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Conformation of a polymer chain at the θ' point: Connection to the external perimeter of a percolation cluster

Antonio Coniglio
Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215

Naeem Jan
Physics Department, St. Francis Xavier University, Antigonish, Nova Scotia, Canada B2S 1C0

Imtiaz Majid and H. Eugene Stanley
Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215
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We present an argument that the statistics of polymer rings at the θ' point in two dimensions is exactly given by the statistics of the external perimeter ("hull") of a percolation cluster. As a consequence, the fractal dimension $d_f(\theta')$ of a polymer chain at the θ' point coincides with that of the hull of the percolating cluster, $d_f(\theta')=d_H$. Here θ' is the coil-globule transition point for a special interaction parameter. We also discuss conditions under which the θ' point may be related to the conventional θ point.

Consider a long flexible polymer chain. In a dilute solution of good solvent or at high temperatures one customarily neglects the van der Waals attraction between the monomers, and the chain assumes a shape controlled solely by the hard-core repulsion. The statistics of real polymers under these conditions are known to correspond to those of a self-avoiding random walk (SAW).[1,2] What happens under conditions (such as a poor solvent) where we cannot neglect the attraction? At high T, the chain retains the excluded volume or SAW statistics of the zero-attraction limit. However, as T is decreased, the attractive interaction plays an increasingly significant role and "suddenly" at a critical temperature $T_c=\theta$ the chain undergoes a dramatic phase transition to the collapsed phase (Fig. 1).[3] Since the fractal dimension of the swollen chain is typically $d_f=1.71\simeq\frac{5}{3}$,[1] while the fractal dimension of the collapsed state is $d_f=d=3$, a small change in T leads to a huge change in the volume occupied by the chain. Many biological, chemical, and physical systems capitalize on this amplification feature by evolving systems that operate near the θ point; one example is the collapse transition in DNA.[4]

At present, the basic physics in the neighborhood of the θ point is still not understood. For example, although we know how the mass scales with distance for the dilute polymer and for the collapsed state, there are many conflicting results for the θ point[5-15] for $d=2$, in contrast to the exact result $d_f=2$ at the critical dimension $d_c=3$. Here we present a model that may shed light on this problem. We argue that the polymer chain at the θ' point has the same statistics and therefore the same fractal dimension as a new and extremely simple random walk, which reproduces the hulls of all the clusters at the percolation threshold. This walk, introduced by Weinrib and Trugman[16] who called it a smart kinetic walk (SKW), chooses the next step with equal probability from among all available possibilities that do not result in self-intersection, except at the origin, and do not lead to self-trapping; it therefore has the unique feature that the only means of termination is to re-

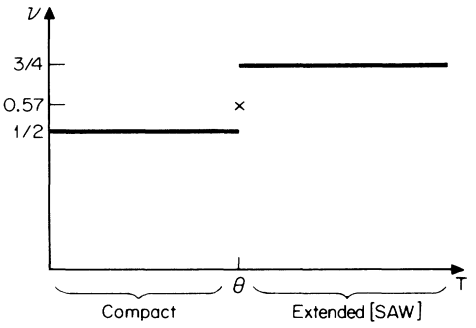

FIG. 1. Temperature dependence of $\nu=d_f^{-1}$ for a polymer solution or "interacting SAW." For any $T>\theta'$, the system has the same behavior as a pure SAW, while for $T<\theta'$ it is identical to a compact object.

visit the origin. The end result of this walk is an ensemble of self-avoiding polygons. Weinrib and Trugman also showed that on the honeycomb lattice these self-avoiding polygons are generated with the same statistics as the hulls of the clusters at the percolation threshold of the triangular lattice. This result implies that the fractal dimension of an SKW is identical to the hull of a percolating cluster.

A variation of the SKW consists, in addition to the above constraints, in avoiding the self-intersection at the origin, and in this case it grows forever. Such a walk was introduced independently by Kremer and Lyklema[17] who named it indefinitely growing self-avoiding walk (IGSAW). Weinrib and Trugman gave strong arguments that the fractal dimension of the IGSAW is the same as that of the SKW. This prediction is supported by very accurate numerical work which gives for both walks $d_f \simeq 1.75$,[17,18] in agreement with the numerical value for the hull of the percolating cluster $d_H \simeq 1.75$,[19] and a conjectured exact result.[20,21] $d_H = 1 + \nu_p^{-1} = 1.75$, where $\nu_p = \frac{4}{3}$ is the percolation connectedness length exponent.

Our starting point is the simple SAW. The SAW can be generated on a computer by choosing an origin and then adding successive steps of the walk with equal probability. Henceforth we consider the honeycomb lattice: The first step has weight $\frac{1}{3}$ (three choices) and subsequent steps have weight $\frac{1}{2}$ (two choices); if the walk steps on a previously visited site, the walk stops. A typical SAW configuration is given in Fig. 2(a). The SAW exponent for $d=2$ is known[22] exactly to be $\nu = \frac{3}{4}$, where ν is defined by $\langle R_N^2 \rangle \sim N^{2\nu}$ and $\langle R_N^2 \rangle$ is the square of the radius of gyration averaged over all chain configurations of N steps. Instead of the SAW, sometimes it is more convenient to study self-avoiding rings. These are made of all self-avoiding walks which return to the origin. It is known[2] that the fractal dimension of the self-avoiding rings is the same as that of the SAW.

The SAW is a good model only for the limit of a very good solvent. For a less good solvent, one conventionally uses the nearest-neighbor interacting SAW (ISAW): each SAW configuration is weighted by a factor, $\exp(\varepsilon N_{\mathrm{NN}})$, where N_{NN} is the number of nearest-neighbor (NN) monomer pairs in the walk and $\varepsilon = E/kT$ is the dimensionless NN interaction energy. The ISAW as well as the NN interacting self-avoiding rings reproduces the θ point and the collapsed state. However, it is very impractical from the computational point of view since the probability of generating a very long chain of, say, 100 steps without a *single* self-intersection is extremely low.

We now argue that SKW generates interacting self-avoiding rings at $T=\theta'$. Consider the honeycomb lattice shown in Fig. 2 with the origin as indicated (○). In order to generate the SKW [Fig. 2(d)],[16] the first step is made in a random direction and the hexagons on either side of the chosen direction are assigned + and −, respectively. For the second and subsequent steps we first assign to the hexagon at the vertex a + (or −) with probability 0.5 and make a step to ensure the separation of the two regions + and −. Note that at the end of the sixth step the sign of the hexagon at the vertex of the walk is already determined and, hence, the next step (bold line) has a weight of 1, whereas the previous steps have a weight $\frac{1}{2}$ except for the first with weight $\frac{1}{3}$. The walk will eventually terminate by a revisit to the origin, having generated a self-avoiding ring. We note that some of the steps have weight $\frac{1}{2}$ and some have weight 1, whereas each step of a noninteracting self-avoiding ring always has weight $\frac{1}{2}$ except for the first with weight $\frac{1}{3}$. Therefore, the weight for a self-avoiding ring model of N steps is given by $W_{\mathrm{ring}} = \frac{1}{3}(\frac{1}{2})^{N-1}$ while W_{SKW} has an extra factor of 2 for each bond or step with a weight of 1. In this example there are five such bonds: three to avoid self-intersection (bold lines), the other two to avoid self-trapping (wavy lines); therefore $W_{\mathrm{SKW}} = W_{\mathrm{ring}} \exp(5 \ln 2)$.

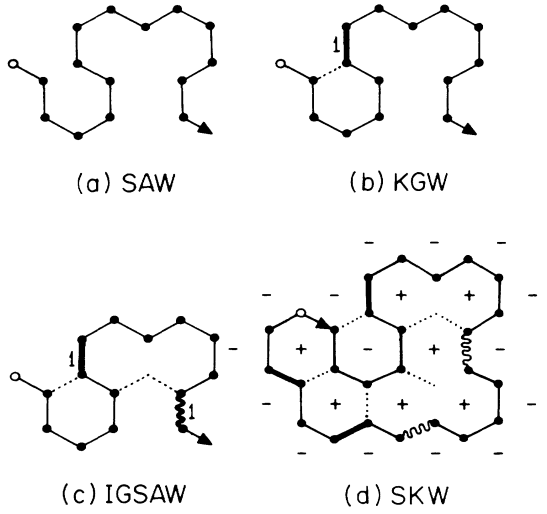

FIG. 2. Three identical configurations (*a*, *b*, and *c*) of $N=15$ steps of the SAW, KGW, and IGSAW on the honeycomb lattice, each with its own weight. The IGSAW configuration coincides with an SKW before coming back to the origin. The arrows indicate the future direction of the walks. (a) SAW. All the light lines correspond to weight $\frac{1}{2}$, except for the first step, which has weight $\frac{1}{3}$. The total weight for the SAW is thus $W_{\mathrm{SAW}} = \frac{1}{3}(\frac{1}{2})^{N-1}$. (b) KGW. The KGW has for each step the same weight as for the SAW except for that step chosen necessarily to avoid self-intersection, which has weight 1 (bold line). This step occurs immediately after the walker steps to a site that is a NN to a previously visited site (connected by a dotted line). The weight for such configuration is $W_{\mathrm{KGW}} = W_{\mathrm{SAW}} \exp(\varepsilon^*)$, with $\varepsilon = \ln 2$. (c) IGSAW. For the IGSAW there are two steps that have weight 1, and $W_{\mathrm{IGSAW}} = W_{\mathrm{SAW}} \exp(2\varepsilon^*)$. The first occurs, as in the KGW, to avoid self-intersection (bold line), while the second occurs to avoid self-trapping (wavy line). "Wavy" steps occur only if a pair of NNN sites has been visited (two dotted bonds). (d) An SKW configuration; note that the first 14 steps have the same configuration and weight as in (c).

In general, for a configuration with N_1 of such bonds, $W_{\mathrm{SKW}} = W_{\mathrm{ring}} \exp(N_1 \ln 2)$; we will show that in a given configuration N_1 is given by one plus the number of hexagons that contain two steps of the walk which are not connected on that hexagon [see Fig. 3(a)], plus twice the number of hexagons that contain three steps of the walk not connected on this hexagon.

To prove the validity of this rule, consider first the walk in its evolution, before it has returned back to the origin.

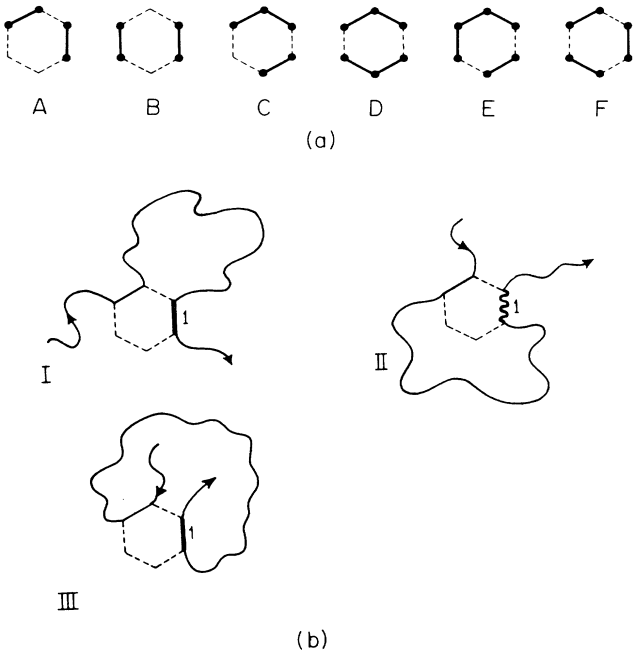

FIG. 3. (a) The number of steps in a SKW before coming back to the origin that have weight 1 is given by the number of hexagonal plaquettes in configurations *A*, *B*, *C*, *D*, and *E* plus twice the number of plaquettes in configuration *F*. The full lines are the steps of the walk in that hexagonal plaquette. (b) All topologically different configurations of a SKW that contain a plaquette of type *A*. These configurations show that one of the two bonds always has a weight 1. In I and III the step represented by bold lines avoids self-intersection. In II the step represented by a wavy line avoids self-trapping. Note that there are three more configurations obtained by reversing the arrow in I, II, and III. In this case the weight 1 step is the opposite one.

Also exclude for the moment the case when the walk comes within one lattice constant of the origin. Under these circumstances we show that each time one of the plaquettes of Fig. 3(a) is realized it implies that one of the bonds of the plaquette has weight 1 except for plaquette *F* for which two bonds have weight 1. This can be checked using the example of Fig. 2(c) where the bold and wavy bonds are shown which have weight 1. In general we note that the local configuration *A* can be part of the walk in one of the three different topological configurations; in all cases one of the two bonds always has weight 1 [Fig. 3(b)]. The same analysis can be repeated for all the other local configurations of Fig. 3(a). When we consider the complete ring, due to the fact that the origin has been revisited, there is one plaquette near the origin not included in those of Fig. 3(a) which contains always one bond with weight 1 [see, e.g., Fig. 2(d)]. This concludes the proof. Note that $N_1 = N_{NN} + N'_{NNN}$ when N_{NN} is the number of NN monomers and N'_{NNN} is a subset of next-nearest-neighbor (NNN) monomers [Fig. 3(b)].

Finally, if we define an interacting self-avoiding ring with an interaction $\varepsilon = E/kT$ for each nearest neighbor and NNN pair contributing to N_1, the weight of this ring is $W_{ring} = W_{SAW}\exp(\varepsilon N_1)$ which coincides with W_{SKW} at $\varepsilon^* = \varepsilon/k\theta' = \ln 2$, corresponding to a particular temperature $T = \theta'$. In this way we have mapped exactly the SKW on the interacting self-avoiding rings at the particular temperature $T = \theta'$. This is the main result of the present work.

Before concluding, we note that θ' is a higher order critical point. The phase diagram of the interacting rings is given in Fig. 1. Because of the mapping of the SKW onto the NNN interacting rings with $T = \theta'$, SKW should have 1 of the 3 critical exponents of Fig. 1. We rule out the $T < \theta'$ exponent since $\nu > \frac{1}{2}$ for the SKW[23] and $\nu = \frac{1}{2}$ for the ISAW with $T < \theta'$. We can virtually rule out the $T > \theta'$ exponent since high-precision numerical work[16,19] and the possible exact result[20,21] report $\nu = \frac{4}{7}$ quite distinct from the SAW value of $\frac{3}{4}$.[22] Since the exponent ν seems distinct from the SAW and from the collapsed phase, θ' corresponds to a higher order critical point.

If the special interaction is in the same universality class as the NN interaction, then the θ' point describes also the statistics of the θ point. *We have no way of testing this intriguing possibility.* It is nonetheless interesting to examine the appropriate numerical data. We conclude that experimental results (Table I) and some calculations agree well,[12,14] but other calculations do not.[5] For this reason, we have undertaken our own numerical calculation for the θ point using a new method, which is done in the following manner. We consider the kinetic growth walk (KGW)[24-26] recently introduced as a model for a growing polymer. The KGW avoids direct self-intersection and thus the next step is chosen with equal probability from among the unvisited nearest-neighbor sites [Fig. 2(b)]. The walk terminates when there are no unvisited nearest neighbors. Using the same reasoning as before, it is possible to show that the KGW on the honeycomb lattice is equivalent to a NN interacting SAW at a particular temperature $\varepsilon^* = \ln 2$. This corresponds to a temperature just above the θ temperature. Since a KGW is a NN ISAW with weight $\exp(\varepsilon^* N_{NN})$,[27] we can generate any ISAW from a KGW weighted by $\exp[(\varepsilon - \varepsilon^*)N_{NN}]$. We have generated many long KGW's (up to 700 steps) on the honeycomb lattice and weighted each configuration with the appropriate Boltzmann factor; our analysis gives $\nu = 0.575 \pm 0.025$, which agrees well with calculations for IGSAW, SKW, and the hull of the percolating cluster (Table I).[21]

One might ask the question whether there is a walk

TABLE I. Comparison between ν for polymers and polymer models with ν for nonpolymer models. Flory theory gives $\frac{2}{3}$.

	ν
Experiments on θ-point polymers	0.56[a]
Monte Carlo (this paper)	0.57
SKW	0.57 ± 0.01[b]
IGSAW	0.567 ± 0.003[c]
Hull of percolating cluster	0.57[d]

[a]Reference 10.
[b]Reference 18.
[c]Reference 17.
[d]References 19 and 20.

which describes the ISAW at the θ' point. The analysis obtained above for determining the weights of the interacting rings can be used to show that the IGSAW maps onto an interacting SAW with NN and NNN interactions. The only difference now is that there is *no* one-to-one correspondence between the set of all N step ISAW (as some conformations will eventually lead to trapping) and the set of N-step IGSAW's (which do not contain any conformation that can be trapped by subsequent steps). However, the following argument can be used to show that the fractal dimension of the two walks is the same. In fact we can define the SAW problem in a different way. Starting from the origin one can generate extremely long chains of N' steps. If we consider the statistics of that part of the chain made on the first N steps ($N \ll N'$), we expect that this will reproduce the same fractal dimension of the standard SAW, due to the self-similarity of a typical configuration of the long chain.[28] The SAW configurations which are made of the first N steps of a long chain exclude the possibility of ending in a cul-de-sac and therefore coincide with the IGSAW configuration. This argument is consistent with the fact that self-avoiding rings and SAW have the same fractal dimensions. We are unable at present to predict γ, the exponent describing the number of distinct self-avoiding walks. The partition function $Z_N = \sum \exp(\varepsilon N_{\rm NN})$ asymptotically diverges as $Z_N \sim \mu^N \times N^{\gamma-1}$, where μ is the connectivity constant. This cannot be obtained from the partition function of the rings[2] or equivalently the SKW. However γ is equal to 1 by construction[17] for the IGSAW and one may be tempted to conclude that $\gamma = 1$ also at the θ' point. We believe that although the cul-de-sac configurations do not contribute to the fractal dimension, we cannot rule out that they contribute to the enhancement factor and thus might lead to a γ slightly different from 1.

In conclusion, it appears that the SKW describes the statistics of a polymer chain at the θ' point, and can be found very accurately to give $\nu = 0.57$. This prediction is remarkably close to the experimental value $\nu = 0.56$.[10] Since the SKW is equivalent to the hull of the percolating cluster we have the intriguing result that a polymer chain at the θ' point in $d = 2$ appears to have the same statistics as the hull of the percolating cluster.

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