Lattice Theory for Multicomponent Mixtures of Copolymers with Internal Degrees of Freedom in Heterogeneous Systems

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ABSTRACT: We have generalized the lattice theory recently presented by Evers, Scheutjens, and Fleer (*Macromolecules* **1990**, *23*, 5221) by extending it to the case where the polymer segments possess internal degrees of freedom. The theory is able to describe the adsorption from a multicomponent mixture of arbitrary composition of polymers and solvents where the segments of a polymer may be of different types and possess internal degrees of freedom. The use of internal states results in effective segment–segment interaction parameters, which are temperature and density dependent. This simple polymer model has previously been useful for describing the existence of a lower consolute point occurring in some aqueous polymer solutions and for predicting the conformational equilibrium of poly(ethylene oxide) in homogeneous solutions. We also present results from an application of our extended theory on the adsorption of Pluronic (a triblock copolymer) from aqueous solution. The nontrivial and prominent increase of the Pluronic adsorption as the temperature of the solution reaches the cloud point from *below* is accurately reproduced by the theory.

I. Introduction

Since the original work on polymer adsorption from solution by Scheutjens and Fleer,[1] the discrete lattice theory has developed in several directions. Some of the more important extensions deal with the description of the polymer. Polyelectrolytes constitute an important class of polymers, where the long-range electrostatic interaction may significantly alter the monomer distribution. An exploratory study with charges included was performed by Papenhuijzen et al.[2] using the Scheutjens–Fleer theory augmented with a description of the electrostatic contribution to the free energy of the system on a mean-field Poisson–Boltzmann level. Recently, Leermakers and Scheutjens[3] modeled the steric hindrance of the C–C bond rotation by introducing different weights for gauche and trans conformations. This extension of the original Scheutjens–Fleer theory also prohibits direct back-folding. Furthermore, we have suggested[4] that, by introducing internal degrees of freedom of the polymer segments, an effective temperature- and density-dependent polymer–solvent interaction parameter can be obtained. Such or similar extension is essential for modeling the lower consolute point in the binary polymer–solvent systems.

A more fundamental extension is to go beyond the random mixing (mean field) approximation. A significant step in that direction has been made by Leermakers.[5] The gist of his approach is not only to count the distribution of monomers, but also to consider the directions of bonds between adjacent monomers. Finally, a large improvement was recently made by Evers, Scheutjens, and Fleer.[6] Previously, the lattice theory was presented for a two-component system: polymer and solvent. Evers et al.[6] made the theory more general by formulating it for a multicomponent mixture, even without a solvent, of arbitrary composition. Moreover, they proposed a numerical procedure which efficiently treats the constraint of the filled lattice space.

In this contribution we report a generalization of the formalism of Evers et al.[6] by extending it to the case where the polymer model contains internal degrees of freedom (states). Furthermore, the description of the internal states is made more general than in our previous report.[4] Here we will consider the case where *all* segment types may possess an *arbitrary* number of internal states. The presented theory is thus able to describe adsorption from a multicomponent mixture of arbitrary composition where each component consists of one or several segments. The segments of a polymer may be of the same type (homopolymer) or they may be different (block copolymer, alternating copolymer, etc). Finally, each segment type may possess one or several internal states which may provide us with an effective segment–segment interaction which is temperature and density dependent. This dependence is achieved by using a restricted number of parameters which all have physical interpretations.

The paper is organized as follows. In section II we give a short account of experimental results which motivate our extended polymer model with internal states. Other proposed mechanisms of rationalizing the existence of a lower consolute point are also included. In section III we give a brief presentation of the lattice model, basic concepts of our extension, and some important results. In particular, comparison of central quantities given by Evers et al. and those of the present theory is pursued. The theory has been employed for describing the adsorption of Pluronic[7] (a triblock copolymer) on a hydrophobic surface. Some initial results are given in section IV, while a more extended report is given elsewhere.[8] The paper ends with three appendices. In the first one, Appendix A, a more complete derivation of our extended theory is given. Appendix B contains numerical aspects of implementing the theory, and most important indexes and variables are compiled in Appendix C.

II. Background

Some important polymers display a reduced solubility in aqueous solution at elevated temperatures. Above a certain temperature the solution separates into two phases, one rich and one poor in the polymer. The existence of a lower consolute point is often discussed in terms of a more repulsive polymer–solvent interaction, or equivalently in a more attractive polymer–polymer interaction, at higher temperature. Of course, at a sufficiently high temperature a one-phase region is encountered again, provided the polymer is chemically stable at these temperatures. The location of the lower consolute point depends on the properties of the constituents of the system.

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An aqueous solution of poly(ethylene oxide) (PEO) displays a lower consolute point in the range of 350–450 K,[9,10] depending on the molecular mass, whereas a solution of the more hydrophobic poly(propylene oxide) (PPO) separates at 280–320 K.[9,11] Hydrophobically substituted cellulose ethers, such as ethyl(hydroxyethyl)cellulose (EHEC), which are frequently used in industrial applications, constitute a third example of polymers having a lower consolute point.

Several mechanisms have been proposed for explaining the temperature-dependent interaction between polymer and solvent. Kjellander and Florin[12] pointed out that PEO could very well be accommodated in a tetrahedrally structured water solution. They proposed that this coupling causes a zone of an enhanced water structure about the PEO chains. If this region is stable enough against degradation at increased temperature, this structure would promote a phase separation.

In a second proposal by Goldstein,[13] it is suggested that the polymer segments may be either hydrogen bonded or nonbonded to adjacent solvent molecules. This extension of the Flory–Huggins theory causes the effective segment–segment interaction parameter to be temperature dependent, and by suitable choice of parameters, a two-phase coexistence region occurs in the binary polymer–solvent phase diagram.

In our laboratory, Karlström[14] has proposed a third mechanism. The gist of his approach is that the conformation of a polymer segment may vary with temperature, and that different conformations interact unequally with adjacent polymer segments and solvent molecules. From quantum mechanical calculations,[15] the conformations of the OCCO segment were divided into two classes or states: one being polar and having the lowest energy but a low statistical weight, and one being less polar or nonpolar and having the higher energy but a higher statistical weight. (The latter class will be referred to as the nonpolar, although some of the conformations constituting the class have small dipole moments.) At low temperature the polar state is dominating, thus a more favorable polymer–solvent interaction is obtained, whereas at increasing temperature, the nonpolar state becomes progressively more important, which results in a more unfavorable polymer–solvent interaction.

It cannot be ruled out, and in fact, it is even likely that all three descriptions contain parts which are relevant for the existence of a lower consolute point, at least for some system. However, it appears that the mechanism of Karlström has some advantages. It provides, for example, an explanation of the resulting clouding phenomena of nonionic surfactant solutions in solvents other than water, i.e., in formamide,[16] and the similarity of the PEO–dextran–water and PEO–dextran–formamide phase diagrams.[17] The approach is also consistent with recently observed ^{13}C NMR chemical shifts of PEO in aqueous solution, in organic solvents, and in pure PEO.[18] The chemical shift data support conformational changes with temperature and composition variations, and the shift changes are semiquantitatively predicted by the model given a fit of the shifts of the two classes of conformations.

Copolymers of ethylene oxide (EO) and propylene oxide (PO) are frequently used as stabilizing additives in colloidal suspensions since the different characters of the blocks provide both anchoring groups and dangling tails, which increase the stabilization. Recent measurements by Tiberg et al.[8] on such triblock copolymers have shown a number of interesting adsorption properties. Inspired by the successful predictions found by employing Karlström's polymer model on phase diagrams of the PEO–dextran–solvent system[17,19] and EHEC–water systems,[20] as well as the encouraging results from the PEO–water system,[4,21] we have chosen to describe the phase behavior and adsorption of block copolymers of PEO–PPO type by a similar approach. Since both segment types display an increased effective attraction at higher temperature, it is essential to describe both types with internal degrees of freedom.

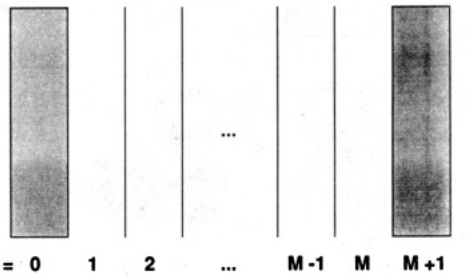

Figure 1. Illustration of the two surfaces (in the case of a planar geometry) and the intervening space which is divided into layers parallel to the surfaces and the labeling of the surface and intervening layers.

III. Theory

A. Model. The space between two impenetrable and smooth surfaces, planar or curved, is divided into M parallel layers (see Figure 1). Within each layer, the Bragg–Williams approximation of random mixing is applied, and thus all lattice sites in a layer are equivalent. A lattice site has a given number of nearest neighbors, which is determined by the lattice topology. A given number of these are found in the same layer, whereas the others are located in the two adjacent layers.

The lattice between the surfaces is completely filled by solvent and polymer molecules. The different types of solvent(s) and polymer(s) are collectively referred to as the components of the system. A polymer consists of several segments, and these may be of different types. The different segment types are referred to as species. It is assumed that the volumes of polymer segments and solvent molecules are the same, and that they occupy one lattice site each.

Close to the surface the mixture becomes heterogeneous because solvent and polymers interact unequally with the surface, and because of the restricted number of conformations possible for the polymers. A central quantity of the theory is the species potential, which depends on the distance from the surface and the species. If the potential profiles are known, the segment density profiles can be calculated using Boltzmann statistics.

B. Internal Degrees of Freedom. Our extension of the lattice theory formulated by Evers et al.[6] is that each segment type exists in one of several states (see Figure 2). Each state is characterized by an energy term and an entropy term, which contribute to the internal free energy, and by interaction parameters describing the nearest-neighbor interaction with segments in different states. Thus, the interaction parameters describe the interaction among segments in given states. Since the interaction between two segments depends on their states *and* since the population of the states (the state distribution) depends on temperature and density of neighbors (cf. eq 6), the model leads to an effective (averaged over all pairs of states) segment–segment interaction which is temperature as well as density dependent. The virtue of the internal degrees of freedom is that we obtain an effective segment–segment interaction *without* explicitly specifying a functional form

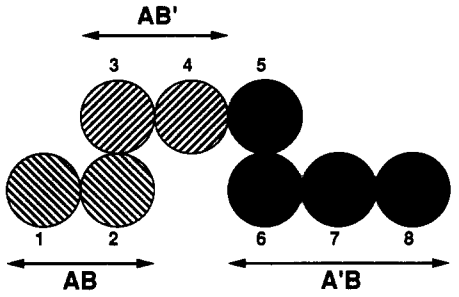

Figure 2. Illustration of a component (polymer) in a given conformation on a two-dimensional cubic lattice. The component consists of eight segments of which segments of ranks 1–4 are of type A and 5–8 are of type A′. Segments of type A have two internal states, AB and AB′, whereas species A′ has only one state, A′B. Segments of ranks 1 and 2 are in state AB and 3 and 4 are in state AB′.

of $\chi_{\text{segment-segment}}(T,\phi)$. Instead, the dependence emerges as a *consequence* of a physically plausible model employing a restricted number of parameters of which all have clear meaning.

The total internal free energy of the system is given by

$$\beta A_{\text{int}} = \sum_i \sum_A n_{Ai} \sum_B P_{ABi}[\beta U_{AB} + \ln (P_{ABi}/g_{AB})] \quad (1)$$

where $\beta = (kT)^{-1}$; $\sum_i$ denotes a sum over layers, $\sum_A$ a sum over all species (segment types), and $\sum_B$ a sum over all states of species A; n_{Ai} is the number of sites in layer i occupied by segments of type A; and P_{ABi} is the fraction of species A in layer i which are in state B. There are three contributions to the internal free energy represented by the bracket, viz. U_{AB}, which is the internal energy of state B of species A, $kT \ln g_{AB}$, where g_{AB} is the degeneration factor of state B of species A, and $kT \ln P_{ABi}$, an entropy term arising from the mixing of the states. In the application to PEO and related polymers, U_{AB} and g_{AB} describe the equilibrium between the conformation classes of the polymer segments. Since the nonpolar class has the higher internal energy and the larger degeneration, $U_{\text{EO,nonpolar}} > U_{\text{EO,polar}}$ and $g_{\text{EO,nonpolar}} > g_{\text{EO,polar}}$.

State and Segment Distributions. The derivation of the state and segment distributions originates from the canonical partition function and the related grand canonical partition function of the system. In the theory of Evers et al.,[6] the canonical partition function Q is given by

$$Q = \Omega \exp(-\beta U) \quad (2)$$

where Ω is the configurational degeneration and U the configurational energy, both depending on the space configuration (the spacial arrangement of the molecules). The internal degrees of freedom is included in the theory by extending Q according to

$$Q = Q_{\text{int}} \Omega \exp(-\beta U) \quad (3)$$

where Q_{int} is the canonical partition function of the internal degrees of freedom and is given by $Q_{\text{int}} = \exp(-\beta A_{\text{int}})$. In eq 3, Q depends on the spacial configuration as well as on the state distribution given by $\{P_{ABi}\}$.

The configurational degeneration is not affected by the presence of internal states. Thus Ω could be taken from Evers et al.[6] after a generalization to curved surfaces or from us[4] after an extension to a multicomponent system. The configurational energy is obtained by adding all nearest-neighbor contributions, including surface interactions, and becomes in the absence of internal degrees of freedom

$$\beta U = \frac{1}{2}\sum_{i=0}^{M+1} L_i \sum_A^s \sum_{A'}^s \phi_{Ai} \chi_{AA'} \langle \phi_{A'i} \rangle \quad (4)$$

where ϕ_{Ai} is the volume fraction of sites in layer i occupied by species A, $\chi_{AA'}$ is the Flory–Huggins interaction parameter for the species pair A–A′, and $\langle ... \rangle$ denotes an average over layers $i-1$, i, and $i+1$, including surface layers. The superindex s of the species summation symbol implies that the surface species are included in the sum as well. In the case of internal degrees of freedom, U is easily generalized to

$$\beta U = \frac{1}{2}\sum_{i=0}^{M+1} L_i \sum_A^s \sum_{A'}^s \sum_B \sum_{B'} \phi_{Ai} P_{ABi} \chi_{BB'} \langle P_{A'B'i} \phi_{A'i} \rangle \quad (5)$$

where $\chi_{BB'}$ is the Flory–Huggins interaction parameter for the energy associated with transferring a segment of type A in state B from a solution of pure A in state B to a solution of pure A′ in state B′. An often used adsorption parameter is $\chi_s \equiv -\beta(u_{BS} - u_{B'S})$ where u_{BS} is the adsorption energy of a polymer segment (of type B) and $u_{B'S}$ that of a solvent molecule (segment of type B′) at a surface (segment of type S) (see ref 1 and references given therein). The parameter is related to Flory–Huggins interaction parameters through $\chi_s \equiv -\lambda_{10}(\chi_{BS} - \chi_{B'S})$, since only a fraction (λ_{10}) of all nearest neighbors are used in the adsorption process as compared to all neighbors used in the definition of the interaction parameter. (λ_{10} depends on the lattice topology and is 0.25 in the case of a hexagonal lattice.)

The selection of the most important term of the grand canonical partition function specifies one state and one conformational distribution, which will be referred to as the equilibrium distributions. The aim is to obtain expressions of the *state* equilibrium distribution as well as of the *segment* equilibrium distribution, the latter being uniquely determined by the conformational equilibrium distribution.

The state distribution $\{P_{ABi}\}$ can be derived from the partition function, and as explicitly shown in Appendix A, it is given by the implicit set of nonlinear equations

$$P_{ABi} = \frac{X_{AB}}{\sum_B X_{AB}}$$

$$X_{AB} \equiv g_{AB} \exp[-\beta U_{AB} - \sum_{A'}^s \sum_{B'} \chi_{BB'} \langle P_{A'B'i} \phi_{A'i} \rangle] \quad (6)$$

valid for all species, states, and layers. The numerator gives the weight of finding the species A in layer i which are in state B, whereas the denominator is a normalization factor. As expected, eq 6 shows that a state is favored by a high degeneration, a low internal energy, and a favorable interaction (small χ) with its neighboring segments.

The expression of the segment distribution is more complex due to the connectivity of the chains, and because segments of a chain may reside in different layers. The determination of the segment distribution requires (i) an expression of the relative free energy of placing an unconnected segment in a layer and (ii) a method of taking into account the constraint that two connected segments in a chain have to be located in the same or two adjacent layers. The former is given by the species potential, which may be derived from the partition function and the packing constraints. Moreover, the species potential u_{Ai} may be divided into two parts: one species-independent u'_i and

one species-dependent u_{Ai}^{int} according to

$$u_{Ai} = u'_i + u_{Ai}^{int} \tag{7}$$

(Here we retain the notation of the species potential of Evers et al.[6] although our extension leads to an entropic contribution to u^{int}, which thus has a character of free energy.) If the species potentials are defined with respect to bulk solution, i.e., $u_A^b = 0$, then the two parts are given by

$$\beta u'_i \equiv \alpha_i + \sum_x \frac{\phi_x^b}{r_x} + \frac{1}{2}\sum_{A'}\sum_{A''}\phi_{A'}^b \chi_{A'A''}\phi_{A''}^b$$

$$\beta u_{Ai}^{int} \equiv \sum_{A'}^{s} \chi_{AA'}(\langle\phi_{A'i}\rangle - \phi_{A'}^b) \tag{8}$$

where ϕ_x^b is the bulk volume fraction of component x, ϕ_A^b is the bulk volume fraction of species A, and α_i are Lagrangian multipliers to be determined. The corresponding expressions for the case of internal degrees of freedom becomes, as also explicitly shown in Appendix A

$$\beta u'_i \equiv \alpha_i + \sum_x \frac{\phi_x^b}{r_x} + \frac{1}{2}\sum_{A'}\sum_{A''}\sum_{B'}\sum_{B''}\phi_{A'}^b P_{A'B'}^b \chi_{B'B''} P_{A''B''}^b \phi_{A''}^b$$

$$\beta u_{Ai}^{int} \equiv \sum_B \left[P_{ABi}\left(\beta U_{AB} + \ln\frac{P_{ABi}}{g_{AB}}\right) - P_{AB}^b\left(\beta U_{AB} + \ln\frac{P_{AB}^b}{g_{AB}}\right)\right] + \sum_{A'}^{s}\sum_B\sum_{B'}\chi_{BB'}(P_{ABi}\langle P_{A'B'i}\phi_{A'i}\rangle - P_{AB}^b P_{A'B'}^b \phi_{A'}^b) \tag{9}$$

where P_{AB}^b is the fraction of species A in state B in bulk and is given by a relation similar to eq 6 (eq A.7.13). The species-independent potential u'_i ensures that the space is completely filled in layer i by a suitable choice of α_i and is related to the lateral pressure in a continuous model. In bulk, u' becomes zero. The species-dependent term u_{Ai}^{int} has two contributions: the internal free energy for species A being in layer i subtracted by the corresponding quantity in bulk, and the mixing energy for species A being in layer i subtracted by the mixing energy for species A being in bulk. In both cases averages are taken over the relevant state distributions. At distances far away from the surface, P_{ABi} approaches P_{AB}^b, ϕ_{Ai} approaches ϕ_A^b, and hence u_{Ai}^{int} becomes zero.

The second aspect of the determination of the segment distribution is to take into account the chain connectivity. If only monomers are present, the volume fraction ϕ_{Ai} of monomer A in layer i is simply related to the bulk volume fraction ϕ_A^b according to

$$\phi_{Ai} = G_{Ai}\phi_A^b \tag{10}$$

where the weighting factor G_{Ai} for species A in layer i is given by

$$G_{Ai} = \exp(-\beta u_{Ai}) \tag{11}$$

since the species potentials were defined to be zero in bulk. The matter becomes more complex for polymers. Since the internal states do not introduce any further complications, the procedure given by Evers et al.[6] or the equivalent matrix method[4] generalized to copolymers can be applied. In the latter approach, the *segment* distribution expressed in terms of n_{xsi}, the number of sites in layer i occupied by segments of rank s belonging to component x, is given by

$$n_{xsi} = C_x\{\Delta_i^T\cdot[\prod_{s'=r_x}^{s+1}(\mathbf{W}^{t(x,s')})^T]\cdot\mathbf{s}\}\{\Delta_i^T[\prod_{s'=2}^{s}\mathbf{W}^{t(x,s')}]\cdot\mathbf{p}(x,1)\} \tag{12}$$

where C_x is a normalization factor (determined either by the number of molecules of type x or by the bulk volume fraction of component x, depending on external condition), $\mathbf{W}^{t(x,s)}$ a tridiagonal matrix containing elements which contain factors describing the lattice topology and weighting factors for segment of rank s belonging to component x, and $\mathbf{p}(x,1)$ a vector describing the distribution of the first segment of component x among the layers. From n_{xsi} the desired segment volume fractions are easily obtained. The *species* volume fraction ϕ_{Ai}, needed in eq 9, is given by

$$\phi_{Ai} = \frac{1}{L_i}\sum_x\sum_{s=1}^{r_x}\delta_{A,t(x,s)}n_{xsi} \tag{13}$$

where the Kronecker δ selects segments of rank s of component x only if it is of type A. Thus, given the species potentials u_{Ai}, the species volume profiles ϕ_{Ai} for polymers are obtained by eqs 11–13, and these equations together with eqs 7 and 9 form an implicit set of nonlinear equations for the segment distributions.

Free Energy of Interaction. In a number of applications, such as stabilization of colloidal solutions, it is of great importance to be able to model the forces among colloids with adsorbed polymers. From the lattice theory it is possible to obtain the free energy of interaction, and hence the force, between the two surfaces mediated by the intervening solution. The free energy of interaction $A^{int}(M)$ at a surface distance M is the difference between the excess surface free energy at a surface separation M and at an infinite separation according to

$$A^{int}(M) = A^\sigma(M) - A^\sigma(\infty) \tag{14}$$

If all components are in equilibrium with the bulk, the excess surface free energy $A^\sigma(M)$ is given by

$$\beta A^\sigma(M) = -\sum_x n_x - \sum_{i=1}^{M} L_i\alpha_i - \frac{1}{2}\sum_{i=1}^{M}\sum_A\sum_{A'}\sum_B\sum_{B'}n_{Ai}P_{ABi}\chi_{BB'}\langle P_{A'B'i}\phi_{A'i}\rangle \tag{15}$$

A comparison with the data of Evers et al. shows that only the last term is formally modified by the presence of internal degrees of freedom, but it should be kept in mind that the other two terms are affected indirectly.

IV. Adsorption of Pluronic

Ellipsometry measurements by Tiberg et al.[8] on an aqueous solution of Pluronic PE 6200, a PEO–PPO–PEO block copolymer, show that the polymer adsorbs sparsely to hydrophobic surfaces at low bulk concentration and at temperatures well below the cloud point. However, at increased bulk concentration or at increased temperature the adsorption becomes larger, and as the cloud point is approached, the adsorption increases without limit.

Pluronic PE 6200 is modeled as a linear triblock copolymer with 49 segments, of which 37 are assigned to PO and the others to EO equally distributed on each side of the PPO block. The EO segments are described with two states and we are using the same EO–EO, EO–water, and internal EO parameters as previously[4,14] (see Table I). In accord with section II, the PO segments are also

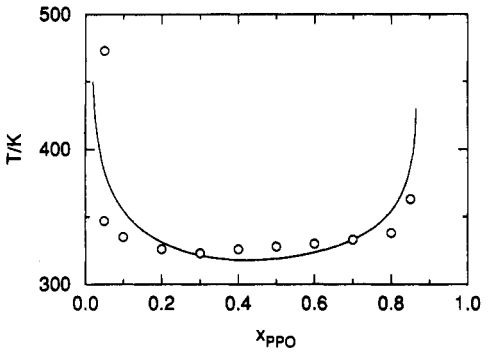

Figure 3. Phase diagram for the PPO–water system: experimental points from ref 9 for a molecular mass of 400 g mol^{-1} (open circles) and calculated phase boundary from eq A.7.12 by using hexagonal lattice, $r_{PPO} = 7$, and relevant parameters given in Table I (full line). The unit of the abscissa is weight and volume fraction, respectively.

Table I
Internal-State Parameters (U_{AB} and g_{AB}), Surface Interaction Parameters ($\chi_{B,surface}$), and Flory–Huggins Interaction Parameters ($\chi_{BB'}$) for the Heterogeneous Pluronic–Water System (Energy in kJ mol^{-1})

species	state	state no.	U_{AB}	g_{AB}	$kT\chi_{B,surface}$[a]
water		1	0	1	10.0
EO	polar	2	0[b]	1[b]	6.7
	nonpolar	3	5.086[b]	8[b]	3.5
PO	polar	4	0[c]	1[c]	6.7
	nonpolar	5	11.5[c]	60[c]	3.5

$kT\chi_{BB'}$

state no.	2	3	4	5
1	0.6508[b]	5.568[b]	1.7[c]	8.5[c]
2		1.266[b]	0[d]	1.3[e]
3			1.3[e]	0[d]
4				1.4[c]

[a] The values corresponds to adsorption parameters $kT\chi_{polar} = 0.825$ and $kT\chi_{nonpolar} = 1.625$ kJ mol^{-1} (see text for definition). [b] From ref 14. See also ref 4. [c] From fit to experimental data[9] of the PPO–water phase diagram (see text). [d] Taken to be equal. [e] Taken to be equal.

modeled by using two states. The corresponding parameters were obtained by fitting the calculated PPO–water phase diagram (using eq A.7.12) to the experimental one given by Malcolm and Rowlingson.[9] The resulting parameters are compiled in Table I and the phase diagrams are given in Figure 3. The model qualitatively predicts the lower consolute point, although the phase boundary is not sufficiently flat. A more accurate, and thus elaborated approach, where the unequal volumes of a water molecule and a PO segment are taken into account, is likely to improve this matter. However, this is beyond the scope of the present investigation and, furthermore, is not important for the understanding of the adsorption of Pluronic. In order to keep the description as simple as possible, the four EO–PO cross-interaction parameters are chosen as the average of the corresponding interaction parameters of EO and PO, respectively. The surface interaction parameters are selected to correspond to a hydrophobic surface, and again the polar and nonpolar segments of EO and PO are treated pairwise equally (cf. Table I). In a more refined approach, the larger hydrophobic character of PO, as compared to EO, should have been considered fully by using different polymer segment–polymer segment as well as polymer segment–surface interaction parameters. Such an approach improves the overall agreement with experimental data,[8] but at the present stage, sufficient experimental data for an unambiguous determination of separate parameters are still lacking.

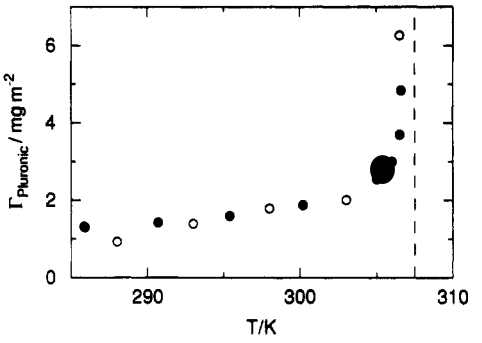

Figure 4. Amount of adsorbed Pluronic PE 6200 from an aqueous solution as a function of temperature: experimental ellipsometry results from ref 8 at a bulk weight fraction of 1×10^{-3} (open circles) and calculated results at a bulk volume fraction of 2×10^{-3} (filled circles). The dashed line denotes the cloud point of the experimental system. The calculated data have been rescaled; see text.

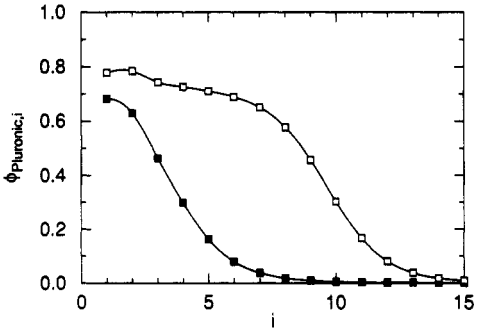

Figure 5. Calculated segment volume fraction profile of Pluronic PE 6200 at $T = 298$ K (filled symbols) and at $T = 319.5$ K (open symbols). The cloud point of the model is 319.6 K.

The amount adsorbed in the heterogeneous model system is obtained from a self-consistent solution of the species and state distributions (see Appendix B). Since the ellipsometry measurements give the adsorbed amount in excess of the bulk concentration, the excess adsorbed amount per surface site, $\Gamma_x \equiv \sum_i(\phi_{xi} - \phi_x^b)$, is used for the calculation.

Figure 4 shows the adsorption of Pluronic PE 6200 as a function of the temperature at a given bulk concentration. The calculated temperatures have been rescaled such that the experimental and theoretical cloud points are close. The motivation for the rescaling is that it is the temperature *deviation* from the cloud point, and not the absolute temperature itself, which governs the adsorption. (The rescaling is equivalent to a homogeneous scaling of all interaction parameters.) Moreover, the calculated excess amount has been transferred from excess number of segments per lattice site to weight per area by using the mean segment mass of 54.3 g mol^{-1} and a length of lattice site of 4 Å. It is clear from Figure 4 that the model reproduces the salient small increase of adsorbed amount at low temperature, the transition to larger adsorption some degrees below the cloud point, and the unlimited increase as the cloud point is approached.

Figure 5 displays the segment volume fraction profile at two temperatures. At the lower one, well below the cloud point, the adsorption is restricted to the first few layers. However, at the higher temperature, just below the cloud point, the region of high polymer concentration is extended further out, and the number of adsorbed segments per lattice site increases from $\Gamma_x = 2.4$ to $\Gamma_x = 6.7$.

From the reasonable lattice size used in Figure 4 and the results shown in Figure 5 it is clear that the adsorbed Pluronic molecules form a rather compact monolayer at the lower temperature. However, at higher temperature, close to the cloud point, an enhanced adsorption takes place in the form of multilayers, which could be viewed as the onset of the phase separation. This is further corroborated by the fact that the volume fraction of Pluronic in the first few layers at 319.5 K is ≈0.75, which is comparable to its volume fraction in the polymer-rich phase, 0.71, at the cloud point of 319.6 K, the latter obtained from a Pluronic PE 6200–water phase diagram (calculated from eq A.7.12, diagram not shown).

A more detailed examination of the Pluronic system is given by Tiberg et al.[8] Here we will conclude that the presented theory makes it possible to describe copolymers in a heterogeneous system where the polymer constituents display a reduced water solubility at elevated temperatures. The use of internal states enables a simple description of effective segment–segment interactions which are temperature and density dependent by employing a physically plausible model with a restricted number of parameters. Such or similar effective interactions are crucial for describing the adsorption occurring in systems, such as an aqueous Pluronic solution, close to their cloud points.

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Appendix A. Theory

In this appendix we derive the heterogeneous lattice theory for the case of internal degrees of freedom. In order to make the derivation coherent, some of the ideas and concepts of Evers et al. and of us are briefly restated. For a more detailed introduction of basic concepts, we refer to the original papers, in particular refs 1, 4, and 6.

A. Model. Consider the space between two impenetrable surfaces, either planar, cylindrical, or spherical. The layers parallel to, or concentric with, the surfaces are numbered from $i = 1$ to $i = M$, and the surface layers are labeled $i = 0$ and $i = M + 1$, respectively (see Figure 1). Within each of these layers, the Bragg–Williams approximation of random mixing is applied. Each of the layers contains L_i lattice sites, and in the case of curved surfaces, the number of sites depends on the layer number.[4] The number of nearest-neighbor sites, z, as well as the fraction of these sites in the same layer, λ_{ii}, and the fraction of these in adjacent layers $i' = i \pm 1$, $\lambda_{ii'}$, are dependent on the lattice topology.[1] In the case of a planar hexagonal lattice, $\lambda_{ii} = 0.5$. We will consider the case where each site is occupied by one segment. Since we require that segments in layer i have an equal number of nearest neighbors in layer i' as segments in layer i' have in layer i, the $\lambda_{ii'}$'s are subjected to the flux constraint

$$L_i\lambda_{ii'} = L_{i'}\lambda_{i'i} \qquad i, i' = 0, 1, ..., M + 1 \qquad \text{(A.1.1)}$$

The lattice between the surfaces is completely filled with n_x components (molecules of type x), each component consisting of r_x segments. The order number of a segment in a linearly connected chain is referred to as the rank of the segment and is labeled s. The segments of one component may all be of the same type or different types. The segment types, which will be referred to as species, are labeled A, A′, etc. Each species can attain one of several states labeled B, B′, etc. (see Figure 2). A species is associated with each surface and the component–surface interaction is described on an equal footing with the component–component interaction.

The species labeling is global; e.g., the summation over all species refers to all species of the system irrespective of the component(s) in which they occur. In contrast, the state labeling is local; e.g., the summation over all states refers to only those states associated with a species which is either given explicitly, as in Figure 2, or given by the context.

Since density gradients only exist perpendicular to the surfaces, average number and average volume fractions in each lattice layer are employed. The most important of those are as follows: n_{xi}, the number of sites in layer i occupied by segments belonging to component x; n_{Ai}, the number of sites in layer i occupied by segments of type A; and n_{Axi}, the number of sites in layer i occupied by segments of type A belonging to component x. The corresponding volume fractions, ϕ_{xi}, ϕ_{Ai}, and ϕ_{Axi}, are defined according to $\phi_{xi} \equiv n_{xi}/L_i$, etc. Obviously, the volume fractions for the surface species are fixed and equal to 1 for layers $i = 0$ and $M + 1$ and equal to 0 for the remaining layers (provided that the two surfaces are identical).

The concept of conformation and its degeneration plays an important role. A conformation c of component x is defined by an ordered set of layer numbers $k(x,s,c)$; $s = 1, r_x$, where $k(x,s,c)$ is the layer where the segment of rank s of component x in conformation c is located. The degeneration of a component x in conformation c, neglecting self-exclusion, becomes $\omega_{xc}z^{r(x)-1}$ where

$$\omega_{xc} = L_{k(x,c,1)}\prod_{s=2}^{r_x}\lambda_{k(x,c,s-1),k(x,c,s)} \qquad \text{(A.1.2)}$$

$L_{k(x,c,1)}$ gives the number of possibilities of placing the first segment, and the product of λ elements is the probability of placing the remaining $s - 1$ segments according to conformation c.

B. Partition Function. The grand canonical partition function of the system is given by

$$\Xi(\{\mu_x\},\{L_i\},T) = \sum_{\forall\{n_{xc}\}}\sum_{\forall\{P_{ABi}\}} Q(\{n_{xc}\},\{P_{ABi}\},\{L_i\},T) \times \exp[\beta\sum_x n_x\mu_x] \qquad \text{(A.2.1)}$$

where n_{xc} is the number of components x in conformation c, $\{n_{xc}\}$ a set of n_{xc} which completely fills the space between the surfaces, P_{ABi} the fraction of species A in layer i which is in state B, $\{P_{ABi}\}$ a set of P_{ABi} such that the sum over states amounts to 1 for each species in each layer, Q the canonical partition function, μ_x the chemical potential of component x, and $\beta \equiv (kT)^{-1}$, where k is the Boltzmann constant and T the absolute temperature.

It will be convenient to deal with the free energy contributions from the configurational and internal degrees of freedom separately, and hence we factorized the canonical partition function according to

$$Q(\{n_{xc}\},\{P_{ABi}\},\{L_i\},T) = Q_{int}(\{n_{xc}\},\{P_{ABi}\},\{L_i\},T)Q_{conf}(\{n_{xc}\},\{P_{ABi}\},\{L_i\},T) \qquad \text{(A.2.2)}$$

where Q_{int} is the partition function of the internal degrees of freedom, which becomes unity in the case of no internal degrees of freedom, and Q_{conf} the configurational partition function. In eq A.2.2 it is explicitly shown that Q_{int} (and

the internal free energy) may depend on the conformation distribution and Q_{conf} (and the configurational free energy) on the state distribution. This will be the case for our model, and in fact, it constitutes the coupling between the configurational and the internal degrees of freedom. Furthermore, the configurational partition function is traditionally separated into two factors[1,6] according to

$$Q_{conf}(\{n_{xc}\},\{P_{ABi}\},\{L_i\},T) = \Omega(\{n_{xc}\},\{L_i\}) \times \exp[-\beta U(\{n_{xc}\},\{P_{ABi}\},\{L_i\})] \quad (A.2.3)$$

where Ω is the configurational degeneration, which will be modeled as being independent of the internal states, and U the configurational interaction energy, which will depend upon the state distribution.

Thermodynamic quantities of the heterogeneous system have to be given with respect to some reference state. As in the Flory–Huggins theory,[22] we select the components in separated and pure amorphous systems as the reference state, but complement it with the condition of fixed but otherwise arbitrary state distributions of the separated components. (Note the different meaning of internal state and reference state.) By similar factorization, the canonical partition function of component x in the pure amorphous system is given by

$$Q^*_x = Q^*_{x,int}\Omega^*_x \exp[-\beta U^*_x] \quad (A.2.4)$$

Since the components are separated in the reference state, the corresponding quantities of the reference state are given by $Q^* = \Pi_x Q^*_x$, $Q^*_{int} = \Pi_x Q^*_{int,x}$, $\Omega^* = \Pi_x \Omega^*_x$, and $U^* = \sum_x U^*_x$, which together with eqs A.2.2–A.2.4 results in

$$Q = Q^* \frac{Q_{int}}{Q^*_{int}} \frac{\Omega}{\Omega^*} \exp[-\beta(U - U^*)] \quad (A.2.5)$$

C. Internal Degrees of Freedom. Each state of each species is characterized by terms contributing to the internal free energy and by interaction parameters describing the nearest-neighbor interaction with species in different states. The internal free energy of state B of species A, μ_{AB}, is modeled as

$$\beta\mu_{AB} = \beta U_{AB} - \ln g_{AB} \quad (A.3.1)$$

where U_{AB} is the internal energy and g_{AB} the degeneration factor of state B of species A, thus being conformational independent. For each species, only the differences between μ_{AB} are relevant for the state equilibrium. Thus, U_{AB} contains an arbitrary energy scaling term and g_{AB} an arbitrary degeneration factor, both of which are the same for all states of a given species but may differ among the species. An additional contribution to the internal free energy of a species arises from the different ordering (mixing) of the states of a species in a given layer. The contribution to the state mixing entropy from state B of species A in layer i amounts to

$$S_{mix,ABi}/k = -P_{ABi} \ln P_{ABi} \quad (A.3.2)$$

The internal free energy of a segment of type A is obtained by adding the contributions given by eqs A.3.1 and A.3.2 according to

$$\beta A_{int,Ai} = \sum_B (P_{ABi}\beta\mu_{AB} - S_{mix,ABi}/k) = \sum_B P_{ABi}\left[\beta U_{AB} + \ln \frac{P_{ABi}}{g_{AB}}\right] \quad (A.3.3)$$

The total internal free energy of the system is found by weighting $A_{int,Ai}$ with the number of species A in layer i and summing over species as well as over layers, which gives

$$\beta A_{int} = \sum_{i=1}^{M}\sum_A n_{Ai}\sum_B P_{ABi}\left[\beta U_{AB} + \ln \frac{P_{ABi}}{g_{AB}}\right] \quad (A.3.4)$$

For the reference state of separated pure amorphous systems we have

$$\beta A^*_{int} = \sum_x\sum_A n_x r_{Ax}\sum_B P^*_{AB}\left[\beta U_{AB} + \ln \frac{P^*_{AB}}{g_{AB}}\right] \quad (A.3.5)$$

where r_{Ax} denotes the number of segments of type A in component x. Moreover, we have to specify the state distribution of the reference state; however, the choice is arbitrary for the physical properties of the heterogeneous system of our interest. An obvious alternative is $P^*_{AB} = 0$ for all B except B = B′ where $P^*_{AB'} = 1$, for all species, which gives

$$\beta A^*_{int} = \sum_x\sum_A n_x r_{Ax}[\beta U_{AB'} - \ln g_{AB'}] \quad (A.3.6)$$

If we select the energy scale such that $U_{AB'} = 0$ and the degeneration scale such that $g_{AB'} = 1$ for each species

$$\beta A^*_{int} = 0 \quad (A.3.7)$$

is obtained. Thus, the reference state can always be selected such that the internal free energy of it is zero.

Finally, the partition function of the internal degrees of freedom is, as usual, related to the free energy according to

$$Q_{int} = \exp[-\beta A_{int}] \quad (A.3.8)$$

and a similar relation holds for the reference state.

D. Configurational Degeneration. According to the Flory–Huggins theory,[22,23] the entropy due to mixing of the components is simply the conformational degeneration, i.e., the number of distinguishable ways of realizing the mixing. Within the mean-field approximation, the number of ways of placing the first chain of component x in conformation c is

$$\omega(1) = \omega_{xc} z^{r_x - 1}\prod_{s=1}^{r_x}\frac{[L_{k(x,c,s)} - \nu_{k(x,c,s)}]}{L_{k(x,c,s)}} = \omega_{xc} z^{r_x-1}\prod_{i=1}^{M}\prod_{\nu_i=0}^{r_{xci}-1}\frac{[L_i - \nu_i]}{L_i} \quad (A.4.1)$$

where ω_{xc} is the degeneration in the absence of self-exclusion given by eq A.1.2. and ν_i the number of previously placed segments in layer i. The number of ways of placing n_{xc} chains of component x in configuration c becomes $\omega(n_{xc}) = \omega(1)^{n_{xc}}$, where ν_i runs from 0 to $n_{xc}r_{xci} - 1$, and moreover, the number of distinguishable ways of placing n_x chains of component x is $\omega(n_x) = \Pi_c \omega(n_{xc})/n_{xc}!$, where ν_i runs to $n_x r_{xi} - 1$. Finally, the number of distinguishable ways of placing n chains becomes $\omega(n) = \Pi_x \omega(n_x)$, where ν_i runs to $L_i - 1$. Since $\Omega = \omega(n)$, the degeneration of a multicomponent system in a curved lattice becomes

$$\Omega = \left[\prod_x z^{n_x(r_x-1)}\prod_c \frac{\omega_{xc}^{n_{xc}}}{n_{xc}!}\right]\left[\prod_{i=1}^{M}\frac{L_i!}{L_i^{L_i}}\right] \quad (A.4.2)$$

The degeneration of the amorphous reference state follows from the use of conversions $\omega_{xc} \to L_x$ (L_x is the number of lattice sites of the pure amorphous system of component x, $L_x = n_x r_x$), $L_i \to L_x$, and $n_{xc} \to n_x$ in eq A.4.2, which

results in

$$\Omega^* = \prod_x \frac{(n_x r_x)!}{n_x!}\left[\frac{z}{n_x r_x}\right]^{n_x(r_x-1)} \qquad (A.4.3)$$

as also given by Flory.[22]

The configurational contribution to the mixing entropy is obtained by combining eqs A.4.2 and A.4.3, and by employing Stirling's approximation, it simply becomes

$$\ln\frac{\Omega}{\Omega^*} = -\sum_x\sum_c n_{xc}\ln\frac{n_{xc}r_x}{\omega_{xc}} \qquad (A.4.4)$$

If $r_x = 1$ for all x, i.e., all components consist of only one segment, the conversions $c \rightarrow i$ and $\omega_{xc} \rightarrow L_i$ lead to $\ln(\Omega/\Omega^*) = \sum_x\sum_{i=1}^{M} n_{xi}\ln\phi_{xi}$, and in the case of a homogeneous solution, where i becomes redundant, we retrieve $\ln(\Omega/\Omega^*) = \sum_x n_x \ln\phi_x$, as expected.

E. Interaction Energy. Within the mean-field approximation the interaction energy is given by

$$\beta U = \frac{1}{2}\sum_{i=0}^{M+1} L_i \sum_A^s\sum_{A'}^s\sum_B\sum_{B'}\phi_{Ai}P_{ABi}\chi_{BB'}\langle P_{A'B'i}\phi_{A'i}\rangle \qquad (A.5.1)$$

where $\langle x_i\rangle \equiv \sum_{i'=0}^{M+1}\lambda_{ii'}x_{i'}$. In our case of only nearest-neighbor interactions, the sum over i' in the definition of $\langle x_i\rangle$ contains at most three terms. The notation $\sum^s$ implies that the sum includes the surface species as well. In eq A.5.1, $\chi_{BB'}$ denotes the Flory–Huggins interaction parameter traditionally defined as $\chi_{BB'} = \beta z[\epsilon_{BB'} - (\epsilon_{BB} + \epsilon_{B'B'})/2]$ where $\epsilon_{BB'}$ is the interaction energy on a site volume basis between species A in state B and species A′ in state B′. In expressions like eq A.5.1, the state summation variable B is always associated with the species summation variable A, B′ and A′, etc.

The interaction energy for the reference state is obtained by summing over the contributions from the pure amorphous systems according to

$$\beta U^* = \sum_x \beta U^*_x = \frac{1}{2}\sum_x n_x r_x \sum_A\sum_{A'}\sum_B\sum_{B'}\phi^*_{Ax}P^*_{AB}\chi_{BB'}P^*_{A'B'}\phi^*_{A'x} \qquad (A.5.2)$$

where $n_x r_x$ denotes the number of lattice sites of component x and ϕ^*_{Ax} the volume fraction of species A in the pure reference solution of component x, or equivalently, the fraction of segments of type A in component x.

In the absence of internal degrees of freedom, eq A.5.1 reduces to

$$\beta U = \frac{1}{2}\sum_{i=0}^{M+1} L_i \sum_A^s\sum_{A'}^s \phi_{Ai}\chi_{AA'}\langle\phi_{A'i}\rangle \qquad (A.5.3)$$

which applied to planar geometry ($L_i \rightarrow L$) is in agreement with eq 34 of ref 6. Since the state labeling becomes redundant in the case of no internal degrees of freedom (only one state per species), the notation $X_{AA'}$ may be used instead of $\chi_{BB'}$ and the sum over states may be dropped, as in eq A.5.3.

F. Equilibrium Distribution. If the system is not too close to a phase transition, the properties of the system are accurately described by the sets $\{n_{xc}\}$ and $\{P_{ABi}\}$ which give the largest term of the double sum in eq A.2.1 and fulfill the constrains

$$\sum_x\sum_c n_{xc}r_{xci} = L_i \quad \forall i \qquad (A.6.1)$$

$$\sum_B P_{ABi} = 1 \quad \forall A \text{ and } \forall i \qquad (A.6.2)$$

where r_{xci} is the number of segments in component x in conformation c which are in layer i. The sets giving the maximal term will be denoted as the equilibrium distributions and they are conveniently obtained by forming the function

$$f = \ln\Xi + \sum_{i=1}^{M}\alpha_i\Big(L_i - \sum_x\sum_c n_{xc}r_{xci}\Big) + \sum_A\sum_{i=1}^{M}\gamma_{Ai}\Big(1 - \sum_B P_{ABi}\Big) \qquad (A.6.3)$$

where the Lagrangian multipliers α_i and γ_{Ai} have been introduced to release the constraints in $\{n_{xc}\}$ and $\{P_{ABi}\}$. The extreme value (maximum) of f is given by

$$0 = \frac{\partial f}{\partial n_{x'c'}} \quad \forall n_{x'c'} \in \{n_{xc}\} \qquad (A.6.4)$$

$$0 = \frac{\partial f}{\partial P_{A'B'i'}} \quad \forall P_{A'B'i'} \in \{P_{ABi}\} \qquad (A.6.5)$$

where the primes denote the members of the sets which belong to the equilibrium distributions. With the use of eqs A.2.1 and A.6.3, eqs A.6.4 and A.6.5 are transformed to

$$0 = \frac{\partial \ln Q}{\partial n_{x'c'}} + \beta\mu_{x'} - \sum_{i=1}^{M}\alpha_i r_{x'c'i} \qquad (A.6.6)$$

$$0 = \frac{\partial \ln Q}{\partial P_{A'B'i'}} - \gamma_{A'i'} \qquad (A.6.7)$$

where $n_x = \sum_c n_{xc}$ have been used. In order to determine $\{n_{xc}\}$ and $\{P_{ABi}\}$, $\ln Q$ has to be expanded. Substitution of eqs A.3.8, A.3.4, A.4.4, and A.5.1 in eq A.2.5 gives the useful expansion

$$\ln Q = \ln Q^* - \left\{\sum_{i=1}^{M}\sum_A n_{Ai}\sum_B P_{ABi}\left[\beta U_{AB} + \ln\frac{P_{ABi}}{g_{AB}}\right] - \beta A^*_{int}\right\} - \sum_x\sum_c n_{xc}\ln\frac{n_{xc}r_x}{\omega_{xc}} - \left\{\frac{1}{2}\sum_{i=0}^{M+1}\sum_A^s\sum_{A'}^s\sum_B\sum_{B'}n_{Ai}P_{ABi}\chi_{BB'}\langle P_{A'B'i}\phi_{A'i}\rangle - \beta U^*\right\} \qquad (A.6.8)$$

From the condition expressed in eq A.6.7 and the expansion of $\ln Q$, the equilibrium distribution $\{P_{ABi}\}$ can be determined. A direct substitution of eq A.6.8 in eq A.6.7, and use of the fact that the state distribution of the amorphous reference state is fixed, give an equation from which $\gamma_{A'i'}$ can be eliminated by employing the constraint

given by eq A.6.2. The result is the implicit equation

$$P_{ABi} = \frac{X_{AB}}{\sum_B X_{AB}}$$

$$X_{AB} \equiv g_{AB} \exp[-\beta U_{AB} - \sum_{A'}^{s}\sum_{B'} \chi_{BB'} \langle P_{A'B'i}\phi_{A'i}\rangle] \quad \text{(A.6.9)}$$

where the prime notation for equilibrium distributions has been dropped.

Now we turn to $\{n_{xc}\}$. Substitution of eq A.6.8 in the condition for $\{n_{xc}\}$ given by eq A.6.6, and the use of the definition $(\partial \ln Q^*)/(\partial n_{xc}) \equiv -\beta\mu^*_x$ as well as the identity $n_{Ai} = \sum_x \sum_c n_{xc} r_{Axci}$, where r_{Axci} is the number of species of type A in component x in conformation c which are in layer i, give

$$0 = -\beta\mu^*_x - \left\{\sum_{i=1}^{M}\sum_A r_{Axci}\sum_B P_{ABi}\left[\beta U_{AB} + \ln\frac{P_{ABi}}{g_{AB}}\right] - \frac{\partial(\beta A^*_{int})}{\partial n_x}\right\} - \ln\frac{n_{xc}r_x}{\omega_{xc}} - 1 - \left\{\sum_{i=1}^{M}\sum_A^s\sum_{A'}^s\sum_B\sum_{B'} r_{Axci}P_{ABi}\chi_{BB'}\langle P_{A'B'i}\phi_{A'i}\rangle - \frac{\partial(\beta U^*)}{\partial n_x}\right\} + \beta\mu_x - \sum_{i=1}^{M}\alpha_i r_{xci} \quad \text{(A.6.10)}$$

Component-dependent, but conformational-independent, quantities in eq A.6.10 are brought together and define the component-dependent constant C_x according to

$$\ln C_x \equiv \beta(\mu_x - \mu^*_x) - \ln r_x - 1 + \frac{\partial(\beta A^*_{int})}{\partial n_x} + \frac{\partial(\beta U^*)}{\partial n_x} + \sum_A \beta r_{Ax} u_A^{ref} \quad \text{(A.6.11)}$$

where u_A^{ref} has been introduced for latter use. As in the formulation by Evers et al.,[6] we define a species potential u_{Ai}, here extended by contributions from the internal degrees of freedom, according to

$$\beta u_{Ai} \equiv \alpha_i + \sum_B\left\{P_{ABi}\left[\beta U_{AB} + \ln\frac{P_{ABi}}{g_{AB}}\right] + \sum_{A'}^{s}\sum_{B'} P_{ABi}\chi_{BB'}\langle P_{A'B'i}\phi_{A'i}\rangle\right\} + \beta u_A^{ref} \quad \text{(A.6.12)}$$

and a species weighting factor G_{Ai} by

$$G_{Ai} \equiv \exp[-\beta u_{Ai}] \quad \text{(A.6.13)}$$

From eqs A.6.10–A.6.13 the probability of finding component x in conformation c is compactly expressed as

$$P_{xc} \equiv \frac{n_{xc}}{n_x} = \frac{C_x}{n_x}\omega_{xc}\prod_{i=1}^{M}\prod_A (G_{Ai})^{r_{Axci}} \quad \text{(A.6.14)}$$

which, thus, specifies the equilibrium distribution of $\{n_{xc}\}$, although also in an implicit form. (The species weighting factors and the species potentials are functions of the volume fractions, which depend on the conformation distribution.) In the case of no internal degrees of freedom, eq A.6.14 remains formally unchanged, but the expressions of the species potential as well as of the constants C_x become simplified and are in agreement with those given by Evers et al. (eq 39 substituted into eq 16 and eq 19 of ref 6).

G. Segment Distribution. The segment distribution will be derived from $\{n_{xc}\}$, but the functional relation becomes more complex than that for the state distribution due to the connectivity of the chains. In eq A.6.14 each segment in the chain contributes with one species weighting factor to the probability of the conformation. The change of the product indexes i and A to s gives

$$P_{xc} = \frac{C_x}{n_x}\omega_{xc}\prod_{s=1}^{r_x} G_{t(x,s),k(x,c,s)} = \frac{C_x}{n_x}[L_{k(x,c,1)}G_{t(x,1),k(x,c,1)}]\left[\prod_{s=2}^{r_x} G_{t(x,s),k(x,c,s)}\lambda_{k(x,c,s-1),k(x,c,s)}\right] \quad \text{(A.7.1)}$$

where $t(x,s)$ denotes the type of segment s of component x and the second equality is obtained by employing eq A.1.2. The form of eq A.7.1 suggests that the probability of the conformations could be calculated with a matrix scheme. Accordingly, the transition matrix $\mathbf{W}^A$ is defined as

$$\mathbf{W}^A \equiv \mathbf{G}^A(\lambda)^T \quad \text{(A.7.2)}$$

where $\mathbf{G}^A$ is a diagonal matrix with the elements $(\mathbf{G}^A)_{ii} \equiv G_{Ai}$ and λ a tridiagonal matrix with $(\lambda)_{ij} \equiv \lambda_{ij}$. Moreover, let the vector $\mathbf{p}(x,s)$, with the elements $[\mathbf{p}(x,s)]_i$, be the number distribution among the layers of segments of rank s belonging to component x, and at this stage the influence of segments beyond rank s on the distribution is not included. Then, the relation between the distribution of the first segments in molecules of type x, $\mathbf{p}(x,1)$, and the distribution of segments of rank s, $\mathbf{p}(x,s)$, becomes

$$\mathbf{p}(x,s) = \left[\prod_{s'=2}^{s}\mathbf{W}^{t(x,s')}\right]\cdot\mathbf{p}(x,1) \quad \text{(A.7.3)}$$

where $\prod_{j=1}^{n}\mathbf{W}^j \equiv \mathbf{W}^n \ldots \mathbf{W}^1$; the order is relevant since $\mathbf{W}^A$ does not generally commute under multiplication. By employing the identification $L_{k(x,c,1)}G_{t(x,1),k(x,c,1)} = \mathbf{p}_{k(x,c,1)}(x,1)$ as the start distribution and $G_{t(x,s),k(x,c,s)}\lambda_{k(x,c,s-1),k(x,c,s)} = (\mathbf{W}^{t(x,c)})_{k(x,c,s-1),k(x,c,s)}$ as the transition matrix, eq A.7.1 can be rewritten as

$$P_{xc} = \frac{C_x}{n_x}\left[\prod_{s=2}^{r_x}(\mathbf{W}^{t(x,s)})_{k(x,c,s),k(x,c,s-1)}\right]\mathbf{p}_{k(x,c,1)}(x,1) \quad \text{(A.7.4)}$$

By summing over all conformations, which implies a sum over the layer indexes, the first bracket becomes a product of $\mathbf{W}$ matrices premultiplied by $\mathbf{s}^T \equiv (1, 1, \ldots, 1)$ and postmultiplied by $\mathbf{p}(x,1)$, which arose from the last factor of eq A.7.4. Since the probabilities of the left-hand side sum up to 1, we obtain

$$\frac{C_x}{n_x} = \frac{1}{\mathbf{s}^T\cdot\mathbf{p}(x,r_x)} \quad \text{(A.7.5)}$$

after having used eq A.7.3.

The segment distribution may now be obtained by a procedure originally devised by Rubin and DiMarzio[24] and later extended by us. A generalization of eq 41 of ref 4 to

a multicomponent system gives the number of segments of rank s of component x in layer i, n_{xsi}, according to

$$n_{xsi} = C_x\{\Delta_i^T\cdot[\prod_{s'=r_x}^{s+1}(\mathbf{W}^{t(x,s')})^T]\cdot\mathbf{s}\}\{\Delta_i^T\cdot[\prod_{s'=2}^{s}\mathbf{W}^{t(x,s')}]\cdot\mathbf{p}(x,1)\} \quad (A.7.6)$$

where Δ_i denotes a column vector with components δ_{ij} ($j = 1, ..., M$), and the product index s' in the first bracket runs in the negative direction. From eq A.7.6, the number of species A of component x in layer i, the number of segments of component x in layer i, and the number of species A in layer i are obtained according to

$$n_{Axi} = \sum_{s=1}^{r_x}\delta_{A,t(x,s)}n_{xsi} \quad (A.7.7)$$

$$n_{xi} = \sum_{A} n_{Axi} \quad (A.7.8)$$

$$n_{Ai} = \sum_{x} n_{Axi} = \sum_{x}\sum_{s=1}^{r_x}\delta_{A,t(x,s)}n_{xsi} \quad (A.7.9)$$

Equations A.7.6–A.7.9 show that the amount of component x is proportional to C_x. In the case of the canonical ensemble (fixed amount), C_x is given by eq A.7.5, i.e.

$$C_x = n_x[\mathbf{s}^T\cdot\mathbf{p}(x,r_x)]^{-1} \quad (A.7.10)$$

where n_x is the (desired) number of particles of type x and $[\mathbf{s}^T\cdot\mathbf{p}(x,r_x)]$ the number of "surviving" chains after $r_x - 1$ steps given by eq A.7.3. In the case of the grand canonical ensemble (fixed chemical potential), we consider a homogeneous bulk solution which is in equilibrium with the heterogeneous system. Following Evers et al.,[6] a reference potential u_A^{ref} is selected such that the species potential u_A becomes zero in the bulk. By applying eq A.7.8 to the bulk solution, the normalization constant becomes

$$C_x = \phi_x^b/r_x \quad (A.7.11)$$

where ϕ_x^b is the volume fraction of component x in bulk. In order to determine u_A^{ref} such that $u_A = 0$ in bulk, an expression of the chemical potential of component x in the homogeneous bulk relative to the pure amorphous state, $\mu_x - \mu^*_x$, is needed. Extending the procedure of Evers et al.[6] to the case of internal degrees of freedom, we arrive after some manipulations at

$$\beta(\mu_x - \mu^*_x) = r_x\sum_A\sum_B\phi^*_{Ax}\left\{P^b_{AB}\left[\beta U_{AB} + \ln\frac{P^b_{AB}}{g_{AB}}\right] - P^*_{AB}\left[\beta U_{AB} + \ln\frac{P^*_{AB}}{g_{AB}}\right]\right\} + \ln\phi_x^b + 1 - r_x\sum_{x'}\frac{\phi^b_{x'}}{r_{x'}} - \frac{r_x}{2}\sum_A\sum_{A'}\sum_B\sum_{B'}[(\phi^b_A - \phi^*_{Ax})P^b_{AB}\chi_{BB'}P^b_{A'B'}(\phi^b_{A'} - \phi^*_{A'x}) + \phi^*_{Ax}\phi^*_{A'x}\chi_{BB'}(P^*_{AB}P^*_{A'B'} - P^b_{AB}P^b_{A'B'})] \quad (A.7.12)$$

where ϕ^b_A denotes the volume fraction of species A in bulk. The fraction of species A which is in state B in the bulk, P^b_{AB}, is given by

$$P^b_{AB} = \frac{X^b_{AB}}{\sum_B X^b_{AB}}$$

$$X^b_{AB} \equiv g_{AB}\exp[-\beta U_{AB} - \sum_{A'}\sum_{B'}\chi_{BB'}P^b_{A'B'}\phi^b_{A'}] \quad (A.7.13)$$

The reference potential is found from substitutions of eqs A.3.7, A.5.2, A.7.11, and A.7.12 into eq A.6.11 and it becomes

$$\beta u_A^{ref} = \sum_x\frac{\phi^b_x}{r_x} - \sum_B P^b_{AB}\left[\beta U_{AB} + \ln\frac{P^b_{AB}}{g_{AB}}\right] + \frac{1}{2}\sum_{A'}\sum_{A''}\sum_{B'}\sum_{B''}\phi^b_{A'}P^b_{A'B'}\chi_{B'B''}P^b_{A''B''}\phi^b_{A''} - \sum_{A'}\sum_B\sum_{B'}P^b_{AB}\chi_{BB'}P^b_{A'B'}\phi^b_{A'} \quad (A.7.14)$$

which also reduces to the expression given by Evers et al.[6] in the case of no internal degrees of freedom (eq 44 of ref 6). The final expression of the species potential is now obtained by substituting the reference potential into eq A.6.12. By noticing that u_{Ai} may be separated into a species-independent part u'_i and a species-dependent part u^{int}_{Ai}, we at last obtain

$$u_{Ai} = u'_i + u^{int}_{Ai} \quad (A.7.15)$$

where

$$\beta u'_i \equiv \alpha_i + \sum_x\frac{\phi^b_x}{r_x} + \frac{1}{2}\sum_{A'}\sum_{A''}\sum_{B'}\sum_{B''}\phi^b_{A'}P^b_{A'B'}\chi_{B'B''}P^b_{A''B''}\phi^b_{A''}$$

$$\beta u^{int}_{Ai} \equiv \sum_B\left[P_{ABi}\left(\beta U_{AB} + \ln\frac{P_{ABi}}{g_{AB}}\right) - P^b_{AB}\left(\beta U_{AB} + \ln\frac{P^b_{AB}}{g_{AB}}\right)\right] + \sum_{A'}^{s}\sum_B\sum_{B'}\chi_{BB'}(P_{ABi}\langle P_{A'B'i}\phi_{A'i}\rangle - P^b_{AB}P^b_{A'B'}\phi^b_{A'}) \quad (A.7.16)$$

H. Free Energy and Surface Forces. The free energy of the heterogeneous system with respect to the amorphous reference state is

$$\beta(A - A^*) \equiv -\ln\frac{Q}{Q^*} = \beta(A_{int} - A^*_{int}) - \ln\frac{\Omega}{\Omega^*} + \beta(U - U^*) \quad (A.8.1)$$

where eqs A.2.5 and A.3.8 have been used. The contribution from the mixing entropy given by eq A.4.4 can be further modified by employing the conformational equilibrium distribution described by eq A.6.14, and with the help of eq A.6.13 and the identity $n_{Ai} = \sum_x\sum_c n_{xc}r_{Axci}$, we arrive at

$$\ln\frac{\Omega}{\Omega^*} = -\sum_x n_x\ln C_x r_x + \sum_{i=1}^{M}\sum_A n_{Ai}\beta u_{Ai} \quad (A.8.2)$$

Substitution of eq A.8.2 and the expressions of A_{int}, A^*_{int}, U, and U^* given by eqs A.3.4, A.3.5, A.5.1, and A.5.2, respectively, into eq A.8.1 gives the free energy $A - A^*$ in terms of C_x and u_{Ai} as well as in volume fractions. Further substitution of C_x defined by eq A.6.11 and u_{Ai} defined by eq A.6.12 results in the following expression of the free

energy:

$$\beta(A - A^*) = -\sum_x n_x + \sum_x n_x\beta(\mu_x - \mu^*_x) - \sum_{i=1}^{M} L_i\alpha_i - \frac{1}{2}\sum_{i=1}^{M}\sum_{A}\sum_{A'}\sum_{B}\sum_{B'} n_{Ai}P_{ABi}\chi_{BB'}\langle P_{A'B'i}\phi_{A'i}\rangle \quad (A.8.3)$$

The excess surface free energy of the system is given by

$$A^\sigma = (A - A^*) - \sum_x n_x(\mu_x - \mu^*_x) \quad (A.8.4)$$

where the sum extends only over components of the system which are in equilibrium with the bulk solution. Finally, the free energy of interaction between the two surfaces at separation M, with respect to infinite separation, is given by $A^\sigma(M) - A^\sigma(\infty)$.

Appendix B. Numerical Aspects

The numerical solution comprises a self-consistent determination of the species distribution $\{n_{Ai}\}$ as well as of the state distribution $\{P_{ABi}\}$. Given a fixed state distribution, the species distribution is determined by $\phi_{Ai} = n_{Ai}/L_i$, eqs A.6.12, A.6.13, A.7.2, A.7.6, A.7.7, and A.7.9, whereas the state distribution is given by eq A.6.9 for a constant species distribution. There are two strategies for solving the interdependent distributions: simultaneously or alternately in an iterative process. Since the latter approach generally requires less storage, it is normally preferred.

Evers et al. have described an elegant procedure for determining the species distribution which avoids the difficulties of handling the packing constraints.[6] They introduced a set of unconstrained variables x_{Ai} according to

$$x_{Ai} \equiv -\beta(u_{Ai} - \bar{u}) + \frac{1}{Mn_A}\sum_x \ln\,[\mathbf{s}^T\cdot\mathbf{p}(x,r_x)] \quad (B.1)$$

where the average segment potential is defined by $\bar{u} \equiv (1/Mn_A)\sum_{i=1}^{M}\sum_A u_{Ai}$ and n_A denotes the number of species in the system. Through a number of steps the Langrange multipliers α_i (which also depend on the species until convergence is achieved and thus are labeled α_{Ai}) can be calculated from eq A.6.12 for a given set of x_{Ai}. Hence, at convergence

$$\sum_A \phi_{Ai} = 1 \quad \forall\, i \qquad \alpha_{Ai} = \alpha_i \quad \forall\, A \quad (B.2)$$

where $\alpha_i = (1/n_A)\sum_A \alpha_{Ai}$ should be fulfilled. The variation of $\{x_{Ai}\}$, such that eq B.2 is satisfied, is efficiently performed by a Newton–Raphson procedure, where the solution of the nonlinear set of equations $f_{Ai}(\{x_{Ai}\}) = 0$ is sought, where

$$f_{Ai} = \alpha_{Ai} - \alpha_i \quad A = 1, 2, ..., n_A - 1, \forall\, i$$
$$\sum_{A'}\phi_{A'i} - 1 \quad A = n_A, \forall\, i \quad (B.3)$$

Appendix C. Important Symbols

Variables

A	total free energy, eq A.8.3
A^σ	excess surface free energy, eq A.8.4
A_{int}	total internal free energy
C_x	component-dependent constant, eq A.6.11
G_{Ai}	species weighting factor, eq A.6.13
$\mathbf{G}^A$	diagonal matrix containing G_{Ai}
g_{AB}	degeneration of state B of species A
k	Boltzmann constant
$k(x,c,s)$	layer where the segment of rank s of component x in conformation c is located
L_i	number of sites in layer i
L_x	number of segments of all molecules of type x
n_x	number of component x
n_{xc}	number of component x in conformation c
n_{xi}	number of sites in layer i occupied by segments belonging to component x
n_{Ai}	number of sites in layer i occupied by segments of type A
n_{Axi}	number of sites in layer i occupied by segments of type A belonging to component x
n_{xsi}	number of sites in layer i occupied by segments of rank s belonging to component x
P_{ABi}	fraction of species A in layer i which are in state B
P^b_{AB}	fraction of species A which are in state B in bulk
P^*_{AB}	fraction of species A which are in state B in reference state
P_{xc}	probability of conformation c for component x, eq A.6.14
$\mathbf{p}(x,s)$	number distribution of segments of rank s belonging to component x
Q	canonical partition function
Q_{conf}	configurational canonical partition function
Q_{int}	partition function of the internal degrees of freedom
r_x	number of segments in component x
r_{Ax}	number of segments of type A in component x
r_{xci}	number of segments in component x in conformation c which are in layer i
r_{Axci}	number of segments of type A in component x in conformation c which are in layer i
$\mathbf{s}$	column vector with unit elements
T	absolute temperature
$t(x,s)$	species type of segment of rank s belonging to component x
U	total interaction energy
U_{AB}	internal energy of state B of species A
u^{ref}_A	reference potential of species A, eq A.7.14
u_{Ai}	species potential, eq A.6.12
$\mathbf{W}^A$	transition matrix, eq A.7.2
z	coordination number of the lattice
α_i	Lagrangian multiplier related to volume constrains
γ_{Ai}	Lagrangian multiplier related to the internal states
Δ_i	column vector with components δ_{ij} for all j
$\lambda_{ii'}$	fraction of nearest-neighbor sites in layer i' viewed from a site in layer i
μ_{AB}	internal free energy of state B of species A
μ_x	chemical potential of component x
Ξ	grand canonical partition function
ϕ_{xi}	fraction of sites in layer i occupied by segments belonging to component x
ϕ_{Ai}	fraction of sites in layer i occupied by segments of type A
ϕ_{Axi}	fraction of sites in layer i occupied by segments of type A belonging to component x

ϕ_x^b	fraction of sites occupied by segments belonging to component x in bulk
ϕ_A^b	fraction of sites occupied by species A in bulk
ϕ^*_{Ax}	fraction of sites occupied by species A belonging to component x in pure amorphous x
$\chi_{BB'}$	Flory–Huggins interaction parameter between species A in state B and species A′ in state B′
Ω	configurational degeneration
ω_{xc}	combinatory factor related to the degeneracy of component x in conformation c neglecting self-exclusion, eq A.1.2

Indexes

A	species (type of segment)
B	state
b	homogeneous bulk solution
c	conformation
i	layer number
s	segment rank
T	transpose
x	component (type of molecule)
*	amorphous reference state

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