Phase Equilibria of Lattice Polymer and Solvent: Tests of Theories against Simulations

William G. Madden*

Central Research and Development Department and Polymer Products Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19880-0356

Adriana I. Pesci and Karl F. Freed

The James Frank Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. *Received April 25, 1989; Revised Manuscript Received July 13, 1989*

ABSTRACT: Computer simulations are performed to determine the coexistence curve for an incompressible polymer–solvent mixture on a simple cubic lattice in three dimensions. This model is isomorphic to that of a compressible pure polymer when the solvent molecules are regarded as vacanoies. Coexistence is established by letting the system separate into two phases, with the polymer-rich phase condensed against an adhesive boundary. A slight degree of polydispersity ($M_w/M_n = 1.084$) is included to take advantage of an especially efficient simulation algorithm. Comparison is made against the theories of Flory, of Guggenheim, and of Freed and co-workers. The Guggenheim quasichemical approximation is found to be in best agreement with the simulation results. The standard Flory lattice theory ("Flory–Huggins theory") proves accurate at very high polymer volume fractions but is poor at lower concentrations. The simulations reveal deficiencies in existing implementations of the Freed theory that can be eliminated by the inclusion of additional diagrams. Bulk-phase simulations were conducted to evaluate the term-by-term accuracy of the approximate theories in their predicted corrections to the Helmholtz free energy and internal energy of mixing. The Guggenheim and Freed theories are found to give good representations of the first-order perturbation term in the cohesive forces. They also agree well with one another in their predictions for the athermal Helmholtz free energy of mixing. However, the most elaborate implementation of the Freed theory now available gives a second-order term that is incorrect in both sign and magnitude. The quasichemical approximation in the Guggenheim theory gives a reasonable estimate of this term, but a cruder version of the Freed theory ("extended mean field theory") is in best overall agreement with simulation. This result suggests refinements of the systematic Freed theory that are necessary to reproduce the simulations. It is shown that the second-order term from extended mean field theory can be used in conjunction with accurate lower-order results to give improved agreement with simulations at intermediate densities.

I. Introduction

Lattice models have played an important role in the theory of polymer solutions since Flory,[1-3] Huggins,[4,5] Miller,[6] and Guggenheim[7-9] introduced and developed them in the early 1940s. Because the length scales appropriate to macromolecular systems are often much larger than the size of individual atoms, lattice models for polymers have proven more robust than corresponding models for small molecules. The solution of the lattice model requires approximations, the choice of which lead to differing results. The theories of Huggins, Miller, and Guggenheim are all equivalent in the athermal limit. Flory's version (the form usually called "Flory–Huggins" theory) is, even for athermal systems, equivalent to the other theories only in the limit of infinite lattice coordination number or in an infinite dimensional space. All these early workers differ in the way they introduce temperature dependence into their theories. The nature of their development makes it difficult to improve on these theories in a systematic fashion.

The original lattice models for polymeric solutions and blends were created specifically for application to an incompressible polymer–solvent or polymer–polymer mixture. It has been known since 1939 that the lattice theory for an incompressible alloy can be mapped onto a "lattice–gas" model in which one component can be interpreted as an empty site or "hole".[10] Only in the last dozen years or so has the same isomorphism been invoked for the equations of state for melt polymers, polymer blends, and compressible polymer solutions. Originally, Sanchez and Lacomb used Flory's version of the polymer lattice theory to obtain equations of state for melt polymers.[11] More recently, Panayiotou and Vera[12] and Kumar, Reid, and Suter[13] have interpreted various versions of the Guggenheim polymer–solvent lattice theory as polymer–hole theories for dense macromolecular systems.

Recently, Freed[14] noted that advances in field theory for spin systems enabled one to couple the spins into monodisperse chains of arbitrary complexity and with arbitrary branching characteristics. Using field theoretic techniques and making the requisite translations of spins into particles, Freed and co-workers[14-19] have developed the first completely rigorous and systematic analysis of the macromolecular lattice models. Instead of the usual approximate counting of microstates, Freed's technique begins with a rigorous formulation of the partition function on the lattice and expands the Helmholtz free energy as a series of integrals. These integrals are then represented as diagrams analogous to the familiar Mayer cluster diagrams for small molecule liquids and solutions in the continuum. The terms can then be grouped so as to provide an expansion in the reciprocal of the lattice coordination number z. The effects of nearest-neighbor interactions are evaluated via a perturbation expansion in the interaction energies whose individual coefficients are represented in similar fashion and further expanded in powers of z^{-1}. The technical complexity of the calculation dictates that only a few lower-order terms in this secondary expansion can be evaluated. The terms that are zeroth order in z^{-1} correspond to the limit of infinite coordina-

0024-9297/90/2223-1181$02.50/0

tion number. Since the individual integrals that arise in the theory are always tractable, the only limitations in the Freed theory are the assumption that the Helmholtz free energy is analytic in the expansion variables and the sheer number of integrals that arises as the two expansions are carried out to higher-order terms. This approach has recently been reformulated by Freed and Bawendi[19] using more conventional theoretical tools.

In order to test these theories unambiguously, comparison must be made against computer simulation results for specific lattice models. Despite the longstanding efforts in this area, no simple lattice model for a macromolecular system has been characterized as well as the model systems for small molecules in the continuum. We present here the first multichain simulation results for the coexistence curve of lattice polymers in the presence of solvent (or holes), and we explore the temperature and composition dependence of the internal energy of mixing and other properties. These simulation results are then compared with the Flory, Guggenheim, and Freed approximations to the standard lattice model.

II. Lattice Models

We consider a system made up of N_p polymer molecules each containing r beads (mers) and N_s monomeric solvent molecules (or holes) confined to a lattice. The polymer beads and solvent molecules interact via the nearest-neighbor potentials $-\epsilon_{pp}$, $-\epsilon_{ps}$, and $-\epsilon_{ss}$. The static structure and all excess properties of mixing are completely determined by the single parameter $\Delta\epsilon_{ps} = \epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}$. Except near the critical point, the excess Helmholtz free energy of mixing can be written as a perturbation series

$$\beta(\Delta A^{mix} - \Delta A_0^{mix})/N = \epsilon^* a_1 + (\epsilon^*)^2 a_2 + (\epsilon^*)^3 a_3 + \ldots \quad (1)$$

where $\beta = 1/k_B T$ is the reciprocal temperature, $\epsilon^* = \beta\Delta\epsilon_{ps}$, $N = rN_p + N_s$ is the total number of lattice sites, and ΔA_0^{mix} is the free energy of mixing of the infinite temperature (athermal) reference system. This latter quantity is of obvious entropic origin. The internal energy of mixing can be similarly expanded

$$\beta\Delta\epsilon^{mix}/N = \epsilon^* e_1 + (\epsilon^*)^2 e_2 + (\epsilon^*)^3 e_3 + \ldots \quad (2)$$

where the coefficients e_n are related to the a_n through $\Delta E^{mix} = [\partial(\beta\Delta A^{mix})/\partial\beta]_{N_p,N_s}$. Since the reference system is athermal, the perturbation series is identical with an expansion in reciprocal temperature. The a_n then do not depend on temperature, and

$$e_n = n a_n \quad (3)$$

For a theory that includes second- and higher-order terms, the distinction between the a_n and the e_n is a reflection of the temperature dependence of the entropy (structure). For an expansion about an athermal reference system, $e_1 = \Delta E_0^{mix}/(N\Delta\epsilon_{ps})$.

For the Flory version of the lattice theory,[1-3] the athermal free energy of mixing takes on the familiar form

$$\beta\Delta A_0^{mix}/N = \phi_s \ln \phi_s + [\phi_p/r] \ln \phi_p \quad (4)$$

where $\phi_s = N_s/N$ and $\phi_p = rN_p/N$ are the volume fractions of solvent and polymer, respectively, and $\phi_s + \phi_p = 1$. Equation 4 is appropriate for the mixing of monomers with any diffuse molecule occupying r sites. In the Flory theory, the term e_1 (= a_1) is approximated (consistently) by an expression appropriate to the mixing of uncorrelated monomers

$$e_1 = (z/2)\phi_s\phi_p \quad (5)$$

and all the other e_n and a_n are identically zero. In this notation, the original Flory χ parameter is then $\epsilon^* z/2$. The Flory lattice theory is therefore a first-order perturbation theory about the athermal reference system with a somewhat crude estimate of both the zeroth- and the first-order terms. When written in terms of the χ parameter, Flory's expression for the free energy of mixing gives no hint of its lattice origin. This has sometimes been seen as an advantage for the Flory version of the theory, suggesting that it is somehow more suitable than other lattice theories for polymers in continuum space. Though seductive, this argument is misleading. The details of the lattice vanish for excess properties of mixing only because the architecture of the molecules, including their chain character, has been entirely discarded. This assumption has no greater validity in the continuum than on a lattice. In both cases, spatial correlations of the mers can make significant contributions to the thermodynamics of the mixture.

In the Guggenheim theory,[7-9] some local effects of the connectivity of the chain are retained. Guggenheim's result for the mixing of athermal chains is identical with that of Huggins[4,5] and of Miller[6] and may be written as a correction to the Flory expression

$$\beta\Delta A_0^{mix}/N = \phi_s \ln \phi_s + (\phi_p/r) \ln \phi_p + (z/2)[\phi_s \ln \Theta_s/\phi_s + (q/r)\,\phi_p \ln \Theta_p/\phi_p] \quad (6)$$

where $\Theta_p = qN_p/(N_s + qN_p)$ and $\Theta_s = 1 - \Theta_p$ are the surface fractions of polymer and solvent. The quantity $zq = zr - 2r + 2$ represents the maximum number of noncovalent contacts that may be made by the beads of a linear polymer of length r. Guggenheim provides expressions for the probability of various kinds of noncovalent contact on the lattice both in the athermal limit[7] and within the context of the quasichemical (Bethe) approximation.[8]

Using Guggenheim's complete expressions,[8,9] one may construct a first-order perturbation theory analogous to Flory's, but with a more sophisticated treatment of the reference system. Panayiotou and Vera called this first-order Guggenheim theory the random mixing approximation.[12] The resulting expression for e_1 is given by

$$e_1 = (z/2)\Theta_p\phi_s = (z/2)(q/r)\Theta_s\phi_p \quad (7)$$

In the quasichemical approximation, the internal energy of mixing is of a similar form

$$\Delta E^{mix} = (z/2)\Theta_p\phi_s\Gamma_{ps}\epsilon^* = (z/2)(q/r)\Theta_s\phi_p\Gamma_{sp}\epsilon^* \quad (8)$$

where

$$\Gamma_{ps} = \Gamma_{sp} = 2/[1 + (1 + 4\Theta_p\Theta_s f)^{1/2}] \quad (9)$$

and $f = \exp(\epsilon^*) - 1$. Guggenheim's quasichemical approximation to the lattice model can be expanded in ϵ^* and put into perturbation form. Terms to all orders in ϵ^* appear, but only the e_1 and e_2 terms prove significant in this application.

The theories of Freed and co-workers are intentionally of the form of eq 1 with the expressions for ΔA_0^{mix} and for the a_n written in terms of an expansion in z^{-1}

$$\beta\Delta A_0^{mix}/N = \xi_0^{(0)} + z^{-1}\xi_1^{(0)} + z^{-2}\xi_2^{(0)} + z^{-3}\xi_3^{(0)} + \ldots \quad (10)$$

and

$$a_n = \xi_0^{(n)} + z^{-1}\xi_1^{(n)} + z^{-2}\xi_2^{(n)} + z^{-3}\xi_3^{(n)} + ... \qquad (11)$$

The $\xi_j^{(n)}$ are simple polynomial expressions in ϕ_p and ϕ_s. The theory is constructed so that the terms $\xi_0^{(0)}$ and $\xi_0^{(1)}$ are just the Flory expressions for ΔA_0^{mix} and a_1.

Bawendi and Freed have carried out the expansion of ΔA_0^{mix} to $O(z^{-2})$, and recently Pesci and Freed have obtained expressions for a_1 to $O(z^{-2})$, a_2 to $O(z^{-1})$, and a_3 to $O(z^0)$. A subset of the higher-order $\xi_0^{(n)}$ may be used to construct an "extended mean field" theory[16] which, in the spirit of the original Flory approximation, represents the higher-order fluctuations as those in a mixture of spatially uncorrelated monomers. In the Freed formalism, it is the $\xi_j^{(n)}$ ($j \neq 0$) which systematically introduce the architecture of the polymer. The detailed expressions are somewhat complicated and are available elsewhere for a number of quite general cases.[15,17]

It is worth noting one crucial philosophical difference between the approach of Freed et al. and some earlier workers (notably Huggins and Guggenheim). In the earlier theories, the configurational integrals for individual polymer molecules are factored out of the full N-body partition function and are assumed to be independent of composition. Consequently, they do not appear in the final expressions for the excess chemical potentials (or the pressure). Without this assumption, earlier theories do not reduce to the isolated chain thermodynamics at vanishing ϕ_p. However, as ϕ_p is increased, there is a strong coupling of intra- and intermolecular effects on polymer configurations (nearly cancelling at the highest densities or concentrations), and the assumption that these prefactors do not depend on concentration over a wide range of concentration is therefore clearly incorrect. The Freed approach does not involve factoring out the intramolecular partition function and, in principle, accounts for the changes in the intramolecular structure as a function of concentration.

Whether the truncated expansions in ϵ^* and in z^{-1} are adequate to this task at all volume fractions is at the very least questionable. In the limit of infinite dilution, the Freed approach, if carried out to all orders, would properly reduce to a product of single-molecule partition functions and thus formally provides a theory for the isolated polymer molecule in solution. However, the properties of dilute and semidilute polymer solutions are often not susceptible to the simple expansions of eq 2, 10, and 11. For a good solvent, in the semidilute regime, the osmotic pressure is known to scale as $\phi_p^{9/4}$. This result is consistent with both scaling[20] and renormalization group[21] analyses but is difficult to reconcile with any straightforward polynomial expression.

III. Simulation Methods

Computer simulations were performed by using the combination of Wall/Mandel reptations[22] and Olaj/Mansfield pseudokinetics[23,24] described in previous reports.[25,26] Though the kinetic aspects of the algorithm are most useful in the calculation of properties that depend on global chain conformations, it has also been established[26] that for properties accumulated on a bead-by-bead basis the algorithm can reduce (by an order of magnitude or more) the length of a simulation required to achieve a desired statistical uncertainty. This class of properties includes the energies of mixing and the densities of coexisting phases, which are the fundamental data used in most of the analyses undertaken here. The pseudokinetic simulations produce a polydisperse sample characterized by a square-mound distribution of molecular weights.[25] Except at noted, the number-averaged molecular weight M_n was set at exactly 100 (beads), and the minimum and maximum molecular weights were 50 and 150, respectively. These parameters lead to the dispersity ratios $M_w/M_n = 1.084$ and $M_z/M_w = 1.065$ (to within one part in one thousand). It is not intended that the distribution achieved in these simulations be representative of any realizable polymer sample (though the technique permits wide latitude in the construction of the distribution of molecular weights[23,24]). Rather, the breadth and shape of the molecular weight distribution were chosen so as to produce results that can be compared reliably against analytical theories for monodisperse samples while the peculiar efficiencies of the pseudokinetic aspects of the algorithm are retained. The consequences of the finite chain length and the modest degree of polydispersity are considered further below.

The methods most often used to establish phase equilibria for small molecule liquids involve simulation in ensembles which require that additional molecules be inserted into an already dense system.[27-31] Such methods are limited to situations where there is adequate room in the system to accommodate the inserted species with reasonable frequency. The sheer size of a polymer molecule prevents the direct simulation of truly macromolecular systems at high concentration using algorithms based on any simple insertion technique. Semigrand canonical methods require only that one species of a mixture be transformed into another.[32] Sariban and Binder[33] have been able to apply the semigrand methodology to a sample consisting of two lattice polymers and a small fixed number of holes. This system was chosen to have a high degree of symmetry (the two polymers were identical except for the cross interaction between them), and molecules of one polymer species were transformed into the other subject to a constraint of a fixed difference in their chemical potentials. Because of the enormous size difference between a polymer molecule and a solvent molecule, the semigrand methods are not obviously appropriate in the determination of polymer–solvent (or polymer–hole) equilibria.

In recent work, Madden has used the pseudokinetic simulation method to study the interfaces of lattice polymers with hard walls,[25,26] with solvent (vacuum),[25] and with other polymeric phases.[34] Though the geometry of a planar slab was employed in the simulations, it was established[26] that relatively thin polymeric slabs achieve a bulk character in their interiors. The interfaces between two such polymeric slabs or between one slab and another medium are thus representative of the interfaces with bulk polymer phases under similar conditions. Heterogeneous simulations of this sort are essentially similar to an experiment in which several phases are simultaneously present and in equilibrium within a sealed vessel.

In the case of canonical Monte Carlo or molecular dynamics simulations of small molecules, the coexisting liquid/vapor densities deduced from similar simulations were found not to be in quantitative agreement with the results of simulations employing bulk geometries and the more elegant statistical mechanical methods mentioned earlier. The observed differences were attributed to the premature truncation of a continuous potential of formally infinite range. It is straightforward to correct for this truncation in bulk geometries, but the problem is less easily addressed in inhomogeneous samples.[35] For a nearest-neighbor lattice model, the interbead poten-

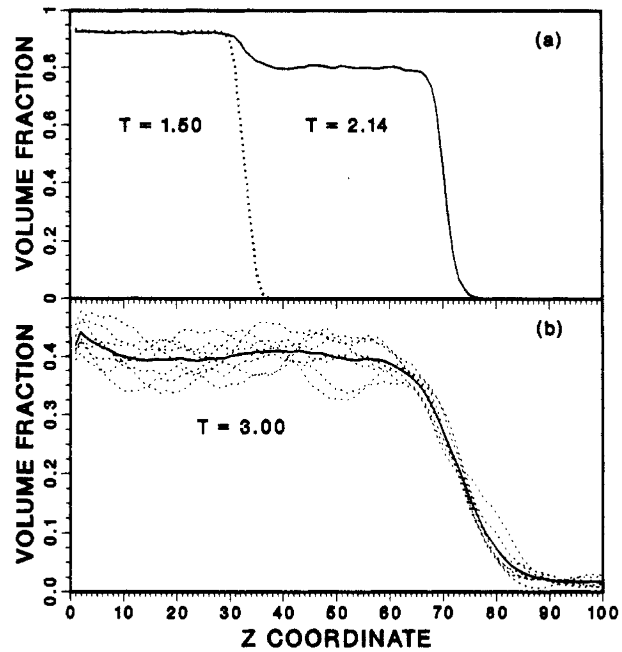

Figure 1. Volume fraction of polymer as a function of distance from adsorbing wall: (a) comparison of polymer–solvent (dotted curve) simulation and polymer–polymer–solvent (solid curve) simulation at low temperature; (b) high-temperature simulations. Solid curve is the average of eight individual simulations.

tial is rigorously of finite range, and such considerations are not an issue. We therefore analyze the bulklike regions observed in heterogeneous simulations performed with slab geometries and determine the properties of the coexisting phases. In those cases where several immiscible polymers (differing only in the strength of the nearest-neighbor interaction energies) were found to coexist simultaneously with a phase of pure solvent (or vacuum), a single simulation developed two bulk regions, each containing a different polymer. With an appropriate rescaling of the temperature, each of these simulations yielded two data points for the figures reported here. In all cases, the coexisting densities obtained from single layer or multiple layer geometries were found to be in good agreement, provided that only one polymeric species was present in the interior of any one layer. Most of the simulations reported here were originally obtained for a variety of other purposes. They vary in duration from 5000 moves or attacks per chain to over 100 000 moves or attacks per chain (at the highest temperature). Equilibrium was established in prior relaxation runs 2–10 times longer in duration.

IV. Results and Discussion

Figure 1a compares the observed bead density (polymer volume fraction) in a polymer–solvent (polymer–vacuum) simulation with that observed in a polymer–polymer–solvent (polymer–polymer–vacuum) simulation at relatively low temperatures. In each case, the sample is adsorbed on an adhesive wall at $z = 0$, whose influence has been shown to vanish within a few lattice layers.[25] The figure shows the magnitude of the spatial fluctuations in density typically found in these simulations and demonstrates that consistent results are obtained from simulations employing single-slab and two-slab geometries. At $T = 3.00$, the highest temperature employed in simulations using the slab geometry, considerably larger fluctuations are observed. The results of a series of *eight* polymer–solvent simulations at $T^* = 3.00$ are

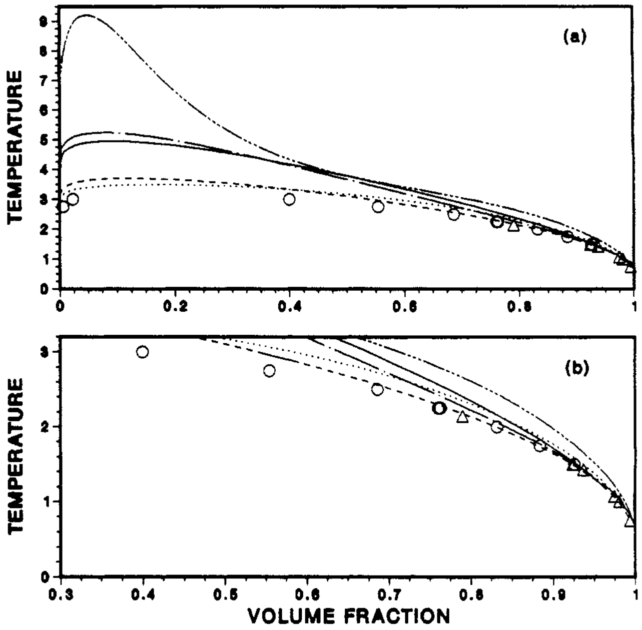

Figure 2. Coexistence curves from simulation compared with the predictions of lattice theories: circles, single-layer simulations; triangles, double-layer simulations; —, Flory; ···, GRM; - - -, GQC; – · –, EMF; - - - - -, PF3; (a) full curves; (b) expanded scale.

reported in Figure 1b. Each of these simulations is as long or longer than the simulations shown in Figure 1a. Though most of the fluctuations are removed in the average density profile (also shown), the large magnitude of the density fluctuations in the individual runs illustrates the difficulty of achieving reliable bulk phase properties at this highest temperature. The increased density fluctuations observed at $T^* = 3.00$ appear to be a result of the reduced contribution from the pseudokinetics at the observed volume fraction (mean $\phi_p = 0.401$). With use of the same spatial domain to obtain a bulk ϕ_p for each of the runs at $T^* = 3.00$, the standard deviation of the mean is found to be 0.003. For all the averages reported here, this represents a worst case result. For other volume fractions, we do not have available the requisite block averages to perform a meaningful statistical analysis. However, from the magnitude of the observed *spatial* fluctuations in the bulk region and from comparison of duplicate runs available at several of the lower temperatures, we conclude that the uncertainties in the bulk ϕ_p are smaller than the size of the symbols used to plot the data.

A. Coexistence Curve. Figure 2 presents the coexistence curve for the polymer–solvent (polymer–vacuum) system obtained by averaging the bead densities over the central region of each slab. Only a single polymer species is present in the averaging region. For those simulations in which two immiscible polymers are present, the two polymer species share conformal potentials, differing only in the magnitudes of their energetic parameters. The temperature in each bulk region is reported on a scale appropriate to the polymer present in that phase: $T^* = k_B T / \Delta\epsilon_{0i}$, where 0 indicates solvent and i indicates polymer species i which is present in that bulk region. The spatial range over which averages were taken was varied in order to ensure that the results were not sensitive to any specific definition of the limits of the bulk region. Between 7 and 12 lattice layers adjacent to each interface were typically excluded from the bulk averages within any given phase. Except as noted, all points correspond to a sample with $M_n = 100$ and

Table I
Simulation Results

ϕ_p	T^*	$\Delta E^{mix}/N\Delta\epsilon_{ps}$
	Bulk Runs	
0.900	1.750	0.2330
0.900	2.500	0.2403
0.900	3.000	0.2433
0.900	5.000	0.2485
0.900	∞	0.2553
0.800	2.250	0.3857
0.800	3.000	0.4014
0.800	∞	0.4349
0.700	2.250	0.4546
0.700	2.500	0.4721
0.700	3.000	0.4909
0.700	5.000	0.5181
0.700	8.000	0.5300
0.700	15.000	0.5393
0.700	25.000	0.5437
0.700	50.000	0.5464
0.700	∞	0.5511
0.600	2.750	0.5112
0.600	3.000	0.5213
0.600	∞	0.6027
0.500	3.000	0.5055
0.500	5.000	0.5557
0.500	8.000	0.5755
0.500	15.000	0.5901
0.500	25.000	0.5951
0.500	50.000	0.6006
0.500	∞	0.6022
0.400	15.000	0.5401
0.400	∞	0.5535
0.400	∞	0.5529
0.300	10.000	0.4445
0.300	∞	0.4612
0.200	10.000	0.3218
0.200	20.000	0.3279
0.200	∞	0.3328
0.200	∞	0.3329
0.100	10.000	0.1710
0.100	20.000	0.1739
0.100	∞	0.1761
0.100	∞	0.1762
	Coexistence Runs	
0.924	1.500	0.1696
0.790	2.143	0.3912
0.981	1.000	0.0364
0.937	1.429	0.1685
0.994	0.750	0.0044
0.975	1.071	0.0859
0.994	0.750	0.0031
0.925	1.500	0.1634
0.926	1.500	0.2231
0.884	1.750	0.2651
0.884	1.750	0.2860
0.832	2.000	0.3444
0.760	2.250	0.4164
0.763	2.250	0.4120
0.762	2.250	0.4183
0.686	2.500	0.4805
0.400	3.000	0.4413
0.023	3.000	0.0362

$M_w/M_n = 1.084$. At $T^* = 2.25$ we have also obtained results from two additional simulations with $M_w/M_n = 1.004$, and at $T^* = 1.75$ we have also obtained results from a simulation with $M_n = 200$ and $M_w/M_n = 1.084$. As seen in Table I, the bulk densities calculated from these simulations are superposable on the results obtained for $M_n = 100$ and $M_w/M_n = 1.084$, and in fact cannot be distinguished in the figures.

The asymmetry of the coexistence curve is clearly evident and is principally a consequence of the contribution of the size of the polymeric species to the athermal part of the free energy of mixing. Except at the highest temperatures a dilute (vapor) phase is not observed and is not expected in simulations of finite duration. The critical temperature cannot be determined precisely from simulations of this nature but would appear to lie in the interval $T^* = 3.2$–3.5. The critical temperature varies with M_w, as does the critical volume fraction.[37] However, the approximate lattice theories suggest that the shapes of the coexistence curves are nearly identical for two polymer samples of very different average molecular weight until the temperature of the sample of lower mean molecular weight approaches its critical temperature. The agreement of two simulations at $T^* = 1.75$, one with $M_n = 100$ ($M_w = 108$) and the other with $M_n = 200$ ($M_w = 217$), provides a specific test of this prediction.

Because the simulations were performed on polydisperse samples, the overall sample is only "quasibinary", and the system critical point will move slightly off the maximum in a plot of T vs ϕ. Stockmayer[36] has examined the effects of polydispersity on the critical point within the context of the Flory lattice theory, which should be adequate to assess the magnitude of the effect. For the rather narrow distributions used here, Stockmayer's equations predict that the critical temperature and the critical volume fraction $\phi_{p,c}$ in the polydisperse system will be within 1% of the monodisperse critical parameters. This result, coupled with the observed insensitivity of the coexisting volume fraction to variation in M_w/M_n at $T^* = 2.25$, leads us to infer that, for all $\phi_p > \phi_{p,c}$, the coexistence curve is not substantially affected by the polydisperse nature of our samples. However, for $T^* > 2.75$, we do observe some detachment of smaller chains from the surface. This detached material is of lower molecular weight ($M_n = 60$–70) than that in the denser phase ($M_n = 100$). Though we believe this result to be correct for the polydisperse sample actually simulated, all of the approximate lattice theories (in their monodisperse forms) predict minute polymer concentrations in the dilute phase at these temperatures or a temperature comparably close to the predicted critical points. Simulations of a monodisperse sample would therefore not be expected to show significant amounts of polymer in the dilute phase at any temperature considered here, even though the polymer concentration on the higher concentration side of the coexistence curve would in all cases be nearly identical with that reported in Table I.

Also shown in Figure 2 are the predictions of a number of approximate lattice theories for a mixture of monodisperse chains with $r = M_n = 100$ and a monomer solvent. (No significant differences are observed with $r = M_w = 108.4$.) For $\phi_p > 0.9$, all theories give quite similar results, with the original Flory theory (F) and the quasichemical version of the Guggenheim theory (GQC) in best agreement with the simulation results. For lower ϕ_p, the predictions of the approximate theories diverge dramatically. The Flory lattice theory becomes especially poor, predicting a critical temperature of about 4.95. In contrast, the quasichemical theory is in good agreement with the simulation results at all temperatures below 2.5. The coexistence curve obtained by using this approximation does, however, depart from the simulation results at higher temperatures and predicts a critical temperature of about 3.7. The Guggenheim random mixing (GRM) result seems slightly better near the critical point but is poorer than either the GQC or Flory results at higher volume fractions. The extended mean field theory (EMF) produces a coexistence curve that improves slightly on the lower-order Flory mean field results, except near the

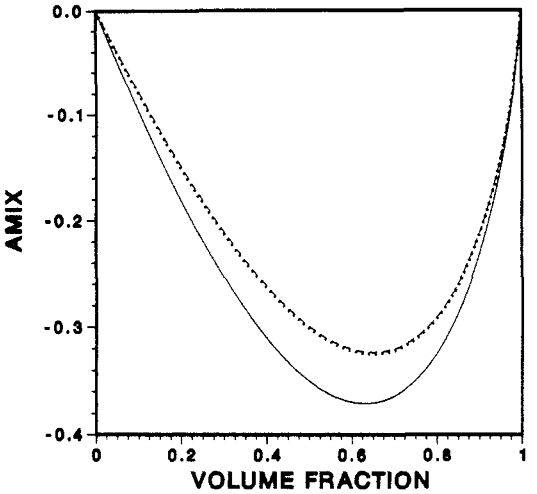

Figure 3. Athermal Helmholtz free energies of mixing ($\beta \Delta A_0^{\text{mix}}$) from lattice theories: —, Flory; ···, Huggins–Miller–Guggenheim (HMG); - - -, Bawendi–Freed.

critical point. Surprisingly, the third-order Pesci–Freed theory (PF3) produces a coexistence curve with a peculiar shape, including a region of positive curvature at intermediate volume fractions. This feature is not seen in the predictions of the other approximate lattice theories nor is it suggested by the simulation results. **[Note Added in Proof**: The Pesci–Freed theory is the most elaborate published implementation of the Freed formalism. In implementing that theory, Pesci and Freed neglect certain diagrammatic corrections of order r^{-1} in the thermal expansion of the free energy. While such terms are individually small and are collectively negligible at sufficiently high molecular weight, they prove comparable to other terms of order r^{-1} retained by these workers. Prompted by the present comparison, the Freed expansion has been recomputed through second order in ϵ with all molecular weight dependencies retained. While the internal energy of mixing changes only slightly, the coexistence curves are quite sensitive to the inclusion of these additional terms. The new expressions yield results for ΔA_0^{mix} and e_1 that are nearly identical with those shown for the Guggenheim random mixing approximation. The revised expressions completely eliminate all anomalies and produce a more accurate coexistence curve than any of the theories considered here. These results will be presented elsewhere.[42]]

B. Athermal Limit and Energies of Mixing. Figure 3 compares the athermal free energies of mixing for chains with $r = 100$ by using the Flory lattice theory, the Huggins/Miller/Guggenheim (HMG) theory, and the Bawendi–Freed (BF) theory[15] (second order in z^{-1}). The BF theory is the athermal limit of the Pesci–Freed theory. Though the athermal free energy of mixing is not easily obtained via simulation, Dickman and Hall[37] have applied Widom's potential distribution theory[38] to athermal computer simulations of short chains at low-to-intermediate volume fractions. These workers established that both the HMG expression and the BF expressions offer significant improvement over the Flory result for such systems. The technique used by Dickman and Hall provides a prediction for the probability of inserting an additional chain into the system. The calculated insertion probability is directly related either to the pressure or to the excess chemical potential of solvent, depending on the interpretation of the monomeric species as either holes or particles. More recently, Hertando and Dickman[39] have used the density of a thermal lattice polymer at a hard wall to determine the pressure of neat polymer (or solvent chemical potential) at higher polymer volume fractions densities and higher molecular weights. Again, the Bawendi–Freed and HMG theories are found to be more accurate than the Flory theory, though somewhat larger discrepancies between the theories and simulations are observed for long chains at lower volume fractions.

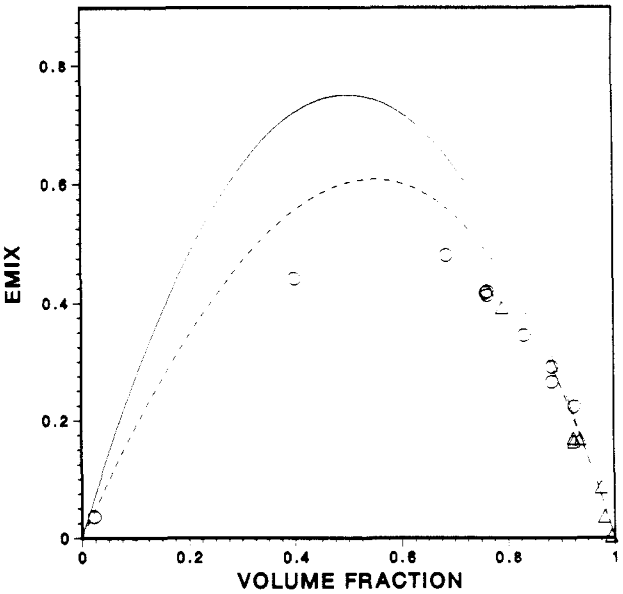

Figure 4. Internal energy of mixing ($\Delta E^{\text{mix}}/N\Delta\epsilon_{\text{ps}}$) along coexistence curve: circles, single-layer simulations; triangles, double-layer simulations; —, Flory; - - -, GRM.

Figure 3 is entirely consistent with the results of Dickman and Hall. For chains with $r = 100$, the HMG and BF theories are found to predict free energies of mixing in close agreement over the full range of ϕ_{p}. The Flory theory gives significantly different results at all but the highest volume fractions. However, it is the excess chemical potentials, derivatives of the free energy of mixing, which determine the coexistence curve. Further, the dilute phase has only a minute concentration of polymer, except near the critical temperature. At these lower temperatures, the coexisting concentration in this regime is effectively achieved when the chemical potential of the solvent in the mixture equals its pure bulk value (a condition of zero pressure in the polymer–hole interpretation). This condition arises from a delicate cancellation of the athermal chemical potential with correction terms arising from the intermolecular forces. Thus, the very small differences between the HMG and Bawendi–Freed theories can lead to somewhat larger differences in the predicted coexistence curves than a cursory examination of Figure 3 would suggest.

Though the direct simulation of chemical potentials and free energies of mixing is exceedingly difficult for the polymer–solvent system at high ϕ_{p}, the internal energy of mixing is easily accessible. Figure 4 reports the internal energies of mixing ($\Delta E^{\text{mix}}/N\Delta\epsilon_{\text{ps}}$) obtained from averages of a typical bead potential over the bulk regions of the inhomogeneous simulations used in the construction of Figure 2. Also shown are the Flory and GRM results, for which internal energies of mixing are independent of temperature. Both differ substantially from the simulation results. Figure 5 shows the internal energies of mixing obtained from a series of bulk simulations (homogeneous samples with no interfaces and no coexisting phases) along the isotherms $T^* = 3.00$ ($\epsilon^* = 1/3$) and $T^* = \infty$ ($\epsilon^* = 0$, the athermal limit). The calculations at $T^* = \infty$

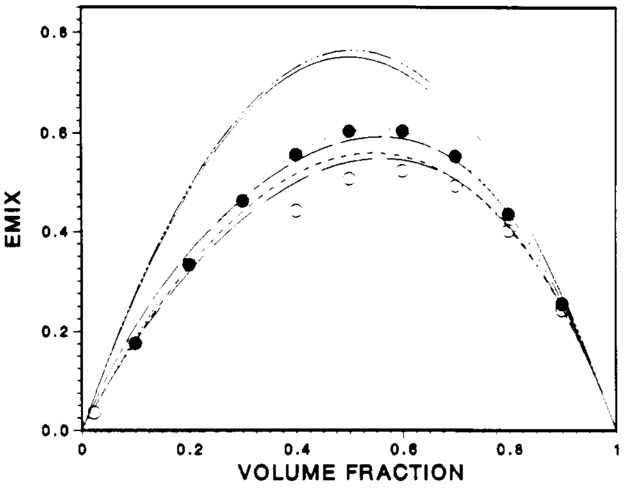

Figure 5. Internal energy of mixing along isotherms: solid circles, simulation at $T^* = \infty$ (e_1); open circles, simulation at $T^* = 3.00$; —, Flory; ···, GRM; - - -, GQC; — — —, Pesci–Freed (first order); — - - - -, Pesci–Freed (third order); —·—, GRM + e_2(EMF).

give a direct determination of e_1. For $\phi_p \geq 0.9$, the data obtained at the two temperatures are in nearly quantitative agreement, suggesting that only the leading term in the ϵ^* expansion is required for the construction of an accurate theory for the internal energy of mixing. This volume fraction corresponds to a compressible polymer at melt density, and its weak temperature dependence indicates that the contact probability for unlike beads at finite temperature is only very slightly perturbed by the inclusion of the cohesive forces. From the lattice fluid viewpoint, this result is consistent with the physical picture underlying the accurate perturbation theories developed for small-molecule liquids at high density. There, the set of pair distribution functions is determined almost entirely by the repulsive parts of the intermolecular potentials and is largely unaffected by the inclusion of weakly varying attractive forces. From the viewpoint of a polymer–solvent solution, the same data suggest that, for $\phi_p \geq 0.9$, the solvent is near its Henry's law condition. At lower volume fractions, the internal energy of mixing at finite temperature departs dramatically from its value in the infinite temperature limit, and higher-order theories are clearly required.

Figure 5 also shows the predictions of the various lattice theories for the internal energy of mixing. Both the Flory lattice theory and the GRM approximation are rigorously first-order. The GRM result is in quantitative agreement with the first-order simulation results, but except at high volume fractions, the predictions of the Flory theory are quite poor. The failures of the Flory theory can therefore be attributed not only to the absence of higher-order contributions in ϵ^* but also to its poor prediction of the first-order contribution. In fact, its success at high polymer volume fraction is quite clearly a consequence of a cancellation of errors between its somewhat crude estimates for the athermal free energy of mixing and for the correction for the cohesive forces. Even though the coexistence curve from the full PF3 theory was found to be in poor agreement with the simulation results, Pesci and Freed's prediction for e_1 is in very good agreement with the simulation result and is only slightly poorer than the GRM prediction. The published version of the Pesci–Freed approach omits some terms of order r^{-1} in the ϵ^* dependence of the free energy of mixing. The form used in these calculations omits all molecular weight dependences in the thermal portion of the free energy of mixing. Such terms should be unimportant for most real polymer molecules.

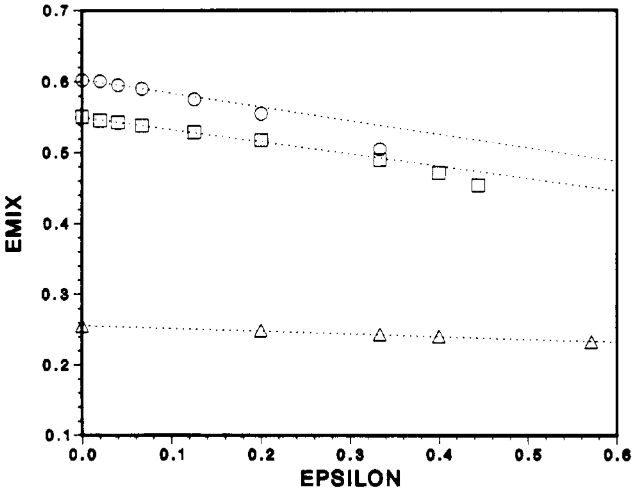

Figure 6. Internal energy of mixing as a function of ϵ^*: points are simulations; lines are fits to simulation data at low ϵ^*; circles, $\phi_p = 0.5$; squares, $\phi_p = 0.7$; triangles, $\phi_p = 0.9$.

A first-order perturbation theory provides an upper bound on the net correction to the thermal part of the Helmholtz free energy of mixing, and since either the infinite-temperature state or the finite-temperature state may be regarded as the reference system, the Helmholtz free energy of mixing at $T^* = 3.00$ (or any higher temperature) is rigorously bounded by the two sets of simulation results reported in the figure.[40,41] Also shown are the results for the full third-order Pesci–Freed theory at $T^* = 3.00$. These are clearly worse than the corresponding first-order results and indicate errors in higher-order terms. The remaining two curves on the figure are the results for $T^* = 3.00$ of the Guggenheim quasichemical approximation (GQC) and a modified Guggenheim theory introduced below (denoted GRM + e_2(EMF)). Both show a significant improvement over the other theories at all volume fractions. [The results of the recomputed lattice theory are better still.[42]]

C. Higher-Order ϵ^* Contributions. In order to assess the importance of individual higher-order terms in the ϵ^* expansion, we undertook a series of bulk simulations at increasingly higher ϵ^* (lower temperature) for $\phi_p = 0.5, 0.7$, and 0.9. The results are shown in Figure 6. The highest values of ϵ^* were chosen so that the system remained within the single-phase region. First-order convergence would be indicated if the energies of mixing were independent of ϵ^*. This is nearly so at $\phi_p = 0.9$, where the data fall on a straight line with a slight negative slope (indicating a small second order contribution). At the lower densities, the data deviate substantially from the $\epsilon^* = 0$ limit in a nonlinear fashion, demonstrating that terms through at least third order in ϵ^* must be retained.

We have estimated the second-order contribution to the ϵ^* expansion of the internal energy of mixing at $\phi_p = 0.5$, $\phi_p = 0.7$, and $\phi_p = 0.9$ by fitting the simulation data in the neighborhood of $\epsilon^* = 0$ to a straight lines and to quadratic equations. The two fitting procedures give estimates for e_1 and e_2 that are in complete agreement with one another. At each density, the second-order theory gives a straight line in the figure, and our best estimates for these lines are indicated in Figure 6. The figure makes clear that terms beyond second-order are required at $\phi_p = 0.5$ and $\phi_p = 0.7$. However, the magnitude (and even the sign) of the e_3 term was found to be sensitive to the order of the polynomial used in the fit,

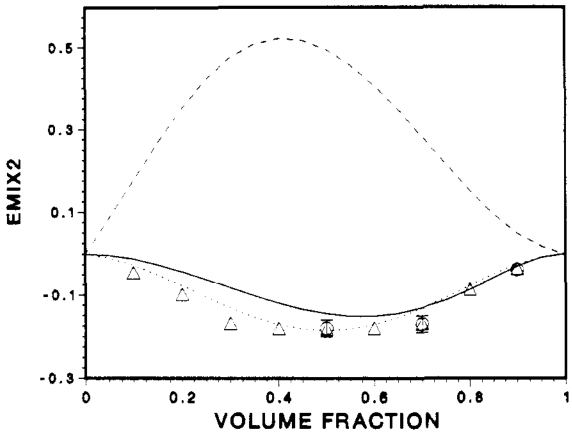

Figure 7. Second-order terms e_2: circles, slopes of the lines in Figure 6; triangles, finite difference of simulation results at high temperature; —, GQC; ···, EMF; - - -, Pesci–Freed.

and the magnitudes of both the e_3 and e_4 terms so obtained were comparable to that of the e_2 term. We are therefore led to believe that, at $\phi_p = 0.5$ and $\phi_p = 0.7$, both the third- and fourth-order terms are not negligible at coexistence temperatures, but we are not even able to predict their individual signs with confidence.

The predictions from the three theories for e_2 are compared in Figure 7 for the complete range of ϕ_p. At most volume fractions, the second-order term was established by finite difference using the previously reported result for $T^* = \infty$ and one additional simulation at a high, but finite, temperature ($20 \leq T^* \leq 50$). Also shown are the three points determined at $\phi_p = 0.5$, 0.7, and 0.9 from the fits shown in Figure 6. The error bars shown for these volume fractions are the standard deviation of the e_2 coefficient as determined by the fitting program. The quasichemical approximation and the extended mean field theory both predict that the e_2 term is negative and that it becomes substantial at intermediate volume fractions. The second-order term from the EMF theory appears to be in better overall agreement with the simulation over the full range of volume fractions. The Pesci–Freed results disagree in both magnitude and sign with the simulation estimates and are skewed to lower, rather than higher, volume fractions. The errors in this term are a significant source of the overall error in the Pesci–Freed results at high ϕ_p. [The e_2 obtained from the recomputed lattice theory[42] is even better than that obtained from the EMF.]

Though the simulation data do not yield unambiguous estimates for the e_3 term, Figure 8 compares the predictions for this term obtained from the extended mean field theory and from the Guggenheim quasichemical approximation. The $\xi_j^{(3)}$ from the Freed theory are not available for $j > 0$. The Guggenheim theory produces negative, but very small, third-order terms. Higher-order terms within the theory are also minute, and the Guggenheim quasichemical approximation is therefore found to be effectively second-order in this application. In contrast, the third-order terms for the EMF theory are positive. Our attempts to fit the simulation data do not preclude positive third-order terms such as those arising from the EMF, providing that there are higher-order terms that are substantial and negative. [In the recomputed theory,[42] the EMF e_3 is negative and quite small.] However, at low temperatures and low enough densities, the collapse of unscreened chains ought not be well described by any theory that cannot account for chain connectivity, and considerable caution must be exercised in applying any polymer mean field theory under such circumstances.

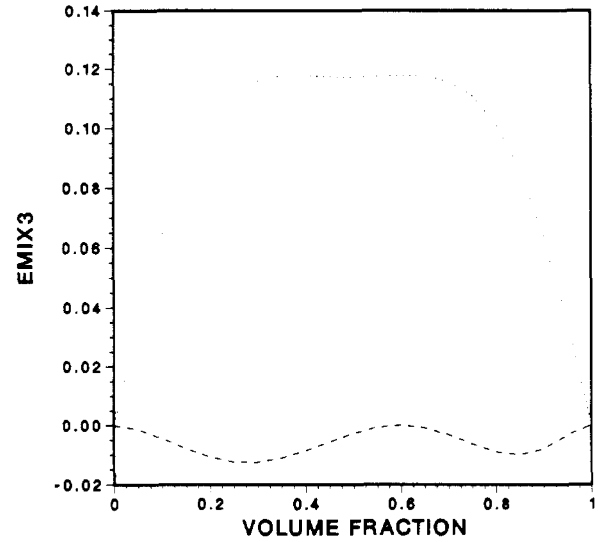

Figure 8. Third-order terms e_3: – – –, GQC; ···, EMF.

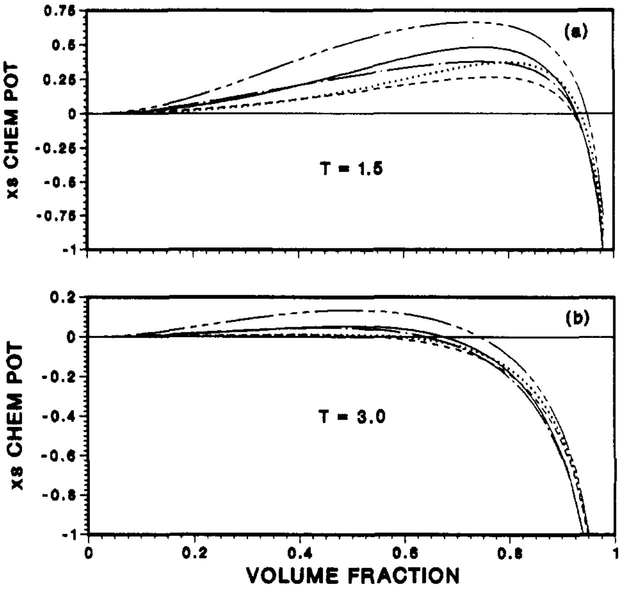

Figure 9. Excess chemical potential of solvent ($\beta\Delta\mu^e_s$) at $T^* = 1.5$ and at $T^* = 3.0$. The key is as in Figure 1.

D. Chemical Potential and Chain Dimensions. The excess solvent chemical potential $\beta\mu^e_s$, defined as the difference between the chemical potential of solvent in the mixture and the chemical potential when pure, is displayed in Figure 9 for two temperatures. Since all the lattice theories predict negligible polymer in the solvent-rich phase, the controlling condition for phase equilibrium is $\beta\mu^e_s = 0$ (a condition of zero pressure in the lattice fluid model). At the lower temperature and lower volume fractions, the $\beta\mu^e_s$ curves for the theories diverge substantially from one another, but they are closely spaced as they intersect the line $\beta\mu^e_s = 0$. The Pesci–Freed curve differs from the others mostly because of its anomalous second order term. At the higher temperature, the general shapes of the curves are more similar, but they cross the line $\beta\mu^e_s = 0$ at rather different volume fractions, leading to the diverging coexistence curves of Figure 2. At more negative values of $\beta\mu^e_s$ (higher pressures), the theories converge to two distinct limiting curves. Under these high-volume-fraction conditions, only the zeroth- and first-order terms contribute. The Pesci–Freed and Guggenheim theories are in good agreement for these two terms and thus coalesce to form one curve. The Flory

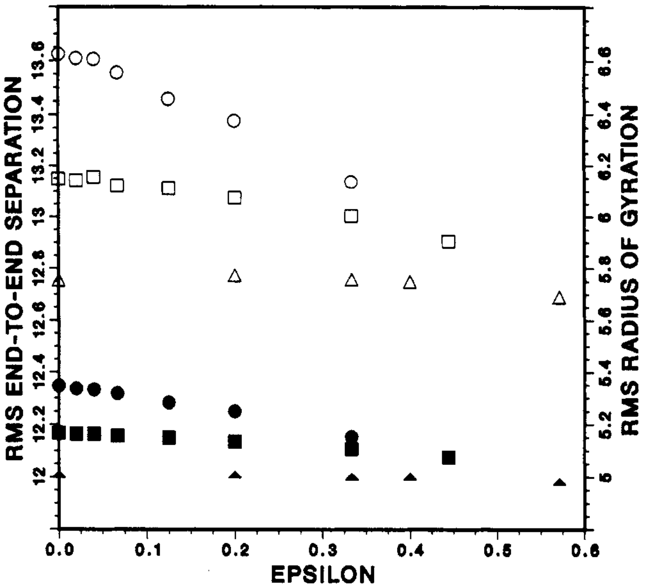

Figure 10. Root-mean-square end-to-end separation (open points, left scale) and root-mean-square radius of gyration (solid points, right scale) as a function of ϵ^*: circles, $\phi_p = 0.5$; squares, $\phi_p = 0.7$; triangles, $\phi_p = 0.9$.

and EMF theories share common zeroth- and first-order terms, different from the other three theories, and thus have a different limiting form. Since very negative values of μ^e_s correspond to high pressures in the lattice fluid model, this may be of some significance in applying a lattice fluid theory to equation of state data for melt polymer at high pressure. Under such circumstances, the deficiencies observed for the Freed theories at low (coexistence) pressures may no longer apply.

Figure 10 shows how the root-mean-square end-to-end separations and the root-mean-square radii of gyration depend on ϵ^* at three volume fractions. These quantities reflect the global conformation of the chains, and their variations provide crude measures of changes in intramolecular structure. The pseudokinetic algorithm has been shown to be especially effective in improving the statistical uncertainties for such properties when compared with more conventional simulation techniques.[26] However, the figure shows more scatter than those for the corresponding internal energies of mixing because these quantities are intrinsically more difficult to obtain with good precision. The figure illustrates clearly that the conformational properties of the chains are not invariant to composition. The scale of the figure is quite expanded, and the magnitude of the changes are admittedly small. At lower ϕ_p, the effects are known to be more pronounced.[2,3] Though the theories of Freed and co-workers are not now constructed so as to permit the extraction of these data, the structural changes revealed in the figure as well as more subtle, local configurational changes are implicitly included in their expression for the Helmholtz free energy. The traditional lattice theories do not have embedded within them any information concerning the large scale structure of the chains.

E. Further Comparisons. The work of Dickman and Hall[37,39] and the results presented in Figure 5 suggest that both the HMG theory and the most elaborate of the Freed theories give good representations for the free energy of mixing of athermal chains and for e_1. The extended mean field theory was found to be in best overall agreement with the simulation estimates for e_2. Figure 11 presents the coexistence curves obtained when these empirical results are used a guide in the selection of appropriate approximations. In view of Figures 3 and 5, one would expect that a first-order Pesci–Freed theory should give results similar to the Guggenheim random mixing approximation. This proves to be true at high volume fractions ($\phi_p > 0.8$), but the Pesci–Freed result again departs from the simulation in a fashion similar to that observed in Figure 2 for the full Pesci–Freed theory. A qualitatively similar departure is observed if *either* the A_0^{mix} term or the a_1 term in the Guggenheim theory is replaced with the corresponding term from the Pesci–Freed theory. We therefore conclude that the errors in the Pesci–Freed prediction of the critical point arise from the very minor differences shown in Figure 3 and 5, which become exaggerated upon differentiation.

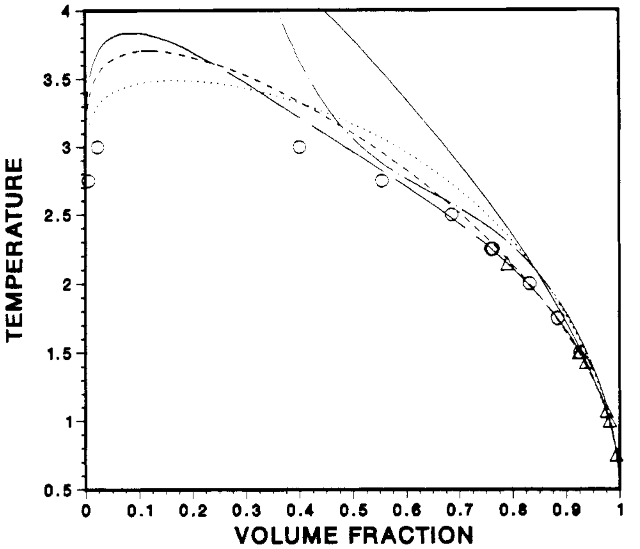

Figure 11. Coexistence curves from modified lattice theories: circles and triangles, simulations; ···, GRM; - - -, GQC; — — —, GRM + e_2(EMF); — · —, Pesci–Freed (first-order); —, Flory.

Figure 11 also shows the coexistence curve obtained when the extended mean field (EMF) second-order term is added to the random mixing theory. At high and intermediate polymer volume fractions, this supplemented Guggenheim theory agrees better with the simulations than does the prediction of the quasichemical approximation because it includes a better estimate of the second-order term. At lower volume fractions, the supplemented Guggenheim theory lacks the necessary higher-order terms to give an accurate coexistence curve. The inclusion of the third-order term from the extended mean field theory (not shown) does not alter the coexistence curves significantly and, in any case, gives a correction to the Helmholtz free energy of mixing in a direction opposite of that which Figure 6 suggests is required. The first-order Pesci–Freed theory can also be supplemented with the EMF second-order term. For clarity, the resulting coexistence curve is not shown in the figure. It is in excellent agreement with the supplemented Guggenheim theory for $\phi_p > 0.8$ but at lower volume fractions departs from the simulation coexistence curve in the same manner as other versions of the Pesci–Freed theory.

The results presented thus far have shown that the classic Flory form of the lattice theory ("Flory–Huggins theory") does not give a good representation of either the zeroth-order or the first-order perturbation terms. Nor does it include any estimate of the higher-order terms shown to be important at intermediate and low volume fractions. Yet, the Flory–Huggins form has been applied successfully to correlate a wide variety of experimental data. In doing so, of course, the parameters of the lattice model must be fit to experimental variables, with the understanding that this process will simultaneously ameliorate the caricature of the real world as a lattice and the errors attendant to Flory's specific approximations within that model. If one treats the simulation results for the coexistence curve as quasiexperimental data, one can fit the data to the Flory form. With the chain length retained at 100, we find that any adjustment of the length scale (the lattice constant) and the energy scale (χ parameter) in the Flory theory can give a much better representation of the data in the critical region but only at the expense of any reasonable agreement at higher volume fractions. In contrast, if r is set equal to 9 in the Flory equation and no adjustments are made to the length and energy scales, the resulting coexistence curve fits the simulation data with $M_n = 100$ rather well for $\phi_p > 0.65$. In this regime, the results from the Flory theory with $r = 9$ agree with the simulation results about as well as the GQC results shown in Figure 2. The predicted critical temperature is also approximately correct, but the critical volume fraction is much too high ($\phi_p = 0.3$). It is not possible, in this instance, to associate the renormalized mer size with the inability of the lattice to represent the additional configurational freedom available to real molecules in the continuum. With the chain length so shortened, each renormalized mer would represent about 45 rather than 4 potential contacts of the simulation beads, and the process might be regarded as somehow approaching the large z limit, where the Flory approximations are known to be more accurate. However, we know of no criterion that predicts the renormalized Flory chain ought to be of length 9. The magnitude and perhaps even the direction of the length renormalization seem here to be a haphazard consequence of errors in the original Flory assumptions and entirely devoid of physical meaning. Fits to a different set of quasiexperimental data for the same model would probably yield different fitting parameters, possibly with a less drastic renormalization of chain lengths. Nevertheless, considerable caution should be exercised in the interpretation of the parameters obtained from *any* fit of the Flory equation to experimental data.

V. Summary and Conclusions

We have obtained the coexistence curve for a incompressible mixture of polymer and solvent (or for a compressible polymer) on a simple cubic lattice and have compared these coexistence curves with those predicted from several version of the lattice theory for polymer solutions. We observe the following:

(1) The standard Flory form of the lattice theory gives very good results at high volume fractions but makes a very poor prediction of the critical temperature.

(2) The Guggenheim theory, both in the random mixing approximation and in the quasichemical approximation, gives better overall agreement with the simulation data than the Flory form. However, at higher volume fractions, the random mixing approximation is poorer than the Flory form of the theory, while the quasichemical approximation shows a net improvement.

(3) An extended mean field theory provides some modest improvement over the basic Flory theory at high volume fractions. However, the more elaborate Pesci–Freed theory is unexpectedly poor in this application, predicting coexistence curves which show strong departures from the simulation results. [The completely self-consistent implementation by Dudowitcz, Freed, and Madden gives a coexistence curve in excellent agreement with simulation.[42]]

(4) Direct calculations of the first-order term in the perturbation expansion for the nearest-neighbor interactions show that the mean field theories (including the Flory theory) give poor estimates for this quantity at lower volume fractions. However, both the Guggenheim theory and the Pesci–Freed theory represent the first-order term quite well.

(5) Estimates of the second-order term were obtained by finite differences of simulation results. The extended mean field theory and the Guggenheim quasichemical approximation were found to be in qualitative agreement with the simulation results, but the Pesci–Freed prediction is too large and of opposite sign. [The revised lattice theory[42] yields a good estimate for e_2.]

(6) Simulation studies of homogeneous polymer solutions indicate that still higher-order terms are required to represent the free energy of mixing at intermediate volume fractions. None of the available theories presently provides the required corrections. Serious theoretical issues may prevent the construction of reliable equations for the free energy of mixing in the semidilute regime using any straightforward expansion. The quality of the predictions of the theories near the critical point of the polymer–solvent mixture may therefore be accidental. These fundamental difficulties arise because of differences in size and morphology of polymer and solvent molecules. They should be much less important when applied to polymer blends with low concentration of solvent or holes.

(7) The second-order term from the extended mean field theory may be added to the Guggenheim theory in place of the quasichemical approximation and provides an improved agreement with the coexistence curves obtained from simulation. This may be worthwhile because the quasichemical approximation does not provide an analytical expression for ternary mixtures.[13] This augmented Guggenheim theory will be useful for compressible polymer blends and for compressible polymer–solvent systems. [Using the reformulated Freed theory for the lower-order terms, a comparably accurate result may be obtained entirely within the Freed formalism.[42]]

(8) When the basic Flory theory is applied to the simulation results as though they were experimental data on real polymers, a good fit for moderate to high polymer volume fractions can be obtained only if the chain length in the Flory lattice equation is drastically reduced. The meaning of this fit is obscure at best and impels caution in the interpretation of fitting parameters when the Flory theory is applied to real systems.

The coexistence curve for the polymer–solvent system probably represents one of the most severe tests for any lattice theory. In part, this arises from the size difference between the two components. Unlike a mixture of monomers or one made up of two linear polymers, the typical solvent molecule is structurally distinct from a polymer bead, and each component of the mixture can participate in a different number of contacts. The conditions for coexistence are subtle and require a precise cancellation of terms that contain contributions on the length scales of both the polymer and the monomer. This is not easy to achieve, and the failure of any or all of these theories in this series of tests need not preclude their use in other applications. The Flory–Huggins equation has the virtues of mathematical simplicity and apparent detachment from its lattice origins. It can be readily incorporated into theories for polymers in complicated situations and can be confidently expected to give qualitatively correct results. It also provides a framework for the definition of a state-dependent χ parameter which, because it extracts the most significant aspects of the polymeric contributions to the thermodynamics of mixtures, plays a role in macromolecular solutions not unlike that of the activity in ordinary mixtures. The Guggenheim theories appear to be quite accurate for athermal solutions of lattice polymers at all densities and are capable of providing accurate theories for dense or concentrated polymer mixtures at lower temperatures as well. The Freed theories can be shown to match, or nearly match, the Guggenheim theories for the zeroth- and first-order terms in the ϵ^* expansion of the Helmholtz free energy. Only the Freed theory can easily incorporate the most general of polymer architectures[42] (including cross-linking), and only the Freed theory admits to systematic improvements. The results of this study are expected to provide insights into the construction of improved approximations within that formalism. In some applications, an approximate resummation to all orders in ϵ^* may be required.

Acknowledgment. At The University of Chicago, this research is supported, in part, by grants from the National Science Foundation (DMR86-14358, condensed matter theory program) and from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660; **1942**, *10*, 51.
(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter XII.
(3) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.
(4) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440; *J. Phys. Chem.* **1942**, *46*, 151; *Ann. N.Y. Acad. Sci.* **1942**, *41*, 1.
(5) Huggins, M. L. *Physical Chemistry of High Polymers*; Wiley: New York, 1958.
(6) Miller, A. R. *Proc. Cambridge Philos. Soc.* **1942**, *39*, 54; **1943**, *39*, 54.
(7) Guggenheim, E. A. *Proc. R. Soc. London, Ser. A* **1944**, *183*, 203.
(8) Guggenheim, E. A. *Proc. R. Soc. London, Ser. A* **1944**, *183*, 213.
(9) Guggenheim, E. A. *Mixtures*; Oxford University Press: Oxford, 1952.
(10) Cernuschi, F.; Eyring, H. *J. Chem. Phys.* **1939**, *7*, 547.
(11) Sanchez, I. C.; Lacomb, R. H. *Macromolecules* **1978**, *11*, 1145.
(12) Panayiotou, C.; Vera, J. H. *Polym. J.* **1982**, *14*, 681.
(13) Kumar, S. K.; Reid, R. C.; Suter, U. W. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1985**, *30*, 66; *Ind. Eng. Chem. Fundam.* **1987**, *26*, 2532.
(14) Freed, K. F. *J. Phys. A* **1985**, *18*, 871.
(15) Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1986**, *85*, 3007; *J. Chem. Phys.* **1988**, *88*, 2741.
(16) Bawendi, M. G.; Freed, K. F.; Mohanty, U. *J. Chem. Phys.* **1987**, *87*, 5534.
(17) Pesci, A. I.; Freed, K. F. *J. Chem. Phys.* **1989**, *90*, 2003, 2017.
(18) Nemirovsky, A. M.; Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 7272. Bawendi, M. G.; Freed, K. F.; Mohanty, U. *J. Chem. Phys.* **1986**, *84*, 7036. Pesci, A. I.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 7342.
(19) Freed, K. F.; Bawendi, M. G. *J. Phys. Chem.* **1989**, *93*, 2194.
(20) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(21) Freed, K. F. *Renormalization Group Theories of Macromolecules*; Wiley-Interscience: New York, 1979.
(22) Wall, F. T.; Mandel, J. *J. Chem. Phys.* **1975**, *63*, 4592.
(23) Olaj, O. F.; Lantschbauer, W.; Pelinka, K. H. *Chemie Kunststoffe Aktuelle* **1978**, *32*, 199; Olaj, O. F.; Lantschbauer, W. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 847.
(24) Mansfield, M. L. *J. Chem. Phys.* **1982**, *77*, 1554.
(25) Madden, W. G. *J. Chem. Phys.* **1987**, *87*, 1405.
(26) Madden, W. G. *J. Chem. Phys.* **1988**, *88*, 3934.
(27) Adams, D. J. *Mol. Phys.* **1976**, *32*, 647; **1979**, *37*, 211.
(28) Shing, K. S.; Gubbins, K. E. *Mol. Phys.* **1982**, *46*, 1109. Shing, K. S.; Chung, S. T. *J. Phys. Chem.* **1987**, *91*, 1674.
(29) Romano, S.; Singer, K. *Mol. Phys.* **1979**, *37*, 1765.
(30) Powles, J. G. *Mol. Phys.* **1980**, *41*, 715.
(31) Panagiotopoulos, A. Z. *Mol. Phys.* **1980**, *61*, 813.
(32) Kofke, D. A.; Glandt, E. D. *Mol. Phys.* **1988**, *64*, 1105.
(33) Sariban, A.; Binder, K. *J. Chem. Phys.* **1987**, *86*, 5869. Sariban, A.; Binder, K.; Heermann, D. W. *Colloid Polym. Sci.* **1987**, *265*, 424.
(34) Madden, W. G., unpublished results.
(35) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Oxford University Press: Oxford, 1982; p 178.
(36) Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 588.
(37) Dickman, R.; Hall, C. K. *J. Chem. Phys.* **1986**, *85*, 3023.
(38) Widom, B. *J. Chem. Phys.* **1963**, *39*, 2805.
(39) Hertando, A.; Dickman, R. *J. Chem. Phys.* **1988**, *89*, 7577.
(40) Friedman, H. L. *A Course in Statistical Mechanics*; Prentice Hall: Englewood Cliffs, NJ, 1985; p 185.
(41) Hansen, J. P.; McDonald, R. *Theory of Simple Liquids*, 2nd ed.; Academic: London, 1986, p 153.
(42) Dudowitcz, J.; Freed, K. F.; Madden, W. G. *Macromolecules*, submitted for publication.