STATISTICAL MECHANICS OF POLYMER MODELS

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1 Introduction

The standard models used in the statistical mechanics of polymers are combinatorial structures such as self-avoiding walks, lattice polygons and lattice trees. These systems have been studied by combinatorial and probabilistic approaches, by numerical methods including Monte Carlo techniques, and using a variety of techniques from statistical mechanics. There are many challenging open questions, partly motivated by problems from molecular biology, especially for the more physically relevant models in low dimensions. These include questions about entanglement complexity of ring polymers, phase transitions such as polymer adsorption and polymer collapse, and extensions to random copolymers. In this report, we survey this area and highlight aspects that were discussed at the BIRS workshop, May 10-15, 2003, as well as important open questions. There are a number of books [1, 2, 3] and review articles [4, 5] which give useful background information.

2 Polymer Models

Polymer models have attracted serious attention from mathematicians and physicists since the 1950's. In the simplest case of linear polymer molecules, the polymer consists of a set of identical monomers attached sequentially. The monomers can be numbered $j = 0, 1, 2, \ldots n$ and we say that the polymer has $n + 1$ monomers or a degree of polymerization of $n + 1$. If the polymer is in dilute solution, so that each polymer molecule can be regarded as behaving independently, the polymer will behave differently depending on the quality of the solvent. If the solvent is *good* then the essential features are (i) the flexibility and connectivity of the polymer and (ii) the fact that monomers take up space to the exclusion of other monomers. This space exclusion is called the *excluded volume effect* and it is this phenomenon which makes the problem difficult to model. Random walk models capture the flexibility and connectivity but do not model the excluded volume effect. The model which has been used since the 1950's is a *self-avoiding walk* on a lattice.

Consider the d-dimensional hypercubic lattice $\mathbb{Z}^d$ where the vertices are the integer points in $\mathbb{R}^d$ and the edges connect pairs of vertices which are unit distance apart. An n-edge self-avoiding walk on $\mathbb{Z}^d$ is a set of vertices $j = 0, 1, 2, \ldots n$ such that vertices j and $j + 1$ are unit distance apart on the lattice and all the vertices of the walk are distinct vertices in the lattice. Suppose for example that $d = 2$ (ie the square lattice) and, to be definite, let the walk start at the origin. If we write c_n for the number of distinct n-edge self-avoiding walks then $c_1 = 4$, $c_2 = 12$ and $c_3 = 36$. The first

interesting question is the number of 4-edge walks, c_4. We have to consider the number of ways for the walk to self-intersect at the fourth step. It is easy to see that $c_4 = 3c_3 - 8 = 100$.

One can construct upper and lower bounds on c_n by counting subsets and supersets. If we attach a coordinate system to the lattice $\mathbb{Z}^d$ in the obvious way then we see that walks which only add steps in positive coordinate directions are self-avoiding so $c_n \geq d^n$. Similarly, if we consider all walks except those with a step which is an immediate reversal of the previous step, then we have $c_n \leq 2d(2d-1)^{n-1}$. An early result about the asymptotic behaviour of c_n is due to Hammersley [6] who showed that the limit

$$\lim_{n\to\infty} n^{-1} \log c_n = \inf_{n>0} n^{-1} \log c_n \equiv \kappa_d \tag{1}$$

exists. κ_d is the *connective constant* of the lattice $\mathbb{Z}^d$. The above inequalities imply that $\log(d) \leq \kappa_d \leq \log(2d-1)$ and it is not too difficult to improve these bounds although the precise value of κ_d is not known for any $d \geq 2$. (Using non-rigorous numerical methods we know the value of κ_2 very precisely [7, 8] and we have fairly precise estimates also for $d = 3$ [9].)

A related question is how quickly the limit is approached. For any d, Hammersley and Welsh [10] showed that

$$\kappa_d \leq n^{-1} \log c_n \leq \kappa_d + O(n^{-1/2}) \tag{2}$$

so that c_n increases no faster than $e^{\kappa_d n + O(\sqrt{n})}$. Hara and Slade [11, 12] showed that, for $d \geq 5$, $c_n = A_d e^{\kappa_d n}(1 + o(1))$ and it is generally believed that a similar result holds for $d = 4$ but with a log correction and that, for $d = 2, 3$,

$$c_n = A_d n^{\gamma_d - 1} e^{\kappa_d n}(1 + o(1)). \tag{3}$$

The critical exponent γ_2 is thought to have the value $43/32$ [13, 14] and there is a good numerical estimate of γ_3 [9]. If equation (3) were true, then

$$\lim_{n\to\infty} \frac{c_{n+1}}{c_n} = e^{\kappa_d}. \tag{4}$$

Equation (4) has up to now only been proved for $d \geq 5$ [11, 12]; the best that is known for $d = 2, 3, 4$ is that

$$\lim_{n\to\infty} \frac{c_{n+2}}{c_n} = e^{2\kappa_d}, \tag{5}$$

which was proved by Kesten [15] based on a pattern theorem argument. A *pattern* is any fixed self-avoiding walk; a specific pattern P is said to occur in another self-avoiding walk ω if a translate of P is a subwalk of ω. A *proper pattern* or *Kesten pattern* is a pattern which can occur three times (ie as three distinct subwalks) in at least one long self-avoiding walk. Given a proper pattern P, Kesten's pattern theorem says that all but exponentially few sufficiently long self-avoiding walks contain P with a positive density. More precisely, given P there exists an $\epsilon > 0$ such that

$$\limsup_{n\to\infty} n^{-1} \log c_n(\epsilon n, P) < \kappa_d, \tag{6}$$

where $c_n(\epsilon n, P)$ is the number of n-step self-avoiding walks in which the pattern P occurs at most ϵn times. Kesten's Pattern Theorem has had many applications beyond the proof of equation (5) and some of these are discussed later in this report.

For a polymer in dilute solution in a good solvent, a standard assumption for the self-avoiding walk model is that each n-step walk, starting at the origin, is an equally likely configuration for the polymer. Then, for example, there is interest in the average metric properties of the polymer and their dependence on the excluded volume effect. One metric property is the end-to-end distance of a walk, that is the euclidean distance between the 0'th and the n'th vertex of an n-step walk. Letting s_n denote the root mean square end-to-end distance over all n-step self-avoiding walks, it is believed that

$$s_n = B_d n^{\nu_d}(1 + o(1)). \tag{7}$$

For n-step random walks on $\mathbb{Z}^d$, it is known that the root mean square end-to-end distance equals $n^{1/2}$. For $d \geq 5$, it is known that equation (7) holds with $\nu_d = 1/2$ but for $d \leq 4$, the best that is known rigorously is that $s_n \leq n$. Numerical and other evidence suggests that $\nu_2 = 3/4$ [13, 14], $\nu_3 \approx 0.588$ [16, 17] and $\nu_4 = 1/2$ with logarithmic corrections. Other measures of the polymer's size (in units of length) such as the root mean square radius of gyration are also expected to have the form given in equation (7) where the amplitude B_d may be dependent on the particular measure but the exponent ν_d is not.

Define the generating function

$$C(x) = \sum_n c_n x^n. \tag{8}$$

The series converges for $x < x_c = e^{-\kappa_d}$ and diverges for $x \geq x_c$. The functional form given in (3) implies that, close to x_c, the generating function $C(x)$ behaves as

$$C(x) \sim \frac{A_d}{(x_c - x)^{\gamma_d}}, \tag{9}$$

and this is an example of a *scaling function*. Given a point y in $\mathbb{Z}^d$, let $c_n(0, y)$ be the number of n-step self-avoiding walks starting at the origin and ending at y. The generating function

$$G_x(0, y) = \sum_n c_n(0, y) x^n \tag{10}$$

is known as the *two point function* and x_c is also its radius of convergence for any $y \neq 0$. Note that assuming equations (3) and (7) hold implies [1] that

$$\sum_y |y|^2 G_x(0, y) \sim \text{const.}(x_c - x)^{-2\nu_d - \gamma_d}. \tag{11}$$

It was observed numerically [18] that critical exponents such as ν and γ depend on the dimensionality of the problem but not on the particular lattice being studied, although the connective constant is a lattice dependent property. This is the idea of *universality*; certain aspects of the problem (such as critical exponents) do not depend on microscopic details of the model but change if parameters such as dimensionality change. In 1972 de Gennes [19] pointed out that self-avoiding walks are the zero spin space dimension case of a spin model in D spin dimensions and d spatial dimensions. Critical exponents depend on d and D but not on the lattice being considered. Because of the connection to spin models $C(x)$, defined above, is called the *susceptibility* and γ is the *susceptibility critical exponent*. Off-lattice models are thought to have the same exponents as these lattice models provided that the forces are repulsive and short-ranged [17, 20]. Similarly, lattice walks with other forms of short range repulsion, such as neighbour-avoiding walks [21] and spread out walks, have the same critical exponents. The exponent value $\nu_3 \approx 0.588$ has been observed experimentally in light scattering measurements of the radius of gyration of very long polymers in dilute solution in good solvents [22].

Based on the assumption of universality, it is also expected that there is a continuum model which is obtained from an appropriate *scaling limit*, where the step lengths of an n-step walk on the lattice are scaled by a function of n ($(Bn)^{-\nu_d}$, say, for some B) and then $n \to \infty$, and that this model has the same critical exponents as the original lattice model. This assumption combined with nonrigorous renormalization group techniques and conformal field theory arguments led to conjectured values for critical exponents such as γ_d and ν_d [13, 14, 17]. For $d \geq 5$, Hara and Slade [11, 12] proved that such a scaled self-avoiding walk converges in distribution to Brownian motion, i.e. Brownian motion is the scaling limit of self-avoiding walks. For $d = 4$, it is believed, but not yet proved, that the scaling limit is also Brownian motion but with a logarithmic scaling correction. Most recently, for $d = 2$, Lawler *et al* [23] proved that if the scaling limit exists for self-avoiding walks and if it satisfies an appropriate conformal invariance condition, then the scaling limit must be stochastic Loewner evolution with speed $\kappa = 8/3$, $SLE_{8/3}$; SLE_κ is a family of stochastic processes

introduced by Schramm [24] that is parametrized by a one-dimensional Brownian motion with speed κ. The critical exponents for $SLE_{8/3}$ can be obtained rigorously and the results of Lawler *et al* [23] predict the same critical exponents as the conformal field theory arguments. The same critical exponents had also been predicted using 2D quantum gravity arguments [25]. For this approach, one considers a polymer model on a random planar graph instead of on a lattice and then Knizhnik *et al*'s [26] KPZ map is used to predict critical exponents [27]. Evidence from numerical studies is consistent with all these critical exponent predictions, and hence the evidence is mounting that the assumptions underlying these predictions for $d \leq 4$ must be valid for self-avoiding walk models.

Ring polymers have a particular interest because of their connection to circular DNA molecules. In three dimensions they can be knotted or linked and we shall return to these phenomena in a later section. In the same way that self-avoiding walks are a model of linear polymers, ring polymers can be modelled by self-avoiding polygons. A *self-avoiding polygon* on the lattice $\mathbb{Z}^d$ is a connected subgraph of the lattice with all vertices of degree 2. Self-avoiding polygons are counted modulo translation. Let p_n be the number of self-avoiding polygons with n edges. On the square lattice ($d = 2$), $p_4 = 1$, $p_6 = 2$ and $p_8 = 7$. We note that for n even

$$\sum_{y:|y|=1} c_{n-1}(0, y) = 2np_n. \tag{12}$$

It is known [28] that

$$\lim_{n\to\infty} n^{-1} \log p_n = \sup_{n>0} n^{-1} \log p_n = \kappa_d \tag{13}$$

so that the numbers of polygons and self-avoiding walks grow at the same exponential rate. It is believed that $p_n \sim \text{const.} n^{\alpha-3} e^{\kappa_d n}$ where α is the heat capacity exponent in the associated spin model. Self-avoiding walks and polygons are expected to have the same metric exponent ν and hyperscaling connects the exponents α and ν by the relation $2 - \alpha = d\nu$ [1]. Define the generating function

$$P(x) = \sum_n p_n x^n. \tag{14}$$

$P(x)$ converges for $x < x_c$ and diverges for $x > x_c$. If hyperscaling holds and the conjectured values for ν are correct then $\alpha < 1$ in all dimensions and $P(x)$ converges at $x = x_c$ [1].

The value of the connective constant κ is not known rigorously for any lattice but there is a non-rigorous argument [13, 14] for the honeycomb lattice that $\kappa = \log \sqrt{2 + \sqrt{2}}$. The best estimates of the connective constant for other lattices come from exact enumeration of walks or polygons and, in two dimensions, much longer series are available for the numbers of polygons.

There are corresponding lattice models of branched polymers. The two most widely used are *lattice animals* (ie connected subgraphs of the lattice) and *lattice trees* (lattice animals with no cycles). If a_n and t_n are the numbers of lattice animals and lattice trees with n vertices (counted up to translation) then it is known that the limits

$$\lim_{n\to\infty} n^{-1} \log a_n \equiv \log \lambda \tag{15}$$

and

$$\lim_{n\to\infty} n^{-1} \log t_n \equiv \log \lambda_0 \tag{16}$$

exist, and that $\lambda_0 < \lambda$. It is believed that $a_n \sim \text{const.} n^{-\theta} \lambda^n$ and $t_n \sim \text{const.} n^{-\theta_0} \lambda_0^n$ and that $\theta = \theta_0$. Parisi and Sourlas [29] gave arguments for the values of θ in two and three dimensions and Brydges and Imbrie [30, 31] have now given a rigorous version of these arguments. For sufficiently large dimensions, Hara and Slade [32] proved $\theta_0 = 5/2$ and that ν, the radius of gyration exponent for trees, is $1/4$. Also, Derbez and Slade [33] proved that the scaling limit for high dimensional trees is integrated super-Brownian excursion (ISE).

Recently an analogue of Kesten's pattern theorem has been proved for lattice animals by Madras [34]. His approach to the proof differs from the approach that applies to the self-avoiding walk case and his approach can also be applied to obtain a pattern theorem for other lattice clusters such as lattice trees. One consequence of his theorem is the following ratio limit:

$$\lim_{n\to\infty} \frac{a_{n+1}}{a_n} = \lambda. \tag{17}$$

We can also consider connected subgraphs of the lattice with fixed homeomorphism type. For given d, suppose that the maximum vertex degree of the graph defining the homeomorphism type τ is less than or equal to $2d$. Let $g_n(\tau)$ be the number of embeddings of τ (lattice subgraphs homeomorphic to τ) in $\mathbb{Z}^d$ with n edges. Then

$$\lim_{n\to\infty} n^{-1} \log g_n(\tau) = \kappa_d \tag{18}$$

independent of τ [35]. Given any lattice subgraph homeomorphic to τ, each edge of τ corresponds to a path, called a *branch*, of the lattice subgraph. For the study of polymer networks it is also of interest to consider $\hat{g}_n(\tau)$, the number of n-edge embeddings of τ in $\mathbb{Z}^d$ with the property that each branch of the embedding has $O(n)$ edges. In this case one can also prove that

$$\lim_{n\to\infty} n^{-1} \log \hat{g}_n(\tau) = \kappa_d \tag{19}$$

independent of τ [36, 37]. Duplantier [38] has predicted the τ dependence on the critical exponent γ_τ for $\hat{g}_n(\tau)$, assuming that $\hat{g}_n(\tau) = A_d n^{\gamma_\tau - 1} e^{\kappa_d n}(1 + o(1))$. Holmes *et al* [39] have proved Gaussian behaviour in dimension greater than four for a related model, in which the branches of the embedding are composed of mutually avoiding spread-out self-avoiding walks.

2.1 Exactly solvable models

From the above discussion it is clear that rigorous results on self-avoiding walks are difficult to obtain and hence there has been some interest in devising simpler models which are exactly solvable and can be used to explore phenomena such as universality and the forms of scaling functions. As an example we shall consider Dyck paths. These are walks on the square lattice where

1. steps are allowed in the $(1,1)$ and $(1,-1)$ directions,
2. the walk starts at the origin and ends on the line $y = 0$, and
3. no vertex of the walk has negative y-coordinate.

Let the number of Dyck paths with n edges be d_n and define the generating function

$$D(z) = \sum_{n\geq 0} d_n z^n \tag{20}$$

where $d_0 = 1$ by convention. By a factorization argument

$$D(z) = 1 + z^2 D(z)^2 \tag{21}$$

so that

$$D(z) = \frac{1 - \sqrt{1 - 4z^2}}{2z^2} \tag{22}$$

from which we see that $d_n \sim$ const. $n^{-3/2} 2^n$. For these walks the connective constant is $\log 2$ and the critical exponent corresponding to γ is $-1/2$. In general for such directed models, the value of the connective constant gives a lower bound on the connective constant for self-avoiding walks but the exponent tells us nothing about the value of γ for self-avoiding walks, although it is reassuring to see a form similar to that in eqn (3). One can extend this type of analysis to other exactly solved sets of walks [3, 40]. If the set is larger (ie grows at an exponentially faster rate) then one obtains a better bound on the connective constant of self-avoiding walks. Another way to extend these models is by adding energy terms to model adsorption or collapse, as discussed in later sections. We note also that some progress has been made recently towards understanding why some lattice models are exactly solvable and others are apparently difficult to solve [41, 42].

3 Phase Transitions in Polymer Models

For polymers in a poor solvent or interacting with a surface, short range attractive interactions between monomers or between monomers and surface molecules cannot be ignored. For these situations the assumption that each polymer configuration is equally likely is not valid. Instead the standard model is a self-avoiding walk model for which the probability that a particular n-step walk occurs is now assumed to be a function of temperature and one or more appropriate "local" features of the self-avoiding walk such as the number of vertices of the walk in the surface, in the case of a polymer interacting with a surface. These models are called interacting self-avoiding walk models. For such models, one of the main questions of interest is whether or not a phase transition occurs for the model, ie whether or not there exists a temperature, T_c, at which the limiting free energy for the model is non-analytic.

Two interacting self-avoiding walk models have received a great deal of attention, namely, self-avoiding walk models of the adsorption transition and self-avoiding walk models of the collapse transition. There are also versions of these models for self-avoiding polygons, lattice trees, lattice animals, and lattice subgraphs with fixed homeomorphism type. Recently, there has also been much interest in interacting random copolymer models where there is a random distribution in the polymer of more than one type of monomer. There are versions of adsorption and collapse models for random copolymers and in addition there are models of the localization transition. We discuss progress on the study of these interacting polymer models next.

3.1 Adsorption at a surface

In this case, the typical situation is to consider a polymer in dilute solution where the polymer is tethered to a surface. It is assumed that there is a short range interaction between the monomers and the surface. For the self-avoiding walk model of this situation, the surface is represented by the hyperplane $z = 0$ in $\mathbb{Z}^d$, where a point in $\mathbb{Z}^d$ is assumed to have coordinates $(x, y, ..., z)$. The main results were obtained by Hammersley *et al* [43] who investigated two self-avoiding walk models of adsorption. For the first model, the walk is tethered to the surface and cannot penetrate it. In this case, $c_n^+(v)$, the number of self-avoiding walks in $z \geq 0$, starting at the origin, and with $v + 1$ vertices in $z = 0$, is considered. Each walk counted in $c_n^+(v)$ is considered to be equally likely and, more generally, the probability of an n-step walk with $v + 1$ vertices (or visits) to $z = 0$ is assumed to have the form

$$\frac{e^{\beta v}}{Q_n^+(\beta)} \tag{23}$$

for β real and where the normalization term, $Q_n^+(\beta)$, is given by

$$Q_n^+(\beta) = \sum_v c_n^+(v) e^{\beta v} \tag{24}$$

and is known as the *partition function* for the model. The limiting free energy is defined to be

$$\mathcal{F}^+(\beta) = \lim_{n\to\infty} n^{-1} \log Q_n^+(\beta), \tag{25}$$

where the limit has been proved to exist for all β and is a convex nondecreasing function of β [43]. Hammersley *et al* proved further that there exists $\beta_c^+ > 0$ for this model such that

$$\begin{aligned} \mathcal{F}^+(\beta) &= \kappa_d \qquad \text{for } \beta \leq \beta_c^+ \\ \text{and } \mathcal{F}^+(\beta) &> \kappa_d \qquad \text{for } \beta > \beta_c^+ \end{aligned} \tag{26}$$

and hence $\beta = \beta_c$ is a point of nonanalyticity of $\mathcal{F}^+(\beta)$. Given any β, let $\langle v_n(\beta)\rangle$ be the expected number of visits of an n-edge self-avoiding walk to the surface $z = 0$. Because of the convexity of $\mathcal{F}^+(\beta)$,

$$\lim_{n\to\infty} \frac{\langle v_n(\beta)\rangle}{n} = \frac{d\mathcal{F}^+(\beta)}{d\beta} \tag{27}$$

and this derivative exists for almost all β. At each such β value for $\beta > \beta_c^+$, the derivative is known to be positive. It is not known, however, if $\mathcal{F}^+(\beta)$ is continuously differentiable at $\beta = \beta_c^+$. β_c is known as the *adsorption transition critical point*. For $\beta < \beta_c^+$, contacts with the surface are not favoured enough to overcome the loss of entropy that would result from frequent visits to the surface, while for $\beta > \beta_c^+$ this no longer holds and the walk is considered adsorbed to the surface since there is a non-zero fraction of vertices of the walk in the surface.

Hammersley *et al* [43] also considered a related model in which the surface is penetrable. In this case the partition function is given by

$$Q_n(\beta) = \sum_v c_n(v) e^{\beta v}, \tag{28}$$

where $c_n(v)$ is the number of n-step self-avoiding walks starting at the origin with $v+1$ vertices in $z = 0$. The limiting free energy, given by

$$\mathcal{F}(\beta) = \lim_{n\to\infty} n^{-1} \log Q_n(\beta), \tag{29}$$

exists and is a convex nondecreasing function of β [43]. In this case, there exists $\beta_c \geq 0$ such that

$$\begin{aligned} \mathcal{F}(\beta) &= \kappa_d \qquad \text{for } \beta \leq \beta_c \\ \text{and } \mathcal{F}(\beta) &> \kappa_d \qquad \text{for } \beta > \beta_c \end{aligned} \tag{30}$$

and it is also known that $\beta_c < \beta_c^+$. For both models, it is believed that at the critical point $\lim_{n\to\infty} \frac{\langle v_n(\beta)\rangle}{n} = 0$, however, this has not been proved. It is also believed, based on numerical evidence, that $\beta_c = 0$.

Exactly solvable, eg partially directed walk and Dyck path, versions of these models have been investigated. As an example we shall consider the adsorption of Dyck paths. Let $d_n(v)$ be the number of n-edge Dyck paths with v visits to the line $y = 0$ and define

$$G(x,z) = \sum_{n,v} d_n(v) x^v z^n. \tag{31}$$

An equation for G can be obtained by the factorization argument used in section 2.1, giving

$$G(x,z) = 1 + xz^2 D(z) G(x,z) \tag{32}$$

or, equivalently,

$$G = \frac{2}{2 - x + x\sqrt{1-4z^2}}. \tag{33}$$

G is singular when the square root is zero (ie when $z = 1/2$) and when the denominator is zero. These two branches meet at $x_c = 2$ which is the location of the adsorption transition in this model. The model shares some of the broad general features of the self-avoiding walk model of polymer adsorption but, of course, the two models disagree in detail. Interestingly, there is evidence that they have the same value (1/2) for the crossover exponent, which describes the shape of the free energy curve in the adsorbed phase, close to the phase transition. More complicated and interesting directed walk models can also be solved exactly using a variety of different and complementary approaches [3, 40].

3.2 The Collapse Transition

Experimental evidence [44] shows that for high molecular weight polymers in dilute solution, either as the temperature or solvent quality is reduced the polymers go from typically being spread out in a coil-like configuration to being compact in a ball-like configuration. This transition occurs over a short temperature range, providing evidence for the existence of what's known as the *collapse phase transition*. This transition is thought to be driven by a combination of a short range attraction of

monomers with each other and a short range repulsion between monomers and solvent molecules. For the standard self-avoiding walk model of this phenomenon, the energy of a configuration is assumed to be proportional to the number of nearest neighbour contacts of the walk; a *nearest neighbour contact* of a self-avoiding walk is defined to be any edge of the lattice which joins two vertices of the walk but is not an edge of the walk. In this case the partition function of the model is

$$Q_n^{isaw}(\beta) = \sum_{\ell} c_n(\ell) e^{\beta \ell} \tag{34}$$

where $c_n(\ell)$ is defined to be the number of n-step self-avoiding walks starting at the origin with ℓ nearest neigbour contacts. The limit which defines the limiting free energy for this model,

$$\lim_{n\to\infty} n^{-1} \log Q_n^{isaw}(\beta) \equiv \mathcal{F}^{isaw}(\beta) \tag{35}$$

has been proved to exist for all $\beta \leq 0$ [45], however, the standard approach for proving this limit exists does not work for $\beta > 0$. It is believed that $\mathcal{F}^{isaw}(\beta)$ exists for all β and the numerical evidence suggests that there exists a critical point, known as the *collapse transition critical point* or the θ-point, at $\beta = \beta_c^{isaw}$ where $\mathcal{F}^{isaw}(\beta)$ is nonanalytic and such that

$$s_n = \begin{cases} B_d n^{\nu_d} & \text{for } \beta > \beta_c \\ B_d^c n^{\nu_d^c} & \text{for } \beta = \beta_c \\ C_d n^{1/d} & \text{for } \beta < \beta_c \end{cases}, \tag{36}$$

where it is believed that $\nu_d^c = 1/2$ for all $d \geq 3$ and $\nu_2^c = 4/7$. For the corresponding self-avoiding polygon model, it can be proved that the limiting free energy does exist for all β [45], however, the existence of the collapse transition critical point has not been proved for either the walk or polygon model. Numerical evidence [45] suggests that the critical point is the same for the self-avoiding walk and polygon models. For $d > 3$, it is believed that mean field theory should hold for interacting self-avoiding walks but this has not been proved. The $d = 4$ case has been studied by Prellberg and Owczarek [46] using Monte Carlo methods.

In the lattice animal version of this model, it is useful to introduce a two variable partition function

$$Q_n^{ianimal}(\beta_1, \beta_2) = \sum_{\ell, s} a_n(\ell, s) e^{\beta_1 \ell + \beta_2 s} \tag{37}$$

where $a_n(\ell, s)$ is the number of n-vertex lattice animals having ℓ nearest neighbour contacts and s solvent contacts, ie edges in the lattice from a vertex in the animal to a vertex not in the animal. In this case, one can prove that the corresponding limiting free energy, $\mathcal{F}^{ianimal}$, exists and is a convex function for all β_1 and β_2 [47]. Furthermore, by exploiting the connection between lattice animals and percolation clusters it is possible to prove that there exists at least one critical point for $\mathcal{F}^{ianimal}$ (corresponding to the bond percolation critical point) where a collapse transition is believed to occur. It is believed that there is a whole curve of collapse transition critical points in the (β_1, β_2)-plane [47, 48].

While the proof of the existence of a collapse phase transition for self-avoiding walks remains elusive, there are some exactly solvable models of collapse. Brak *et al* [49] derived an exact expression for the generating function $G(x, y) = \sum_{n,\ell} e_n(\ell) x^\ell y^n$ where $e_n(\ell)$ is the number of n-step partially directed walks on the square lattice with ℓ nearest-neighbour contacts and showed that this implied that the free energy was non-analytic. There are also other exactly solved models of collapse [50] and also exactly solved models of self-interacting walks interacting with a surface [40]. Dhar [51] has also solved a directed animal model of collapse.

3.3 Random Copolymers

Polymers are frequently composed of more than one type of monomer, eg biopolymers such as proteins are composed of different types of amino acids. In some circumstances local interaction

properties are dependent on the specific type of monomer involved in the interaction. To investigate the effect this has on phase transitions, there has been much interest in the study of random copolymers.

For the standard self-avoiding walk model, the relevant situation is when the randomness is quenched, that is, we assume that the sequence of monomer types making up a linear polymer is randomly chosen according to a given probability distribution but that once it is chosen the polymer's monomer sequence is fixed. In the simplest model there are two types of monomers, A and B, and the monomer sequence or *colouring* of a linear polymer composed of n monomers is given by a sequence $\chi = \chi_1, \chi_2, ..., \chi_n$, where the χ_i are independent and identically distributed random variables equal to A with probability p and B with probability $1-p$. Once chosen χ is fixed and then each configuration of the polymer with the same energy is considered to be equally likely. Thus for the case of random copolymer adsorption at an impenetrable surface we suppose that only the A monomers interact with the surface. Given a colouring χ, the partition function is then given by

$$Q_n^+(\beta|\chi) = \sum_{v_A} c_n^+(v_A|\chi) e^{\beta v_A}, \tag{38}$$

where $c_n^+(v_A|\chi)$ is the number of n-step self-avoiding walks, starting at the origin, confined to $z \geq 0$, with j'th vertex ($j > 0$) coloured by χ_j, and with v_A A-vertices in $z = 0$. Now in order to investigate the adsorption transition, one is interested in the *limiting quenched average free energy*

$$\bar{\kappa}(\beta) \equiv \lim_{n\to\infty} \langle n^{-1} \log Q_n^+(\beta|\chi) \rangle \tag{39}$$

where $\langle\cdot\rangle$ denotes the expected value over all colourings χ. The limit defining $\bar{\kappa}(\beta)$ has been proved to exist and $\bar{\kappa}(\beta)$ is a convex nondecreasing function of β [52]. Furthermore there exists a critical point $\beta = \beta_c^{rca+}(p) \geq \beta_c^+$ corresponding to an adsorption phase transition for this model and $\beta_c^{rca+} > \beta_c^+$ for $0 < p < 1$. It has also been proved [52] that the limiting free energy is *self-averaging* for this model, that is,

$$\lim_{n\to\infty} n^{-1} \log Q_n^+(\beta|\chi) = \bar{\kappa}(\beta) \tag{40}$$

with probability one and bounds have been obtained on the extent of this self-averaging [53, 54] for finite values of n. Similar results can be obtained for the case of adsorption at a penetrable surface. It is also known under mild additional conditions that the energy, the average number of surface contacts, self-averages but there remain open questions regarding the self-averaging of other thermodynamic quantities such as the heat capacity [55].

The case of homopolymer adsorption at a penetrable surface can also be generalized to investigate a phenomenon known as *localization at a surface* for random copolymers. In this case we suppose that there is an interface at $z = 0$ separating two different solvents or two liquid phases. It is assumed that A monomers interact with the liquid in $z > 0$, B monomers interact with the liquid in $z < 0$, and all monomers (regardless of type) interact equally with the interface $z = 0$. Experimental evidence for related systems indicates that in the appropriate temperature regime the polymer is localized near the surface and intersects it frequently while for other temperatures the polymer is either found primarily above or below the interface and hence delocalized. Given χ, the relevant three parameter partition function is now given by

$$Q_n^{loc}(\alpha, \beta, \gamma|\chi) = \sum_{v_A, v_B, w} c_n(v_A, v_B, w|\chi) e^{\alpha v_A + \beta v_B + \gamma w}, \tag{41}$$

where $c_n(v_A, v_B, w|\chi)$ is the number of n-step self-avoiding walks, starting at the origin, with j'th vertex ($j > 0$) coloured by χ_j, and with v_A A-vertices in $z > 0$, v_B B-vertices in $z < 0$, and w vertices in $z = 0$. The *limiting quenched average free energy*

$$\bar{\kappa}(\alpha, \beta, \gamma) \equiv \lim_{n\to\infty} \langle n^{-1} \log Q_n^{loc}(\alpha, \beta, \gamma|\chi) \rangle \tag{42}$$

has been proved to exist and it is a convex nondecreasing function of α, β, γ [56, 57]. Focussing on $p = 1/2$ for convenience, for $\gamma = 0$ there exist two symmetric phase boundaries (one with $\beta \geq \alpha$ and

the other with $\beta \leq \alpha$) in the (α, β)-plane that bound the localized phase. The two phase boundaries intersect at the origin in this case and, for example, if one stays in the half-plane $\beta \leq \alpha$ there is a curve of critical points corresponding to a phase transition from the localized phase to the phase in which the polymer is delocalized into $z > 0$. Further rigorous results are known regarding the γ dependence of the phase diagram but many interesting open questions remain. In particular for $\alpha = \beta = 0$, the model is equivalent to homopolymer adsorption at a penetrable surface so that the critical value of γ is β_c which is believed to be zero (but this is not yet proved). For all $\gamma > \beta_c$, the point $(0, 0, \gamma)$ is in the localized phase.

There are no exactly solvable models for localization of a random copolymer at a surface. However, the first models used to study these phenomena were (bilateral) Dyck path models [58, 59]. Qualitatively the results are the same for the Dyck path models and the self-avoiding walk models, but it is possible to prove some stronger results in the case of Dyck path models. In particular, Biskup and den Hollander [59] obtained results about path properties. For the self-avoiding walk model no corresponding path results are available.

As it is difficult to obtain rigorous results for models of homopolymer collapse, the analysis of random copolymer collapse is even more difficult and few results have been obtained [60].

4 Random Knotting and Entanglement Complexity

Ring polymers in three dimensions behave like simple closed curves in $\mathbb{R}^3$ and can be knotted or linked. Knots and links have been observed in circular DNA molecules and are thought to act as topological obstructions to cellular processes such as replication.

4.1 Frisch-Wasserman-Delbruck Conjecture

In the 1960s Frisch and Wasserman, and Delbruck, conjectured that sufficiently long ring polymers would be knotted with high probability. To address this question mathematically we need a model of a ring polymer, and the first model for which a result of this nature was obtained was a polygon on the simple cubic lattice $\mathbb{Z}^3$. Let p_n be the number of n-edge polygons on this lattice and p_n^o be the number of these that are unknotted. It is known [61] that

$$\lim_{n\to\infty} n^{-1} \log p_n^o \equiv \kappa_o < \kappa_3 \tag{43}$$

so that unknotted polygons are exponentially rare in the set of polygons, for n large. The key ingredients in the proof of this result are:

(i) There are no "antiknots" - that is, if k is a given knot type and ϕ is the unknot then there does not exist a knot k' such that $k \# k' = \phi$. This means that a knotted circle cannot be unknotted by tying a second knot at a different location in the circle.

(ii) A knotted ball pair is a 3-ball B^3 and a 1-ball B^1, properly embedded in B^3 such that the pair (B^3, B^1) is not homeomorphic to the trivial ball pair (in which B^1 is a diameter of the 3-ball $\{x, y, z | x^2 + y^2 + z^2 \leq 1\}$). Given a knot type k we can construct an embedding (τ) of an arc (ie a 1-ball) in $\mathbb{Z}^3$ such that the union of the dual 3-cells forms a 3-ball and the ball pair is knotted. Moreover, if the vertices of degree 1 of B^1 are connected by an arc entirely outside B^3, the resulting simple closed curve has knot type k.

(iii) Using Kesten's pattern theorem one can proved that the arc τ occurs at least once on all but exponentially few sufficiently long polygons.

These arguments can be extended in various ways. Somewhat weaker results can be obtained for some cases of polygons in $\mathbb{R}^3$ (not lying on a lattice) such as equilateral polygons and Gaussian random polygons [62]. For instance, for Guassian random polygons, Diao *et al* [62] proved that there exists a constant $\epsilon > 0$ such that Gaussian random polygons with n edges are knotted with probability at least $1 - e^{-n^\epsilon}$ for n sufficiently large. For the lattice case one can prove that prime knots are exponentially rare and, indeed, that the typical knots in long polymers are very complex [35].

4.2 Polygons with Fixed Knot Type

Suppose that we fix the knot type of the polygons and write $p_n(k)$ for the number of n-edge polygons in $\mathbb{Z}^3$ with knot type k. Perhaps surprisingly we do not know if the limit

$$\lim_{n\to\infty} n^{-1} \log p_n(k) \tag{44}$$

exists (except when $k = \phi$, the unknot). Arguments similar to those outlined in section 4.1 can be used to establish that

$$\limsup_{n\to\infty} n^{-1} \log p_n(k) < \kappa_3 \tag{45}$$

for every k, and a concatenation of polygons with knot types k_1 and k_2 shows that

$$p_{n_1}(k_1)p_{n_2}(k_2) \leq 2p_{n_1+n_2}(k_1\#k_2). \tag{46}$$

Setting $k_1 = k$, $k_2 = \phi$ then establishes that

$$\liminf_{n\to\infty} n^{-1} \log p_n(k) \geq \kappa_o \tag{47}$$

but it is an open question as to whether this is an equality or a strict inequality.

There are many numerical (Monte Carlo) investigations of polygons (both lattice polygons and various off-lattice models in $\mathbb{R}^3$) with fixed knot type [63, 64, 65]. The evidence suggests that, for $k \neq \phi$, the probability that an n-edge polygon has knot type k, increases for small n, goes through a maximum, and decreases for large n. The location of the maximum depends on k and increases as the knot becomes more complex. Very little is known rigorously about this behaviour.

4.3 Localization of knots

For a given knot type, is the knot typically localized in a long polygon of this knot type? This question sounds somewhat nebulous (since knotting is a topological property) but it can be made more precise by imagining splitting the n-edge polygon into two arcs of length m and $n - m$, connecting each of these up to form two separate polygons (eg by running parallel rays from the end points of an arc to a point at infinity) and checking the knot types of the resulting (infinite) simple closed curves. If one of them (the one originally having m edges, say) is of knot type k and the other is unknotted we can say that the knot is localized in an arc of length m. If $m = o(n)$ for typical polygons we can regard the knot as typically localized for large n.

This was a contentious question for many years with evidence being presented for both points of view. It is probably fair to say that the numerical evidence now favours localization [66]. Again the evidence is numerical and nothing is known rigorously. A related question is how the mean square radius of gyration depends on knot type. If we write $\langle R_n^2(k)\rangle$ for the mean square radius of gyration for n-edge (lattice) polygons with knot type k, then a reasonable guess is that

$$\langle R_n^2(k)\rangle = A(k)n^{2\nu(k)}(1 + B(k)n^{-\Delta(k)} + ...) \tag{48}$$

Numerical evidence suggests that the exponents $\nu(k)$ and $\Delta(k)$ are independent of k and, perhaps, that the amplitude $A(k)$ is independent of k [64]. This would be consistent with knots being localized and all the knot dependence appearing in the correction-to-scaling term, with knot-dependent amplitude $B(k)$.

4.4 Topological Restrictions and Excluded Volume

Consider a model of a ring polymer in $\mathbb{R}^3$ where there is no excluded volume. For instance, think of an equilateral ring polymer constrained to form a ring so that its first and last vertices are identical. This is just a random walk in $\mathbb{R}^3$, constrained to return to the origin at its last step. The mean-square radius of gyration $\langle R_n^2\rangle \sim n^{2\nu}$ where n is the number of steps in the walk (or bonds in the ring) and

$\nu = 1/2$. Suppose now that the ring is constrained to have a given knot type. Does this topological restriction change the value of ν from its random walk value of $1/2$ to the excluded volume value of about 0.588? This question has been investigated numerically (by Monte Carlo techniques) and there is evidence that the topological restriction changes the universality class to that of polymers with excluded volume (ie $\nu \approx 0.588$) [67].

4.5 Connections to DNA experiments

Knots and links can act as topological obstructions to various cellular processes. For instance, in mitosis the two circular DNA molecules cannot separate during the formation of the daughter cells because they are linked, and bacteria cannot express genes on knotted plasmids. Organisms have a collection of enzymes (eg topoisomerases) which effect strand passages in DNA so that DNA molecules can be linked and unlinked, or knotted and unknotted, by these strand passages; the cell abhors topological entanglement in its genetic material, and uses topoisomerases to solve problems arising from such entanglements. There is considerable interest in understanding the mode of action of these enzymes and there has been a fruitful collaboration between topologists and molecular biologists to design and analyse experiments to probe the action of these enzymes [68, 69]. From the topological point of view the circular DNA molecule can be considered as a sum of two string tangles, with a numerator construction to form one or more (possibly knotted or linked) circles. The tangles which typically appear in the biological problems are rational tangles and the classification of these is well-understood. The biological assumption is that the action of the enzyme is confined to the tangle confined in a single 3-ball. By examining the products produced by the action of the enzyme on a given substrate (say an unknotted circular DNA molecule) one can deduce the probable mechanism of enzyme binding and action, in terms of how the broken DNA strands are spatially arranged before religation [70].

4.6 Knot Invariants and Knot Energies

A *knot invariant* is any function defined on the set of simple closed curves in $\mathbb{R}^3$ which is a constant for all simple closed curves with a fixed knot type k. If a simple closed curve's knot type is unknown, knot invariants can be useful for either determining the knot type or at least reducing the number of knot type possibilities. They can also be used as a way to compare two knot types, or, for example, measure the "complexity" of a knot. For example, the *minimum crossing number*, the minimum number of crossings in a regular projection of a knot, is a knot invariant. In the standard knot tables, the knot types are listed according to their minimum crossing number. *Thickness* is a geometrically based knot invariant of recent interest which has been defined and studied in [71, 72]. Recently there has also been much interest in the study of *knot energies*, real-valued and non-negative functions, usually only defined for either the space of smooth knots or the space of polygonal knots. The global minimum of such a function over a given knot type is another example of a knot invariant and any knot which is a global minimizer is referred to as an "ideal" representative of the knot type with respect to the given energy function. Just as with the case of crossing number, these knot energies provide ways to characterize and compare different knot types and sometimes they offer the advantage that they are easy to compute. Some examples of knot energies are möbius energies [73] and ropelength [74].

Since a wide variety of knot energy functions have been proposed and studied, it is important to develop criteria for assessing and comparing these functions so that one can use a "good" energy function for a given purpose. Diao *et al* [75] have developed criteria for assessing knot energies defined on equilateral polygonal knots. Equilateral polygonal knots are frequently used in computational studies and the knot energies used for these are often discrete versions of energy functions defined for smooth knots. Ideally a knot invariant derived from a knot energy function would be able to distinguish between all knot types; but this is something that would be difficult to prove. Failing that, one might ask that it would be able to distinguish a knot from the unknot. The minimum energy configuration for a given knot type may not be unique and may even be singular (ie edges may intersect or overlap) and hence one might ask that the minimum configuration at least be non-

singular. Also one might prefer the $n \to \infty$ limit (for n the number of edges in the polygon) to be well defined and, if the energy is a discrete version of an energy for smooth knots, that the limit be the smooth knot energy. Not all knot energies in use satisfy all these properties, however, there are some that do [75].

5 Conclusion

This is a rich field from which challenging combinatorial, probabilistic, topological, and geometrical problems have arisen. Significant advances have been made recently in, for example, understanding scaling limits in high dimensions and in the plane. However, there remain many interesting open problems especially in the study of interacting polymer and copolymer models, in the study of the entanglement complexity of polymers, and regarding finding efficient computational approaches for studying these models.

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