The role of three body interactions in polymer collapse in two dimensions

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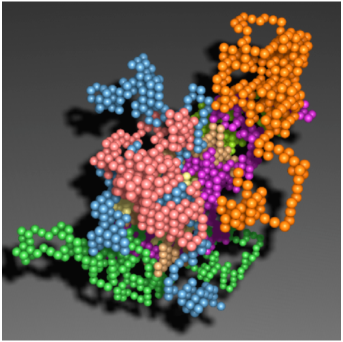
Modelling of Polymers in Solution

- Polymers: long chains of monomers
- "Coarse-Graining": beads on a chain
- "Excluded Volume":
  minimal distance between beads
- Contact with solvent:
  effective short-range interaction
- Good/bad solvent:
  repelling/attracting interaction



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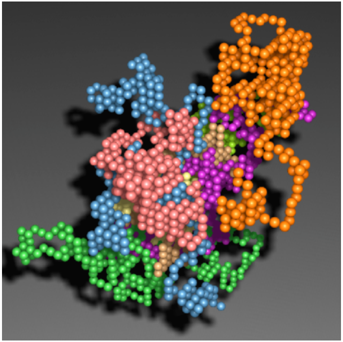


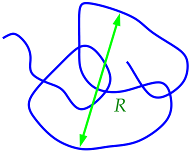
A Model of a Polymer in Solution

Random Walk + Excluded Volume + Short Range Attraction

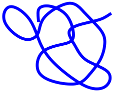
A Polymer Phase Transition: Collapse (θ-point)

- *Polymers are often 'Fractal': length n, spatial extension $R \sim n^{\nu}$ and the mass $m \propto n \sim R^{d_{fractal}}$ giving $\nu = 1/d_{fractal}$.*
- *$d_{fractal}$ changes discontinuously dependent with temperature*
- *That is, a "Phase transition" occurs as temperature is changed: Polymer Collapse, aka Coil-Globule Transition, aka Θ-Point*

Consider two spatial dimensions ($d = 2$):



$T > T_c$: good solvent swollen phase (coil): $d_{fractal} = 4/3$

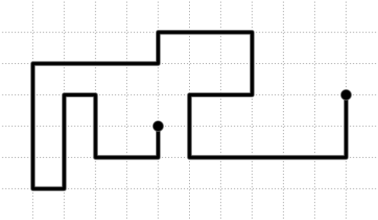


$T = T_c$: Θ-polymer: $d_{fractal} = 7/4$

$T < T_c$: poor solvent — collapsed phase (liquid-like globule): $d_{fractal} = d = 2$

The Canonical Polymer Lattice Model

- *Polymer → self-avoiding random walk (SAW)*
- *Physical space → regular lattice eg $\mathbb{Z}^3$ or $\mathbb{Z}^2$*
- *Sites — beads — monomers — not always valid*

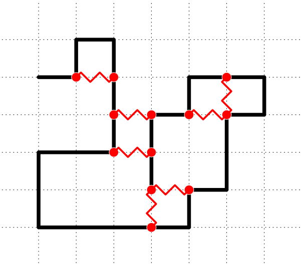


Key idea: Universality

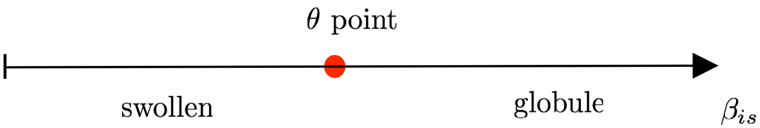
THE CANONICAL COLLAPSING POLYMER LATTICE MODEL

Interacting Self-Avoiding Walk (ISAW)

- *Start with a self-avoiding walk (SAW) and add 'interactions'*
- *Quality of solvent → short-range interaction energy* $-\varepsilon_{is}$
- *Inverse temperature* $\beta_{is} = \varepsilon_{is}/k_B T$
- *Interactions are between (non-consecutive) nearest neighbours*



Classical collapse transition



The θ point

- High temperature "swollen or "extended" phase $d_f < d$
- θ-point collapse transition is a second order phase transition
- Low temperature partially dense (but disorded) globule $d_f = d$ — liquid-like drop
- de Gennes' general description (1975) as a "tricritical point"
- The standard theory (de Gennes 1975, Stephen 1975, Duplantier 1982) of the collapse transition is based on the $n \to 0$ limit of the magnetic tri-critical $\phi^4 - \phi^6$ O(n) field theory

Quantities of interest

The partition function

$$Z_n(\beta) = \sum_{configurations} e^{\beta \varepsilon_{is} m_{nn}}$$

where m_{nn} is the number of nearest-neighbour pairs (contacts) and $-\varepsilon_{is}$ is the energy associated with each nearest neighbour pair.
The free energy

$$\kappa_n(\beta_{is}) = \frac{1}{n} \log Z_n(\beta_{is})$$

and the thermodyanmic limit is

$$K(\beta_{is}) = \lim_{n \to \infty} \kappa_n(\beta_{is})$$

QUANTITIES OF INTEREST

The internal energy, which is the first derivative of κ_n with respect to β_{is}

$$u_n(\beta_{is}) = \frac{1}{n}\langle m_{nn}\ \varepsilon_{is}\rangle$$

with

$$U(\beta_{is}) = \lim_{n\to\infty} u_n$$

.

The specific heat, which is the second derivative,

$$c_n(\beta_{is}) = \frac{1}{n}\left(\langle m_{nn}^2\ \varepsilon_{is}^2\rangle - \langle m_{nn}\ \varepsilon_{is}\rangle^2\right)$$

with

$$C(\beta_{is}) = \lim_{n\to\infty} c_n$$

.

At fixed temperature

For any fixed temperature we expect

$$R_n^2 \sim A n^{2\nu}$$

the value of ν *depends on the whether* $T > T_t$, $T = T_t$ *or* $T < T_t$.

For $T \geq T_t$ *we expect*

$$Z_n \sim B e^{Kn} n^{\gamma - 1}$$

while for $T < T_t$ *we expect*

$$Z_n \sim B e^{Kn} e^{K_s n^{(d-1)/d}} n^{\gamma - 1}$$

where K_s *is a surface free energy.*

The change in the exponents ν *and* γ *herald a phase transition.*

Scaling in the three phases

At high temperatures — small β — Swollen Phase

In two dimensions, $\nu = 3/4$ while $\gamma = 43/32$

At the transition — $\beta = \beta_t$ — θ-point

In two dimensions, $\nu = 4/7$ while $\gamma = 8/7$

At low temperatures — large β — Globule Phase

In two dimensions, $\nu = 1/2$ while in three dimensions $\nu = 1/3$.

SCALING AROUND THE θ POINT

As the critical temperature is approached the specific heat is expected to behave as

$$c_\infty(T) \sim B|T_t - T|^{-\alpha} \ ,$$

For finite lengths n

$$c_n(T) \sim n^{\alpha\phi}\, \mathcal{C}((T - T_t)n^{\phi})$$

The exponents α and ϕ are related via

$$2 - \alpha = \frac{1}{\phi} \ .$$

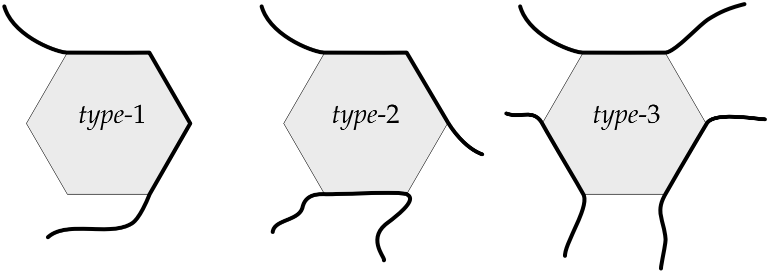
Duplantier-Saleur (DS) model

Duplantier and Saleur (1987) predicted the standard θ-point behaviour in two dimensions

which has been subsequently supported by work of Prellberg and Owczarek (1994) on the Manhattan lattice.

- Considered SAW on the honeycomb lattice in the presence of percolating vacancies (annealed) with probability p
- Equivalent to ISAW-type model with interactions around a face
- In particular to a model where faces visited three times are given a Boltzmann weight, ω_3, being equal to the square of the weight of those visited twice, ω_2
- That is, $\omega_3 = \omega_2^2 = \frac{1}{(1-p)^2}$
- Collapse point is when $\omega_2 = 2$, at percolation point ($p = 1/2$)

Three types of face on the honeycomb lattice



$$\omega_3 = \omega_2^2$$

SCALING AROUND THE θ POINT IN TWO DIMENSIONS

- Model related to hulls of percolating clusters
- Exponents from $O(n=1)$ Ising model in "critical" low temperature phase ($q=1$ Potts at critical point)
- It was hence predicted that

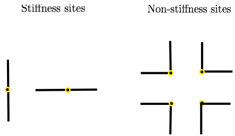
$$\phi = 3/7 \approx 0.43 \quad \text{and} \quad \alpha = -1/3 \; .$$

- The specific heat does *not* diverge at the transition
- It was also predicted the $d_f = 7/4$ at the θ-point.

Adding stiffness to ISAW

Adding stiffness

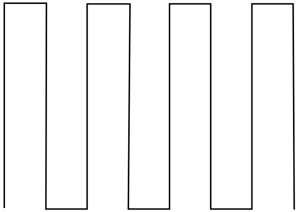
- Models natural rigidity of polymers
- though it implies sites to monomer mapping is incomplete with adding stiffness
- In 1998 Bastolla and Grassberger studied the canonical model in three dimensions and added a weight for bends
- Later, in 2009, a model with weights for ‘stiffness sites’ studied by Krawczyk, Owczarek and Prellberg in two dimensions



SEMI-FLEXIBLE ISAW AT LOW TEMPERATURES

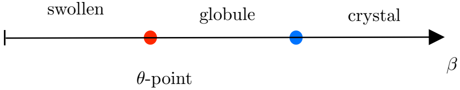
At low temperatures and sufficient stiffness a polymer crystal can occur

A rectangular "polymer" crystal

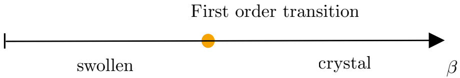


Semi-flexible ISAW

- Two transitions or one — depends on stiffness
- For small stiffness

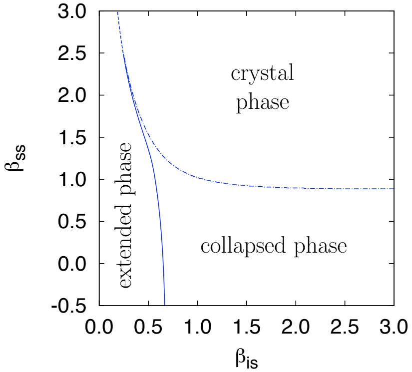


- For large stiffness



Adding stiffness to ISAW

If one considers both nearest-neighbour interactions (β_{is}) and stiffness (β_{ss}) one finds



Phase transition for semi-flexible polymers

Swollen – Globule

This is the θ transition: convergent specific heat and divergent free energy third derivative, $\alpha = -1/3$ in two dimensions.

Swollen – Crystal

First order in both two and three dimensions

Globule – Crystal

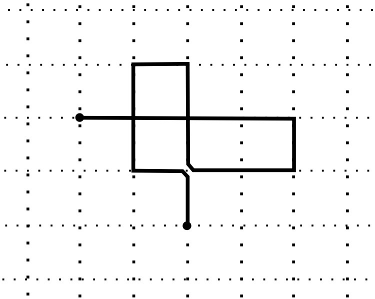
Second order in two dimensions with estimated $\alpha \approx 0.6(2)$

Meeting point

Unknown

Self-avoiding trails (SAT)

Trails, or bond avoiding walks, were introduced by Malakis in 1976 to model polymers with loops.

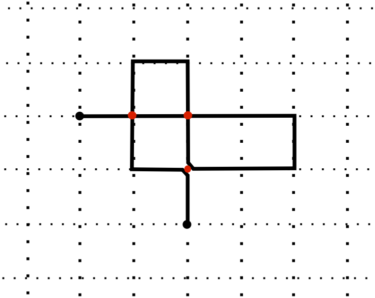


HISTORY OF SAT ANALYSIS

- Malakis suggested that SAW and SAT are in the same universality class
- Shapir and Oono introduced a field theoretic approach to trails in 1984
- They conjectured that SAW and SAT are in the same universality class
- Guttmann (1985) confirmed this from series work that SAT and SAW are in the same universality class with $\nu = 3/4$ in two dimensions.

ISAT ON THE SQUARE LATTICE— DIFFERENT MODEL OF POLYMER COLLAPSE

- Start with self-avoiding trails (bond avoiding walks) = same universality class as SAW
- Interactions were added by associating an energy with doubly occupied sites — both crossings and touching.



ISAT ON THE SQUARE LATTTICE

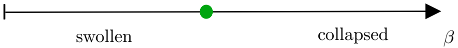
The partition function

$$Z_n(\beta) = \sum_{SAT} e^{\beta \varepsilon_{int} m_{int}}$$

where m_{int} is the number of intersections, both crossing and touchings are counted equally and $-\varepsilon_{int}$ is the energy associated with each intersection.

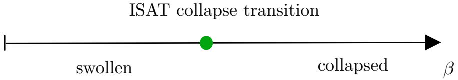
This leads to a single phase transition on varying β.

ISAT collapse transition



ISAT on the square latttice — different model of polymer collapse

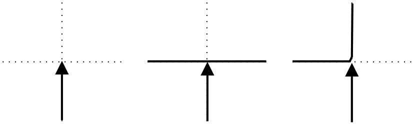
A single phase transition on varying temperature but broken Universality ?



- Shapir and Oono found a “new” tricritical point (that is, not the de Gennes θ-point)
- Lim A Guha, Y Shapir (1988) analysed ISAT on the triangular lattice via series found a divergent specific heat
- H Meirovitch, H A Lim (1989) analysed ISAT on the square lattice using a Monte Carlo method gave $\phi = 0.807(5)$ for the ISAT collapse transition

Kinetic SAT (KSAT)

A dynamic random walk: a kinetic growth trail on the square lattice



Probability of next step $\frac{1}{3}$ 1 1

$= \frac{1}{3} \times 1$ $= \frac{1}{3} \times 3$ $= \frac{1}{3} \times 3$

Mapping to ISAT model

This kinetic growth trail gives configurations of SAT with a ISAT Boltzmann weight of $e^{\beta \varepsilon_{int}} = 3$. (H. Meirovitch, I. S. Chang, and Y. Shapir (1989) and Bradley (1990))

SQUARE LATTICE KSAT SCALING

Owczarek and Prellberg (1995) studied KSAT. It was conjectured that

$$R_n^2(T) \sim An\,(\log n)^2 \ .$$

and estimated

$$\phi = 0.88(7)$$

They also analysed surface exponents and showed they were not consistent with θ-point values.

Square lattice ISAT Collapse transition

An alternate theory

Grassberger and Hegger 1996 suggest renormalisation argument implies ISAT collapse is first order: they gave numerical evidence in three dimensions but could not verify the conjecture on the square lattice.

Square lattice ISAT simulations

Owczarek and Prellberg 2006, used PERM Monte Carlo on the square lattice has shown that there is a collapse transition with a strongly divergent specific heat, and the exponents have been estimated as

$$\phi = 0.84(3) \quad \text{and} \quad \alpha = 0.81(3)\ .$$

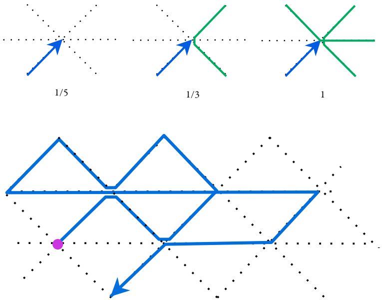
Square lattice ISAT Collapse transition

Transfer matrix calculations

- Foster 2009 suggested that the mapping between magnetic model and single polymer (there is a difference of ensembles here) is not straightforward with the ν exponent not mapped as normal. This may be related to a first order nature to the transition that was conjectured.
- In fact it was conjectured that ISAT on the square lattice are in the Blote-Nienhuis loop model universality class

Clearly there is something special about square lattice ISAT so study another lattice....

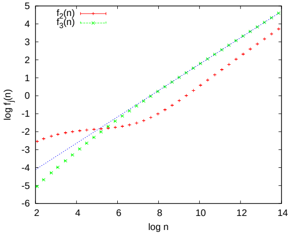
KINETIC GROWTH TRAILS ON THE TRIANGULAR LATTICE



An example of a trail with 13 steps on the triangular lattice. This trail has six singly visited sites, two doubly-visited sites and one triply-visited site (with probability $\frac{1}{5}\frac{1}{3}1$).
This trail is produced by the growth process with probability $(\frac{1}{6})(\frac{1}{5})(\frac{1}{5})(\frac{1}{5})(\frac{1}{5})(\frac{1}{3})(\frac{1}{5})(\frac{1}{5})(1)(\frac{1}{3})(\frac{1}{5})(\frac{1}{5})(\frac{1}{3})$.

FLUCTUATIONS IN TRIANGULAR KSAT

Fluctuations demonstrate divergent behaviour



$$\alpha = 0.847(3) \quad \text{and} \quad \phi = 0.867(3) \ .$$

Canonical Static ISAT - triangular lattice

Different to kSAT

- *Associate an energy $-\varepsilon$ with each doubly-visited site and an energy -2ε with each triply-visited site.*
- *For each SAT we count the number $m_2(\varphi_n)$ of doubly-visited sites and $m_3(\varphi_n)$ of triply-visited sites of the lattice and give that configuration a Boltzmann weight $\omega^{m_2+2m_3}$, where $\omega = \exp(\beta\varepsilon)$.*

The partition function of the canonical ISAT model is then given by

$$Z_n^{(2)}(\omega) = \sum_{SAT} \omega^{m_2+2m_3} \ .$$

Collapse transition for tri-ISAT

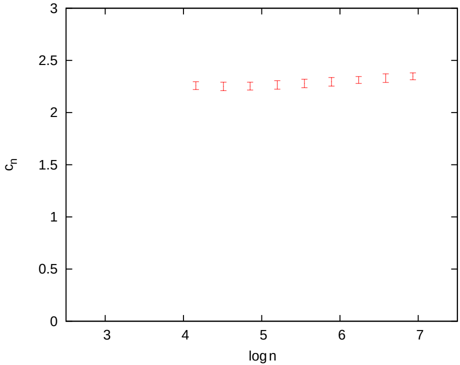


Figure: Plot of the value of the maximum of the specific heat $c_n = \max_\omega c_n^{(2)}$ against $\log n$. This suggests that the specific heat does not diverge as the polymer length is increased.

FREE ENERGY THIRD DERIVATIVE

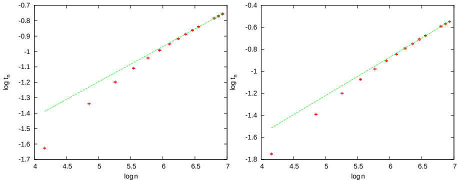


Figure: Plot of the height of the peaks of $t_n^{(2)}(\omega)$, the third derivative of the free energy with respect to temperature against n. The third derivative has two peaks: one positive and one negative in value.

They show a weak divergence: values 0.23(6) and 0.35(6) for $(1+\alpha)\phi$ were found: this is consistent with the ISAW θ-point value of $2/7 \approx 0.28$.

Therefore it is tempting to conjecture that the canonical ISAT model on the triangular lattice has a collapse transition that lies in the θ-point universality class, rather than square lattice ISAT collapse universality class.

The extended model of self-interacting trails (eISAT)

We associate an energy $-\varepsilon_2$ with each doubly-visited site and a different energy $-\varepsilon_3$ with each triply-visited site. For each SAT we assign a Boltzmann weight $\omega_2^{m_2}\omega_3^{m_3}$, where $\omega_j = \exp(\beta\varepsilon_j)$.

The partition function of the eISAT model is then given by

$$Z_n(\omega_2, \omega_3) = \sum_{SAT} \omega_2^{m_2(\varphi_n)} \omega_3^{m_3(\varphi_n)} \ .$$

We can define a one temperature family paramerized by k, where $\omega_3 = \omega_2^k$, with

$$Z_n^{(k)}(\omega) = \sum_{SAT} \omega^{m_2(\varphi_n)+km_3(\varphi_n)} \ .$$

The canonical model has $k = 2$

KSAT MAPPING

The KSAT progress gives SAT configurations with Boltzmann weights

$$\omega_2 = 5/3 \qquad \text{and} \qquad \omega_3 = 25/3$$

Alternatively

$$\omega = 5/3 \qquad \text{with} \qquad k = k_G \equiv \frac{\log(25/3)}{\log(5/3)} \approx 4.15 \neq 2 \ .$$

So the KSAT process does not map to any temperature of the canonical ISAT on the triangular lattice.

eISAT WITH $k = k_{KGT}$

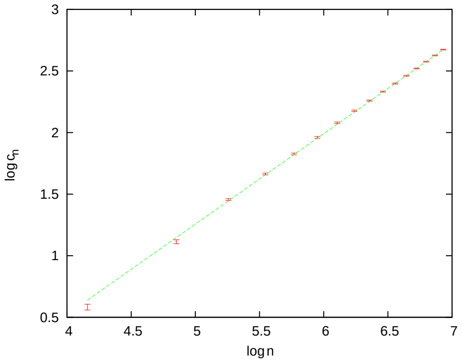


Figure: Plot of the logarithm of $c_n = \max_\omega c_n^{(k_G)}$, the value of the maximum of the specific heat, against $\log n$. The straight line has slope $\alpha\phi = 0.734$.

CROSSOVER SCALING FOR THE SPECIFIC HEAT IN $k = k_{KGT}$

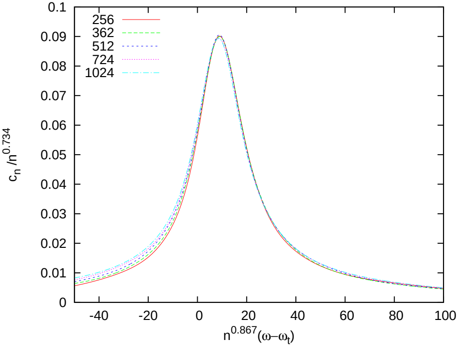


Figure: Scaling plot of the specific heat around the transition temperature, using the exponents from the growth process.

eISAT with $k = 0$

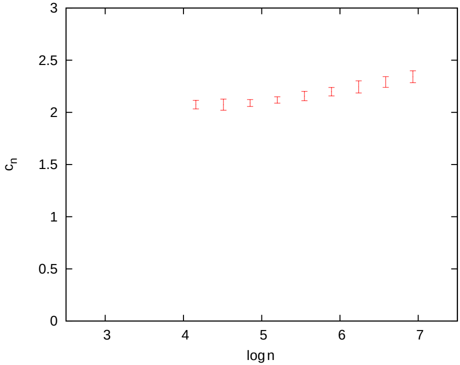


Figure: Plot of the value of the maximum of the specific heat $c_n = \max_\omega c_n^{(0)}$ against $\log n$ for $k = 0$ eISAT model. This suggests that the specific heat does not diverge as the polymer length is increased, as is the case in the canonical model ($k = 2$).

THIRD DERIVATIVE IN $k = 0$ MODEL

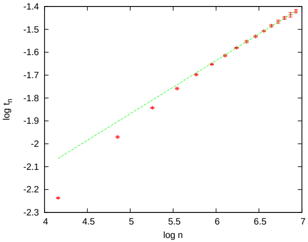


Figure: Plot of the height of one of the peaks of $t_n^{(0)}(\omega)$, the third derivative of the free energy with respect to temperature against n.

$$(1+\alpha)\phi \approx 0.23(6)$$

$k = \infty$ – 'Triple' model

Consider

$$Z_n^{(triple)}(\omega) = \sum_{\varphi_n \in \Omega_n} \omega^{m_3(\varphi_n)} \ .$$

$k = \infty$ – 'TRIPLE' MODEL

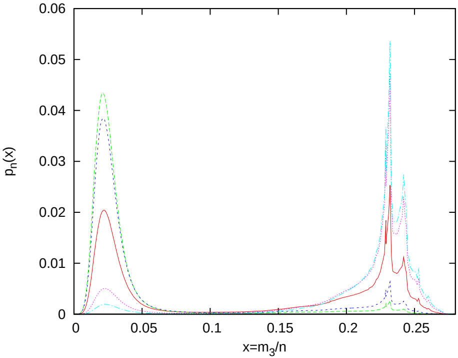


Figure: Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the *Triple* model at temperatures near, and at, the temperature at which the specific heat attains its maximum for length $n = 1024$. The specific heat attains its maximum at $\omega = \omega_{max} = 7.41$ and the distribution is plotted for this value and at $\omega = 7.31, 7.34, 7.48, 7.52$: the plots move from left to right as ω is increased.

$k = \infty$

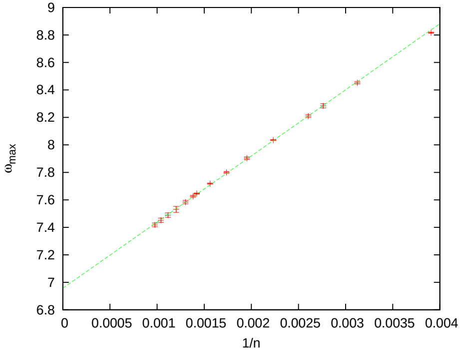


Figure: Plot of the location, ω_{max}, of the peak of the specific heat against $1/n$ for the *Triple* model.

FLUCTUATIONS

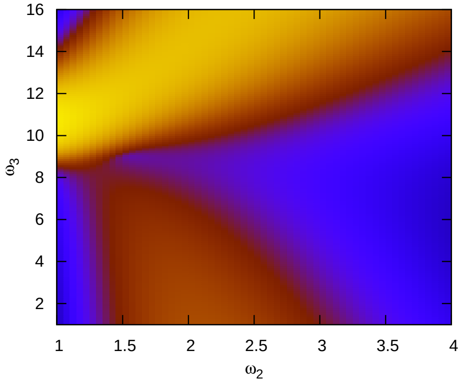


Figure: Density plot of the logarithm of the largest eigenvalue λ_{max} of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length $n = 128$ (the lighter the shade, the larger the value).

COLLAPSED PHASE FOR CANONICAL MODEL — GLOBULE

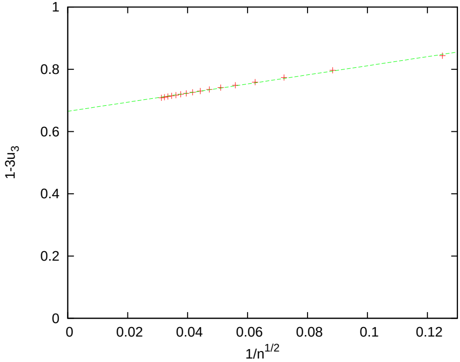


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(\omega_2, \omega_3) = (4, 16)$ in the collapsed liquid-drop-like globule phase. As the length increases this reaches a non-zero value.

A GLOBULE WHEN $k = 0$

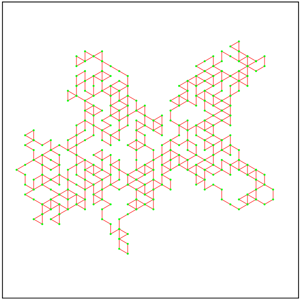


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (5, 1)$, which is in the globule phase: it looks disordered and rather more like a liquid-like globule than a crystal.

Collapsed phase when $k = 6$

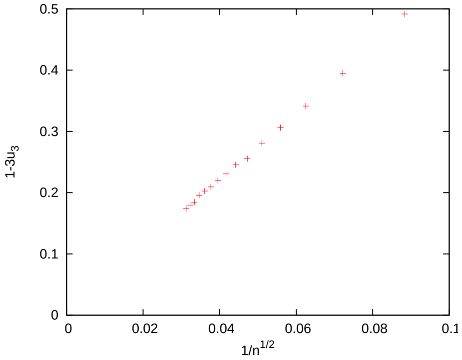


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(1.58, 15.6)$ in the hypothesised frozen (crystal-like) phase. As the length increases this quantity vanishes.

A 'crystal' in the Triple model

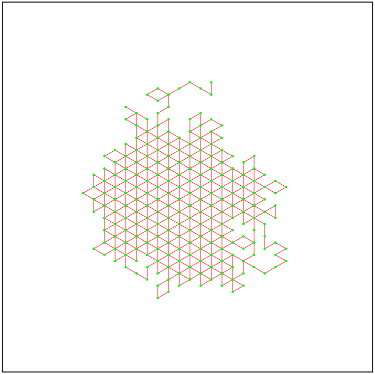


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

Phase diagram

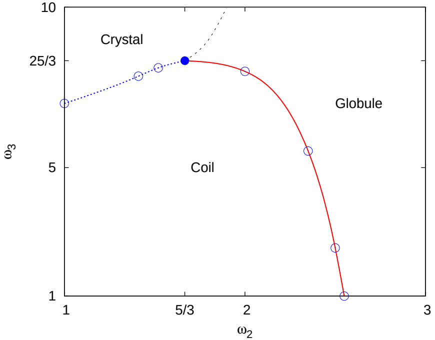


Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The filled circle is at the location of the kinetic growth point, and the open circles represent estimates of the collapse transition for various values of *k*.

Triangular lattice eISAT Conclusions

By studying an extended ISAT model on the triangular lattice we have found

- three phases: swollen, globule and crystal-like
- similar to semi-flexible ISAW despite stiffness is absent
- the meeting point of three phase boundaries seems multi-critical
- Kinetic growth dynamic model gives this multi-critical point exactly
- Square lattice ISAT model only has this multi-critical point
- This multicritical point — 'meeting point' in the semi-flexible ISAW model

J. Doukas, A. L. Owczarek and T. Prellberg, *Phys. Rev. E*, **82**, 031103 (12pp), 2010

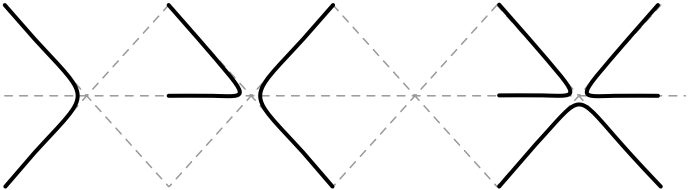
Loop models

So where does the story go now...

- The configurations of the exactly solved Loop models (á la Blöte-Nienhuis) are neither the full set of self-avoiding walks or trails
- They are paths on a lattice that can share sites, but usually not edges, and importantly unlike trails do not *cross*

INTERACTING GROOVES ON THE TRIANGULAR LATTICE

Recently we looked at Grooves: look mum, no crossings!

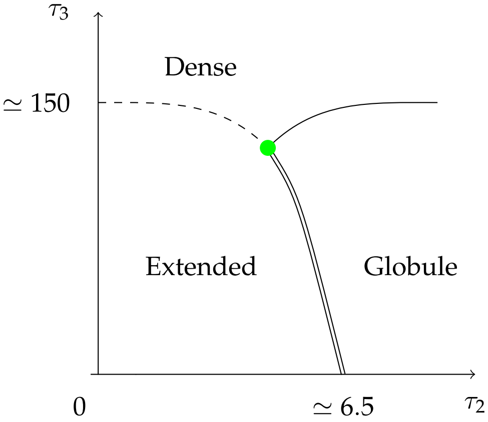


1-*visited* 2-*visited* 3-*visited*

$$Z_n(\tau_2, \tau_3) = \sum_{Grooves} \tau_2^{m_2(\varphi_n)} \tau_3^{m_3(\varphi_n)} \quad .$$

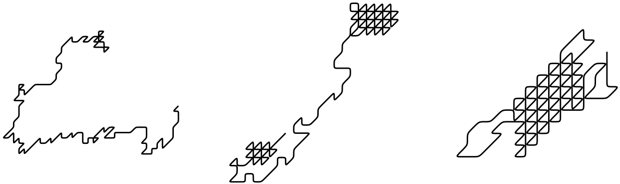
- Related to $O(n)$-model type configurations

Phase diagram for generalised Interacting Grooves (IG) on the triangular lattice



- Extended(Coil) to Dense transition looks first order again

Configuartions: Swollen to Fully Dense



Configurations in Extended, 'at first order' Transition and Dense regions

First order nature of Swollen to Dense

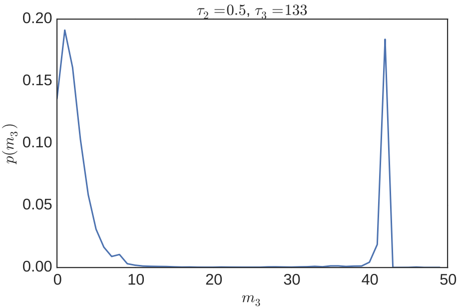


Figure: The distribution of the number of triply visited sites m_3 is clearly bimodal at the point when τ_2 and τ_3 cross the line of suspected first-order transitions.

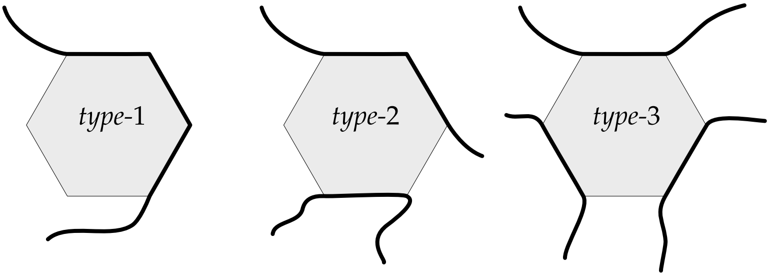
BACK TO THE FUTURE: WALKS AGAIN

- Want to look at fully flexible walk model that incorporates three-body interactions
- That is, no stiffness
- Back to self-avoiding walks — no trails or grooves

Generalised DS model

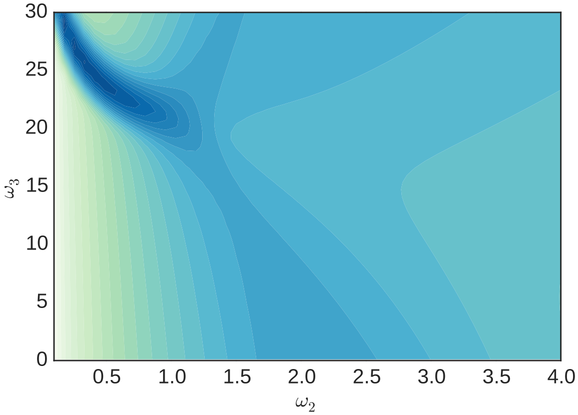
Consider model of Duplantier and Saleur on the Honeycomb lattice again

- Just generalise to arbitrary ω_3 and ω_2



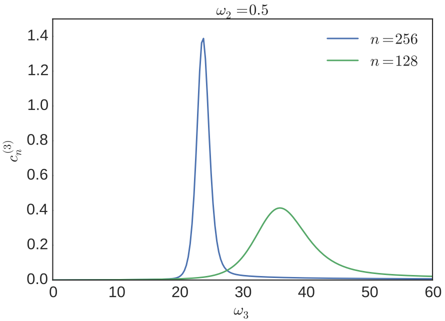
$$Z_n(\omega_2, \omega_3) = \sum_{Walks} \omega_2^{m_2(\varphi_n)} \omega_3^{m_3(\varphi_n)} \ .$$

Fluctuations in our model



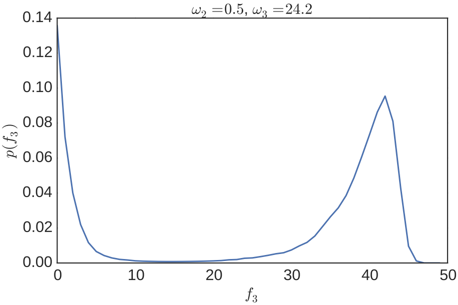
Density plot of the logarithm of the largest eigenvalue of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length 256. Darker shades (colours) represent larger values.

SPECIFIC HEAT FOR $\omega_2 = 0.5$



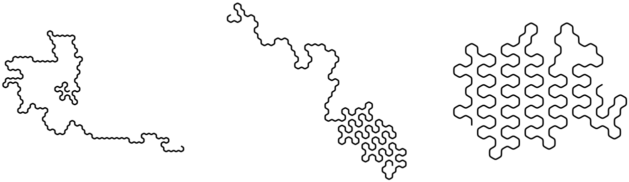
Specific heat peak increases rapidly with length

DISTRIBUTION OF TRIPLY VISITED FACES



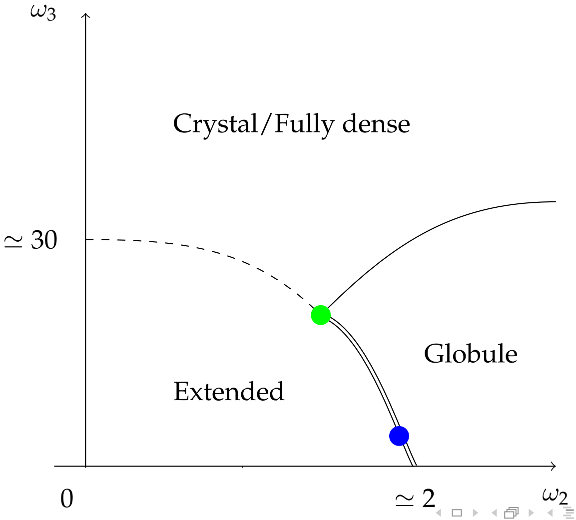
The distribution of the number of *type*-3 faces f_3 is clearly bimodal at the point when ω_2 and ω_3 cross the line of suspected first-order transitions

CONFIGURATIONS



Configurations that illustrate the co-existence of fully dense and swollen parts of the polymer, demonstrating the first-order nature of the transition as ω_3 is increased at fixed $\omega_2 = 0.5$.

CONJECTURED PHASE DIAGRAM FOR GENERALISED DS WALKS



CONCLUSIONS

- Our generalised DS interacting walk model incorporating three-body interactions displays a phase diagram similar to interacting trails and grooves
- No need for stiffness, touching or crossings
- Universality is being restored to this picture
- Beautiful new theory: *Vernier, Jacobsen, Saleur* (2015)
- Outstanding issues of crossings being tackled: *Nahum* et al (2015)

A Bedini, A. Owczarek, T Prellberg. *J. Phys. A: Math. and Theor*, **49**, 214001 (16pp), 2016

Outstanding questions

- Is the dense phase resulting from stiffness the same as that produced from three-body interactions?
- multi-critical points
- dense-globule transition characterisation
- adsorption — *Chris Bradly*
- Three dimensions
- Thanks to collaborators: *Andrea Bedini, Jason Doukas and Jarek Krawczyk*

Research in action

Figure: Research in action