Lattice Theories and Simulation Studies of Polymer Solutions on BCC and FCC Lattices

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ABSTRACT: The basic theoretical structure of all lattice theories for polymer solutions suggests that they will become increasingly accurate as the coordination number of the lattice is increased. Monte Carlo simulations have been performed for polymer chains of length 10 and 40 with monomeric solvent on three-dimensional body-centered cubic (BCC) and face-centered cubic (FCC) lattices. The energies of mixing and radii of gyration have been obtained and compared with standard lattice theories. The simulation data show that higher-order energetic terms are more significant on the high coordination number lattices than on the simple cubic lattice, in apparent contradiction to conventional wisdom. For the quantities considered, common lattice theories are shown to be no better for BCC and FCC lattices than was established in previous tests against simulations conducted on simple cubic lattices.

1. Introduction

Since the 1940s, lattice models have played an essential role in the theory of polymer solutions and are still of significant interest today. This continuing importance arises for a variety of reasons. First, they possess most of the essential features that make the thermodynamics of polymer solutions a uniquely difficult challenge. Second, lattice models are more amenable to analytic solution than most other theories for polymer solutions.[1−20] Third, one can introduce compressibility effects in a relatively easy manner.[21,22] Finally, lattice models are easily simulated using Monte Carlo methods.[23−37] This allows for a careful assessment of the approximations in the model and in the various analytic theories. This assessment has been made for a variety of linear and branched polymeric systems, including polymer solutions, polymer melts, and melt polymer blends.

The four main lattice theories for polymer melts and polymer solutions are the Flory−Huggins (FH) theory,[1,2] the Huggins−Miller−Guggenheim (HMG) family of theories,[3−10] the BGY polymer lattice theory developed by Lipson and co-workers[11−14] and the lattice cluster theory (LCT) of Freed and co-workers.[15−20] With the exception of the BGY polymer theory, these theories can be tested against simulation with no ambiguities concerning the choice of parameters. Most of the explicit tests of these theories have been against computer simulation results on the simple cubic lattice.[23−30,32−36] This is thought to provide a fairly severe test of the theories since the coordination number, z, of the simple cubic lattice is only 6. It is widely believed that all these theories become more accurate as the coordination number increases. In the limit of infinite coordination number, all the theories become equivalent to the Flory−Huggins theory, which in turn is the exact result on an infinite dimensional lattice.

An important exception to this focus on simple cubic lattices is the elegant determination of the polymer−solvent phase equilibrium of Mackie et al.[31] These workers employ an extension of the Gibbs ensemble method,[38,39] that has proven highly successful in a variety of off-lattice simulations. In order to maintain constant lattice pressure (equivalent to constant excess chemical potential of solvent), they must add and remove entire layers of the lattice while redistributing the polymers in the available space. This method can be made more efficient by working in a peculiar three dimensional lattice that has a coordination number of 26. (Numbers larger than 12 are possible because the class of interacting sites includes neighbors of several different spacings.) These workers show that their method agrees well at lower temperatures with simulations performed using an interfacial method previously introduced by Madden,[28,30] and this method gives improved results near the critical temperature. Much of their analysis focuses on the critical region of the phase diagram, which was inaccessible in the earlier interfacial studies. Wolfgart *et al.*[37] have also simulated polymers on a high coordination number lattice. However, the only finite energy in their model is an intramolecular attraction that leads to chain collapse at low temperatures. Their results are not relevant to the present study.

When applied to real polymeric systems coordination numbers are generally chosen to be higher than $z = 6$ but considerably less than $z = 26$. Typical choices are in the 10−12 range for those lattice theories that require an explicit specification.[22,40−41] This leaves open the question of whether the absolute accuracy of the earlier tests adequately assess the practical merits of the various theories. We report here some simple tests of these lattice theories on body-centered cubic (BCC) and face centered cubic (FCC) lattices, where the coordination numbers of 8 and 12 are more in the range of those actually chosen in fitting polymer solution data to the functional forms derived from lattice theories.

2. Simulation Details

The model is standard. In a simulation cell whose dimensions are $L_x \times L_y \times L_z$, the number of sites N is given by $N = \nu L_x L_y L_z$, where ν is 1 for the simple cubic lattice, 2 for the BCC lattice, and 4 for the FCC lattice. There are N_p linear polymer chains of length n. The beads of each chain are sequentially assigned to n nonoverlapping adjacent sites on the lattice. The remaining $N_s = N - nN_p$ sites are regarded as either

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solvent or holes. The volume fraction (site fraction) of polymer is $\phi_p = nN_p/N$, while that of solvent or holes is $\phi_s = N_s/N$. In principle, nearest neighbor interactions ϵ_{ss}, ϵ_{ps}, and ϵ_{pp} can be specified, but the only thermodynamically relevant energy for two-component bulk mixtures is the interchange energy[2,9,42]

$$\Delta\epsilon = 2\epsilon_{ps} - \epsilon_{ss} - \epsilon_{pp} \tag{1}$$

The system as defined above represents an incompressible binary lattice mixture. Of course, the monomeric solvent molecules may be interpreted as holes and the results are then those for a compressible neat polymer. The reported energies of mixing can be converted to configurational energies using standard transformations.[42]

Polymer beads are allowed to move in several standard ways: (1) A polymer end bead can move into one of the z sites adjacent to its covalently bonded neighbor. (2) An interior bead that is not collinear with its two covalently bonded neighbors can move to one of the nearby equivalent sites that are consistent with the connectivity of the chain. Including the null move, there are two such sites on a SC lattice and up to four such sites on a BCC or FCC lattice.

Each move is accepted with probability $\max(1,\exp[-\beta\Delta E])$, where ΔE is the energy change associated with the trial move. Overlap of two polymer beads leads to an infinite energy and therefore always results in rejection of the move. When a move is accepted, a solvent molecule (or hole) is assigned to the lattice site formerly occupied by the polymer bead. More elaborate movement schemes are possible, but were found to be unnecessary in the studies reported here.

3. Lattice Theories

The Flory–Huggins equation[1,2] is the most commonly employed result obtained from polymer lattice theories. It results from a "mean field" theory in which the polymer conformations are presumed to be independent of both concentration and temperature. The result is an exceptionally simple form for the Helmholtz free energy of mixing, reminiscent of regular solution theory for small molecules:

$$\frac{\Delta A^{\mathrm{MIX}}}{NkT} = \frac{\phi_s}{N_s}\ln(\phi_s) + \frac{\phi_p}{nN_p}\ln(\phi_p) + \frac{z\Delta\epsilon}{2kT}\phi_s\phi_p \tag{2}$$

As a mean field theory, it has only a linear dependence on reciprocal temperature and the only role the coordination number plays is in scaling the temperature. In applications to real polymer solutions, the quantity $z\Delta\epsilon/2kT$ is replaced by the parameter χ. With this substitution, the functional form of the Flory–Huggins equation can be obtained in a number of other ways,[43] each of which makes approximations as drastic as those made in the lattice derivation. The FH equation is often regarded as the defining equation for the function $\chi(\phi_p,T)$, which has a much weaker dependence on the thermodynamic variables than does the full free energy of mixing. For our purposes, however, the precise lattice result, eq 1, is required.

The Guggenheim quasichemical theory[8–10] is the most elaborate and self consistent implementation of the more detailed approach originally taken by Huggins and Miller.[3–7] It considers more carefully the local solvation of a polymer bead and has been found to give much better estimates of the various contact probabilities in an athermal solution. The functional form for the free energy of mixing is slightly more complicated than that of the FH equation:[44]

$$\begin{aligned}\frac{\Delta A^{\mathrm{MIX}}}{NkT} = {} & \phi_s\ln(\phi_s) + \frac{\phi_p}{n}\ln(\phi_p) + {}\\ & \frac{z}{2}\left[\phi_s\ln\left(\frac{\theta_s}{\phi_s}\right) + \frac{q_p\phi_p}{n}\ln\left(\frac{\theta_p}{\phi_p}\right)\right] + {}\\ & \frac{z}{2}\left[\phi_s\ln\left(\frac{1-\theta_p\Gamma}{\theta_s}\right) + \frac{q_p\phi_p}{n}\ln\left(\frac{1-\theta_s\Gamma}{\theta_p}\right)\right]\end{aligned} \tag{3}$$

where

$$\Gamma = \frac{2}{1 + \{1 + 4\theta_p\theta_s[\exp(\beta\Delta\epsilon) - 1]\}^{1/2}} \tag{4}$$

$\theta_p = q_pN_p/(N_s + q_pN_p)$ and $\theta_s = 1 - \theta_p$ are the surface fractions of polymer and solvent, and $zq_p = N_p(z-2) + 2$. The equations above are specific to a monomeric solvent. The Flory Huggins result is recovered in the limit of large z, where $\theta_p \rightarrow \phi_p$ and $\theta_s \rightarrow \phi_s$. A linearized version of the Guggenheim–Huggins–Miller approach, obtained by setting $\Gamma = 1$, has been dubbed the "Random Mixing" approximation (GRM).[22,40]

In the lattice BGY theory for polymers, the thermal contributions to the free energy of mixing, are estimated using an integral equation first introduced by Yvon[45] for small molecule liquids and rediscovered some years later by Born and Green.[46] The derivation begins with a full off-lattice BGY (or YBG) equation. An assumption is made that there exists a reliable theory for the hard core (athermal) polymer mixture. The superposition approximation[47] is applied to the three body distribution functions and the equations are then mapped onto the lattice. An analytical result is obtained by inserting contact probabilities from whichever lattice theory has been chosen to describe the athermal reference system. Versions of the BGY lattice theory have been obtained using both the Flory–Huggins[1,2] and the Huggins–Miller–Guggenehim[3–10] contact probabilities. Tests against computer simulation have shown the latter to be the more accurate, and the resulting expression for the free energy of mixing is

$$\begin{aligned}\frac{\Delta A^{\mathrm{MIX}}}{NkT} = {} & \frac{\Delta A_0^{\mathrm{MIX}}}{NkT} - {}\\ & \frac{z\phi_s}{2}\ln\{\theta_s + \theta_p\exp[-\beta(\epsilon_{ps} - \epsilon_{ss})]\} - {}\\ & \frac{q_pz\phi_p}{2n}\ln\{\theta_p + \theta_s\exp[-\beta(\epsilon_{ps} - \epsilon_{pp})]\}\end{aligned} \tag{5}$$

The reference free energy, $\Delta A_0^{\mathrm{MIX}}$ is given by eq 3 with $\Delta\epsilon = 0$. An earlier version of the lattice BGY theory uses the Flory–Huggins reference system and is recovered in the large z limit of eq 5. One peculiarity of the BGY theory is that it does not automatically yield the single energetic quantity $\Delta\epsilon$ that should rigorously arise in any lattice theory.[42] This is probably a result of the map of the continuum BGY onto the lattice and the use of the superposition approximation for the triplet distribution functions. The theory will therefore give different predictions for polymer/hole and polymer/solvent systems that are rigorously isomorphic. In previous tests on binary mixtures, the BGY lattice theory has been shown to be very competitive with other lattice theories when one sets $\epsilon_{ss} = \epsilon_{pp}$, giving $\Delta\epsilon = 2(\epsilon_{ps}$

$- \epsilon_{pp}) = 2(\epsilon_{ps} - \epsilon_{ss})$.[12] To be consistent with this earlier work, this is the parameter set used in all the calculations below. It should be noted that a successful off-lattice version of the BGY polymer theory has also been developed.[48] This theory does not suffer from any inconsistencies associated with the BGY lattice theory.

The most elaborate lattice theory for melt polymers, polymer blends and polymer solutions is the lattice cluster theory.[15-20] It is based on an exact formal decomposition of the partition function, somewhat analogous to the Mayer cluster theory but highly specific to the lattice. The mathematics are quite complex, but the result can be expressed in the form of a Taylor expansion in $\Delta\epsilon/kT$

$$\frac{\Delta A^{\mathrm{MIX}}}{NkT} = a_0 + a_1\left(\frac{\Delta\epsilon}{kT}\right) + a_2\left(\frac{\Delta\epsilon}{kT}\right)^2 + a_3\left(\frac{\Delta\epsilon}{kT}\right)^3 + ... \quad (6)$$

where the coefficients a_n are themselves expanded in powers of z^{-1}

$$a_n = \zeta_n^{(0)} + \zeta_n^{(1)}\frac{1}{z} + \zeta_n^{(2)}\left(\frac{1}{z}\right)^2 + ... \quad (7)$$

Each of the coefficients $\zeta_n^{(j)}$ is independent of temperature but depends on volume fraction, molecular weight, lattice architecture and molecular connectivity. All coefficients can be evaluated analytically, but an increasingly large number of individual integrals (represented in the theory as Mayer-like graphs) must be evaluated to produce higher order terms in the expansions. Examination of the original sources shows that the actual expressions for the $\zeta_n^{(j)}$ are formidable, ugly enough perhaps to prevent some workers from using the theory. However, they are merely polynomial expansions and very easy to evaluate using a personal computer of modest capacity. Freed and co-workers[21] have presented these expansions in very general form that not only allow one to include not only thermal (energetic) effects but also allow one to consider the consequences of lattice architecture, polymer branching, and cross-linking. The existing expressions can therefore be applied to a wide range of experimental situations without further theoretical development. No other theory for polymer solutions, melts, or blends has this capability.

In order to include the effects of lattice architecture within LCT, one must evaluate a very large number of complex integrals (graphs) by integrating over the Brillouin zone of the lattice in question. At present, closed form expressions are available to second order in $\Delta\epsilon$ and (for each such term) to second order in $1/z$ for a hypercubic lattice in a $z/2$ dimensional space. We designate this implementation as LCT2. No expressions of equivalent power and generality exist on the BCC and FCC lattices. However, the Flory–Huggins theory, the Guggenheim QCT and Guggenheim-based version of BGY lattice theory *presume* that the architecture is of importance only to the extent that it alters the coordination number z. We cannot test this idea directly without performing simulations on higher dimensional cubic lattices, which are beyond our capabilities. However, the z-dependent lattice theories (GQC, BGY, and LCT) begin to crowd the Flory–Huggins result at higher values of z.[20] Consequently, one is inclined to dismiss any secondary lattice-specific dependences as unimportant. Some of the results presented below suggest that dismissal to be premature. Nevertheless, we will compare our three-dimensional BCC simulation results against LCT theory for a *four*-dimensional hypercubic system. Both lattice systems have a coordination number of 8. Similarly, three-dimensional FCC results will be compared against LCT theory for a *six*-dimensional hypercubic lattice, both with coordination number 12.

In order to motivate the actual tests undertaken here, it is worth reviewing some of the significant results of earlier work. Prior tests of the various lattice theories against computer simulations for polymer and solvent (or polymer and holes) on the simple cubic lattice reveal the following.

(1) For athermal systems, the standard Flory–Huggins treatment gives a poor estimation of the lattice pressure (excess solvent chemical potential), strongly suggesting that its representation of the athermal free energy of mixing is inadequate. In contrast, both the lattice-cluster-theory and the Huggins–Miller–Guggenheim theories give lattice pressures in rather good agreement with experiment, with the LCT having, perhaps, a slight edge.[23-27]

(2) The internal energy of mixing in the athermal limit (the first-order term in an expansion in $\Delta\epsilon/kT$) is reproduced nearly quantitatively by the LCT and the GQC lattice theories.[20] The BGY theory is rigorously identical to the GQC theory at this level.[12] The FH result is quite poor.[20] Since this first-order term is determined by the athermal polymer–solvent contact probabilities, an accurate value for this quantity is an indirect assessment of the athermal free energies.

(3) The second-order terms in the expansion of the internal energy of mixing and the free energy of mixing have been estimated by finite difference of high temperature simulation results.[20,30] This term is everywhere negative. Both the LCT and the BGY theories give excellent representations of this quantity.[12,20] The GQC predictions are excellent at high polymer volume fractions, but significantly poorer at lower volume fractions.[20,30] There are no second- and higher-order contributions in the standard Flory–Huggins theory. However, the $z \rightarrow \infty$ limit of the LCT provides higher-order expressions analogous to the first-order term in FH theory. This "extended mean field" theory (EMF) predicts a second-order term in reasonably good agreement with the simulation estimates.[20,30]

(4) Plots of $\Delta E^{\mathrm{MIX}}/\Delta\epsilon$ vs $\Delta\epsilon/kT$ indicate that the expansion has converged at first order when $\phi_p > 0.9$ and at second order for $\phi_p > 0.8$.[30] However, very substantial contributions from third- and possibly fourth-order terms are evident at intermediate volume fractions (<0.65).[29,30] Such terms are a direct result of the chain character of the polymer molecules. For thermodynamically significant temperatures, third- and higher-order terms are very small in all the lattice theories. For the BGY and GQC theories, the connectivity does not survive the requisite subtractions of the pure component energies. The only higher-order terms available from the LCT are EMF contributions in which the chain connectivity has been explicitly ignored to simplify the calculation. All the lattice theories are thus effectively second-order in $\Delta\epsilon/kT$, and all fail to reproduce the energy of mixing data at intermediate-to-low volume fractions.

(5) Coexistence curves for polymer + solvent seem to deviate from the simulation results on the polymer-rich side whenever the theory begins to show significant errors in ΔE^{MIX}.[20,30] The quality of the theory on the polymer poor side has little effect on this calculation

except near the critical temperature because the coexisting solution is exceedingly dilute in polymer. Indeed, the polymer solvent coexistence curve at intermediate-to-high volume fractions can be mapped out to three or four digit accuracy within any of the theories merely by determining the ϕ_p at which the excess solvent chemical potential vanishes. The polymer chemical potential itself need not be considered until significant polymer dissolves in the polymer poor phase. This can extend up to about 0.8 or 0.9 of the critical solution temperature, depending on chain length.

(6) Near the critical point, the situation is considerably different. None of the lattice theories should be expected to be highly accurate in this region, since all are "mean field" in the sense that they have an analytic expansion in this region. On the basis of a fairly limited exploration of the high-temperature coexistence curve on the simple cubic lattice, it was clear in ref 20 that the FH theory gave a grossly incorrect critical temperature (at least 50% too high). A quantitative assessment of the critical temperature for the other theories is somewhat more difficult because of the uncertainty in the critical temperature. On the basis of the results of ref 20, Mackie *et al.*[31] characterized the GQC critical temperature as about 20% too high for chains of length 100 on the simple cubic lattice. This seems about right. In their own $z = 26$ simulations, Mackie *et al.* found that the FH critical temperature was now in error by only about 25%, but the GQC theory remains in error by about 20%. Our own calculations confirm this and show that the LCT and BGY theories give results nearly identical to those of the GQC theory for the $z = 26$ case.

The direct consequence of items 1 through 5 is that much of what we observe in the thermodynamics of polymer solvent systems can be deduced by a careful examination of the temperature and volume-fraction dependence of ΔE^{MIX}, a quantity that is very easily obtained via simulation. Consequently, the bulk of our efforts are devoted to an examination of ΔE^{MIX}. When the two species are both polymeric, the picture is not so simple. Theories that are very comparable for the polymer–solvent system can give dramatically different results for blends and for blend equations of state.[34–37]

Results

We have performed simulations of polymer solutions on the BCC and FCC lattices that correspond to the conditions reported in an earlier study on a simple cubic lattice.[29] Detailed mixing data were taken for chains of length 10 and 40. Volume fractions of polymer were varied between 0.1 and 0.9 at two temperatures. For all lattices one of these temperatures is $T^* \equiv kT/\Delta\epsilon = \infty$. The other temperature is lattice-dependent and selected to give $\chi = z\Delta\epsilon/2kT = 1$. This corresponds to $T^* = 3.0$ for the SC lattice, $T^* = 4.0$ for the BCC lattice and $T^* = 6.0$ for the FCC lattice. It should be noted that, while these are equivalent temperatures according to the Flory–Huggins equation, they are not comparably related in any of the other theories. On the basis of preliminary calculations using LCT, GQC, and BGY and the general behavior observed in the simulation studies of Madden *et al.*[20,30] and of Mackie *et al.*,[31] we believe that the reported data are all supercritical for $n = 10$ but may sometimes be below the critical temperature for $n = 40$, particularly on the lattices with higher coordination number. We return to this point below.

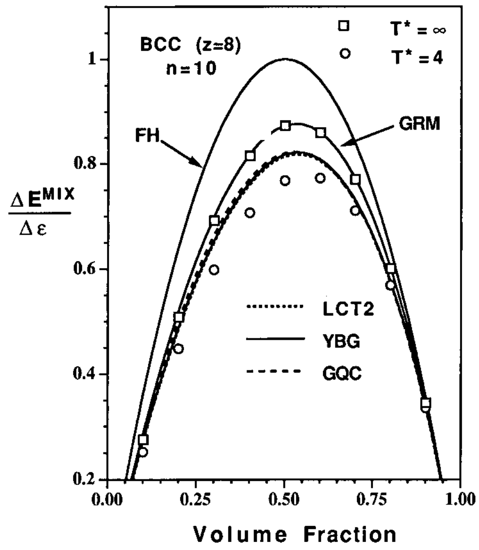

Figure 1. Internal energy of mixing (per lattice site) for chains of length 10 on a BCC lattice as a function of polymer volume fraction.

Each run was typically carried out for 150 000 attempted moves per polymer bead. A number of quantities were monitored including the radii of gyration, R_g, and the internal energy of mixing. For the athermal system, the internal energy of mixing is defined as

$$\frac{\Delta E_0^{\mathrm{MIX}}}{\Delta\epsilon} = \lim_{\Delta\epsilon\to 0} \frac{\Delta E^{\mathrm{MIX}}}{\Delta\epsilon} \qquad (8)$$

and can be calculated directly in an athermal simulation. In the language of the lattice theories, this is the "random mixing" limit. We will use this terminology, even though it is perhaps not quite appropriate for the actual athermal systems. Depending on the thermodynamic state the uncertainty in ΔE^{MIX} estimated via block averages is between 1 part in 2000 at high volume fractions and 1 part in 200 at lower volume fractions. In all cases the uncertainties in ΔE^{MIX} are smaller than size of the symbol used in the figures shown here. Uncertainties in the radii of gyration are 2% or less. Box sizes were 13 unit cells on an edge for the FCC studies (8788 lattice sites), 18 for the BCC studies (8192 sites), and 20 for the SC studies (8000 sites). Previous experience indicates that these boxes are large enough to make finite size effects negligible for the chain lengths and the thermodynamic states considered here.

Figures 1–4 compare $\Delta E^{\mathrm{MIX}}/N\Delta\epsilon$ for polymer + solvent on the BCC and FCC lattices. The polymer chains were 10 or 40 beads in length and the temperatures corresponded to $\chi = 0$ and $\chi = 1$. The analogous results for simple cubic systems have previously been reported by Falsafi and Madden.[29] The results for the FCC, BCC, and SC cases are quite similar. The athermal simulation results are uniformly higher than the calculation at finite temperature, a direct consequence of the negative second order term in the expansion of ΔE^{MIX} in $\Delta\epsilon/kT$. The finite temperature result is always skewed toward higher volume fractions, and this becomes more pronounced at the higher molecular weight.

The general accuracy of the lattice theories is also similar on the three lattices. The Flory–Huggins result is uniformly poor, except for $\phi_p > 0.9$. The Guggenheim random mixing result is essentially quantitative for $T^* = \infty$ on all lattices, as is the athermal limit of LCT. The athermal LCT result is not shown in the figures because

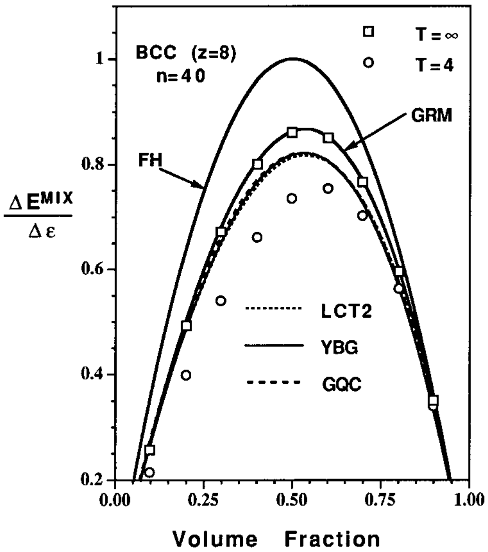

Figure 2. Internal energy of mixing (per lattice site) for chains of length 40 on a BCC lattice as a function of polymer volume fraction.

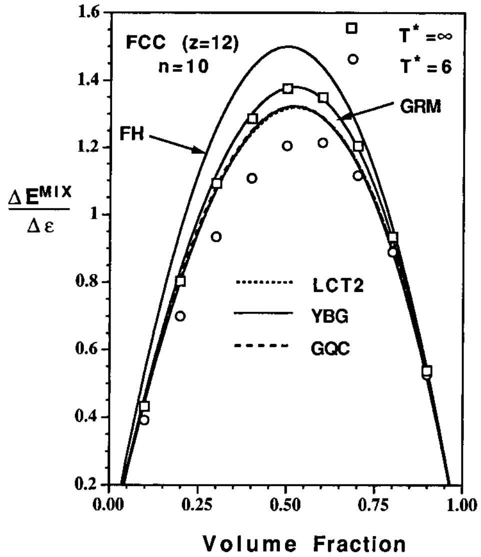

Figure 3. Internal energy of mixing (per lattice site) for chains of length 10 on a FCC lattice as a function of polymer volume fraction.

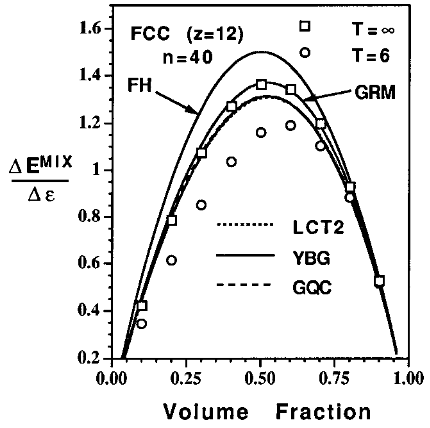

Figure 4. Internal energy of mixing (per lattice site) for chains of length 40 on a FCC lattice as a function of polymer volume fraction.

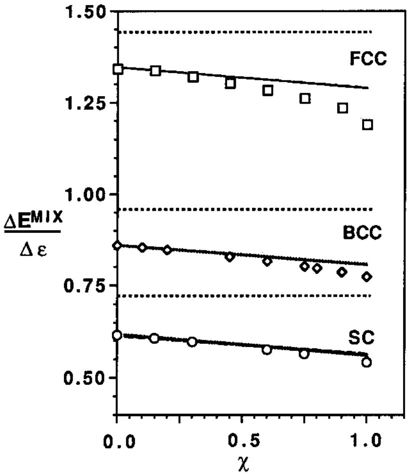

Figure 5. Internal energy of mixing (per lattice site) for chains of length 10 on SC, BCC, and FCC lattices as a function of $\chi = z\Delta\epsilon/2kT$ at $\phi_p = 0.60$. The horizontal dotted lines represent the FH result for each lattice. The GQC, LCT2, and BGY results are also shown and are indistinguishable on the scale of the ordinate.

it is completely indistinguishable from the GRM result on these high coordination number lattices. At the lower temperature, the more successful of the theories (LCT2, BGY, and GQC) all are quite accurate for larger volume fractions ($\phi_p \geq 0.8$) but begin to show significant overestimations of ΔE^{MIX} for $\phi_p < 0.7$). As anticipated, the three theories yield very similar results for the $z = 8$ case and are virtually indistinguishable for the $z = 12$ system. The more sophisticated theories also give results increasingly closer to the Flory–Huggins prediction as the coordination number increases.

Though the theories agree well with one another at the higher coordination numbers, they do not show any improved agreement with simulation when the temperature is low. Indeed, the theoretical results for $z = 12$ appear to be poorer at lower volume fractions than those for $z = 8$. Figure 5 shows a plot of ΔE^{MIX} for chains of length 10 vs $\chi = z\Delta\epsilon/2kT$ at $\phi_p = 0.6$, the highest polymer volume fraction for which there is evidence of significant contribution from higher-order terms. The intercept at $\chi = 0$ is the athermal result. The slope of the straight line departing from this result yields the second-order contribution to the expansion in $\Delta\epsilon$. Any deviation from this straight line represents contributions from third- and higher-order terms. The expansion of the ordinate required to represent all three lattices on the same figure tends to suppress the display of nonlinear terms in the SC and BCC lattices. These have previously been shown to be significant for the SC lattice.[20,29] It is quite clear that there is no reduction in the contribution of the nonlinear terms as the coordination number increases. Also shown are the predictions of the FH, GQC, BGY, and LCT2 cases. The Flory–Huggins prediction appears as a horizontal line for each lattice. The other three lattice theories are indistinguishable on the figure. The straight-line character of the plots reveals why we refer to these theories as "effectively second-order". For the high coordination number lattices, they are essentially quantitative through second order but completely lacking in the substantial third- and higher-order character needed to explain the simulation data for $\phi_p \leq 0.6$. Results for simulations with $n = 40$ (not shown) are very similar.

Figure 6 shows the "nonrandom" contribution to $\Delta E^{\mathrm{MIX}}/z\Delta\epsilon$ for all three lattices for chains of length 40 over the full range of volume fractions. This nonrandom contribution is obtained by subtracting the "random mixing" result (in the nomenclature of ref 22) for each

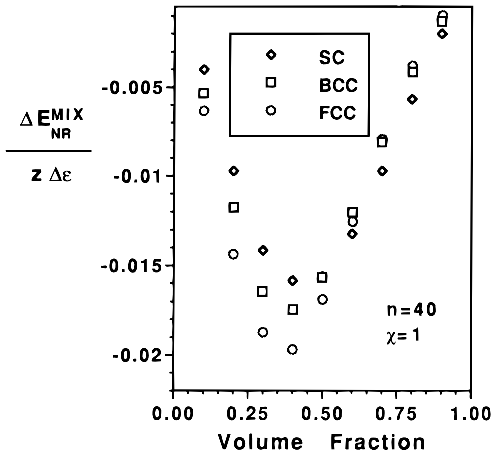

Figure 6. *Nonrandom* contribution to the internal energy of mixing for chains of length 40 on SC, BCC, and FCC lattices as a function of $\chi = z\Delta\epsilon/2kT$. For this figure only, the energy of mixing is also reduced by the coordination number z.

lattice from the corresponding result obtained in the finite temperature simulations:

$$\frac{\Delta E^{\rm MIX}_{\rm NR}}{\Delta\epsilon} \equiv \frac{\Delta E^{\rm MIX}}{\Delta\epsilon} - \frac{\Delta E^{\rm MIX}_{T=\infty}}{\Delta\epsilon} \qquad (9)$$

$\Delta E^{\rm MIX}_{\rm NR}$ represents the sum of second and higher terms in the internal energy of mixing. For this figure only, the energies are reduced by $z\Delta\epsilon$, which suppresses the obvious dilation of energy scales as $z \rightarrow \infty$. In these units, this nonrandom contribution to the internal energy of mixing vanishes for all volume fractions when $z \rightarrow \infty$. We note that the $\chi = 1$ temperatures may penetrate the two-phase region for $n = 40$ chains but are comfortably above the expected critical temperatures for $n = 10$ chains. (This assessment is made from the lattice theories themselves and the observation that they tend to *over*estimate the critical temperature.) The results for these shorter chains (not shown) are very similar to those seen in Figure 6. Since the relationships among the various lattice results are unaffected by the magnitude and sign of $T - T_{\rm c}$ it seems unlikely that any peculiarities in these results are a consequence of a penetration into the two-phase region.

Careful inspection of Figure 6 shows that the magnitude of the higher-order contributions become smaller within increasing z for $\phi_{\rm p} \geq 0.7$. This is the behavior predicted by the GQC, LCT, and BGY theories and coincides with the range of volume fractions for which these theories are accurate. For $\phi_{\rm p} < 0.7$, an unexpected reordering of the results occurs, and Figure 6 shows a dramatic *increase* in the magnitude of the nonrandom contributions to $\Delta E^{\rm MIX}$ on the higher coordination number lattices. A virtually identical reordering is observed for chains with $n = 10$ (not shown). In both cases, this means that there is a higher than expected number of polymer–solvent contacts, $N_{\rm ps}$, on the FCC and BCC lattices. The energy and free energy of mixing therefore converge more slowly than any existing implementations of the lattice theories would lead one to expect. As in previous studies,[20,29,30] we attribute this discrepancy to the failure of the theories to account properly for changes in the polymer conformations as the sample becomes more dilute. The Flory–Huggins and Guggenheim theories explicitly invoke a composition-independent intramolecular partition function that implies invariant polymer chain conformations. The BGY theory implicitly shares the assumptions of its reference theories.

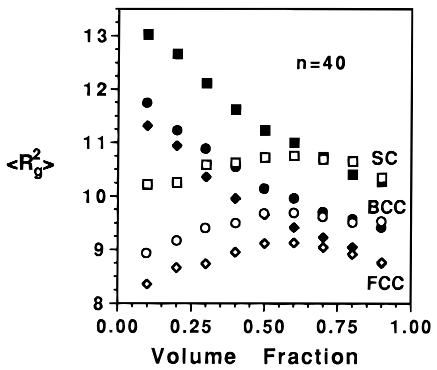

Figure 7. Mean square radii of gyration for chains of length 40 (in units of the bond length) on SC, BCC, and FCC lattices as a function of polymer volume fraction. The filled symbols correspond to $T^* = \infty$. The open symbols correspond to the temperatures associated with $\chi = 1$ ($T^* = 3$ for SC, $T^* = 4$ for BCC, and $T^* = 6$ for FCC). Key: SC, squares; BCC, circles; FCC, triangles.

The full LCT theory, in contrast, *does* include intrachain contributions at all levels in the expansion in $\Delta\epsilon$. However, the results shown are from LCT2, the lattice cluster theory truncated at second order in $\Delta\epsilon$ and at second order in z^{-1} (for each term in $\Delta\epsilon$). The graphs that contribute at second order seem to include only indirect correlations that we attribute to intramolecular encounters (or avoidances) of beads fairly far apart on the backbone. We therefore suspect that the features observed in Figure 6 result from changes in the number of contacts of beads not very distant along the chain backbone.

Figure 7 shows how the radii of gyration, $R_{\rm g}$, change with volume fraction for chains of length 40 on the three lattices. The $R_{\rm g}$ values for the high coordination number lattices are always smaller than those for the simple cubic case because of the increased number of tightly wrapped configurations that are possible on these lattices. The radii of gyration for the athermal systems show substantial expansion as polymer volume fraction decreases. Melt screening no longer holds, and the effects of excluded volume dominate. Despite these changes in conformation, the Guggenheim, LCT, and BGY theories are highly successful in the athermal limit, presumably because the expansion of the chains allows for the maintainence of a fairly uniform local composition. The radii of gyration at the $\chi = 1$ temperatures are markedly different. They are always smaller than the corresponding radii in the athermal simulations and tend to decrease at the lowest volume fractions. This is not unexpected, since the solvent quality is much reduced at these lower temperatures.

Ironically, the radii of gyration at $\chi = 1$ are arguably more uniform than the corresponding athermal results, but the theories are quite deficient at lower volume fractions. This is puzzling until one realizes that the energy of mixing is sensitive only to local distributions of polymer beads about solvent molecules. The very fact that the radii of gyration have been reduced from their athermal limiting values indicates that the chains have responded in a significant way to the reduction in temperature and the attendant changes in the character of the solvent. The effect on $R_{\rm g}$ is a concatenation of local conformational changes that cause the chains to shrink substantially. For single chains, this is traditionally understood as an increase in *intra*molecular polymer–polymer contacts. For the solutions at intermediate volume fractions, this must take place while increasing the number of polymer–solvent contacts, N_{ps}, and inexorably reducing the *total* polymer–polymer contacts (because $2N_{pp} = znN_p - N_{ps}$).

We speculate that this preferential intramolecular contact may arise because of the tendency of the chains to perform a partial wrap around individual solvent molecules at lower volume fractions and lower temperatures. This allows for a larger number of polymer–solvent contacts than would otherwise be expected and biases the chain conformation toward smaller dimensions. The smaller volume occupied by the chain then leads to a higher likelihood that polymer–polymer contacts will be *intra*molecular. This picture also suggests an explanation for why there is an enhancement of the nonrandom contribution to ΔE^{MIX} as one proceeds from the SC to the BCC to the FCC lattice. Given a specific polymer–solvent contact, it requires an excursion of three bonds for a *recontact* to occur in a SC lattice but only two bonds on a BCC lattice and only one bond on a FCC lattice. The opportunities for multiple contacts between a chain and an individual solvent molecule are thus much larger on the BCC and FCC lattices. Indeed, 12 sequential beads of a single FCC polymer can completely enclose an individual solvent molecule. This is not possible on either a BCC or SC lattice.

If this interpretation is correct, the counterintuitive trend observed for $\phi_p < 0.7$ in Figure 6, might not be seen in $z = 8$ and $z = 12$ simulations on a hypercubic lattice, which share the recontact constraints of the three dimensional SC system. The expected smooth convergence with increasing z may in fact hold at all volume fractions. On the other hand, the physical solvation pattern of the FCC lattice is similar to that in the continuum. The magnitude of these nonrandom contributions may therefore be very significant for off-lattice systems and must be borne in mind when applying these lattice theories to real polymer solutions.

The LCT has the potential for discriminating between the four-dimensional hypercubic lattice and the BCC lattice or between the six-dimensional hypercubic lattice and the FCC lattice. This requires that the entire host of diagrams contributing at all levels be re-evaluated using integrations over the Brillouin zones of the BCC and FCC lattices. However, the extensive agreement between the existing hypercubic implementations of the LCT and Bravais-silent Guggenheim and BGY theories for $z = 8$ and $z = 12$ and the excellent predictions of LCT for the $\Delta\epsilon^2$ term for the internal energy[20,29] suggest that lattice-dependent differences will not appear in the LCT until the difficult-to-obtain $\Delta\epsilon^3$ term. We emphasize, however, that we do not expect the higher-order terms to be absent on these hypercubic lattices. We merely expect that they might not be so exaggerated relative to the three-dimensional SC case.

Finally, we consider the implications of the various theories on the coexistence curves for polymer and solvent on the three lattices. Figures 8–10 show the coexistence curves predicted by the various lattice theories. No simulation results for the coexistence curves are available for the high coordination number lattices. As expected, the LCT2, BGY, and GQC theories give curves in close agreement at moderate-to-high polymer volume fractions. Nearer the critical point, the theories depart from one another. This departure is more substantial for the solutions with $n = 40$ chains than for the solutions with $n = 10$. However, the theories agree increasingly more closely as the coordination number increases. This is not surprising, since their predictions for the energies and free energies of mixing are so similar. In fact, the coexistence curves generally

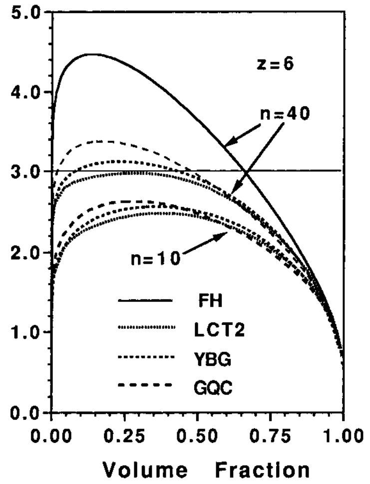

Figure 8. Coexistence curves for chains of length 10 and 40 on a simple cubic (SC) lattice. The Flory–Huggins (FH) results for chains of length 10 are supressed for clarity. This result lies among the curves for chains of length 40.

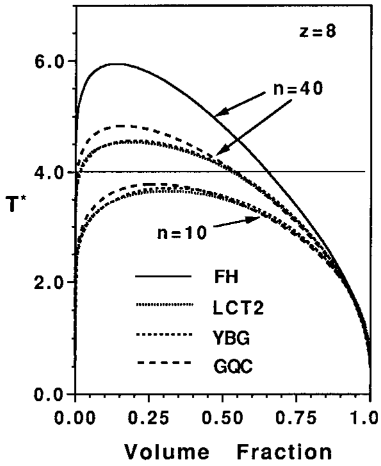

Figure 9. Coexistence curves for chains of length 10 and 40 on a body-centered cubic cubic (BCC) lattice. The Flory–Huggins (FH) results for chains of length 10 are again supressed for clarity.

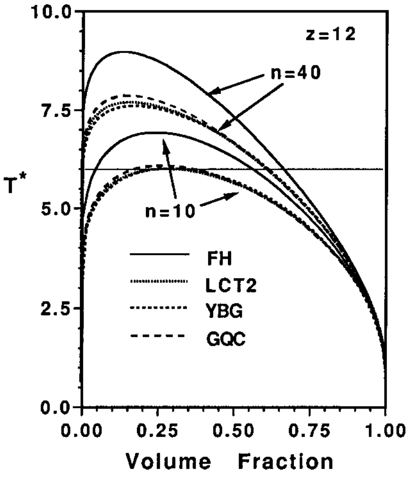

Figure 10. Coexistence curves for chains of length 10 and 40 on a face-centered cubic cubic (FCC) lattice. The Flory–Huggins (FH) results for chains of length 10 are shown.

agree less well than the energies of mixing, showing just how subtle the match of chemical potentials must be near the critical point. On the basis of the present calculations, we cannot establish how accurate these coexistence curves are. However, the persistent overestimation of the internal energy of mixing by each of the lattice theories at all coordination numbers must almost certainly result in corresponding overestimates of the solution critical temperatures.

A reasonable argument can be made that the results for these lattices should be compared at constant T/T_c. This is difficult (since the critical temperatures are not known) and awkward (since different temperatures would be needed for each lattice and for each molecular weight). Still, we can roughly assess the consequences of such a comparison using the results presented in Figures 8–10, as well as some supplementary calculations. We estimate that—at the outside—the FCC T/T_c might be about about 20% lower than the SC value for fixed $T^* = T/\Delta\epsilon$. (This depends on molecular weight and the theoretical prediction of T_c. The available evidence suggests that we should not take the theoretical predictions of T_c too seriously.) Even if we were to use $\chi = 0.8$ as the FCC condition most closely comparable to the SC lattice with $\chi = 1$, Figure 5 shows that the FCC result still contains large contributions from higher-order terms. These contributions will only become more significant at lower volume fractions where the real anomalies kick in. Thus, we do not believe that any major readjustment of our conclusions would be required if the simulation had been performed at constant T/T_c. The higher-order terms in $\Delta\epsilon/k_BT$ will remain significant for BCC and FCC lattices in three dimensions.

Summary and Conclusions

Monte Carlo simulations of polymer and monomeric solvent have been performed on BCC and FCC lattices. These lattices have coordination numbers more typical of those that would be commonly employed in applying such theories to real polymer–solvent systems. The simulation results were compared with standard theories for polymer and solvent on a lattice. Though fundamental theory suggests that all the lattice theories (including the relatively crude Flory–Huggins theory) should become increasingly accurate as one proceeds to lattices of increasing coordination number, such systematic improvement is observed only at high polymer volume fractions. For intermediate and low-volume fractions, the deficiencies of the predictions of the standard theories for the internal energy of mixing become larger as the coordination number of the lattice increases. While the consequences on the coexistence curve have not been determined for these lattices, these results seem consistent with those of Mackie et al.,[31] who obtained the coexistence curve of polymer and solvent for a three-dimensional, high coordination number lattice. We suggest that convergence of the theories at high coordination number is slower on a series of lattices with fixed dimensionality than it would be for a series of hypercubic lattices in higher dimensional spaces. However, this slow convergence may reflect the actual situation in real polymer–solvent systems.

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