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The mean field to Ising crossover in the critical behavior of polymer mixtures: a finite size scaling analysis of Monte Carlo simulations

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Abstract. — Monte Carlo simulations of the bond fluctuation model of symmetrical polymer mixtures (chain lengths $N_A = N_B = N$) are analyzed near the critical temperature $T_c(N)$ of their unmixing transition. Two choices of interaction range are studied, using a square-well potential with effective coordination number $z_{\text{eff}} = 14$ or $z_{\text{eff}} = 5$, respectively, at a volume fraction $\phi = 0.5$ of occupied lattice sites, and chain lengths in the range $8 \leq N \leq 512$. A linear relation between $N$ and $T_c(N)$ is established, $T_c(N) = AN + B$, where the correction term $B$ is positive for $z_{\text{eff}} = 14$ but negative for $z_{\text{eff}} = 5$. The critical behavior of the models is analyzed via finite size scaling techniques, paying attention to the crossover from three-dimensional Ising-like behavior to mean-field behavior, using a formulation based on the Ginzburg criterion. It is shown that the location of the crossover does not depend on $z_{\text{eff}}$, consistent with the expected entropic origin of the mean-field behavior for long chains. However, despite large numerical efforts only a crude estimation of the crossover scaling function of the order parameter (describing the coexistence curve of the blends) and of the singular chain length dependence of the associated critical amplitude is possible. These results are discussed in the context of pertinent theories and related experiments.

1. Introduction.

The critical behavior of polymer mixtures has become the subject of intensive research in recent years [1-29]. There are many reasons for this interest. E.g., while Ginzburg-type criteria [30-35] imply that for binary (AB) mixtures of flexible polymers in the symmetrical case (chain lengths $N_A = N_B = N$) for $N \to \infty$ the critical behavior is described by the Landau theory [36] (mean-field critical exponents), the universality principle [37, 38] implies that very near to the critical temperature $T_c$ one should see the same critical exponents as for the three-dimensional Ising model [38-40]. This prediction has been indeed verified both by computer

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simulation [2-4, 17-21] and experiments [5-15]. The crossover from fluctuations-dominated Ising-like critical behavior very near \( T_c \) to classical mean-field like behavior farther away from \( T_c \) has found longstanding attention theoretically, in particular for the gas-liquid critical points in simple fluids [41-57]. The crossover behavior is found to be controlled by two variables [57] — a microscopic cutoff wavenumber \( \Lambda_0 \) of the critical fluctuations at short wavelengths, and a system-dependent parameter, the « Ginzburg number \( G_i \) », which may be expressed in terms of the (mean-field) critical amplitude \( \xi_{\text{MF}}^* \) of the correlation length \( \xi \) of order parameter fluctuations,
\[
\xi = \xi_{\text{MF}}^* (t - t_0)^{-1/2}, \quad t = 1 - T/T_c
\]
of the scattering function \( S(q \to 0) \) at zero wavenumber \( q \to 0 \), at critical concentration (or density respectively)
\[
S(q \to 0) = \hat{C}_+^\text{MF} (t - t_0)^{-1}
\]
and of the order parameter \( \langle |m| \rangle \),
\[
\langle |m| \rangle = \hat{B}^\text{MF} t^{1/2}
\]
This Ginzburg number then can be written as (\( v_0 \) is the volume per molecule in the case of small molecules or the volume per monomer in the case of polymer mixtures) [35, 57]
\[
G_i = \left( \frac{3}{4 \pi} \right)^2 \frac{1}{(\hat{B}^\text{MF})^4} (\hat{C}_+^\text{MF})^2 \left( \frac{v_0}{(\xi_{\text{MF}}^*)^3} \right)
\]
For \( |t| \gg G_i \), the classical mean field theory holds while for \( |t| \ll G_i \) the Ising critical behavior applies [37-39],
\[
\xi = \xi_+^* (t - t_0)^{-\nu}, \quad S(q \to 0) = \hat{C}_+^* (t - t_0)^{-\gamma}, \quad \langle |m| \rangle = \hat{B}(t)^{\beta}
\]
with exponents [10]
\[
\nu \approx 0.63, \quad \gamma \approx 1.24, \quad \beta \approx 0.325.
\]
If one could disregard the cutoff parameter \( \Lambda_0 \), the crossover between these two types of critical behavior would simply be controlled by one universal function of the variable \( t/G_i \) for each quantity of interest; it appears that such a universal crossover scaling description is at least a reasonable approximate description for simple fluids [57]. However, there the situation is obscured by the fact that the Ginzburg number \( G_i \) is never very small (e.g. \( G_i = 0.014 \) for \( \text{CO}_2 \) [53] or \( G_i = 0.025 \) for \( \text{H}_2\text{O} \) [53]), and since the crossover spans several decades of the reduced variable \( t/G_i \), one leaves the critical region where power-laws such as equations (1-3), (5) would be a reasonable description for \( t/G_i \gg 1 \) altogether.

Now polymer mixtures are, in principle, ideally suited to study such problems, since \( G_i \) can be made arbitrarily small for long enough chains. This is seen inserting the results of the Flory-Huggins [58, 59] theory for the critical behavior in equation (4), namely [30-33]
\[
\xi_{\text{MF}}^* = \frac{v_0^3}{6} \sqrt{2N}, \quad \hat{C}_+^\text{MF} = N/4, \quad \hat{B}^\text{MF} = \sqrt{3},
\]
which yields
\[
G_i = \frac{3^5}{2^5 \pi^2 N} \approx 2.308/N.
\]
Note that apart from the chain length there are no material-dependent parameters in equations (7, 8), which reflect the fact that the mean-field behavior of polymer mixtures derives from the entropy of Gaussian coils [30-34]. Consequently, it is implied that in terms of the variable $t/G_0 = Nt/2.308$ all symmetric polymers should exhibit the same behavior, irrespective of the chain lengths and their chemical nature, etc., if the universal crossover scaling description suggested by the theory [47, 56, 57] holds. Since this reasoning can be extended to somewhat asymmetric polymer mixtures [7] — all what happens is a change of the factor relating $G_0$ and the chain lengths $N_A, N_B$, it is somewhat disturbing that the recent experiments indicate problems with this universal crossover scaling description [10]. In the present paper we address this problem extending our simulation approach [17-21] to the bond fluctuation model [60-62] of symmetrical polymer mixtures. By studying the critical region of this model for a wide range of chain lengths, from $N = 8$ to $N = 512$, we provide further evidence to the fact [18, 19] that Flory-Huggins theory [58, 59] yields the correct exponent in the variation of $T_c(N)$ with $N$, $T_c(N) \propto N$, although the prefactor in this linear relation is not reliably predicted. These results [18, 19] have been corroborated by a recent elegant experimental study [22] and a reformulation [26] of the polymer reference interaction site model (PRISM) theory [23-25], and thus it is clear that the earlier result [23-25] $T_c(N) \propto \sqrt{N}$ was due to an artefact of the mean spherical approximation decoupling scheme.

It is hoped that the additional data given in the present paper will be useful as a further test of various approximate theories [26-28] for the thermodynamics of polymer mixtures, and thus contribute to our theoretical understanding of an important class of materials [29].

In section 2 we now summarize the main characteristics of the present model and the finite size scaling analysis used to extract information on critical properties from the simulation data. Section 3 surveys these critical properties for the various chain lengths studied, discussing also our conclusions for $T_c(N)$. Section 4 presents details on crossover phenomena in finite size scaling. Section 5 discusses our attempts to numerically estimate the crossover scaling function of the order parameter, using the variable $tN$ (which is simply proportional to $t/G_0$, as discussed above), and discusses the related problem of the chain length dependence of critical amplitudes. Comparing data for two different versions of the model (in the present model the interaction range is very short, effective coordination number $z_{\text{eff}} \approx 5$, while in previous work we used [17-21] $z_{\text{eff}} \approx 14$), we are able to investigate to what extent crossover phenomena are universal. Section 6 then contains our conclusions.

2. A brief review of the model and the techniques of simulation and analysis.

The bond fluctuation model [60-62] is a coarse-grained model of flexible polymers, where «effective monomers» block all 8 sites of an elementary cube of the simple cubic lattice for further occupation, and are joined by «effective bonds», represented by vectors $\ell$ from the set P(200), P(210), P(211), P(300) and P(310). Here and in the following all lengths are measured in units of the lattice spacing, and the symbol P stands for all permutation and sign combinations of the Cartesian coordinates $(\ell, \ell, \ell)$. One imagines that each effective bond corresponds to the end-to-end distance of a group of $n = 3-5$ successive chemical monomers along the backbone of the chain [63, 64]. Thus it is natural that the length $\ell$ of the effective bond is not fixed but can fluctuate in some range. Previous work [61, 62] has demonstrated that for a volume fraction $\phi = 0.5$ of occupied lattice sites the static and dynamic properties of long chains correspond to chains in dense polymer melts, excluded volume interactions being screened out on a length $\xi \approx 6$, i.e. about two average bond lengths. At this volume fraction the acceptance rate of the attempted moves, random displacements of the effective monomers by one lattice spacing, is still reasonably large ($A \approx 0.15$ [62]), and hence the coils renew their configurations reasonably fast. The athermal version of the model can be vectorized rather
efficiently, about 2 million attempted monomer moves per second are reached at CRAY-YMP processors [65].

This model of polymer melts can be straightforwardly extended to simulate symmetrical blends by associating two types of identities, A and B, with the chains, and introducing pairwise interactions \( \epsilon_{AA}(r) \), \( \epsilon_{AB}(r) \) and \( \epsilon_{BB}(r) \) between AA, AB and BB pairs of monomers at separation \( r \). Only two special choices of these interaction parameters, and two choices for the range of this interaction are considered.

(i) The interaction is nonzero only for monomers of different kind \( (\epsilon_{AA} = \epsilon_{BB} = 0) \) and for the smallest distance that two monomers can have, namely \( P(200) \); note that smaller distances between the center of mass of two effective monomers cannot occur due to their extended size and the excluded volume interaction. We then denote \( \epsilon = \epsilon_{AB} \).

(ii) The interaction \( \epsilon(r) = -\epsilon_{AA}(r) = -\epsilon_{BB}(r) = \epsilon_{AB}(r) \) is nonzero and constant for all three bond vectors \( P(200), P(210), P(211) \) that contribute to the first peak of the radial distribution function \( g(r) \) between monomers [61]. This medium range interaction is probably physically more realistic, but the program executes about a factor of two slower than the choice (i), since in computing the energy change \( \Delta E \) caused by an attempted hop of a monomer one has to search for « neighbors » in a larger surrounding region. Thus the performance of the code in the presence of these interactions is only about 500 000 attempted monomer moves per second.

Since in the Flory-Huggins theory [58, 59] the critical temperature of a polymer mixture is written, for a selfavoiding walk model of chains of \( N \) steps in the dense limit \( (\phi = 1) \), as \( k_B T_c = z 6\bar{\nu}N/2 \), with \( \bar{\nu} = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2 \), where \( z \) is the coordination number of the lattice, it is of interest to estimate the analog of \( z \) for the present model containing these extended monomers. We define an effective coordination number in terms of the radial distribution function \( g(r) \) around the center of gravity of a monomer as

\[
z_{\text{eff}} = \sum_r \epsilon(r) g(r)/r \quad ,
\]

\( \epsilon \) without argument being the strength of the (constant) interaction potential, as defined above. Using the results of reference [61] we find \( z_{\text{eff}} \approx 5 \) for model (i) and \( z_{\text{eff}} \approx 14 \) for model (ii). Note that these numbers include contributions from neighbors along the chain, which do not contribute to the unmixing of chains [2-4]. Due to a small temperature dependence of the coil configurations there is also a very weak temperature dependence of \( z_{\text{eff}} \) to be expected, but this was not investigated.

In a semi-grand canonical ensemble description of a symmetric polymer mixture, where chains may switch their identity \( A \leftrightarrow B \), but the total number of chains is constant, the temperature \( T \) and the chemical potential difference \( \Delta \mu \) between A and B-monomers are the (given) independent thermal variables. Phase separation and also the critical point occur at \( \Delta \mu = 0 \), because the system is symmetric against a change of chain « labels » A, B and simultaneous change of volume fractions \( \phi_A \leftrightarrow \phi_B \). Denoting the numbers of A-chains in the cubic box of linear dimension \( L \) as \( n_A \), the number of B-chains as \( n_B \), the basic observable of interest is the « order parameter » \( m \),

\[
m = \Delta n/n \quad , \quad n = n_A + n_B \quad , \quad \Delta n = n_A - n_B \quad .
\]

A realisation of the semi-grand canonical ensemble is easily obtained if one considers in the simulation apart from the local hops of monomers, which only lead to relaxation of the chain configurations and diffusion of the chains, a second type of move, where one attempts to « relabel » a chain \( A \leftrightarrow B \). This means, a chain of one type is replaced by a chain of the other
type but in an identical configuration, if the move is accepted. Of course, in both kinds of motions the Metropolis transition probabilities involving the energy change $\Delta E$ have to be considered, as is standard in Monte Carlo sampling [2-4, 18, 20, 66].

Using histogram techniques [20, 67] the probability distribution $P_L(m)$ of the order parameter as well as its low order moments are obtained from the simulation in an effective way, as described in detail in [20]. Due to a large investment of computer time on the CRAY-YMP 8/32 at the Höchstleistungsrechenzentrum (HRLZ) in Jülich and due to this economical data analysis, it has been possible to study systems up to chain lengths of $N = 512$ effective monomers on lattices up to linear dimensions of $L = 160$, i.e. systems containing 256 000 monomers. Altogether about 3 000 hours CPU time were needed for the data discussed in the present paper. As discussed in [18, 20, 62, 65], a significant fraction of computer time is needed to prepare a well-equilibrated initial configuration of the polymer melt with the largest chain length at each lattice size. Configurations at the same values of $L$ but values of $N$ smaller by some power of 2 are easily produced by cutting the chains in pieces of equal length and further equilibration. These configurations are stored and reused as starting configuration for the blend simulations (where arbitrary assignment of labels A, B realize fully ordered starts — with only A-chains — or fully disordered starts, with random mixtures of A and B, for instance).

These data for $\langle |m| \rangle$, $\langle m^2 \rangle$, $\langle m^4 \rangle$ and suitable ratios of these moments are then analyzed by standard finite size scaling techniques [2-4, 17-21, 66, 68-70]. Figures 1-3 present some examples of our data for the model case (i); more data for case (ii) can be found in references [17, 18, 20]. It is seen that for the choices of $L$ which were analyzed there is indeed a very strong finite size rounding of both $\langle |m| \rangle$ and the response functions $S_{\text{coll}}$, $S'_{\text{coll}}$ in the critical region, rather than displaying the power laws written in equation (5). The response functions $S_{\text{coll}}$, $S'_{\text{coll}}$ are defined here in terms of fluctuation relations

$$S_{\text{coll}} = n\langle m^2 \rangle - \langle m \rangle^2 , \quad (n = \langle m^2 \rangle \text{ for } \Delta \mu = 0) , \quad (11)$$

$$S'_{\text{coll}} = n\langle m^2 \rangle - \langle |m| \rangle^2 . \quad (12)$$

Note that equations (11), (12) are defined in such a way [66] that $S_{\text{coll}}$ is proportional to the scattering function $S(q \to 0)$ above $T_c$ for a critical volume fraction $\phi_A^{\text{crit}} = \phi_B^{\text{crit}} = (1 - \phi)^2$ in the thermodynamic limit ($n \to \infty$), while $S_{\text{coll}}$ is proportional to the scattering function $S(q \to 0)$ below $T_c$ for a path along one branch of the coexistence curve (for $n \to \infty$). Of course, due to the symmetry of our model both branches are equivalent, and thus $S(q \to 0)$ at the A-rich branch coincides with $S(q \to 0)$ at the B-rich branch at the same temperature. Although a finite system does not show any spontaneously broken symmetry and thus for $\Delta \mu = 0$ we have a vanishing order parameter $\langle m \rangle$ for all nonzero temperatures and finite $n$, the use of $\langle |m| \rangle$ as measure of the effective order parameters and in equation (12) ensures a smooth approach to the thermodynamic limit,

$$\lim_{n \to \infty} \langle |m| \rangle_{\Delta \mu = 0} = \lim_{\Delta \mu \to 0} \lim_{n \to \infty} \langle m \rangle_{\Delta \mu}$$

The histogram reweighting technique [20, 67] allows to obtain data at $\Delta \mu \neq 0$ from reweighting histograms taken at $\Delta \mu = 0$ with appropriate factors $\exp(\Delta \mu \ mN n/2 \ k_B T)$. In this way, data for $S_{\text{coll}}$ at constant $\langle m \rangle \neq 0$ have been generated, as discussed in more detail in references [18, 20]. Since Flory-Huggins theory [32, 58, 59] predicts that $S^{-\frac{1}{2}}_{\text{coll}}(\phi_A)$ vanishes at the spinodal

$$S^{-\frac{1}{2}}_{\text{coll}}(\phi_A) \propto \chi_{sp}(\phi_A) - \chi , \quad (13)$$
Fig. 1. — Order parameter $\langle |m| \rangle$ (a) and order parameter susceptibilities $S_{\text{coll}} = n (\langle m^2 \rangle - \langle m \rangle^2)$, $S'_{\text{coll}} = n (\langle m^2 \rangle - \langle |m| \rangle^2)$ (b) plotted vs. temperature for $N = 64$ and three choices of $L$ as indicated in the figure. Open symbols (triangles, squares, and circles) denote the data directly observed at those temperatures where the actual simulations were made, including error bars indicating the size of statistical errors, while broken curves indicate the multihistogram extrapolation based on the use of all data on $P_\perp (m)$ at all considered temperatures. Full curves are based on a finite size scaling extrapolation towards the thermodynamic limit. The broken curve with stars (marked «spinodal») in (a) is obtained from an extrapolation of $S_{\text{coll}}^{-1}$ to the point $S_{\text{coll}}^{-1} = 0$ at constant $\langle m \rangle$ as linear function of $\epsilon/k_B T$. In (b) the upper set of curves for $k_B T/\epsilon \approx 10$ refers to $S_{\text{coll}}'$ while the lower set of curves refers to $S'_{\text{coll}}$. 
Fig. 2. — Ratio of moments $\langle m^2 \rangle / \langle |m| \rangle^2$ vs. temperature for $N = 64$ (a) and $N = 256$ (b). Different curves result from histogram extrapolations for different choices of $L$ as indicated in the figure.

From a plot of the inverse structure factor versus the Flory-Huggins-parameter $\chi$ at constant volume fraction $\phi_A$ of A-monomers one can locate the spinodal $\chi_{sp}(\phi_A)$ from a linear extrapolation. In our model, $\phi_A = \phi (1 + \langle m \rangle) / 2$ and approximately one can assume that $\chi \propto \epsilon / k_B T$: thus $\chi_{sp}(\phi)$ corresponds to a spinodal temperature $T_{sp}(\langle m \rangle)$ and it is the quantity $\epsilon / k_B T_{sp}(\langle m \rangle)$ obtained from linear extrapolation of $S_{coll}^{-1}(\langle m \rangle)$ vs. $\epsilon / k_B T$ that is included in...
Fig. 3. — Finite size scaling plots of the scaled order parameter, $L' \langle |m| \rangle$, (a), the scaled susceptibility $S_{\text{coll}}$ below $T_c$, $L^2 \langle (m^2) - \langle |m| \rangle^2 \rangle$, (b), and the scaled susceptibility $S_{\text{coll}}$ above $T_c$, $L^2 \langle (m^2) - \langle m \rangle^2 \rangle$, versus the scaled temperature distance $L'' t$ (a, b) or $L'' t'$ (c), where $t = 1 - T/T_c$, $t' = 1 - T_c/T$, $k_B T_c / \epsilon = 9.9264$, and the scaling exponents $u = 1.526$, $v = 0.5482$. Full straight lines on these log-log-plots indicate asymptotic power laws (where $x$ is the abscissa variable) as quoted in the figure.
figure 1. Of course, the « spinodal curve » intrinsically is a mean-field concept and thus should be viewed with precautions. For $\phi_A = \phi_A^{\text{MF}}$, equation (13) reduces to equation (2), of course, so the mean-field value for exponent $\gamma = 1$ is automatically implied, rather than the correct value (Eq. (5)). Therefore $T_{sp}(\langle m \rangle = 0)$ must lie above the actual critical temperature $T_c$, as also observed experimentally [7-10], cf. figure 1a. But one expects that the difference $T_{sp}(\langle m \rangle = 0) - T_c$ vanishes as $N \to \infty$.

We now summarize the finite-size scaling equations [68-71] used to analyze the « raw data » for $\langle |m| \rangle$, $S_{\text{coll}}$ and $S_{\text{coll}}$ obtained for different linear dimensions $L$ from our simulation:

$$\langle |m|^k \rangle = L^{-kv} f_k(L^u t) \quad k = 1, 2, \ldots$$

where $f_k$ is a suitable scaling function and $u$, $v$ are characteristic exponents. In the Ising critical region [40]

$$v = \beta / \nu = 0.515, \quad u = 1 / \nu = 1.587$$

while in the mean-field critical region for $d = 3$ hyperscaling does not hold, and then $L$ does no longer scale with the correlation length $\xi \propto |t|^{-\nu}$ but rather a « thermodynamic » length [71]

$$\ell \propto (\langle |m| \rangle^{-2} S_{\text{coll}})^{1/d} \propto (|t|^{-2\beta_{\text{MF}} + \gamma_{\text{MF}}^3/N})^{1/d} = N^{1/3} |t|^{-2/3}$$

One therefore obtains, using $d = 3$ and $\beta_{\text{MF}} = \frac{1}{2}$, $\gamma_{\text{MF}} = 1$

$$v = \beta_{\text{MF}} d (2 \beta_{\text{MF}} + \gamma_{\text{MF}}) = \frac{3}{4}, \quad u = d (2 \beta_{\text{MF}} + \gamma_{\text{MF}}) = \frac{3}{2}.$$  

In the mean-field critical region, bulk (homogeneous) fluctuations of the order parameter dominate, and control the finite size rounding [71]. Therefore the mean-field correlation length $\xi_{\text{MF}} \propto |t|^{-\nu_{\text{MF}}}$ with $\nu_{\text{MF}} = 1/2$ does not enter the finite size scaling description. In the asymptotic non-mean-field critical region, however, the important order parameter fluctuations

\[ \text{Fig. 3 (continued).} \]
in a finite size system are spatially inhomogeneous ones, and therefore then $L$ scales with $\xi$. It turns out that in the crossover region from mean-field behavior there is a smooth matching between all these lengths, see figure 4. It now depends on whether the linear dimension $L$ exceeds $\xi_{\text{cross}} \propto N$ or not if equations (15) or equation (16) should be used in the finite size scaling law, equation (14). In view of the smoothness of the crossover it is clear, that for $L \approx \xi_{\text{cross}}$ neither of these sets of exponents will lead to a reasonable scaling, and it may then be practically more useful to treat $u$, $v$ as adjustable «effective exponents» which may smoothly interpolate between their theoretical limits equations (15), (16). While for $N \approx 32$ the fit of the data to master curves by plotting $\langle |m|^L \rangle$ vs. $L^\nu t$ works very well, if one fixes $u$, $v$ at the «Ising values» quoted in equation (15), this is no longer true for $N \approx 64$, see figure 3. But a reasonable fit (over a restricted range of $L$ which always is comparable to $N$, cf. Tab. 1) is possible with these effective exponents, as expected.

**Fig. 4.** — Crossover scaling of characteristic lengths for a polymer mixture. For $t \gg G$, (i.e. $-\log t$ to the left of $-\log G$) one has mean field behavior, with two characteristic lengths $\xi_{\text{MF}} \propto \sqrt{N} t^{-1/2}$ and $\xi \propto N^{1/3} t^{-2/3}$. These lengths smoothly merge in the crossover regime ($t = G$) and in the non-mean-field critical region a single characteristic length $\xi \propto N^{1-\nu} t^{-\nu}$ takes over.

**Table 1.** — Critical temperatures, effective critical exponents and effective critical amplitudes as a function of chain length. Also shown is the interval ($L_{\text{min}}$, $L_{\text{max}}$) from which these estimates are derived.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$B_{\text{eff}}$</th>
<th>$\beta_{\text{eff}}$</th>
<th>$C_{\text{eff}}^+$</th>
<th>$\dot{C}_{\text{eff}}^-$</th>
<th>$\gamma_{\text{eff}}$</th>
<th>$k_B T_{c/\xi}$</th>
<th>$(L_{\text{min}}, L_{\text{max}})$</th>
<th>$u$</th>
<th>$v$</th>
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<tbody>
<tr>
<td>8</td>
<td>1.18</td>
<td>0.325</td>
<td>225</td>
<td>52</td>
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<td>0.9693</td>
<td>(24, 40)</td>
<td>1.59</td>
<td>0.51</td>
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<td>16</td>
<td>1.27</td>
<td>0.325</td>
<td>260</td>
<td>72</td>
<td>1.24</td>
<td>2.2892</td>
<td>(24, 48)</td>
<td>1.59</td>
<td>0.51</td>
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<tr>
<td>32</td>
<td>1.25</td>
<td>0.325</td>
<td>500</td>
<td>130</td>
<td>1.24</td>
<td>4.845</td>
<td>(40, 64)</td>
<td>1.59</td>
<td>0.51</td>
</tr>
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<td>64</td>
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<td>0.359</td>
<td>850</td>
<td>240</td>
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<td>9.9261</td>
<td>(48, 80)</td>
<td>1.526</td>
<td>0.548</td>
</tr>
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<td>128</td>
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<td>0.389</td>
<td>1700</td>
<td>700</td>
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<td>20.69</td>
<td>(48, 80)</td>
<td>1.570</td>
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<tr>
<td>256</td>
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<td>0.42</td>
<td>4000</td>
<td>1700</td>
<td>1.0787</td>
<td>40.9</td>
<td>(64, 160)</td>
<td>1.563</td>
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<td>0.402</td>
<td>8200</td>
<td>3500</td>
<td>1.042</td>
<td>82.27</td>
<td>(96, 160)</td>
<td>1.626</td>
<td>0.653</td>
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<tr>
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<td>$\sqrt{3}$</td>
<td>0.5</td>
<td></td>
<td></td>
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<td></td>
<td>3/2</td>
<td>3/4</td>
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</table>
A delicate point is the precise estimation of the critical temperature. Choosing ratios such as

\[ U_{ij}^{L_t} = \langle |m| \rangle_{ij}^{L_t} / \langle |m| \rangle \] \[ \text{with } L_t = ij \] \[ (17) \]

one concludes from equation (14) that they depend on a single scaling combination \( L^t \) only,

\[ U_{ij}^{L_t} = f_{ij}^{L_t} (L^t) , \] \[ (18) \]

with \( f_{ij}^{L_t} \) being another suitable scaling function. Plotting now ratios \( U_{ij}^{L_t} \) vs. \( t \) for different choices of \( L \), one expects that all such curves should intersect in a common intersection point \( f_{ij}^{L_t}(0) \) for \( t = 0 \). Figure 2 shows that this works reasonably well for \( N = 64 \), while for \( N = 256 \) considerable scatter is apparent. This must be expected since for \( N = 256 \) a larger range of \( L \) is covered and part of the data fall in the region where \( L \) is distinctly smaller than \( \xi_{\text{cross}} \). Since part of the scatter seen in figure 2b is due to statistical and systematic errors involved in the histogram reweighting technique, a more sophisticated data analysis (considering corrections to finite size scaling) does not seem to be warranted.

Figure 3 then shows an example for the « data collapsing » obtained for \( N = 64 \) for the three quantities \( \langle |m| \rangle \), \( \langle m^2 \rangle \) and \( \langle m^2 \rangle - \langle |m| \rangle^2 \). We estimate here that the systematic deviation seen between the curves for the three different choices of \( L \) should be mostly due to corrections to finite size scaling rather than statistical and systematic errors of the « raw data ». The same is true for \( N \approx 32 \), where \( u, v \) were not allowed to vary but rather fixed at their Ising values. In contrast, for \( N \approx 128 \) statistical and systematic errors in the data become more of a problem, simply because for the larger lattice sizes at \( T_c \) critical slowing down of order parameter fluctuations is a severe problem \([66]\) and also the chain configurations remain highly correlated over large times. Thus the non-monotonic variation of effective exponents and effective amplitudes with \( N \) in table I needs to be taken with corresponding precautions.

An alternative way of checking for the effective exponent \( v \) to be used in equation (14) is to study directly, the variation of the order parameter \( \langle |m| \rangle \) at \( T_c \), which according to equation (14) should vary as \( \langle |m| \rangle _{T_c} \propto L^{-\nu} \). Alternatively, one can study the variation of the response function \( n [ \langle m^2 \rangle _{T_c} - \langle |m| \rangle _{T_c}^2 ] \) with \( L \) at \( T_c \), or equivalently the variation of \( (S_{\text{coll}})_\text{max} \). Since \( n = L^3 \phi / (8N) \), we expect that \( (S_{\text{coll}})_\text{max} \propto L^{-3 \phi / 2} / N \). Figure 5 checks for such power laws. The data are indeed compatible with such an interpretation in terms of an effective exponent \( v \). The estimates resulting for \( v \) from either \( \langle |m| \rangle _{T_c} \) or \( (S_{\text{coll}})_\text{max} \) are roughly in agreement with each other and in most cases also compatible with the numbers which resulted from the data collapsing of the temperature dependence (Tab. I). A similar behavior for the model (ii) with longer range of interaction, mentioned above, has already been documented \([18]\). A more refined description of this crossover will be attempted in section 4.

3. Chain length dependence of critical properties.

The critical temperature \( T_c(N) \) is found to scale linearly with \( N \) for both models (i) and (ii) for large \( N \) ; however, unexpectedly the corrections to this leading behavior are different (Fig. 6) : while for case (i) one approaches the asymptotic value \( k_b T_f / N \varepsilon = 0.16124 \) for large \( N \) from below, for case (ii) one approaches this value from above. In both cases these data can be fitted to straight lines with a « free-end »-correction,

\[ k_b T_f / \varepsilon = 0.16124 N - 0.227 , \] \[ \text{model (i)} \] \[ (19) \]

\[ k_b T_f / \varepsilon = 2.15 N + 1.35 , \] \[ \text{model (ii)} \] \[ (20) \]
Fig. 5. — Log-log plot of the order parameter at $T_c$, $\langle |m| \rangle_{T_c}$ (a) and of the maximum value of the response function, $(S_{\text{coll}})^\text{max} = n(\langle m^2 \rangle - \langle |m|^2 \rangle)^\text{max}$ (b) versus $L$. All choices of $N$ are included. Straight-line fits are indicated for $N = 16$ and $N = 256$.

but the sign of this correction differs. While one could physically interpret a positive correction as a contribution due to extra interactions that free ends can have with nonbonded neighbors [19, 20], we now doubt whether such a simple interpretation is correct in view of the different sign found for model (I). We have no interpretation to offer for this difference in sign. It is
interesting to note, however, that in the revised versions of PRISM decouplings [26] slightly different schemes yield different sign of the correction for the same model, which indicates also that it is not straightforward to understand precisely the origin of this correction. It is also interesting that for model (i) one has to go to fairly large $N$ until one reaches the asymptotic behavior, unlike model (ii). This fact might be due to the smallness of $z_{\text{eff}}$, which leads to rather low ordering temperatures for $N \approx N_{s}$ in case (i), and hence rather strong fluctuation effects leading to a suppression of $T_{c}$ may be expected. However, in the model of Sariban and Binder

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Fig. 6. — Variation of the observed normalized critical temperature $k_{B} T_{c}/(\varepsilon N)$ with $N^{1/2}$, for model (i) \{only $\varepsilon_{AB} \neq 0$, $z_{\text{eff}} \approx 5$\} and for the «most symmetric» model (ii) \{$\varepsilon_{AB} = -\varepsilon_{AA} = -\varepsilon_{BB} = \varepsilon$, $z_{\text{eff}} = 14$\}.

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**Table:**

- **Chain length dependence of critical temperatures**
  - $k_{B} T_{c}/N\varepsilon$ vs. $N^{1/2}$
  - Data points: 0.00, 0.08, 0.12, 0.16, 0.20
  - $N^{1/2}$ values: 0.0, 0.1, 0.2, 0.3, 0.4
  - $N$ values: 8, 16, 32, 64, 128, 256

**Diagram a):**

- Graph showing the variation of $k_{B} T_{c}/N\varepsilon$ with $N^{1/2}$.
- Data points: 0.00, 0.08, 0.12, 0.16, 0.20
- $N^{1/2}$ values: 0.0, 0.1, 0.2, 0.3, 0.4
- $N$ values: 8, 16, 32, 64, 128, 256

**Diagram b):**

- Graph showing the variation of $k_{B} T_{c}/N\varepsilon$ with $N^{1/2}$.
- Data points: 2.00, 2.50, 3.00
- $N^{1/2}$ values: 0.0, 0.1, 0.2, 0.3
- $N$ values: 256, 128, 64, 32, 16
[2-4] which also has $\zeta_{\text{eff}} \approx 3$ a positive correction similar to equation (20) was nevertheless found.

Discussing the magnitude of the coefficient of the leading term, we would expect a reduction by a factor of 2 times the ratio of the effective coordination numbers, i.e. roughly a factor of 6 (the factor of 2 comes from the fact that in case (ii) all pairs of monomers between different chains contribute but only AB-pairs contribute for case (i)). In reality the ratio between both factors in roughly 13, indicating for case (i) a stronger discrepancy between the model and Flory-Huggins-prediction $\{k_B T_c (\phi) f = \zeta_{\text{eff}} N \phi/2 \approx 1.25 N\}$ than in case (ii). A similar trend was observed for the simple self-avoiding walk model of references [2-4] as well. If we would take the prefactor in equation (19) as an estimate of an effective coordination number between nonbonds neighbors, we would obtain the very small value $\zeta_{\text{eff}} \approx 0.64$. This shows that Flory-Huggins theory can hardly estimate the scale for the critical temperature reasonably, although it yields the exponent of the chain length dependence correctly.

As discussed already in reference [3], the order parameter should exhibit a crossover scaling from mean-field behavior to non-mean-field like behavior as follows

$$\langle |m| \rangle = \tilde{B}_{\text{MF}}^{1/2} \tilde{M} (t/t_*) = \sqrt{3} t^{1/2} \tilde{M} (2.3 N t)$$  \hspace{1cm} (21)

where in the last step we have used $\tilde{B}_{\text{MF}} = \sqrt{3}$ (Eq. (7)) and inserted equation (8). In order that equation (21) reduces to equation (5) we must have [3, 18] $\tilde{M} (\xi) \propto \xi^{\beta - 1/2}$ and hence

$$\tilde{B} (N) \propto N^{(\beta - 1/2)} \approx N^{-0.176}$$  \hspace{1cm} (22)

In order to check for equation (22) we followed the procedure described in reference [20] and fitted data for $\langle |m| \rangle$ which are not affected by finite size effects (for the largest choice of $L$ in each case) directly to the equation $\langle |m| \rangle = \tilde{B} t^{\beta}$ imposing the Ising model value for $\beta$ ($\beta = 0.325$). Figure 7 gives our results. It is seen that two regimes must be distinguished. For short chains ($N \leq \approx 32$) equation (22) is not yet valid and rather one finds that the data are compatible with a law proposed for semidilute binary blends in a common solvent [72-74], where an exponent $x$ describing the reduction of the $x$-parameter due to excluded volume enters

$$\tilde{B} (N) \propto N^{(\beta - 1/2) \psi (1 + x)} \approx N^{-0.0317} \hspace{1cm} (x \approx 0.22).$$  \hspace{1cm} (23)

Equation (23) results if one considers chains in the crossover regime from dilute to semidilute solutions, where chains have started overlapping and interacting, and one can describe this interaction by rescaling them in terms of «blobs» which have the size of the screening length of excluded volume interactions. Inside one blob, there are no monomers of other chains, and thus the number of pairwise contacts that lead to unmixing is greatly reduced. A scaling theory for these effects yields also equation (23). Previous work where also the volume fraction $\phi$ of the monomers was varied over a wide range [4] was shown to be in good agreement with equation (23) [75]. The fact that our data for $N \leq 32$ are described by equation (23) can be understood that the screening length of excluded volume forces $\xi_{\text{exc}} \approx 6$ for $\phi = 0.5$ [62] and this is comparable to the gyration radii for small $N$ ($\sqrt{\langle R_{\text{gyr}}^2 \rangle} \approx 12.26$ for $N = 16$, $\sqrt{\langle R_{\text{gyr}}^2 \rangle} \approx 17.5$ for $N = 32$). Unfortunately, only in this regime where the effective exponent $\beta_{\text{eff}}$ agrees with the Ising exponent $\beta = 0.325$ (Tab. 1) can the associated critical amplitude $\tilde{B}$ accurately estimated; for larger $N$ we can fit rather precisely an effective amplitude $\tilde{B}_{\text{eff}}$ (corresponding to a critical behavior described by $\beta_{\text{eff}}$, see Tab. 1), but an amplitude $\tilde{B}$ corresponding to $\beta = 0.325$ can be estimated only within large errors, as figure 7 shows. This problem could only be resolved if data closer to $T_c$ (i.e., for larger $L$) were available. It is
obvious from table I that the effective amplitude $B_{\text{eff}}$ has an $N$-dependence rather different from equation (22): probably it smoothly interpolates between the Ising value for short chains and the mean-field result $\sqrt{3}$ that one obtains for $N \to \infty$ with $\beta = 1/2$.

The effective critical exponents $\beta_{\text{eff}}$, $\gamma_{\text{eff}}$ etc. and the associated effective critical amplitudes quoted in table I for model (i) with $z_{\text{eff}} = 5$ and in table I of reference [18] for model (ii) with $z_{\text{eff}} = 14$ are estimated from a relatively narrow «window» of lattice sizes around $L_m = (L_{\min} + L_{\max})/2$ and temperatures where the correlation length $\xi$ is comparable to $L_m$. Therefore the $N$-dependence of these effective critical exponents simply reflects the fact that for different chain lengths $N$ we work in different portions of the crossover scaling diagram for the characteristic lengths, figure 4, some of the data correspond to $\ell / \xi_{\text{crossover}} > 1$ and other data to $\ell / \xi_{\text{crossover}} < 1$. Note that $\xi_{\text{crossover}} \propto N$ and $\ell \propto \xi$ for $\xi > \xi_{\text{crossover}}$ and the rounded temperature region of our data corresponds to $\xi = L_m$, and hence it makes sense to analyze our
data for $\beta_{\text{eff}}$, $\gamma_{\text{eff}}$ etc. not as functions of $1/N$ but rather of $L_m/N$ (Fig. 8): the variable $L_m/N$ should simply be proportional to the variable $\xi/\xi_{\text{cross}}$, which translates into $t/G$, if figure 4 is involved. Although there is some scatter, figure 8 is compatible with a smooth crossover from mean-field values for $L_m/N \ll 1$ (or $\xi/\xi_{\text{cross}} \ll 1$, respectively) to Ising-model values [40, 76] for $L_m/N \gg 1$ (or $\xi/\xi_{\text{cross}} \gg 1$, respectively). Figure 8 may be of interest for the interpretation of experiments, since effective exponents are easily defined in terms of logarithmic derivatives [57]

$$g_{\text{eff}}(t) = -\frac{d \{ \log S(q \to 0) \}}{d \{ \log (-t) \}}, \quad \beta_{\text{eff}} = \frac{d \log \langle |m| \rangle}{d \log (t)}$$  (24)

they are convenient for the discussion of crossover phenomena. Numerous theoretical predictions can be found in literature for $\gamma_{\text{eff}}(t)$, e.g. [47, 56, 57], while the crossover of the other quantities displayed in figure 8 to our knowledge has not been treated explicitly. Our data for $\gamma_{\text{eff}}$ are compatible with the finding [47, 56, 57] that $\gamma_{\text{eff}}(t)$ varies monotonously with $\log (-t)$ between both limits and that the maximum slope of this variation occurs for about $\gamma_{\text{eff}} \approx 1.12$, i.e. halfway in between both limiting values. Unfortunately the larger scatter of our data does not warrant a more detailed comparison with these predictions at this stage.

Fig. 8. — Semi-log plot of the effective exponent $\gamma_{\text{eff}}$ of the collective scattering function $S_{\text{coll}}(q \to 0)$ [upper part], of the order parameter exponent $\beta_{\text{eff}}$ [middle part] and the ratio of critical amplitudes $\hat{C}_+^{\text{eff}}/\hat{C}_-^{\text{eff}}$ [lower part] versus the crossover scaling variable $L_m/N$, which is proportional to the ratio of characteristic lengths $Z/\xi_{\text{cross}}$. Asymptotic limits are shown as dashed straight lines. Curves through the points are only a guide to the eye to show how the various crossover scaling functions could look like.

From figure 4 we conclude that for \( t = G_t \approx 2.3 / N \) (Eq. (8)) we must have \( \xi_{\text{cross}} \propto N \) and hence it clearly matters whether \( L / \xi_{\text{cross}} \gg 1 \) (then the finite size rounding occurs in the non-mean field, Ising-like regime) or whether \( L / \xi_{\text{cross}} \ll 1 \) (then the finite size rounding occurs in the mean-field critical regime). This consideration clearly suggests that data such as shown in figure 5 for the model (i) with \( z_{\text{eff}} \approx 3 \) [77] should be analyzed in terms of the crossover scaling variable \( L / \xi_{\text{cross}} \propto L / N \). We thus expect [18, 21]

\[
N^{1/2} \langle |m| \rangle_{T_c} = \tilde{m}(L / N),
\]

\[
N^2 L^{-3} n (\langle m^2 \rangle - \langle |m| \rangle^2) = \tilde{S}(L / N),
\]

where consistency with equations (14), (15) for \( L / N \gg 1 \) and with equations (14), (16) for \( L / N \ll 1 \) requires that the scaling functions \( \tilde{m}(\zeta) \), \( \tilde{S}(\zeta) \) have the following behavior for small or large values of the argument \( \zeta = L / N \), respectively:

\[
\tilde{m}(\zeta) \propto \zeta^{-\beta_1}, \; \zeta \gg 1, \quad \tilde{m}(\zeta) \propto \zeta^{-3/4}, \; \zeta \ll 1,
\]

\[
\tilde{S}(\zeta) \propto \zeta^{-2 \beta_1}, \; \zeta \gg 1, \quad \tilde{S}(\zeta) \propto \zeta^{-3/2}, \; \zeta \ll 1.
\]

We can derive equations (25), (26) by generalizing equation (14) stating that \( L \) scales with the «thermodynamic length» \( \ell(t) \propto N^{1/3} t^{-2/3} \) and including \( t / G_t \propto N t \) as a second scaling variable:

\[
\langle |m|^k \rangle = (LN^{-1/3})^{-3k/4} \tilde{f}_k(LN^{-1/3} t^{2/3}, N t)
\]

\[
N^{k/4} L^{-3k/4} \tilde{f}_k(L / N, N t)
\]

where \( \tilde{f}_k \) is derived from \( \tilde{f}_k \) changing variables \( \xi_1 = LN^{-1/3} t^{2/3}, \; \xi_2 = N t \) to variables \( \xi_1 \xi_2^{-2/3}, \; \xi_2 \). Splitting off a factor \( L / N )^{3k/4} \) leads to \( \langle |m|^k \rangle \propto N^{-k/2} \tilde{f}_k(L / N, N t) \). The thermodynamic mean field limit is obtained. Of course, by replacing the second argument \( N t \) by infinity and requiring \( \tilde{f}_k \propto \xi_1^{3/4} \) which gives \( \langle |m| \rangle \propto t^{1/2} \) and the powers of \( LN^{-1/3} \) indeed cancel out. Note that \( h = L^3 \phi / 8 \) in our model and hence equation (26) simply can be also written as \( \langle m^2 \rangle - \langle |m| \rangle^2 \propto N^{-1} \tilde{S}(L / N) \). From equation (29) we obtain hence simply equations (25), (26) putting \( t = 0 \) in \( \tilde{f}_k \) in equation (29). Alternative and more detailed derivations of equations (25), (26) can be found in references [18, 21].

Figure 9 replots the data of figure 5 and compares them to corresponding results for the model with \( z_{\text{eff}} = 14 \) [18, 21]. It is seen that one obtains a relatively good data collapsing and the crossover between the two power laws proposed in equations (27), (28) can be recognized easily. Comparison of figures 9a, c shows gratifyingly that on the abscissa scale the position of the crossover is the same, \( L / N \approx 0.9 \) independent of the value of \( z_{\text{eff}} \). Such a «universality» of the crossover is indeed expected — note that the Ginzburg number \( G_i \) in equation (8) does not depend on such details of the model as well, it is solely controlled by the chain length. This fact is due to the entropic origin of the coefficient of the gradient in the free energy functional of polymer mixtures [30-34]. While changing the interaction range in our model of polymer mixtures changes strongly the location of \( T_c \) relative to the strength of the interaction, compare equations (19) and (20), it does not change the position of the crossover between Ising and mean-field critical behavior (measured by a particular value \( t_{\text{cross}} / G_i = c_1 \) or \( L_{\text{cross}} / N = c_2 \), respectively), as long as this range is small in comparison to the polymer coil sizes of interest.
An important observation, however, is that the constant where the crossover occurs (defined in terms of the intersection of straight-line extrapolation on log-log plots, as in Fig. 9) depends on the nature of the quantity that is analyzed. E.g., the constant $c_2 = 0.9$ for the crossover of the order parameter (Figs. 9a, c) but $c_2' = 1.8$ for the crossover of the scattering function. This implies the Ising critical region for $S_{\text{coll}}$ is narrower than for $\langle |m| \rangle$.

It is interesting to compare the numerical value for these constants ($c_2, c_2'$) describing this universal crossover to the universal constant $C$ introduced by Bates et al. [7] for describing the crossover in the scattering function $S(q \to 0)$ at critical composition of the mixture in the one crossover scaling

order parameter at the critical point

![Graph a)](image)

maximal susceptibility

![Graph b)](image)

Fig. 9. — Log-log plot of $N^{1/2} \langle |m| \rangle_{T_c}$ (a) and $L^{-1} N \langle \langle m^2 \rangle \rangle - \langle |m| \rangle^2_{\text{max}}$ (b) vs. $L/N$ for the model (i) with $z_{\text{eff}} = 5$. Different symbols represent the various chain lengths used, as indicated in the figure. Straight lines indicate the expected power laws, as quoted in the figure. Part (c) shows data corresponding to (a) but for the model (ii) with $z_{\text{eff}} = 14$. 
phase region \((t = 0)\). Their expression for the temperature distance \(t_{\text{cross}}\) where the crossover occurs for a symmetrical mixture \((N_A = N_B = N, \ g_A = g_B = N, \ \phi_c = 1/2)\) reduces to

\[
-t_{\text{cross}} = C v_m^2 \frac{[2/(n \phi_c^2)]^2}{[2/N \phi_c][2 R^2/N \phi_c]} = C v_m^2 N^2/R^6,
\]

\(v_m\) being the volume taken by a monomer. First we convert \((- t_{\text{cross}})\) into the correlation length \(\xi_{\text{cross}}\), figure 4, see also equation (7)

\[
\xi_{\text{cross}}^2 = 2 R^2/( - t_{\text{cross}}) = 2 R^2/(C v_m^2 N^2).
\]

Using now \(R = \ell \sqrt{N/6}\) where \(\ell\) is the length of an effective bond \((\ell \approx 2.63\) in our case, measuring lengths in units of the lattice spacing, \(v_m = 2\) then for \(\phi = 0.5\) we further obtain

\[
\xi_{\text{cross}} = \sqrt{2} \ell^4 N/(36 v_m \sqrt{C}) \approx 0.935 N/\sqrt{C}.
\]

Bates et al. [7] suggest \(C = 0.29 \pm 0.08\) which yields \(\xi_{\text{cross}} \approx 1.74 N\). If we could identify \(\xi_{\text{cross}}\) with the values for \(L\) where we see crossover for the order parameter \(L_{\text{cross}} \approx 0.9 N\), or the scattering function, \(L_{\text{cross}} \approx 1.8 N\), we obtain nearly the same constant in the latter case. This finding is an indirect support for the usefulness of equation (30), and we suspect that some problems noted in the literature [10] with equation (30) are probably due to an inappropriate identification of \(t_{\text{cross}}\) from the experimental data.

5. Thermal crossover for the coexistence curve.

While the simulations have provided compelling evidence for the crossover from Ising-like criticality to mean-field behavior in the framework of the size-dependence of critical properties at \(T_c\) (Figs. 5, 9, Sect. 4), these size-dependences are not observable in any real experiment. Conversely, one readily can study the thermal crossover for the scattering function,

\[
S(q \to 0) = \hat{C}^{\text{MF}}_+ ( - t)^{-1} \tilde{s}(t/G_c) = \frac{N}{4} ( - t)^{-1} \tilde{s}(2.3 N t),
\]

and in principle also the thermal crossover for the coexistence curve (Eq. (21)) should be experimentally accessible.
Using our data for $\langle |m| \rangle$ for the largest value of $L$ in a temperature « window » near $T_c$, which we believe is neither significantly affected by size effects (very near $T_c$) nor by saturation effects (at low temperatures where the order parameter gets large), we arrive at a picture as shown in figure 10. Again it is clear that short chain lengths do not satisfy equation (21). Since equation (21) directly leads to the power law equation (22) which we failed to see for $N \leq 32$ either, the lack of scaling for small $N$ is at least consistent with our analysis of critical amplitudes, figure 7. Chain lengths $N = 64 - 512$ show the expected scaling, at least roughly. It clearly appears that also for $N = 512$ we still have not reached the regime of mean-field behavior yet. In this crossover scaling plot, our data span roughly two decades in the variable $Nt$, and this is clearly not enough to span the full crossover region.

![Crossover scaling](image)

Fig. 10. — Log-log plot of $N^{1/2} \langle |m| \rangle$ vs. $Nt$ to check for the validity of crossover scaling, equation (21), for the model (i) with $z_{\text{eff}} = 5$ (a) and the model (ii) with $z_{\text{eff}} = 14$ (b). Different symbols show various chain lengths $N_t$, as indicated. Only such data were included for which the $L$-dependence was thought to be negligibly small, and data at lower temperatures being plagued by saturation effects of the order parameter also were omitted. Straight lines indicate the Ising power law $\propto (Nt)^{3/4}$, valid for $Nt \gg 1$ and the mean field power law $\propto (Nt)^{1/2}$, valid for $Nt \gg 1$. 
analytical studies of the crossover scaling function $\tilde{s}(t/G_i)$ based on renormalization group calculations [47, 56, 57] also reveal that the crossover is spread out over several decades in the variable $t/G_i$, and sharp kinks should not be expected. Figure 10 thus gives qualitative evidence for the expected behavior, but due to the various interesting effects (« blob effects » for small $N$, finite size effects for small $t$, corrections to scaling due to the saturation of the order parameter for large $t$, systematic errors due to inaccuracy of $T_c$, statistical errors, . . . ) we are not able to give a precise estimation of $\tilde{m}(t/G_i)$.

In order to try an alternative estimation of the scaling function, we use the fits for $\langle |m| \rangle$ and $S_{\text{coll}}$ in terms of effective exponents and amplitudes and treat these results in a scaling plot similar to figure 10. Of course, each power law on the log-log plot gives a straight line, but using the same interval ($0.001 < t < 0.1$) for the different values of $N$, the fan of straight lines defines as a sort of envelope the crossover scaling function. In this way we estimate the scaling function for $\langle |m| \rangle$ consistent with figure 10 but with slightly better precision. The crossover scaling function for $S_{\text{coll}}$ can in this way also estimated, at least roughly. Figure 11b is our counterpart to estimates of the crossover scaling function for $S(q \to 0)$ as function of $t/G_i$ discussed extensively in the literature [47, 56, 57]. Since figure 11b defines this crossover scaling function only in a rather crude way, we have not attempted a quantitative comparison.

6. Conclusions.

In this paper we have undertaken a major computational effort to analyze the critical behavior of symmetrical polymer mixtures by means of extensive Monte Carlo simulations of the bond fluctuation model. Particular attention has been paid to the variation of critical temperatures and « effective » critical exponents and amplitudes with chain length. Two choices for the interaction range between the monomers were compared. The main findings can be summarized as follows.

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**Fig. 11.** — a) Log-log plot of $N^{1/2} \langle |m| \rangle$ vs. $N t$ as in figure 10, but using the fits resulting from finite size scaling, $\langle |m| \rangle = \tilde{B}_{\text{eff}} t^{\beta_{\text{eff}}}$ rather than raw data. b) Log-log plot of $N^{-2} S_{\text{coll}}$ vs. $N (-t)$, using the fits resulting from finite size scaling, $S_{\text{coll}} = C^\text{eff}_{+} (-t)^{-\tau_{\text{eff}}}$ as quoted in table I.
(i) The scaling of the critical temperature with chain length $N$ can be well described by a linear relation, $T_c(N) = AN + B$, where the constants $A$, $B$ are strongly model-dependent. Flory-Huggins theory overestimates the coefficient $A$ typically by a large factor (in our case a factor 3-4, for a volume fraction of $\phi = 0.5$ occupied lattice sites). There does not seem to exist a simple interpretation for the « free end-correction » term $B$. We find that $B$ even can be either positive or negative.

(ii) In a temperature region accessible to simulations (and experiments), i.e. $0.001 < |t| < 0.1$, the crossover from Ising-like critical behavior for small $N$ to mean-field like behavior for large $N$ is described by a gradual change of « effective » exponents and « effective » critical amplitudes from the one class to other. While very short chains due to remaining effects of excluded volume interactions behave differently, for chain lengths $N \approx 32$ we find a behavior that is rather universal, in particular it does not depend on the interaction range of our model. This shows directly the entropic origin of the mean field behavior in large chain mixtures, as is of course expected. The change of effective exponents can also be interpreted in terms of crossover scaling functions, where one studies the quantities of interest in a suitably scaled form as functions of the crossover variable $t/G_c \propto Nt$. The resulting crossover scaling functions for the order parameter $\langle |m| \rangle$ (which describes the coexistence curve) and $S(q \to 0)$ (describing the critical scattering at the critical volume fraction in the one-phase region) have been estimated, at least crudely. These crossover scaling functions are spread out over several decades in the variable $Nt$ and are in qualitative agreement with corresponding theoretical predictions.

(iii) Evidence for the success of a crossover scaling description of finite size rounding at the critical point has been presented. Since there the crossover seems to be somewhat sharper, one can estimate a constant intended to locate the center of the crossover region, first introduced by Bates et al. [7]. We confirm the numerical value of this (universal) constant, for the scattering

Fig. 11 (continued).
function $S(q \to 0)$, but find a different constant for the crossover of the order parameter. This reiterates our above statements, that really the crossover is spread out over a broad region of the crossover scaling variables ($L/N$ in finite size scaling or $Nt$ in the thermal approach to $T_c$, respectively). Therefore one must be careful by which procedure one extracts estimates for this constant describing the center of the crossover region either from simulation data or experiment.

(iv) In the asymptotic Ising-like critical region, the critical amplitudes must have a singular dependence on the chain length $N$. Although this is a necessary consequence of crossover scaling, only crude and qualitative evidence for this behavior was found, since for large $N$ extremely large lattice sizes would be required to reach this Ising region fully despite an effort for this study (and a preceding one [18-21]) which took already about 3 000 hours CRAY-YMP time (on a single processor) this does not seem feasible yet.

(v) Our data suggest that suitable polymer mixtures should allow the experimental verification of theoretical concepts on the description of Ising-mean field crossover nicely. It is hoped that our investigation is useful for such efforts. On the theoretical side, we suggest that the crossover scaling of the order parameter also should be considered in detail. To our knowledge, emphasis has mainly been on $S(q \to 0)$ and the specific heat in the one-phase region.

Overall speaking, as far as simulations can tell, symmetric polymer mixtures seem fairly well understood now. After some initial confusion about closure approximations in integral equation theories of polymer mixtures [23-25], which now seems settled [26], our data should also be useful to test such approximate analytical theories in more detail.

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[77] Analogous data for the model (ii) with $z_H \approx 14$ have already been presented in figure 15 of reference 18 and are hence not repeated here.

[78] Very recently, this has been attempted in Meier G., Schwahn D., Mortensen K. and Janssen S., preprint, where data for several polymer mixtures are interpreted in terms of the crossover scaling description of References [56, 57].