware of any previous work on the weak segregation regime of AB-BC systems.

Model. – Let ϕ be the volume fraction of the AB diblock; f and αf the fractions of the A and C components in the AB and BC copolymers, respectively; and N and βN the respective monomer numbers. For simplicity we assume equal monomer volume and statistical segment length for all species. We work in terms of a vector of fluctuations ψ ,

$$\psi = \{\psi_A, \psi_B, \psi_C\}, \quad (1)$$

where ψ_i is the deviation of the volume fraction of species i from its mean value. It is straightforward to calculate the correlation functions

$$G_{ij}(q) = \langle \psi_i(q) \psi_j(-q) \rangle \quad (2)$$

using the RPA [18], including three Flory χ parameters χ_{AB} , χ_{AC} , and χ_{BC} . It is convenient to define the basis set

$$\mathbf{e}_0 = \sqrt{\frac{1}{3}} \{1, 1, 1\}, \quad \mathbf{e}_1 = \sqrt{\frac{2}{3}} \left\{ \frac{1}{2}, -1, \frac{1}{2} \right\}, \quad \mathbf{e}_2 = \sqrt{\frac{1}{2}} \{1, 0, -1\}, \quad (3)$$

where $\psi \cdot \mathbf{e}_0$ is a volume-changing fluctuation and $\psi \cdot \mathbf{e}_1$ and $\psi \cdot \mathbf{e}_2$ are physical fluctuations in an incompressible system. The fluctuation $\psi \cdot \mathbf{e}_1 = \sqrt{3/2}(\psi_A + \psi_C)$ corresponds to separating the A and C blocks from the B block, and is primarily a microphase separation mode, since

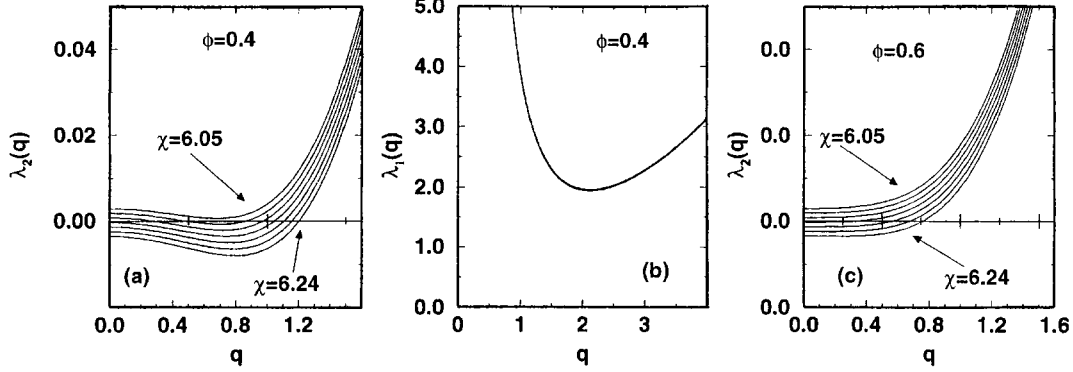


Fig. 1. – Fluctuation eigenvalues as a function of wave vector (units of R_g^{-1} , where R_g is the radius of gyration) for $f = 0.17$, $\alpha = 1$, $\beta = 1$, $r_{AC} = 0.49$, $r_{BC} = 2.9$, for $\phi = 0.4$ and $\phi = 0.6$ and a range of χ values. Variations of λ_1 with χ are shown, but not visible (b).

it is prohibited at $q = 0$ by chain connectivity. The other mode, $\psi \cdot \mathbf{e}_2 = \sqrt{1/2}(\psi_A - \psi_C)$, corresponds to demixing the A and C blocks, and in the limit $q \rightarrow 0$ corresponds to demixing the blend. Hence we term this a macrophase separation mode. A general fluctuation at $q \neq 0$ is an admixture of these two modes, while only mode \mathbf{e}_2 is present for $q = 0$.

The spinodal is given by the determinant of the 2×2 matrix of $G_{ij}(q)$ in the incompressible $\{\mathbf{e}_1, \mathbf{e}_2\}$ subspace,

$$\Gamma(q) = G_{11}(q)G_{22}(q) - G_{12}(q)^2, \quad (4)$$

where $G_{ab}(q) = \mathbf{e}_a \cdot \mathbf{G} \cdot \mathbf{e}_b$. $\Gamma(q)$ is a product of the fluctuation eigenvalues. These eigenvalues have minima at $q = 0$ (macrophase separation) or $q_* \neq 0$ (microphase separation). The spinodal point is given by that eigenmode whose eigenvalue first vanishes upon reducing the temperature. For $q = 0$ this eigenmode is \mathbf{e}_2 , while otherwise it is an admixture of \mathbf{e}_1 and \mathbf{e}_2 . The small- q expansion of Γ has the form

$$\Gamma(q) = \frac{a_0 + a_1q^2 + a_2q^4 + a_3q^6 + \dots}{b_1q^2}. \quad (5)$$

To parametrize the problem, we let $\chi \equiv \chi_{AB}N$, $r_{AC} \equiv \chi_{AC}/\chi_{AB}$, and $r_{BC} \equiv \chi_{BC}/\chi_{AB}$. The phase diagram may now be calculated in the (χ, ϕ) -plane, with r_{AC} , r_{BC} , f , α , β as independent material parameters. Obviously the system is far richer (and more complicated) than that of simple diblocks. Rather than systematically calculating phase diagrams, we first discuss the nature of macro- and micro-phase separation, and then examine the character of the possible Lifshitz points.

Microphase vs. macrophase separation. – In the AB/AB limit ($\chi_{AC} = 0$, $\chi_{AB} = \chi_{BC}$) macrophase separation cannot occur; while for large enough χ_{AB} macrophase separation is possible. The nature of the unstable modes can be seen by examining the eigenvalues $\lambda_1(q)$ and $\lambda_2(q)$ of the fluctuation matrix (in the 2-dimensional incompressible subspace).

Typical results are shown in fig. 1 for a blend with $f = 0.17$, $\beta = \alpha = 1.0$, $r_{AC} = 0.49$, $r_{BC} = 2.9$, for compositions $\phi = 0.4$ and $\phi = 0.6$. One eigenvalue (λ_1) diverges at $q = 0$, and the other (λ_2) is finite. We term these the *microphase* and *macrophase* modes, respectively. In the limit $q \rightarrow 0$, the microphase mode corresponds to \mathbf{e}_1 and the macrophase mode to \mathbf{e}_2 ,

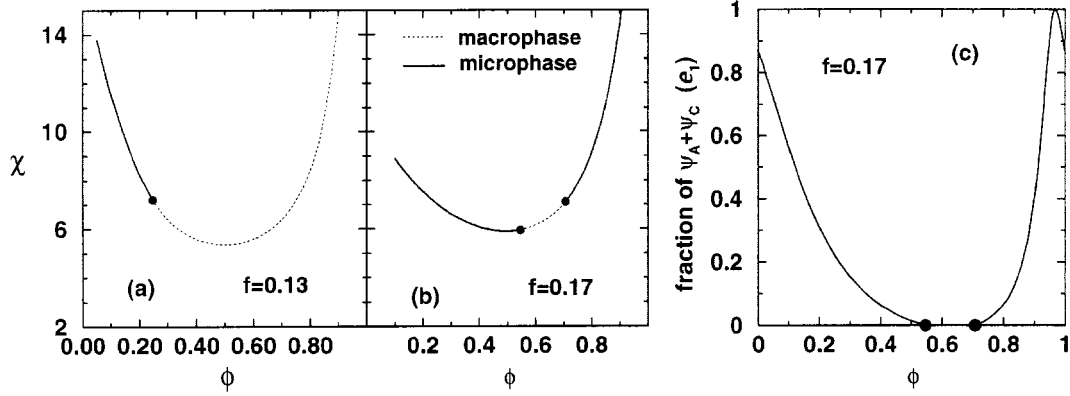


Fig. 2. – Spinodal diagrams for $\beta = 1, \alpha = 1$, for $f = 0.13$ (a) and $f = 0.17$ (b), for $\alpha = 1, \beta = 1$, $r_{AC} = 0.49, r_{BC} = 2.9$. Thick lines denote microphase spinodals, dotted lines denote macrophase (liquid-liquid) spinodals, and the filled circles are the microphase endpoints. (c) shows the contribution of the microphase separation mode $e_1 \sim \psi_A + \psi_C$ along the microphase separation lines for $f = 0.17$.

while at finite q these modes are (orthogonal) linear combinations of e_1 and e_2 . For $\phi = 0.4$ a microphase separation transition spinodal is located at $\chi = 6.063$, at which point the local minimum in $\lambda_2(q)$ becomes negative at finite q , fig. 1a (note that there are actually non-zero cubic terms ψ^3 in the free energy at this point, so that the spinodal is preempted by a first-order transition). For $\phi = 0.6$, however, the spinodal occurs to macrophase separation, since λ_2 first becomes negative (fig. 1c), upon increasing χ , for $q = 0$. The microphase mode (λ_1 , not shown) has a minimum at finite q , but remains positive. We define the *microphase endpoint* as the termination of the spinodal line for microphase separation on the spinodal line for macrophase separation. For this system microphase endpoints occur at $\phi = 0.546$ and $\phi = 0.706$ (fig. 2b). The instability of the macrophase mode can be easily understood, since an A-B homopolymer melt requires $\chi N \sim 2$ for macrophase separation, and the corresponding A-B diblock melt requires $\chi N \simeq 10.5$ for microphase separation. Hence pure microphase separation is more costly, and if the system can take advantage of some macrophase separation (*i.e.* including some component of the eigenvector e_2), it will do so.

Spinodal diagrams are shown in fig. 2a, b. Since the two diblocks are identical in architecture and molecular weight, the phase behaviour results solely from the chemical differences between A and C, through the χ parameters. Lowering the the temperature induces an instability to either macrophase or microphase separation, depending on copolymer asymmetry and blend composition. For diblocks with $f = 0.13$ the disordered phase is unstable to macrophase separation for $\phi \gtrsim 0.246$, and to microphase separation for blends with $\phi \lesssim 0.246$ (fig. 2). The asymmetry about $\phi = 0.5$ is due to the distinct temperature dependence of the three χ parameters. Generally the bimodal associated with the macrophase spinodal preempts the microphase endpoint and we expect, with increasing χ , macrophase-macrophase coexistence, macrophase-microphase coexistence, and microphase-microphase coexistence. As the copolymers become more symmetric, the region of macrophase separation narrows, and the critical point for macrophase separation coincides with the microphase endpoint at a copolymer volume fraction $f_L \simeq 0.17$ (fig. 2b). Such a point is in fact a Lifshitz point.

Figure 2c shows the portion of the eigenmode for the microphase instability which is in fact the microphase eigenmode e_1 , along the lines of microphase transitions for $f = 0.17$. At the Lifshitz point (and the other microphase endpoint) there is an infinitesimal amount of

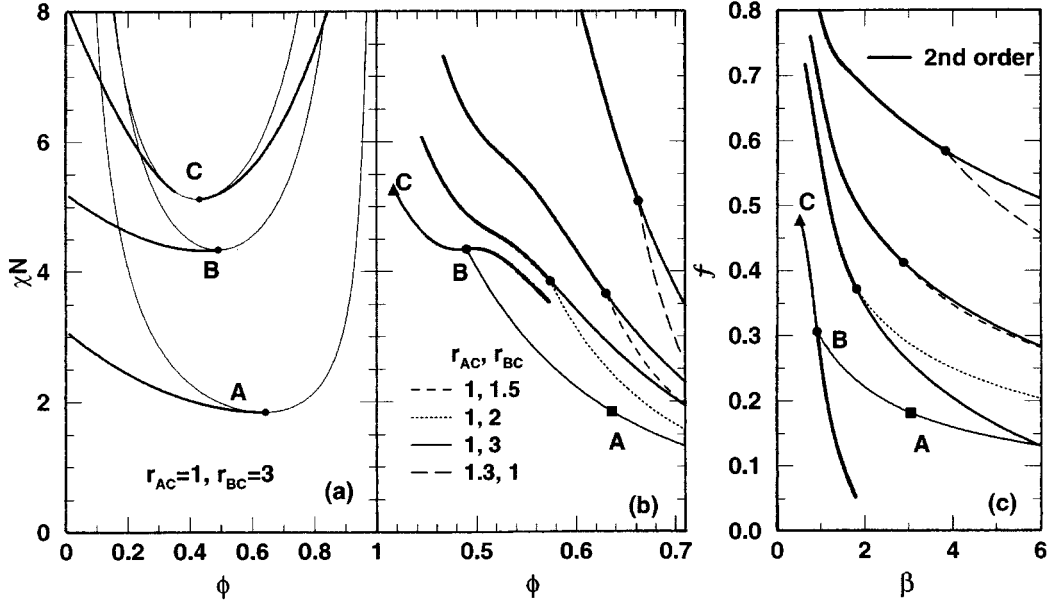


Fig. 3. – (a): Microphase (thick lines) and macrophase (thin lines) spinodals for points A (■), B, and C (▲) in (b) and (c), for $r_{AC} = 1, r_{BC} = 3$. First-order Lifshitz points are denoted by •. (b) and (c): Lines of Lifshitz points for various r_{AB}, r_{BC} . Thin lines are first-order Lifshitz points for $\alpha = 1$, which end on lines of second-order Lifshitz points (thick lines) at •'s. Along the second-order lines $\alpha \neq 1$, except for the intersection with the first order lines. The ranges of the second-order lines are $\alpha \in (0.590, 1.30)[r_{AC} = 1, r_{BC} = 1.5]$, $\alpha \in (0.592, 2.32)[r_{AC} = 1, r_{BC} = 2]$, $\alpha \in (0.709, 5.00)[r_{AC} = 1, r_{BC} = 3]$, $\alpha \in (0.64, 1.08)[r_{AC} = 1.3, r_{BC} = 1]$, where low α is to the left and high α to the right in (b) and (c).

e_1 , and the majority of the instability is in the macrophase mode, e_2 . As the pure system is approached (either $\phi = 0$ or $\phi = 1$) the fraction of e_1 increases but, interestingly, does not approach 1. This is due to the chemical asymmetry between A and C.

Lifshitz points. – As with a homopolymer blend, the critical composition ϕ_c is given by $\partial a_0 / \partial \phi = 0$, yielding $\phi_c = \sqrt{\beta} / (1 + \sqrt{\beta})$ [24]. At ϕ_c the critical point χ_c for macrophase separation is given by $a_0 = 0$. If $a_1 > 0$ macrophase separation occurs directly from the disordered state; while for $a_1 < 0$ microphase separation at finite wave number q_* occurs directly from the disordered state, hence preempting macrophase separation. The limit $q_* = 0$ defines a point at which the line of microphase separation transitions meets the spinodal for macrophase separation, determined by $a_0 = a_1 = 0$. By tuning the material parameters we can easily find a first-order Lifshitz point, where $a_0 = a_1 = 0$ at the critical point, ϕ_c ; and a second-order Lifshitz point, at which $a_0 = a_1 = a_2 = 0$ at ϕ_c [15]. In principle, one may tune the material parameters further to find third- ($a_3 = 0$), fourth- ($a_4 = 0$), and fifth- ($a_5 = 0$) order Lifshitz points. For example, for fixed r_{AB}, r_{BC} and α a second-order Lifshitz point can be found by adjusting β, f , and χ . A third-order Lifshitz point can, in principle, then be found by adjusting α so that $a_3 = 0$; and r_{AB} and r_{BC} could then be adjusted to find fourth and fifth-order Lifshitz points (with $a_4 = 0$ and $a_5 = 0$, respectively). This is quite a large parameter space, and we have succeeded only in finding first- and second-order Lifshitz points.

Figure 3 shows lines of Lifshitz points calculated for various parameters (b,c), and representative spinodal diagrams (a). We stress that the binodals for macrophase separation, as well

as various microphase structures, will considerably complicate these diagrams. Nonetheless, the Lifshitz points (*e.g.*, fig. 3a) **A** and **C** are the lowest- χ features in their phase diagrams, and should be accessible directly from the disordered state. The Lifshitz lines are shown both in the (χ, ϕ) -plane (indicating where in the phase diagram to look), as well as in the (f, β) -plane, indicating the trajectory in architecture space. The first-order Lifshitz lines for $\alpha = 1$ end, at small β , on a second-order Lifshitz line which traces out a trajectory in (β, α, f) space. The projections of these lines onto the (f, β) -plane are shown as thick lines in fig. 3b,c. The second-order lines end at small β (and α) where a stable root no longer exists; at this point (such as **C**) the coefficient a_3 approaches zero, although our numerics cannot find a stable solution with $a_0 = a_1 = a_2 = a_3 = 0$ (which would signify a third-order Lifshitz point). The nature of the spinodal diagram for **C** suggests that the macrophase separation window could indeed vanish at third-order Lifshitz point for certain values of the parameters. The higher-order Lifshitz behavior is indicative of more than one length scale competing for stability, as would be expected for diblocks which each have a preferred lengthscale. For large β (and α), the second-order Lifshitz lines remain stable and do not end.

Summary. – We have examined some aspects of phase separation in AB/BC diblock copolymer blends. Both macro- and micro-phase separation can occur, and microphase separation is a combination of the fundamental macrophase and microphase eigenmodes. We have demonstrated the possibility of Lifshitz points of first and second order, and our calculations (limited at present by numerical precision) suggest that Lifshitz points of up to 5th order are, in principle, possible. This is the first prediction of which we are aware for higher-order Lifshitz points. Clearly, these calculations are illustrative of a rich phase behaviour which can be mapped by varying architecture and the three χ -parameters. Future work should address the nature of the ordered microphase-separated phases, and allow for composition fluctuations. In particular, particularly strong fluctuations are expected near higher-order Lifshitz points (the upper critical dimension for a k -th-order Lifshitz point is $d_c = 4(1 + k)$).

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