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

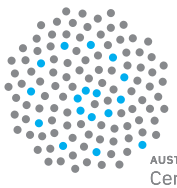
[†] Aleks Owczarek, [†] Andrea Bedini, and [‡] Thomas Prellberg

[†] School of Mathematics and Statistics, The University of Melbourne

[‡] School of Mathematical Sciences, Queen Mary University of London

December, 2015

Guttmann 2015 — 70 and counting

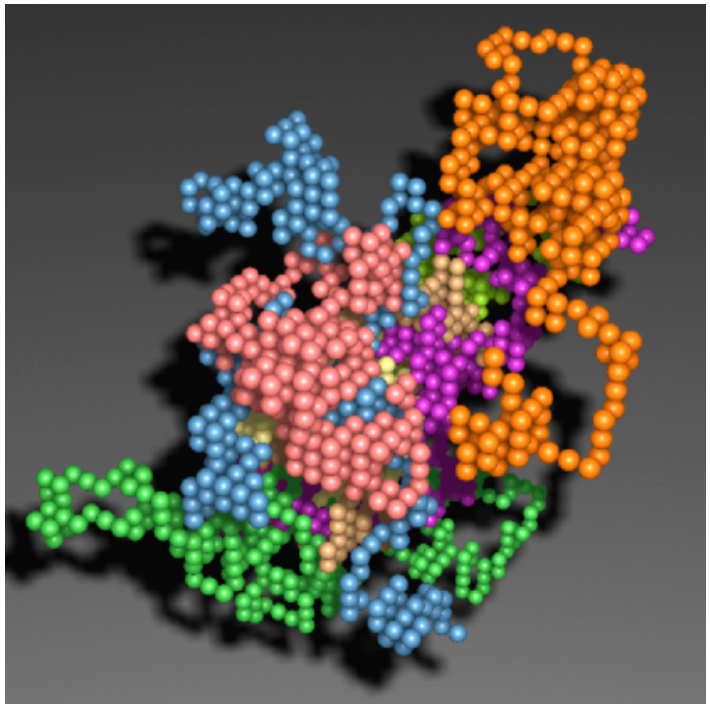


AUSTRALIAN RESEARCH COUNCIL
Centre of Excellence for Mathematics and Statistics of Complex Systems

THE UNIVERSITY OF MELBOURNE

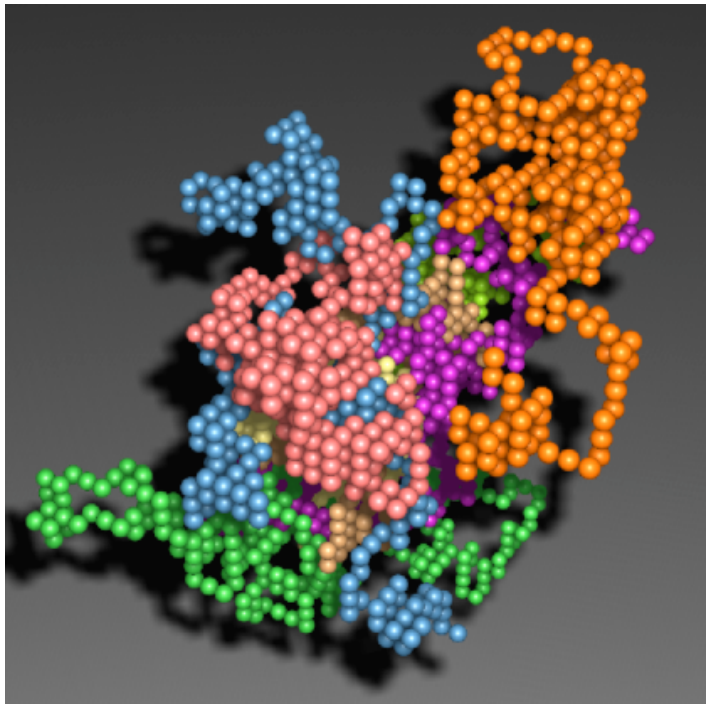
Modelling of Polymers in Solution

- 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



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

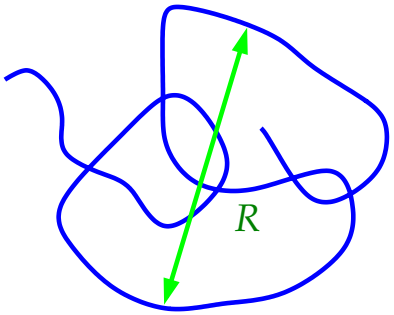


A Model of a Polymer in Solution

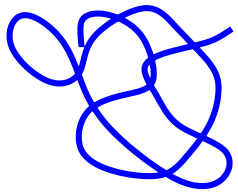
Random Walk + Excluded Volume + Short Range Attraction

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 $\nu = 1/d_{fractal}$.*
- *A "Phase transition" occurs as temperature is changed: Polymer Collapse, aka Coil-Globule Transition, aka Θ-Point*



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

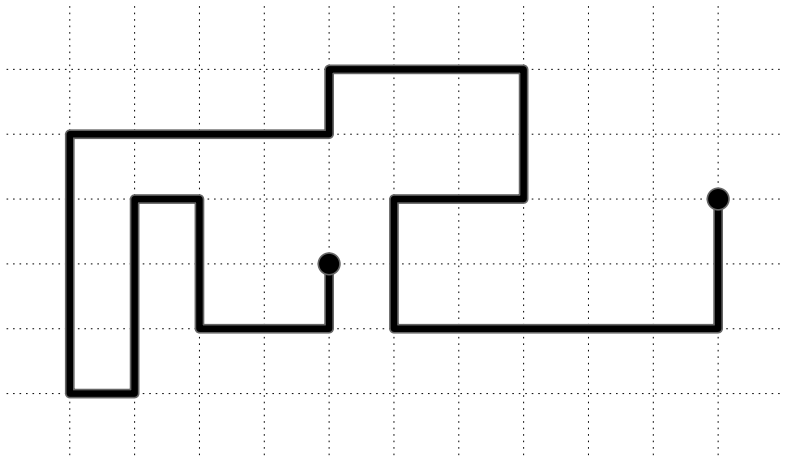


$T = T_c$: Θ-polymer: $d_{fractal} = 7/4$

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

The Canonical Polymer Lattice Model

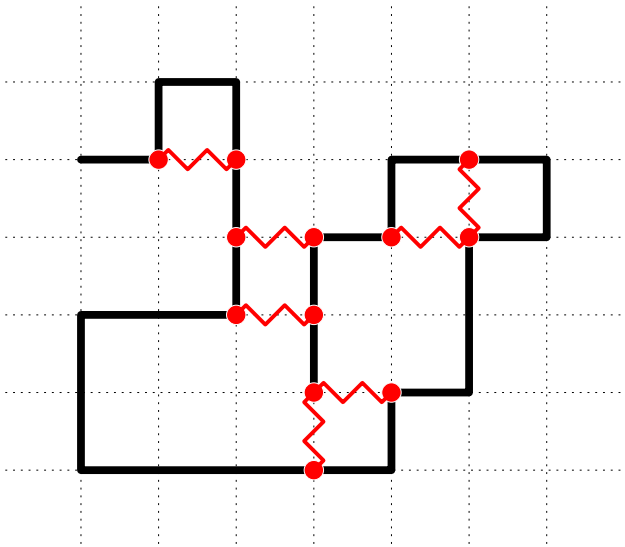
- *Polymer* $\rightarrow$ *self-avoiding random walk (SAW)*
- *Physical space* $\rightarrow$ *regular lattice eg* $\mathbb{Z}^3$ *or* $\mathbb{Z}^2$
- *Sites — beads — monomers — not always valid*



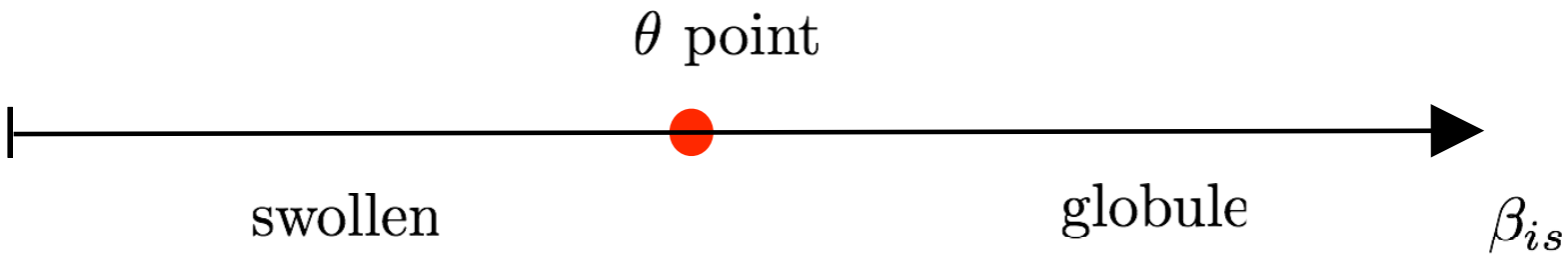
The Canonical Collapsing Polymer Lattice Model

Interacting Self-Avoiding Walk (ISAW)

- *Start with a SAW and add 'interactions'*
- *Quality of solvent* $\rightarrow$ *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

- θ-point collapse transition is a critical phenomenon
- That is, a second order phase transition
- High temperature "swollen or "extended" phase sometimes called "coil"
- Low temperature partially dense globule
- de Gennes' general description (1975) as a "tricritical point"
- Much work since on exponent values, scaling subtleties and various extensions

Scaling around the θ point: Classic crossover scaling

One expects that the singular part of the thermodynamic specific heat behaves as

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

where $\alpha < 1$ for a second-order phase transition. For finite lengths n

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

with $0 < \phi < 1$ if the transition is second-order and

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

if the transition is first-order. The exponents α and ϕ are related via

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

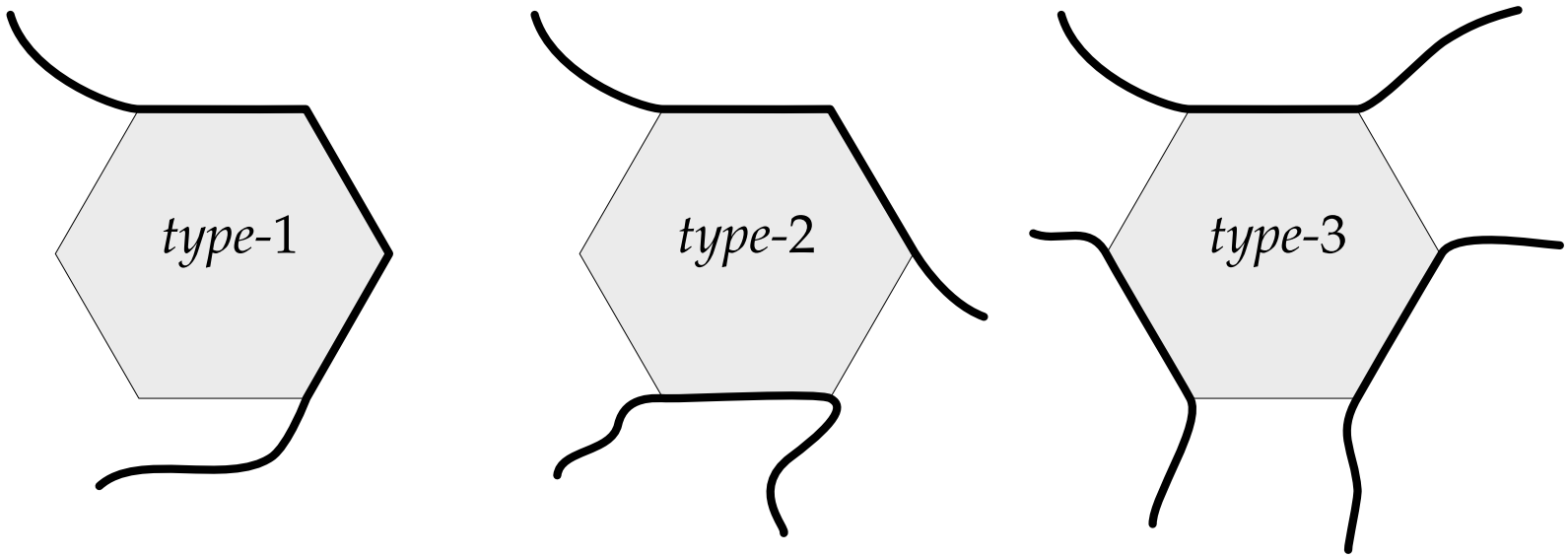
DS MODEL FOR POLYMER COLLAPSE

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

which has been subsequently supported 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, say ω_3, is equal to the square of those listed 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

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

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

- Note that this implies that the specific heat does *not* diverge at the transition (exponent $\alpha\phi = -1/7$). However, the third derivative of the free energy with respect to temperature will diverge with exponent

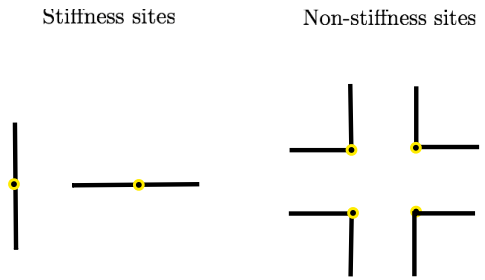
$$(1 + \alpha)\phi = 2/7$$

- It was also predicted the $\nu = 4/7$ at the θ-point.

Adding stiffness to ISAW

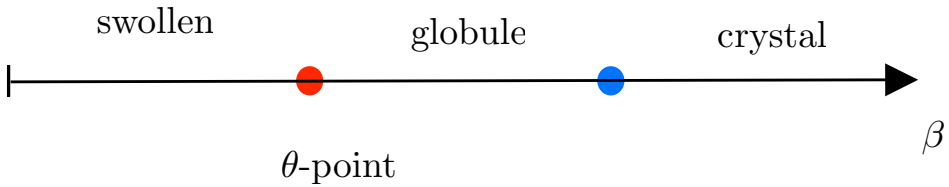
Adding stiffness

- 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
- At low temperatures and sufficient stiffness a polymer crystal can occur

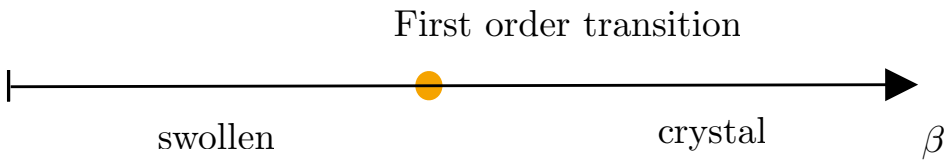


SEMI-FLEXIBLE ISAW

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

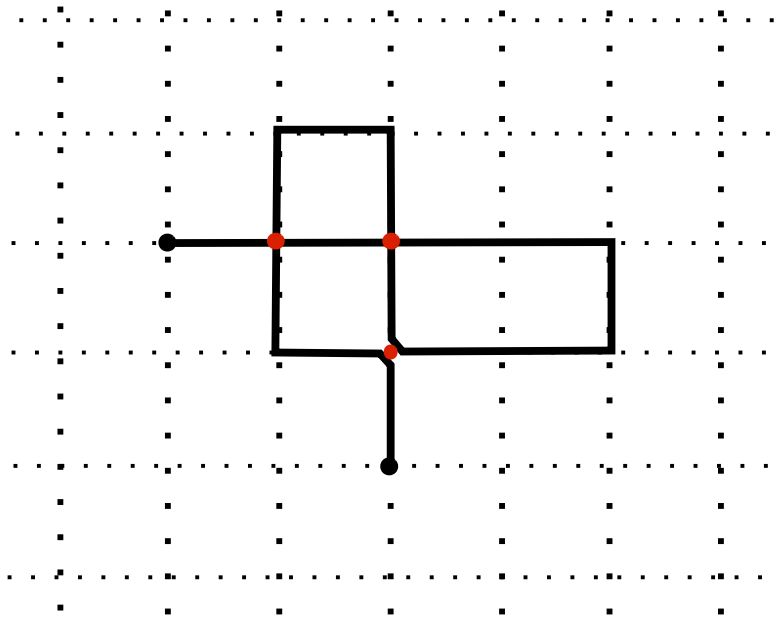


- For large stiffness



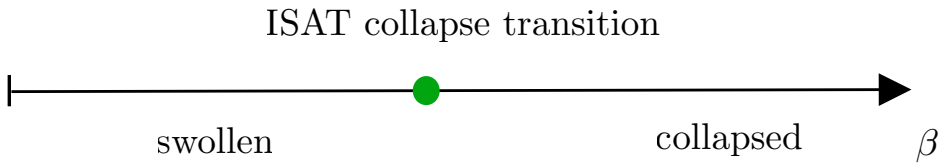
ISAT ON THE SQUARE LATTICE— DIFFERENT MODEL OF POLYMER COLLAPSE

- 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 — DIFFERENT MODEL OF POLYMER COLLAPSE

A single phase transition on varying temperature.



- 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 tranistion

SQUARE LATTICE ISAT SCALING

Owczarek and Prellberg (1995) studied ISAT via Kinetic Growth algorithm. It was estimated

$$\phi = 0.88(7)$$

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

The extended model of self-interacting Trails (eISAT) on the Triangular Lattice

J. Doukas, A. O and T. Prellberg (2010) considered an extended model on the triangular lattice

Differentiate between the number of times the Trail crosses or touches

- *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

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

Phase diagram for extended ISAT model on the triangular lattice

Two low temperature phases, one fully dense

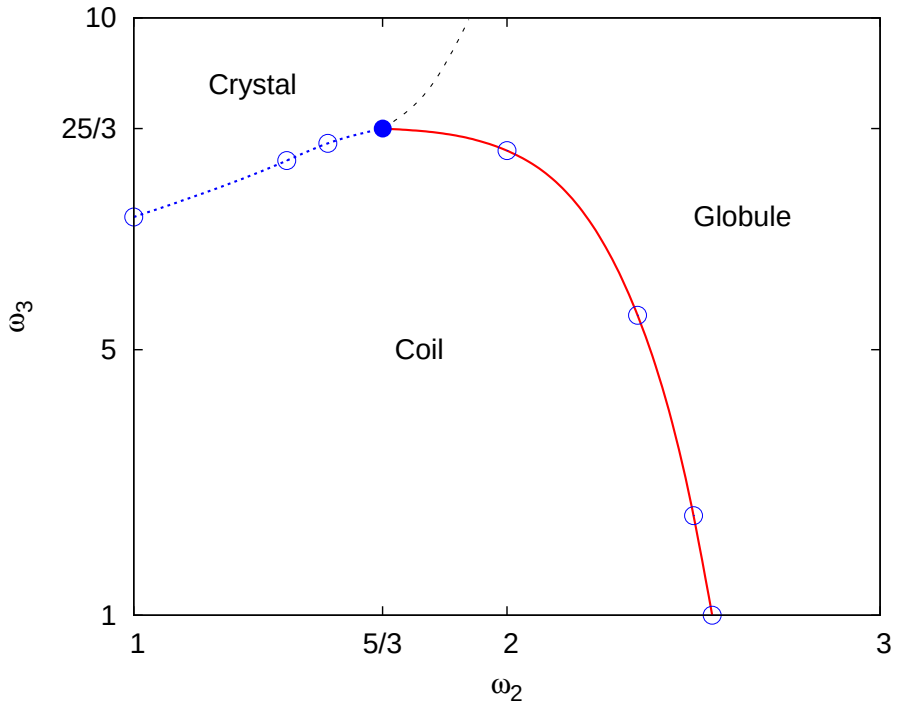


Figure : The Coil-Crystal transition looks first order

COIL-CRYSTAL TRANSITION

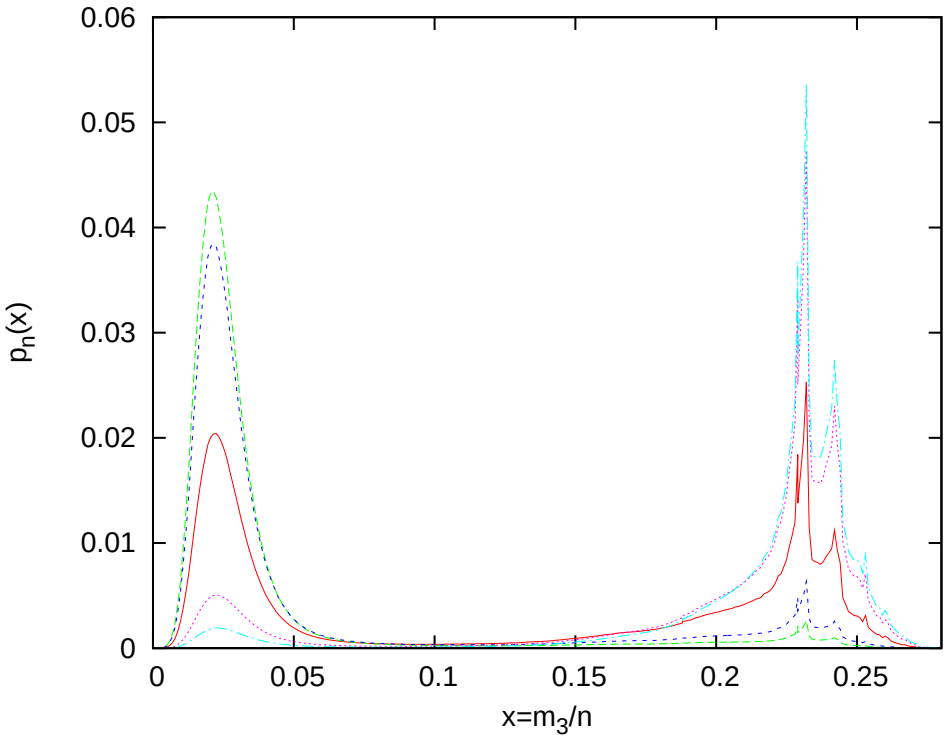


Figure : Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the *Triple* model at temperatures near, and at, the temperature at which the specific heat attains its maximum for length $n = 1024$.

THE DENSE 'CRYSTAL'-LIKE PHASE

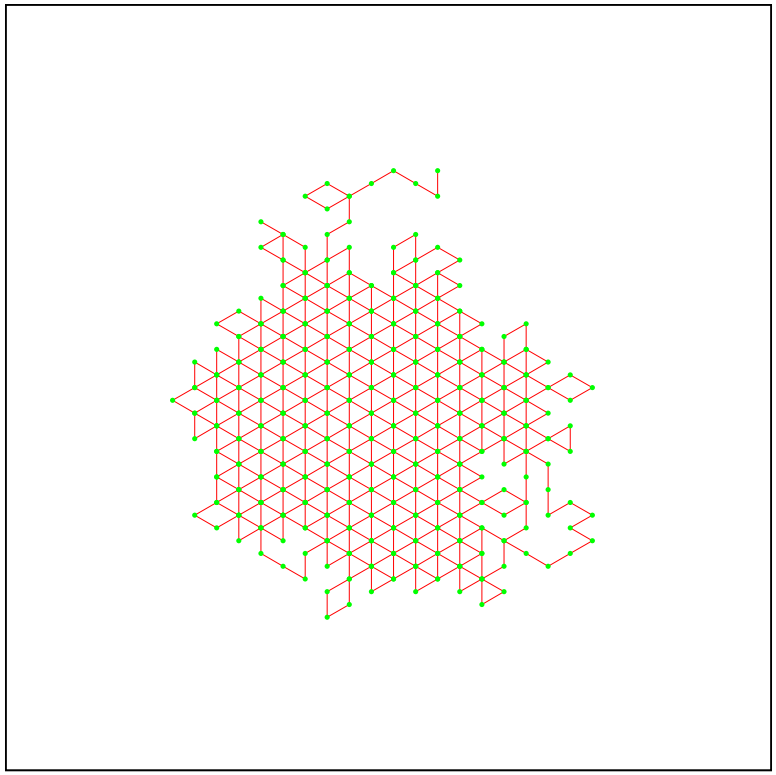
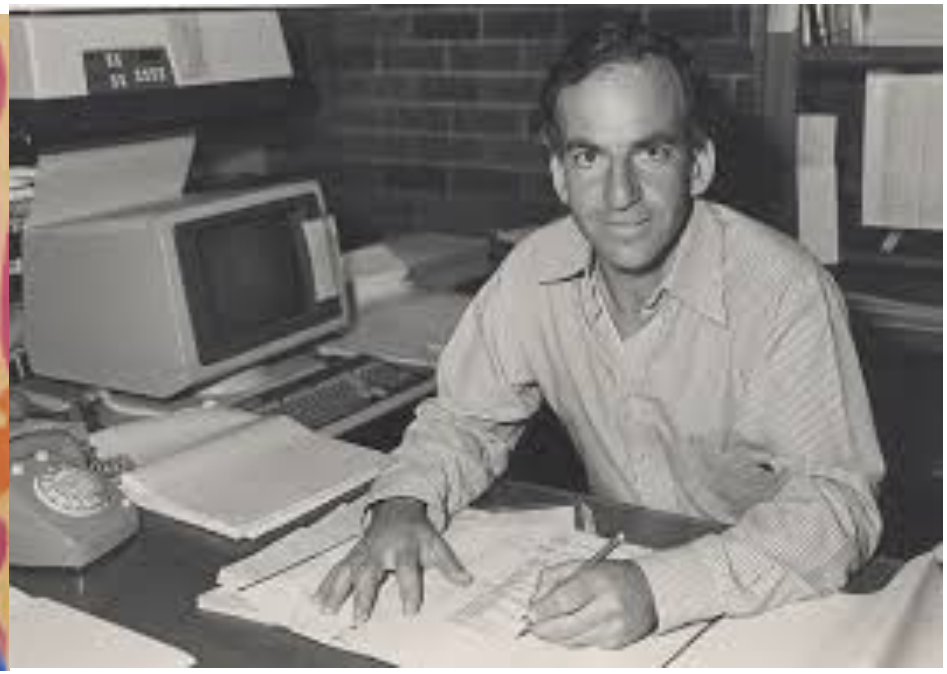


Figure : A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

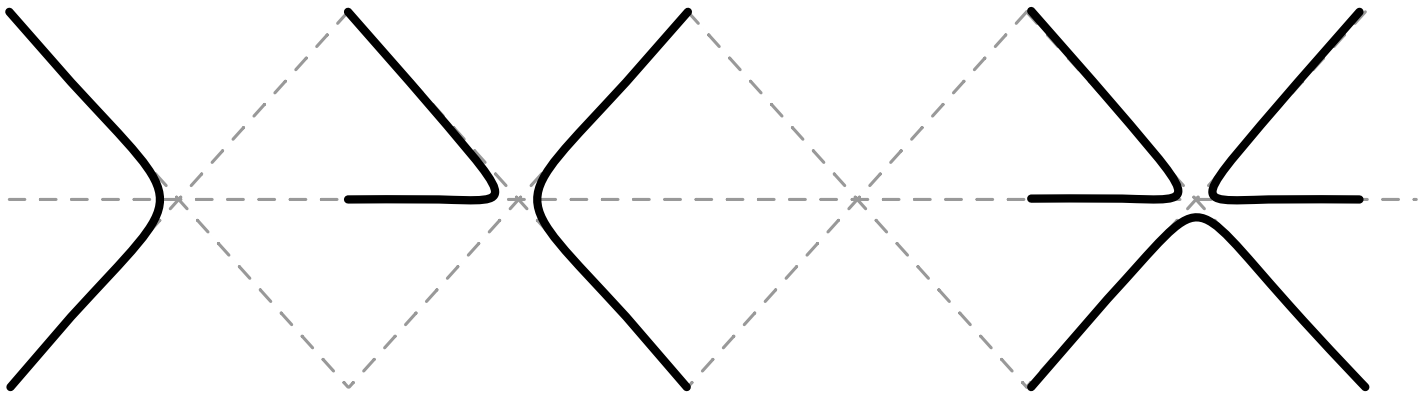
Get groovy: Tony in the swinging '60s (80's)

Get groovy: Tony in the swinging '60s (80's)



Interacting Grooves on the triangular lattice

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

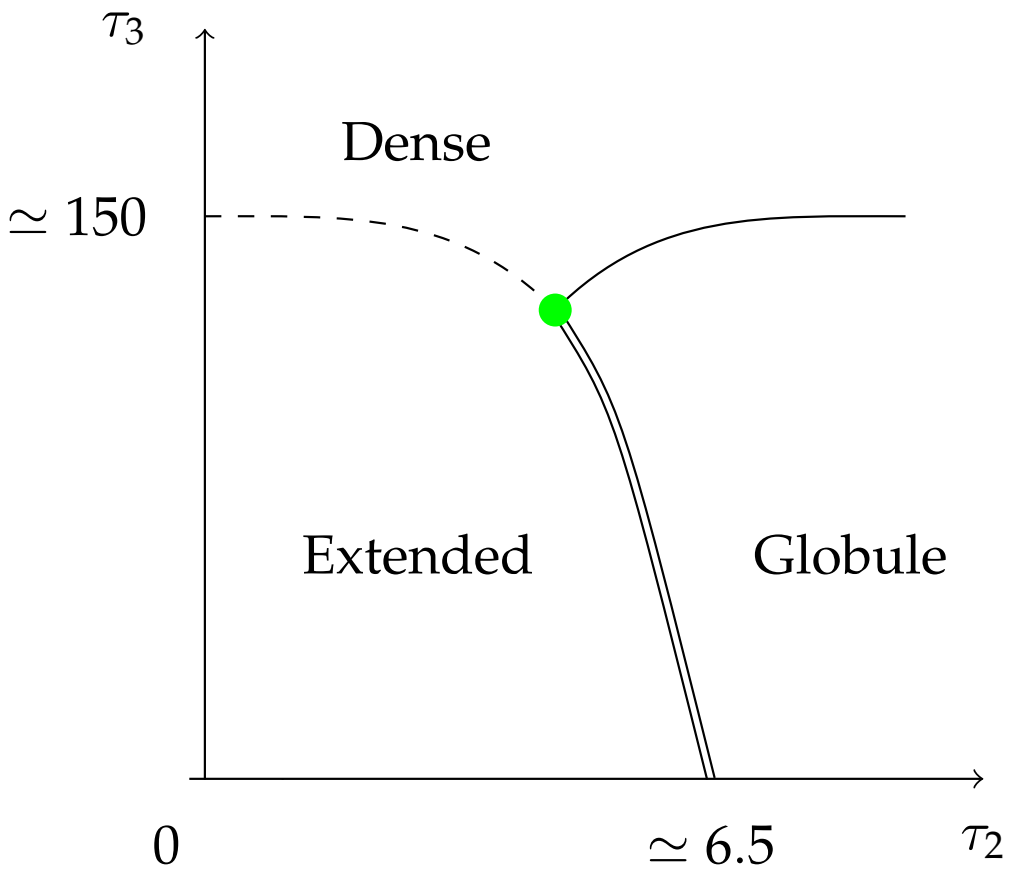


1-*visited* 2-*visited* 3-*visited*

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

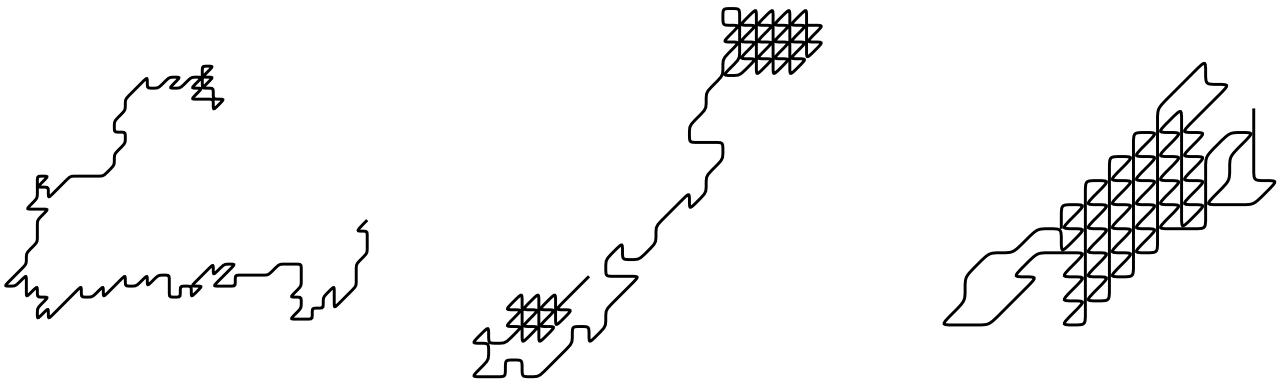
- Related to $O(n)$-model type configurations

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

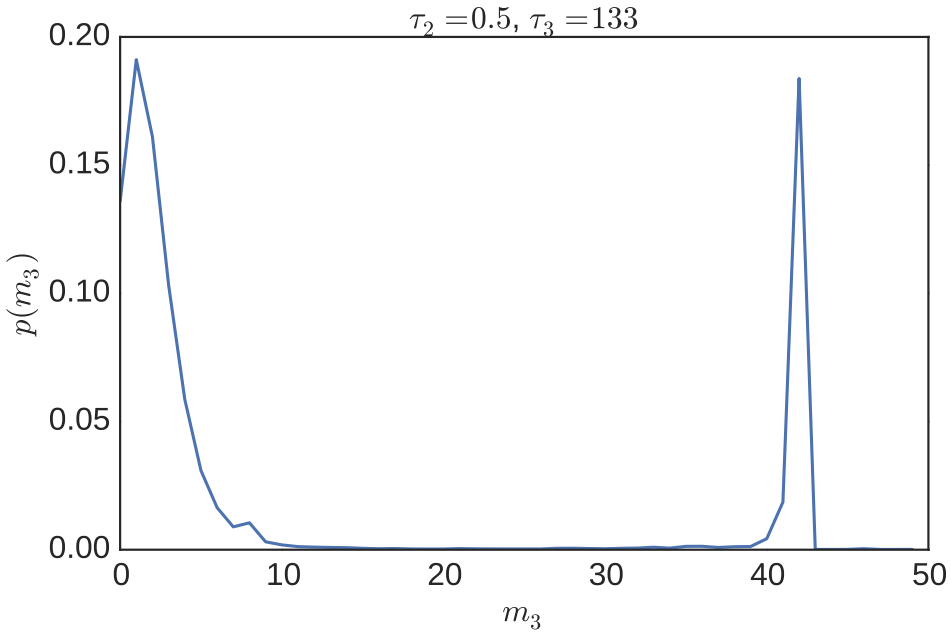


Figure : The distribution of the number of triply visited sites m_3 is clearly bimodal at the point when τ_2 and τ_3 cross the line of suspected first-order transitions.

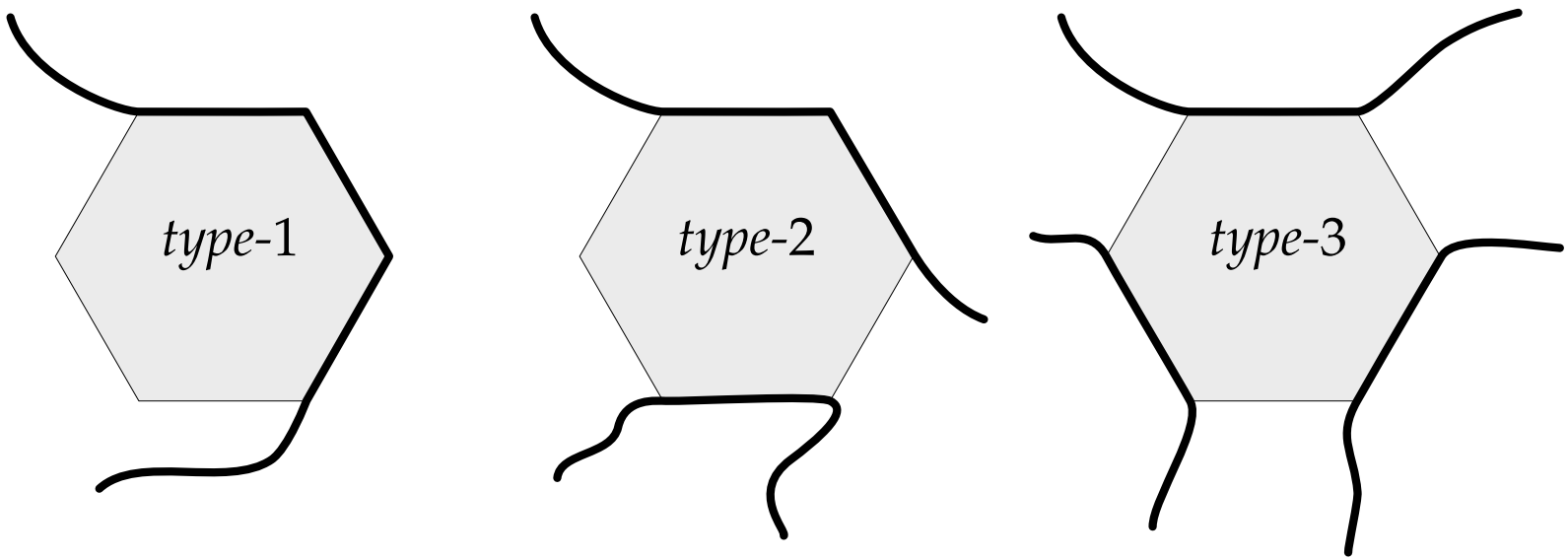
BACK TO THE FUTURE: WALKS AGAIN

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

Generalised DS model

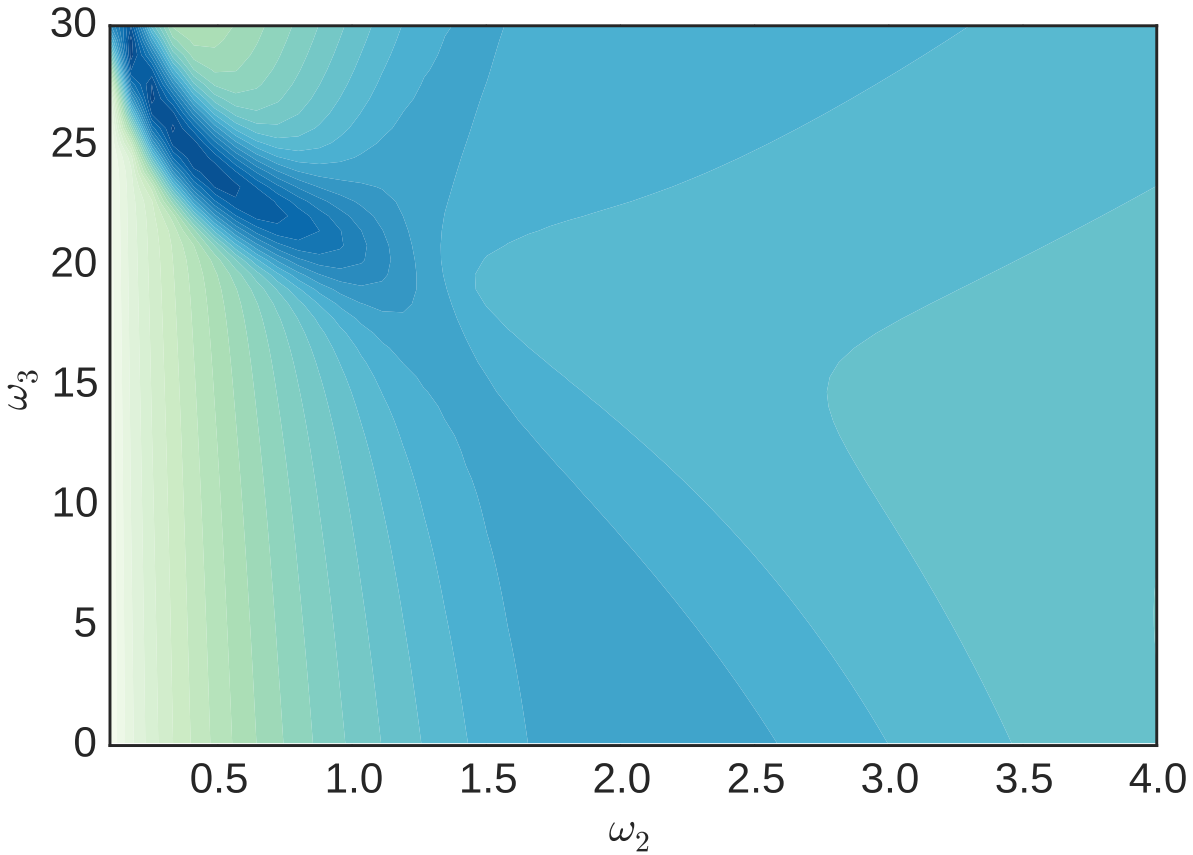
Consider model of Duplantier and Saleur on the Honeycomb lattice again

- Just generalise to arbitrary ω_3 and ω_2



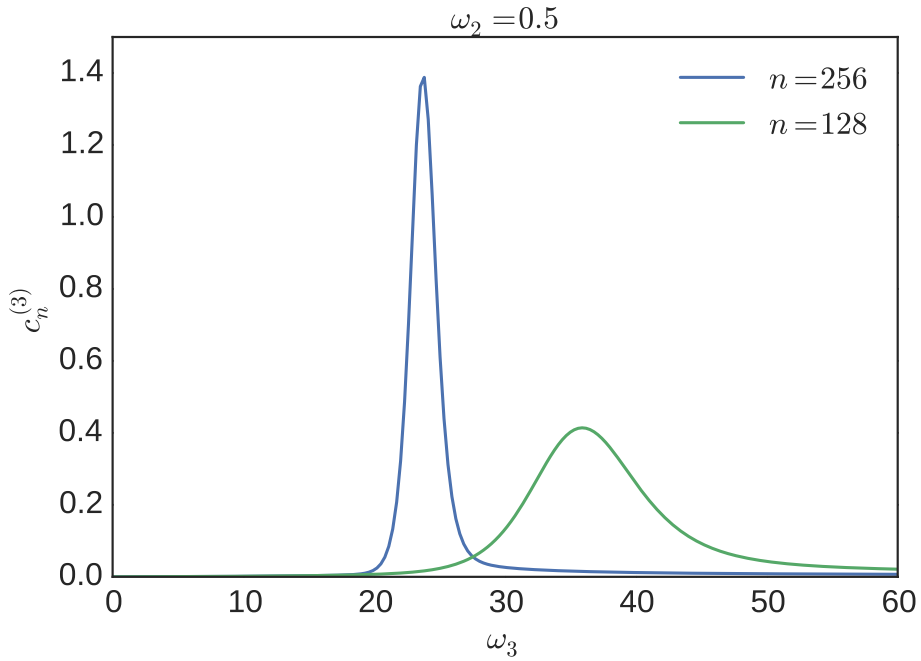
$$Z_n(\omega_2, \omega_3) = \sum_{Walks} \omega_2^{m_2(\varphi_n)} \omega_3^{m_3(\varphi_n)} \ .$$

FLUCTUATIONS IN OUR MODEL



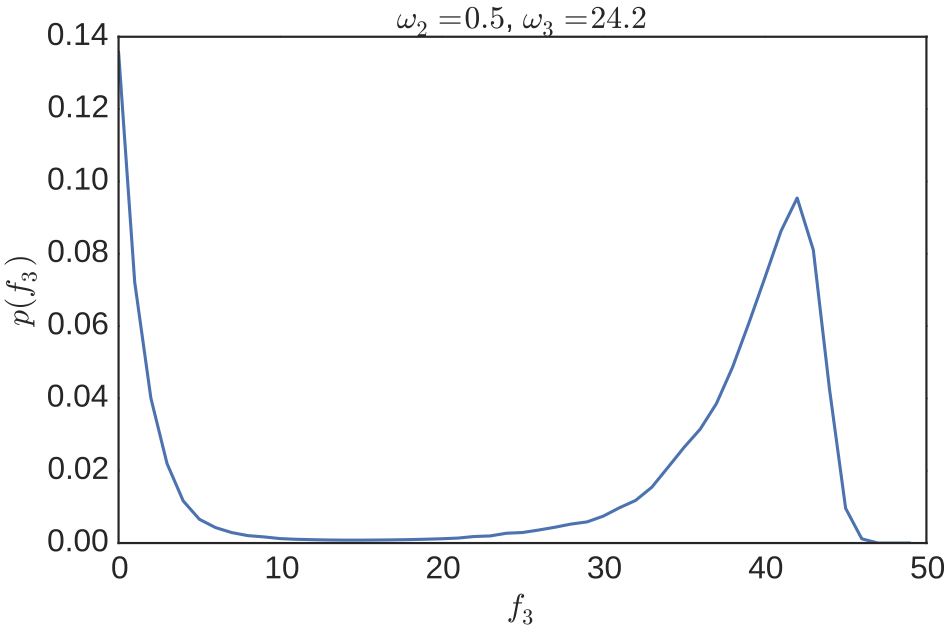
Density plot of the logarithm of the largest eigenvalue of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length 256. Darker shades (colours) represent larger values.

SPECIFIC HEAT FOR $\omega_2 = 0.5$



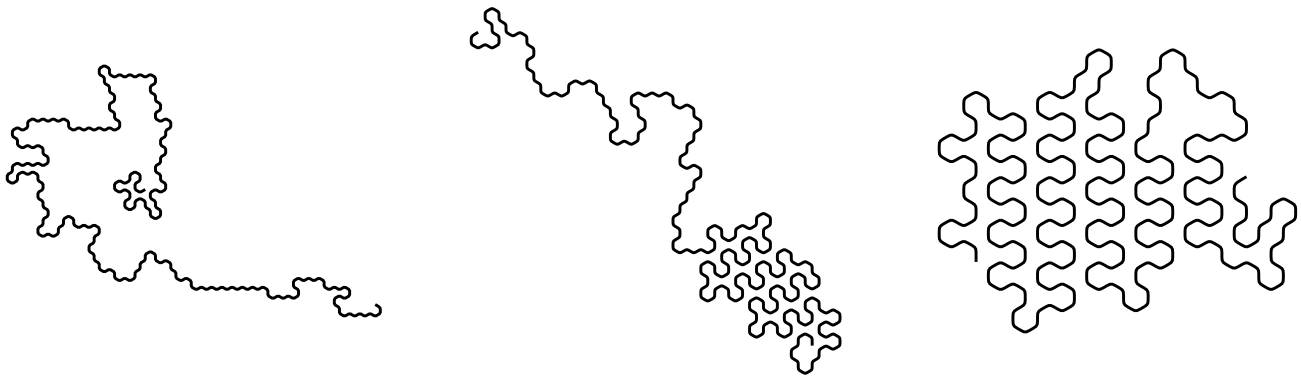
Specific heat peak increases rapidly with length

DISTRIBUTION OF TRIPLY VISITED FACES



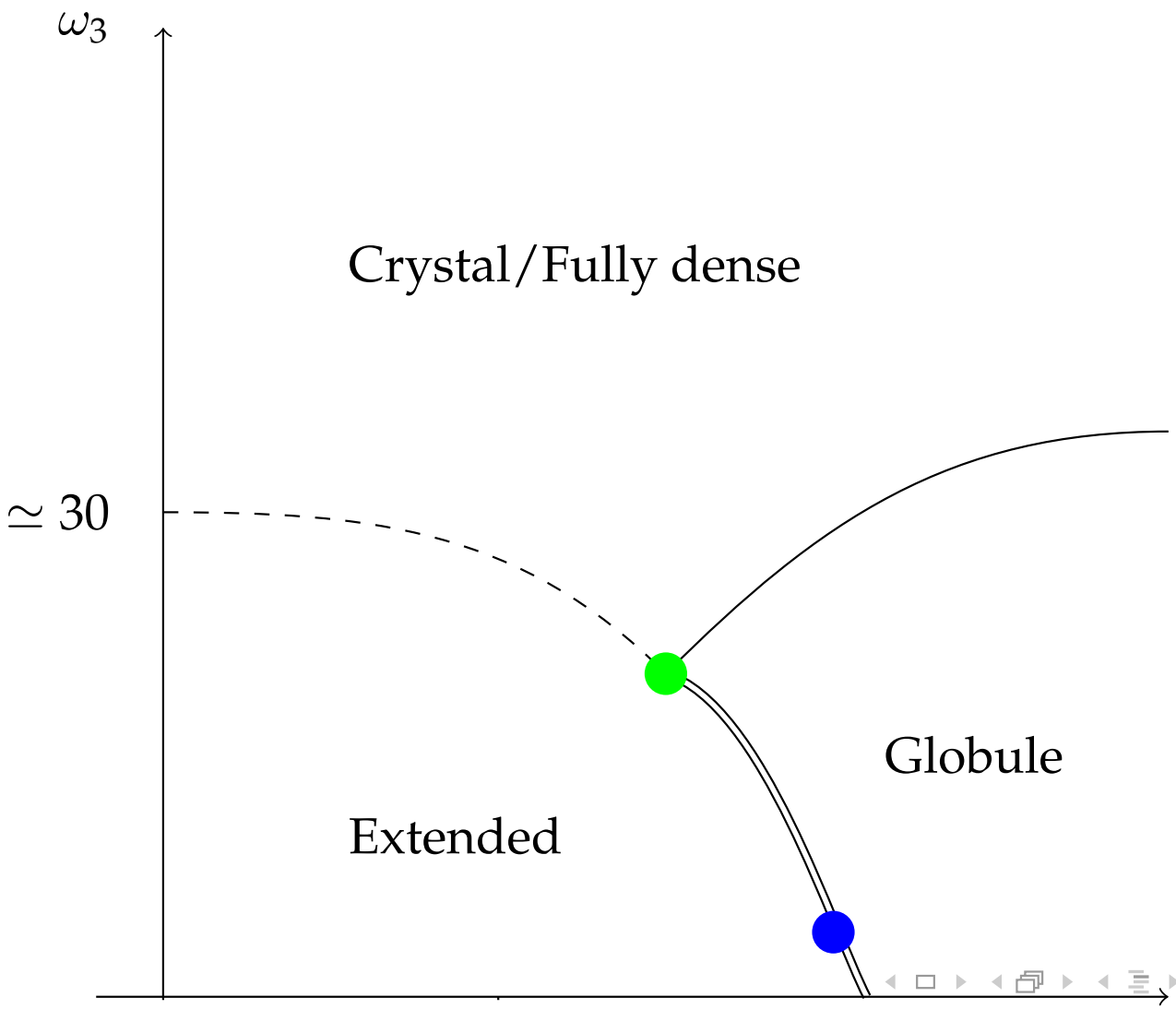
The distribution of the number of *type*-3 faces f_3 is clearly bimodal at the point when ω_2 and ω_3 cross the line of suspected first-order transitions

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)
- Interplay of theory and numerical work — à la Tony

Thanks Tony !