

Adsorptionlike Collapse of Diblock Copolymers

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A linear copolymer made of two reciprocally attracting N -monomer blocks collapses to a compact phase through a novel transition, whose exponents are determined with extensive Monte Carlo simulations in two and three dimensions. In the former case, an identification with the statistical geometry of suitable percolation paths allows one to predict that the number of contacts between the blocks grows like $N^{9/16}$. In the compact phase the blocks are mixed and, in two dimensions, also zipped, in such a way to form a spiral, double chain structure.

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Our knowledge of the conformational properties in solution of single, isolated polymers with inhomogeneous sequence, is still extremely limited [1]. A major challenge in statistical physics is the description of the possible conformational transitions of such systems, their universal scaling behaviors, and the nature of the different phases in finite dimensional situations. In the last few decades a similar program has been accomplished, to a substantial extent, for homopolymers [2], while for heteropolymers, so far, most insight is limited to approaches of mean field type [1,3].

Block copolymers [3,4] are interesting as members of the large family of heteropolymers, like proteins or polyampholytes, characterized by the above inhomogeneity. These copolymers are important as interface stabilizing agents and can display intriguing phenomena of microphase separation, a major topic in soft condensed matter research. The status of the art, as far as studies of hetero- and copolymer conformational transitions are concerned, suggests to us to investigate in detail, without resorting to mean field approximations, prototype problems involving relatively simple molecular architectures. Of particular interest will be those transitions which possibly reveal peculiar to systems with chain inhomogeneity, without counterpart in the homopolymer case.

In this Letter we address one of such problems, the collapse from the high temperature (T) swollen state to the low- T compact state of a copolymer whose two equally long blocks, A and B , attract each other with short-range forces. A physical realization could be that of oppositely charged A and B , immersed in a screening solvent. Another case, involving AA and BB attraction, rather than repulsion, is one in which the monomers of A are able to establish hydrogen bonds with those of B , which add to the van der Waals forces, thus creating extra AB attractive interactions. In the first instance we consider here the effect of AB attractive interactions acting alone. In both two dimensions (2D) and 3D, the collapsed phase has an approximate alternating, periodic structure, as far as the space distribution of A and B monomers is concerned. We determine numerically, and exactly in 2D, the exponents

of this collapse, showing that it has qualitative features in common with adsorption phenomena [5]. Nevertheless, the universality class coincides with neither that of adsorption [5], nor that of theta collapse of homopolymers [6].

We model the diblock copolymer by a self-avoiding walk (SAW) w of length $|w| = 2N$ steps (monomers) on square and cubic lattice. The walk w consists of N consecutive monomers of type A (w_A), followed by N monomers of type B (w_B). The Hamiltonian is $H(w) = -\sum_{i \in w_A, j \in w_B} \epsilon$, where ϵ is a positive energy, and the sum runs over pairs $\langle i, j \rangle$ of lattice sites visited by the copolymer (the AB junction excluded), which are nearest neighbors (nn). The scaling regime can be described by the ν exponent governing the asymptotic behavior of the canonical average radius of gyration,

$$\langle R_g \rangle = \frac{\sum_w \exp[-H(w)/T] R(w)}{\sum_w \exp[-H(w)/T]} \sim N^\nu, \quad (1)$$

where the sums extend to all $2N$ -step configurations w of the copolymer, with radius $R(w)$ relative to the center of mass. In the swollen, high- T regime one should expect $\nu = \nu_{\text{SAW}}$, with $\nu_{\text{SAW}} = 3/4$ [7] and 0.588 [8] in 2D and 3D, respectively. In a compact, low- T phase, $\nu = 1/d$. Another important quantity is the specific heat $C = \frac{1}{N} \partial \langle H \rangle / \partial T$, which at a conformational transition between high- T and low- T regimes is expected to obey the scaling:

$$C \sim N^{2\phi-1} F[(T - T_c)N^\phi] \quad (2)$$

for large N and for T close to the transition temperature T_c , F being a suitable scaling function. For $T = T_c$, ν should take a peculiar value, ν_c .

By extensive Monte Carlo sampling we computed $\langle R_g \rangle$, C , and $\langle H \rangle$ for N up to 800 in both 2D and 3D. The sampling was based on a multiple Markov chain method, which has been shown to be particularly suitable to deal with polymers at low T [9]. Several Markov chains, each one designed to sample at a different T , are generated in parallel [10]. The sampling at low T is then considerably enriched by swapping configurations between chains contiguous in T . Since each Markov chain is ergodic, so is the

composite one [9]. This procedure dramatically reduces the correlations within each chain. Both in 2D and 3D the simulations have been performed by using 25 parallel chains covering a range from $T = \infty$ to deeply inside the collapsed phase ($T = 0.5$).

Our data for C (Fig. 1) signal clearly the presence of a transition, with peaks in the T -dependence sharpening and growing with N , consistently with Eq. (2). The corresponding T_c and ϕ could be deduced from the N dependence of the height, $h(N)$, and position, $T_c(N)$, of these peaks. Indeed, in the scaling limit we expect $h(N) \sim N^{2\phi-1}$ and $T_c(N) - T_c(\infty) \sim N^{-\phi}$, for increasing N [$T_c(\infty) = T_c$]. Since a linear least squares fit of the log of h gives a very large χ^2 statistical error, we consider $h(N) = AN^{2\phi-1}(1 + B/N)$ where a scaling correction $1/N$ is included. The least squares fit in this case gives a lower χ^2 and we obtained (see Fig. 2) $\phi = 0.56 \pm 0.02$ in 2D and $\phi = 0.60 \pm 0.01$ in 3D. These values of ϕ allowed us to extrapolate $T_c(\infty)/\epsilon = 1.5 \pm 0.2$ and $T_c(\infty)/\epsilon = 2.9 \pm 0.2$, in 2D and 3D, respectively. From log-log plots of $\langle R_g \rangle$ vs N we also estimated ν at several temperatures. At $T = T_c$ we obtained $\nu_c = 0.748 \pm 0.008$ in 2D and $\nu_c = 0.583 \pm 0.007$ in 3D. In fact, ν stays approximately constant for $T \geq T_c$. Only for $T < T_c$, ν decreases, approaching values consistent with a compact phase ($\nu \sim 1/d$) for low T .

The ν_c estimates appear fully compatible with the exponents appropriate to a swollen SAW. In this respect the new collapse is analogous to a polymer adsorption on an attractive, impenetrable wall [5]. Indeed, at an adsorption transition one also finds $\nu_{\text{ads}} = \nu_{\text{SAW}}$. However, the ϕ 's determined here are definitely different from those describing the growth with N of the number of polymer-wall

contacts in adsorption ($\phi_{\text{ads}} = 1/2$ and $\phi_{\text{ads}} = 0.496 \pm 0.004$ in 2D [5] and 3D [11], respectively). Further analogies with adsorption are revealed by the large N behavior of the average energy (or $\langle N_{AB} \rangle$) per monomer. Figure 3 indicates crossings of the various $\langle H \rangle/N$ curves. The T range at which the crossings concentrate signals the transition and is consistent with the estimated T_c . Moreover $\langle H \rangle/N \rightarrow 0$ for $T > T_c$ and $\langle H \rangle/N \rightarrow \text{const}$ for $T < T_c$ (Fig. 3 inset). This behavior is different from what is found for the theta collapse, where the energy density curves do not cross each other, and $\langle H \rangle/N$ is asymptotically nonzero for all temperatures. The average number of polymer-wall contacts at opposite sides of an adsorption transition behaves similarly to $\langle N_{AB} \rangle$ here. In addition, as in adsorption, at $T = T_c$ we find that $-\langle H \rangle/N \sim N^{\phi-1}$. By fitting this behavior, we obtained alternative ϕ estimates ($\phi = 0.55 \pm 0.04$ and $\phi = 0.61 \pm 0.03$, in 2D and 3D, respectively), fully consistent with those based on C .

Apart from being a transition from a swollen to a compact state, the copolymer collapse has nothing in common with a homopolymer theta collapse, which is characterized by a peculiar $\nu_\theta \neq \nu_{\text{SAW}}$ [$\nu_\theta = 4/7$ (2D) and $1/2$ (3D) [2,6]]. Also the ϕ_θ is clearly different from the ϕ 's here ($\phi_\theta = 3/7$ in 2D [6] and $\phi_\theta = 1/2$ in 3D [2]). The copolymer collapse is indeed a novel transition, determined by the peculiar inhomogeneous backbone sequence and by its interactions.

In both 2D and 3D, typical configurations sampled at low T present a maximal alternance of A and B monomers, compatibly with the constraint of forming a diblock chain. In 2D (Fig. 4) A and B are also zipped on each other, and the resulting double chain structure forms spirals. The zipped, double chain represents a concrete realization of a polymer with orientation dependent interactions. For

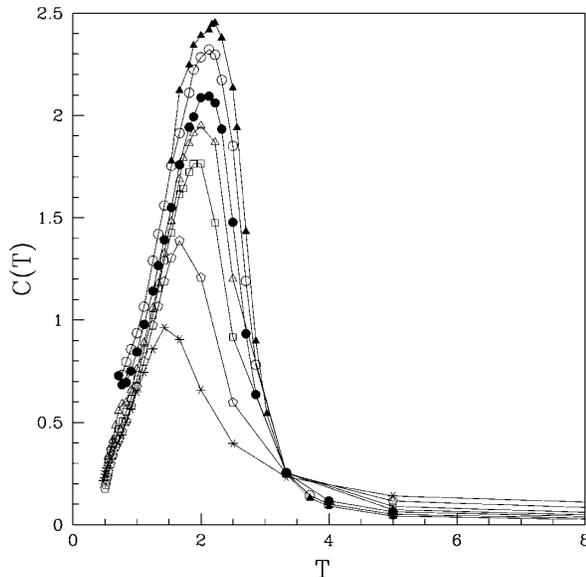


FIG. 1. Specific heat in 2D as a function of T for $N = 50$ (*), 100 (◇), 200 (□), 300 (Δ), 400 (●), 600 (○), and 800 (filled triangles).

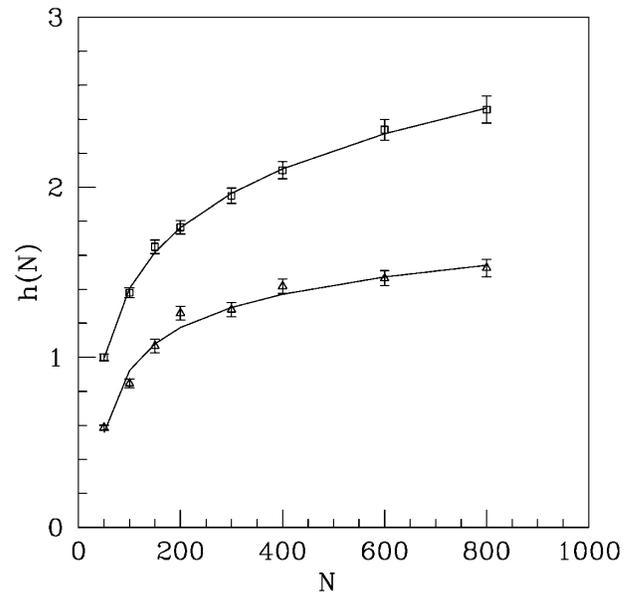


FIG. 2. Fits of $h(N)$ in 2D (triangles) and 3D (squares).

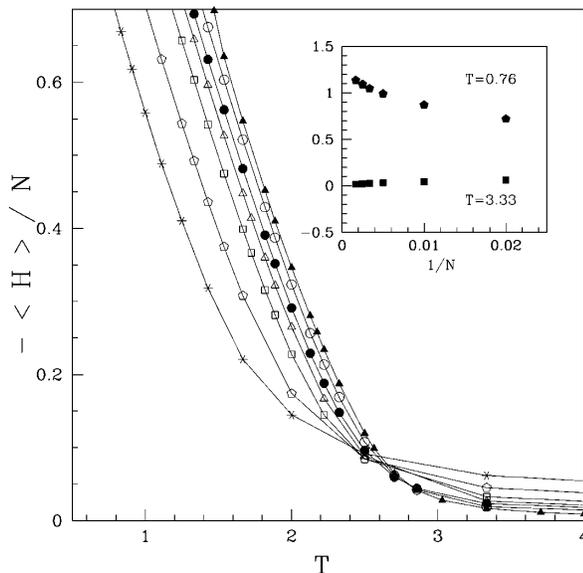


FIG. 3. $\langle H \rangle / N$ vs T in 3D for $N = 50$ (*), 100 (\diamond), 200 (\square), 300 (Δ), 400 (\bullet), 600 (\circ), and 800 (filled triangles). The inset shows the convergence of $\langle H \rangle / N$ to 0 for $T > T_c$ and to a constant for $T < T_c$.

models of such polymers, spiral compact phases have been recently observed in 2D [12]. In 3D the compact phase has more complex, unzipped configurations and substantial entropy. On the other hand, the A and B monomers are not segregated, and their alternance in space realizes an approximately periodic microphase structure.

By assuming $\nu_c = 3/4$, we can predict ϕ exactly in 2D, following a strategy of identification with geometric percolative objects, which in the past revealed extremely fruitful for homopolymer problems [6,13,14]. The idea is that the statistics of suitably chosen percolative contours could reproduce the critical behavior of interacting polymers in the conditions of interest. The homopolymer at the theta point in 2D is known to have the same statistics as the external perimeter (hull) of a critical percolation cluster [15], and this coincidence is at the basis of the full exact characterization of theta scaling [6,13,14]. On the square lattice, the incipient infinite cluster of the percolation problem for elementary squares (only squares with an edge in common are connected) is expected to have an externally accessible hull which, besides assuming the configurations of a self-avoiding ring, has the fractal dimension $D_{c1} = 1/\nu_{SAW} = 4/3$ of a swollen SAW [16]. This has been recently established on a rigorous basis in Ref. [17]. External accessibility means there should exist at least one path of connected vacant squares by which any neighborhood of the hull be connected to points at infinite distance. We identify our A and B blocks at the transition with the two halves in which the externally accessible hull of the cluster is divided by two diametrically opposite, distant points (Fig. 5). The identification of A and B with the copolymer blocks at collapse will make sense, provided the reciprocal nn contacts of these halves have a fractal

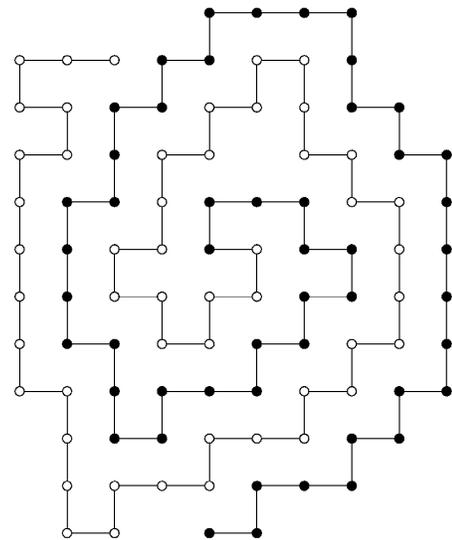


FIG. 4. Typical configuration at low T ($T = 0.5 < T_c$) in $d = 2$ for $N = 100$. Filled and empty circles denote, respectively, A and B monomers.

dimension matching the correct ϕ exponent, as shown below. This fractal dimension results from an effective AB attraction. The fact that A and B are identified with externally accessible hull portions excludes from the count the full hull self-contacts possibly produced by the presence of inaccessible reentrances (Fig. 5). Indeed, such reentrances cannot be included in A or B , and it is in virtue of their exclusion that the accessible hull has a fractal dimension $D_{c1} < D_{\text{hull}} = 7/4$. In Ref. [17] Coulomb gas results for the $T = 0$ loop gas are used to determine the dimensions of various fractal sets in the cluster of the hexagon percolation problem, for which it is easier to discuss geometry and effective interactions of these sets. In view of the peculiar connectivity of the hexagonal lattice, hull reentrances are always accessible by at least one path of vacant hexagons. Thus, external accessibility requires now existence of at least two distinct vacant paths joining the neighborhood of the hull to infinity [17]. The probability with respect to all percolative configurations of a given hull profile can be interpreted as the result of a decision process (between being occupied or vacant) for the hexagons progressively touched by the hull itself. It is thus easy to realize that AB nn contacts have the same effect as attractive interactions in a polymer problem. Indeed, while normally each step of the hull involves a decision for a new hexagon (and thus a probability factor $1/2$, the hexagon percolation threshold, in the total weight), at an AB contact the involved hexagon has already made his decision, and no factor is required. Thus, AB contacts increase the probability of the hull configuration. Besides determining D_{c1} exactly, the methods of Ref. [17] allow us to conclude that the set of AB contacts described above must have a fractal dimension $D_{c2} = 3/4$, which coincides with that of the “red” hexagons (squares in our case), i.e., of those hexagons whose removal would

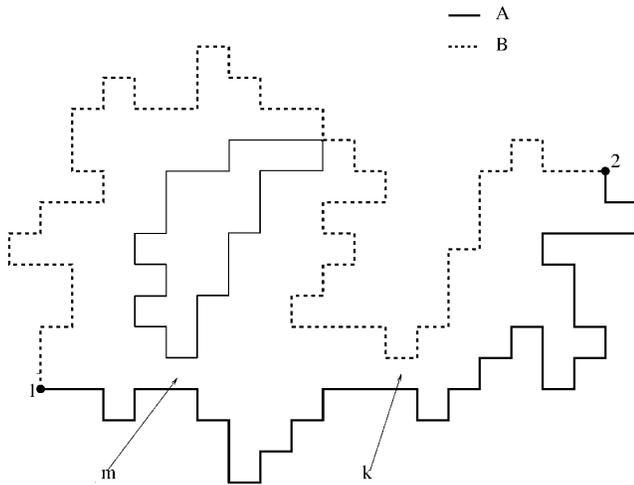


FIG. 5. Points 1 and 2 separate the accessible hull portions A and B. The light-continuous line represents an inaccessible reentrance of the hull. k : Red square corresponding to AB nn contacts. m : Contact of A with a hull reentrance. The union of A and B has fractal dimension $4/3$. By including in the hull definition also inaccessible reentrances, the dimension becomes $7/4$.

interrupt the cluster connection between the opposite distant points [18]. D_{c1} and D_{c2} are also expected to be universal with respect to different lattice structures [17] and thus should hold also for the square lattice. The proposed identification leads to $\phi = 9/16$: indeed, for N steps accessible half-perimeters, the average number of contacts should scale like $N^{D_{c2}/D_{c1}}$. $D_{c2}/D_{c1} = 9/16 = 0.56\dots$ is strikingly close to our numerical determination, supporting the correctness of our assumptions [19].

In summary, we gave a description of the collapse undergone by a copolymer with two reciprocally attracting blocks. We could determine with high precision, and exactly in 2D, the exponents of this new transition, which has analogies with homopolymer adsorption and theta collapse, but falls in a universality class different from both. The low- T dense phase is not segregated and, in 2D, turns out to be spiral, with zipped A and B. To our knowledge, the exact determination of ϕ in 2D is the first application of percolation results to a genuinely inhomogeneous polymer problem. We checked that the universality class of the transition remains the same if, more consistently with the physical picture of oppositely charged blocks, AA and BB repulsions are included in the Hamiltonian. A natural extension of our study consists of a systematic exploration of the phase diagram in regions where, e.g., the AA and BB interactions are also attractive and compete with the AB one. This corresponds to a copolymer in which the difference between AA (or BB) and AB interactions is

produced by hydrogen bonds. This competition generates a very rich phase diagram, with both segregated and unsegregated compact phases and interesting new transitions.

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 - [18] Since also inaccessible hull reentrances can produce red hexagons (or squares; see Fig. 5) we argue that these are, at most, a finite fraction of the total of red hexagons.
 - [19] Based on the identification of a ring polymer at the theta point with the full cluster hull, one can similarly establish that two halves of a homopolymer at the theta point have a number of contacts $\sim N^{\phi_\theta}$, where $\phi_\theta = 3/7$.