Critical Phenomena and "Crossover Scaling" in Model Systems for Soft Condensed Matter

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Critical points where phase separation between coexisting phases sets in are quite common in systems such as micellar solutions, polymer solutions, mixtures of homopolymers and copolymers, and related soft matter systems. While the asymptotic critical behavior associated with this phase separation should be the same as for simple Ising ferromagnets, the mesoscopic scale of the molecular constituents of these systems often causes a broad regime of parameters where simple mean-field type behavior is observed. Determination of the conditions for which a crossover between these two types of critical phenomena occurs constitutes a crucial test of our understanding of the effective interactions in these systems. In this report, two representative examples are described: (i) a ternary system of solvent plus polymer A plus polymer B, where solvent–polymer unmixing competes with polymer–polymer phase separation; (ii) a melt of random copolymers, where macroscopic phase separation and microphase separation compete. As a prelude, the Ising to mean-field crossover is studied by Monte Carlo simulation of an Ising magnet with a large but finite interaction range, providing accurate reference data for a crossover scaling description. It also is shown that new and more efficient simulation algorithms need to be (and have been) developed in order to be able to tackle such problems.

1 Introduction

"Soft condensed matter" is a synonym for a class of systems that are somewhere in between simple fluids and "hard" solids: Colloidal dispersions, gels, microemulsions, membranes, polymeric materials, etc. These systems have very broad industrial applications (production of lubricants, detergents, paints, perfumes, food industry, biotechnology and pharmaceutical industry, etc.), and much empirical knowledge has been accumulated about them; however, only rather recently these systems have moved into the mainstream of scientific basic research, and many aspects of their behavior are still not completely understood. In particular, the "soft" character of these materials can, to a large extent, be attributed to a delicate interplay between energy and entropy on the atomistic scale, giving rise to non-trivial mesoscopic structure, and the interactions between effective units on the mesoscopic scale are often entropic in origin. Understanding how to control the mesoscale structure and the effective interactions is a key aspect in order to systematically improve the properties of these materials and to develop novel applications.

One phenomenon that is decisively influenced by the nature and range of effective interactions on the mesoscale is the critical behavior associated with the onset of phase sepa-

ration into two distinct phases that coexist with each other. For instance, if the quality of a solvent used to dissolve flexible polymers is deteriorated by lowering its temperature T below the so-called "Theta temperature" Θ, phase separation may occur into a polymer-rich solution and a phase consisting essentially of pure solvent, with very few isolated and collapsed chains remaining in this solution. For very high molecular weight (or, equivalently, chain length N) of the polymer, the phase diagram is very asymmetric, the critical concentration ϕ_{crit} of the polymer being rather small, and for $N \to \infty$ one even has $\phi_{\mathrm{crit}} \to 0$, and the critical temperature $T_{\mathrm{c}}(N) \to \Theta$. This particular limit causes a special crossover of critical properties from one class of behavior to another one, which has been intensively studied by experiments, theory, and simulation, and is now rather well understood. However, when we consider the extension to the case where two kinds of polymers (A, B) are dissolved in the same solution, the situation becomes much more intricate: In the polymer-rich solution, one must expect that a further phase separation occurs, into a phase rich in polymer A and another phase rich in polymer B. Thus, in the same polymer solution, two rather different types of phase separation occur and compete with each other, and the subtle interplay of these phenomena is clearly of interest. This problem will be described in more detail in Section 3.

In problems of the type described above, a generic characteristic length scale occurs, such as the gyration radius of a polymer coil, which in a sense is analogous to the range of interactions in a system of small molecules, as far as the character of the critical phenomena is concerned. In order to understand the basic notions of how one can "move" from one type of critical behavior to another, it is therefore useful to study the model problem of a simple Ising lattice system, where the range of exchange interactions between the magnetic moments can be varied to a great extent (Section 2).

Instead of considering competition between two types of regular phase separation, where ultimately the spatial inhomogeneity develops on macroscopic scales, it is also possible to have a competition between macroscopic phase separation and mesophase ordering. While periodically modulated mesophase structures are rather well understood for systems such as liquid crystals, monodisperse block copolymers, etc., a more irregular form of mesophase or "microphase separation" is expected for random copolymers, where monomers of type A and monomers of type B alternate along the chain backbone in an irregular fashion. Such random heteropolymers can be viewed as a crude, qualitative model of biopolymers, which makes their study of particular interest as well. First steps to simulate the phase transitions of random copolymer melts will be described in Section 4.

For all these problems, critical points can be located by extensions of the well-known "finite-size scaling" technique, which requires very accurate computer simulation results over a broad range of lattice sizes for the models studied. "Brute-force"-type application of supercomputers would not lead very far—due to the mesoscopic length scales involved (medium interaction range or coil size, etc.) very large systems are needed, and near critical points the problem of strongly correlated system configurations ("critical slowing down") presents an additional complication. For the heteropolymers, the low temperatures of interest imply that glass-like relaxation is an additional problem, and very efficient sampling techniques are needed to cope with this problem. Thus, a key feature of the present project has been the development of new and more efficient algorithms, as well as their careful testing and demonstration of viability. Consequently, physical applications are still in their early stages.

2 A Prelude: The Ising to Mean-Field Crossover in the Medium-Range Ising Model

The Ising model is a lattice model for a uniaxial ferromagnet, where variables ("spins") $S_i = \pm 1$ designate whether the magnetic moment at a lattice site i is oriented up or down along the preferred axis. Ferromagnetic order is induced by an exchange-type interaction energy ($E = -J_{ij} S_i S_j$) with a positive "exchange constant" J_{ij} between spins at sites i and j.

In statistical mechanics, this is the prototype model to study phase transitions, and it is also the "yard stick" against which the efficiency of computer simulation programs, algorithms, analysis techniques, etc. is measured (for a detailed account, see the recent review Ref. **?**, which actually grew out of the earlier stages of this NIC (HLRZ) project). The "order parameter", namely the magnetization per spin (units are chosen such that the magnetic moment per spin is unity), $m = \sum_i \langle S_i \rangle / N$, where N is the number of lattice sites and $\langle \cdots \rangle$ denotes a thermal average, vanishes when the Curie temperature T_c is approached from below, $m \propto (1 - T/T_c)^\beta$, with $\beta = 1/8$ if the lattice is two-dimensional, while this "critical exponent" $\beta \approx 0.325$ if the lattice is three-dimensional. Accurate estimation of critical temperatures and exponents, for various choices of lattice structure, interaction range R [defined as $R^2 = \sum_{j(\neq i)} r^2 J_{ij} / \sum_{j(\neq i)} J_{ij}$, where $r \equiv |\vec{r}_i - \vec{r}_j|$ and $\vec{r}_i, \vec{r}_j$ are the lattice vectors pointing from the origin to the sites i, j], etc., has been a prominent goal of Monte Carlo simulations of this model for a long time.[1] Only in the limit $R \to \infty$ (or, equivalently, $z = \sum_{j(\neq i)} J_{ij} \to \infty$, assuming that all interaction constants J_{ij} equal a constant J for $r < R_m$ and $J_{ij} \equiv 0$ for $r > R_m$[1]) the problem becomes trivial: Then $T_c = zJ/k_B$ (k_B = Boltzmann's constant) and $\beta = 1/2$, i.e., mean-field theory (or, equivalently, the Weiss molecular-field theory) holds exactly.

We now wish to find T_c and the critical exponents (of the magnetization and of other quantities, such as the magnetic susceptibility, i.e., the response function to an external magnetic field H, $\chi = (\partial m / \partial H_T)_{H=0} \propto |1 - T/T_c|^{-\gamma}$, γ being another critical exponent) for the case where R is large but finite. This problem is difficult because of "crossover": For small enough distance $t \equiv T/T_c - 1$ from the critical point, the exponents will take the universal values of the "Ising universality class", but the region where they can be observed will decrease with increasing R. Outside this region, one finds "effective exponents", e.g., $\gamma_{\mathrm{eff}}(t) \equiv -d \ln \chi / d \ln |t|$. Since the power law $\chi = \hat{\chi} |t|^{-\gamma}$ implies a straight line with slope γ on a log–log plot of χ vs. $|t|$, the effective exponent is simply the "local slope" of the corresponding function on the log–log plot. Figure 1 gives an example for the susceptibility exponent γ_{eff}^- (the superscript minus stands for the sign of t) for $T < T_c$ and $d = 2$ dimensions (where one knows that $\gamma = 7/4$ exactly while the mean-field result is always $\gamma_{\mathrm{MF}} = 1$).[2] One can see that there is a nontrivial (and in this case even nonmonotonic) variation of the effective exponent with the scaling variable tR^2, and there is no analytic theory available that would yield this information! Also for a Monte Carlo simulation such an estimation of effective exponents is a tour de force; therefore, significant error bars as shown in the figure are still inevitable, and the full crossover (which spreads out over 5 decades in tR^2!) cannot be displayed for a single choice of R, but only by combining many values of R—that probe different parts of the crossover scaling function—in a single plot.

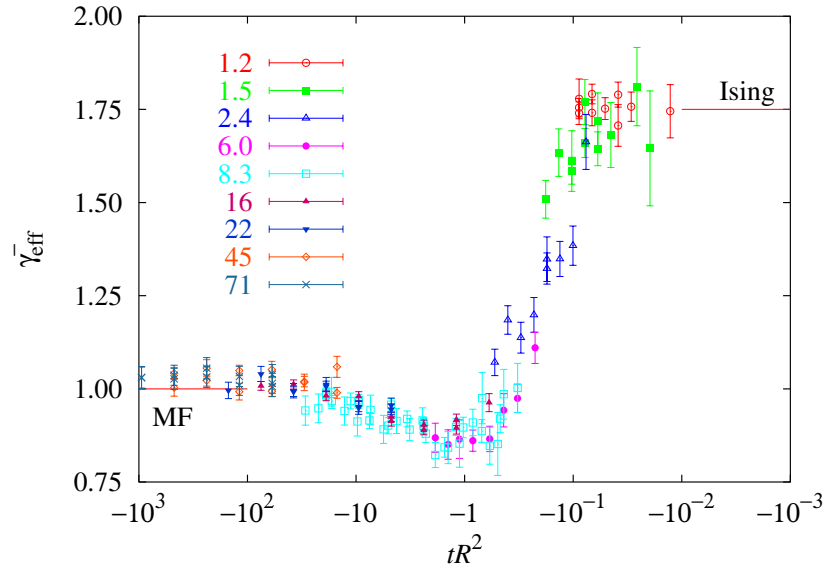Why is such a study so difficult? To answer this question, we recall that Monte Carlo

Figure 1. Effective susceptibility exponent $\bar{\gamma}_{\text{eff}}$ of the two-dimensional Ising square lattice for various choices of the interaction range R (denoted by different symbols, as given by the key in the figure), plotted vs. the crossover scaling variable tR^2 (note the logarithmic scale of the abscissa).

studies amount to simulating a finite $L \times L$ lattice (in $d = 2$) with periodic boundary conditions, and for finite lattices critical singularities are in fact rounded: Asymptotically, for $L \to \infty$, this rounding of singularities is described by finite-size scaling theory (see, e.g., Ref. **?** for a review), and actually this theory is needed for a precise location of T_{c} and estimation of critical exponents from the simulation.[1,3–5] However, when R is large, the asymptotic region of finite-size scaling is only reached when $L/R^2 \gg 1$ (in $d = 2$) or even $L/R^4 \gg 1$ (in $d = 3$), and thus it follows at once that huge lattice sizes L are needed. For the standard single-spin-flip Monte Carlo algorithm,[3,4] which suffers from "critical slowing down" (i.e., subsequently generated system configurations in the critical region are correlated over a "time" $\tau \propto L^z$ Monte Carlo steps (MCS) per lattice site, with a "dynamic exponent" $z \approx 2.1$[4,5]), this task would be hopeless even for the most powerful supercomputers available today! However, this difficulty could be overcome by an elegant extension of the single cluster algorithm[6] to systems with long-range interactions.[7] The cluster algorithms of Refs. 6, 7 reduce the critical slowing down dramatically ($\tau \propto \ln L$ in $d = 2$[4,5]). The important point of the algorithm of Luijten and Blöte[7] is that, despite the long-range interaction, the computational effort scales only linearly (and *not* quadratically) with the number of sites in the generated cluster.

Even with the availability of this novel algorithm, the need to study very large linear lattice dimensions with very high statistical accuracy, for many choices of the three parameters L, t and R, made the use of a very powerful computer such as the CRAY-T3E indispensable: Due to the relatively small correlation time τ, the task could be split over many processors collecting the data within a reasonable total time.

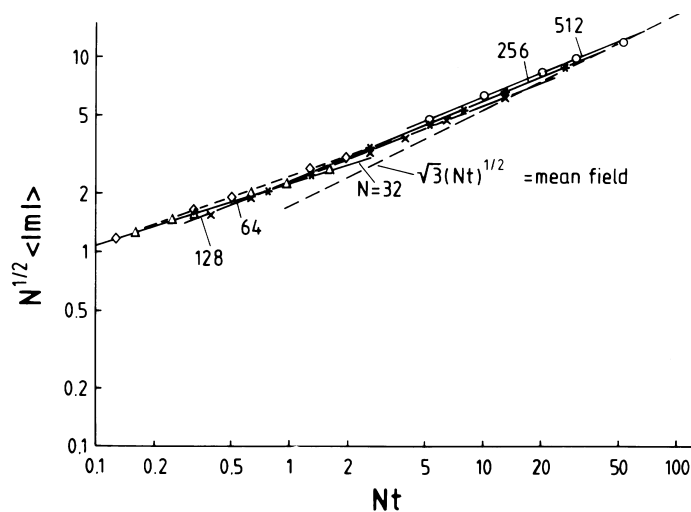Why is such an Ising to mean-field crossover relevant for soft matter systems? This

Figure 2. Plot of the scaled order parameter $\langle|m|\rangle N^{1/2}$ of symmetrical polymer mixtures plotted vs. the scaled temperature distance $N|t|$ from the critical point. Different symbols denote the different chain lengths investigated, as indicated in the figure. Broken straight line shows the mean-field result. All data refer to simulations of the bond fluctuation model of polymer chains on the simple cubic lattice, for a density $\phi = 1/2$ of occupied sites.

question is most easily answered for a binary polymer mixture (A, B), with symmetrical chain lengths $N_A = N_B = N$ (unlike the following section, we do not consider the additional effects of a solvent here). Given the fact that a flexible polymer chain in a melt has a random-walk-like structure, i.e., the gyration radius R_g scales like $R_g = bN^{1/2}$, b being the size of an effective segment, we conclude that each chain takes a volume $V = (4\pi/3)R_g^3 \propto b^3 N^{3/2}$. However, the density of segments of the chain inside this volume is rather small, $\rho = N/V \propto b^{-3}N^{-1/2}$; much smaller than the total segment density in the melt ($\rho \propto b^{-3}$). As a consequence, one concludes[8] that $N^{1/2}$ chains must share the same volume and that each chain interacts with $z = N^{1/2}$ "neighbors". Upon noting that the order parameter of a polymer mixture [$m = (n_A - n_B)/(n_A + n_B)$, n_A, n_B being the number of chains of type A, B, respectively] corresponds to the magnetization of the Ising problem, one can essentially provide a mapping between the medium-range Ising problem and symmetrical polymer mixtures.[9] In fact, these arguments are supported both by experiments[10] and by direct simulations[11] of symmetrical polymer mixtures—although some problems do remain.[10] So far, the existing direct simulations of critical properties of polymer mixtures (e.g., Fig. 2[11]) do give some evidence for crossover because of the curvature seen on the log–log plot, but the data do not allow to obtain effective exponents via logarithmic derivatives yet. Extending studies such as shown in Fig. 2 belongs to the goals that are still under consideration in the present project.

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3 Critical Phenomena in Ternary Systems: Polymer A + Polymer B + Solvent

As for Fig. 2, we use the bond fluctuation model on the three-dimensional simple cubic lattice, but now the density ρ of monomers is not fixed at the melt density, but rather a dynamical variable controlled by the appropriate chemical potential. In this model, effective monomers are modeled by elementary cubes on the lattice (all the 8 corners of the cube being blocked from further occupation), and are connected by effective bonds which may have lengths $b = 2$, $\sqrt{5}$, $\sqrt{6}$, 3 or $\sqrt{10}$ lattice spacings (on the simple cubic lattice).[12, 13] The idea behind this model is to perform, for a chemically realistic model of a chain, a coarse-graining along the backbone of the chain: about $n \approx 5$ chemical monomers correspond to one "effective bond" of the bond fluctuation model. The spread of effective bond lengths b is thought to come from the various conformational structures that a group of n monomers may take, due to the various choices of torsional angles. From such a mapping, one may conclude that a lattice spacing physically corresponds to about 2Å, and the physical degree of polymerization N_p corresponds to the chain length N via $N = N_p/n$.[14]

In order to deal with two types of chains (A, B), we choose chain lengths N_A, N_B, and interaction parameters $\varepsilon_{AA}(\vec{r})$, $\varepsilon_{BB}(\vec{r})$, and $\varepsilon_{AB}(\vec{r})$. For simplicity, all these interactions are taken of the square-well type, i.e., constant and nonzero up to the range R_m (we choose $R_m = \sqrt{6}$) and zero elsewhere. Only the most symmetric case is considered, namely $N_A = N_B = N$ and $\varepsilon_{AA} = \varepsilon_{BB} = -\varepsilon_{AB}$. Thus, the internal structure and length of the two types of chains are identical; they differ only by their label (A or B). The solvent is not accounted for explicitly (it is just represented by the vacant sites). If we would consider a dense melt (volume fraction of occupied sites $\phi = 1/2$ or larger[14]), only the combination $\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2$ of the interaction constants would matter, and the only phase transition to consider is a phase separation between an A-rich phase and a B-rich phase (this was the situation treated in the model of Fig. 2). However, for small ϕ (or small monomer density $\rho = \phi/8$, remembering that each monomer blocks 8 lattice sites) this phase separation between two polymer phases competes with the phase separation between polymer and solvent.

As an example, the phase diagram of such a system is shown for the case of $N = 20$ in Fig. 3. Even for relatively short chains (such as $N = 20$) the construction of this phase diagram becomes very difficult, since in the grand-canonical ensemble polymer chains have to be inserted in a very dense system (note that $\rho_{\text{coex}}^{(2)}(\tau) \geq 0.5$ for $T^* = T/\varepsilon_{AB} < 1.70$). Even the use of the well-know "configurational bias" algorithm[15] would not allow to carry out such simulations with the necessary accuracy. Therefore the recently invented "recoil growth" algorithm,[16] which is a generalization of the "configurational bias" algorithm suitable for very dense polymer systems, has been adapted to the present problem,[17] and the data shown in Fig. 3 are actually generated with this method. The idea behind all these techniques[15–17] is that a chain is not inserted into a dense system in one step—which would never be an accepted Monte Carlo move, since the excluded volume condition would always be violated—but one inserts only one end of the chain, and from there on it is "grown" segment by segment. This growth is not done blindly, but rather occurs in a biased way, so that the chain "searches" for empty regions of the system into which it can still grow. Of course, in the simulation one must correct for the applied bias, and great care is required in order to ensure that the algorithm respects the "detailed balance" condition—we refer the
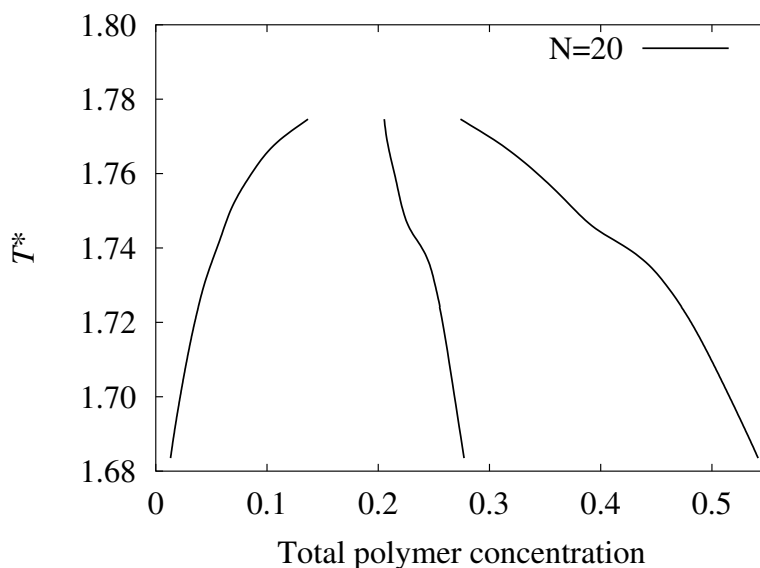
Figure 3. Phase diagram in the plane of variables $T^* = T/\varepsilon_{AB}$ and polymer concentration (or volume fraction of occupied sites) ϕ, for a binary polymer solution with $N_A = N_B = N = 20$. The curves were obtained from simulations of the bond fluctuation model for three lattice linear dimensions ($L = 40$, $L = 60$, and $L = 80$, respectively). The "gap" near $T^* = 1.78$ corresponds to the vicinity of the critical point, where the numerical data are strongly affected by finite-size rounding. The left part of the coexistence curve ($\rho_{coex}^{(1)}$) separates the solvent-rich phase from the two-phase region, the right part ($\rho_{coex}^{(2)}$) separates the two-phase region from the polymer-rich phase. The curve in the center of the two-phase region is the *rectilinear diameter*, $\rho_{rd}(T) = [\rho_{coex}^{(1)}(T) + \rho_{coex}^{(2)}(T)]/2$. Note that the phase separation between A-rich and B-rich polymer phases (curve not shown) hits the coexistence curve $\rho_{coex}^{(2)}(T)$ at a "critical end point" (CEP), causing a singularity both in $\rho_{coex}^{(2)}(T)$ and in $\rho_{rd}(T)$, just above $T^* = 1.74$.

interested reader to the original literature for these technical details.[15–17]

Figure 3 highlights the effect of the polymer A–polymer B phase separation (that occurs in the polymer-rich phase) on the polymer–solvent phase diagram: When the critical line of the A–B-separation hits the coexistence curve $\rho_{coex}^{(2)}(T)$ at the "critical end point" (CEP) the coexistence curve shows a rather pronounced wiggle. This anomaly in the phase diagram, however, does not lead to a particular crossover for the critical exponents. Only when the CEP would coincide with the polymer–solvent critical point, the two coincident critical phenomena would change their character into a "tricritical" phenomenon,[18] and interesting crossover scaling would occur. To realize this tricritical point, other choices than $\varepsilon_{AA} = \varepsilon_{BB} = -\varepsilon_{AB}$ have to be considered.

A special behavior is also predicted[19] for the good solvent case, $\varepsilon_{AA} = \varepsilon_{BB} = 0$, $\varepsilon_{AB} \neq 0$. Now, there is no polymer–solvent phase separation, and polymer A–polymer B phase separation can occur only if ϕ exceeds some critical value ϕ_p, of the same order as the overlap concentration ϕ^*. For ϕ slightly less than ϕ_p, instead of bulk phase separation one expects large aggregates of slightly overlapping A-chains, separated from large aggregates of slightly overlapping B-chains (Fig. 4). The phase transition at $\phi \to \phi_p$ then is a kind of continuum percolation of soft spheres, each sphere representing a whole poly-
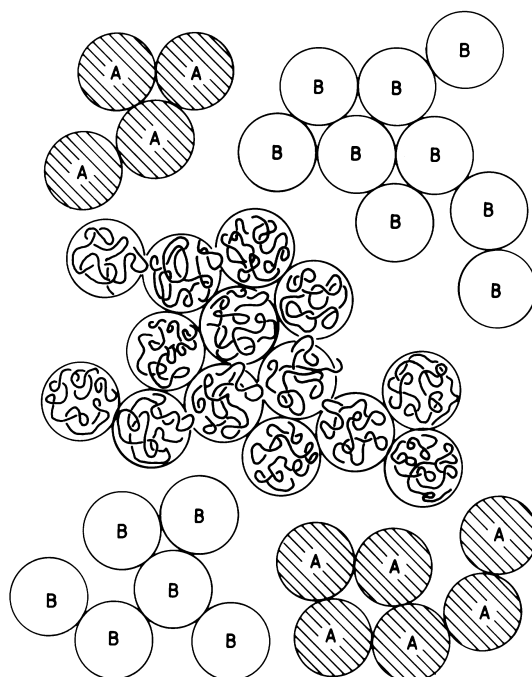
Figure 4. Qualitative picture of a system consisting of polymer A + polymer B + solvent, under good solvent conditions, but with large repulsive interaction ε_{AB}, for a volume fraction ϕ slightly less than a "percolation concentration" ϕ_{p} where macroscopic aggregates of chains of one type appear.

mer chain. Due to the huge lattice linear dimensions that would be required to study this transition, somewhat more powerful computers than presently available are clearly needed.

4 Phase Separation in Melts of Random Copolymers

A random copolymer is composed of two types of monomers A and B, which form a random sequence with average composition f (only $f = 1/2$ is studied here) and a parameter λ that describes the correlation of composition along the chain. For $\lambda = 0$, the sequence is completely uncorrelated, while for $\lambda = -1$ we have a regularly alternating copolymer ($ABABAB\dots$) and for $\lambda = +1$ we have homopolymers (the ratio of A and B-homopolymers is determined by f). Note that the random sequence, once created, is fixed, since this sequence is determined by the chemical synthesis of the chain.

Such random copolymers are often studied with a motivation to understand biopolymers; remember that a single strand of DNA is a (quasi-random) sequence of 4 types of amino acids (the detailed sequence then contains the genetic information). Here, however, we do not have biologically motivated questions, such as protein folding, in mind, but rather ask what is the phase behavior of a melt of short copolymer chains (of chain lengths $N = 5, 10, 20$), as a function of the blockiness parameter λ and the (repulsive) interaction ε_{AB} between monomers of different kind. In the block-copolymer case, one knows that
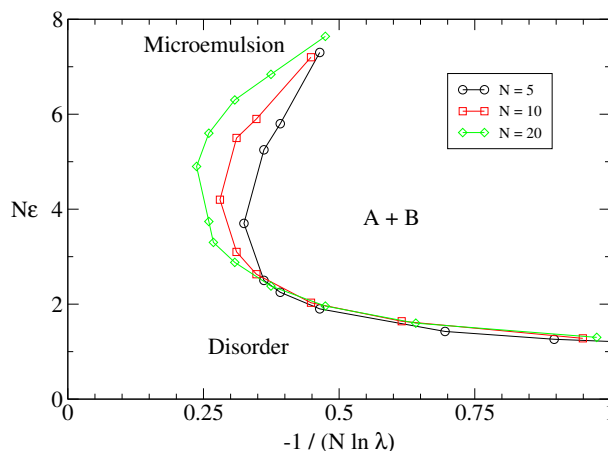
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Figure 5. Phase diagram of a random copolymer melt of composition $f = 1/2$ (50% A and 50% B). For small λ, only a disordered phase is found, as well as for small ε (i.e., $\varepsilon_{AB}/k_B T$) at all choices of λ. For large enough λ one encounters, with increasing ε, phase separation into chains with an excess of A or B-monomers, as shown by the curves. For still larger ε a phase transition occurs to a new type of phase whose nature is still under investigation (see text). Note that the x-axis parameter $1/(N \ln \lambda)$ is the ratio of the correlation length $1/\ln \lambda$ of the disorder along one polymer chain and the polymer length N. The polymer model is again the bond fluctuation model, as in the previous section.

a microphase separation occurs where an alternating arrangement of A-rich and B-rich domains is stable ("lamellar mesophase"), but it is clear that this structure will get more and more disrupted as the randomness increases. Note also that the randomness has the effect that individual (short) chains have a notable surplus in A or B—the composition $f = 1/2$ holds only on average. As a consequence, macroscopic phase separation into A-rich and B-rich phases is possible, and has actually been found in our simulations (Fig. 5, see Ref. **?** for details). However, in the region where both λ and $\varepsilon_{AB}/k_B T$ are large, an additional phase occurs which could be a kind of "microemulsion" (see the configuration snapshot, Fig. 6), or a lamellar mesophase somewhat distorted by randomness, or a two-phase region between a microemulsion and the lamellar phases. Note that microemulsions normally form in ternary systems A, B plus surfactant (which stabilizes A–B interfaces), and depending on the compositions of these constituents also regions of lamellar order or two-phase-coexistence regions occur in the phase diagram, in addition to a sponge-like phase. It could be that our melt of random copolymers is a kind of disordered analog of such a simple microemulsion.

In order to be able to obtain the results shown in Figs. 5 and 6, it was first of all necessary to develop a new, more efficient version of the "slithering snake" algorithm in order to be able to equilibrate the model system, and long runs at the CRAY-T3E were indispensable to establish the large-scale structures seen in Fig. 6. Very recently, a new generalization of the configurational-bias algorithm (where chains are removed in one part of the lattice and "regrown" in another part) was developed,[21] which hopefully will allow to clarify the open questions about the phase diagram and critical behavior of this system.
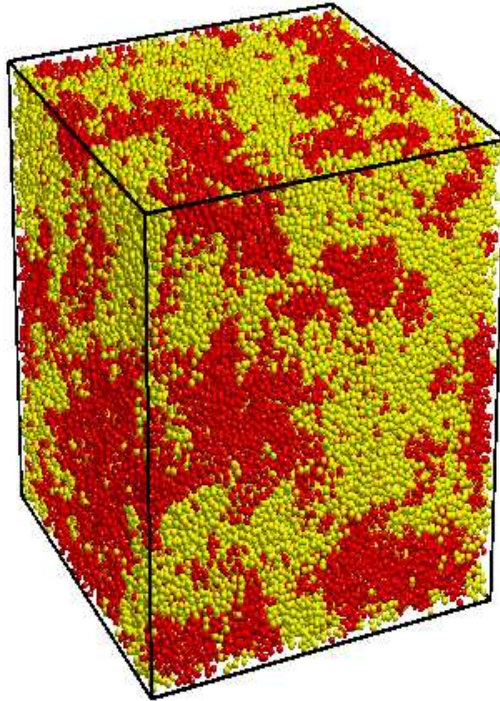
Figure 6. Snapshot of a microemulsion-like state of a random copolymer melt, for system parameters $N = 10$, $\lambda = 0.75$, $\varepsilon_{AB}/k_{\mathrm{B}}T = 0.8$, and a 120^3 lattice.

5 Concluding Remarks

In this paper, it has been shown that various types of phase separation in soft matter systems (polymer–solvent, polymer A–polymer B, random copolymers with excess of one kind of monomer versus excess of the other type of monomer) give rise to very interesting phase diagrams and interesting critical phenomena. However, the large scale provided by the large characteristic lengths, together with the common difficulties of polymer simulations (slow configurational relaxation of long chains, difficult chain insertions in dense systems, etc.), render the study of such phenomena by means of large-scale computer simulations particularly difficult. Developing new algorithms targeted to ease these problems, together with the availability of huge computer resources on very efficient parallel supercomputers, has proven crucial in order to achieve progress.

Acknowledgements

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