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Born–Green–Yvon Treatment of Concentrated Polymer Solutions

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ABSTRACT: The thermodynamics and configurational statistics of a concentrated polymer solution are treated by using the Born–Green–Yvon integral equation approach, and equations are derived for thermodynamic mixing quantities, including the noncombinatorial contribution to the entropy of mixing. These incorporate terms arising from bare potential interactions and correlations through third bodies. Using these results we investigate the shifts in the upper critical solution temperature as a function of the energy parameters.

I. Introduction

Developments in the theoretical treatment of concentrated polymer solutions have lagged behind those in the theory of small-molecule solutions. There are two major approaches in analyzing experimental data on polymer solutions. Flory–Huggins theory,[1] the polymer analogue of regular solution theory, is a lattice model in which expressions for the energy (ΔU_{mix}) and combinatorial entropy ($\Delta S_{\text{mix}} = \Delta S_c$) of mixing are formulated, assuming that the components are randomly mixed on the lattice. The free energy of mixing (ΔA_{mix}) is given by

$$\Delta A_{\text{mix}} = \beta^{-1}(s \log \phi_1 + N \log \phi_2 + \chi s \phi_2) \qquad (1)$$

where β is the inverse temperature in energy units, s is the number of solvent molecules, N is the number of polymer chains (each of which has n monomers), ϕ_1 and ϕ_2 are the volume (site) fractions of solvent and monomer, respectively, and χ, the interaction parameter, is defined by

$$\chi = \Omega\beta(\epsilon_{12} - {}^1\!/_2\epsilon_{11} - {}^1\!/_2\epsilon_{22}) \qquad (2)$$

Ω is the coordination number of the lattice and ϵ_{22}, ϵ_{12}, and ϵ_{11} are the monomer–monomer, monomer–solvent, and solvent–solvent interaction energies for the different kinds of nearest-neighbor interactions on the lattice.

Modifications to Flory–Huggins theory have involved more sophisticated estimates of ΔS_c[2] and, in particular, considering the ϵ's to be free, rather than potential, energies.[3] The latter tactic enables χ to be divided into an entropic (χ_S) and an enthalpic (χ_H) component; the former is taken to be a correction term representing the noncombinatorial contributions to ΔS_{mix}, while the latter is related to ΔH_{mix}. Often, however, χ_S is greater in magnitude than χ_H, and a molecular interpretation for χ_S has remained a problem.

Flory–Huggins theory is easy to apply and has been widely used in analyzing experimental data, yet it fails to explain one interesting property of polymer solutions: the second critical point (the lower critical solution temperature) which is reached upon raising the temperature of the mixture.

This phenomenon has been qualitatively understood by considering the large differences in thermal expansivities of the two components. Two theories, similar in appearance, have evolved, and both attempt to quantify this important feature. Corresponding states theory, developed by Prigogine et al.[4] and extended and widely applied by Patterson and co-workers,[5] was the first, but a later description of Flory[6] has been more widely used. In both treatments the pure and mixed components obey the same reduced equation of state, and the solution is assumed to be randomly mixed. The advantage of Flory's approach is that he relates the reduction parameters to experimentally determinable properties such as the density and thermal expansion and pressure coefficients of the pure components. One or two adjustable parameters are used, and the expressions for the various thermodynamic quantities contain terms which, separately, reflect the contact energy and free volume differences of the two components. A volume change on mixing is therefore incorporated and produces a negative (temperature-dependent) contribution to both ΔU_{mix} and ΔS_{mix}. The result is[7] that as the temperature is increased $-T\Delta S_{\text{mix}}$ becomes positive and eventually dominates, therefore yielding a positive ΔA_{mix} and hence a second critical point.

The equation-of-state theories have been successful in predicting trends and properties which the random-mixing description does not reflect; a drawback is that these treatments yield little insight on the molecular level as to the nature of the interactions which give rise to the bulk properties of the solution.

Detailed microscopic descriptions do exist for a single chain; a major advance in this area was the work of Edwards,[8] who considered the "growth" of a chain as a diffusion process in a field which, in turn, is generated by the presence of the other monomers. Recall that the mean square end-to-end length of a linear polymer has the asymptotic behavior

$$\langle R_n^2 \rangle \sim n^{2\nu} \qquad (3)$$

where $\nu = {}^3\!/_5$ for a single chain in a good solvent. The

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result is valid for $c < c^*$, where c^* represents the local concentration experienced by a monomer in an isolated coil. Above c^*, $\nu = {}^1/_2$ and, on the right side of eq 3, there appears a multiplicative function of concentration.[9] Several alternative derivations of the Edwards result followed,[10] and these were all subsequently reconciled by using integral equation methods. There are a number of such techniques[11] and the one which we shall use is the Born–Green–Yvon (BGY) method, the formalism of which will be outlined in the next section. The starting point is a linked hierarchy of distribution functions which provides an exact configurational description of the system. The objective of these approaches is to produce an expression for the pair distribution function and then make use of this to calculate thermodynamic or configurational properties. For example, the probability density of finding two particles within volume elements $d\vec{r}_1$ and $d\vec{r}_2$ about $\vec{r}_1$ and $\vec{r}_2$, respectively, is given (in the canonical ensemble) by

$$p_2(\vec{r}_1,\vec{r}_2) = \frac{\lambda^N}{(N-2)!}\,\frac{\int\cdots\int (d\vec{r}^N/d\vec{r}_1\,d\vec{r}_2)\exp(-\beta U(\vec{r}^N))}{Q(N,V,T)} \tag{4}$$

where Q is the canonical partition function, N is the number of (identical) particles, $U(\vec{r}^N)$ is the total intermolecular potential, and λ is a constant which arises out of the integration over momentum coordinates. Then, if we ignore the momentum terms (being eventually interested in the differences in state functions)

$$U = \frac{2\pi N}{\rho}\int_0^\infty dr_{12}\, r_{12}^2 p_2(\vec{r}_1,\vec{r}_2)\phi(\vec{r}_{12}) \tag{5}$$

where ρ is the number density, r_{12} is the distance, and $\phi(r_{12})$ is the pair potential between particles at $\vec{r}_1$ and $\vec{r}_2$. U can then be integrated with respect to $1/T$ to obtain the free energy. For the case of a solution, the entropy of mixing (ΔS_{mix}) is then given by

$$\Delta S_{\text{mix}} = \Delta S|_{T=\infty} + (\Delta U/T) - \int_0^{1/T}\Delta U(1/T)\, d(1/T) \tag{6}$$

At high temperatures ($T \to \infty$) it is reasonable to assume that the solution is randomly mixed and we use a combinatorial estimate (ΔS_c) for $\Delta S|_{T=\infty}$. In this paper we use the Flory–Huggins expression for ΔS_c but more sophisticated approximations[2] could be used, and an expression for the noncombinatorial contribution (ΔS_{nc}) to the entropy of mixing is then just obtained from $\Delta S_{\text{mix}} - \Delta S_c$.

The work on polymer solutions presented here is an extension of a BGY description for a single chain which evolved over the course of several papers[12-14] by Whittington and co-workers. The authors were able to clarify the relationship between previous results (for $c < c^*$) by showing that the different values for ν in eq 3 could be obtained by making different approximations in truncating the BGY hierarchy. Other integral-equation techniques have been used to investigate some of the thermodynamic and configurational properties of an isolated ring polymer,[15] and the configurational properties of an isolated linear chain.[16]

Fixman and Peterson[17] have studied the crossover from the dilute to semidilute regimes using a BGY treatment in which the polymer *molecules* are considered effectively as point particles. The interpolymer interaction is approximated by using a Flory–Krigbaum potential.

In this paper we use the BGY approach to study a two-component polymer solution. Thus, we start with an exact configurational description of the system and, through the application of well-defined approximations, are able to increase systematically the range and complexity of interparticle correlations. This work makes clear exactly what approximations will recover the random-mixing and Edwards[18] results for $c > c^*$.

Section II covers the formalism and the configuration of a polymer chain in solution. In section III we derive approximate but analytic expressions for the thermodynamic quantities and examine the effects of contributions to the pair correlation function which arises from first the bare potential and then third-body terms. In section IV we present some numerical results and discuss the different approximations used.

II. Formalism and Configuration of a Single Chain

We consider a solution consisting of N linear polymer chains, each having n monomers, and s solvent molecules. We write the total number of particles as $N_0 = s + nN$. The configurational partition function (Z) in the canonical ensemble is given by

$$Z = \int d\vec{r}^{N_0}\exp[-\beta U(\vec{r}^{N_0})] \tag{7}$$

where the potential energy U is given by the sum of pair-wise additive terms.

$$\begin{aligned} U = {} & \sum_{M=1}^{N}\sum_{i=2}^{n} \upsilon(\vec{r}_{iM} - \vec{r}_{(i-1)M}) + \sum_{M=1}^{N}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} u(\vec{r}_{iM} - \vec{r}_{jM}) + \\ & \sum_{L=1}^{N-1}\sum_{M=L+1}^{N}\sum_{i=1}^{n}\sum_{j=1}^{n} u(\vec{r}_{iL} - \vec{r}_{jM}) + \sum_{M=1}^{N}\sum_{i=1}^{n}\sum_{j=1}^{s} q(\vec{r}_{iM} - \vec{r}_j) + \\ & \sum_{k=1}^{s-1}\sum_{l=k+1}^{s} w(\vec{r}_k - \vec{r}_l) \end{aligned} \tag{8}$$

υ is a connectivity potential, acting between first-neighbor monomers on the same chain, and u, q, and w are respectively the monomer–monomer, monomer–solvent, and solvent–solvent interaction potentials. Here $\vec{r}_k$ is the position of the kth solvent particle and $\vec{r}_{iM}$ is the position of the ith monomer on the Mth polymer chain.

The probability that the two monomers labeled iL and jM are in volume elements $d\vec{r}_{iL}$ and $d\vec{r}_{jM}$ about $\vec{r}_{iL}$ and $\vec{r}_{jM}$ is $p_2(\vec{r}_{iL},\vec{r}_{jm})\, d\vec{r}_{iL}\, d\vec{r}_{jm}$ where

$$p_2(\vec{r}_{iL},\vec{r}_{jM}) = Z^{-1}\int (d\vec{r}^{N_0}/d\vec{r}_{iL}\, d\vec{r}_{jM})\exp(-\beta U(\vec{r}^{N_0})) \tag{9}$$

The response of the system to a perturbation in the location of the monomer labeled iL is given by the gradient with respect to $\vec{r}_{iL}$ of p_2, so that

$$\begin{aligned} -\beta^{-1}\nabla_{iL}p_2(\vec{r}_{iL},\vec{r}_{jM}) = {} & p_2(\vec{r}_{iL},\vec{r}_{jM})\nabla_{iL}u(\vec{r}_{iL} - \vec{r}_{jM}) + \\ & \int d\vec{r}_{(i-1)L}\, p_3(\vec{r}_{iL},\vec{r}_{(i-1)L},\vec{r}_{jM})\nabla_{iL}\upsilon(\vec{r}_{(i-1)L} - \vec{r}_{iL}) + \\ & \int d\vec{r}_{(i+1)L}\, p_3(\vec{r}_{iL},\vec{r}_{(i+1)L},\vec{r}_{jM})\nabla_{iL}\upsilon(\vec{r}_{(i+1)L} - \vec{r}_{iL}) + \\ & \sum_f \int d\vec{r}_{fL}\, p_3(\vec{r}_{iL},\vec{r}_{fL},\vec{j}_{M})\nabla_{iL}u(\vec{r}_{fL} - \vec{r}_{iL}) + \\ & \sum_S\sum_f \int d\vec{r}_{fS}\, p_3(\vec{r}_{iL},\vec{r}_{fS},\vec{r}_{jM})\nabla_{iL}u(\vec{r}_{fS} - \vec{r}_{iL}) + \\ & \sum_k \int d\vec{r}_k\, p_3(\vec{r}_{iL},\vec{r}_k\vec{r}_{jM})\nabla_{iL}q(\vec{r}_k - \vec{r}_{iL}) \end{aligned} \tag{10}$$

Note that the effect of moving one of the two particles in question is to create a restoring force on that particle. This arises in part from the direct interaction between the two monomers, as embodied in the first term on the right-hand side, and in part from interactions through a third body, the latter being either another monomer or a solvent molecule.

We shall first consider the configurational properties of a single chain, and the starting point will be eq 10 with $iL = nL$ and $jM = 1L$; the third term on the right-hand side of eq 10 will therefore not contribute. The objective is to understand how the different molecular interactions affect the position of monomer nL given that of $1L$. Having decided to work at the level of pairwise correlations, we shall need another expression for the triplet probability density (p_3), which will necessarily be approximate. In the connectivity term p_3 can be rewritten in terms of conditional probabilities, and

$$\begin{aligned} p_3(\vec{r}_{nL},\vec{r}_{(n-1)L},\vec{r}_{1L}) &= p(\vec{r}_{nL}|\vec{r}_{(n-1)L},\vec{r}_{1L})p(\vec{r}_{(n-1)L}|\vec{r}_{1L})p(\vec{r}_{1L}) \\ &\approx p(\vec{r}_{nL}|\vec{r}_{(n-1)L})p(\vec{r}_{(n-1)L}|\vec{r}_{1L})p(\vec{r}_{1L}) \end{aligned} \tag{11}$$

where we have made use of a Markov approximation in going from the first line to the second.

In the remaining terms which contain p_3, the triplet function is decomposed into a product of pair functions by using the Kirkwood superposition approximation, for example

$$p_3(\vec{r}_{1L},\vec{r}_{nL},\vec{r}_{fS}) \approx \frac{p_2(\vec{r}_{1L},\vec{r}_{nL})p_2(\vec{r}_{nL},\vec{r}_{fS})p_2(\vec{r}_{fS},\vec{r}_{1L})}{p(\vec{r}_{1L})p(\vec{r}_{fS})p(\vec{r}_{nL})} \tag{12}$$

Equation 10 therefore becomes

$$\begin{aligned} \beta^{-1}\nabla_{nL}p_2(\vec{r}_{1L},\vec{r}_{nL}) = -p_2(\vec{r}_{1L},\vec{r}_{nL})\nabla_{nL}u(\vec{r}_{1L}-\vec{r}_{nL}) - \\ p(\vec{r}_{1L})\int \mathrm{d}\vec{r}_{(n-1)L}\, p(\vec{r}_{nL}|\vec{r}_{(n-1)L})p(\vec{r}_{(n-1)L}|\vec{r}_{1L}) \times \\ \nabla_{nL}v(\vec{r}_{(n-1)L}-\vec{r}_{nL}) - \\ \sum_f \int \mathrm{d}\vec{r}_{fL}\, \frac{p_2(\vec{r}_{1L},\vec{r}_{nL})p_2(\vec{r}_{1L},\vec{r}_{fL})p_2(\vec{r}_{fL},\vec{r}_{nL})}{p(\vec{r}_{1L})p(\vec{r}_{fL})p(\vec{r}_{nL})}\nabla_{nL}u(\vec{r}_{fL}-\vec{r}_{nL}) - \\ \sum_S\sum_f \int \mathrm{d}\vec{r}_{fS}\, \frac{p_2(\vec{r}_{1L},\vec{r}_{nL})p_2(\vec{r}_{1L},\vec{r}_{fS})p_2(\vec{r}_{fS},\vec{r}_{nL})}{p(\vec{r}_{1L})p(\vec{r}_{fS})p(\vec{r}_{nL})} \times \\ \nabla_{nL}u(\vec{r}_{fS}-\vec{r}_{nL}) - \\ \sum_k \int \mathrm{d}\vec{r}_k\, \frac{p_2(\vec{r}_{1L},\vec{r}_{nL})p_2(\vec{r}_{1L},\vec{r}_k)p_2(\vec{r}_k,\vec{r}_{nL})}{p(\vec{r}_{1L})p(\vec{r}_k)p(\vec{r}_{nL})}\nabla_{nL}q(\vec{r}_k-\vec{r}_{nL}) \end{aligned} \tag{13}$$

In order to make the integrals tractable this equation is further simplified by using the independence approximation for $p_2(\vec{r}_{1L},\vec{r}_{nL})$ in the last three terms on the right-hand side i.e.

$$p_2(\vec{r}_{1L},\vec{r}_{nL}) = p(\vec{r}_{1L})p(\vec{r}_{nL}) \tag{14}$$

and the result is that in each of these terms, as in the connectivity term, the position of monomer nL will depend only indirectly on that of monomer $1L$, through a third body which is another monomer or a solvent molecule.

We now must specify the forms of the different potentials; the connectivity potential is chosen such that $p(\vec{r}_{nL}/\vec{r}_{(n-1)L})$ is nonzero only when the connected pair are a bond distance (a) apart

$$v(r) = \beta^{-1}\delta(|\vec{r}| - a) \tag{15}$$

where $\vec{r}$ is the vector between the two particles. Also

$$u(\vec{r}) = \beta^{-1}\delta(\vec{r})\int \mathrm{d}\vec{r}\, [\exp(\beta u(\vec{r})) - 1] = \beta^{-1}\delta(\vec{r})y_u \tag{16}$$

$$q(\vec{r}) = \beta^{-1}\delta(\vec{r})y_q \tag{17}$$

where y_u and y_q represent the excluded volume which is a result of monomer–monomer and monomer–solvent interactions. When one makes the appropriate substitutions into eq 13 and uses the symmetry of the distribution functions about the origin, the resulting expression is

$$\begin{aligned} p(\vec{r}_{nL}|\vec{r}_{1L}) = \int \mathrm{d}\vec{r}_{(n-1)L}\, p(\vec{r}_{(n-1)L}|\vec{r}_{1L})p(\vec{r}_{nL}|\vec{r}_{(n-1)L}) - \\ y_u p(\vec{r}_{nL}|\vec{r}_{1L})|_{\vec{r}_{nL}=\vec{r}_{1L}} - y_u\sum_f p(\vec{r}_{fL}|\vec{r}_{1L})p(\vec{r}_{nL}|\vec{r}_{fL})|_{\vec{r}_{nL}=\vec{r}_{fL}} - \\ y_u\sum_S\sum_f p(\vec{r}_{fS}|\vec{r}_{1L})p(\vec{r}_{nL}|\vec{r}_{fS})|_{\vec{r}_{nL}=\vec{r}_{fS}} - \\ y_q\sum_k p(\vec{r}_k|\vec{r}_{1L})p(\vec{r}_{nL}|\vec{r}_k)|_{\vec{r}_{nL}=\vec{r}_k} \end{aligned} \tag{18}$$

The probability of finding the last monomer in the Lth chain at $\vec{r}_{nL}$, given the first monomer $1L$ at $\vec{r}_{1L}$, can be thought of in terms of successfully completing an n-step self-avoiding walk (SAW). The first term on the right-hand side of eq 18 is the chain-propagating term which, given the positions of the first and next-to-last monomers, adds monomer nL onto the chain at $\vec{r}_{nL}$. The effect of all of the other terms is to reduce the probability of completing the n-step walk, taking into account the other particles which may already be occupying the desired position. If $\vec{r}_{1L} = \vec{r}_{nL}$, then placing monomer nL there would yield an (n −1)-step polygon; if $\vec{r}_{fL} = \vec{r}_{nL}$, the results would be a "tadpole", with the loop being made up of monomers fL to nL and the tail composed of monomers $1L$ to $(f - 1)L$. Similarly, a monomer from a different chain, or a solvent molecule, could interfere with the completion of the walk. Considering the effects from intrachain terms alone, the description resembles a counting theorem derived by Sykes,[19] which expresses the number of n-step SAWs in terms of the numbers of (n −1)-step polygons and tadpoles.

Equation 18 is also related to the Edwards[18] description; considering only the first term on the right-hand side, differentiating both sides with respect to n (the degree of polymerization), and expanding $p(\vec{r}_{(n-1)L}|\vec{r}_{1L})$ about $(\vec{r}_{nL} - \vec{r}_{(n-1)L})$ to second order gives a diffusion equation in the absence of a field. By reinstatement of the solvent and additional monomer terms the effect of the resulting field is incorporated. The monomer–monomer interactions comprise intra- and intermolecular contacts, and it is expected that the former should dominate for c below c^* and the latter above c^*.

III. Derivation of Thermodynamic Quantities

In this section we are concerned with the effects of interparticle correlations on the bulk thermodynamic properties of the solution. Thus, we shall first derive forms for the pair distribution functions which incorporate the effects of direct interactions between particles and shall make use of these to obtain expressions for the free energy and noncombinatorial entropy of mixing, as described in the Introduction. Then the consequences of including the indirect interactions through a third body will be considered. Most of the work which follows makes use of a lattice model, although a limited continuum model is also discussed briefly.

Starting with eq 10 for $\nabla_{iL}p_2(\vec{r}_{iL},\vec{r}_{jM})$, the Kirkwood approximation is used for all the triplet distribution functions; both sides are divided by $p_2(\vec{r}_{iL};\vec{r}_{jM})$, and the independence approximation is made for the remaining pair distribution functions on the right-hand side. It is now possible to integrate with respect to $\vec{r}_{iL}$ and as the remaining (singlet) distribution functions are constant for a particular (monomer or solvent) species these are included in the integration constant (and labeled c) to give, for the monomer–monomer case

$$p_2(\vec{r}_{iL},\vec{r}_{jM}) = \exp[-\beta u(\vec{r}_{iL} - \vec{r}_{jM}) + c] \tag{19}$$

with similar forms being derived for the monomer–solvent and solvent–solvent pairs. The solution is now considered to occupy a lattice of N_0 sites and coordination number Ω. $u(\vec{r})$, $q(\vec{r})$, and $w(\vec{r})$ are all chosen to be step potentials, each having the well width equal to a lattice spacing, with well depths of magnitude ϵ_{22}, ϵ_{12}, and ϵ_{11}, respectively. The above pair distribution function is normalized by using the condition

$$\sum_{\vec{r}_{iL}}\sum_{\vec{r}_{jM}} p_2(\vec{r}_{iL},\vec{r}_{jM}) = 1 \tag{20}$$

and for N_0 large the result is

$$p_2(\vec{r}_{iL},\vec{r}_{jM}) = \exp[-\beta u(\vec{r}_{iL} - \vec{r}_{jM})]/N_0^2 \qquad (21)$$

The resulting expression for ΔU (from eq 21 and the lattice analogue of eq 5) has an explicit temperature dependence, but is still similar in form to the random-mixing result. In fact, the latter can be derived with the BGY approach by making the independence approximation on the right-hand side of eq 10 and continuing as described above. The new expressions for ΔU and ΔA_{mix} reduce to the random-mixing forms in the limit of high temperature.

Nearest neighbors on the lattice interact with energies which depend on the type of particles involved; therefore, it is to be expected that occupation of a lattice site will depend on the particles present in neighboring sites. Consider two particular sites, adjacent on the lattice, labeled 1 and 2. Suppose that site 1 is occupied by a (any) monomer, m. Then, the probabilities can be renormalized such that

$$p^\dagger(s,\vec{r}_2|m,\vec{r}_1) = Ap(s,\vec{r}_2|m,\vec{r}_1) \qquad (22)$$

A representing the normalization constant, to satisfy

$$p^\dagger(s,\vec{r}_2|m,\vec{r}_1) + p^\dagger(m,\vec{r}_2|m,\vec{r}_1) = 1 \qquad (23)$$

where s represents a solvent molecule, and the same normalization constant applies to both conditionals. Similarly

$$p^\dagger(s,\vec{r}_2|s,\vec{r}_1) + p^\dagger(m,\vec{r}_2|s,\vec{r}_1) = 1 \qquad (24)$$

These are normalization conditions for probabilities which are generic, in the sense that they involve unlabeled species. Using, for example

$$p_2(m,\vec{r}_1;m,\vec{r}_2) = \sum_{iL}\sum_{jM} p_2(iL,\vec{r}_1;jm,\vec{r}_2) = \phi_2^2 \exp[-\beta u(\vec{r}_1 - \vec{r}_2)] \qquad (25)$$

as well as eq 22–24, and that $p(m,\vec{r})$, $p(s,\vec{r})$ are just the volume (site) fractions of monomer (ϕ_2) and solvent (ϕ_1), respectively, the new renormalized probabilities are

$$p^\dagger(m,\vec{r}_2|m,\vec{r}_1) = \frac{\phi_2 \exp(-\beta\epsilon_{22})}{\phi_2 \exp(-\beta\epsilon_{22}) + \phi_1 \exp(-\beta\epsilon_{12})} \qquad (26)$$

$$p^\dagger(m,\vec{r}_2|s,\vec{r}_1) = \frac{\phi_2 \exp(-\beta\epsilon_{12})}{\phi_2 \exp(-\beta\epsilon_{12}) + \phi_1 \exp(-\beta\epsilon_{11})} \qquad (27)$$

with analogous expressions for $p(s,\vec{r}_2|m,\vec{r}_1)$ and $p(s,\vec{r}_2|s,\vec{r}_1)$. These renormalized conditional probabilities are now used to find U through

$$U = \tfrac{1}{2} \sum_{\text{no. of monomers}}{}' [\epsilon_{22}p^\dagger(m,\vec{r}_2|m,\vec{r}_1) + \epsilon_{12}p^\dagger(s,\vec{r}_2|m,\vec{r}_1)] + \tfrac{1}{2} \sum_{\text{no. of solvent molecules}}{}' [\epsilon_{11}p^\dagger(s,\vec{r}_2|s,\vec{r}_1) + \epsilon_{12}p^\dagger(m,\vec{r}_2|s,\vec{r}_1)] \qquad (28)$$

where the primed sums are taken over the Ω nearest neighbors of $\vec{r}_1$ on the lattice. The result is

$$U = \frac{\Omega nN}{2}\left[\frac{\epsilon_{22}\phi_2 \exp(-\beta\epsilon_{22}) + \epsilon_{12}\phi_1 \exp(-\beta\epsilon_{12})}{\phi_2 \exp(-\beta\epsilon_{22}) + \phi_1 \exp(-\beta\epsilon_{12})}\right] + \frac{\Omega s}{2}\left[\frac{\epsilon_{12}\phi_2 \exp(-\beta\epsilon_{12}) + \epsilon_{11}\phi_1 \exp(-\beta\epsilon_{11})}{\phi_2 \exp(-\beta\epsilon_{12}) + \phi_1 \exp(-\beta\epsilon_{11})}\right] \qquad (29)$$

and setting the ϵ's equal to one another recovers the random-mixing result, which is also obtained from eq 29 in the high-temperature limit. Equation 29 leads directly to expressions for ΔS_{nc} and ΔA_{mix} (see Appendix) and therefore to $\partial\mu_1/\partial\phi_2$ and $\partial^2\mu_1/\partial\phi_2^2$. ΔS_{nc} is given by

$$\frac{\Delta S_{\text{nc}}}{N_0} = \frac{\Omega\phi_2}{2T}\left[\frac{\epsilon_{22}\phi_2 \exp(-\beta\epsilon_{22}) + \epsilon_{12}\phi_1 \exp(-\beta\epsilon_{12})}{\phi_2 \exp(-\beta\epsilon_{22}) + \phi_1 \exp(-\beta\epsilon_{12})}\right] + \frac{\Omega\phi_1}{2T}\left[\frac{\epsilon_{12}\phi_2 \exp(-\beta\epsilon_{12}) + \epsilon_{11}\phi_1 \exp(-\beta\epsilon_{11})}{\phi_2 \exp(-\beta\epsilon_{12}) + \phi_1 \exp(-\beta\epsilon_{11})}\right] + \frac{k_{\text{B}}\Omega\phi_2}{2} \log\,[\phi_2 \exp(-\beta\epsilon_{22}) + \phi_1 \exp(-\beta\epsilon_{12})] + \frac{k_{\text{B}}\Omega\phi_1}{2} \log\,[\phi_2 \exp(-\beta\epsilon_{12}) + \phi_1 \exp(-\beta\epsilon_{11})] \qquad (30)$$

where k_{B} is the Boltzmann constant. ΔS_{nc} vanishes when the ϵ's are equal to one another, or as the temperature approaches infinity.

In the section which follows we compare numerical results produced by using this level of BGY and using the random-mixing theory; in addition, we investigate how changing the balance between the different ϵ's affects the critical temperature.

We now consider the effect of relaxing the rigid lattice constraint by following the same approach as described above, but working in the continuum. The singlet probabilities are now number densities, for example $p(m) = nN/V$ (V being the volume of the space), and

$$\int\int p_2(m,\vec{r}_1;s,\vec{r}_2)\, \mathrm{d}\vec{r}_1\, \mathrm{d}\vec{r}_2 = p(m)p(s)V^2 \qquad (31)$$

Scaled potentials are used where, as in the lattice case, the form of the $\vec{r}$ dependence ($\psi(\vec{r})$) is constant but the well depths vary depending on the kind of interaction. Using the unrenormalized p_2's to find ΔU involves expanding the exponentials to order $O(\beta\epsilon)$, and then the denominators such that βU is of order $O(\beta\epsilon)^2$. Then, instead of summing over all possible lattice positions, we integrate over a separation distance $\vec{r}$, and in doing this a hard core is imposed, having the same radius for both solvent and monomers. At this level the forms for ΔU and ΔS_{nc} are strictly analogous to the lattice results. The renormalization procedure also closely follows the approach described above, except that it is now necessary to integrate over a volume element (v) large enough to contain one particle, i.e.

$$\int_v \mathrm{d}\vec{r}_2\, [p^\dagger(s,\vec{r}_2|m,\vec{r}_1) + p^\dagger(m,\vec{r}_2|m,\vec{r}_1)] = 1 \qquad (32)$$

After the renormalization constant is simplified (by taking a high-temperature limit), the renormalized conditional probabilities have the form

$$p^\dagger(m,\vec{r}_2|m,\vec{r}_1) = \frac{p(m)(1 - \beta\epsilon_{22}\psi(\vec{r}))}{1 - \beta\psi(\vec{r})(\phi_2\epsilon_{22} + \phi_1\epsilon_{12})} \qquad (33)$$

Using these to obtain expressions for ΔU and ΔS_{nc} yields equations which are analogous to those derived with the solution occupying a lattice. We conclude that the restrictions present in this limited continuum model, which enabled us to carry out all of the manipulations analytically, are still too severe to alter significantly the description from that of the lattice. A more effective approach would involve changing the size of the hard core as well as the form of $\psi(\vec{r})$ such that these variables would depend on the nature of the particles. In fact, we intend to pursue this by using computational techniques.

Finally, we investigate the effects of including indirect pairwise correlations through a third body. Once again we start with the exact expression for ∇p_2 in terms of the different p_3's (see eq 10). The Kirkwood approximation is used on all of the triplet functions, and both sides are divided by the p_2 of interest to give $\nabla \ln p_2$ on the left-hand side. Next, instead of using the independence approximation in each remaining p_2 on the right-hand side, we make use of the renormalized conditional probabilities derived above (eq 27 and 28) in all but the connectivity term; the latter is treated as before. The justification for simplifying the connectivity term in this manner is that for a solution above c^* connectivity effects might be expected to have the same order of magnitude as in pure polymer. Although the BGY description is applicable over the entire concentration range, use of both the Kirkwood and the independence approximation implies that $c > c^*$.

Once all the substitutions have been made, a high-temperature expansion is performed and the result is an expression for $\nabla_1 \log p_2(m,\vec{r}_1;m,\vec{r}_2)$ which contains terms to order $O(\beta\epsilon)^2$. Still working on a lattice, potentials having r dependence $\psi(\vec{r}_{12})$ and varying well depths (ϵ_{11}, ϵ_{12}, ϵ_{22}) are used and both sides are integrated with respect to $\vec{r}_1$. Normalization of the resulting expression for p_2 is tedious but straightforward, taking into account the sums over the positions of the third interacting particle in the different terms. In performing the required sums over $\vec{r}_1$ and $\vec{r}_2$ we note that the dominant contribution comes from the situation in which these two positions are separated by more than one shared site.

The new p_2's are now renormalized by using the conditions outlined in eq 23 and 24 giving, for example

$$\begin{aligned}p^{\dagger}(m,\vec{r}_2|s,\vec{r}_1) = \{&\phi_2 \exp[-\beta\psi(\vec{r}_{12})\epsilon_{12} - \phi_1\phi_2\beta^2(\epsilon_{12} - \epsilon_{22}) \times \\ &(\epsilon_{12} - \epsilon_{11})\sum_{\vec{r}_3}\psi(\vec{r}_{13})\psi(\vec{r}_{23})]\}/ \\ &\{\phi_2 \exp[-\beta\psi(\vec{r}_{12})\epsilon_{12} - \phi_1\phi_2\beta^2(\epsilon_{12} - \epsilon_{22})(\epsilon_{12} - \\ &\epsilon_{11})\sum_{\vec{r}_3}\psi(\vec{r}_{13})\psi(\vec{r}_{23})] + \\ &\phi_1 \exp[-\beta\psi(\vec{r}_{12})\epsilon_{11} - \phi_1\phi_2\beta^2(\epsilon_{12} - \epsilon_{11})^2\sum_{\vec{r}_3}\psi(\vec{r}_{13})\psi(\vec{r}_{23})]\}\end{aligned} \quad (34)$$

If we compare this with eq 27, it is clear how interactions through a third body contribute to the more sophisticated expressions. The new terms vanish when either ϕ_1 or ϕ_2 is zero, and when the ϵ's are all equal to one another; all of these cases represent conditions under which there will be no competition for sites between different types of particles, and in particular, when the ϵ's are equal the conditional probabilities will reduce to volume fractions.

In the work which follows

$$\begin{aligned}\psi(r_{ij}) &= +1 \qquad \vec{r}_j,\vec{r}_j \text{ adjacent} \\ &= 0 \qquad \vec{r}_i,\vec{r}_j \text{ nonadjacent} \\ &= \infty \qquad \vec{r}_i = \vec{r}_j\end{aligned} \quad (35)$$

In order for interactions through a third particle to affect the conditional probabilities it must be adjacent to both $\vec{r}_1$ and $\vec{r}_2$, which are themselves adjacent. It is therefore necessary to choose lattices which can accommodate three simultaneously nearest-neighbor sites, for example the face-centered-cubic (fcc) lattice. Two coordination numbers are now of interest: Ω, as before, represents the number of immediate neighbors surrounding a site, while Ω' is the number of locations at which a third particle may interact with both members of a neighboring pair.

The renormalized probabilities can now be used to derive a new expression for U (using eq 28); each of the sums over $\vec{r}_3$ will produce Ω' contributions. A simplified version of U follows, in which terms are retained to order $O(\beta\epsilon)^2$

$$U = (\Omega/2)(B_0 + \beta B_1 + \beta^2 B_2) \quad (36)$$

where

$$B_0 = nN\phi_2\epsilon_{22} + 2nN\phi_1\epsilon_{12} + s\phi_1\epsilon_{11}$$

$$B_1 = -nN\phi_1[\phi_2(\epsilon_{12} - \epsilon_{22})^2 + \phi_1(\epsilon_{12} - \epsilon_{11})^2]$$

$$\begin{aligned}B_2 = {}& ^1\!/_2 nN\phi_1[\phi_2(2\phi_2 - 1)(\epsilon_{12} - \epsilon_{22})^3 + \phi_1(2\phi_1 - 1)(\epsilon_{12} - \\ &\epsilon_{11})^3] + \Omega' nN\phi_1{}^2\phi_2(\epsilon_{11} - \epsilon_{22})[\phi_2(\epsilon_{12} - \epsilon_{22})^2 - \phi_1(\epsilon_{12} - \epsilon_{11})^2]\end{aligned}$$

B_0 is just the random-mixing result and when the ϵ's are equal to one another this is the only remaining term.

Equations 29 and 36 are equivalent but for the third-body terms, and high-temperature expansions of the two differ only in those contributions containing Ω'; notice that these vanish when $\epsilon_{11} = \epsilon_{22}$. As before, expressions for ΔS_{nc}, ΔA_{mix} (see Appendix), $\partial\mu_1/\partial\mu_2$, and $\partial^2\mu_1/\partial\phi_2{}^2$ can be obtained; for ΔS_{nc} the result is

$$\begin{aligned}\frac{\Delta S_{\mathrm{nc}}}{N_0} = \frac{\Omega}{2}\Bigg\{&\frac{-\phi_1\phi_2 k_{\mathrm{B}}\beta^2}{2}[\phi_2(\epsilon_{12} - \epsilon_{22})^2 + \phi_1(\epsilon_{12} - \epsilon_{11})^2] + \\ &\frac{\phi_1\phi_2 k_{\mathrm{B}}\beta^3}{3}[\phi_2(2\phi_2 - 1)(\epsilon_{12} - \epsilon_{22})^3 + \phi_1(2\phi_1 - 1)(\epsilon_{12} - \epsilon_{11})^3] \\ &+ \frac{2\Omega'\phi_1{}^2\phi_2{}^2 k_{\mathrm{B}}\beta^3}{3}(\epsilon_{11} - \epsilon_{22})[\phi_2(\epsilon_{12} - \epsilon_{22})^2 - \phi_1(\epsilon_{12} - \epsilon_{11})^2]\Bigg\}\end{aligned} \quad (37)$$

Only the final term on the right-hand side arises from third-body effects. As expected, when the ϵ's are all equal ΔS_{nc} goes to zero, and when $\epsilon_{11} = \epsilon_{22}$ the third-body contributions vanish, as in eq 36 for U. Although the first term is never positive, the terms in β^3 can have either sign depending on the balance between the interaction energies. The corresponding result for the chemical potential of the solvent (μ_1) relative to that of pure solvent ($\mu_1{}^0$) is

$$\begin{aligned}\beta(\mu_1 - \mu_1{}^0) = {}&\phi_2(1 - 1/n) + \log \phi_1 + \\ &\frac{\Omega\phi_2{}^2\beta}{2}(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}) + \frac{\Omega\phi_2{}^2\beta^2}{4}[(1 - 2\phi_2)(\epsilon_{12} - \epsilon_{22})^2 - \\ &2\phi_1(\epsilon_{12} - \epsilon_{11})^2] + \frac{\Omega\phi_2{}^2\beta^3}{12}\{2\phi_1(3\phi_1 - 1)(\epsilon_{12} - \epsilon_{11})^3 + \\ &(6\phi_2{}^2 - 6\phi_2 + 1)(\epsilon_{12} - \epsilon_{22})^3 + \\ &2\Omega'(\epsilon_{11} - \epsilon_{22})[2\phi_1\phi_2(\phi_2 - \phi_1)(\epsilon_{12} - \epsilon_{22})^2 + \\ &\phi_1{}^2(\phi_1 - 3\phi_2)(\epsilon_{12} - \epsilon_{11})^2]\}\end{aligned} \quad (38)$$

We now make use of the expressions derived in this section to calculate some numerical results.

IV. Numerical Results and Discussion

The expressions for the chemical potential, incorporating only bare terms (see Appendix) and third-body terms (eq 38), clearly depend on all the ϵ parameters, not just through the balance as reflected in χ. Hence, we expect that different values of ϵ_{11}, ϵ_{12}, and ϵ_{22}, with χ fixed, will lead to differences in the phase separation behavior. We have investigated this effect by numerically calculating the concentration and temperature dependence of the chemical potential. An example with no third-body interactions is given in Figure 1, which shows the variation in the concentration dependence of the chemical potential for three different sets of ϵ parameters, with χ fixed. The temperature is chosen to be close to the critical temperature for the case where $\epsilon_{11} = \epsilon_{22}$. It is apparent that this temperature is well above the critical temperature for the case with $\epsilon_{12} = \epsilon_{22}$ and well below that for $\epsilon_{12} = \epsilon_{11}$. Thus, the critical temperature can be shifted in either direction from the symmetrical case, by changing the balance of the ϵ parameters.

This is demonstrated even more clearly by the data in Table I. Once again we have chosen to vary the ϵ parameters, keeping $\Delta\epsilon = \epsilon_{12} - {}^1\!/_2\epsilon_{11} - {}^1\!/_2\epsilon_{22}$ fixed. In each case the critical temperature was located by determining numerically the temperature at which $\partial\mu_1/\partial\phi_2$ (Appendix) first showed a positive sign. Consider first the results when only the bare interactions contribute ($\Omega' = 0$). With $\Delta\epsilon$ and ϵ_{12} fixed, as ϵ_{11} decreases, T_{c} decreases. The onset of phase separation is a reflection of the balance between

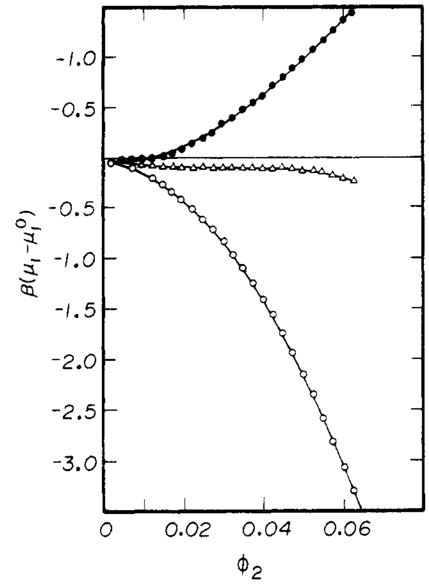

Figure 1. $\beta(\mu_1 - \mu_1^0)$ vs. ϕ_2 for T = 112.8 K: (●) $\epsilon_{22}/k_B = 0$, $\epsilon_{11}/k_B = \epsilon_{12}/k_B = 20$ (K); (▵) $\epsilon_{12}/k_B = 10$ (K), $\epsilon_{11}/k_B = \epsilon_{22}/k_B = 0$; (○) $\epsilon_{11}/k_B = 0$; $\epsilon_{12}/k_B = \epsilon_{22}/k_B = 20$ (K).

Table I
Change in the Critical Temperature As ϵ_{11}, ϵ_{12}, and ϵ_{22} Are Varied with $\Delta\epsilon = \epsilon_{12} - {}^1/_2\epsilon_{11} - {}^1/_2\epsilon_{22}$ Fixed[a]

ϵ_{11}/k_B, K	ϵ_{1}/k_B, K	ϵ_{22}/k_B, K	$T_c(\Omega' = 0)$, K	$T_c(\Omega' = 4)$, K
40	30	0	240.7	240.8
20	20	0	234.5	234.3
15	20	5	229.5	229.5
10	20	10	223.1	223.1
0	20	20	205.8	203.5
0	30	40	180.2	167.3
0	40	60	137.5	143.0

[a] $\Omega = 12$ and $n = 1000$.

energetic and entropic contributions to $\Delta A_{\rm mix}$. In the expression for $\Delta S_{\rm nc}$ which includes only the direct interactions (eq 30) a high-temperature expansion to order $O(\epsilon\beta)^2$ yields the first term (right-hand side) of eq 37. For ϕ_2 very small (ϕ_{2c} is generally less than 0.04) as ϵ_{11} decreases $\Delta S_{\rm nc}$, which is negative, decreases and therefore so does $\Delta S_{\rm mix}$. The effect of this is to discourage mixing but in fact T_c is being lowered due to energetic effects. This can be demonstrated by taking a high-temperature expansion of $\Delta U_{\rm mix}$ (using eq 29) to order $O(\beta\epsilon)$. Dropping terms of order $O(\phi_2^2)$, it can be seen that as ϵ_{11} decreases, with ϵ_{12} and $\Delta\epsilon$ fixed, $\Delta U_{\rm mix}$ decreases. Thus, $\Delta A_{\rm mix}$ is being dominated by energetic contributions in this critical region.

When third-body interactions are incorporated, T_c is decreased for all but one of the cases examined, and this difference grows with $|\epsilon_{11} - \epsilon_{22}|$. If we consider the term containing Ω' in the equation for $\partial\mu_1/\partial\phi_2$ (using eq 38), we find that, typically, ϕ_{2c} is very small and therefore the first term in brackets will dominate. The sign of this term will be positive if $\epsilon_{22} - \epsilon_{11}$ is negative and negative if this factor is positive. Thus, for the set $\{40,30,0\}$, although $\epsilon_{22} - \epsilon_{12}$ is larger than $\epsilon_{11} - \epsilon_{12}$, ϕ_2 is small and therefore T_c is almost unchanged in going from $\Omega' = 0$ to $\Omega' = 4$. Conversely, the set $\{0,30,40\}$ produces a decrease in T_c of almost 13 K. The combination of having $\epsilon_{11} - \epsilon_{12}$ dominate and $\epsilon_{22} - \epsilon_{11}$ positive means that the incorporation of third-body effects causes a reduction in $\partial\mu_1/\partial\mu_2$, and therefore T_c is lowered.

The last example shown in Table I seems to contradict this explanation: $\epsilon_{11} - \epsilon_{22}$ is large and ϵ_{22} is greater than ϵ_{11}, yet T_c increases in going from the first to the second column. Recall that the above argument depends on ϕ_{2c} being small. In the other cases this is so, ϕ_{2c} ranging between about 0.01 and 0.04. In the last case, however, although ϕ_{2c} is ~0.04 when $\Omega' = 0$, it increases greatly (to ~0.23) when $\Omega' = 4$ and therefore both terms will contribute, producing a less predictable shift in the critical temperature. The equations which determine the critical conditions are complicated, and it is difficult to go beyond a qualitative analysis of these trends. However, for the case in which only the bare potential contributions are included it is useful to examine simplified forms, in which terms are retained only to order $O(\beta\epsilon)^2$ in $\beta\partial\mu_1/\partial\phi_2$ and $\beta\partial^2\mu_1/\partial\phi_2^2$. As a rough approximation we take ϕ_{2c} to be the Flory–Huggins value $(1/(1 + n^{1/2}))$, substitute this into the equation $\partial^2\mu_1/\partial\phi_2^2 = 0$, and then let n go to infinity. This yields a quadratic equation for T_c, the solution of which is

$$T_c = \{-\Omega(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}) + [\Omega^2(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})^2 + 2\Omega\{(\epsilon_{22} - \epsilon_{12})^2 - 2(\epsilon_{11} - \epsilon_{12})^2\}]^{1/2}\}/2k_B \quad (39)$$

with χ fixed, the change in T_c is determined by the change in $(\epsilon_{22} - \epsilon_{12})^2 - 2(\epsilon_{11} - \epsilon_{12})^2$.

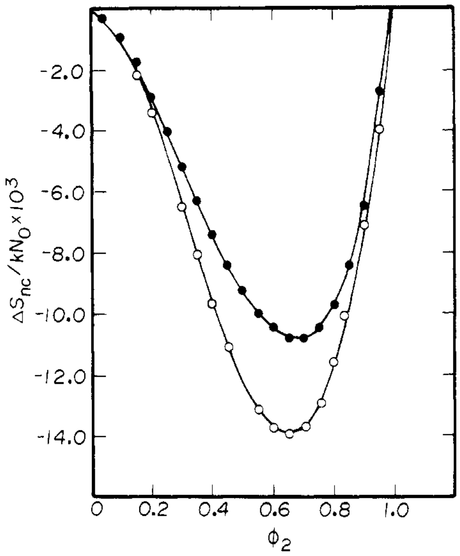

Figure 2. $\Delta S_{\rm nc}/k_B N_0$ vs. ϕ_2, T = 110.4 K, n = 1000, Ω = 12, $\epsilon_{11}/k_B = \epsilon_{12}/k_B = 20$ (K), $\epsilon_{22}/k_B = 0$; using eq 37 and incorporating (○) direct interactions, $\Omega' = 0$; (●) direct and third-body interactions, $\Omega' = 4$.

In Figure 2 we compare the concentration dependence of the noncombinatorial contribution to the entropy of mixing, when only bare contributions (eq 30) and both bare and third-body contributions (eq 37) are included. The noncombinatorial entropy change is negative, as expected for a system with no volume change on mixing. The minimum in this case is at a value of ϕ_2 other than 0.5; this is because, for $\epsilon_{11} = \epsilon_{12} \neq \epsilon_{22}$, the expression is no longer symmetrical in ϕ_1 and ϕ_2. For the example given, the effect of third-body interactions is to decrease the magnitude of $\Delta S_{\rm nc}$. In order to estimate the contribution from these terms, consider the case when $\phi_2 = 0.5$. The final term in eq 37 then simplifies to $(\Omega\Omega' k_B\beta^3/96)[(\epsilon_{11} - \epsilon_{22})^2(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})]$. The sign is given by the sign of χ and the magnitude is proportional to $(\epsilon_{11} - \epsilon_{22})^2$.

In deriving the results of section III we have made a number of approximations. By far the most important of these is the assumption of a lattice structure which has implied that the volume change on mixing is zero. In spite of these approximations, we have obtained interesting results on nonrandom mixing contributions to thermodynamic functions, including contributions through third bodies. We wish to stress that the Born–Green–Yvon formulation presented here is not restricted to a lattice case, and we intend to pursue the numerical solutions of the BGY equations for a continuum model of a concentrated polymer solution.

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Appendix

This appendix contains complete expressions for the free energy of mixing and the chemical potential, based on the results of section III. For the case in which only bare potential interactions are incorporated, the free energy change upon mixing (ΔA_{mix}) is given by

$$\Delta A_{\mathrm{mix}} = \beta^{-1}[N \log \phi_2 + s \log \phi_1] - (\Omega/2)(nN\epsilon_{22} + s\epsilon_{11}) - (\beta^{-1}\Omega/2)\{nN \log [\phi_2 \exp(-\beta\epsilon_{22}) + \phi_1 \exp(-\beta\epsilon_{12})] + s \log [\phi_2 \exp(-\beta\epsilon_{12}) + \phi_1 \exp(-\beta\epsilon_{11})]\} \tag{A.1}$$

This yields the following expression for the chemical potential of the solvent (μ_1) relative to that of pure solvent ($\mu_1{}^0$):

$$\beta(\mu_1 - \mu_1{}^0) = [\phi_2(1 - 1/n) + \log \phi_1] - \beta\Omega\epsilon_{11}/2 - (\Omega/2) \log [\phi_1 \exp(-\beta\epsilon_{11}) + \phi_2 \exp(-\beta\epsilon_{12})] - \frac{\Omega}{2}\left\{\phi_2{}^2\left[\frac{\exp(-\beta\epsilon_{12}) - \exp(-\beta\epsilon_{22})}{\phi_1 \exp(-\beta\epsilon_{12}) + \phi_2 \exp(-\beta\epsilon_{22})}\right] + \phi_1\phi_2\left[\frac{\exp(-\beta\epsilon_{11}) - \exp(-\beta\epsilon_{12})}{\phi_1 \exp(-\beta\epsilon_{11}) + \phi_2 \exp(-\beta\epsilon_{22})}\right]\right\} \tag{A.2}$$

Finally, ΔA_{mix} for the case in which third-body terms are included is

$$\Delta A_{\mathrm{mix}} = \beta^{-1}(s \log \phi_1 + N \log \phi_2) + (\Omega/2) \times [nN\phi_1(\epsilon_{12} - \epsilon_{22}) + s\phi_2(\epsilon_{12} - \epsilon_{11})] - (\Omega nN\phi_1\beta/4)[\phi_2(\epsilon_{12} - \epsilon_{22})^2 + \phi_1(\epsilon_{12} - \epsilon_{11})^2] + (\Omega nN\phi_1\beta^2/12)[\phi_2(2\phi_2 - 1) \times (\epsilon_{12} - \epsilon_{22})^3 + \phi_1(2\phi_1 - 1)(\epsilon_{12} - \epsilon_{11})^3] + (\Omega\Omega' nN\phi_1{}^2\phi_2\beta^2/6)(\epsilon_{11} - \epsilon_{22})[\phi_2(\epsilon_{12} - \epsilon_{22})^2 - \phi_1(\epsilon_{12} - \epsilon_{11})^2] \tag{A.3}$$

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