Thermodynamic and topological properties of copolymer rings with a segregation/mixing transition

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Abstract

Two ring polymers close to each other in space may be either in a segregated phase if there is a strong repulsion between monomers in the polymers, or intermingle in a mixed phase if there is a strong attractive force between the monomers. These phases are separated by a critical point which has a $\theta$-point character. The metric and topological properties of the ring polymers depend on the phase, and may change abruptly at the critical point. In this paper we examine the thermodynamics and linking of two ring polymers close in space in both the segregated and mixed phases using a cubic lattice model of two polygons interacting with each other. Our results show that the probability of linking is low in the segregated phase, but that it increases through the critical point as the model is taken into the mixed phase. We also examine the metric and thermodynamic properties of the model, with focus on how the averaged measures of topological complexity are related to these properties.

Keywords: Links, lattice polygons, polymer collapse, Monte Carlo methods.

1 Introduction

Mutually attracting pairs of circular or ring polymers in solution undergo a transition from a segregated to a mixed phase at a critical temperature. The metric and topological properties of the polymers are different in the segregated and mixed phases, changing at the critical temperature from expanded spatially segregated conformations to more compact conformations in the mixed phase where the two polymers interpenetrate. In [1] the segregation-mixing transition of a polymer-polymer-solvent mixture is discussed in chapter IV.4. There it is argued that in a good solvent the polymer coils behave like hard spheres which cannot interpenetrate (they are segregated). In a poor solvent, however, the coils tend to exclude the solvent and are driven together increasing the local concentration which, if high enough, should drive the system through a $\theta$-transition into
a collapsed phase. This should also occur if there is a strong attractive interaction between the polymer coils, where they exclude solvent molecules by mixing in close proximity to one another.

In this paper we aim to model the segregated-mixed phases in a model of a system composed of a pair of proximate ring polymers which may be linked, especially when they are in the mixed phase. We use a cubic lattice closed self-avoiding walk model (lattice polygons) where the proximity is modelled by forcing the polygons to have at least one pair of vertices (one vertex in each polygon) a unit distance apart. See figure 1(a) for an example. The two polygons are both self-avoiding and mutually avoiding in the lattice.

Our model is also useful as a model for a particular class of diblock copolymers with figure eight connectivity composed of two polygons joined together by sharing a single step (see figure 1b). Each polygon is a block in the copolymer, and both polygons are in a good solvent but there is a short range interaction between vertices located in each of the two polygons. If the interaction is a strong attractive force, then the two polygons in the figure eight will tend to interpenetrate, otherwise they will segregate due to an entropic repulsion between them. One may also consider ring formation in a uniform 4-star polymer with two A-arms and two B-arms. The star polymer can be cyclized to form an A ring and a B ring, in conditions with different interaction strengths between the two rings, resulting in different extents of linking of the two rings.

We shall focus (in particular) on the metric and topological properties of our model in the segregated and mixed phases. Our aim is to address the following questions:

- How do configurational properties (such as mean extension, shape and entanglement) depend on the strength of the interaction between the component polygons (or blocks)?
- How do topological properties of the system (such as the complexity of linking between the component polygons) differ in the segregated and mixed phases?
- How does topological complexity, as measured in terms of the link spectrum, depend on the degree of mixing?

The configurational and topological properties of the model could be different in the segregated and mixed phases. In the segregated phase the component polygons tend to be separated in space, and so the degree of linking between them will be low, while in the mixed phase they may be strongly intermingled with a high degree of linking. It is not clear a priori that the transition will be strongly signalled in the configurational properties of the model. While the segregated phase will have the scaling properties of a self-avoiding walk, as the model crosses the critical point into the mixed phase the two polygons might form ribbon-like structures [2, 3]. If this is all that happens then the critical exponents of the mixed phase will still be given by self-avoiding walk exponents. The interactions between different parts of the ribbon boundaries could lead to further collapse, similar to that of a self-avoiding walk having gone through a θ-transition into its dense phase. This transition should be signalled in the linking (and in the mean topological invariants such as linking number) of the two components, and the critical properties (such as the radius of gyration exponent) might be different on the two sides of the transition.

The plan of the paper is as follows. In section 2 we describe the model and its partition function and free energy. Section 3 contains some theorems establishing the existence of a transition from a segregated phase to a mixed phase. In section 4 we discuss the Monte Carlo methods used to sample configurations and consider the results of the simulations (and in particular the metric and shape properties of the system as a function of the attractive interaction). Results on the topological
2 The model

We model circular polymers as lattice self-avoiding polygons of length \(n\). These are embeddings of simple closed curves in the simple cubic lattice \(\mathbb{Z}^3\). The embeddings are also simple closed curves in \(\mathbb{R}^3\) with well defined topological properties (knots and links). In this paper the lattice polygons are mutually avoiding and placed in \(\mathbb{Z}^3\) such that a pair of vertices (one vertex in each polygon) are a unit distance apart (see figure 1). We label the two polygons by \(A\) and \(B\) respectively so that this is a model of two adjacent rings \(A\) and \(B\) which may be linked, or parts of a copolymer with a figure eight connectivity and two blocks, each a ring of the figure eight.

A **mutual contact** between polygons \(A\) and \(B\) is a pair of vertices \((v_A, v_B)\), such that \(v_A \in A\) and \(v_B \in B\) and the distance between \(v_A\) and \(v_B\) is equal to one: \(d(v_A, v_B) = 1\). An interaction between the two polygons (or blocks in the copolymer) is introduced by introducing an energy \(\epsilon_m\) associated with each mutual contact, and then defining the parameter \(\beta_m = -\frac{\epsilon_m}{k_B T}\) where \(k_B\) is Boltzmann’s constant and \(T\) is the absolute temperature. Denoting the number of conformations of the lattice model of total length \(2n\) (each polygon component of length \(n\)) with \(k_m\) mutual contacts by \(p^{(2)}_{2n}(k_m)\), the equilibrium properties of the system are given by the partition function

\[
Z_{2n}(\beta_m) = \sum_{k_m} p^{(2)}_{2n}(k_m)e^{\beta_m k_m}.
\]  

(1)

Entropy dominates the model when \(\beta_m \leq 0\) and the two component polygons tend to stay separated (this is a **segregated phase** due to the mutual avoidance between the polygons inducing a short-ranged repulsion between them). When \(\beta_m > 0\) is large enough, then the mutual contacts induce an attraction between the component polygons, and one expects this to increase the number of mutual contacts. In this case one expects the most likely conformations to be those where the two polygons interpenetrate strongly in a **mixed phase**.

The free energy per unit length is given by \(f_{2n}(\beta_m) = \frac{1}{2n} \log Z_{2n}(\beta_m)\) and by taking \(n \to \infty\) the
limiting free energy of the model is obtained:
\[
f(\beta_m) = \lim_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m). \tag{2}
\]

It is not known that this limit exists for all values of \( \beta_m \in \mathbb{R} \) but we shall show that it exists for \(-\infty < \beta_m \leq 0\) and is equal to \( \kappa_3 = \log \mu_3 \) where \( \kappa_3 \) is the connective constant and \( \mu_3 \) is the growth constant of cubic lattice self-avoiding walks \([4]\) (see section 3). When \( \beta_m > 0 \) the situation is more complicated and we shall rely on Monte Carlo simulations to explore the model in this regime.

3 Some rigorous results

In this section we obtain some bounds on the partition function \( Z_{2n}(\beta_m) \) and use these to prove the existence of the thermodynamic limit when \( \beta_m \leq 0 \) and the existence of a phase transition in the system. We also obtain some similar results for fixed link type.

Attach the coordinate system \((x_1, x_2, x_3)\) to \( \mathbb{Z}^3 \) so that the coordinates of the vertices are all integers. Write \( p_n \) for the number of \( n \)-edge polygons (modulo translation) so that \( p_{2m+1} = 0 \), \( p_4 = 3 \), \( p_6 = 22 \), etc. Hammersley \([4]\) has shown that \( \lim_{n \to \infty} \frac{1}{n} \log p_n = \log \mu_3 \) where \( \mu_3 \) is the growth constant of self-avoiding walks on this lattice. Similarly, if we write \( q_n \) for the corresponding number of polygons on the square lattice \( \mathbb{Z}^2 \) then \( \lim_{n \to \infty} \frac{1}{n} \log q_n = \log \mu_2 \) where \( \mu_2 \) is the growth constant of self-avoiding walks on the square lattice.

**Theorem 1.** If \(-\infty < \beta_m \leq 0\) then
\[
\lim_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) = \kappa_3 = \log \mu_3.
\]

**Proof:** To obtain an upper bound consider \( \beta_m = 0 \). Embed a polygon with \( n \) edges in \( p_n \) ways and embed a second \( n \)-edge polygon in a box of side \( 2n \) centred on the first polygon, This implies that
\[
Z_{2n}(0) \leq p_n^2 e^{o(n)} \quad \text{so that}
\]
\[
\limsup_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) \leq \limsup_{n \to \infty} \frac{1}{2n} \log Z_{2n}(0) \leq \log \mu_3, \quad \text{if } \beta_m \leq 0.
\]

To get a lower bound construct two polygons, one \((\sigma_1)\) with \( n-2 \) edges and the other \((\sigma_2)\) with \( n \) edges. For \( \sigma_1 \) translate the right-most top-most edge a unit distance to the right and add two edges to reconnect the polygon to form \( \sigma_3 \). Translate \( \sigma_3 \), and rotate it if necessary, so that its right-most edge is unit distance from an edge of \( \sigma_2 \) and there are exactly two vertices of \( \sigma_3 \) that are unit distance from vertices of \( \sigma_2 \). This gives the bound
\[
Z_{2n}(\beta_m) \geq p_n p_{n-2} e^{2\beta_m/2}
\]
since exactly two new mutual contacts are created. Taking logarithms, dividing by \( 2n \) and letting \( n \to \infty \) gives
\[
\liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) \geq \log \mu_3
\]
which completes the proof. \( \Box \)

**Theorem 2.** If \( \beta_m > 0 \) and \( 0 < \alpha < 1 \) then
\[
\liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) \geq \frac{\alpha}{2} \left[ \log \mu_2 + \beta_m \right] + (1 - \alpha) \log \mu_3.
\]
Since \( \alpha \in (0, 1) \) is arbitrary, this shows that
\[
\liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) \geq \max \left( \frac{1}{2} \left[ \log \mu_2 + \beta_m \right], \log \mu_3 \right).
\]

Proof: Construct a polygon \( \sigma_1 \) in the plane \( x_1 = 0 \) with \( \lfloor \alpha n \rfloor \) edges, \( 0 < \alpha < 1 \). Let \( \sigma_2 \) be a translate of \( \sigma_1 \) in the plane \( x_1 = 1 \). Let \( \sigma_3 \) be a polygon in \( \mathbb{Z}^3 \) with \( n - \lfloor \alpha n \rfloor \) edges and with no vertices with \( x_1 > -1 \). Similarly, let \( \sigma_4 \) be a polygon in \( \mathbb{Z}^3 \) with \( n - \lfloor \alpha n \rfloor \) edges and with no vertices with \( x_1 < 2 \). Concatenate \( \sigma_1 \) and \( \sigma_3 \) to obtain a polygon with \( n \) edges and, similarly, concatenate \( \sigma_2 \) and \( \sigma_4 \). The two resulting polygons have \( \lfloor \alpha n \rfloor \) pairs of vertices unit distance apart so that they contribute a Boltzmann factor \( \exp[\beta_m \lfloor \alpha n \rfloor] \) to the partition function \( Z_{2n}(\beta_m) \). \( \sigma_1 \) can be chosen in \( \mu_2^{\lfloor \alpha n \rfloor + o(n)} \) ways, \( \sigma_2 \) can be chosen in only one way, while \( \sigma_3 \) and \( \sigma_4 \) can each be chosen in \( \mu_3^{n - \lfloor \alpha n \rfloor + o(n)} \) ways. This construction gives a lower bound on \( Z_{2n}(\beta_m) \)
\[
Z_{2n}(\beta_m) \geq q_{\lfloor \alpha n \rfloor} \mu_2^{\lfloor \alpha n \rfloor} e^{\beta_m \lfloor \alpha n \rfloor} / 4 = \mu_2^{\lfloor \alpha n \rfloor + o(n)} \mu_3^{2(n - \lfloor \alpha n \rfloor) + o(n)} e^{\beta_m \lfloor \alpha n \rfloor}.
\]
Taking logarithms of the above, dividing by \( 2n \), and letting \( n \to \infty \), the claimed lower bound is obtained.

\[ \square \]

**Theorem 3.** \( \liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) \) is non-analytic at \( \beta_m^0 \) where \( 0 \leq \beta_m^0 \leq 2 \log \mu_3 - \log \mu_2 \).

Proof: We can rewrite the result of theorem 2 as
\[
\liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}(\beta_m) \geq \alpha \left[ \frac{1}{2} (\log \mu_2 + \beta_m) - \log \mu_3 \right] + \log \mu_3
\]
and this is equal to \( \log \mu_3 \) when
\[
\frac{1}{2} (\log \mu_2 + \beta_m) - \log \mu_3 = 0, \quad \text{for } 0 < \alpha < 1.
\]
This shows that the limiting infimum is greater than \( \log \mu_3 \) when \( \beta_m > 2 \log \mu_3 - \log \mu_2 \). Therefore the limiting infimum is singular at some \( \beta_m^0 \) where
\[
0 \leq \beta_m^0 \leq 2 \log \mu_3 - \log \mu_2
\]
which completes the proof.

\[ \square \]

### 3.1 Bounds on the free energies of linked conformations

The free energies of linked conformations of specified links can also be bounded using arguments similar to the above. We proceed by recalling that the growth constant of unknotted polygons is defined by the limit [5]
\[
\lim_{n \to \infty} \frac{1}{n} \log p_n(\emptyset) = \log \mu_{\emptyset}.
\]
It is known that \( \mu_{\emptyset} < \mu_3 \) [5, 6]. One may similarly define the growth constant \( \mu_K \) of knotted polygons of knot type \( K \) by
\[
\limsup_{n \to \infty} \frac{1}{n} \log p_n(K) = \log \mu_K.
\]
It is known that $\mu_0 \leq \mu_K < \mu_3$ \cite{7}

Denote the number of linked conformations of link type $L$, with polygon components of length $n$ each, and with $k_m$ mutual contacts, by $p^{(2)}_{2n}(k_m, L)$. The partition function is

$$Z^{(2)}_{2n}(\beta_m, L) = \sum_{k_m} p^{(2)}_{2n}(k_m, L) e^{\beta_m k_m}$$

and it is a sum of weighted conformations of fixed linked type $L$ and total length $2n$.

An example of a linked conformation in our model is shown in figure 2. This conformation is a Hopf-link and it has weight $e^{13\beta_m}$ (since $k_m = 13$) in the partition function. More generally, the two components of a lattice link of link type $L$ are lattice knots of knot types $K_1$ and $K_2$ respectively. In many cases $K_1 = K_2 = \emptyset$ (for example, if $L$ is the Hopf link, as shown in figure 2), but $K_1$ and $K_2$ could be (necessarily) non-trivial knots for certain link types, or could be chosen to be given knot types.

We generalize theorem 1 as follows.

**Theorem 4.** Suppose that $L$ is a 2-component link with components of knot types $K_1$ and $K_2$. Then, if $-\infty < \beta_m \leq 0$,

$$\log \mu_0 \leq \liminf_{n \to \infty} \frac{1}{2n} \log Z^{(2)}_{2n}(\beta_m, L) \leq \limsup_{n \to \infty} \frac{1}{2n} \log Z^{(2)}_{2n}(\beta_m, L) < \log \mu_3.$$ 

In the event that $K_1 = K_2 = \emptyset$, then $\lim_{n \to \infty} \frac{1}{2n} \log Z^{(2)}_{2n}(\beta_m, L) = \log \mu_0 < \log \mu_3$.

Proof: An upper bound is obtained by first noting that $Z^{(2)}_{2n}(\beta_m, L) \leq Z^{(2)}_{2n}(0, L)$, and then counting the number of conformations of the component polygons independently, times the number of ways they may be placed so that the link may be recovered. Each component polygon is a placement of a simple closed polygon of fixed knot type, say $K_1$ for the first polygon, and $K_2$ for the second polygon. This shows that

$$Z^{(2)}_{2n}(1, L) \leq n^3 p_n(K_1) p_n(K_2)$$

Taking logarithms, dividing by $2n$ and letting $n \to \infty$, gives

$$\limsup_{n \to \infty} \frac{1}{2n} \log Z^{(2)}_{2n}(\beta_m, L) \leq \frac{1}{2} (\log \mu_{K_1} + \log \mu_{K_2}) < \log \mu_3.$$

Figure 2: A linked conformation of two polygons with one mutual contact shown. The total number of mutual contacts between the two polygons is $k_m = 13$, while each polygon component has length $n = 14$. In this case the link type is $L = 2^7_1$, the Hopf link.
In the event that the two component polygons of the link are both the unknot, then $K_1 = K_2 = \emptyset$ and

$$\limsup_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L) \leq \log \mu_\emptyset.$$ 

**Figure 3:** A schematic diagram with a construction to create a link in the cubic lattice. The link is represented by a tangle $T$ drawn inside a square in the $x_3 = 0$ plane of the lattice. By subdividing the cubic lattice, the tangle can be pushed onto the edges in the $x_3 = 0$ plane and only stepping into the $x_3 = 1$ plane to create overpasses in the projection. Moreover, one component of the tangle has endpoints in the left-most boundary of the square while the other has endpoints in its right-most boundary. By adding edges at $A$ and $B$ respectively, the components of $T$ can be closed into polygons such that the bottom and top edges of $T$ are in different components. The top edge of an unknotted polygon $\sigma_1$ is concatenated to the bottom edge of $T$ at $A$, and the bottom edge of an unknotted polygons $\sigma_2$ is concatenated to the top edge of $T$ at $B$.

Consider the schematic diagram in figure 3 to find the lower bound. A link $L$ is represented as a two-dimensional tangle $T$ which is embedded in the $x_3 = 0$ plane of the cubic lattice, accommodating overpasses in $T$ by stepping into the $x_3 = 1$ plane. The embedding of $T$ is completed into a link by closing each component into a polygon such that the edge with lexicographic least midpoint (the bottom edge), and the edge with lexicographic most midpoint (the top edge), are in different components of the tangle. This is shown as $A$ and $B$ in figure 3.

Proceed by concatenating the top edge of an unknotted polygon $\sigma_1$ onto the bottom edge $A$, and the bottom edge of a second unknotted polygon $\sigma_2$ onto the top edge $B$, as illustrated. Assume that the length of the first component in the embedded tangle $T$ is $m_1$, and of the second component, $m_2$. Fix the length of $\sigma_1$ to be $n - m_1$, and of $\sigma_2$ to be $n - m_2$. This creates a link $L$ of link type determined by $T$, and since the overpasses in $T$ are accommodated by overstepping into the $x_3 = 1$ plane, there is at least one mutual contact between the components of $T$, as required. There are $j_m \geq 1$ mutual contacts in $L$, and $j_m \leq 4(m_1 + m_2)$ since a polygon of length $m_1$ has at most 4 mutual contacts for each vertex, and since $\sigma_1$ and $\sigma_2$ do not contribute any such mutual contacts.

Since the orientation of the top edge of $\sigma_1$ has to match that of $A$, there are $p_{n-m_1}(\emptyset)/2$ choices for $\sigma_1$. Similarly, there are $p_{n-m_2}(\emptyset)/2$ choices for $\sigma_2$. This shows that

$$p_{n-m_1}(\emptyset) p_{n-m_2}(\emptyset) e^{j_m j_m} \leq 2^2 Z_{2n}^{(2)}(\beta_m, L).$$

Take logarithms, divide by $2n$, and let $n \to \infty$. Since $m_1$ and $m_2$ are fixed, this shows that

$$\log \mu_\emptyset \leq \liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L).$$

This completes the proof. $\square$
Lower bounds on the free energies of linked conformations of the model in figure 1(a) are determined using a construction similar to that in the proof of theorem 2. A schematic diagram is shown in figure 4. The intersection of the $x_3 = 0$ and $x_3 = 1$ planes and $\mathbb{Z}^3$ is a slab $S$ of height 1. (That is, $S$ consists of two square lattice planes a distance one apart in the $x_3$-direction). Let $T$ be a tangle diagram of a link of type $L$. Then $T$ can be realised as two self-avoiding walks in $S$ such that the endpoints of the self-avoiding walks are in a plane $x_1 = k$, and with the self-avoiding walks confined to the lattice points in $S$ with $x_1 \leq k$. We next translate the tangle, and extend the endpoints of its component self-avoiding walks by adding steps, if necessary, into the $x_1 > k$ sublattice such that the two component self-avoiding walks have the same lengths $\ell$, and the the four endpoints have coordinates $(m, 0, 0)$, $(m, 0, 1)$, $(m, 1, 0)$ and $(m, 1, 1)$ where $(m, 0, 0)$ and $(m, 1, 0)$ are the endpoints of one self-avoiding walk, and $(m, 0, 1)$ and $(m, 1, 1)$ are the endpoints of the second self-avoiding walk. By adding two edges to close off the tangle into a linked pair of polygons, the link $L$ is realised as a lattice link of type $L$. We assume that there are $c_0$ mutual contacts between the component self-avoiding walks.

![Figure 4: Schematic of a tangle T embedded in a slab S and two polygons σ₁ and σ₂, each of length n, concatenated onto the components of the tangle. Since σ₂ is a translation of σ₁ one step along the x₃-direction, the number of mutual contacts between them is n.](image)

As shown in figure 4, let $\sigma_1$ be a square lattice self-avoiding polygon in the $x_3 = 0$ plane, and $\sigma_2$ be the translate of $\sigma_1$ one step in the $x_3$-direction. If the length of $\sigma_1$ is $n$, then there are $n$ mutual contacts between the pair of polygons $(\sigma_1, \sigma_2)$. This pair can be translated together and concatenated on the link $L$ by placing the left-most and nearest edge (the bottom edge) of $\sigma_1$ one step in the $x_1$-direction to the edge joining the endpoints $(m, 0, 0)$ and $(m, 1, 0)$. Then $\sigma_2$ has its bottom edge one step in the $x_1$-direction from the edge joining the endpoints $(m, 0, 1)$ and $(m, 1, 1)$. The concatenation gives a lattice link of type $L$, with total length $2\ell + 2n + 2$. The total number of mutual contacts is $c_0 + n$. This shows that

$$Z_{2^{\ell+2n+2}}^{(2)}(\beta_m, L) \geq q_n \beta_m^{c_0+n},$$

since the number of choices for $\sigma_1$ is $q_n$, the number of square lattice polygons of length $n$.

By taking logarithms of equation (6), dividing by $2n$ and then taking $n \rightarrow \infty$, the following theorem is proven.

**Theorem 5.** If $\beta_m > 0$ then $\liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L) \geq \frac{1}{2} (\log \mu_2 + \beta_m).$ \hfill $\square$

The corollary of theorems 2 and 5 is that there is, for some link types, a critical point $\beta_m^{(L)}$.

**Corollary 1.** Suppose that $L$ is a link with components each of knot type the unknot. Then the limit $\liminf_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L)$ is non-analytic at a critical point $\beta_m^{(L)}$, where $0 \leq \beta_m^{(L)} < 2 \log \mu_0 - \log \mu_2$. 

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Note that if \( \beta_m \leq 0 \), then by theorem 4, \( \lim_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L) = \log \mu_0 \). On the other hand, if \( \beta_m > 0 \), then by theorem 5, \( \lim \inf_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L) \geq \frac{1}{2} \left( \log \mu_2 - \log \mu_2 \right) \). This lower bound is greater than \( \log \mu_0 \) if \( \beta_m > 2 \log \mu_0 - \log \mu_2 \). Thus, there is a non-analyticity at a critical point \( \beta_m^{(L)} \in [0, 2 \log \mu_0 - \log \mu_2] \) in \( \lim \inf_{n \to \infty} \frac{1}{2n} \log Z_{2n}^{(2)}(\beta_m, L) \) as claimed. \( \square \)

Since \( \mu_0 < \mu_3 \) the upper bound in corollary 1 is strictly smaller than the upper bound given in theorem 3. In addition, note that the probability of seeing a link of type \( L \) (and with both components the unknot), is

\[
P_{2n}(L) = \frac{Z_{2n}^{(2)}(\beta_m, L)}{Z_{2n}(\beta_m)}.
\]

By theorems 1 and 4,

\[
P_{2n}(L) = K \left( \frac{\mu_0}{\mu_3} (1 + o(1)) \right)^{2n} \to 0, \quad \text{if } n \to \infty \text{ and } \beta_m \leq 0.
\]

Since \( |\mu_3 - \mu_0| \approx 10^{-6} \) [8, 9], the convergence of \( P_{2n}(L) \) to zero is numerically very slow and not significant until walks have lengths of \( O(10^6) \), this effect will not be visible in our data, and the probability of linking as a particular fixed link type \( L \) will be a function of the local geometry of the polygons in the lattice and the value of \( \beta_m \).

## 4 Results: Thermodynamic and metric properties

### 4.1 Monte Carlo method

Conformations of the lattice model were sampled from the Boltzmann distribution using a Markov chain Monte Carlo algorithm. The elementary moves were a combination of pivot moves for self-avoiding polygons [10] and local Verdier-Stockmayer style moves [11]. The Verdier-Stockmayer moves were introduced to increase the mobility of the Markov Chain when the algorithm samples at large positive values of \( \beta_m \) [12, 13] where there is a strong interaction between the component polygons which reduces the success rates of the pivot moves.

Sampling was also improved by implementing the elementary moves using a Multiple Markov Chain algorithm with chains distributed along a sequence of parameters \( (\beta_m^{(j)}) \) for \( j = 1, 2, \ldots, M \). Along each parallel chain Metropolis sampling was implemented to sample from the Boltzmann distribution at a fixed \( \beta_m^{(j)} \), and chains were swapped using the protocols of Multiple Markov Chain sampling [14, 12, 13]. The collection of parallel multiple Markov chains is itself a Markov Chain with stationary distribution the product of the Boltzmann distributions along each chain (see reference [12, 13]).

In this paper we sampled along \( M \approx 50 \) parallel chains, and we were able to obtain sufficiently uncorrelated samples for systems of total size \( 2n \in \{96, 200, 296, 400, 600, 800\} \) and for the \( \beta_m^{(j)} \) equally spaced in the interval \([-0.3, 1.0] \). We counted a single iteration as \( O(1) \) pivot moves, and \( O(n) \) local Verdier-Stockmayer style moves. By spacing the reading of data along each Markov chain, we were able to sample approximately \( 2.5 \times 10^4 \) conformations that are essentially uncorrelated at each fixed value of \( \beta_m^{(j)} \) for a total of at least \( 1.25 \times 10^6 \) data points for each value of \( n \). The simulations were expensive in terms of CPU time. For example, for \( 2n = 600 \) and \( M \approx 50 \) a total of 25,000 uncorrelated conformations were sampled over three months of CPU time. In figure 6 we show some examples of conformations taken along the chains for different values of \( \beta_m^{(j)} \).
Figure 5: (a) Plot of the average number of mutual contacts per monomer, \( \langle k_m \rangle/2n \) and (b) the corresponding variance \( Var(k_m)/2n \) as a function of \( \beta_m \). Different symbols refer to different values of \( n \) (see legend). In panel (b) the dashed vertical line highlights the location of the most asymptotic crossings that we consider as the best estimate of the transition.

Figure 6: Top row: Pairs of lattice polygons, each of \( n = 100 \) steps sampled at different values of \( \beta_m \)’s (0.0, 0.4, 0.6). Their corresponding, topologically equivalent, simplified versions after the smoothing and shrinking procedure via the BFACF algorithm are reported in the middle row while the minimal representation of the associated link type is reported in the bottom row.

4.2 Thermodynamic properties

The results in section 2 show that there should be two regimes in the model, namely a segregated regime for negative or small positive values of \( \beta_m \), and a mixed regime of interpenetrating components when \( \beta_m \) is large and positive. The segregated regime is characterized by states where the two polygons are separated from one another with a low density of mutual contacts between them, while the mixed phase has the two components close together in the same local space so that the number of mutual contacts is increased.

A sharp change in the average energy per monomer \( \langle k_m \rangle/(2n) \) is consistent with the two regimes being separated by a phase boundary (see section 3). This is also seen in the variance of \( \langle k_m \rangle \) defined by

\[
Var(k_m) = \langle k_m^2 \rangle - \langle k_m \rangle^2. \tag{9}
\]
Estimates of \( \langle k_m \rangle / (2n) \) and the normalized variance \( Var(k_m)/(2n) \) are plotted as functions of \( \beta_m \) for various values of \( n \) in figure 5(a) and in figure 5(b), respectively. For \( \beta_m < \beta_m^* \), \( \langle k_m \rangle / (2n) \), tends to zero with increasing \( n \). In this phase the small and decreasing number of mutual contacts per monomer is consistent with the two component polygons being largely segregated in space. This is the segregated phase, as explained in section 3. For \( \beta_m > \beta_m^* \) the curves of \( (k_m)/(2n) \) are increasing as \( n \) increases. In this mixed phase the two polygons have large non-zero energy per monomer (that is, a high incidence of mutual contacts), consistent with the two component polygons having sections near to each other in the lattice as they share the same volume in space. Our data are consistent with \( \langle k_m \rangle \to A n \) as \( n \) increases with \( 2 < A < 3 \). This shows that the mixed phase is not an extended ribbon with the two polygons forming its boundary, but is a denser phase where strands in each polygon have a high number of contacts per monomer (between 2 and 3) with the other component. The segregated-mixed transition as \( \beta_m \) is taken through its critical value is also seen in the peak forming in \( Var(k_m)/2n \) when plotted as a function of \( \beta_m \), see figure 5(b). With increasing \( n \) the peaks move to smaller values of \( \beta_m^* \). This behaviour is consistent with theorems 1 and 2, since in the infinite \( n \) limit the variance is equal to zero in the segregated phase, has a jump discontinuity at the critical point, and then decreases with increasing \( \beta_m \).

The data in figure 5(b) strongly suggest that the transition at \( \beta_m^* \) is asymmetric (that is, in the limit \( n \to \infty \) the variance is zero if \( \beta < \beta_m^* \) but it characteristically increases as \( \beta < \beta_m^* \)). In these circumstances the intersections of the variances for different values of \( n \) in figure 5(b) are a good estimator of the location of the critical point as \( n \to \infty \). This gives the estimate of \( \beta_m^* = 0.31 \pm 0.01 \). The asymmetry of the transition is consistent with the results of section 3.

### 4.3 Metric and shape properties

The size and metric scaling of lattice links can be examined by calculating metric quantities such as the mean square radius of gyration \( R_j^2 \) for \( j \in \{1, 2\} \) for components \( j = 1 \) or \( j = 2 \). As expected the behaviour of \( R_j^2 \) does not depend on \( j \) and we improve the estimate of this metric observable by averaging over the two components: \( R_j^2 = (R_1^2 + R_2^2)/2 \). This quantity, scaled by the power \( n^{2\nu} \) is reported, as a function of \( \beta_m \), in figure 7(a) and (b), and for lengths \( n \in \{48, 100, 148, 200, 300, 400\} \). Since the metric scaling of the self-avoiding walk has exponent \( \nu_{SAW} = 0.587297(7) \) \[15\] it should be the case that the ratio \( R_j^2/n^{2\nu_{SAW}} \) is a constant for \( \beta_m < 0 \) (in the segregated regime). This is seen in figure 7(a) where the data for \( \beta \leq \beta_m^* \approx 0.3 \) collapse to a constant close to 0.1, with little dependence on \( n \). This is evidence that for these values of \( \beta_m \) the system is in a segregated phase where the self-avoidance between the two polygons separates them in space, and each polygon has the properties of a ring polymer in a good solvent, with associated metric exponent \( \nu \).

For values of \( \beta_m > \beta_m^* \) the model is instead in a mixed phase. Here the ratio \( R_j^2/n^{2\nu} \) with \( \nu = \nu_{SAW} \) is dependent on both \( n \) and \( \beta_m \), decreasing either with increasing \( \beta_m \) or with increasing \( n \), as seen in figure 7(a). The collapsed nature of the model is exposed by plotting \( R_j^2/n^{2/3} \) against \( \beta_m \), showing collapse of the data for different values of \( n \) to an underlying curve for large values of \( \beta_m \), see figure 7(b). These observations are consistent with the model passing through a phase transition into a mixed and collapsed phase where the interpenetrating components explore states with a high (local) density of monomers. Note that in this figure the critical point \( \beta_m^* \) separating the segregated and mixed phases has value approximately 0.3, that is, consistent with the one estimated using the variance of the mutual number of contact (see figure 5(b)).

The collapse of the data for large \( \beta_m > \beta_m^* \) is consistent with the two polygons interpenetrating
each other in a phase with high mutual contacts. This indicates that the mixed phase may be characterized by compact conformations in a collapsed phase and that the lattice link transitions through a $\theta$-point at $\beta_m^\ast$ from an expanded and segregated phase into a collapsed and mixed phase.

The transition between a segregated (and expanded or free) phase for negative $\beta_m$, and a mixed (and collapsed) phase for large positive $\beta_m$, is also suggested by other metric observables. For instance, in figure 7(c) and (d) the mean separations between the centres of mass $d_{cm}$ of the two polygon components are examined. The $\beta_m$ dependence of this measure is reported in figure 7(c) while in figure 7(d) the scaled version $d_{cm}/n^\nu$ is plotted. In both cases the data decrease with increasing $\beta_m$, consistent with the model entering a compact phase where the centres of mass of the two components are close to each other. Note that in (c) $d_{cm}$ increases with $n$ in the segregated phase, and this growth is shown in (d) to be at the expected rate of $O(n^\nu)$, the typical length scale of the model. The curves in (c) intersect pairwise close to a critical value $\beta_m^\ast \approx 0.4$, slightly larger than the estimate suggested by the data of figure 7(a), but not inconsistent with the expected segregated-mixed transition.

The configurational properties of the model change as it crosses over from the segregated phase to the mixed phase. The interaction between the two polygon components, due to both the self-avoidance repulsion, and the short ranged interaction induced by weighted mutual contacts, deform the components in the two phases, and this may be seen by measuring the asphericity and prolateness of components. In the segregated phase the conformations may be similar to that shown in figure 6 (left), while the mixed phase has interpenetrated components as shown in figure 6 (middle and right). In the segregated phase the polygon components are aspherical when the components are segregated, but transitioning into the mixed phase reduces the degree of asphericity as the two components collapse by forming mutual contacts and interpenetrate into a locally dense conformation. This is seen in figure 8(a) where the average asphericity $\Delta = (\Delta_1 + \Delta_2)/2$ is highest in the segregated phase but decreases once the model transitions through a critical value of $\beta_m$ into the
mixed phase. In the segregated phase the data are collapsed into a horizontal line (independent of both $\beta_m$ and $n$) with the asphericity $\Delta \approx 0.08$ over the entire range of the segregated phase). In the mixed phase $\Delta$ decreases with increasing $\beta_m$ and increasing $n$.

The degree of prolateness of the model (plotted in figure 8(b)) presents a more nuanced picture, and our data are more noisy. They suggest a relatively constant (in $\beta_m$) value in the segregated phase that increases and appears to peak in the mixed phase at a location that moves to smaller values of $\beta_m$ with increasing $n$ approaching the expected value $\beta_m^*$. When $\beta_m \leq 0$ the main effect is entropic repulsion where the two curves are mutually repelling (for entropic reasons), leading to the two components being prolate. As $\beta_m$ increases towards its critical value the two components will start to intermingle but there will still be parts of each component that are not intermingled (so that the components are not completely mixed). These intermingled parts might feel a stronger entropic repulsion resulting in a more prolate shape. For large $\beta_m$ the mutual attraction dominates, and this will overcome the entropic repulsion and give a more spherical shape when the two components are mixed. Clearly, from the figure, this effect is small.

Figure 9: Percentage of the volume fraction of the region shared by both polygons as a function of $\beta_m$.

A natural observable for the segregated/mixed transition is based on the estimate of the overlap volume fraction, $V_o/V$, namely the volume of the box shared by the two polygons scaled by the total volume of the box containing the full system [16]. This is shown as a function of $\beta_m$ in figure 9.
the overlap is relatively small (although not zero) and its value increases very mildly with $n$. When $\beta_m > \beta_m^*$ the overlap volume fraction $V_o/V$ steadily increases approaching an asymptotic value that for $n = 400$ approaches the 80% of the system volume. This indicates a very strong interpenetration of the two rings when the system is well inside the mixed phase ($\beta_m = 1$).

## 5 Topological entanglement

### 5.1 Linking probability and average linking number

A first characterization of the topological mutual entanglement that forms in the system is provided by the estimate of the probability that the two polygons are topologically linked. In general two disjoint simple closed curves $C_1$ and $C_2$ are topologically unlinked (or splittable) if there exists a homeomorphism $H$ of $\mathbb{R}^3$ onto itself, $H : \mathbb{R}^3 \to \mathbb{R}^3$, such that the images $H(C_1)$ and $H(C_2)$ can be separated by a plane [17]. This definition is not convenient computationally and we relied instead on the notion of linking based on the computation of the 2-variable Alexander polynomial $\Delta(t,s)$ of the link diagram. This is done by encoding crossings (overpasses and underpasses in a planar projection of the polygon pair) and calculating $\Delta(t,s)$ from the encoding. For details see reference [17].

$\Delta(t,s)$ is not a perfect invariant able to distinguish all link types, but if we restrict ourselves to the identification of link types with minimal crossing number at most 7 its resolution will be sufficient for the analysis of the data. The calculation of $\Delta(t,s)$ could be prohibitively costly if the number of crossings $n_c$ after a planar projection is very large. This occurs in particular when the two polygons are strongly overlapping in the mixed phase (that is, for $\beta_m$’s sufficiently large). The number of crossings was decreased by simplifying the polygons while keeping the topology unaltered using BFACF moves [18, 19] at low temperature [20, 21]. This reduces the system to components of close to minimal length compatible with the linked state. See figure 6 for some examples of simplified configurations. This implementation almost always reduced the number of crossings in the projections to well below 50, reducing the CPU time devoted to calculating $\Delta(t,s)$. Notice that if a component is reduced to length $n \leq 6$, then the pair cannot be linked for geometric reasons, so that a calculation of $\Delta(t,s)$ is not necessary.

The calculation of $\Delta(t,s)$ proceeded by performing 100 independent projections onto randomly oriented planes of the simplified configurations, then choose amongst these the projection $P$ with the least number of crossings. $\Delta(t,s)$ is then calculated using $P$ for $t, s \in \{2, 3\}$. This gives four values which are compared to the values computed from the explicit expression of $\Delta(t,s)$ for link types up to 7 crossings (see for instance [22]). Those cases where the Alexander polynomial is not trivial but does not correspond to a link with 7 or fewer mutual crossings in its minimal projection, are classified as complex links.

In figure 10(a) we show the probability $P_{\text{link}}$ of topologically linked pairs of polygons (i.e. $\Delta(t,s) \neq 0$) as a function of $\beta_m$ and for different values of $n$. There are clear qualitative trends seen in this graph and, in particular, $P_{\text{link}}$ increases with $\beta_m$. For $\beta_m \lesssim 0.4$ $P_{\text{link}}$ increases rapidly with $\beta_m$ as the model transitions from the segregated into the mixed phase. At large values of $\beta_m$ (well inside the mixed phase), $P_{\text{link}}$ appears to settle on a value close to 0.9 at the larger values of $n$. We do not give data for $n = 300$ or $n = 400$ when $\beta_m \gtrsim 0.4$ because of a possibility of false positives for the unlink. There are link types with $\Delta(s,t) = 0$ but which are topologically linked. These link types start to appear in the standard knot table as having minimal crossing numbers

\[ \Delta(s,t) = 0 \]
In our model as $\beta_m$ increases the link types are of increasing complexity. Computing $\Delta(s,t)$ for some of these link types, however, gives $\Delta(s,t) = 0$, and they are classified as being the unlink. This causes overcounting of unlinks in our data at large $n$ and high $\beta_m$, as well as undercounting of non-trivial links as a consequence. The result is that $P_{\text{link}}$ would be systematically underestimated in figure 10(a) at large values of $n$ and $\beta_m$.

A simpler way to measure the complexity of the linked states of the polygon pairs is by computing their linking number $Lk$. The linking number $Lk(C_1,C_2)$ of a pair of closed curves $(C_1,C_2)$ is calculated by summing positive and negative mutual crossings in a simple projection of $(C_1,C_2)$ [23]. The linking number defines homological linking of $(C_1,C_2)$, namely, two curves are homologically linked if and only if $Lk(C_1,C_2) \neq 0$ [17]. In figure 10(b) we report the average absolute value of $Lk(C_1,C_2)$, as a function of $\beta_m$. These graphs of $|Lk|$ increase for all values of $\beta_m$ with $n$ and with increasing $\beta_m$ at fixed $n$. The increase is large in the mixed phase when $\beta_m > \beta_m^*$. It shows that both increasing $n$, and increasing $\beta_m$, increase the complexity of the links in the mixed phase, an effect which is much less pronounced in the segregated phase where the probability of linking is low.

### 5.2 Link spectrum

In figure 11 we examine aspects of the link spectrum measured as a function of $\beta_m$ by plotting the percentage of the most popular links (with minimal crossing number up to 7 and with percentage at least 1%) as detected in our simulations. As expected, the population of unlinks is very large for $\beta_m < 0$ (approaching 100%), and decreases as $\beta_m$ is increased and the mixed phase is approached.

For sufficiently large values of $\beta_m$ and sufficiently large values of $n$, the proportion of unlinks stabilizes at very low levels. Concomitantly with this, the simplest link type (the Hopf link, $2_1^2$) has a non-monotonic behaviour reaching a maximum at values of $\beta_m$ that decrease as $n$ increases. This non-monotonic behaviour is common to all link types with $n_c \leq 6$ and for the $7_2^2$ and $7_2^2$ links. The other 7 crossings links also show this behaviour but their populations are too small (below 1%) for this to be significant.

The fact that for large $n$ and well inside the mixed phase the complexity of the linked pairs is rapidly increasing is also suggested by the rapid increase of the populations of topologically linked pairs $(\Delta(t,s) \neq 0)$ having $n_c > 7$. This is reported in figure 12 together with two examples of...
linked pairs of polygons with $n_c = 8$. Again, the fact that for $n \geq 300$ the curves seem to approach a constant value could be due to the failure of the two-variable Alexander polynomial in detecting more complex links at large $\beta_m$.

Finally, in figure 13 we report the link spectrum as a function of $\beta_m$ where each panel presents data for a different value of $n$. In all cases the unlink dominates the segregated phase, but its incidence decreases sharply when $\beta_m \approx 0.3$ while the incidence of linked conformations increases into the mixed phase. The Hopf link ($2_2^1$) dominates the linked conformations in the mixed phase but it also peaks close to $\beta_m \approx 0.3$. More complex links also appear, albeit at smaller proportions, as $\beta_m$ increases, and the simplest of these similarly peak at $\beta_m \approx 0.3$. It appears from our data that the number of link types multiplies in the mixed phase with increasing values of $n$, and while the incidence of specific link types decreases with increasing $n$ and $\beta_m$, we know from figure 10 that the sum over all these link types increases with $\beta_m$ into the mixed phase. This may indicate that the increase in the number of link types compensates for the reduction in the incidence of any specific link type, so that the proportion of linked conformations dominate state space.

5.3 Metric and energy properties at fixed link type

In figure 14 the number of mutual contacts in pairs of unlinked polygons is plotted as a fraction of the total number of mutual contacts. This fraction is (expectedly) close to one if $\beta_m$ is negative, showing that almost all conformations are unlinked. Increasing $\beta_m$ towards its critical value reduces this fraction, and this is consistent with both an increase in the total number of contacts due the components starting to approach one another, and with an increase in the proportion of linked conformations where the polygons are closer together and so contain larger numbers of mutual
Figure 12: Percentage of the population of link types having $\Delta(t,s) \neq 0$ with $n_c > 7$. To give a glimpse of the complexity of the links found in the mixed state two examples with $n_c = 8$ are reported. The top right refers to a $8_8^2$ link (Lk=1) and was found in a polygon pair with $n = 48$ while the bottom right is a $8_1^2$ link (Lk=4) and was found in a polygon pair with $n = 100$. In both cases the configurations reported are those simplified by the smoothing algorithm based on BFACF moves, see text.

Figure 13: Percentage of the population of some link types as a function of $\beta_m$ (black: 0, red: 2, blue: 4, green: 5, cyan: 6, magenta: 6). Different panels refer to different values of $n$.

contacts. This observation is supported by noting that the ratio of contacts between links of type $2_1^2$ and all polygons in the first instance, and between $2_1^3$ and unlinked states are high in the segregated phase, showing that linked states of type $2_1^3$ contain, on average, a higher density of mutual contacts.

Data on the mean square radius of gyration paint an interesting picture. Deep in the segregated
phase the unlink dominates state space and so the ratio of $\langle R^2_g \rangle_{01}$ to $\langle R^2_g \rangle$ is approximately equal to 1. This is also the case deep in the mixed phase – unlinked states have about the same size as the average conformation (since the polygons are mixed and together collapsed into a dense conformation minimizing the $\langle R^2_g \rangle$). Near the critical point the situation is more interesting. As the proportion of linked states increases as $\beta_m$ approaches its critical value from below, the ratio $\langle R^2_g \rangle_{01} / \langle R^2_g \rangle$ increases because linked states are smaller than unlinked states. This ratio should exceed 1 (which it does). Passing through the transition causes collapse of both unlinked and linked states, and so the ratio should settle down to 1 again, as it does. This picture is reaffirmed in the figures plotting the ratios $\langle R^2_g \rangle_{21} / \langle R^2_g \rangle$ and $\langle R^2_g \rangle_{21} / \langle R^2_g \rangle_{01}$ showing that the link 2 is larger than the unlink and the average of all states in the segregated phase, but are about the same size in the mixed (collapsed) phase.

6 Discussion

To investigate the thermodynamics, metric and topological properties of a pair of polymer rings undergoing a segregated to mixed phase transition, we have considered a pair of polygons on the simple cubic lattice constrained to have a pair of vertices (one from each polygon) unit distance apart. The polygons are self- and mutually avoiding and, in addition, there is a short range potential between pairs of vertices in the two polygons. When this potential is repulsive or weakly attractive the two polygons are largely separated in space but when the potential is sufficiently attractive the polygons interpenetrate and form a more compact object in a mixed phase.

In section 3 we prove that the limiting free energy exists when the potential is repulsive, and we establish bounds when it is attractive that establish the existence of a phase transition from a segregated phase to one where there are many inter-polygon contacts. We use a Monte Carlo
approach to investigate configurational properties such as the expected number of inter-polygon contacts, and the radius of gyration of a polygon as a function of the strength of the potential. The mean number of contacts increases as the potential becomes more attractive and increases rapidly in the region of the transition. The radius of gyration scales differently (with size) in the segregated and compact phases and there are changes in the asphericity and prolateness.

In section 5 we looked at the extent of linking of the two polygons as a function of the strength of the potential, both by computing the 2-variable Alexander polynomial (as a detector of topological linking) and the linking number (as a detector of homological linking). As the potential becomes more attractive the linking probability and the link complexity both increase, with a relatively sharp increase around the transition region. It is clear that, in the compact phase where there is considerable interpenetration of the polygons, the linking probability is high.

A related experimental situation is as follows. Consider a uniform 4-star polymer with two A-arms and two B-arms with the ends of the arms functionalized so that the system can be cyclized to form an A ring and a B ring, forming a figure eight. The A and B arms carry opposite charges so that they are attracted to one another and the strength of the attraction can be modified by changing the pH or the ionic strength. Prepare the system (i.e., the 4-star) at some fixed pH and ionic strength, and after equilibration, carry out a cyclization reaction. At high ionic strength or where charges are suppressed by varying the pH, the A and B arms will repel or weakly attract and there should be little interpenetration so that, after cyclization, there should be little linking. Conversely, with large charge densities and low ionic strength there should be considerable interpenetration and linking.

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