Multi-critical polymer collapse

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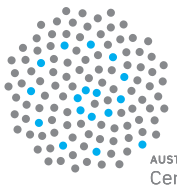
Statistical Physics of Lattice Polymers, 2010



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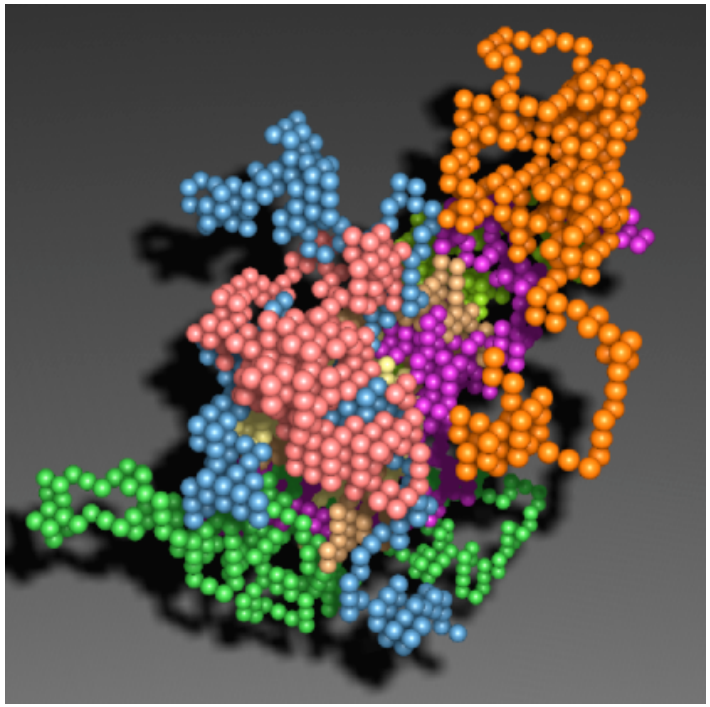
Modelling of Polymers in Solution

- 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



Modelling of Polymers in Solution

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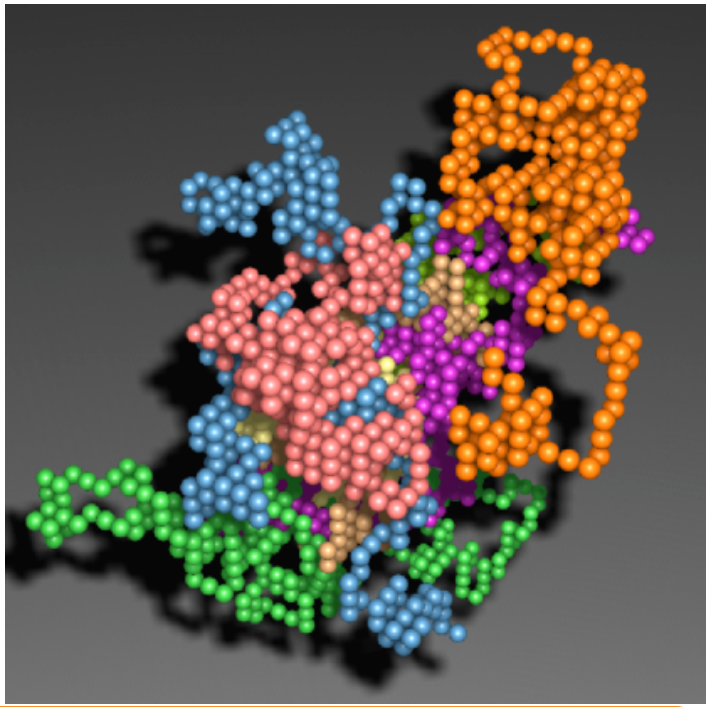
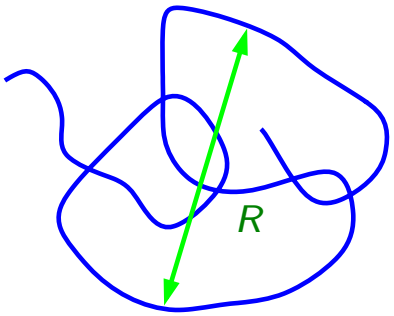


A Model of a Polymer in Solution

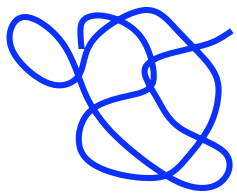
Random Walk + Excluded Volume + Short Range Attraction

A Polymer Phase Transition: Collapse (θ-point)

- *Let the length of the polymer be* **n** *monomers so its mass* $m \propto n$ *and its spatial extension* R
- *Then one finds that mass* $m \sim R^{d_{fractal}}$ *with* $d_{fractal}$ *discontinuously dependent to temperature.*
- *A phase transition occurs as temperature is changed:*
- *Polymer Collapse, aka Coil-Globule Transition, aka Θ-Point*



$T > T_t$: good solvent swollen phase (coil): $d_{fractal} < d$

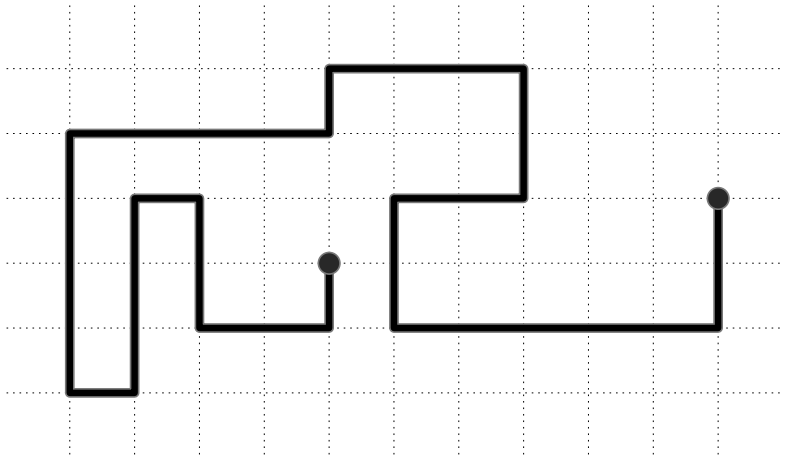


$T = T_t$: Θ-polymer: $d_{fractal} \approx 2$

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

The Canonical Polymer Lattice Model

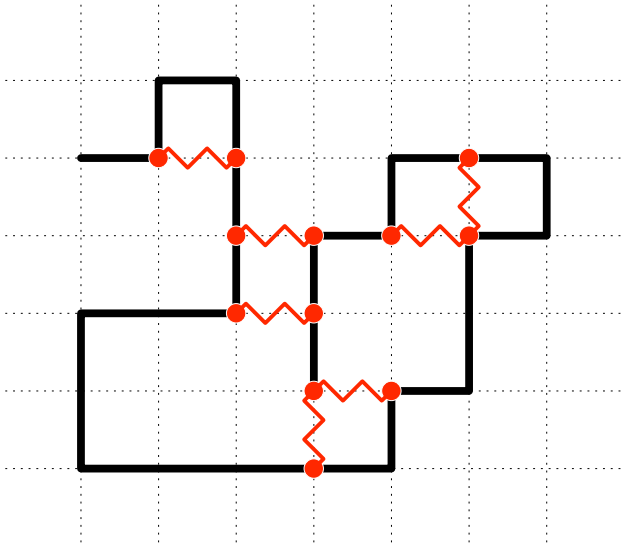
- *Polymer* $\longrightarrow$ *self-avoiding random walk (SAW)*
- *Physical space* $\longrightarrow$ *regular lattice eg* $\mathbb{Z}^3$ *or* $\mathbb{Z}^2$
- *Sites — beads — monomers — not always valid*



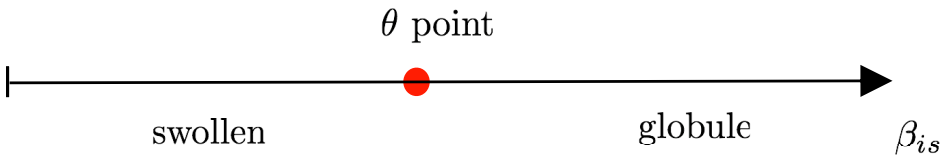
The Canonical Collapsing Polymer Lattice Model

Interacting Self-Avoiding Walk (ISAW)

- *Start with a SAW and add 'interactions'*
- *Quality of solvent* $\longrightarrow$ *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
- de Gennes' general description (1975) as a "tricritical point"
- Much work since on exponent values, scaling subtleties and various extensions

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

$$R_n^2 \sim An^{2\nu}$$

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

$$Z_n \sim Be^{K\,n} n^{\gamma-1}$$

while for $T < T_t$ we expect

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

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

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

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

where $\alpha < 1$ for a second-order phase transition. The singular part of the thermodynamic limit internal energy behaves as

$$U(T) \sim B|T_t - T|^{1-\alpha} ,$$

if the transition is second-order, and there is a jump in the internal energy if the transition is first-order (an effective value of $\alpha = 1$).

Scaling around the θ point

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

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

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

Scaling around the θ point in two dimensions

The work of Duplantier and Saleur (1987) predicted the standard θ-point behaviour in two dimensions, which has been subsequently verified Prellberg and Owczarek (1994). It is expected that

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

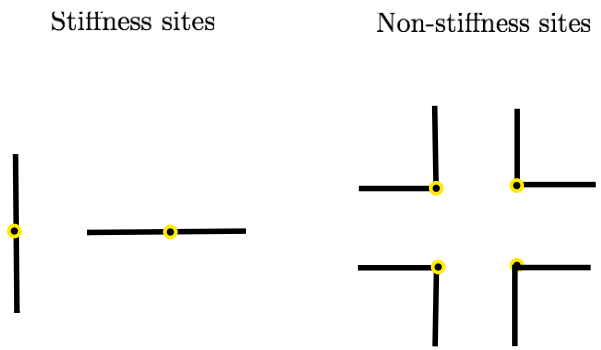
Note that this implies that the specific heat does *not* diverge at the transition. However, the third derivative of the free energy with respect to temperature will diverge with exponent

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

Adding stiffness to ISAW

Adding stiffness

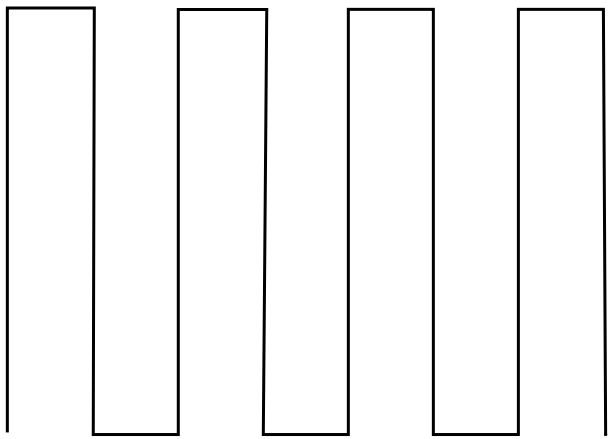
- Models natural rigidity of polymers
- though it implies sites to monomer mapping is incomplete with adding stiffness
- In 1998 Bastolla and Grassberger studied the canonical model in three dimensions and added a weight for bends
- Later, in 2009, a model with weights for 'stiffness sites' studied by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



Semi-flexible ISAW at low temperatures

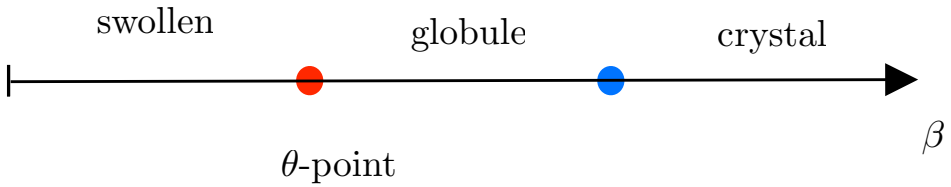
At low temperatures and sufficient stiffness a polymer crystal can occur

A rectangular "polymer" crystal

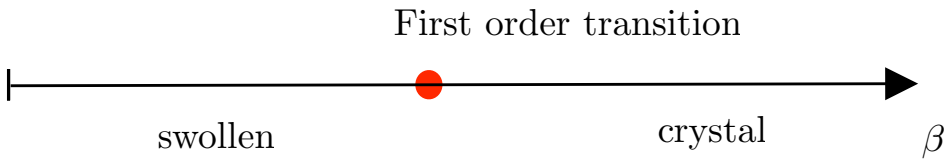


Semi-flexible ISAW

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

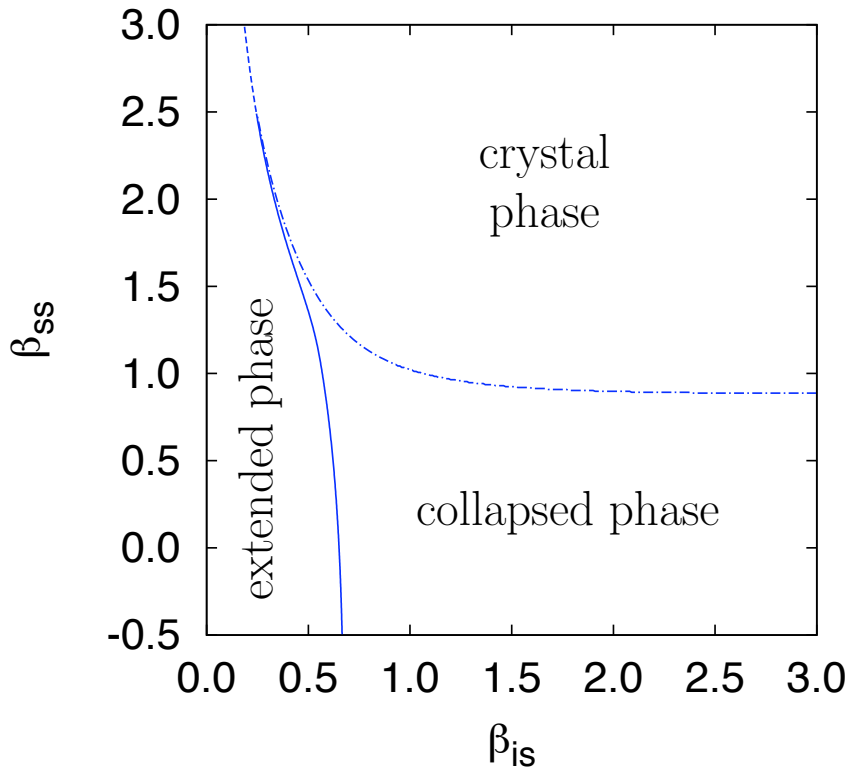


- For large stiffness



Adding stiffness to ISAW

If one considers both nearest-neighbour interactions and stiffness one finds



Phase transition for semi-flexible polymers

Swollen – Globule

This is the θ transition: convergent specific heat and divergent free energy third derivative

Swollen – Crystal

First order in both two and three dimensions

Globule – Crystal

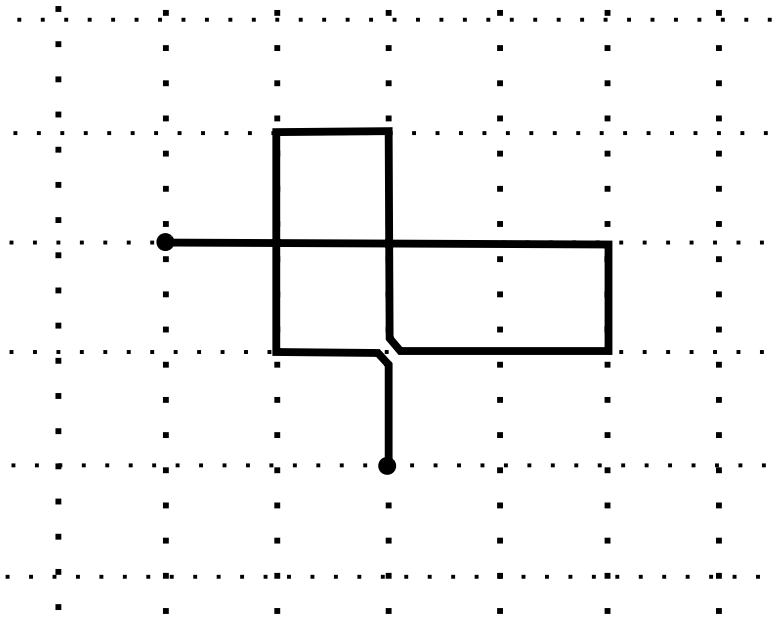
Second order in two dimensions with estimated $\alpha \approx 0.4$

Meeting point

Unknown

Self-avoiding trails (SAT)

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

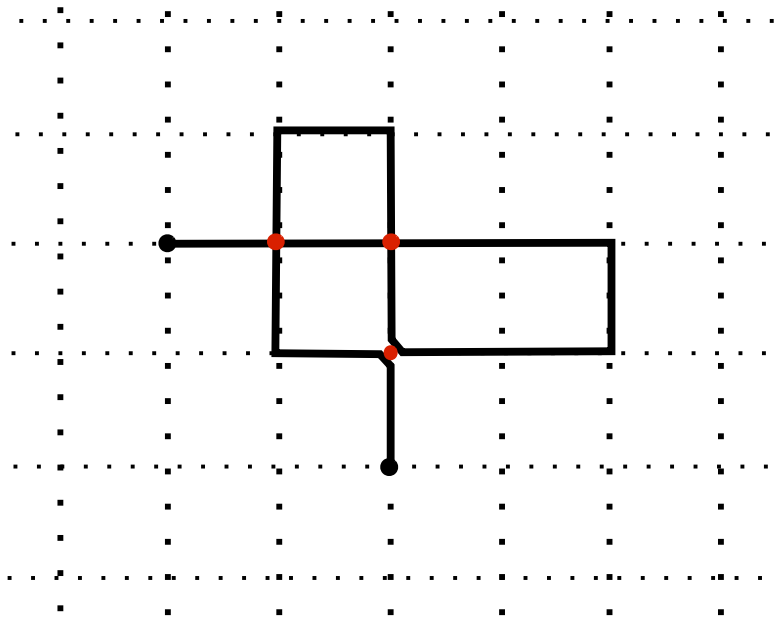


History of SAT

Trails were studied by Shapir and Oono in 1984.

ISAT on the square lattice

Interactions were added by associating an energy with doubly occupied sites — both crossings and touching.



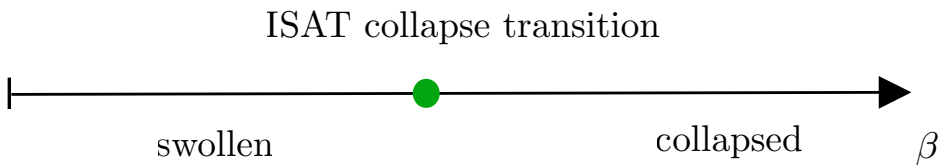
ISAT on the square latttice

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.

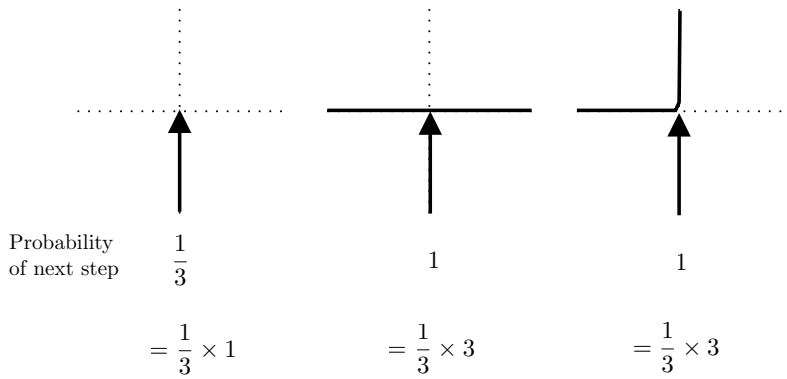


ISAT

H. A. Lim, A. Guha, and Y. Shapir (1988)

Kinetic SAT (KSAT)

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



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))

Transition

Previous work, Owczarek and Prellberg 2006, 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

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

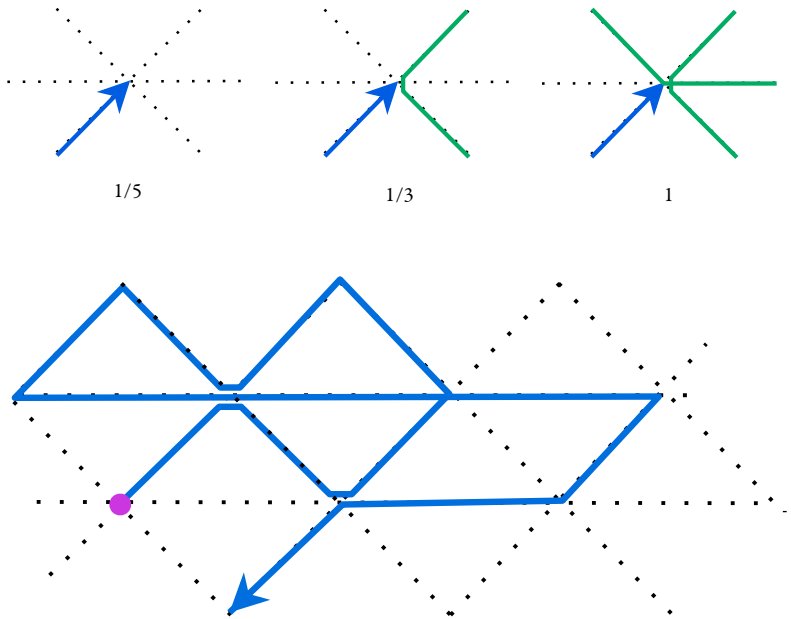
At $T = T_t$ it was predicted by Owczarek and Prellberg (1995) that

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

Other ideas

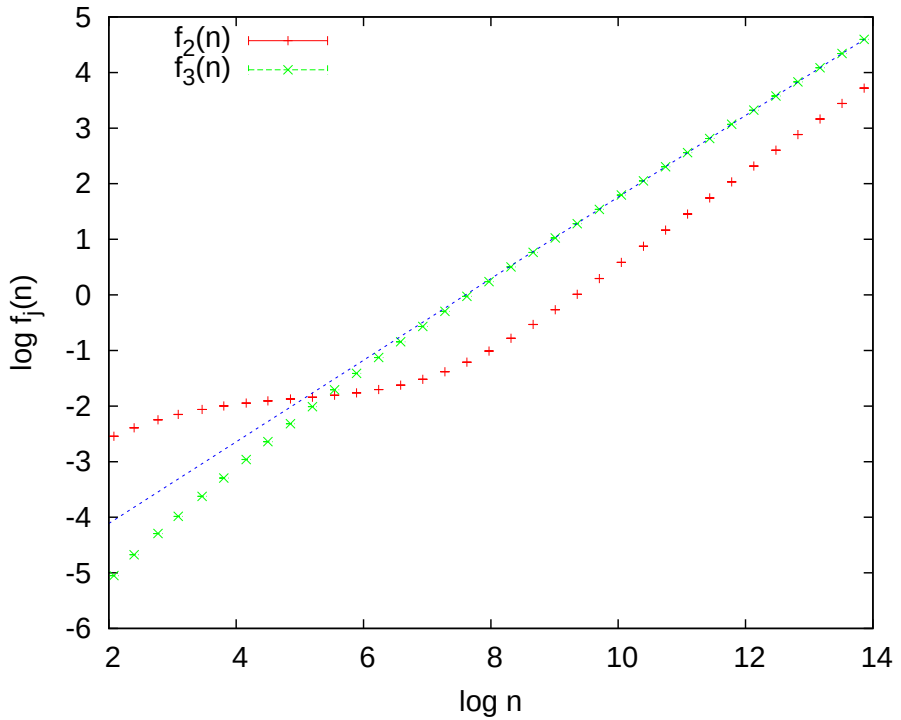
- Grassberger and Hegger 1996 suggest renormalisation argument implies ISAT collapse is first order: they gave numerical evidence in three dimensions.
- Foster 2009 suggested that the mapping between grand ensemble and canonical is not straightforward with ν exponent not appped as normal.

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 KSAT



Doubly and Triply Visits

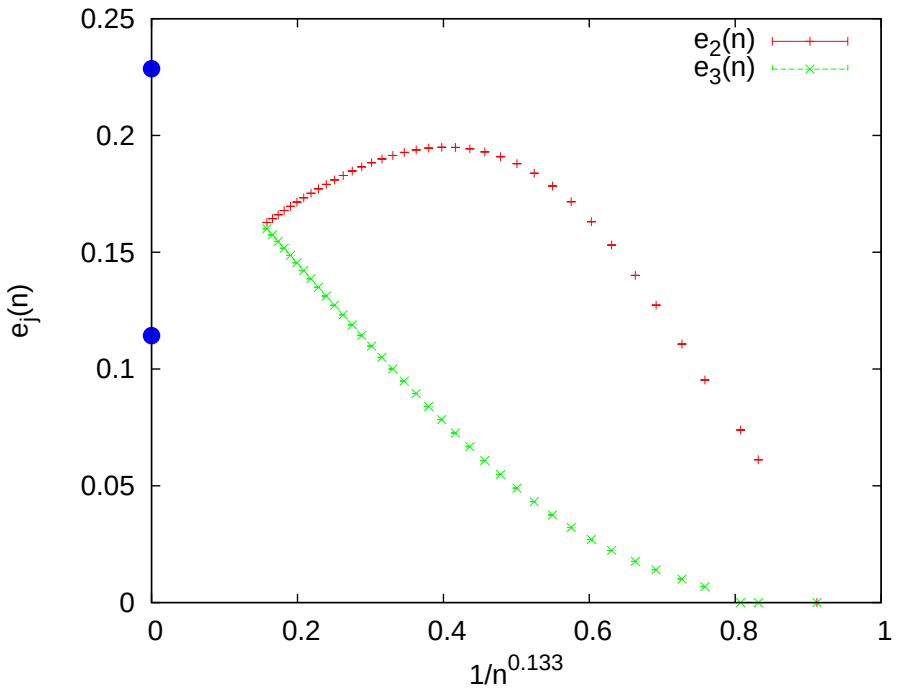


Figure: Plot of the average numbers of doubly, $e_2(n)$, and triply, $e_3(n)$, visited sites against $1/n^{0.133}$. Their asymptotic values, $E_2 = 4/35 \approx 0.114$ and $E_3 = 8/35 \approx 0.228$ respectively are marked as filled circles.

Canonical Model

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

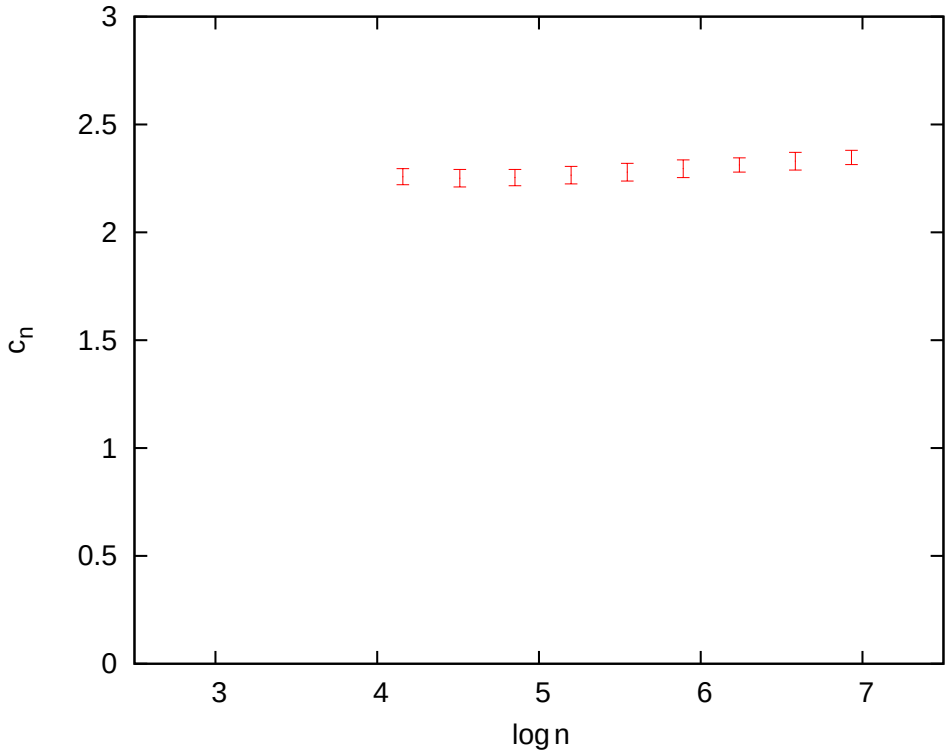


Figure: Plot of the value of the maximum of the specific heat $c_n = \max_\omega c_n^{(2)}$ against $\log n$. This suggests that the specific heat does not diverge as the polymer length is increased.

Free Energy Third Derivative

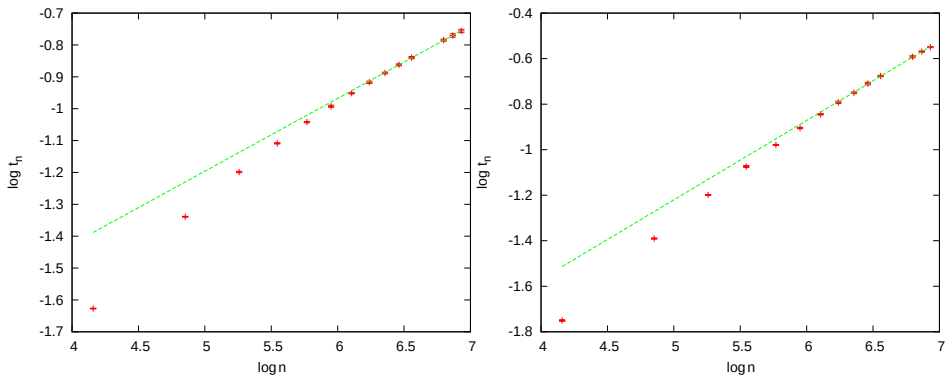


Figure: Plot of the height of the peaks of $t_n^{(2)}(\omega)$, the third derivative of the free energy with respect to temperature against n. The third derivative has two peaks: one positive and one negative in value.

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 $k = k_{KGT}$

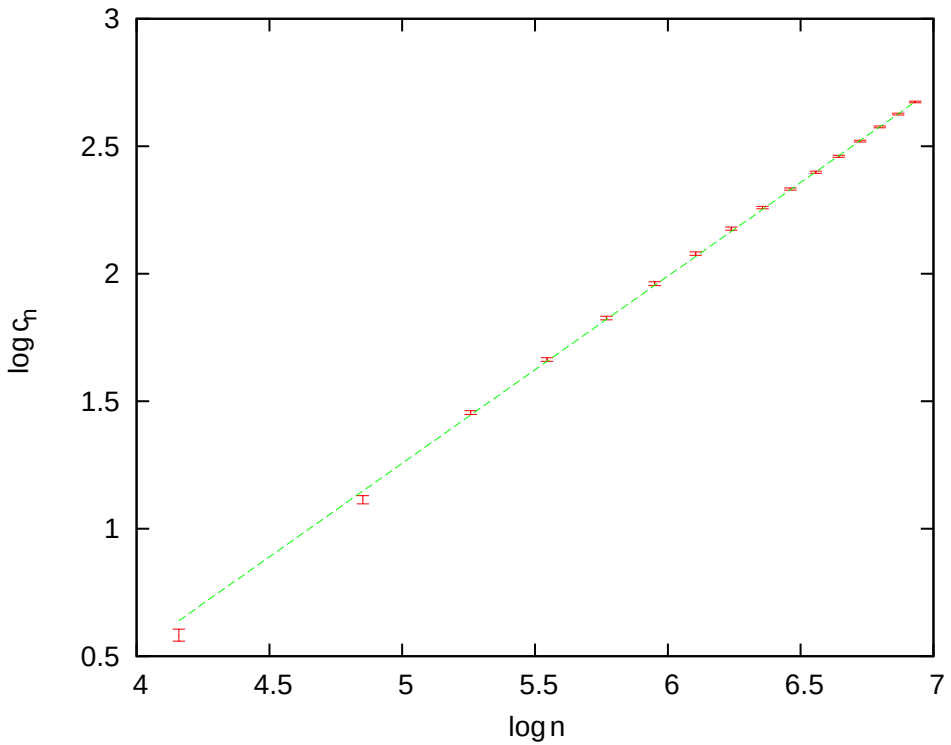


Figure: Plot of the logarithm of $c_n = \max_\omega c_n^{(k_G)}$, the value of the maximum of the specific heat, against $\log n$. The straight line has slope 0.734.

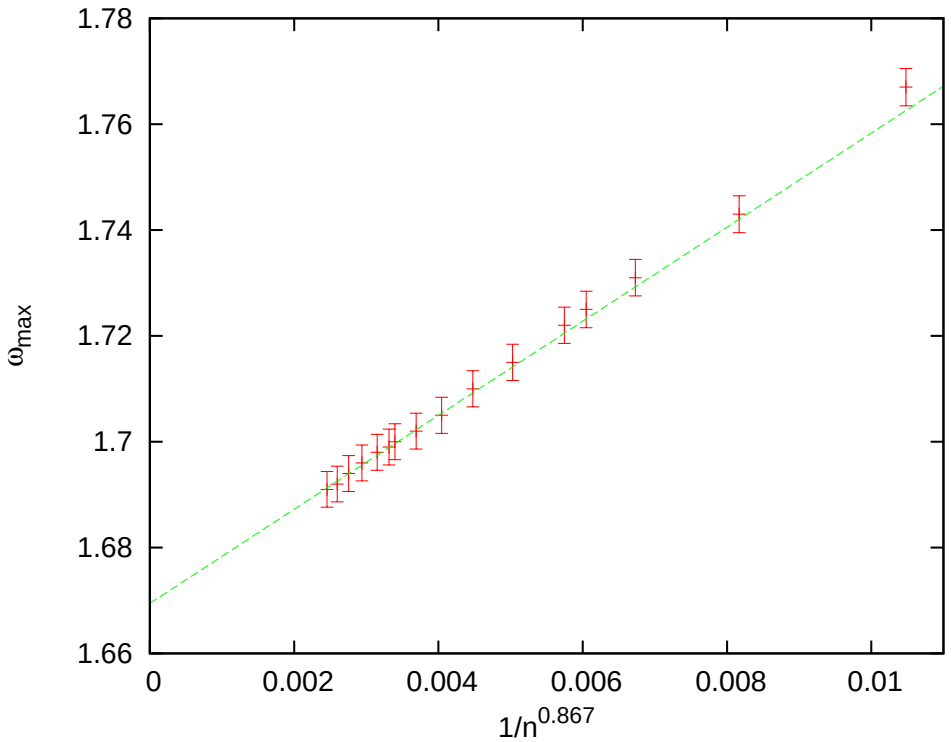


Figure: Plot of the location, ω_{max}, of the peak of the specific heat against $1/n^{0.867}$.

Specific heat in $k = k_{KGT}$

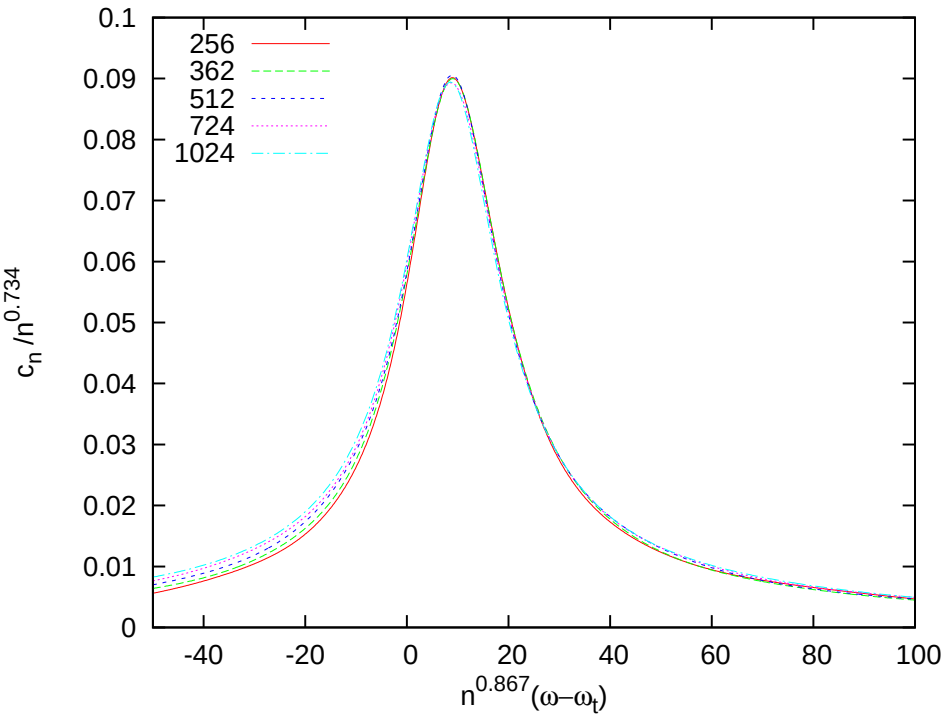


Figure: Scaling plot of the specific heat around the transition temperature, using the exponents from the growth process.

eISAT with $k = 0$

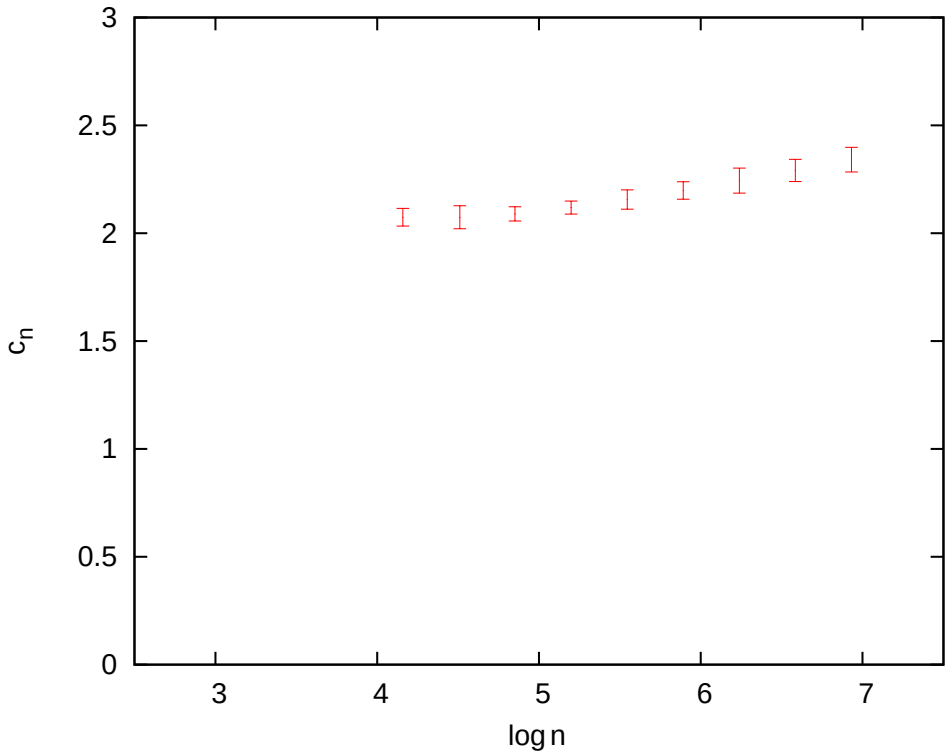


Figure: Plot of the value of the maximum of the specific heat $c_n = \max_\omega c_n^{(0)}$ against $\log n$ for $k = 0$ EISAT model. This suggests that the specific heat does not diverge as the polymer length is increased, as is the case in the canonical model ($k = 2$).

Third derivative in $k = 0$ model

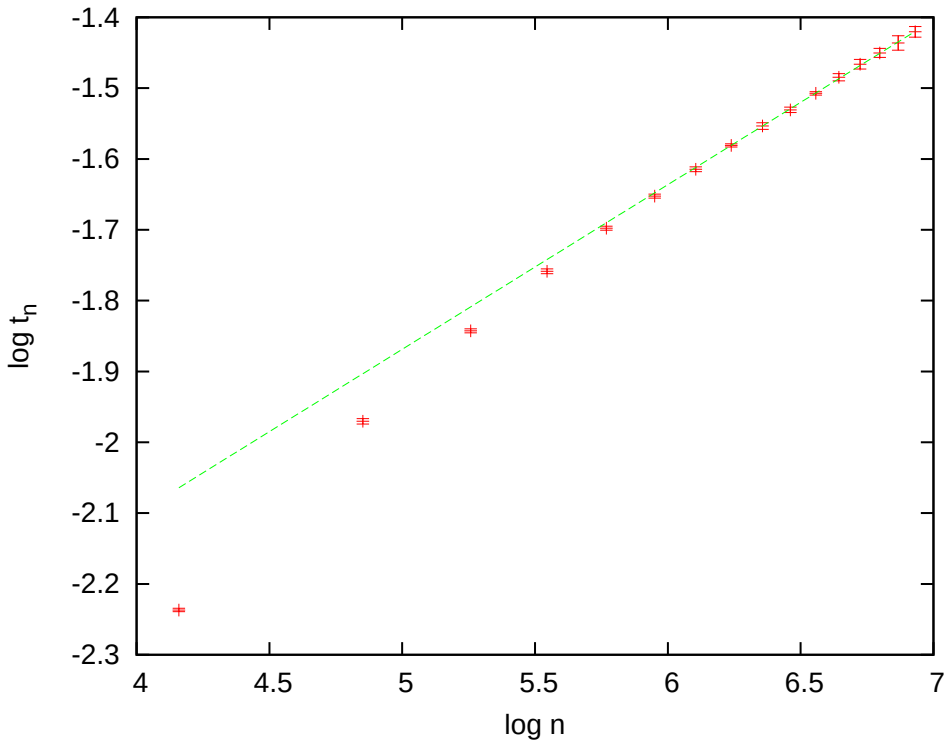


Figure: Plot of the height of one of the peaks of $t_n^{(0)}(\omega)$, the third derivative of the free energy with respect to temperature against n. The third derivative has two peaks: one positive and one negative in value. The figure shows $t_n = \min_\omega t_n^{(0)}$ which is the larger in absolute value and the one seemingly less affected by corrections to scaling.

$k = \infty$ – 'Triple' model

Consider

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

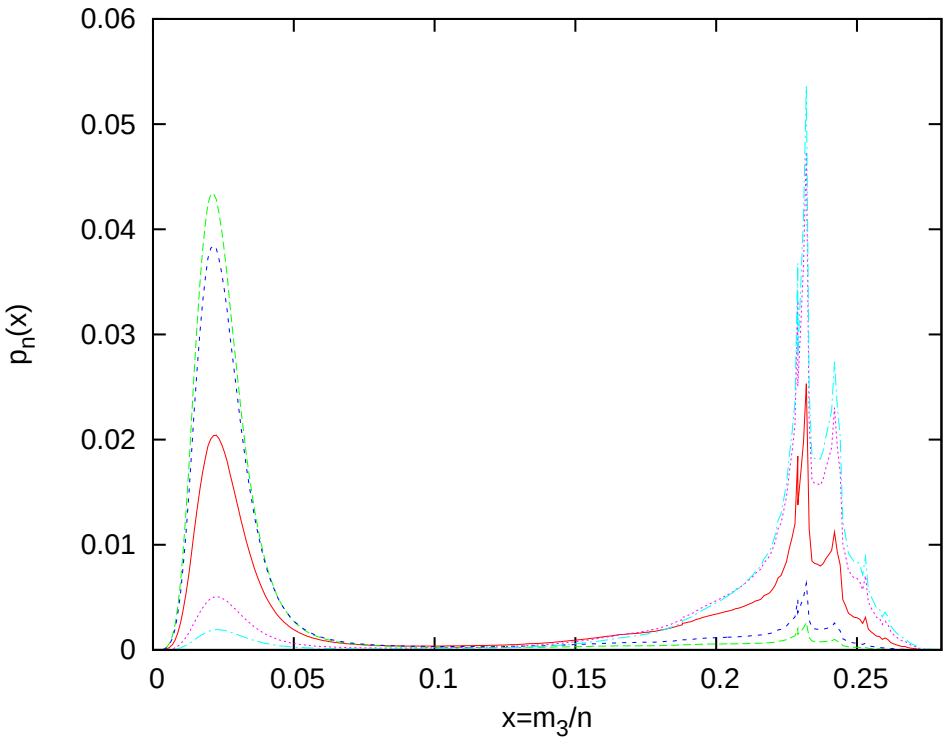


Figure: Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the *Triple* model at temperatures near, and at, the temperature at which the specific heat

$k = \infty$

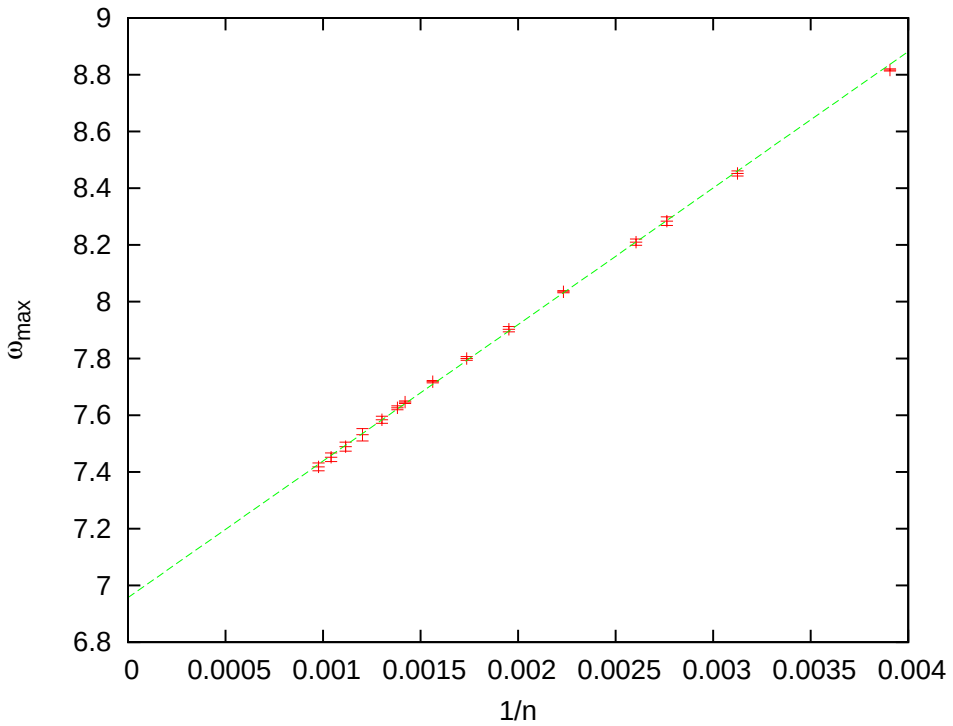


Figure: Plot of the location, ω_{max}, of the peak of the specific heat against $1/n$ for the *Triple* model.

$k = 6$

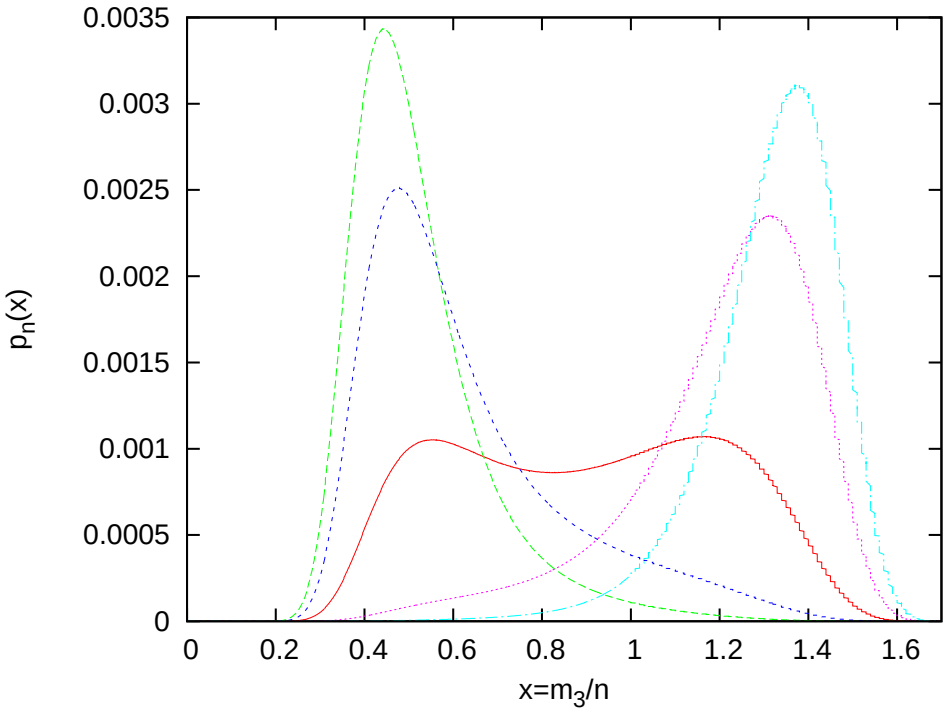


Figure: Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the $k = 6$ model at temperatures near, and at, the temperature at which the specific heat attains its maximum for length $n = 1024$. The specific heat attains its maximum at $\omega = \omega_{max} = 1.419$ and the distribution is plotted for this value and at $\omega = 1.410, 1.414, 1.425, 1.430$: the plots move from left to right as ω is increased.

Fluctuations

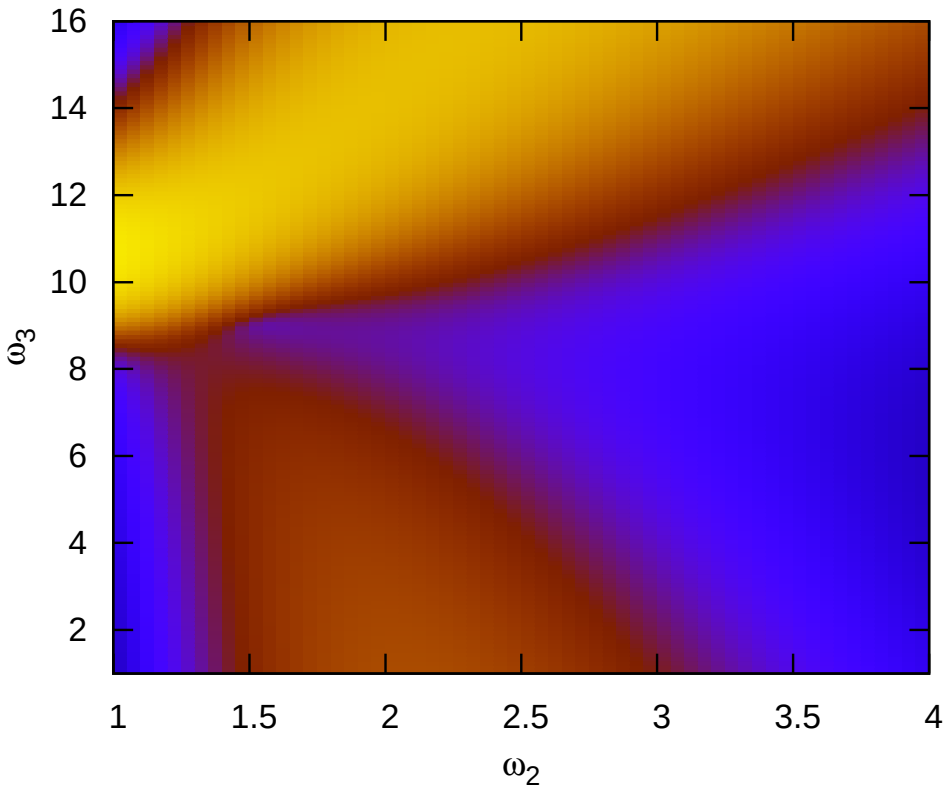


Figure: Density plot of the logarithm of the largest eigenvalue λ_{max} of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length $n = 128$ (the lighter the shade, the larger the value).

Collapsed phase for canonical model — globule

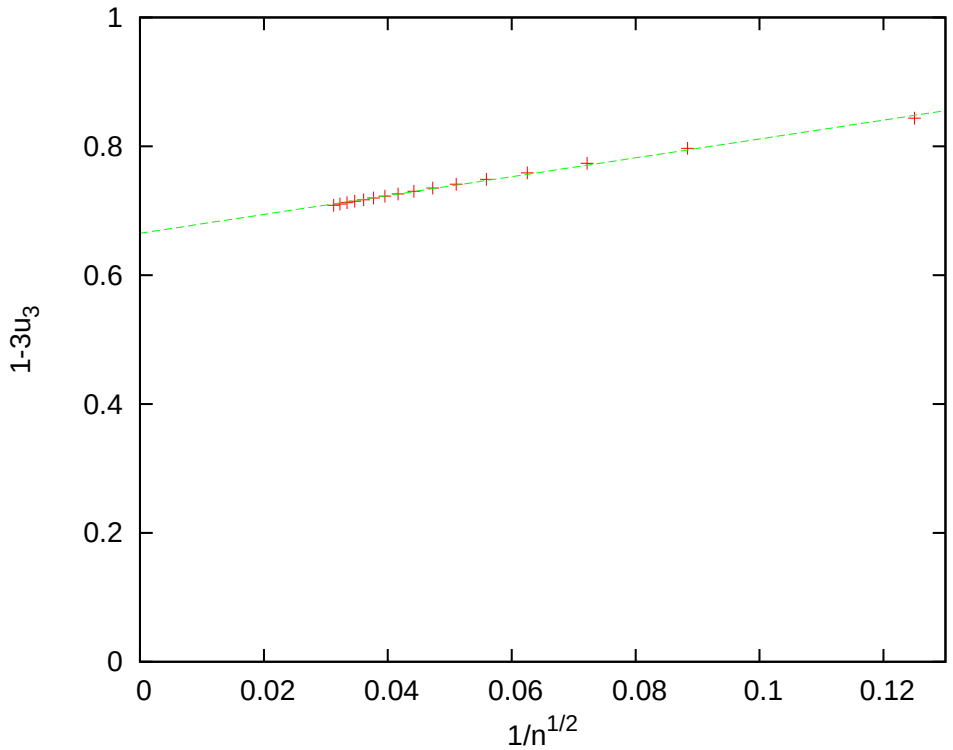


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(\omega_2, \omega_3) = (4, 16)$ in the collapsed liquid-drop-like globule phase. As the length increases this reaches a non-zero value.

A globule when $k = 0$

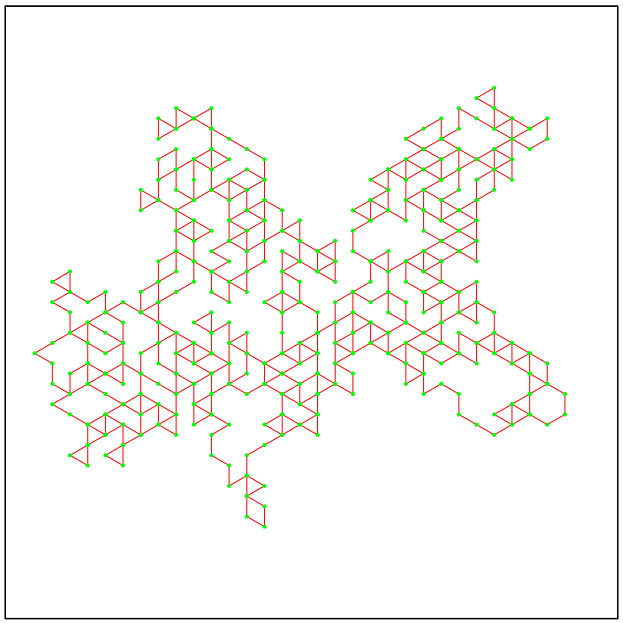


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (5, 1)$, which is in the globule phase: it looks disordered and rather more like a liquid-like globule than a crystal.

Collapsed phase when $k = 6$

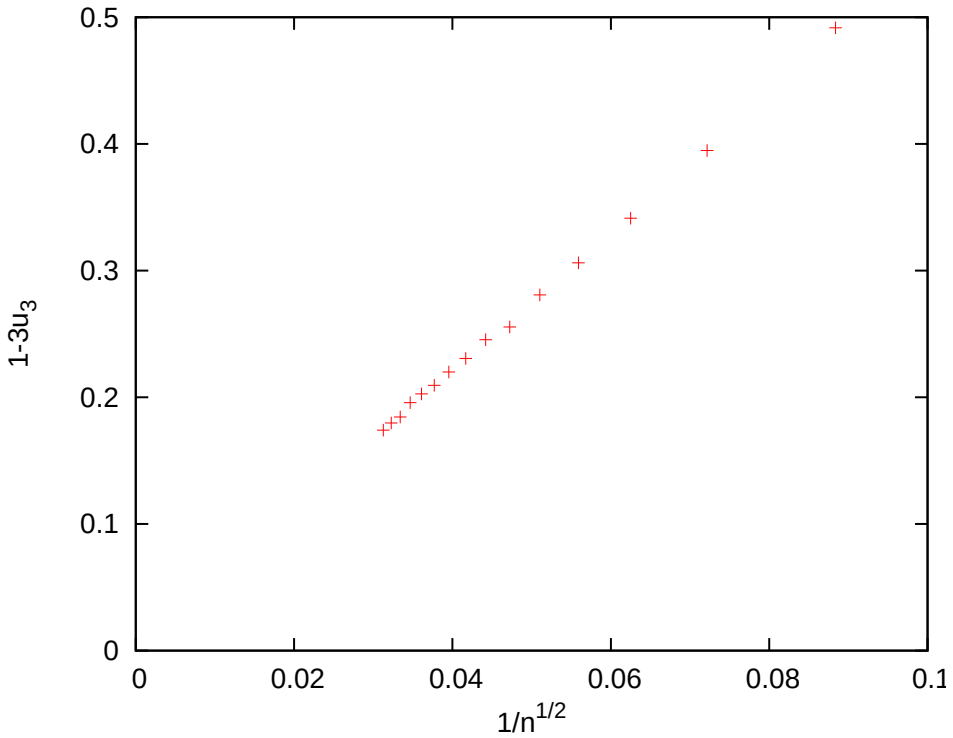


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(1.58, 15.6)$ in the hypothesised frozen (crystal-like) phase. As the length increases this quantity vanishes.

A 'crystal' in the Triple model

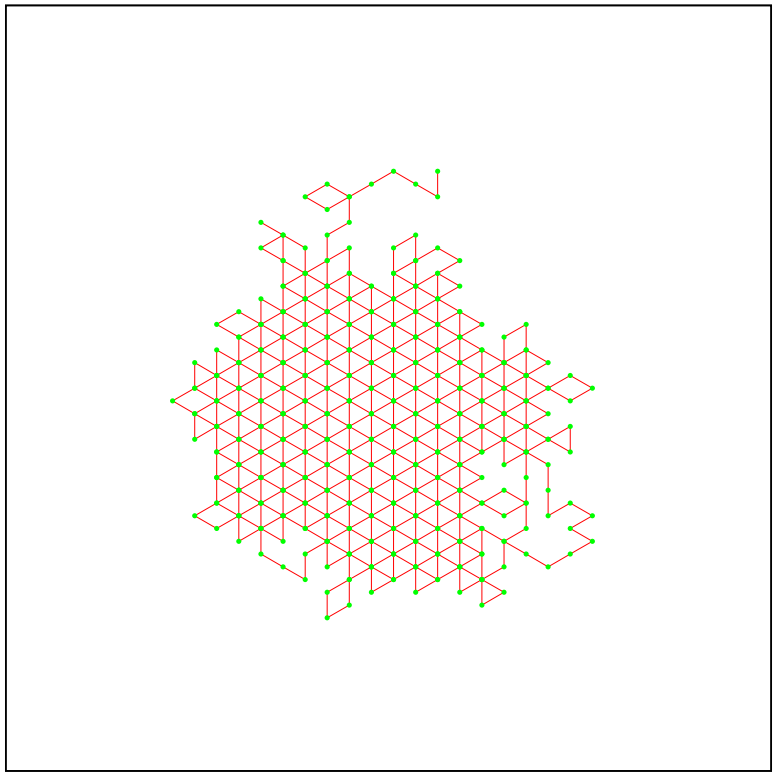


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

Phase diagram

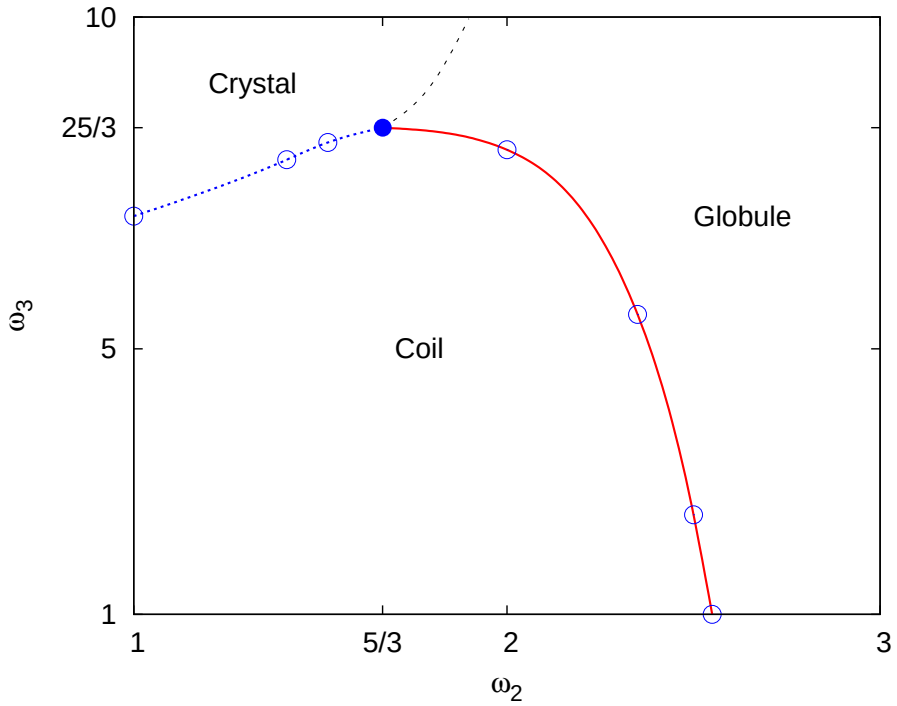


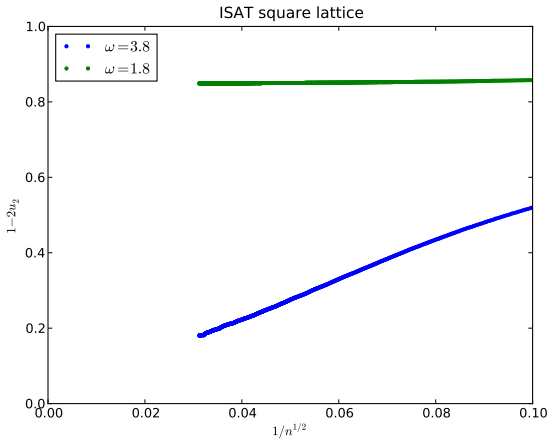
Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The filled circle is at the location of the kinetic growth point, and the open circles represent estimates of the collapse transition for various values of k.

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
- Now investigating cubic lattice (with Andrea Bedini)

Postscript



This means we can finally deduce for the square lattice

Square Lattice ISAT

Multi-critical collapse