

**University of Massachusetts Amherst**

---

**From the Selected Works of William MacKnight**

---

1988

# Computer Simulation of a Binary Polymer Mixture in Three Dimensions

William MacKnight, *University of Massachusetts Amherst*

P. Cifra

F. E. Karasz



Available at: [https://works.bepress.com/william\\_macknight/176/](https://works.bepress.com/william_macknight/176/)

# Computer Simulation of a Binary Polymer Mixture in Three Dimensions

P. CIFRA,\* F. E. KARASZ, and W. J. MACKNIGHT, *Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003*

## Synopsis

The behavior of a binary polymer mixture was simulated on a cubic lattice over both the miscibility and immiscibility regions. The number and distribution of interactions in the mixture were found to be different from the mean-field picture; however, the observed phase behavior agrees with that predicted by the mean-field theory and is not affected by the observed concentration fluctuations. The relationship between the phenomenological  $\chi$  parameter and the heterosegmental interaction energy was investigated. Polymer chains show nearly ideal behavior, even for strongly interacting mixtures; this simplifies the theoretical treatment of polymer mixtures analogous to homopolymer melts.

## INTRODUCTION

Polymer blending is a useful means for preparing new polymeric materials. The thermodynamics of polymer mixing has been successfully treated by the Flory-Huggins (FH) theory for a long time. As is well known this theory works well for dense systems of flexible chains, as opposed to dilute systems. It can explain both the UCST and LCST behavior observed in polymer mixtures by allowing the interaction parameter  $\chi$  to vary appropriately with temperature.<sup>1,2</sup> The theory has been extended to mixtures formed by copolymers.<sup>1,3</sup>

Here we present the results of a Monte-Carlo simulation of a dense binary polymer mixture. This method allows nonrandomness in mixing to arise from (1) energetic preferences present in the mixture and (2) correlations within the system due to the connectivity of segments, neither of which is accounted for in the mean-field treatment. In a previous two-dimensional simulation of the same system<sup>4</sup> we observed deviations from mean-field behavior as well as a considerable expansion of the polymer chains in the miscibility region. Unlike two-dimensional dense systems, which show nonideality,<sup>5,6</sup> three-dimensional dense systems of chains obey mean-field theory.<sup>7</sup> Similarly, in the present work we observed the phase-separation transition to have a mean-field character. In comparison with the two-dimensional case only a slight expansion of the chains was observed in the miscibility region; the behavior of the chains was nearly ideal.

\*Permanent address: Polymer Institute, Slovak Academy of Sciences 842 36 Bratislava, Czechoslovakia.

## CALCULATION PROCEDURE

A dense binary system of 484 flexible chains each consisting of 20 segments was simulated on a cubic lattice. The lattice consisted of  $22 \times 22 \times 22$  sites, 9.09% of which were voids; periodic boundary conditions were imposed on the system, and estimates and comparisons indicated that finite size effects were minimal. Half of the self-avoiding chains were designated as type A and the second half as type B. In addition to the simple volume-exclusion interactions within and between chains, an interaction energy  $\epsilon$  was included in the total energy of the system whenever A and B segments occupied adjacent lattice sites. Using a negative, positive, or zero reduced interaction energy,  $\epsilon' = \epsilon/k_B T$ , we simulated a miscible, immiscible, or athermal system, respectively. In the athermal system individual chains have the properties of those in a one component homopolymer melt. Starting from an arbitrary configuration of the system, we applied  $5 \times 10^7$  reptation moves to the chains, thereby obtaining equilibrium thermodynamic averages for each state.<sup>8</sup> During the sampling, each chain move was accepted or rejected according to Metropolis' rules;<sup>9</sup> the properties of the system were monitored continuously to determine when the system had reached equilibrium. No hysteresis was observed in the phase transition, since sufficiently long equilibration times were permitted in each state. The number of heterocontacts per chain and the chain end-to-end distance were accumulated during the sampling as principal descriptors of the system. The end-to-end distance of both A and B chains could be sampled over the same thermodynamic average because of the equivalency of the chains in this system.

Recently, results on analogous systems have been reported by Sariban and Binder.<sup>10</sup> Using a grand canonical ensemble, they present results of calculations of compositions of phases formed during phase separation and focus mainly on critical exponents and amplitudes in their system. In contrast in the present study we employ a canonical ensemble and present results in the form of heterocontacts in the system at a 1:1 component composition.

## RESULTS AND DISCUSSION

We first calculated the equilibrium mean-square end-to-end separation in the homopolymer melt using  $\epsilon' = 0$ . The result,  $\langle R^2 \rangle = 30.04$  in lattice spacing units, is in good agreement with the result of Olaj et al.,<sup>11</sup>  $\langle R^2 \rangle = 29.62$ , corresponding to the volume fraction of chains,  $\phi = 1$ . The result of Okamoto<sup>12</sup> and that of de Vos and Bellemans<sup>13</sup> when extrapolated to higher concentrations also agree with our value.

We then performed the calculation for the binary mixture using a nonzero  $\epsilon'$ . The results are shown in Figure 1, where the average number of heterocontacts per chain  $\bar{N}_{AB}$  is plotted as a function of  $\epsilon'$ . One can see a diffuse mixing/unmixing transition where a large number of heterocontacts corresponds to a miscible system and a small number of heterocontacts corresponds to an immiscible system, in which the chains are separated into domains. The center of the transition occurs at a critical value of the interaction energy,  $\epsilon'_c = 0.05$ . The transition is narrower in comparison with the two-dimensional case discussed previously. This occurs because three-dimensional chains have additional contacts available, each making a contribution  $\epsilon'$  to the total

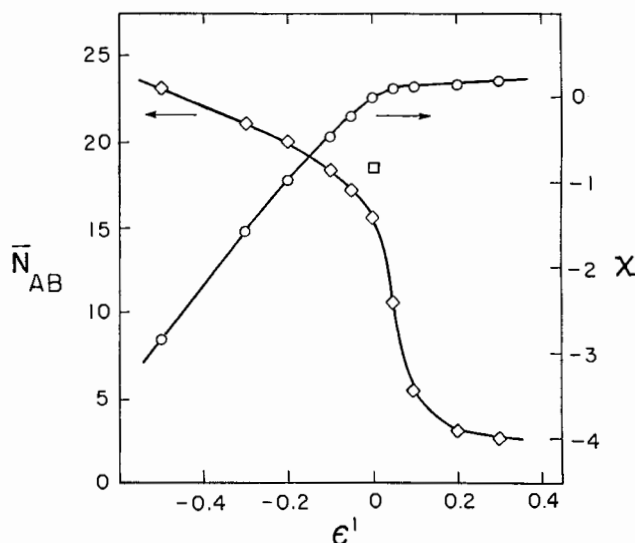


Fig. 1. Transition curve showing the dependence of  $\bar{N}_{AB}$  and  $\chi$  on  $\epsilon'$ ; ( $\square$ ) the value for the athermal system obtained from FH theory.

energy of the system. The transition is sharp in the immiscibility region where the system undergoes phase separation into domains. It is more diffuse in the miscibility region where intermixing of A and B chains provides space for continuous changes in properties with an increasing attractive A-B interaction.

For the athermal mixture,  $\epsilon = 0$ , a value of  $\bar{N}_{AB} = 15.35$  was obtained, which is a little smaller than that predicted from the FH theory,  $\bar{N}_{AB} = 18.17$ . The latter was obtained using  $N(z-2)\phi_A\phi_B$  for the total number of heterocontacts in the system, where  $N$  is the total number of sites in the mixture;  $z$  is the lattice coordination number,  $z = 6$ ; and  $\phi_i$  is the volume fraction of component  $i$ . Our value was obtained starting from two different initial configurations corresponding to  $N_{AB} = 10$  and 20; 15.35 was the limiting value approached from either side, a further indication that hysteresis was absent in this simulation.

Using the results presented above, there are two representations for the total A/B interaction free energy,  $\Delta F_{int}$ . One is the mean-field expression from FH theory, which assumes that the number of heterocontacts is proportional to the product of the volume fractions of A and B. The other expression stems from our approach where the total number of contacts depends on  $\epsilon'$ . For each  $\epsilon'$  we have a corresponding number of heterocontacts,  $\bar{N}_{AB}(\epsilon')$  per chain. Equating the two expressions for  $\Delta F_{int}$ , we obtain a relationship between the phenomenological  $\chi$  parameter and the true molecular constant  $\epsilon'$ :

$$\Delta F_{int}/RT = \chi\phi_A\phi_B = \epsilon'n_{ch}\bar{N}_{AB}(\epsilon')/N \quad (1)$$

where  $\Delta F_{int}/RT$  is related to the free energy per unit volume of the system, and  $n_{ch}$  is the total number of chains in the system. The dependence of  $\chi$  on  $\epsilon'$  is also depicted in Figure 1. The dependence is linear in the miscible regime

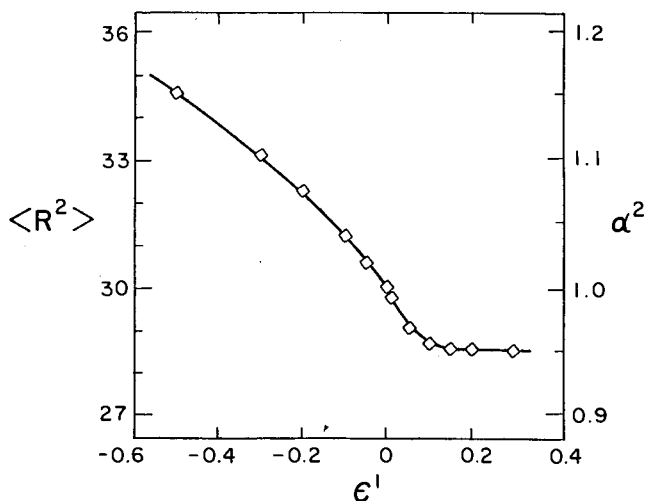


Fig. 2. Mean square end-to-end distance  $\langle R^2 \rangle$  and the square of the expansion coefficient  $\alpha^2$  are shown as a function of  $\epsilon'$ .

and is thereby analogous to two-dimensional systems; however, in the immiscible region saturation occurs as the chains become segregated into domains, and  $\chi$  asymptotically approaches a maximum of 0.25 with increasing  $\epsilon'$ . Thus the calculated  $\chi_{\max}$  in this work is close to 0.3, which was observed for the planar square lattice;<sup>4</sup> therefore, the estimates are not very sensitive to the lattice approximation or change of dimensionality. The existence of an upper positive limit of  $\chi_{\max}$  is consistent with the fact that large positive  $\chi$  parameters are not observed in real polymer mixtures, whereas negative values are common. Using eq. (1), the value of  $\chi_c$  which corresponds to the critical value,  $\epsilon'_c = 0.05$ , is found to be 0.11. This agrees with the value  $\chi_c = 2/p = 0.1$  predicted from FH theory;  $p$  is the degree of polymerization of both types of chains.

We have also investigated the dependence of coil dimension on  $\epsilon'$ . As mentioned above, the size of the chains for  $\epsilon' = 0$  agrees with the value for the homopolymer melt. The dependence of  $\langle R^2 \rangle$  and the square of the expansion coefficient  $\alpha^2$  on  $\epsilon'$  are shown in Figure 2;  $\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_{\epsilon'=0}$ . As  $\epsilon'$  increases beyond zero,  $\langle R^2 \rangle$  decreases only slightly below the athermal value as chains are repelled from the A-B domain interfaces. Still larger  $\epsilon'$  values result in an increasing number of chains aggregating into domains in which each chain then experiences a homopolymer melt-like environment. With decreasing  $\epsilon'$  in the  $\epsilon' < 0$  region, the favorable A-B interaction causes the chains to expand monotonically. The largest calculated value here for  $\alpha$  is 1.07, which corresponds to  $\chi = -2.81$ . The chain expansion in the miscible region is thus less pronounced than that for the two-dimensional system; the perturbation of the chain dimensions by the A-B interaction in the three dimensional case is thus small, and the chain behavior is more nearly ideal.

We conclude that the Monte-Carlo simulation results differ somewhat from those of the mean-field approximation of random mixing in the region investigated. However, the observed concentration fluctuations have no effect on the observed phase-separation transition, which is accurately described by

the mean-field theory. The observation that chains behave nearly ideally over a broad range of interactions implies a considerable simplification in the theoretical treatment of such systems. Powerful techniques such as the random phase approximation can, therefore, be used for mixtures of strongly interacting polymers.

The computations were performed using the IBM 3090/400 Supercomputer Facility at Cornell University. We thank AFOSR 86-0100 for support.

### References

1. G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **16**, 1827 (1983).
2. R. Koningsveld, in *Integration of Fundamental Polymer Science and Technology*, L. A. Kleintjens and P. J. Lemstra, Eds., Elsevier, 1985.
3. D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
4. P. Cifra, F. E. Karasz, and W. J. MacKnight, submitted for publication; P. Cifra, F. E. Karasz, and W. J. MacKnight, *Polymer Comm.*, **28**, 180 (1987).
5. P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, 1979.
6. A. Baumgartner, *Polymer*, **23**, 334 (1982).
7. P. G. de Gennes, *J. Physique Lett. (Paris)*, **38**, L441 (1977).
8. F. T. Wall and F. Mandel, *J. Chem. Phys.*, **63**, 4592 (1975).
9. N. Metropolis, A. N. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).
10. A. Sariban and K. Binder, *J. Chem. Phys.*, **86**, 5859 (1987).
11. O. F. Olaj and W. Lantschbauer, *Makromol. Chem., Rapid Commun.*, **3**, 847 (1982).
12. H. Okamoto, *J. Chem. Phys.*, **79**, 3976 (1983).
13. E. de Vos and A. Bellemans, *Macromolecules*, **7**, 847 (1974).

Received November 23, 1987

Accepted April 26, 1988