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Two-stage collapse of a polymer chain in two dimensions

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I show that for a certain range in its parameter space, a self-attracting self-avoiding loop (SASAL) can be mapped onto the hull of a percolation cluster in two dimensions. The inside (outside) of this loop attracts itself with interaction energy ε_+ (ε_-). This mapping is used to argue that if $\varepsilon_+ > \varepsilon_-$, the collapse of the SASAL occurs in not one but two stages as the temperature is reduced: the SASAL first collapses to form a "branched polymer" and then at lower temperatures collapses still further to become a compact globule.

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At high temperatures, a polymer chain in a good solvent behaves essentially as if it were a self-avoiding walk (SAW): Its mean radius of gyration grows as $\langle R \rangle \sim N^{\nu}$, where ν has the same value as for the SAW and N is the molecular weight [1]. As the temperature T is reduced, however, the short-ranged van der Waals attraction between monomers becomes increasingly important. At low temperatures, the polymer chain is in a collapsed state, and the exponent ν takes on the value $1/d$, where d is the dimension of space.

For decades, it was believed that the collapse must always occur at a single temperature, the theta temperature T_θ. If there is a single collapse transition, it is a tricritical point [1]. Recently, however, Orlandini *et al.* [2] discovered that a certain self-attracting self-avoiding trail on the Sierpinski gasket collapses in two stages: between the high-temperature SAW phase and the fully collapsed low-temperature phase, there is a lattice animal or "branched polymer" phase. They also presented numerical evidence that, as the temperature is reduced, a self-attracting 2-tolerant trail on the square lattice collapses to form a branched polymer. (A 2-tolerant trail can visit a site no more than twice.)

The results of Orlandini *et al.* are intriguing, but they suffer from certain limitations. The Sierpinski gasket is a regular fractal lattice with the appealing attribute that many problems can be exactly solved on it. However, critical phenomena on the Sierpinski gasket are pathological in several important respects [3]. In addition, both of the models studied by Orlandini *et al.* have only partial self-avoidance: self-avoiding trails can revisit sites but not bonds. Finally, the self-attracting 2-tolerant trail was studied using exact enumerations of relatively short walks, and so the correct asymptotic behavior may not have been found. It is therefore unclear whether there are real polymer chains that have a branched polymer phase.

Perhaps the most important tool used in the theory of the θ polymers in two dimensions (2D) has been the mapping introduced by Coniglio *et al.* [4]. These workers showed that at its collapse transition, a self-attracting polymer ring on the hexagonal lattice can be mapped onto the surface (or "hull") of a percolation cluster at threshold. Since it has been proven that the radius-of-gyration exponent ν is $\frac{4}{7}$ for the perimeter of a percolation cluster at threshold in 2D [5], the value of the size exponent at the tricritical point ν_t must also be $\frac{4}{7}$. Similar approaches to the collapse transition of a polymer chain in 2D have been developed by others [6,7].

In this Rapid Communication, I consider a certain self-attracting self-avoiding loop (SASAL) in 2D. The inside of the loop attracts itself with interaction energy ε_+, while the outside of the loop attracts itself with energy ε_-. The energies ε_+ and ε_- may differ. I demonstrate that for a range of parameter values, the SASAL can be mapped onto the hull of a percolation cluster in 2D. This mapping generalizes the mapping of Coniglio *et al.* to the case $\varepsilon_+ \neq \varepsilon_-$. The mapping is used to argue that the SASAL has three distinct phases—in addition to the high-temperature phase and the fully collapsed low-temperature phase, there is a lattice animal phase. If $\varepsilon_+ > \varepsilon_-$, the collapse of the SASAL occurs in not one but two stages as the temperature is reduced: the SASAL first collapses to form a "branched polymer" and then at lower temperatures collapses still further to become a compact globule. The SASAL is therefore a strictly self-avoiding loop in 2D Euclidean space that has a two-stage collapse analogous to that found by Orlandini *et al.*

Consider the equilibrium statistical mechanics of a self-avoiding loop (SAL) of N occupied bonds on the hexagonal lattice (Fig. 1). For simplicity, we shall take one of the bonds in the loop to be held fixed. Note that the lattice dual to the hexagonal lattice is a triangular lattice. If one of the edges of a hexagon is occupied, we will say that the triangular lattice site at the center of this hexagon is "adjacent" to the occupied edge. Similarly, we say that this site is adjacent to the SAL itself.

To assign an energy to a given loop configuration L, we first color the dual lattice sites adjacent to the loop. Sites inside the loop are colored black, while sites outside the loop are colored white. We assign an energy $\varepsilon_+ \geq 0$ to the black sites and an energy $\varepsilon_- \geq 0$ to the white sites. Let the number of black sites be $n_+(L)$ and the number of white sites be $n_-(L)$. The energy of a configuration L is $E(L) = \varepsilon_+ n_+(L) + \varepsilon_- n_-(L)$.

For $\varepsilon_+ = \varepsilon_- = 0$, our SASAL is a SAL without self-attraction. On the other hand, if either ε_+ or ε_- is posi-

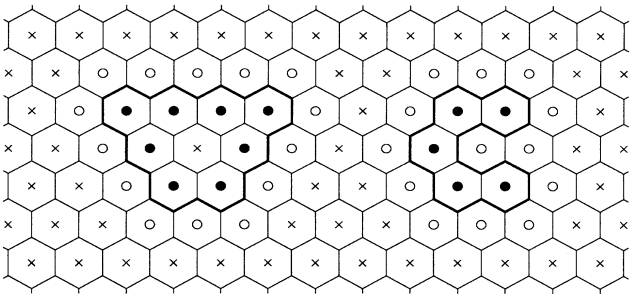

FIG. 1. Two SASAL's of 22 monomers (bold solid lines) on the hexagonal lattice (solid lines). Sites on the dual triangular lattice are black (solid circles), white (open circles), or uncolored (×'s). The SASAL on the left has energy $8\varepsilon_+ + 14\varepsilon_-$, while the one on the right has energy $5\varepsilon_+ + 13\varepsilon_-$.

tive, the loop is self-attracting, since configurations L with the smallest values of $n_+(L)$ and $n_-(L)$ have the lowest energies (Fig. 1).

Our SASAL reduces to the polymer loop of Coniglio *et al.* [4] for $\varepsilon_+ = \varepsilon_-$. The study of this polymer loop has provided considerable insight into the nature of the θ point in 2D. To understand the physical significance of our SASAL for general values of ε_+ and ε_-, consider the case $\varepsilon_+ > \varepsilon_-$. In this case, the inside of the SAL attracts itself more strongly than the outside does. A polymer loop adsorbed on a solid substrate is usually modeled by a 2D SASAL. If the polymer loop has different side groups on its inner and outer "surfaces," and if the inner side groups attract each other more strongly than the outer side groups do, then the polymer loop should be modeled by a SASAL with $\varepsilon_+ > \varepsilon_-$.

SASAL's have also been studied as simple models of 2D "vesicles" [8–10]. The inner surface of a real three-dimensional vesicle could attract itself more strongly than the outer surface does if the inner and outer surfaces have different chemical compositions. Vesicles of this kind can be treated using techniques similar to those applied here, and will be discussed elsewhere [11].

Just as in the case of the self-attracting polymers introduced by Coniglio *et al.* [4] and Duplantier and Saleur [6], there are attractive interactions between nearest-neighbor and next-nearest-neighbor pairs of monomers in our SASAL. There are interactions only between nearest-neighbor pairs of monomers in traditional lattice models of the θ point [1]. Our SASAL has a single collapse transition when $\varepsilon_+ = \varepsilon_-$. This transition is referred to as a θ' point to distinguish it from the usual θ point [4].

The partition function for a loop of N monomers is

$$Z(x,y,N) = \sum_{L'} x^{n_+(L')} y^{n_-(L')} . \tag{1}$$

Here $\beta \equiv T^{-1}$, $x \equiv \exp(-\beta\varepsilon_+)$, $y \equiv \exp(-\beta\varepsilon_-)$, and the sum runs over all SAL configurations L'. The Boltzmann weight of the loop configuration L is

$$w(L,x,y,N) = x^{n_+(L)} y^{n_-(L)} / Z(x,y,N) . \tag{2}$$

I will now show that for $x+y=1$, our SASAL can be mapped onto the hull of a site percolation cluster on the hexagonal lattice. Following Ref. [12], we shall take the hull of a percolation cluster to be a SAL on the hexagonal lattice. Consider an arbitrary bond in the hull. By definition, one of the triangular lattice sites adjacent to this bond is occupied, while the other is not. If the triangular lattice sites inside the hull and adjacent to it are occupied, the hull is an external percolation hull; otherwise, it is an internal percolation hull.

Consider an arbitrary self-avoiding loop L on the hexagonal lattice. The number of triangular lattice sites that are adjacent to L and that are inside [outside] the loop will be denoted $n_+(L)$ [$n_-(L)$]. The probability that a given bond B belongs to an external percolation hull of length N is given by

$$P(p,N) = \sum_{L'} p^{n_+(L')} (1-p)^{n_-(L')} . \tag{3}$$

Here the sum runs over all SAL's L' of length N that contain B. If it is given that the bond B belongs to an external hull of length N, the probability of a particular external hull configuration L is

$$p(L,p,N) = p^{n_+(L)} (1-p)^{n_-(L)} / P(p,N) . \tag{4}$$

We are now ready to construct our mapping. Combining Eqs. (3) and (4) with Eqs. (1) and (2), we obtain

$$Z(p,1-p,N) = P(p,N) , \tag{5}$$

and

$$w(L,p,1-p,N) = p(L,p,N) . \tag{6}$$

Analogous relations exist between the SASAL and internal percolation hulls, but these will not be needed, and so we will not pause to discuss them.

We have shown that for $x+y = \exp(-\beta\varepsilon_+) + \exp(-\beta\varepsilon_-) = 1$, our SASAL is equivalent to an external percolation hull for site percolation on the hexagonal lattice with $p=x$. Accordingly, we will refer to the line $x+y=1$ in the parameter space of the SASAL as the "percolation line."

I shall now discuss the phase diagram of the SASAL. We shall confine our attention to the case $\varepsilon_+ \geq \varepsilon_-$. In our discussion, we will use the mapping just described in combination with what is known about the behavior of percolation hulls in 2D.

At $T=\infty$, the self-avoiding loop is not self-attracting, and it has the same scaling properties as a SAW. Thus, the radius-of-gyration exponent ν is exactly $\frac{3}{4}$ [13]. The mean area A enclosed by the SASAL scales as $A \sim N^{3/2}$, and so the area enclosed by the SASAL has fractal dimension 2 [8,10]. Throughout its entire high-temperature phase, the scaling properties of the loop are the same as at $T=\infty$. As the temperature is reduced from infinity, on the other hand, the effect of the attractive interactions becomes more important. At low temperatures, the SASAL collapses and the radius-of-gyration exponent takes on the value $\nu = \frac{1}{2}$.

Consider the case $\varepsilon_+ = \varepsilon_-$. For $x = y = \frac{1}{2}$, the SASAL is equivalent to the external hull of a site percolation

cluster on the triangular lattice at $p=\frac{1}{2}$. Using this fact, Coniglio *et al.* [4] argued that $x=y=\frac{1}{2}$ is the θ' point, and that $T_{\theta'}=\varepsilon_+/\ln 2$. The value of ν at the θ' point, ν_t, is exactly $\frac{4}{7}$.

We now turn to the case $\varepsilon_+ > \varepsilon_-$. Recall that for $x+y=1$, the SASAL is equivalent to the hull of a percolation cluster with $p=x$. For $p<p_c=\frac{1}{2}$, only finite percolation hulls exist. In this regime, percolation clusters with linear dimensions large compared to the correlation length ξ have the same fractal dimension as lattice animals in 2D [14]. Using a transfer-matrix method, Derrida and Stauffer [15] obtained the estimate $D=1.5607\pm0.0004$ for the fractal dimension of lattice animals in 2D. Comparable estimates were obtained by others [16,17]. The fractal dimension of the hull cannot exceed the fractal dimension of the cluster itself, and so the fractal dimension of the hull of a lattice animal must certainly be less than 2. Thus, the segment of the percolation line with $p<p_c$ cannot lie in the low-temperature phase of the SASAL. This segment cannot lie in the high-temperature phase of the SASAL either, as I now argue. A 2D lattice animal has fractal dimension $D=1.5607\pm0.0004$, and so its hull encloses an area with a fractal dimension of roughly 1.56. This means that the SASAL encloses an area with a fractal dimension $D=1.5607\pm0.0004$ on the segment of the percolation line with $p<\frac{1}{2}$. In contrast, the area enclosed by the SASAL in its high-temperature phase has fractal dimension 2. Hence, the segment of the percolation line with $p<p_c$ cannot lie in the high-temperature phase of the SASAL.

We have seen that the segment of the percolation line with $p<\frac{1}{2}$ lies in a phase distinct from both the high- and low-temperature phases, as shown in Fig. 2. In this phase, the SASAL has the same fractal dimension as the hull of a 2D lattice animal. We refer to this phase of the SASAL as the "lattice animal" or "branched polymer" phase.

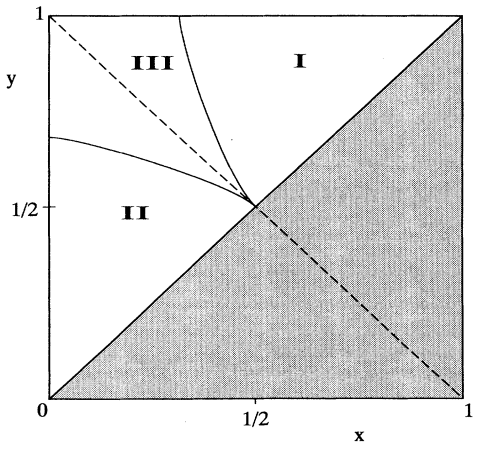

FIG. 2. Schematic phase diagram of the SASAL for $x \leq y$. The high-temperature, low-temperature, and lattice animal phases are labeled I, II, and III, respectively. The dashed line is the percolation line $x+y=1$.

Although the fractal dimension of the hull of a 2D lattice animal has not yet been determined, there is reason to believe that it is the same as that of the lattice animal itself. Lubensky and Isaacson [18] argued that trees and lattice animals are in the same universality class, and this is supported by numerical evidence (see Ref. [19] and references therein). Clearly, the bulk and hull fractal dimensions coincide for trees. Accordingly, I expect that the same is true of lattice animals. If this is so, the fractal dimension of a lattice animal hull is roughly 1.56 in 2D. (None of the results that follow depends on the validity of this speculation.)

At first sight, it is perhaps surprising that the SASAL has a phase in which its scaling behavior is the same as that of the hull of a lattice animal. To shed light on this, we consider the SASAL with $\varepsilon_+ > 0$ and $\varepsilon_- = 0$. For simplicity, we shall discuss the case in which $N=4M+2$, where M is a positive integer, but similar considerations hold for general values of N. An allowed conformation of the SASAL can be constructed as follows: We begin with a tree of M occupied sites on the *dual* triangular lattice. (A tree is a cluster of sites with no loops.) The corresponding SASAL configuration on the hexagonal lattice consists of those bonds that belong to one and only one hexagon with an occupied dual lattice site at its center. It can be shown that this configuration is a ground state of the SASAL, and that all the ground states of the SASAL can be constructed in this fashion [11].

In the limit in which $\varepsilon_+ \to \infty$ and $\varepsilon_- = 0$, only the ground-state configurations of the SASAL are allowed states. Thus, for $x=0$ and $y=1$ the SASAL with $N=4M+2$ monomers can be mapped onto a tree of M sites on the dual lattice. We conclude that for $x=0$ and $y=1$ the SASAL has the same scaling behavior as a lattice tree. Since lattice trees are in the same universality class as lattice animals [18,19], we have confirmed the existence of a lattice animal phase.

Let us now consider the general case in which $0<\varepsilon_-<\varepsilon_+<\infty$. In this case, the SASAL must pass through the lattice animal phase as the temperature is reduced because $y=x^{\varepsilon_-/\varepsilon_+}$. Thus, the collapse of the SASAL does not occur at a single temperature. Instead, two distinct phase transitions occur as the temperature is reduced. When the temperature is reduced below a certain temperature T_1, the attraction between the inner walls of the SASAL leads to its partial collapse. For temperatures less than T_1 but greater than a second transition temperature T_2, the SASAL is treelike (Fig. 3). As the temperature is further reduced, the attraction between the branches of the SASAL becomes increasingly important. At the transition temperature $T=T_2$, the

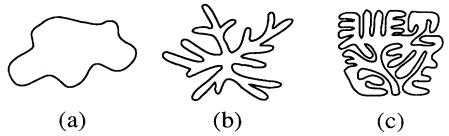

FIG. 3. Sketches of the SASAL for (a) $T>T_1$, (b) $T_1>T>T_2$, and (c) $T_2>T$.

SASAL undergoes a second collapse. For $T < T_2$, the SASAL is fully collapsed and its fractal dimension is 2 [20]. This sequence of phase transitions is strikingly similar to that found by Orlandini *et al.* [2] in their study of a self-attracting self-avoiding trail on the Sierpinski gasket.

As we have already noted, for $x = 0$ and $y = 1$ the SASAL can be mapped onto a lattice tree without self-attraction. More generally, the SASAL reduces to a self-attracting lattice tree with contact interactions for $x = 0$ and $0 \leq y \leq 1$. As y is reduced from 1, the attraction between the branches of the tree becomes increasingly important, and, at a critical value of y, the tree collapses. This collapse transition has recently been studied by exact enumeration [21]. Now consider the case in which ε_+ is finite but is still greater than ε_-. The collapse transition at $T = T_2$ should be in the same universality class as the collapse of a self-attracting tree with contact interactions in 2D. The transition that occurs at $T = T_1$ has not yet been studied, however. Monte Carlo or exact enumeration studies of this phase transition would be of considerable interest.

In summary, I have shown that for a range of parameter values, a certain self-attracting self-avoiding loop can be mapped onto the hull of a percolation cluster in 2D. This mapping was used to argue that the SASAL has three phases, one of which is a "branched polymer" phase. If $\varepsilon_+ > \varepsilon_-$, the collapse of the SASAL occurs in two stages as the temperature is reduced: the SASAL first collapses to form a "branched polymer," and then at lower temperatures collapses still further to become a compact globule.

In this Rapid Communication, I considered a SASAL on the hexagonal lattice with a particular kind of monomer-monomer interaction, so that analytical results could be obtained. However, I believe that the results obtained here are quite general, and apply to *any* adsorbed polymer loop whose inner "surface" attracts itself more strongly than the outer "surface" does.

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