

Scattering from mixtures of flexible and stiff polymers

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The random phase approximation (RPA) is used to calculate the scattering function for multicomponent mixtures of flexible and stiff polymers. These calculations will be useful for the qualitative interpretation of small angle neutron scattering (SANS) data from binary mixtures of polymer liquid crystals and flexible polymers in the isotropic phase region. They can predict the spinodal line as well as the isotropic-to-nematic phase transition line. Depending on the volume fraction of the rigid polymer and on the relative values of the Flory–Huggins and Maier–Saupe interaction parameters, either the spinodal line or the isotropic-to-nematic phase transition is reached first.

INTRODUCTION

The random phase approximation (RPA) has been developed^{1–6} to describe the phase separation thermodynamics (spinodal line) of flexible polymer blend mixtures from the one-phase region. Since its introduction, the de Gennes formula¹ has been instrumental in helping experimentalists extract Flory–Huggins interaction “chi” parameters from binary compatible blend mixtures. This approach has been extended to multicomponent systems^{2–6} using either a direct calculation approach^{2–3} or an elegant matrix notation approach.^{4–6} Both agree and differ only in the manner in which the formalism is set up.

The RPA gives surprisingly good results for blends, melts, and concentrated solutions of flexible polymers despite the crudeness of the approximations involved (linear response, mean field). It is not as good around and below the overlap concentration because of the importance of concentration fluctuations. The RPA which neglects a large number of interactions (as shown in Fig. 1) is expected to work even better for stiff polymers for which loop interactions are less probable (these are inexistent for rigid rods). However, the RPA is still not an “exact” statement for rigid rods because it neglects ternary interactions.

The RPA has also been applied by Doi *et al.*^{7–9} to stiff polymers in solution. For instance, static scattering functions were investigated for dilute and semidilute solutions of rigid rods. This formalism was able to predict the nematic phase transition that occurs above the overlap concentration. Small scattering vector, Q , expansions of the static structure factor have been presented.⁹ Moreover, Holyst and Schick^{10,11} have recently used a field theory approach along with a random phase approximation to examine the stability¹⁰ and correlations¹¹ in a rigid-flexible diblock copolymer system.

A combination of the above mentioned approaches is used here to describe multicomponent blend mixtures of stiff polymers including mixtures of rigid rods and flexible components (the two extreme limits in stiffness) in a unified manner. The results obtained here reproduce those of Doi *et al.*^{7–9} in the limit where the flexible component is replaced by a solvent and agree with those reported by Holyst and Schick.^{10,11} Even though the formalism can

describe an intermediate degree of stiffness (or flexibility) for each of the member components of the blend, specific examples corresponding to mixtures of rigid rods and flexible (freely jointed chains) polymers will be considered. The formalism will be presented for a compressible polymer mixture as well as an incompressible mixture. The ideal (sometimes called “bare”) structure factors and their moments averaged over orientations will be presented in order to consider specific examples.

COMPRESSIBLE MULTICOMPONENT MIXTURES OF STIFF POLYMERS

We consider a polymer system consisting of n kinds of stiff (i.e., semiflexible) polymers, and use the matrix notation approach introduced by Akcasu.^{4–6} Some of these components could be copolymers. Component I , for example, has a degree of polymerizations N_I , volume fraction ϕ_I , monomer volume v_I , and segment size l_I . For stiff polymers, the averaged fluctuating density is defined as

$$\langle \rho(Q, \mathbf{u}) \rangle = \sum_{\alpha i} \langle \exp(-i\mathbf{Q} \cdot \mathbf{r}_{\alpha i}) \delta(\mathbf{u} - \mathbf{u}_{\alpha i}) \rangle, \quad (1)$$

where monomer i in polymer α is located at position $\mathbf{r}_{\alpha i}$ and is oriented along direction $\mathbf{u}_{\alpha i}$ and where $\langle \dots \rangle$ represents an average over conformations (i.e., over $\mathbf{r}_{\alpha i}$ and $\mathbf{u}_{\alpha i}$).

Following the standard RPA formalism, we define externally applied (weakly perturbing) potentials \mathbf{U} (\mathbf{U} is an n -component vector that can depend on Q , but not on monomer orientations) and intersegment potentials $\mathbf{W}(\mathbf{u}, \mathbf{u}')$ ($n \times n$ matrix), where \mathbf{u} and \mathbf{u}' represent the directions of two test segments. Within the mean field approach, the RPA equations give the mean response of the averaged densities $\langle \rho(Q, \mathbf{u}) \rangle$ ($\langle \rho \rangle$ is an n vector) in terms of the response functions for the bare system $\mathbf{X}_0(Q, \mathbf{u}, \mathbf{u}')$ ($n \times n$ matrix) and for the interacting system $\mathbf{X}(Q, \mathbf{u}, \mathbf{u}')$. In this matrix notation approach, bold face characters are used to represent n vectors, $n \times n$ matrices, as well as three-dimensional Cartesian vectors such as direction \mathbf{u} . The RPA equations in the matrix form are

RANDOM PHASE APPROXIMATION

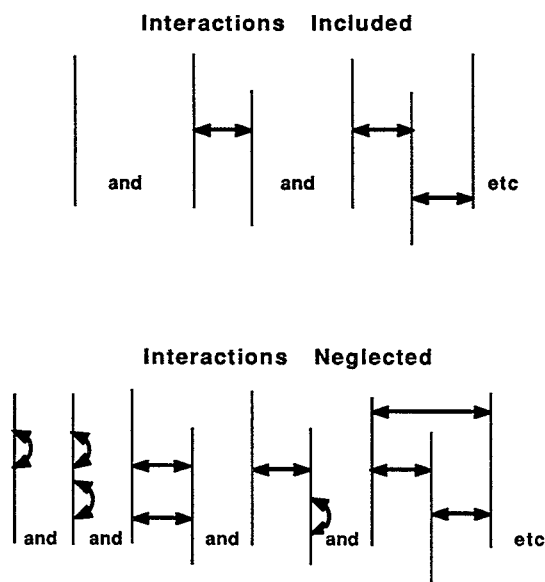


FIG. 1. Schematic representation of the interactions that are taken into account and those that are neglected in the random phase approximation.

$$\langle \rho(Q, \mathbf{u}) \rangle = - \int d\mathbf{u}' X_0(Q, \mathbf{u}, \mathbf{u}') \left[\mathbf{U}/k_B T + \int d\mathbf{u}_1 \mathbf{W}(\mathbf{u}', \mathbf{u}_1) \langle \rho(Q, \mathbf{u}_1) \rangle / k_B T \right], \quad (2a)$$

along with

$$\langle \rho(Q, \mathbf{u}) \rangle = - \int d\mathbf{u}' X(Q, \mathbf{u}, \mathbf{u}') \mathbf{U}/k_B T. \quad (2b)$$

Note that these two sets of equations can be combined to give

$$\mathbf{X}(Q, \mathbf{u}, \mathbf{u}') = X_0(Q, \mathbf{u}, \mathbf{u}') - \int d\mathbf{u}_1 d\mathbf{u}_2 X_0(Q, \mathbf{u}, \mathbf{u}_1) \times \mathbf{W}(\mathbf{u}_1, \mathbf{u}_2) X(Q, \mathbf{u}_2, \mathbf{u}') / k_B T, \quad (3)$$

which are the general RPA integral equations for compressible blend mixtures. Note that these equations are similar to the Ornstein-Zernicke relations.¹² Since the intersegment interactions become weaker when two test segments are parallel to each other, the interaction potentials are taken to be proportional to $\sin(\alpha)$, where α is the angle between the two test segments [$\sin(\alpha) = |\mathbf{u}_1 \times \mathbf{u}_2|$, where \times is the vectorial product]. In order to proceed further, Doi *et al.*⁷⁻⁹ assumed the following expansion:

$$\sin(\alpha) = (\pi/4) \{ 1 - (15/16) \times (\mathbf{u}_1 \mathbf{u}_1 - \mathbf{I}/3) : (\mathbf{u}_2 \mathbf{u}_2 - \mathbf{I}/3) + \dots \}, \quad (4)$$

where $\mathbf{u}_i \mathbf{u}_i$ represents a second rank tensor, \mathbf{I} is the second rank unity tensor, and the column $(:)$ represents the scalar product of two second rank tensors. Neglecting higher order terms effectively decouples the \mathbf{u}_1 and \mathbf{u}_2 integrations in the RPA equations therefore making calculations tractable analytically. The interaction potentials can therefore be assumed to be

$$\mathbf{W}(\mathbf{u}_1, \mathbf{u}_2) = \mathbf{W}_0 - \mathbf{W}_1 (\mathbf{u}_1 \mathbf{u}_1 - \mathbf{I}/3) : (\mathbf{u}_2 \mathbf{u}_2 - \mathbf{I}/3). \quad (5)$$

\mathbf{W}_0 and \mathbf{W}_1 ($n \times n$ matrices) are assumed here to contain unknown potential parameters. (Note that Doi *et al.*⁷⁻⁹ relate their scalar counterparts through: $W_1/W_0 = 15/16$ for rigid rods). The \mathbf{W}_1 potentials are the Maier-Saupe interaction parameters. The \mathbf{u}_1 and \mathbf{u}_2 integrations become

$$\begin{aligned} & \int d\mathbf{u}_1 \int d\mathbf{u}_2 X_0(Q, \mathbf{u}, \mathbf{u}_1) \mathbf{W}(\mathbf{u}_1, \mathbf{u}_2) X(Q, \mathbf{u}_2, \mathbf{u}_3) \\ &= \left\{ \int d\mathbf{u}_1 X_0(Q, \mathbf{u}, \mathbf{u}_1) \right\} \mathbf{W}_0 \left\{ \int d\mathbf{u}_2 X(Q, \mathbf{u}_2, \mathbf{u}_3) \right\} \\ & \quad - \left\{ \int d\mathbf{u}_1 X_0(Q, \mathbf{u}, \mathbf{u}_1) (\mathbf{u}_1 \mathbf{u}_1 - \mathbf{I}/3) \right\} \\ & \quad : \mathbf{W}_1 \left\{ \int d\mathbf{u}_2 X(Q, \mathbf{u}_2, \mathbf{u}_3) (\mathbf{u}_2 \mathbf{u}_2 - \mathbf{I}/3) \right\}. \end{aligned} \quad (6)$$

We use the following identity valid for uniaxial symmetry:

$$\begin{aligned} & \int d\mathbf{u}' X_0(Q, \mathbf{u}, \mathbf{u}') [\mathbf{u}' \mathbf{u}' - \mathbf{I}/3] \\ &= (3/2) [\mathbf{q} \mathbf{q} - \mathbf{I}/3] \int d\mathbf{u}' X_0(Q, \mathbf{u}, \mathbf{u}') \\ & \quad \times [(\mathbf{q} \cdot \mathbf{u}')^2 - 1/3] \end{aligned} \quad (7)$$

(where the unit vector $\mathbf{q} = \mathbf{Q}/|\mathbf{Q}|$ has been used to represent the longitudinal direction) and define the following orientational moments ($n \times n$ matrices):

$$\begin{aligned} X_0(Q) &= \int d\mathbf{u} \int d\mathbf{u}' X_0(Q, \mathbf{u}, \mathbf{u}'), \\ X(Q) &= \int d\mathbf{u} \int d\mathbf{u}' X(Q, \mathbf{u}, \mathbf{u}'), \\ \mathbf{R}_0(Q) &= (3/2) \int d\mathbf{u} \int d\mathbf{u}' X_0(Q, \mathbf{u}, \mathbf{u}') \\ & \quad \times [(\mathbf{q} \cdot \mathbf{u})^2 - 1/3], \\ \mathbf{R}(Q) &= (3/2) \int d\mathbf{u} \int d\mathbf{u}' X(Q, \mathbf{u}, \mathbf{u}') \\ & \quad \times [(\mathbf{q} \cdot \mathbf{u})^2 - 1/3], \\ \mathbf{T}_0(Q) &= (9/4) \int d\mathbf{u} \int d\mathbf{u}' X_0(Q, \mathbf{u}, \mathbf{u}') \\ & \quad \times [(\mathbf{q} \cdot \mathbf{u})^2 - 1/3] [(\mathbf{q} \cdot \mathbf{u}')^2 - 1/3]. \end{aligned} \quad (8)$$

Note that the matrices \mathbf{R} and \mathbf{R}_0 are not symmetric in the case of copolymers where one of the blocks is flexible and the other one is rigid. Note also that $\mathbf{R}(Q)$ is a generalized (Q dependent) orientational order parameter.

We integrate Eqs. (3) over \mathbf{u} and \mathbf{u}' to obtain

$$\mathbf{X}(Q) = \mathbf{X}_0(Q) - \mathbf{X}_0(Q) \cdot [\mathbf{W}_0/k_B T] \cdot \mathbf{X}(Q) \\ + (2/3)\mathbf{R}_0^T(Q) \cdot [\mathbf{W}_1/k_B T] \cdot \mathbf{R}(Q), \quad (9)$$

where $\mathbf{R}_0^T(Q)$ is the transpose matrix and we have used $[\mathbf{q}\mathbf{q} - \mathbf{I}/3]:[\mathbf{q}\mathbf{q} - \mathbf{I}/3] = 2/3$. First, multiplying Eqs. (3) by $[(\mathbf{q} \cdot \mathbf{u})^2 - 1/3]$ and then integrating over \mathbf{u} and \mathbf{u}' gives another set of equations

$$\mathbf{R}(Q) = \mathbf{R}_0(Q) - \mathbf{R}_0(Q) \cdot [\mathbf{W}_0/k_B T] \cdot \mathbf{X}(Q) \\ + (2/3)\mathbf{T}_0(Q) \cdot [\mathbf{W}_1/k_B T] \cdot \mathbf{R}(Q). \quad (10)$$

These sets of coupled equations (9) and (10) can be solved by eliminating $\mathbf{R}(Q)$ in order to obtain after a few manipulations,

$$\mathbf{X} = \{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\}^{-1} \\ \times \{\mathbf{X}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0\}, \quad (11)$$

where the (Q) argument has been dropped, the temperature (in energy units) $k_B T$ dividing the \mathbf{W}_0 and \mathbf{W}_1 potentials has been omitted for notation convenience and $\mathbf{M} = [\mathbf{I} - (2/3)\mathbf{T}_0 \cdot \mathbf{W}_1]$ has been defined. The isotropic-to-nematic transition is obtained by the characteristic equation $\det\{\mathbf{M}\} = 0$ (where \det represents the determinant of a matrix). If the van der Waals interactions were "turned off" ($\mathbf{W}_0 = 0$), then \mathbf{M} would be the denominator of \mathbf{X} so that \mathbf{X} would blow up if $\det(\mathbf{M}) = 0$. This argument for determining the isotropic-to-nematic transition line is the same as Doi *et al.*'s⁸ for lyotropic solutions of rigid rods. Above certain critical values of \mathbf{W}_1 's the blend forms the nematic phase. As in the case of purely flexible mixtures, the spinodal condition is

$$\det\{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\} = 0. \quad (12)$$

Note that the isotropic case (i.e., if orientational correlations were neglected) is obtained when $\mathbf{W}_1 = 0$ as

$$\mathbf{X}(Q)^{-1} = \mathbf{X}_0(Q)^{-1} + \mathbf{W}_0, \quad (13)$$

which is the result for multicomponent compressible blends of flexible polymers.

Since blend mixtures of completely rigid rods do not exist in the one-phase region, the approach described here will be applied to mixtures of rigid and flexible polymers. The case of polymer solutions (Doi *et al.*'s results⁸) can be recovered when one of the components is taken to be a solvent.

INCOMPRESSIBLE MULTICOMPONENT MIXTURES OF STIFF POLYMERS

Using the matrix notation approach⁴⁻⁶ that was introduced to describe multicomponent (consider n components) flexible polymer systems, the RPA equations are reviewed here for an incompressible polymer mixture. The idea is to isolate a "matrix" component (denoted component M) from the "rest" of the blend (denoted R). The various correlations are described through a scalar part

$\mathbf{X}_{MM}^0(Q)$, a vector part $\mathbf{X}_{MR}^0(Q)$, and a matrix part $\mathbf{X}_{RR}^0(Q)$, and similarly for potentials \mathbf{W} 's. The RPA equations for the n -vector fluctuating densities $\langle \rho(u) \rangle$ are

$$\langle \rho(u) \rangle = - \int d\mathbf{u}' \mathbf{X}_0(\mathbf{u}, \mathbf{u}') \left[\mathbf{U}/k_B T + \lambda \mathbf{E} \right. \\ \left. + \int d\mathbf{u}_1 \mathbf{W}(\mathbf{u}', \mathbf{u}_1) \langle \rho(\mathbf{u}_1) \rangle / k_B T \right], \quad (14a)$$

$$\langle \rho(u) \rangle = - \int d\mathbf{u}' \mathbf{X}(\mathbf{u}, \mathbf{u}') \mathbf{U}/k_B T, \quad (14b)$$

where $\langle \rho(u) \rangle = \text{Col}[\langle \rho_R(u) \rangle, \langle \rho_M(u) \rangle]$, \mathbf{E} is an n vector with all terms equal to unity and the Q dependence has been omitted for simplicity in notation. λ is a Lagrange multiplier that is to be determined using the incompressibility constraint

$$\langle \rho_M \rangle + \mathbf{E}_R^T \cdot \langle \rho_R \rangle = 0, \quad (15)$$

where $\langle \rho_M \rangle = \int d\mathbf{u} \langle \rho_M(u) \rangle$ and $\langle \rho_R \rangle = \int d\mathbf{u} \langle \rho_R(u) \rangle$.

Following the same procedure as in the previous section, we obtain sets of equations for the orientational moments which are solved to give

$$\{\mathbf{X}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0\}^{-1} \{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 \\ + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\} \langle \rho \rangle = - [\mathbf{U} + \lambda \mathbf{E}], \quad (16)$$

along with

$$\mathbf{X}^{-1} \langle \rho \rangle = -\mathbf{U}. \quad (17)$$

Here also the $k_B T$ term dividing the potentials has been omitted for notation convenience. Following Akcasu,⁶ we introduce an $n \times (n-1)$ matrix $\mathbf{P} = \text{Col}[\mathbf{I}, -\mathbf{E}_R^T]$, where \mathbf{I} is the $(n-1) \times (n-1)$ identity matrix and \mathbf{E}_R^T is an $(n-1)$ row vector comprising only ones. Using the \mathbf{P} matrix, the incompressibility statement becomes: $\langle \rho \rangle = \mathbf{P} \langle \rho_R \rangle$ and Eq. (14b) becomes $\mathbf{X}_{RR}^{-1} \langle \rho_R \rangle = -\mathbf{P}^T \mathbf{U}$. Multiplying Eq. (16) on the left by \mathbf{P}^T and using the fact that $\mathbf{P}^T \cdot \mathbf{E} = 0$, one can eliminate the potentials \mathbf{U} and obtain

$$\mathbf{X}_{RR}^{-1} = \mathbf{P}^T \cdot \{\mathbf{X}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0\}^{-1} \\ \times \{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\} \cdot \mathbf{P}. \quad (18)$$

This is a general result that states that the incompressibility constraint can be applied by sandwiching the $n \times n$ matrix $\mathbf{X}^{-1}(Q)$ (obtained for compressible mixtures) between \mathbf{P}^T and \mathbf{P} in order to obtain the $(n-1) \times (n-1)$ matrix of structure factors $\mathbf{X}_{RR}^{-1}(Q)$ for the remaining components. For example, in a binary blend mixture of flexible polymers, the sandwiching procedure has the effect of adding the diagonal elements and subtracting the off-diagonal elements; i.e., $\mathbf{P}^T \mathbf{W}_0 \mathbf{P} = W_{AA}^0 + W_{BB}^0 - W_{AB}^0 - W_{BA}^0 = -2k_B T \chi_{AB}$ which defines the Flory-Huggins interaction parameter χ_{AB} in terms of the interaction potentials W_0 's ($k_B T$ is the temperature in energy units).

Given the various structure factors $\mathbf{X}_{RR}(Q)$, the small angle neutron scattering (SANS) cross section $d\Sigma(Q)/d\Omega$ is readily obtained as

$$\frac{d\Sigma(Q)}{d\Omega} = \mathbf{B}^T \cdot \mathbf{X}_{RR}(Q) \cdot \mathbf{B}, \quad (19)$$

where the $(n-1)$ -component vector \mathbf{B} contains the relative scattering length densities. For example, $B_A = (b_A/v_A - b_M/v_M)$, where b_A and b_M are the scattering lengths of components A and M (matrix component), respectively, and the v 's are the monomer volumes.

The incompressibility assumption has been extensively used for flexible polymer blend mixtures. It is not known how reasonable this approximation would be for mixtures of flexible and stiff polymers. The results derived here will be applied in the next sections to investigate binary mixtures of flexible and rigid polymers.

BINARY BLEND OF A FLEXIBLE AND A RIGID ROD POLYMERS

This case is simple enough to give compact tractable results. Assuming that component A is flexible (freely jointed chains) and B is rigid (rigid rod polymers) and imposing the incompressibility condition, the following result can be obtained:

$$\begin{aligned} X_{AA} = & \left\{ (2/3)R_{BB}^0 W_{BB}^1 X_{AA}^0 + [1 - (2/3)T_{BB}^0 W_{BB}^1] \right. \\ & \times X_{AA}^0 X_{BB}^0 \left. \right\} / \left\{ (2/3)R_{BB}^0 W_{BB}^1 [1 - 2\chi_{AB} X_{AA}^0] \right. \\ & + (X_{AA}^0 + X_{BB}^0 - 2\chi_{AB} X_{AA}^0 X_{BB}^0) [1 \\ & \left. - (2/3)T_{BB}^0 W_{BB}^1] \right\}, \quad (20) \end{aligned}$$

where $X_{AB}^0 = R_{AA}^0 = R_{AB}^0 = R_{BA}^0 = T_{AA}^0 = T_{AB}^0 = 0$ and the remaining ideal structure factors can readily be calculated

$$\begin{aligned} X_{AA}^0(Q)/N_A \phi_A v_A = & \{ [1 + j_0(Ql_A)] N_A / [1 - j_0(Ql_A)] \\ & - 2j_0(Ql_A) [1 - j_0^N(Ql_A)] / \\ & [1 - j_0(Ql_A)]^2 \} / N_A^2, \quad (21a) \end{aligned}$$

$$\begin{aligned} X_{BB}^0(Q)/N_B \phi_B v_B = & \int_0^1 dx j_0^2(Ql_B N_B x/2) \\ & = 2[\cos(Ql_B N_B) - 1] / (Ql_B N_B)^2 \\ & + 2\text{Si}(Ql_B N_B) / Ql_B N_B, \quad (21b) \end{aligned}$$

$$\begin{aligned} R_{BB}^0(Q)/N_B \phi_B v_B = & (3/2) \int_0^1 dx (x^2 - 1/3) j_0^2(Ql_B N_B x/2) \\ & = (3/2) \{ 2[5 - \cos(Ql_B N_B)] / 3(Ql_B N_B)^2 \\ & - 2\sin(Ql_B N_B) / (Ql_B N_B)^3 \\ & - 2\text{Si}(Ql_B N_B) / 3Ql_B N_B \}, \quad (21c) \end{aligned}$$

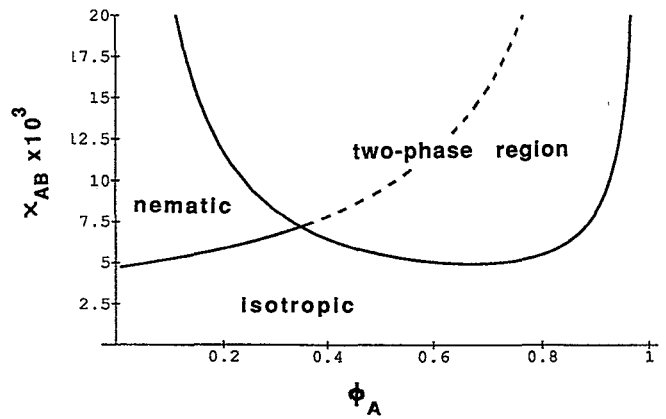


FIG. 2. Phase diagram for a binary blend mixture of a flexible (A component) and a rigid (B component) polymers with: $N_A=200$, $N_B=800$, $v_A=v_B=1$, and $W_{BB}^1/k_B T \chi_{AB}=0.4$ as predicted by the RPA.

$$\begin{aligned} T_{BB}^0(Q)/N_B \phi_B v_B = & (9/4) \int_0^1 dx (x^2 - 1/3) j_0^2(Ql_B N_B x/2) \\ & = (9/4) \{ -10/9(Ql_B N_B)^2 + \cos(Ql_B N_B) \\ & \times [2/9(Ql_B N_B)^2 - 4/(Ql_B N_B)^4] + \sin(Ql_B N_B) \\ & \times [4/(Ql_B N_B)^5 - 2/3(Ql_B N_B)^3] \\ & + 2\text{Si}(Ql_B N_B) / 9(Ql_B N_B) \}, \quad (21d) \end{aligned}$$

where $j_0(X) = \sin(X)/X$ is the spherical Bessel function of order zero and $\text{Si}(X)$ is the sine integral function:

$$\text{Si}(X) = \int_0^X dt \sin(t)/t. \quad (22)$$

The isotropic-to-nematic transition is determined by the condition $[1 - (2/3)T_{BB}^0 W_{BB}^1] = 0$, whereas the spinodal line is obtained when the denominator of X_{AA} is equal to zero. These conditions are evaluated in the thermodynamic limit ($Q=0$) in Fig. 2 for a Maier-Saupe interaction parameter $W_{BB}^1/k_B T = 0.4\chi_{AB}$ and for $N_A=200$, $N_B=800$, $v_A=v_B=1$. When the volume fraction of component A (ϕ_A) is low, the isotropic-to-nematic phase transition is reached first whereas at high ϕ_A the spinodal line is reached first. Because the isotropic-to-nematic phase transition is of first order¹⁰ ("weakly" first order transition), a narrow two-phase channel¹⁰ should exist between the isotropic and the nematic phases. Because of the approximation involved (RPA, no nematic interaction for the flexible polymers, etc.) such a channel is not predicted in our calculations.¹⁰ The RPA formalism is not valid beyond the spinodal line.

BINARY MIXTURE OF A FLEXIBLE AND A RIGID ROD DIBLOCK COPOLYMER

In the case of a diblock copolymer with flexible A blocks (freely jointed chains) and rigid B blocks (rigid rods), the intercomponent ideal structure factors are no longer null therefore leaving only: $R_{AA}^0 = R_{AB}^0$

$=T_{AA}^0=T_{AB}^0=0$. The volume fractions become related to the molecular weights: $\phi_A=N_A v_A/(N_A v_A+N_B v_B)$, $\phi_B=1-\phi_A$. The general result in the matrix form reduces in this

case to the following generalization of the Liebler formula¹³ to include chain stiffness:

$$X_{AA}=\{(2/3)W_{BB}^1[R_{BB}^{02}X_{AA}^0-2R_{BA}^0R_{BB}^0X_{AB}^0+R_{BA}^0X_{BB}^0]+[1-(2/3)T_{BB}^0W_{BB}^1](-X_{AB}^{02}+X_{AA}^0X_{BB}^0)\}/\{(X_{AA}^0+2X_{AB}^0+X_{BB}^0+2\chi_{AB}X_{AB}^{02}-2\chi_{AB}X_{AA}^0X_{BB}^0)[1-(2/3)T_{BB}^0W_{BB}^1]+(2/3)W_{BB}^1[R_{BA}^{02}+2R_{BA}^0R_{BB}^0+R_{BB}^0]- (4/3)\chi_{AB}W_{BB}^1[R_{BB}^{02}X_{AA}^0-2R_{BA}^0R_{BB}^0X_{AB}^0+R_{BA}^0X_{BB}^0]\}, \quad (23)$$

where the ideal structure factors X_{AA}^0 , X_{BB}^0 , R_{BB}^0 , and T_{BB}^0 are given in the previous section and the remaining ones are given below

$$X_{AB}^0(Q)/(N_A\phi_A v_A N_B\phi_B v_B)^{1/2}=\{[1-j_0(Ql_A)^{N_A}]/N_A[1-j_0(Ql_A)]\} \int_0^1 dx j_0(Ql_B N_B x/2)\cos(Ql_B N_B x/2) \\ =\{[1-j_0(Ql_A)^{N_A}]/N_A[1-j_0(Ql_A)]\}\text{Si}(Ql_B N_B)/Ql_B N_B \quad (24)$$

$$R_{BA}^0(Q)/(N_A\phi_A v_A N_B\phi_B v_B)^{1/2}=\{[1-j_0(Ql_A)^{N_A}]/N_A[1-j_0(Ql_A)]\} \int_0^1 dx [3x^2-1/2]j_0(Ql_B N_B x/2)\cos(Ql_B N_B x/2) \\ =\{[1-j_0(Ql_A)^{N_A}]/N_A[1-j_0(Ql_A)]\}(3/2)\{-\cos(Ql_B N_B)/(Ql_B N_B)^2 \\ -\text{Si}(Ql_B N_B)/3(Ql_B N_B)+\sin(Ql_B N_B)/(Ql_B N_B)^3\}. \quad (25)$$

These results agree with those reported by Holyst and Schick.¹¹ The structure factor $X_{AA}(Q)$ has been plotted in Fig. 3 using the following parameters: $N_A=200$, $N_B=800$, $v_A=v_B=1$, $\chi_{AB}N=19$ (where $N=N_A+N_B$), and for three values of the Maier-Saupe interaction parameter: $W_{BB}^1/k_B T\chi_{AB}=0, 0.4$, and 0.6 . Orientational ordering is seen to increase as the Maier-Saupe parameter increases. The location of the peaks in Fig. 3 corresponds to $Ql_N N_B=2\pi, 4\pi$ and depends only on the length of the rigid rods ($l_N N_B$). Figure 4, on the other hand, represents the effect of varying

the relative molecular weight of the flexible block with $v_A=v_B=1$, $\chi_{AB}N=15$, $W_{BB}^1/k_B T\chi_{AB}=0.4$ and N_A/N taking on three different values: $N_A/N=0.2, 0.7$, and 0.8 . The first curve corresponds to a point in the phase diagram which is closer to the isotropic-to-nematic phases transition line than to the isotropic-to-lamellar transition line. The other two curves correspond to points that are closer to the isotropic-to-lamellar spinodal line instead. The word "lamellar" is used to name the ordered phase even though this could have another morphology since the RPA cannot

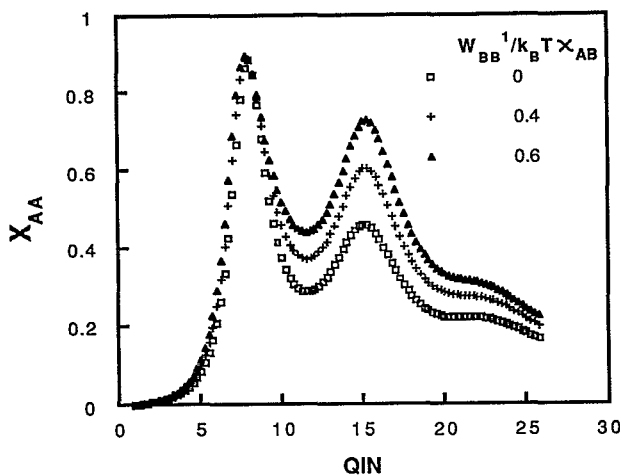


FIG. 3. Structure factor for a melt of diblock copolymers made of flexible freely jointed (A component) and rigid (B component) blocks with: $N_A=200$, $N_B=800$, $v_A=v_B=1$, $l_A=l_B=1$, and $\chi_{AB}N=19$ (where $N=N_A+N_B$). The three curves correspond to $W_{BB}^1/k_B T\chi_{AB}=0, 0.4$, and 0.6 .

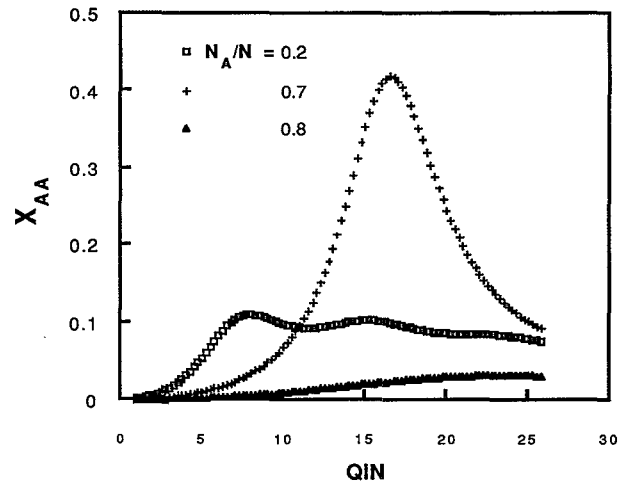


FIG. 4. Structure factor for a melt of diblock copolymers made of flexible freely jointed (A component) and rigid (B component) blocks with: $\chi_{AB}N=15$ (where $N=N_A+N_B$), $W_{BB}^1/k_B T\chi_{AB}=0.4$, $v_A=v_B=1$ and $l_A=l_B=1$. The three curves correspond to $N_A/N=0.2, 0.7$, and 0.8 , respectively.

predict the symmetry of the ordered phase. Figure 4 shows that when the rigid rods get shorter, the number of peaks decreases (from two to one) because the first peak occurs at higher Q so that the higher order peaks are completely "damped" out. Note that the RPA works better¹⁰ for cases where $N_A < N_B$.

Various phase diagrams for diblock copolymers have been investigated by Holyst and Schick.¹¹ For instance, our Fig. 3 is similar to their¹¹ Fig. 3(a). The sharpness of the peaks in Fig. 3 points to the fact that the domain boundaries (in direct space) are sharper in this system. When the rigid rods get shorter (Fig. 4), this sharpness decreases leading to a regular sinusoidal profile for the density of rigid rods. It should be emphasized that the peaks observed here are the results of taking orientational moments of the structure factor for a rigid rod; these peaks appear even in the ideal (unperturbed) rigid rod case [$R_{BB}^0(Q)$ and $T_{BB}^0(Q)$, e.g., show peaks at $Q/N_B = 2\pi, 4\pi$]. In practice, due to polydispersity, such sharp peaks may not be observable experimentally.

CONCLUSIONS

Using the RPA formalism, general expressions for the static structure factor for melt and blend mixtures of stiff polymers have been derived. Both spinodal and nematic phase transitions are built into the formalism. Upon cooling, the isotropic-to-nematic transition could occur either before or after the spinodal transition depending on the volume fraction of the rigid polymer components and on the relative strength of the Flory–Huggins (χ 's) and Maier–Saupe (W_i 's) interaction parameters. The RPA approach breaks down beyond the spinodal transition line. Specific results have been presented in the cases of a binary homopolymer blend and of a diblock copolymer where one of the components is rigid and the other one flexible. The formalism presented here agrees with previously reported results by Doi *et al.*^{7–9} and Holyst and Schick.^{10,11} It could

be useful for the qualitative interpretation of SANS data from mixtures of liquid crystals and flexible polymers. In a binary mixture, the flexible component could be deuterated in order to increase the contrast offered to neutrons. In our applications of the present RPA formalism to mixtures of flexible and rigid polymers, nematic interactions between flexible (freely jointed) chains have been neglected. In order to recover the narrow two-phase channel between the isotropic and nematic phases (observed in lyotropic system^{14,15} for example), these interactions should be included.¹⁰ The inclusion of non-mean-field effects yields a more complete picture¹⁰ (the calculations, however, become nontractable analytically).

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