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Torsion of polygons in $\mathcal{Z}^3$

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Abstract. The torsion of polygons and self-avoiding walks in the cubic lattice is a measure of the self-entanglement of these objects. We consider several definitions of torsion in polygons, and introduce a fugacity conjugate to the torsion in our models. We study the thermodynamic behaviour of these models using probabilistic methods and rigorous methods from statistical mechanics. In particular, we prove that at least one of our models has a non-analyticity in its free energy, corresponding to a transition between phases with high and low torsion.

1. Introduction

There has been recent interest in the use of geometrical measures of entanglement complexity to describe the conformational properties of linear and ring polymers [1–3]. Most interest has focused on the writhe of the polymer as a measure of the extent of supercoiling. For ribbon models of double-stranded polymers (such as DNA [4] and some polysaccharides [5]) one can also consider the twist of one boundary curve about the other, and there is an important conservation theorem relating the twist and the writhe to the linking number of the two boundary curves [6]. A lattice ribbon model has been developed [7], and this has been used to investigate universal properties of ribbons, both numerically [8] and analytically [9]. An interesting extension of this model would be to include a twist fugacity term, which would allow one to concentrate on structures with a large twist, as is the case for DNA.

In this paper we build the necessary theoretical tools by considering the simpler case of a single-stranded polymer. For single-stranded polymers a twist does not exist, but we can define the torsion of the polymer backbone which captures some of the same local information. Biopolymers such as proteins and DNA can exist in helical forms and torsion reflects the extent of helicity of the polymer chain.

We shall be concerned with a lattice model of a ring polymer and specifically with self-avoiding polygons in the simple cubic lattice Z^3. Lattice models have the advantage that we can use combinatorial methods to attack the problem, so that we shall be able to prove several results about the asymptotic behaviour of various averages of the torsion of a polygon. However, the usual way to define the torsion of a curve in R^3 relies on the curve being differentiable and having a tangent vector which is stationary nowhere [10]. Since lattice polygons are piecewise linear we take a different approach to the definition of torsion [11]. The approach which we use counts the number of signed dihedral angles (which are either $\pm\pi/2$) since we want to measure the deviation from planarity. Alternatively we can simply count the number of these dihedral angles, and we shall argue that these two schemes capture information about different structures in the polymer.

In section 2 we define three measures of the torsion of a polygon, corresponding to three different ways of weighting the local torsional contributions, i.e. the dihedral angles. In section 3 we prove some rigorous results about these three measures of torsion, and show that a thermodynamic potential of at least one of them exhibits a singularity as the fugacity associated with torsion is varied. In section 4 we prove some rigorous results about densities of dihedral angles and investigate the connection of these results to the form of the thermodynamic potentials.

2. Definitions

We begin by defining some notation. Let p_n be the number of n-edge (unrooted, unoriented) self-avoiding polygons in the simple cubic lattice Z^3. Polygons are considered to be distinct if they cannot be superimposed by translation. For instance, $p_4 = 3$ and $p_6 = 22$. A polygon is made up of a sequence of line segments, each of which comprises one or more colinear edges, and each three successive line segments define a dihedral angle. The dihedral angle can be 0 or π, in which case the three line segments are coplanar, or $\pm\pi/2$ (the sign is fixed using a right-hand rule). In the cubic lattice we shall be interested in defining torsion as a measure of non-planarity. Consequently, we focus on dihedral angles of size $\pm\pi/2$. We abuse the terminology above by ignoring dihedral angles of size 0 or π, and we take *dihedral angle* to mean a non-planar dihedral angle (of sizes $\pi/2$ or $-\pi/2$ in the cubic lattice). That is, a *positive dihedral angle* is a dihedral angle of $\pi/2$, and a *negative dihedral angle* is a dihedral angle of $-\pi/2$. In each n-edge polygon there can be a number m of dihedral angles, with $0 \leqslant m \leqslant n$. Numbering these dihedral angles $i = 1, 2, \ldots, m$, and writing $\tau_i = \pm 1$ according to the sign of the ith angle, we define

$$t = \sum_i \tau_i \tag{2.1}$$

and

$$\tilde{t} = \sum_i |\tau_i|. \tag{2.2}$$

We call t the *torsion* of the polygon and $\tilde{t}$ the *absolute torsion* of the polygon [11]. When we consider the signed sum, the polygon must be oriented and we therefore write $p_n(t)$ for the number of *oriented* n-edge polygons with torsion t. Therefore

$$\sum_{t=-n}^{n} p_n(t) = 2p_n. \tag{2.3}$$

Similarly we write $\tilde{p}_n(\tilde{t})$ for the number of non-oriented n-edge polygons with absolute torsion equal to $\tilde{t}$. Clearly

$$\sum_{\tilde{t}=0}^{n} \tilde{p}_n(\tilde{t}) = p_n. \tag{2.4}$$

We can associate a weight with either the torsion or the absolute torsion of a polygon, and we define the corresponding generating functions

$$Z_n(\beta) = \sum_{t=-n}^{n} p_n(t) \mathrm{e}^{\beta t} \tag{2.5}$$

and

$$\tilde{Z}_n(\beta) = \sum_{\tilde{t}=0}^{n} \tilde{p}_n(\tilde{t}) \mathrm{e}^{\beta \tilde{t}}. \tag{2.6}$$

Note that $Z_n(\beta)$ is symmetric in β since $p_n(t) = p_n(-t)$, whereas $\tilde{Z}_n(\beta)$ is an increasing function of β. We can define a third generating function, related to (2.5), by first defining $\bar{p}_n(t) = 2p_n(t)$ if $t > 0$ and $\bar{p}_n(0) = p_n(0)$. Then

$$\bar{Z}_n(\beta) = \sum_{t=0}^{n} \bar{p}_n(t) \mathrm{e}^{\beta t} = \sum_{t=-n}^{n} p_n(t) \mathrm{e}^{\beta |t|}. \tag{2.7}$$

The utility of this definition will become apparent in the next section.

3. Thermodynamic limits

3.1. Existence of thermodynamic limits

We can define quantities related to the three generating functions (2.5)–(2.7) which play the role of free energies per vertex, i.e.

$$F_n(\beta) = n^{-1} \log Z_n(\beta) \tag{3.1}$$

$$\tilde{F}_n(\beta) = n^{-1} \log \tilde{Z}_n(\beta) \tag{3.2}$$

$$\bar{F}_n(\beta) = n^{-1} \log \bar{Z}_n(\beta). \tag{3.3}$$

Hereafter we shall refer to these quantities as *free energies*.

In this section we show that each of these functions has a limit as n goes to infinity. The approach is to concatenate pairs of polygons, and establish that the generating functions satisfy generalized supermultiplicative inequalities.

The top and bottom edges of an oriented polygon are defined by a lexicographic ordering of the edges by the coordinates of their midpoints. The top edge is the one with the lexicographically largest midpoint, and the bottom edge is the one with the lexicographically smallest midpoint. Let $\mathcal{P}$ be an oriented polygon in Z^3 with n edges and torsion $t - s$, and let $\mathcal{Q}$ be an oriented polygon in Z^3 with m edges and torsion s. We call e_p the top edge of $\mathcal{P}$ and e_q the bottom edge of $\mathcal{Q}$. In order to concatenate $\mathcal{P}$ and $\mathcal{Q}$, we need to have e_p and e_q parallel and with opposite orientations. This implies that, once we have chosen $\mathcal{P}$ in $p_n(t-s)$ ways, we can choose $\mathcal{Q}$ in $p_m(s)/4$ ways. Now we can translate $\mathcal{Q}$ so that the midpoints of e_p and e_q differ by unity in their first coordinates (with all other coordinates identical, and e_q with the larger first coordinate). We concatenate $\mathcal{P}$ and $\mathcal{Q}$ by deleting e_p and e_q and by adding two new edges to join the endpoints of e_p and e_q. This gives a new oriented polygon $\mathcal{P} \oplus \mathcal{Q}$. Observe that removal of an edge in any polygon can decrease or increase the torsion by at most three units, and similarly addition of an edge to make a new polygon can change the torsion by up to three units. Thus, the torsion of $\mathcal{P} \oplus \mathcal{Q}$ can range from up to six less to up to six more than the sum of the torsions of $\mathcal{P}$ and $\mathcal{Q}$. Then $\mathcal{P} \oplus \mathcal{Q}$ has $n + m$ edges and torsion of at least $t - 6$ and at most $t + 6$. Without loss of generality, we will assume from now on that $n \geqslant m$. Thus

$$\sum_{s} p_n(t-s) p_m(s) \leqslant 4 \sum_{k=-6}^{6} p_{n+m}(t+k) \tag{3.4}$$

and the summation over s is over all those values of s which gives a non-zero contribution to the sum.

Similarly, for the absolute torsion we can show that

$$\sum_s \tilde{p}_n(t-s)\tilde{p}_m(s) \leqslant 2\sum_{k=-6}^{6} \tilde{p}_{n+m}(t+k). \tag{3.5}$$

We now show that (3.5) can be used to prove that $\tilde{Z}_n(\beta)$ satisfies a generalized supermultiplicative inequality. A similar argument will show that (3.4) implies that $Z_n(\beta)$ also satisfies a supermultiplicative inequality, but we will not repeat the proof here. Multiply (3.5) by $e^{\beta t}$ and sum over t (remembering that we have $n \geqslant m$, and that $\tilde{p}_m(\ell) = 0$ if $\ell > m$)

$$\sum_{t=0}^{n}\sum_{s=0}^{t} \tilde{p}_n(t-s)\tilde{p}_m(s)e^{\beta(t-s)}e^{\beta s} \leqslant 2\sum_{k=-6}^{6}\sum_{t=0}^{n+m} \tilde{p}_{n+m}(t+k)e^{\beta(t+k)}e^{-\beta k} \tag{3.6}$$

which gives

$$\begin{aligned}\tilde{Z}_n(\beta)\tilde{Z}_m(\beta) \leqslant 2\{&e^{6\beta}\tilde{Z}_{n+m}(\beta) + e^{5\beta}\tilde{Z}_{n+m}(\beta) + \cdots + e^{\beta}\tilde{Z}_{n+m}(\beta) + \tilde{Z}_{n+m}(\beta)\\ &+e^{-\beta}(\tilde{Z}_{n+m}(\beta) - \tilde{p}_{n+m}(0)) + e^{-2\beta}(\tilde{Z}_{n+m}(\beta) - \tilde{p}_{n+m}(0) - \tilde{p}_{n+m}(1)) + \cdots\}\end{aligned} \tag{3.7}$$

thus

$$\begin{aligned}\tilde{Z}_n(\beta)\tilde{Z}_m(\beta) &\leqslant 2\Bigg[\left(\sum_{j=-6}^{6} e^{j\beta}\right)\tilde{Z}_{n+m}(\beta) - \left(\sum_{j=1}^{6} e^{-j\beta}\right)\tilde{p}_{n+m}(0) - \left(\sum_{j=2}^{6} e^{-j\beta}\right)\tilde{p}_{n+m}(1)\\ &\quad -\left(\sum_{j=3}^{6} e^{-j\beta}\right)\tilde{p}_{n+m}(2) - \left(\sum_{j=4}^{6} e^{-j\beta}\right)\tilde{p}_{n+m}(3)\\ &\quad -\left(\sum_{j=5}^{6} e^{-j\beta}\right)\tilde{p}_{n+m}(4) - e^{-6\beta}\tilde{p}_{n+m}(5)\Bigg]\\ &\leqslant 2\left(\sum_{j=-6}^{6} e^{j\beta}\right)\tilde{Z}_{n+m}(\beta)\end{aligned} \tag{3.8}$$

so that $\log \tilde{Z}_n(\beta)$ is a generalized supermultiplicative sequence.

Note that

$$\tilde{Z}_n(\beta) \leqslant e^{\kappa_3 n} \qquad \text{if } \beta \leqslant 0 \tag{3.9}$$

where κ_3 is the connective constant of polygons† in Z^3, and

$$\tilde{Z}_n(\beta) \leqslant e^{(\kappa_3+\beta)n} \qquad \text{if } \beta > 0. \tag{3.10}$$

Thus, $\lim_{n\to\infty} n^{-1}\log\tilde{Z}_n(\beta) = \lim_{n\to\infty}\tilde{F}_n(\beta) = \tilde{\mathcal{F}}(\beta)$ exists and is finite for $\beta < \infty$ [14]. Similarly, we can prove that $\lim_{n\to\infty} n^{-1}\log Z_n(\beta) = \lim_{n\to\infty} F_n(\beta) = \mathcal{F}(\beta)$ exists and is finite for $\beta < \infty$.

It remains to prove that $\bar{F}_n(\beta)$ converges to a limit. We first consider the case $\beta \leqslant 0$. Taking again (3.4), multiplying both sides by $e^{\beta|t|}$, using the triangle inequality $|t| \leqslant |t-s| + |s|$, and summing over t gives

$$\sum_{t=-n}^{n}\sum_{s=-m}^{m} p_n(t-s)p_m(s)e^{\beta|t-s|}e^{\beta|s|} \leqslant 4\sum_{k=-6}^{6}\sum_{t=-(n+m)}^{n+m} p_{n+m}(t+k)e^{\beta|t|} \tag{3.11}$$

† The connective constant of polygons is defined by the limit $\lim_{n\to\infty}\frac{1}{n}\log p_n = \kappa_d$ in d-dimensions [12, 13]. The connective constant of self-avoiding walks is defined by replacing p_n by c_n (the number of self-avoiding walks of n steps) and it is equal to κ_d.

which implies, using the inequality $||t+k|-|k|| \leqslant |t|$, that

$$\bar{Z}_n(\beta)\bar{Z}_m(\beta) \leqslant 4 \sum_{k=-6}^{6} \mathrm{e}^{-\beta|k|} \bar{Z}_{n+m}(\beta). \tag{3.12}$$

Hence, $\lim_{n\to\infty} n^{-1} \log \bar{Z}_n(\beta) = \lim_{n\to\infty} \bar{F}_n(\beta) = \bar{\mathcal{F}}(\beta)$ exists and is finite for $\beta \leqslant 0$.

For $\beta \geqslant 0$ we observe that

$$\sum_{t=-n}^{n} p_n(t)\mathrm{e}^{\beta t} \leqslant \sum_{t=-n}^{n} p_n(t)\mathrm{e}^{\beta|t|} \leqslant 2\sum_{t=0}^{n} p_n(t)\mathrm{e}^{\beta t} \leqslant 2\sum_{t=-n}^{n} p_n(t)\mathrm{e}^{\beta t} \tag{3.13}$$

so taking logarithms, dividing by n and letting $n \to \infty$ we have

$$\lim_{n\to\infty} n^{-1} \log Z_n(\beta) = \lim_{n\to\infty} n^{-1} \log \bar{Z}_n(\beta) \tag{3.14}$$

or $\mathcal{F}(\beta) = \bar{\mathcal{F}}(\beta)$ for $\beta \geqslant 0$.

3.2. Convexity and monotonicity

We prove convexity of the function $F_n(\beta) = n^{-1} \log Z_n(\beta)$ by using the Cauchy–Schwartz inequality, i.e.

$$\begin{aligned} Z_n(\beta_1)Z_n(\beta_2) &= \sum_{t=-n}^{n} p_n(t)\mathrm{e}^{\beta_1 t} \sum_{s=-n}^{n} p_n(s)\mathrm{e}^{\beta_2 s} \\ &\geqslant \left(\sum_{t=-n}^{n} p_n(t)\mathrm{e}^{\frac{\beta_1+\beta_2}{2}t} \right)^2 \\ &= \left(Z_n\left(\frac{\beta_1+\beta_2}{2}\right)\right)^2 \end{aligned} \tag{3.15}$$

which implies that

$$\frac{1}{n} \log Z_n\left(\frac{\beta_1+\beta_2}{2}\right) \leqslant \frac{1}{2}\left(\frac{1}{n}\log Z_n(\beta_1) + \frac{1}{n}\log Z_n(\beta_2)\right) \tag{3.16}$$

i.e. that $F_n(\beta)$ is a convex function of β. Since $\mathcal{F}(\beta)$ is the limit of a sequence of convex functions, it is convex in $\beta \in (-\infty, \infty)$. It is therefore continuous in $\beta \in (-\infty, +\infty)$, and differentiable almost everywhere [15].

Using the Cauchy–Schwartz inequality for $\bar{F}_n(\beta)$ and $\tilde{F}_n(\beta)$ we obtain convexity, continuity and differentiability (almost everywhere) also for $\bar{\mathcal{F}}(\beta)$ and $\tilde{\mathcal{F}}(\beta)$. Moreover, both of these limiting free energies are monotonic non-decreasing functions of β $\forall\beta \in R$, since $\forall\beta_1, \beta_2 \in R$, with $\beta_1 \leqslant \beta_2$, we have $\mathrm{e}^{\beta_1|t|} \leqslant \mathrm{e}^{\beta_2|t|}$ $\forall t \in R$ and $\mathrm{e}^{\beta_1\tilde{t}} \leqslant \mathrm{e}^{\beta_2\tilde{t}}$ $\forall\tilde{t} \in R^+$. Also $\mathcal{F}(\beta)$ is a monotonic non-decreasing function of β, for $\beta \geqslant 0$, since it is equal to $\bar{\mathcal{F}}(\beta)$. Since $Z_n(\beta) = Z_n(-\beta)$ we also observe that $\mathcal{F}(\beta) = \mathcal{F}(-\beta)$, and consequently, $\mathcal{F}(\beta)$ is decreasing with β if $\beta < 0$.

3.3. Bounds on the free energies

In this section we use bounds on the generating functions in order to obtain bounds on free energies in our models. If $\beta = 0$, then $Z_n(0) = 2p_n$, and by the definition of the free energy we obtain

$$\mathcal{F}(0) = \kappa_3. \tag{3.17}$$

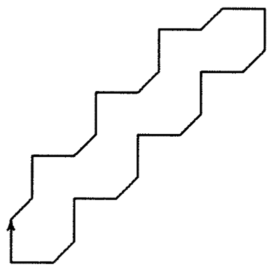

Figure 1. A polygon of length n and torsion $n-6$.

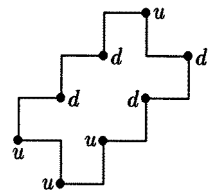

Figure 2. One can construct a polygon in which every edge is the middle edge of a dihedral angle by adding edges up, or down, at every second vertex of a planar polygon.

If $\beta > 0$, then

$$Z_n(\beta) = \sum_{t=-n}^{n} p_n(t)\mathrm{e}^{\beta t} \leqslant \mathrm{e}^{\beta n} \sum_{t=-n}^{n} p_n(t) = 2\mathrm{e}^{\beta n} p_n \tag{3.18}$$

which implies:

$$\mathcal{F}(\beta) \leqslant \kappa_3 + \beta. \tag{3.19}$$

Figure 1 is an example of a polygon with n edges and torsion $n-6$. A similar construction can be carried out for any even n greater than or equal to 12. Hence $p_n(n-6) > 0$, and we find that $Z_n(\beta) \geqslant \mathrm{e}^{\beta(n-6)} p_n(n-6)$. Since every edge in a polygon counted by $p_n(n-6)$, except for at most six, is the middle edge of a right-handed (positive) dihedral angle, it fixes the orientation of edges adjacent to it. Thus, at least $(n-2)$ edges in the polygon have their orientations fixed if the polygon has torsion $n-6$ (in the sense that when we have specified the orientations of two edges, then the rest are also determined). Thus, $p_n(n-6) = \mathrm{e}^{\mathrm{o}(n)}$, and we conclude that $\mathcal{F}(\beta) \geqslant \beta$ if $\beta > 0$. On the other hand, $\mathcal{F}(\beta)$ is monotonic increasing, and so $\mathcal{F}(\beta) \geqslant \mathcal{F}(0) = \kappa_3$ if $\beta > 0$. Thus

$$\mathcal{F}(\beta) \geqslant \max\{\beta, \kappa_3\}. \tag{3.20}$$

Since $\mathcal{F}(\beta) = \mathcal{F}(-\beta)$, these results also give a lower and upper bound if $\beta < 0$.

We turn our attention now to $\tilde{Z}_n(\beta)$. If $\beta = 0$ then $\tilde{Z}_n(0) = p_n$, and thus $\tilde{\mathcal{F}}(0) = \kappa_3$. If $\beta > 0$ then an upper bound on $\tilde{Z}_n(\beta)$ is found by

$$\tilde{Z}_n(\beta) = \sum_{t\geqslant 0} \tilde{p}_n(t)\mathrm{e}^{\beta t} \leqslant \mathrm{e}^{\beta n} \sum_{t\geqslant 0} \tilde{p}_n(t) = p_n \mathrm{e}^{\beta n}. \tag{3.21}$$

Hence

$$\tilde{\mathcal{F}}(\beta) \leqslant \kappa_3 + \beta. \tag{3.22}$$

On the other hand, $\tilde{Z}_n(\beta) \geqslant \mathrm{e}^{\beta n} \tilde{p}_n(n)$. A polygon which is counted by $\tilde{p}_{3n}(3n)$ can be constructed from a planar polygon with $2n$ (n even) edges and all adjacent edges at right angles as follows. We create dihedral angles by inserting a new edge in the polygon, perpendicular to the plane containing it, at every second vertex. This new edge is chosen to be either up or down, as illustrated in figure 2. In this way, exactly n edges are added to the polygon, resulting in a new polygon of length exactly $3n$. This new polygon must be closed, thus exactly $n/2$ of the new edges must be in the up direction, and exactly $n/2$ in the down direction. Thus, we can construct it in at least $\binom{n}{n/2}$ ways. Hence

$$\tilde{Z}_{3n}(\beta) \geqslant e^{3\beta n}\tilde{p}_{3n}(3n) \geqslant e^{3\beta n}\binom{n}{n/2} p^*_{2n} \tag{3.23}$$

where p^*_n is the number of polygons in Z^2 with all adjacent edges at right angles. One can show that $\lim_{n\to\infty} \frac{1}{n}\log p^*_n \geqslant \frac{1}{2}\log 2$. Using this bound, taking logarithms, dividing by $3n$ and letting $n \to \infty$ in the above (note that $\tilde{\mathcal{F}}(\beta)$ is a monotonic non-decreasing function of β) gives

$$\tilde{\mathcal{F}}(\beta) \geqslant \max\{\tfrac{2}{3}\log 2 + \beta, \kappa_3\}. \tag{3.24}$$

If $\beta < 0$ then $\tilde{Z}_n(\beta) \leqslant p_n$ which gives

$$\tilde{\mathcal{F}}(\beta) \leqslant \kappa_3. \tag{3.25}$$

For a lower bound, note that $\tilde{Z}_n(\beta) \geqslant \tilde{p}_n(0)$ where $\tilde{p}_n(0)$ is the number of planar polygons in three dimensions. This gives the lower bound

$$\tilde{\mathcal{F}}(\beta) \geqslant \kappa_2 \tag{3.26}$$

where κ_2 is the connective constant in Z^2. ($\tilde{p}_n(0)$ equals three times the number of polygons in two dimensions.)

The relation between the free energies $\mathcal{F}(\beta)$ and $\tilde{\mathcal{F}}(\beta)$ is given by the following theorem. We note that $\mathcal{F}(0) = \tilde{\mathcal{F}}(0) = \kappa_3$, so that these agree at least at one point. We prove that if $\beta > 0$, then $\tilde{\mathcal{F}}(\beta)$ is an upper bound on $\mathcal{F}(\beta)$. If $\beta < 0$, then $\tilde{\mathcal{F}}(\beta) \leqslant \kappa_3 \leqslant \mathcal{F}(\beta)$. From equation (3.20), and since $\mathcal{F}(\beta) = \mathcal{F}(-\beta)$, $\tilde{\mathcal{F}}(\beta) < \mathcal{F}(\beta)$ if $\beta < -\kappa_3$.

Theorem 3.1. If $\beta \leqslant 0$, then $\tilde{\mathcal{F}}(\beta) \leqslant \mathcal{F}(\beta)$, and the inequality is strict if $\beta < -\kappa_3$. If $\beta \geqslant 0$, then $\tilde{\mathcal{F}}(\beta) \geqslant \mathcal{F}(\beta)$.

Proof. We have already considered the case $\beta \leqslant 0$. So assume that $\beta > 0$. Let $l = (\tilde{t} - t)/2$ and let $\tilde{q}_n(\tilde{t}, l)$ be the number of polygons with n edges, having absolute torsion $\tilde{t}$ and torsion equal to $\tilde{t} - 2l$. Then

$$\begin{aligned}\tilde{Z}_n(\beta) &= \sum_{\tilde{t}=0}^{n}\sum_{l=0}^{\tilde{t}} \tilde{q}_n(\tilde{t}, l)e^{\beta(\tilde{t}-l)}e^{\beta l} \\ &\geqslant \sum_{\tilde{t}=0}^{n}\sum_{l=0}^{\tilde{t}} \tilde{q}_n(\tilde{t}, l)e^{\beta(\tilde{t}-l)}e^{-\beta l} \\ &= \sum_{\tilde{t}=0}^{n}\sum_{l=0}^{\tilde{t}} \tilde{q}_n(\tilde{t}, l)e^{\beta(\tilde{t}-2l)}.\end{aligned} \tag{3.27}$$

Now write $q_n(\tilde{t}, t)$ for the number of polygons with n edges, having absolute torsion $\tilde{t}$ and torsion t. Since $t = \tilde{t} - 2l$ the last inequality can be written as

$$\begin{aligned}\tilde{Z}_n(\beta) &\geqslant \sum_{\tilde{t}=0}^{n}\sum_{t=-\tilde{t}}^{\tilde{t}} q_n(\tilde{t}, t)e^{\beta t} \\ &= \sum_{\tilde{t}=0}^{n}\sum_{t=-n}^{n} q_n(\tilde{t}, t)e^{\beta t} \\ &= \sum_{t=-n}^{n} p_n(t)e^{\beta t} = Z_n(\beta)\end{aligned} \tag{3.28}$$

and the result follows after taking logarithms, dividing by n and letting n go to infinity. □

As noticed in equation (3.14), if $\beta \geqslant 0$, then $\bar{\mathcal{F}}(\beta) = \mathcal{F}(\beta)$. The situation is more difficult to analyse if $\beta < 0$; we show in the following theorem that $\bar{\mathcal{F}}(\beta) = \kappa_3$ for all $\beta < 0$. The proof is based on a 'most popular' class argument (see for instance [16]).

Theorem 3.2. The limiting free energy corresponding to the excess torsion is independent of β for $\beta \leqslant 0$, and is equal to κ_3.

Proof. We first note that $\bar{Z}_n(-\infty) = p_n(0)$ and $\bar{Z}_n(0) = 2p_n$. Clearly $\bar{Z}_n(-\infty) \leqslant \bar{Z}_n(0)$. If we concatenate two polygons, each having n edges, one having torsion k and the other having torsion $-k$, we obtain the inequality

$$\sum_k p_n(k) p_n(-k) \leqslant \sum_{l=-6}^{6} p_{2n}(l). \tag{3.29}$$

If we classify polygons by torsion there must be a most popular class, say those polygons having torsion equal to $\pm k^*$. That is,

$$p_n(k^*) \geqslant p_n(k) \qquad \forall |k| \leqslant n \tag{3.30}$$

and

$$p_n(k^*) \geqslant 2p_n/(2n+1). \tag{3.31}$$

Since $p_n(k^*) = p_n(-k^*)$ this gives

$$\left(\frac{2p_n}{2n+1}\right)^2 \leqslant p_n(k^*) p_n(-k^*) \leqslant \sum_k p_n(k) p_n(-k) \leqslant \sum_{l=-6}^{6} p_{2n}(l). \tag{3.32}$$

Let l^* be the value of l such that $-6 \leqslant l \leqslant 6$ and $p_{2n}(l^*) \geqslant p_{2n}(l)$ for $-6 \leqslant l \leqslant 6$. Then

$$\left(\frac{2p_n}{2n+1}\right)^2 \leqslant 13 p_{2n}(l^*). \tag{3.33}$$

If $\beta \leqslant 0$, then

$$2p_{2n} \geqslant \bar{Z}_{2n}(\beta) \geqslant p_{2n}(l^*) \mathrm{e}^{\beta |l^*|} \geqslant \left(\frac{2p_n}{2n+1}\right)^2 \frac{\mathrm{e}^{\beta |l^*|}}{13}. \tag{3.34}$$

Taking logarithms, dividing by $2n$ and letting n go to infinity gives

$$\lim_{n\to\infty} n^{-1} \log \bar{Z}_n(\beta) = \kappa_3 \qquad \forall \beta \leqslant 0. \tag{3.35}$$

□

We noted that $\mathcal{F}(\beta)$ is a convex function, and is differentiable almost everywhere in its domain. Moreover, if $\mathcal{F}(\beta)$ is differentiable at β, then

$$\frac{\mathrm{d}}{\mathrm{d}\beta} \mathcal{F}(\beta) = \lim_{n\to\infty} \frac{1}{n} \frac{\mathrm{d}}{\mathrm{d}\beta} \log Z_n(\beta) = \lim_{n\to\infty} \frac{\langle t \rangle_n}{n} \tag{3.36}$$

where $\langle t \rangle_n = \sum_{t=-n}^{n} t p_n(t) \mathrm{e}^{\beta t} / Z_n(\beta)$ is the mean torsion. $\langle t \rangle_n / n$ is the mean torsion per edge. In the next theorem, we adapt the tossing of a biased coin to prove that the limiting value of the mean torsion per edge is positive for any $\beta > 0$. In particular, this means that $\mathcal{F}(\beta)$ is strictly increasing for all $\beta > 0$.

Theorem 3.3. The mean torsion per edge and the mean excess torsion per edge are both positive for every positive β in the infinite n limit.

Proof. The mean value of the torsion is

$$\langle t\rangle_n = \frac{\sum_{t=-n}^{n} t p_n(t) \mathrm{e}^{\beta t}}{\sum_{t=-n}^{n} p_n(t) \mathrm{e}^{\beta t}}. \tag{3.37}$$

Since $\mathcal{F}(\beta) = \bar{\mathcal{F}}(\beta)\ \forall \beta > 0$, we only have to consider the mean torsion. The theorem is an immediate consequence of the following result.

For any $\beta > 0$ there exists an $\epsilon > 0$ such that

$$\lim_{n\to\infty} \frac{\langle t\rangle_n}{n} \geqslant \left(2\left(\frac{\mathrm{e}^{\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right) - 1\right)\epsilon. \tag{3.38}$$

Proof. The proof of the last result is as follows. Suppose that i, j and k are the canonical unit vectors. Let P be the following walk: $[-i, k, -i, -i, -k, i, j, k, -i, -k, -i, k, -i]$. The union of the dual 3-cubes of P is a topological 3-ball C, and P contains two positive and one negative dihedral angles. A reflection of P (to obtain the walk P^*) through its centre of mass leaves its endpoints and C unchanged. P^* contains two negative and one positive dihedral angles. P is also a Kesten pattern [17], and since the endpoints of P and P^* are the same vertices of C, one can choose to insert either P or P^* into C in any given polygon containing C. Let α_n be a class of polygons with at least $\lfloor\epsilon n\rfloor$ occurrences of C, each containing either P or P^*, and fixed outside the union of exactly $\lfloor\epsilon n\rfloor$ of the C's. By Kesten's pattern theorem [18] the number of such classes of polygons is at least $(1-\mathrm{e}^{-\gamma n})2^{-\lfloor\epsilon n\rfloor} p_n$, where $\gamma > 0$ is a small number and p_n is the number of polygons with length n. The factor of $2^{-\lfloor\epsilon n\rfloor}$ appears because each class α_n represents $2^{\lfloor\epsilon n\rfloor}$ polygons. (This is a consequence of the binomial choice of either P or P^* in each C.) Suppose that the contribution to the torsion of a polygon in the class α_n from the fixed part outside the union of the C's is t, and let there be t_+ occurrences of the pattern P and t_- occurrences of the pattern P^* in the C's (thus, $t_+ + t_- = \lfloor\epsilon n\rfloor$). In the partition function, the weight of each P is e^{β}, and of P^* is $\mathrm{e}^{-\beta}$. Since the P and P^* are independent and binomially distributed, the normalized contribution of the class α_n to the partition function is

$$\mathrm{e}^{\beta t} \sum_{t_+=0}^{\lfloor\epsilon n\rfloor} \binom{\lfloor\epsilon n\rfloor}{t_+} \left(\frac{\mathrm{e}^{\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right)^{t^+} \left(\frac{\mathrm{e}^{-\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right)^{\lfloor\epsilon n\rfloor - t_+} = \mathrm{e}^{\beta t}. \tag{3.39}$$

Similarly, the normalized contribution to the numerator in (3.37) is

$$\begin{aligned} &\mathrm{e}^{\beta t} \sum_{t_+=0}^{\lfloor\epsilon n\rfloor} (t + t_+ - t_-) \binom{\lfloor\epsilon n\rfloor}{t_+} \left(\frac{\mathrm{e}^{\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right)^{t_+} \left(\frac{\mathrm{e}^{-\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right)^{\lfloor\epsilon n\rfloor - t_+} \\ &\qquad = \mathrm{e}^{\beta t}\left(t + 2\left(\frac{\mathrm{e}^{\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right) - 1\right)\lfloor\epsilon n\rfloor. \end{aligned} \tag{3.40}$$

The contribution from the class α_n^*, the mirror image of α_n, is similarly obtained (by replacing t with $-t$):

$$\mathrm{e}^{-\beta t}\left(-t + 2\left(\frac{\mathrm{e}^{\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right) - 1\right)\lfloor\epsilon n\rfloor. \tag{3.41}$$

Without loss of generality, we can assume that $t \geqslant 0$. In that case, the combined contribution to the numerator in (3.37) from the class α_n and its mirror image is

$$t(\mathrm{e}^{\beta t} - \mathrm{e}^{-\beta t}) + \left[2\left(\frac{\mathrm{e}^{\beta}}{\mathrm{e}^{\beta}+\mathrm{e}^{-\beta}}\right) - 1\right]\lfloor\epsilon n\rfloor(\mathrm{e}^{\beta t} + \mathrm{e}^{-\beta t}). \tag{3.42}$$

For $\beta > 0$ the first term is always non-negative, and so we can get a lower bound on the numerator by ignoring it. This gives a lower bound for each of the classes α_n. Let ω_n be the set of polygons with fewer than $\lfloor \epsilon n \rfloor$ occurrences of P or P^* in C, and fixed outside the union of the C's. For any $\epsilon > 0$ it can be shown, using standard techniques (see for example [19]), that q_n grows exponentially with n. On the other hand, the pattern theorem for polygons [20], states that there exists an $\epsilon_0 > 0$, such that for every positive $\epsilon < \epsilon_0$, the number of polygons in ω_n is exponentially small, compared with all polygons. We conclude that q_n is bounded from above and below by $e^{-\gamma_1 n} p_n \geqslant q_n \geqslant e^{-\gamma_2 n} p_n$ if n is large, where $0 < \gamma_1 < \gamma_2$, and for every positive $\epsilon < \epsilon_0$. We now assume that $\epsilon < \epsilon_0$ is fixed. Let R be the minimum contribution to the numerator in (3.37) by a polygon in ω_n, and S be the maximum contribution to the partition function by a polygon in ω_n. Using these bounds, and the contributions from the classes α_n, the mean torsion for n large enough is bounded from below as

$$\frac{\langle t \rangle_n}{n} \geqslant \frac{(1 - e^{-\gamma n}) p_n [(2(\frac{e^{\beta}}{e^{\beta} + e^{-\beta}}) - 1) \frac{\lfloor \epsilon n \rfloor}{n}](e^{\beta t} + e^{-\beta t}) + e^{-\gamma_2 n} p_n R}{p_n (e^{\beta t} + e^{-\beta t}) + e^{-\gamma_1 n} p_n S} \tag{3.43}$$

since each class α_n contains $2^{\lfloor \epsilon n \rfloor}$ polygons. Now taking $n \to \infty$ we obtain

$$\lim_{n \to \infty} \frac{\langle t \rangle_n}{n} \geqslant \left(2 \left(\frac{e^{\beta}}{e^{\beta} + e^{-\beta}} \right) - 1 \right) \epsilon. \tag{3.44}$$

□

We have already seen that $\bar{\mathcal{F}}(\beta) = \kappa_3$ if $\beta \leqslant 0$. In particular, this means that the mean absolute torsion per edge is zero if $\beta < 0$. The left derivative of $\bar{\mathcal{F}}(\beta)$ is also zero at $\beta = 0$, and by theorem 3.3 the right derivative at β is either 0 or positive. If it is positive, then there is a jump discontinuity at $\beta = 0$ in the first derivative of $\bar{\mathcal{F}}(\beta)$, which indicates a *first-order* transition in this model. In addition, since $\mathcal{F}(\beta) = \bar{\mathcal{F}}(\beta)$ if $\beta \geqslant 0$, and $\mathcal{F}(\beta) = \mathcal{F}(-\beta)$, this also indicates a first-order transition in the mean torsion. If the right derivative at $\beta = 0$ is 0, on the other hand, then we have a continuous transition in the excess torsion model, while we cannot make any statements about the mean torsion.

The mean absolute torsion, on the other hand, is positive at $\beta = 0$, in contrast to the results above. We prove this in the next theorem.

Theorem 3.4. The mean absolute torsion per edge is positive at $\beta = 0$ in the infinite n limit.

Proof. Let P be the following walk: $[i, j, k]$. Then P contains exactly one dihedral angle. By the pattern theorem for polygons there exists a $\gamma > 0$ and an $\epsilon > 0$ (dependent on P), such that a fraction $(1 - e^{-\gamma n})$ of all n-polygons contains P at least $\lfloor \epsilon n \rfloor$ times. The mean absolute torsion, $\langle \tilde{t}_n \rangle$, of n-polygons per edge is bounded below by

$$\frac{\langle \tilde{t}_n \rangle}{n} \geqslant \frac{(1 - e^{-\gamma n}) p_n \lfloor \epsilon n \rfloor + e^{-\gamma n} p_n . 0}{n p_n} = (1 - e^{-\gamma n}) \frac{\lfloor \epsilon n \rfloor}{n}. \tag{3.45}$$

Thus $\lim_{n \to \infty} \frac{\langle \tilde{t}_n \rangle}{n} \geqslant \epsilon > 0$. □

4. The density function of dihedral angles

The number of polygons of length n with a 'density' ϵ of dihedral angles is $\tilde{p}_n(\lfloor \epsilon n \rfloor)$. In this section we study absolute torsion by focusing our attention on the *density function* $\tilde{\rho}(\epsilon) = \lim_{n \to \infty} n^{-1} \log \tilde{p}_n(\lfloor \epsilon n \rfloor)$ of dihedral angles. We first prove that this density function is well defined, in the sense that the limit exists. The density function is related to the free energy by a Legendre transform: $\tilde{\mathcal{F}}(\beta) = \sup_{0 \leqslant \epsilon \leqslant 1} (\tilde{\rho}(\epsilon) + \epsilon \beta)$, and conversely $\tilde{\rho}(\epsilon) = \inf_{\beta} (\tilde{\mathcal{F}}(\beta) - \epsilon \beta)$, see [21] for details. Consequently, knowledge of the density function is equivalent to knowledge of the free energy. However, there are some results which are easier to prove using the density function. In this section we will consider the asymptotic behaviour of $\tilde{\mathcal{F}}(\beta)$ by first finding some properties of the density function.

Theorem 4.1. The limit $\lim_{n\to\infty} n^{-1}\log\tilde{p}_n(\lfloor\epsilon n\rfloor) = \tilde{\rho}(\epsilon)$ exists and is a concave function of ϵ in [0, 1].

Proof. $\tilde{p}_n(\lfloor\epsilon n\rfloor)$ is the number of polygons of length n with $\lfloor\epsilon n\rfloor$ dihedral angles. Observe that $\epsilon\in[0,1]$. It now follows from concatenation that

$$\tilde{p}_n(\lfloor\epsilon n\rfloor)\tilde{p}_m(\lfloor\delta m\rfloor) \leqslant \sum_{i=-6}^{6}\tilde{p}_{n+m}(\lfloor\epsilon n\rfloor + \lfloor\delta m\rfloor + i). \tag{4.1}$$

Since $\lfloor a+b\rfloor - 1 \leqslant \lfloor a\rfloor + \lfloor b\rfloor \leqslant \lfloor a+b\rfloor + 1$, the above can be simplified to

$$\begin{aligned}\tilde{p}_n(\lfloor\epsilon n\rfloor)\tilde{p}_m(\lfloor\delta m\rfloor) &\leqslant 3\sum_{i=-8}^{8}\tilde{p}_{n+m}(\lfloor\epsilon n + \delta m\rfloor + i)\\ &\leqslant 51\tilde{p}_{n+m}(\lfloor\epsilon n + \delta m + i(n,m)\rfloor)\end{aligned} \tag{4.2}$$

where $i(n,m)$ is that value of i which maximizes the summand above and $|i(n,m)|\leqslant 8$.

Put $\delta = \epsilon$ in (4.2), and define $\tilde{q}_n(\lfloor\epsilon n\rfloor) = \tilde{p}_n(\lfloor\epsilon n\rfloor)/51$. Then

$$\tilde{q}_n(\lfloor\epsilon n - i(n,m)\rfloor)\tilde{q}_m(\lfloor\epsilon m\rfloor) \leqslant \tilde{q}_{n+m}(\lfloor\epsilon(n+m)\rfloor). \tag{4.3}$$

Suppose that n is given, and for fixed m, $n = Nm + r$. Applying the above inequality to $\tilde{q}_n(\lfloor\epsilon n\rfloor)$ recursively gives

$$\begin{aligned}\tilde{q}_n(\lfloor\epsilon n\rfloor) &\geqslant \tilde{q}_{mN+r}(\lfloor\epsilon(mN+r)\rfloor) \geqslant \tilde{q}_{mN}(\lfloor\epsilon(mN)\rfloor)\tilde{q}_r(\lfloor\epsilon r - i(mN,r)\rfloor)\\ &\geqslant \cdots \geqslant \prod_{l=1}^{N}\tilde{q}_m(\lfloor\epsilon m - i(ml, m(l-1)))\rfloor\tilde{q}_r(\lfloor\epsilon r - i(mN,r)\rfloor)\end{aligned} \tag{4.4}$$

where all the $i(a,b)$ are between -8 and 8. For a fixed value of m, there is a value of l which minimizes $\tilde{q}_m(\lfloor\epsilon m - i(ml, m(l-1))\rfloor)$. Let this value be l_m, and define $z_m = i(ml_m, m(l_m-1))$. Then $|z_m|\leqslant 8$. Replacing the $i(ml, m(l-1))$ above by z_m gives

$$\tilde{q}_n(\lfloor\epsilon n\rfloor) \geqslant [\tilde{q}_m(\lfloor\epsilon m - z_m\rfloor)]^N\tilde{q}_r(\lfloor\epsilon r - i(mN,r)\rfloor). \tag{4.5}$$

Take logarithms of this equation, divide by $n = mN + r$, and take $n\to\infty$ by letting $N\to\infty$. This gives

$$\liminf_{n\to\infty}\frac{1}{n}\log\tilde{q}_n(\lfloor\epsilon n\rfloor) \geqslant \frac{1}{m}\log\tilde{q}_m(\lfloor\epsilon m - z_m\rfloor). \tag{4.6}$$

Put $\epsilon = \delta$ in (4.2), and define $j(n,m) = i(n,m) + z_{n+m}$. Then $|j(n,m)|\leqslant 16$ and by arguing as in equation (4.3), we obtain

$$\tilde{q}_n(\lfloor\epsilon n - j(n,m)\rfloor)\tilde{q}_m(\lfloor\epsilon m\rfloor) \leqslant \tilde{q}_{n+m}(\lfloor\epsilon(n+m) - z_{n+m}\rfloor) \tag{4.7}$$

and consequently

$$\tilde{q}_m(\lfloor\epsilon m - z_m\rfloor) \geqslant \tilde{q}_k(\lfloor\epsilon k - j(k,m)\rfloor)\tilde{q}_{m-k}(\lfloor\epsilon(m-k)\rfloor) \tag{4.8}$$

where $k < m$. Substitute the above into equation (4.6), then

$$\liminf_{n\to\infty}\frac{1}{n}\log\tilde{q}_n(\lfloor\epsilon n\rfloor) \geqslant \frac{1}{m}\log\tilde{q}_k(\lfloor\epsilon k - j(k,m)\rfloor) + \frac{1}{m}\log\tilde{q}_{m-k}(\lfloor\epsilon(m-k)\rfloor). \tag{4.9}$$

Now take the lim sup of the above by letting $m \to \infty$, and for each value of m choose k such that $\tilde{q}_k(\lfloor \epsilon k - j(k,m) \rfloor) > 0$. Since $|j(k,m)| \leqslant 16$, we need at most 33 different values of k, and k stays therefore finite as $m \to \infty$. Consequently

$$\liminf_{n\to\infty} \frac{1}{n} \log \tilde{q}_n(\lfloor \epsilon n \rfloor) \geqslant \limsup_{m\to\infty} \frac{1}{m} \log \tilde{q}_m(\lfloor \epsilon(m) \rfloor) \tag{4.10}$$

and the limit exists, so that we can define

$$\tilde{\rho}(\epsilon) = \lim_{n\to\infty} \frac{1}{n} \log \tilde{p}_n(\lfloor \epsilon n \rfloor). \tag{4.11}$$

To see that $\tilde{\rho}(\epsilon)$ is concave, put $n = m$ in (4.2). This gives

$$\tilde{q}_n(\lfloor \epsilon n \rfloor)\tilde{q}_n(\lfloor \delta n \rfloor) \leqslant \tilde{q}_{2n}(\lfloor (\epsilon + \delta)n + i(n,n) \rfloor). \tag{4.12}$$

Take logarithms, divide by n and let $n \to \infty$. □

We are interested in the behaviour of $\tilde{\rho}(\epsilon)$, especially for small ϵ. This will give information on the asymptotic behaviour of the free energy as $\beta \to -\infty$.

Theorem 4.2. $\tilde{\rho}(\epsilon)$ is continuous at $\epsilon = 0$ and the right derivative at $\epsilon = 0$ is infinite. In addition, $\tilde{\rho}(0) = \kappa_2$ and there exists a positive number α_0 such that $\tilde{\rho}(1-\alpha) < \kappa_3$ for all $\alpha < \alpha_0$.

Proof.

(1) *We first prove continuity of $\tilde{\rho}(\epsilon)$ at $\epsilon = 0$, and the existence of α_0.* Note that $\tilde{\rho}(0) = \kappa_2$ since all polygons with no dihedral angles are planar. To prove continuity at $\epsilon = 0$, we must show that $\lim_{\epsilon\to 0} \tilde{\rho}(\epsilon) = \kappa_2$. Since $\kappa_3 > \kappa_2$, it follows that for small ϵ, $\tilde{\rho}(\epsilon) > \tilde{\rho(0)} = \kappa_2$. We now show that for any $\delta > 0$, $\lim_{\epsilon\to 0} \tilde{\rho}(\epsilon) \leqslant \delta + \kappa_2$. This establishes continuity at $\epsilon = 0$.

Let $\tilde{p}_n(t)$ be the number of polygons with n edges and absolute torsion t. Define c_n to be the number of self-avoiding walks of length n (in Z^3) and let $c_n^{(2)}$ be the number of self-avoiding walks of length n in Z^2. The connective constants for c_n and $c_n^{(2)}$ exist [12] and they are defined by $\lim_{n\to\infty} \frac{1}{n} \ln c_n = \kappa_3$, and $\lim_{n\to\infty} \frac{1}{n} \ln c_n^{(2)} = \kappa_2$ respectively. ¿From the existence of these limits, given $\delta > 0$ $\exists m = m(\delta)$ such that $c_m \leqslant \mathrm{e}^{(\kappa_3+\delta)m}$ and $c_m^{(2)} \leqslant \mathrm{e}^{(\kappa_2+\delta)m}$.

Choose $m < n$, and subdivide each polygon of length n into M subwalks of length m, with a remaining subwalk of length r, where $0 \leqslant r < m$ (thus $M = (n-r)/m$). If the total absolute torsion is t, then at most t of these subwalks are non-planar (that is, contain at least one dihedral angle). Thus

$$\begin{aligned}
\tilde{p}_n(t) &\leqslant \sum_{k=0}^{t} \binom{M}{k} c_m^k [c_m^{(2)}]^{M-k} c_r \\
&\leqslant \sum_{k=0}^{t} \binom{M}{k} \mathrm{e}^{(\kappa_3+\delta)km} \mathrm{e}^{(\kappa_2+\delta)(M-k)m} \mathrm{e}^{(\kappa_3+\delta)r} \\
&= \sum_{k=0}^{t} \binom{M}{k} \mathrm{e}^{(\kappa_3-\kappa_2)km} \mathrm{e}^{\kappa_2 Mm} \mathrm{e}^{\delta Mm} \mathrm{e}^{(\kappa_3+\delta)r} \\
&\leqslant \mathrm{e}^{\delta Mm} \mathrm{e}^{\kappa_2 Mm} \mathrm{e}^{(\kappa_3+\delta)m} \sum_{k=0}^{t} \binom{M}{k} \mathrm{e}^{(\kappa_3-\kappa_2)km}.
\end{aligned} \tag{4.13}$$

Let $t = \lfloor \epsilon n \rfloor$, take logarithms and divide by n

$$\frac{1}{n} \ln \tilde{p}_n(\lfloor \epsilon n \rfloor) \leqslant \frac{\delta Mm}{n} + \frac{\kappa_2 Mm}{n} + \frac{(\kappa_3+\delta)m}{n} + \frac{1}{n} \log \sum_{k=0}^{\lfloor \epsilon n \rfloor} \binom{M}{k} \mathrm{e}^{(\kappa_3-\kappa_2)km}. \tag{4.14}$$

Examine the final term; for small $\epsilon < 1/3m$ the maximum term in the summand when $k = \lfloor \epsilon n \rfloor$ is:

$$\frac{1}{n}\log\sum_{k=0}^{\lfloor \epsilon n\rfloor}\binom{M}{k}e^{(\kappa_3-\kappa_2)km} \leqslant \frac{1}{n}\log\left[(\lfloor \epsilon n\rfloor+1)\binom{M}{\lfloor \epsilon n\rfloor}e^{(\kappa_3-\kappa_2)\lfloor \epsilon n\rfloor m}\right]$$
$$= \frac{1}{n}\log(\lfloor \epsilon n\rfloor+1) + \frac{1}{n}\log\binom{M}{\lfloor \epsilon n\rfloor} + (\kappa_3-\kappa_2)\lfloor \epsilon n\rfloor m/n.$$

The combinatorial term in the last inequality can be bounded as follows from above:

$$\frac{1}{n}\log\binom{M}{\lfloor \epsilon n\rfloor} = \frac{1}{n}\log\binom{\frac{n-r}{m}}{\lfloor \epsilon n\rfloor} \leqslant \frac{1}{n}\log\binom{\lfloor \frac{n}{m}\rfloor}{\lfloor \epsilon n\rfloor}. \tag{4.15}$$

Since $\frac{1}{n}\log\binom{\lfloor \frac{n}{m}\rfloor}{\lfloor \epsilon n\rfloor} = \frac{1}{n}\lfloor \frac{n}{m}\rfloor \log(\lfloor \frac{n}{m}\rfloor/(\lfloor \frac{n}{m}\rfloor - \lfloor \epsilon n\rfloor)) + \frac{1}{n}\lfloor \epsilon n\rfloor \log((\lfloor \frac{n}{m}\rfloor - \lfloor \epsilon n\rfloor)/\lfloor \epsilon n\rfloor) \to -\frac{1}{m}\log(1-\epsilon m) - \epsilon\log\epsilon + \epsilon\log(\frac{1}{m}-\epsilon)$ as $n\to\infty$, it follows that

$$\lim_{n\to\infty}\frac{1}{n}\log\tilde{p}_n(\lfloor \epsilon n\rfloor) \leqslant \delta + \kappa_2 + (\kappa_3-\kappa_2)\epsilon m$$
$$-\frac{1}{m}\log(1-\epsilon m) - \epsilon\log\epsilon + \epsilon\log\left(\frac{1}{m}-\epsilon\right). \tag{4.16}$$

Now letting $\epsilon \to 0$ with δ (and hence m) fixed we obtain

$$\lim_{\epsilon\to 0}\lim_{n\to\infty}\frac{1}{n}\log\tilde{p}_n(\lfloor \epsilon n\rfloor) \leqslant \delta + \kappa_2. \tag{4.17}$$

Since δ is arbitrarily small, this proves continuity.

Since $\tilde{\rho}(\epsilon)$ is continuous in $[0, 1)$, the above implies that there exists an $\epsilon_m > 0$ such that $\epsilon_m = \min\{\epsilon|\tilde{\rho}(\epsilon) = \kappa_3\}$. Finally, the existence of α_0 follows from Kesten's pattern theorem [20]: If α is small, then almost all edges are in dihedral angles, and the density of the pattern $\{i, i\}$ is low, and so $\tilde{\rho}(1-\alpha) < \kappa_3$. Choose α_0 to be the maximum which makes this true.

(2) *We next prove that the right derivative of $\tilde{\rho}(\epsilon)$ is infinite at $\epsilon = 0$.* Let $p_n^{(2)}(\lambda n, Q)$ be the number of n-edge polygons in Z^2 which contain a given pattern (a subwalk) Q at least λn times. By Kesten's pattern theorem there exists a $\lambda_0(Q)$ such that for all $\lambda \leqslant \lambda_0(Q)$

$$p_n^{(2)}(\lambda n, Q) = e^{\kappa_2 n + o(n)} \tag{4.18}$$

provided that Q is a Kesten pattern. (A Kesten pattern is a subwalk which can occur three times in a self-avoiding walk.) We choose Q to be the pattern in figure 3. By changing it as shown to Q' it contributes $+1$ to the torsion of the resulting polygon, and $+3$ to the number of dihedral angles.

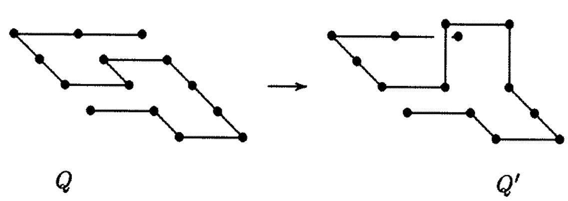

Figure 3. The pattern Q can be changed into a non-planar pattern Q' which gives a contribution of $+1$ to the torsion or $+3$ to the number of dihedral angles in a polygon.

Take $0 < \epsilon < \lambda < \lambda_0(Q)$. Then we can select $\lfloor \epsilon n \rfloor$ patterns Q from any $\lfloor \lambda n \rfloor$ to create a polygon with absolute torsion $3\lfloor \epsilon n \rfloor$. This gives a lower bound on the number of polygons with absolute torsion $3\lfloor \epsilon n \rfloor$, which we express as follows

$$\tilde{p}_n(3\lfloor \epsilon n \rfloor) \geqslant \binom{\lfloor \lambda n \rfloor}{\lfloor \epsilon n \rfloor} p_n^{(2)}(\lambda n, Q). \tag{4.19}$$

Taking the logarithm of this, dividing by n and letting $n \to \infty$ gives

$$\tilde{\rho}(3\epsilon) \geqslant \lambda \log \lambda - \epsilon \log \epsilon - (\lambda - \epsilon) \log(\lambda - \epsilon) + \kappa_2 \tag{4.20}$$

for any $\epsilon > 0$. Note that the function $f(\epsilon) = \lambda \log \lambda - \epsilon \log \epsilon - (\lambda - \epsilon) \log(\lambda - \epsilon)$ has an infinite right derivative at $\epsilon = 0$, for any fixed $\lambda > 0$. Since $\tilde{\rho}(0) = \kappa_2$, and is continuous at $\epsilon = 0$, it follows that $\tilde{\rho}(\epsilon)$ has infinite right derivative at $\epsilon = 0$. □

We next state a similar theorem about the behaviour of $\tilde{\rho}(\epsilon)$ at $\epsilon = 1$.

Theorem 4.3. $\tilde{\rho}(\epsilon)$ is continuous at $\epsilon = 1$ and the left derivative at $\epsilon = 1$ is equal to minus infinity.

We omit the details of the proof but note that the idea is similar to the proof of theorem 4.2. □

We now examine the consequences of these theorems for the asymptotic behaviour of the free energy. Define $\epsilon_m = \min\{\epsilon | \tilde{\rho}(\epsilon) = \kappa_3\}$. Then ϵ_m exists by theorem 4.2. It follows that

$$\lim_{n \to \infty} \frac{1}{n} \log \tilde{p}_n(\lfloor \epsilon_m n \rfloor) = \kappa_3 \tag{4.21}$$

and the number of polygons p_n is dominated (exponentially) by polygons with a 'density' $\frac{\lfloor \epsilon_m n \rfloor}{n}$ of dihedral angles. Figure 4 is a schematic diagram of $\tilde{\rho}(\epsilon)$. It is not clear whether the maximum is attained at a single point, or in an interval. (If it is attained in an interval, then there is a first-order phase transition between the high- and low-density phases).

The right derivative of $\tilde{\rho}(\epsilon)$ at $\epsilon = 0$ is $+\infty$, as shown in theorem 4.2. The Legendre transform

$$\tilde{\mathcal{F}}(\beta) = \sup_{\epsilon} \{\tilde{\rho}(\epsilon) + \epsilon \beta\} \tag{4.22}$$

connects the density function to the free energy [21, 22]. By equation (4.20) we have

$$\tilde{\rho}(3\epsilon) \geqslant \log \left(\frac{\lambda^\lambda}{\epsilon^\epsilon (\lambda - \epsilon)^{(\lambda - \epsilon)}} \right) + \kappa_2 \tag{4.23}$$

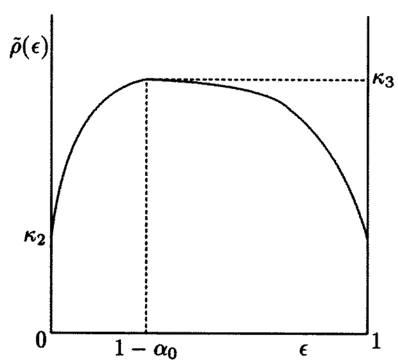

Figure 4. The density function $\tilde{\rho}(\epsilon)$.

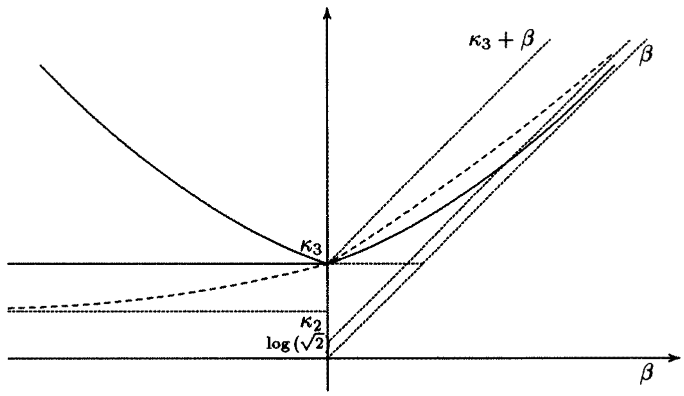

Figure 5. A schematic graph of the free energies.

where $0 < \epsilon < \lambda < \lambda_0$. But

$$\begin{aligned}3\epsilon\beta + \log\left(\frac{\lambda^\lambda}{\epsilon^\epsilon(\lambda-\epsilon)^{(\lambda-\epsilon)}}\right) &= 3\epsilon\beta + \lambda\log\lambda - (\lambda-\epsilon)\log(\lambda-\epsilon) - \epsilon\log\epsilon \\ &\geqslant \epsilon(3\beta + \log\lambda - \log\epsilon) - (\lambda-\epsilon)\log\left(1-\frac{\epsilon}{\lambda}\right) \\ &> 0 \qquad \text{if } 3\beta + \log\lambda > \log\epsilon \end{aligned} \tag{4.24}$$

and, for every β, there is such an ϵ. Thus $\tilde{\mathcal{F}}(\beta) > \kappa_2$ for all finite β. On the other hand, $\tilde{\mathcal{F}}(\beta)$ is asymptotic to κ_2 as $\beta \to -\infty$. To see this, note that from equations (4.16) and (4.22) for any $\delta > 0$, there is an m such that

$$\tilde{\mathcal{F}}(\beta) \leqslant \delta + \kappa_2 + \sup_\epsilon\{\epsilon(\log 2 + (\kappa_3 - \kappa_2)m + \beta)\}. \tag{4.25}$$

If β is sufficiently negative at $\log 2 + (\kappa_3 - \kappa_2)m + \beta < 0$, then the above supremum is attained at $\epsilon = 0$, and $\tilde{\mathcal{F}}(\beta)$ is within δ of κ_2. Theorem 4.3 implies that the free energy, $\tilde{\mathcal{F}}(\beta)$, never reaches its asymptote as $\beta \to \infty$. The free energies are sketched in figure 5.

5. Discussion

We have introduced three measures of the torsion of a self-avoiding polygon, which we call the *torsion*, the *excess torsion* and the *absolute torsion*. By attaching a fugacity (β) we define appropriate generating functions, and limiting quantities which correspond to free energies. We obtain rigorous results about the dependence of these free energies on their corresponding torsion fugacities, and show that the free energy corresponding to the excess torsion is non-analytic at $\beta = 0$. The mean excess torsion increases as $\sqrt{n}$ [23] for $\beta = 0$ but as the first power of n for positive β.

The mean torsion is clearly zero at $\beta = 0$ and we prove that it increases linearly with n for positive β (and decreases linearly with n for negative β), while the mean absolute torsion increases linearly with n for all $\beta > -\infty$.

We expect that at large positive β the mean torsion and the excess torsion are both dominated by polygons with helical structures, and that the mean absolute torsion is dominated by highly non-planar structures. At large negative β the mean torsion is dominated by helical structures (but of the opposite side), the mean excess torsion is dominated by polygons in which the positive and negative contributions to the torsion roughly cancel, and the mean absolute torsion is dominated by planar structures.

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References

[1] Arteca G A and Mezey P G 1992 *Biopolymers* **32** 1609
[2] Janse van Rensburg E J, Orlandini E, Sumners D W, Tesi M C and Whittington S G 1993 *J. Phys. A: Math. Gen.* **26** L981
[3] Vologodskii A V and Cozzarelli N R 1994 *Ann. Rev. Biophys. Biomol. Struct.* **23** 609
[4] Bauer W R, Crick F H C and White J H 1980 *Sci. American* **243** 118
[5] Rees D A 1973 Polysaccharide conformation *MTP Int. Review of Science, Organic Chemistry, Series One* vol 7 (London: Butterworths)
[6] White J H 1969 *Am. J. Math.* **91** 693
[7] Janse van Rensburg E J, Orlandini E, Sumners D W, Tesi M C and Whittington S G 1994 *Phys. Rev.* E **50** 4279
[8] Orlandini E, Janse van Rensburg E J and Whittington S G 1996 *J. Stat. Phys.* **82** 1159
[9] Janse van Rensburg E J, Orlandini E, Sumners D W, Tesi C and Whittington S G 1996 *J. Stat. Phys.* **85** 103
[10] Struik D J 1988 *Lectures on Classical Differential Geometry* (New York: Dover)
[11] Alexandrov A D and Reshetniyak Y G 1989 *General Theory of Irregular Curves* (Dordrecht: Kluwer)
[12] Hammersley J M 1957 *Proc. Camb. Phil. Soc.* **53** 642
[13] Hammersley J M 1961 *Proc. Camb. Phil. Soc.* **57** 516
[14] Hille E 1948 *Functional Analysis and Semi-groups (AMS Colloq. Publ. 31)* (New York: American Mathematical Society)
[15] Hardy G H, Littlewood J E and Pòlya G 1952 *Inequalities* 2nd edn (New York: Cambridge University Press)
[16] Hammersley J M, Torrie G M and Whittington S G 1982 *J. Phys. A: Math. Gen.* **15** 539
[17] Soteros C E, Sumners D W and Whittington S G 1992 *Math. Proc. Camb. Phil. Soc.* **111** 75
[18] Kesten H 1963 *J. Math. Phys.* **4** 960
[19] Madras N and Slade G 1992 *The Self-avoiding Walk* (Boston, MA: Birkhauser)
[20] Sumners D W and Whittington S G 1988 *J. Phys. A: Math. Gen.* **21** 1689
[21] Madras N, Soteros C E and Whittington S G 1988 *J. Phys. A: Math. Gen.* **21** 4617
[22] Ellis R S 1985 *Entropy, Large Deviations and Statistical Mechanics (A Series of Comprehensive Studies in Mathematics 271)* (Berlin: Springer)
[23] Tesi M C 1996 Geometrical entanglement in lattice models of ring polymers: Torsion and writhe *Preprint*