Lattice Models of Polymer Entanglements

Connections for Women: Discrete Lattice Models in Mathematics, Physics and Computing

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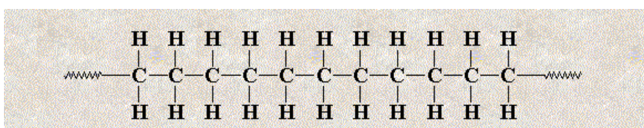
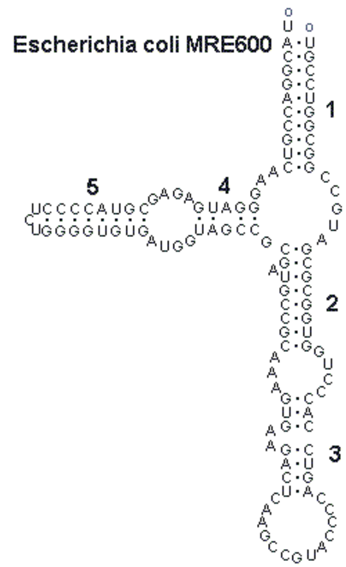
Introduction to Polymers

Polymer: Large molecule made of repeated molecular units called *monomers*; if there is more than one type of monomer *Copolymer*



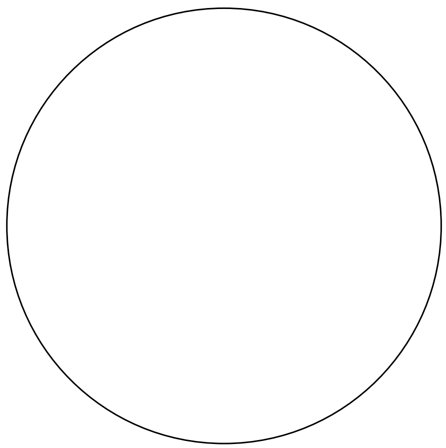
homopolymer - polyethylene



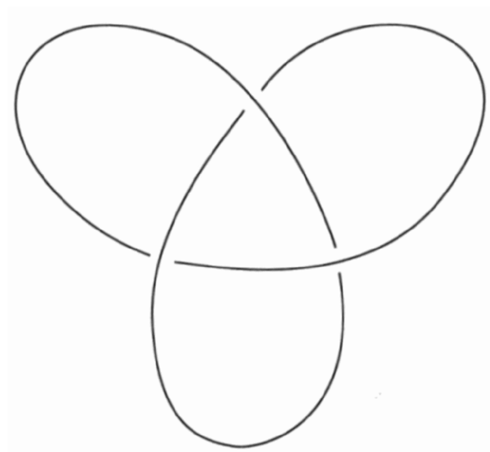
copolymer

Fundamental Question of Interest: What properties of polymer solutions are primarily a result of the fact that a polymer is a very large molecule made up of repeated molecular units?

Introduction to Random Knotting: What is a Knot?



unknot ϕ



trefoil 3_1

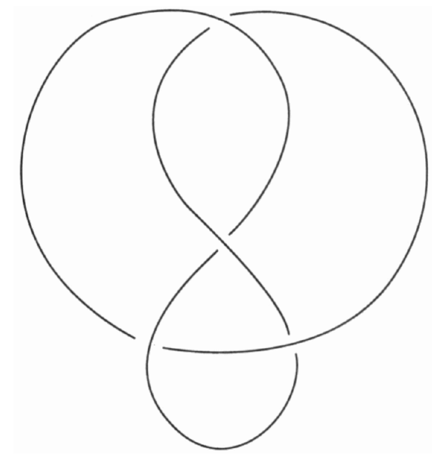
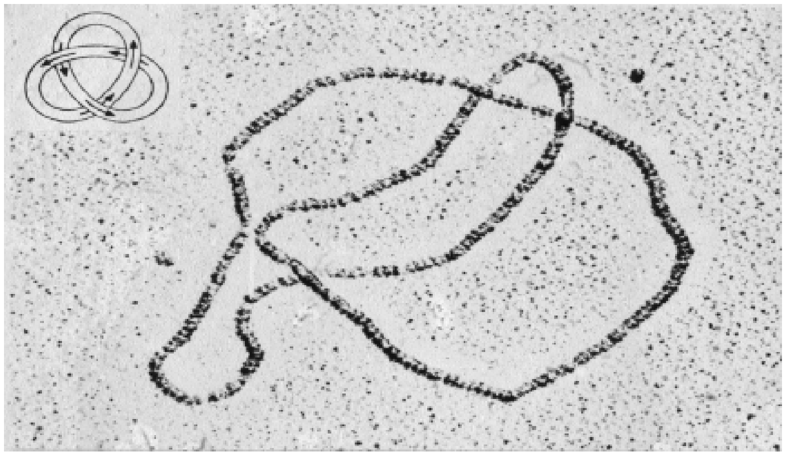


figure-eight 4_1

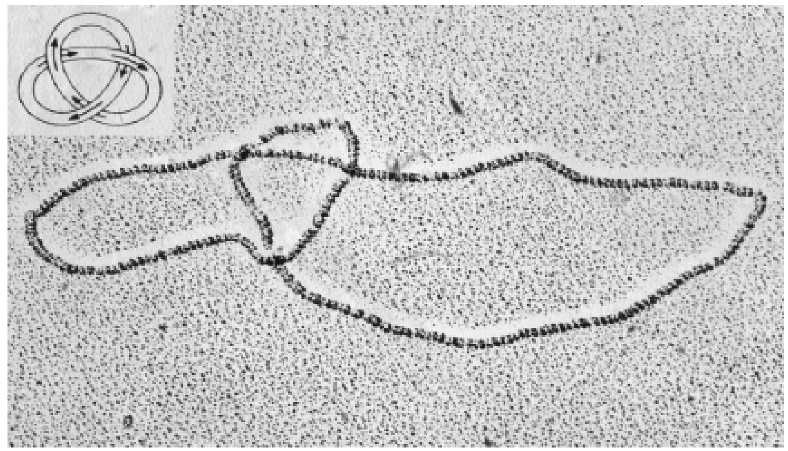
A *knot* is an embedding of a simple closed curve in $\mathbb{R}^3$. Two knots are *equivalent* if they are *ambient isotopic*, i.e. if one can be continuously transformed into the other. The *knot types* are the equivalence classes.

A knot K has a *prime* knot decomposition, $K = K_1 \# K_2 \# ... \# K_p$

Knots and Polymers



right-handed trefoil

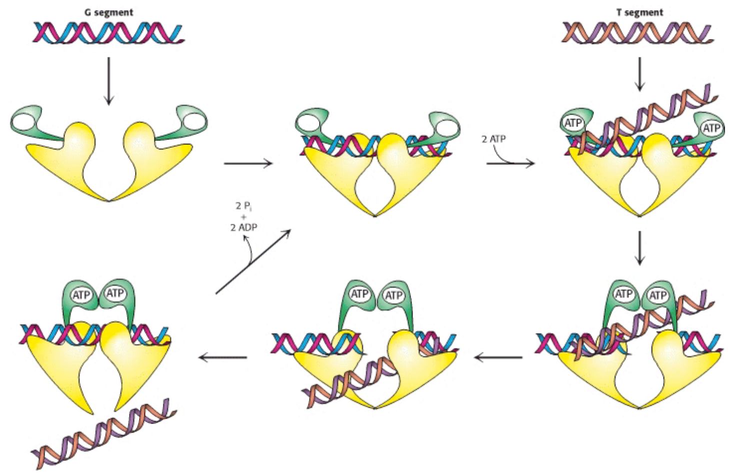


left-handed trefoil

Electron micrographs of recA coated DNA.

Reproduced with permission of author from: Determination of the absolute handedness of knots and catenanes of DNA. Mark A. Krasnow, Andrzej Stasiak, Sylvia J. Spengler, Frank Dean, Theo Koller, Nicholas R. Cozzarelli. Nature 304, 559-560 11 08 1983 Letter

DNA type II Topoisomerase



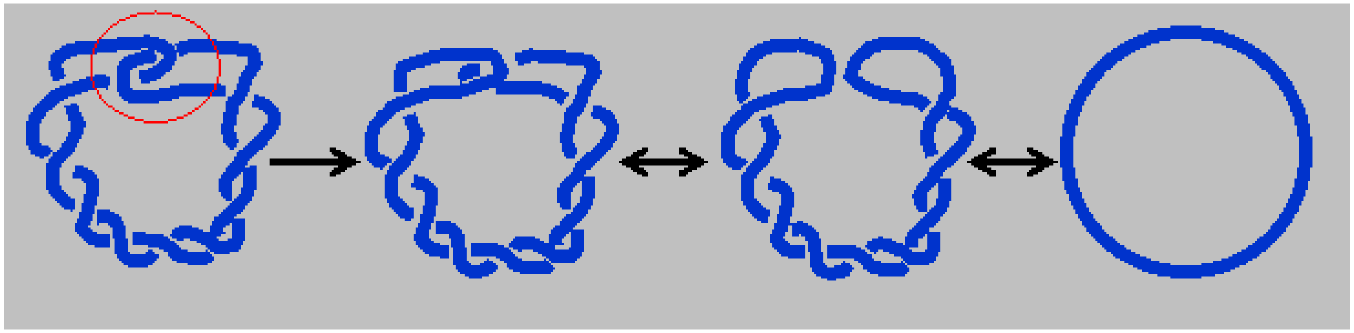
passes one part of DNA through another via enzyme-bridged transient break

Biochemisty, 5th edition, Berg JM, Tymoczko JL, Stryer L. New York: W H Freeman; 2002

Knots in Nature

Knots and links have been observed in circular DNA molecules - DNA highly compacted and self-entangled in cell nucleus. Knots topologically obstruct cellular processes such as replication.

Topoisomerases: enzymes that pass one part of a DNA molecule through another via enzyme-bridged transient break in the DNA. Act locally on the DNA to remove topological (global) obstructions.



http://www.math.fsu.edu/~jmann/KnotOnMtn.htm

QUESTION: If local strand passages occur at random locations, how efficient is this action at changing knot type?

D.W. Sumners, Program in Mathematics and Molecular Biology (PMMB) Short Course, Berkeley, June 22 - July 3 1998

FIRST STEP: How likely is a knot in a "random" polygon?

Random Knotting in Self-Avoiding Polygons

Frisch-Wasserman Delbruck Conjecture:

In the 1960's Frisch and Wasserman, and Delbruck, conjectured that sufficiently long ring polymers would be *knotted* (not the unknot) with high probability.

Frisch & Wasserman (1961) (JAmChemSoc **83** 3789), Delbruck (1962) Math. Problems in the Biol. Sci.

Proved for various polymer models:

Sumners and Whittington (1988) and Pippenger (1989) for self-avoiding polygons:

All but exponentially few sufficiently long self-avoiding polygons (SAP) on the simple cubic lattice ($\mathbb{Z}^3$) are knotted.

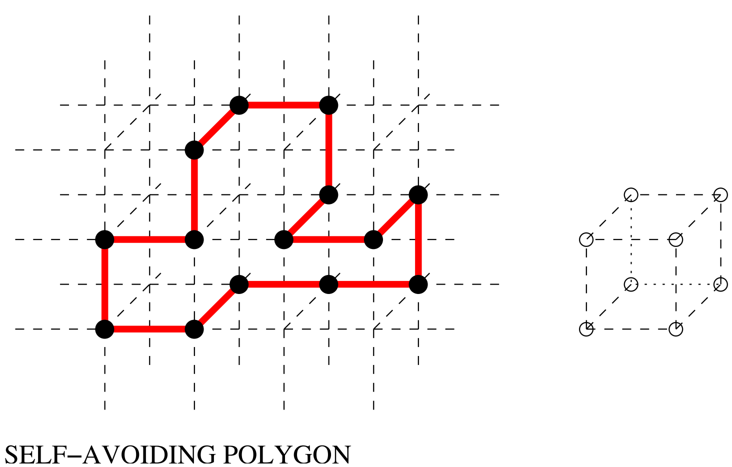
Diao, Pippenger and Sumners (1994) for Gaussian random polygons in 3-space.

Diao (1995) for Equilateral polygons in 3-space.

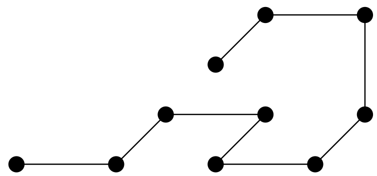
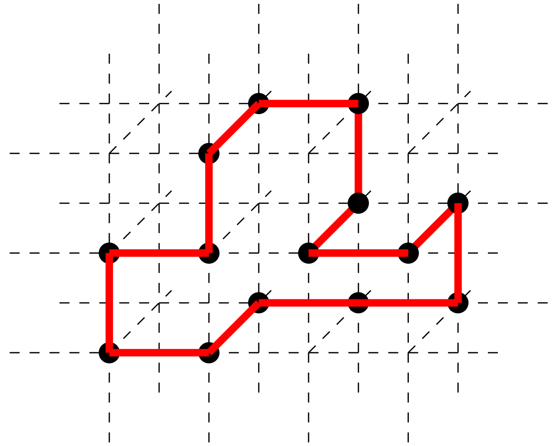
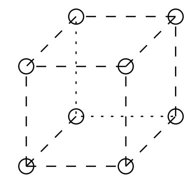
Lattice Models of Ring Polymers

Lattice Model Assumptions: a ring polymer *configuration is represented by a self-avoiding polygon* in $\mathbb{Z}^3$; in *dilute solution* (hence polymer-polymer interactions can be ignored); at *equilibrium* s.t. two *equal energy size n configurations are equally likely*; two configurations identical if one is translate of the other

Advantages of lattice models: excluded volume property easily incorporated
substantial conformational freedom available
combinatorial and asymptotic analysis possible
values of some critical exponents expected to be exact



Properties of Self-avoiding Walks (SAWs) and Polygons (SAPs)

c_n: the number of n-step SAWs starting at the origin

p_n: the number of n-step SAPs up-to-translation

Square Lattice ($d = 2$): $c_1 = 4$, $c_2 = 12$, $c_3 = 36$, $c_4 = 3c_3 - 8 = 100$;

$$p_4 = 1,\ p_6 = 2,\ p_8 = 7$$

$c_{71} \approx 41 \times 10^{29}$ $(d = 2)$ $\qquad$ $c_{30} = 270569905525454674614 \approx 2 \times 10^{20}$ $(d = 3)$

$p_{110} \approx 97 \times 10^{39}$ $(d = 2)$ $\qquad$ $p_{32} = 53424552150523386 \approx 5.3 \times 10^{16}$ $(d = 3)$

(Jensen JPA **36** (2003) 5731–45) $\qquad$ (Clisby *et al* JPA **40** (2007) 10973–1017)

www.ms.unimelb.edu.au/∼ iwan/saw/series/sqsaw.ser $\qquad$ www.math.ubc.ca/∼slade/

$c_{36} = 2941370856334701726560670 \approx 2.9 \times 10^{24}$ $(d = 3)$ (Schram et al. arXiv:1104.2184v1 Apr. 2011)

Smallest knotted SAPs are trefoils with $n = 24$ edges and $p_{24}(3_1) = 3328$

(Y Diao JKTR **2** (1993) 413–25; JSP **74** (1994) 1247–54); Scharein *et al* JPA **42** (2009) 475006

Simplest Model: Each SAP of size n (number of edges) is considered equally likely.

p_n - # of distinct (up to translation) n-edge SAPs in $\mathbb{Z}^3$

$p_n(\phi)$ - # of distinct (up to translation) n-edge UNKNOTTED SAPs in $\mathbb{Z}^3$

$p_n(K)$ - # of distinct (up to translation) n-edge knot type K SAPs in $\mathbb{Z}^3$

As $n \to \infty$ Sumners and Whittington (1988) (JPA **21**, 1689–94) $\Rightarrow$

$$\boxed{Prob.\ \ of\ Knotting = 1 - \frac{p_n(\phi)}{p_n} = 1 - e^{-(\kappa-\kappa_o)n+o(n)}}$$

Soteros, Sumners and Whittington (1992) (MathProcCambPhilSoc **111** 75) $\Rightarrow$

$$\boxed{Prob.\ \ of\ Knot\text{-}type\ K = \frac{p_n(K)}{p_n} \to 0}$$

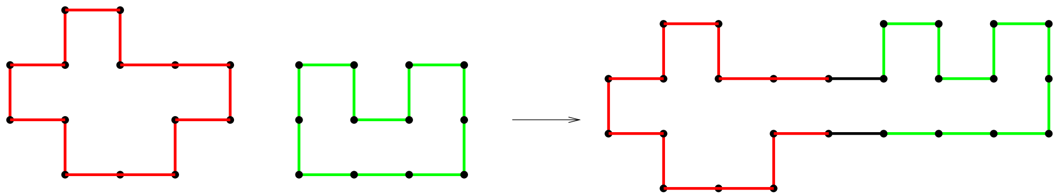
Orlandini *et al* (1998) (IMA Vol.Math.Appl. **103** 9; JPA **31** 5953) Monte Carlo evidence consistent with

$$\boxed{p_n(K) \sim A_K n^{\theta_o + f_K} e^{\kappa_o n}}$$

f_K - # prime knots in K's knot decomp.

Properties of Self-avoiding Polygons (SAPs) in $\mathbb{Z}^d$

Standard Concatenation Argument



$$\boxed{p_n p_m \leq (d-1)p_{n+m} \quad ; \; p_n \leq (2d)^n} \Rightarrow \boxed{\lim_{n\to\infty} \frac{1}{2n} \log p_{2n} \equiv \log \mu_d = \kappa_d}$$

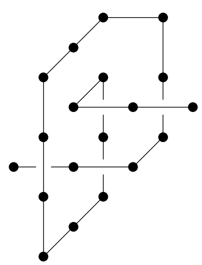
(Hammersley Proc.Camb.Phil.Soc. **58** (1961), 235–8)

$$\boxed{p_n(\phi)p_m(\phi) \leq 2p_{n+m}(\phi) \quad ; \; p_n(\phi) \leq p_n} \Rightarrow \boxed{\lim_{n\to\infty} \frac{1}{2n} \log p_{2n}(\phi) \equiv \log \mu_0 = \kappa_0}$$

(Sumners and Whittington JPA **21** (1988), 1689–94)

$$\boxed{\kappa_o < \kappa_3 \quad \Rightarrow Prob.\ of\ Knotting = 1 - \frac{p_n(\phi)}{p_n} = 1 - e^{-(\kappa-\kappa_o)n+o(n)}}$$

Key ingredient: Pattern theorem (Kesten, 1963) used to prove that "tight trefoil" pattern occurs at least once in all but exponentially few sufficiently long SAPs.



Pattern Theorem for Self-avoiding Polygons (SAPs) in $\mathbb{Z}^d$

Theorem 1 (Kesten Pattern Theorem 1963) *Given any proper SAW pattern* P, $\exists\ \epsilon_P > 0$ *such that*

$$\limsup_{n\to\infty} \left(\frac{c_n(\epsilon_P n, P)}{c_n} \right)^{1/n} < 1. \tag{1}$$

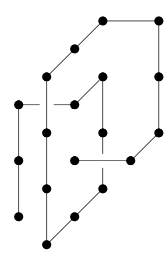
Corollary 1 (Sumners and Whittington 1988) *Given any proper SAP pattern* P, $\exists\ \epsilon_P > 0$ *such that*

$$\limsup_{n\to\infty} \left(\frac{p_n(\epsilon_P n, P)}{p_n} \right)^{1/n} < 1. \tag{2}$$

$p_n(\epsilon_P n, P)$: # of n edge SAPs which contain AT MOST $\epsilon_P n$ translates of P

$\Rightarrow$ all but exponentially few sufficiently long SAPs contain more than $\epsilon_P n$ translates of P

NOT a proper SAP pattern:



Sumners and Whittington (1988) (JPA 21 1689):

$$\kappa_o \equiv \lim_{n\to\infty} n^{-1} \log p_n(\phi) < \lim_{n\to\infty} n^{-1} \log p_n \equiv \kappa$$

Hence for n large enough unknotted polygons are exponentially rare in the set of polygons and

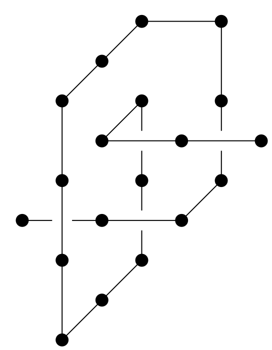
$$Prob.\ of\ Knotting = 1 - \frac{p_n(\phi)}{p_n} = 1 - e^{-(\kappa-\kappa_o)n+o(n)}$$

Key ingredients in the proof:

(i) There are no "antiknots" - that is, if k is a given knot type then there does not exist a knot k' such that $k\#k' = \phi$.

(ii) There exists a "tight pattern" τ such that if it occurs as a subwalk of a SAP, then the SAP cannot be an unknot.

(iii) The pattern theorem due to Kesten (1963) can be used to prove that τ occurs at least once as a subwalk on all but exponentially few sufficiently long SAPs. This relies on the fact that the number of SAWs and SAPs have the same exponential growth rate.



$p_n(K)$ - # of distinct (up to translation) n-edge SAPs in $\mathbb{Z}^3$ with knot type K

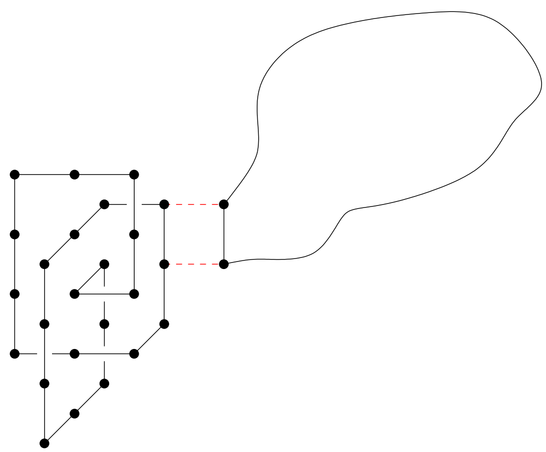
Soteros, Sumners and Whittington (1992) **(MathProcCambPhilSoc 111 75):**

$$\limsup_{n\to\infty} n^{-1}\log p_n(K) < \lim_{n\to\infty} n^{-1}\log p_n \equiv \kappa$$

Open Questions:

Does the following limit exist for $K \neq \phi$?

$$\kappa_K \equiv \lim_{n\to\infty} n^{-1}\log p_n(K)$$



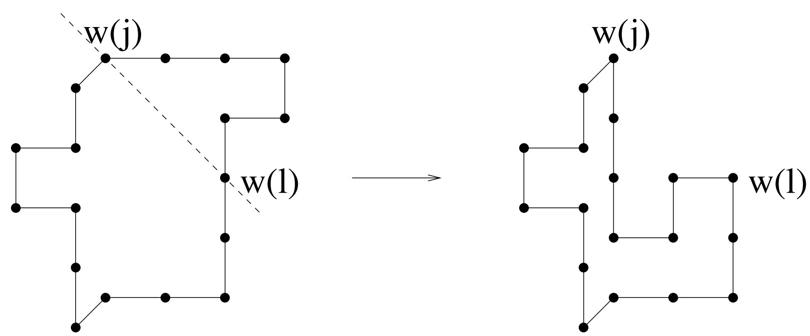
$$\Rightarrow p_{n-m}(\phi) \leq p_n(K) \Rightarrow \kappa_o \leq \kappa_K$$

$$\kappa_K = \kappa_o ?$$

Markov Chain Monte Carlo Methods for Studying SAPs

Pivot Moves: (Lal (1969) MolPhys 17 57)

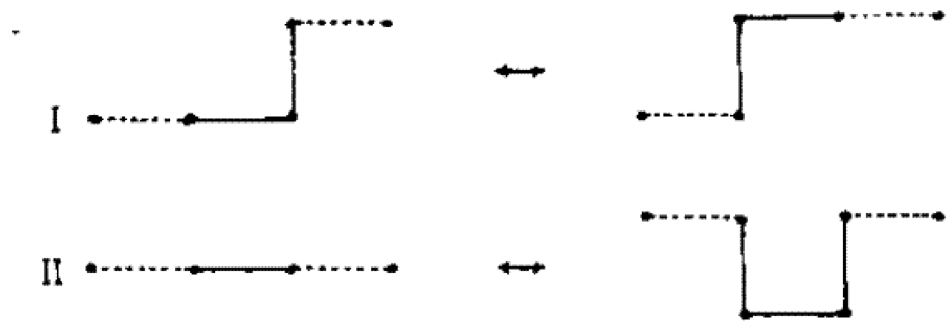
Pick two vertices $\omega(j)$ and $\omega(l)$ of SAP $\omega := \omega(0), \omega(1), ..., \omega(n-1)$ at random. Next choose an operation at random from a set of lattice preserving operations. Perform the chosen operation on a path of the polygon from $\omega(j)$ to $\omega(l)$.



Madras *et al* (1990) (JSP **58** 159–83) proved: the resulting Markov Chain is irreducible on the state space of all n-edge SAPs. Transition matrix can be chosen to be symmetric and aperiodic and hence at equilibrium each n-edge SAP is equally likely.

Efficient algorithm for sampling from the set of all n-edge SAPs.

BFACF Moves: **(Berg & Foester (1981), Aragao de Carvalho & Caracciolo (1983), Aragao de Carvalho *et al* (1983))**



Janse van Rensburg and Whittington (1990) (JPA **24** 5553) proved: the resulting Markov Chain is irreducible on the state space of all (variable length) SAPs with fixed knot type K.

Given $\beta < \beta_c$, transition probilities can be chosen so the chain is aperiodic and its equilib. dist. is

$$\pi(\omega) = \frac{e^{\beta n}}{\sum_m p_m(K) e^{\beta m}} = \frac{e^{\beta n}}{Q(\beta)}, \qquad \omega \ n\text{-edge SAP knot type } K.$$

Sokal and Thomas (1988) proved: the exponential autocorrelation time (the relaxation time of the slowest mode) of the BFACF algorithm is infinite. Plus integrated autocorr. time increases as $\beta \to \beta_c$.

Note that Expected # of edges in SAP $= \dfrac{\sum_n n p_n(K) e^{\beta n}}{Q(\beta)} = \dfrac{d \log Q(\beta)}{d\beta}$

Thus as $\beta \to \beta_c$, the average polygon size increases.

Combining pivots and BFACF moves can reduce the problem - resulting chain is irreducible on the set of all SAPs.

Alternatively, a Multiple Markov Chain Monte Carlo approach can be used.

Multiple MCMC Method for Variable Length SAPs

Choose a sequence $\beta_1 < \beta_2 < ... < \beta_M$.

For the ith subchain use BFACF moves (+ pivots) and transition probabilities that yield stationary distribution π_i on state space $\mathcal{S}^*$

$$\pi_i(\omega) = \frac{e^{\beta_i n}}{\sum_m p_m^* e^{\beta_i m}}, \qquad \omega \ n\text{-edge SAP in } \mathcal{S}^*$$

p_m^* ($= p_m(K)$ or p_m) is the number of m-edge SAPs in $\mathcal{S}^*$.

After t time steps in each subchain, a neighboring pair of subchains (say i and $i+1$) is chosen at random and a swap of subchain i's SAP ($S_t^{(i)}$) with subchain $(i+1)$'s SAP ($S_t^{(i+1)}$) is attempted with Metropolis acceptance probability:

$$\min\{1, \frac{\pi_i(S_t^{(j)})\pi_j(S_t^{(i)})}{\pi_i(S_t^{(i)})\pi_j(S_t^{(j)})}\}$$

Orlandini *et al* (1996) (JPA **29** L299) proved: the resulting Markov Chain has equil. dist.

$$\pi((\omega_1, \omega_2, ..., \omega_M)) = \prod_{i=1}^{M} \pi_i(\omega_i), \qquad \omega_i \in \mathcal{S}^*, i = 1, ..., M.$$

In practice this improves the autocorrelations times with suitable choice of $\beta_1, ..., \beta_M$.

Monte Carlo Estimates

$$P_n(Knotted) = 1 - \frac{p_n(\phi)}{p_n} = 1 - e^{-(\kappa-\kappa_o)n+o(n)}$$

Janse van Rensburg and Whittington (1990) (JPA **23** 3573–90): studied n-edge SAPs on the FCC lattice (smallest trefoil has 16 edges) $n \leq 1600$.

Janse van Rensburg (Contemporary Math. 304 (2002) 137-151): n-edge SAPs for $n \leq 4000$

$\kappa - \kappa_o = (4.15 \pm 0.32) \times 10^{-6}$ (simple cubic)

$\kappa - \kappa_o = (5.91 \pm 0.32) \times 10^{-6}$ (fcc)

$\kappa - \kappa_o = (5.82 \pm 0.32) \times 10^{-6}$ (bcc)

$$p_n(K) = A_K n^{\alpha(K)-3} e^{\kappa_o n}(1 + \frac{B}{n^\Delta} + \ldots)$$

Orlandini *et al* (1998) (IMA Vol.Math.Appl. **103** 9; JPA **31** 5953): studied fixed knot type

$\mu(\phi) = e^{\kappa_o} = 4.6852$ $\quad \mu(3_1) = e^{\kappa_{3_1}} = 4.6832$ $\quad \mu(4_1) = e^{\kappa_{4_1}} = 4.6833$

$\mu(6_2) = e^{\kappa_{6_2}} = 4.6844$ $\quad \mu(3_1\#3_1) = e^{\kappa_{3_1\#3_1}} = 4.6800$ $\quad \mu(3_1\#4_1) = e^{\kappa_{3_1\#4_1}} = 4.6841$

If assume all equal, then $\mu(\phi) = 4.6836 \pm 0.0038$ (95% conf. int.).

Results consistent with $\alpha(K) = \alpha(\phi) + N_f$, N_f # prime knots in K's knot decomp.

Recent Numerical Results

$$p_n(K) = A_K n^{\alpha(K)-3} e^{\kappa_o n}(1 + \frac{B}{n^\Delta} + ...)$$

Janse van Rensburg and Rechnitzer developed new approximate enumeration method based on "atmospheres of polygons" (JPA 2008 41:105002, JKTR 2011 20 p 1145)

For two prime knots K and L, as $n \to \infty$:

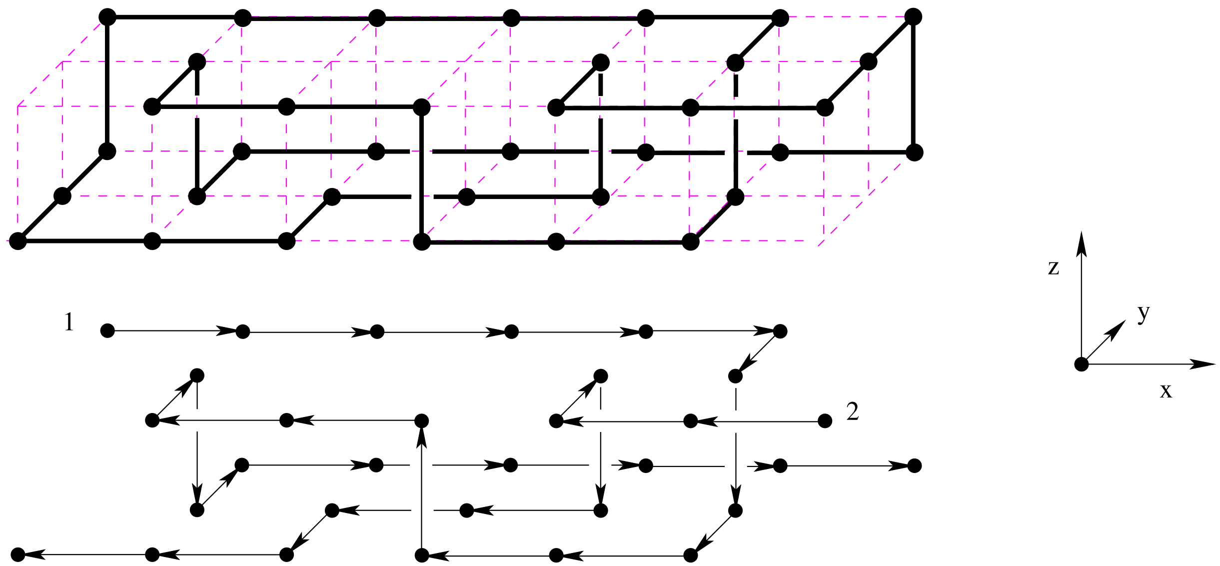
$$\frac{p_n(K)}{p_n(L)} \approx \frac{A_K}{A_L}$$

Numerical evidence (using atmospheric moves and GAS sampling) shows that this limiting constant is universal (lattice independent, at least for SC, FCC, BCC). (JPA 2011 44 162002, 165001)

"estimate that a long random polygon is approximately 28 times more likely to be a trefoil than a figure-eight, independent of the underlying lattice, giving an estimate of the intrinsic entropy associated with knot types in closed curves"

Limiting ratio also studied by different methods in Baiesi, Orlandini and Stella (J. Stat. Mech. Theor. Exp. 2010 P06012)

SAPs in $\infty \times N \times M$ Tubes



Markov Chain Like Properties (Transfer Matrix Arguments)

$\alpha > 0$ and $\kappa(N, M) > 0$ s.t. as $n \to \infty$ (Soteros 1998 IMA Vol.Math.App. **1**03 101–33)

$$\boldsymbol{p_n(N, M) = \alpha e^{n\kappa(N,M)} + o(e^{n\kappa(N,M)})}$$

$$\boldsymbol{p_n(N, M, \bar{P}) = \bar{\alpha} e^{n\kappa(N,M,\bar{P})} + o(e^{n\kappa(N,M,\bar{P})})}$$

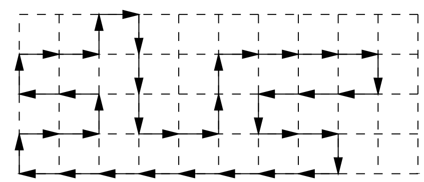
where $\kappa(N, M, \bar{P}) < \kappa(N, M)$

$\Rightarrow$ Knotting Prob $= 1 - \frac{p_n(N,M,\phi)}{p_n(N,M)} = 1 - e^{-(\kappa(N,M) - \kappa_0(N,M))n + o(n)} \to 1$ as $n \to \infty$

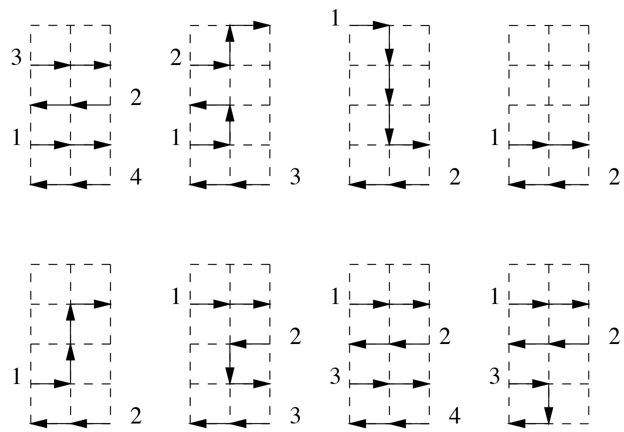
Outline of Pattern Theorem Proof (Soteros 1998): Based on transfer-matrix approach of Alm and Janson (1990) Communic. Stat. Stoch. Models **6** 169-212 for SAWs in one-dimensional lattices.

The transfer-matrix $G(x)$ is an $L \times L$ matrix where L is the number of possible configurations of a polygon in a subset of the tube with span b.

a)



b)



$$g_{i,j}(x) = \begin{cases} x^{e_i} & \text{if configuration } i \text{ can } \textit{hook up} \text{ to configuration } j \\ 0 & \text{otherwise.} \end{cases}$$

$G(x)$ is non-negative, irreducible and aperiodic and Frobenius theory implies nice properties for its spectral radius, $\rho(x)$.

The generating function $H(x) = \sum_m p_{2m}(N, M)x^{2m} = Q_a(x) + Q_b(x)$ where

$$Q_b(x) \propto \frac{1}{\det(I - G(x))}$$

thus $H(x)$ is analytic for $|x| < x_0$ and has a second order pole when $|x| = x_0$ where x_0 is such that $\rho(x_0) = 1$.

This implies that there exists $\alpha > 0$ such that as $n \to \infty$

$$\boldsymbol{p_n(N, M) = \alpha x_0^{-n} + o(x_0^{-n})}$$

i.e. $\kappa(N, M) = -\log x_0$.

Removing pattern P from all polygons corresponds to deleting a row and column in $G(x)$ and Frobenius theory implies there exists $\bar{x}_0 < x_0$ and $\bar{\alpha} > 0$ such that

$$\boldsymbol{p_n(N, M, \bar{P}) = \bar{\alpha}\bar{x}_0^{-n} + o(\bar{x}_0^{-n})}$$

i.e. $\kappa(N, M, \bar{P}) = -\log \bar{x}_0 < \kappa(N, M)$.

For any non-negative integer valued $additive\ functional$ ψ defined for SAPs, there exists $\gamma_\psi > 0$ (determined from eigenvalues and eigenvectors of G) s.t. as $n \to \infty$

$$\mathbb{E}[\psi(X)] = \gamma_\psi n + O(1)$$

Transfer-Matrix calculations for small L and M

$L = 1$

system	valid sections	valid 2-spans	β	$\frac{\eta_1 \xi_1}{\beta}$	$x_0 = \mu^{-1}$
(1,1)-prism	20	108	2.951241	2.336134 10^{-2}	0.547397
(1,2)-prism	814	9702	3.621382	0.636925 10^{-2}	0.437382
(1,3)-prism	44,484	963,096	4.105161	0.182089 10^{-2}	0.388795
(1,4)-prism	4,065,078	129,413,546			

$L = 0$

system	column states	β	$\frac{\eta_1 \xi_1}{\beta}$	$x_0 = \mu^{-1}$
(0,1)-prism	1	1	1	1.000000
(0,2)-prism	3	2.500000	1.0 10^{-1}	0.707107
(0,3)-prism	8	2.841143	2.433445 10^{-2}	0.594616
(0,4)-prism	20	3.107643	0.719011 10^{-2}	0.536749
(0,5)-prism	50	3.330234	2.461838 10^{-3}	0.501896
(0,6)-prism	126	3.523772	0.946299 10^{-3}	0.478782
(0,7)-prism	322	3.696418	0.399452 10^{-3}	0.462427
(0,8)-prism	834	3.853173	1.821891 10^{-4}	0.450302
(0,9)-prism	2187			0.440989
(0,10)-prism	5797			0.433634

Transfer-Matrix and Polymer Entanglements Summary

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