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]. It is known as Θ-collapse and has been widely investigated in the past years using various methods such as mean field approximations [2], exact enumerations of interacting self-avoiding walks on lattices [3], Monte Carlo [4], transfer matrix [5] and field theoretical calculations [6]. In two dimensions the exponents of the Θ-collapse have been related to the fractal properties of the percolation cluster and are believed to be known exactly [7].

The study of the conformational properties and phase transitions of macromolecules with inhomogeneous or random sequences of monomers is an interesting frontier in nowadays polymer statistics [8]. These systems pose new theoretical and numerical challenges, compared to their more standard, homogeneous counterparts. Particularly interesting is in general the possibility that the inhomogeneities along the chain could lead to transitions and universality classes of scaling behavior, which are not realized for homopolymers [9,10]. Moreover, the most complex versions of models of this class are also expected to be useful for the description of phenomena like protein folding [11], DNA denaturation [12] and RNA secondary structure formation [13]. 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 zipping transition. By zipping 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 unzipped to 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 zipping 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 to 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 the attractive interactions between monomers of the two blocks are established through a preferential formation of hydrogen bonds. The attractive interactions between the two blocks, besides zipping, tend also 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 [14], a model of diblock copolymer with some of the features discussed above has been studied in both two dimensions (2D) and 3D. In that model the two blocks were represented by two halves of a self avoiding walk (SAW) on hypercubic lattice, and attractive interactions were acting 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 as possible monomers of the other block. The transition of the diblock copolymer from a high T swollen to a low T compact phase, had analogies with both polymer adsorption on a wall, and Θ-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,
The swollen phase could exist for temperatures just below the transition, could not be excluded. If this were the case, the adsorption-like collapse found in Ref. 13 would correspond to a zipping and a further transition to the compact globular phase should be expected to take place at a lower $T$.

In the present article we extend the model of Ref. 15 in 2D 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 adsorption-like collapse of Ref. 13 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 also the first order collapse has interesting features, 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 2D 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. The mapping onto percolative stochastic geometry we discuss here is, to our knowledge, the first example of exact results derivation for a genuinely inhomogeneous polymer problem in 2D. The connection with percolation geometry shows also that the physics of zipping is closely connected with that of the $\Theta$-point transition, for which a representation in terms of percolation geometry has been established already 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 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 appear also 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 properly these more complicated systems.

This paper is organized as follows: In Section II we present the model and the main features of the phase diagram. In Sections III and IV we discuss the numerical results obtained by exact enumerations and Monte Carlo simulations, respectively. In Section V using recent results for crossing probabilities of percolation paths in 2D, 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. THE MODEL AND PHASE DIAGRAM

We model the 2D diblock copolymer by an interacting SAW on the square lattice. In the configuration $w$ 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:

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

(1)

where $N_{AB}(w)$ and $N_3(w)$ are the number of $A-B$ and of 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

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

(2)

where

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

(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 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 (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 configurations 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, with (d) sampled in the vicinity of the transition to the compact state; notice 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 the 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.

One can easily understand now why the 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, also the zipped-compact transition temperature 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

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

where the sums extend to all $N$-steps 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

$$R_g(N, T) \sim N^{\nu_c} R [(T - T_c)N^\delta]$$
where \( \nu_c \) and \( \phi \) are the exponents characterizing the transition and \( R \) is a scaling function that is assumed to approach a positive constant if its argument approaches zero.

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

\[
C(N, T) \sim N^{2\phi-1} C \left[ (T - T_c)N^\phi \right] \tag{6}
\]

where \( C \) 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 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 \( N \to \infty \) 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 one. However, as \( \delta \) is increased, the two sets of peaks get clearly separated and extrapolations yield two distinct transition temperatures. We focus here on the characterization of the high \( T \) transition from the swollen to the zipped phase. The scaling form of Eq. (3) 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. (3) and (4) one has:

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

and

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

For the calculation of the critical exponents we formed first the finite \( N \) approximants, for instance

\[
\nu_c(N) \equiv \frac{\ln(R_g(N + 2)/R_g(N))}{\ln((N + 2)/N)} \tag{9}
\]

(here \( R_g(N) \) is a shorthand notation for \( R_g(N, T_c(N)) \)) and then extrapolated \( \nu_c(N) \) to \( N \to \infty \). 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 to the radius of the half-chain, or single block, which at the critical temperature should scale as:

\[
R'_g(N, T = T_c) \sim \left( \frac{N}{2} \right)^{\nu'_c} \tag{10}
\]

\[\]

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)      |

![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 \( N = 12, 14, \ldots 30 \). The double peak structure for \( \delta = 0 \) suggests the sequence of two transitions, swollen-zipped and zipped-collapsed.](image)

The values of the exponents \( \phi \) and \( \nu_c \) vary slightly along the line (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 the line (1); the most reliable estimates for \( \nu_c \) and \( \phi \) should be those for large \( \delta \), where the lines (1) and (3) 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. [25] for the transition at \( \delta = 0 \) and will be derived in detail in Section V.

As for the 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 to achieve much larger copolymer lengths.

\[ \text{Fig. 4.} \quad \text{Solid lines: Specific heat from exact enumerations for } N = 12, 14, \ldots, 30 \text{ for } \delta = 0 \text{ (a) and } \delta = -1.5 \text{ (b). Circles: Monte Carlo results for } N = 30. \]

**IV. MONTE CARLO SIMULATIONS**

In order to sharpen and extend the results of exact enumerations, in particular concerning the properties of the 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, being difficult to construct a Markov chain sufficiently "mobile" 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 converge is rapid. Most recently this method has been used successfully to investigate collapse transitions in homopolymers \[21\], hethopolymers \[11\], and adsorption in \( \Theta \)-solvent \[20\].

First one defines a Metropolis based Markov chain for a temperature \( T \). This procedure makes use of a hybrid algorithm based on pivot \[24\] as well as on local moves \[25\]. 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 Fig. 1 (b,c,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 \[27\]. These moves are particularly effective for dense chains, and even more effective for the zipped chains, where typically one side of each half-chain is free and can hold a new kink. The resulting algorithm is a little 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. 3(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 \( m \approx 40 \) 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 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 \[4\] we expect, as \( N \) increases,

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

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. \[13\] 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 \( 1/N^{2\Delta} \), but the best fit is obtained for \( \Delta = 1 \). The estimated value of \( \phi \) allowed us to extrapolate \( T_c \).
by plotting $T_c(N)$ vs. $1/N^\phi$. This gives $T_c = 1.51(4)$ ($\beta_c = 0.66(2)$).

![Graph](image)

**FIG. 5.** $\delta = 1.5$: Plot of the specific heat vs. $\beta$, for chains of various lengths. For $N = 300$ and $N = 400$ 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 $C/N^{2\beta-1}$ vs. $(\beta-\beta_c)N^\phi$, with $\phi = 9/16 = 0.5625$ and $\beta_c = 0.66$.

The inset of Fig. 5 shows a plot of $C/N^{2\beta-1}$ 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. On the contrary, for the 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 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 $E/N$ (b,c). For lower temperatures $P$ develops a double peak structure (d,e,f). In the case (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 $R_S^2$ defined in (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

$$R_S^2(N) \sim \rho_c N^{2\nu} \quad (12)$$

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

and an interesting quantity to be computed is the ratio $\rho_c/\rho_g$, which is expected to be universal. For non interacting SAW’s on a square lattice, exact enumerations and Monte Carlo simulations give $\rho_c/\rho_g \approx 7.13$ (see references in [23]). Figure 7 shows the ratio $R_S^2/R_e^2$ 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 $\rho_c/\rho_g = 7.15(5)$ in agreement with the value expected for non interacting SAW’s. In the proximity of the zipping transition the curves start to bend downwards and at $\beta_c \approx 0.66$ they cross each other almost in a unique point (see inset). At the crossing point our estimate of the universal amplitude is $\rho_c/\rho_g = 6.35 \pm 0.20$ which is definitively different from the amplitudes 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 $\rho_e/\rho_g$ [22].

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 does not scale anymore like the radius of gyration, as assumed in Eqs. (12,13). For sufficiently low temperatures, $\rho_e/\rho_g$ starts to grow back indicating that the compact phase is characterized by 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 Fig. 2(e,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(a). 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 a behavior is stronger than in the case $\delta = 1.5$ since here the coexistence is between two phases (the swollen and the compact) with a rather large difference in energy, therefore the double peak structure of $P$ can be noticed already for small $N$.

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 others. We have chosen in particular the case $\delta = 0$, since it was considered in Ref. [13].

In Fig. 9 we plot the specific heat as a function of $\beta$ for several $N$ values. For the smallest chains ($N = 60, 80$), one observes a peak in the specific heat with a shoulder at 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 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 $N = 200$ 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 has first 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 sensible 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 of 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 from Fig. 7 here $R_e^2/R_g^2$ drops and increases again in a narrow range of $\beta$ values indicating that the zipped phase is restricted to a small temperature interval.

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 predict exact values for the exponents. A preliminary, less precise version of the arguments below was given in Ref. [15].

It is well-known that, in 2D, 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 to the fact that the relevant percolative set appropriate for the zipping is not the hull, as for the homopolymer $\Theta$-point.

Like in the $\Theta$-point case, here it is convenient to con-
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, also the equivalent diblock copolymer problem realized here by percolation paths will be on 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 Refs. [18, 19]. One further realizes that this effective ring polymer problem is characterized by attractive interactions. These originate from the fact that, at threshold \((p = p_c = 1/2)\), multiple visitations [28] by the hull of the same occupied, or vacant, hexagon, give higher probability to the realization of a ring configuration. Indeed, when the contour proceeds essentially straight, to each new step corresponds a new hexagon whose state (occupied or vacant) has to be determined. So, 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 higher global probability. This is equivalent to an attractive interaction favoring the multiple visitations of the same hexagon.

It is convenient here 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:

\[
P_l(r, R) \approx (r/R)^{x_l}
\]

where:

\[
x_l = \frac{l^2 - 1}{12}
\]

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].

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

**FIG. 13.** Path crossing configurations for (a) a dashed and a solid line and (b) two dashed 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.

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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. [14, 17] 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 percolating cluster (see Fig. 13(a)). This identification allows 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 \(D_\Theta = D_{l=2} = 2 - x_{l=2} = 7/4\).

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 in 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 the points 1 and 2. In force of the definition, the backbone does not include the 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 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 as double dashed area in Fig. 13(b).

![Diagram](image-url)

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 correspondence to the so-called "red" hexagons.

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 of the effective interactions determining the shape of the two backbone sides, we expect them to be essentially local, like 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.

For the calculation of the fractal dimension of the external perimeter of the backbone one can use Eqs. (14,15) taking two continuous paths and a dashed one. 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, also of its backbone.

Therefore we now take \( t = 3 \) for the exponents defined in Eq. (15). In this case we find that the external perimeter of the backbone scales as \( L_{bb} \sim R^{2-\nu_3} = R^{4/3} \), which implies a fractal dimension \( D_3 = 4/3 \). 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 identify a dimension \( D_4 = 2 - \nu_4 = 3/4 \). 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 \( \phi = 9/16 \). Now the numerical determinations of \( \nu_c \) and \( \phi \) at the zipping transition are remarkably consistent with these values, making the conjecture extremely plausible [30].

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, are strongly supporting 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 2D, 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 adsorption-like collapse occurring at \( \delta = 0 \) and first detected in Ref. [17]. In spite of the fact that most tests are not able to put into clear evidence the existence of two successive transitions, the only multiritical behavior which can be characterized coming from the high
temperature region seems to definitely 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 to such conclusion comes from our determination of the universal amplitude ratio between squared end-to-end distance and radius of gyration of the polymer.

Another interesting aspect 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 swollen to spiral state found in oriented polymers \cite{31,32}, i.e. chains to which an overall orientation is assigned and where different energies are associated to 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 attracted already some attention in the recent literature \cite{31,32}, mainly because of the relevance that such transition can have for biopolymers. Imbert et al. \cite{31} 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. \cite{32} 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 to a zipped phase. By its construction their model has no other transitions to 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 distance 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 \cite{13}. Another open issue is the effect of disorder on the interaction between monomers for the zipping transition, which would allow to understand the behavior of models of polymers more relevant for applications to chemistry or biology than a simple diblock.

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