Weak Segregation Theory of Microphase Separation in Associating Binary Homopolymer Blends

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ABSTRACT: In this paper we study the phase behavior of blends of associating homopolymers A and B in the weak segregation regime. The homopolymers are "associating" in the sense that hydrogen bonds are possible between the A chains and the B chains. Hydrogen bonds between two A chains, or between two B chains, are not possible. Each B chain can form at most one hydrogen bond, whereas each A chain might form bonds with several B chains, leading to the formation of block copolymer-like clusters. If the hydrogen bonds are strong enough, the system might undergo a microphase separation transition. However, due to the reversible nature of the hydrogen bonds, the system is in dynamic equilibrium, enabling it to adapt its cluster composition to changing conditions. Therefore, to construct the phase diagram, the free energy should be minimized *simultaneously* with respect to the cluster composition and the parameters describing the microstructure. We show that in the weak segregation regime this minimization can be split into two independent steps. In the first step, one determines what the cluster composition would have been if the system were homogeneous. In the second step, this composition is inserted into the expression for the Landau free energy *without the nonlocal term*. We show that the error made in the first step (neglecting the change in cluster composition due to the presence of the microstructure) exactly cancels the error made in the second step (omission of the nonlocal term from the Landau free energy). For the simplest associating homopolymer blend the phase diagram is presented.

1. Introduction

Much attention has been paid to the phase behavior of covalently bonded AB-block copolymers for the situation where there is a net repulsion between the two monomer types A and B. The presence of the covalent bonds prevents a separation between the A blocks and the B blocks over macroscopic distances, and in order to reduce the number of unfavorable AB interactions, the system undergoes a transition to a microphase-separated state. The same phenomenon can occur if the blocks are connected not by chemical bonds but by reversible "physical" interactions such as hydrogen bonds. This has the advantage that there is no need to synthesize molecules having complicated architectures. Instead, it is sufficient to blend suitably functionalized homopolymers. These homopolymers will automatically associate to form block copolymer-like clusters, which can undergo a microphase separation transition on lowering of the temperature, provided that the hydrogen bonds are strong enough. Due to the reversible nature of the hydrogen bonds, the system is in dynamic equilibrium, and clusters are continuously formed and broken. Nevertheless, in a macroscopic system, the number density of clusters of a given type is not fluctuating in time, and statistical equilibrium averages are the same as in a covalently bonded system having the same composition. In particular, the free energy difference between the homogeneous state and a microphase-separated state *having the same cluster composition* is the same as it is for covalently bonded copolymers,[1−3] including the so-called nonlocal term. However, since the system is in dynamic equilibrium, the cluster composition in a microphase-separated state is in fact slightly different from that in the homogeneous state. Therefore, to find the free energy difference between these two states, one should consider it not only as a function of the parameters of the microstructure but also as a function of the cluster composition, and one should minimize it *simultaneously* with respect to all parameters. The aim of this paper is to show that in the weak segregation regime this procedure can be simplified by splitting it into two independent steps. In the first step, one determines what the cluster composition would have been if the system were homogeneous. In the second step, this composition (which differs slightly from the actual composition!) is inserted into the local part of the Landau expansion of $\Delta F_{\mathrm{micro}}$, where $\Delta F_{\mathrm{micro}}$ is the free energy difference between the homogeneous state and the microphase-separated state. Finally, the resulting expression is minimized with respect to the parameters of the microstructure. As we will show further on, the error made in the first step (neglecting the composition change due to the presence of the microstructure) cancels exactly the error made in the second step (omitting the nonlocal term from the Landau free energy).

In refs 4−8, associating homopolymers were studied experimentally. Poly(4-vinylpyridine) (P4VP) was used as a model polymer in combination with various end-functionalized oligomers. The latter consist of a long alkyl tail and a functional headgroup that can make a hydrogen bond with the nitrogen of the pyridine groups of P4VP. The clusters resemble comb copolymers, and the system is able to undergo a transition to a regular microphase-separated state. The theoretical study of such systems was initiated by Tanaka. In ref 9, Tanaka and co-workers considered a blend of two monodisperse homopolymers capable of reversibly connecting to each other to form a diblock cluster, which is the most basic example of associating homopolymers. By calculation of the scattering function within the random phase approximation and determination of the condition for divergence, the spinodals for micro- and for macrophase

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separation were calculated. Reference 10 considers a mixture of long A chains capable of forming hydrogen bonds at several places, distributed evenly along the chain, and short B chains capable of forming one hydrogen bond only at one of their ends. The arising clusters are comb copolymer-like, with the A chains forming the backbone and the B chains forming the teeth. Spinodals for micro- and macrophase separation were found, but since the free energy of the microstructure was not calculated, the binodals were determined from the free energy of the homogeneous phase alone. Although this is not correct if one of the coexisting phases is microphase separated, in the weak segregation regime, where the free energy of the microstructure is small, it is not too bad of an assumption. In refs 11 and 12 phase diagrams of associating homopolymers forming diblock clusters respectively comb clusters were determined via Monte Carlo computer simulations, and compared with theoretical spinodals. In ref 13, the results obtained in ref 10 concerning the comb system were improved upon by calculating the free energy of microphase separation, taking this free energy contribution into account in the calculation of the binodals. However, the change in cluster composition due to the presence of the microstructure was not accounted for. Also, it was conjectured that in view of the annealed character of the system, the nonlocal contribution to the Landau free energy of the microstructure[1−3] should not be taken along in the calculation. The main objective of the present paper is to prove that in the weak segregation regime both approximations (which are, each by itself, not justified) exactly cancel each other, thus showing the correctness of the procedure. For illustration we will calculate the phase diagram of associating homopolymers forming diblock clusters for a typical set of parameter values.

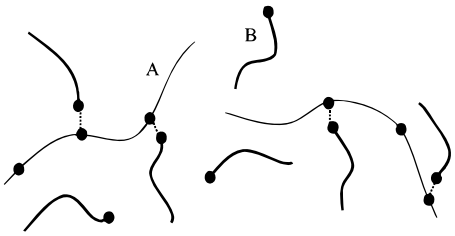

Figure 1. Associating homopolymers. All chains of the same sort are identical. A black dot represents a group capable of forming a hydrogen bond. Hydrogen bonds (denoted by a dotted line) are only possible between an A chain and a B chain. The system is in dynamic equilibrium in the sense that hydrogen bonds are continuously being formed and broken.

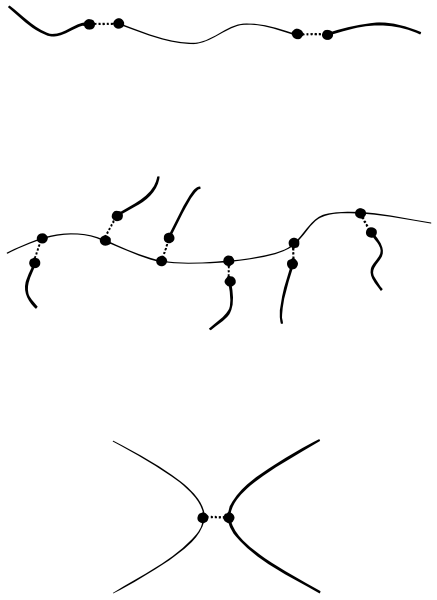

Figure 2. Cluster types. Depending on the number of associating groups per A chain, their distribution along the chain, and the position of the associating group on the B chain, various cluster types are possible. The figure shows clusters resembling triblock copolymers, comb copolymers, and star copolymers.

2. Model

Consider a molten blend of two associating monodisperse homopolymers A and B. Let N_α be the number of segments in a molecule of type α = A/B. Each segment may consist of several chemical monomers. It is assumed that the A and the B chains have the same statistical segment length, and that both segment types have the same excluded volume, which will be taken as the unit of volume. Between the A and B segments a net weakly repulsive interaction is present, which is as usual quantified by the segmental Flory−Huggins interaction parameter χ. Between the A and B chains hydrogen bonding is possible. On each A chain, one or more monomers are capable of forming a hydrogen bond. It is assumed that the number of these active sites and their positions along the chain are the same for all A chains. The B chains, which are identical to each other as well, have only one active site along the chain, to avoid the possibility of ring formation (the presence of rings in the molecules would greatly complicate the calculation of the correlation functions). It is assumed that hydrogen bonding is only possible between an A chain and a B chain and not between two A chains or two B chains. See Figure 1 for illustration. By definition, a *sticker segment* is a segment containing a monomer capable of forming a hydrogen bond. It is assumed that each segment contains at most one such monomer. The formation of a hydrogen bond is accompanied by a decrease in energy and a decrease in entropy. In a certain temperature range, these hydrogen bonds are thermally reversible. Following Tanaka, a group of chains connected by hydrogen bonds will be called a *cluster* (for convenience, a nonbonded homopolymer is also considered to be a cluster). Apart from the trivial homopolymeric clusters, all clusters resemble covalently bonded block copolymers. Depending on the number and the positions of the sticker segments one can obtain clusters resembling diblock copolymers, triblock copolymers, comb copolymers, star copolymers, etc. (see Figure 2 for illustration). In deriving the theory it will prove to be convenient to assume the presence of an underlying lattice. Each lattice site is occupied by exactly one segment. Of course, this lattice is just an aid in deriving the equations, and the final results should be independent of the lattice. At this point we introduce some definitions. Let z be the number of nearest neighbors of a lattice site (the so-called coordination number of the lattice). Let s denote a cluster type, and n_s the total number of clusters of type s. Let N_s^α be the number of monomers of type α = A/B in a cluster of type s, and let $N_s = N_s^A + N_s^B$ be the total number of monomers in such a cluster. Let n_α be the total number of homopolymer chains (bonded and nonbonded) of type α = A/B.

3. Free Energy of Homogeneous State

A cluster composition $\{n_s\}$ can only be realized if the following constraint is satisfied:

$$\sum_s n_s N_s^\alpha = n_\alpha N_\alpha \quad \alpha = \mathrm{A/B} \tag{1}$$

Our first aim is to find an expression for the free energy of the homogeneous state having cluster composition $\{n_s\}$. To define this free energy, a reference state is required. For this we take the (hypothetical) state where the A chains and the B chains are separated and crystallized. To facilitate finding the entropy, we first assume that the homopolymers are distinguishable (for instance, they are numbered) and that they have a head and a tail. Afterward the equations are corrected for the fact that the molecules are in fact indistinguishable. The entropy has three contributions. The first contribution is the entropy associated with the various ways of combining the homopolymers to form the clusters. The second contribution is the entropy associated with the formation of a homogeneous melt (containing both the entropy of disorientation,[14] and the entropy of mixing), and third there is the entropy change associated with the formation of the hydrogen bonds. The first contribution can be found as follows. Place the A homopolymers in line, head down. This can be done in $n_A!$ ways. Number in an arbitrary way the different cluster types $\{s\}$. Then, going from the left to the right along the line of A homopolymers, construct first the clusters of type s_1, then the clusters of type s_2, etc. Since in this way the places where the B homopolymers have to be attached are fixed, the number of ways in which the B chains can be attached is simply $n_B!$. However, in this way permutations of different clusters of the same type are counted separately, and each realization of the n_s clusters of type s appears $n_s!$ times. Therefore, the total number of ways to construct the clusters is

$$\frac{n_A! n_B!}{\prod_s n_s!} \equiv \exp(\Delta S_1/k_B) \tag{2}$$

where k_B is Boltzmann's constant. Since the A and B homopolymers are assumed to be distinguishable for the moment, the n_s clusters of the same type s are distinguishable as well. To find the second contribution ΔS_2 to the entropy, we follow Flory[14] and assume the presence of an underlying lattice with coordination number z. Each segment occupies exactly one lattice site. Within the lattice description, the quantity $\exp(\Delta S_2/k)$ is just the total number of ways to place the clusters on the lattice. Since the clusters are distinguishable, and have no internal symmetries due to the fact that the homopolymers are distinguishable, one obtains[14]

$$\frac{\Delta S_2}{k_B} = \sum_s n_s(N_s - 1)\ln(z-1) - \sum_s n_s N_s + \sum_s n_s \ln(n_A N_A + n_B N_B) \tag{3}$$

To correct for our assumption that the molecules are distinguishable, the quantity $k_B(\ln n_A! n_B!)$ must be subtracted from the entropy. Taking this correction into account, and combining eq 2 with eq 3, the entropy ΔS of the homogeneous state with respect to the state where the A and B chains are separated and crystallized becomes

$$\frac{\Delta S}{k_B} = \sum_s n_s(N_s - 1)\ln\frac{(z-1)}{e} - \sum_s n_s \ln\frac{n_s}{V} \qquad V \equiv n_A N_A + n_B N_B \tag{4}$$

where V is the volume of the system measured in units of the volume of a segment. In deriving eq 4 it was assumed that the molecules have a "head" and a "tail". The validity of this assumption depends on the distribution of the sticker segments along the chain. In the model used in ref 13, for instance, all A segments are capable of forming hydrogen bonds, while the (short) B chains have only one sticker segment at one of their ends (the arising clusters resemble comb copolymers). In that case the A chains are symmetric, while the B chains are not, and one should subtract from eq 4 the term $n_A \ln 2$, which is constant and of no importance. Therefore, we can take eq 4 to be valid generally. It is now straightforward to write down the total free energy F_{hom} of the homogeneous state as a function of its composition:

$$\frac{F_{hom}}{k_B T} = \sum_s n_s \ln\frac{n_s}{V} - \sum_s n_s(N_s - 1)\ln\frac{(z-1)}{e} + \frac{\Delta F_{hb}}{k_B T}\sum_s n_s N_s^{hb} + \chi\frac{n_A N_A n_B N_B}{n_A N_A + n_B N_B} \tag{5}$$

Here ΔF_{hb} is the (constant) free energy change associated with the formation of one hydrogen bond, and N_s^{hb} is the number of hydrogen bonds in a cluster of type s, which is (for nontrivial clusters!) equal to the number of B chains in the cluster.

4. Microphase Separation in Covalently Bonded Block Copolymers

A microphase-separated state can be characterized by its coarse grained concentration profile $\psi(\vec{x})$, which is the deviation of the local fraction of A monomers from the average value. In the weak segregation regime, the free energy difference ΔF_{micro} between the homogeneous state and a microphase-separated state can be approximated by its Landau expansion in powers of $\psi(\vec{x})$:

$$\frac{\Delta F_{micro}}{k_B T} \cong \frac{F_{Landau}}{k_B T} \equiv \sum_{n=2}^{4}\frac{1}{n!}\frac{1}{V^{n-1}}\sum_{\vec{q}_1,\ldots,\vec{q}_n} \times \gamma_n(\{n_s\}, \vec{q}_1, \ldots, \vec{q}_n)\,\psi(\vec{q}_1)\ldots\psi(\vec{q}_n)$$

$$\psi(\vec{q}) = \int d\vec{x}\, e^{i\vec{q}\cdot\vec{x}}\,\psi(\vec{x}) \quad \psi(\vec{x}) = \rho_A(\vec{x}) - f_A \qquad f_A = \frac{n_A N_A}{n_A N_A + n_B N_B} \tag{6}$$

In refs 1−3 general expressions were derived for the so-called vertex functions $\gamma_n(\{n_s\},\vec{q}_1, \ldots, \vec{q}_n)$. In the weak segregation regime, the second- and the fourth-order terms of the Landau free energy are of the same order of magnitude (the third-order term is either of the same order of magnitude, or smaller). For many block copoly-

mer systems (but not for random copolymers), the Landau free energy is on the order of ψ^4. We give here the explicit expression for the second-order vertex, γ_2, because we will need it further on:

$$\gamma_2(\{n_s\},q) = \frac{\overline{\gamma_{AA}} + \overline{2g_{AB}} + \overline{g_{BB}}}{\overline{g_{AA}}\,\overline{g_{BB}} - \overline{g_{AB}}^2} - 2\chi \equiv \tilde{\gamma}_2(\{n_s\},q) - 2\chi$$

$$\overline{g_{\alpha\beta}}(q) = \sum_s \rho_s g^s_{\alpha\beta}(q) \qquad \rho_s = \frac{n_s}{V} = \frac{n_s}{\sum_\sigma n_\sigma N_\sigma} \tag{7}$$

$g_{\alpha_1\ldots\alpha_n}$ is the nth order correlation function of molecule type s. We will not reproduce the full expressions for the third- and the fourth-order vertices.[1−3] The fourth-order vertex, γ_4, has a contribution that vanishes for monodisperse melts (more precisely, it vanishes if the number of molecules types does not exceed the number of monomer types). This contribution is generally called the "nonlocal term", because in real space representation it couples points in space that are arbitrarily far apart. For our purpose it is relevant to give its general form[3] in Fourier representation

$$\gamma_4^{\text{nonlocal}}(\vec{q}_1, \ldots, \vec{q}_4) = \delta_K(\vec{q}_1 + \vec{q}_2)\,\delta_K(\vec{q}_3 + \vec{q}_4) \times \sum_{\alpha\beta\gamma\delta} \Gamma_{\alpha\beta\gamma\delta}(q_1, q_3) z_\alpha(q_1) z_\beta(q_2) z_\gamma(q_3) z_\delta(q_4) + \ldots$$

$$\Gamma_{\alpha\beta\gamma\delta}(q_1,q_3) = \overline{g_{\alpha\beta}(q_1)g_{\gamma\delta}(q_3)} - \sum_{\mu\nu} \overline{g_{\alpha\beta\mu}}(q_1, -q_1, 0)\,\overline{g_{\mu\nu}}^{-1}(0)\,\overline{g_{\gamma\delta\nu}}(q_3, -q_3, 0) \tag{8}$$

Greek lower case letters denote monomers types, $\delta_K = \pm 1$ is the Kronecker δ, and the dots represent the two remaining (distinct) terms obtained by permuting $\vec{q}_1$, ..., $\vec{q}_4$.

5. Microphase Separation in Associating Homopolymers

Since the clusters that are present in associating homopolymer melts resemble block copolymers, there can be a microphase separation transition provided that the hydrogen bonds are strong enough. To construct the phase diagram taking into account the possibility of microphase separation, the total free energy

$$F_{\text{total}}(\{n_s\},\psi) = F_{\text{hom}}(\{n_s\}) + \Delta F_{\text{micro}}(\{n_s\}, \psi) \tag{9}$$

has to be minimized *simultaneously* with respect to the cluster composition, $\{n_s\}$, and with respect to the concentration profile, ψ. It follows from eq 9 that $\Delta F_{\text{micro}}(\{n_s\},\psi)$ represents the difference in free energy between the microphase-separated state and the honmogenous state *having the same composition*. It is important to realize that the expression for $\Delta F_{\text{micro}}(\{n_s\},\psi)$ coincides with that for covalently bonded copolymers, because both the energy and the entropy do not depend on whether the bonds between the A and B chains are reversible or not. In particular, its Landau expansion contains the nonlocal term. In the weak segregation regime we have $\Delta F_{\text{micro}} \ll F_{\text{hom}}$, and so it seems to be justified first to minimize $F_{\text{hom}}(\{n_s\})$ with respect to $\{n_s\}$, to insert the resulting cluster composition $\{n_s^\circ\}$ into $\Delta F_{\text{micro}}(\{n_s\},\psi)$, followed by the minimization of $\Delta F_{\text{micro}}(\{n_s^\circ\},\psi)$ with respect to the parameters describing ψ (for instance, the period and the amplitude of the microstructure). However, this procedure is wrong. To explain why, it is convenient to introduce first a simpler notation. Let h denote the total free energy, f the free energy of the homogeneous phase, and g the free energy change due to the presence of the microstructure. Moreover, let $\vec{x}$ represent the cluster composition $\{n_s\}$, and let $\vec{y}$ represents the set of parameters describing ψ. Then eq 9 can be written as

$$h(\vec{x},\vec{y}) = f(\vec{x}) + g(\vec{x},\vec{y}) \quad f \gg g \tag{10}$$

If $\vec{x}_0$ minimizes f, that is, if

$$\nabla f(\vec{x}_0) = 0 \tag{11}$$

then in a first approximation the minimum value of h (for a fixed value of $\vec{y}$) is given by

$$h_{\min}(\vec{y}) \cong f(\vec{x}_0) + g(\vec{x}_0,\vec{y}) - \frac{1}{2}\nabla_x g(\vec{x}_0,\vec{y}) \cdot [\nabla^2 f(\vec{x}_0)]^{-1} \cdot \nabla_x g(\vec{x}_0,\vec{y}) \tag{12}$$

where $\nabla^2 f(x_0)$ is considered to be a matrix, $\nabla_x g(\vec{x}_0,\vec{y})$ is considered to be a vector, and the dots denote matrix multiplications. Assuming that the derivatives of f and g are of the same order of magnitude as the functions themselves, the third term on the right-hand side of eq 9 (in the following we will refer to this term as "the correction term") is negligible compared to the second term (because $f \gg g$). It is then justified to make the approximation

$$h_{\min}(\vec{y}) \cong f(x_0) + g(\vec{x}_0,\vec{y}) \tag{13}$$

and the minimum of h can be found by the minimization of $g(\vec{x}_0,\vec{y})$ with respect to $\vec{y}$. However, this argument is based on the assumption that the derivative of g with respect to x_i is of the same order of magnitude as g itself, whereas in the case of eq 9 this requirement is not satisfied, as can be seen in the following explanation. We remind the reader that the function g corresponds to the Landau free energy, eq 6, and that the parameter set $\vec{x}$ corresponds to the composition $\{n_s\}$. The derivative of the third- (fourth-) order vertex with respect to n_s is of the same order of magnitude as the third- (fourth-) order vertex itself, and so the contributions of these vertexes to the correction term in eq 12 *are* negligible. However, for the second-order vertex the situation is different. Its general form was given in eq 7. In the weak segregation regime, γ_2 is a small parameter on the order of ψ^2, but this is only due to the subtraction of 2χ; the quantity $\tilde{\gamma}_2$ itself is *not* a small parameter. Since after differentiation with respect to n_s the constant 2χ disappears, the derivative of γ_2 is on the order of unity, and *not* on the order of ψ^2. Therefore, the corresponding contribution to the correction term in eq 12 has the same order of magnitude as g and cannot, therefore, be neglected. We will see that this contribution cancels exactly the nonlocal term in g. To evaluate the correction term, we have to find an expression for $\nabla^2 F_{\text{hom}}/k_B T$. First we argue that the parameter set $\vec{x}$ contains more parameters than the composition $\{n_s\}$ alone. By definition, it contains all parameters with respect to which the free energy F^{hom} must be minimized. The problem is that the minimization of eq 5 has to be done under the constraints given by eq 1. This is equivalent with minimizing $\tilde{F}_{\text{hom}}$ without constraints, where $\tilde{F}_{\text{hom}}$ is

defined by

$$\frac{\tilde{F}_{\mathrm{hom}}}{k_{\mathrm{B}}T} = \frac{F_{\mathrm{hom}}}{k_{\mathrm{B}}T} + \lambda_{\mathrm{A}}\Big(\sum_s n_s N_s^{\mathrm{A}} - n_{\mathrm{A}}N_{\mathrm{A}}\Big) + \lambda_{\mathrm{B}}\Big(\sum_s n_s N_s^{\mathrm{B}} - n_{\mathrm{B}}N_{\mathrm{B}}\Big) \quad (14)$$

To establish the connection with eq 10, one should realize that the Lagrange multipliers λ_α have to be included in the parameter set $\vec{x}$, so there exists the correspondence $\vec{x} \leftrightarrow \{n_s,\lambda_\alpha\}$. Differentiation of eq 14 (use eq 5) shows that the Hessian $\nabla^2 F_{\mathrm{hom}}/k_{\mathrm{B}}T$ has the following form:

$$\nabla^2 F_{\mathrm{hom}}/k_{\mathrm{B}}T = \begin{bmatrix} n_s^{-1} & 0 & 0 & N_s^{\mathrm{A}} & N_s^{\mathrm{B}} \\ 0 & n_\sigma^{-1} & 0 & N_\sigma^{\mathrm{A}} & N_\sigma^{\mathrm{B}} \\ 0 & 0 & \vdots & \vdots & \vdots \\ N_s^{\mathrm{A}} & N_\sigma^{\mathrm{A}} & \dots & 0 & 0 \\ N_s^{\mathrm{B}} & N_\sigma^{\mathrm{B}} & \dots & 0 & 0 \end{bmatrix} \quad (15)$$

In appendix A it is shown how this matrix can be inverted. The result is

$$(\nabla^2 F_{\mathrm{hom}}/k_{\mathrm{B}}T)_{s\sigma}^{-1} = \delta_{s\sigma}n_\sigma - \sum_{\alpha\beta} n_s N_s^\alpha n_\sigma N_\sigma^\beta G_{\alpha\beta}^{-1}$$

$$G_{\alpha\beta} = \sum_s n_s N_s^\alpha N_s^\beta \quad (16)$$

The matrix elements $\nabla^2 F_{\mathrm{dis}}/k_{\mathrm{B}}T)_{s\lambda}^{-1}$, $(\nabla^2 F_{\mathrm{dis}}/k_{\mathrm{B}}T)_{\lambda\mu}^{-1}$, etc. need not be evaluated, since they give no contribution to the correction term because the Landau free energy does not depend on λ_α. Finally we have to calculate the derivative $\partial g/\partial x$, which corresponds to

$$\frac{\partial g}{\partial x} \leftrightarrow \begin{cases} \dfrac{\partial}{\partial n_s}\dfrac{1}{2V}\displaystyle\sum_{\vec{q}} \gamma_2(\vec{q})\psi(\vec{q})\psi(-\vec{q}) = \\ \qquad \dfrac{1}{2V^2}\displaystyle\sum_{\vec{q}} g^s_{\alpha\beta}(q) z_\alpha(q) z_\beta(q)\psi(\vec{q})\psi(-\vec{q}) \\ \dfrac{\partial}{\partial \lambda_i}\dfrac{1}{2V}\displaystyle\sum_{\vec{q}} \gamma_2(\vec{q})\psi(\vec{q})\psi(-\vec{q}) = 0 \end{cases} \quad (17)$$

We used $n_s = V\rho_s$. Combining eqs 12, 16, and 17, the correction term $\Delta F_{\mathrm{corr}}/k_{\mathrm{B}}T$ is found to be

$$\Delta F_{\mathrm{corr}}/k_{\mathrm{B}}T = -\frac{1}{8V^4}\sum_{q_1q_2\alpha\beta\gamma\delta}\Bigg(\sum_s n_s g^s_{\alpha\beta}(q_1) g^s_{\gamma\delta}(q_2) - \sum_{\mu\nu}\sum_s n_s g^s_{\alpha\beta}(q_1) N_s^\mu\, G_{\mu\nu}^{-1} \sum_\sigma n_\sigma g^s_{\gamma\delta}(q_2) N_s^\nu\Bigg)\psi(q_1) \times \psi(-q_1)\psi(q_2)\psi(-q_2) z_\alpha(q_1) z_\beta(q_1) z_\gamma(q_2) z_\delta(q_2) \quad (18)$$

The second term between the brackets can be simplified by using

$$g^s_{\alpha\beta}(q) N_\mu^s = g^s_{\alpha\beta\mu}(q,-q,0)$$

$$G_{\alpha\beta} \equiv \sum_s n_s N_s^\alpha N_s^\beta = V\sum_s \rho_s g^s_{\alpha\beta}(0) \quad (19)$$

and so, using the abbreviation $\bar{A} = \sum \rho_s A_s$

$$\Delta F_{\mathrm{corr}}/k_{\mathrm{B}}T = -\frac{1}{8V^3}\sum_{q_1q_2}\sum_{\alpha\beta\gamma\delta}\Bigg(\overline{(g_{\alpha\beta}(q_1) g_{\gamma\delta}(q_2)} - \sum_{\mu\nu}\overline{g_{\alpha\beta\mu}}(q_1,-q_1,0)\bar{g}_{\mu\nu}^{-1}(0)\overline{g_{\gamma\delta\nu}}(q_2,-q_2,0))\Bigg)\psi(q_1) \times \psi(-q_1)\psi(q_2)\psi(-q_2) z_\alpha(q_1) z_\beta(q_1) z_\gamma(q_2) z_\delta(q_2) \quad (20)$$

By direct substitution of eq 8 into the Landau free energy eq 6, one can check that the correction term given in eq 20 is, apart from a minus sign, equal to the nonlocal term. It follows that they cancel each other on the right-hand side of eq 12. This finishes our proof of the fact that the minimization of eq 9 can be split into two independent steps, provided that the nonlocal term is omitted from the Landau free energy.

6. Associating Homopolymers Forming Diblock Clusters: Phase Diagram

Next we apply the theory to the most simple case. The A chains and the B chains have the same number of monomers and the same Kuhn segment length. Moreover, the A and B monomers have the same excluded volume (these are not essential assumptions, and the calculation could easily be adapted to a more general situation). We define a segment length l in such way that l is much smaller than the contour length of the chain, but on the other hand l is large enough to ensure that the distance between two monomers separated by a distance l along the chain obeys random walk statistics. There is some freedom in the choice of l, but of course the final results will not depend on this choice. Let N be the number of segments per chain; then $N \propto l^{-1}$. All chains have exactly one sticker segment at one of their end points, so there are only three types of clusters possible: a free A chain, a free B chain, and a symmetric diblock copolymer. Let n be the total number of homopolymer chains (bonded and unbonded), and let f be the fraction of A chains. Let pn be the number of diblock copolymer-like clusters. The χ parameter is inversely proportional to N (because it is the interaction energy *per segment*), and we will assume that it is inversely proportional to the temperature as well. This motivates the definition of a rescaled temperature t by

$$\chi = \frac{1}{Nt} \quad (21)$$

The free energy of the homogeneous state has been given in eq 5. Before proceeding, we have to find an expression for the free energy change ΔF_{hb} associated with the formation of a hydrogen bond. The *entropic* part of ΔF_{hb} can be written as a sum of two contributions. The first contribution is due to a loss in orientational entropy: the chemical groups forming the hydrogen bond must be precisely aligned. Usually it is written as $-k_{\mathrm{B}} \ln q$, where typically[16] $q \approx 100$. Its interpretation is that at infinite temperature 1 out of $q + 1$ contacts between a sticker A segment and a sticker B segment would lead to a hydrogen bond. The second contribution to the entropy is due to a loss in translational entropy. In the lattice model, this is accounted for by requiring that the two bonded segments occupy two adjacent lattice sites. This spatial localization corresponds to the volume of one segment, and the corresponding translational entropy loss would be dependent on the choice

of the segment length l. Since the translational entropy penalty is in reality independent of l, we have to correct for this by adding the term $-k_B \ln l$, which is equivalent to adding $k_B \ln N$ (because $l \propto N^{-1}$). Besides the entropic contributions to ΔF_{hb}, there is also an energetic contribution, which we assume to be independent of the temperature. Combining all terms, the free energy change ΔF_{hb} upon the formation of a hydrogen bond can be written as

$$\Delta F_{hb}/k_B T = -\frac{a}{t} + \ln \frac{q}{N} \tag{22}$$

The free energy density eq 5 of the homogeneous state becomes

$$\frac{F_{hom}}{nk_B T} = (f-p)\ln(f-p) + (1-f-p)\ln(1-f-p) + p\ln p + \frac{f(1-f)}{t} + p + p\left(-\frac{a}{t} + \ln q\right) - p\ln(z-1) \tag{23}$$

For the coordination number z one could insert an effective value, but since the factor $(z-1)$ can be absorbed into q (see eq 23) and q is an adjustable phenomenological parameter, the last term in eq 23 may be omitted. Note that the dependence on N has disappeared, as it should, since the free energy must be independent of the choice of the segment length. For a and q, we take characteristic values. A rough estimate for q can be found as follows. The entropy change upon formation of a hydrogen bond is on the order[16] of $\Delta S = 40\ J\ K^{-1}\ mol^{-1}$, which corresponds to a value of $q = \exp(\Delta S/k_B) = 100$. The value of a is, roughly speaking, the ratio between the interaction energy of a hydrogen bond and the dispersive interaction energy of the *whole* chain, and so it depends not only on the chemical nature of the A and B monomers and the character of the hydrogen bond but also on the number of monomers per chain. In an experimental situation, the value of a can be changed continuously by changing the chain length. For our calculation, we chose $a = 1.65$ in order to obtain an interesting phase diagram. The phase diagram is calculated by splitting the minimization in two independent steps, the correctness of which was proven in the previous sections. First we minimize eq 23 with respect to p, thus obtaining the number of diblock clusters in the *homogeneous* state as a function of the temperature t. Next we calculate the expression for the Landau free energy (without the nonlocal term!) for a blend of A homopolymers, B homopolymers, and AB-diblock copolymers, inserting for p the value obtained for the homogeneous state. The reader who is interested in the calculation of the vertex functions is referred to refs 17 and 18 (ref 18 explains how to calculate the correlation functions for homopolymers and diblock copolymers, and ref 17 shows how to obtain from this the second- and the third-order vertex functions, and the local part of the fourth-order vertex function). We make the first harmonic approximation[18] and take into consideration only the lamellar, the hexagonal, and the bcc lattice symmetries. The periodicity of the lattice is assumed to be determined by the position of the minimum of the second-order vertex, which is, at least for the system under consideration, justified in the weak segregation regime.[18] To construct the phase diagram in the (f,t) plane, we determine, for fixed temperature t and composition f, the free energies of the homogeneous state, the lamellar state, the hexagonal state, and the bcc state. For fixed t, we plot the lowest of these four free energy values as a function of f. By constructing common tangents, one arrives at the phase diagram displayed in Figure 3. Note that the regions of stability of the various phases are separated from each other by narrow two-phase regions. The reason for this is explained by Figure 4: the free energy as a function of f has a kink at the phase transition points.

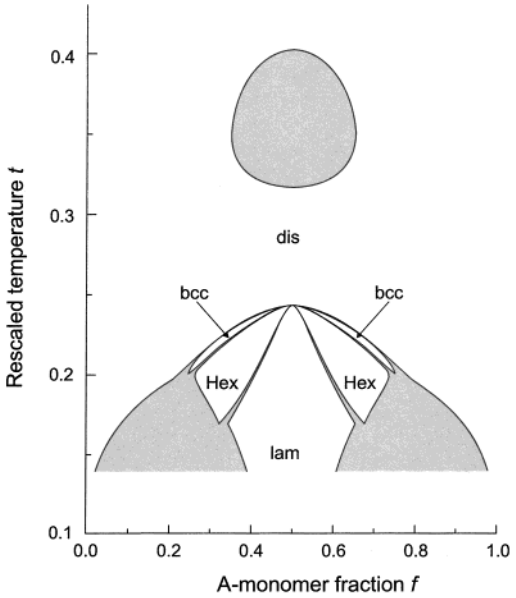

Figure 3. Phase diagram of associating AB homopolymer blend forming symmetric diblock copolymer-like clusters. Values of the parameters: $q = 120$; $a = 1.65$. Horizontal axis: A monomer fraction f. Vertical axis: rescaled temperature t. White area: 1-phase region. Gray area: 2-phase region.

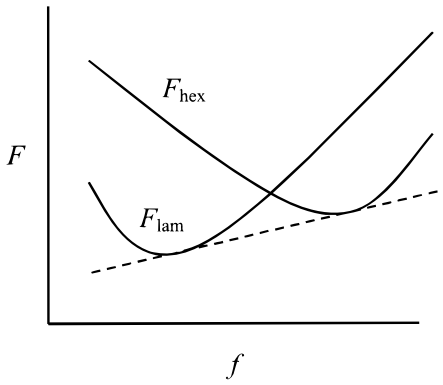

Figure 4. Qualitative explanation of the existence of narrow two-phase regions separating the regions of stability of two different phases. The solid curves give the free energies of the lamellar phase and the hexagonal phase as a function of the fraction f of A monomers. Due to the difference in slope at the intersection point, the free energy has a kink. The dotted line represents the common tangent used to determine the compositions of the coexisting phases.

7. Summary

In this paper we investigated theoretically the phase behavior of monodisperse associating AB-homopolymer blends in the weak segregation regime. We assumed that hydrogen bonds are only possible between an A chain and a B chain and not between two chains of the same sort and that each B chain can form no more than one hydrogen bond. The clusters present in the system

resemble covalently bonded block copolymers, and there can be a transition to a microphase-separated state provided that the hydrogen bonds are strong enough. To construct the phase diagram, one has to minimze the free energy simultaneously with respect to the cluster composition and the parameters of the microphase separation. The main result of this paper is to prove that in the weak segregation regime this procedure can be simplified considerably by splitting it into two independent steps. In the first step, one determines what the composition would have been if the system were homogeneous. In the second step, this composition is inserted into the expression for the Landau free energy, as it was derived for covalently bonded copolymers, but without taking along the nonlocal term. Subsequently, this expression is minimized with respect to the parameters of the microstructure. We showed that the error made in the first step (the assumption that the cluster composition is not influenced by the presence of the microstructure) cancels exactly the error made in the second step (omission of the nonlocal term from the Landau free energy). Our result justifies the calculation made in ref 13.

Appendix A

In this appendix we calculate the inverse of the matrix **H** defined by

$$\mathbf{H} = \begin{bmatrix} n_s^{-1} & 0 & 0 & \mathrm{N}_s^{\mathrm{A}} & N_s^{\mathrm{B}} \\ 0 & n_\sigma^{-1} & 0 & N_\sigma^{\mathrm{A}} & N_\sigma^{\mathrm{B}} \\ 0 & 0 & \ddots & \vdots & \vdots \\ N_s^{\mathrm{A}} & N_\sigma^{\mathrm{A}} & \cdots & 0 & 0 \\ N_s^{\mathrm{B}} & N_\sigma^{\mathrm{B}} & \cdots & 0 & 0 \end{bmatrix} \tag{A1}$$

Rewrite it as the sum of a diagonal matrix **g** and a block matrix **A**

$$\mathbf{H} = \mathbf{g} + \mathbf{A} \tag{A2}$$

where

$$\mathbf{g} = \begin{bmatrix} n_s^{-1} & 0 & \cdots & 0 & 0 \\ 0 & n_\sigma^{-1} & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \ldots & K^{-1} & 0 \\ 0 & 0 & \ldots & 0 & K^{-1} \end{bmatrix}$$

$$\mathbf{A} = \begin{bmatrix} 0 & 0 & \cdots & N_s^{\mathrm{A}} & N_s^{\mathrm{B}} \\ 0 & 0 & \cdots & N_\sigma^{\mathrm{A}} & N_\sigma^{\mathrm{B}} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ N_s^{\mathrm{A}} & N_\sigma^{\mathrm{A}} & \cdots & 0 & 0 \\ N_s^{\mathrm{B}} & N_\sigma^{\mathrm{B}} & \cdots & 0 & 0 \end{bmatrix} \tag{A3}$$

The constant K is introduced in order to make the matrix **g** invertible; afterward, the limit $K \to \infty$ is taken.

One can write

$$\mathbf{H}^{-1} = \mathbf{g}^{-1}(1 + \mathbf{A}\mathbf{g}^{-1})^{-1} = \mathbf{g}^{-1}(1 - \mathbf{B} + \mathbf{B}^2 - \mathbf{B}^3 + \ldots)$$

$$\mathbf{B} \equiv \mathbf{A}\mathbf{g}^{-1} = \begin{bmatrix} 0 & 0 & \cdots & KN_s^A & \mathrm{KN}_s^{\mathrm{B}} \\ 0 & 0 & \cdots & KN_\sigma^{\mathrm{A}} & KN_\sigma^{\mathrm{B}} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ n_s N_s^A & n_\sigma N_\sigma^{\mathrm{A}} & \cdots & 0 & 0 \\ n_s N_s^B & n_\sigma N_\sigma^{\mathrm{B}} & \cdots & 0 & 0 \end{bmatrix} \tag{A4}$$

After introducing the abbreviations

$$x_s^\alpha = KN_s^\alpha \quad y_s^\alpha = n_s N_s^\alpha \tag{A5}$$

the matrix **B** can be written as

$$\mathbf{B} = \begin{bmatrix} 0 & x_s^\alpha \\ y_s^\alpha & 0 \end{bmatrix} \tag{A6}$$

Straightforward calculation shows that (there is a summation over repeated indices)

$$\mathbf{B}^2 = \begin{bmatrix} x_s^{\alpha_1} y_s^{\alpha_1} & 0 \\ 0 & y_{s_1}^\alpha x_{s_1}^\beta \end{bmatrix} \quad \mathbf{B}^3 = \begin{bmatrix} 0 & x_s^{\alpha_1} y_{s_1}^{\alpha_1} x_{s_1}^\alpha \\ y_{s_1}^\alpha x_{s_1}^{\alpha_1} y_s^{\alpha_1} & 0 \end{bmatrix}$$

$$\mathbf{B}^4 = \begin{bmatrix} x_s^{\alpha_1} y_{s_1}^{\alpha_1} x_{s_1}^{\alpha_2} y_\sigma^{\alpha_2} & 0 \\ 0 & y_{s_1}^\alpha x_{s_1}^{\alpha_1} y_{s_2}^{\alpha_1} x_{s_2}^\beta \end{bmatrix} \tag{A7}$$

and so forth. We are only interested in the upper left part of the matrix, since the matrix has to be contracted with the vector $\vec{\Delta}x_x(x,y)$, which has zero α components.

$$(1 - \mathbf{B} + \mathbf{B}^2 - \mathbf{B}^3 + \ldots)_{s\sigma} = \delta_{s\sigma} + y_s^{\alpha_1} x_\sigma^{\alpha_1} + x_s^{\alpha_1} y_{s_1}^{\alpha_1} x_{s_1}^{\alpha_2} y_\sigma^{\alpha_2} + x_s^{\alpha_1} y_{s_1}^{\alpha_1} x_{s_1}^{\alpha_2} y_{s_2}^{\alpha_2} x_{s_2}^{\alpha_3} y_\sigma^{\alpha_3} + \ldots = \delta_{s\sigma} + y_s^\alpha \Big(\sum_{k=0}^{\infty} C^k\Big)_{\alpha\beta} x_\sigma^\beta = \delta_{s\sigma} + Kn_s N_s^\alpha (1 - C)_{\alpha\beta}^{-1} N_\sigma^\beta$$

$$C_{\alpha\beta} = Kn_s N_s^\alpha N_\sigma^\beta \tag{A8}$$

Multiplying with g^{-1} and taking the limit $K \to \infty$ leads to

$$H_{s\sigma}^{-1} = \delta_{s\sigma} n_\sigma - \sum_{\alpha\beta} n_s N_s^\alpha n_\sigma N_\sigma^\beta G_{\alpha\beta}^{-1}$$

$$G_{\alpha\beta} = \sum_s n_s N_s^\alpha N_s^\beta \tag{A9}$$

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