

# SANS from Homogeneous Polymer Mixtures: A Unified Overview

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An overview of various modeling methods used to understand small angle neutron scattering (SANS) data from homogeneous polymer systems is presented. First, calculations of single macromolecule structure factors are reviewed for many chain architectures and monomer block configurations such as linear, ring, star branched, comb grafted chains and regular "starburst" dendrimers either in the homopolymer or copolymer forms. Then, the different methods used to model "concentration" effects in polymer solutions (dilute, semidilute, concentrated), polymer melts and blend mixtures are summarized on the basis of the random phase approximation. Polymer chain stiffness is also included in the formalism so that mixtures of liquid crystals and flexible polymers in the single-phase region can be described. Specific examples are included along with various SANS data that were analyzed within this framework. This overview is meant to be a guide to help build up models in order to understand SANS data from many homogeneous polymer systems. It is not meant to be complete and is not an exhaustive review of the literature in the field. Most of the results discussed have been previously published and are brought together here in a unified self-contained approach.

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## 1 Introduction

Since its introduction in the early 1970s, the small angle neutron scattering (SANS) method has had a substantial impact on polymer research. When used with partially deuterated polymers, SANS permits a close monitoring of macromolecular conformations in polymer solutions, melts, and blend mixtures. This advantage has made it a unique tool for the understanding of the morphology of polymer materials and of the relationship between their structures and physical properties.

Macromolecular systems can be modeled fairly well owing to the pioneering work of many scientists such as P. Debye (flexible chains, etc.), P. Flory (gaussian chains, theta temperature, etc.), H. Kuhn (polymer chain stiffness, etc.), W. Stockmayer (gelation, branching, etc.), B. Zimm (dilute solutions, normal modes, etc.), P.G. de Gennes (random phase approximation, scaling ideas, etc.), H. Yamakawa (wormlike chains, etc.), H. Benoit (star polymers, multicomponent description, etc.), A.Z. Akcasu (high concentration method, first cumulant, etc.), K.F. Freed (renormalization group theory) to name only a few. The SANS technique has shown with no ambiguity, for instance, that polymer coils form random walk trajectories when they are in the melt or bulk states [1]. This means that correlations between monomers along the chain backbone are screened by other surrounding chains, so that the chain “forgets” quickly (after one step) about where its other parts are [2]. SANS has been most valuable for the monitoring of chain conformations in a wide variety of polymer systems (solutions, melts, solids) and with a wide array of experimental conditions. It has also proven its usefulness, during the last few years, as a thermodynamic probe used to map out phase diagrams of polymer blend mixtures.

Blending of polymers is necessary for better controlled physical properties of polymeric materials. Unfortunately, most polymer blends are immiscible. The binary mixtures that are known to be miscible have been very valued systems for studying the thermodynamics of phase separation. Conformations in the miscible region, concentration fluctuations close to the immiscible region as well as the delimitation of the spinodal line have been well understood for a number of polymer blend systems using the SANS technique with deuterium labeling of one of the components. Our description of homopolymer and/or copolymer blends stops at the spinodal line in the sense that heterogeneous multiphase systems fall outside of the scope of this overview which is devoted to homogeneous single-phase mixtures only.

Advances in the modeling of polymer systems, such as the random phase approximation (RPA) [3, 4], thoroughly reviewed here, have made it possible to analyze SANS data from widely different and seemingly complicated mixtures of various polymer architectures at various concentrations and temperatures. Old modeling methods, such as the inverse Zimm formula [5] (which is the basis of the Zimm Plot), or more recent modeling methods such as the high concentration method [6–8], fall within the scope of the present overview and are

discussed in detail since they constitute major tools for the understanding of SANS data from polymer solutions. Some misgivings as to the validity of using such "mean field" approaches to describe polymer solutions (where concentration fluctuations are important) have been presented in the literature [4, 9, 10]. A generalization of de Gennes' RPA formula [3, 4] based on a direct computations method [11, 12] or on a multicomponent matrix approach [13–15] are also reviewed and reproduced in an appendix in order to clarify what assumptions are made for its derivation. Another calculation [16] applied the RPA to ternary polymer blends. A further generalization of the multicomponent RPA method to include polymer chain stiffness is included. These recent results will be useful for the qualitative treatment of mixtures of liquid crystals and flexible polymers in the single-phase region. They can predict the isotropic-to-nematic phase transition as well as the spinodal line.

On the other hand, advances in chemical synthesis have made possible the polymerization of many complicated chain architectures. Linear, ring, star branched and comb grafted chains can be made now with high regularity, monodispersity and controlled sequencing of different chemical blocks. For instance, stars can be synthesized with a fraction (say one third) of one arm deuterated, copolymer combs can be made with chemically different monomeric units for the side branches and the backbone, etc. "Dendrimers" [17] ("starburst" or "combburst") are regular polymers that grow through multifunctional polymerization reactions starting from an initiator core and branching outward with a multiplication of the number of monomeric blocks from one generation to the next. Structure factors for "starburst" dendrimers are presented here as a guide to "build up" such quantities for other chain architectures. Polymer networks have been the subject of a number of SANS investigations [18]; however, as yet, their structure factor has not been successfully calculated making them inappropriate to include in this overview.

The paper is divided into the two main essential parts needed to work out a model for a generic polymer system: first, the single-chain structure factor, and then the inter-chain correlations contribution (also called "concentration" effects). Gaussian coil and random walk statistics are assumed for most of the paper, although, when possible, chain rigidity and chain swelling (or collapse) are included in order to show how these could be taken into account. A simple model, referred to as the "sliding rod" model [19], is used, for instance, to describe polymer chain stiffness between the gaussian coil limit and the rigid rod limit. Many other semiflexible chain models exist [20] but are not included here because of our focus on the simplest models and concepts possible. Monodisperse polymers are assumed throughout the paper. After discussing the two main pieces needed to work out a model (single-chain and inter-chain contributions), some specific examples are discussed and results taken from my recent research topics are included. Subject matters are covered at a basic tractable level.

## 2 Form Factors, Structure Factors

### 2.1 Definitions

In order to introduce some notation and definitions, we consider a polymer block with  $n$  monomers of segment length  $b$ . Defining  $r_{ij}$  as the interdistance between two monomers  $i$  and  $j$  in that block, and  $Q$  as the scattering wave-number (often called scattering “vector”), various types of correlations can be considered depending on the number of summations involved:

$$E(Q) = \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{1n}] \rangle \quad (2.1)$$

$$F(Q) = (1/n) \sum_{i=1}^n \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{1i}] \rangle \quad (2.2)$$

$$P(Q) = (1/n^2) \sum_{i,j=1}^n \langle \exp[-i\mathbf{Q} \cdot \mathbf{r}_{ij}] \rangle. \quad (2.3)$$

$E(Q)$ ,  $F(Q)$  and  $P(Q)$  are the correlations between chain extremities, the form factor and the structure factor respectively and  $\langle \dots \rangle$  represents an average over all possible chain conformations. Note that these expressions are normalized such that they become unity at the zero  $Q$  limit.

The radius of gyration is defined as:

$$R_g^2 = (1/2n^2) \sum_{i,j=1}^n \langle r_{ij}^2 \rangle \quad (2.4)$$

and the low  $Q$  expansion of the structure factor is:

$$P(Q) = 1 - (QR_g)^2/3 \quad (2.5)$$

regardless of what model is used to describe chain statistics. However, the full chain correlations at finite  $Q$  can be calculated only after a chain model is specified. A few simple cases are considered here: flexible gaussian chains, rigid rods, “sliding rods” for semiflexible chains and freely-jointed chains.

### 2.2 Ideal Gaussian Polymer Blocks

Gaussian coils are characterized by a gaussian probability distribution [2] for the monomers and describe adequately flexible polymer blocks. Ideal chains follow random walk statistics, i.e.,

$$\langle r_{ij}^2 \rangle = b^2 |i - j| \quad (2.6)$$

( $b$  being the segment length) as is the case for polymer melts, relaxed polymer solids and polymer solutions under theta conditions (when monomer–monomer and monomer–solvent interactions are equivalent). The polymer chain quickly

“forgets” (after one step) about where its other segments are and the radius of gyration is  $R_g = b(n/6)^{1/2}$ .

In this case, a natural scattering variable is introduced as  $\alpha = Q^2 b^2/6$  so that:

$$E_G(\alpha n) = \exp[-\alpha(n-1)] \quad (2.7)$$

$$\begin{aligned} F_G(\alpha n) &= (1/n) \sum_{i=1}^n \exp[-\alpha(i-1)] \\ &= [1 - \exp(-\alpha n)]/[1 - \exp(-\alpha)]n \end{aligned} \quad (2.8)$$

$$\begin{aligned} P_G(\alpha n) &= (1/n^2) \sum_{i,j=1}^n \exp[-\alpha|i-j|] \\ &= 1/n + 2\{1 - [1 - \exp(-\alpha n)]/[n(1 - \exp(-\alpha))]\}/ \\ &\quad [n(1 - \exp(-\alpha))]. \end{aligned} \quad (2.9)$$

Note that for  $\alpha \ll 1$  and  $n \gg 1$ , but keeping  $\alpha n$  finite, more familiar form and structure factors are recovered:

$$F_G(\alpha n) = [1 - \exp(-\alpha n)]/\alpha n \quad (2.10)$$

$$P_G(\alpha n) = 2[\exp(-\alpha n) - 1 + \alpha n]/(\alpha n)^2. \quad (2.11)$$

This form for  $P_G(\alpha n)$  is the widely used Debye function. Note that for homopolymer chains,  $n$  is large (large degree of polymerization) and  $\alpha$  is small (SANS instruments do not “see” monomer chemistry) so that these last expressions can be used. However, for short block copolymers,  $n$  is not necessarily large and the more general equations are more appropriate to use.

### 2.3 Swollen/Collapsed Gaussian Polymer Blocks

Within Flory’s mean field approximation, biased random walk statistics are characterized by:

$$\langle r_{ij}^2 \rangle = b^2 |i-j|^{2\nu} \quad (2.12)$$

where  $\nu$  is the excluded volume parameter that takes on values between  $\nu = 1/3$  for collapsed chains, to  $\nu = 3/5$  for fully swollen chains, via  $\nu = 1/2$  for ideal coils (note that fully swollen chains become ideal coils in 4 dimensional space). The radius of gyration is in this case:  $R_g = b[n^{2\nu}/(2\nu+1)(2\nu+2)]^{1/2}$ . The various correlation factors become:

$$E_G(\alpha n) = \exp[-\alpha(n-1)^{2\nu}] \quad (2.13)$$

$$F_G(\alpha n) = (1/n) \sum_{i=1}^n \exp[-\alpha(i-1)^{2\nu}] \quad (2.14)$$

$$P_G(\alpha n) = (1/n^2) \sum_{i,j=1}^n \exp[-\alpha|i-j|^{2\nu}]. \quad (2.15)$$

Due to the fact that these progressions cannot be summed, the continuous chain limit ( $\alpha \ll 1$  and  $n \gg 1$ , but keeping  $\alpha n$  finite) is taken so that the following results can be obtained:

$$F_G(\alpha n) = [1/2\nu X^{1/2\nu}] \gamma(1/2\nu, X) \quad (2.16)$$

$$P_G(\alpha n) = [1/\nu X^{1/2\nu}] \{ \gamma(1/2\nu, X) - [1/X^{1/2\nu}] \gamma(1/\nu, X) \} \quad (2.17)$$

where  $X = \alpha n^{2\nu}$  has been defined and  $\gamma(a, X)$  is the incomplete gamma function:

$$\gamma(a, X) = \int_0^X dt \exp(-t) t^{a-1}. \quad (2.18)$$

Note that  $\gamma(a, \infty) = \Gamma(a)$  is the gamma function. This structure factor ( $P_G(\alpha n)$ ) reproduces the Debye function in the limit  $\nu = 1/2$ . The high  $Q$  limit ( $\alpha \gg 1$ ) of the structure factor is:

$$P_G(\alpha n) = [1/\nu X^{1/2\nu}] \{ \Gamma(1/2\nu) - [1/X^{1/2\nu}] \Gamma(1/\nu) \} \quad (2.19)$$

which varies from  $3\Gamma(3/2)/(\alpha^{3/2} n)$  for fully collapsed chains to  $2/(\alpha n)$  for ideal chains to  $5\Gamma(5/6)/3(\alpha^{5/6} n)$  for fully swollen chains. Flory introduced a characteristic transition temperature (called theta temperature and defined for infinite molecular weights) for which the monomer–monomer, solvent–solvent and monomer–solvent interactions are equivalent making the chain appear “ideal” (as if it were in a bulk environment). Below this temperature, chains start collapsing while above it, they start swelling.

## 2.4 The Temperature Blob Model

In cases of intermediate degrees of chain swelling, the temperature blob approach [21] has been useful in modeling excluded volume effects. It consists in defining a blob comprising a number  $n_\tau$  of monomers that obey ideal chain statistics while the blobs themselves show excluded volume effects:

$$\begin{aligned} \langle r_{ij}^2 \rangle &= b^2 |i - j|; & |i - j| < n_\tau \\ \langle r_{ij}^2 \rangle &= n_\tau b^2 (|i - j|/n_\tau)^{2\nu}; & |i - j| > n_\tau. \end{aligned} \quad (2.20)$$

This approach involves two parameters ( $\nu$  and  $n_\tau$ ) to describe chain swelling and is characterized by an unphysical break of chain statistics at  $|i - j| = n_\tau$ . Due to the awkwardness of the numerical generation of the structure factor when  $\nu \neq 1/2$ , a simple Debye function with swollen radius of gyration is often used (in an adhoc fashion) to fit scattering data from polymer solutions.

## 2.5 Rigid Rods

For rigid rods, the natural scattering variable is  $\alpha = Qb$ , and the conformational averaging becomes an averaging over orientations. Here also, in order to obtain compact analytical results, one has to go to the continuous chain limit ( $\alpha \ll 1$

and  $n \gg 1$ , but keeping  $\alpha n$  finite) which gives:

$$E_R(\alpha n) = \sin(\alpha n)/\alpha n \quad (2.21)$$

$$F_R(\alpha n) = (1/n) \sum_i \sin(\alpha i)/\alpha i = \text{Si}(\alpha n)/\alpha n \quad (2.22)$$

$$\begin{aligned} P_R(\alpha n) &= (1/n^2) \sum_{i,j}^n \sin[\alpha|i-j|]/[\alpha|i-j|] \\ &= 2\{[\cos(\alpha n) - 1]/\alpha n + \text{Si}(\alpha n)\}/\alpha n \end{aligned} \quad (2.23)$$

where the sine integral function has been defined as:

$$\text{Si}(\alpha n) = \int_0^{\alpha n} dt \sin(t)/t. \quad (2.24)$$

Note that in cases where the large  $n$  assumption is not valid, precise form and structure factors should be generated by performing the summations numerically.

Various models are available [20] to describe semiflexible chains. Some are based on expansions either close to the gaussian coil or to the rigid rod limits, while others interpolate between these two chain stiffness limits. One of these, the sliding rod model [19], is described here because of its inherent simplicity.

## 2.6 The Sliding Rod Model

The sliding rod model assumes that the chain behaves as a rigid rod for contour lengths corresponding to a characteristic number  $n_c$  of monomers ( $bn_c$  is used as a stiffness parameter reminiscent of the Kuhn length) whereas longer chain portions follow ideal chain gaussian statistics (flexible coils). The structure factor is given by:

$$\begin{aligned} P_{SR}(\alpha_1 n, \alpha_2 n) &= (1/n^2) \left\{ \sum_{i-j=1}^{n_c} \sin[\alpha_1|i-j|]/\alpha_1|i-j| \right. \\ &\quad \left. + \sum_{i-j=n_c+1}^n \exp(-\alpha_2|i-j|) \right\} \end{aligned} \quad (2.25)$$

where  $\alpha_1 = Qb$  and  $\alpha_2 = Q^2 b^2/6$ . Defining structure factors for a rigid rod  $P_R(\alpha_1 n)$  and a gaussian coil  $P_G(\alpha_2 n)$  (see above), one obtains:

$$\begin{aligned} P_{SR}(\alpha_1 n, \alpha_2 n) &= (1/n^2) \{ n_c^2 P_R(\alpha_1 n) \\ &\quad + (n - n_c - 1)^2 P_G(\alpha_2 n - \alpha_2 n_c - \alpha_2) \}. \end{aligned} \quad (2.26)$$

## 2.7 Freely-Jointed Chains

Freely jointed chains are another form of flexible chains because of the free rotation of the universal joint between monomers; however, monomers are



assumed to be rigid “sticks” of size  $b$ . In this case, the structure factor can be calculated:

$$P_{\text{FJC}}(\alpha n) = \frac{\{[1 + j_0(\alpha)]n/[1 - j_0(\alpha)] - 2j_0(\alpha)[1 - j_0^2(\alpha)]\}}{[1 - j_0(\alpha)]^2/n^2} \quad (2.27)$$

where  $\alpha = Qb$  and  $j_0(\alpha) = \sin(\alpha)/\alpha$  is the spherical Bessel function of order zero.

Now that self correlations within the same block (or chain) have been calculated, we will introduce cross correlations between different blocks.

## 2.8 Inter-Block Cross Correlations

Consider two polymer blocks A and C with  $n_A$  and  $n_C$  monomers of segment lengths  $b_A$  and  $b_C$  in each, separated by a third block B with  $n_B$  monomers of segment length  $b_B$ . Correlations between the A and C blocks are [22]:

$$\begin{aligned} P(\alpha_A n_A, \alpha_C n_C) &= (1/n_A n_C) \sum_{i=1}^{n_A} \sum_{j=1}^{n_C} \langle \exp[-\mathbf{Q} \cdot \mathbf{r}_{ij}] \rangle \\ &= F(\alpha_A n_A) E(\alpha_B n_B) F(\alpha_C n_C) \end{aligned} \quad (2.28)$$

where completely free joints (random bond angles) have been assumed between blocks A/B and B/C and angular correlations have been neglected.  $E(\alpha n)$  and  $F(\alpha n)$  could be for rigid rods or gaussian coils depending on the stiffness of the A, B, and C blocks.

Now that the needed tools for calculating intra-block and interblock correlations have been developed, we will consider various polymer architectures in the next sections.

## 3 Structure Factors for Various Chain Architectures

### 3.1 Linear Chain

Consider a linear chain with  $N$  monomers of segment length  $b$ . The static scattering function is defined as:  $S(Q) = N^2 P(\alpha N)$ . For convenience in notation, it can also be written as:

$$S(Q) = N + N^2 Q[\alpha, N] \quad (3.1)$$

where:

$$Q[\alpha, N] = (2/N^2) \sum_{k=1}^N (N - k) E(\alpha k) \quad (3.2)$$

represents the non-self ( $i \neq j$ ) correlations. Here,  $\alpha = Q^2 b^2 / 6$  if the chain is

flexible or  $\alpha = Qb$  if it is a rigid rod. Note that:

$$Q[\alpha, N] = P(\alpha, N) - 1/N \quad (3.3)$$

and that  $Q[0, N] = (N - 1)/N$ . Efforts are being made to keep  $N$  finite (for the sake of describing short blocks) to the extent possible.

### 3.2 Ring Homolymer

Since modeling rigid rings is trivial. We assume gaussian statistics (ideal chains). Consider a ring polymer of  $N$  monomers of segment length  $b$ . The static scattering function is given by the following identical expressions:

$$S(Q) = \sum_{i,j}^N \exp[-\alpha|i-j|(1-|i-j|/N)] \quad (3.4a)$$

$$= N + 2N \sum_k^N (1-k/N) \exp[-\alpha k(1-k/N)] \quad (3.4b)$$

$$= N \sum_k^N \exp[-\alpha k(1-k/N)] \quad (3.4c)$$

$S(Q)$  can be readily calculated [23] in the continuous chain limit ( $\alpha \ll 1$  and  $N \gg 1$ , but keeping  $\alpha N$  finite) as:

$$N^2 [\exp(-U^2)/U] \int_0^U dt \exp(t^2) \quad (3.5)$$

where  $U = (\alpha N)^{1/2}/2$  and the Dawson integral can be generated numerically (it is part of some computer libraries).

### 3.3 Diblock Linear Copolymer

Consider a diblock A and B linear copolymer ( $n_A, n_B, \alpha_A, \alpha_B$ ). The static scattering function  $S(Q)$  is the sum of three contributions:

$$S(Q) = S_{AA}(Q) + S_{BB}(Q) + 2S_{AB}(Q) \quad (3.6)$$

where:

$$S_{AA}(Q) = n_A^2 P(\alpha_A n_A) \quad (3.7a)$$

$$S_{BB}(Q) = n_B^2 P(\alpha_B n_B) \quad (3.7b)$$

$$S_{AB}(Q) = n_A n_B F(\alpha_A n_A) F(\alpha_B n_B). \quad (3.7c)$$

Note that  $S_{AB}(Q)$  can also be written as:

$$S_{AB}(Q) = [n^2 P(\alpha n) - n_A^2 P_A(\alpha_A n_A) - n_B^2 P_B(\alpha_B n_B)]/2 \quad (3.7d)$$

where  $\alpha = (\alpha_A n_A + \alpha_B n_B)/n$  and  $n = n_A + n_B$ .

### 3.4 Diblock Ring Copolymer

Consider a diblock A and B cyclic copolymer ( $n_A, n_B, \alpha_A, \alpha_B$ ). As in the linear case, the scattering function is the sum of three contributions with, however:

$$S_{AA}(Q) = \sum_{i,j}^{n_A} \exp[-\alpha_A |i-j|(1-|i-j|/n)] \quad (3.8a)$$

$$= n_A + 2n_A \sum_k^{n_A} (1-k/n_A) \exp[-\alpha_A k(1-k/n)] \quad (3.8b)$$

which becomes in the continuous limit:

$$= 2n_A^2 \exp(-\alpha_A n/4) \int_0^1 ds (1-s) \exp[\alpha_A n(n_A s/n - 1/2)^2] \quad (3.8c)$$

where  $n = n_A + n_B$ . As for homopolymer rings, this integral has to be performed numerically.

The cross correlations structure factor  $S_{AB}(Q)$  can be obtained using Eq. (3.7d) where  $n^2 P(\alpha n)$  becomes the structure factor for the full  $n$  monomer ring.

### 3.5 Alternating Copolymer

Consider a regularly alternating linear copolymer (Fig. 1) of  $N_A$  blocks A and  $N_B$  blocks B with  $N$  being the total number of blocks ( $N = N_A + N_B$ ). Each A(B) block is comprised of  $n_A$  ( $n_B$ ) monomers. Two cases will be considered: (1)  $N$  is odd and (2)  $N$  is even.

When  $N$  is odd,  $N_A = (N+1)/2$  and  $N_B = (N-1)/2$ ; the A/A scattering functions are:

$$S_{AA}(Q) = N_A S_{AA}^S(Q) + N_A^2 S_{AA}^I(Q) \quad (3.9)$$

The self block correlations are straightforward to evaluate:

$$S_{AA}^S(Q) = n_A^2 P(\alpha_A n_A) \quad (3.10)$$

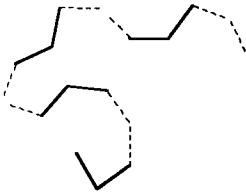


Fig. 1. Regularly alternating block copolymer

and the inter block correlations are:

$$S_{AA}^I(Q) = 2(n_A^2/N_A^2) \sum_{k=1,2}^{N_A} (N_A - k) F^2(\alpha_A n_A) E(\alpha_A n_A)^{(k-1)} E(\alpha_B n_B)^k \quad (3.11)$$

where  $(N_A - k)$  is the number of A/A block combinations that are separated by  $2k$  blocks. In the case of gaussian chains:

$$S_{AA}^I(Q) = n_A^2 F_G^2(\alpha_A n_A) E_G(-\alpha_A n_A) Q_G[\alpha_A n_A + \alpha_B n_B, N_A]. \quad (3.12)$$

Similarly for the A/B scattering function:

$$S_{AB}(Q) = 2(n_A n_B / N_A N_B) \sum_{k=1,2}^{N_A} (N_A - k) F(\alpha_A n_A) F(\alpha_B n_B) E(\alpha_A n_A)^{(k-1)} E(\alpha_B n_B)^{(k-1)} \quad (3.13)$$

and for gaussian chains:

$$S_{AB}(Q) = (N_A N_B n_A n_B) F_G(\alpha_A n_A) F_G(\alpha_B n_B) E_G(-\alpha_A n_A) E_G(-\alpha_B n_B) Q_G[\alpha_A n_A + \alpha_B n_B, N_A]. \quad (3.14)$$

When  $N$  is even,  $N_A = N_B = N/2$  and the corresponding results are:

$$S_{AA}^I(Q) = n_A^2 F_G^2(\alpha_A n_A) E_G(-\alpha_A n_A) Q_G[\alpha_A n_A + \alpha_B n_B, N_A] \quad (3.15)$$

$$S_{AB}(Q) = (N_A N_B n_A n_B) F_G(\alpha_A n_A) F_G(\alpha_B n_B) E_G(-\alpha_A n_A) E_G(-\alpha_B n_B) \{Q_G[\alpha_A n_A + \alpha_B n_B, N_A + 1] + Q_G[\alpha_A n_A + \alpha_B n_B, N_A]\} / 2. \quad (3.16)$$

The B/B and B/A scattering functions are obtained by interchanging the A and B indices. The total scattering function is the sum of all contributions:

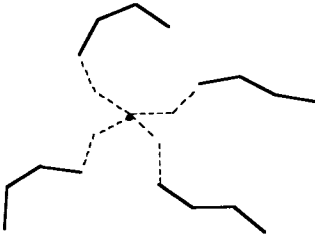
$$S(Q) = S_{AA}(Q) + S_{BB}(Q) + 2S_{AB}(Q) \quad (3.17)$$

provided that the monomers have the same scattering length densities. If not, then the scattering intensity is obtained by weighing the static scattering functions by the appropriate contrast factors (as will be discussed later).

### 3.6 Star Branched Copolymer

Consider a star branched polymer with  $N_b$  branches (Fig. 2). Each branch is composed of two monomeric blocks A and B (copolymer) of  $n_A$  and  $n_B$  monomers respectively (the A block is assumed to be at the outside of the branch). The single-branch correlations  $S_{sb}(Q)$  involve the scattering functions  $S_{AA}^{sb}(Q)$ ,  $S_{BB}^{sb}(Q)$ , and  $S_{AB}^{sb}(Q)$  that were derived [24] for diblock copolymers:

$$S_{sb}(Q) = S_{AA}^{sb}(Q) + S_{BB}^{sb}(Q) + 2S_{AB}^{sb}(Q) \quad (3.18)$$



**Fig. 2.** Four-arm star branched copolymer with three outer A blocks and two inner B blocks

$$\begin{aligned}
 S_{AA}^{sb}(Q) &= n_A^2 F^2(\alpha_A n_A) \\
 S_{BB}^{sb}(Q) &= n_B^2 F^2(\alpha_B n_B) \\
 S_{AB}^{sb}(Q) &= n_A n_B F(\alpha_A n_A) F(\alpha_B n_B),
 \end{aligned} \tag{3.19}$$

while the inter-branch correlations:

$$S_{ib}(Q) = S_{AA}^{ib}(Q) + S_{BB}^{ib}(Q) + 2S_{AB}^{ib}(Q) \tag{3.20}$$

involve triblock correlations that were calculated for alternating copolymers ( $N = 3$  in the preceding section) with  $n_A$  monomers in each of the two outside A blocks and  $2n_B$  monomers in block B:

$$\begin{aligned}
 S_{AA}^{ib}(Q) &= n_A^2 F^2(\alpha_A n_A) E(\alpha_B 2n_B) \\
 S_{BB}^{ib}(Q) &= n_B^2 F^2(\alpha_B n_B) \\
 S_{AB}^{ib}(Q) &= n_A n_B F(\alpha_A n_A) E(\alpha_B n_B) F(\alpha_B n_B).
 \end{aligned} \tag{3.21}$$

The total static scattering function is therefore the sum of the two contributions:

$$S(Q) = N_b S_{sh}(Q) + N_b(N_b - 1) S_{ib}(Q). \tag{3.22}$$

Here also, the various self and cross correlations have to be weighed by the contrast factors in order to obtain the scattered intensity.

### 3.7 Copolymer Comb

Consider a regular copolymer “comb” (Fig. 3) made of  $N_A$  side branches ( $n_A$  monomers in each) and  $N_B$  backbone blocks ( $n_B$  monomers in each). Note that usually  $N_B = N_A + 1$  and that the backbone units are called blocks only for convenience. The various correlation terms involved are [22]:

$$S_{AA}(Q) = N_A S_{AA}^S(Q) + N_A(N_A - 1) S_{AA}^I(Q) \tag{3.23}$$

$$S_{AA}^S(Q) = n_A^2 P(\alpha_A n_A) \tag{3.24}$$

$$S_{AA}^I(Q) = n_A^2 F^2(\alpha_A n_A) Q[\alpha_B n_B, N_A]$$

$$S_{BB}(Q) = (N_B n_B)^2 P(\alpha_B N_B n_B) \tag{3.25}$$

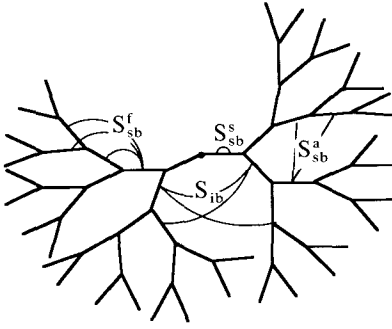


Fig. 4. Dendrimer polymer gel with two branches, five generations and a doubling of the number of units at each generation

The intra-branch self correlations term in the scattering function involves monomer–monomer correlations within the same block. Since there are  $f^{(k-1)}$  blocks in generation  $k$ , the total number of blocks per branch,  $n_B$ , is:

$$n_B = \sum_{k=1}^N f^{k-1} = (f^N - 1)/(f - 1) \quad (3.29)$$

therefore giving (gaussian monomers are assumed):

$$S_{sb}^s(Q) = n^2 P_G(\alpha n). \quad (3.30)$$

The intra-branch cross-correlations between blocks that originate at the same stem involve summations over blocks in generations  $k$  and  $l$  respectively and form factors internal to each block:

$$S_{sb}^f(Q) = 2n^2 [F_G(\alpha n)]^2 \sum_{k=1}^N f^{k-1} \sum_{r=k+1}^N f^{r-k} \exp[-\alpha n(r - k - 1)]. \quad (3.31)$$

These summations can be easily performed giving an analytical expression:

$$S_{sb}^f(Q) = 2n^2 \{ [F_G(\alpha n)]^2 / [\exp(-\alpha n) - 1] \} \\ \times \{ f^N \exp(-\alpha n N) [\exp(\alpha n N) - \exp(\alpha n)] / \\ [\exp(\alpha n) - 1] - f(f^N - 1)/(f - 1) \}. \quad (3.32)$$

Similarly, for the intra-branch cross-correlations between blocks that originate from different stems, three summations are involved: the previous two (over  $k$  and  $r$ ) and a third summation over the number of stem points ( $m$ ) that have to be crossed in order to join the two blocks under consideration:

$$S_{sb}^a(Q) = 2n^2 [F_G(\alpha n)]^2 \sum_{k=2}^N f^{k-1} \sum_{m=1,3}^{2k-3} (f - 1) f^{(m-1)/2} \\ \times \exp[-\alpha n(m - 1)] \\ \times \left\{ 1 + 2 \sum_{r=k+1}^N f^{r-k} \exp[-\alpha n(r - k)] \right\}. \quad (3.33)$$

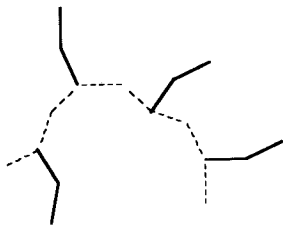


Fig. 3. Copolymer comb with four side branches equally spaced along the chain backbone

$$S_{AB}(Q) = 2(n_A n_B / N_A N_B) F(\alpha_A n_A) \sum_k^{N_B - 1} k F(\alpha_B n_B k). \quad (3.26)$$

If the B monomers are flexible (gaussian statistics)  $S_{AB}(Q)$  becomes:

$$S_{AB}(Q) = 2(n_A n_B / N_A N_B) F(\alpha_A n_A) N_A \{1 - F_G(\alpha_B n_B N_A)\} / [\exp(\alpha_B n_B) - 1] \quad (3.27)$$

or if they are rigid, then:

$$\begin{aligned} S_{AB}(Q) = & 2(n_A n_B / N_A N_B) F(\alpha_A n_A) (N_A / \alpha_B n_B) \\ & \times \{ [1 - \cos(\alpha_B n_B N_A)] \sin(\alpha_B n_B) \\ & + [1 - \cos(\alpha_B n_B)] \sin(\alpha_B n_B N_A) \} / \{ [1 - \cos(\alpha_B n_B)]^2 \\ & + \sin^2(\alpha_B n_B) \} \end{aligned} \quad (3.28)$$

regardless of whether the A monomers are flexible (use  $F_G(\alpha_A n_A)$ ) or rigid (use  $F_R(\alpha_A n_A)$ ). Note that orientational correlations have been neglected.

### 3.8 Starburst Dendrimer

Consider a regular starburst dendrimer [17] formed of  $N_b$  branches. Each branch is formed of  $N$  generations of monomeric blocks going from the first generation at the core to higher generations outside. The number of blocks is multiplied by a factor  $f$  (usually  $f = 2$ ) in going from one generation to the next. Note that the “functionality” parameter is defined here as  $f + 1$ . Each block is composed of  $n$  monomers forming gaussian links with segment length  $b$ .

The calculations of the various structure factors for a dendrimer are rather straightforward [25], but somewhat tedious. There are four main contributions to these correlations: (1) one intrabranched self-correlations part,  $S_{sb}^s$ , (2) one intra-branch cross-correlations part between blocks that originate from the same stem,  $S_{sb}^f$ , (3) one intra-branch cross-correlations part between blocks that originate from different stems,  $S_{sb}^a$ , and (4) one interbranch correlations part  $S_{ib}$ . These various correlations are sketched in Fig. 4.

In other words, in going from block  $k$  to a block  $r$ , one has to meet  $m$  stems with  $(f - 1)f^{(m-1)/2}$  as the number of possibilities. The summations, here also, can be performed giving:

$$S_{sb}^a(Q) = 2n^2 [F_G(\alpha n)]^2 \{ (f - 1) / [f \exp(-2\alpha n) - 1] \} \\ \times \{ A(Q) + B(Q) \} \quad (3.34)$$

$$A(Q) = [f^{2N} \exp(-2\alpha n N) - f^2 \exp(-2\alpha n)] / \\ [f^2 \exp(-2\alpha n) - 1] - (f^N - f) / (f - 1) \\ B(Q) = 2 \{ f^N \exp(-\alpha n N) [f^N \exp(-\alpha n N) - f \exp(-\alpha n)] / \\ [f \exp(-\alpha n) - 1] \\ - f \exp(-\alpha n) [f^{2N} \exp(-2\alpha n N) - f^2 \exp(-2\alpha n)] / \\ [f^2 \exp(-2\alpha n) - 1] - f^N \exp(-\alpha n N) [\exp(\alpha n N) - \exp(\alpha n)] / \\ [\exp(\alpha n) - 1] + f \exp(-\alpha n) (f^N - f) / \\ (f - 1) \} / [f \exp(-\alpha n) - 1] .$$

Note that this term is proportional to  $(f - 1)$  and goes to zero for star-branched polymers ( $f = 1$ ).

Finally, the inter-branch correlations are:

$$S_{ib}(Q) = n^2 [F_G(\alpha n)]^2 \sum_{k=1}^N f^{k-1} \sum_{r=1}^N f^{r-1} \exp[-\alpha n(r+k-2)] \quad (3.35)$$

and are summed up to give:

$$S_{ib}(Q) = n^2 [F_G(\alpha n)]^2 [f^N \exp(-\alpha n N) - 1]^2 / \\ (f \exp(-\alpha n) - 1)^2 . \quad (3.36)$$

The total scattering function is the sum of all of these partial structure factors:

$$S(Q) = N_b [S_{sb}^s(Q) + S_{sb}^f(Q) + S_{sb}^a(Q)] + N_b (N_b - 1) S_{ib}(Q) . \quad (3.37)$$

This scattering function goes to the square of the total number of monomers in the gel,  $(nN_b n_B)^2$ , at the zero  $Q$  limit as it should.

The calculations presented here agree with those of Burchard et al. [26] who used cascade theory to investigate the case corresponding to  $f = 2$ . In order to derive these results, we have assumed ideal gaussian monomer blocks that can cross each other ("phantom" chains). This is unrealistic for high functionality where the monomer density becomes so high that the reaction sites get screened therefore stopping the polymerization reaction after about 10 generations. Moreover, monomer blocks that are far from the core find themselves in "stretched" configurations (with enhanced excluded volume) due to the lack of available space. Excluded volume can be incorporated either at the outset in which case the summations would have to be performed numerically or in an ad-hoc fashion (as mentioned before). The approach presented here is, however,



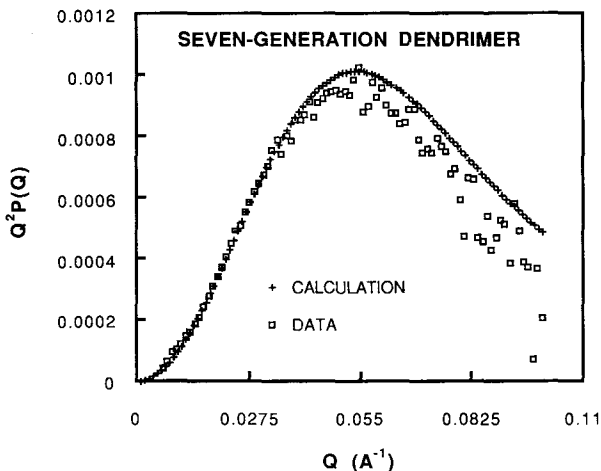


Fig. 5. Kratky plot for SANS data taken from solutions of starburst polyamidoamine dendrimers with seven generations in deuterated water (extrapolated to zero concentration) and comparison with the gaussian blocks dendrimer model with  $b = 0.48$  nm,  $n = 10$ ,  $N = 7$ ,  $N_b = 3$  and  $f = 2$ . Salt was added to the solution in order to screen out the coulomb interactions

a first start in the modeling of such complicated structures as shown in Fig. 5 where SANS data taken from solutions of starburst polyamidoamine dendrimers with seven generations in deuterated water are compared with various models including the gaussian blocks dendrimer model described here (with  $b = 0.48$  nm,  $n = 10$ ,  $N = 7$ ,  $N_b = 3$  and  $f = 2$ ). In order to reach the single dendrimer scattering limit, low concentrations (less than 1% volume fraction) were measured and data were extrapolated to zero concentration.

## 4 Dilute Polymer Solutions

The single-chain structure factors calculated in the previous sections correspond to the infinite dilution limit. This limit also corresponds to zero scattering intensity and is not useful so that concentration effects have to be included in the modeling of polymer solutions. First, Zimm's single-contact approximation [5] is reviewed for dilute polymer solutions; then, a slight extension of that formula which applies to semidilute solutions, is discussed.

### 4.1 Zimm's Single Contact Approximation

Consider a dilute polymer solution with  $N_p$  polymer molecules of  $N$  monomers each. The polymer volume fraction  $\phi_p$  is often used as the concentration parameter; it is given by:  $\phi_p = NN_p v_p / (NN_p v_p + N_s v_s)$ , where  $v_p$  and  $v_s$  are the

monomeric and solvent molecule volumes respectively and  $N_s$  is the number of solvent molecules. Note that, sometime, the polymer concentration  $C_p = N_p/V$  ( $V = NN_p v_p + N_s v_s$  being the total sample volume) is used instead.

Zimm's approximation [5] assumes that inter-chain interactions occur only through single contacts. Given two monomers  $i$  and  $j$  that belong to two different chains (say, called 1 and 2), the two-chain distribution function is:

$$P(\mathbf{r}_{1i}, \mathbf{r}_{2j}) = P(\mathbf{r}_{1i})P(\mathbf{r}_{2j}) \left\{ 1 - v \sum_{k,1}^N \delta(\mathbf{r}_{1k,21}) \right\} \quad (4.1)$$

where  $P(\mathbf{r})$  is the single-chain distribution function,  $\mathbf{r}_{1k,21} = \mathbf{r}_{1k} - \mathbf{r}_{21}$ ,  $v$  is the excluded volume during the binary interaction, and  $\delta(\mathbf{r})$  is the Dirac delta function. The scattering function for the whole sample is the sum of two (single-chain and inter-chain) contributions which are:

$$S(Q) = N_p S_{sc}(Q) + N_p(N_p - 1)S_{ic}(Q) \quad (4.2)$$

$$S_{sc}(Q) = N^2 P(\alpha N) \quad (4.3)$$

$$S_{ic}(Q) = - (v/V) N^4 P^2(\alpha N)$$

where we have neglected the Fourier transform of the average polymer density (which is identically zero except at  $Q = 0$  which is an experimentally irrelevant limit):

$$\langle \rho(Q) \rangle = (1/N) \sum_i^N \langle \exp(-i\mathbf{Q} \cdot \mathbf{r}_i) \rangle \sim \delta(Q). \quad (4.4)$$

This is equivalent to assuming a constant polymer density ( $\langle \rho(\mathbf{r}) \rangle$ ) in configuration space. The second virial coefficient  $A_2$  is related to  $v$  as follows:

$$N^2 v = 2M_w^2 A_2 / N_{av} \quad (4.5)$$

where  $M_w$  and  $N_{av}$  are the polymer molecular weight and Avogadro's number respectively. The scattering function is therefore ( $N_p$  being always large):

$$S(Q) = N_p N^2 P(\alpha N) \{ 1 - v C_p N^2 P(\alpha N) \}. \quad (4.6)$$

This formula describes dilute solutions ( $C_p < 1/vN^2$ ) fairly well despite the fact that it ignores macromolecular shape changes during binary chain interactions.

## 4.2 The Inverse Zimm Formula

The inverse Zimm formula involves the following approximate form:

$$\begin{aligned} S^{-1}(Q) &= \{ 1 + v C_p N^2 P(\alpha N) \} / N_p N^2 P(\alpha N) . \\ &= 1/N_p N^2 P(\alpha N) + v/V . \end{aligned} \quad (4.7a)$$

or in terms of volume fractions:

$$S^{-1}(Q) = (v_p^2/V) \{ 1/N \phi_p v_p P(\alpha N) + v/v_p^2 \}. \quad (4.7b)$$

This formula is the basis of the Zimm Plot which consists in plotting the inverse of the scattering intensity,  $S^{-1}(Q)$ , vs  $Q^2$  which shows a linear variation at low  $Q$  and in dilute solutions. Extrapolated values ( $Q \rightarrow 0$ ,  $C_p \rightarrow 0$ ) of the intercept and the slope yield the degree of polymerization  $N$  and the excluded volume  $v$  (or second virial coefficient  $A_2$ ) respectively. Zimm's formula can describe scattering data accurately well into the semidilute concentration region. This region is defined for concentrations above an overlap concentration  $C_p^*$  which is defined in either of the two following ways:

$$C_p^* = M_w/N_{av}R_g^3 \quad \text{or} \quad C_p^* = 3M_w/4\pi N_{av}R_g^3 \quad (4.8)$$

where  $R_g$  is the macromolecular radius of gyration defined before. Note that this overlap concentration does not correspond to a "critical" state of the system. The inverse Zimm formula, which is the "approximation of an approximation", works surprisingly well due to the fact that the second approximation,  $(1-x) \sim 1/(1+x)$ , re-sums higher order terms which account for series of single-contacts. It applies whether gaussian or rigid rod statistics are assumed. Actually, for rigid rods, Zimm's single contact approximation works better because the third and higher virial coefficients are small. Zimm's single contact approximation, however, neglects orientational correlations which can be important in semidilute solutions of rigid rods. Because it does not account for all possible correlations, the inverse Zimm scattering formula is essentially a mean field treatment.

Some misgivings as to the use of such a mean field approach to describe polymer solutions have been presented in the literature [4, 9]. For instance, the mean field approach cannot explain the experimentally observed molecular weight dependence of the excluded volume  $v$  and does not account for entanglements. A renormalization group description of polymer solutions exists in the literature [10]. It is more successful than the mean field description for dilute and semidilute solutions where concentration fluctuations are non-negligible (especially in good solvents). For instance, it can account for the molecular weight dependence of the excluded volume  $v$ . However, due to my lack of knowledge concerning this research area, these are not included here. Moreover, scaling theory arguments [4, 9] and Monte Carlo predictions [27] are available for dilute and semidilute polymer solutions. These, however, cannot be used to fit experimental data (scaling theory cannot predict prefactors and Monte Carlo calculations can be used only to compare trends).

## 5 Concentrated Polymer Solutions

A characteristic concentration  $C_p^{**}$  can be defined [28] to separate the semidilute and concentrated regions:

$$C_p^{**} = C_p^*(R^2/R_0^2)^4 \quad (5.1)$$

where  $R^2$  and  $R_\theta^2$  are the end-to-end chain distances at zero concentration and under theta conditions respectively. As the concentration increases, excluded volume effects start being screened so that they become negligible in polymer melts whereby random walk statistics are recovered (zero second virial coefficient). In semidilute and concentrated regions, one could define concentration blobs between entanglement points. Chains would display excluded volume effects within a concentration blob but the blobs themselves would follow random walk statistics. This approach will not be pursued here. Instead, we will discuss a justification of Zimm's inverse formula in terms of series of single-contacts (the Benoit–Benmouna model [29]) and review the “high concentration method” [6–8] which is an alternative to the Zimm approach and permits the separation of single-chain and interchain structure factors by performing measurements from samples with different deuterated polymer fractions (keeping the total polymer concentration constant).

### 5.1 The Benoit–Benmouna Model

For non-dilute concentrations ( $C_p > 1/vN^2$ ), a binary interaction between two macromolecules can occur either through a direct contact, or through a series of contacts [29] with other chains (third, fourth, etc.). If  $k$  chains are involved, the scattering function is:

$$S(Q) = N_p N^2 P(\alpha N) \{ 1 - v C_p N^2 P(\alpha N) + v^2 C_p^2 N^4 P^2(\alpha N) + \dots + (-v)^k C_p^k N^{2k} P^k(\alpha N) \}. \tag{5.2}$$

This series can be re-summed to give the inverse Zimm formula:

$$S(Q) = N_p N^2 P(\alpha N) / \{ 1 + v C_p N^2 P(\alpha N) \} \tag{5.3}$$

RANDOM PHASE APPROXIMATION

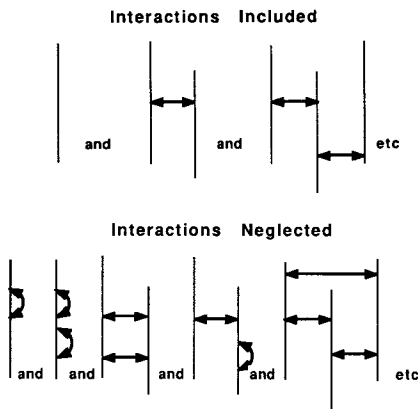


Fig. 6. Schematic representation of the inter-chain interactions that are included or neglected in the random phase approximation

which still does not contain contributions from multiple contacts between two chains. Also neglected are “loop” (sometime called “ring”) interactions within a chain, multiple contacts with other chains, etc. (see Fig. 6). The loop interactions are the ones that account for excluded volume effects and the multiple contacts properly account for the molecular weight dependence of the excluded volume (second virial coefficient) in the renormalization group theory [10]. Moreover, ternary interactions (neglected in the mean field approach) are non negligible in highly branched systems (such as star polymers with a large number of branches).

Effects due to macromolecular shape changes during single-contact interactions can, within the Benoit–Benmouna theory, be included in an ad-hoc fashion by renormalizing the single-chain structure factor to make it concentration dependent. This approach is often used to describe polymer solutions up to the concentrated region.

## 5.2 The High Concentration Method

Consider a polymer solution consisting of protonated and deuterated polymers (concentrations  $C_H$  and  $C_D$  respectively) that have the same degree of polymerization  $N$ . The scattered intensity is proportional to the structure factors for the polymer–polymer correlations  $S_{HH}(Q)$ ,  $S_{DD}(Q)$ ,  $S_{HD}(Q)$ , polymer–solvent correlations  $S_{PS}(Q)$ , and solvent–solvent correlations  $S_{SS}(Q)$ . The protonated, deuterated and solvent molecule scattering lengths are called  $a_H$ ,  $a_D$  and  $a_S$  and  $\{a_p\}$  is the average polymer scattering length. The scattered intensity can be expressed in terms of an absolute cross section as:

$$\begin{aligned} d\Sigma(Q)/d\Omega = & [a_D^2 S_{DD}(Q) + a_H^2 S_{HH}(Q) + 2a_D a_H S_{DH}(Q) \\ & + 2a_S \{a_p\} S_{PS}(Q) + a_S^2 S_{SS}(Q)]/V. \end{aligned} \quad (5.4a)$$

Assuming an incompressible polymer solution allows the elimination of the last two terms:

$$\begin{aligned} d\Sigma(Q)/d\Omega = & [(a_D/v_D - a_S/v_S)^2 v_D^2 S_{DD}(Q) + (a_H/v_H - a_S/v_S)^2 v_H^2 S_{HH}(Q) \\ & + 2(a_D/v_D - a_S/v_S)(a_H/v_H - a_S/v_S)v_D v_H S_{DH}(Q)]/V. \end{aligned} \quad (5.4b)$$

The various structure factors can be split, here also, into single-chain ( $P_D^S(Q)$ , etc.) and interchain ( $P_{DD}^I(Q)$ , etc) parts:

$$\begin{aligned} v_D^2 S_{DD}(Q)/V = & N_D \phi_D v_D [P_D^S(Q) + \phi_D P_{DD}^I(Q)] \\ v_H^2 S_{HH}(Q)/V = & N_H \phi_H v_H [P_H^S(Q) + \phi_H P_{HH}^I(Q)] \\ v_D v_H S_{DH}(Q)/V = & (N_D \phi_D v_D N_H \phi_H v_H)^{1/2} (\phi_D \phi_H)^{1/2} P_{DH}^I(Q). \end{aligned} \quad (5.5)$$

The high concentration method assumes that deuteration does not change chain conformations and interactions (provided that the total polymer concentration is kept constant); i.e., that  $P_D^S(Q) = P_H^S(Q)$  (call it  $P_S^S(Q)$ ) and

$P_{DD}^I(Q) = P_{HH}^I(Q) = P_{DH}^I(Q)$  (call it  $P_I(Q)$ ) along with  $N_D = N_H$  (call it  $N$ ) and  $v_D = v_H$  (call it  $v_P$ ). Defining a “total” polymer–polymer structure factor  $P_T(Q) = P_S(Q) + \phi_P P_I(Q)$ , the main result is obtained in terms of the various contrast factors:

$$\{A_P^2\} = (a_D/v_P - a_S/v_S)^2 \phi_D/\phi_P + (a_H/v_P - a_S/v_S)^2 \phi_H/\phi_P \quad (5.6)$$

$$\{A_P\}^2 = [(a_D/v_P - a_S/v_S)\phi_D/\phi_P + (a_H/v_P - a_S/v_S)\phi_H/\phi_P]^2$$

as:

$$d\Sigma(Q)/d\Omega = [\{A_P^2\} - \{A_P\}^2] N\phi_P v_P P_S(Q) + \{A_P\}^2 N\phi_P v_P P_T(Q) . \quad (5.7)$$

where we have defined the following:  $\{\dots\}$  is a composition averaging and  $\phi_P$  is the total polymer volume fraction ( $\phi_P = \phi_D + \phi_H$ ), so that  $\{A_P\} = a_H\phi_H/\phi_P + a_D\phi_D/\phi_P$  is the average polymer scattering length.

The first contrast factor can be simplified as:

$$[\{A_P^2\} - \{A_P\}^2] = (a_H/v_H - a_D/v_D)^2 \phi_D\phi_H/\phi_P^2 \quad (5.8)$$

where  $\phi$ 's are the volume fractions. The structure factors  $P_S(Q)$  and  $P_T(Q)$  can, therefore, be obtained by performing two measurements (where only  $\phi_D/\phi_H$  is varied, keeping  $\phi_P = \phi_D + \phi_H$  constant). Because  $P_T(Q)$  represents correlations from all monomers with equal weighting, it has a weak  $Q$  dependence. Note that, if the incompressibility assumption had not been made, one would need four different sample compositions instead, in order to determine the four unknown structure factors  $P_S(Q)$ ,  $P_T(Q)$ ,  $S_{PS}(Q)$  and  $S_{SS}(Q)$ .

This method applies for whatever polymer concentration. In practice, it is preferable to use high concentrations in order to increase the signal-to-noise ratio and therefore minimize counting time. However, it can also be applied to semidilute or even dilute solutions where Zimm plots are useful. It also applies not only to linear polymers but also to any form of chain architecture and to deuterated/protonated mixtures in non-solvent matrices such as polymer blends or polymer networks provided that changing the deuterated fraction does not change the homogeneous nature of the mixture (i.e., no change to the chain conformations and interactions).

## 6 Multicomponent Blends of Flexible Homopolymers and Copolymers

### 6.1 The de Gennes Formula

Consider a binary polymer blend (A and B components) of gaussian chains with degrees of polymerization  $N_A$ ,  $N_B$ , volume fractions  $\phi_A$ ,  $\phi_B$ , and monomeric volumes  $v_A$ ,  $v_B$ , respectively. When the blend is a homogeneous phase mixture,

de Gennes [3–4] used the Random Phase Approximation (RPA) to derive an expression for the structure factors of the fully interacting system,  $S_{AA}(Q)$ ,  $S_{BB}(Q)$ ,  $S_{AB}(Q)$ , in terms of those of the “ideal” (non-interacting) system  $S_{AA}^0(Q)$ ,  $S_{BB}^0(Q)$ .  $S_{AA}^0(Q)$  and  $S_{BB}^0(Q)$  are the single chain structure factors (note that  $S_{AB}^0(Q) = 0$  except for A/B copolymers). Assuming effective interaction potentials  $W_{AA}$ ,  $W_{BB}$  and  $W_{AB}$  between A and B monomers, the linear responses of the fluctuating densities  $\langle \rho_A(Q) \rangle$  and  $\langle \rho_B(Q) \rangle$  to externally applied (weakly perturbing) potentials  $U_A$  and  $U_B$  are given by:

$$\begin{aligned} \langle \rho_A(Q) \rangle &= -X_{AA}^0(Q)[U_A + W_{AA}\langle \rho_A(Q) \rangle + W_{AB}\langle \rho_B(Q) \rangle]/k_B T \\ \langle \rho_B(Q) \rangle &= -X_{BB}^0(Q)[U_B + W_{BA}\langle \rho_A(Q) \rangle + W_{BB}\langle \rho_B(Q) \rangle]/k_B T \end{aligned} \quad (6.1)$$

where  $X_{AA}^0(Q)$ , etc., represent “bare” response functions. The isothermal incompressibility ( $\langle \rho_A(Q) \rangle + \langle \rho_B(Q) \rangle = 0$ ) condition allows the elimination of one of the equations. The fluctuation-dissipation theorem relates the response functions to the structure factors as follows:  $X_{AA}^0(Q) = \phi_A v_A S_{AA}^0(Q)/N_A$ , etc. Recall that  $S_{AA}^0(Q) = \langle \rho_A(-Q)\rho_A(Q) \rangle$ . Moreover interacting response functions,  $X_{AA}(Q) = \phi_A v_A S_{AA}(Q)/N_A = N_A \phi_A v_A P(\alpha_A N_A)$ , etc., can be introduced through:

$$\langle \rho_A(Q) \rangle = -X_{AA}(Q)(U_A - U_B)/k_B T \quad (6.2)$$

so that the externally applied potentials can be eliminated from these coupled equations. De Gennes’ formula therefore relates the interacting response to the bare response functions:

$$1/X_{AA}(Q) = 1/X_{AA}^0(Q) + 1/X_{BB}^0(Q) - 2\chi_{AB}/v_0 \quad (6.3)$$

where  $v_0 = (v_A v_B)^{1/2}$  is the “lattice cell” volume and the Flory–Huggins interaction “chi” parameter  $\chi_{AB}$  has been defined as:

$$\chi_{AB} = W_{AB}/k_B T - (W_{AA} + W_{BB})/2k_B T. \quad (6.4)$$

$\chi_{AB}$  appears here as a universal parameter. However, it was found experimentally to depend on a number of factors [30–33] such as temperature, molecular weight, composition, inter-monomer distance (and therefore on the scattering vector  $Q$ ), isotopic constitution, tacticity, microstructure, etc. These dependencies are shortcomings of the crude RPA description. The scattered intensity (macroscopic cross section  $d\Sigma(Q)/d\Omega$ ) is given by:

$$\begin{aligned} (a_A/v_A - a_B/v_B)^2/d\Sigma(Q)/d\Omega &= 1/N_A \phi_A v_A P_G(\alpha_A N_A) \\ &+ 1/N_B \phi_B v_B P_G(\alpha_B N_B) - 2\chi_{AB}/v_0 \end{aligned} \quad (6.5)$$

where we have used scattering length densities  $a_A/v_A$ , etc. This de Gennes formula has found wide use in polymer blends and has been instrumental in determining spinodal points (value of  $\chi_{AB}$  for which the scattered intensity becomes infinite) and mapping out phase diagrams. Zimm’s formula is recovered from the de Gennes formula by taking  $N_A = N$ ,  $N_B = 1$  and defining the

excluded volume by:  $v = v_p^2/v_s \phi_s - 2\chi_{PS} v_p^2/v_0$  ( $v$  is the excluded volume,  $v_s$  is the solvent molecule volume,  $v_0$  is the cell volume, and  $V$  is the sample volume).

## 6.2 The Benoit–Akcasu Generalization

Benoit et al. [11–12] and Akcasu et al. [13–15] have extended de Gennes' formula to describe multicomponent polymer systems. Their results are reproduced in Appendix A in a matrix form (following Akcasu [13–15]). Consider a number of components (noted A, B, etc.) with degrees of polymerization  $N_A$ , etc., volume fractions  $\phi_A$ , etc., monomer volumes  $v_A$ , etc. Some of these components could be block copolymers. Having one of the components (called “matrix” component) as a homopolymer simplifies the calculations. The main result is:

$$\mathbf{X}^{-1}(\mathbf{Q}) = \mathbf{X}_0^{-1}(\mathbf{Q}) + \mathbf{V}(\mathbf{Q}) \quad (6.6a)$$

where  $\mathbf{X}_0(\mathbf{Q})$  and  $\mathbf{X}(\mathbf{Q})$  are the bare and interacting system response matrices respectively and  $\mathbf{V}(\mathbf{Q})$  is an excluded volumes matrix (note that  $v_0^2 \mathbf{V}(\mathbf{Q})$  and not  $\mathbf{V}(\mathbf{Q})$  alone has the dimension of a volume). Equivalently:

$$\mathbf{X}(\mathbf{Q}) = \mathbf{X}_0(\mathbf{Q}) \cdot [\mathbf{I} + \mathbf{V}(\mathbf{Q}) \cdot \mathbf{X}_0(\mathbf{Q})]^{-1} \quad (6.6b)$$

where  $\mathbf{I}$  is the identity matrix. The macroscopic scattering cross section (scalar quantity) is obtained as:

$$d\Sigma(\mathbf{Q})/d\Omega = \mathbf{A}^T \cdot \mathbf{X}(\mathbf{Q}) \cdot \mathbf{A} \quad (6.7)$$

where  $\mathbf{A}$  is a column vector ( $\mathbf{A}^T$  is the corresponding row vector) containing the scattering length densities of the various components (A, B, etc.) and that of the “matrix” (M) component; for example,  $\mathbf{A}_A = (a_A/v_A - a_M/v_M)$ . Appendix A describes multicomponent systems of homopolymers and copolymers. If only copolymers were present, then the “matrix” component would have to be one of the copolymer blocks; this situation involves more complicated expressions which are derived in Appendix B.

In the case of a compressible polymer mixture, the RPA yields the same result but with the potentials matrix  $\mathbf{W}$  replacing the excluded volumes matrix  $\mathbf{V}$ :

$$\mathbf{X} = \mathbf{X}_0 [\mathbf{I} + \mathbf{W} \cdot \mathbf{X}_0]^{-1}$$

Moreover the components of vector  $\mathbf{A}$  change to become  $\mathbf{A}_A = a_A/v_A$ , etc. An Ornstein–Zernike (OZ) approach (referred to as the integral equation theory) describing multicomponent compressible polymer blend mixtures has been extensively investigated [35]. The multicomponent OZ equation relates the “direct” correlations matrix  $\mathbf{C}$  and the “total” (i.e., direct and indirect) correlations matrix  $\mathbf{H}$  as:

$$\mathbf{H} = \mathbf{X}_0 \mathbf{C} \mathbf{X}_0 + \mathbf{X}_0 \mathbf{C} \mathbf{H} \quad (6.8a)$$



By definition, the structure factor is the sum of single-chain (“bare”)  $X_0$  and interchain  $H$  structure factors:  $X = X_0 + H$ . The formal solution to the OZ equations:

$$H = X_0 C X_0 [I - X_0 C]^{-1} \quad (6.8b)$$

is identical to the RPA equation for compressible mixtures provided that a Mean Spherical Approximation (MSA) closure relation,  $C = -W/k_B T$ , is used for large intermonomer distances. The RPA approach considers the mean field potentials  $W$ 's merely as parameters whereas realistic constraints (both for large and short distances) are used in order to solve the integral equations.

### 6.3 Three Component Flexible Homolymer Blend

The multicomponent RPA formalism [11–15] is applied, here, to a ternary incompressible mixture [11–16] of homopolymers (A, B, C). Assuming that component C is the “matrix” component, one is left with  $2 \times 2$  matrices for components A and B:

$$\begin{aligned} X_{AA}^0(Q) &= N_A \phi_A v_A P(\alpha_A N_A) \\ X_{BB}^0(Q) &= N_B \phi_B v_B P(\alpha_B N_B) \\ X_{AB}^0(Q) &= 0 \end{aligned} \quad (6.9)$$

and the third component, C, enters only through:

$$\begin{aligned} V_{AA}(Q) &= 1/X_{CC}^0(Q) - 2\chi_{AC}/v_0 \\ V_{BB}(Q) &= 1/X_{CC}^0(Q) - 2\chi_{BC}/v_0 \\ V_{AB}(Q) &= 1/X_{CC}^0(Q) + \chi_{AB}/v_0 - \chi_{AC}/v_0 - \chi_{BC}/v_0 \end{aligned} \quad (6.10)$$

where the  $N$ 's,  $\phi$ 's, and  $v$ 's are the degrees of polymerization, volume fractions, and monomeric volumes respectively. As customary,  $v_0$  is defined as the volume of the reference cell. The single-chain structure factors  $P(\alpha N)$ 's are taken to be Debye functions for flexible polymers:

$$P(\alpha_A N_A) = 2[\exp(-Q^2 R_{gA}^2) - 1 + Q^2 R_{gA}^2]/Q^4 R_{gA}^4, \quad (6.11)$$

and the radius of gyration is given in terms of the statistical length  $b_A$  as  $R_{gA}^2 = N_A b_A^2/6$ . Partial structure factors can be obtained as:

$$\begin{aligned} X_{AA}(Q) &= X_{AA}^0(1 + V_{BB} X_{BB}^0)/[(1 + V_{AA} X_{AA}^0)(1 + V_{BB} X_{BB}^0) \\ &\quad - V_{AB}^2 X_{AA}^0 X_{BB}^0] \\ X_{BB}(Q) &= X_{BB}^0(1 + V_{AA} X_{AA}^0)/[(1 + V_{AA} X_{AA}^0)(1 + V_{BB} X_{BB}^0) \\ &\quad - V_{AB}^2 X_{AA}^0 X_{BB}^0] \\ X_{AB}(Q) &= -X_{AA}^0 V_{AB} X_{BB}^0/[(1 + V_{AA} X_{AA}^0)(1 + V_{BB} X_{BB}^0) \\ &\quad - V_{AB}^2 X_{AA}^0 X_{BB}^0] \end{aligned} \quad (6.12)$$

where the Q-dependence has been dropped for convenience. Note that the spinodal point is reached when the denominator of the partial structure factors vanishes.

The neutron scattered intensity (macroscopic differential scattering cross section  $d\Sigma(Q)/d\Omega$ ) is given by:

$$\begin{aligned} d\Sigma(Q)/d\Omega = & (a_A/v_A - a_C/v_C)^2 X_{AA}(Q) + (a_B/v_B - a_C/v_C)^2 X_{BB}(Q) \\ & + 2(a_A/v_A - a_C/v_C)(a_B/v_B - a_C/v_C) X_{AB}(Q) \end{aligned} \quad (6.13)$$

where the  $a$ 's are the monomeric scattering lengths for the different components. Note that, due to the incompressibility assumption, this result is independent of the contrast between components A and B. Note also that the three components (A, B, C) do not have to be linear chains; they could correspond to whatever chain architecture provided that the single-chain structure factors are known.

#### 6.4 Blend Mixture of a Copolymer and a Homopolymer (Both Flexible)

We assume, now, that the three component blend considered in the previous section consists of a copolymer A/B (could be a diblock, triblock, etc, or an alternating copolymer) and a homopolymer C [11–15]. The notation and formalism of the previous section hold but now  $X_{AB}^0(Q) \neq 0$  (note that  $X_{AB}^0(Q)$  shows a peak in the scattering function). The partial structure factors become:

$$\begin{aligned} X_{AA}(Q) = & \{X_{AA}^0(1 + V_{BA}X_{AB}^0 + V_{BB}X_{BB}^0) \\ & - X_{AB}^0(V_{BA}X_{AA}^0 + V_{BB}X_{BA}^0)\}/\Delta \\ X_{BB}(Q) = & \{X_{BB}^0(1 + V_{AB}X_{BA}^0 + V_{AA}X_{AA}^0) \\ & - X_{BA}^0(V_{AB}X_{BB}^0 + V_{AA}X_{AB}^0)\}/\Delta \\ X_{AB}(Q) = & \{-X_{AA}^0(V_{AA}X_{AB}^0 + V_{AB}X_{BB}^0) \\ & + X_{AB}^0(1 + V_{AA}X_{AA}^0 + V_{AB}X_{BA}^0)\}/\Delta \end{aligned} \quad (6.14)$$

where:

$$\begin{aligned} \Delta = & (1 + V_{AA}X_{AA}^0 + V_{AB}X_{BA}^0)(1 + V_{BA}X_{AB}^0 + V_{BB}X_{BB}^0) \\ & - (V_{AA}X_{AB}^0 + V_{AB}X_{BB}^0)(V_{BA}X_{AA}^0 + V_{BB}X_{BA}^0). \end{aligned} \quad (6.15)$$

The  $V$ 's and the bare structure factors  $X_{AA}^0(Q)$  and  $X_{BB}^0(Q)$  are still given by the same expressions as in the previous section, and:

$$X_{AB}^0(Q) = (\phi_A \phi_B v_A v_B)^{1/2} S_{AB}^0(Q)/(N_A N_B)^{1/2} \quad (6.16)$$

and  $S_{AB}^0(Q)$  are given in Sect. 3 for diblock, and alternating copolymers for example.

## 7 Multicomponent Blends of Stiff Homopolymers and Copolymers

### 7.1 General RPA Equations for Mixtures of Stiff Polymers

Consider a number  $n$  of stiff polymer components (here “stiff” is used to mean “semiflexible”) and define orientation-dependent ideal and interacting response ( $n \times n$ ) matrices  $\mathbf{X}_0(\mathbf{Q}, \mathbf{u}, \mathbf{u}')$  and  $\mathbf{X}(\mathbf{Q}, \mathbf{u}, \mathbf{u}')$  respectively. In this case, orientational correlations have to be included in addition to the usual isotropic ones. Doi et al. [36–38] have developed the theory for solutions of stiff homopolymers. Their formalism is applied in Appendices C and D to multicomponent blend mixtures of stiff polymers without and with the incompressibility condition respectively. The interaction potentials comprise anisotropic (also called nematic) contributions as well as the usual isotropic ones:

$$\mathbf{W}(\mathbf{u}', \mathbf{u}'') = \mathbf{W}_0 - \mathbf{W}_1(\mathbf{u}'\mathbf{u}'' - \mathbf{I}/3):(\mathbf{u}'\mathbf{u}'' - \mathbf{I}/3), \quad (7.1)$$

where  $\mathbf{u}'$  and  $\mathbf{u}''$  represent the orientations of two test rods. The  $\mathbf{W}_1$  potential factors are the Maier–Saupe interaction parameters. The main result for the case of compressible stiff polymer mixtures (see Appendix C) is:

$$\begin{aligned} \mathbf{X} &= \{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\}^{-1} \\ &\times \{\mathbf{X}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0\} \end{aligned} \quad (7.2)$$

where the matrix  $\mathbf{M} = [\mathbf{I} - (2/3)\mathbf{T}_0 \cdot \mathbf{W}_1]$  has been used,  $k_B T$  dividing the potential parameters has been omitted for notational convenience, and the following orientational moments ( $n \times n$  matrices) of the ideal structure factors have been defined:

$$\begin{aligned} \mathbf{X}_0(\mathbf{Q}) &= \int d\mathbf{u} \int d\mathbf{u}' \mathbf{X}_0(\mathbf{Q}, \mathbf{u}, \mathbf{u}') \\ \mathbf{X}(\mathbf{Q}) &= \int d\mathbf{u} \int d\mathbf{u}' \mathbf{X}(\mathbf{Q}, \mathbf{u}, \mathbf{u}') \\ \mathbf{R}_0(\mathbf{Q}) &= (3/2) \int d\mathbf{u} \int d\mathbf{u}' \mathbf{X}_0(\mathbf{Q}, \mathbf{u}, \mathbf{u}') [(\mathbf{q} \cdot \mathbf{u})^2 - 1/3] \\ \mathbf{R}(\mathbf{Q}) &= (3/2) \int d\mathbf{u} \int d\mathbf{u}' \mathbf{X}(\mathbf{Q}, \mathbf{u}, \mathbf{u}') [(\mathbf{q} \cdot \mathbf{u})^2 - 1/3] \\ \mathbf{T}_0(\mathbf{Q}) &= (9/4) \int d\mathbf{u} \int d\mathbf{u}' \mathbf{X}_0(\mathbf{Q}, \mathbf{u}, \mathbf{u}') [(\mathbf{q} \cdot \mathbf{u})^2 - 1/3][(\mathbf{q} \cdot \mathbf{u}')^2 - 1/3]. \end{aligned} \quad (7.3)$$

where  $\mathbf{q}$  is the unit vector along  $\mathbf{Q}$ . Although the incompressibility assumption is expected to be a reasonable one for flexible polymer mixtures, it is not known whether it could also be realistic for mixtures of flexible and rigid polymers. Making that assumption, the general result (for incompressible mixtures of stiff polymers) (see Appendix D) is:

$$\begin{aligned} \mathbf{X}_{RR}^{-1} &= \mathbf{P}^T \cdot \{\mathbf{X}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0\}^{-1} \\ &\times \{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\} \cdot \mathbf{P} \end{aligned} \quad (7.4)$$

where we have followed Akcasu [15] and introduced an  $n \times (n - 1)$  matrix  $\mathbf{P} = \text{Col}[\mathbf{I}, -\mathbf{E}_R^T]$  ( $\mathbf{I}$  is the  $(n - 1) \times (n - 1)$  identity matrix and  $\mathbf{E}_R^T$  is an  $(n - 1)$  row vector comprising only ones) in order to apply the incompressibility constraint at the outset.

The isotropic-to-nematic transition is defined by the characteristic equation  $\text{Det}\{\mathbf{M}\} = 0$  (where  $\text{Det}$  represents the determinant of a matrix). If the Van der Waals interactions were "turned off" ( $\mathbf{W}_0 = 0$ ) so that only nematic interactions are left, then  $\mathbf{M}$  would be the denominator of  $\mathbf{X}$  so that  $\mathbf{X}$  would blow up for this condition ( $\text{Det}\{\mathbf{M}\} = 0$ ). Above certain critical values of  $W_1$ 's the blend forms the nematic phase. As in the case of purely flexible mixtures, the spinodal condition is:

$$\text{Det}\{\mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3)\mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0\} = 0. \quad (7.5)$$

Here also  $k_B T = 1$  has been set. 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 (results from Doi et al. [36–38]) can be recovered when one of the components is taken to be a solvent.

## 7.2 Binary Blend of a Flexible and a Rigid Rod Polymers

In the case of a binary incompressible mixture of stiff homopolymers (components are named A and B), the above equations simplify. 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:

$$\begin{aligned} X_{AA} = & \{(2/3)R_{BB}^0 W_{BB}^1 X_{AA}^0 + [1 - (2/3)T_{BB}^0 W_{BB}^1] X_{AA}^0 X_{BB}^0\} / \\ & \{(2/3)R_{BB}^0 W_{BB}^1 [1 - 2\chi_{AB} X_{AA}^0] \\ & + (X_{AA}^0 + X_{BB}^0 - 2\chi_{AB} X_{AA}^0 X_{BB}^0)[1 - (2/3)T_{BB}^0 W_{BB}^1]\} \end{aligned} \quad (7.6)$$

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.

$$\begin{aligned} X_{AA}^0(Q)/N_A \phi_A v_A = & \{[1 + j_0(Qb_A)] N_A / [1 - j_0(Qb_A)] \\ & - 2j_0(Qb_A) [1 - j_0^N(Qb_A)] / \\ & [1 - j_0(Qb_A)]^2\} / N_A^2 \end{aligned} \quad (7.7a)$$

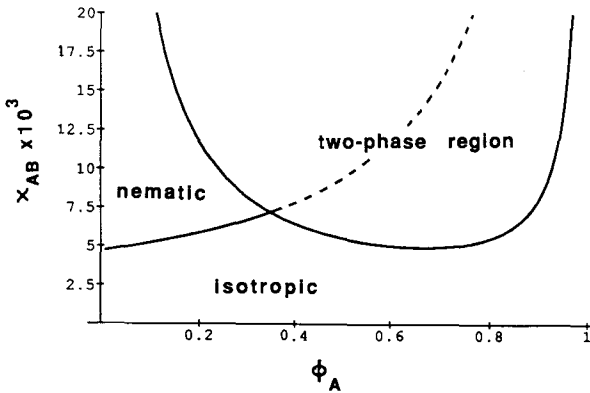
$$\begin{aligned} X_{BB}^0(Q)/N_B \phi_B v_B = & \int_0^1 dx j_0^2(Qb_B N_B x / 2) \\ = & 2[\cos(Qb_B N_B) - 1] / (Qb_B N_B)^2 \\ & + 2\text{Si}(Qb_B N_B) / Qb_B N_B \end{aligned} \quad (7.7b)$$

$$\begin{aligned}
R_{BB}^0(Q)/N_B \phi_B v_B &= (3/2) \int_0^1 dx (x^2 - 1/3) j_0^2(Qb_B N_B x/2) \\
&= (3/2) \{ 2[5 - \cos(Qb_B N_B)]/3(Qb_B N_B)^2 \\
&\quad - 2\sin(Qb_B N_B)/(Qb_B N_B)^3 \\
&\quad - 2\text{Si}(Qb_B N_B)/3Qb_B N_B \} \quad (7.7c)
\end{aligned}$$

$$\begin{aligned}
T_{BB}^0(Q)/N_B \phi_B v_B &= (9/4) \int_0^1 dx (x^2 - 1/3)^2 j_0^2(Qb_B N_B x/2) \\
&= (9/4) \{ -10/9(Qb_B N_B)^2 + \cos(Qb_B N_B) \\
&\quad \times [2/9(Qb_B N_B)^2 - 4/(Qb_B N_B)^4] \\
&\quad + \sin(Qb_B N_B)[4/(Qb_B N_B)^5 - 2/3(Qb_B N_B)^3] \\
&\quad + 2\text{Si}(Qb_B N_B)/9(Qb_B N_B) \} \quad (7.7d)
\end{aligned}$$

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

The isotropic-to-nematic transition is determined by the condition  $[1 - (2/3)T_{BB}^0 W_{BB}^1/k_B T] = 0$  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. 7 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 ( $\phi_A$ ) is low, the isotropic-to-nematic phase transition is reached first whereas at high  $\phi_A$  the spinodal line is reached first. In the second case, the macromolecules do not have a chance to orient themselves before the spinodal line is reached. This RPA approach is a generalization of the Doi et al. [36–38] results (that were developed for lyotropic polymer liquid crystals) to describe thermotropic polymer mixtures. Both approaches cannot, however,



**Fig. 7.** 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

reproduce the narrow two-phase region between the isotropic and nematic phases as observed experimentally or as predicted by the lattice model approach [44]. Because the isotropic-to-nematic phase transition is a first order transition, the nematic phase can be obtained only after separation into two phases (one nematic and one isotropic) upon heating. The RPA formalism presented here is not valid beyond the spinodal line.

### 7.3 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 equal to zero 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 Leibler formula [39] to include chain stiffness:

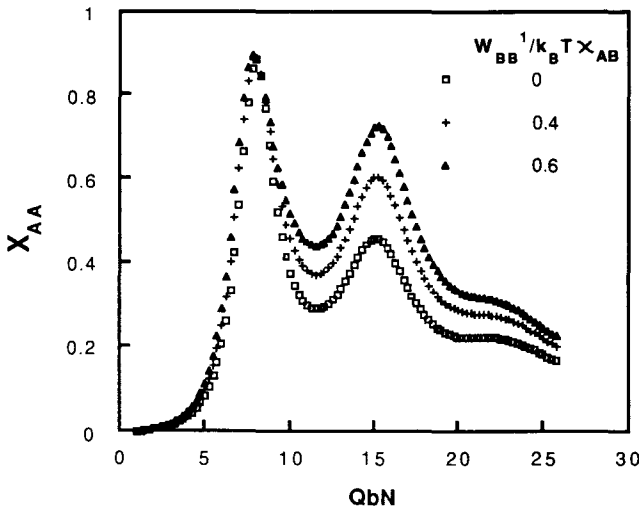
$$\begin{aligned} X_{AA} = & \{ (2/3) W_{BB}^1 [R_{BB}^{02} X_{AA}^0 - 2R_{BA}^0 R_{BB}^0 X_{AB}^0 + R_{BA}^{02} X_{BB}^0] \\ & + [1 - (2/3) T_{BB}^0 W_{BB}^1] (-X_{AB}^{02} + X_{AA}^0 X_{BB}^0) \} / \\ & \{ (X_{AA}^0 + 2X_{AB}^0 + X_{BB}^0 + 2\chi_{AB} X_{AB}^{02} - 2\chi_{AB} X_{AA}^0 X_{BB}^0) \\ & \times [1 - (2/3) T_{BB}^0 W_{BB}^1] \\ & + (2/3) W_{BB}^1 [R_{BA}^{02} + 2R_{BA}^0 R_{BB}^0 + R_{BB}^{02}] \\ & - (4/3) \chi_{AB} W_{BB}^1 [R_{BB}^{02} X_{AA}^0 - 2R_{BA}^0 R_{BB}^0 X_{AB}^0 + R_{BA}^{02} X_{BB}^0] \} \quad (7.8) \end{aligned}$$

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:

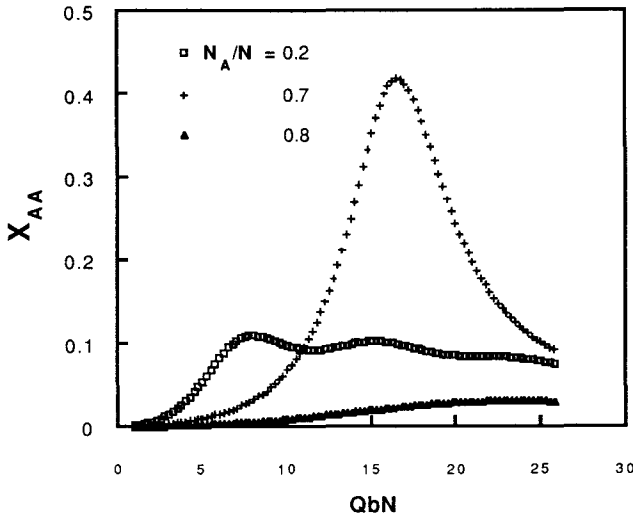
$$\begin{aligned} X_{AB}^0(Q) / (N_A \phi_A v_A N_B \phi_B v_B)^{1/2} \\ = & \{ [1 - j_0(Qb_A)^{N_A}] / N_A [1 - j_0(Qb_A)] \} \\ & \times \int_0^1 dx j_0(Qb_B N_B x / 2) \cos(Qb_B N_B x / 2) \\ = & \{ [1 - j_0(Qb_A)^{N_A}] / N_A [1 - j_0(Qb_A)] \} \text{Si}(Qb_B N_B) / Qb_B N_B \quad (7.9a) \end{aligned}$$

$$\begin{aligned} R_{BA}^0(Q) / (N_A \phi_A v_A N_B \phi_B v_B)^{1/2} \\ = & \{ [1 - j_0(Qb_A)^{N_A}] / N_A [1 - j_0(Qb_A)] \} \\ & \times \int_0^1 dx [3x^2 - 1/2] j_0(Qb_B N_B x / 2) \cos(Qb_B N_B x / 2) \\ = & \{ [1 - j_0(Qb_A)^{N_A}] / N_A [1 - j_0(Qb_A)] \} (3/2) \{ -\cos(Qb_B N_B) / \\ & (Qb_B N_B)^2 - \text{Si}(Qb_B N_B) / 3(Qb_B N_B) \\ & + \sin(Qb_B N_B) / (Qb_B N_B)^3 \} \quad (7.9b) \end{aligned}$$

These results agree with those reported by Holyst and Schick [40–41]. The structure factor  $X_{AA}(Q)$  has been plotted in Fig. 8 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 Figure 8 corresponds to  $Qb_B N_B = 2\pi, 4\pi$  and depends only on the length of the rigid rods ( $b_B N_B$ ). The peaks observed here are a characteristic 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  $T_{BB^0}(Q)$ , for example, show peaks at  $Qb_B N_B = 2\pi, 4\pi$ ). Figure 9, 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 phase 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 predict the symmetry of the ordered phase. Figure 9 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. The sharpness of the peaks in Figure 8 points to the fact that the domain boundaries (in direct space) are



**Fig. 8.** Structure factor for a melt of diblock copolymers made of flexible freely-jointed (A component) and rigid (B component) blocks with:  $N_A = 200$ ,  $N_B = 800$ ,  $v_A = v_B = 1$ ,  $b_A = b_B = b$ , 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. 9.** Structure factor for a melt of diblock copolymers made of flexible freely-jointed (A component) and rigid (B component) blocks with:  $\chi_{AB}N = 19$  (where  $N = N_A + N_B$ ),  $W_{BB}^1/k_B T \chi_{AB} = 0.4$ ,  $v_A = v_B = 1$  and  $b_A = b_B = b$ . The three curves correspond to  $N_A/N = 0.2, 0.7$ , and  $0.8$  respectively

sharper in this system. When the rigid rods get shorter (Figure 9), this sharpness decreases leading to a regular sinusoidal profile for the density of rigid rods. Various phase diagrams for diblock copolymers have been investigated by Holyst and Schick [41]. Here also, it is emphasized that the RPA approach should be considered only for qualitative observations because it cannot predict the narrow two-phase channel between the nematic and isotropic regions which is due to non-mean field contributions.

Now that the RPA has been applied to various polymer mixtures, specific cases are considered in the following sections along with SANS data analyzed with arguments similar to the ones discussed in the previous sections.

## 8 Specific Examples

In the following sections, examples of SANS investigations from polymer systems are considered. Simple cases involving polymer solutions and blends are described in order to demonstrate the modeling approaches discussed here. These examples have been borrowed from my recent work in collaboration with other scientists at the National Institute of Standards and Technology.



### 8.1 Semidilute Solution of Deuterated Polystyrene in Dioctyl Phthalate

A semidilute solution [42] of high molecular weight deuterated polystyrene ( $M_w = 1.95 \times 10^6$  g/mole,  $M_w/M_n = 1.64$ ) in dioctyl phthalate (DOP) at a volume fraction of 2.83% of polystyrene was measured by SANS at room temperature. A characteristic intensity behavior  $I(Q)$  was obtained after data correction (solvent incoherent scattering, empty cell scattering and usual background corrections, etc.) and was circularly averaged. The reduced  $I(Q)$  data was then fitted to the following form:

$$(a_p/v_p - a_s/v_s)^2/I(Q) = 1/N\phi_p v_p P_G(\alpha N) + 1/\phi_s v_s - 2\chi_{ps}/v_0 \quad (8.1)$$

where the same notation is being used: degree of polymerization:  $N = 18750$ , polymer volume fraction:  $\phi_p = 2.83\%$ , molar volumes:  $v_p = 100 \text{ cm}^3$ ,  $v_s = 398 \text{ cm}^3$ , contrast factor:  $(a_p/v_p - a_s/v_s)^2 N_{av} = 5.57 \times 10^{-3} \text{ mole/cm}^4$ , Debye function:

$$P_G(\alpha N) = 2[\exp(-\alpha N) - 1 + \alpha N]/(\alpha N)^2 \quad (8.2)$$

with fully swollen radius of gyration:

$$\alpha N = Q^2 R_g^2 = Q^2 b^2/(2v + 1)(2v + 2) \quad (8.3)$$

and  $v = 0.6$  (good solvent conditions). Results of the fit were: segment length:  $b = 0.725 \text{ nm}$  and interaction parameter:  $\chi_{ps}/v_0 = 9.68 \times 10^{-4} \text{ mole/cm}^3$ . The spinodal value is  $\chi_{ps}/v_0 = 1/2N\phi_p v_p + 1/2\phi_s v_s = 1.297 \times 10^{-3} \text{ mole/cm}^3$ . The experimentally obtained and the calculated intensities are shown in Fig. 10 for comparison.

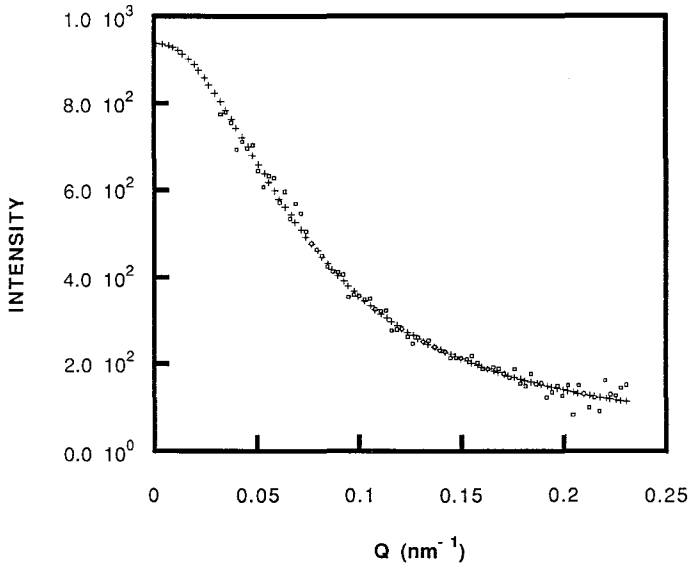
### 8.2 Binary Blend of Deuterated Polystyrene and Poly(vinyl methyl ether)

Consider a binary polymer blend [43] of deuterated polystyrene, PSD, ( $M_w = 1.95 \times 10^5$  g/mole,  $M_w/M_n = 1.02$ ) and poly(vinyl methyl ether), PVME, ( $M_w = 1.59 \times 10^5$  g/mole,  $M_w/M_n = 1.3$ ) with a composition of 48.4% PSD (volume fraction). SANS data were taken at various temperatures ranging from ambient to  $160^\circ\text{C}$ . De Gennes's RPA formula:

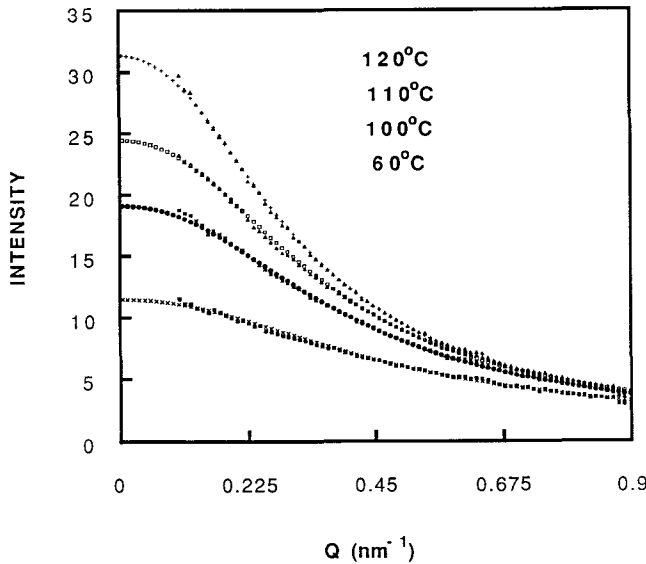
$$(a_A/v_A - a_B/v_B)^2/d\Sigma(Q)/d\Omega = 1/N_A \phi_A v_A P_G(\alpha_A N) + 1/N_B \phi_B v_B P_G(\alpha_B N) - 2\chi_{AB}/v_0 \quad (8.4)$$

was used to fit the reduced data (Fig. 11) with A as the PSD component and B as the PVME component and with:  $N_A = 1741$ ,  $N_B = 2741$ ,  $v_A = 100 \text{ cm}^3/\text{mole}$ ,  $v_B = 55.4 \text{ cm}^3/\text{mole}$ ,  $(a_A/v_A - a_B/v_B)^2 N_{av} = 6.07 \times 10^{-3} \text{ mole/cm}^4$ ,  $\phi_A = 48.4\%$ , etc. Results of the fits were:  $b_{\text{PSD}} = 0.8 \text{ nm}$ ,  $b_{\text{PVME}} = 0.6 \text{ nm}$  and:

$$\chi_{\text{PSD/PVME}}/v_0 = 9.73 \times 10^{-4} - 0.416/T, \quad (\text{in mole/cm}^3) \quad (8.5)$$



**Fig. 10.** SANS from deuterated polystyrene ( $M_w = 1.95 \times 10^6$  g/mol) in dioctyl phthalate solution (3% polymer weight fraction). Experimental data (arbitrary units) and results of the fit to the inverse Zimm formula are plotted



**Fig. 11.** SANS from deuterated polystyrene/poly(vinyl methyl ether) at equal compositions (50%/50% weight fractions). Experimental data (macroscopic cross section) and fits to the de Gennes formula are plotted for four temperatures: 60 °C, 100 °C, 110 °C and 120 °C (from bottom to top)

where  $T$  is the absolute temperature (Fig. 12). The PSD/PVME blend is a lower critical solution temperature (LCST) system and shows spinodal decomposition for  $\chi_{\text{PSD/PVME}} = 1.23 \times 10^{-5}$  mole/cm<sup>3</sup> (value which makes the right-hand side of de Gennes's equation equal to zero); i.e., at 160°C. These results agree with previously reported values [31] for this system.

### 8.3 Ternary Blend of Deuterated Polystyrene/ Poly(vinyl methyl ether)/Protonated Polystyrene; The High Concentration Method

Consider a ternary homopolymer blend mixture of PSD, PVME and protonated polystyrene (PSH). PSD and PVME have the same molecular weights as in the previous section and for PSH:  $M_w = 1.90 \times 10^5$  g/mole,  $M_w/M_n = 1.04$ . The extra parameters needed to describe the blend are:  $N_{\text{PSH}} = 1827$ ,  $v_{\text{PSH}} = 100$  cm<sup>3</sup>/mole,  $(a_{\text{PSH}}/v_{\text{PSH}} - a_{\text{PVME}}/v_{\text{PVME}})^2 N_{\text{av}} = 1.79 \times 10^{-4}$  mole/cm<sup>4</sup>. Three compositions corresponding to the same PVME volume fraction were measured by SANS:

sample 1: 48.4%/51.6%/0% PSD/PVME/PSH

sample 2: 36%/51.1%/12.9% PSD/PVME/PSH

sample 3: 23.8%/50.6%/25.6% PSD/PVME/PSH .

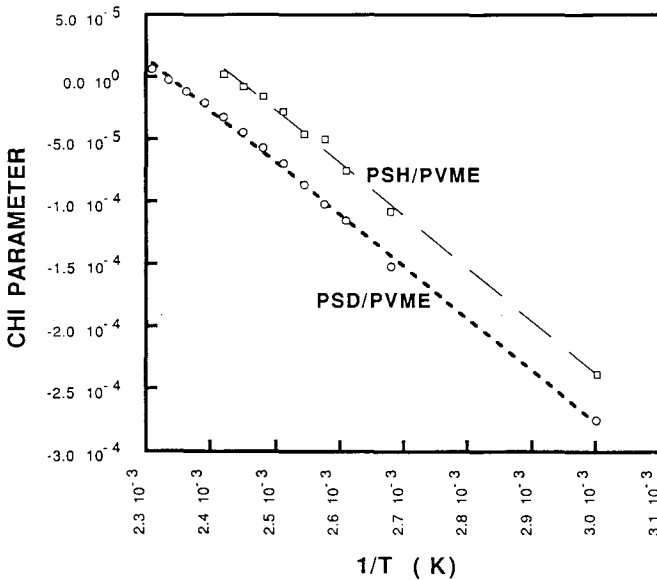


Fig. 12. Flory-Huggins  $\chi/v_0$  parameters for deuterated polystyrene/poly(vinyl methyl ether) and protonated polystyrene/poly(vinyl methyl ether) interactions. The first one was obtained from binary (PSD/PVME) mixtures (50%/50% weight fraction) and the second one from ternary (PSD/PVME/PSH) blend mixtures (23.8%/25.6%/50.6%)

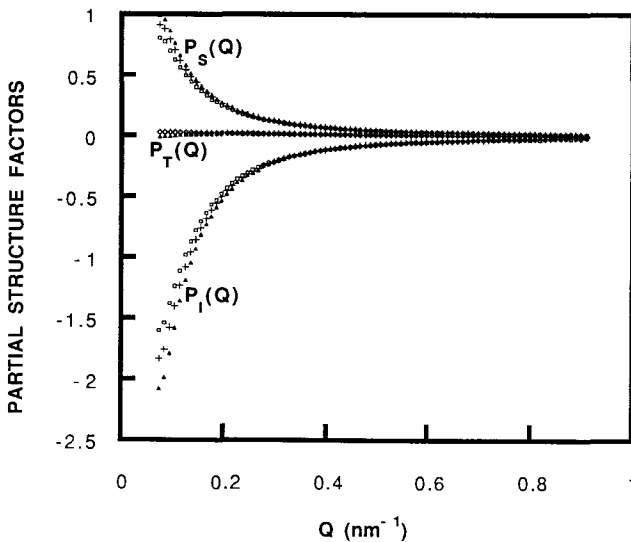
The high concentration method is used, here, to extract single-chain, interchain and total scattering structure factors. The scattering cross section for each sample is given by:

$$\begin{aligned} d\Sigma(Q)/d\Omega = & (a_C/v_P - a_A/v_P)^2 [\phi_A \phi_C / \phi_P^2] N \phi_P v_P P_S(Q) \\ & + [(a_A/v_P - a_B/v_B) \phi_A / \phi_P \\ & + (a_C/v_P - a_B/v_B) \phi_C / \phi_P]^2 N \phi_P v_P P_T(Q), \end{aligned} \quad (8.6)$$

where  $N_A = N_C = N$ ,  $v_A = v_C = v_P$ ,  $\phi_A + \phi_C = \phi_P$ .  $P_S(Q)$ ,  $P_T(Q)$  and the inter-chain structure factor ( $P_I(Q) = [P_T(Q) - P_S(Q)]/\phi_P$ ) can be extracted by combining data taken for pairs of samples (sample pairs 1-2, 2-3 and 1-3) with the proper weighing factors. The results are shown in Fig. 13. A number of observations can be made. For instance, the various structure factors extracted from different pairs of samples are slightly different due to the fact that the high concentration method assumptions hold only approximately (conformations may change from sample to sample,  $P_{AA}^I(Q)$ ,  $P_{AC}^I(Q)$  and  $P_{CC}^I(Q)$  may not be identical, the system may not be completely incompressible, etc.). Moreover, the interchain structure factors  $P_I(Q)$  are negative as they should. Recall that, for example,

$$P_{AC}^I(Q) = - [V/Nv_P] \int d^3R [1 - g_{AC}(R)] \exp[-i\mathbf{Q} \cdot \mathbf{R}] \quad (8.7)$$

where  $g_{AC}(R)$  is the pair distribution function representing monomer packing and  $\mathbf{R}$  is the inter-monomers distance.  $P_{AC}^I(Q)$  is obviously a very complicated



**Fig. 13.** Single-chain  $P_S(Q)$ , interchain  $P_I(Q)$  and total  $P_T(Q)$  structure factors for a blend mixture of deuterated and protonated polystyrene (PSD, PSH) in poly(vinyl methyl ether) (PVME). The total PVME fraction was 51% and the PSD fractions were varied from 49% to 24%. The three curves correspond to sample pairs 1-2, 2-3 and 1-3 in each case

quantity to model directly in blend systems. It contains information about the various monomer–monomer interaction potentials, about monomer packing, and about overall chain conformations. For instance,  $P_{AC}^I(Q)$  depends not only on AC interactions (represented by the  $\chi_{AC}$  “chi” parameter) but also on the other ones ( $\chi_{AB}$ ,  $\chi_{BC}$ ). In order to investigate slight changes in the “chi” parameter due to deuteration, the RPA is used, instead, to analyze the SANS data from one of the ternary blends in the next section.

#### *8.4 Ternary Blend of Deuterated Polystyrene/ Poly(vinyl methyl ether)/Protonated Polystyrene; The RPA Method*

Consider one of the ternary blend mixtures described in the previous section. Data from sample 3 were taken from room temperature to 160°C and are analyzed [43], using the RPA formalism for a ternary blend. The three components are called: A: PSD, B: PVME, C: PSH. Also, temperature dependencies for the two known chi parameters ( $\chi_{PSD/PVME}/v_0$  and  $\chi_{PSD/PSH}/v_0$ ) were assumed [31, 32]:

$$\begin{aligned}\chi_{PSD/PVME}/v_0 &= 9.73 \times 10^{-4} - 0.416/T \\ \chi_{PSD/PSH}/v_0 &= -2.9 \times 10^{-6} + 0.0020/T.\end{aligned}\quad (8.8)$$

Results of the fits showed that  $\chi_{PSH/PVME}/v_0$  has the following temperature dependence:

$$\chi_{PSH/PVME}/v_0 = 10.6 \times 10^{-4} - 0.436/T.\quad (8.9)$$

This dependence suggests a spinodal temperature for the PSH/PVME system of 140°C which is in agreement with cloud point measurements. Figure 12 shows that the temperature dependence of  $\chi_{PSD/PVME}$  and  $\chi_{PSH/PVME}$  are parallel indicating that deuteration brings about a uniform shift in the spinodal temperature. This result, however, may not hold for other compositions.

## 9 Discussion

Monodisperse polymer blocks have been assumed all along. Polydispersity effects could be introduced in an ad-hoc fashion by assuming a molecular weight distribution (such as the Zimm–Schultz):

$$W(n) = [a/\langle n \rangle \Gamma(a + 1)] (a/\langle n \rangle)^a \exp(-an/\langle n \rangle)\quad (9.1)$$

where  $\langle n \rangle$  is the number average degree of polymerization,  $a$  is a measure of the polydispersity, and  $\Gamma(a + 1)$  is the gamma function. The weight average degree

of polymerization is

$$n_w = \langle n^2 \rangle / \langle n \rangle = \langle n \rangle (a + 1) / a \quad (9.2)$$

so that the degree of polydispersity is  $\varepsilon = (n_w - \langle n \rangle) / \langle n \rangle = 1/a$ . Averaging over this distribution has the following effect:

$$\langle \exp(-\alpha n) \rangle = (1 + \alpha \langle n \rangle \varepsilon)^{-1/\varepsilon} \quad (9.3)$$

and the Debye function becomes:

$$\langle P(\alpha n) \rangle = 2[(1 + \alpha \langle n \rangle \varepsilon)^{-1/\varepsilon} - 1 + \alpha \langle n \rangle \varepsilon] / (1 + \varepsilon) \alpha^2 \langle n \rangle^2 \quad (9.4)$$

Note that the same symbol  $\langle \dots \rangle$  was used before to denote a conformational average while here it denotes a molecular weight average. Averaging over molecular weight distributions cannot always be done exactly. In cases where the degree of polymerization ( $n$ ) appears in complicated expressions, "preaveraging" approximations ( $\langle f(n)g(n) \rangle \sim \langle f(n) \rangle \langle g(n) \rangle$ ) have to be resorted to. Random copolymers, for instance, could be modeled as regularly alternating copolymers with polydisperse blocks [22].

With the advent of "formula manipulation" computer programs that perform analytical manipulations (Mathematica [45] was extensively used by this author), lengthy results for the various structure factors for multicomponent polymer mixtures are readily obtained and can form the basis of FORTRAN codes that can be used to fit neutron scattering data. This approach is preferable to performing the matrix inversions numerically because it involves an initial careful setting up of the general RPA formulas only. Also analytical functional forms are preferable to direct numerical calculations (matrix inversions, etc.) in least-squares fitting where these functions are evaluated thousands of times. This approach which consists in handling very complicated analytical forms to fit the data could be referred to as "semi-analytical".

The RPA theory works surprisingly well for homogeneous flexible polymer systems considering the crude approximations involved (mean field and linear response). It works better for concentrated solutions, melts and blends. It is also often used for dilute and semidilute solutions. It, however, breaks down in non-homogeneous (such as phase decomposing) systems and close to the critical point where equivalent tools are not yet available. Renormalization group theory, on the other hand, works well in dilute and semidilute polymer solutions because it can account for loop interactions within one chain and for higher level interchain (multiple) contacts; but breaks down in melts and blends. Moreover, scaling arguments are available for the estimation of exponents in polymer solutions. Scaling theory can be tested using neutron scattering (log-log plots); however, it cannot predict prefactors and cannot, therefore, be used to directly fit scattering data. The RPA itself has its own drawbacks; it cannot, for example, describe compact polymer systems (such as stars with a large number of arms or starburst dendrimers) in the semidilute region where these show local "liquid-like" ordering (appearance of an interparticle peak in the scattering function). It can however, describe these systems in the concentrated region (where chains

interpenetrate). The effect of Coulomb interactions (in polyelectrolytes for example) or dipolar interactions (in ionomers for example) have not been discussed here. These interactions (as well as hydrogen bonding) increase the long range order therefore enhancing density fluctuations and making the mean field assumption (inherent in the RPA) a weaker approximation.

The Flory-Huggins "chi" parameter was introduced as a universal parameter. It has been found to depend on a number of experimental variables (molecular weight, composition, microstructure, tacticity, intermonomer distance, etc.) so that it has become an empirical parameter used to disguise our inadequacies in the knowledge of polymer systems. Modeling efforts leading to a better microscopic understanding of the origin of monomer-monomer and/or monomer/solvent interactions are needed. Van der Waals interactions between atoms (represented by electronic polarizabilities) could form the basis of such efforts. Other outstanding topics that require modeling efforts include: structure factor for polymer networks, effects of shear on the scattering function (the RPA may not be appropriate to use in the presence of shear), simple non-mean field treatments of polymer solutions that could be used to fit scattering data, prediction of phase diagrams for stiff copolymer mixtures, etc.

When the SANS technique was introduced, twenty years ago, data analysis consisted mainly of observations of relative trends of parameters (such as the radius of gyration) obtained by performing standard plots (such as the Guinier plot) and the SANS technique was not "exciting". However, modeling tools such as the ones described here have made SANS a very precise technique that is rich in information making it an increasingly used method (despite the fact that SANS spectra look "dull" compared to other spectra) with applications ranging from cutting edge science all the way to applied routine characterization. Newly introduced methods (such as the High Concentration Method or the Random Phase Approximation) have brought renewed interest in this technique. A recent literature search by this author of the Chemical Abstracts database based on the two keywords "neutron" and "polymer" came up with 480 articles that were published between 1980 and 1990, 424 of which used the SANS technique. New experimental methods both in the synthesis of ingenious polymer structures as well as in making judicious sample environments (such as the shear cell) are opening up new horizons to the SANS technique. Shearing, for instance, is making this "equilibrium" tool valuable for the investigation of rheology problems as well. Kinetic measurements (time slicing of the data) is allowing dynamic studies of chain conformations and concentration fluctuations to be made. Phase separation of blends occurs so rapidly that the peak in the scattering function (characterizing the later stages of spinodal decomposition) forms and disappears into the very low-Q region rapidly. A few systems (such as polycarbonate/polymethyl metacrylate) are characterized by slow phase separation kinetics which coupled with the availability of low-Q instruments and of time slicing will permit the investigation of the intermediate stages of spinodal decomposition. Theoretical back up is available both in early and late stages and predictions are being tested using light scattering.

It is unfortunate that research in the area of polymer solutions has been deserted during the past ten years in favor of blend work. With the advent of shear cells, it is expected that research in polymer solutions will become “fashionable” again. For instance, the phenomenon of shear-induced apparent demixing of high molecular weight polystyrene in semidilute solutions (in DOP for example) is not understood. Kinetics measurements will hopefully permit a close monitoring of the remixing effect after shear cessation as well.

The RPA formalism has been generalized to describe mixtures of stiff and flexible polymers. Eventhough this generalization reproduces the main expected features (isotropic-to-nematic transition for example), it cannot reproduce experimental phase diagrams observed in lyotropic liquid crystals for instance, whereby a narrow two-phase region (channel) is observed between the isotropic and nematic phases. The approach described here is a mere generalization of the Doi et al. approach [36–38] to describe thermotropic polymer liquid crystal mixtures. Most SANS measurements on liquid crystalline polymers have focussed on the investigation of chain conformations in oriented systems. There is a need for data in the isotropic region which cannot be reached in most systems. However, with slightly hydrogen bonded blends of flexible and rigid polymers, there is hope for extracting both the Flory-Huggins and the Maier-Saupe interaction parameters and investigating their dependences on temperature, molecular weight, and composition.

## 10 Appendices

### *Appendix A: Multicomponent Random Phase Approximation for Homopolymer and Copolymer Mixtures*

Consider a polymer system consisting of  $n$  components. These could be homopolymer mixtures or homopolymer and copolymer mixtures. In order to simplify the calculations, we consider that at least one of the components (that we call “matrix” component) is a homopolymer. The formalism presented here is a straightforward extension of the two-component case in an  $n$ -vector and  $n \times n$  matrix notation [13]:

$$\langle \rho(\mathbf{Q}) \rangle = -\mathbf{X}_0(\mathbf{Q})[\mathbf{U}/k_B T + (\mathbf{W}/k_B T) \cdot \langle \rho(\mathbf{Q}) \rangle] + \lambda \mathbf{E} \quad (\text{A.1a})$$

$$\langle \rho(\mathbf{Q}) \rangle = -\mathbf{X}(\mathbf{Q})\mathbf{U}/k_B T \quad (\text{A.1b})$$

$$\mathbf{E}^T \cdot \langle \rho(\mathbf{Q}) \rangle = 0 \quad (\text{A.1c})$$

where  $\langle \rho(\mathbf{Q}) \rangle$  and  $\mathbf{U}$  are the vector density and externally applied potentials,  $\mathbf{X}_0(\mathbf{Q})$  and  $\mathbf{X}(\mathbf{Q})$  are the bare and interacting system structure factor matrices,  $\mathbf{W}$  is the monomer-monomer interaction potentials matrix,  $\mathbf{E}$  is a vector with all components equal to unity and  $\lambda$  is a Lagrange multiplier introduced to help impose the incompressibility constraint (incompressibility equation:  $\mathbf{E}^T \cdot \langle \rho(\mathbf{Q}) \rangle$ )



= 0). The idea is to isolate the “matrix” component (denoted component M) from the “rest” of the blend (denoted R). Matrix  $\mathbf{X}_0(Q)$  is formed of 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  $\mathbf{W}$ . Assuming that no copolymer is shared between the “matrix” component and the remaining  $(n - 1)$  components imposes  $\mathbf{X}_{MR}^0(Q) = \mathbf{0}$  therefore simplifying the calculations. With the M–R separation, the RPA equations become:

$$\langle \rho_M \rangle = -X_{MM}^0 U_M / k_B T - X_{MR}^0 U_R / k_B T - (\mathbf{X}_0 \cdot \mathbf{W})_{MM} \langle \rho_M \rangle / k_B T \\ - (\mathbf{X}_0 \cdot \mathbf{W})_{MR} \langle \rho_R \rangle / k_B T - \lambda (X_{MM}^0 + \mathbf{X}_{MR}^0 \cdot \mathbf{E}_R), \quad (\text{A.2a})$$

$$\langle \rho_R \rangle = -X_{RM}^0 U_M / k_B T - X_{RR}^0 U_R / k_B T - (\mathbf{X}_0 \cdot \mathbf{W})_{RM} \langle \rho_M \rangle / k_B T \\ - (\mathbf{X}_0 \cdot \mathbf{W})_{RR} \langle \rho_R \rangle / k_B T - \lambda (X_{RM}^0 + \mathbf{X}_{RR}^0 \cdot \mathbf{E}_R), \quad (\text{A.2b})$$

$$\langle \rho_M \rangle = -X_{MM} U_M / k_B T - X_{MR} U_R / k_B T \quad (\text{A.2c})$$

$$\langle \rho_R \rangle = -X_{RM} U_M / k_B T - X_{RR} U_R / k_B T \quad (\text{A.2d})$$

$$\langle \rho_M \rangle + \mathbf{E}_R^T \cdot \langle \rho_R \rangle = 0 \quad (\text{A.2e})$$

where  $\mathbf{E}_R$  is an  $(n - 1)$ -vector with all terms equal to unity and  $\mathbf{E}_R^T$  denotes its transpose. Extracting  $\lambda$  from Eq. (A.2a) and replacing it in Eq. (A.2b) yields an equation for  $\langle \rho_R \rangle$ , which with the help of Eq. (A.2e) becomes:

$$\langle \rho_R \rangle = -X_{RR}^0 \{ U_R / k_B T + (-\mathbf{W}_{RM} \cdot \mathbf{E}_R^T + \mathbf{W}_{RR}) \cdot \langle \rho_R \rangle / k_B T \\ - \mathbf{E}_R (X_{MM}^0)^{-1} [-\mathbf{E}_R^T + X_{MM}^0 (-\mathbf{W}_{MM} \mathbf{E}_R^T + \mathbf{W}_{MR}) / k_B T] \langle \rho_R \rangle \} \\ + (\mathbf{X}_{RR}^0 \cdot \mathbf{E}_R) U_M / k_B T \quad (\text{A.3a})$$

$$\langle \rho_R \rangle = -X_{RM} U_M / k_B T - X_{RR} U_R / k_B T. \quad (\text{A.3b})$$

Defining an excluded volumes matrix:

$$\mathbf{V} = -\mathbf{W}_{RM} \mathbf{E}_R^T / k_B T + \mathbf{W}_{RR} / k_B T + \mathbf{E}_R \mathbf{E}_R^T / X_{MM}^0 \\ + \mathbf{E}_R \mathbf{E}_R^T \mathbf{W}_{MM} / k_B T - \mathbf{E}_R \mathbf{W}_{RM}^T / k_B T \quad (\text{A.4})$$

the RPA equations become ( $\mathbf{I}$  is the identity matrix):

$$\mathbf{X}_{RR}(Q) = \mathbf{X}_{RR}^0(Q) \cdot [\mathbf{I} + \mathbf{V}(Q) \cdot \mathbf{X}_{RR}^0(Q)]^{-1} \quad (\text{A.5})$$

or if one drops the RR indices (in another form):

$$\mathbf{X}^{-1}(Q) = \mathbf{X}_0^{-1}(Q) + \mathbf{V}(Q). \quad (\text{A.6})$$

Note that without the incompressibility assumption (and without using the Lagrange multiplier  $\lambda$ ), one would arrive to an identical equation for  $n \times n$  matrices but with  $\mathbf{W}$  replacing  $\mathbf{V}(Q)$ . Note also that  $\mathbf{V}(Q)$  has the dimension of inverse volume.

This generalization of de Gennes' formula to multicomponent homopolymer and copolymer blends can describe a wide variety of situations. After a slight generalization (described in Appendix B) it can also, describe the case of pure copolymer mixtures whereby a copolymer has to be shared between M and R. Using Appendix A, one could obtain this limit (pure copolymer mixtures) by

assuming a fictitious homopolymer (say component Z) in the mixture to be the matrix component, then taking the limit  $\phi_Z \rightarrow 0$ . This method is cumbersome because of the fact that the Z component appears in the denominator of the various terms of  $V(Q)$  which diverge if proper care is not taken. Moreover, this procedure involves inverting  $(n+1) \times (n+1)$  matrices for an  $n$ -component problem. The general situation [15] where a copolymer is shared between R and M is discussed in Appendix B.

### *Appendix B: Multicomponent Random Phase Approximation for Pure Copolymer Mixtures*

In the case where  $\mathbf{X}_{MR}^0(Q) \neq 0$ ; i.e., if a copolymer is shared between R and M, we follow Akcasu [15] and 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. (A.1b) becomes:  $\mathbf{X}_{RR}^{-1} \langle \rho_R \rangle = -\mathbf{P}^T \mathbf{U} / k_B T$ . Multiplying:

$$\mathbf{X}_0^{-1} \{ \mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 / k_B T \} \cdot \langle \rho \rangle = - [\mathbf{U} / k_B T + \lambda \mathbf{E}] \quad (\text{B.1})$$

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:

$$\mathbf{X}_{RR}^{-1} = \mathbf{P}^T \cdot \mathbf{X}_0^{-1} \{ \mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 / k_B T \} \cdot \mathbf{P}. \quad (\text{B.2})$$

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.,  $\mathbf{P}^T \mathbf{W}_0 \mathbf{P} = (\mathbf{W}_{AA}^0 + \mathbf{W}_{BB}^0 - \mathbf{W}_{AB}^0 - \mathbf{W}_{BA}^0) / k_B T = -2\chi_{AB}$  which defines the Flory-Huggins interaction parameter  $\chi_{AB}$  in terms of the interaction potentials  $W_0$ 's. Of course, the approaches of Appendices A and B agree in common cases (for example in the case of a copolymer A-B and homopolymer C mixture).

### *Appendix C: Compressible Binary Blend Mixture of Stiff Polymers*

We consider a polymer system consisting of  $n$  kinds of stiff polymers, and use the matrix notation approach introduced by Akcasu [13–15]. Some of these components could be copolymers. Component I has a degree of polymerizations  $N_1$ , volume fraction  $\phi_1$ , monomer volume  $v_1$ , and segment size  $b_1$ . For stiff polymers, the averaged fluctuating density is defined as:

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

where monomer  $i$  in polymer  $\alpha$  is located at position  $\mathbf{r}_{\alpha i}$  and is oriented along direction  $\mathbf{u}_{\alpha i}$  and where  $\langle \cdots \rangle$  represents an average over conformations (i.e., over distributions of  $\mathbf{r}_{\alpha i}$  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 inter-segment 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  $\langle \boldsymbol{\rho}(Q, \mathbf{u}) \rangle$  ( $\langle \boldsymbol{\rho} \rangle$  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:

$$\langle \boldsymbol{\rho}(Q, \mathbf{u}) \rangle = - \int d\mathbf{u}' \mathbf{X}_0(Q, \mathbf{u}, \mathbf{u}') \left[ \mathbf{U}/k_B T + \int d\mathbf{u}'' \mathbf{W}(\mathbf{u}', \mathbf{u}'') \langle \boldsymbol{\rho}(Q, \mathbf{u}'') \rangle / k_B T \right] \quad (\text{C.2a})$$

along with:

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

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

$$\mathbf{X}(Q, \mathbf{u}, \mathbf{u}') = \mathbf{X}_0(Q, \mathbf{u}, \mathbf{u}') - \int d\mathbf{u}_1 d\mathbf{u}_2 \mathbf{X}_0(Q, \mathbf{u}, \mathbf{u}_1) \times \mathbf{W}(\mathbf{u}_1, \mathbf{u}_2) \mathbf{X}(Q, \mathbf{u}_2, \mathbf{u}') / k_B T \quad (\text{C.3})$$

which are the general RPA integral equations for compressible blend mixtures. Note that these equations are similar to the Ornstein–Zernicke relations [35]. Since the inter-segment interactions become weaker when two test segments are parallel to each other, the interaction potentials are taken to be proportional to  $\sin(\alpha)$  where  $\alpha$  is the angle between the two test segments ( $\sin(\alpha) = |\mathbf{u}' \times \mathbf{u}''|$  where  $\times$  is the vectorial product). In order to proceed further, Doi et. al. [36–38] assumed the following expansion:

$$\sin(\alpha) = (\pi/4) \{ 1 - (15/16)(\mathbf{u}' \cdot \mathbf{u}' - \mathbf{I}/3) : (\mathbf{u}'' \cdot \mathbf{u}'' - \mathbf{I}/3) + \cdots \} \quad (\text{C.4})$$

where  $\mathbf{u}' \cdot \mathbf{u}'$  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  $\mathbf{u}'$  and  $\mathbf{u}''$  integrations in the RPA equations therefore making calculations tractable analytically. The interaction potentials can, therefore, be assumed to be:

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

$\mathbf{W}_0$  and  $\mathbf{W}_1$  ( $n \times n$  matrices) are assumed, here, to contain unknown potential parameters (Note that Doi et al. [36–38] relate their scalar counterparts through:  $W_1/W_0 = 15/16$  for rigid rods). The  $\mathbf{W}_1$  potential factors are the

Maier–Saupe interaction parameters. The  $\mathbf{u}_1$  and  $\mathbf{u}_2$  integrations become:

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

We use the following identity:

$$\begin{aligned} \int d\mathbf{u}' \mathbf{X}_0(\mathbf{Q}, \mathbf{u}, \mathbf{u}') [\mathbf{u}' \mathbf{u}' - \mathbf{I}/3] &= (3/2) [\mathbf{q} \mathbf{q} - \mathbf{I}/3] \\ & \quad \times \int d\mathbf{u}' \mathbf{X}_0(\mathbf{Q}, \mathbf{u}, \mathbf{u}') [(\mathbf{q} \cdot \mathbf{u}')^2 - 1/3] \end{aligned} \quad (\text{C.7})$$

(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):

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

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.

We integrate Eq. (C.3) over  $\mathbf{u}$  and  $\mathbf{u}'$  to obtain:

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

where  $\mathbf{R}_0^T(\mathbf{Q})$  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 Eq. (C.3) by  $[(\mathbf{q} \cdot \mathbf{u}')^2 - 1/3]$  and then integrating over  $\mathbf{u}$  and  $\mathbf{u}'$  gives another set of equations:

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

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

$$\begin{aligned} \mathbf{X} &= \left\{ \mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 + (2/3) \mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0 \right\}^{-1} \\ & \quad \times \left\{ \mathbf{X}_0 + (2/3) \mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \right\} \end{aligned} \quad (\text{C.11})$$

where the  $(\mathbf{Q})$  argument and the temperature ( $k_B T$ ) have been dropped for notation convenience and  $\mathbf{M} = [\mathbf{I} - (2/3) \mathbf{T}_0 \cdot \mathbf{W}_1/k_B T]$  has been defined. Note that the isotropic case (i.e., if orientational correlations were neglected) is

obtained when  $W_1 = 0$  as:

$$\mathbf{X}(\mathbf{Q})^{-1} = \mathbf{X}_0(\mathbf{Q})^{-1} + \mathbf{W}_0/k_B T \quad (\text{C.12})$$

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

### *Appendix D: Incompressible Multicomponent Mixture of Stiff Polymers*

Using the matrix notation approach [13–15] that was introduced to describe multicomponent (here also consider  $n$  components) flexible polymer systems, the RPA equations are reviewed here for an incompressible stiff polymer mixture. As before, 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  $X_{MM}^0(\mathbf{Q})$ , a vector part  $\mathbf{X}_{MR}^0(\mathbf{Q})$  and a matrix part  $\mathbf{X}_{RR}^0(\mathbf{Q})$ , and similarly for potentials  $W$ 's. The RPA equations for the  $n$ -vector fluctuating densities  $\langle \rho(\mathbf{u}) \rangle$  are:

$$\begin{aligned} \langle \rho(\mathbf{u}) \rangle = & - \int d\mathbf{u}' \mathbf{X}_0(\mathbf{u}, \mathbf{u}') [\mathbf{U}/k_B T + \lambda \mathbf{E} \\ & + \int d\mathbf{u}'' \mathbf{W}(\mathbf{u}', \mathbf{u}'') \langle \rho(\mathbf{u}'') \rangle / k_B T] \end{aligned} \quad (\text{D.1a})$$

$$\langle \rho(\mathbf{u}) \rangle = - \int d\mathbf{u}' \mathbf{X}(\mathbf{u}, \mathbf{u}') \mathbf{U} / k_B T \quad (\text{D.1b})$$

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

$$\langle \rho_M \rangle + \mathbf{E}_R^T \cdot \langle \rho_R \rangle = 0. \quad (\text{D.1c})$$

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

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

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

( $k_B T$  has been omitted) along with:

$$\mathbf{X}^{-1} \langle \rho \rangle = - \mathbf{U} \quad (\text{D.3})$$

Here also, we use the  $n \times (n-1)$  matrix  $\mathbf{P}$  to apply the incompressibility constraint and obtain:

$$\begin{aligned} \mathbf{X}_{RR}^{-1} = \mathbf{P}^T \cdot \{ \mathbf{X}_0 + (2/3) \mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \}^{-1} \\ \times \{ \mathbf{I} + \mathbf{X}_0 \cdot \mathbf{W}_0 (2/3) \mathbf{R}_0^T \cdot \mathbf{W}_1 \cdot \mathbf{M}^{-1} \cdot \mathbf{R}_0 \cdot \mathbf{W}_0 \} \cdot \mathbf{P} \end{aligned} \quad (\text{D.4})$$

This result generalizes the one obtained in Appendix B to include chain stiffness.

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