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Toward an Integrated Analytic Description of Demixing in Ternary Solutions of Nonideal Uncharged Lattice Polymers, Hard Particles, and Solvent

H. M. Schaink* and J. A. M. Smit

Physical and Macromolecular Chemistry, Leiden Institute of Chemistry,
Gorlaeus Laboratoria, University of Leiden, Postbus 9502,
2300 RA Leiden, The Netherlands

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ABSTRACT: We present a new analytic scheme for the description of the phase behavior of solutions of lattice polymers and hard particles. The theory covers mixtures containing short polymers (i.e., the radius of gyration smaller than the hard particle radius) as well as mixtures containing very long polymers. The lattice polymers have excluded volume interactions, and the hard particles can have a spherical, convex, or dumbbell shape. The theory combines the Flory theory for polymer solutions, the Boublik−Nezbeda equation of state for isotropic fluids of hard particles, and a simple correction term for the reduction of polymer configurations near a wall. In order to be able to integrate these different approaches, typical properties of the hard particles, such as the average number of surface−fluid contacts of a particle, are expressed in terms of lattice sites using a simple numerical simulation. These simulation results are fitted for general use by simple second-order polynomials. The resulting equation of state predicts entropy-driven as well as energy-driven demixing and restabilization. As examples, the ternary mixtures lattice polymer + solvent + (hard spheres or hard dumbbells) are discussed, as well as the comparison with the Flory theory for two different polymers and a solvent.

Introduction

It is well known that addition of polymer molecules to a colloidal or protein solution may give rise to a segregation into a polymer-enriched and a colloid-enriched phase. Most of the experimental and theoretical[1−6] work in this field has dealt with mixtures in which the molecular mass of the polymer molecules is considerably smaller than the molecular mass of the colloids. However there is also evidence of phase separation in mixtures in which the molecular mass of the polymers is considerably larger than that of the colloidal particles.[7−12] It is reasonable to expect that the phase behavior in these two regimes can be derived from a single model. Indeed as the length of the polymer chains varies from short to long, there should be a gradual change in the thermodynamic properties. Here we will present a lattice theory which comprehends these type of mixtures in the long polymer limit, as well as in the short polymer limit.

The use of lattice models has a long history in polymer physics. The most frequently used model was introduced in 1945 by P. Flory.[13] Since then various modifications of this theory have been given.[14−17] The Flory type of approach has been applied successfully to several systems, such as mixtures of polymers,[18] polyelectrolytes,[19] solutions of polymers and rigid rods,[20] and polymer solutions near flat interfaces.[21−23]

Various attempts have been made to incorporate the Flory theory in the description of polymer + hard spheres + solvent, with varying success. Baskir et al. have tried to model the interaction between a polymer solution and a single sphere,[24] and Fleer et al. have tried to modify the theory of a polymer solution between two flat interfaces to a theory of a solution between two large spheres.[25] The validity of these theories is restricted to mixtures with dilute hard sphere concentrations. Furthermore these methods become numerically cumbersome for systems which contain very long polymer molecules. Another option is to study these mixtures by numerical simulation. Frenkel and Meijer[26] have recently published results of MC simulations of mixtures of ideal athermal lattice polymers and hard spheres. However, the neglect of excluded volume interactions of the polymers may have serious consequences for the calculated phase behavior.

Our goal is to gain insight concerning the factors that are important in the phase behavior of macromolecular solutions that presently cannot be studied with the techniques described above. Examples of such systems are the aqueous solutions of small globular proteins and high molecular weight biopolymers.[8−12] For sufficiently high salt concentrations, it was shown by Wang and Bloomfield[27] that the osmotic pressure of aqueous solutions of globular proteins can be well represented by the Carnahan−Starling equation of state for hard particles.[28,29]

Here we will present a simple analytic theory for a ternary system which contains many hard particles, lattice polymers, and solvent molecules. This theory interpolates between the equation of state of a hard particle solution and that of a lattice polymer solution. We assume that the configuration of hard particles is not affected by the presence of the lattice (i.e., the center of mass of a particle does have to coincide with a lattice site), while the polymer and solvent molecules are located on the lattice. The theory combines the Flory theory for polymer solutions (including excluded volume interactions), the Boublik−Nezbeda equation of state for hard convex particles and hard dumbbells[30,31] (which reduces to the Carnahan−Starling equation in the case of spherical particles[28−31]), and a simple correction term accounting for the reduction in entropy caused by the reduction of the number of possible polymer configurations in the first layer near the particle surface. Using a descriptive parameter, it is possible to set this term so that it corresponds to a simple estimate of the effect of the depletion of polymer segments in the first layer

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near the particle surface.[32] This correction term is a rather drastic simplification of the problem, but it has the advantage that it keeps the treatment analytic. The models which take the reduction in the number of polymer configuration more accurately into account are computationally intensive.[21,22,26] In principle, a refinement of the present theory can be developed in which several fluid layers around the hard particles are considered, by modifying existing theories for polymer solutions near a flat wall[21,22,32] and inclusion of correlation between the hard particles. The present theory, however, may describe at least semiquantitatively thermodynamic processes such as entropy-driven phase separation[26] and restabilization.[25,33] This is a feature which is not captured by a standard Flory treatment of phase separation,[18,19] where also energetic effects are needed to explain these phenomena.

In the present theory we make the lattice constant so large that one solvent molecule occupies exactly one lattice site, and the lattice polymers consist of segments which also occupy one lattice site. Our lattice model predicts that the length of the polymer chains has only a slight influence on the phase behavior. The hard particles that we consider here have a radius that is at least 2.5 times larger than the lattice constant. This is in order to assure that the number of lattice sites inside the hard particles does not vary too strongly as the particle moves through the lattice. A description of the physical properties (such as the volume) of a single hard particle in terms of the lattice sites can be easily obtained by placing the hard particle a number of times randomly in the lattice. In Appendix A of this paper, we elaborate such a scheme for spherical particles. Using the results obtained in Appendix A, it is possible to generalize the treatment from spheres to fused spheres (dumbbells). It appears that a ternary mixture of polymers + fused spheres + solvent has a stronger tendency to undergo an entropy-driven phase separation than a mixture that contains single spheres.

In principle it is also possible to treat cases with ellipsoidal or spherocylindrical particles with the developed equation of state. However a theory for these particles requires other input parameters than those obtained in Appendix A. However, these input parameters can be obtained along a similar route.

The relevance of the possibility of studying multicomponent mixtures which contain polymers and nonspherical hard particles lies in the fact that many protein and colloidal particles do not have a spherical shape. For instance some globular proteins may form dimers depending on the solvent conditions.[34,35] Hence it is interesting to study systems which contain fused spheres.

The actual application to the present theory to realistic protein + polymer solutions requires also numerical values for the interaction energies. The Flory parameters for the polymer−polymer interaction are extensively tabulated (see, for instance, ref 36). The energy parameter required by the present theory for the polymer−protein interaction is basically unknown and must be extracted from experimental results.

The present theory can be generalized straightforward to systems which contain several species of hard particles and polymers. Possible applications of such a generalization are the study of the phase equilibrium under influence of a dimerization reaction of the hard particles and the calculation of protein-partitioning coefficients in phase-separated polymer solutions. Thus the theory of Abbott et al.[37,38] for protein partitioning, which is restricted to dilute concentrations of spherical particles, may be extended to the more concentrated regime.

In the next section we will derive an expression for the Helmholtz free energy and the spinodal for the ternary mixture consisting of hard particles, polymers, and solvent molecules. Although this derivation is focused on the case in which the hard particles have a spherical shape, it is possible in any stage of the derivation to replace the spheres by nonspherical particles. The expressions given are valid for both spherical and nonspherical particles. Furthermore the generalization to multicomponent mixtures containing different hard particles and different linear polymers is straightforward.

A discussion of typical phase diagrams predicted by the present theory is also given.

Theory

The Ternary System: Lattice Polymers + Hard Spheres + Solvent Molecules. In the statistical thermodynamical description of mixtures, the interactions between all species of molecules have to be taken into account. For the ternary system hard spheres + polymers + solvent, the most difficult problem is the interaction between the hard sphere and the polymer. The polymer may become adsorbed on the surface of the sphere. However such an adsorption is accompanied by a considerable reduction of the number of possible polymer configurations and hence a reduction of the entropy. Obviously the free energy of such a mixture is the result of a delicate balance between the entropic and attractive forces.

Here we will derive an expression for the Helmholtz free energy for the general system hard particles + lattice polymers + solvent. The entropic part and the internal energy part of the free energy are treated separately. In principle it is possible to construct a more refined description on the basis of the theories given in refs 21 and 22, in which the interplay between entropic and energy effects is accounted for. However such a description, which is in study, is expected no longer to be simple.

The theory that we will present below is a lattice theory. In order to be able to describe the properties of the hard particles in terms of lattice sites, we have to express the properties of a single hard particle in these terms. For spherical particles this will be done in the appendix. Here we will give only two definitions which we will use frequently in the following sections. A lattice site which is located on the surface of a sphere is called a s-site, and a lattice site that does not belong to the sphere and which has one or more s-sites as a nearest neighbor will be called a f-site.

Entropy. First we calculate the entropy of the system. Consider a three-dimensional lattice which consists of N lattice sites. Each lattice site has z nearest neighbors, and the lattice constant is given by a. The volume of this system is equal to V. Within this lattice we place N_1 hard spheres with radius R. The centers of mass of the spheres do not need to coincide with a lattice point. The volume of a hard sphere encloses on average $v(>1)$ lattice sites. Thus the total number of sites that is enclosed by N_1 hard spheres is given by N_1v. The total number of possible configurations of the N_1 hard spheres is given by $\Omega(N_1,0,0)$. The actual value of $\Omega(N_1,0,0)$ is related to the entropy of the hard sphere system according to the familiar result of statistical mechanics:[39]

$$\Omega(N_1,0,0) = \exp(S_{HS}/k_B) \qquad (1)$$

Here k_B represents the Boltzmann constant. The entropy, S_{HS}, can be calculated from an equation of state for hard spheres. However the previous arguments also hold for nonspherical hard particles. Therefore we use the Boublik−Nezbeda equation of state for isotropic fluids of hard particles[30,31] and find the following:

$$\frac{S_{\mathrm{HP}}}{N_1 k_{\mathrm{B}}} = \frac{-3}{2} \ln T - \ln \eta + (1 - Q^2)\ln(1 - \eta) - \frac{(Q^2 + 3Q)\eta - 3Q\eta^2}{(1 - \eta)^2} + \text{const} \quad (2)$$

in which T denotes the temperature and the packing fraction of the hard particles η is given by

$$\eta = \frac{N_1 v}{N} \quad (3)$$

In eq 2 we have also introduced a geometrical factor, Q, which depends on the shape of the hard particle. In ref 30, an explicit expression for Q can be found. Here we will consider two examples. Equation 2 reduces to the entropy as predicted by the Carnahan–Starling equation of state for hard spheres[28,29] when $Q = 1$. For $Q = 1.5$, we have a equation of state for fused spheres which has a third virial coefficient which is accurate within 1.1%.[31]

For each of these hard particle configurations, there remain $N - N_1 v$ lattice sites that can be filled by N_2 polymer molecules which consists of m monomers and N_3 solvent molecules. There are $\Omega^*(N_2,0)$ ways to arrange the N_2 polymer molecules on the $N - N_1 v$ lattice sites. When all polymers are placed on the lattice, there is only one way to distribute the N_3 solvent molecules on the remaining free lattice sites. Thus $\Omega^*(N_2,N_3) = \Omega^*(N_2,0)$. It is possible to calculate the number of polymer configurations, $\Omega^*(N_2,N_3)$, using a Flory scheme[13,14,39] or a more sophisticated method.[15−17] Using this result, it is found that the total number of hard particle and polymer configurations is given by:

$$\Omega(N_1,N_2,N_3) = \Omega^*(N_2,N_3)\Omega(N_1,0,0) \quad (4)$$

With eq 4, it is possible to calculate the entropy of the mixture on its rudimentary form. Using the Flory scheme,[13,14,39] we find the following:

$$\frac{\Delta S'}{N k_{\mathrm{B}}} = \frac{S_{\mathrm{HS}}}{N k_{\mathrm{B}}} - \frac{\varphi_2}{m} \ln\left(\frac{\varphi_2}{\varphi_2 + \varphi_3}\right) - \varphi_3 \ln\left(\frac{\varphi_3}{\varphi_2 + \varphi_3}\right) \quad (5)$$

where we have introduced the polymer volume fraction $\varphi_2 = mN_2/N$ and the solvent volume fraction $\varphi_3 = N_3/N$. It should be noted that the volume fractions obey the sum rule $\eta + \varphi_2 + \varphi_3 = 1$.

In the derivation of eq 5, we have assumed that the spheres only occupy space and do not hinder the polymers. This is clearly an oversimplification, since a polymer is subject to a considerable reduction of the number of possible configurations when polymer segments have contacts with a surface. Now will we present a simple correction for this reduction.

A polymer segment that is in contact with the surface of a sphere has either 1, 2, or 3 surface sites of the sphere as nearest neighbor, depending on its location on the sphere. This is due to the lattice on which the system is defined. The average conformational entropy loss[23,40] associated with a single polymer segment on the sphere is given by:

$$k_{\mathrm{B}} L \equiv k_{\mathrm{B}} \ln\left(\frac{z - \alpha^* - 1}{z - 1}\right) = k_{\mathrm{B}} \sum_{i=1}^{3} \gamma_i \ln\left(\frac{z - i - 1}{z - 1}\right) \quad (6a)$$

Here we have introduced γ_i to represent the fraction of fluid sites around a sphere that has i contacts with the spheres. In the appendix we have calculated the value of α^* as a function of the radius of the sphere.

Similarly when a polymer segment makes contact with the surfaces of two different spheres, the average loss of conformational entropy is given by:

$$k_{\mathrm{B}} \ln\left(\frac{z - 2\alpha^* - 1}{z - 1}\right) \quad (6b)$$

However, we have found that the contribution of these configurations, which can be calculated using the contact value of the hard sphere pair correlation function,[31,41] does not affect the results of the calculations presented here. Therefore we neglect the contributions involving eq 6b. Then the total loss of the conformational entropy is given by:

$$\frac{S_{\mathrm{con}}}{N k_{\mathrm{B}}} = \varphi_{\mathrm{f},2} L \quad (7)$$

Here $\varphi_{\mathrm{f},2}$ is the volume fraction of the polymer segments that are located in the layer of f-sites. A simple assumption for the ratio of $\varphi_{\mathrm{f},2}$ and the volume fraction of f-sites, φ_{f}, is given by:

$$\frac{\varphi_{\mathrm{f},2}}{\varphi_{\mathrm{f}}} = \left(\frac{\varphi_2}{1 - \eta}\right)^x \quad (8)$$

In eq 8 we have introduced the parameter x. The case $x = 1$ corresponds to a homogeneous distribution of polymer segments over the $N - N_1 v$ lattice sites that are not occupied by the hard particles. The case $x = 2$ corresponds to a simple estimate[32] of the number of polymer segments in the first layer near a flat rigid wall. Equation 8 is of course a simplification of the depletion effects that have been found in polymer solutions near a rigid wall.[21−23,32] The same is true for the assumption that only the polymer segments in the first layer around the spheres contribute to the configurational entropy, S_{con}. Inclusion of more layers around the spheres makes the equation of state more complex. This will not be considered here.

The total entropy predicted by the present model is found by combining eqs 5 and 7:

$$\Delta S = \Delta S' + S_{\mathrm{con}} \quad (9)$$

Equation 9 differs in four aspects from the Flory-type excess entropy for the ternary polymer1 + polymer2 + solvent mixture. The first difference is caused by the fact that a sphere has no multiple internal configurations. This causes a considerable reduction of the entropy with respect to the polymer1 + polymer2 + solvent mixture. Second, the positions of the spheres are not restricted by the presence of the lattice. This causes an increase of the entropy with respect to the polymer1 + polymer2 + solvent mixture. The third difference is the reduction in the entropy due to S_{con}. Finally, the fourth difference is caused by the possibility of depletion effects near the surfaces of the hard particles. Such depletion effects are not found in the ternary solutions with two species of polymer chains.

Internal Energy. Next we calculate the contribution of the internal energy to the excess Helmholtz free energy. We assume an effective interaction between lattice sites that are nearest neighbors. When a site is occupied by (a part of) a molecule of species i and a nearest neighboring site is occupied by (a part of) a molecule of species j, then the interaction energy between these sites is given by e_{ij}. The description of polymer–polymer, polymer–solvent, and solvent–solvent interactions is the same as the one used in the theory of binary polymer + solvent mixtures. A simple Flory approach yields to a good approximation for the energy contribution of these interactions:

$$\frac{\Delta U'}{N} = \chi_{23} k_{\mathrm{B}} T \frac{\varphi_2 \varphi_3}{(1 - \eta)} \quad (10)$$

where χ_{23} is the usual Flory χ parameter[13,14,39] of the polymer + solvent system

$$\chi_{23} = \frac{z(2e_{23} - e_{22} - e_{33})}{2k_{\mathrm{B}} T} \quad (11)$$

Next we will focus our attention on the interactions in which the spherical particles are involved. A spherical particle interacts with its neighborhood via the lattice sites which are located on its surface. The lattice sites which are inside (and not on the surface of) the sphere do not contribute to the interaction energy. This implies that we have to estimate the total number of surface lattice sites (s-sites) of all the spherical particles and the number of their nearest neighbor sites outside the sphere (f-sites).

In Appendix A, we calculate $\langle n_s \rangle$ and $\langle n_f \rangle$, the average numbers of s- and f-sites for a single sphere. For a system with N_1 spheres, the total number of s- and f-sites is to a good approximation given by $N_i = N_1 \langle n_i \rangle$ (i = s, f). This corresponds to a volume fraction:

$$\varphi_i = \frac{N_i}{N} = \eta \frac{\langle n_i \rangle}{v} \ (i = s, f) \tag{12}$$

The total number of sites that contribute to the sphere–sphere contacts can be calculated using the contact value of the pair correlation function.[31,41,42] It turns out that this number is very small with respect to N_f. Therefore we will set this number equal to zero.

Next we consider the polymer–sphere contacts. The fraction of f-sites that are occupied by the polymer segments is given by eq 8. Then we find for the total number of sphere–polymer contacts:

$$N_{12}^* = \frac{\alpha_{sf}}{2} N_s \frac{\varphi_{f,2}}{\varphi_f} \tag{13}$$

In eq 13 we have introduced α_{sf}, the average number of contacts between a single s-site and its nearest neighbor f-sites. The value of α_{sf} is calculated in the appendix as a function of the sphere radius R.

The space that is not occupied by polymers and spheres is taken in by the solvent. So we find that the number of f-sites that are occupied by solvent molecules is given by:

$$N_{f,3} = N_f - N_{f,2} \tag{14}$$

Therefore, the total number of sphere–solvent contacts becomes

$$N_{13}^* = \frac{\alpha_{sf}}{2} N_s \frac{\varphi_{f,3}}{\varphi_f} \tag{15}$$

where $\varphi_{f,3}$ is given by $\varphi_{f,3} = \varphi_f - \varphi_{f,2}$ (see also eq 8).

Collecting the results, we find for the total contribution of the interaction energy:

$$\Delta U = k_B T \chi_{23} \frac{\varphi_2 \varphi_3}{(1 - \eta)} + \varphi_{12}^* e_{12} + \varphi_{13}^* e_{13} \tag{16}$$

where we have introduced the volume fractions $\varphi_{1j}^* = N_{1j}^*/N$. In eq 16 we have included the polymer–solvent, polymer–polymer, and solvent–solvent contributions given in eq 10.

Now we are able to present the expression for the Helmholtz free energy:

$$\Delta A = \Delta U - T\Delta S \tag{17}$$

where ΔS is given in eq 9.

Spinodal. With expression 17 for the Helmholtz energy, it is possible to make predictions of the phase behavior of a ternary mixture of lattice polymers + hard spheres + solvent molecules. When the volume of the system does not change during the phase transition, it is found that a ternary mixture is thermodynamically stable when:[43]

$$\mathrm{Sp}(\Delta A) \equiv \Delta A_{11} \Delta A_{22} - (\Delta A_{12})^2 > 0 \tag{18}$$

In eq 18 we have introduced the notation $\Delta A_{ij} = (\partial^2 \Delta A / \partial N_i \partial N_j)_N$. It should be noted that in explicit calculation of eq 18 the incompressibility condition $N_3 = N - N_1 v - N_2 m$ has to be taken into account.

First we will consider the entropic part of eq 18. When we apply the the spinodal condition to eq 5, we find the following:

$$\left(\frac{N}{k_B}\right)^2 \mathrm{Sp}(\Delta S') = v F(Q,\eta) \frac{\varphi_2 + \varphi_3/m}{\varphi_2 \varphi_3} \tag{19}$$

with

$$F(Q,\eta) = \frac{1 + (6Q - 2)\eta + (9Q^2 - 6Q + 1)\eta^2 - 4Q^2\eta^3 + Q^2\eta^4}{\eta(1 - \eta)^4}$$

Equation 19 is positive for all the physical realistic values of η, φ_2, and φ_3. As a result, no entropy-driven demixing can be found with the approximations that underlie eq 5.

This situation changes when we include the contribution of the configuration entropy. Using eqs 5–9 and 19, we find the following:

$$\left(\frac{N}{k_B}\right)^2 \mathrm{Sp}(\Delta S) = v F(Q,\eta) \left[\frac{\varphi_2 + \varphi_3/m}{\varphi_2 \varphi_3} - x(x - 1) \frac{\eta {\varphi_2}^{x-2} \langle \eta_f \rangle}{(1 - \eta)^x v} L \right] - \left(\frac{\langle n_f \rangle x {\varphi_2}^{x-1}}{(1 - \eta)^{x+1}} L \right)^2 \tag{20}$$

Here it should be noted that L, which is defined in eq 6a, always has a negative value. Therefore eq 20 can become negative only when the term proportional to L^2 cancels the other terms. This happens when the ratio $\langle n_f \rangle^2/v$ is sufficiently large (for given values of the shape factor Q and chain length m). Thus inclusion of the configurational entropy may give rise to entropy-driven demixing.

It is also possible to obtain an analytic expression for the spinodal condition of the Helmholtz free energy. Using eqs 16–18 and 20, we find the following:

$$\mathrm{Sp}(\Delta A) = k_B^2 T^2 \mathrm{Sp}(\Delta S) + \mathrm{Sp}(\Delta U) - k_B T \mathrm{Cr}(\Delta S, \Delta U) \tag{21}$$

with

$$\mathrm{Sp}(\Delta U) = \frac{-(\alpha e k_B T)^2}{N^2 (1 - \eta)^4}$$

and the cross-terms

$$\mathrm{Cr}(\Delta S, \Delta U) = \Delta S_{11} \Delta U_{22} + \Delta S_{22} \Delta U_{11} - 2\Delta S_{12} \Delta U_{12} = \frac{k_B T}{N^2} \left(4\chi_{23} v \frac{F(Q,\eta)}{1 - \eta} + \frac{2x\alpha e \langle n_f \rangle}{(1 - \eta)^4} \left(\frac{\varphi_2}{1 - \eta} \right)^{x-1} L \right)$$

where we have introduced $\alpha = \alpha_{sf} \langle n_s \rangle$ and $e = (e_{13} - e_{12})/k_B T$. The function $F(Q,\eta)$ is defined in eq 19.

For comparison we also give the expression of the spinodal of the ternary polymer1 + polymer 2 + solvent mixture:[19]

$$\left(\frac{1}{\varphi_1 m_1} + \frac{1}{\varphi_3} - 2\chi_{13} \right) \left(\frac{1}{\varphi_2 m_2} + \frac{1}{\varphi_3} - 2\chi_{23} \right) - \left(\frac{1}{\varphi_3} + \chi_{12} - \chi_{13} - \chi_{23} \right)^2 = 0 \tag{22}$$

The definition of the Flory interaction parameters χ_{ij} is similar to eq 11. This equation can only predict phase separation when at least one of the interaction parameters χ_{ij} is not equal to zero. In the following section, we will make comparisons of the predictions made by eqs 21 and 22.

Results

The spinodal condition as obtained in eqs 18–21 differs significantly from the spinodal predicted by the usual Flory theory for the ternary polymer1 + polymer2 + solvent mixture (eq 22). The most striking difference

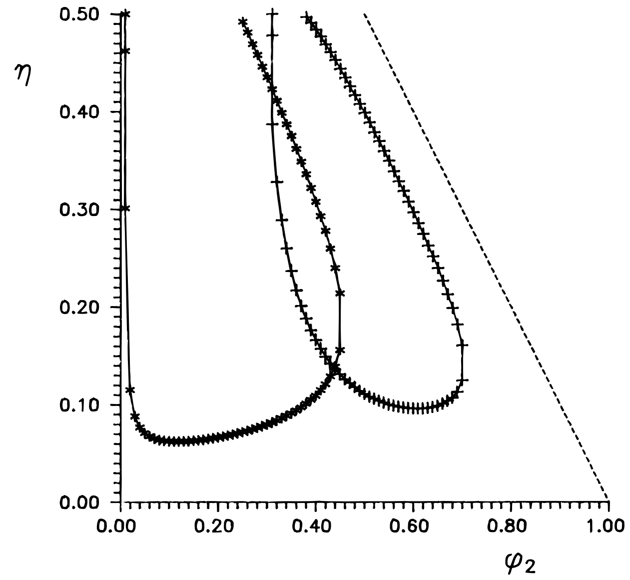

Figure 1. Phase diagram of the athermal ternary mixture hard spheres ($R = 5.25$) + lattice polymers ($m = 50$) + solvent for for two different distributions of polymer segments (see eq 8): homogeneous distribution ($x = 1$; *) and a single depletion layer ($x = 2$; +). The dashed line indicates $\eta + \varphi_2 = 1$.

is that the present equation of state is capable of predicting an entropy-driven phase separation, whereas in the Flory theory demixing only occurs as a result from an imbalance between the different energy parameters e_{ij} (see eq 11).

Essential for the entropy-driven demixing predicted by the present model is the configurational entropy, S_{con}, which depends on the number of polymer segments that are in direct contact with the surface of the hard particles. In the previous section, we considered two different assumptions for the distribution of the polymer segments. The first of these assumptions ($x = 1$ in eqs 8 and 20) states that the polymer segments are distributed homogeneously over the sites that are accessible for the polymers. This situation corresponds to the case in which depletion effects are absent. We also consider the case $x = 2$, which gives a simple estimate of the number of polymer segments in the first layer.[32] This estimate gives a rudimentary description of depletion. In Figure 1 it can be seen that the case without depletion has a stronger tendency to demix than the case with depletion. This is caused by the fact that there are more polymer segments in the first fluid layer when depletion is absent than in the case with depletion. As a result of this larger number of polymer segments in the first layer, there is a larger reduction of the configurational entropy with respect to the case with depletion. Comparison of Figure 1 with the results of ref 4 shows that the case $x = 1$ predicts the phase separation at polymer volume fractions that are at least 1 order of magnitude smaller than than the results of ref 4. For this reason we will consider in what follows only the case $x = 2$.

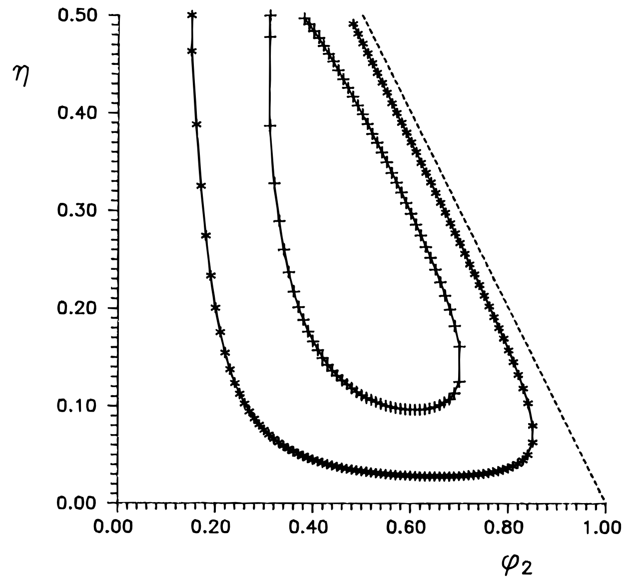

Figure 2. Phase diagram of the athermal ternary mixture hard spheres + lattice polymers ($m = 50$) + solvent for various hard sphere radii: $R = 5.25$ (+) and $R = 12$ (*). See also Figure 1.

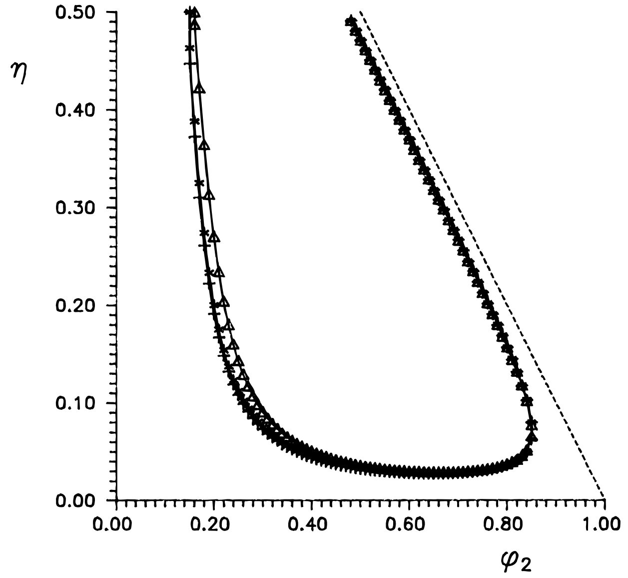

Figure 3. Phase diagram of the athermal ternary mixture hard spheres ($R = 12$) + lattice polymers + solvent for various chain lengths: $m = 10$ (△), $m = 50$ (*), and $m = 100$ (+). See also Figure 1.

We have seen that the entropy-driven phase separation is favored by large values of the ratio $\langle n_f \rangle^2/v$. Since the number of f-sites, $\langle n_f \rangle$, is a surface property, we have $\langle n_f \rangle \sim R^2$. Likewise, we have for the volume of a particle $v \sim R^3$, so we find $\langle n_f \rangle^2/v \sim R$, i.e., the present equation of state predicts entropy-driven phase separation for mixtures containing particles which are sufficiently large. Here it should be noticed that the ratio $\langle n_f \rangle^2/v$ is a property of the particles, independent of the actual number of polymer segments that are located in the layer of f-sites. In Figure 2 we give some phase diagrams which illustrate the influence of the hard sphere radius on the entropy-driven phase separation.

Another molecular parameter which influences the shape of the phase diagram is the chain length, m, of the polymer. The only part of the spinodal condition which depends on the chain length is given by eq 19. In Figure 3 it can be seen that increase of the chain length increases the tendency to demix, although this effect is not so pronounced as the effect that is caused by the change of the volume of the hard particle. This is because the spinodal becomes independent of the chain length for very large chains, as can be concluded from eq 21.

In Figures 1–3 it can be seen that the phase diagram exhibits a miscibility gap for certain chain lengths and sphere radii. The reason for this type of behavior can

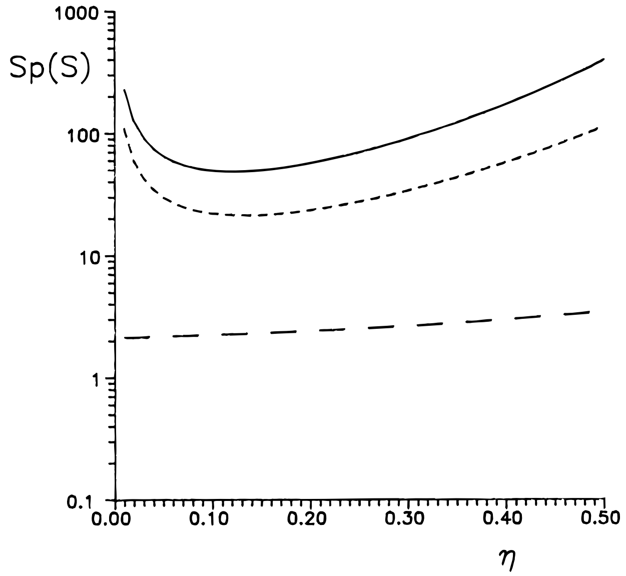

Figure 4. Sp($\Delta S'$) (eq 19; solid line), $F(\eta, Q = 1)$ (dotted line), and $(\varphi_2 + \varphi_3/m)/(\varphi_2\varphi)$ (dashed line) as a function of the volume fraction spheres, η.

be found when one considers eq 19. In this equation there are clearly two different identifiable parts: a hard sphere part

$$vF(Q = 1,\eta)$$

and a part that results from the presence of the polymer and solvent molecules

$$\frac{\varphi_2 + \varphi_3/m}{\varphi_2\varphi_3}$$

This latter part is a monotonic function, whereas the hard sphere contribution exhibits a minimum between $0.1 < \eta < 0.3$ (see Figure 4). When the contribution of the configurational entropy (eq 21) is also taken into account, then it is likely that the spinodal condition of the total entropy in the first instance has two zero points in the neighborhood of the minimum of $F(Q,\eta)$. What happens physically is the following. At low sphere volume fractions, η, the polymers and the spheres are completely miscible. As η increases, then it is possible that the system reaches a value for η at which the configurational entropy causes the system to demix. When η is increased still further, the contribution of the hard spheres to the entropy increases in importance. Under certain circumstances this may give rise to a complete miscibility of the spheres and the polymers at high η. This effect is known as restabilization.[25,33]

Clustering of particles is a frequently met phenomenon. For instance certain proteins can form stable dimers, depending on the solvent conditions, like temperature, pH, and added salt.[34,35] Here we will study how deviations of the spherical shape of the hard particles affect the tendency to phase separate.

Nonspherical particles have a larger surface/volume ratio than spherical particles. As a result there are more surface sites involved in the particle−polymer interactions when the particles of a given volume are taken to be unspherical. This gives rise to an increased tendency to undergo an entropy-driven phase separation. On the other hand, we find that the hard particle part, $F(Q,\eta)$, of the spinodal increases roughly by a factor of 1.8 as the spheres are replaced by fused spheres. This latter change enhances the tendency to mix. The change in phase behavior is determined by the competition between these two effects. Here it should be noted that the tendency to demix becomes larger as the spheres (and fused spheres) become larger. This is because the ratio $\langle n_f\rangle^2/v$, which determines whether or not entropy demixing occurs, is proportional to the radius of the spheres. We illustrate this change in demixing behavior by comparing the predictions of the present equation of state for a solution of spheres + polymers ($Q = 1$) and a solution of fused spheres + polymers ($Q = 1.5$). The volume of a fused sphere is taken to be equal to that of a single sphere. When the fused spheres are large enough, it is possible to apply the results concerning the lattice properties of a single sphere, as obtained in the appendix, also to the fused spheres. The loss of surface sites where the two spheres are fused together is estimated in Appendix B. In Figure 5 it is illustrated how the phase diagram changes when mixtures which contain fused spheres of volume v are considered instead of spheres with the same

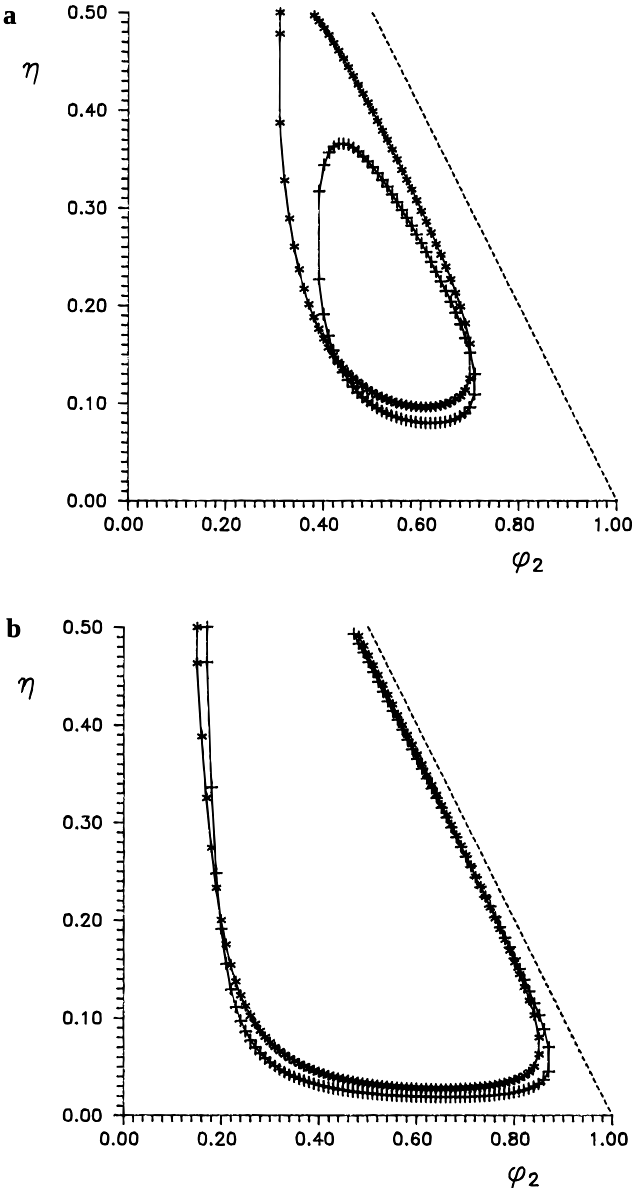

Figure 5. Comparison of the phase diagrams of the ternary mixtures spheres + polymers + solvent and fused spheres + polymers ($m = 50$) + solvents: (a) $R = 5.25$ (*), $R_{\mathrm{eff}} = 5.25$ (+) and (b) $R = 12$ (*), $R_{\mathrm{eff}} = 12$ (+). See also Figure 1.

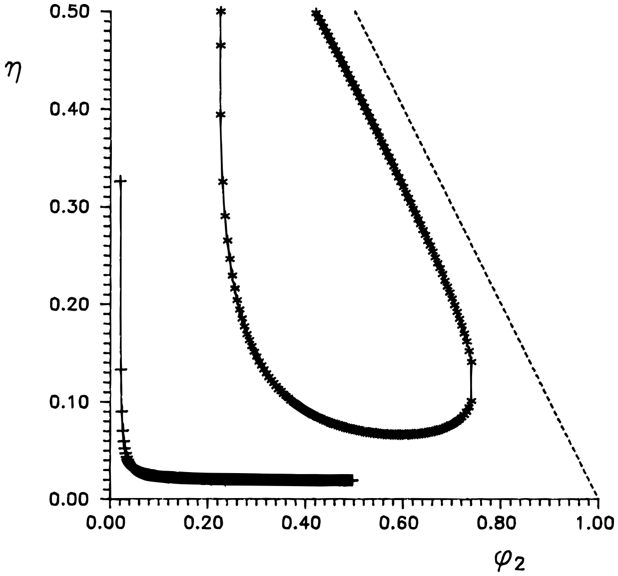

Figure 6. Comparison of the phase diagrams of the ternary mixtures spheres + polymers2 + solvent ($R = 5$, $v = 224$, $m_2 = 224$, $e_{12} = 0.05$; *) and polymers1 + polymers2 + solvents ($m_1 = 224$, $m_2 = 224$, $e_{12} = 0.05$; +). See also Figure 1.

volume. It can be seen that the changes in the phase diagram as a result from the change from spheres to fused spheres are rather drastic. For the mixture with the smaller spheres ($R = 5.25$), the change to fused spheres causes a decrease in demixing behavior, while for the mixtures with the larger spheres an increased demixing behavior is observed.

Next we consider the more complete spinodal in which the contribution of the internal energy is incorperated. Inspection of eq 21 shows that the demixing tendency is enhanced when $\chi_{23} > 0$ and/or $e < 0$. The case $\chi_{23} > 0$ corresponds to a poor solvent for the polymer. For the energy parameter $e = e_{13} - e_{12}$ are three different possibilities which give rise to $e < 0$: (1) The repulsion between the polymers and the hard particles dominates over the repulsion between the hard particles and the solvent, (2) the attraction between the hard particles and the solvent is larger than the attraction between the hard particles and the polymers, and (3) the hard particles and the solvent attract each other, while the hard particles and the polymers repel each other.

As a final example of the capabilities of the present equation of state, we will study how the phase diagram changes as the hard particle unfolds into a chain. The initial state is for instance a globular protein in a polymer solution, the final state is the denatured protein in the same solution. In order to model the polymer1 + polymer2 + solvent mixture, we use the Flory spinodal given in eq 22. First, when the interaction energies are negligible, we find that the states in which only hard particles or only polymers are present are completely mixed. In that case demixing only occurs when some of the spheres are denatured, and the phase diagram is similar to the ones given in Figures 2 and 3. Next we will consider what happens when there is a slight repulsion between the spheres and the polymers. Here we will consider a ternary system containing polymers which have a chain length that is equal to the volume, v, of the hard particles ($R = 5$; $v = 224$) and with a slight repulsion ($e_{12} = 0.05k_BT$; $k_BT = 1$) between the two species of molecules. The results of these calculations are given in Figure 6. It can be seen that the spinodal curve shifts to lower volume fractions as the sphere unfolds itself. This shift becomes larger as the volume of the hard particle or the interaction energy increases.

Discussion and Conclusions

We have presented a simple analytic equation of state for ternary mixtures containing hard particles, polymer, and solvent molecules. This equation of state is a combination of the Flory theory for polymers,[13,14,39] the Boublik−Nezbeda equation of state for the isotropic fluids of hard particles,[30,31] and a correction term for the reduction of the configurational entropy.[23,40]

We have chosen to use the Flory lattice theory because it allows, with the above-mentioned additional approaches, an explicit formulation of the spinodal. Simultaneously the excluded volume interaction between the polymer chains is taken into account. The validity of the Flory theory is expected to hold in the concentrated polymer regime. However, we know that Flory's theory fails quantatively in the so-called semidilute regime of the polymers.[32,44] In this regime the scaling approach would be a nice alternative. On the other hand, it must be realized that although the exponents of the scaling are well known, there is still a lack in knowledge in the proportionality constants of these laws. This impedes a straightforward development of spinodals along this route.

The choice of the Boublik−Nezbeda equation of state was inspired by the fact that it has, despite its simplicity, an exact second virial coefficient and a third virial coefficient that is either exact (for hard convex particles) or almost exact (within 1.1% for dumbbells).[30,31] Therefore the Boublik−Nezbeda equation is superior in comparison to an excluded volume treatment[14,37] which predicts an incorrect third virial coefficient. A disadvantage of the Boublik−Nezbeda equation is that it is not capable to predict the transition to crystalline or liquid crystalline states. The fluid−solid transition of hard spheres takes place at a volume fraction, $\eta = 0.49$.[41,42] Therefore we have not considered systems which have hard particle volume fractions that are larger than 0.5. The use of the Boublik−Nezbeda equation has enabled us to show that the shape of the hard particle can have an effect on the phase equilibria. A similar observation was made by Asakura and Oosawa,[3] using a different theory.

In order to estimate the reduction of the configurational entropy, we have used a simple model in which only one layer of fluid sites around the hard particles is taken into account. This is of course a very simplified representation of the real situation in which depletion effects are to be expected which extend over several fluid layers. In principle it is possible to achieve a more complete description of the depletion effect. However such a description would no longer be simple. The first aim of the present paper is the presentation of the simplest version of this theory.

In our estimate of the reduction of the configurational entropy, we have considered two cases: (1) the homogeneous distribution of polymer segments in the space that is not occupied by the hard particles ($x = 1$ in eqs 8 and 20) and (2) a simple estimate distribution of polymer segments in the first fluid layer due to depletion ($x = 2$). We have found that the depletion free model ($x = 1$) has stronger tendency to demix than the model with depletion. In fact it demixes at polymer volume fractions that are 1 order of magnitude smaller than the calculated coexistence curves presented in ref

4. For this reason we have mainly considered the model with a simple description of depletion.

It would be of interest to make a comparison of the predictions of our theory with recent simulation results concerning the phase behavior of mixtures containing hard spheres and ideal lattice polymers.[26] Within the Flory formalism, ideal polymers are best mimicked under θ conditions (i.e., $\chi_{23} = 0.5$). However, even then a comparison with ref 26 is difficult because in ref 26 a single lattice site can be occupied by several polymer segments. Therefore the system studied in ref 26 does not obey the incompressibility condition $N = N_1 v + N_2 m + N_3$. Such an incompressibility condition is inherent to a Flory scheme, like the one we have presented in the previous sections. This discrepancy implies that the chemical potentials, μ_i, of the system studied in ref 26 are completely different from the chemical potentials that follow from our theory. Therefore it is not possible to make a direct comparison with ref 26, where the phase diagrams are expressed as functions of η and $z = \exp(\mu_2)$.

Most of the theories developed so far for the ternary hard sphere + polymer + solvent mixture are restricted to the case in which the hard spheres are large with respect to the polymer molecules.[3−6] These theories are bound to fail in the case where the hard particles are so small that they are able to penetrate the polymer molecules to some extent. On the other hand, the theory of Abbott et al.[37,38] for protein partitioning in polymer solutions is restricted to the situation in which the concentration of hard particles is very small. The equation of state we have presented here predicts that the spinodal becomes independent of the length of the polymer chains, when these chains are sufficiently large. Such independence of the chain length is recently observed in BSA + dextran[10] and whey isolate + dextran solutions.[11] Although the phase separations in mixtures of hard spheres, solvent, and large polymers and mixtures which contain short polymers are usually treated separately, it is likely that these are limiting cases which can be approached from a single physical picture. The theory presented here should not be considered as the conclusive answer to the problems concerning the phase behavior of these mixtures. It is more a stepping stone toward an integrated description of ternary mixtures consisting of hard particles + solvent + either long or short polymers. The first improvement of the present theory should be the a priori calculation of the polymer segment distribution in the first few fluid layers around the hard particles, using a modification of existing theories for polymer solutions near a flat rigid surface.[21−23,32] Then it would be no longer necessary to use a descriptive parameter in order to account for the depletion effects. Work along this route is presently in progress.

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Appendix A: Single Sphere in the Lattice

A single hard sphere interacts via its surface with its surrounding. In our case the surrounding is a lattice on which lattice polymers and solvent molecules are located. Therefore it is necessary to express the physical properties of the surface of the sphere in terms of the lattice. This will be done in this appendix.

Table A1. Number of s-Sites, $\langle n_s \rangle$, and f-Sites, $\langle n_f \rangle$, and Thickness of the Layer of s-Sites, d_s, and f-Sites, d_f, as a Function of the Radius of the Sphere

R	$\langle n_s \rangle$	$\langle n_f \rangle$	d_s	d_f
2.5	43.7	69.0	0.8810	0.7129
5.0	224.1	285.4	0.8535	0.7827
7.5	533.8	630.3	0.8479	0.8032
10.0	974.0	1106.1	0.8446	0.8126
12.5	1544.5	1711.8	0.8421	0.8173
15.0	2245.2	2447.4	0.8403	0.8200
17.5	3076.5	3313.6	0.8390	0.8219
20.0	4038.6	4310.5	0.8381	0.8232
25.0	6354.3	6695.8	0.8368	0.8250
30.0	9191.7	9602.7	0.8358	0.8261
35.0	12 551.5	13 031.9	0.8352	0.8269
40.0	16 433.1	16 982.9	0.8347	0.8275
50.0	25 763.5	26 451.9	0.8340	0.8282
75.0	58 224.6	59 259.4	0.8330	0.8293
100.0	103 732.0	105 113.2	0.8326	0.8297
200.0	416 076.1	418 842.2	0.8318	0.8304

Table A2. Average Number of Contacts of a s-Site with Neighboring f-Sites, α_{sf}, a f-Site with Neighboring s-Sites, α_{fs}, and a f-Site with Neighboring f-Sites, α_{ff}, and the Effective Factor, α^*, Needed for the Calculation of the Entropy Correction as a Function of the Sphere Radius

R	α_{sf}	α_{fs}	α_{ff}	α^*
2.5	2.382	1.401	2.023	1.453
5.0	2.071	1.601	2.178	1.690
7.5	1.976	1.664	2.257	1.763
10.0	1.931	1.696	2.295	1.799
12.5	1.905	1.716	2.316	1.822
15.0	1.887	1.730	2.329	1.837
17.5	1.875	1.740	2.339	1.848
20.0	1.866	1.747	2.346	1.857
25.0	1.854	1.758	2.355	1.869
30.0	1.845	1.766	2.361	1.877
35.0	1.839	1.771	2.365	1.883
40.0	1.835	1.775	2.369	1.888
50.0	1.829	1.781	2.374	1.894
75.0	1.821	1.789	2.379	1.902
100.0	1.817	1.793	2.382	1.907
200.0	1.811	1.799	2.386	1.913

We will use a numerical scheme in which the sphere is placed randomly in the lattice. Then the properties of the surface are examined for this particular position of the sphere in the lattice. The results presented here are averaged over 1000 different positions of the sphere. This procedure is applied for spheres with a diameter that varies between $5 \leq 2R \leq 400$ lattice units.

We have determined the following properties: (1) the number of s-sites, $\langle n_s \rangle$, (2) the number of f-sites, $\langle n_f \rangle$, (3) the volume of the sphere, v (which should obey $v = 4\pi R^3/3$), (4) the number of single, double, and triple contacts between the f- and s-sites (as viewed from the layer of f-sites), and (5) the number of f-sites that are also the nearest neighbor of another f-site.

The results of the evaluation of 1−5 are given in Tables A1 and A2.

The results of 1−3 can be used to calculate the average thickness of the layers with s- and f-sites:

$$d_s = \left(\frac{3}{4\pi}\right)^{1/3} (v^{1/3} - (v - \langle n_s \rangle)^{1/3}) \qquad \text{(a1)}$$

$$d_f = \left(\frac{3}{4\pi}\right)^{1/3} ((v + \langle n_f \rangle)^{1/3} - v^{1/3}) \qquad \text{(a2)}$$

Next we consider the contacts between the different sites. It is easy to show for two spheres in contact that

Table A3. Fit Parameters Needed for the Calculation of α_{sf}, α_{fs}, α_{ff}, α^*, d_s, and d_f Using Eq a5

y	a	b	c
α_{sf}	1.804 333 42	1.210 061 66	0.586 972 40
α_{fs}	1.801 492 24	−1.056 861 14	0.147 866 60
α_{ff}	2.397 177 51	−1.119 284 95	0.445 754 62
α^*	1.915 732 42	−1.146 958 62	−0.019 349 98
d_s	0.831 925 56	0.115 323 62	0.016 083 33
d_f	0.832 162 93	−0.174 090 67	−0.312 700 04

the number of contacts between their s-sites depends on the orientation of the vector that links the centers of masses of the spheres, with respect to the axes of the lattice. A similar directional preference can be found in the interaction between a sphere and a polymer segment (or solvent molecule). This directional preference is an artifact of the lattice. In order to avoid it, we treat the s- and f-sites in mean-field approximation. For the calculation of the interaction energies, we need to know the average number of contacts between a single s-site and the neighboring f-sites. This can be found by combining the results of 1 and 4. For the correction factor, α^*, needed for the calculation of the reduction of the configurational entropy due to polymer segments present in the first fluid layer around the sphere, we also need the results of 4 (see eq 6).

The results of 5 are needed when a better description of the entropy is made on basis of the theories of Helfand[22] or Scheutjens and Fleer.[21] Not shown in the tables are the results concerning α_{fg}, the number of contacts between a f-site and sites which are located in the second fluid layer around the sphere. However, these can be easily extracted from:

$$\alpha_{fg} = 6 - \alpha_{fs} - \alpha_{ff} \tag{a4}$$

The results presented in Tables A1 and A2 can be easily represented by a second-order polynomial:

$$y = a + b\left(\frac{1}{R}\right) + c\left(\frac{1}{R}\right)^2 \tag{a5}$$

The fit parameters a−c are presented in Table A3. This fit equation reproduces the results of Tables A1 and A2 within 1%. Equation a5 can also be used to extrapolate the lattice properties to spheres with radius $R > 200$. The accuracy of such an extrapolation can be estimated by comparing the values of the coefficient a for the pair α_{sf} and α_{fs}, which should become equal in the limit of infinitely large spheres. A similar statement also holds for the pair d_{sf} and d_{fs}.

Appendix B: Contact Region of Fused Spheres

Consider two spheres (with radius R) which are in contact. The lattice sites that form the surface of the spheres are assumed to be distributed homogeneously over the surface layer. On this manner we remove any trivial effects which are related with the orientation of the spheres in the lattice. The contact region of sphere 1 is defined to be that part of the surface layer of sphere 1 in which the s-sites of molecule 1 has an s-site of sphere 2 as a nearest neighbor. We estimate the reduction of the number of f-sites due to a contact region using the formula for the overlap volume of two different spheres with radii R_1 and R_2:

$$V_{ov} = \frac{\pi}{12a}[-3(R_1^2 - R_2^2)^2 + 8(R_1^3 + R_2^3)a - 6(R_1^2 + R_2^2)a^2 + a^4] \tag{b1}$$

where a represents the separation between the centers of masses of the spheres. In order to calculate the contact region of sphere 1, we have $a = 2R$, $R_1 = R$, and $R_2 = R + d_f$. On a similar manner, the contact region of sphere 2 can be calculated. So we find for the reduction of f-sites:

$$\langle n_f\rangle_c = \frac{\pi}{12}\left(\frac{d_f}{R}\right)^2(4R^3 - Rd_f^2 - d_f^3) \tag{b2}$$

The total number of f-sites around a fused sphere is given by:

$$\langle n_f\rangle_{\text{fused sphere}} = 2\langle n_f\rangle_s - \langle n_f\rangle_c \tag{b3}$$

where $\langle n_f\rangle_s$ is the number of f-sites around a single sphere that is one-half of the fused sphere. It can be seen from eq b3 that the correction term becomes negligibly small for large spheres.

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