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Influence of Nematic Fluctuations on the Phase Separation of Polymer Blends

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A blend of two polymers often exhibits a phase transition on cooling from a single mixed phase to two homogeneous phases, each rich in a different polymer. The standard Flory–Huggins theory describes the dependence of the phase transition on the molecular weights of the two polymers, the composition of the blend, and the interaction parameter χ but does not include the effect of polymer stiffness. Yet it is well-known that when there is a large difference in flexibility, such as in a blend of rods and coils, the system will phase separate for entropic reasons alone; this was first shown by Flory.[1,2] It is therefore reasonable to expect that differences in the statistical segment lengths of even flexible polymer species can lead to an entropic contribution $\Delta\chi$ to the effective interaction parameter χ_{eff}. In this paper, we calculate $\Delta\chi$ in the limit where the two components are both quite flexible and show that it is proportional to the square of the difference in statistical segment lengths, in units of a composition-averaged statistical segment length.

Our approach is to use a Landau–Ginzburg expansion developed to study liquid crystalline polymers.[3] The free energy is written as an expansion in two order parameters, namely, concentration and orientation density. This approach was first adopted by Carton and Leibler[4] to study the conformations of Gaussian chains near polymer–solvent or polymer–polymer interfaces. In our case, we calculate the expansion coefficients from a model of wormlike chains within the random-phase approximation. We obtain the coefficients as functions of the total length of the polymer in units of the persistence length of the chain. We then integrate over the orientational degrees of freedom to find the contribution of orientational, i.e., nematic, fluctuations to χ_{eff}.

Other approaches could also be used to estimate the effect of chain stiffness on phase separation. The cluster expansion of Freed and Bawendi[5] yields an entropic contribution to χ_{eff} that arises from differences in monomer shape.[6] In addition, the polymer RISM integral equation theory of Schweizer and Curro[7] has been applied to an athermal binary blend of different statistical segment lengths.[8] Schweizer and Curro find that $\Delta\chi$ is *negative*, indicating that a difference in stiffness enhances miscibility. Their approach gives specific numerical estimates of χ_{eff} but cannot yield analytic expressions for χ_{eff} as a function of volume fraction and statistical segment lengths.

In the preceding paper, Bates, Schulz, Rosedale, and Almdal[9] have estimated χ_{eff} for four binary polymer blends with different statistical segment lengths. They find that $\Delta\chi$ is *positive*, in contradiction with the results of Schweizer and Curro. Our result provides an explanation of the sign difference between the RISM theory and the experiments and is in qualitative agreement with the data of Bates et al.[9]

The standard approach to calculating the contributions of fluctuations is to start with an effective Hamiltonian $\mathcal{H}_{\text{eff}}$ of the same form as the Landau-Ginzburg free energy.[10] Therefore, the first step is to calculate the Landau–Ginzburg free energy within the random-phase approximation from a microscopic model of chains with bending rigidity. Details of this calculation will be provided elsewhere;[3] here it suffices to state the assumptions underlying the calculations. We consider an incompressible blend of two semiflexible homopolymers of species 1 and 2. For simplicity, we assume that the chains consist of rigid segments of fixed length a_0 and that both polymers contain N segments of equal volume v_0. The average composition ϕ is the mean volume fraction of species 1. The flexibilities of the pure homopolymers are characterized by dimensionless elastic constants κ_1 and κ_2; the persistence lengths are $\kappa_1 a_0$ and $\kappa_2 a_0$. We assume that species 1 is more rigid so that $\kappa_1 > \kappa_2$.

In calculating the mean-field free-energy functional, we retain two interaction parameters. The isotropic interaction between segments is characterized by the conventional Flory parameter χ, which favors demixing of the two homopolymers. We also include a quadrupolar interaction characterized by a Maier–Saupe parameter $\tilde{w}$ that favors mutual alignment of segments. This interaction could arise from anisotropic interactions or from steric excluded-volume interactions.[11]

Finally, we introduce two order parameters. The first describes the deviation of the average local composition from the average global composition:

$$\varphi(\vec{r}) = \phi(\vec{r}) - \phi \qquad (1)$$

The second order parameter is the standard local nematic tensor order parameter

$$S^{ij}(\vec{r}) = v_0\left\langle \sum_1 \int \mathrm{d}s \left(u_1^i(s)\, u_1^j(s) - \frac{1}{3}\delta^{ij} \right) \delta(\vec{r}-\vec{r}_1(s)) + \sum_2 \int \mathrm{d}s \left(u_2^i(s)\, u_2^j(s) - \frac{1}{3}\delta^{ij} \right) \delta(\vec{r}-\vec{r}_2(s)) \right\rangle \qquad (2)$$

where the blend is assumed to be isotropic on average and the angular brackets represent a thermal ensemble average. The sums run over all chains of species 1 and 2; $\vec{r}_1(s)$ is the position vector and $\vec{u}_1(s)$ is the tangent vector of segment s on a chain of species 1.

The Landau–Ginzburg free-energy expansion then has the form ($\beta \equiv 1/k_{\mathrm{B}}T$):

$$\beta\mathcal{F} = \rho_0 \int \mathrm{d}\vec{r}\ [(A-\chi)\varphi^2 + (\tilde{B}-\tilde{w})S^{ij}S^{ij} - \tilde{C}_3\varphi S^{ij}S^{ij} + \tilde{C}_4\varphi^2 S^{ij}S^{ij}] \qquad (3)$$

where we have truncated the expansion in φ and $\overleftrightarrow{S}$ at second order in each order parameter and have retained only the terms that give contributions to $\Delta\chi$. The monomer density is $\rho_0 = 1/v_0$. In order to simplify the free energy, we introduce a scalar orientational order parameter S. Since $\overleftrightarrow{S}$ is a traceless symmetric tensor, it must have the form

$$\overleftrightarrow{S} \equiv S\left(\hat{n}_i\hat{n}_j - \frac{1}{3}\delta^{ij}\right) \qquad (4)$$

where $\hat{n}$ is a local director. Once we substitute eq 4 into eq 3, we obtain new coefficients B, C_i, w, etc., for terms involving the scalar S which are related to the coefficients $\tilde{B}$, etc., by a factor of $^2/_3$; for example

$$B = \tilde{B}\left(\hat{n}_i\hat{n}_j - \frac{1}{3}\delta_{ij}\right)^2 = {}^2/_3\tilde{B} \qquad (5)$$

By using $\mathcal{F}[\phi,\mathcal{S}]$ as an effective Hamiltonian $\mathcal{H}_{\text{eff}}$, we can

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now write

$$\beta\mathcal{H}_{\text{eff}} = \rho_0 \int \mathrm{d}\vec{r}\, [(A - \chi)\varphi^2 + (B - w)S^2 - C_3\varphi S^2 + C_4\varphi^2 S^2] \quad (6)$$

We assume that the coefficients in the effective Hamiltonian can be approximated by the corresponding coefficients in the Landau–Ginzburg free energy. We stress that the coefficients A, B, C_i, etc., are *not* unknown parameters. The parameter A is the coefficient of the φ^2 term obtained by expanding the Flory–Huggins free energy in powers of φ:

$$\mathcal{F}_{\text{fh}} = \frac{\phi_1}{N}\log\phi_1 + \frac{\phi_2}{N}\log\phi_2 + \chi\phi_1\phi_2 \quad (7)$$

where $\phi_1 = \phi + \varphi$ and $\phi_2 = 1 - \phi - \varphi$. The coefficients B, C_i, etc., are functions of N/κ_1 and N/κ_2 that we have calculated from a microscopic model of wormlike chains with bending elasticity.[12] The coefficients are given in the flexible ($N \gg \kappa_1$) limit by

$$B = \frac{15}{4\bar{\kappa}},\quad C_3 = \frac{15}{4\bar{\kappa}}\Delta,\quad C_4 = \frac{15}{4\bar{\kappa}}\Delta^2 \quad (8)$$

where

$$\bar{\kappa} \equiv \phi\kappa_1 + (1 - \phi)\kappa_2 \quad (9)$$

is a composition-weighted average of the elastic constants and

$$\Delta = (\kappa_1 - \kappa_2)/\bar{\kappa} \quad (10)$$

is a dimensionless difference between the elastic constants. The parameter B is the coefficient of the S^2 term of the Landau–de Gennes expansion of the nematic free energy for a homopolymer of elastic constant $\bar{\kappa}$.[13,14] Finally, the coupling terms involving both φ and S describe the change in the orientational entropy when the concentrations of the two species are inhomogeneous. The physical interpretation of the coupling terms is more transparent when we rewrite the effective Hamiltonian as follows:

$$\beta\mathcal{H}_{\text{eff}} = \rho_0 \int \mathrm{d}\vec{r} \left[(A - \chi)\varphi^2 + \left(\frac{B}{1 + \varphi\Delta} - w\right)S^2\right] \quad (11)$$

By expanding the S^2 term in eq 11 in powers of φ, we recover the coefficients C_3 and C_4 given by eq 8. We have also used a density-functional approach similar to that of Tang and Freed[15] to show that the coefficients of all terms of the form $\varphi^n S^2$ should be given by the expansion of $BS^2/(1 + \varphi\Delta)$. The φ dependence of the S^2 term in eq 11 reflects the decrease in the free energy when polymers of species 1, which are stiffer, are concentrated in regions of high orientational order and polymers of species 2, which are more flexible, are concentrated in regions of low orientational order. If the two species have equal stiffnesses, then $\Delta = 0$ and there is no coupling between concentration and orientation. The coefficient C_3 was also obtained by Fredrickson and Leibler for a blend of two semiflexible homopolymers.[16]

To obtain $\Delta\chi$, we must deduce the effective free-energy functional in terms of φ alone by integrating over the orientational degrees of freedom. This effective free energy is given by

$$\beta\mathcal{F}_{\text{eff}}[\varphi] = -\log \int \mathcal{D}S\, e^{-\beta\mathcal{H}_{\text{eff}}} \quad (12)$$

where $\mathcal{H}_{\text{eff}}$ is given by eq 11. If we factor out the terms independent of S, we find

$$\beta\mathcal{F}_{\text{eff}}[\varphi] = \rho_0 \int \mathrm{d}\vec{r}\, (A - \chi)\varphi^2 - \log \int \mathcal{D}S \exp\left[-\rho_0 \int \mathrm{d}\vec{r} \left(\frac{B}{1 + \varphi\Delta} - w\right)S^2\right] \quad (13)$$

At this point, it is convenient to make the integrals dimensionless by rescaling $\vec{x} = \vec{r}/\kappa a_0$. The monomer density is then replaced by a dimensionless monomer density $\rho = (\bar{\kappa} a_0)^3/v_0$. After performing the Gaussian integral over S, we obtain

$$\beta\mathcal{F}_{\text{eff}}[\varphi] = \rho \int \mathrm{d}\vec{x}\, (A - \chi)\varphi^2 + \frac{1}{2}\int \mathrm{d}\vec{x} \log\left(\frac{B}{1 + \varphi\Delta} - w\right) \quad (14)$$

In this and subsequent equations, constant terms are discarded. Next, we expand the logarithm to obtain the φ^2 term:

$$\beta\mathcal{F}_{\text{eff}}[\varphi] = \rho \int \mathrm{d}\vec{x} \left[(A - \chi)\varphi^2 + \frac{1}{4\rho}\frac{B(B - 2w)}{(B - w)/^2}\Delta^2\varphi^2\right] \quad (15)$$

We now define $\Delta\chi$ by

$$\mathcal{F}_{\text{eff}}[\varphi] = \rho \int \mathrm{d}\vec{x}\, [A - (\chi + \Delta\chi)]\varphi^2 \quad (16)$$

and obtain our principal result

$$\Delta\chi = \frac{1}{4}\frac{B(2w - B)}{(B - w)^2}\frac{v_0}{(\bar{\kappa} a_0)^3}\left(\frac{\kappa_1 - \kappa_2}{\bar{\kappa}}\right)^2 \quad (17)$$

This expression can be recast in terms of the statistical segment lengths a_1 and a_2 of the two species. By comparing expressions for the mean-square end-to-end distance, we find that $2\kappa_i a_0 = a_i$. The final expression for $\Delta\chi$ is then given by

$$\Delta\chi \propto \frac{v_0}{\bar{a}^3}\left(\frac{a_1 - a_2}{\bar{a}}\right)^2 \quad (18)$$

We have also performed a one-loop calculation of $\Delta\chi$ by expanding the expression eq 13 in powers of φ *before* performing the Gaussian integrals over S. In that case, we have also included square-gradient terms in S. The details of this calculation are not provided here, but the result is nearly identical to eq 17. The form is the same, except that the factor $^1/_4$ in front is replaced by a factor of order unity, and the factor $2w - B$ is replaced by $cw - B$, where

$$c = \frac{2I_0}{2I_0 - I_1} \quad (19)$$

and I_0 and I_1 are integrals given by

$$I_0 = \int \frac{\mathrm{d}^3 q}{1 + g(q)},\quad I_1 = \int \frac{\mathrm{d}^3 q}{(1 + g(q))^2} \quad (20)$$

The function $g(q)$ arises from the gradient expansion of the Landau–Ginzburg free energy and is given by

$$g(q) = \frac{13}{63}q^2 + \frac{2}{7}(q_x q_y + q_y q_z + q_z q_x) + O(q^4) \quad (21)$$

Since the coefficient of the q^4 term of $g(q)$ is tedious to calculate and is required for the convergence of I_0, we have not attempted to calculate these integrals. However, the fact that the inclusion of gradient terms does not destroy the form of eq 18 is reassuring.

We turn now to a discussion of our result in eq 17. The first point to be noted is the sign of the correction $\Delta\chi$. Evidently, our result can have either sign, depending on the magnitude of the Maier–Saupe interaction w. Within our model, w is an unknown parameter that can arise from excluded-volume interactions or from anisotropic interactions between monomers. We can, however, set a bound on w by observing that for $w > B$ the mixture is nematic. Since we are interested in isotropic blends of flexible polymers, w must satisfy $w < B$. For a weak Maier–Saupe interaction ($w < {}^1/_2 B$), we obtain $\Delta\chi < 0$, indicated that orientational fluctuations promote *mixing* of the two polymer species. This is consistent with the results of Schweizer and Curro,[8] who found that $\Delta\chi < 0$ for *athermal* blends of polymers with different stiffnesses. For a strong Maier–Saupe interaction ($w > {}^1/_2B$), on the other hand, we obtain $\Delta\chi > 0$, implying that orientational fluctuations promote *demixing* of the two components. The physical interpretation of these results is straightforward. The coefficient B parametrizes the strength of the orientational entropy of mixing of the two polymers. Thus, the position of the nematic–isotropic transition is roughly determined by the competition between the Maier–Saupe parameter w, which favors local segmental alignment, and the orientational entropy of mixing B, which favors isotropization. From eq 8 we see that B depends inversely on the average stiffness of the two polymers; thus, the orientational entropy of mixing is decreased if the average stiffness increases, and a smaller w is sufficient to drive the system to the nematic phase. In the case where $w < B$, the system is in the isotropic phase, but if w is sufficiently strong, our result indicates that it can give rise to strong orientational correlations which promote demixing. Bates et al.[9] showed that $\Delta\chi$ is positive for all the mixtures they have studied. This implies that w lies in the range ${}^1/_2B < w < B$ for all of the blends they studied. Note that the lower bound of this window depends on the approximations used in calculating $\Delta\chi$. From the one-loop calculation, we obtain the range $B/c < w < B$.

The sensitivity of the sign of $\Delta\chi$ to the magnitude of w raises the question of how large the Maier–Saupe parameter could be for flexible polymer blends. Recent experiments by Ylitalo, Zawada, and Fuller,[17] as interpreted by Olmsted and Milner,[18] suggest that w can indeed be of order B for flexible polymers. Ylitalo et al. performed simultaneous measurements of infrared dichroism and birefringence on polybutadiene oligomers embedded in polybutadiene melts and networks to measure the orientational coupling. Olmsted and Milner[18] constructed a model to describe oligomers embedded in a host melt which includes a Maier–Saupe interaction on all bonds. By comparing their model to the data of Ylitalo et al., Olmsted and Milner estimate the Maier–Saupe parameter to be $w \approx 0.9B$ for polybutadiene. This result is based on completely different considerations from ours but lies within our range of ${}^1/_2B < w < B$.

Finally, we consider the magnitude of the renormalization $\Delta\chi$. Bates et al.[9] have studied binary blends of four polyolefins, namely, polyethylene, poly(ethylenepropylene), poly(ethylene/ethylethylene) (a random copolymer), and poly(ethylethylene). From their data, we find that $\Delta\chi$ is of the right order of magnitude when the Maier–Saupe parameter lies roughly in the range $0.5B < w < 0.6B$. Thus, if w lies at the lower end of the allowed range $0.5B < w < B$, eq 17 yields a shift in χ that is comparable in magnitude to the values obtained by Bates et al.[9]

In summary, we have shown that a difference in chain flexibility in a binary polymer blend can give rise to orientational fluctuations that renormalize the Flory χ parameter. These fluctuations, in turn, can lead to a substantial shift in the critical point and phase boundaries. Our result for the shift $\Delta\chi$ is appealing because of its simplicity and because the necessary parameters can be obtained from measurements on the pure blend components. Finally, we note that the preceding paper by Bates et al.[9] shows that there is indeed a strong correlation between the magnitude of χ and the difference in statistical segment length for several polymer blends.

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References and Notes

(1) Flory, P. J. *Proc. R. Soc. London* **1956**, *A234*, 73.
(2) Flory, P. J. *Adv. Polym. Sci.* **1984**, *59*, 1.
(3) Liu, A. J.; Fredrickson, G. H., to be published.
(4) Carton, J.-P.; Leibler, L. *J. Phys. (Fr.)* **1990**, *51*, 1683.
(5) Freed, K. F.; Bawendi, M. G. *J. Phys. Chem.* **1989**, *93*, 2194.
(6) Freed, K. F.; Pesci, A. I. *J. Chem. Phys.* **1987**, *87*, 7342.
(7) Schweizer, K. S.; Curro, J. G. *Chem. Phys.* **1990**, *149*, 105.
(8) Schweizer, K. S.; Curro, J. G. *Phys. Rev. Lett.* **1988**, *60*, 809.
(9) Bates, F. S.; Schulz, M. F.; Rosedale, J. H.; Almdal, K. *Macromolecules*, preceding paper in this issue.
(10) See, for example: Amit, D. J. *Field Theory, the Renormalization Group, and Critical Phenomena*; World Scientific: Singapore, 1984.
(11) Luckhurst, G. R.; Zannoni, C. *Nature* **1977**, *267*, 412.
(12) Saito, N.; Takahashi, K.; Yunoki, Y. *J. Phys. Soc. Jpn.* **1967**, *22*, 219.
(13) ten Bosch, A.; Maissa, P., Sixou, P. *J. Phys. Lett. (Fr.)* **1983**, *44*, L105.
(14) Rusakov, V. V.; Shliomis, M. I. *J. Phys. Lett. (Fr.)* **1985**, *46*, L935.
(15) Tang, H.; Freed, K. F. *J. Chem. Phys.* **1991**, *94*, 1572.
(16) Fredrickson, G. H.; Leibler, L. *Macromolecules* **1990**, *23*, 531.
(17) Ylitalo, C. M.; Zawada, J. A.; Fuller, G. G., to be published.
(18) Olmsted, P. D.; Milner, S. T., to be published.