Macromolecules **1981**, *14*, 727–736

Theory of Inhomogeneous Multicomponent Polymer Systems

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ABSTRACT: A new theory of inhomogeneous multicomponent systems is developed, starting from the functional integral representation of the partition function. The theory can be used to determine the interfacial properties and microdomain structures of a combination of homopolymers, block copolymers, monomers, and solvents. For the case of no polymers present, our theory reduces to that of Cahn and Hilliard for small molecules. In our approach, the general free energy functional is optimized by the saddle-function method, subject to constraints of no volume change with mixing and constancy of the individual particle numbers, to obtain new equations for the mean fields acting on the polymers. We are thus able to restrict density fluctuations in the system, without introducing an "ad hoc" term involving a vanishing compressibility into the free energy. In addition, by using the gradient expansion for the interaction energy, we demonstrate explicitly the absence of all "kinetic" terms involving the (inverse) degree of polymerization from the mean-field equations, when we choose to introduce the local, homogeneous Flory–Huggins free energy for reference. The mathematical formalism is worked out in detail for the multicomponent homopolymer–solvent system, and it is shown how to extend the theory to include block copolymers. Finally, in order to give a definite example, the variation of the interfacial properties with molecular weight and interaction parameter is worked out numerically for the simplest case of a homopolymer–solvent system. The numerical method is discussed in detail. Applications to more complicated systems will be given in the future.

1. Introduction

There has been a great deal of activity in practical and theoretical studies of polymer blends recently.[1-3] In this paper we focus on phase separation phenomena in homopolymer and copolymer mixtures, and we formulate a new theoretical treatment of inhomogeneous multicomponent polymer systems which includes the effects of small molecules, such as monomers or solvents. Although a great deal of theoretical work has been done on phase separation,[4-12] small-molecule and homopolymer effects on interfacial properties and microdomain formation in block copolymers have received relatively little attention. In our work we treat more complex problems such as the effect of homopolymers, monomers, and solvents on the block copolymer morphology.[13-16]

In order to achieve this goal, we felt it was necessary to develop a theory in which small molecules and macromolecules were treated equally in the basic formulation, and we used the functional integral representation of the partition function, as developed by Edwards,[17] Freed,[18] Helfand,[19] and others. Helfand's work[4-7] emphasized the importance of severely restricting overall density fluctuations in inhomogeneous polymer systems, and he accomplished this by adding an "ad hoc" term to the free energy, which depends inversely on the small compressibility of the system and directly on the square of the deviation from the average density. In the limit of a vanishing compressibility this term becomes indeterminate and has to be treated in a special manner. Because the constant-density constraint generates a great deal of mathematical and numerical complexity,[6,20] we felt a new approach to the problem was necessary.

In section 2 we introduce the functional integral technique and minimize the free energy functional by using the saddle-function method, subject to the constraints of no volume change locally upon mixing, with a constant number of particles for all the components. This leads to a new set of equations for the polymer mean fields, which depend on unknown Lagrangian multipliers corresponding to the constraints. The unknown quantities can be determined for a given system from the constancy of the chemical potential for the various components in the different phases.

Since a hypothetical locally homogeneous Flory–Huggins free energy is often introduced for reference, we consider this case and demonstrate explicitly the subtraction of the so-called "kinetic terms", which vary inversely as the degree of polymerization, from the expression for the free energy. In section 3 we use a gradient expansion for the interaction energy, valid for a short-range potential, and discuss the multicomponent homopolymer–solvent system in detail. We obtain expressions for the total free energy and the interfacial tension. The modifications necessary to include copolymers are given in section 4, and in section 5 we calculate the binodal curves and exhibit interfacial profiles and interfacial tensions for a single homopolymer–solvent mixture, as a function of molecular weight and interaction parameter. This example is worked out in detail, along with a description of numerical methods (given in Appendix B), in order to demonstrate the application of the new and unfamiliar mean-field equations to a simple case. Section 6 contains the conclusions, and in Appendix A we derive expressions for the interfacial tension (for a one-dimensional system) which isolate the nonlocal short-range contributions from the polymer chain contributions and demonstrate the reduction of our theory to that of Cahn and Hilliard[21] when no polymers are present.

2. Partition Function for Multicomponent Homopolymer–Solvent Mixtures

We denote the number of polymer chains of type p by $\tilde{N}_p = N_p/Z_p$, where N_p is the number of monomer units and Z_p is the degree of polymerization. N_s is the number of solvent molecules of type s, and the index κ will be used to label either polymer or solvent molecules. Since $Z_s = 1$, we have $\tilde{N}_s = N_s$.

In terms of a functional integral representation, the partition function for the homopolymer–solvent mixture is given by[17-19]

$$\mathbf{Z} = \left(\prod_{\kappa}\frac{Z_{\kappa}^{\tilde{N}_{\kappa}}}{\tilde{N}_{\kappa}!}\right)\int\left(\prod_{s}\prod_{i=1}^{N_s}\mathrm{d}^3r_{si}\right)\left(\prod_{p}\prod_{j=1}^{\tilde{N}_p}\delta\mathbf{r}_{pj}(\cdot)P[\mathbf{r}_{pj}(\cdot)]\right)e^{-\beta V} \tag{2-1}$$

where Z_κ is the partition function due to the kinetic energy and V is the intermolecular potential. The integral is over all space curves $\mathbf{r}(\cdot)$, which represent possible configurations of the macromolecules. The probability density functional for a given space curve is denoted by $P[\mathbf{r}(\cdot)]$ and is assumed to be of standard Wiener form, i.e.

$$P[\mathbf{r}_p(\cdot)] \propto \exp\left[-\frac{3}{2b_p^2}\int_0^{Z_p}\mathrm{d}t\ \dot{r}_p^{\,2}(t)\right] \tag{2-2}$$

b_p being the Kuhn statistical length of a single segment of the polymer.[5] We write out the intermolecular potential explicitly in terms of all the space curves, defining $\hat{W} = \beta V$ and using $k_{\mathrm{B}}T$ as the unit of energy

$$\hat{W} = \hat{W}(\{\mathbf{r}_{si}\},\{\mathbf{r}_{pj}(\cdot)\}) = \tfrac{1}{2}\sum_{\substack{ss'\\ii'}} W_{ss'}(\mathbf{r}_{si} - \mathbf{r}_{s'i'}) + \sum_{\substack{sp\\ij}}\int_0^{Z_p}\mathrm{d}t\ W_{sp}[\mathbf{r}_{si} - \mathbf{r}_{pj}(t)] + \tfrac{1}{2}\sum_{\substack{pp'\\jj'}}\int_0^{Z_p}\mathrm{d}t\int_0^{Z_{p'}}\mathrm{d}t'\ W_{pp'}[\mathbf{r}_{pj}(t) - \mathbf{r}_{p'j'}(t')] \tag{2-3}$$

In terms of microscopic particle densities

$$\hat{\rho}_p(\mathbf{r}) = \hat{\rho}_p(\mathbf{r};\{\mathbf{r}_{pi}(\cdot)\}) = \sum_{i=1}^{\tilde{N}_p}\int_0^{Z_p}\mathrm{d}t\ \delta[\mathbf{r} - \mathbf{r}_{pi}(t)] \tag{2-4}$$

$$\hat{\rho}_s(\mathbf{r}) = \hat{\rho}_s(\mathbf{r};\{\mathbf{r}_{si}\}) = \sum_{i=1}^{N_s}\delta(\mathbf{r} - \mathbf{r}_{si}) \tag{2-5}$$

the potential can be conveniently written in a compact form

$$\hat{W} = \tfrac{1}{2}\sum_{\kappa\kappa'}\int\mathrm{d}^3r\int\mathrm{d}^3r'\,\hat{\rho}_\kappa(\mathbf{r})W_{\kappa\kappa'}(\mathbf{r} - \mathbf{r}')\hat{\rho}_{\kappa'}(\mathbf{r}') \tag{2-6}$$

and introducing the δ function, we get

$$e^{-\hat{W}} = \int[\prod_\kappa\delta\rho_\kappa(\cdot)]\prod_\kappa\delta[\rho_\kappa(\cdot) - \hat{\rho}_\kappa(\cdot)]e^{-W} \tag{2-7}$$

where

$$W = W(\{\rho_\kappa(\cdot)\}) = \tfrac{1}{2}\sum_{\kappa\kappa'}\int\mathrm{d}^3r\int\mathrm{d}^3r'\,\rho_\kappa(\mathbf{r})W_{\kappa\kappa'}(\mathbf{r} - \mathbf{r}')\rho_{\kappa'}(\mathbf{r}') \tag{2-8}$$

Using the integral representation of the δ function

$$\delta[\rho_\kappa(\cdot) - \hat{\rho}_\kappa(\cdot)] = \mathcal{N}\int\delta\omega_\kappa(\cdot)\exp\left\{\int\mathrm{d}^3r\ \omega_\kappa(\mathbf{r})[\rho_\kappa(\mathbf{r}) - \hat{\rho}_\kappa(\mathbf{r})]\right\} \tag{2-9}$$

where the limits of integration of ω_κ are $-i\infty$ to $+i\infty$ and $\mathcal{N}$ is a normalization constant, the expression for the partition function finally becomes

$$\mathbf{Z} = \left(\prod_\kappa\frac{Z_\kappa^{\tilde{N}_\kappa}}{\tilde{N}_\kappa!}\right)\mathcal{N}\int[\prod_\kappa\delta\rho_\kappa(\cdot)\delta\omega_\kappa(\cdot)]\times\prod_\kappa\mathcal{Q}_\kappa^{\tilde{N}_\kappa}\exp\left\{\sum_\kappa\int\mathrm{d}^3r\ \omega_\kappa(\mathbf{r})\rho_\kappa(\mathbf{r}) - W\right\} \tag{2-10}$$

and it is this integral which we wish to evaluate by the saddle-function method.[19]

The quantities $\mathcal{Q}_\kappa$ are given by

$$\mathcal{Q}_s = \int\mathrm{d}^3r\ e^{-\omega_s(\mathbf{r})} \tag{2-11}$$

$$\mathcal{Q}_p = \int\delta\mathbf{r}(\cdot)P[\mathbf{r}(\cdot)]\exp\left\{-\int_0^{Z_p}\mathrm{d}t\ \omega_p[\mathbf{r}(t)]\right\} = \int\mathrm{d}^3r\int\mathrm{d}^3r_0\ Q_p(\mathbf{r},Z_p|\mathbf{r}_0) \tag{2-12}$$

and the function $Q_p(\mathbf{r},t|\mathbf{r}_0)$, which can be interpreted as a (unnormalized) distribution function for a chain of t repeat units to start at $\mathbf{r}_0$ and end at $\mathbf{r}$, can be shown to satisfy the modified diffusion equation[19]

$$\frac{\partial Q_p}{\partial t} = \frac{b_p^2}{6}\nabla^2 Q_p - \omega_p Q_p \tag{2-13}$$

with

$$Q_p(\mathbf{r},0|\mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0) \tag{2-14}$$

Sometimes it is convenient to work with the integral of Q_p over all starting positions $\mathbf{r}_0$

$$q_p(\mathbf{r},t) = \int\mathrm{d}^3r_0\ Q_p(\mathbf{r},t|\mathbf{r}_0) \tag{2-15}$$

and in this case

$$\frac{\partial q_p}{\partial t} = \frac{b_p^2}{6}\nabla^2 q_p - \omega_p q_p \tag{2-16}$$

with

$$q_p(\mathbf{r},0) = 1 \tag{2-17}$$

and

$$\mathcal{Q}_p = \int\mathrm{d}^3r\ q_p(\mathbf{r},Z_p) \tag{2-18}$$

Returning to the partition function, eq 2-10, we use Stirling's approximation for large $\tilde{N}_\kappa$ and write

$$\mathbf{Z} = \mathcal{N}\int[\prod_\kappa\delta\rho_\kappa(\cdot)\delta\omega_\kappa(\cdot)]\exp\{-\mathcal{F}(\{\rho_\kappa(\cdot)\},\{\omega_\kappa(\cdot)\})\} \tag{2-19}$$

where the free energy functional is given by

$$\mathcal{F}(\{\rho_\kappa(\cdot)\},\{\omega_\kappa(\cdot)\}) = W(\{\rho_\kappa(\cdot)\}) - \sum_\kappa\int\mathrm{d}^3r\ \omega_\kappa(\mathbf{r})\rho_\kappa(\mathbf{r}) + \sum_\kappa\int\mathrm{d}^3r\ \frac{\rho_\kappa(\mathbf{r})}{Z_\kappa}\left\{\ln\left(\frac{N_\kappa}{Z_\kappa Z_\kappa\mathcal{Q}_\kappa}\right) - 1\right\} \tag{2-20}$$

Using the saddle-function method, we obtain the free energy, given by the minimization of the functional, eq 2-20, with respect to ρ_κ and ω_κ, subject to the constraints of no volume change locally upon mixing

$$\sum_\kappa[\rho_\kappa(\mathbf{r})/\rho_{0\kappa}] = 1 \tag{2-21}$$

and a constant number of particles

$$\int\mathrm{d}^3r\ \rho_\kappa(\mathbf{r}) = N_\kappa \tag{2-22}$$

Here $\rho_{0\kappa}$ is the density of pure material in monomer segments per unit volume. The minimization yields equations for the equilibrium density and the mean fields acting on the polymers. Denoting the Lagrangian multipliers, corresponding to the constraints eq 2-21 and 2-22 by $\eta(\mathbf{r})$ and λ_κ, respectively, we write the variational equations as

$$\frac{\delta W}{\delta\rho_\kappa(\mathbf{r})} - \omega_\kappa(\mathbf{r}) + \frac{\eta(\mathbf{r})}{\rho_{0\kappa}} - \lambda_\kappa = 0 \tag{2-23}$$

and

$$\rho_\kappa(\mathbf{r}) + \frac{\tilde{N}_\kappa}{\mathcal{Q}_\kappa}\frac{\delta\mathcal{Q}_\kappa}{\delta\omega_\kappa(\mathbf{r})} = 0 \tag{2-24}$$

Equation 2-24 gives immediately

$$\rho_s(\mathbf{r}) = \frac{N_s}{\mathcal{Q}_s}e^{-\omega_s(\mathbf{r})} \tag{2-25}$$

and

$$\rho_p(\mathbf{r}) = \frac{N_p}{Z_p\mathcal{Q}_p}\int_0^{Z_p}\mathrm{d}t\ q_p(\mathbf{r},t)q_p(\mathbf{r},Z_p - t) \tag{2-26}$$

As we will see later, eq 2-23 expresses the constancy of the chemical potential. Once the unknown quantities $\eta(\mathbf{r})$ and λ_κ are determined, eq 2-23 can be used to obtain an expression for the mean-field ω_κ, which occurs in the equation of motion for q_p.

It may be noted that if $\omega_\kappa(\mathbf{r})$, $\eta(\mathbf{r})$, and λ_κ satisfy eq 2-23, so do $\omega_\kappa(\mathbf{r}) + a_\kappa$, $\eta(\mathbf{r}) + c$ and $\lambda_\kappa + c/\rho_{0\kappa} - a_\kappa$, where c and a_κ are constants. In this paper, we choose a_κ so that $\mathcal{Q}_\kappa$, given by eq 2-11 and 2-12, satisfies the relation $\mathcal{Q}_\kappa = N_\kappa/\rho_{0\kappa}$.

The above analysis differs from that of Helfand[19] in several ways. First, we have derived a general form for the free energy density, starting from the partition function and the general form of the intermolecular potential. Second, we have applied the saddle-function method to the functional integral, eq 2-19, with the constraint of no volume change upon mixing, giving rise to new expressions for the mean field. This constraint is automatically built into our theory and does not have to be added separately to the free energy in terms of a vanishing compressibility, as in previous work.[4-7,20]

We end this section by showing how the general free energy expression, eq 2-20, reduces to the Flory–Huggins form for a uniform system. For this purpose it is convenient to introduce the symmetric form of the potential energy, which vanishes for interactions between like molecules

$$U_{\kappa\kappa'}(\mathbf{r}) = W_{\kappa\kappa'}(\mathbf{r}) - \frac{1}{2\rho_{0\kappa}\rho_{0\kappa'}}(W_{\kappa\kappa}(\mathbf{r})\rho_{0\kappa}^{\ 2} + W_{\kappa'\kappa'}(\mathbf{r})\rho_{0\kappa'}^{\ 2}) \tag{2-27}$$

so that eq 2-8 becomes

$$W = {}^1\!/_2\sum_\kappa W_{\kappa\kappa}\rho_{0\kappa}N_\kappa + {}^1\!/_2\sum_{\kappa\kappa'}\int \mathrm{d}^3r \int \mathrm{d}^3r'\, \rho_\kappa(\mathbf{r})U_{\kappa\kappa'}(\mathbf{r}-\mathbf{r}')\rho_{\kappa'}(\mathbf{r}') \tag{2-28}$$

where

$$W_{\kappa\kappa} = \int \mathrm{d}^3r\, W_{\kappa\kappa}(\mathbf{r}) \tag{2-29}$$

For a uniform system, ρ_κ and ω_κ are constant, and from eq 2-16 and 2-26 we find

$$q_p(t) = e^{-\omega_p t} \tag{2-30}$$

$$\rho_\kappa = \rho_{0\kappa}e^{-\omega_\kappa Z_\kappa} \tag{2-31}$$

Using these relations, valid only for a uniform system, in eq 2-20, we find

$$\mathcal{F} = v f_\mathrm{h} \tag{2-32}$$

where v is the volume and the homogeneous free energy density is given by

$$f_\mathrm{h} = {}^1\!/_2\sum_\kappa W_{\kappa\kappa}\rho_{0\kappa}\rho_\kappa + {}^1\!/_2\sum_{\kappa\kappa'} U_{\kappa\kappa'}\rho_\kappa\rho_{\kappa'} + \sum_\kappa \frac{\rho_\kappa}{Z_\kappa}\left[\ln\left(\frac{\rho_\kappa}{Z_\kappa \mathcal{Z}_\kappa}\right) - 1\right] \tag{2-33}$$

where in the above expression

$$U_{\kappa\kappa'} = \int \mathrm{d}^3r\, U_{\kappa\kappa'}(\mathbf{r}) \tag{2-34}$$

Equation 2-33 can be rewritten in standard Flory–Huggins form[22] by noting that the chemical potential of the pure material is

$$\mu_{0\kappa} = \frac{1}{2}W_{\kappa\kappa}\rho_{0\kappa} + \frac{1}{Z_\kappa}\left[\ln\left(\frac{\rho_{0\kappa}}{Z_\kappa \mathcal{Z}_\kappa}\right) - 1\right] \tag{2-35}$$

so that eq 2-33 becomes

$$f_\mathrm{h} = \sum_\kappa \rho_\kappa\mu_{0\kappa} + \frac{1}{2}\sum_{\kappa\kappa'} U_{\kappa\kappa'}\rho_\kappa\rho_{\kappa'} + \sum_\kappa \frac{\rho_\kappa}{Z_\kappa}\ln\left(\frac{\rho_\kappa}{\rho_{0\kappa}}\right) \tag{2-36}$$

Taking into account variation of the volume with particle number, the chemical potential of the uniform system is given by

$$\mu_\kappa = \mathrm{D}f_\mathrm{h}/\mathrm{D}\rho_\kappa \equiv \frac{\partial f_\mathrm{h}}{\partial \rho_\kappa} + \frac{1}{\rho_{0\kappa}}\left(f_\mathrm{h} - \sum_{\kappa'}\rho_{\kappa'}\frac{\partial f_\mathrm{h}}{\partial \rho_{\kappa'}}\right) \tag{2-37}$$

Making use of eq 2-36, we obtain finally

$$\mu_\kappa = \mu_{0\kappa} + \sum_{\kappa'} U_{\kappa\kappa'}\rho_{\kappa'} + \frac{1}{Z_\kappa}\left[\ln\left(\frac{\rho_\kappa}{\rho_{0\kappa}}\right) + 1\right] - \frac{1}{\rho_{0\kappa}}\left[\frac{1}{2}\sum_{\kappa'\kappa''} U_{\kappa'\kappa''}\rho_{\kappa'}\rho_{\kappa''} + \sum_{\kappa'}\frac{\rho_{\kappa'}}{Z_{\kappa'}}\right] \tag{2-38}$$

In the following sections we will often write the free energy density of the inhomogeneous system in terms of a "local" homogeneous free energy density of the Flory–Huggins form, eq 2-36. It should be borne in mind, however, that this procedure is arbitrary and does not imply the validity of the relations eq 2-30 and 2-31 in general.

3. Gradient Expansion

For a short-range potential, we may carry out a gradient expansion of eq 2-28

$$W = {}^1\!/_2\sum_\kappa W_{\kappa\kappa}\rho_{0\kappa}N_\kappa + {}^1\!/_2\sum_{\kappa\kappa'} U_{\kappa\kappa'}\int \mathrm{d}^3r\, \rho_\kappa(\mathbf{r})\rho_{\kappa'}(\mathbf{r}) - {}^1\!/_{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\int \mathrm{d}^3r\, \vec{\nabla}\rho_\kappa(\mathbf{r})\cdot\vec{\nabla}\rho_{\kappa'}(\mathbf{r}) + \ldots \tag{3-1}$$

where $W_{\kappa\kappa'}$ and $U_{\kappa\kappa'}$ are given by eq 2-29 and 2-34 and

$$V_{\kappa\kappa'} = \int \mathrm{d}^3r\, r^2 U_{\kappa\kappa'}(\mathbf{r}) \tag{3-2}$$

In terms of the local homogeneous free energy density, eq 2-33, W is given by

$$W = \int \mathrm{d}^3r \left\{ f_\mathrm{h} - \sum_\kappa \frac{\rho_\kappa}{Z_\kappa}\left[\ln\left(\frac{\rho_\kappa}{Z_\kappa \mathcal{Z}_\kappa}\right) - 1\right] - \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\, \vec{\nabla}\rho_\kappa(\mathbf{r})\cdot\vec{\nabla}\rho_{\kappa'}(\mathbf{r}) \right\} \tag{3-3}$$

and the appearance of the ln term in this expression is the result of having to subtract the corresponding term in f_h.

Making use of eq 3-3, we rewrite the variational eq 2-23 in the form

$$\frac{\mathrm{D}f_\mathrm{h}}{\mathrm{D}\rho_\kappa} - \frac{1}{Z_\kappa}\ln\left(\frac{\rho_\kappa}{Z_\kappa \mathcal{Z}_\kappa}\right) + \frac{1}{6}\sum_{\kappa'} V_{\kappa\kappa'}\nabla^2\rho_{\kappa'} - \omega_\kappa + \frac{\zeta(\mathbf{r})}{\rho_{0\kappa}} - \lambda_\kappa = 0 \tag{3-4}$$

where

$$\zeta(\mathbf{r}) = \eta(\mathbf{r}) - (f_\mathrm{h} - \sum_\kappa \rho_\kappa\, \partial f_\mathrm{h}/\partial\rho_\kappa) \tag{3-5}$$

and we have used the definition of the operator $\mathrm{D}/\mathrm{D}\rho_\kappa$, given by eq 2-37. In the bulk homogeneous phase, the mean field is a constant and according to eq 2-31

$$\omega_\kappa^{\ b} = -\frac{1}{Z_\kappa}\ln\left(\frac{\rho_\kappa^{\ b}}{\rho_{0\kappa}}\right) \tag{3-6}$$

and the chemical potential is given by

$$(\mathrm{D}f_\mathrm{h}/\mathrm{D}\rho_\kappa)_b = \mu_\kappa^{\ b} \tag{3-7}$$

so that in the bulk eq 3-4 becomes

$$\mu_\kappa^{\ b} + \frac{1}{Z_\kappa}\ln\left(\frac{Z_\kappa \mathcal{Z}_\kappa}{\rho_{0\kappa}}\right) + \frac{\zeta^b}{\rho_{0\kappa}} - \lambda_\kappa = 0 \tag{3-8}$$

Note that there is no ambiguity in which of the bulk homogeneous phases one takes, since the chemical potential $\mathrm{D}f_{\mathrm{h}}/\mathrm{D}\rho_\kappa$ must have the same value in all such phases.

Solving this equation for λ_κ and substituting back in eq 3-4, we get

$$\frac{\mathrm{D}f_{\mathrm{h}}}{\mathrm{D}\rho_\kappa(\mathbf{r})} - \left[\omega_\kappa(\mathbf{r}) + \frac{1}{Z_\kappa}\ln\left(\frac{\rho_\kappa(\mathbf{r})}{\rho_{0\kappa}}\right)\right] + \frac{[\zeta(\mathbf{r}) - \zeta^b]}{\rho_{0\kappa}} + \frac{1}{6}\sum_{\kappa'} V_{\kappa\kappa'}\,\nabla^2\rho_{\kappa'}(\mathbf{r}) = \mu_\kappa{}^b \quad (3\text{-}9)$$

The left-hand side of this equation can be identified as the expression for the chemical potential of the component κ in an inhomogeneous system so that eq 3-9 simply relates the fact that the chemical potential must be spatially constant. In the following, it is convenient to define

$$\Delta\mu_\kappa = \mathrm{D}f_{\mathrm{h}}/\mathrm{D}\rho_\kappa - \mu_\kappa{}^b = \mathrm{D}\Delta f/\mathrm{D}\rho_\kappa \quad (3\text{-}10)$$

where

$$\Delta f = f_{\mathrm{h}} - \sum_\kappa \rho_\kappa\mu_\kappa{}^b \quad (3\text{-}11)$$

Note that both $\Delta\mu_\kappa$ and Δf vanish in the bulk phases.

The other unknown Lagrangian multiplier in eq 3-9 can be determined by making use of eq 2-25, valid in general for an inhomogeneous system

$$\frac{\zeta(\mathbf{r}) - \zeta^b}{\rho_{0s}} = \frac{\Delta\zeta}{\rho_{0s}} = -\Delta\mu_s - \frac{1}{6}\sum_{\kappa'} V_{s\kappa'}\,\nabla^2\rho_{\kappa'} \quad (3\text{-}12)$$

and from eq 3-9 and 3-12 we obtain the desired equation for the polymer mean field

$$\omega_p = \Delta\mu_p - \frac{1}{Z_p}\ln\left(\frac{\rho_p}{\rho_{0p}}\right) - \frac{\rho_{0s}}{\rho_{0p}}\left(\Delta\mu_s + \frac{1}{6}\sum_{\kappa'} V_{s\kappa'}\,\nabla^2\rho_{\kappa'}\right) + \frac{1}{6}\sum_{\kappa'} V_{p\kappa'}\,\nabla^2\rho_{\kappa'} \quad (3\text{-}13)$$

We note that $V_{\kappa\kappa} = 0$ from the definitions given by eq 2-27 and 3-2, and we remark that all $1/Z_p$ "kinetic terms" cancel out of the final result for the mean field, as demonstrated explicitly in the hompolymer–solvent example discussed in section 5. The appearance of these terms in our expressions is due to the fact that we preferred to write the free energy density in terms of the Flory–Huggins form for convenience, as mentioned earlier. Although the equation for ω_p does not contain $1/Z_p$ terms, the equation of motion for q_p still depends on Z_p through the variable t, as well as through the expression for ρ_p, eq 2-26. In addition, the boundary conditions depend on Z_p and thereby influence the solution for the interfacial density profiles.

From eq 2-20 and 3-3 we obtain for the free energy

$$\mathcal{F} = \int \mathrm{d}^3r \left\{ f_{\mathrm{h}} - \sum_\kappa \rho_\kappa\left[\omega_\kappa + \frac{1}{Z_\kappa}\ln\left(\frac{\rho_\kappa}{\rho_{0\kappa}}\right)\right] - \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\,\vec{\nabla}\rho_\kappa\cdot\vec{\nabla}\rho_{\kappa'} \right\} \quad (3\text{-}14)$$

Making use of the relation

$$\sum_\kappa \rho_\kappa\,\mathrm{D}f_{\mathrm{h}}/\mathrm{D}\rho_\kappa = f_{\mathrm{h}} \quad (3\text{-}15)$$

as well as eq 3-12, eq 3-9 gives

$$\sum_\kappa \rho_\kappa\mu_\kappa{}^b = f_{\mathrm{h}} - \sum_\kappa \rho_\kappa\left[\omega_\kappa + \frac{1}{Z_\kappa}\ln\left(\frac{\rho_\kappa}{\rho_{0\kappa}}\right)\right] + \frac{1}{6}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\rho_\kappa\,\nabla^2\rho_{\kappa'} - \rho_{0s}\left(\Delta\mu_s + \frac{1}{6}\sum_{\kappa'} V_{s\kappa'}\,\nabla^2\rho_{\kappa'}\right) \quad (3\text{-}16)$$

and eq 3-14 for the free energy becomes

$$\mathcal{F} = \sum_\kappa \mu_\kappa{}^b N_\kappa + \gamma A \quad (3\text{-}17)$$

where γ is the interfacial tension, A is the interfacial area, and

$$\gamma A = \int \mathrm{d}^3r \left\{ \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\vec{\nabla}\rho_\kappa\cdot\vec{\nabla}\rho_{\kappa'} + \rho_{0s}\Delta\mu_s \right\} \quad (3\text{-}18)$$

In deriving eq 3-18 we have used the fact that the molecular densities are constant in the asymptotic bulk phases. Equations 3-13, for the mean field, and 3-18, for the interfacial tension, are the main results of this section.

4. Extension to Block Copolymers

Suppose in the multicomponent system the pair of polymers designated by A and B are linked to form a block copolymer AB. Then in writing down the partition function eq 2-1, we must replace $\tilde{N}_{\mathrm{A}}!\tilde{N}_{\mathrm{B}}!$ by $\tilde{N}_{\mathrm{AB}}!$, where $\tilde{N}_{\mathrm{AB}} = N_{\mathrm{A}}/Z_{\mathrm{A}} = N_{\mathrm{B}}/Z_{\mathrm{B}}$. Also, in writing down the free energy functional from eq 2-10, we must change $\mathcal{Q}_{\mathrm{A}}\mathcal{Q}_{\mathrm{B}}$ to $\mathcal{Q}_{\mathrm{AB}}$, where

$$\mathcal{Q}_{\mathrm{AB}} = \int\int\int \mathrm{d}^3r\,\mathrm{d}^3r_0\,\mathrm{d}^3r'\,Q_{\mathrm{A}}(\mathbf{r},Z_{\mathrm{A}}|r_0)Q_{\mathrm{B}}(\mathbf{r}',Z_{\mathrm{B}}|\mathbf{r}_0) \quad (4\text{-}1)$$

and Q_{A} and Q_{B} satisfy the same diffusion eq 2-13 as before.[19] In deriving eq 4-1, we have simply used the fact that the two homopolymers are connected to form the block copolymer. The free energy functional eq 2-20 now becomes

$$\mathcal{F} = W - \sum_\kappa \int \mathrm{d}^3r\,\omega_\kappa(\mathbf{r})\rho_\kappa(\mathbf{r}) + \sum_s N_s\left[\ln\left(\frac{N_s}{Z_s\mathcal{Q}_s}\right) - 1\right] + \sum_p \tilde{N}_p\left[\ln\left(\frac{\tilde{N}_p}{Z_p\mathcal{Q}_p}\right) - 1\right] + \tilde{N}_{\mathrm{AB}}\left[\ln\left(\frac{\tilde{N}_{\mathrm{AB}}}{Z_{\mathrm{AB}}\mathcal{Q}_{\mathrm{AB}}}\right) - 1\right] \quad (4\text{-}2)$$

where the subscript p refers only to homopolymers, while κ refers to all solvents, homopolymers, and A or B components of block copolymers. The kinetic contribution to the partition function is $Z_{\mathrm{AB}} = Z_{\mathrm{A}}Z_{\mathrm{B}}$, and the interaction energy W is given as before by eq 3-3. All other equations are the same as for homopolymers, with the exception of eq 2-26, which for block copolymers is replaced by

$$\rho_{\mathrm{A}}(\mathbf{r}) = -\tilde{N}_{\mathrm{AB}}\frac{\delta\ln\mathcal{Q}_{\mathrm{AB}}}{\delta\omega_{\mathrm{A}}(\mathbf{r})} = \frac{\tilde{N}_{\mathrm{AB}}}{\mathcal{Q}_{\mathrm{AB}}}\int_0^{Z_{\mathrm{A}}}\mathrm{d}t\,q_{\mathrm{A}}(\mathbf{r},t)\int \mathrm{d}^3r_0\,Q_{\mathrm{A}}(\mathbf{r},Z_{\mathrm{A}} - t|\mathbf{r}_0)q_{\mathrm{B}}(\mathbf{r}_0,Z_{\mathrm{B}}) \quad (4\text{-}3)$$

with a similar equation for $\rho_{\mathrm{B}}(\mathbf{r})$. In what follows we will neglect the homopolymer contribution to the free energy functional, eq 4-2, since this has been discussed in detail in the earlier sections.

Using the gradient expansion, as well as the saddle-function method, we write the free energy of the block copolymers alone in the same form as in the previous section

$$\mathcal{F} = \int \mathrm{d}^3r \left\{ f_{\mathrm{h}} - \sum_{\kappa=\mathrm{A,B}} \rho_\kappa\left[\omega_\kappa + \frac{1}{Z_\kappa}\ln\frac{\rho_\kappa}{Z_\kappa}\right] - \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\,\vec{\nabla}\rho_\kappa\cdot\vec{\nabla}\rho_{\kappa'} \right\} + \tilde{N}_{\mathrm{AB}}\left[\ln\left(\frac{\tilde{N}_{\mathrm{AB}}}{\mathcal{Q}_{\mathrm{AB}}}\right) + 1\right] \quad (4\text{-}4)$$

where we have used eq 2-25 for the solvent mean field. The chemical potentials for the pure A and B components in the definition of f_h by eq 2-36 do not have any physical significance in the present context, since A and B are linked to form a copolymer and they just contribute additive terms in the final expression for the free energy.

Unlike the case of homopolymers, for block copolymers we cannot write the free energy with respect to the bulk macroscopic phases, as in eq 3-17, because the block copolymer system forms a periodic microdomain structure and macroscopic regions, where the density of the individual components is constant, do not exist. Here we choose for reference a hypothetical uniform or "molten" state in which the density is

$$\rho_{u\kappa} = \phi_{0\kappa}\rho_{0\kappa} \tag{4-5}$$

and $\phi_{0\kappa}$ is the *overall* macroscopic volume fraction of component κ. First we determine the Lagrangian multipliers λ_κ and $\zeta(\mathbf{r})$, which occur in the variational eq 3-4, with respect to quantities in the uniform state. From eq 3-4, choosing $\omega_{A,B}$ to be zero in this state, we get

$$\frac{Df_h}{D\rho_A} - \left(\frac{Df_h}{D\rho_A}\right)_u - \left[\omega_A + \frac{1}{Z_A}\ln\left(\frac{\rho_A}{\rho_{uA}}\right)\right] + \frac{\Delta\zeta(\mathbf{r})}{\rho_{0A}} + \frac{1}{6}\sum_\kappa V_{A\kappa}\nabla^2\rho_\kappa = 0 \tag{4-6}$$

where $\Delta\zeta(\mathbf{r}) = \zeta(\mathbf{r}) - \zeta_u$, with a similar equation for the B component of the copolymer. As in eq 3-12, the quantity $\Delta\zeta(\mathbf{r})$ can be determined from the solvent relation

$$\frac{\Delta\zeta}{\rho_{0s}} = \left(\frac{Df_h}{D\rho_s}\right)_u - \frac{Df_h}{D\rho_s} - \frac{1}{6}\sum_\kappa V_{s\kappa}\nabla^2\rho_\kappa \tag{4-7}$$

and the derivative for the uniform state can be calculated by using eq 4-5. Combining eq 4-6 and 4-7, we obtain the relation

$$\int d^3r \left\{f_h - (f_h)_u - \sum_{\kappa=A,B}\rho_\kappa\left[\omega_\kappa + \frac{1}{Z_\kappa}\ln\left(\frac{\rho_\kappa}{\rho_{u\kappa}}\right)\right] + \Delta\zeta(\mathbf{r}) - \frac{1}{6}\sum_{\kappa\kappa'}V_{\kappa\kappa'}\,\vec{\nabla}\rho_\kappa\cdot\vec{\nabla}\rho_{\kappa'}\right\} = 0 \tag{4-8}$$

where we have made use of eq 2-21 and 3-15. With this result the free energy can be expressed as

$$\mathcal{F} = \mathcal{F}_u + \int d^3r\,[{}^1\!/\!_{12}\sum_{\kappa\kappa'}V_{\kappa\kappa'}\vec{\nabla}\rho_\kappa\cdot\vec{\nabla}\rho_{\kappa'} - \Delta\zeta(\mathbf{r})] - \tilde{N}_{AB}\ln\left(\frac{\mathcal{Q}_{AB}}{v}\right) \tag{4-9}$$

Here v is the volume,

$$\mathcal{F}_u = v(f_h)_u - \sum_{\kappa=A,B}\tilde{N}_\kappa\ln\left(\frac{\rho_{u\kappa}}{Z_\kappa}\right) + \tilde{N}_{AB}\left[\ln\left(\frac{\tilde{N}_{AB}}{v}\right) + 1\right] \tag{4-10}$$

and we have used the fact that in the uniform state $\Delta\zeta(\mathbf{r})$ and $\omega_{A,B}$ vanish, so that $\mathcal{Q}_u = v$.

Our goal at this point has changed from that of the earlier sections. We can no longer unambiguously define an interfacial tension (except perhaps for very narrow interfaces) and we are now interested in the *absolute* minimum of $\Delta\mathcal{F} = \mathcal{F} - \mathcal{F}_u$ for different periodic microdomain structures with different sizes of the unit cell. In the process of carrying out these calculations, we will still obtain the interfacial density profiles, but we must be guided by experiment as to which structures to choose for a given system. However, there is no guarantee that under certain conditions a disordered microdomain structure would not give a lower free energy than the ordered microdomain structure.

For a periodic structure we require

$$\begin{aligned}\rho_\kappa(\mathbf{r} + \mathbf{R}_n) &= \rho_\kappa(\mathbf{r})\\ \omega_p(\mathbf{r} + \mathbf{R}_n) &= \omega_p(\mathbf{r})\\ Q_p(\mathbf{r} + \mathbf{R}_n,t|\mathbf{r}_0 + \mathbf{R}_n) &= Q_p(\mathbf{r},t|\mathbf{r}_0)\end{aligned} \tag{4-11}$$

where $\mathbf{R}_n$ is some lattice vector. It is convenient to define a quantity

$$\bar{Q}_p(\mathbf{r},t|\mathbf{r}_0) = \sum_n Q_p(\mathbf{r} + \mathbf{R}_n,t|\mathbf{r}_0) \tag{4-12}$$

which satisfies the same diffusion equation (eq 2-13) as Q_p, with the initial condition

$$\bar{Q}_p(\mathbf{r},0|\mathbf{r}_0) = \sum_n \delta(\mathbf{r} - \mathbf{r}_0 - \mathbf{R}_n) \tag{4-13}$$

It is sufficient to solve for $\bar{Q}_p$ in a unit cell (volume Ω) since $\bar{Q}_p(\mathbf{r} + \mathbf{R}_n,t|\mathbf{r}_0) = \bar{Q}_p(\mathbf{r},t|\mathbf{r}_0)$, and we may express all quantities of interest in terms of $\bar{Q}_p$, i.e.

$$q_p(\mathbf{r},t) = \int_\Omega d^3r_0\,\bar{Q}_p(\mathbf{r},t|\mathbf{r}_0) \tag{4-14}$$

$$\rho_A(\mathbf{r}) = \frac{N_A}{\mathcal{Q}_{AB}}\int_0^{Z_A} dt\; q_A(\mathbf{r},Z_A - t)\int_\Omega d^3r'\,\bar{Q}_A(\mathbf{r},t|\mathbf{r}')q_B(\mathbf{r}',Z_B) \tag{4-15}$$

and

$$\mathcal{Q}_{AB} = \frac{v}{\Omega}\int_\Omega d^3r\; q_A(\mathbf{r},Z_A)q_B(\mathbf{r},Z_B) \tag{4-16}$$

The numerical evaluation of these equations for block copolymer microstructures in the presence of solvents and homopolymers will be presented in future publications.

5. Applications to Homopolymer–Solvent System

As an illustration of the earlier formulation, we discuss the calculation of the density profiles and asymptotic densities for a homopolymer–solvent mixture. The corresponding case for infinite molecular weight has been given earlier by Helfand and Sapse.[5] For convenience we change the degree of polymerization variable in eq 2-16 for the distribution function so that t lies in the range 0–1 (i.e., $t \rightarrow Zt$). With b_p as the unit of length, eq 2-16 becomes

$$\frac{1}{Z}\frac{\partial q(x,t)}{\partial t} = \frac{1}{6}\frac{\partial^2 q(x,t)}{\partial x^2} - \omega_p(x)q(x,t) \tag{5-1}$$

We also choose to work with volume fractions

$$\phi_\kappa = \rho_\kappa/\rho_{0\kappa} \tag{5-2}$$

which are equal to the reduced densities if there is no volume change upon mixing. In terms of these quantities, eq 2-26 for the polymer density becomes

$$\phi_p(x) = \int_0^1 dt\; q(x,t)q(x,1 - t) \tag{5-3}$$

and

$$\phi_s(x) = 1 - \phi_p(x) \tag{5-4}$$

The boundary conditions for eq 5-1 are

$$q(\pm\infty,t) = \exp[-tZ\omega_p(\pm\infty)] \tag{5-5}$$

and according to eq 2-17

$$q(x,0) = 1 \tag{5-6}$$

Making use of eq 2-31, we can express eq 5-5 as

$$q(\pm\infty,t) = \exp[t\ln\phi_p(\pm\infty)] \tag{5-7}$$

The Flory–Huggins form for the free energy density of the homopolymer–solvent system gives, from eq 3-11, with k_BT as the unit of energy

$$\Delta f = \rho_p(\mu_{0p} - \mu_p{}^b) + \rho_s(\mu_{0s} - \mu_s{}^b) + \rho_{0s}\left(\chi\phi_p\phi_s + \phi_s \ln \phi_s + \frac{\rho_{0p}}{\rho_{0s}}\frac{\phi_p}{Z}\ln \phi_p\right) \tag{5-8}$$

where $\chi = U_{ps}\rho_{0p}$ is the usual Flory–Huggins parameter.[22] Using the fact that $\Delta f = 0$ in the asymptotic phases, we find from eq 5-8

$$\Delta\mu_p = F_p(x) - F_p(\pm\infty) \tag{5-9}$$

where

$$F_p(x) = \frac{\rho_{0s}}{\rho_{0p}}\left[\chi\phi_s{}^2(x) + \frac{\rho_{0p}}{Z\rho_{0s}}\ln \phi_p(x) + \left(1 - \frac{\rho_{0p}}{Z\rho_{0s}}\right)\phi_p(x)\right] \tag{5-10}$$

Similarly to eq 5-9, we obtain

$$\Delta\mu_s = F_s(x) - F_s(\pm\infty) \tag{5-11}$$

where

$$F_s(x) = \chi\phi_p{}^2(x) + \ln \phi_s(x) + \left(1 - \frac{\rho_{0p}}{Z\rho_{0s}}\right)\phi_p(x) \tag{5-12}$$

The asymptotic volume fractions $\phi_p(\pm\infty)$ [or $\phi_s(\pm\infty)$] are obtained from the relations

$$F_p(\infty) = F_p(-\infty)$$
$$F_s(\infty) = F_s(-\infty) \tag{5-13}$$

and the result for the polymer mean field, eq 3-13, becomes

$$\omega_p(x) = \left[F_p(x) - F_p(\pm\infty) - \frac{1}{Z}\ln \phi_p(x)\right] - [F_s(x) - F_s(\pm\infty)] - \frac{1}{3}\chi\sigma^2\phi_p{}''(x) \tag{5-14}$$

The range of interaction of the parameter σ is assumed to be of the order of b_p (a few angstroms).

At this point it is interesting to compare our theory with that of Helfand and Sapse.[5] In the limit of vanishing compressibility and for a homogeneous system, the free energy densities in both theories reduce to the Flory–Huggins form. However, the chemical potential is different. In Helfand's work the chemical potential in the limit of vanishing compressibility ϵ is given by[5]

$$\mu_{\text{Helfand}} = \mu_{\text{Flory-Huggins}} + \psi(\mathbf{r}) \tag{5-15}$$

where

$$\psi(\mathbf{r}) = \lim_{\epsilon\to 0}\frac{1}{\epsilon}\left(\sum_\kappa \frac{\rho_\kappa(\mathbf{r})}{\rho_{0\kappa}} - 1\right) \tag{5-16}$$

is an undetermined function. Now the condition of a constant chemical potential requires

$$\mu_{\text{F-H}}(\infty) + \psi(\infty) = \mu_{\text{F-H}}(-\infty) + \psi(-\infty) \tag{5-17}$$

Next Helfand chooses $\psi(\infty) = \psi(-\infty)$, so that his chemical potential in the asymptotic phases reduces to the Flory–Huggins form (aside from an additive constant). This allows him to determine $\psi(\mathbf{r})$ and to solve for the asymptotic densities.

In our theory no undetermined function occurs, and our chemical potential automatically reduces to the Flory–Huggins form in the bulk phases. In addition, the derivation of the polymer mean-field equations for finite molecular weight is straightforward in our formalism.

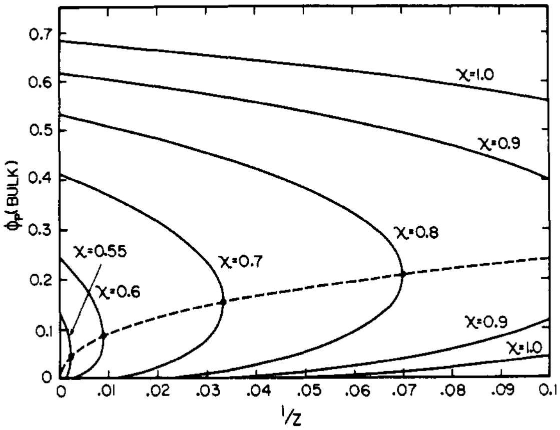

Figure 1. Bulk concentration values of polymer in the polymer-rich and solvent-rich phases for a homopolymer–solvent system as a function of the (inverse) degree of polymerization Z. The binodal curves shown are for different values of χ, and the dotted line is the locus of critical points, where the interface broadens and the interfacial tension falls to zero (Figure 4). As is well-known, for $\chi < {}^1/_2$ a two-phase region does not form for any value of Z.

The corresponding expression for the surface tension, eq 3-18, becomes

$$\gamma = \int_{-\infty}^{\infty} dx \left\{F_s(x) - F_s(\pm\infty) - \frac{\chi\sigma^2}{6}[\phi_p{}'(x)]^2\right\} \tag{5-18}$$

where the interfacial area A cancels on both sides of this equation because of the one-dimensional nature of the integral.

The numerical method of solving the above equation is presented in Appendix B. We now proceed to a discussion of the results for a homopolymer–solvent system, shown in Figures 1–4 for a range of molecular weights and interaction parameters.

In Figure 1 we show the results of the calculation of the binodal curves for the homopolymer–solvent system, assuming $\rho_{0p} = \rho_{0s}$. These curves are obtained from the numerical solution of eq 5-13, which state that the chemical potential of any component must be the same in both phases. Instead of varying the temperature T, as in standard phase diagrams, we have calculated the binodals for different values of χ, at fixed T, as a function of the (inverse) molecular weight Z. The binodals are asymmetrical and the phase diagram is skewed because the size ratio of the polymer molecules to solvent molecules, $Z\rho_{0s}/\rho_{0p}$, is greatly different from unity. The spinodal curves (not shown) are obtained from eq 5-8, using eq 5-4

$$\frac{\partial^2\Delta f}{\partial\phi_s{}^2} + \frac{\partial^2\Delta f}{\partial\phi_p{}^2} - 2\frac{\partial f}{\partial\phi_s}\frac{\partial f}{\partial\phi_p} = 0 \tag{5-19}$$

which may be solved analytically for different values of χ and Z. The point of tangency of the binodal and spinodal curves is the critical point, which is determined by the vanishing of both the first and second derivatives of the chemical potential, giving[2]

$$(\phi_p)_c = (\rho_{0p}/Z\rho_{0s})^{1/2}/[1 + (\rho_{0p}/Z\rho_{0s})^{1/2}] \tag{5-20}$$

The locus of critical points is shown by the dotted line in Figure 1, for $\rho_{0p} = \rho_{0s}$. The associated critical value of χ, below which no phase separation occurs, is[2]

$$\chi_c = {}^1\!/\!_2[1 + (\rho_{0p}/Z\rho_{0s})^{1/2}] \tag{5-21}$$

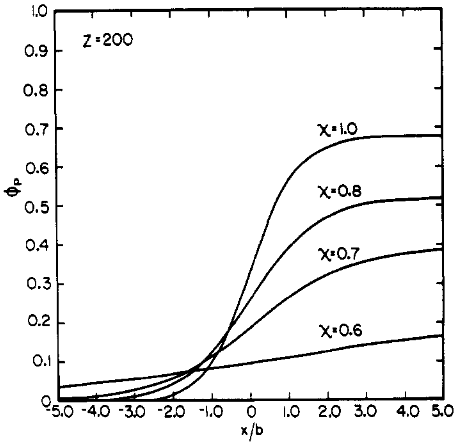

Figure 2. Interfacial concentration profiles for a polymer with degree of polymerization $Z = 200$ and a solvent for varying values of χ. The solvent concentration profiles are obtained from $\phi_p + \phi_s = 1$, and the distance from the interface is measured in units of the Kuhn length b.

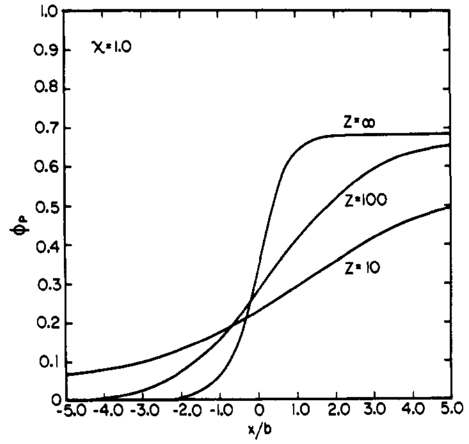

Figure 3. Interfacial concentration profiles for polymers with varying degrees of polymerization and a solvent for $\chi = 1.0$. The solvent concentration profiles are obtained from $\phi_p + \phi_s = 1$, and the distance from the interface is measured in units of the Kuhn length $b_p \equiv b$.

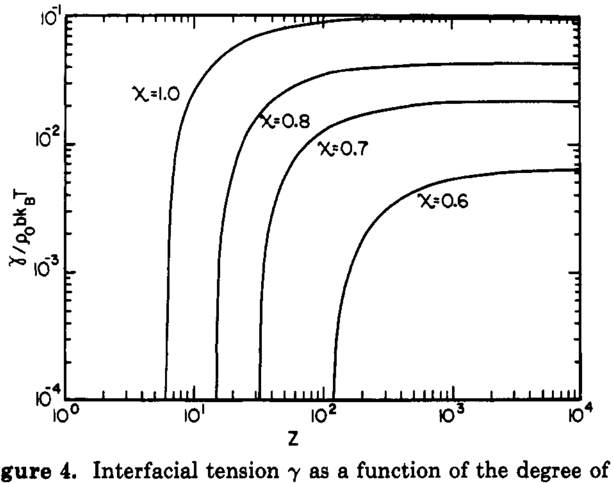

Figure 4. Interfacial tension γ as a function of the degree of polymerization for a polymer–solvent system with different values of the interaction parameter χ. The vertical scale is in reduced units, and typically $\rho_0 b k_B T \sim 15$ dyn/cm, using $b = 6$ Å, $\rho_{0p} = \rho_{0s} = 0.01$ mol/cm^3 with $T = 298$ K.

with the limiting value of 0.5 for $Z \rightarrow \infty$, as shown in Figure 1. Qualitatively the curves in Figure 1 can be easily understood by noting that for a decrease in molecular weight, a larger χ is required to obtain similar concentrations of polymer in the bulk phases. This means that for smaller molecules, the increased entropy loss upon demixing must be offset by a gain in the enthalpy for phase separation to occur.

The remaining diagrams, Figures 2–4, refer to the properties of the interface itself. Before discussing these figures, we comment on the validity of our microscopic calculations, noting that they are based on the mean-field approximation used in section 2. The simplest estimate of the validity of mean-field theory is due to de Gennes.[3] He considers a polymer chain of volume $R_p^3 \simeq b_p^3 Z^{3/2}$ and defines a parameter P which is equal to the *average* number of other chains occupying this volume

$$P \simeq (\rho_{0p}/Z)\phi_p R_p^3 \tag{5-22}$$

where ρ_{0p}/Z is the number of chains per unit volume. Since $\rho_{0p} = b_p^{-3}$, eq 5-22 becomes

$$P \simeq \phi_p Z^{1/2} \tag{5-23}$$

If $P \gg 1$, fluctuations in the average mean field are unimportant. On the other hand, if P is of order unity, fluctuation effects are large and the mean-field approximation breaks down. For the theoretical curves shown in Figures 2–4, eq 5-23 can easily be applied to determine the importance of fluctuations on a given density profile in order to see where our mean-field description (without fluctuations) becomes invalid.

Figure 2 shows the interfacial concentration profiles for a polymer ($Z = 200$) and a solvent for different values of the interaction parameter χ. Since we are working with volume fractions, we have $\phi_s + \phi_p = 1$, so that the concentration of solvent can be read from the top down in this figure. As usual, the distance from the interface is measured in units of the Kuhn length b. According to the binodal curves shown in Figure 1, for fixed Z and decreasing χ the bulk polymer concentration decreases and approaches the critical value, given by eq 5-20. Figure 2 shows the broadening of the interface as χ approaches χ_c, given by eq 5-21. The corresponding values of the interfacial tension for fixed Z and varying χ are shown in Figure 4. Figure 3 shows the broadening of the interface with decreasing molecular weight for a fixed value of χ. This corresponds to a trajectory along the single binodal shown in Figure 1, as well as a path along one of the curves shown in Figure 4.

In general, it appears that the interfacial profiles are rather narrow, with most of the variation in density taking place within a few b spacings. Detailed comparison of the homopolymer–solvent calculations with experiment is difficult, however. Although the interfacial thickness of microdomains in block copolymers has been studied in detail,[23-25] less microscopic investigation has been carried out on the kinematics of phase separation in incompatible homopolymer blends. The difficulty here is that successful application of the small-angle X-ray scattering technique to the determination of interfacial widths requires that phase separation take place by nucleation and growth throughout the system. If the phase separation is allowed to proceed to completion, however, a macroscopic phase boundary results, and the interfacial profile has to be measured by some other technique.[26] In some cases demixing can also occur by spinodal decomposition,[27] but our theoretical calculations do not apply directly to this phenomenon. We hope that future experimental work on incompatible polymer–solvent systems using X-ray scattering will allow the calculations presented in this section to be tested.

6. Conclusions

We have derived new mean-field equations for an inhomogeneous multicomponent mixture of block copolymers, homopolymers, monomers, and solvents, including nonlocal or gradient terms to lowest order. The corresponding results for the free energy and the interfacial tension (where applicable) are also given. For the homopolymer–solvent mixture, the reference state is taken to be the homogeneous bulk phase away from the interface. For a block copolymer–solvent system, a hypothetical uniform state, in which the different components have a constant density, is chosen for reference. The homopolymer–solvent system is worked out in detail numerically for a range of molecular weights and interaction parameters. Unfortunately, there are little experimental data available for comparison with this simple case. Future work will deal with more complicated cases, such as the effect of solvents, monomers, and homopolymers on block copolymer microdomain morphology. The mean-field approach has proved quite successful for a description of the microdomain formation in "pure" block copolymers.[6,7] It will be interesting to see whether this success will be maintained by a good quantitative description of more complicated systems.

Acknowledgment. We thank L. M. Marks for developing the computer programs used to evaluate the interfacial density profiles and surface tensions and for assistance with the numerical calculations. We are indebted to Professor M. Tribus for comments regarding the constant-density constraint, and we thank Dr. R. H. Marchessault and Professor K. F. O'Driscoll for discussions and encouragement during the course of this work.

Appendix A

We derive some alternate expressions for the interfacial tension of a homopolymer–solvent mixture, valid for a one-dimensional system, which distinguish between the macromolecular and nonlocal energy contributions to this quantity. We define a "conjugate" distribution function by

$$q_p^\dagger(x,t) = q_p(x,Z_p - t) \qquad \text{(A-1)}$$

and change the degree of polymerization variable from t to Z_pt. Equation 2-26 for the polymer density is then given by

$$\rho_p = \rho_{0p}\int_0^1 \mathrm{d}t\; q_p q_p^\dagger \qquad \text{(A-2)}$$

and the equations of motion because

$$\frac{1}{Z_p}\frac{\partial q_p}{\partial t} = \frac{b_p^2}{6}\frac{\partial^2 q_p}{\partial x^2} - \omega_p q_p \qquad \text{(A-3)}$$

$$\frac{1}{Z_p}\frac{\partial q_p^\dagger}{\partial t} = \frac{b_p^2}{6}\frac{\partial^2 q_p^\dagger}{\partial x^2} - \omega_p q_p^\dagger \qquad \text{(A-4)}$$

with

$$q_p(x,0) = q_p^\dagger(x,1) = 1 \qquad \text{(A-5)}$$

Differentiating eq 3-9 and multiplying by ρ_κ gives

$$\sum_\kappa \rho_\kappa \frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{\mathrm{D}\Delta f}{\mathrm{D}\rho_\kappa} + \frac{1}{6}\sum_{\kappa'} V_{\kappa\kappa'}\frac{\mathrm{d}^2\rho_{\kappa'}}{\mathrm{d}x^2}\right\} - \sum_p\left(\rho_p\frac{\mathrm{d}\omega_p}{\mathrm{d}x} + \frac{1}{Z_p}\frac{\mathrm{d}\rho_p}{\mathrm{d}x}\right) + \frac{\mathrm{d}\Delta\zeta}{\mathrm{d}x} = 0 \qquad \text{(A-6)}$$

Integrating this expression and using the relation

$$\rho_p\frac{\mathrm{d}\omega_p}{\mathrm{d}x} = -\rho_{0p}\frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{1}{Z_p}q_p(x,1) + \int_0^1 \mathrm{d}t\,\frac{b_p^2}{6}\left(\frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} - q_p\frac{\partial^2 q_p^\dagger}{\partial x^2}\right)\right\} \qquad \text{(A-7)}$$

derived using eq A-2 to A-5, gives

$$\Delta\zeta + \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\left(2\rho_\kappa\frac{\mathrm{d}^2\rho_{\kappa'}}{\mathrm{d}x^2} - \frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\frac{\mathrm{d}\rho_{\kappa'}}{\mathrm{d}x}\right) - \sum_p\frac{\rho_p}{Z_p} + \sum_p \rho_{0p}\left\{\frac{1}{Z_p}q_p(x,1) + \int_0^1 \mathrm{d}t\,\frac{b_p^2}{6}\left(\frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} - q_p\frac{\partial^2 q_p^\dagger}{\partial x^2}\right)\right\} = 0 \qquad \text{(A-8)}$$

where the constant of integration can be shown to vanish by noting that $\Delta\zeta$ vanishes for $|x| \to \infty$ and using eq 2-31 for a homogeneous system. Integrating eq A-8 once more gives

$$-\int \mathrm{d}x\,\Delta\zeta = \sum_p \rho_{0p}\frac{b_p^2}{3}\int \mathrm{d}x\int_0^1 \mathrm{d}t\,\frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} - \frac{1}{4}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\int \mathrm{d}x\,\frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\frac{\mathrm{d}\rho_{\kappa'}}{\mathrm{d}x} \qquad \text{(A-9)}$$

and using this result, eq 3-18 for the interfacial tension can be written

$$\gamma = \int \mathrm{d}x\left(\frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\frac{\mathrm{d}\rho_{\kappa'}}{\mathrm{d}x} - \Delta\zeta\right) = \sum_p \rho_{0p}\frac{b_p^2}{3}\int \mathrm{d}x\int_0^1 \mathrm{d}t\,\frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} - \frac{1}{6}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\int \mathrm{d}x\,\frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\frac{\mathrm{d}\rho_{\kappa'}}{\mathrm{d}x} \qquad \text{(A-10)}$$

which shows that in the absence of polymers, the interfacial tension for a mixture of small-molecule liquids arises from the nonlocal term alone, a result noted by earlier authors.[21,28]

Another expression for the interfacial tension can be derived starting from eq 3-9 and making use of eq 2-21

$$\sum_\kappa \frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\left\{\frac{\mathrm{D}\Delta f}{\mathrm{D}\rho_\kappa} + \frac{1}{6}\sum_{\kappa'} V_{\kappa\kappa'}\frac{\mathrm{d}^2\rho_{\kappa'}}{\mathrm{d}x^2}\right\} - \sum_p\frac{\mathrm{d}\rho_p}{\mathrm{d}x}\left[\omega_p + \frac{1}{Z_p}\ln\left(\frac{\rho_p}{\rho_{0p}}\right)\right] = 0 \qquad \text{(A-11)}$$

Integrating eq A-11 and using the relation

$$\omega_p\frac{\mathrm{d}\rho_p}{\mathrm{d}x} = \rho_{0p}\frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{1}{Z_p}q_p(x,1) + \int_0^1 \mathrm{d}t\left(\frac{b_p^2}{6}\frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} + \frac{1}{Z_p}q_p\frac{\partial q_p^\dagger}{\partial t}\right)\right\} \qquad \text{(A-12)}$$

derived using eq A-2 to A-5, gives

$$\Delta f + \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'} \frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\frac{\mathrm{d}\rho_{\kappa'}}{\mathrm{d}x} - \sum_p \rho_{0p}\left\{\frac{1}{Z_p} q_{\mathrm{p}}(x,1) + \int_0^1 \mathrm{d}t\left(\frac{b_p^2}{6}\frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} + \frac{1}{Z_p} q_p \frac{\partial q_p^\dagger}{\partial t}\right)\right\} - \sum_p \frac{\rho_p}{Z_p}\left[\ln\left(\frac{\rho_p}{\rho_{0p}}\right) - 1\right] = 0 \quad \text{(A-13)}$$

where the constant of integration vanishes because Δf vanishes for $|x| \to \infty$, and in the homogeneous phase we have

$$q_p(x,t) = (\rho_p/\rho_{0p})^t \quad \text{(A-14)}$$

according to eq 2-30 and 2-31. Integrating eq A-13 again gives

$$\int \mathrm{d}x\ \Delta f = \sum_p \rho_{0p}\frac{b_p^2}{6}\int \mathrm{d}x \int_0^1 \mathrm{d}t\ \frac{\partial q_p}{\partial x}\frac{\partial q_p^\dagger}{\partial x} - \frac{1}{12}\sum_{\kappa\kappa'} V_{\kappa\kappa'}\int \mathrm{d}x\ \frac{\mathrm{d}\rho_\kappa}{\mathrm{d}x}\frac{\mathrm{d}\rho_{\kappa'}}{\mathrm{d}x} + \sum_p \frac{1}{Z_p}\int \mathrm{d}x\left\{\rho_p \ln\left(\frac{\rho_p}{\rho_{0p}}\right) + \rho_{0p}\int_0^1 \mathrm{d}t\ q_p\frac{\partial q_p^\dagger}{\partial t}\right\} \quad \text{(A-15)}$$

and noting the result eq A-10, we obtain

$$\gamma = 2\left\{\int \mathrm{d}x\ \Delta f - \sum_p \frac{1}{Z_p}\int \mathrm{d}x\left[\rho_p \ln\left(\frac{\rho_p}{\rho_{0p}}\right) + \rho_{0p}\int_0^1 \mathrm{d}t\ q_p \frac{\partial q_p^\dagger}{\partial t}\right]\right\} \quad \text{(A-16)}$$

In the special case where the polymers have infinite molecular weights ($Z_p = \infty$), this equation reduces to

$$\gamma = 2\int \mathrm{d}x\ \Delta f \quad \text{(A-17)}$$

a result which was obtained by Helfand and Sapse[4] and used in our previous work.[20]

Appendix B

In this appendix, we give a brief description of our numerical method. First, we discretize the variables x and t

$$\begin{aligned} x &= (i - N)\Delta x \qquad i = 0, ..., 2N \\ t &= j\Delta t \qquad j = 0, ..., M \end{aligned} \quad \text{(B-1)}$$

where $\Delta t = 1/M$, and we write $q(x,t)$ as $q(i,j)$. Typically $N = 100$, and the choice of Δx depends on the interfacial thickness. In our work M was chosen in the range 100–200. The discrete version of the modified diffusion equation is obtained by using the Crank–Nicholson scheme[29]

$$\frac{1}{Z}\frac{q(i,j) - q(i,j-1)}{\Delta t} = \frac{1}{12}\left[\frac{q(i+1,j) + q(i-1,j) - 2q(i,j)}{(\Delta x)^2} + \frac{q(i+1,j-1) + q(i-1,j-1) - 2q(i,j-1)}{(\Delta x)^2}\right] + \frac{1}{2}\omega(i)[q(i,j) + q(i,j-1)] \quad \text{(B-2)}$$

which has the following tridiagonal form in i

$$Aq(i+1,j) + B_i q(i,j) + Aq(i-1,j) = D_{i,j-1} \quad \text{(B-3)}$$

with the given boundary values

$$\begin{aligned} q(0,j) &= \exp[t \ln \phi_p(-\infty)] \\ q(2N,j) &= \exp[t \ln \phi_p(\infty)] \end{aligned} \quad \text{(B-4)}$$

In eq B-3 $D_{i,j-1}$ involves only $\omega(i)$, $q(i+1,j-1)$, $q(i,j-1)$, and $q(i-1,j-1)$.

We begin with a guess for $\phi_p(x)$ which interpolates between $\phi_p(\pm\infty)$ and we use eq 5-14 to obtain an initial guess for $\omega(i)$. This, together with $q(i,j-1)$ ($i = 0, ..., 2N$), determines the coefficients B and D in eq B-3. The tridiagonal difference eq 5-18 is then easily solved, with the help of the boundary conditions, eq B-4, to yield $q(i,j)$ ($i = 0, ..., 2N$). Thus, starting from the initial condition $q(i,0) = 1$ ($i = 0, ..., 2N$), we obtain $q(i,j)$ and so on.

From this set of $q(i,j)$, we obtain the new density profile $\phi_p^{(1)}(x)$, using eq 5-3 and the trapezoidal rule. $\omega_p^{(1)}(i)$ is then obtained by using $\phi_p^{(1)}(x)$ and eq 5-14. For each guess $\omega_p(i)$, we thus compute from the equations its "image" $\omega_0^{(1)}(i)$. We then repeat the interation with the new guess

$$\omega_p^{\text{new}}(i) = \omega_p(i) + \lambda[\omega_p^{(1)}(i) - \omega_p(i)] \quad \text{(B-5)}$$

where λ is some relaxation parameter. The iteration is continued until the self-consistency condition

$$\max_{i=0,...,2N} |\omega_p(i) - \omega_p^{(1)}(i)| \le \epsilon \quad \text{(B-6)}$$

is achieved. Typically we used $\epsilon \simeq 10^{-6}$–10^{-7} in our calculations.

To improve the convergence, we apply a modified secant method[30] after a few iterations, briefly described below. Let $\omega_1(i), \omega_2(i), ..., \omega_L(i)$ be a series of successive guesses, and $\omega_1^{(1)}(i), ..., \omega_L^{(1)}(i)$ their corresponding "images". To improve the convergence we use as our next guess

$$\omega(i) = \omega_L(i) + \sum_{l=1}^{L-1} P_l[\omega_l(i) - \omega_L(i)] \quad \text{(B-7)}$$

and determine the coefficients p_l by minimization of

$$\sum_i \{G_L(i) + \sum_{l=1}^{L-1} p_l[G_l(i) - G_L(i)]\}^2 \quad \text{(B-8)}$$

where

$$G_l(i) = \omega_l(i) - \omega_l^{(1)}(i) \quad \text{(B-9)}$$

In other words, the optimum p_l is given by the solution of the set of linear equations

$$\sum_{l'} p_{l'}\{\sum_i [G_{l'}(i) - G_L(i)][G_l(i) - G_L(i)]\} + \sum_i G_L(i)[G_l(i) - G_L(i)] = 0 \quad \text{(B-10)}$$

and these are used in eq B-7.

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Theory of Interfacial Tension in Ternary Homopolymer–Solvent Systems

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ABSTRACT: A recent theory of inhomogeneous multicomponent polymer systems is used to calculate the interfacial tension and width in ternary homopolymer–homopolymer–solvent mixtures. We consider symmetric systems where the polymer–solvent interaction parameters are equal ($\chi_{AS} = \chi_{BS}$), as well as asymmetric systems ($\chi_{AS} \neq \chi_{BS}$). A number of phase diagrams are presented, corresponding to different degrees of miscibility of the components and different values of the molecular weights of the homopolymers. The maxima in the interfacial tension curves as a function of solvent concentration are generally found to be shifted to lower concentrations than the minima in the interfacial width curves. Scaling relations are derived which explain this shift, as well as the dependence of the interfacial tension on molecular weight for symmetric systems. Calculations of the interfacial tension are given for styrene–polystyrene–polybutadiene mixtures.

1. Introduction

The study of polymer compatibility and incompatibility remains an active and important area of applied and fundamental research.[1,2] The development of new techniques of measuring the interfacial tension in multicomponent systems gives a direct quantitative measure of the microscopic compatibility of such systems.[3] In this paper we develop the theory of the interfacial tension in ternary homopolymer–solvent mixtures, which complements the traditional thermodynamic calculations of phase diagram binodal curves.[4,5]

We extend our earlier work on unsymmetrical polymer–polymer interfaces (assuming infinite molecular weight) in the presence of solvent[6] to deal with ternary homopolymer–solvent systems in general. We make use of a new formulation of inhomogeneous multicomponent systems developed recently and discussed in detail elsewhere.[7] Briefly, in our theory we optimize the general free energy functional of the homopolymer–solvent system using the saddle function method, subject to the constraint of no volume change locally upon mixing, and obtain new equations for the mean fields acting on the polymers. These equations are given (without derivation) in section 2 and are expressed in terms of the chemical potential corresponding to a locally homogeneous Flory–Huggins free energy density. The equations are solved numerically by a self-consistent procedure described elsewhere,[7] and phase diagrams are presented for symmetric systems, where the polymer–solvent interaction parameters are equal ($\chi_{AS} = \chi_{BS}$), as well as for asymmetric systems ($\chi_{AS} \neq \chi_{BS}$). Plots of the interfacial tension and width are given for varying amounts of solvent in the system. All of our present calculations are restricted to monodisperse systems.

In order to obtain a better undstanding of the trends observed in the results of the numerical work we develop a number of scaling relations,[8] which are checked against the exact numerical calculations. Although all of our phase diagrams have been studied earlier experimentally[9-12] and theoretically,[4,5,13,14] the corresponding plots of the interfacial tension and width (as well as the interfacial profiles) are presented here for the first time. Finally, we calculate the interfacial tension for a polymerization path in the styrene–polystyrene–polybutadiene system and find good agreement with recent measurements by Reiss and coworkers.[3]

2. Theory

A detailed account of the theory of inhomogeneous multicomponent polymer systems has been presented in an earlier publication.[7] Here we summarize the equations required for the analysis of the ternary homopolymer–homopolymer–solvent mixture. The reader who is interested in the derivation of these equations, as well as a discussion of the theory, is referred to our earlier work.[7]

The mean-field equations for $q_\kappa(x,t)$ (κ = A, B), which is proportional to the probability density that the end of a molecule of type κ and degree of polymerization $Z_\kappa t$ is at x, are

$$\begin{aligned}\frac{1}{Z_A}\frac{\partial q_A(x,t)}{\partial t} &= \frac{1}{6}\frac{\partial^2 q_A(x,t)}{\partial x^2} - \omega_A(x)q_A(x,t)\\ \frac{1}{Z_B}\frac{\partial q_B(x,t)}{\partial t} &= \frac{1}{6}\frac{\partial^2 q_B(x,t)}{\partial x^2} - \omega_B(x)q_B(x,t)\end{aligned} \tag{2-1}$$

where x is measured in terms of the Kuhn statistical length b, which is assumed to be the same for the two polymers in model calculations, and Z_κ is the degree of polymeri-