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Reviews

Static Scattering from Multicomponent Polymer Systems: Theoretical Models

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ABSTRACT: This paper deals with the generalization of the standard equation for scattering, $1/\mathbf{S}(\mathbf{q}) = 1/\mathbf{S}^0(\mathbf{q}) + \mathbf{V}$, to multicomponent polymer systems and shows that the same result holds if it is written in matrix form. Three different methods are used: the Ornstein–Zernike formalism, the Random-Phase Approximation, and the Edwards Hamiltonian method. We compare these three methods in order to see how they work for multicomponent polymer systems. As a side result, we rederive the Flory–Huggins free energy without using a lattice model, and we generalize this to take into account Gaussian fluctuations in multicomponent systems.

1. Introduction

The properties of multicomponent polymer systems are the subject of intensive investigations because of their potential applications and the number of fundamental questions that are raised when one deals with the correlations between various species in the systems.[1–4] One of the most challenging problems comes from the coupling of intra- and intermolecular correlations. Several methods have been proposed to solve this problem, and the main purpose of this review is to present and compare three of them.

(i) The first method is based on a direct extension of the Ornstein–Zernike (OZ) formalism to macromolecular systems. This method was developed in simple liquid theories[5] along with diagrammatic techniques and was shown to be very useful for macromolecular systems by Benoit and co-workers[6] and Curro and Schweizer.[7]

(ii) The second method uses the Random-Phase Approximation (RPA) and was first suggested by Pines and Noziéres from strongly interacting electron systems.[8] Its extension to polymer systems was due to de Gennes[1] and later developed substantially by Leibler.[2]

(iii) The third method uses the Edwards Hamiltonian and is more familiar among field theorists and functional analysts. It has been intensively used to investigate equilibrium properties of polymer systems.[9–11]

In this paper we rederive, using these three different methods, the general result for multicomponent polymer systems[4,6,12,13]

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{V} \tag{1a}$$

where $\mathbf{S}(\mathbf{q})$ and $\mathbf{S}_0(\mathbf{q})$ are the total and bare structure matrices, respectively, $\mathbf{V}$ is the interaction matrix, $\mathbf{q}$ is the magnitude of the wave vector $\mathbf{q} = (4\pi/\lambda)[\sin(\theta/2)]$, λ is the wavelength of the incident radiation, and θ is the scattering angle. The equation for a binary polymer–solvent system was first derived by Zimm by using the single contact approximation.[14] It can be written in the form

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{V} \tag{1b}$$

where $\mathbf{V} = 1/\varphi_s - 2\chi_{ps}$, φ_s is the volume fraction of solvent, and χ_{ps} is the polymer–solvent interaction parameter. In the case of a binary mixture of two homopolymers τ and σ, the corresponding result was derived by de Gennes using

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the Random-Phase Approximation[1]

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}^0_\tau(\mathbf{q})^{-1} + \mathbf{S}^0_\sigma(\mathbf{q})^{-1} - 2\chi_{\sigma\tau} \qquad (1c)$$

Equations 1b and 1c are usually referred to as Zimm's and de Gennes' formulas, respectively. This review is the first of a series that will deal with the applications of eqs 1a–1c to various systems made of polymer mixtures.

2. Definitions and Notations

In a scattering experiment, one measures the intensity $I(\mathbf{q})$, which is given by

$$I(\mathbf{q}) = \mathbf{a}^{\mathrm{T}}\cdot\mathbf{S}(\mathbf{q})\cdot\mathbf{a} \qquad (2)$$

where $\mathbf{a} = \mathrm{col}\,(a, ..., a_z)$ is a column vector whose elements a_σ are the scattering lengths of monomers σ, $\mathbf{a}^{\mathrm{T}}$ is its transpose, and z is the number of components. $\mathbf{S}(\mathbf{q})$ is a $z \times z$ square matrix whose elements $\mathbf{S}_{\sigma\tau}(\mathbf{q})$ are defined by

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \langle \rho^\sigma_{\mathbf{q}} \rho^\tau_{-\mathbf{q}} \rangle \qquad (3a)$$

where $\rho^\sigma_{\mathbf{q}}$ is the density of monomers of species σ. In the discrete representation, we have

$$\rho^\sigma_{\mathbf{q}} = \sum_{\alpha=1}^{n^\sigma} \sum_{i\in\alpha}^{N_\sigma} e^{i\mathbf{q}\cdot\mathbf{R}_{\alpha i}{}^\sigma} \qquad (3b)$$

and in the continuous representation

$$\rho^\sigma_{\mathbf{q}} = \sum_{\alpha=1}^{n^\sigma} \int_0^{N_\sigma} \mathrm{d}s\; e^{i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)} \qquad (3c)$$

Here $\mathbf{R}^\sigma_{\alpha i}$ or $\mathbf{R}^\sigma_\alpha(s)$ denotes the position of a monomer (i or s along the chain) belonging to chain α of type σ. There are n^σ chains of type σ per unit volume, and their degree of polymerization is N_σ. Then substituting eq 3b or eq 3c into eq 3a yields

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \sum_\alpha^{n^\sigma} \sum_\beta^{n^\tau} \sum_{i\in\alpha}^{N_\sigma} \sum_{j\in\beta}^{N_\tau} \langle e^{i\mathbf{q}\cdot[\mathbf{R}_\alpha{}^\sigma(s) - \mathbf{R}_\beta{}^\tau(s')]} \rangle \qquad (4a)$$

or

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \sum_\alpha^{n^\sigma} \sum_\beta^{n^\tau} \int_0^{N_\sigma} \mathrm{d}s \int_0^{N_\tau} \mathrm{d}s'\; \langle e^{i\mathbf{q}\cdot[\mathbf{R}_\alpha{}^\sigma(s) - \mathbf{R}_\beta{}^\tau(s')]} \rangle \qquad (4b)$$

The symbol $\langle ... \rangle$ designates an equilibrium average in the interacting system. The elements of the bare structure matrix $\mathbf{S}_0$ have exactly the same definitions, but the equilibrium average is taken with respect to the distribution function in the noninteracting system (i.e., intramolecular distribution function). When we deal with a solution where the solvent has been taken out of the matrix formulation by the use of an incompressibility condition, the interaction matrix $\mathbf{V}$ represents the usual short-range excluded-volume matrix. It can be expressed in terms of the solvent volume fraction φ_s and the Flory–Huggins interaction parameters $\chi_{\sigma\tau}$ as

$$\mathbf{V} = (1/\varphi_s)\mathbf{E} - \alpha \qquad (5a)$$

$\mathbf{E}$ is a square matrix where all elements are units; α is a square matrix of the same order with elements

$$\alpha_{\sigma\tau} = \chi_{\sigma s} + \chi_{\tau s} - \chi_{\sigma\tau}(1 - \delta_{\sigma\tau}) \qquad (5b)$$

The Kronecker delta function $\delta_{\sigma\tau}$ is introduced to ensure that $\chi_{\sigma\sigma} = 0$, as it should. These quantities will be defined later in terms of real potentials. In the first and second methods, we shall use the discrete representations, but the Edwards Hamiltonian method is used more commonly with the continuous representation of monomers along chains. Therefore, we shall keep this representation here also.

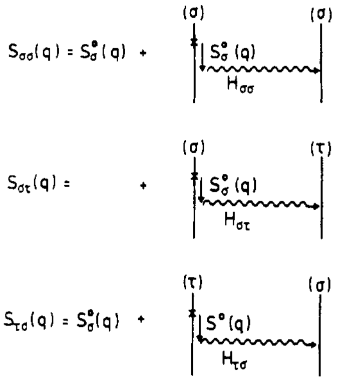

Figure 1. Diagrammatic representations of eqs 7a–7c (two-component systems).

3. Ornstein–Zernike (OZ) Formalism

Here we shall present this method in a slightly more systematic way than has been applied before. We note that the partial structure factors $\mathbf{S}_{\sigma\tau}(\mathbf{q})$ of eq 4a can be written as a sum of two terms: one describes intramolecular correlations and gives rise to $\mathbf{S}^0_{\sigma\tau}(\mathbf{q})$, and the other describes intermolecular correlations. We introduce the correlation matrix (intermolecular) $\mathbf{H}$ to designate them: Therefore, we write the standard equation, which is first in the OZ formalism:

$$\mathbf{S}(\mathbf{q}) = \mathbf{S}_0(\mathbf{q})[1 + \mathbf{H}(\mathbf{q})] \qquad (6)$$

where 1 is the unit matrix. For homopolymers, this equation gives (z-component system)

$$\mathbf{S}_{\sigma\sigma}(\mathbf{q}) = \mathbf{S}^0_\sigma(\mathbf{q}) + \mathbf{S}^0_\sigma(\mathbf{q})\,\mathbf{H}_{\sigma\sigma}(\mathbf{q}) \qquad (7a)$$

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \mathbf{S}^0_\sigma(\mathbf{q})\,\mathbf{H}_{\sigma\tau}(\mathbf{q}) \qquad (7b)$$

$$\mathbf{S}_{\tau\sigma}(\mathbf{q}) = \mathbf{S}^0_\tau(\mathbf{q})\,\mathbf{H}_{\tau\sigma}(\mathbf{q}) \qquad (7c)$$

The diagrammatic representation, which illustrates the normalization with respect to the intramolecular factor, is given in Figure 1.

For copolymers, the matrix $\mathbf{S}_0$ has nonzero off-diagonal elements, and the interspecies correlations are found both in intra- and intermolecular functions. For a two-component system, eq 6 gives explicitly

$$\mathbf{S}_{\sigma\sigma}(\mathbf{q}) = \mathbf{S}^0_\sigma(\mathbf{q}) + \mathbf{S}^0_\sigma(\mathbf{q})\,\mathbf{H}_{\sigma\sigma}(\mathbf{q}) + \mathbf{S}^0_{\sigma\tau}(\mathbf{q})\,\mathbf{H}_{\tau\sigma}(\mathbf{q}) \qquad (8a)$$

and

$$\mathbf{S}_{\tau\sigma}(\mathbf{q}) = \mathbf{S}^0_{\tau\sigma}(\mathbf{q}) + \mathbf{S}^0_{\tau\sigma}(\mathbf{q})\,\mathbf{H}_{\sigma\sigma}(\mathbf{q}) + \mathbf{S}^0_\tau(\mathbf{q})\,\mathbf{H}_{\tau\sigma}(\mathbf{q}) \qquad (8b)$$

The expressions for $\mathbf{S}_{\tau\tau}(\mathbf{q})$ and $\mathbf{S}^0_{\sigma\tau}(\mathbf{q})$ can be deduced by interchanging the indices σ and τ. The diagrammatic representation of these two equations is given in Figure 2.

The second step in the OZ formalism is to introduce the direct correlation matrix $\mathbf{C}$, which is related to $\mathbf{H}$ by the well-known relationship

$$\mathbf{H} = \mathbf{C} + \mathbf{H}\cdot\mathbf{C} \qquad (9a)$$

or equivalently

$$\mathbf{H} = (\mathbf{I} - \mathbf{C})^{-1}\cdot\mathbf{C} \qquad (9b)$$

where we note that factors such as n^σ and N_σ are lumped into the definition of $\mathbf{C}$. One can also introduce direct and total correlation functions between monomers denoted $c_{(\sigma,i;\,\tau,j)}$ and $h_{(\sigma,i;\,\tau,j)}$, respectively. $(\sigma,i;\tau,j)$ is the correlation

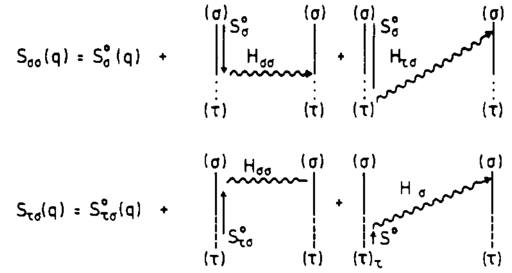

Figure 2. Diagrammatic representations of eqs 8a and 8b (diblock copolymer $\sigma\tau$).

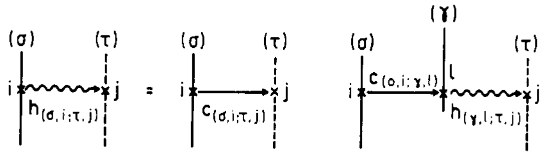

Figure 3. Diagrammatic representation of eq 11 for homopolymers.

between monomer i on chain σ and monomer j on chain τ. These monomer–monomer correlation functions are related with the interspecies correlation functions by the following equations:

$$\mathbf{H}_{\sigma\tau} = \sum_i^{N_\sigma}\sum_j^{N_\tau} h_{(\sigma,i;\,\tau,j)} \tag{10a}$$

$$\mathbf{C}_{\sigma\tau} = \sum_i^{N_\sigma}\sum_j^{N_\tau} c_{(\sigma,i;\,\tau,j)} \tag{10b}$$

Furthermore, we assume that h and c are related by the usual OZ equations:[15]

$$h_{(\sigma,i;\,\tau,j)} = c_{(\sigma,i;\,\tau,j)} + \sum_\gamma \sum_{l\in\gamma}^{N_\gamma} c_{(\sigma,i;\,\gamma,l)} h_{(\gamma,l;\,\tau,j)} \tag{11}$$

We can obtain a similar equation for intraspecies correlations $h_{(\sigma,i;\,\sigma,j)}$. This equation can be illustrated by the diagram of Figure 3.

Equation 11 is valid for homopolymers and copolymers without distinction. It was illustrated for homopolymers in Figure 3 for simplicity. We note the summation over all species γ present in the mixture including σ and τ. If only two species, σ and τ, are present, then the right-hand side of eq 11 contains three terms, two of them corresponding to $\gamma = \sigma$ and $\gamma = \tau$. Summing both sides of eq 11 over all monomers i and j and using eq 10 and the following approximation[16]

$$\sum_i^{N_\sigma} c_{(\sigma,i;\,\gamma,l)} = \sum_i^{N_\sigma}\sum_l^{N_\gamma} c_{(\sigma,i;\,\gamma,l)} \tag{12}$$

we obtain

$$\mathbf{H}_{\sigma\tau} = \mathbf{C}_{\sigma\tau} + \sum_\gamma \mathbf{C}_{\sigma\gamma}\mathbf{H}_{\gamma\tau} \tag{13}$$

which corresponds to eq 9a in matrix form. Substituting eq 9b into eq 6 yields

$$\mathbf{S}(\mathbf{q}) = \mathbf{S}_0(\mathbf{q})\cdot[\mathbf{I} - \mathbf{C}]^{-1} \tag{14a}$$

The reciprocal form of this equation reads

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) - \mathbf{C}\cdot\mathbf{S}_0^{-1}(\mathbf{q}) \tag{14b}$$

Since $\mathbf{S}_0(\mathbf{q})$ is always known for the system under investigation, it remains to specify $\mathbf{C}$ to solve the problem completely. In simple liquid theories,[5] there are several approximations that relate $\mathbf{C}$ to $\mathbf{H}$ in addition to the OZ equation (eq 13), thereby closing the set. These methods have not yet been extended to macromolecules except for a few attempts using the Mean Spherical Approximation or the Percus–Yevick Approximation.[7,17] Here we use the following approximation, which turns out to be good for multicomponent homopolymer and copolymer mixtures:

$$\mathbf{C} = -\mathbf{V}\cdot\mathbf{S}_0(\mathbf{q}) \tag{15}$$

We see immediately that the combination of eqs 14b and 15 gives the expected result (see eq 1a).

To summarize this method, we note that it is based on three equations: eqs 6, 9a, and 15. The first two equations are basically definitions of $\mathbf{H}$ and $\mathbf{C}$. All the approximations in this model are in eq 15, which gives $\mathbf{C}$ in terms of $\mathbf{S}_0$ and $\mathbf{V}$. We have not used the incompressibility condition, and we have not even specified what the system is. This is done when we write explicitly $\mathbf{S}_0$ and $\mathbf{V}$. In the next section, we describe another method, the RPA.

4. RPA

To illustrate the steps of this method, we shall consider the case of a ternary system before writing the general equation in matrix form. Aside from pedagogical reasons, the resulting equations for the ternary system will be particularly useful in forthcoming papers.

4.1. Ternary Mixtures. Consider a mixture of three polymer species σ, τ, and γ and let us write the density fluctuations $\delta\rho_\sigma(\mathbf{q})$, ..., in response to the external perturbations $\delta U_\sigma(\mathbf{q})$, ..., etc.

$$\delta\rho_\sigma(\mathbf{q}) = -\chi_\sigma^0[\delta U_\sigma(\mathbf{q}) + \delta U_0(\mathbf{q}) + kT\chi_{\sigma\tau}\delta\rho_\tau(\mathbf{q}) + kT\chi_{\sigma\gamma}\delta\rho_\gamma(\mathbf{q})] \tag{16a}$$

$$\delta\rho_\tau(\mathbf{q}) = -\chi_\tau^0[\delta U_\tau(\mathbf{q}) + \delta U_0(\mathbf{q}) + kT\chi_{\tau\sigma}\delta\rho_\sigma(\mathbf{q}) + kT\chi_{\tau\gamma}\delta\rho_\gamma(\mathbf{q})] \tag{16b}$$

$$\delta\rho_\gamma(\mathbf{q}) = -\chi_\gamma^0[\delta U_\gamma(\mathbf{q}) + \delta U_0(\mathbf{q}) + kT\chi_{\gamma\sigma}\delta\rho_\sigma(\mathbf{q}) + kT\chi_{\gamma\tau}\delta\rho_\tau(\mathbf{q})] \tag{16c}$$

The bare response functions are related to bare structure factors by the known formula

$$kT\chi_\sigma^0(\mathbf{q}) = \mathbf{S}_\sigma^0(\mathbf{q}); \qquad \sigma = \tau, \gamma, ... \tag{16d}$$

$\delta U_0(\mathbf{q})$ is a potential that acts uniformally on all species to ensure the incompressibility of the total system:

$$\delta\rho_0(\mathbf{q}) + \delta\rho_\tau(\mathbf{q}) + \delta\rho_\gamma(\mathbf{q}) = 0 \tag{16e}$$

$\chi_{\sigma\tau}$, etc., are the Flory–Huggins interaction parameters and should not be confused with the response functions. These parameters are conceptually defined in terms of real potentials $W_{\sigma\tau}$ by (the precise definition of the potentials $W_{\sigma t}$ will be given later)

$$\chi_{\sigma\tau} = W_{\sigma\tau} - \frac{1}{2}(W_{\sigma\sigma} + W_{\tau\tau}) \tag{16f}$$

which is proportional to the energy required to break two bonds $\sigma\sigma$ and $\tau\tau$ and form bonds $\sigma\tau$. Substituting the incompressibility condition (16e) into eq 16c gives

$$\delta U_0(\mathbf{q}) = -\delta U_\gamma(\mathbf{q}) + \left(\frac{1}{\chi_\gamma^0(\mathbf{q})} - kT\chi_{\sigma\gamma}\right)\delta\rho_\sigma(\mathbf{q}) + \left(\frac{1}{\chi_\gamma^0(\mathbf{q})} - kT\chi_{\tau\gamma}\right)\delta\rho_\tau(\mathbf{q}) \tag{17a}$$

This equation defines the potential that ensures the incompressibility of the system in terms of its properties. Substituting eq 17a into eqs 16a and 16b gives a set of two equations relating the two independent variables $\delta\rho_\sigma(\mathbf{q})$ and $\delta\rho_\tau(\mathbf{q})$:

$$[1 - \psi_{\sigma\sigma}(\mathbf{q})]\, \delta\rho_\sigma(\mathbf{q}) - \psi_{\sigma\tau}(\mathbf{q})\, \delta\rho_\tau(\mathbf{q}) = -\chi^0_\sigma(\mathbf{q})\, \delta U'_\sigma(\mathbf{q}) \tag{17b}$$

$$-\psi_{\tau\sigma}(\mathbf{q})\, \delta\rho_\sigma(\mathbf{q}) + [1 - \psi_{\tau\tau}(\mathbf{q})]\, \delta\rho_\tau(\mathbf{q}) = -\chi^0_\tau(\mathbf{q})\, \delta U'_\tau(\mathbf{q}) \tag{17c}$$

where

$$\psi_{\sigma\tau}(\mathbf{q}) = -\chi^0_\sigma(\mathbf{q}) \left[\frac{1}{\chi^0_\gamma(\mathbf{q})} - 2kT\chi_{\sigma\gamma}\right] \tag{18a}$$

$$\psi_{\sigma\tau}(\mathbf{q}) = -\chi^0_\sigma(\mathbf{q}) \left[\frac{1}{\chi^0_\gamma(\mathbf{q})} - kT\chi_{\sigma\gamma} - kT\chi_{\tau\gamma} + kT\chi_{\sigma\tau}\right] \tag{18b}$$

$$\psi_{\tau\sigma}(\mathbf{q}) = -\chi^0_\tau(\mathbf{q}) \left[\frac{1}{\chi^0_\gamma(\mathbf{q})} - kT\chi_{\sigma\gamma} - kT\chi_{\tau\gamma} + kT\chi_{\sigma\tau}\right] \tag{18c}$$

$\psi_{\tau\tau}(\mathbf{q})$ can be deduced from eq 18a by interchanging the indices σ and τ. The potential $\delta U'$ is defined as

$$\delta U'_{\sigma,\tau}(\mathbf{q}) \equiv \delta U_{\sigma,\tau}(\mathbf{q}) - \delta U_\gamma(\mathbf{q}) \tag{18d}$$

One can see the connection between ψ's and the direct correlation functions in the preceding model by defining the quantities

$$U_\sigma(\mathbf{q}) = \frac{1}{\mathbf{S}^0_\gamma(\mathbf{q})} - 2\chi_{\sigma\gamma} \tag{19a}$$

$$U_{\sigma\tau}(\mathbf{q}) = \frac{1}{\mathbf{S}^0_\gamma(\mathbf{q})} - \chi_{\sigma\gamma} - \chi_{\tau\gamma} + \chi_{\sigma\tau} \tag{19b}$$

Equation 18 becomes

$$\psi_{\sigma\sigma}(\mathbf{q}) = -U_\sigma(\mathbf{q})\, \mathbf{S}^0_\sigma(\mathbf{q}) \tag{20a}$$

$$\psi_{\sigma\tau}(\mathbf{q}) = -U_{\sigma\tau}(\mathbf{q})\, \mathbf{S}^0_\sigma(\mathbf{q}) \tag{20b}$$

$$\psi_{\tau\sigma}(\mathbf{q}) = -U_{\sigma\tau}(\mathbf{q})\, \mathbf{S}^0_\tau(\mathbf{q}) \tag{20c}$$

or in matrix form

$$\psi(\mathbf{q}) = -\mathbf{U}(\mathbf{q})\cdot\mathbf{S}_0(\mathbf{q}) \tag{20d}$$

Solving eqs 17a–17c, one can obtain the total structure factors $\mathbf{S}_{\sigma\tau}(\mathbf{q})$ in the interacting system:

$$-kT\delta\rho_\sigma(\mathbf{q}) = \mathbf{S}_{\sigma\sigma}(\mathbf{q})\, \delta U'_\sigma(\mathbf{q}) + \mathbf{S}_{\sigma\tau}(\mathbf{q})\, \delta U'_\tau(\mathbf{q}) \tag{21a}$$

$$-kT\delta\rho_\tau(\mathbf{q}) = S_{\tau\sigma}(\mathbf{q})\, \delta U'_\sigma(\mathbf{q}) + \mathbf{S}_{\tau\tau}(\mathbf{q})\, \delta U'_\tau(\mathbf{q}) \tag{21b}$$

The results are

$$\mathbf{S}_{\sigma\sigma}(\mathbf{q}) = \mathbf{S}^0_\sigma(\mathbf{q})[1 + U_\tau(\mathbf{q})\, \mathbf{S}^0_\tau(\mathbf{q})]/\mathcal{D}(\mathbf{q}) \tag{22a}$$

$$\mathbf{S}_{\tau\tau}(\mathbf{q}) = \mathbf{S}^0_\tau(\mathbf{q})[1 + U_\sigma(\mathbf{q})\, \mathbf{S}^0_\sigma(\mathbf{q})]/\mathcal{D}(\mathbf{q}) \tag{22b}$$

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \mathbf{S}_{\tau\sigma}(\mathbf{q}) = -U_{\sigma\tau}(\mathbf{q})\, \mathbf{S}^0_\sigma(\mathbf{q})\, \mathbf{S}^0_\tau(\mathbf{q})/\mathcal{D}(\mathbf{q}) \tag{22c}$$

where the denominator $\mathcal{D}(\mathbf{q})$ is the determinant of eqs 17b and 17c:

$$\mathcal{D}(\mathbf{q}) = [1 + U_\sigma(\mathbf{q})\, \mathbf{S}^0_\sigma(\mathbf{q})][1 + U_\tau(\mathbf{q})\, \mathbf{S}^0_\tau(\mathbf{q})] - U_{\sigma\tau}{}^2(\mathbf{q})\, \mathbf{S}^0_\sigma(\mathbf{q})\, \mathbf{S}^0_\tau(\mathbf{q}) \tag{22d}$$

If component γ is a solvent

$$\mathbf{S}^0_\gamma(\mathbf{q}) = \varphi_s \tag{23a}$$

and we have the known results where U_σ, etc., coincide with the ordinary excluded volume parameters. $\mathbf{U} = \mathbf{V}$; in this case, eqs 22a–22d can be written in matrix form as

$$\mathbf{S}(\mathbf{q}) = [1 + \mathbf{V}\cdot\mathbf{S}_0(\mathbf{q})]^{-1}\mathbf{S}_0(\mathbf{q}) \tag{23b}$$

which leads to eq 1a.

4.2. Matrix Formulation of the RPA. This formulation has already been done by Akcasu and Tombakuglu[4] in its dynamical version, and we only briefly reproduce their equations. One notes that eqs 16a–16c can be written in a compact form as

$$\delta\rho(\mathbf{q}) = -\chi_0(\mathbf{q})[\delta\mathbf{U}(\mathbf{q}) + \delta U_0\xi + \chi\delta\rho(\mathbf{q})] \tag{24}$$

where $\delta\rho(\mathbf{q}) = \mathrm{col}\ (\delta\rho_\sigma, \delta\rho_\tau, ...)$, $\xi = \mathrm{col}\ (1, 1, 1, ..., 1)$, $\delta\mathbf{U} = \mathrm{col}\ (\delta U_\sigma, \delta U_\tau, ...)$ are column vectors. The incompressibility condition in eq 16e reads

$$\xi^{\mathrm{T}}\cdot\delta\rho = 0; \qquad \xi^{\mathrm{T}} \equiv (1, 1, ...) \tag{25}$$

The procedure by which one isolates one component, say γ, by using the incompressibility condition and writing the potential δU_0 in terms of the properties of the mixture is done in the same way as in the preceding section (4.1). One writes explicitly eq 21 for component γ:

$$\delta\rho_\gamma(\mathbf{q}) = -\chi^0_\gamma(\mathbf{q})[\delta\mathbf{U}_\gamma(\mathbf{q}) + \delta U_0 + kT\chi_{\gamma\sigma}\delta\rho_\sigma(\mathbf{q}) + kT\chi_{\gamma\tau}\delta\rho_\tau(\mathbf{q}) + ...] \tag{26a}$$

Solving this equation for δU_0 and substituting the result into eq 24, one arrives at

$$\delta\rho(\mathbf{q}) = -\chi_0[\delta U' + kT\mathbf{U}(\mathbf{q})\, \delta\rho(\mathbf{q})] \tag{26b}$$

with

$$\delta\mathbf{U}' = \begin{pmatrix} U_\sigma & - & \delta U_\gamma \\ U_\tau & - & \delta U_\gamma \\ & \cdot & \\ & \cdot & \\ U_Z & \dot{-} & \delta U_\gamma \end{pmatrix} \tag{26c}$$

and the elements of $\mathbf{U}(\mathbf{q})$ are defined in eqs 19a and 19b. Solving eq 26b in the form

$$\delta\rho(\mathbf{q}) = -\chi(\mathbf{q})\delta U' \tag{27a}$$

yields the result

$$\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0{}^{-1} + \mathbf{U}(\mathbf{q}) \tag{27b}$$

and if γ is a solvent $\mathbf{U}(\mathbf{q}) \equiv \mathbf{V}$, eq 27b coincides with eqs 1a–1c. To summarize this method, we say that it is based on eq 24, which contains the unknown and uniform potential δU_0. This potential is expressed in terms of other properties of the system using the incompressibility assumption, and this leads to extracting one component from the mixture, which will play the role of matrix or eventually solvent. The next method is based on the Edwards Hamiltonian written in terms of the collective coordinates or monomer densities.

5. Edwards Hamiltonian Method

Our starting point is the Edwards Hamiltonian, which is written in terms of the monomer coordinates for a two-components system as

$$\beta\mathcal{H}(\{\mathbf{R}_\alpha^\sigma(s)\}) = \sum_{\sigma=1}^{z}\sum_{\alpha\in\sigma}^{n^\sigma}\frac{3}{2l_\sigma}\int_0^{N_\sigma}\left(\frac{\partial\mathbf{R}_\alpha^\sigma(s)}{\partial s}\right)^2 \mathrm{d}s + \sum_{\sigma=1}^{z}\sum_{\tau=1}^{z}\sum_{\alpha\in\sigma}^{N_\sigma}\sum_{\beta\in\tau}^{N_\tau}\int_0^{N_\sigma}\mathrm{d}s\int_0^{N_\tau}\mathrm{d}s'\ W_{\sigma\tau}(\mathbf{R}_\alpha^\sigma(s) - \mathbf{R}_\beta^\tau(s')) \quad (28)$$

where β in front of the Hamiltonian $\mathcal{H}$ is equal to $1/kT$. The first term represents the Wiener measure, which is appropriate for Gaussian chains, and the second describes the interactions between all chains of the same or different components. Usually the interaction potentials are assumed to be short ranged and replaced by pseudopotentials:

$$W_{\sigma\tau}(\mathbf{R}_\alpha^\sigma(s) - \mathbf{R}_\beta^\tau(s')) \simeq W_{\sigma\tau}\delta((\mathbf{R}_\alpha^\sigma(s) - \mathbf{R}_\beta^\tau(s')) \quad (29a)$$

where $W_{\sigma\tau}$ is a constant describing the strength of the potential. The formalism, however, works also for long-ranged interactions $W_{\sigma\tau}(\mathbf{R}_\alpha^\sigma(s) - \mathbf{R}_\beta^\tau(s'))$. Equation 29a is only used for thermodynamic forces, but if we have charged polymers in the system, we would have to add a long-range. Coulombic potential as

$$W_{\sigma\tau}(\mathbf{R}_\alpha^\sigma(s) - \mathbf{R}_\beta^\tau(s')) = \sum_{\mathbf{q}} W_{\sigma\tau}(\mathbf{q})e^{i\mathbf{q}\cdot(\mathbf{R}_\alpha{}^\sigma(s)-\mathbf{R}_\beta{}^\tau(s'))} \quad (29b)$$

where $W_{\sigma\tau}(\mathbf{q})$ varies like $\mathbf{q}^{-2}$ for bare Coulombic interactions. Equation 28 can be written in a compact form as

$$\mathcal{H}(\{\mathbf{R}_\alpha^\sigma(s)\}) + \mathcal{H}(\{\mathbf{R}_\alpha^\sigma(s)\}) + \mathcal{H}_1(\{\mathbf{R}_\alpha^\sigma(s)\}) \quad (30)$$

where $\mathcal{H}_0$ is the Hamiltonian of the noninteracting chains (bare Hamiltonian) and $\mathcal{H}_1$ represents the interactions between chains. $\{\mathbf{R}_\alpha^\sigma(s)\}$ denotes all monomer coordinates in the system and l_σ is the step length of species σ. Knowing the Hamiltonian, one can write the partition function

$$Z(\{\mathbf{R}_\alpha^\sigma(s)\}) = \frac{1}{\prod_{\sigma=1}^{Z} n^\sigma!}\int \mathcal{D}\mathbf{R}_\alpha^\sigma(s)\prod_{\sigma=1}^{Z}\prod_{\alpha=1}^{n^\sigma} e^{-\beta\mathcal{H}(\{\mathbf{R}_\alpha{}^\sigma(s)\})} \quad (31a)$$

which is a functional integral over all monomer position coordinates $\{\mathbf{R}_\alpha^\sigma\}$. All thermodynamic properties can be deduced from Z and in particular the free energy, which is given by

$$\beta F = -\log Z(\{\mathbf{R}_\alpha^\sigma(s)\}) \quad (31b)$$

We shall discuss later in this section the connection of F with the Flory–Huggins free energy and its extension to include the effects of fluctuations. Our aim now is to write the Hamiltonian in terms of the collective variables $\rho_\mathbf{q}^\sigma$ because this form is more convenient than $\mathcal{H}(\{\mathbf{R}_\alpha^\sigma(s)\})$. $\rho_\mathbf{q}^\sigma$ was already defined in eq 3c, and the argument $\mathbf{q}$ is put in the index for simplicity in the notations. Here since we are essentially dealing with correlations in density fluctuations, we shall not make a distinction between $\rho_\mathbf{q}^\sigma$ and $\delta\rho_\mathbf{q}^\sigma$ unless specified otherwise. We have

$$\delta\rho_\mathbf{q}^\sigma = \rho_\mathbf{q}^\sigma - \rho_0^\sigma\frac{1}{\Omega}\delta(\mathbf{q}) \quad (32)$$

where ρ_0^σ is the mean density of component σ, Ω is the volume of the system, and $\delta(\mathbf{q})$ is the Dirac delta function. For $\mathbf{q} \neq 0$, $\delta\rho_\mathbf{q}^\sigma$ and $\rho_\mathbf{q}^\sigma$ are equal.

The partition function $Z(\{\mathbf{R}_\alpha^\sigma(s)\})$ can be transformed to collective coordinates by the following procedure[10,11,18]

$$Z(\{\rho_\mathbf{q}^\sigma\}) = \int \mathcal{D}\mathbf{R}_\alpha^\sigma(s)\prod_{\sigma=1}^{Z}\prod_{\alpha=1}^{n^\sigma}\prod_{\mathbf{q}>0}\delta(\rho_\mathbf{q}^\sigma - \sum_{\alpha=1}^{N_\sigma}\int_0^{N_\sigma} e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)})e^{-\beta\mathcal{H}} \quad (33a)$$

The next step is to rewrite the delta function as follows

$$\delta(\rho_\mathbf{q}^\sigma - \sum_{\alpha}\int_0^{N_\sigma}\mathrm{d}s\ e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)}) = \int \mathrm{d}g_{-\mathbf{q}}^\sigma\ e^{ig_{-\mathbf{q}}{}^\sigma(\rho_\mathbf{q}{}^\sigma - \sum_{\alpha=1}{}^{n^\sigma}\int_0{}^{N_\sigma}\mathrm{d}s e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)})} \quad (33b)$$

where we have introduced the new field variables $g_{-\mathbf{q}}^\sigma$. Combining the last two equations gives

$$Z(\{\rho_\mathbf{q}^\sigma\}) = \int \mathcal{D}\mathbf{R}_\alpha^\sigma(s)\int \delta g_{-\mathbf{q}}^\sigma \times e^{i\sum_\mathbf{q}\sum_\sigma\{g_{-\mathbf{q}}{}^\sigma\rho_\mathbf{q}{}^\sigma - g_{-\mathbf{q}}{}^\sigma\sum_\alpha\int_0{}^{N_\sigma}\mathrm{d}s e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)}\}}e^{-\beta\{\mathcal{H}_0+\mathcal{H}_1\}} \quad (33c)$$

This functional integral can be evaluated by standard methods. First, we must note that $\mathcal{H}_1$ can be immediately expressed in terms of collective coordinates $\rho_\mathbf{q}^\sigma$ (see eqs 27–29). We have

$$\beta\mathcal{H}_1(\{\rho_\mathbf{q}^\sigma\}) = \sum_\mathbf{q}\sum_{\sigma\tau} W_{\sigma\tau}\rho_\mathbf{q}^\sigma\rho_{-\mathbf{q}}^\tau \quad (33d)$$

We shall assume here that the $W_{\sigma\tau}$ values are constant, confining ourselves to short-range interactions expressed by delta functions. The main problem is to transform $\mathcal{H}_0$ and the integral over monomer coordinates in the exponent. The common procedure consists of expanding this term as follows:

$$e^{-i\sum_\mathbf{q}\sum_\sigma g_{-\mathbf{q}}{}^\sigma\sum_\alpha\int_0{}^{N_\sigma}\mathrm{d}s e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)}} \approx 1 - i\sum_\mathbf{q}\sum_\sigma g_{-\mathbf{q}}^\sigma\sum_\alpha\int_0^{N_\sigma} e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)} - \frac{1}{2!}\sum_{\mathbf{qk}}\sum_{\sigma\tau} g_{-\mathbf{q}}^\sigma g_{-\mathbf{k}}^\tau\sum_{\alpha\beta}^{n^\sigma n^\tau}\int_0^{N_\sigma}\mathrm{d}s\int_0^{N_\tau}\mathrm{d}s'\ e^{-i\mathbf{q}\cdot\mathbf{R}_\alpha{}^\sigma(s)}e^{-i\mathbf{k}\cdot\mathbf{R}_\beta{}^\tau(s')} + \text{etc.} \quad (34a)$$

Putting eq 34a back into eq 33c, one can perform the $\mathcal{D}(\{\mathbf{R}_\alpha^\sigma(s)\})$ integral, which involves in addition to eq 34a the factor $e^{-\beta\mathcal{H}_0}$. One can easily see that the first term gives 1, the second is 0, and the third term gives

$$-\sum_{\mathbf{q}>0}\sum_{\sigma\tau} g_\mathbf{q}^\sigma g_{-\mathbf{q}}^\tau \mathbf{S}_{\sigma\tau}^0(\mathbf{q}) \quad (34b)$$

where $\mathbf{S}_{\sigma\tau}^0(\mathbf{q})$ is defined in eq 4b, the average being performed with respect to the bare Hamiltonian $\mathcal{H}_0$ and higher order terms are neglected (Gaussian approximation): In a way, higher order terms are not completely neglected because of the following approximation, which is often used in polymer solution theories (as in the former models of sections 3 and 4):

$$1 - \sum_\mathbf{q}\sum_{\sigma\tau}^{z} g_\mathbf{q}^\sigma g_{-\mathbf{q}}^\tau \mathbf{S}_{\sigma\tau}^0(\mathbf{q}) \approx e^{-\sum_\mathbf{q}\sum_{\sigma,\tau} g_\mathbf{q}{}^\sigma g_{-\mathbf{q}}{}^\tau \mathbf{S}_{\sigma\tau}{}^0(\mathbf{q})} \quad (34c)$$

Combining eqs 33c, 33d, and 34c gives the result

$$Z(\{\rho_\mathbf{q}^\sigma\}) = \int\prod_\sigma \mathcal{D}\rho_\mathbf{q}^\sigma e^{-\beta\mathcal{H}(\{\rho_\mathbf{q}^\sigma\})} \quad (35a)$$

where the Gaussian integral over the field variable $g_{-\mathbf{q}}^\sigma$ has been performed and $\mathcal{H}(\{\rho_{\mathbf{q}}^{\sigma}\})$ is finally given by

$$\beta\mathcal{H}(\{\rho_{\mathbf{q}}^{\sigma}\}) = \sum_{\sigma\tau}\rho_{\mathbf{q}}^{\sigma}\{(\mathbf{S}_{\sigma\tau}^{0})^{-1}(\mathbf{q}) + W_{\sigma\tau}\}\rho_{-\mathbf{q}}^{\tau} \qquad (35b)$$

and

$$\mathbf{S}_{\sigma\tau}^{-1}(\mathbf{q}) = (\mathbf{S}_{\sigma\tau}^{0})^{-1}(\mathbf{q}) + W_{\sigma\tau} \qquad (35c)$$

To understand eq 35c, let us write the definition of $\mathbf{S}_{\sigma\tau}(\mathbf{q})$:

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \langle\rho_{\mathbf{q}}^{\sigma}\rho_{-\mathbf{q}}^{\tau}\rangle \qquad (35d)$$

where the average is performed with respect to the total potential in the interacting system:

$$\mathbf{S}_{\sigma\tau}(\mathbf{q}) = \frac{1}{Z(\{\rho_{\mathbf{q}}\})}\int\mathcal{D}(\{\rho_{\mathbf{q}}\})\rho_{\mathbf{q}}^{\sigma}\rho_{-\mathbf{q}}^{\tau}e^{-\beta\mathcal{H}(\{\rho_{\mathbf{q}}^{\sigma}\})} \qquad (35e)$$

where

$$Z(\{\rho_{\mathbf{q}}^{\sigma}\}) = \int\mathcal{D}(\{\rho_{\mathbf{q}}\})e^{-\beta\mathcal{H}(\{\rho_{\mathbf{q}}\})} \qquad (35f)$$

This functional integral is Gaussian, and the result is given in eq 35c or

$$\langle\rho_{\mathbf{q}}^{\sigma}\rho_{-\mathbf{q}}^{\tau}\rangle = \mathbf{S}_{\sigma\tau}(\mathbf{q}) = \{(\mathbf{S}_{\sigma\tau}^{0})^{-1}(\mathbf{q}) + W_{\sigma\tau}\}^{-1} \qquad (35g)$$

This is of course the central result we are seeking by using the Edwards Hamiltonian method. The remaining task is to express the real interaction potentials $W_{\sigma\tau}$ in terms of Flory–Huggins interaction parameters $\chi_{\sigma\tau}$ (which has already been announced in eq 16f). First, we note that eq 35c does not take the incompressibility requirement into account; the latter is expressed by

$$\sum_{\tau=1}\rho_{\mathbf{q}}^{\tau} = 0 \quad (\mathbf{q} \neq 0) \qquad (36a)$$

or

$$\rho_{\mathbf{q}}^{1} + \sum_{\tau=2}\rho_{\mathbf{q}}^{\tau} = 0 \qquad (36b)$$

where we have isolated component 1 whose density is minus the sum of densities of all other components (but any of the z components can be isolated this way). Eliminating $\rho_{\mathbf{q}}^{1}$ from the Hamiltonian in eq 35b gives

$$\beta\mathcal{H}(\{\rho_{\mathbf{q}}\}) = \rho_{\mathbf{q}}^{1}((\mathbf{S}_{11}^{0})^{-1} + W_{11})\rho_{-\mathbf{q}}^{1} + \sum_{\sigma=2}^{z}\rho_{\mathbf{q}}^{1}((\mathbf{S}_{1\sigma}^{0})^{-1} + W_{1\sigma})\rho_{-\mathbf{q}}^{\sigma} + \sum_{\tau=2}^{z}\rho_{\mathbf{q}}^{\tau}((\mathbf{S}_{\tau1}^{0})^{-1} + W_{\tau1})\rho_{-\mathbf{q}}^{1} + \sum_{\sigma,\tau=2}^{z}\rho_{\mathbf{q}}^{\sigma}((\mathbf{S}_{\sigma\tau}^{0})^{-1} + W_{\sigma\tau})\rho_{-\mathbf{q}}^{\tau} \qquad (36c)$$

Substituting eq 36b into eq 35b, we get the Hamiltonian in the new mixture of $z - 1$ components:

$$\beta\mathcal{H}' = \sum_{\sigma,\tau=2}^{z}\rho_{\mathbf{q}}^{\sigma}\{(\mathbf{S}_{\sigma\tau}^{0})^{-1}(\mathbf{q}) + U_{\sigma\tau}(\mathbf{q})\}\rho_{-\mathbf{q}}^{\tau} \qquad (37a)$$

where we have introduced the interaction parameters $U_{\sigma\tau}(\mathbf{q})$ defined as

$$U_{\sigma\tau}(\mathbf{q}) = \mathbf{S}_{11}^{0}(\mathbf{q})^{-1} - \mathbf{S}_{1\sigma}^{0}(\mathbf{q})^{-1} - \mathbf{S}_{\tau1}^{0}(\mathbf{q})^{-1} + W_{\sigma\tau} + W_{11} - W_{1\sigma} - W_{\tau1} \qquad (37b)$$

If the isolated component 1 is a solvent, we have

$$\mathbf{S}_{11}^{0}(\mathbf{q}) = \varphi_1 = \rho_0^1\{\sum_{\sigma=1}^{z}\rho_0^{\sigma}\}^{-1} \qquad (37c)$$

and

$$\mathbf{S}_{1\sigma}^{0}(\mathbf{q}) = \mathbf{S}_{\tau1}^{0}(\mathbf{q}) = 0 \qquad (37d)$$

Using eq 16f, we find that

$$W_{\sigma\tau} + W_{11} - W_{1\sigma} - W_{\tau1} = \chi_{\sigma\tau} - \chi_{1\sigma} - \chi_{\tau1} \qquad (37e)$$

Substituting eqs 37c–37e into eq 37b yields

$$U_{\sigma\tau} = \frac{1}{\varphi_1} - \chi_{1\sigma} - \chi_{1\tau} + \chi_{\sigma\tau} \qquad (38)$$

which are identical with the usual excluded-volume parameters $V_{\sigma\tau}$ (see eqs 5a and 5b where s should be replaced by 1). Therefore, eq 37a and 38 give the final result, which in matrix form is identical with the general result (eq 1a).

Before closing this section, let us make some comments on the free energy that can be obtained from eq 35 including density fluctuations.

6. Free Energy with Density Fluctuations

The partition function as obtained in eqs 35a and 35b can be written as

$$Z(\{\rho_{\mathbf{q}}\}) = e^{-\beta F_0}\int\mathcal{D}\rho_{\mathbf{q}}e^{-\sum_{\sigma,\tau}{}^{z}\{\rho_{\mathbf{q}}{}^{\sigma}((\mathbf{S}_{\sigma\tau}{}^{0})^{-1}(\mathbf{q})+W_{\sigma\tau})\rho_{-\mathbf{q}}{}^{\tau}\}} \qquad (39)$$

where we have included the factor $e^{-\beta F_0}$ describing the free energy at $\mathbf{q} = 0$ and collecting combinatorial numbers which are given by the Flory–Huggins formula[1,19] (see Appendix A for details)

$$\beta F_0 = \sum_{\sigma=1}^{z}\frac{\rho_0^{\sigma}}{N_{\sigma}}\log\rho_0^{\sigma} + \sum_{\sigma\tau}\rho_0^{\sigma}W_{\sigma\tau}\rho_0^{\tau} \qquad (40a)$$

Note that to obtain the free energy of mixing a reference state has to be subtracted (see ref 1, p 71). This subtraction of the reference state is already done if we write down eq 39. Note further that up to now we have not used the incompressibility constraint as has been done by Olvera de la Cruz et al.[20] This incompressibility constraint can be built in afterwards by using for the potentials $W_{\sigma\tau} = W_0 + \epsilon_{\sigma\tau}$, where W_0 is the hard core potential, and taking the limit $W_0 \rightarrow \infty$. This method has been used in a previous paper.[13]

Introducing the Flory–Huggins interaction parameter (see eq 16f), we can derive the free energy of mixing as

$$\beta F_{0_{\mathrm{mix}}} = \sum_{\sigma=1}^{z}\frac{\rho_0^{\sigma}}{N_{\sigma}}\log\rho_0^{\sigma} + \sum_{\sigma\neq\tau}\chi_{\sigma\tau}\rho_0^{\sigma}\rho_0^{\tau} \qquad (40b)$$

Therefore, the total free energy including the effects of fluctuations is given by

$$\beta F = -\log Z(\{\rho_{\mathbf{q}}\}) \qquad (41a)$$

or

$$\beta F = \beta F_{0_{\mathrm{mix}}} + \sum_{\mathbf{q}>0}\log(\mathrm{Det}\{\mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{W}\}) \qquad (41b)$$

Replacing log (Det { }) by Tr log { } (Tr = trace) and approximating $\sum_{\mathbf{q}}$ by an integral as

$$\sum_{\mathbf{q}>0} \simeq \frac{\Omega}{(2\pi)^3}\int d^3\mathbf{q}$$

one can put eq 41b in the form

$$\beta F = \sum_{\sigma=1}^{z} \frac{\rho_0^\sigma}{N_\sigma} \log \rho_0^\sigma + \sum_{\sigma \neq \tau} \chi_{\sigma\tau} \rho_0^\sigma \rho_0^\tau - \frac{\Omega}{(2\pi)^3} \int d^3\mathbf{q}\ \mathrm{Tr} \log \{\mathbf{S}_{\sigma\tau}^0(\mathbf{q})^{-1} + W_{\sigma\tau}\} \quad (42)$$

It is interesting to compare this form with the local free energy proposed by de Gennes[1] to investigate spinodal decomposition in polymer mixtures, i.e.,

$$\beta F(\{\rho_\sigma(\mathbf{r})\}) = \sum_{\sigma} \frac{\rho_0(\mathbf{r})}{N_\sigma} \log \rho_0 + \sum_{\sigma \neq \tau} \chi_{\sigma\tau} \rho_\sigma(\mathbf{r})\ \rho_\tau(\mathbf{r}) + \sum_{\sigma} K_\sigma |\nabla \sigma_\tau(\mathbf{r})|^2 \quad (43)$$

where the gradient term is introduced to describe fluctuations in the long-wavelength limit. We note that the corresponding partition function is

$$Z = \int \mathcal{D}\{\rho_\sigma(\mathbf{r})\} e^{-\beta F(\{\rho_\sigma(\mathbf{r})\})} \quad (44)$$

To follow the usual procedure, we expand the free energy around the mean $\mathbf{S}_\sigma^0$ and we denote the fluctuation $\phi_\sigma(\mathbf{r})$ by

$$\delta\rho_\sigma(\mathbf{r}) \equiv \phi_\sigma(\mathbf{r}) = -\mathbf{S}_\sigma^0 + \mathbf{S}_\sigma(\mathbf{r}) \quad (45)$$

We obtain

$$Z = e^{-\beta F_{0_{\mathrm{mix}}}} \int \mathcal{D}\{\phi(\mathbf{r})\} e^{(1/2)\sum_{\sigma\tau}\{(\partial^2 F/\partial\rho_\sigma{}^0 \partial\rho_\tau{}^0) + K_\sigma \delta_{\sigma\tau} \nabla^\sigma \nabla^\tau\} \phi_\sigma \phi_\tau} \quad (46a)$$

where $F_{0_{\mathrm{mix}}}$ is the Flory–Huggins free energy of mixing (see eq 34b). (Remember that the reference state has already been subtracted.) The final form of the free energy is

$$\beta F = \beta F_{0_{\mathrm{mix}}} + \sum_{\sigma} \mathrm{Tr} \log \left\{ \frac{\partial^2 F}{\partial \rho_\sigma^0 \partial \rho_\tau^0} + \mathbf{q}^2 K_{\sigma\tau} \right\} \quad (46b)$$

which is an approximation of eq 42, noting that for a binary polymer system

$$\frac{\partial^2 F}{\partial \rho_\sigma^0 \partial \rho_\tau^0} = \frac{1}{N_\sigma \rho_\sigma^0} + \frac{1}{N_\tau \rho_\tau^0} \quad (46c)$$

and

$$K_{\sigma\tau} = \frac{1}{3} \left\{ \frac{\mathrm{Rg}_\sigma{}^2}{N_\sigma \rho_\sigma^0} + \frac{\mathrm{Rg}_\tau{}^2}{N_\tau \rho_\tau^0} \right\} \quad (46d)$$

where Rg_σ and Rg_τ are the radii of gyration of polymers σ and τ, respectively. A generalization of eq 40 was also discussed by Akcasu and Sanchez.[21] One must note, however, that in order to describe correctly the phase separation process, one has to go beyond the Gaussian approximation used to arrive at eq 42. Higher order vertex functions have been introduced by Leibler[2] to investigate the microphase separation transition in block copolymers. The same functions were also introduced by Fredrickson[22] to investigate similar phenomena in other systems. Such a discussion is beyond the scope of this paper.

7. Conclusions

The purpose of this review was to rederive the general result for the static scattering matrix for a multicomponent polymer mixture by using three different methods. The Ornstein–Zernike method was used in a slightly more general way than the method orginally used by Benoit et al.[6] This required an expression for the direct correlation matrix $\mathbf{C}(\mathbf{q})$, which was assumed to be given by $-\mathbf{V}\cdot\mathbf{S}_0(\mathbf{q})$. The second method was a static version of the dynamic RPA matrix formulation proposed by Akcasu and Tombakuglu.[4] The third method was based on the Edwards Hamiltonian representation. This paper gives a unified picture on the way to deal with static scattering from multicomponent polymer mixtures and hints at possible extensions to more complex phenomena such as spinodal decomposition, dynamics near the equilibrium state, etc.

As a side result, we also derived the free energy of mixing the Flory–Huggins without using a lattice model. We further extended the free energy to treat Gaussian fluctuations above the spinodal transition. Near the spinodals, which are given by det $(\mathbf{S}_0{}^{-1} + \mathbf{V}) = 0$, higher order fluctuations have to be treated, or alternatively one can use the scaling approach that has been applied by Binder[23] to such systems.

Appendix A

Here we derive the Flory–Huggins free energy from the Edwards Hamiltonian, and we show that we have to include combinational terms to find the correct expression. We start from the partition function for a binary system polymer (one component) + solvent

$$Z = \frac{1}{n_{\mathrm{p}}!} \frac{1}{n_{\mathrm{s}}!} \int \prod_{\mathbf{q}} \delta\rho_{\mathbf{q}} \delta c_{\mathbf{q}} e^{-\beta \mathcal{H}(\{\rho_{\mathbf{q}}\},\{c_{\mathbf{q}}\})} \quad (\mathrm{A1})$$

where n_{p} is the number of polymer molecules (chains) and n_{s} is the number of solvent molecules. The appearance of $n_{\mathrm{p}}!$ and $n_{\mathrm{s}}!$ in Z is due to the classical Gibbs paradox. (Molecules of the same species are indistinguishable.) The Edwards Hamiltonian $\mathcal{H}(\{\rho_{\mathbf{q}}\},\{c_{\mathbf{q}}\})$ is given by

$$\mathcal{H}(\{\rho_{\mathbf{q}}\},\{c_{\mathbf{q}}\}) = \sum_{\mathbf{q}=0}^{\infty} \left\{ \left(\frac{1}{\mathbf{S}^0(\mathbf{q})} + W_{\mathrm{pp}} \right) \rho_{\mathbf{q}} \rho_{-\mathbf{q}} + \left(\frac{1}{c_0} + W_{\mathrm{ss}} \right) c_{\mathbf{q}} c_{-\mathbf{q}} + 2 W_{\mathrm{sp}} \rho_{\mathbf{q}} c_{-\mathbf{q}} \right\} \quad (\mathrm{A2})$$

where $\mathbf{S}^0(\mathbf{q})$ is the bare structure factor of the polymer, c_0 is the solvent concentration, W_{pp}, W_{ss}, and W_{sp} are the polymer–polymer interaction, the solvent–solvent interaction, and the polymer–solvent interaction potentials, $\{\rho_{\mathbf{q}}\}$ are the concentration fluctuations for the polymers, and $\{c_{\mathbf{q}}\}$ are the concentration fluctuations for the solvent. Note that this Edwards Hamiltonian (eq A2) as well as those for the multicomponent systems used in the main text, are also appropriate for compressible systems. This has been shown implicitly in ref 24 and later in ref 25 where the corresponding structure factors for compressible systems have been calculated. The limit of incompressible systems can be taken by using infinite hard core potentials as we have shown in ref 13. From the Hamiltonian we separate first the $\mathbf{q} = 0$ term, i.e.

$$\beta \mathcal{H} = \beta \mathcal{H}_0(\rho_0, c_0) + \sum_{\mathbf{q}>0} \beta \mathcal{H}'(\{\rho_{\mathbf{q}}\},\{c_{\mathbf{q}}\}) \quad (\mathrm{A3})$$

with

$$\beta \mathcal{H}_0(\rho_0, c_0) = \left(\frac{1}{N\rho_0} + W_{\mathrm{pp}} \right) \rho_0{}^2 + \left(\frac{1}{c_0} + W_{\mathrm{ss}} \right) c_0{}^2 + 2 W_{\mathrm{sp}} c_0 \rho_0 \quad (\mathrm{A4})$$

where N is the degree of polymerization of the polymers.

The partition function is now given by

$$Z = e^{-\beta F} = e^{-\beta F_0}\int\prod_{\mathbf{q}>0}\delta\rho_\mathbf{q}\delta c_\mathbf{q}e^{-\beta\sum_{\mathbf{q}>0}{}^{*}\mathcal{H}'(\{\rho_\mathbf{q}\}\{c_\mathbf{q}\})} \equiv e^{-\beta F_0}e^{-\beta\Delta F} \tag{A5}$$

where

$$\beta F_0 = \beta\mathcal{H}_0 + \log n_\mathrm{p}! + \log n_\mathrm{s}! \tag{A6}$$

We know that

$$\rho_0 = n_\mathrm{p}N/\Omega$$

$$c_0 = n_\mathrm{s}/\Omega \tag{A7}$$

where Ω is the volume of the system, which we put equal to 1; i.e., $\Omega \equiv 1$. Using Stirling's approximation

$$\log n! = n\log n - n \tag{A8}$$

we find immediately

$$\beta F_0 = \frac{\rho_0}{N}\log\frac{\rho_0}{N} + c_0\log c_0 + W_\mathrm{pp}\rho_0^{\,2} + W_\mathrm{ss}c_0^{\,2} + 2W_\mathrm{ps}\rho_0c_0 \tag{A9}$$

which is the total free energy (without fluctuations) of the solution. Calculating the free energy of mixing by subtracting the proper reference state (see de Gennes,[1] p 71) we find the classical Flory–Huggins free energy.

$$\beta F_0 = \frac{\rho_0}{N}\log\rho_0 + c_0\log c_0 + \chi_\mathrm{ps}\rho_0c_0 \tag{A10}$$

Appendix B

For readers who are not familiar with the functional integral formalism, we derive eq 41b of the main text.

To find the contribution ΔF from the fluctuations for the free energy of the Flory–Huggins type, we take from Appendix A

$$e^{-\beta\Delta F} = \int\prod_{\mathbf{q}>0}\delta\rho_\mathbf{q}^\sigma\delta c_\mathbf{q}e^{-\sum_{\mathbf{q}>0}\sum_{\sigma,\tau}\rho_\mathbf{q}{}^\sigma((1/\mathbf{S}^0)+\mathbf{V})_{\sigma\tau}\rho_{-\mathbf{q}}{}^\tau}$$

$$\equiv \int\prod_{\mathbf{q}>0}\delta\rho_\mathbf{q}e^{-\sum_{\mathbf{q}>0}\sum_{\sigma,\tau}\rho_\mathbf{q}{}^\sigma M_\mathbf{q}{}^{\sigma\tau}\rho_{-\mathbf{q}}} \tag{B1}$$

We introduce new variables $\tilde{\rho}_\mathbf{q}^\sigma$ by an unitary transformation

$$\rho_\mathbf{q}^\sigma = \sum_\lambda U_\mathbf{q}^{\sigma\lambda}\tilde{\rho}_\mathbf{q}^\lambda \tag{B2}$$

where $U_\mathbf{q}^{\sigma\lambda}$ is an unitary matrix, which diagonalizes $\mathbf{M}$. Note that $\det\mathbf{U} = 1$, so that the Jacobian from the transformation from $\rho_\mathbf{q}$ to $\tilde{\rho}_\mathbf{q}$ is one.

Thus, we get

$$e^{-\beta\Delta F} = \int\prod_{\mathbf{q}>0}\delta\tilde{\rho}_\mathbf{q}^\sigma\delta c_\mathbf{q}e^{-\sum_{\mathbf{q}>0}\sum_{\sigma,\tau}\sum_{\lambda,\mathbf{k}}\tilde{\rho}_\mathbf{q}{}^\lambda U_\mathbf{q}{}^{\sigma\lambda}M_\mathbf{q}{}^{\sigma\tau}U_{-\mathbf{q}}{}^{\tau\mathbf{k}}\tilde{\rho}_{-\mathbf{q}}{}^\mathbf{k}} \tag{B3}$$

where we introduce a new matrix

$$\Lambda_{\lambda\kappa} = \sum_{\lambda,\kappa}U_\mathbf{q}^{\sigma\lambda}M_\mathbf{q}^{\sigma\tau}U_{-\mathbf{q}}^{\tau\kappa} \tag{B4}$$

which has now only diagonal elements, i.e.

$$\Lambda_{\lambda\kappa} = \Lambda_{\kappa\kappa}\delta_{\lambda\kappa} \tag{B5}$$

Thus, we get

$$e^{-\beta\Delta F} = \int\prod_{\mathbf{q}>0}\delta\tilde{\rho}_\mathbf{q}^\sigma e^{-\sum_{\mathbf{q}>0}\sum_\kappa\Lambda_{\kappa\kappa}|\rho_\mathbf{q}{}^\kappa|^2} = \prod_{\mathbf{q}>0}\prod_\kappa\frac{1}{\Lambda_{\kappa\kappa}} =$$

$$\prod_{\mathbf{q}>0}\frac{1}{\det\Lambda_\mathbf{q}} \equiv \prod_{\mathbf{q}>0}\frac{1}{\det\mathbf{M}_\mathbf{q}} \tag{B6}$$

since

$$\det\Lambda = \det\mathbf{M}$$

because

$$\det\mathbf{U} = 1$$

Thus, we find

$$e^{-\beta\Delta F} = e^{-\sum_{\mathbf{q}>0}\log(\det\mathbf{M})} \tag{B7}$$

and

$$\beta\Delta F = \sum_{\mathbf{q}>0}\log\left(\det\left(\frac{1}{\mathbf{S}^0(\mathbf{q})} + \mathbf{V}\right)\right) \tag{B8}$$

which is the fluctuation term in the Gaussian approximation.

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