Polymer Blends and Polymer Solutions: A Born–Green–Yvon Integral Equation Treatment†

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Received April 20, 1990; Revised Manuscript Received September 5, 1990

ABSTRACT: A description of polymer blends and polymer solutions is presented by making use of the Born–Green–Yvon integral equation technique. Expressions for the internal energy of mixing and free energy of mixing are derived without requiring the assumption of random mixing. At this stage the treatment describes an incompressible mixture on a lattice; extensions to the case of a compressible mixture are discussed. For the polymer–solvent case comparisons are made with recent simulation results as well as with predictions of other theories describing incompressible lattice solutions. For the case of polymer blends the phase diagram of a mixture exhibiting an upper critical solution temperature in investigated; qualitative comparisons are made with some simulation data on polymer blends. In addition, some of the effects on the miscibility of the system upon varying the degree of polymerization of one or both of the components are also examined.

I. Introduction

Over the past 10–15 years there has been a growing interest in polymer blends. Once it became apparent that causes of miscibility in binary mixtures of polymers were not rare curiosities, the formulation of polymer blends became a possible route to new materials. Concurrent with the rising interest in practical possibilities for these systems has been a desire to develop theoretical treatments that would lead to predictions about their equilibrium and dynamic properties. This study focuses on equilibrium problems, and it is noted that interest in such theories is enhanced by the fact that simple experimental measurements on blended systems do not generally yield a reliable picture of the effects of changing temperature and composition on miscibility. Over the past few years there has been some theoretical activity in this area, and several new treatments have appeared. Sanchez and Balazs[1] have extended the lattice fluid model,[2] incorporating a new energy term to account for the presence of strong interactions between unlike components. Painter et al.[3] have published a series of papers that incorporate Flory–Huggins theory combined with another term reflecting the strength of the mixed-component interaction. This is accomplished via an equilibrium constant that, for the cases studied by these authors, is obtained through infrared studies of the mixture and the pure components. Curro and Schweizer[4–6] have made use of the reference interaction site model (RISM), originally developed by Chandler and co-workers[7] for the study of small-molecule fluids and mixtures, to investigate the properties of polymer mixtures that are athermal or that have a weak interaction between unlike components. This is the only off-lattice model that leads to predictions about equilibrium properties. Finally, there have appeared a series of papers by Freed and co-workers[8] treating the case of an incompressible mixture on a lattice. In these papers corrections to Flory–Huggins theory are developed from first principles (i.e., from the partition function) as an expansion in powers of the inverse of the lattice coordination number and the interaction energy.

Despite these developments more progress is needed before the equilibrium behavior of these systems can be considered predictable. Some important progress will no doubt be made as the aforementioned theories are extended and compared to simulation results and experimental data. However, while simulation data on compressible blends have been obtained for lattice models, there is still no lattice model for a compressible mixture that does not make some use of the assumption of random mixing.[9] Current discussion in the literature leads to the perception that miscibility in a blend is driven by a combination of the effects of strong interactions between unlike components and differing degrees of thermal expansion. Thus a random mixing description is not entirely appropriate. In addition, it is common to see both criticism and spirited defense of lattice models; a theory that could be solved in both the lattice and continuum versions would yield insight regarding the questions surrounding this debate.

The work that follows represents the first stage in the development of a theory that will be used to tackle these issues. Section II contains a description of an integral equation treatment for binary mixtures[10] that may be applied to study solutions varying in nature from a binary mixture of small molecules to a polymer–solvent mixture to a polymer blend. The effects of nonrandom mixing appear naturally when this approach is used. At the current stage of development, the description applies to a lattice model of an incompressible mixture. In sections III and IV results are presented for the polymer–solvent and polymer blend case, respectively, making comparisons with simulation studies where possible. Section V is a summary and a discussion of future directions.

II. A Born–Green–Yvon Treatment of a Binary Mixture

This treatment is based on a theory for simple fluids that was developed by Born and Green[11a] and Yvon[11b] (with related work by Kirkwood[12]). Henceforth it shall be referred to BGY. Some of the details of the treatment discussed here were formulated in an earlier work[10] that focused on the polymer–solvent case; connections with this earlier paper will be made where appropriate. At the heart of the original BGY description is the relationship developed between the N- and the $(N-1)$-particle distribution functions, expressed through a set of linked integrodifferential equations. With explicit expressions for the distribution functions in hand, calculation of thermodynamic properties is straightforward.[13] However, at this point the complexity of the description is equivalent to dealing with the entire partition function. To make

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† This paper is dedicated to the memory of D. A. Holden, a colleague and a friend.

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further progress an approximation is needed to "close" the hierarchy at a level that still contains information about the correlations between particles in solution.[14] The standard treatment in related theories of simple fluids is to close at the level of the pair distribution function; this requires a second relationship between the triplet and the pair distribution functions that will necessarily be an approximate one. Two closure relationships are used in the work described here:

$$p_3(l_1,l_2,l_3) = p(l_1)\, p(l_2)\, p(l_3) \qquad (1)$$

$$p_3(l_1,l_2,l_3) = [p_2(l_1,l_2)\, p_2(l_2,l_3)\, p_2(l_3,l_1)]/[p(l_1)\, p(l_2)\, p(l_3)] \qquad (2)$$

On the left side in both equations is the triplet probability density for finding particles one, two, and three at positions l_1, l_2, and l_3, respectively. In eq 1, which makes use of the independence approximation, this triplet density is expressed as a product of the single-particle densities, equivalent to the number densities. All correlations between positions of these three particles are eliminated through use of the independence approximation. In eq 2 the Kirkwood superposition approximation is used. Here the triplet probability density is expressed as a product of the pair probability densities divided by the product of the singlet densities. In other words, the three-body correlations are accounted for through a product of the two-body correlations. The Kirkwood approximation is the most commonly used closure approximation in integral equation descriptions such as BGY, because it means that interesting information is retained in a description that is now solvable. However, this approximation treats all pairs equivalently, whether or not they involve connected segments. Through the further approximations of considering only nearest-neighbor interactions and placing the system on a lattice (of coordination number z), expressions can be developed[13] for the pair probability densities involving both the pure-component pairs and the mixed pair. These expressions would be analogous to eqs 26 and 27 of ref 10, if site (or volume) fractions which account for the connected nearest-neighbors of a segment had been used. In the case of a binary mixture there will be only one mixed-pair interaction; generalization to ternary or higher order mixtures would involve additional expressions of a form similar to those developed here. At this level of development no vacancies have been incorporated, either for the pure components or for the solution. Thus at the current stage the description is for an incompressible lattice mixture.

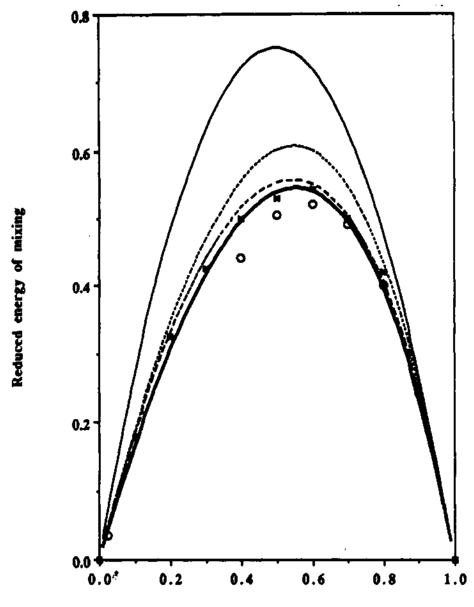

Figure 1. $\Delta E_{\mathrm{mix}}/N_0\Delta\epsilon$ plotted against ϕ_2; $r_1 = 1$, $r_2 = 100$, $\beta\Delta\epsilon = 3.00$. ○, simulation results; —, BGY; -, FH; - - -, GRM; – – –, GQC; *, EMF (data extracted from ref 18).

Making use of the expressions for the nearest-neighbor distribution functions, it is straightforward to work out the form of ΔE_{mix}.[13] The most closely related expression previously developed, eq 29 in ref 10, represents the contribution from the mixed state only. In the present work the introduction of nearest-neighbor connectivity of the chain affects the expressions for the pair probability densities and also is accounted for in summing the contributions to ΔE_{mix}. The full expression can be expanded in powers of $\beta = 1/k_{\mathrm{B}}T$ and to $\mathcal{O}(\beta^3)$ is given by

$$\beta\Delta E_{\mathrm{mix}}/N_0 = (zq_2\xi_1\phi_2/2r_2)(\beta\Delta\epsilon) - (z\beta^2\phi_1\phi_2/2)[\phi_2(\epsilon_{12} - \epsilon_{22})^2 + \phi_1(\epsilon_{12} - \epsilon_{11})^2] + (z\beta^3\phi_1\phi_2/4)[\phi_2(2\phi_2 - 1)(\epsilon_{12} - \epsilon_{22})^3 + \phi_1(2\phi_1 - 1)(\epsilon_{12} - \epsilon_{11})^3] \qquad (3)$$

ϵ_{11} and ϵ_{22} are the pure-component interaction energies between segments of types 1 and 2, respectively, while ϵ_{12} represents the mixed interaction energy; $\Delta\epsilon = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$, ϕ_1 and ϕ_2 are the volume or site fractions of the two components, and r_1 and r_2 are their respective degrees of polymerization. N_0 is the total number of lattice sites, and z is the coordination number of the lattice, which represents the number of nearest neighbors to any lattice site. In the expansion of the complete expression, the first term obtained ($\mathcal{O}(\beta)$) is, in fact, the Flory–Huggins term; that given in eq 3 reflects the decision to use Guggenheim's version of random mixing, which accounts for the connectivity between a segment and its covalently bonded neighbors in the chain.[13] Thus, ξ_1 and ξ_2 can be thought of as site fractions modified to account for the fact that for all but the end monomers of the polymer chain, two of the nearest neighbors of any segment are connected monomers. This means that instead of a chain of degree of polymerization r_1 having zr_1 nearest neighbors, as it would in Flory–Huggins theory, it has zq_1 where

$$zq_1 = zr_1 - 2r_1 + 2 \qquad (4)$$

There is a similar relationship between q_2 and r_2 for component 2. Now these modified site fractions are given by

$$\xi_1 = q_1N_1/(q_1N_1 + q_2N_2) \qquad \xi_2 = q_2N_2/(q_1N_1 + q_2N_2) \qquad (5)$$

where N_1 and N_2 are the number of molecules of types 1 and 2, respectively. When $r_1 = r_2 = 1$, the case of a binary mixture of small molecules is obtained. The expanded form of ΔE_{mix} is presented here because it will be useful in section III for making comparisons with results from simulation studies and other theories. The temperature dependence of ΔE_{mix} can now be exploited to obtain the free energy of mixing, making use of the relationship

$$\Delta E_{\mathrm{mix}} = [\partial(\Delta A_{\mathrm{mix}}/T)/\partial(1/T)]_V \qquad (6)$$

This is in contrast to Flory–Huggins theory[15] where the expression for ΔE_{mix} shows no temperature dependence. In that case, the expression for ΔS_{mix} (which is purely combinatorial) is developed separately, and the two are then combined to give ΔG_{mix} ($=\Delta A_{\mathrm{mix}}$, since there is no volume change on mixing).

To use eq 6, an integration with respect to $1/T$ must be carried out. For the lower limit, this fraction approaches

0, and therefore T approaches infinity. If a reasonable picture of the solution at very high temperature is taken to be one in which athermal mixing occurs, then the two components are randomly mixed. An estimate of the combinatorial contribution to ΔS_{mix}, labeled ΔS_{c}, will therefore be needed: Here the version developed by Guggenheim[16] is used, as opposed to the familiar expression from Flory–Huggins theory (which was used in obtaining the previous BGY formulation[10]) because, as noted above, it incorporates some of the local effects of chain connectivity. The Guggenheim estimate is

$$-\Delta S_{\mathrm{c}}/N_0k_{\mathrm{B}} = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + (z/2)[(q_1/r_1)\phi_1\ln(\xi_1/\phi_1) + (q_2/r_2)\phi_2\ln(\xi_2/\phi_2)] \tag{7}$$

Putting eqs 3, 6, and 7 together and expanding to $\mathcal{O}(\beta^3)$, the resulting expression for ΔA_{mix} is

$$\beta\Delta A_{\mathrm{mix}}/N_0 = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + (z/2)[(q_1/r_1)\phi_1\ln(\xi_1/\phi_1) + (q_2/r_2)\phi_2\ln(\xi_2/\phi_2)] + \beta(zq_2/2r_2)\xi_1\phi_2\Delta\epsilon - \beta^2(z\phi_1\phi_2/4)[\phi_2(\epsilon_{12}-\epsilon_{22})^2 + \phi_1(\epsilon_{12}-\epsilon_{11})^2] + \beta^3(z\phi_1\phi_2/12)[\phi_2(2\phi_2-1)(\epsilon_{12}-\epsilon_{22})^3 + \phi_1(2\phi_1-1)(\epsilon_{12}-\epsilon_{11})^3] \tag{8}$$

The unexpanded version is included in the Appendix. Equation 8 can be compared with eq A.3 of ref 10, which was derived for the case in which both direct and indirect pairwise interactions are included. Terms associated with the combinatorial entropy differ somewhat in the two equations, as does the term that is leading order in β. As indicated above, this reflects some accounting in the present treatment for the effects of connectivity. Terms of $\mathcal{O}(\beta^2,\beta^3)$ agree in the two equations when $\epsilon_{11} = \epsilon_{22}$; when this condition is met, the contributions from the indirect pairwise interactions vanish from eq A.3. The chemical potentials of each component can be obtained directly from eq 8; with these relationships, the conditions for phase equilibria can be established, and the coexistence curve mapped out. Because the nature of these relationships is complex, closed-form expressions for the critical temperature and composition have not been derived.

In the expression for ΔE_{mix} (eq 3) and therefore in those which follow, two energy terms appear: $(\epsilon_{12} - \epsilon_{11})$ and $(\epsilon_{12} - \epsilon_{22})$. This is in contrast to the usual mean-field result in which the only energy term is the sum of these two, often denoted $\Delta\epsilon$. For the compressible model, in which vacant lattice sites appear, it is expected that there will be more than one energy term. However, as Madden has recently proved,[17] for an incompressible lattice model only $\Delta\epsilon$ is important in determining the thermodynamic properties of the solution. The fact that two energy terms arise in the BGY model at this stage is likely due to the use of the Kirkwood superposition approximation for all the triplet probability densities. In particular, it could be the triplet probabilities that involve connected monomers for which this approximation is the least satisfactory. The result is the introduction of what might be considered as another degree of freedom in the description at this level; for the purposes of the work that follows ϵ_{11} shall be considered to be identical with ϵ_{22}, leaving only the difference $\epsilon_{12} - \epsilon_{22} = \epsilon_{12} - \epsilon_{11} = \Delta\epsilon/2$ to play a role. Using this condition, eqs 3 and 8 now become

$$\beta\Delta E_{\mathrm{mix}}/N_0 = (zq_2\xi_1\phi_2/2r_2)(\beta\Delta\epsilon) - (z\phi_1\phi_2/8)(\beta\Delta\epsilon)^2 + (z\phi_1\phi_2(\phi_2-\phi_1)^2/32)(\beta\Delta\epsilon)^3 \tag{3$'$}$$

$$\beta\Delta A_{\mathrm{mix}}/N_0 = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + (z/2)[(q_1/r_1)\phi_1\ln(\xi_1/\phi_1) + (q_2/r_2)\phi_2\ln(\xi_2/\phi_2)] + (zq_2\xi_1\phi_2/2r_2)(\beta\Delta\epsilon) - (z\phi_1\phi_2/16)(\beta\Delta\epsilon)^2 + (z\phi_1\phi_2(\phi_2-\phi_1)^2/96)(\beta\Delta\epsilon)^3 \tag{8$'$}$$

III. Polymer–Solvent Solutions

Ultimately a theoretical description is accountable to experimental data. However, at this stage in the development of this theory the model is for an incompressible mixture. Since it is not possible to separate the contributions to experimental results that arise from free-volume effects, the most appropriate comparisons to be made at this point are with computer simulation results for an incompressible lattice mixture. Recently, Madden et al.[18] have published data on such systems, and these simulation results will be used as the first test of the BGY theory developed here.

These simulations were done on the simple cubic lattice ($z = 6$), for a solution of solvent ($r_1 = 1$) and polymer chains ($r_2 = 100$). Here the focus will be on results for the energy of mixing and the coexistence curve. In Figure 1 the BGY results are compared with the simulation results for $\Delta E_{\mathrm{mix}}/N_0\Delta\epsilon$ as a function of composition, with $(\beta\Delta\epsilon) = 3.00$; comparison is made in the same figure with Flory–Huggins theory (FH), the Guggenheim quasi-chemical (GQC)[19] and random-mixing (GRM)[18] approximations, and the closest of the Freed group results, the extended mean-field theory (EMF).[18] All theoretical treatments are for incompressible mixtures. With respect to the BGY results it should be noted that having imposed the constraint $\epsilon_{11} = \epsilon_{22}$, *there are no adjustable parameters used in making this comparison.* It can be seen that the BGY curve is as close, if not closer, to the simulation data than any of the other plots. Equation 3′ is an expansion in powers of $\beta\Delta\epsilon$. Madden et al.[18] comment that the Guggenheim version of random mixing is in quantitative agreement with the simulation results for the athermal mixture. Since GRM has been used for the athermal limit of the BGY description, similar agreement in the first-order terms for $\beta\Delta E_{\mathrm{mix}}/N_0$ follows. It is possible to compare quantitatively the BGY and simulation estimates of the second-order coefficient in the expansion of $\beta\Delta E_{\mathrm{mix}}/N_0$, i.e., the coefficient to the term of order $(\beta\Delta\epsilon)^2$ in eq 3′. In Figure 2 the BGY results for both the second- and third-order coefficients are plotted with the simulation data; the agreement for the second-order term is excellent. The third-order term makes a much smaller contribution and is expected that higher order terms would follow this trend.

A comparison of simulation and theoretical results for the coexistence curve is a more demanding test of a theory, since here the agreement must be good over a wide range of both composition and temperature. Figure 3, in which the reduced temperature $(k_{\mathrm{B}}T/\Delta\epsilon)$ is plotted against volume fraction of polymer (ϕ_2), shows such a comparison. Only that portion of the curve to the right of the critical point is shown; the simulation data indicate that to the left of the critical point the binodal rapidly approaches very small values of ϕ_2, and hence the theoretical curves were all obtained by solving for $\mu_1 - \mu_1{}^\circ = 0$. The various theoretical estimates begin to diverge most dramatically as the critical composition is approached from the right. The BGY curve is as close, if not closer, than the best of the other treatments. Flory–Huggins theory drastically overestimates the critical temperature, as does the Guggenheim random mixing prediction. The Guggenheim quasi-chemical approximation is relatively close, and the EMF

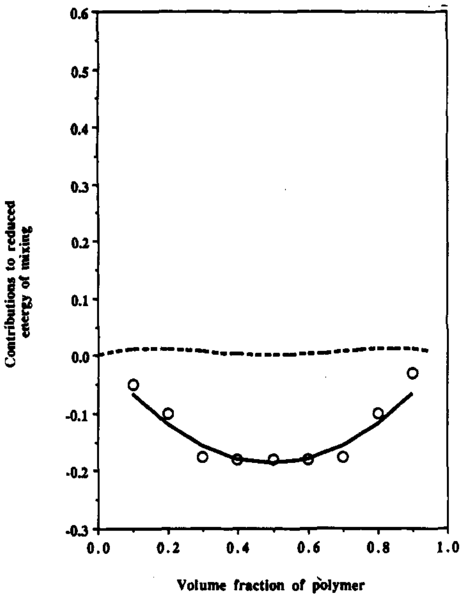

Figure 2. Second- and third-order coefficients ($\mathcal{O}(\beta^2,\beta^3)$) from eq 3′ plotted against ϕ_2; ○, estimates from simulation data; —, BGY result for $\mathcal{O}(\beta^2)$; - - -, BGY result for $\mathcal{O}(\beta^3)$.

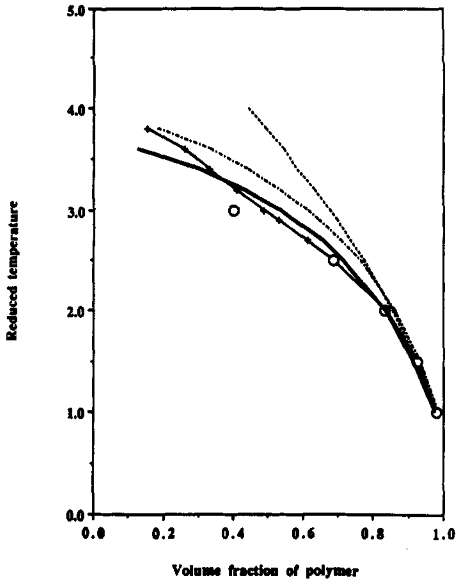

Figure 3. Portion of the coexistence curve for polymer–solvent case. $\beta/\Delta\epsilon$ is plotted against ϕ_2; ○, simulation results; —, BGY; - - -, FH; - · -, GRM; *, EMF (data extracted from ref 18).

theory of Freed and co-workers does better still. Again, the excellent agreement using BGY has been obtained without any adjustable parameters other than the initial choice of $\epsilon_{11} = \epsilon_{22}$.

The BGY, GQC, and EMF treatments all give comparable fits for this case. In the following section GQC will be used again, for the case of an incompressible blend, and so further comparisons with BGY will be made. Freed and co-workers[8] have examined the case of blends, but this work was done before the lattice cluster formalism was developed; quantitative comparison with BGY would be rather difficult at this stage. From the descriptions of the EMF theory (and related versions)[8] it would appear that in this approach all correlations at a particular level are included in developing the expression for the change in free energy upon mixing. In the BGY treatment, use of the Kirkwood superposition approximation implies that all levels of a particular set of correlations are kept. It is not clear that these two apparently very different "philosophies" result in significant differences in quantitative predictions for the incompressible polymer–solvent mixture. This could be a result of restricting the range of interactions to those involving only nearest neighbors. Additional comparisons must await further developments involving blends and/or compressible mixtures.

IV. Polymer Blends

Since the limitations on miscibility are of interest, the investigation of a phase diagram developed by using BGY will be the focus of this section. One could imagine cases involving an upper critical solution temperature (UCST), a lower critical solution temperature (LCST), or (very rarely for the case of blends) both.[20] The last situation makes up an interesting but small class; in this work an example involving an UCST will be studied. For the case of a polymer solution, a LCST is usually associated with the large difference in thermal expansion coefficients between the two components. In the case of a polymer blend this difference would not be typically very large; instead, one might be tempted to look for an analogy with small-molecule mixtures that exhibit LCSTs. In those cases the usual rationale for a LCST involves an extended network of contacts between unlike molecules. As the temperature is increased, this network is disrupted and phase separation results.[21] Thus, the mixed-component interaction energy should be favorable but not so favorable (i.e., more so than both of the pure-component energies) that it cannot be overcome by k_BT as T is raised. It would seem that more information about ϵ_{12} relative to ϵ_{11} and ϵ_{22} is needed than just the balance represented by $\Delta\epsilon$. However, for an incompressible lattice model only this one parameter is legitimate. Thus, whether one believes that the origin of the LCST in blends arises from differences in thermal expansion or from sensitivities to the relative strengths of the mixed and pure interaction energies, a compressible model is needed to investigate the phenomenon. A discussion on LCSTs using the BGY approach must therefore wait until the compressible model has been developed.

The model chosen here for analysis using BGY is a blend, occupying a simple cubic lattice ($z = 6$), in which both components have 1000 repeat units. Setting ϵ_{11} and ϵ_{22} to be equal (as before) with $(\epsilon_{12} - \epsilon_{ii})/k_B = 0.3$ (K), Figure 4 illustrates what happens to the composition dependence of ΔA_{mix} as a function of temperature. The critical temperature is at approximately 530 K, and as T is lowered from this point the appearance of a local maximum illustrates the phase-separation process. The intersections of a tangent with the two minima yield points on the binodal, while contributions to the spinodal may be obtained from the composition at the points of inflection on either side of the local maximum. The symmetry in this plot is a reflection of having the same degree of polymerization and identical pure interaction energies for each of the two components.

It does not take a significant increase in the magnitude of $(\epsilon_{12} - \epsilon_{ii})/k_B$ to yield a system in which the two components are completely immiscible. The data shown in Figure 5 confirm that this is due to the small contribution of ΔS_{mix} to ΔA_{mix} for the case of a blend. In this figure the contribution of the entropy of mixing to the reduced free energy of mixing is illustrated, plotted against composition for different values of the ratio r_2/r_1. In each case $r_2 = 1000$, and the different choices of r_1 result in the mixture changing in nature from that of a blend ($r_2/r_1 = 1$; $r_2 = 1000$) to a system approaching the polymer solvent case ($r_2/r_1 = 50$; $r_1 = 20$); the data for $r_2/r_1 = 1000$ were 2 orders of magnitude greater than that shown and are not

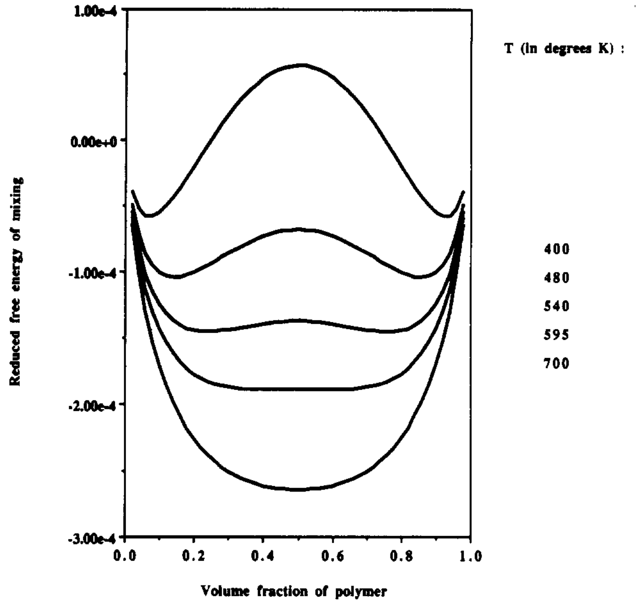

Figure 4. $\beta \Delta A_{mix}/N_0$ plotted against ϕ_2. From the bottom curve to the top T is given by 660, 580, 530, 480, 400 K.

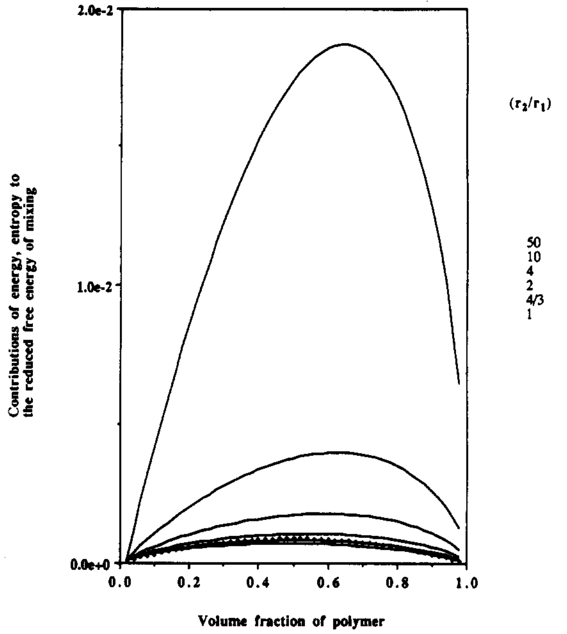

Figure 5. Contributions of ΔS_{mix} and ΔE_{mix} to $\beta \Delta A_{mix}/N_0$, plotted against ϕ_2. The solid curves are for the contribution of ΔS_{mix}, with (r_2/r_1) (from bottom to top) equal to 1, $^4/_3$, 2, 4, 10, 50. + gives a representative contribution of ΔE_{mix}.

included. A representative curve showing the reduced internal energy of mixing is also given. Note that for the case of a blend the energetic and entropic terms are of comparable magnitude (hence the limited miscibility), but once the chain length of one of the components becomes significantly smaller (by approximately an order of magnitude), the increase in the entropy of mixing results in a strong driving force promoting miscibility. This is illustrated even more dramatically in Figure 6, which shows how the critical temperature changes with the ratio r_2/r_1. The ordinate is the function $\{(2k_BT_c/z\Delta\epsilon)[(r_1)^{-1/2} + (r_2)^{-1/2}]^2\}$, which is predicted by Flory–Huggins theory to be a constant equal to 2. The symbols represent calculations using the BGY treatment. For $r_2/r_1 = 1$ the UCST is found at about 530 K, as noted above. As r_1 decreases, there is a rapid decrease in the critical temperature until r_1 reaches a value of about 100; after that the decline is less dramatic. An analogous effect, the lowering of T_c for a polymer–solvent system as the molecular weight of the polymer is lowered, has been well-documented experimentally.[22] Both the BGY and FH treatments predict such a trend, but the difference between the two increases with the molecular weight of the polymer. This can be seen by comparing the difference in T_C for the polymer–solvent case with $r_2 = 100$ (Figure 2), with the difference for $r_2 = 1000$, which is apparent in Figure 6 as r_2/r_1 becomes large (i.e., as the polymer–solvent limit is approached).

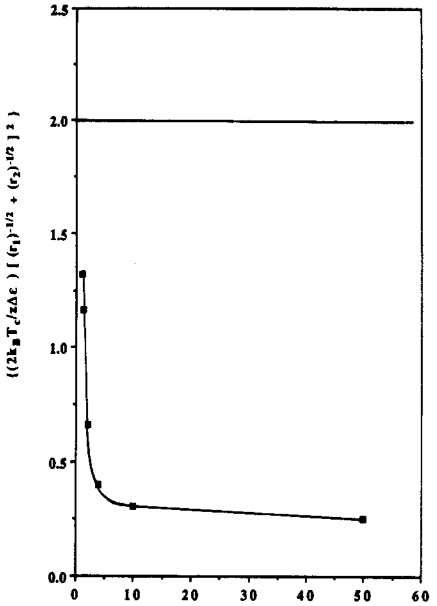

Figure 6. $\{(2k_BT_c/z\delta\epsilon)[(r_1)^{-1/2} + (r_2)^{-1/2}]^2\}$ plotted against (r_2/r_1). The line at ordinate = 2.0 represents the Flory–Huggins prediction. The symbols are the results of calculations using the BGY treatment; the curve has been added as a visual aid.

It is also feasible to use BGY to investigate the progression from a binary mixture of small molecules to a binary mixture of polymers by varying both r_2 and r_1. The data in Figure 7 illustrate how the value of $k_BT_c/\Delta\epsilon$ changes as a function of r_2 ($=r_1$). The Flory–Huggins prediction, shown in Figure 7 as an unbroken line, is that $k_BT_c/\Delta\epsilon$ is equal to $rz/2$ when $r_2 = r_1$; recall that $z = 6$. The BGY results (calculated for a series of choices for r_2) show essentially straight-line behavior for small r, with increasing curvature as r becomes larger.

For the polymer–solvent case it has been possible to make comparisons with computer simulation data; for the case of blends it is difficult to imagine the algorithm that would permit the evaluation of equilibrium properties of such mixtures without the inclusion of vacancies. Thus, quantitative comparisons are not possible at this point. However, in a recent paper Sariban and Binder[23] do compare some of their simulation results on blends-plus-voids to the predictions of the Flory–Huggins and Guggenheim quasi-chemical treatments without voids. Figure 8 compares the Sariban and Binder (SB) result for the coexistence curve from simulations of chains having 32 repeat units on a simple cubic lattice, where the volume fraction of voids is equal to 0.6, with the results for FH, GQC, and BGY. The Flory–Huggins estimate of the critical temperature is very high; Sariban and Binder note that Flory–Huggins can also be developed for a three-component system, and when the case of a blend with voids is treated the critical temperature is reduced but is still much higher than the simulation result. Although the Guggenheim model does better, BGY clearly is the

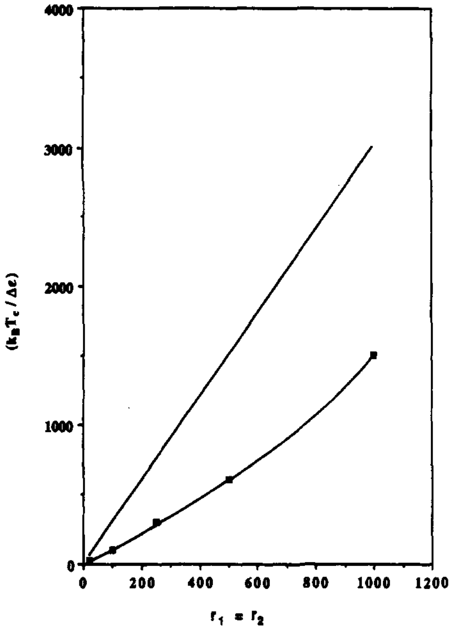

Figure 7. $k_BT_c/\Delta\epsilon$ plotted against r_2 ($=r_1$). The solid line represents the predictions of Flory–Huggins theory. The symbols are the results of calculations using the BGY treatment; the curve has been added as a visual aid.

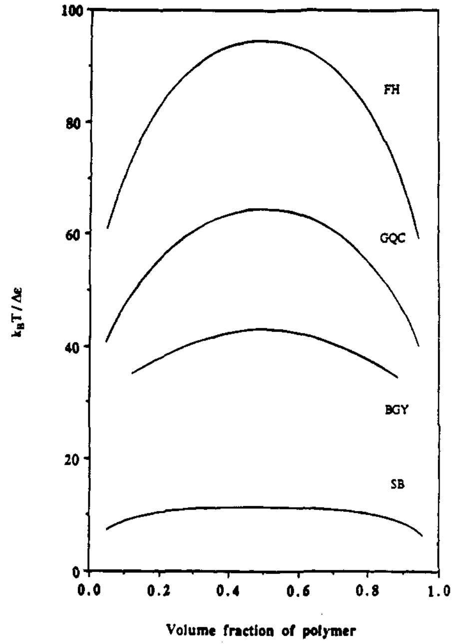

Figure 8. $2\beta/\Delta\epsilon$ plotted against ϕ_2 for $r_2 = r_1 = 32$. From bottom to top: simulation results, labeled SB, adapted from ref 20; BGY; GQC; FH.

closest to the simulation results. This is evident both in terms of the critical temperature and in the shape of the coexistence curve. In the simulation results the flatness of the curve near T_c is a reflection of the non-mean-field character of the system. Both FH and GQC are mean-field treatments; the BGY treatment described here is also expected to be a mean-field one, although non-mean-field behavior has been associated with the BGY approach for several problems.[24,25]

V. Summary and Future Directions

An equilibrium description of a two-component system on a lattice has been developed by using the Born–Green–Yvon formalism and explicitly applied to the cases of a polymer solution and a polymer blend. Favorable quantitative comparison with simulation results for the case of the polymer–solvent mixture indicate this to be a promising approach. In addition, the qualitative features of the results for the polymer blend are physically reasonable. Comparison with experimental data must await extension of this description to the case in which free volume effects have been incorporated. At the current level, however, there are still aspects worthy of further investigation. Use of the independence and the Kirkwood approximations (eq 1) have resulted in the appearance of two energy parameters where one is expected; refinements with respect to the nature of the closure relationships used should be investigated. In addition, there is a question of whether the critical exponents for both the single-chain and the phase-separation problems can be extracted.[26]

At the next level of this theory, currently under development, the effects of free volume will become apparent. It will then be possible to compare quantitative lattice simulation results on blends with this model and to make comparisons with other treatments that incorporate free volume.[1–6] In addition, it will be necessary to formulate relationships between the microscopic parameters, which must appear in any statistical mechanical theory, and macroscopic observables. Concurrent with this effort will be the extension of this treatment to the continuum. The BGY approach was formulated as a continuum description,[11,12] so the basic model remains the same. However, analytic solutions are not to be expected. With the lattice results providing a first guess, iterative solutions involving numerical techniques will be appropriate. The results discussed here represent an encouraging start to a theoretical treatment that ultimately may provide quantitative predictive power for experimentalists.

Acknowledgment. I am grateful that there is an organization to acknowledge for financial support of this work, viz., the donors of the Petroleum Research Fund, administered by the American Chemical Society. The initial inspiration of S. G. Whittington should be recognized, and I have also benefited from discussions with W. G. Madden, and C. J. T. Landry.

Appendix

The unexpanded version of the expression for ΔA_{mix} is

$$\beta\Delta A_{\mathrm{mix}}/N_0 = [(1/r_1) - (z/2)]\phi_1 \ln \phi_1 + [(1/r_2) - (z/2)]\phi_2 \ln \phi_2 + (z/2)[\phi_1 \ln (\xi_1/\phi_1) + \phi_2 \ln (\xi_2/\phi_2)] - (z/2)\{\phi_2 \ln [1 + (\phi_1/\phi_2) \exp(-\beta(\epsilon_{12} - \epsilon_{22}))] + \phi_1 \ln [1 + (\phi_2/\phi_1) \exp(-\beta(\epsilon_{12} - \epsilon_{11}))]\} \quad (A.1)$$

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(13) A description richer in technical detail is currently being prepared. Interested readers are welcome to correspond with me. Added in proof: In the description now being prepared factors of ξ are incorporated in a self-consistent fashion, and the first term on the right-hand side of eq 3 appears naturally.

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(26) Two examples: First, consider the relationship between the mean-square end-to-end length of a chain ($\langle R_n^2 \rangle$) and the number of segments (n) which, for n large, is

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

For a mean-field treatment, $2\nu = 1$, whereas for a real chain in dilute solution (c is below c^*, the overlap concentration), in a good solvent, the value is believed to be close to 1.2. Another example is relevant to the case of a coexistence curve. As the critical point (T_c, ϕ_c) is approached, the composition dependence of the temperature can be described as

$$(T - T_c)/T_c \sim (\phi - \phi_c)^\beta \qquad \text{(ii)}$$

A mean-field model, for example, the Flory–Huggins or Guggenheim quasichemical models, yields $\beta = {}^1/_2$, while results using the Ising model show $\beta \cong {}^5/_{16}$; the latter more closely represents the behavior of real systems.