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On knots in a model for the adsorption of ring polymers

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Abstract. The occurence of knots in a model of a ring polymer interacting with a surface is considered. The polymer is described by a self-avoiding polygon (SAP) and interacts with the surface through a short-range interaction. It is proven rigorously that, for all non-zero temperatures, all except exponentially few SAPs contain a knot. We also show that the average knot complexity grows at least linearly with the length of the polymer, for sufficiently long polymers.

1. *Introduction*

The statistical mechanics of polymers has witnessed great progress ever since the discovery by de Gennes (1972) of a relation between physical quantities of long polymer chains and the properties of a ferromagnet near its critical temperature. This relation has led to a rather good and complete knowledge of the critical properties of linear polymers, especially in two dimensions where Coulomb gas and conformal invariance techniques have yielded whole classes of exactly known exponents (for an introduction, see e.g. Duplantier 1990).

Looking for new and interesting problems, researchers in the statistical mechanics of polymers have turned their attention in recent years to the investigation of geometrical and topological properties of polymers. Such quantities are especially relevant in the study of certain biopolymers such as DNA. One of the most interesting subjects in this respect is the occurence of knots in ring polymers.

When such a polymer is immersed in a good solvent, it can be modelled conveniently as a self-avoiding polygon on a lattice, e.g. the cubic lattice Z^3. The degree of polymerization of the polymer then corresponds to the number of vertices n of this polygon. As usual in equilibrium statistical mechanics, time averages over the dynamical history of the polymer are replaced by ensemble averages over the set of all polygons with n vertices. Each such polygon can be considered as an embedding of the circle in Z^3 and so one can ask the question whether or not such a polygon is knotted. A polygon is said to be unknotted when it can be deformed in a continuous way into a circle. A very important result in this respect was obtained by Sumners and Whittington (1988) who showed that the fraction of unknotted polygons goes to zero exponentially fast when $n \to \infty$. Stated more precisely, if p_n is the number of n-step polygons and p_n^0 is the number of unknotted n-step polygons, these authors showed that there exists a strictly positive constant α such that

$$\frac{p_n^0}{p_n} = \exp\left(-\alpha n + \mathrm{o}(n)\right). \tag{1.1}$$

There exist numerical estimates of the constant α appearing in (1.1) (Janse van Rensburg and Whittington 1990).

It is not enough to know that long polymers are knotted; one also wants to study how the 'complexity' of a knot changes with n. This problem was studied by Soteros *et al* (1992) who introduced the concept of a good measure of knot complexity. These authors where then able to show that for n large enough, all but exponentially few self-avoiding polygons have a complexity which is greater then Sn where S is some constant. Following this pioneering work the knotting properties of self-avoiding polygons were studied in various circumstances such as when the polygon is confined in a slab (Tesi *at al* 1994), or when attractive interactions between the monomers are introduced and the polymer collapses into a globule at low temperatures (Janse van Rensburg and Whittington 1990).

In this paper we study how the knot probability and complexity behave when two monomers of the polymer are attached to a surface, and when in addition the monomers can gain energy by adsorbing onto this surface. It is well known by now that in this case there exists a critical temperature below which a macroscopic fraction of the monomers are adsorbed on the surface (De'Bell and Lookman 1993). When the temperature approaches zero all monomers should be adsorbed on the surface and, as a planar self-avoiding curve is always unknotted, one thus expects that the knot probability will go to zero. In this paper we study this model using mathematically rigorous techniques. We will be able to prove that the fraction of unknotted polygons (defined with appropriate Boltzmann weights involving the inverse temperature β and the number of monomers in the surface) still goes to zero exponentially fast with a constant $\alpha(\beta)$ that is strictly positive (when $\beta < \infty$). In a forthcoming paper we will present numerical results for the function $\alpha(\beta)$.

This paper is organized as follows. In section 2 we introduce properly defined free energies for the present model and study some of their simple properties. In section 3 we study the Legendre transforms of these free energies which in section 4 will be used to prove the main result stated above. In section 5, we study how the complexity of knots changes when the temperature in our model is varied. Finally, in section 6 we present some concluding remarks.

2. The free energies $F(\beta)$ and $F^0(\beta)$

2.1.

We will work on the cubic lattice Z^3. The (integer) coordinates of the vertices of this lattice will be denoted by $w = (x, y, z)$. A self-avoiding walk (SAW) of n-steps is a sequence $\{w_0, w_1, \ldots w_n\}$ of $(n+1)$ distinct vertices, such that $|w_i - w_{i-1}| = 1$, $1 \leqslant i \leqslant n$. A special subset of the set of all self-avoiding walks is formed by the n-step self-avoiding circuits (SAC). These are n-step SAWs for which $|w_n - w_0| = 1$. In fact, any cyclic permutation of the vertices in a SAC, the reverse permutation of the vertices and any cyclic permutation of the reverse permutation of the vertices give rise to the same geometrical object. This set of $2(n+1)$ SACs will be called an n-step self-avoiding polygon (SAP).

The SAPs which we have defined in this way are not uniquely determined. From now on, by a SAP we will always mean a whole equivalence class of polygons whose edges can be put onto one another after any translation using a vector $v = (v_1, v_2, 0)$. Throughout this paper we will consider SAPs that visit the origin $(0, 0, 0)$ and for which $z_i \geqslant 0$, $0 \leqslant i \leqslant n$.

A *contact* is defined as a vertex of the SAP with $z = 0$. We denote by $p_n(m)$ the number of inequivalent n-step polygons with $m + 1$ contacts $(1 \leqslant m \leqslant n)$.

Each SAP can be considered as an embedding of the circle in Z^3. A SAP is then said to be *unknotted* if it is ambient isotopic to the unknot. We will denote by $p_n^0(m)$ the number of inequivalent n-step unknotted polygons with $m + 1$ contacts that pass through the origin.

We can now introduce the partition functions $Z_n(\beta)$ and $Z_n^0(\beta)$ as

$$Z_n(\beta) = \sum_m p_n(m) \exp(\beta m) \tag{2.1a}$$

and

$$Z_n^0(\beta) = \sum_m p_n^0(m) \exp(\beta m) . \tag{2.1b}$$

We shall, among other results, prove the following:
(i) The limits

$$F(\beta) = \lim_{n\to\infty} \frac{1}{n} \log Z_n(\beta) \tag{2.2a}$$

and

$$F^0(\beta) = \lim_{n\to\infty} \frac{1}{n} \log Z_n^0(\beta) \tag{2.2b}$$

exist for all β.

(ii) Our main result is the following theorem.

Theorem 1. Let $F(\beta)$ and $F^0(\beta)$ be as defined in (2.2); then

$$\alpha(\beta) = F(\beta) - F^0(\beta) > 0 \qquad \forall \beta < \infty . \tag{2.3}$$

If we introduce

$$P_n(\beta) = \frac{Z_n^0(\beta)}{Z_n(\beta)} \tag{2.4}$$

which we will call 'unknot probability', then (2.2) and (2.3) imply that for large n

$$P_n(\beta) = \exp(-\alpha(\beta)n + o(n)) \tag{2.5}$$

i.e. unknotted polygons are exponentially rare.

(iii) If we introduce a measure of the complexity of knots as in Soteros *et al* (1992), then we can show that for sufficiently large n, the average complexity (averaged with Boltzmann weights as in (2.1)) of n-step SAPs grows at least linearly with n.

2.2.

Our first aim is to prove the existence of the limits in (2.2). The proof is a combination of concatenation arguments for SAPs in the bulk (see, e.g. Madras and Slade 1993) and that for SAWs with at least one vertex in a surface (Hammersley *et al* 1982).

First we define the lexicographic ordering in Z^3. We say that $(a_1, a_2, a_3) < (b_1, b_2, b_3)$ if for some j $(1 \leqslant j \leqslant 3)$ we have $a_i = b_i, \forall 1 \leqslant i < j$ and $a_j < b_j$. Without loss of generality we will consider here the set $\mathcal{P}$ of polygons whose lexicographically smallest point is the origin. Next, we consider a special subset $\mathcal{Q}$ of $\mathcal{P}$. To define this set, take the maximum value of x for any vertex of the polygon, i.e determine $x_{\max} = \max_i x_i$. In general there can be several points of the SAP in the plane $x = x_{\max}$ (hereafter referred to as the upper tangent plane). The set $\mathcal{Q}$ then consists of those polygons for which the point $y = z = 0$ is the lexicographically smallest point in the plane $x = x_{\max}$. We will denote the point $(x_{\max}, 0, 0)$ by w_{ex}.

Let $\mathcal{Q}$ contain $q_n^0(m)$ unknotted polygons of n vertices and m contacts, and let

$$B_n^0(\beta) = \sum_m q_n^0(m) \exp \beta m . \tag{2.6}$$

As a first step we now prove that

$$\lim_{n\to\infty} \frac{1}{n} \log B_n^0(\beta)$$

exists.

Therefore, we pick two polygons p_1 (of n_1 steps and m_1 contacts) and p_2 (n_2 steps, m_2 contacts) in $\mathcal{Q}$. We translate p_2 by the vector $(x_{\max}^1 + 1, 0, 0)$ where in an obvious notation $x_{\max}^1 = \max_{i\in p_1} x_i$. Now there are two possibilities. To discriminate these one has to realize that in p_1 there are two bonds going to w_{ex}. One of them will certainly be in either the y ($I = 2$) or in the z ($I = 3$) direction. If the polygon p_2 has the bond going from the origin to the point e_I there is no problem in concatenating p_1 and p_2 into one (n_1+n_2)-step polygon with $m_1 + m_2$ contacts.

In the second case, when p_2 does not contain e_I we can always add four steps (leading to two new contacts) to p_1, translate p_2 by the extra vector e_1 and concatenate the two polygons. Figure 1 shows the two possiblities of how to add these extra steps (contacts).

Going back to the case in which the two polygons can be concatenated immediately, it is trivial to show that we can also add the extra steps/contacts shown in figure 1 to the concatenated polygons (in fact there is a third possibility here, but it is easy to extend the procedure of figure 1 to that case).

From a topological point of view concatenation amounts to a composition of knots (for a gentle introduction to knot theory, see Adams 1994). It is thus clear that a concatenation of two knotted polygons cannot give the unknot. Also notice that the concatenated polygon is still in $\mathcal{Q}$ and has $n_1 + n_2 + 4$ steps and $m_1 + m_2 + 2$ contacts. So, we arrive at the inequality

$$q_{n_1}^0(m_1) q_{n_2}^0(m_2) \leqslant q_{n_1+n_2+4}^0(m_1 + m_2 + 2) . \tag{2.7}$$

Hence,

$$\begin{aligned} B_{n_1}^0(\beta) B_{n_2}^0(\beta) &= \sum_{m_1=1}^{n_1} q_{n_1}^0(m_1) \exp \beta m_1 \sum_{m_2=1}^{n_2} q_{n_2}^0(m_2) \exp \beta m_2 \\ &\leqslant \sum_{m_1=1}^{n_1} \sum_{m_2=1}^{n_2} q_{n_1+n_2+4}^0(m_1 + m_2 + 2) \exp \beta(m_1 + m_2) . \end{aligned}$$

Let $m = m_1 + m_2 + 2$. Then,

$$\begin{aligned} B_{n_1}^0(\beta) B_{n_2}^0(\beta) &\leqslant \exp -2\beta \sum_{m=4}^{n_1+n_2+2} (m-3) q_{n_1+n_2+4}^0(m) \exp \beta m \\ &\leqslant (\exp -2\beta)(n_1 + n_2 - 1) \sum_{m=4}^{n_1+n_2+2} q_{n_1+n_2+4}^0(m) \exp \beta m . \end{aligned}$$

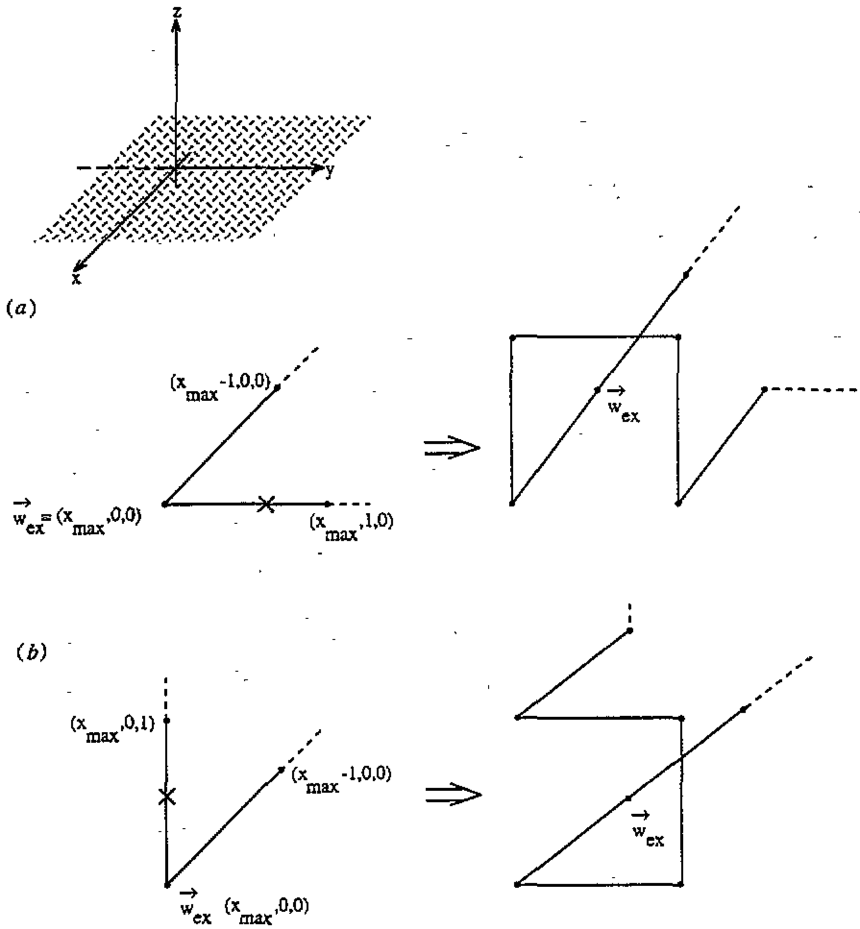

Figure 1. Rules for adding four steps (two contacts) to a polygon at $w_{\rm ex}$. Let i, j, k be unit steps in resp. the x, y, z directions. In (a) the crossed step is removed and replaced by the steps $\{i, k, j, -k, -i\}$. In (b) the crossed step is removed and replaced by the steps $\{i, j, k, -j, -i\}$. The full circles represent parts of the SAP that are not changed.

Adding the (positive) terms in $m = 1, 2, 3$ and $n_1 + n_2 + 4$ $(q_n^0(n-1) = 0)$ shows that

$$B_{n_1}^0(\beta) B_{n_2}^0(\beta) \leqslant (\exp -2\beta)(n_1 + n_2 - 1) B_{n_1+n_2+4}^0(\beta)\,.$$

Finally, we relabel the series $B_{n_1}^0(\beta)$ such that

$$a_4 = a_6 = 1$$

and

$$a_n = B_{n-4}^0(\beta)\,.$$

After taking logarithms on both sides we get

$$\log a_{n_1} + \log a_{n_2} \leqslant -2\beta + \log(n_1 + n_2 - 9) + \log a_{n_1+n_2}\,. \tag{2.8}$$

This shows that $-\log a_n$ is a (generalized) subadditive function of n. Because it is also bounded from below $(a_n = B_{n-4}^0(\beta) \leqslant Z_{n-4}(\beta) \leqslant (6 \exp \beta)^{n-4})$, it finally follows from the theory of subadditive functions (see theorem 2 in Hammersley 1962) that $\lim_{n\to\infty} \frac{1}{n} \log a_n$ exists, and that therefore $\lim_{n\to\infty} \frac{1}{n} \log B_n^0(\beta)$ also exists.

2.3.

The next step is to prove that

$$\lim_{n\to\infty} \frac{1}{n} \log Z_n^0(\beta) = \lim_{n\to\infty} \frac{1}{n} \log B_n^0(\beta) . \tag{2.9}$$

Since the set $\mathcal{Q}$ is a subset of $\mathcal{P}$ it is sufficient to prove that

$$\limsup_{n\to\infty} \frac{1}{n} \log Z_n^0(\beta) \leqslant \lim_{n\to\infty} \frac{1}{n} \log B_n^0(\beta) .$$

Consider any polygon in $\mathcal{P}$ and let k be its lexicographically largest point. There are two values of i such that this polygon contains the bond joining k to $k - e_i$. Take I to be the largest of these and denote by $p_n^0(m; k, I)$ the number of n-step unknotted polygons with m contacts and k and I fixed at a particular value. The number E of possible largest lexicographic points satisfies

$$E \leqslant (2n+1)^2(n+1) \tag{2.10}$$

for any n. We can now concatenate two polygons with the same k and I as follows. Reflect one of the polygons through its upper tangent plane and then translate the polygon by one lattice unit in the e_1-direction. This operation does not change the number of contacts, nor whether the polygon is unknotted or not (though the topological class of the knot may be changed under reflection). We can now concatenate the two polygons in the usual way and will, in this way, create a polygon in $\mathcal{Q}$. Hence, we arrive at the following inequality:

$$p_{n_1}^0(m_1; k, I) p_{n_2}^0(m_2; k, I) \leqslant q_{n_1+n_2}^0(m_1 + m_2) . \tag{2.11}$$

Then, if we define

$$Z_n^0(\beta; k, I) = \sum_{m=1}^{n} p_n^0(m; k, I) \exp(\beta m) \tag{2.12}$$

we have

$$(Z_n^0(\beta; k, I))^2 = \sum_{m_1=1}^{n} \sum_{m_2=1}^{n} p_n^0(m_1; k, I) p_n^0(m_2; k, I) \exp \beta(m_1 + m_2) .$$

If we denote $m = m_1 + m_2$ and use (2.11) we get

$$\begin{aligned}(Z_n^0(\beta; k, I))^2 &\leqslant \sum_{m=1}^{2n} (m-1) q_{2n}^0(m) \exp(\beta m) \\ &\leqslant (2n-1) B_{2n}^0(\beta) .\end{aligned} \tag{2.13}$$

Using Cauchy's inequality in combination with (2.10) gives

$$\begin{aligned}\left[Z_n^0(\beta)\right]^2 &= \left(\sum_{k,I} Z_n^0(\beta; k, I)\right)^2 \\ &\leqslant \sum_{k,I} 1 \sum_{k,I} Z_n^0(\beta; k, I)^2 \\ &\leqslant 4(2n+1)^4(n+1)^2(n-1) B_{2n}^0(\beta)\end{aligned}$$

or

$$Z_n^0(\beta) \leqslant 2(2n+1)^2(n+1)(n-1)^{\frac{1}{2}} B_{2n}^0(\beta)^{\frac{1}{2}}$$

and hence

$$\begin{aligned}\limsup_{n\to\infty} \frac{1}{n} \log Z_n^0(\beta) &\leqslant \limsup_{n\to\infty} \frac{1}{2n} \log B_{2n}^0(\beta) \\ &= \lim_{n\to\infty} \frac{1}{n} \log B_n^0(\beta) .\end{aligned} \tag{2.14}$$

This then proves the existence of $F^0(\beta)$ (see equation (2.2*b*)). In a completely similar way the existence of $F(\beta)$ can be proved.

2.4.

We now show that $F(\beta)$ (and $F^0(\beta)$) are convex functions of β. This is a simple consequence of Cauchy's inequality

$$\left[\sum_k a_k b_k\right]^2 \leqslant \sum_k a_k^2 \sum_l b_l^2 .$$

Indeed we have

$$\begin{aligned} Z_n(\beta_1) Z_n(\beta_2) &= \sum_{m_1} p_n(m_1) \exp(\beta_1 m_1) \sum_{m_2} p_n(m_2) \exp(\beta_2 m_2) \\ &\geqslant \left[\sum_m p_n(m) \exp((\beta_1+\beta_2)m/2)\right]^2 \\ &= Z_n\left(\frac{\beta_1+\beta_2}{2}\right)^2 \end{aligned}$$

or

$$\frac{[F(\beta_1)+F(\beta_2)]}{2} \geqslant F\left(\frac{\beta_1+\beta_2}{2}\right). \tag{2.15}$$

Because $F(\beta)$ is bounded (see subsection 2.5) in any interval, this is sufficient to have convexity. Convexity and boundedness in turn imply that $F(\beta)$ and $F^0(\beta)$ are continuous, that the derivative exists almost everywhere, and that left and right derivatives exist everywhere and are non-decreasing functions of β.

2.5.

To conclude this section, we give bounds for the functions $F(\beta)$ *and* $F^0(\beta)$ *and show that* $\forall\beta \leqslant 0, \alpha(\beta)$ is a constant (and strictly positive).

First, from Madras and Slade (1993), we know that

$$F(\beta = 0) = \log \mu_3 \tag{2.16}$$

where μ_3 is the $d = 3$ connective constant of SAWs and SAPs. Similarly if we define μ_3^0 as

$$F^0(\beta = 0) = \log \mu_3^0 \tag{2.17}$$

it was shown in Tesi *et al* (1994) that (result for the slab of width L with $L \to \infty$)

$$\mu_3^0 < \mu_3 . \tag{2.18}$$

Now, $\forall \beta \leqslant 0$, we have

$$Z_n^0(\beta) \leqslant \sum_m p_n^0(m) = Z_n^0(0) \tag{2.19}$$

and

$$Z_n^0(\beta) \geqslant p_n^0(1) \exp \beta . \tag{2.20}$$

Now, notice that from any polygon of n vertices and two contacts, we can create a polygon of $(n-2)$ vertices and m ($\geqslant 2$) contacts, and vice versa, by shifting the surface at $z = 0$ to $z = 1$. This does not change the knottedness of the polygon. Thus,

$$p_n^0(1) = \sum_m p_{n-2}^0(m) = Z_{n-2}^0(0) . \tag{2.21}$$

Combining (2.19) and (2.20) then gives, $\forall \beta \leqslant 0$

$$Z_{n-2}^0(\beta) \exp \beta \leqslant Z_n^0(\beta) \leqslant Z_n^0(0) .$$

From this it immediately follows that

$$F^0(\beta) = \log \mu_3^0 \qquad \forall \beta \leqslant 0 . \tag{2.22}$$

Similarly, one has

$$F(\beta) = \log \mu_3 \qquad \forall \beta \leqslant 0 \tag{2.23}$$

so that

$$\alpha(\beta) = \log \frac{\mu_3}{\mu_3^0} \qquad \forall \beta \leqslant 0 . \tag{2.24}$$

For $\beta > 0$, we get the following bounds on $F^0(\beta)$. First,

$$Z_n^0(\beta) \geqslant p_n^0(n) \exp(\beta n)$$

or

$$F^0(\beta) \geqslant \log \mu_2 + \beta \tag{2.25}$$

where μ_2 is the connective constant for two-dimensional SAWs and SAPs. The inequality (2.25) also holds for $F(\beta)$.

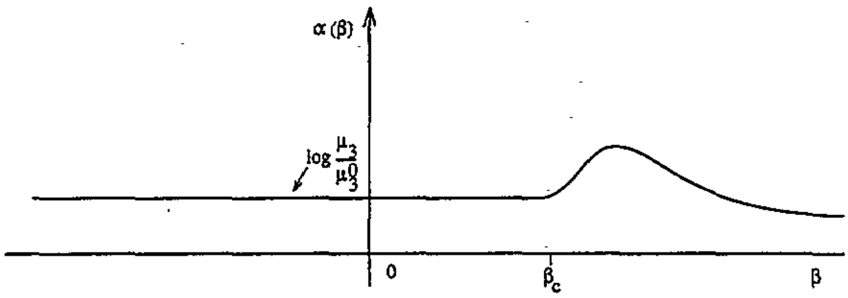

Figure 2. Conjectured behaviour for the function $\alpha(\beta)$. For $\beta \leqslant 0$ and for $\beta \to \infty$ the shape of α shown here is exact.

From equations (2.22) and (2.25) follows the existence of critical temperatures β_c^0 and β_c such that

$$F^0(\beta) = F^0(0) \qquad \forall \beta \leqslant \beta_c^0 \tag{2.26}$$

with

$$\beta_c^0 \leqslant \log \frac{\mu_3^0}{\mu_2}. \tag{2.27}$$

Again, a similar result holds for β_c.

We conclude with an upper bound for $F(\beta)$ (and thus for $F^0(\beta)$) and a conjecture. An evident upper bound for $Z_n(\beta)$ is

$$Z_n(\beta) \leqslant (6 \exp \beta)^n \qquad \forall \beta > 0. \tag{2.28}$$

From equations (2.25) and (2.28) we have

$$\lim_{\beta\to\infty} \frac{1}{\beta} F^0(\beta) = \lim_{\beta\to\infty} \frac{1}{\beta} F(\beta) = 1. \tag{2.29}$$

Finally we conjecture

$$0 < \beta_c < \beta_c^0. \tag{2.30}$$

This conjecture is based on the fact that (2.1b) contains less terms than (2.1a) and thus the latter sum can be expected (in the $n \to \infty$ limit) to be different from its $\beta = 0$ value more easily. Together with (2.3) and (2.24) this conjecture leads to the behaviour for $\alpha(\beta)$ sketched in figure 2. At β_c, $F(\beta)$, and as a consequence $\alpha(\beta)$ starts to increase. Then, at β_c^0 the free energy of unknotted polygons also starts to differ from its infinite temperature value. The maximum in $\alpha(\beta)$ occurs at the point where $F^0(\beta)$ starts to increase more rapidly then $F(\beta)$. At present, it is not clear at which value of the temperature this happens. The existence of a maximum in $\alpha(\beta)$ can also be expected on the basis of numerical work on polygons confined in a slab where the unknot probability is found to decrease if one reduces the distance between the slabs (Tesi *et al* 1994). One can think that increasing β is physically similar to confining the polymer between slabs of decreasing distance. Physically, the bump can be understood as follows. As soon as $\beta > \beta_c$ the polymer starts to shrink in the direction perpendicular to the surface. Confining the polymer in less space increases its knottedness. In a collapse transition this increase can continue all the way down to zero temperature. In the adsorption case, however, the polymer has the ability to extend in the direction parallel to the plane and to decrease thereby its knot probability and decrease its energy. It is the competition between these two effects which probably leads to the bump in figure 2.

We are currently investigating numerically the conjecture (2.30) and the behaviour of $\alpha(\beta)$.

3. The Legendre transforms $\phi(p)$ and $\phi^0(p)$

3.1.

A crucial role in the following will be played by the functions $\phi(p)$ and $\phi^0(p)$ which will be shown to be Legendre transforms of $F(\beta)$ and $F^0(\beta)$, respectively.

We start from (2.7). Defining

$$\begin{aligned} &b_4^0(m) = b_6^0(m) = 1 \qquad &&\forall m \\ &b_n^0(1) = b_n^0(2) = 1 \qquad &&\forall\, n \geqslant 8 \\ &b_n^0(m) = q_{n-4}^0(m-2) && \end{aligned}$$

otherwise we can rewrite (2.7) as

$$b_{n_1}^0(m_1) b_{n_2}^0(m_2) \leqslant b_{n_1+n_2}^0(m_1+m_2)\,. \tag{3.1}$$

Now take p to be a rational number in [0, 1] and denote by I_p the set of all integers n such that pn is an integer. Let n_1 and n_2 be in I_p. Then equation (3.1) implies

$$\log b_{n_1}^0(pn_1) + \log b_{n_2}^0(pn_2) \leqslant \log b_{n_1+n_2}^0(p(n_1+n_2))\,.$$

Because $b_n^0(m)$ is also bounded the following limit exists:

$$\phi^0(p) = \lim_{n\to\infty} \frac{1}{n} \log b_n^0(pn) \tag{3.2}$$

where the limit is taken through integers in I_p.

Secondly, if p and q are in [0, 1] and n is in $I_p \cap I_q$, equation (3.1) gives

$$\log b_n^0(pn) + \log b_n^0(qn) \leqslant \log b_{2n}^0((p+q)n)\,.$$

If we divide by n and let $n \to \infty$ through $I_p \cap I_q \cap I_{(p+q)/2}$ we can see that

$$\tfrac{1}{2}(\phi^0(p) + \phi^0(q)) \leqslant \phi^0\left(\frac{p+q}{2}\right).$$

From Hardy *et al* (1934) it then follows that for all α, β rational in [0, 1] and for all rational p and q

$$\alpha\phi^0(p) + \beta\phi^0(q) \leqslant \phi^0(\alpha p + \beta q)\,. \tag{3.3}$$

The inequality (3.3) allows us to extend the definition (3.2) to all real p in [0, 1]. We take $\phi^0(p)$ to be the continuous concave function of p that coincides with the previous definition of $\phi^0(p)$ at rational p. In a completely analogous way we can, starting from $q_n(m)$, defining $b_n(m)$ as in the beginning of this section, define a continuous and concave function $\phi(p)$ as

$$\phi(p) = \lim_{n\to\infty} \frac{1}{n} \log b_n(pn)\,. \tag{3.4}$$

In the rest of this section we will prove some important properties of $\phi(p)$ and $\phi^0(p)$ and especially their relation with $F(\beta)$ and $F^0(\beta)$.

3.2.

It is rather straightforward to show that

$$\begin{aligned} \phi(0) &= \log \mu_3 \qquad & \phi(1) &= \log \mu_2 \\ \phi^0(0) &= \log \mu_3^0 \qquad & \phi^0(1) &= \log \mu_2 . \end{aligned} \tag{3.5}$$

3.3.

In this subsection we will prove the following lemma.

Lemma 1.

$$\lim_{p\to 1} \frac{\mathrm{d}\phi}{\mathrm{d}p} = \lim_{p\to 1} \frac{\mathrm{d}\phi^0}{\mathrm{d}p} = -\infty . \tag{3.6}$$

Proof. Take any polygon p, element of the set $\mathcal{Q}$. Let p have n vertices and n contacts. We will now describe a process which we call 'trunk formation' to make a polygon of $n+2k$ vertices and n contacts starting from p. Pick k vertices of p (this can be done in $\binom{n}{k}$ ways). Then add vertices as follows:

(i) If w_i is a chosen vertex and none of its neighbours (along the polygon) is chosen, take w_{i+1} and add the vertices $w_i + e_3$ and $w_{i+1} + e_3$.

(ii) If the vertices w_i and w_{i+1} are chosen, but none of their neighbours are, then add the four vertices $w_i + e_3, w_i + 2e_3, w_{i+1} + 2e_3$ and $w_{i+1} + e_3$ to the polygon.

(iii) If the vertices $w_i, w_{i+1}, \ldots, w_{i+j}$ are chosen, add the following $2j$ vertices to the walk

$$\begin{aligned} &w_{i+j-1} + e_3, w_{i+j-1} + 2e_3, \ldots, w_{i+j-1} + je_3 \\ &w_{i+j} + je_3, w_{i+j} + (j-1)e_3, \ldots, w_{i+j} + e_3 . \end{aligned}$$

Notice that in this way we have created a polygon of $n+2k$ vertices and n contacts which is still in $\mathcal{Q}$, and that it is impossible to create knots by trunk formation. We thus arrive at the inequalities

$$q_{n+2k}(n) \geqslant \binom{n}{k} q_n(n) \tag{3.7a}$$

and

$$q^0_{n+2k}(n) \geqslant \binom{n}{k} q^0_n(n) . \tag{3.7b}$$

We will continue with (3.7a) but the same calculations can be done starting from (3.7b). We write $N = n + 2k$, so that

$$\frac{n}{N} = 1 - \frac{2k}{N} .$$

Defining $r = k/N$ we have that $n = (1-2r)N$ and

$$k = \frac{r}{1-2r} n .$$

(we will always have in mind a value of $r \to 0$). Now, we start from (3.7a) and we let $N \to \infty$ through I_{1-2r}. We get

$$\lim_{N\to\infty} \frac{1}{N} \log q_N((1-2r)N) \geqslant \lim_{N\to\infty} \frac{n}{N}\left[\frac{1}{n}\log\binom{n}{k} + \frac{1}{n}\log q_n(n)\right]$$

or

$$\phi(1-2r) \geqslant (1-2r)\left[\lim_{n\to\infty}\frac{1}{n}\log\binom{n}{k} + \phi(1)\right].$$

We then use (Madras *et al* 1988):

$$\lim_{n\to\infty}\frac{1}{n}\log\binom{an}{bn} = a\log a - b\log b - (a-b)\log(a-b)$$

with $a = 1$ and $b = r/(1-2r)$ and get

$$\phi(1-2r) \geqslant (1-2r)\left[-\frac{r}{1-2r}\log\frac{r}{1-2r} - \left(1-\frac{r}{1-2r}\right)\log\left(1-\frac{r}{1-2r}\right) + \phi(1)\right]$$

or

$$\phi(1) - \phi(1-2r) \leqslant r\log\frac{r}{1-2r} + (1-3r)\log\frac{1-3r}{1-2r} + 2r\phi(1).$$

Finally, we take $r \to 0$:

$$\frac{\mathrm{d}\phi}{\mathrm{d}p}(p=1) = \lim_{r\to 0}\frac{\phi(1)-\phi(1-2r)}{2r} \leqslant \lim_{r\to 0}\left[\frac{1}{2}\log\frac{r}{1-2r} + \frac{1-3r}{2r}\log\frac{1-3r}{1-2r}\right] + \phi(1).$$

Then using (3.5) and

$$\lim_{r\to 0}\frac{1-3r}{2r}\log\frac{1-3r}{1-2r} = -\frac{1}{2}$$

we get

$$\frac{\mathrm{d}\phi}{\mathrm{d}p}(p=1) \leqslant -\infty$$

which prooves lemma 1.

3.4.

In this subsection we shall prove that

$$F(\beta) = \sup_{0\leqslant p\leqslant 1}(\phi(p) + \beta p) \tag{3.8a}$$

$$F^0(\beta) = \sup_{0\leqslant p\leqslant 1}(\phi^0(p) + \beta p). \tag{3.8b}$$

Again we will give the proof for the unknotted case. First, from the theory of subadditive functions and from the definition (3.2) we have for finite n

$$\frac{1}{n}\log b_n^0(pn) \leqslant \phi^0(p)$$

or

$$b_n^0(pn) \leqslant \exp n\phi^0(p)$$

so that

$$\begin{aligned}
B_n^0(\beta) &= \sum_m q_n^0(m)\,\mathrm{e}^{\beta m} \\
&= \mathrm{e}^{-2\beta}\sum_m b_{n+4}^0(m+2)\,\mathrm{e}^{\beta(m+2)} \\
&\leqslant n\,\mathrm{e}^{-2\beta}\exp\left\{(n+4)\max_m\left[\phi^0\left(p=\frac{m+2}{n+4}\right)+\beta\frac{m+2}{n+4}\right]\right\} \\
&\leqslant n\,\mathrm{e}^{-2\beta}\exp\left\{(n+4)\sup_p\left[\phi^0(p)+\beta p\right]\right\}.
\end{aligned}$$

Taking logarithms, dividing by n and sending $n \to \infty$ gives

$$F^0(\beta) \leqslant \sup_p\left[\phi^0(p)+\beta p\right].$$

The reverse inequality is obtained as follows:

$$\begin{aligned}
Z_n^0(\beta) &= \sum_m p_n^0(m)\,\mathrm{e}^{\beta m} \geqslant \sum_m q_n^0(m)\,\mathrm{e}^{\beta m} \\
&\geqslant q_n^0(pn)\,\mathrm{e}^{\beta pn}.
\end{aligned}$$

The last inequality holds for all n in I_p (for all rational p). Consequently,

$$\log Z_n^0(\beta) \geqslant \log q_n^0(pn) + \beta pn$$

or

$$F^0(\beta) \geqslant \phi^0(p) + \beta p \qquad \forall p \in Q. \tag{3.9}$$

Hence equation (3.9) holds for all $p \in [0, 1]$ as a consequence of the way in which we constructed $\phi^0(p)$. Therefore

$$F^0(\beta) \geqslant \sup_p[\phi^0(p)+\beta p].$$

This proves (3.8*a*).

3.5.

As a corollary of the results (3.8) we have the following result:

$$\phi^0(p) = \inf_\beta [F^0(\beta) - p\beta] \tag{3.10a}$$

and

$$\phi(p) = \inf_\beta [F(\beta) - p\beta]\,. \tag{3.10b}$$

This is a simple consequence of (3.8) and the fact that $-\phi^0(p)$ and $-\phi(p)$ are convex functions. The result (3.10) is then a simple application of theorem VI.5.3 (e) in Ellis (1985). The result (3.10) is also the reason why we call $\phi^0(p)$ and $\phi(p)$ Legendre transforms of $F^0(\beta)$ and $F(\beta)$.

3.6.

The main result in this paper will be to prove theorem 1. This result will be proved in the next section and will be based on the following lemma.

Lemma 2. Let $F^0(\beta), F(\beta), \phi^0(p)$ and $\phi(p)$ be as defined above, then the following equivalence holds:

$$F(\beta) > F^0(\beta) \qquad \forall \beta < \infty$$

iff

$$\phi(p) > \phi^0(p) \qquad \forall 0 \leqslant p < 1\,.$$

Proof.

(i) Let

$$\phi(p) > \phi^0(p) \qquad \forall 0 \leqslant p < 1$$

or

$$\phi(p) + \beta p > \phi^0(p) + \beta p \qquad \forall 0 \leqslant p < 1\,. \tag{3.11}$$

The left- and right-hand side of (3.11) are both bounded functions on the interval [0, 1]. Thus, they reach their supremum in [0, 1]. Because of lemma 1, the supremum is reached in [0, 1), and so from (3.11)

$$F(\beta) = \sup_{0\leqslant p\leqslant 1} [\phi(p) + \beta p] > \sup_{0\leqslant p\leqslant 1} [\phi^0(p) + \beta p] = F^0(\beta)$$

where we used (3.8).

(ii) Similarly, let

$$\begin{aligned} &F(\beta) > F^0(\beta) \qquad \forall \beta < \infty \\ &F(\beta) - p\beta > F^0(\beta) - p\beta\,. \end{aligned} \tag{3.12}$$

Again, because these functions are bounded on any finite interval, they reach their infimum. From (2.29) it follows that the infimum is reached for finite β so that it follows from (3.10) and (3.12) that

$$\phi(p) > \phi^0(p)\,.$$

As a consequence of lemma 2, a proof that $\phi(p) > \phi^0(p)$ will imply that $\alpha(\beta) > 0$. Such a proof will be given in the next section.

4. Proof of theorem 1

We will prove theorem 1 by showing that $\phi^0(p) < \phi(p)$ if $0 \leqslant p < 1$.

Proof. (i) For any rational p, consider $q_n(pn)$ for $n \in I_p$. A special subset of the polygons in $\mathcal{Q}$ with $n+1$ vertices and $pn+1$ contacts is formed by those polygons which are a concatenation of a polygon of $pn+1$ vertices in the plane $z=0$ with a polygon of $n-pn$ vertices with all $z \geqslant 1$. Consequently,

$$q_n(pn) \geqslant r_{pn} q_{n-pn+1}(1) \tag{4.1}$$

where r_{pn} is the number of $(pn+1)$-step polygons in $\mathcal{Q}$ which have $(pn+1)$ contacts. The factor $q_{n-pn+1}(1)$ stems from the fact that from each polygon of $n-pn$ steps with $z \geqslant 1$ we can make a polygon of $n-pn+2$ vertices and two contacts. The arguments in subsection 2.2 and 2.3 can now be repeated to show that

$$\lim_{n\to\infty} \frac{1}{n} \log r_n = \log \mu_2 \,. \tag{4.2}$$

Taking logarithms in (4.1), dividing by n and sending $n \to \infty$ through I_p we get (note: $n \in I_p \Leftrightarrow n \in I_{1-p}$)

$$\begin{aligned}\phi(p) &= \lim_{n\to\infty} \frac{1}{n} \log q_n(pn)\\ &\geqslant p \lim_{n\to\infty} \frac{1}{np} \log r_{pn} + (1-p) \lim_{n\to\infty} \frac{1}{n(1-p)} \log q_{n-pn+1}(1)\\ &= p \log \mu_2 + (1-p) F(\beta = 0)\,.\end{aligned}$$

Using equation (2.16) finally gives

$$\phi(p) \geqslant p \log \mu_2 + (1-p) \log \mu_3 \,. \tag{4.3}$$

(ii) Secondly, we seek an upperbound to $\phi^0(p)$. To find this, we decompose each polygon in $\mathcal{Q}$ in 'trains' (which are consecutive steps which are contacts) and 'hoops' (which are consecutive steps which are not contacts). Let there be t trains ($t \geqslant 1$). For polygons we have necessarily that the number of hoops, h, must equal t (if $h > 0$). We write

$$q_n^0(pn) = \sum_{t,h} q_n^0(pn; t; h) \tag{4.4}$$

where $q_n^0(pn; t, h)$ is the number of n step unknotted polygons in $\mathcal{Q}$ which have pn contacts, t trains and h hoops. This sum can be further decomposed by indicating the number of steps $m_1', \ldots, m_t'$ in each of the trains, and the number of steps $m_1, \ldots, m_h$ in the hoops. In an obvious notation

$$q_n^0(pn) = \sum_{t,h} \sum_{\{m_i'\}} \sum_{\{m_i\}} q_n^0(pn; t, m_1', \ldots, m_t'; h, m_1, \ldots, m_h)\,. \tag{4.5}$$

To get an upper bound consider all trains and hoops as independent and forget the constraint $t = h$ for $h > 0$ and the constraint that the full polygon should be in $\mathcal{Q}$.

$$q_n^0(pn) \leqslant \sum_t \sum_h \sum_{\{m_j'\}} \sum_{\{m_i\}} \prod_i h_{m_i}^0 \prod_j t_{m_j'} \tag{4.6}$$

where $h_{m_i}^0$ is the number of unknotted hoops of m_i vertices (of course $\sum_i m_i = (1-p)n$) and t'_{m_j} is the number of trains with m_j' vertices ($\sum_j m_j' = pn + 1$). We can now use Kesten's bound (Kesten 1964) on the number of self-avoiding walks to find upper bounds for t'_{m_j}

$$t'_{m_j} \leqslant \mu_2^{m_j'} \exp[\mathrm{o}(m_j')] \,. \tag{4.7}$$

The number $h_{m_i}^0$ can be bounded from above by the number $c_{m_i}^{\bar{T}}$ which gives the number of SAWs of m_i steps which do not contain a trefoil. Because a SAW is not a Jordan curve one has to take care in defining a concept of (un)knottedness for it. This problem has been discussed by Sumners and Whittington (1988) and Janse van Rensburg *et al* (1992). Using the results of these authors, we arrives at

$$h_{m_i}^0 \leqslant c_{m_i}^{\bar{T}} \leqslant \mu_{\bar{T}}^{m_i} \exp[\leq (m_i)] \tag{4.8}$$

where $\mu_{\bar{T}}$ is a connective constant for SAWs which do not contain a (tight) trefoil. Finally,

$$\sum_t \sum_h \sum_{\{m_i'\}} \sum_{\{m_j\}} \leqslant P_D(n) \tag{4.9}$$

where $P_D(n)$ is the number of partitions of n into integers (which do not have to be distinct). From Hardy and Ramanujan (1917)

$$P_D(n) = \frac{1}{4\sqrt{3}n} \exp\left[\pi\sqrt{\frac{2n}{3}} + \mathrm{o}(n)\right]. \tag{4.10}$$

Putting the results (4.7)–(4.10) into (4.6) gives

$$q_n^0(pn) \leqslant \mu_2^{pn} \mu_{\bar{T}}^{n-pn} \exp[\leq (n)]$$

from which finally

$$\phi^0(p) \leqslant p \log \mu_2 + (1-p) \log \mu_{\bar{T}} \,. \tag{4.11}$$

(iii) Finally, using Kesten's pattern theorem, it follows from the work of Sumners and Whittington (1988) that

$$\log \mu_{\bar{T}} < \log \mu_3 \,. \tag{4.12}$$

Hence, from (4.3), (4.11) and (4.12) we get

$$\phi^0(p) < \phi(p)$$

which prooves theorem 1.

5. The complexity of knots

5.1.

In the previous sections, we have investigated the problem of whether or not polymers adsorbed onto a surface contain a knot. Intuitively one suspects that as a polymer gets absorbed it will at first become more entangled and hence some appropriate measure of knot complexity will increase. In this section we study this question rigourously. We therefore first need an appropriate definition of knot complexity. First we remind the reader that any complicated knot K can be uniquely decomposed into prime knots (see, e.g. Adams 1994). We write

$$K = K_1 \# \cdots \# K_n$$

where the operation # represents knot product. A good measure of knot complexity is intuitively any number that can be associated to a knot and that increases as the knot gets more complicated; secondly we demand that when a complicated knot is composed of, for example, r trefoils together with other knots, that its complexity should at least be larger than r times the complexity of a trefoil. More precisely, Soteros *et al* (1992) define a good measure of knot complexity as a function M from the set $\mathcal{K}$ of (equivalence classes of) knots K on to $[0, \infty)$ which satisfies; (i) $M(\text{unknot}) = 0$, (ii) there exists $K \in \mathcal{K}$ such that $M(nK\#L) \geqslant nM(K) > 0, \forall L \in \mathcal{K}$. Examples of such measures of complexity are crossing number, span of any non-trivial Laurent knot polynomial or the log of the order of a knot, etc. By the order of a knot we mean $|\Delta_K(-1)|$ where $\Delta_K(t)$ is the Alexander polynomial of the knot. For these measures the trefoil 3_1 has the property $M(n3_1) \geqslant nM(3_1) > 0$.

In the following M, will be any of these good measures of knot complexity. It was then shown by Soteros *et al* (1992) that for all n which are large enough, all but exponentially few SAPs have an M-complexity which exceeds Sn where S is some constant (we will be more precise below). In the following we will extend this result to SAPs attached to a surface where now S will depend on β.

5.2.

Let $p_n^\lambda(m)$ be the number of n-step polygons with m contact which contain at most $\lfloor n\lambda \rfloor$ trefoils (here $\lfloor x \rfloor$ denotes the largest integer less then or equal to x). Then, using arguments similar to those in section 2 it can be shown that

$$F^\lambda(\beta) = \lim_{n\to\infty} \frac{1}{n} \log \sum_m p_n^\lambda(m)\, \mathrm{e}^{\beta m} \tag{5.1}$$

exists. Furthermore, we can introduce a function $\phi^\lambda(p)$ which can then be shown to be the Legendre transform of $F^\lambda(\beta)$, i.e.

$$\phi^\lambda(p) = \inf_\beta\, [F^\lambda(\beta) - p\beta]\,. \tag{5.2}$$

Finally, lemma 2 can be extended to show that $F(\beta) > F^\lambda(\beta)\ \forall\beta < \infty$, iff $\phi(p) > \phi^\lambda(p)\ \forall 0 \leqslant p < 1$. We now state the following theorem.

Theorem 2. There exists a postive number ζ such that

$$\alpha^{\zeta}(\beta) = F(\beta) - F^{\zeta}(\beta) > 0 \qquad \forall\beta < \infty .$$

That is, for sufficiently large n, the trefoil appears at least $\lfloor n\zeta \rfloor$ times in all but exponentially few n-SAPs.

Proof. Here we give only a brief outline of the proof. Using arguments similar to those in section 4, one can arrive at the following upper bound for $\phi^{\lambda}(p)$:

$$\phi^{\lambda}(p) \leqslant p \log \mu_2 + (1-p) \log \mu_{\lambda} \tag{5.3}$$

where μ_{λ} is a connective constant for SAPs in which the tight trefoil appears at most $\lfloor n\lambda \rfloor$ times. From the work of of Sumners and Whittington (1988) it follows (see also theorem 2.3 in Soteros *et al* 1992) that there exists a positive number ζ such that

$$\log \mu_{\zeta} < \log \mu_3 . \tag{5.4}$$

Combining equations (5.4), (5.3) and (4.3) then leads to the result that there exists a ζ such that

$$\phi^{\zeta}(p) < \phi(p) \tag{5.5}$$

which then proves the theorem, using the above-mentioned extension of lemma 2.

5.3.

Now let M be a good measure of knot complexity and let $M(T)$ be its value for the trefoil. Then, let $E_n^M(\beta)$ be the average M complexity of all n-step SAP, i.e.

$$E_n^M(\beta) = \frac{\sum_W M(W)\, e^{\beta m(W)}}{Z_n(\beta)} \tag{5.6}$$

where the sum is performed over all n-step SAPs W with complexity $M(W)$ and with $m(W)$ contacts.

Then the following theorem holds.

Theorem 3. There exists a positive integer n_T such that for sufficiently large $n > n_T$

$$E_n^M(\beta) > S(\beta)\left(\frac{n}{n_T} - 1\right).$$

Proof. Take ζ as in theorem 2, and take n_T such that $\lfloor (n_T - 1)\zeta \rfloor = 0$ and $\lfloor n_T\zeta \rfloor = 1$. Then for $n > n_T$, the sum in the nominator of (5.6) can be split into a sum over SAPs W_1 which contain less then $\lfloor n\zeta \rfloor$ trefoils and a sum over SAPs W_2 which contain more than $\lfloor n\zeta \rfloor$ trefoils. For a good measure of complexity, one has

$$M(nT\#L) \geqslant nM(T)$$

and thus we get (dropping the walks W_1)

$$E_n^M(\beta) \geqslant \frac{1}{Z_n(\beta)} M(T) \lfloor n\zeta \rfloor \sum_{W_2} \mathrm{e}^{\beta m(W_2)}$$

$$> M(T)\left(\frac{n}{n_T} - 1\right)\left[1 - \mathrm{e}^{-\alpha^{\zeta}(\beta)n + \leq(n)}\right]$$

where we have used theorem 2. Finally because $\alpha^{\zeta}(\beta) > 0$ we know that there exists a $\gamma(\beta)$ such that

$$E_n^M(\beta) > M(T)\left(\frac{n}{n_T} - 1\right)\left[1 - \mathrm{e}^{-\gamma(\beta)n_T}\right]. \tag{5.7}$$

This proves the theorem and gives an explicit form for $S(\beta)$.

The result (5.7) seems to suggest that for sufficiently large n we can expect that

$$E_n^M(\beta) \sim n^{\tau}. \tag{5.8}$$

Numerical work (Janse van Rensburg *et al* 1992) gives the result that for non-interacting SAWs and SAPs, $\tau = 1$. Interpreting τ as a critical exponent leads one to expect that its value can change when one passes through a critical point and thus its value may be different in the phase where the polymer is adsorbed (above β_c). This is very consistent with theorem 3 which only gives a lower bound for τ. On the other hand, numerical work of Janse van Rensburg *et al* (1992) gives indications that τ does not change at the θ-point of the SAP-model. One can eventually argue that critical exponents are determined by local properties and that there exists a class of global (topological) exponents that may be independent of such local 'details'. The possibility of the existence of superuniversal topological exponents is very interesting as it could lead to a change in the usual classification of universality classes. We are currently performing numerical calculations of the knot complexity in the adsorbed phase to get further insight into these issues.

6. Discussion

In this paper we have discussed some topological properties of a model for the adsorption of ring polymers. In our model there is a short-range attraction between the surface and monomers. We have found that, for all non-zero temperatures, a properly defined unknot probability (which takes into account Boltzmann weights) goes to zero exponentially fast in the length n of the polymer. Any good measure of knot complexity is found to increase at least linearly in n with a proportionality factor which depends on temperature. We have made conjectures on the temperature dependence of some of the functions occurring in our results. We have also discussed the possibility of a change in the exponent τ occurring in (5.8). In a forthcoming paper we will verify these conjectures using numerical calculations. It also seems possible to prove the conjecture (2.30) using reasoning similar to that in Hammersley *et al* (1982).

The techniques which we have used here can most likely also be used to prove results about the knot probability for polygons undergoing a θ-transition, or to study the behaviour of a geometrical quantity such as the writhe (see, e.g. Janse van Rensburg *et al* 1993) for polymers attached to a surface.

As for applications, it is by now well established that knots occur in the DNA of some organisms, such as bacteriophages. On the other hand, looking at the organization of DNA in cells, it is known that DNA is attached to large proteins (histones) to form chromosomes. While the surfaces of these proteins are definitely not flat, and our model of a ring polymer is certainly too simple to describe DNA, the present study may be considered as a first humble step towards a physical understanding of the topological behaviour of DNA in such structures as chromosomes. A further step that can be considered is to extend the present work to more realistic models of DNA-like molecules such as the recently introduced lattice ribbons (Janse van Rensburg *et al* 1994).

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