



Monte Carlo investigations of phase transitions: status and perspectives

Kurt Binder^a, Erik Luijten^{a,*}, Marcus Müller^a, Nigel B. Wilding^{a,1},
Henk W.J. Blöte^b

^a*Institut für Physik, Johannes Gutenberg-Universität, Staudinger Weg 7, D-55099 Mainz, Germany*

^b*Department of Physics, Delft University of Technology, P.O. Box 5046,
2600 GA Delft, The Netherlands*

Abstract

Using the concept of finite-size scaling, Monte Carlo calculations of various models have become a very useful tool for the study of critical phenomena, with the system linear dimension as a variable. As an example, several recent studies of Ising models are discussed, as well as the extension to models of polymer mixtures and solutions. It is shown that using appropriate cluster algorithms, even the scaling functions describing the crossover from the Ising universality class to the mean-field behavior with increasing interaction range can be described. Additionally, the issue of finite-size scaling in Ising models above the marginal dimension ($d^* = 4$) is discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Critical phenomena; Ising model; Crossover scaling; Polymers; Finite-size scaling

1. Introduction

It is a common belief that at the present time, about 30 years after the renormalization-group theory of critical phenomena was invented [1], static critical behavior of systems in thermal equilibrium is rather well understood. In particular, this is expected to be true for the most intensively studied case, the Ising universality class [2,3], to which systems such as uniaxial ferromagnets, binary alloys, simple fluids, fluid mixtures, polymer solutions and polymer blends belong [4]. However, in the present work, we shall draw attention to some aspects of critical behavior in Ising-like spin systems which are, even today, still incompletely understood. The first of these concerns the

* Correspondence address: Max-Planck-Institut für Polymerforschung, Postfach 3148, 55021 Mainz, Germany.
E-mail address: erik.luijten@uni-mainz.de (E. Luijten)

¹ Present address: Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, UK.

problem of crossover between the Ising universality class and mean-field critical behavior. This crossover occurs, for instance, when the interaction range (and hence the “Ginzburg number” G entering the Ginzburg criterion [5]) is varied [6–12]. A closely related crossover is found for symmetrical polymer mixtures when the chain length N of the polymers is varied [4,13–23]. A part of this crossover (though typically not the full extent of the crossover scaling function) can be probed experimentally near the critical point of fluids and fluid binary mixtures [24–27]. While the Ginzburg criteria [5,14–16] provide a qualitative understanding of this crossover, the quantitatively accurate theoretical prediction of the crossover scaling function is a challenging problem [28–36], and hence Monte Carlo studies [6–12,17–19] are of great potential benefit. In particular, the question as to what extent (if at all) such crossover scaling functions are universal is an intriguing one [10–12,24–26,36].

Another very interesting crossover which can also be studied is that which occurs near the critical point of unmixing for polymer solutions in a bad solvent [13,37–46]. For chain length $N \rightarrow \infty$ the critical temperature $T_c(N)$ moves towards the Θ -temperature, where a single coil undergoes a transition from a swollen coil to a collapsed globule. This limit corresponds to a tricritical point [13].

Monte Carlo analyses of critical phenomena typically apply finite-size scaling concepts [47–52]. However, care is necessary in the proper application of these methods in the mean-field limit. In fact, the standard formulation of finite-size scaling (“linear dimensions L scale with the correlation length ζ ”) implies that the hyperscaling relation [2,3] between critical exponents should hold [48,53], which is not the case for mean-field exponents (apart from $d = d^* = 4$ dimensions). This problem already arises for Ising models with short-range interactions for $d > d^*$ [54–66], and some disagreements between Monte Carlo results [54,55,57] and theoretical predictions [56,65] have stimulated a long-standing debate (see Ref. [66] for a detailed review).

2. Mean-field to Ising crossover

We consider the Hamiltonian [6,7]

$$\mathcal{H}/k_B T = - \sum_i \sum_{j>i} K(\mathbf{r}_i - \mathbf{r}_j) s_i s_j - h_0 \sum_i s_i, \quad (1)$$

with $s_i = \pm 1$ and an interaction $K(\mathbf{r}) \equiv cR^{-d}$ for $|\mathbf{r}| \leq R$ and zero elsewhere. The critical behavior of this model on d -dimensional lattices can be studied efficiently with a new cluster algorithm adapted for long-range interactions [67].

To analyze the crossover it is instructive to consider the associated Ginzburg–Landau field theory in continuous space,

$$\mathcal{H}(\phi)/k_B T = - \int_V d\mathbf{r} \left\{ \frac{1}{2} \int_{|\mathbf{r}-\mathbf{r}'| \leq R} d\mathbf{r}' \left[\frac{c}{R^d} \phi(\mathbf{r}) \phi(\mathbf{r}') \right] - \frac{1}{2} v \phi^2(\mathbf{r}) - u_0 \phi^4(\mathbf{r}) + h_0 \phi(\mathbf{r}) \right\}, \quad (2)$$

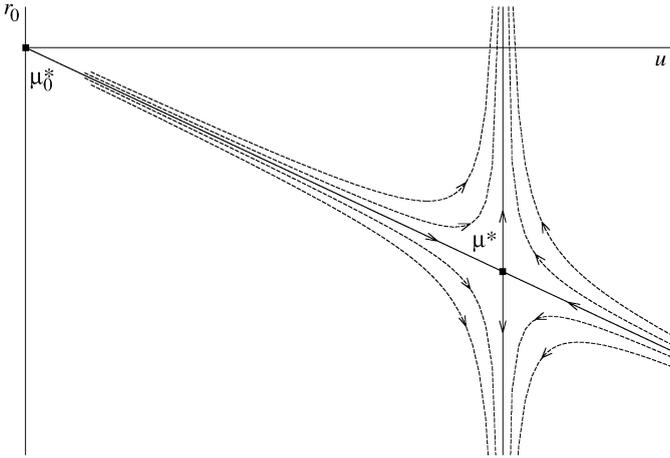


Fig. 1. Qualitative picture of the renormalization trajectory describing the crossover from the Gaussian fixed point $\mu_0^* = (0, 0)$ to the Ising fixed point $\mu^* = (r_0^*, u^*)$.

where $\phi(\mathbf{r})$ is the single-component order-parameter field, v is a temperature-like parameter and u_0 is a constant. After Fourier transformation and suitable rescaling this can be rewritten as (here N is the total number of lattice sites)

$$\begin{aligned} \bar{\mathcal{H}}/k_B T = & \frac{1}{2} \sum_{\mathbf{k}} \left[k^2 + \frac{r_0}{R^2} \right] \psi_{\mathbf{k}} \psi_{-\mathbf{k}} \\ & + \frac{u}{4R^4 N} \sum_{\mathbf{k}_1} \sum_{\mathbf{k}_2} \sum_{\mathbf{k}_3} \psi_{\mathbf{k}_1} \psi_{\mathbf{k}_2} \psi_{\mathbf{k}_3} \psi_{-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3} - \frac{h}{R} \sqrt{\frac{N}{2}} \psi_{\mathbf{k}=0}, \end{aligned} \quad (3)$$

where u is related to u_0 and h to h_0 [7], and r_0 in mean-field theory is the deviation of the temperature from its critical-point value.

We are now interested in identifying the crossover scaling variable associated with the crossover from the Gaussian fixed point $u = 0$ and $r_0 = 0$ to the nontrivial Ising fixed point (Fig. 1). Because of the trivial character of the Gaussian fixed point and the fact the crossover scaling description should hold all the way from the Ising fixed point to the Gaussian fixed point, one can infer the crossover length scale $l_0 = R^{4/(4-d)}$ exactly! This is done by considering a renormalization by a length scale l , such that the wave number changes from k to $k' = kl$, the number of degrees of freedom is reduced from N to $N' = Nl^{-d}$, and ψ_k changes into $\psi'_{k'} = l^{-1} \psi_k$ to leave $\bar{\mathcal{H}}$ invariant. From inspection of the terms in the Hamiltonian one can conclude that the singular part of the free energy must satisfy the scaling relation

$$\tilde{f}_s \left(\frac{r_0}{R^2}, \frac{u}{R^4}, \frac{h}{R} \right) = l^{-d} \tilde{f}_s \left(\frac{r_0}{R^2} l^2, \frac{u}{R^4} l^{4-d}, \frac{h}{R} l^{1+d/2} \right). \quad (4)$$

We see that a finite and nonzero value for the second argument of \tilde{f}_s is retained exactly when l takes the value of the crossover scale l_0 . Thus, we conclude that the singular

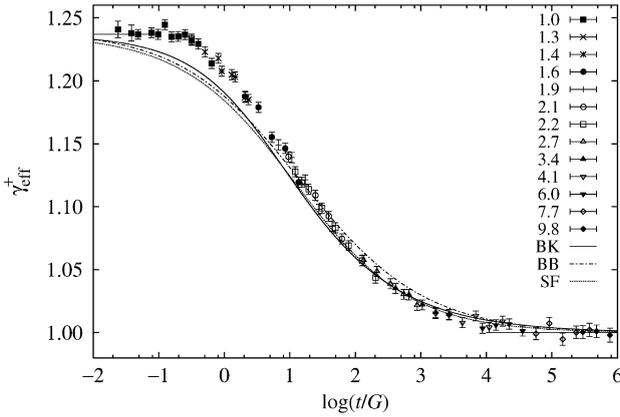


Fig. 2. Effective susceptibility exponent γ_{eff}^* above T_c for the three-dimensional Ising model with variable interaction range R (numbers in the key) plotted versus t/G , along with three theoretical calculations for this quantity; due to Refs. [34] (BK), [30] (BB), and [28,32] (SF), respectively. From Ref. [10].

part of the free energy scales with R as follows:

$$\tilde{f}_s = R^{-4d/(4-d)} \hat{f}_s(\tilde{r}_0 R^{2d/(4-d)}, \tilde{u}, hR^{3d/(4-d)}), \tag{5}$$

where a natural choice of coordinates (Fig. 1) is to measure \tilde{r}_0 and \tilde{u}_0 as distances from the Ising fixed point, unlike in the original Hamiltonian, where r_0 and u_0 are distances from the Gaussian fixed point.

Eq. (5) describes how the temperature distance \tilde{r}_0 from criticality and the magnetic field h scale with the range of interaction R : Note that the crossover exponent is known exactly (unlike other cases of crossover, e.g., between the Ising and Heisenberg universality class in isotropic magnets with varying uniaxial anisotropy [68]). The same result for the crossover exponent follows [6], of course, from simple-minded arguments using the Ginzburg criterion. However, the location of the nontrivial fixed point u^* (Fig. 1), the associated other exponents, and the explicit form of the scaling function \tilde{f}_s cannot be obtained exactly.

The calculation of the scaling function for the free-energy density or its derivatives, such as the susceptibility, is a nontrivial task for both renormalization-group and Monte Carlo calculations. This is demonstrated in Fig. 2 where the effective critical exponent γ_{eff}^+ of the susceptibility for $T > T_c$ is plotted versus the thermal crossover scaling variable t/G , with $t = (T - T_c)/T_c$ being the reduced temperature and $G = G_0 R^{-6}$ the Ginzburg number in $d = 3$, for which $G_0 \approx 0.277$. Note that effective exponents are defined as

$$\gamma_{\text{eff}}^\pm \equiv -d \ln \hat{\chi} / d \ln |t|, \quad \hat{\chi} \equiv k_B T_c(R) (\partial M / \partial h)_T, \tag{6}$$

where \pm refers to $T \gtrless T_c$, respectively, $M = \langle s \rangle_{T,h}$, and the range R is defined from the second moment of the interaction (z being the effective coordination number)

$$R^2 = \frac{\sum_{j \neq i} |\mathbf{r}_i - \mathbf{r}_j|^2 K(\mathbf{r}_i - \mathbf{r}_j)}{\sum_{j \neq i} K(\mathbf{r}_i - \mathbf{r}_j)} = \frac{1}{z} \sum_{j \neq i} |\mathbf{r}_i - \mathbf{r}_j|^2 \quad \text{with } |\mathbf{r}_i - \mathbf{r}_j| \leq R_m. \quad (7)$$

Here the second equality holds only for a square-well potential and values $R_m^2 = 1, 2, 3, 4, 5, 6, 8, 12, 18, 28, 60, 100$, and 160 were studied. From Fig. 2 we see that the Monte Carlo results agree with all the theoretical calculations near the Gaussian fixed point, but do not yield the more rapid increase of γ_{eff}^+ near the Ising fixed point. It is not clear what precise conclusions should be drawn from this discrepancy: some theoretical treatments really rely on extrapolations of low-order renormalization-group expansions in $\varepsilon = 4 - d$, and hence are perhaps rather inaccurate in $d = 3$ dimensions. On the other hand, they clearly relate to the limit where $R \rightarrow \infty$ and $t \rightarrow 0$, with tR^6 fixed – a universal description of the crossover can only be expected in this limit. The Monte Carlo data shown in Fig. 2 also include the range of small R , for which additional corrections to scaling present near the Ising fixed point (other than those attributable to the Ising–mean-field crossover) may come into play.

A rather successful description of the Monte Carlo data could be obtained by a fit to a function given by Anisimov et al. [36]. Their description is also an interpolation formula based on low-order ε -expansions but contains a second parameter (in addition to G) describing a short-wavelength cutoff. However, one disturbing feature of this description is that one needs different amplitudes G_0 in the relation $G = G_0 R^{-6}$ above and below T_c , and the ratio G_0^+/G_0^- is an additional, ad hoc, parameter the significance of which is not understood [36]. Thus, we consider it an as yet unsettled problem as to just on which parameters the crossover scaling description should depend. In this context, we draw attention to the question whether the specific square-well form chosen for the exchange interaction matters. To answer this question, a more general form of $K(\mathbf{r}_i - \mathbf{r}_j)$ was chosen (viz., a superposition of two square-well potentials which differ in range and strength but are chosen such that the same value for R^2 results [11]. While T_c was shown not to be determined by R alone, but depended on $K(\mathbf{r}_i - \mathbf{r}_j)$ in a more detailed way, the same crossover scaling function resulted for all choices of the interaction profile studied [11].

A particular merit of the description of Anisimov et al. [36] is, however, that it can yield a nonmonotonic variation of γ_{eff}^- with t/G : In $d = 3$ a shallow minimum ($\gamma_{\text{eff}}^- \approx 0.96 < \gamma_{\text{MF}} = 1$) occurs for $|t|R^6 = 10^2$ [10] that can be fitted by this theory [36]. Indeed, a very similar minimum has been observed in Ref. [69] from a mean-field expansion for Ising systems with medium-range interactions, see also Ref. [70] for a detailed review. In $d = 2$ dimensions, such a minimum occurs as well and is much more pronounced than in $d = 3$, while above T_c the variation of the effective exponent is still monotonic (Fig. 3). Note that the crossover is again spread out over many decades in

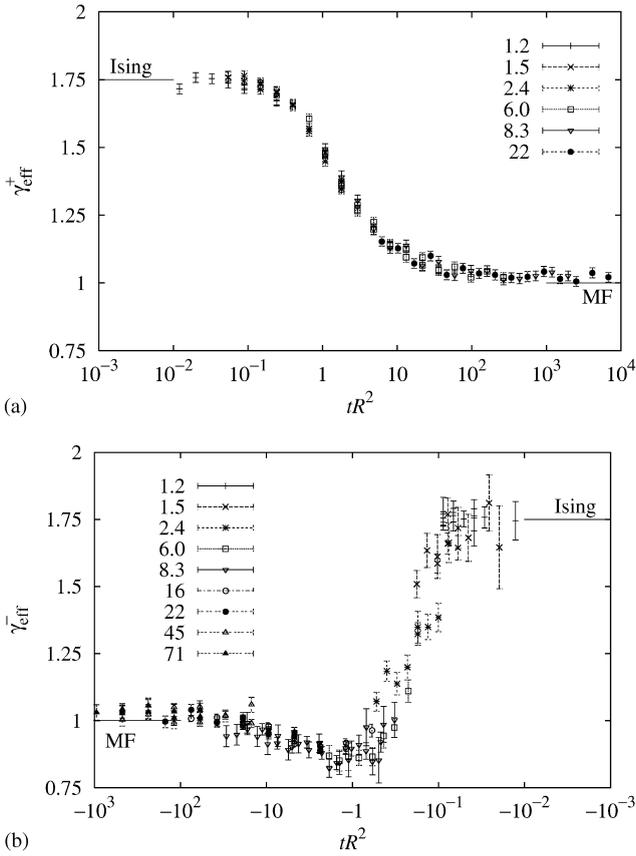


Fig. 3. The effective susceptibility exponent γ_{eff}^* above T_c (a) and below T_c (b), for the two-dimensional Ising model with variable interaction range R (numbers in the key), plotted versus tR^2 . From Ref. [9].

the crossover variable t/G ($G \propto R^{-2}$ in $d=2$), as in $d=3$, and that for $T < T_c$ there are no analytical results whatsoever to compare our Monte Carlo results with! At this point, there is clearly still a gap in our knowledge about critical phenomena.

As a last point in this section, we add a few brief comments about the way in which the Monte Carlo results on effective exponents have been obtained. As is well known [48–52], the Monte Carlo method converges to the exact statistical mechanics of a finite system only; the thermodynamic limit is never addressed directly. The typical situation is that one deals with a $L \times L$ or $L \times L \times L$ box with periodic boundary conditions. The critical singularities are rounded and shifted by the finite size of the system [47–52]. For the precise location of the critical point, a finite-size scaling analysis is required. The principle of finite-size scaling is that the linear dimension L scales with the correlation length ξ . Therefore the k th moment of the magnetization m scales like

$$\langle |M|^k \rangle = L^{-k\beta/\nu} \tilde{M}_k(L/\xi), \tag{8}$$

β and ν being the critical exponents of the order parameter ($\langle m \rangle \propto |t|^\beta$) and the correlation length ($\xi \propto |t|^{-\nu}$), respectively, and \tilde{M}_k being some scaling function. Therefore, the straightforward observation results [48] that these power-law prefactors $L^{-k\beta/\nu}$ cancel out if one considers suitable ratios of moments, such as

$$Q = \langle M^2 \rangle^2 / \langle M^4 \rangle = \tilde{Q}(L/\xi). \quad (9)$$

At T_c we have $\xi \rightarrow \infty$, of course, so $\tilde{Q}(0)$ is simply a constant, independent of the system size L . This justifies the simple recipe to record this ratio for different choices of L and obtain T_c from the intersection point of these ratios [48,51,52]. Note that the ordinate value of this intersection point is a universal constant (only depending on the shape of the system and on the boundary conditions, but not on R , for instance, provided one is in the asymptotic critical region).

However, this recipe so far ignores the crossover from one universality class to the other (as well as corrections to scaling). Nevertheless, it turns out that one can formulate a combined finite-size scaling and crossover scaling description for such problems [6–12,18,19,71]. A simplified description considers the variation of the correlation length, which is $\xi \propto Rt^{-1/2}$ in the mean-field critical region, and $\xi \propto (R^\kappa t)^{-\nu}$ in the Ising critical region [the exponent κ follows from the condition that for $t = t_{\text{cross}} \propto R^{-2d/(4-d)}$ and the corresponding value of ξ , $\xi_{\text{cross}} = \xi(t = t_{\text{cross}}) = l_0 \propto R^{4/(4-d)}$ a smooth crossover between both power laws occurs]. Now, it is of crucial importance to compare L with the crossover length scale ξ_{cross} : If L is much less than ξ_{cross} , then the finite size rounding occurs fully in the mean-field regime, before the crossover to Ising criticality has had a chance to come into play. Actually in this regime the correlation length ξ is not the relevant length to describe the finite size rounding [51,54,55], one rather needs the so-called “thermodynamic length” [55], $\ell_T \propto |t|^{-2/d}$, as will be discussed in Section 4. In this regime ($L \ll \xi_{\text{cross}}$) an accurate determination of T_c is clearly impossible. In order to accurately locate T_c , we need to study the inverse regime, $L \gg \xi_{\text{cross}}$: Only then can one see the mean-field critical behavior farther away from T_c crossing over to the Ising behavior at t_{cross} (remember that this crossover is spread out over several decades!) and the finite-size rounding sets in at a still much smaller value of $|t|$ (where $L \simeq \xi$). Since for large R , ξ_{cross} is also very large ($\xi_{\text{cross}} \simeq l_0 \propto R^{4/(4-d)}$), one needs to simulate very large L and hence such simulations are technically very difficult.

Thus it is not surprising that when this problem was first addressed with single-spin-flip Monte Carlo algorithms [6] a satisfactory description of the full crossover could not be obtained, and the availability of an efficient cluster algorithm [67] was crucial for obtaining meaningful results. In $d = 2$, we could study L up to 800 lattice units, and $R_m = 100$ corresponding to $z = 436$ interacting neighbors (Fig. 4). With these large lattices it is possible to follow the variation of Q almost all the way from the mean-field limit at small L to the Ising limit at large L , and in χ (Fig. 4(a) the Ising asymptote (slope $\frac{3}{4}$ on the log–log plot) is nicely confirmed).

Since we know T_c very precisely and have data for such a wide range of L , it is also possible to carry out runs slightly away from T_c , which are used to study the thermal

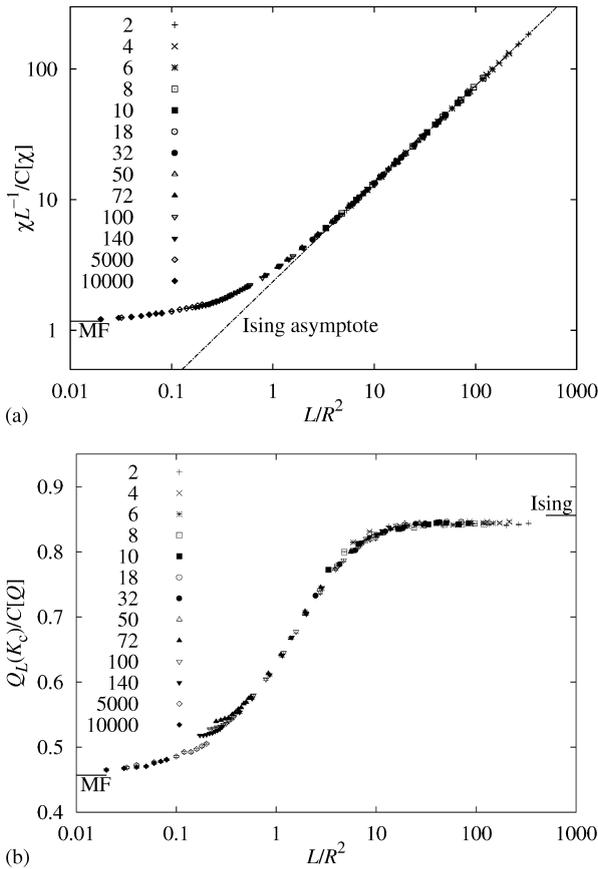


Fig. 4. Finite-size crossover curve for the magnetic susceptibility χ divided by the system linear dimension (a) and the amplitude ratio Q [Eq. (9)] (b) for the two-dimensional Ising model at $K = K_c(R)$ plotted versus the finite-size crossover scaling variable L/R^2 (note that $\xi_{\text{cross}} = l_0 \propto R^2$ in $d = 2$). In both quantities, range-dependent correction factors $C[\chi]$ and $C[Q]$ have been divided out to eliminate some corrections to scaling (see Ref. [8] for a definition of these factors). From Ref. [8].

crossover presented in Figs. 2 and 3. Only data not affected by the finite system size are used for the numerical derivative required in Eq. (6).

3. First steps towards the study of crossover problems in polymer blends and solutions

As is well known [4,13–16], the Ginzburg–Landau–Wilson Hamiltonian for a symmetrical polymer mixture near its critical unmixing point can be mapped on to the Ising model with a medium range of interaction (in $d = 3$ dimensions), $N^{1/2}$ (with N being the chain length of the flexible macromolecule) playing the role of the interaction volume R^3 . Qualitatively, this mapping is understood from the fact that a

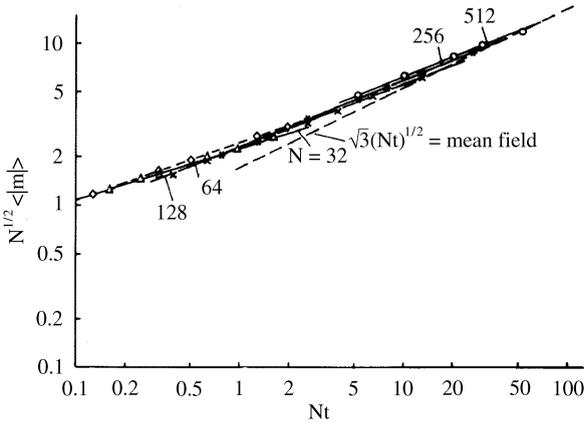


Fig. 5. Crossover scaling plot for the order parameter $\langle |m| \rangle = \langle |\phi_A - \phi_B| \rangle / (\phi_A + \phi_B)$ of a binary polymer mixture (A,B) with symmetrical chain lengths $N_A = N_B = N$. ϕ_A, ϕ_B are the volume fractions of A and B monomers, respectively. The points are simulation results for the bond-fluctuation model on a simple-cubic lattice, using concentration $\phi_v = 0.5$ of vacant sites. Straight lines in this log–log plot indicate power laws with effective exponents, $\langle m \rangle = \hat{B}_{\text{eff}} t^{\beta_{\text{eff}}}$, $t = 1 - T/T_c$. The broken straight line shows the mean-field result, $\langle m \rangle = \sqrt{3}t^{1/2}$, to which the data converge for $N \rightarrow \infty$. From Ref. [19].

polymer coil has a random walk-like configuration. Its gyration radius R_{gyr} scales as $R_{\text{gyr}} \simeq a\sqrt{N/6}$, where a is the size of the monomer. Thus the monomer density of one chain inside the volume that it occupies ($V \propto R_{\text{gyr}}^3$) is very small, $\rho = N/V \propto a^{-3}N^{-1/2}$. Hence in a dense melt ($\rho_{\text{melt}} \simeq a^{-3}$) there are $N^{1/2}$ chains in the same volume, i.e., each chain interacts with $x = N^{1/2}$ “neighbors”. Thus as $N \rightarrow \infty$ one again expects a crossover from Ising-like critical behavior to mean-field like behavior, and this is verified experimentally [20,21] (though the corresponding prediction for the Ginzburg number $G \propto 1/N$ does not seem to work out).

First steps to study this crossover by computer simulation have been performed [18,19] using the bond fluctuation model of symmetrical polymer mixtures [10,72] applying a semi-grand canonical algorithm [17] and histogram reweighting techniques [73,74]. The model and methodology of these simulations have been extensively reviewed elsewhere [4,72] and hence we omit all the technical details here, and simply show an attempt to estimate the crossover scaling function of the order parameter [19] (Fig. 5). Note that polymers are slowly relaxing objects and hence difficult to simulate – no counterpart to the cluster algorithm used for the Ising model [67] is available, and hence the challenge remains to improve substantially the accuracy of studies such as shown in Fig. 5 in order to be able to study the variation of effective exponents for this problem in analogy with Figs. 2 and 3.

If one wishes to compare such simulations for polymer mixtures to experiments on real systems [20,21], an important complication that must be taken into account is the asymmetry in chain length, $N_A \neq N_B$. This leads to two very important technical complications: (i) While in the symmetrical case the coexistence curve (including

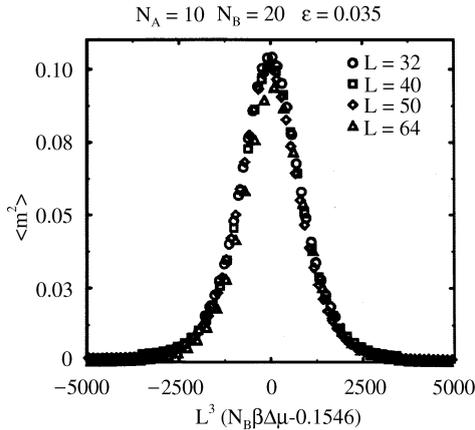


Fig. 6. Finite-size scaling plot for the second moment of the order parameter of an asymmetric polymer mixture ($N_A = 10$, $N_B = 20$) at a temperature $T < T_c$ ($\epsilon = \epsilon_{AB}/T = 0.035$) as a function of the normalized chemical potential difference, in order to locate $\Delta\mu_{\text{coex}}(T)$ by optimizing the “data collapse” for the range of values of L as indicated. From Ref. [22].

the critical point) occurs at a chemical potential difference $\Delta\mu = 0$, for $N_A \neq N_B$ phase coexistence occurs along a nontrivial curve $\Delta\mu_{\text{coex}}(T)$ in the $(\Delta\mu, T)$ plane, and hence one has to search for the critical point $(\Delta\mu_{\text{crit}} = \Delta\mu_{\text{coex}}(T_c), T_c)$ in a two-dimensional variable space. Fig. 6 shows that this problem can also be overcome by finite-size scaling methods, utilizing the scaling behavior appropriate for first-order transitions $\Delta\mu - \Delta\mu_{\text{coex}}(T) \propto L^{-d}$ in d dimensions [51,52] in order to locate $\Delta\mu_{\text{coex}}(T)$ [22]. (ii) Owing to the asymmetry, order parameter density and energy density become coupled, and this “field mixing” effect needs to be disentangled from the finite-size scaling analysis [23]. This problem is well known from computer simulation of fluids and we shall not describe it here, but rather draw attention to a recent review [75].

This field-mixing problem is particularly severe for the unmixing of polymers in solution beneath the Θ -temperature (which formally can be considered as a limiting case of a polymer mixture where $N_B = N$, $N_A = 1$ [4]) (Fig. 7). However, by a suitable transformation of variables, one can construct from ϕ and the energy density u , an appropriate field $\mathcal{M} = (\phi - su)/(1 - sr)$ (where s, r are parameters that can be found from a suitable analysis of the simulations, see Refs. [23,75]), which then scales like the magnetization of the Ising ferromagnets. Fig. 8 shows that the distributions of this variable at criticality nicely coincides with the critical order parameter distribution of the Ising model (actually this mapping can be used as a method for precisely locating the critical point [23,75]).

From analyses of this kind it has been possible to obtain the critical parameters of the model as a function of chain length, see e.g. Fig. 9. The simulation results reproduce nicely the behavior $\rho_c \propto N^{-x}$ with $x \approx 0.37$ found also experimentally [44,45]. However, the simulations also show that the chains at the critical point are

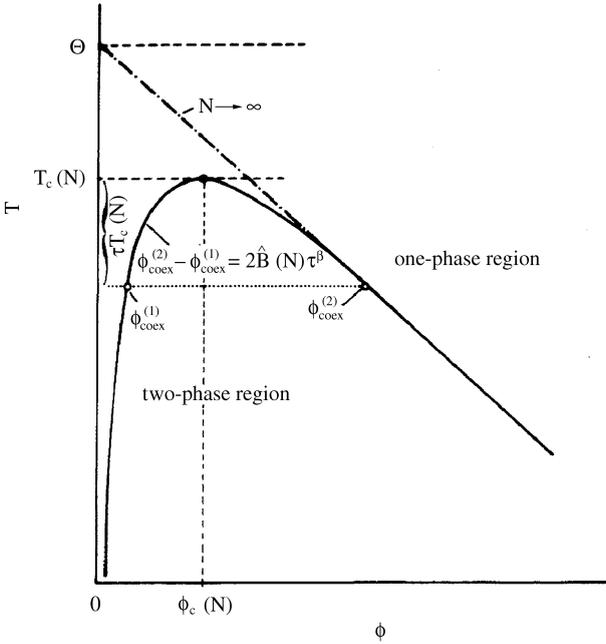


Fig. 7. Schematic phase diagram of a polymer solution using the temperature T and the volume fraction ϕ taken by the effective monomers of the polymer chains as variables. The coexistence curve separates a dilute solution of collapsed chains (at $\phi_{\text{coex}}^{(1)}$) from a semi-dilute solution of overlapping chains (at $\phi_{\text{coex}}^{(2)}$). These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N \rightarrow \infty$ this point merges with the Θ -point of a polymer solution at infinite dilution ($\phi \rightarrow 0$).

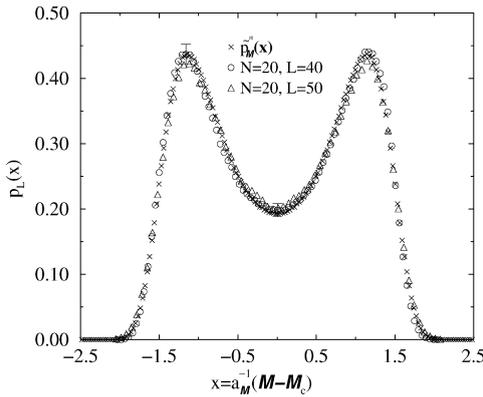


Fig. 8. Critical order-parameter distribution for a polymer solution with chain length $N = 20$, modeled by the bond-fluctuation model on the simple-cubic lattice, for linear dimensions $L = 40$ and 50 , open symbols, and compared to the order-parameter distribution of the Ising model (crosses). From Ref. [46].

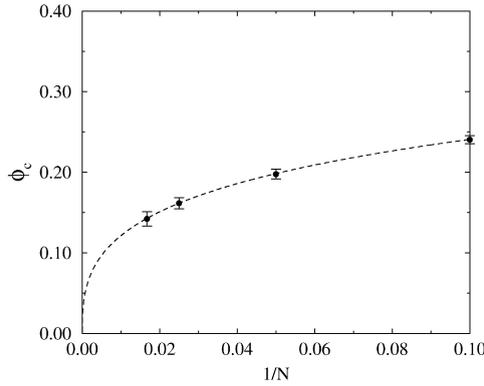


Fig. 9. Estimates of the critical volume fraction ϕ_c of monomers for a polymer solution (modeled by the bond-fluctuation model on the simple-cubic lattice, with an attractive energy between monomers at distances $r \leq \sqrt{6}$) as a function of the inverse chain length. The broken curve represents a fit of the form $\phi_c = (1.1126 + 1.3N^{0.369})^{-1}$. From Ref. [46].

not yet partially collapsed, but are rather ideal, and hence rule out the interpretation of this exponent value (which differs from the classical results $x = \frac{1}{2}$ [44]) as being due to the percolation of partially collapsed chains. Consequently, the physical interpretation of this exponent remains an open question [37,46].

4. Finite-size scaling above the upper critical dimension

Remembering that the correlation length for $d > d^* = 4$ has the mean-field critical behavior $\zeta_b = \zeta_0 t^{-1/2}$, the free-energy density can be written as [76]

$$f_L = L^{-d} \tilde{f} \left\{ t \left(\frac{L}{\zeta_0} \right)^2, uL^{4-d}, hL^{1+d/2} \right\}. \tag{10}$$

Note that here exactly the same powers of L appear as those for l in Eq. (4). For $d > d^*$ there is only the Gaussian fixed point to be considered. But although $u^* = 0$ here and the power of L in the term uL^{4-d} is negative so that $uL^{4-d} \rightarrow 0$ for $L \rightarrow \infty$, the argument uL^{4-d} must not be omitted: u is a “dangerous irrelevant variable” [77], so when we consider the zero-field susceptibility χ and the moment ratio Q [Eq. (9)], we find, using $u \propto \ell_0^{d-4}$,

$$\chi = \left(\frac{\partial^2 f_L}{\partial h^2} \right)_T = L^2 P_\chi \left\{ t \left(\frac{L}{\zeta_0} \right)^2, \left(\frac{L}{\ell_0} \right)^{4-d} \right\}, \tag{11}$$

$$Q = P_Q \left\{ t \left(\frac{L}{\zeta_0} \right)^2, \left(\frac{L}{\ell_0} \right)^{4-d} \right\}. \tag{12}$$

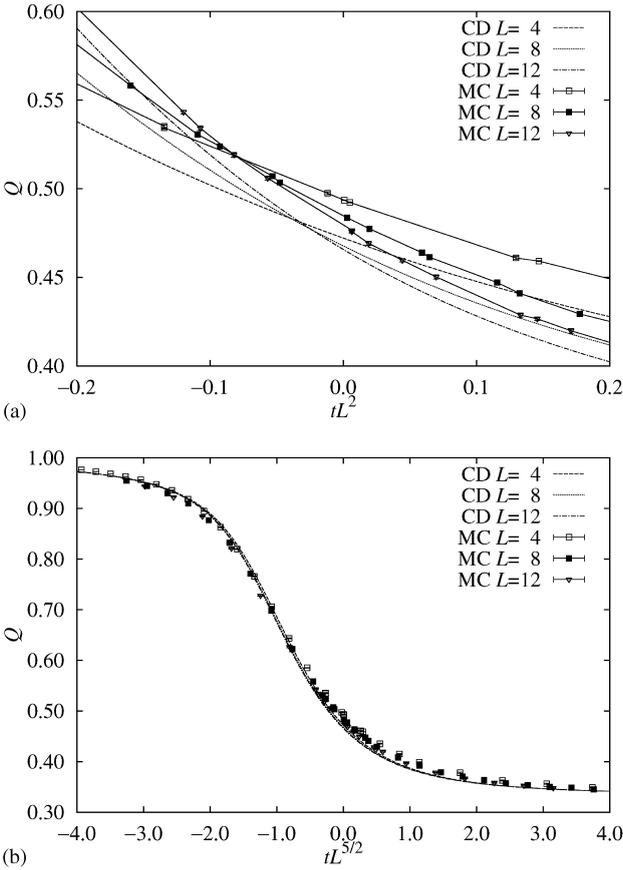


Fig. 10. (a) Plot of Q versus tL^2 for the $d = 5$ Ising model, demonstrating the occurrence of spurious intersections both in the Monte Carlo results [66] and the Chen–Dohm theory [65]. (b) Plot of Q versus the scaling variable $tL^{5/2}$; using parameters ξ_0, ℓ_0 extracted from various limits of the susceptibility [66], the Chen–Dohm theory can be evaluated without any adjustable parameter whatsoever. Note that for $L = 12$ it is already graphically indistinguishable from the “zero-mode” theory. From Ref. [66].

Thus all scaling functions have two arguments, $t(L/\xi_0)^2$ and $(L/\ell_0)^{4-d}$. However, it turns out [54] that a reduction to one-variable scaling occurs for $L \rightarrow \infty$, namely

$$\chi \rightarrow \lim_{L \rightarrow \infty} L^{d/2} \tilde{P}_\chi(tL^{d/2} \xi_0^{-2} \ell_0^{(4-d)/2}), \tag{13}$$

$$Q \rightarrow \lim_{L \rightarrow \infty} \tilde{P}_Q(tL^{d/2} \xi_0^{-2} \ell_0^{(4-d)/2}) = \tilde{P}_Q\{(L/\ell_T)^{d/2}\}, \tag{14}$$

where in the last step we have introduced the “thermodynamic length” $\ell_T \propto t^{-2/d}$ [55], mentioned above.

Eqs. (13) and (14) can be understood from various arguments [54–56]. Brézin and Zinn-Justin argue [56] that in the initial Hamiltonian or the corresponding statistical

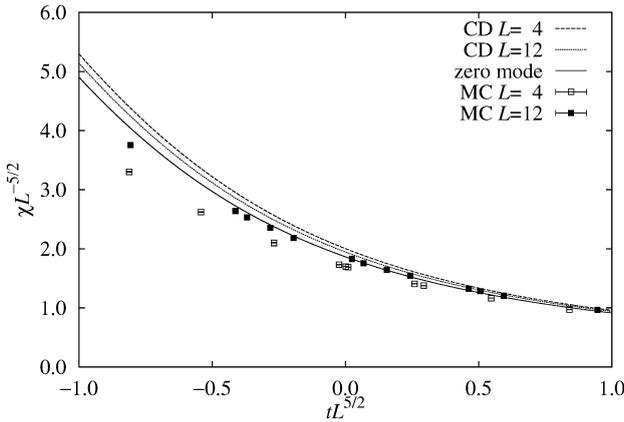


Fig. 11. Plot of the scaled susceptibility $\chi L^{-5/2}$ versus $tL^{5/2}$, including the “zero-mode” result of Ref. [56], as well as the predictions of Chen and Dohm [65] evaluated for the same values of L as the Monte Carlo results shown. From Ref. [66].

weight, one can treat the contribution from the average magnetization M separately,

$$\exp[-\mathcal{H}\{s_i\}/k_B T] = \exp\left\{-\frac{(M^2/M_b^2 - 1)^2}{8k_B T \chi_b/M_b^2} L^d + \dots\right\}, \quad (15)$$

where the dots stand for contributions with nonuniform magnetization, i.e., fluctuations. Here M_b, χ_b are the mean-field bulk magnetization and susceptibility, $M_b = \tilde{M}_b(-t)^{1/2}, \chi_b = \tilde{\chi}_b|t|^{-1}$. The zero-mode theory neglects these fluctuations altogether and there the distribution of the magnetization $P_L(M)$ scales as

$$P_L(M) \propto L^{d/2} \exp\{-[M^2/(\tilde{M}_b^2(-t)) - 1]^2(L/\ell_T)^d/8\}. \quad (16)$$

From this result it is straightforward to derive the above scaling functions \tilde{P}_χ and \tilde{P}_Q explicitly [56].

Since this theory was proposed [54–56] it has been a long-standing problem to verify the predictions by Monte Carlo simulation. In particular, when one plots the moment ratio Q versus temperature deviation from criticality, one should find a universal intersection point at T_c at a value

$$\tilde{P}_Q(0) = 8\pi^2/\Gamma^4(1/4) \simeq 0.456947. \quad (17)$$

However, the Monte Carlo results for small systems seem to intersect at a different value $Q \simeq 0.52$ (Fig. 10). Also, the temperature where this intersection occurs is a little off, but since one does not know T_c beforehand, one could simply imagine that the abscissa in Fig. 10 is mislabeled and T_c must be assigned differently.

Chen and Dohm [64,65] have recently criticized the whole approach sketched above and maintained that one must return to a finite-size scaling description in which both variables $t(L/\xi)^2$ and $(L/\ell_0)^{4-d}$ are kept separate, as in Eqs. (11) and (12). They also obtained the scaling functions P_Q and P_χ in a first-order loop expansion as a

function of these variables. Indeed their result is qualitatively similar to the Monte Carlo data (Fig. 10, broken curves), although in quantitative respects their treatment offers little improvement. This is seen, for instance, in a scaling plot of the susceptibility: The Chen–Dohm theory approaches the zero-mode results from above, while in the regime of interest the Monte Carlo data fall below the zero-mode result (Fig. 11). These discrepancies remain present for considerably larger L than shown here [66].

Thus we arrive at a rather disappointing state of affairs – although for the ϕ^4 theory in $d = 5$ dimensions all exponents are known, including those of the corrections to scaling, and in principle very complete analytical calculations are possible, the existing theories clearly are not so good. Perhaps the discrepancies result because the theory of Ref. [65] is only one-loop order, perhaps because other corrections are missing. While presumably the zero-mode one-parameter scaling is true asymptotically for $L \rightarrow \infty$, the corrections to this limit disappear only rather slowly, as Fig. 10(a) has demonstrated.

5. Concluding remarks

While the estimates of the critical exponents for the $d = 3$ Ising model are impressively accurate [78–80] and analytical [78] and Monte Carlo [79,80] estimates agree within very small error margins, the situation is different for the problems considered in the present paper: Analytical work is restricted to low-order ε -expansions or low-order loop-expansions and discrepancies between theory and simulation occur that are not fully understood. More work will be needed to clarify the situation. Note that the Ising to mean-field crossover considered here really is the simplest example of crossover phenomena, since the crossover exponent is rigorously known – crossover from one nontrivial fixed point to another is presumably more tricky to deal with. And for problems such as the critical point of polymer solutions, even the proper theoretical approach is controversial, and hence it is unclear whether the exponent $x \approx 0.37$ (Fig. 9) is a universal property at all [37–46].

Further problems appear when one is not concerned with bulk critical phenomena in ideal, homogeneous systems, but when one considers inhomogeneous systems, e.g., systems with random quenched disorder (e.g., Ising and Potts models exposed to random fields, spin glasses, etc. [81]). For instance, for a Potts spin glass finite-size scaling is not even understood on the mean-field level, at least for cases where first-order transitions without latent heat occur [82]. Also for systems with a regular inhomogeneity, e.g., Ising films with competing walls which allow for interface localization–delocalization transitions, one has fascinating critical behavior and crossover, of which the details still need to be unraveled [83]. Thus the Monte Carlo investigation of phase transitions – both in equilibrium and in driven systems [84] – will remain an active and challenging field.

Acknowledgements

We thank the HLRZ Jülich for access to a Cray-T3E where part of the computations have been performed. One of us (K.B.) thanks H.-P. Deutsch for a fruitful collaboration that led to the results shown in Fig. 5.

References

- [1] K.G. Wilson, *Phys. Rev. B* 4 (1971) 3174, 3184.
- [2] M.E. Fisher, *Rev. Mod. Phys.* 46 (1974) 597.
- [3] M.E. Fisher, *Rev. Mod. Phys.* 70 (1998) 653.
- [4] K. Binder, *Adv. Polym. Sci.* 112 (1994) 181.
- [5] V.L. Ginzburg, *Fiz. Tverd. Tela* 2 (1960) 2031.
- [6] K.K. Mon, K. Binder, *Phys. Rev. E* 48 (1993) 2498.
- [7] E. Luijten, H.W.J. Blöte, K. Binder, *Phys. Rev. E* 54 (1996) 4626.
- [8] E. Luijten, H.W.J. Blöte, K. Binder, *Phys. Rev. E* 56 (1997) 6540.
- [9] E. Luijten, H.W.J. Blöte, K. Binder, *Phys. Rev. Lett.* 79 (1997) 561.
- [10] E. Luijten, K. Binder, *Phys. Rev. E* 58 (1998) R4060.
- [11] E. Luijten, K. Binder, *Europhys. Lett.* 47 (1999) 311.
- [12] E. Luijten, *Phys. Rev. E* 59 (1999) 4997.
- [13] P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979.
- [14] P.G. de Gennes, *J. Phys. Lett. (Paris)* 38 (1977) L44.
- [15] J.-F. Joanny, *J. Phys. A* 11 (1978) L117.
- [16] K. Binder, *Phys. Rev. A* 29 (1984) 341.
- [17] A. Sariban, K. Binder, *J. Chem. Phys.* 86 (1987) 5859.
- [18] H.-P. Deutsch, K. Binder, *Macromolecules* 25 (1992) 6214.
- [19] H.-P. Deutsch, K. Binder, *J. Phys. II (France)* 3 (1993) 1049.
- [20] G. Maier, D. Schwahn, K. Mortensen, S. Janssen, *Europhys. Lett.* 22 (1993) 577.
- [21] D. Schwahn, G. Meier, K. Mortensen, S. Janssen, *J. Phys. II (France)* 4 (1994) 837.
- [22] M. Müller, K. Binder, *Macromolecules* 28 (1995) 1825.
- [23] M. Müller, N.B. Wilding, *Phys. Rev. E* 51 (1995) 2079.
- [24] M.A. Anisimov, A.A. Povodyrev, V.D. Kulikov, J.V. Sengers, *Phys. Rev. Lett.* 75 (1995) 3146.
- [25] M.A. Anisimov, A.A. Povodyrev, V.D. Kulikov, J.V. Sengers, *Phys. Rev. Lett.* 76 (1996) 4095.
- [26] Y.B. Melnichenko, M.A. Anisimov, A.A. Povodyrev, G.D. Wignall, J.V. Sengers, W.A. Van Hook, *Phys. Rev. Lett.* 79 (1997) 5266.
- [27] J. Jacob, A. Kumar, M.A. Anisimov, A.A. Povodyrev, J.V. Sengers, *Phys. Rev. E* 58 (1998) 2188.
- [28] P. Seglar, M.E. Fisher, *J. Phys. C* 13 (1980) 6613.
- [29] J.F. Nicholl, J.K. Bhattacharjee, *Phys. Rev. B* 23 (1981) 389.
- [30] C. Bagnuls, C. Bervillier, *J. Phys. (France) Lett.* 45 (1984) L-95.
- [31] C. Bagnuls, C. Bervillier, *Phys. Rev. B* 32 (1985) 7209.
- [32] M.E. Fisher, *Phys. Rev. Lett.* 57 (1986) 1911.
- [33] C. Bagnuls, C. Bervillier, *Phys. Rev. Lett.* 58 (1987) 435.
- [34] M.Y. Belyakov, S.B. Kiselev, *Physica A* 190 (1992) 75.
- [35] M.A. Anisimov, S.B. Kiselev, J.V. Sengers, S. Tang, *Physica A* 188 (1992) 487.
- [36] M.A. Anisimov, E. Luijten, V.A. Agayan, S.V. Sengers, K. Binder, *Phys. Lett. A* 264 (1999) 63.
- [37] I.C. Sanchez, *J. Appl. Phys.* 58 (1985) 2871.
- [38] M. Muthukumar, *J. Chem. Phys.* 85 (1986) 4722.
- [39] S. Stepanow, *J. Phys. (Paris)* 48 (1987) 2037.
- [40] A.L. Kholodenko, C. Quian, *Phys. Rev. B* 40 (1989) 2477.
- [41] I.C. Sanchez, *J. Phys. Chem.* 93 (1989) 6983.
- [42] B.J. Cherayil, *J. Chem. Phys.* 95 (1991) 2135.
- [43] D. Lhuillier, *J. Phys. II (Paris)* 2 (1992) 1411.
- [44] B. Widom, *Physica A* 194 (1993) 532.

- [45] S. Enders, B.A. Wolf, K. Binder, *J. Chem. Phys.* 103 (1995) 3809.
- [46] N.B. Wilding, M. Müller, K. Binder, *J. Chem. Phys.* 105 (1996) 802.
- [47] M.E. Fisher, in: M.S. Green (Ed.), *Critical Phenomena*, Academic, New York, 1971.
- [48] K. Binder, *Z. Phys. B* 43 (1981) 119.
- [49] M.N. Barber, in: C. Domb, J.L. Lebowitz (Eds.), *Phase Transitions and Critical Phenomena*, Vol. 8, Academic, New York, 1983.
- [50] V. Privman (Ed.), *Finite Size Scaling and Numerical Simulation of Statistical Systems*, World Scientific, Singapore, 1990.
- [51] K. Binder, in: H. Gausterer, C.B. Lang (Eds.), *Computational Methods in Field Theory*, Springer, Berlin, 1992.
- [52] K. Binder, *Rep. Prog. Phys.* 60 (1997) 487.
- [53] E. Brézin, *J. Phys. (France)* 43 (1982) 15.
- [54] K. Binder, M. Nauenberg, V. Privman, A.P. Young, *Phys. Rev. B* 31 (1985) 1498.
- [55] K. Binder, *Z. Phys. B* 61 (1985) 13.
- [56] E. Brézin, J. Zinn-Justin, *Nucl. Phys. B* 257 (1985) 867.
- [57] Ch. Rickwardt, P. Nielaba, K. Binder, *Ann. Phys. (Leipzig)* 3 (1994) 483.
- [58] K.K. Mon, *Europhys. Lett.* 34 (1996) 399.
- [59] G. Parisi, J.J. Ruiz-Lorenzo, *Phys. Rev. B* 54 (1996) R3698.
- [60] G. Parisi, J.J. Ruiz-Lorenzo, *Phys. Rev. B* 55 (1997) 6082(E).
- [61] E. Luijten, *Europhys. Lett.* 37 (1997) 489.
- [62] K.K. Mon, *Europhys. Lett.* 37 (1997) 493.
- [63] H.W.J. Blöte, E. Luijten, *Europhys. Lett.* 38 (1997) 565.
- [64] X.S. Chen, V. Dohm, *Physica A* 251 (1998) 439.
- [65] X.S. Chen, V. Dohm, *Int. J. Mod. Phys. C* 9 (1998) 1007.
- [66] E. Luijten, K. Binder, H.W.J. Blöte, *Eur. Phys. J. B* 9 (1999) 289.
- [67] E. Luijten, H.W.J. Blöte, *Int. J. Mod. Phys. C* 6 (1995) 359.
- [68] E. Riedel, F. Wegner, *Z. Physik* 225 (1969) 195.
- [69] A. Pelissetto, P. Rossi, E. Vicari, *Phys. Rev. E* 58 (1998) 7146.
- [70] A. Pelissetto, P. Rossi, E. Vicari, preprint cond-mat/9903410.
- [71] K. Binder, H.-P. Deutsch, *Europhys. Lett.* 18 (1992) 667.
- [72] K. Binder, in: K. Binder (Ed.), *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, Oxford University Press, New York, 1995 (Chapter 7).
- [73] A.M. Ferrenberg, R.H. Swendsen, *Phys. Rev. Lett.* 61 (1988) 2635.
- [74] A.M. Ferrenberg, R.H. Swendsen, *Phys. Rev. Lett.* 63 (1989) 1195.
- [75] N.B. Wilding, in: D. Stauffer (Ed.), *Annual Reviews of Computational Physics IV*, World Scientific, Singapore, 1996.
- [76] V. Privman, M.E. Fisher, *J. Stat. Phys.* 33 (1983) 385.
- [77] M.E. Fisher, in: F.J.W. Hahne (Ed.), *Critical Phenomena*, Springer, Berlin, 1983.
- [78] J.C. Le Guillou, J. Zinn-Justin, *Phys. Rev. B* 21 (1980) 3876.
- [79] A.M. Ferrenberg, D.P. Landau, *Phys. Rev. B* 44 (1991) 5081.
- [80] H.W.J. Blöte, E. Luijten, J.R. Heringa, *J. Phys. A* 28 (1995) 6289.
- [81] A.P. Young (Ed.), *Spin Glasses and Random Fields*, World Scientific, Singapore, 1998.
- [82] O. Dillmann, W. Janke, K. Binder, *J. Stat. Phys.* 92 (1998) 57.
- [83] K. Binder, R. Evans, D.P. Landau, A.M. Ferrenberg, *Phys. Rev. E* 53 (1996) 5023.
- [84] J.S. Wang, *J. Stat. Phys.* 82 (1996) 1409.