Modelling dense polymers by self-avoiding walks

EJ Janse van Rensburg
Mathematics and Statistics, York University
– November 2018 –

Collaborator: F Gassoumov

Schloss Dagstuhl

Leibniz-Zentrum für Informatik

Research Supported by a Discovery Grant from NSERC (Canada)
Dense polymer models

- Lattice model of a dense polymer
- Approximate enumeration - flatPERM sampling
- Flory-Huggins theory of dense polymers
- Calculating the square lattice self-avoiding walk Flory-Huggins exponent
- Knotted ring polymers in the cubic lattice
The polymer entropy problem

- Polymer entropy
  - Flory 1940s, Huggins 1940s, ...
- Physical environment – in solvents, melts, gels, mixing, ...
  - 1950s, ...
- Numerical simulation
  - Rosenbluth × 2 1950s
- Polymers in restrictive geometries – slits, slabs, cavities, wedges, ...
  - de Gennes 1970s
- Polymer entanglement and topology
  - de Gennes 1970s, Whittington & Sumners 1980s
A polymer of length $n$ monomers

Confining volume $V$

Monomer concentration $\phi$

- Lattice models of a compressed polymer
- Numerical modelling
Self-avoiding walk in a square
Self-avoiding walks crossing a square

\[ \mathcal{c}_{n,L} = \# \{ \text{walks of length } n \text{ crossing the square of sidelength } L \} \]
Self-avoiding walks crossing a square

\[ \mathcal{c}_{n,L} = \# \{ \text{walks of length } n \text{ crossing the square of sidelength } L \} \]

Let \( n = \lfloor \phi L^2 \rfloor \), then (indirectly) from work of Madras 1993

\[
\mathcal{F}(\phi) = - \lim_{L \to \infty} \frac{1}{L^2} \log \mathcal{c}_{\phi L^2, L}
\]
Self-avoiding walks crossing a square

\[ \mathcal{F}(\phi) = - \lim_{L \to \infty} \frac{1}{L^2} \log \mathcal{C}_{\phi L^2, L} \]

Moreover, \( \mathcal{F}(\phi) < 0 \), and is a convex function of \( \phi \).

\( \mathcal{C}_{\phi L^2, L} \) grows exponentially with \( L^2 \).
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- \( c_n = \#\{\text{self-avoiding walks of length } n \text{ from 0}\} \)

\[ W = 1 \]
\[ P = 1 \]
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- \( c_n = \#\{\text{self-avoiding walks of length } n \text{ from } 0\} \)

\[ W = 1 \times 4 \]
\[ P = 1 \times \frac{1}{4} \]
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- $c_n = \#\{\text{self-avoiding walks of length } n \text{ from } 0\}$

$$W = 1 \times 4 \times 3$$
$$P = 1 \times \frac{1}{4} \times \frac{1}{3}$$
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- \( c_n = \#\{\text{self-avoiding walks of length } n \text{ from 0}\} \)

\[
\langle W \rangle_n = \sum_{|\text{walk}| = n} W(\text{walk}) \cdot P(\text{walk})
\]

\[
W = 1 \times 4 \times 3 \times 3
\]

\[
P = 1 \times \frac{1}{4} \times \frac{1}{3} \times \frac{1}{3}
\]
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- \( c_n = \#\{\text{self-avoiding walks of length } n \text{ from 0}\} \)

\[
W = 1 \times 4 \times 3 \times 3 \times 2 \\
P = 1 \times \frac{1}{4} \times \frac{1}{3} \times \frac{1}{3} \times \frac{1}{2} \\
\langle W \rangle_n
\]
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- \( c_n = \#\{\text{self-avoiding walks of length } n \text{ from 0}\} \)

\[ W = 1 \times 4 \times 3 \times 3 \times 2 \]
\[ P = 1 \times \frac{1}{4} \times \frac{1}{3} \times \frac{1}{3} \times \frac{1}{2} \]

\[ \langle W \rangle_n = \sum_{|\text{walk}|=n} W(\text{walk})P(\text{walk}) \]
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- \( c_n = \#\{\text{self-avoiding walks of length } n \text{ from } 0\} \)

\[
\langle W \rangle_n = \sum_{|\text{walk}|=n} W(\text{walk}) P(\text{walk}) = \sum_{|\text{walk}|=n} 1
\]

- \( W = 1 \times 4 \times 3 \times 3 \times 2 \)
- \( P = 1 \times \frac{1}{4} \times \frac{1}{3} \times \frac{1}{3} \times \frac{1}{2} \)

EJ Janse van Rensburg  Mathematics and Statistics, York University – November 2018 – Collaborator: F Gassoumov
Approximate enumeration of walks in a square

- Rosenbluth algorithm
- $c_n = \#\{\text{self-avoiding walks of length } n \text{ from 0}\}$

- $W = 1 \times 4 \times 3 \times 3 \times 2$
- $P = 1 \times \frac{1}{4} \times \frac{1}{3} \times \frac{1}{3} \times \frac{1}{2}$
- $\langle W \rangle_n = \sum_{|\text{walk}|=n} W(\text{walk})P(\text{walk}) = \sum_{|\text{walk}|=n} 1 = c_n$
Rosenbluth algorithm with pruning and enrichment (Grassberger 1997)

- **Pruning:** if \( W(\text{walk}) < \langle W \rangle_n \) then prune the walk:
  - Compute \( p = \frac{W(\text{walk})}{\langle W \rangle_n} \)
  - With probability \( p \) increase the weight: \( W(\text{walk}) \longrightarrow \frac{1}{p} W(\text{walk}) \)
  - Default put \( W(\text{walk}) = 0 \): stop growing the walk

- **Enrichment:** if \( W(\text{walk}) \geq \langle W \rangle_n \) then enrich the walk:
  - Compute \( r = \frac{W(\text{walk})}{\langle W \rangle_n} \) and \( p = r - \lfloor r \rfloor \)
  - With probability \( p \) put \( c = \lceil r \rceil \) else \( c = \lfloor r \rfloor \)
  - Update \( W(\text{walk}) \longrightarrow 1^c W(\text{walk}) \)
  - Make \( c \) copies of the walk and grow each independently

This is the flatPERM algorithm (Krawczyk & Prellberg 2004)
Rosenbluth algorithm with pruning and enrichment (Grassberger 1997)

- **Pruning:** if $W(walk) < \langle W \rangle_n$ then prune the walk:
  - Compute $p = \frac{W(walk)}{\langle W \rangle_n}$
  - With probability $p$ increase the weight: $W(walk) \rightarrow \frac{1}{p} W(walk)$
  - Default put $W(walk) = 0$: stop growing the walk

- **Enrichment:** if $W(walk) \geq \langle W \rangle_n$ then enrich the walk:
  - Compute $r = \frac{W(walk)}{\langle W \rangle_n}$ and $p = r - \lfloor r \rfloor$
  - With probability $p$ put $c = \lceil r \rceil$ else $c = \lfloor r \rfloor$
  - Update $W(walk) \rightarrow \frac{1}{c} W(walk)$
  - Make $c$ copies of the walk and grow each independently

- This is the flatPERM algorithm (Krawczyk & Prellberg 2004)
flatPERM sampling of confined walks
All walks start in the North-East corner

\[ c_{n,L} = \#\{\text{walks of length } n \text{ vertices in square of sidelength } L-1\} \]

Area of the square is \( V = \#\{\text{sites}\} = L^2 \)

Concentration of vertices ("monomers") is \( \phi = \frac{n}{V} \)

Number of walks at concentration \( \phi \)

\[ c_n(\phi) = \#\{\text{walks of length } n = \lfloor \phi V \rfloor \text{ vertices}\} \]
All walks start in the North-East corner

\[ c_{n,L} = \# \{ \text{walks of length } n \text{ vertices in square of sidelength } L-1 \} \]

Area of the square is \( V = \# \{ \text{sites} \} = L^2 \)

Concentration of vertices ("monomers") is \( \phi = \frac{n}{V} \)

Number of walks at concentration \( \phi \)

\[ c_n(\phi) = \# \{ \text{walks of length } n = \lfloor \phi V \rfloor \text{ vertices} \} \]

- Total finite size free energy per site

\[ F_V(\phi) = -\frac{1}{V} \log c_n(\phi) \]

- Total finite size free energy per unit length

\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \quad \text{and} \quad F_V(\phi) = \phi f_t(\phi) \]
$F_V(\phi)$ for $L = 10$
Flory-Huggins theory

- Flory-Huggins theory for a confined polymer
  - Huggins 1942, Flory 1942, 1953
  - Mean field estimate of number of states or conformations $W$
    \[
    W \approx \frac{V^N}{N!} \left( \frac{n}{V} \right)^{nN} (\gamma - 1)^{nN} \left( \frac{(V/n)!}{(V/n-N)!} \right)^n
    \]
  - Entropy
    \[
    \Delta S = \log W \approx N - N \log 2 + nN(\log(\gamma - 1) - 1) - N \log \frac{N}{V} - (V - nN) \log \frac{V-nN}{V}
    \]

$N$ polymers of length $n$ monomers

Confining volume $V$

Lattice coordination number $\gamma$
• Flory-Huggins “excess entropy” of a confined polymer
  ▶ Entropy of a filled square (put $nN = V$)
    \[ \Delta S^* \approx nN (\log(\gamma - 1) - 1) \]
  ▶ “Excess Entropy”
    \[ \Delta S^e = \Delta S - \Delta S^* \approx -N \log \frac{N}{V} - (V - nN) \log (1 - \frac{nN}{V}) \]
  ▶ Excess Entropy per unit volume
    \[ \Delta S_{\text{site}} = \frac{1}{V} \Delta S^e \approx -\frac{N}{V} \log \frac{N}{V} - (1 - \frac{nN}{V}) \log (1 - \frac{nN}{V}) \]
  ▶ Notice that dependence on $\gamma$ has disappeared
Flory-Huggins “entropy of mixing” (of the polymer in the solvent)

- Concentration of the monomers $\phi = \frac{nN}{V}$
- Cast the excess entropy in terms of $\phi$

$$\Delta S_{\text{site}}(\phi) \approx -\frac{\phi}{n} \log \frac{\phi}{n} - (1 - \phi) \log(1 - \phi)$$

- This is modified by defining the “entropy of mixing”

$$\Delta S_{\text{mix}}(\phi) = \Delta S_{\text{site}}(\phi) - \phi S_{\text{site}}(1) - (1 - \phi) S_{\text{site}}(0) = -\frac{\phi}{n} \log \phi - (1 - \phi) \log(1 - \phi)$$

- Notice that $S_{\text{mix}}(0) = S_{\text{mix}}(1) = 0$
- All constants and linear terms are cancelled by the subtractions
Flory-Huggins theory for a confined polymer

- Monomer-monomer, solvent-solvent and monomer-solvent interactions
  \[ \frac{1}{2} T \chi_{MM} \phi^2, \quad \frac{1}{2} T \chi_{SS} (1 - \phi)^2, \quad T \chi_{MS} \phi(1 - \phi) \]

- “Energy of mixing” when \( T = 1 \)
  \[ E_{\text{mix}} = \chi \phi(1 - \phi), \quad \chi = \chi_{MS} - \frac{1}{2} (\chi_{MM} + \chi_{SS}) \]

- Flory Interaction parameter \( \chi \)

- “Free Energy of mixing” follows from the usual “\( F = U - TS \)”

\[
F_{\text{mix}} = E_{\text{mix}} - S_{\text{mix}} = \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi)
\]
- **Low concentration expansion**

\[
F_{\text{mix}} = E_{\text{mix}} - S_{\text{mix}} = \frac{\phi}{n} \log \phi + \frac{1}{2} (1 - 2\chi)\phi^2 + \frac{1}{6} \phi^3 + \ldots
\]

- **(Edwards) Excluded Volume Parameter** \( \nu = \frac{1}{2} (1 - 2\chi) \)

- **Osmotic pressure** \( \Pi \)

\[
\Pi = \phi^2 \frac{\partial}{\partial \phi} \left( \frac{1}{\phi} F_{\text{mix}} \right) = \frac{1}{V} - \log(1 - \phi) - \phi - \chi \phi^2
\]

- **Open problem:** Determine \( \chi \) for the self-avoiding walk
$F_{mix}$ and $\Pi$
$F_{\text{mix}}$ and $\Pi$
$F_V(\phi)$

-0.6

-0.3

0

0.1

0

0.25

0.50

0.75

1

$F_V(\phi)$
$F_V(\phi)$

-0.6
-0.3
0
0.1

$\phi$

0
0.25
0.50
0.75
1

$F_V(\phi)$

-0.6
-0.3
0
0.1

$\phi$
Modelling dense polymers by self-avoiding walks
$F_V(\phi)$
$F_V(\phi)$
$F_V(\phi)$
$F_V(\phi)$
$F_V(\phi)$
$F_V(\phi)$

![Graph showing $F_V(\phi)$ vs $\phi$ with a downward trend from left to right.](image-url)
$F_V(\phi)$
$F_V(\phi)$
$F_V(\phi)$

![Graph showing the function $F_V(\phi)$ with the axes labeled $\phi$ and $F_V(\phi)$, ranging from $-0.6$ to $0.1$ on the y-axis and from $0$ to $1$ on the x-axis. The graph includes a series of curves representing different values of $\phi$.](image-url)
Flory-Huggins free energy of mixing

\[ F_{\text{mix}}(\phi) = \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi (1 - \phi) \]
- Flory-Huggins free energy of mixing

\[ F_{\text{mix}}(\phi) = \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi (1 - \phi) \]

- “Normalised” to zero by \( F_{\text{mix}}(0) = F_{\text{mix}}(1) = 0 \)
- However, \( F_V(1) \neq 0 \)
- Add in the discarded linear term to obtain an F-H model for \( F_V(\phi) \)

\[ F_V(\phi) = F_{\text{mix}}(\phi) + a_0 \phi = a_0 \phi + \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi (1 - \phi) \]
**Free energy per unit volume**

\[ F_V(\phi) = a_0 \phi + \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi (1 - \phi) \]

**Free energy per unit length**

\[ f_t(\phi) = \frac{1}{\phi} F_V(\phi) = a_0 + \frac{1}{V\phi} \log \phi + \frac{1 - \phi}{\phi} \log(1 - \phi) - \chi \phi \]

**Taking** \( V \) **large and for** \( \phi \gg \frac{1}{V} \)

\[ f_t(\phi) = a_0 + \frac{1 - \phi}{\phi} \log(1 - \phi) - \chi \phi \]
$F_V(\phi)$ for $L = 10$

Two parameter least squares fit:

- $a_0 = 0.1911$
- $\chi = 0.4676$

These are effective values.
$F_V(\phi)$ for $L = 10$

\[ F_V(\phi) = a_0 \phi + \frac{1}{V} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi) \]

- Two parameter least squares fit: $a_0 = 0.1911$ and $\chi = 0.4676$
- These are effective values
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
$f_t(\phi) = -\frac{1}{n} \log c_n(\phi)$
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\( f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \)
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\( f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \)
$$f_t(\phi) = -\frac{1}{n} \log c_n(\phi)$$
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\[ f_t(\phi) = -\frac{1}{n} \log c_n(\phi) \]
\( f_t(\phi) \)

- \( \phi < \phi^* \) — low concentration regime
- \( c_{n,L} = \mu_2^{n+o(n)} \) if \( 0 \ll n \ll L \)
- In the limit \( L \to \infty \), \( f_t(0^+) = -\log \mu_2 \approx -0.97 \)
\[ \phi^* \rightarrow 0 \text{ as } L \rightarrow \infty \]

\[ f_t(\phi) = a_0 + \frac{1}{V} \log \phi + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi_L \phi \]

\[ \lim_{L \rightarrow \infty} f_t(\phi^*) = f_t(0^+) = a_0 - 1 = -\log \mu_2 \]

\[ a_0 = 1 - \log \mu_2 \]
One parameter model for $f_t(\phi)$ for $\phi > \phi^*$:

$$f_t(\phi) = 1 - \log \mu_2 + \frac{1}{V\phi} \log \phi + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi_L \phi$$

For large $V$ the term $\frac{1}{V\phi} \log \phi$ can be left away

$$f_t(\phi) = 1 - \log \mu_2 + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi_L \phi$$

For example, for $L = 10$ ($V = 100$), $\chi_{10} \approx 0.25$
Extrapolate the data

\[ \chi_{\text{saw}} = 0.32(1) \]
Hamiltonian walk

- Number of Hamiltonian walks in a square of side-length $L-1$: $h_L$
Hamiltonian walk

- Number of Hamiltonian walks in a square of side-length $L-1$: $h_L$
  - Corollary of Madras 1993
    $$\kappa_H = \limsup_{L \to \infty} \frac{1}{L^2} \log h_L = \log \mu_H > 0$$
  - The growth constant of Hamiltonian walks of a square: $\mu_H > 1$
  - The connective constant of Hamiltonian walks: $\kappa_H = \log \mu_H$

- Open problem: Estimate $\kappa_H$
- Easy estimate: $\kappa_H \geq \frac{1}{9} \log 2 \approx 0.077$ and $\mu_H \gtrsim 1.08$
The Flory-Huggins free energy is
\[
\lim_{L \to \infty} f_t(\phi) = 1 - \log \mu_2 + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi_{\text{saw}} \phi
\]

Taking \( \phi = 1 \) gives
\[
\kappa_H = \lim_{L \to \infty} f_t(1) = 1 - \log \mu_2 - \chi_{\text{saw}} \approx 0.303
\]

This gives the estimate
\[
h_L = \mu_H^{L^2}, \text{ with } \mu_H \approx 1.35
\]
3 dimensions: ring polymer

Conformational degrees of freedom contribute to entropy
Translational degrees of freedom contribute to entropy
Topological degrees of freedom

Topological constraints contribute to entropy
Knots

$0_1$

$3_1$

$4_1$
# Number of lattice knots of length $N$ and type $K$: $p_N(K)$
Lattice knots

- Number of lattice knots of length $N$ and type $K$: $p_N(K)$
- The number of lattice polygons

$$p_N(K) \sim C \, n^{3-\alpha_K} \, [\mu_3(K)]^N,$$
Lattice knots

- Number of lattice knots of length $N$ and type $K$: $p_N(K)$
- The number of lattice polygons

\[ p_N(K) \sim C n^{3-\alpha_K} [\mu_3(K)]^N, \quad \text{so} \quad \log p_N(K) \sim N \log \mu_3(K) = N \kappa_3(K) \]

- “growth constant” – $\mu_3(K)$
- “connective constant” – $\kappa_3(K) = \log \mu_3(K)$
Three dimensions: lattice knots

- BFACF dynamics in cube of dimension $L^3$
- The confinement restricts state space
- Some states not reachable – same feature in a compressed polymer
- Work in ergodicity class containing shortest knots – “confined knots”
Ergodicty class

Lattice knots

Lattice knots in $L^3$
Ergodicity class

Lattice knots

Minimal knots
Ergodicity class

Lattice knots in $L^3$

Lattice knots

Minimal knots

Confined knots

The confinement restricts state space.

Some states not reachable – same feature in a compressed polymer.
Ergodicty class

- Lattice knots in $L^3$
- Lattice knots
- Minimal knots
- Confined knots

- BFACF dynamics
- The confinement restricts state space
- Some states not reachable – same feature in a compressed polymer
- Space of Confined Knots
Confined knots

- Confined in a volume $V$ – translational degrees of freedom
- \# confined knots in volume $V$: $p_{n,V}(K)$
Confined knots

- Confined in a volume $V$ – translational degrees of freedom
- \# confined knots in volume $V$: $p_{n,V}(K)$
- Free energy per unit volume

\[
F_V(\phi) = -\frac{1}{V} \log p_{n,V}(K)
\]

- $F_V$ is a function of concentration $\phi = \frac{n}{V}$
Lattice model

- Flory-Huggins free energy of mixing (no constant and linear terms)
  \[
  F_{\text{mix}} = \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi (1 - \phi)
  \]
Lattice model

- Flory-Huggins free energy of mixing (no constant and linear terms)
  \[ F_{\text{mix}} = \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi) \]

- Free energy \( F_V(\phi) \)
  \[ F_V(\phi) = a_0 \phi + \frac{\phi}{n} \log \phi + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi) \]

- Osmotic pressure
  \[ \Pi = \phi^2 \frac{\partial}{\partial \phi} \left( \frac{1}{\phi} F_{\text{mix}} \right) = \frac{1}{V} - \log(1 - \phi) - \phi - \chi \phi^2 \]

- GAS algorithm with BFACF dynamics
Animation: high concentration
Animation: low concentration
Flory free energy

- The Flory approximation to the free energy is

\[ f_t(K) = a_0 + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi \phi \]

\[ F_V(K) = f_t(K) \times \phi = a_0 \phi + (1 - \phi) \log(1 - \phi) - \chi \phi^2 \]

- The parameter \( a_0 \) is estimated by noting that

\[ \lim_{\phi \to 0^+} \lim_{L \to \infty} f_t(\phi) = a_0 - 1 = -\log \mu_3(K) \]

- This approximation is given by red dashed curves
$F_V(\phi)$ per unit volume (unknot)
$F_V(\phi)$ per unit volume (unknot)
$F_V(\phi)$ per unit volume (unknot)
$F_V(\phi)$ per unit volume (unknot)
$F_V(\phi)$ per unit volume (unknot)
$F_V(\phi)$ per unit volume (unknot)
$F_V(\phi)$ per unit length ($3_1$ and $4_1$)
$f_t(\phi)$ per unit length (unknot)
Flory interaction parameter $\chi$

Estimate an effective value by fitting $f_t = a_0 + \frac{1-\phi}{\phi} \log(1 - \phi) - \chi\phi$

<table>
<thead>
<tr>
<th>$L$</th>
<th>$\chi_{01}$</th>
<th>$\chi_{31}$</th>
<th>$\chi_{41}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.4265</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>0.3530</td>
<td>0.6906</td>
<td>0.8784</td>
</tr>
<tr>
<td>5</td>
<td>0.3046</td>
<td>0.4482</td>
<td>0.5115</td>
</tr>
<tr>
<td>6</td>
<td>0.2748</td>
<td>0.3564</td>
<td>0.3886</td>
</tr>
<tr>
<td>7</td>
<td>0.2561</td>
<td>0.3053</td>
<td>0.3265</td>
</tr>
<tr>
<td>8</td>
<td>0.2437</td>
<td>0.2760</td>
<td>0.2895</td>
</tr>
<tr>
<td>9</td>
<td>0.2370</td>
<td>0.2569</td>
<td>0.2686</td>
</tr>
<tr>
<td>10</td>
<td>0.2320</td>
<td>0.2471</td>
<td>0.2531</td>
</tr>
<tr>
<td>11</td>
<td>0.2260</td>
<td>0.2383</td>
<td>0.2450</td>
</tr>
<tr>
<td>12</td>
<td>0.2220</td>
<td>0.2325</td>
<td>0.2370</td>
</tr>
<tr>
<td>13</td>
<td>0.2165</td>
<td>0.2231</td>
<td>0.2270</td>
</tr>
<tr>
<td>14</td>
<td>0.2192</td>
<td>0.2180</td>
<td>0.2225</td>
</tr>
<tr>
<td>15</td>
<td>0.2132</td>
<td>0.2193</td>
<td>0.2218</td>
</tr>
</tbody>
</table>

**Table:** Estimated Flory interaction parameters from $f_t$

$\chi = 0.18 \pm 0.03$
Osmotic pressure $\Pi (0_1)$
Osmotic pressure $\Pi (3_1)$
Osmotic pressure $\Pi (4_1)$
Low concentration osmotic pressure – unknot

$\Pi_0$ -0.02

$\phi$

0 0.1 0.2 0.3 0.35

-0.02 0.06
At low concentration the osmotic pressure is negative

Size $S$ of a lattice knot of length $N \ll L$:

$$S = O(N^\nu)$$
At low concentration the osmotic pressure is negative
Size $S$ of a lattice knot of length $N \ll L$:

$$S = O(N^\nu)$$

It touches walls of its confining cube when $S = O(L)$, or when $N = O(L^{1/\nu})$

Concentration where this happens is

$$\phi_0 = \frac{1}{V} O(L^{1/\nu}) \sim L^{1/\nu - 3} = L^{-4/3}$$

(Flory value: $\nu = \frac{3}{5}$)

Since $\Pi V = O(1)$ for $\phi \to 0^+$, plot $\Pi L^3$ against $\phi L^{4/3}$
Low concentration osmotic pressure – unknot

\[ \Pi L^3 \]

\[ \phi_m L^{4/3} \approx 0.37 \]
\[ \phi_c L^{4/3} \approx 1.1 \]
\[ \phi_M L^{4/3} \approx 2.3 \]
Low concentration osmotic pressure – trefoil
Low concentration osmotic pressure – trefoil

\[ \Pi L^3 \]

\[ \phi L^{4/3} \approx 3.7 \]

\[ \phi_0 L^{4/3} \approx 3.7 \]
Low concentration osmotic pressure – figure eight

\[ \Pi(4_1) \]

\[ \varphi \]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \]

\[ -0.05 \quad 0.05 \]
Low concentration osmotic pressure – figure eight

\[ \Pi L^3 \]

\[ \phi L^{4/3} \]

\[ \phi_0 L^{4/3} \approx 4.1 \]
Conclusions

- Flory-Huggins model of $F_V$ for confined compressed square lattice self-avoiding walks
- Flory interaction parameter for square lattice self-avoiding walks:
  $$\chi = 0.32 \pm 0.01$$
- Flory-Huggins model of $F_V$ for cubic lattice confined compressed lattice knots
- Flory interaction parameter for confined cubic lattice knots:
  $$\chi = 0.18 \pm 0.03$$
- Low concentration osmotic pressure is knot type dependent

- Thanks Miklos!