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

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Means, Methods and Results in the Statistical Mechanics of Polymeric Systems II

Stop the difference: 2007 and 2017

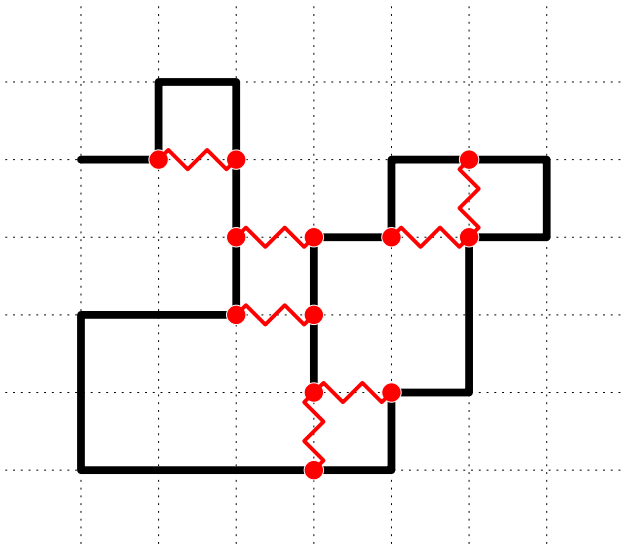
STU'S INSPIRATION: SOME OF HIS PAPERS ABOUT POLYMER COLLAPSE

- Madras, N., et al. "The free energy of a collapsing branched polymer." Journal of Physics A: Mathematical and General 23.22 (1990): 5327.
- Brak, R., A. J. Guttmann, and S. G. Whittington. "On the behaviour of collapsing linear and branched polymers." J. Math. Chem. 8 (1991): 255-267.
- Brak, Richard, Anthony J. Guttmann, and Stuart G. Whittington. "A collapse transition in a directed walk model." J. Phys. A 25.9 (1992): 2437.
- Flesia, S., Gaunt, D. S., Soteros, C. E., and Whittington, S. G. (1994). Statistics of collapsing lattice animals. Journal of Physics A: Mathematical and General, 27(17), 5831.
- Tesi, M. C., Janse van Rensburg, E. J., Orlandini, E., and Whittington, S. G. (1996). Monte Carlo study of the interacting self-avoiding walk model in three dimensions. J. Stat. Phys., 82(1), 155-181.
- Vrbov, Tereza, and Stuart G. Whittington. "Adsorption and collapse of self-avoiding walks in three dimensions: A Monte Carlo study." J. Phys. A 31.17 (1998): 3989.

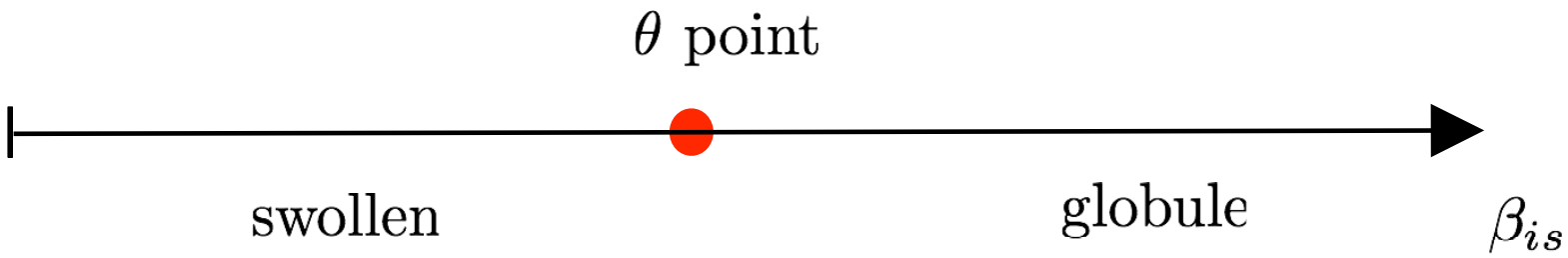
The Canonical Collapsing Polymer Lattice Model

Interacting Self-Avoiding Walk (ISAW)

- *Start with a self-avoiding walk (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

- High temperature "swollen or "extended" phase $d_f > d = 2$
- θ-point collapse transition is a second order phase transition
- Low temperature partially dense globule $d_f = d$
- de Gennes' general description (1975) as a "tricritical point"

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

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

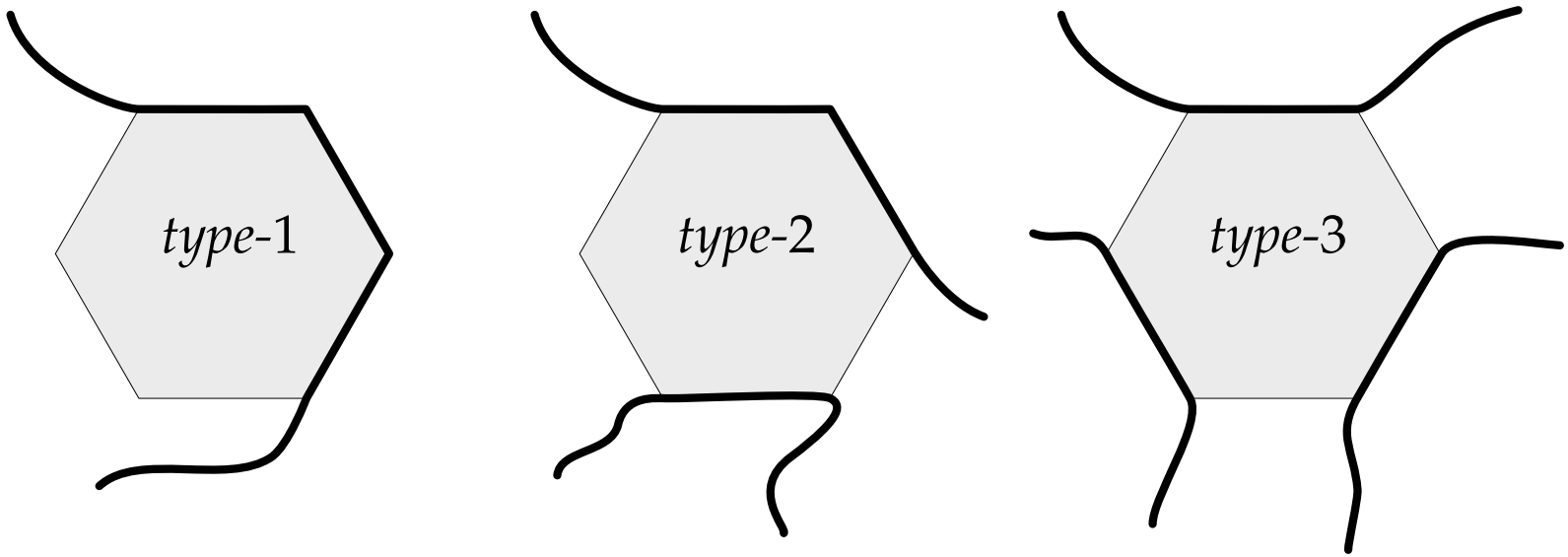
Duplantier-Saleur (DS) model

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

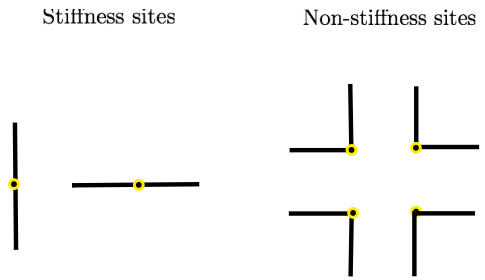
$$\phi = 3/7 \approx 0.43 \quad \text{and} \quad \alpha = -1/3 \, .$$

- 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

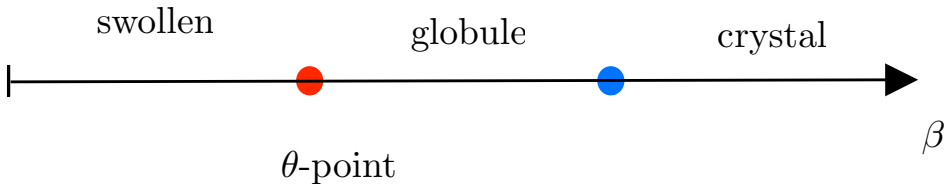
Adding stiffness

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

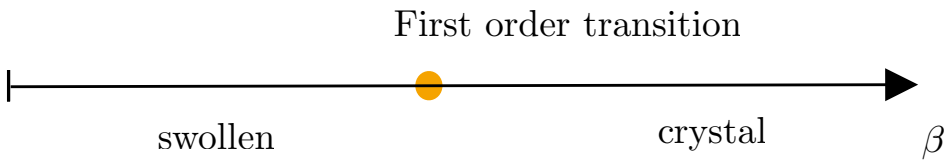


SEMI-FLEXIBLE ISAW

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



- For large stiffness



Phase transition for semi-flexible polymers

Swollen – Globule

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

Swollen – Crystal

First order in both two and three dimensions

Globule – Crystal

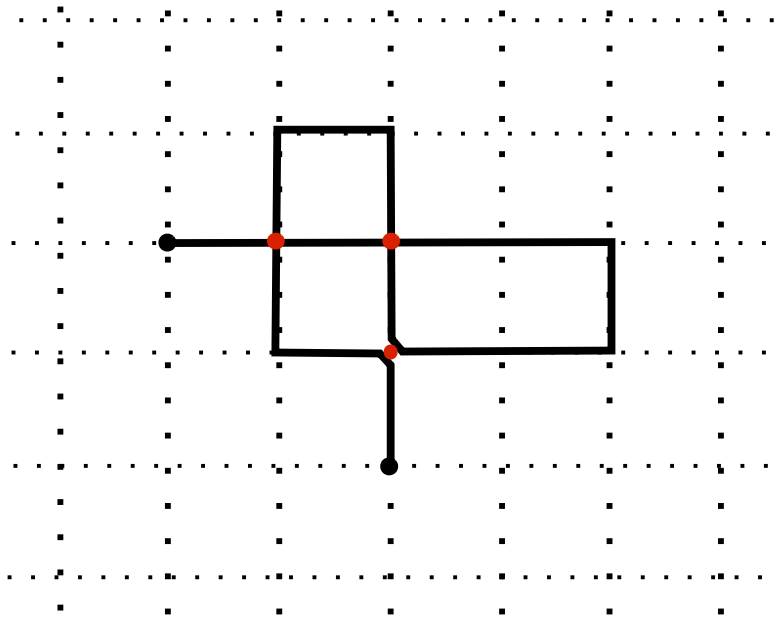
Second order in two dimensions with estimated $\alpha \approx 0.6(2)$

Meeting point

Unknown

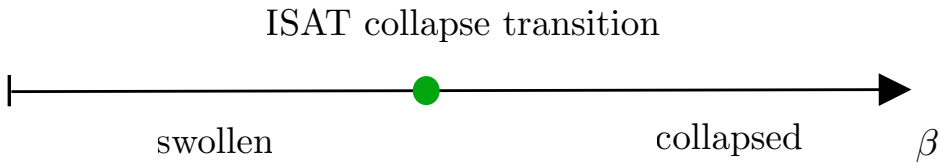
ISAT ON THE SQUARE LATTICE— DIFFERENT MODEL OF POLYMER COLLAPSE

- 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 transition

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.

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....

Means, Methods and Results in the Statistical Mechanics of Polymeric Systems I

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

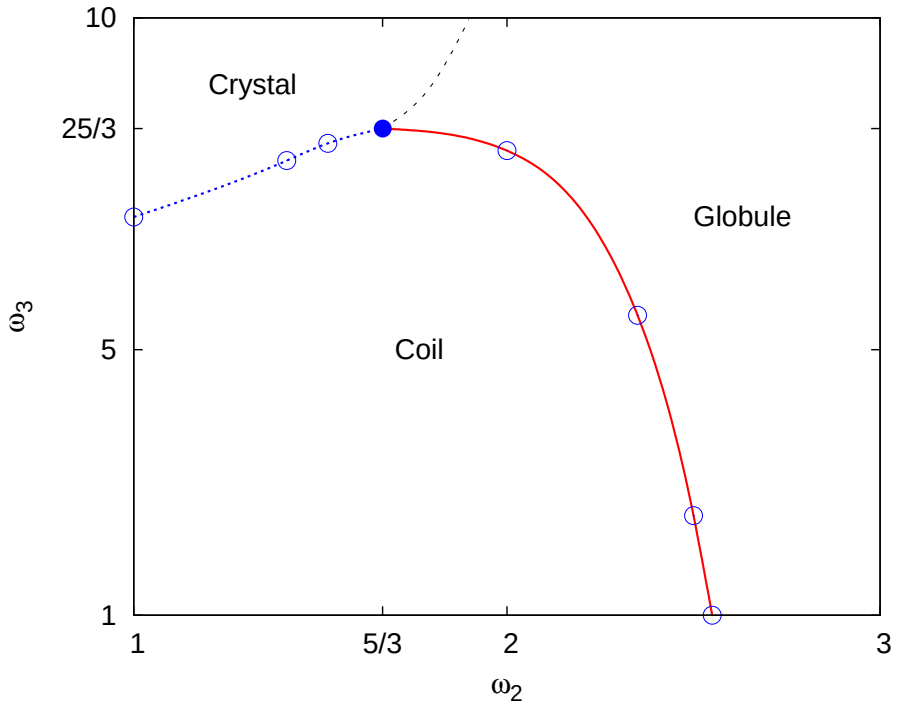


Figure: The Coil-Crystal transition looks first order

Coil-Crystal transition

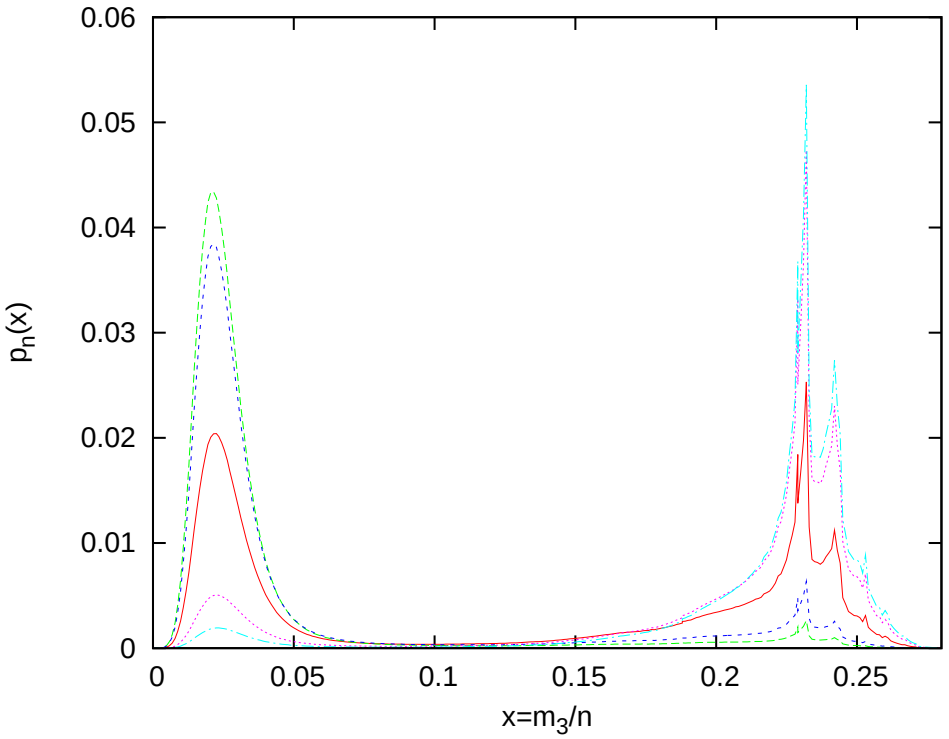


Figure: Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the *Triple* model at temperatures near, and at, the temperature at which the specific heat attains its maximum for length $n = 1024$.

THE DENSE 'CRYSTAL'-LIKE PHASE

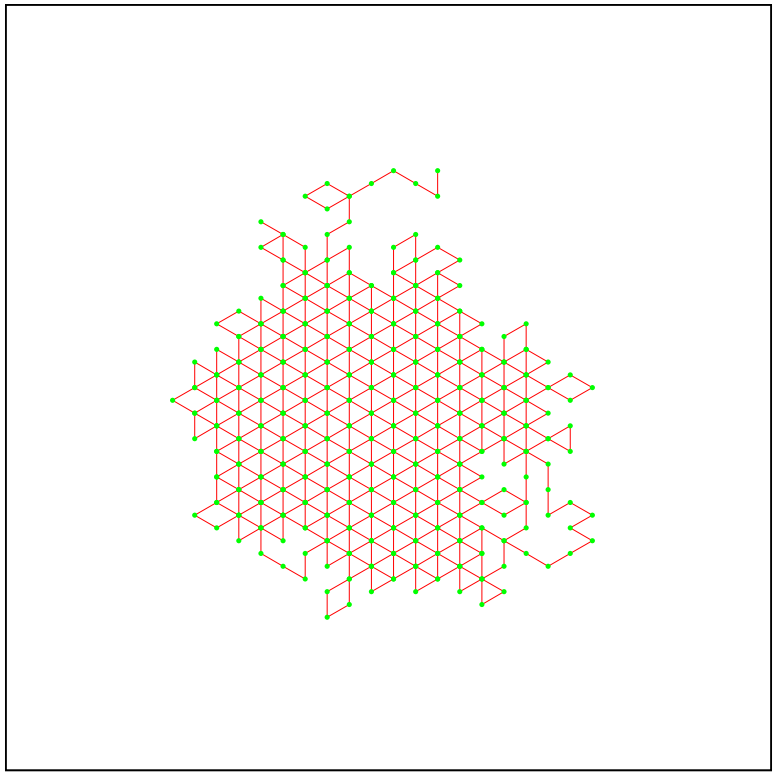


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

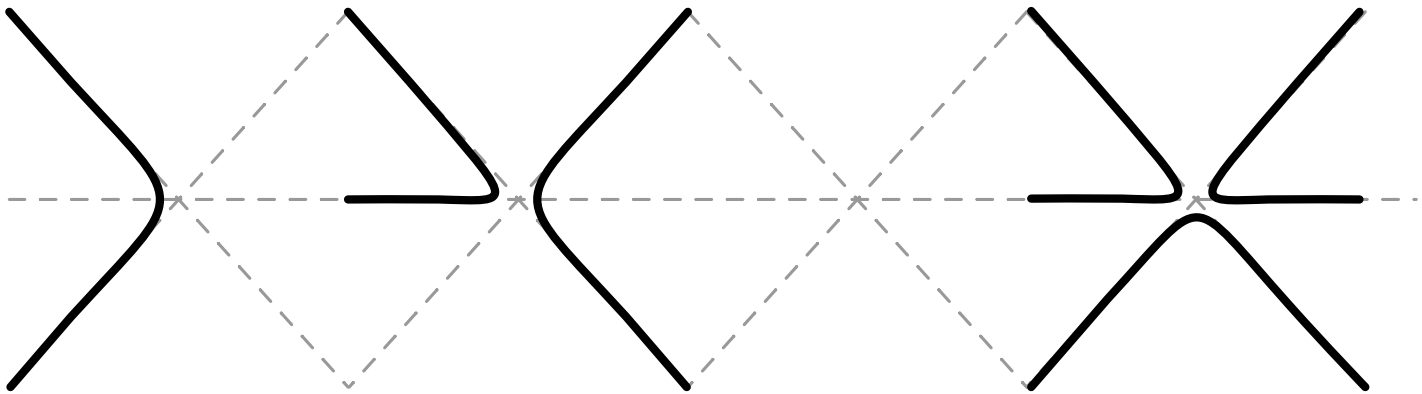
Loop models

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!

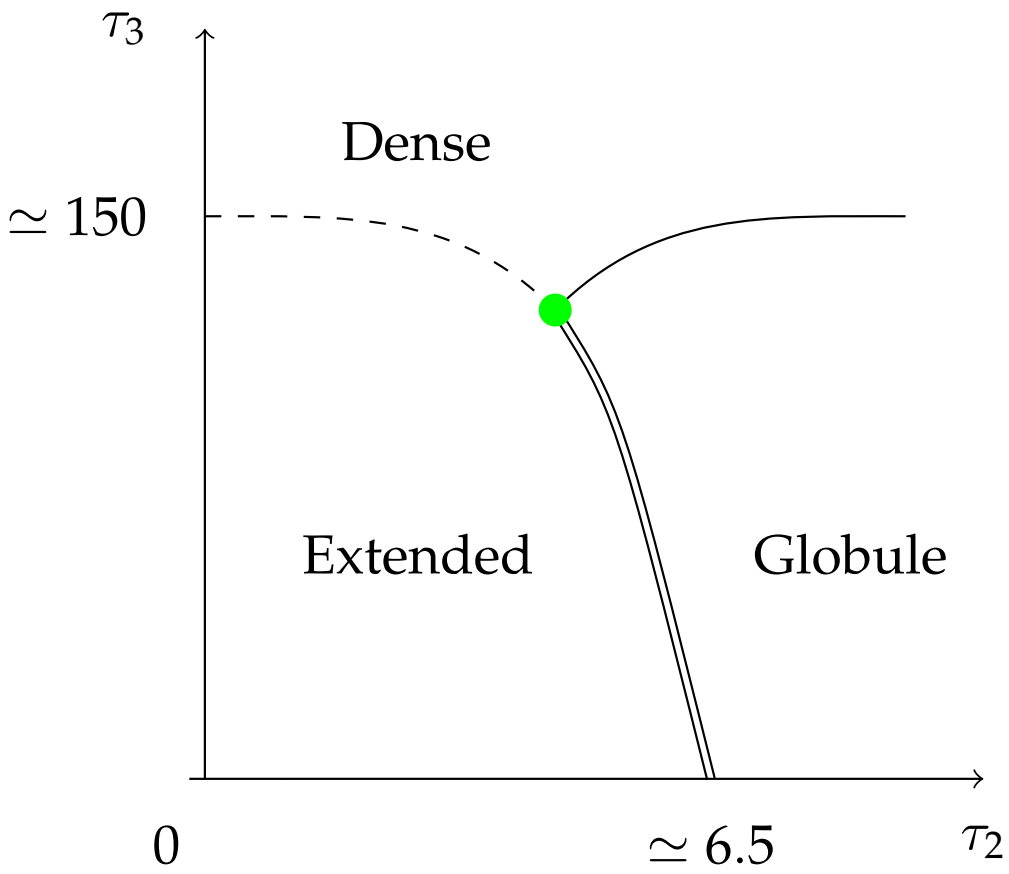


1-*visited* 2-*visited* 3-*visited*

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

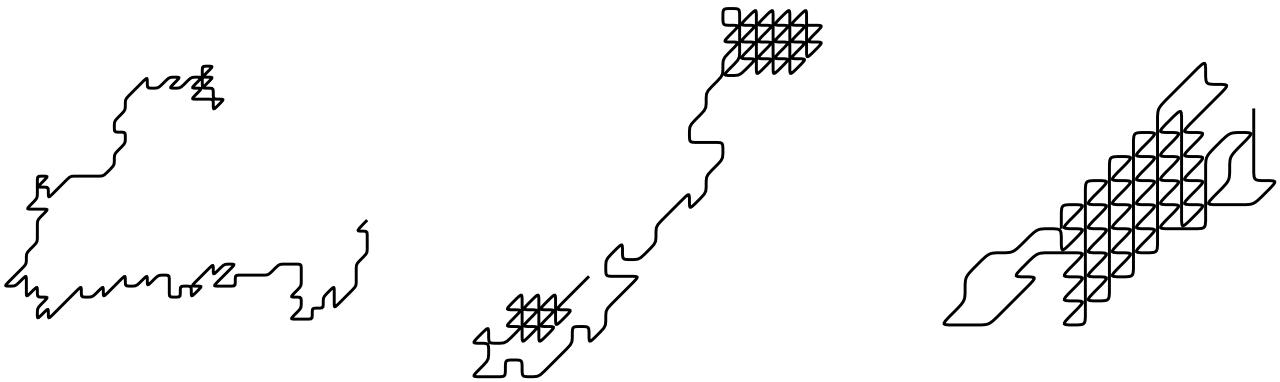
- Related to $O(n)$-model type configurations

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

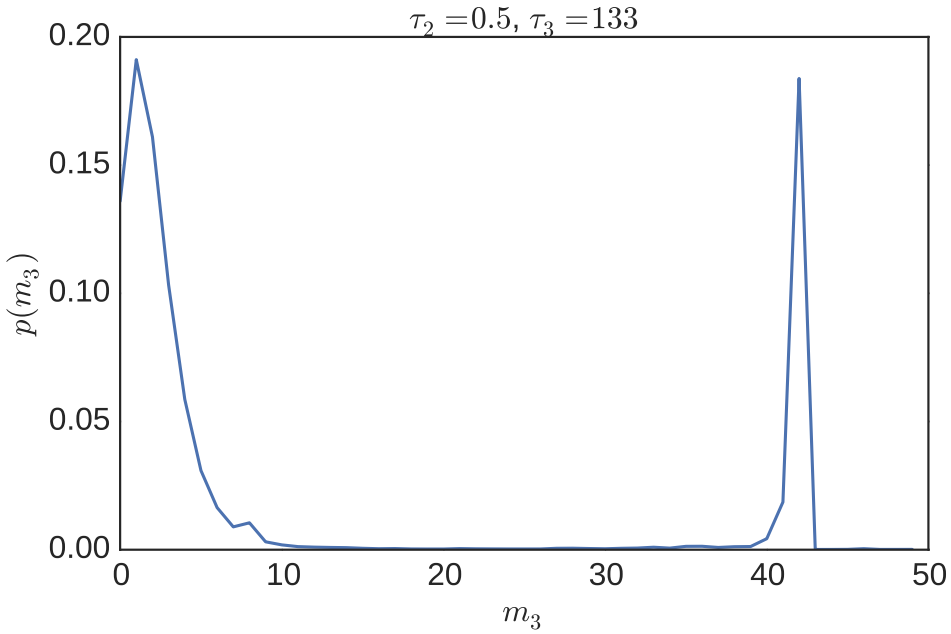


Figure: The distribution of the number of triply visited sites m_3 is clearly bimodal at the point when τ_2 and τ_3 cross the line of suspected first-order transitions.

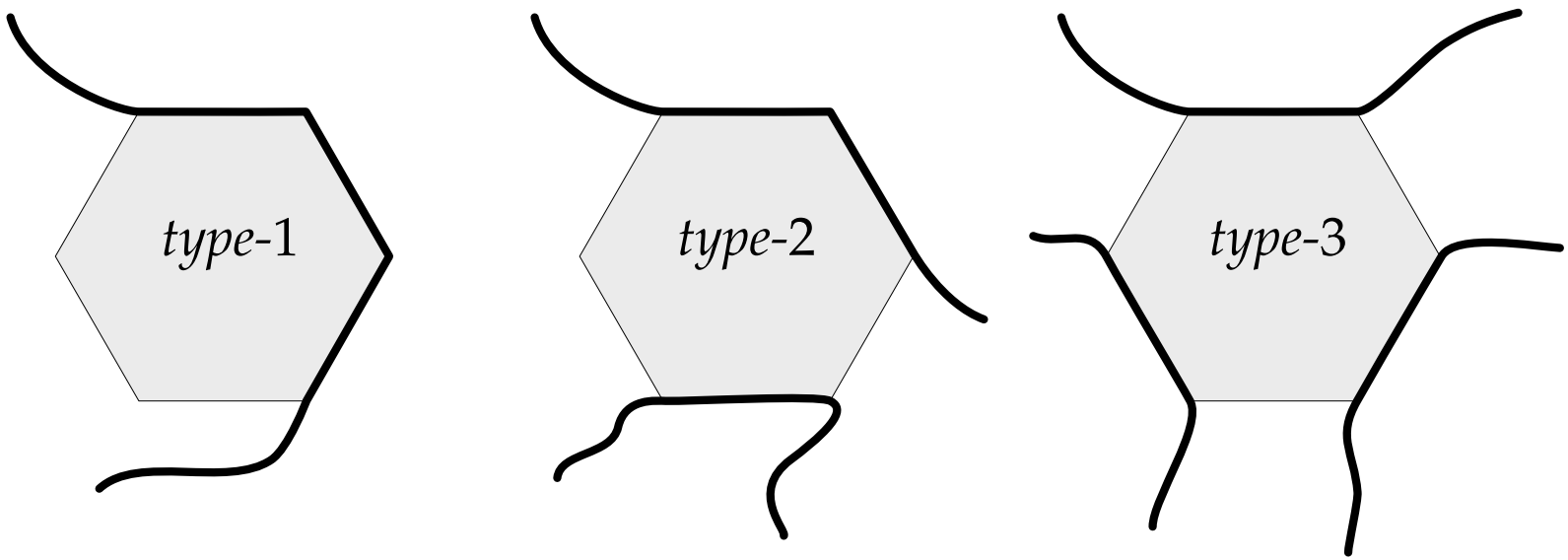
BACK TO THE FUTURE: WALKS AGAIN

- 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

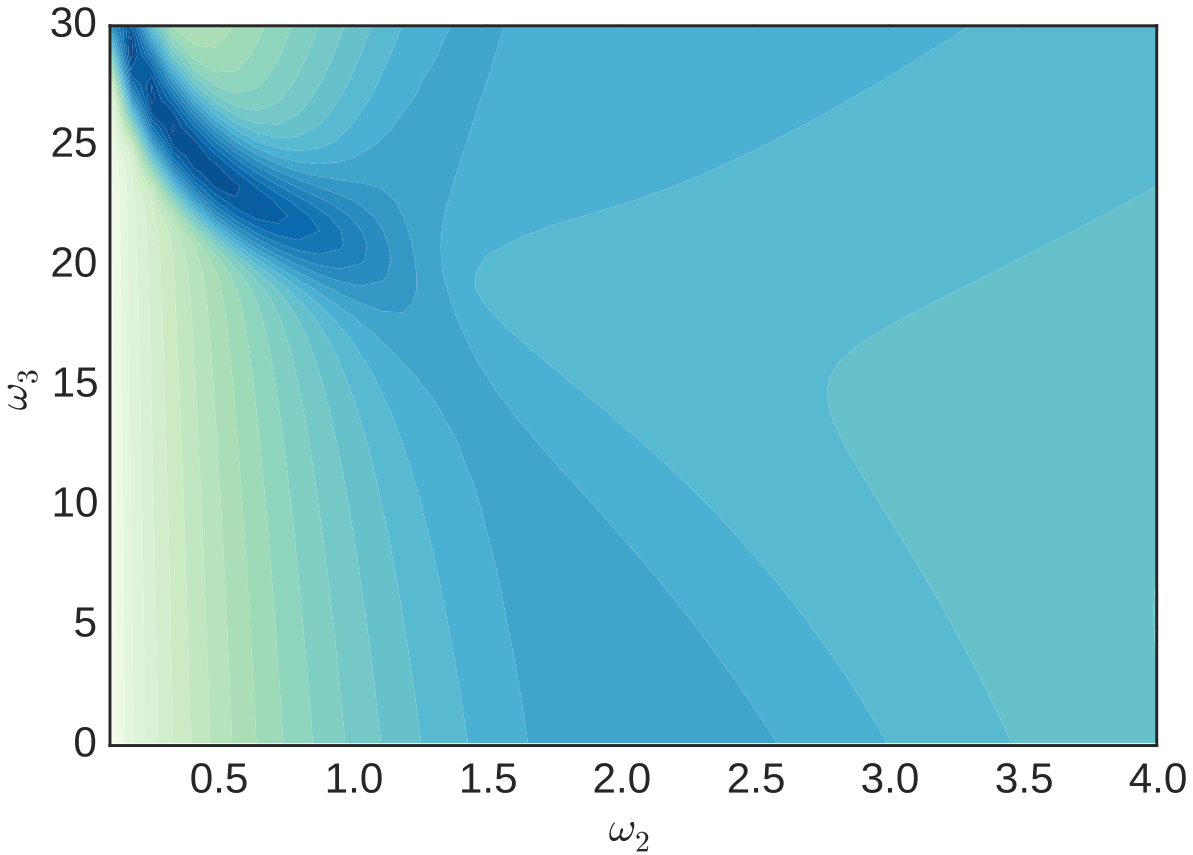
Consider model of Duplantier and Saleur on the Honeycomb lattice again

- Just generalise to arbitrary ω_3 and ω_2



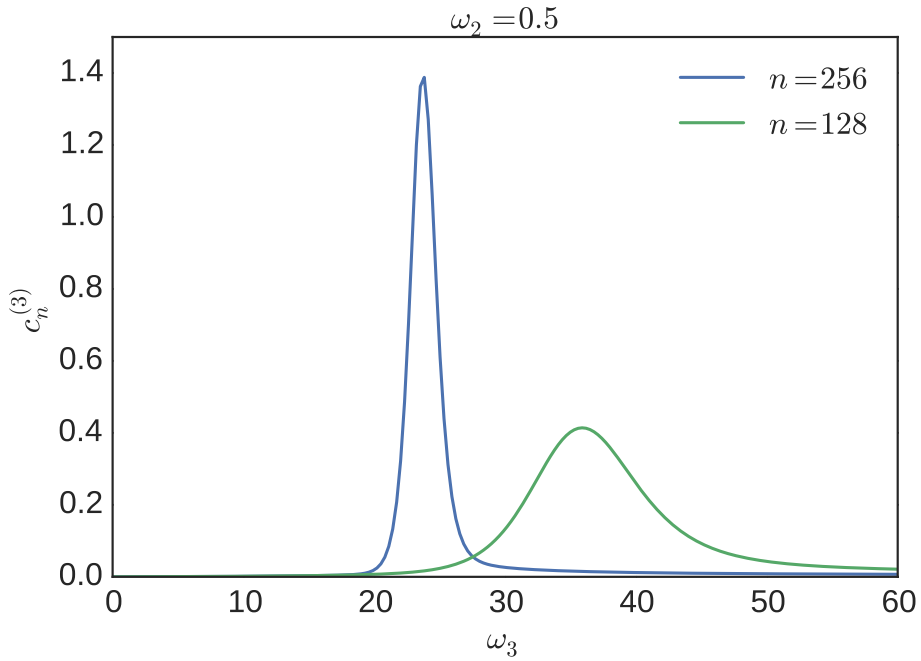
$$Z_n(\omega_2, \omega_3) = \sum_{Walks} \omega_2^{m_2(\varphi_n)} \omega_3^{m_3(\varphi_n)} \ .$$

FLUCTUATIONS IN OUR MODEL



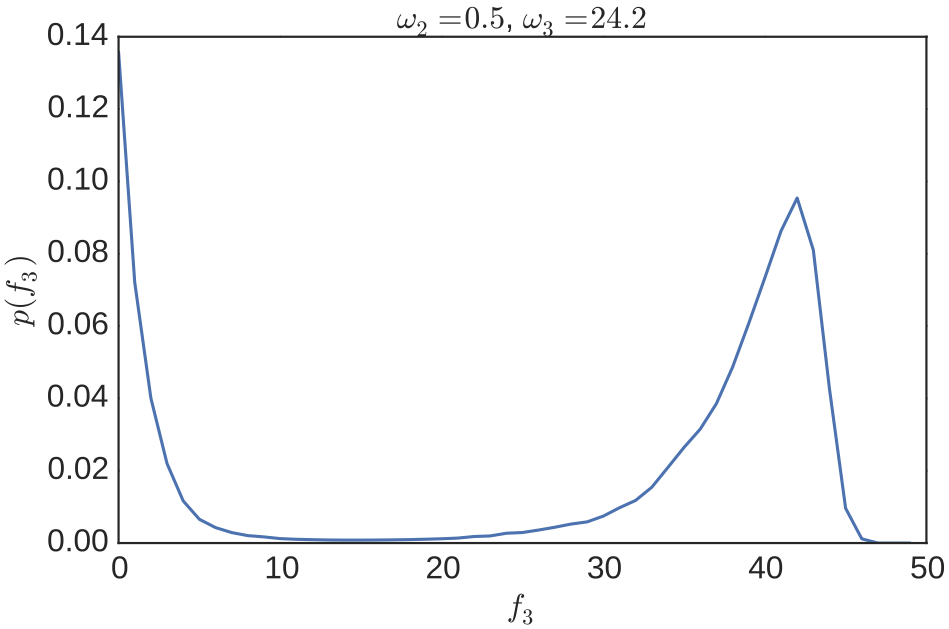
Density plot of the logarithm of the largest eigenvalue of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length 256. Darker shades (colours) represent larger values.

SPECIFIC HEAT FOR $\omega_2 = 0.5$



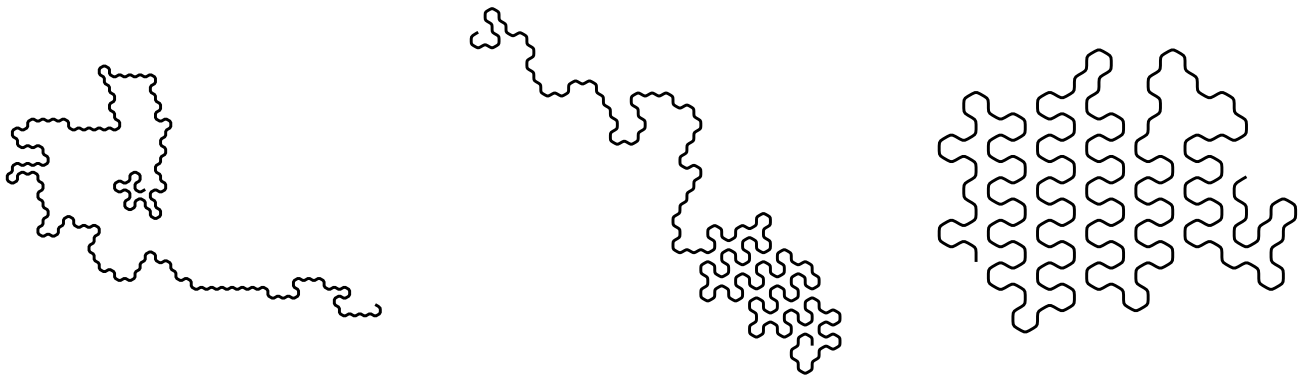
Specific heat peak increases rapidly with length

DISTRIBUTION OF TRIPLY VISITED FACES



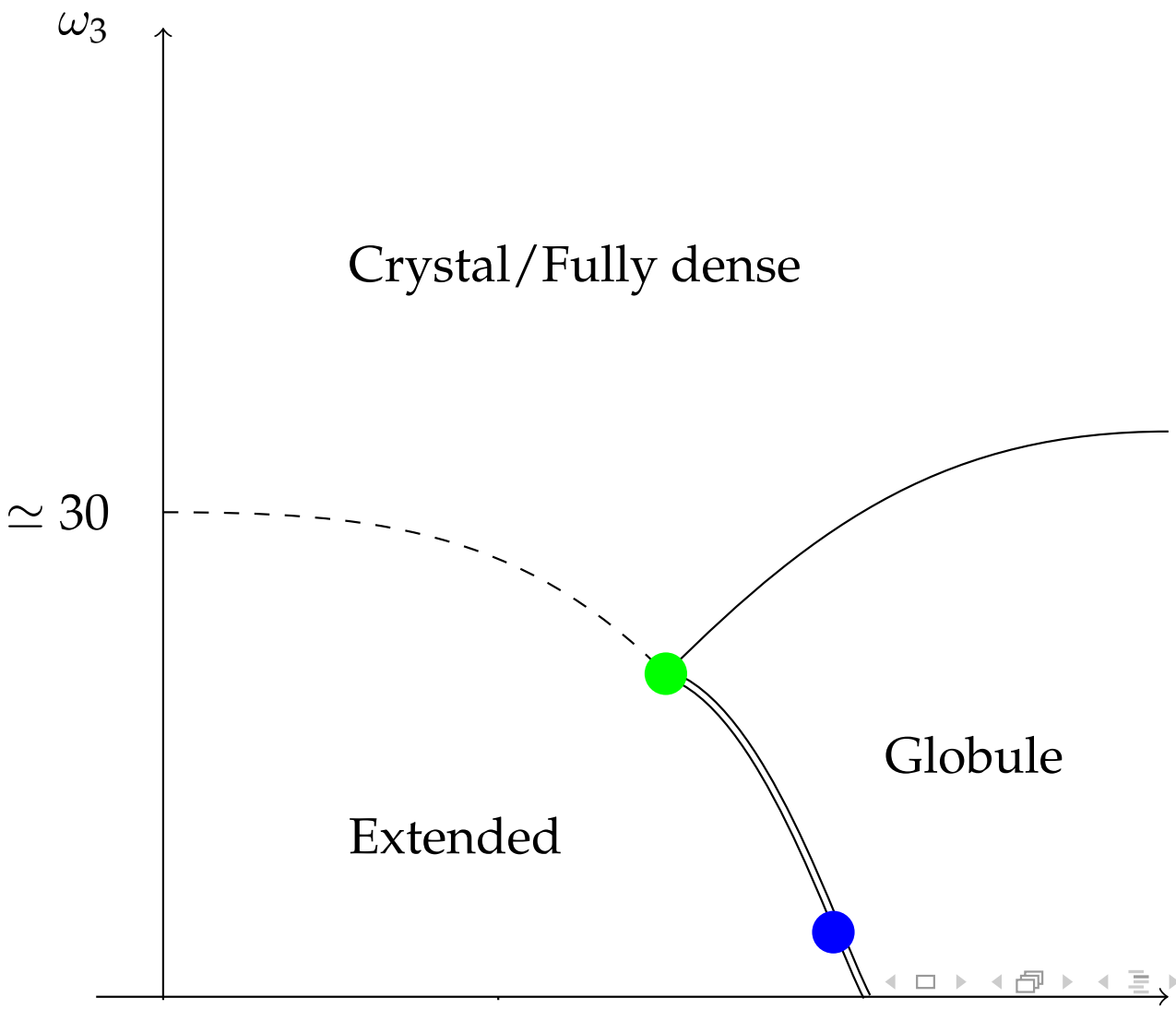
The distribution of the number of *type*-3 faces f_3 is clearly bimodal at the point when ω_2 and ω_3 cross the line of suspected first-order transitions

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)

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

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Here is looking forward to
"Means, Methods and Results in the Statistical Mechanics of Polymeric Systems III"