

## Zippering and collapse of diblock copolymers

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Using exact enumeration methods and Monte Carlo simulations, we study the phase diagram relative to the conformational transitions of a diblock copolymer in two dimensions. The polymer is made of two homogeneous strands of monomers of different species which are joined to each other at one end. We find that, depending on the values of the energy parameters in the model, there is either a first order collapse from a swollen phase to a compact phase of spiral type, or a continuous transition to an intermediate zipped phase followed by a first order collapse at lower temperatures. Critical exponents of the zipping transition are computed, and their exact values are conjectured on the basis of a mapping onto percolation geometry, thanks to recent results on path-crossing probabilities.

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### I. INTRODUCTION

Polymers in solution typically undergo a coil-globule transition from a high temperature ( $T$ ) swollen phase to a low  $T$  phase where the polymer assumes compact conformations. In the case of homopolymers, for which all the monomers are identical, this transition is by now well understood [1,2]. It is known as  $\Theta$  collapse, and has been extensively investigated in the past years using various methods such as mean field approximations [3], exact enumerations of interacting self-avoiding walks on lattices [4], Monte Carlo calculations [5], transfer matrix calculations [6], and field theoretical calculations [7]. In two dimensions the exponents of the  $\Theta$  collapse have been related to the fractal properties of the percolation cluster, and are believed to be known exactly [8].

The study of the conformational properties and phase transitions of macromolecules with inhomogeneous or random sequences of monomers is an interesting frontier in current polymer statistics [9]. These systems pose new theoretical and numerical challenges, compared to their more standard, homogeneous counterparts. Particularly interesting is the possibility that inhomogeneities along the chain could lead to transitions and universality classes of scaling behavior, which are not realized for homopolymers [10,11]. Moreover, the most complex versions of models of this class are also expected to be useful for descriptions of phenomena like protein folding [12], DNA denaturation [13] and RNA secondary structure formation [14]. Thus, an investigation of the universal properties of the simplest among these systems can offer an important gauge of the relevant model ingredients necessary in order to reproduce the basic conformational mechanisms in more sophisticated descriptions.

One of the most elementary conformational transitions (not realized in homopolymers) one can try to describe in relatively simple terms is what we call here a *zippering* transition. By zippering we mean a process in which two strands composing the polymer come in contact in such a way as to form a bound double structure, which remains swollen and does not assume compact configurations. In order to induce a transition from an unzipped state to a zipped state, the minimal inhomogeneity required implies a distinction between

the two strands: if the polymer is made of two blocks composed of monomers of different species (diblock copolymer), and there is a dominant attractive interaction acting between these different monomers, one would expect such a transition to be possible. Of course, the zippering occurring in biomolecules results in general from higher degrees of inhomogeneity than those of a simple diblock copolymer.

From a physical point of view one can think of diblock copolymers with oppositely charged monomers in the two blocks; in the model discussed here the interactions are of short range, and this would correspond to the case of screened Coulomb forces. Another possibility is that attractive interactions between monomers of the two blocks are established through a preferential formation of hydrogen bonds.

Attractive interactions between the two blocks, besides zippering, also tend to produce collapse into a globular compact state, unless some contrasting effect limits the capability of a given monomer to attract monomers of the other block. In a recent paper [15], a model of a diblock copolymer with some of the features discussed above was studied in both two and three dimensions. In this model the two blocks were represented by two halves of a self avoiding walk (SAW) on a hypercubic lattice with attractive interactions between nearest neighbor sites (monomers) visited by the two blocks. So, apart from the steric constraints, there was no interaction mechanism possibly opposing the tendency of a given monomer to be surrounded by as many monomers of the other block as possible. The transition of the diblock copolymer from a high  $T$  swollen phase to a low  $T$  compact phase, had analogies with both polymer adsorption on a wall, and  $\Theta$  collapse, but turned out to belong to a universality class different from both [15]. An intriguing question remained open concerning the very nature of this transition: indeed, the possibility that a zipped, swollen phase could exist for temperatures just below the transition could not be excluded. If this were the case, the adsorptionlike collapse found in Ref. [15] would correspond to a zippering, and a further transition to the compact globular phase should be expected to take place at a lower  $T$ .

In the present paper we extend the model of Ref. [15] in

two dimensions to include an interaction among alternating triplets of different monomers. Depending on its sign, this additional interaction can enhance the tendency of the system either to form compact structures or to take zipped conformations. We draw an accurate phase diagram for the system, in which a zipping transition line is well identified and characterized. Our analysis seems to indicate that the adsorptionlike collapse of Ref. [15] belongs to the zipping universality class as well. Specifically, we find that, depending on the triplet interaction energy, one has either a continuous swollen-zipped transition followed by a first order collapse into compact conformations, or a direct first order swollen-compact transition. Although we mainly focus on the zipping, it turns out that the first order collapse has interesting features as well, since it shows remarkable analogies with that found in homopolymers with orientation dependent interactions, which attracted some attention recently [16].

We will argue that the exact exponents for the zipping transition in two dimensions can be found through an identification between the stochastic geometry of the blocks and that of a percolation cluster backbone [17]. A preliminary form of this argument was presented in Ref. [15]. The relevant dimensions of the percolation cluster can be identified thanks to some recent results for path-crossing probabilities [18]. Our numerical estimates for the zipping exponents are in very good agreement with the conjectured values. To our knowledge, the mapping onto percolative stochastic geometry we discuss here is the first example of exact results derived for a genuinely inhomogeneous polymer problem in two dimensions. The connection with percolation geometry also shows that the physics of zipping is closely connected with that of the  $\Theta$ -point transition, for which a representation in terms of percolation geometry was established long ago [8].

Besides the prototypical importance that zipping acquires here also on the basis of our exact results, one should realize that many of the conformational transitions occurring in biomolecules show aspects which, to some extent, are reminiscent of zipping. This is certainly the case for DNA, in which, upon lowering the temperature below the denaturation one, the conjugate bases form pairs, so that the molecule arranges itself in a double stranded helical structure [13]. Double stranded, zipped structures also appear in the folding of  $\beta$ -hairpin peptides [19]. In the philosophy mentioned at the beginning of this section, one can hope that studies like the one presented here can teach something about how to model these more complicated systems properly.

This paper is organized as follows: In Sec. II we present the model and the main features of the phase diagram. In Secs. III and IV we discuss the numerical results obtained by exact enumerations and Monte Carlo simulations, respectively. In Sec. V, using recent results for crossing probabilities of percolation paths in two dimensions, we conjecture the exact values of the exponents of the zipping transition. Section VI concludes the paper, with a summary of the results and a general discussion.

## II. MODEL AND PHASE DIAGRAM

We model the two-dimensional (2D) diblock copolymer by an interacting SAW on the square lattice. In the configu-

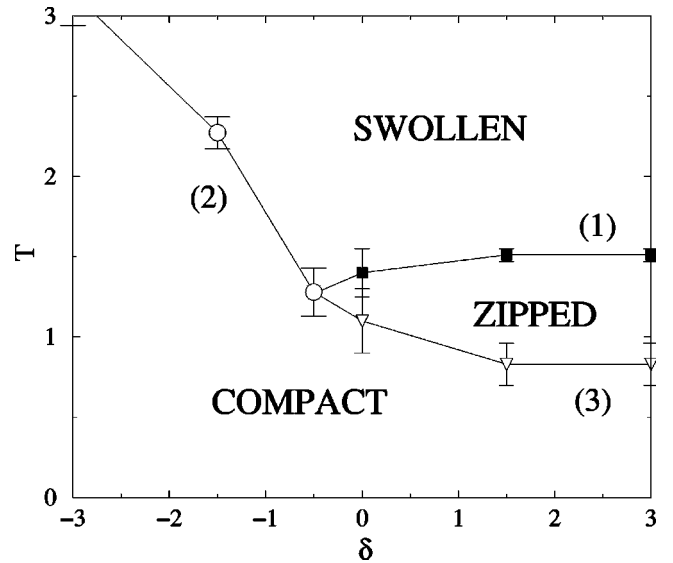


FIG. 1. Phase diagram in the  $\delta$ - $T$  plane. Line (1) is the continuous zipping transition line separating the high temperature swollen phase from the zipped phase. Lines (2) and (3) are of first order type.

ration  $w$  the SAW has  $|w|=N$  vertices (monomers), with  $N$  even, and consists of  $N/2$  consecutive monomers of type  $A$  ( $w_A$ ) followed by  $N/2$  monomers of type  $B$  ( $w_B$ ). A pair of vertices ( $A, B$ ) form a contact if they are a unit lattice distance apart. The interaction between the two blocks  $w_A$  and  $w_B$  is taken into account by assigning an energy  $\varepsilon$  ( $\varepsilon < 0$ ) to each  $A$ - $B$  contact. In addition we introduce a second energy parameter  $\delta$ , associated with contacts formed by a sequence  $A$ - $B$ - $A$  or  $B$ - $A$ - $B$  of neighboring monomers on a line. We refer to these sequences as to *triple* contacts. The Hamiltonian of the system in configuration  $w$  is given by

$$H(w) = N_{AB}(w)\varepsilon + N_3(w)\delta \quad (1)$$

where  $N_{AB}(w)$  and  $N_3(w)$  are the number of  $A$ - $B$  and triple contacts, respectively.

For  $\delta=0$  we recover the model introduced in Ref. [15]; in the present work we consider both signs of  $\delta$ : a positive value of  $\delta$  must prevent the polymer from collapse into compact conformations and favor an intermediate zipped phase, while for a negative  $\delta$  the tendency to collapse is enhanced.

Letting  $c_N(N_{AB}, N_3)$  be the number of copolymer configurations with  $N$  edges,  $N_{AB}$  contacts of type  $A$ - $B$  and  $N_3$  triple contacts, we define the finite- $N$  free energy per monomer

$$F_N(\beta, \delta) = N^{-1} \log Z_N(\beta, \delta), \quad (2)$$

where

$$Z_N(\beta, \delta) = \sum_{N_{AB}, N_3} c_N(N_{AB}, N_3) e^{-\beta(N_{AB}\varepsilon + N_3\delta)} \quad (3)$$

is the partition function and  $\beta=1/T$  [20]. Throughout the rest of the paper we set  $\varepsilon=-1$ . By varying  $T$  and  $\delta$  we have explored the phase diagram of the model (see Fig. 1) on the

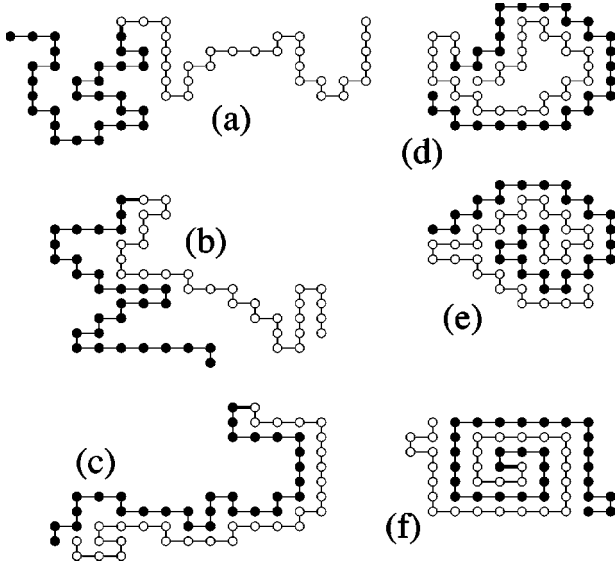


FIG. 2. Typical Monte Carlo equilibrium configurations for an  $N=60$  diblock copolymer: (a) and (b) swollen chains; (c) and (d) zipped chains; (e) and (f) compact chains with  $\delta=1.5$  (e) and  $\delta=-1.5$  (f).

basis of exact enumeration and Monte Carlo simulation results.

As expected, we find a zipped phase in the positive  $\delta$  region, while for negative  $\delta$  there is a direct transition from the swollen to the compact phase. The numerical results show that the line (1) separating the swollen and zipped phases is continuous, while line (2) and (3) are first order. Unfortunately, the numerical methods at our disposal are not sufficiently accurate to determine the precise location of the intersection point between the lines, nor the character of the phase transition in this point, which could be of special type. The location of this intersection point seems to fall at slightly negative values of  $\delta$ .

It is rather instructive to show some typical equilibrium conformations of the copolymer for various values of  $T$  and  $\delta$ , in the three different phases (see Fig. 2). The configurations are snapshots obtained by Monte Carlo simulations: (a) and (b) are conformations in the swollen high  $T$  phase, with (b) close to the zipping transition. (c) and (d) are instead zipped configurations. Note that the pairing of the two strands in (d) follows an opposite orientation with respect to (c). Finally, (e) and (f) are both compact, but of different nature: the latter occurs at  $\delta < 0$  where triple contacts are energetically favored. Therefore, the polymer assumes a spiral-like shape with straight segments turning around the center in order to maximize the number of triple contacts. In case (e),  $\delta$  is positive: the configuration is still of spiral type, but in this case the arms of the spiral are oriented preferentially at  $45^\circ$  with respect to the axes of the square lattice, in order to avoid the formation of triple contacts.

Now one can easily understand why lines (1) and (3) for large  $\delta$  run practically horizontal in the phase diagram of Fig. 1. In the whole zipped phase triple contacts, which cost an energy  $\delta$ , seldom occur [see Fig. 2(c)]; therefore, the zipping temperature should depend rather weakly on  $\delta$ . In addition

the polymer can form compact conformations such as that shown in Fig. 2(e), which also avoids this type of contacts. Hence the zipped-compact transition temperature also should not depend on  $\delta$ , when  $\delta$  is positive and large enough. Both lines (1) and (3) in Fig. 1 should be asymptotically horizontal for large  $\delta$ .

### III. EXACT ENUMERATIONS

Exact enumerations of interacting SAW's are standard techniques for the study of the homopolymer  $\Theta$ -collapse transition [4]. In the present calculation we generated all possible configurations for copolymers up to  $N=30$  monomers, a length which is already sufficient to characterize rather well the critical behavior of the zipping transition.

The occurrence of phase transitions in interacting polymer systems can be detected by studying the large  $N$  behavior of the canonical average squared radius of gyration,

$$R_g^2 = \frac{\sum_w \exp[-\beta H(w)] R^2(w)}{\sum_w \exp[-\beta H(w)]}, \quad (4)$$

where the sums extend to all  $N$ -step configurations  $w$  of the copolymer, with radius  $R(w)$  relative to the center of mass. Indeed, in the proximity of a conformational transition temperature  $T_c$  we expect that

$$R_g(N, T) \sim N^{\nu_c} \mathcal{R}[(T - T_c) N^\phi], \quad (5)$$

where  $\nu_c$  and  $\phi$  are the exponents characterizing the transition, and  $\mathcal{R}$  is a scaling function that is assumed to approach a positive constant if its argument approaches zero.

Another important quantity is the specific heat  $C(N, T) = (1/N) \partial \langle H \rangle / \partial T$ , which for  $N$  large and  $T$  close to  $T_c$  is expected to obey the scaling

$$C(N, T) \sim N^{2\phi-1} \mathcal{C}[(T - T_c) N^\phi], \quad (6)$$

where  $\mathcal{C}$  is again a suitable scaling function.

Figures 3 and 4 show  $dR_g^2/d\beta$  and  $C$  as functions of  $\beta$  for  $\delta=0$  (a) and  $\delta=-1.5$  (b). As the radius of gyration drops at a transition, its derivative  $dR_g^2/d\beta$  shows a peak in correspondence to the transition point.

For  $\delta=-1.5$  both quantities have a single isolated peak, indicating that there is a single transition from a swollen phase to a compact phase. For  $\delta=0$ , instead, the derivative of the radius of gyration has two distinct peaks [Fig. 3(a)], while the picture emerging from the specific heat [Fig. 3(b)] is somewhat more confusing, since the  $N$  dependence of the peak positions and heights is rather irregular, and their extrapolation to  $N \rightarrow \infty$  becomes impossible. Therefore we focus on the peaks of  $dR_g^2/d\beta$ . Extrapolating their positions at  $\delta=0$ , we find the following two estimates of critical temperatures  $T_c=1.40(15)$  and  $T_{2c}=1.1(20)$ , which overlap somewhat within error bars. For this reason it is difficult to discern between two separate, but close, transitions, and a single transition. For positive values of  $\delta$  the two sets of

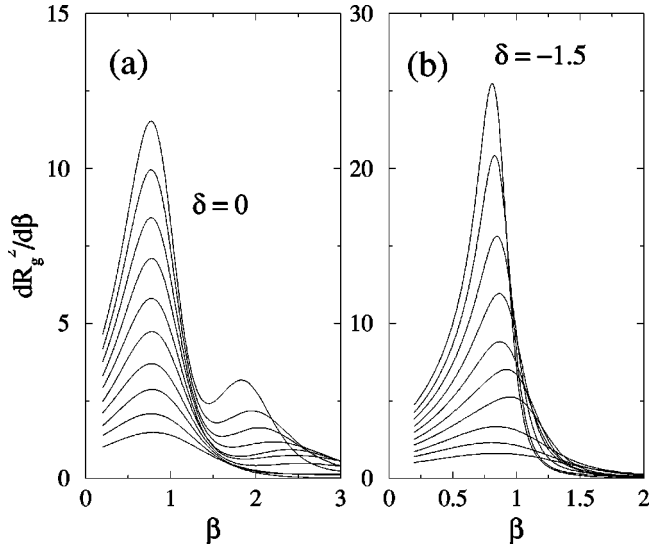


FIG. 3. Derivatives of the squared radius of gyration with respect to the inverse temperature for  $\delta=0$  (a) and  $\delta=-1.5$  (b) and for  $N=12, 14, \dots, 30$ . The double peak structure for  $\delta=0$  suggests a sequence of two transitions: swollen zipped and zipped collapsed.

peaks are clearly separated and extrapolations yield two distinct transition temperatures. Here we focus on the characterization of the high  $T$  transition from the swollen phase to the zipped phase. The scaling form of Eq. (5) implies that  $T_c(N)$ , the temperature where  $dR_g^2/d\beta$  has a maximum, scales for large  $N$  as  $T_c(N) - T_c \sim x_0 N^{-\phi}$ , with  $x_0$  a suitable constant. We calculated both the radius of gyration and specific heat at  $T_c(N)$ ; from Eq. (5) and (6), one has

$$R_g[N, T=T_c(N)] \sim N^{\nu_c} \mathcal{R}(x_0) \quad (7)$$

and

$$C[N, T=T_c(N)] \sim N^{2\phi-1} \mathcal{C}(x_0). \quad (8)$$

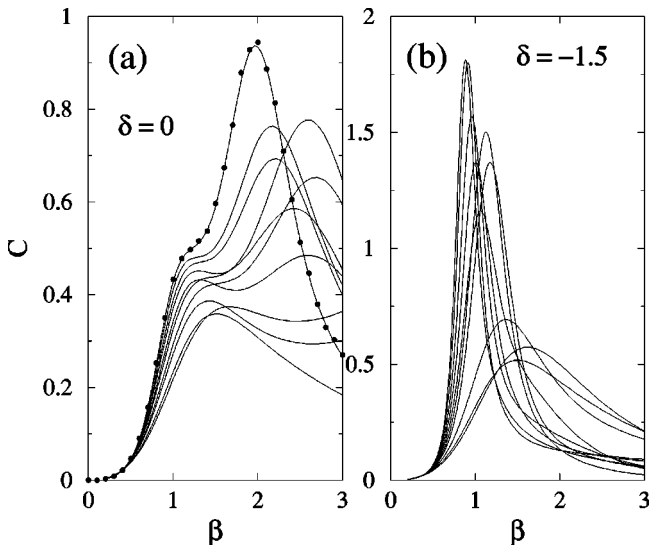


FIG. 4. Solid lines: specific heat from exact enumerations for  $N=12, 14, \dots, 30$  for  $\delta=0$  (a) and  $\delta=-1.5$  (b). Circles: Monte Carlo results for  $N=30$ .

TABLE I. Extrapolated values of  $\nu_c$  and  $\phi$  from the exact enumeration data relative to diblock copolymers up to length  $N=30$ . The exponent  $\nu'_c$  is obtained from the scaling behavior of the radius of one of the blocks.

$\delta$	$\nu_c$	$\phi$	$\nu'_c$
0.0	0.72(1)	0.60(5)	0.74(1)
0.5	0.73(1)	0.58(3)	0.750(5)
1.0	0.73(1)	0.57(3)	0.750(5)
3.0	0.74(1)	0.56(3)	0.750(5)

For the calculation of the critical exponents we first formed the finite  $N$  approximants, for instance

$$\nu_c(N) \equiv \frac{\ln(R_g(N+2)/R_g(N))}{\ln((N+2)/N)} \quad (9)$$

[here  $R_g(N)$  is a shorthand notation for  $R_g(N, T_c(N))$ ], and then extrapolated  $\nu_c(N)$  to  $N \rightarrow \infty$ . The same procedure was followed for  $\phi$ .

The extrapolated values are reported in Table I, together with the exponent  $\nu'_c$ , which is that associated with the radius of the half-chain, or single block, which at the critical temperature should scale as

$$R'_g(N, T=T_c) \sim \left(\frac{N}{2}\right)^{\nu'_c}. \quad (10)$$

The values of the exponents  $\phi$  and  $\nu_c$  vary slightly along line (1) of Fig. 1 when  $\delta$  is increased, while  $\nu'_c$  is rather stable. We believe that the variation of  $\nu_c$  and  $\phi$  is a spurious effect, due to the vicinity of an additional transition in the neighborhood of  $\delta=0$ . It is much more plausible that the exponents are constant along line (1); the most reliable estimates for  $\nu_c$  and  $\phi$  should be those for large  $\delta$ , where lines (1) and (3) of Fig. 1 are clearly separated. The values of  $\nu_c$  and  $\nu'_c$  are consistent (the former only at large  $\delta$ ) with the scaling behavior of a SAW, namely,  $R_g \sim N^{3/4}$ . The value of  $\phi$  is instead consistent with  $\phi=9/16=0.5625$ , which was conjectured in Ref. [15] for the transition at  $\delta=0$ , and will be derived in detail in Sec. V.

As for transition lines (2) and (3), the exact enumeration analysis is not at all conclusive since the scaling behavior of the peaks with the chain length  $N$  is rather irregular, and precise extrapolations turn out to be impossible. This issue will be clarified with the use of Monte Carlo simulations, which allow one to achieve much larger copolymer lengths.

#### IV. MONTE CARLO SIMULATIONS

In order to sharpen and extend the results of exact enumerations, in particular concerning the properties of zipped and collapsed phases, we performed Monte Carlo simulations for various  $N$  and  $\delta$  and for a wide range of temperatures. Since the simulations considered involve sampling at points which include low values of  $T$ , a standard Markov chain Monte Carlo approach is unlikely to be successful, it being difficult to construct a Markov chain sufficiently ‘‘mo-

bile'' at low  $T$  where the interaction energies become relevant. Instead we use a multiple Markov chain technique by which one samples simultaneously at various values of  $T$ , including  $T=\infty$  where convergence is rapid. Most recently this method was used successfully to investigate collapse transitions in homopolymers [21], heteropolymers [11], and adsorption in  $\Theta$  solvent [22].

First one defines a Metropolis based Markov chain for a temperature  $T$ . This procedure makes use of a hybrid algorithm based on pivot [23] as well as on local moves [24]. Pivot moves are of global type, and operate well in the swollen regime, whereas local moves turn out to be essential in speeding up Monte Carlo convergence at low temperatures [21]. In our calculations, each Monte Carlo step consists of  $O(1)$  pivot moves and  $O(N)$  local moves. In this model, however, we have to deal also with a zipped phase where the most probable configurations are characterized by having the two blocks  $A$  and  $B$  paired together, but still not compact [see Figs. 1(b)–1(d)]. To increase the mobility of the Markov chain in this region we added a set of bilocal moves, such as end-end reptation and kink-end (and end-kink) moves [25]. These moves are particularly effective for dense chains, and even more effective for zipped chains, where typically one side of each half-chain is free and can hold a new kink. The resulting algorithm is slightly heavier, but enables the reciprocal sliding of the half-chains and a more efficient exploration of the configuration space. One may then run in parallel a number  $m$  (typically 20–40) of these Markov chains at different temperatures. The sampling at low  $T$  is then considerably enriched by swapping configurations between Markov chains contiguous in  $T$ . The whole process is itself a (composite) Markov chain, obeys detailed balance, and is ergodic [21].

Monte Carlo simulations were performed for three distinct values of  $\delta$ :  $\delta=1.5$ ,  $\delta=-1.5$ , and  $\delta=0$ . As a test of the performance of the multiple Markov chain algorithm we compared the Monte Carlo results with those obtained from the exact enumeration for chains up to  $N=30$  monomers. In all cases analyzed the agreement turned out to be extremely good [see, for instance, Fig. 4(a)].

### A. $\delta=1.5$

In the case  $\delta=1.5$  we considered diblocks of lengths up to  $N=400$ , and sampled at a set of  $m=40$  temperatures typically in the range  $T \in [0.5, \infty]$ . In Fig. 5 we plot the specific heat as a function of  $\beta$  for different  $N$  values. Clearly each curve displays a double peak structure indicating two subsequent transitions. We can rule out the possibility that such double peaked structure is a finite size effect by noting that the peaks sharpen and grow with  $N$ . Let us focus first on the set of peaks at higher temperatures, i.e., on the transition from a swollen phase to a zipped phase. The corresponding  $T_c$  and  $\phi$  could be deduced from the  $N$  dependence of the height,  $h(N)$ , and position,  $T_c(N)$ , of the peak maxima. Indeed, from the scaling behavior [Eq. (6)], we expect, as  $N$  increases,

$$h(N) \sim N^{2\phi-1} \quad \text{and} \quad T_c(N) - T_c \sim N^{-\phi}. \quad (11)$$

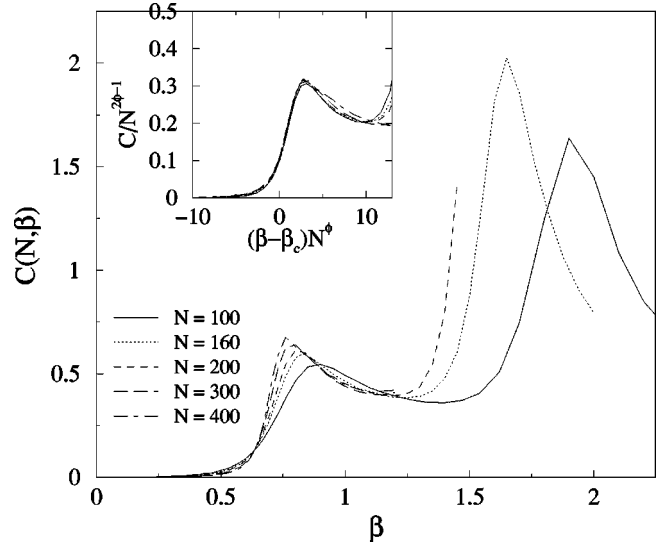


FIG. 5.  $\delta=1.5$ : Plot of the specific heat vs  $\beta$ , for chains of various lengths. For  $N=200, 300$ , and  $400$  the low temperature peak was not reached because of the considerable autocorrelation time caused by low mobility of long collapsed chains. Inset: collapsed specific heat  $C/N^{2\phi-1}$  vs  $(\beta - \beta_c)N^\phi$ , with  $\phi=9/16=0.5625$  and  $\beta_c=0.66$ .

Since a linear least squares fit of  $\log h$  vs  $\log N$  gives a very large  $\chi^2$  statistical error, we fit the data with a function  $A N^{2\phi-1}(1+B/N)$  where a scaling correction  $1/N$  is included. The least squares fit in this case gives  $\phi=0.57 \pm 0.02$ , in agreement with the value  $\phi=9/16=0.5625$  conjectured in Ref. [15], and also with the estimates obtained by exact enumeration. This procedure yields results consistent with a direct extrapolation of effective finite  $N$  exponents. We have also tried to fit the data by using the more general scaling correction  $1/N^\Delta$ , and found that the best fits are those with  $0.5 \leq \Delta \leq 1$  yielding a stable value for  $\phi$ . The estimated value of  $\phi$  allowed us to extrapolate  $T_c$  by plotting  $T_c(N)$  vs  $1/N^\phi$ . This gives  $T_c = 1.51(4)$  [ $\beta_c = 0.66(2)$ ].

The inset of Fig. 5 shows a plot of  $C/N^{2\phi-1}$  vs  $(\beta - \beta_c)N^\phi$ , where we have used  $\phi=9/16$  and the estimate  $\beta_c=0.66$ . As expected, the high temperature peaks collapse onto a single curve quite nicely. Conversely, for a set of peaks at lower temperatures, the same rescaling procedure turns out to be inappropriate. In particular, by using the rescaled variables adequate for the former set of peaks, the positions of the latter set tend to move away from zero while their heights still increase with  $N$ : this is only consistent with a scenario in which a new transition, at a lower  $T=T_{2c}$ , exists. This transition should be also characterized by a crossover exponent greater than  $\phi=9/16$ . We have tried to verify this by looking for two new values  $\beta_{2c}$  and  $\phi_2$  that allow a reasonable fit of the scaling behavior of the second set of peaks. In this way we obtained the rough estimates  $\beta_{2c} \approx 1.0$  and  $\phi_2 \approx 0.7 > 9/16$ . Unfortunately the sampling at low temperatures is not good enough to make such estimates sufficiently sharp. Moreover, in the zipped phase the effective size of an  $N$  monomers system drops to  $N/2$ , making the finite size corrections to scaling more pronounced.

The different nature of the two transitions can be better

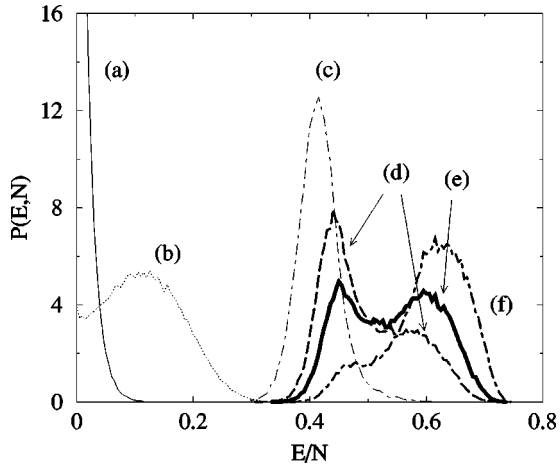


FIG. 6. Plot of  $P(E, N)$  with  $N=200$  and for various temperatures: (a)  $\beta=0.3$ , (b)  $\beta=0.75$ , (c)  $\beta=1.4$ , (d)  $\beta=1.58$ , (e)  $\beta=1.66$ , and (f)  $\beta=1.8$ .

detected from the behavior of  $P(E, N)$ , the probability distribution of the energy  $E$ , for a chain of length  $N$ . Figure 6 shows a plot of  $P(E, N)$  as a function of  $E/N$  for  $N=200$ . At sufficiently high temperatures this quantity has a maximum in  $E=0$ , and decreases rapidly with  $E/N$  [Fig. 6(a)]. As the temperature is lowered the maximum shifts continuously to larger values of  $E/N$  [Figs. 6(b) and 6(c)]. For lower temperatures  $P$  develops a double peak structure [Figs. 6(a)–6(f)]. In the case of Fig. 6(e) the peaks have equal height, while at temperatures below or above it one of the two peaks dominates over the other. This behavior, which persists and becomes more pronounced upon increasing  $N$ , is an indication of phase coexistence; hence the transition at lower  $T$  is of first order type. In terms of specific heat this would mean  $C(T) \sim N$  as  $T=T_{2c}$ , i.e.  $\phi_2=1$ . By extrapolating  $\beta_{2c}(N)$  vs  $1/N$ , we find  $\beta_{2c}=1.2 \pm 0.2$ .

Another way to characterize the different phases of the model consists in looking at the scaling behavior of metric quantities such as  $R_g^2$  defined in Eq. (4), and the mean squared end-to-end distance  $R_e^2(N) = \langle (r_N - r_0)^2 \rangle$ , where  $r_0$  and  $r_N$  are the two end monomers of the copolymer. For large  $N$  we expect

$$R_e^2(N) \sim \rho_e N^{2\nu}, \quad (12)$$

$$R_g^2(N) \sim \rho_g N^{2\nu}, \quad (13)$$

and an interesting quantity to be computed is the ratio  $\rho_e/\rho_g$ , which is expected to be universal [26]. For noninteracting SAW's on a square lattice, exact enumerations and Monte Carlo simulations give  $\rho_e/\rho_g \sim 7.13$  (see Ref. [27], and References in Ref. [26]). Figure 7 shows the ratio  $R_e^2/R_g^2$  as a function of  $\beta$  for several  $N$ . Note that in the range of  $0 < \beta < 0.66$  the curves tend to assume a constant value  $\rho_e/\rho_g = 7.15(5)$ , in agreement with the value expected for non interacting SAW's. In the proximity of the zipping transition the curves start to bend downward, and, at  $\beta_c \approx 0.66$ , they cross each other almost in a unique point (see the inset). At the crossing point our estimate of the universal amplitude

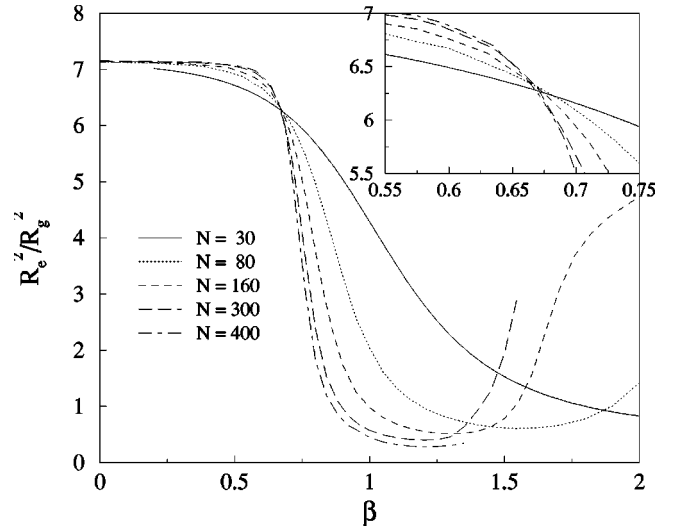


FIG. 7.  $R_e^2/R_g^2$  vs  $\beta$  for  $\delta=1.5$  and for various chain lengths. The  $N=30$  curve is calculated from exact enumerations, while the others are obtained from Monte Carlo simulations. Inset: blowup of the crossing region.

is  $\rho_e/\rho_g = 6.35 \pm 0.20$ , which is definitively different from the amplitude ratio of the SAW universality class. The zipping transition that cannot be distinguished from the swollen phase in terms of the  $\nu$  exponent, is, however, characterized by a different value of the universal ratio  $\rho_e/\rho_g$  [28].

If the temperature is further lowered the  $R_e^2/R_g^2$  curves reach a minimum value that decreases as  $N$  increases. This is an indication that the end-to-end distance in the zipped phase no longer scales like the radius of gyration, as assumed in Eqs. (12) and (13). For sufficiently low temperatures,  $\rho_e/\rho_g$  starts to grow back, indicating that the compact phase is characterized by an end-to-end distance and mean radius of gyration that scale in the same way with  $N$ . As the typical low  $T$  configurations are of spiral type [see Figs. 2(e) and 2(f)] with end points at opposite sides of the spiral, it is natural to expect that  $R_e \sim R_g \sim N^{1/2}$ .

### B. $\delta=-1.5$

For  $\delta < 0$  triple contacts are favored and we expect (as the exact enumerations already indicate) a single transition from swollen directly to compact phase. To investigate the nature of such transition we have performed runs with  $\delta=-1.5$ , for several values of  $N$ , sampling at  $m \approx 30$  different temperatures in the interval  $T \in [1.3, \infty]$ . As in the case  $\delta=1.5$ , we have examined the probability of finding the copolymer in a configuration with energy  $E$ , as a function of the temperature. A plot of  $P$  for  $N=200$  and three different temperatures is shown in Fig. 8. Close to the transition temperature  $P$  has two maxima [see Fig. 8(b)], one at  $E=0$ , and the other at  $E/N \approx 0.7$ . This is a clear indication of a first order transition. The evidence of such behavior is stronger than in the case  $\delta=1.5$ , since here the coexistence is between two phases (the swollen and compact phases) with a rather large difference in energy; therefore, the double peak structure of  $P$  can already be seen for small  $N$ .

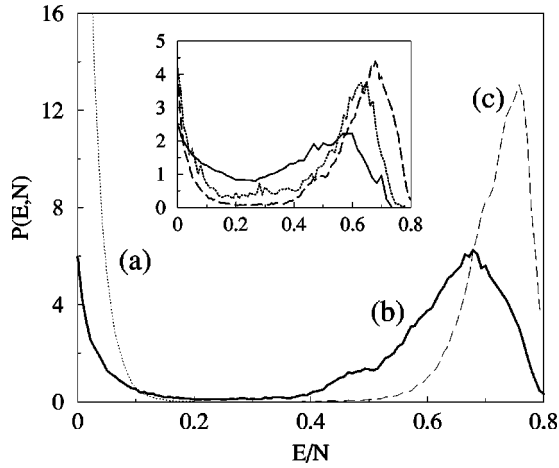


FIG. 8.  $P(E,N)$  vs  $E/N$  for  $\delta = -1.5$  and  $N = 200$  for three different temperatures (a)  $\beta = 0$ , (b)  $\beta = 0.545$ , and (c)  $\beta = 0.6$ . Inset: Plots of  $P(E,N)$  vs  $E/N$  near phase coexistence for  $N = 60$ ,  $\beta = 0.66$  (solid line),  $N = 100$ ,  $\beta = 0.56$  (dotted line), and  $N = 140$ ,  $\beta = 0.545$  (dashed line).

From the analysis of the specific heat peaks we find that they become sharper as  $N$  increases and their height appears to grow with a power of  $N$  slightly exceeding one (the physical upper limit). At the same time, in a plot of energy vs temperature we see curves that seem to approach step functions. These data support the idea that the corresponding transition should be of first order.

### C. $\delta = 0$

The more delicate region to be explored in the phase diagram is the neighborhood of  $\delta = 0$ , where three transition lines meet each other. We have chosen in particular the case  $\delta = 0$ , since it was considered in Ref. [15].

In Fig. 9 we plot the specific heat as a function of  $\beta$  for several  $N$  values. For the smallest chains ( $N = 60$  and  $80$ ), one observes a peak in the specific heat with a shoulder at

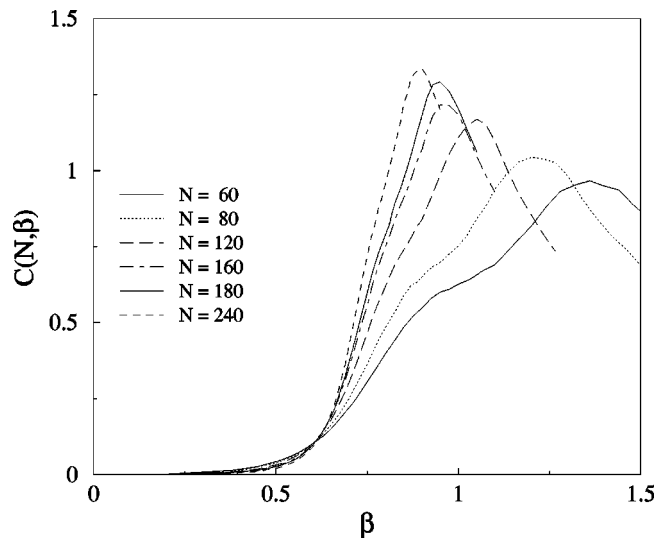


FIG. 9.  $\delta = 0$ : Plot of the specific heat vs  $\beta$ , for various chain lengths.

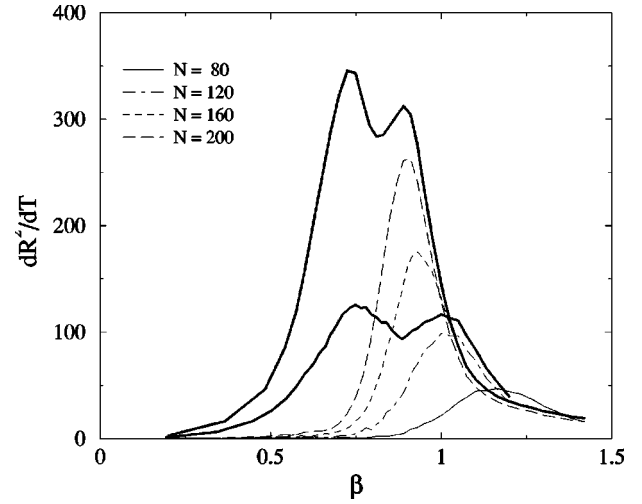


FIG. 10.  $\delta = 0$ . Thin lines: plot of the derivative of the half-chain squared gyration radius, as a function of  $\beta$ . Thick lines: two examples of derivative of the total-chain squared gyration radius ( $N = 120$  and  $200$ ).

smaller  $\beta$ . When the copolymer length is increased the shoulder becomes hardly noticeable. From the specific heat plot one cannot rule out the possibility that the shoulder eventually vanishes leaving out a single transition from a swollen phase to a compact phase. The other possibility is that there are two separate transitions, but very close in temperature.

The presence of two distinct transitions is suggested by a plot of the temperature derivative of the total radius of gyration, shown for  $N = 100$  and  $200$  as thick lines in Fig. 10. In this case one clearly detects two peaks, which although coming closer to each other as  $N$  increases are still noticeable and sharp for  $N$  rather large. The thin lines in Fig. 10 are the temperature derivatives of the radius of gyration of a single block, which show only one peak in correspondence to the low temperature peak of the derivative of the total radius of gyration. This behavior is consistent with the following picture: coming from the swollen phase (small  $\beta$ ), one first has a zipping transition characterized by a drop of the total radius of gyration, while the radius of gyration of a single block still behaves as a SAW and is not sensitive to the zipping transition. However, at lower temperatures, in correspondence to the transition from zipped to compact phase both quantities drop and their derivatives show a peak.

Another quantity which we investigated is the universal amplitude ratio between the end-to-end distance and radius of gyration squared, which is plotted in Fig. 11. Here, as for the  $\delta = 1.5$  case, this universal quantity takes the SAW value  $\sim 7.13$  at high  $T$  and drops in correspondence with the transition. The fact that we find intersections with  $R_e^2/R_g^2 \approx 0.635$  (the same value as for  $\delta = 1.5$ ) strongly suggests the presence of a zipping transition with the same universal properties as that at  $\delta = 1.5$ . Unlike Fig. 7, here  $R_e^2/R_g^2$  drops and increases again in a narrow range of  $\beta$  values, indicating the zipped phase is restricted to a small temperature interval.

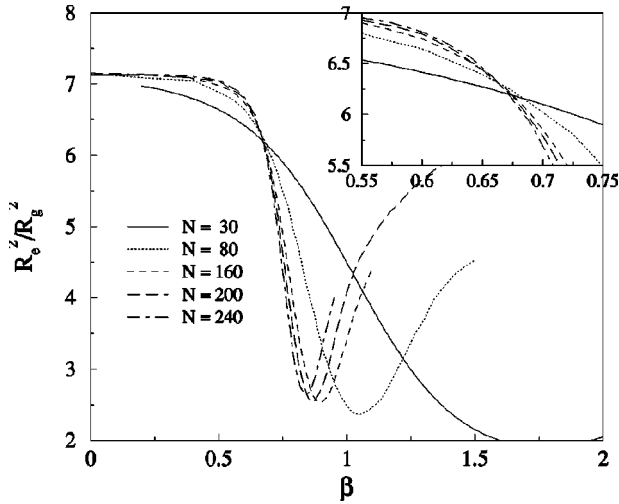


FIG. 11.  $\delta=0$ : Square end-to-end distance over the square gyration radius as a function of  $\beta$ .

In summary, although the numerical evidence is not fully conclusive, our data seem to favor the existence of two separate transitions for  $\delta=0$ . As in the case  $\delta=1.5$ , it is natural to expect that the low  $T$  one (zipped-collapsed) is of first order type.

## V. PERCOLATION PATHS AND EXACT EXPONENTS OF THE ZIPPING TRANSITION

In this section we present a conjecture on the relation between the statistics of some percolation paths at threshold and the diblock copolymer zipping transition. This conjecture leads to a prediction of exact values of the exponents. A preliminary, less precise, version of the arguments below was given in Ref. [15].

It is well known that, in two dimensions, the statistics of a ring polymer at the  $\Theta$  transition is identical to that of the external perimeter, or hull, of a percolation cluster. Through this identification the exact exponents of the  $\Theta$  transition,  $\nu_\Theta=4/7$  and  $\phi_\Theta=3/7$ , were derived [8]. Here we show how similar arguments can be invoked for the zipping transition. The differences are mainly associated with the fact that the relevant percolative set appropriate for the zipping is not the hull, as for the homopolymer  $\Theta$  point, but the backbone of the percolation cluster.

As in the  $\Theta$ -point case, here it is convenient to consider site percolation on a triangular lattice. For this problem the relevant percolation contours, like the hull of a cluster, are in fact strictly self-avoiding paths on the dual, hexagonal lattice. Thus the equivalent diblock copolymer problem realized here by percolation paths will also be on a hexagonal rather than square lattice. On the basis of universality, we expect our results to extend also to the square lattice case.

Let us consider a percolation cluster as sketched in Fig. 12. Its external perimeter is a self-avoiding ring. The ensemble of all possible conformations of an external hull on the lattice can be regarded as a problem of ring polymer (grand canonical) statistics, as discussed in Ref. [8]. One further realizes that this effective ring polymer problem is

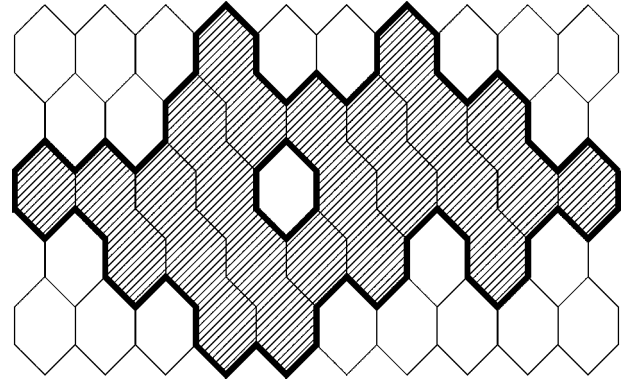


FIG. 12. Percolation cluster of connected occupied hexagons (dashed). Each hexagon is centered on a site of the dual, triangular lattice.

characterized by attractive interactions. These originate from the fact that, at threshold ( $p=p_c=1/2$ ), multiple visitations [29] by the hull of the same occupied, or vacant, hexagon, give a higher probability to the realization of a ring configuration. Indeed, when the contour proceeds essentially in a straight direction, to each new step then corresponds a new hexagon whose state (occupied or vacant) has to be determined. This each step implies a factor  $p_c=1/2$  in the probability weight of the whole configuration. When the contour folds on itself and revisits, after some steps, the perimeter of the same hexagon, the factor  $1/2$  does not apply, resulting in a higher global probability. This is equivalent to an attractive interaction favoring the multiple visitations of the same hexagon.

Here it is convenient to summarize some very recent exact results concerning the fractal dimensions of various percolative sets. Following Ref. [18] we consider an annular region of the hexagonal lattice delimited by an inner circle of small radius  $r$ , and an external one of radius  $R \gg r$ . Two types of paths connecting the two circles are also considered. These paths are formed by connected and self-avoiding sequences of either occupied or empty hexagons. The so-called *path-crossing* probability, namely, the probability that  $l$  non-overlapping paths connect inner to outer circles, was found to behave asymptotically as

$$P_l(r, R) \approx (r/R)^{x_l}, \quad (14)$$

where

$$x_l = \frac{l^2 - 1}{12}. \quad (15)$$

The formula is valid if there is at least a path of each type, and the probability depends only on the total number of these paths, not on their type [18].

Figure 13 shows examples of crossing paths; without resolving the underlying lattice structure, we draw them as solid lines if they connect filled hexagons, while dashed lines are used for paths connecting empty hexagons. As a first example [see Fig. 13(a)] we consider the crossing probability for a continuous and a dashed path, which according to Eqs.



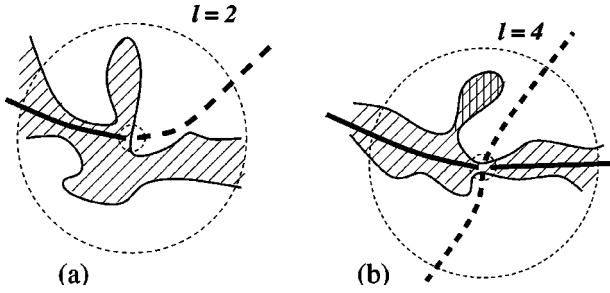


FIG. 13. Path crossing configurations for (a) a dashed line and a solid line and (b) two dashed lines and two solid lines. The probabilities of the configurations yield the fractal dimensions of the external perimeter of the hull (a) and of the cutting hexagons of the backbone (b). The dashed region indicates the percolating cluster of occupied hexagons, while the double dashed region of (b) shows a dangling end, a part of the cluster which does not belong to the backbone.

(14) and (15) decays as  $P_{l=2} \approx (r/R)^{1/4}$ . One recognizes immediately that the set of points for which two of such self-avoiding paths can be drawn are those of the external perimeter or hull of the percolative cluster [see Fig. 13(a)]. This identification allows one to derive the fractal dimension of the hull. Since the area enclosed by the annulus is proportional to  $R^2$ , the perimeter of the hull enclosed in the annulus must scale as  $L_{eh} \sim R^2 P_{l=2} \sim R^{2-x_2} = R^{7/4}$ . Identifying the external hull as a polymer ring at the  $\Theta$  point, one then derives that the latter has a fractal dimension  $D_{\Theta} = D_{l=2} \equiv 2 - x_{l=2} = 7/4$ .

In order to make contact with the diblock copolymer zipping, let us now imagine to identify two points 1 and 2, dividing the cluster hull into two equally long parts (see Fig. 14). By fixing these two points on the cluster perimeter, one automatically defines a backbone as a subset of the whole cluster. The backbone is the union of all connected paths of occupied hexagons, which are strictly self-avoiding (i.e., in each path a given hexagon appears at most once), and join points 1 and 2. Therefore the backbone does not include the

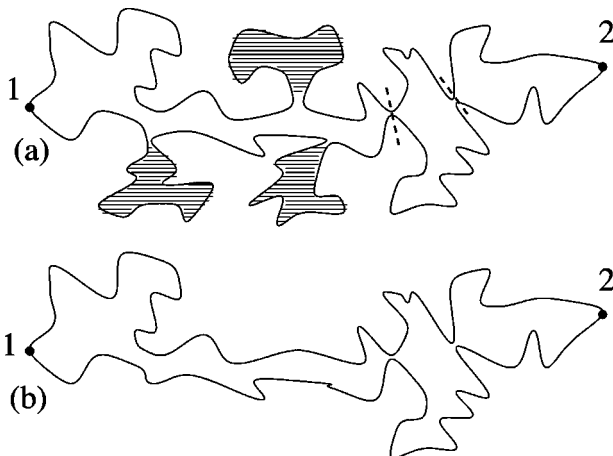


FIG. 14. (a) Schematic representation of a percolation cluster with dangling ends (dashed areas). When these are eliminated one remains with the cluster backbone (b). The dashed segments cut the cluster in corresponding to the so-called ‘‘red’’ hexagons.

so called ‘‘dangling ends,’’ i.e., those branches of the cluster connected to the main body by narrow bridges (i.e., by regions in which only one occupied hexagon is available, making it impossible for a self-avoiding path of hexagons to penetrate and exit at the same time). An example of dangling end is also schematically shown by the double dashed area in Fig. 13(b).

The two points we fix on the contour clearly divide into two sides the perimeter of the backbone. Even if in this case it is not possible to give a simple expression for the effective interactions determining the shape of the two backbone sides, we expect them to be essentially local, as in the case of the hull, and to act differently according to whether they involve close encounters of the same side, or between different sides. This is consistent with the idea that the two sides of the backbone perimeter could represent the statistics of a ring version of the diblock copolymer at the transition, the two parts corresponding, respectively, to blocks *A* and *B*.

To calculate the fractal dimension of the external perimeter of the backbone one can use Eqs. (14) and (15), taking two continuous paths and a dashed path. This configuration clearly identifies the perimeter of the backbone. Indeed, the two continuous paths guarantee that occupied hexagons inside the interior circle belong to a whole path connecting two infinitely distant points. At the same time, a dashed path implies that the vacant hexagons facing the occupied ones belong to the exterior of the cluster, and thus, are also part of its backbone.

Therefore, we now take  $l=3$  for the exponents defined in Eq. (15). In this case we find that the external perimeter of the backbone scales as  $L_{bb} \sim R^{2-x_3} = R^{4/3}$ , which implies a fractal dimension  $D_3 = 4/3$  [30]. This dimension is consistent with that found for the diblock copolymer at the zipping transition. Furthermore, it is natural to associate the switching on of effective attractive interactions between the two backbone sides to the existence of narrow bottlenecks in the backbone itself (corresponding to only one hexagon). These are the so-called cutting or ‘‘red’’ hexagons of the backbone [17], which are visited by the two blocks simultaneously. In order to determine their fractal dimension one has to consider a percolative configuration with two continuous and two dashed paths joining the circles, as sketched in Fig. 13(b). These paths identify a dimension  $D_4 = 2 - x_4 = 3/4$ . Thus, for a backbone with external perimeter equal to  $N$  and an average of  $N_{AB}$  contacts we find  $N \sim R^{D_3}$  and  $N_{AB} \sim R^{D_4}$ . Consequently, the average number of contacts between the backbone sides grows like  $N_{AB} \sim N^{D_4/D_3} = N^{9/16}$ . By identifying the external perimeter of the backbone with the ring diblock copolymer at its transition, one eventually finds  $\nu_c = 3/4$  and  $\phi = 9/16$ . The numerical determinations of  $\nu_c$  and  $\phi$  at the zipping transition are remarkably consistent with these values, making the conjecture extremely plausible [31].

## VI. CONCLUSIONS

In this paper we studied the phase diagram for the collapse transition of a diblock copolymer with attractive interactions between monomers of different species and a triple contact interaction  $\delta$ , which, according to its sign, may either

favor, or unfavor, compactification. In the region of negative  $\delta$  we find a first order transition from a swollen to a compact, spiral phase, while in the positive  $\delta$  region there is a sequence of a continuous zipping transition and a collapse of first order type to compact conformations at a lower temperature.

Our exact enumerations and Monte Carlo simulations yield numerical estimates of the critical exponents  $\nu_c$  and  $\phi$  of the zipping transition, which are consistent with those we could conjecture using recent results for the fractal dimensions of the percolation cluster backbone, from which we expect  $\nu_c = 3/4$  and  $\phi = 9/16$ . The numerically determined exponents, therefore, support the hypothesis that the transition admits a description in terms of percolative stochastic geometry: the two blocks of the copolymer have the same fractal geometry as the two sides of a cluster backbone, and their contacts correspond to the cutting hexagons, or links of the same backbone. This is, to our knowledge, the second example of a percolative representation for a polymer conformational transition in two dimensions, besides that of the  $\Theta$  point. The common percolative roots of these transitions suggests the possibility of a deep link between them, which ought to be elucidated by further studies.

The results obtained for the various transitions appearing in the phase diagram help in clarifying the nature of the adsorptionlike collapse occurring at  $\delta=0$  and first detected in Ref. [15]. In spite of the fact that most tests are not able to put into clear evidence the existence of two successive transitions, the only multicritical behavior which can be characterized as coming from the high temperature region seems definitely to belong to the universality class of the continuous zipping transition identified for positive values of  $\delta$ . Besides the compatibility of the exponent estimates, a very strong support for such conclusion comes from our determination of the universal amplitude ratio between the squared end-to-end distance and the radius of gyration of the polymer.

Other interesting aspects of the phase diagram calculated in this paper are the first order swollen-collapsed and zipped-collapsed transitions found, respectively, for negative and positive values of  $\delta$ . In particular the latter resembles the transition from a swollen to a spiral state found in *oriented* polymers [16], i.e., chains to which an overall orientation is assigned, and where different energies are associated with

contacts between parallel or antiparallel segments of the chain. In fact the analogy between the diblock copolymer in a zipped state and an oriented polymer is very appropriate: in the zipped diblock parallel contacts are of *AB* type, while antiparallel ones are contacts between monomers of equal type. Different energies are clearly associated with the two types of contacts.

It is worthwhile to recall that simple polymer models with some sort of zipping transition already have attracted some attention in recent literature [32,33], mainly because of the relevance that such transition can have for biopolymers. Imbert *et al.* [32] considered a diblock formed by two strands of oppositely charged monomers interacting with each other through long range Coulomb forces and found evidence of the existence of a zipping transition followed by a collapse at lower temperatures. Causo *et al.* [33] considered a simple model for the DNA denaturation transition, in which only the monomers which are at equal distances along the sequence from the center of the chain interact. They found evidence of a first order transition, from a swollen phase to a zipped phase. By its construction their model has no other transitions to a compact state. In their case the first order zipping seems to be due to the selective interactions of monomers along the chain. Also, in our model, if we turn on interactions only between *AB* monomers at equal distances from the center, we find evidence of a first order zipping transition.

Finally, we point out that there are several possible extensions of this work. First of all, it would be interesting to generalize the model to three dimensions and to investigate the properties of the zipping transition in that case [15]. Another open issue is the effect of disorder on the interaction between monomers for the zipping transition, which would allow one to understand the behavior of models of polymers more relevant for applications to chemistry or biology than a simple diblock.

#### ACKNOWLEDGMENTS

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