Anomalous critical behaviour in the polymer collapse transition of lattice trails in two and three dimensions

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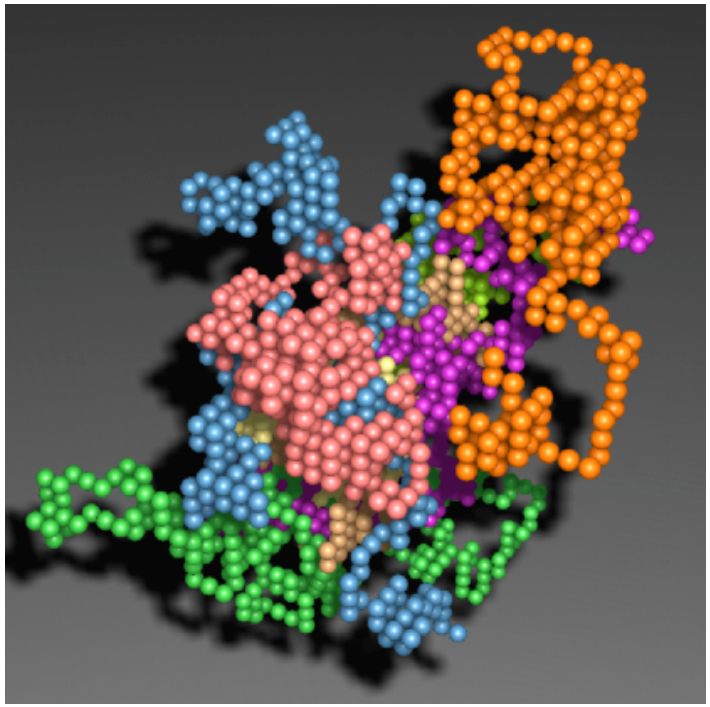
Modelling of Polymers in Solution

- 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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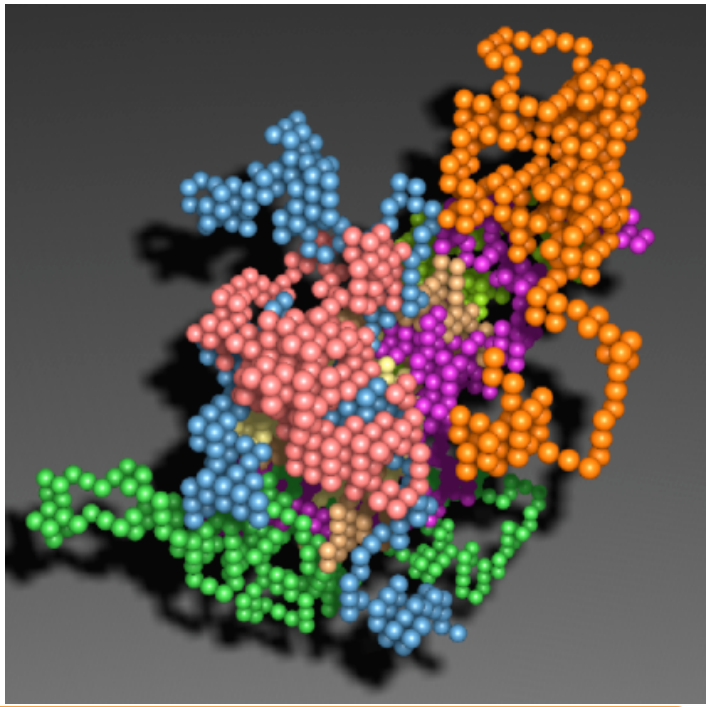
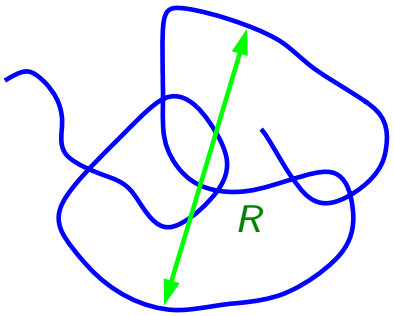


A Model of a Polymer in Solution

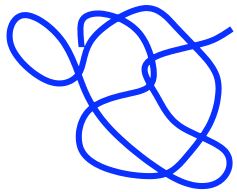
Random Walk + Excluded Volume + Short Range Attraction

A Polymer Phase Transition: Collapse (θ-point)

- *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 on temperature.*
- *A phase transition occurs at* T_t *as the temperature is changed*
- *Polymer Collapse, aka Coil-Globule Transition, aka* Θ*-Point*



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

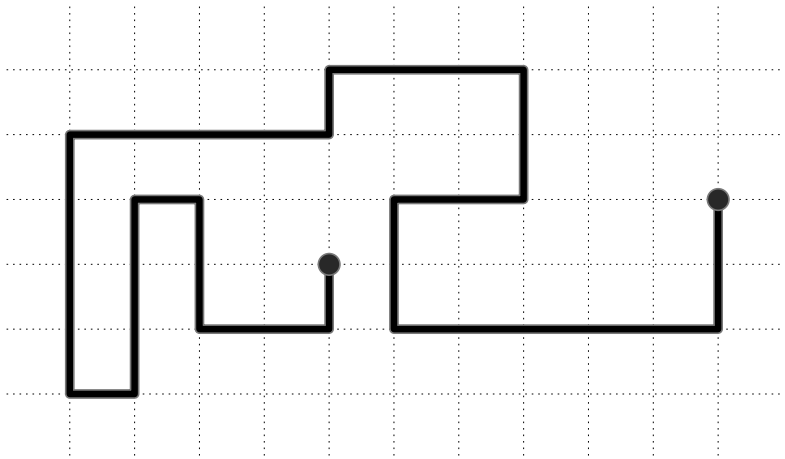


$T = T_t$: Θ-polymer: $d_{fractal} \approx 2$

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

The Canonical Polymer Lattice Model

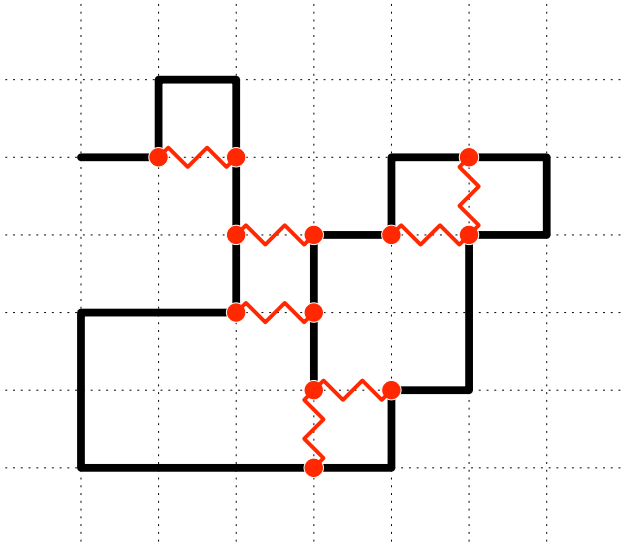
- *Polymer* $\rightarrow$ *self-avoiding random walk (SAW)*
- *Physical space* $\rightarrow$ *regular lattice eg* $\mathbb{Z}^3$ *or* $\mathbb{Z}^2$
- *Sites — beads — monomers — not always valid*



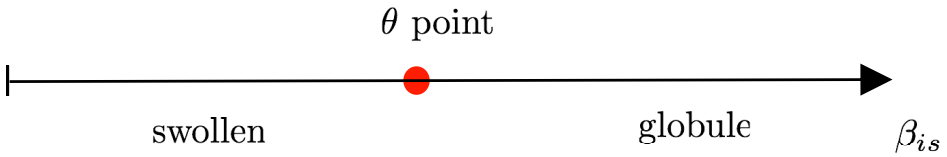
The Canonical Collapsing Polymer Lattice Model

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 second order phase transition
- De Gennes's 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
- Upper critical dimension of three with subtle scaling behaviour in that dimension
- Low temperature phase (globule) is dense but disordered — liquid-like

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

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

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: Classic crossover scaling

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

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

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

Classic crossover scaling

The width of the transition at finite length (say, half-height width of specific heat peak)

$$\Delta T \sim n^{-\phi}$$

.

At finite lengths the *shift* of the transition

$$T_{t,n} - T_t \sim n^{-\psi}$$

obeys $\psi = \phi$ — that is, the shift and width scale together.

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

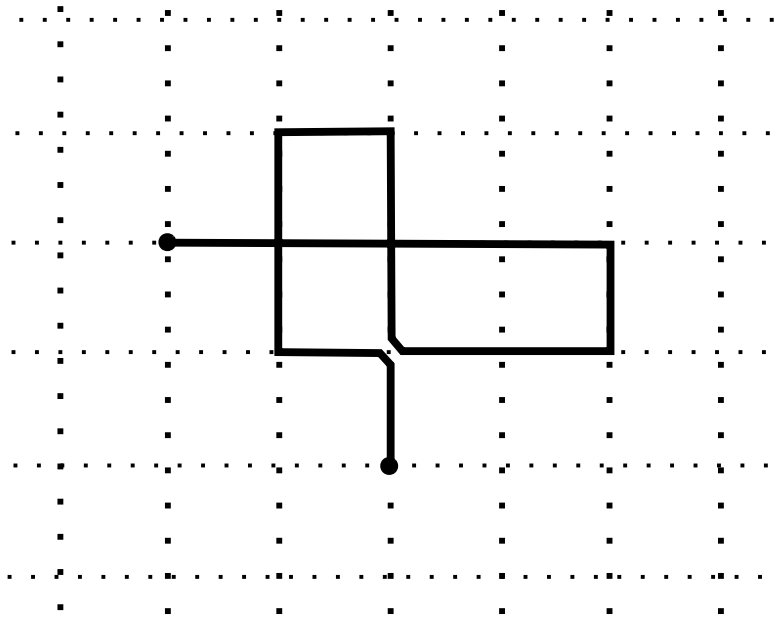
$$\phi = 3/7 \approx 0.43 \quad \text{and} \quad \alpha = -1/3 \, .$$

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

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

Self-avoiding trails (SAT)

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

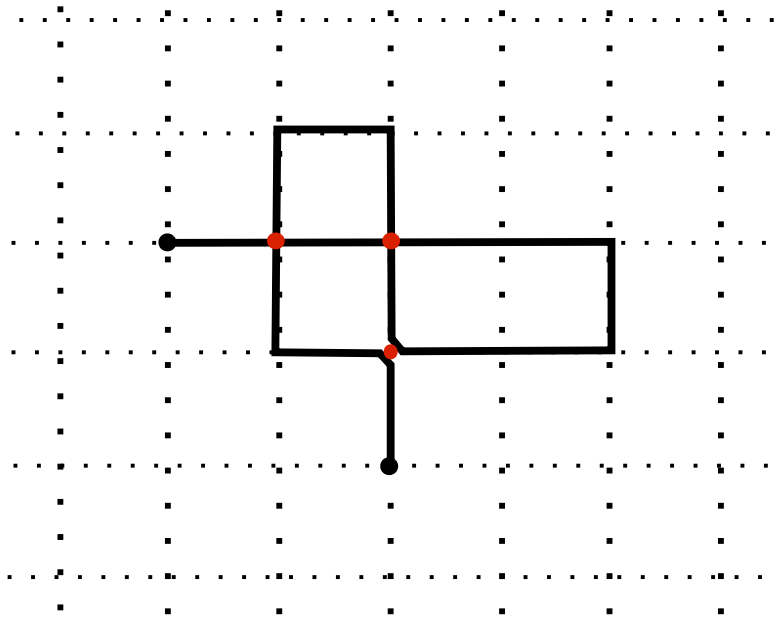


History of SAT analysis

- 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

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



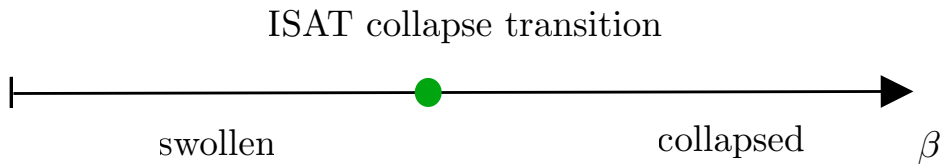
ISAT on the square lattice

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.

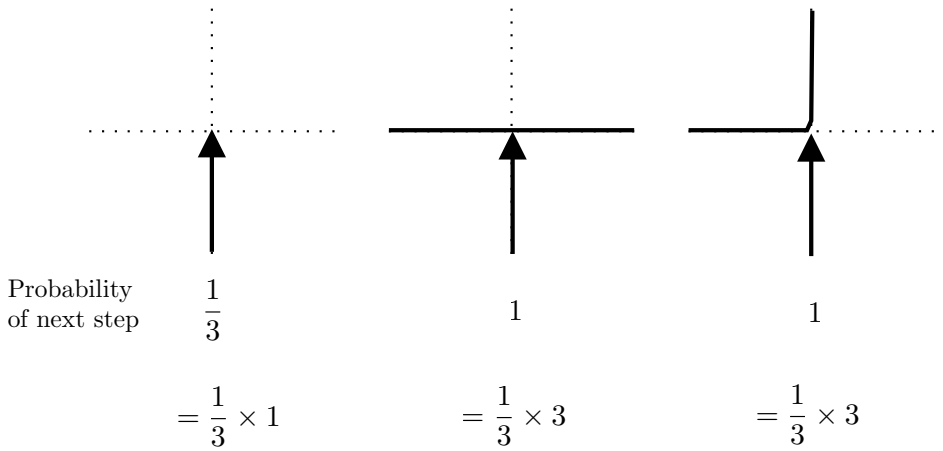


ISAT

- 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

Kinetic SAT (KGT)

A dynamic random walk: 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))

Square lattice KGT scaling

Owczarek and Prellberg (1995) studied KGT. 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

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

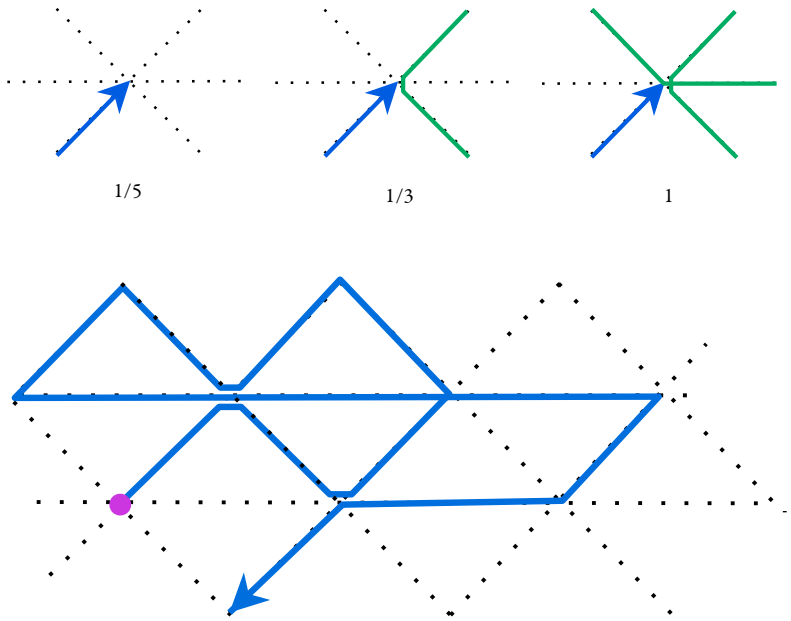
Square lattice ISAT Collapse transition

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 with $\nu = \frac{12}{23}$

Clearly there is something special about square lattice ISAT!

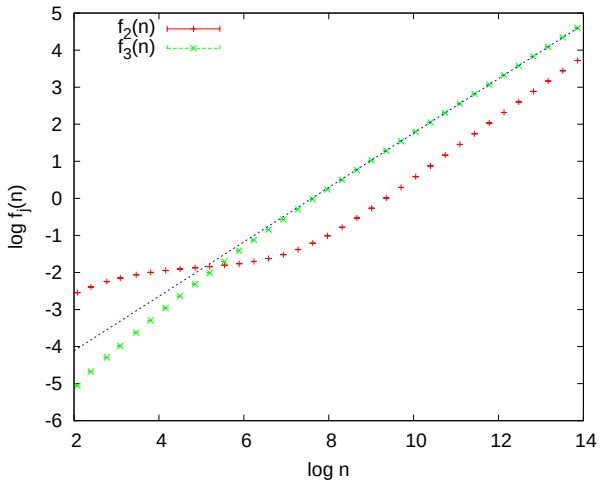
Kinetic growth trails on the triangular lattice



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 KGT

Fluctuations demonstrate divergent behaviour



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

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

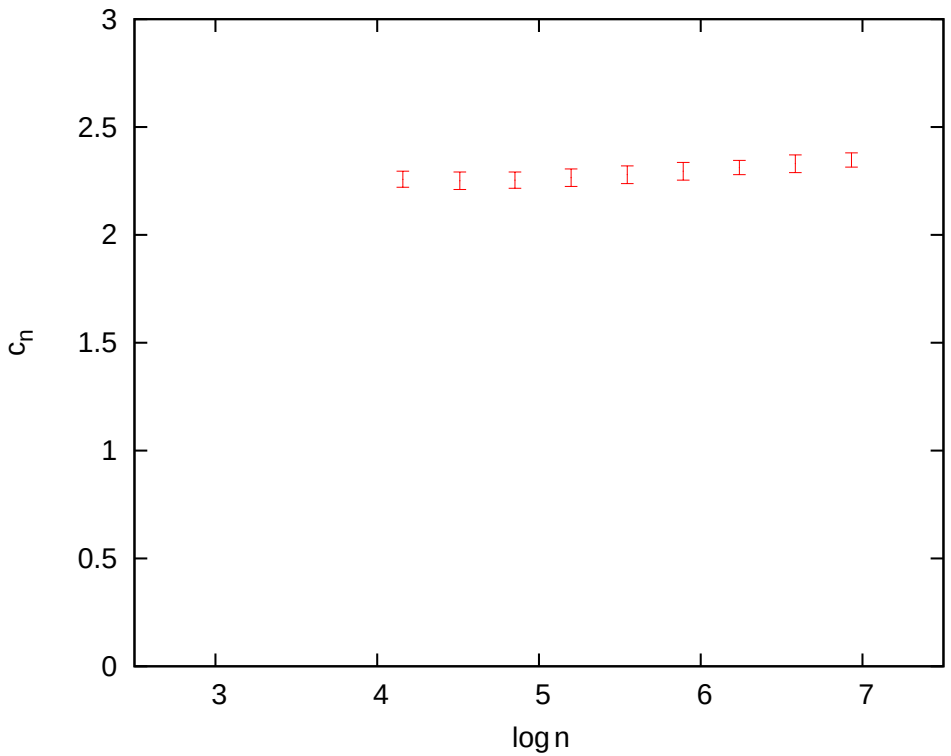


Figure: Plot of the value of the maximum of the specific heat $c_n = \max_\omega c_n^{(2)}$ against $\log n$. This suggests that the specific heat does not diverge as the polymer length is increased.

Free Energy Third Derivative

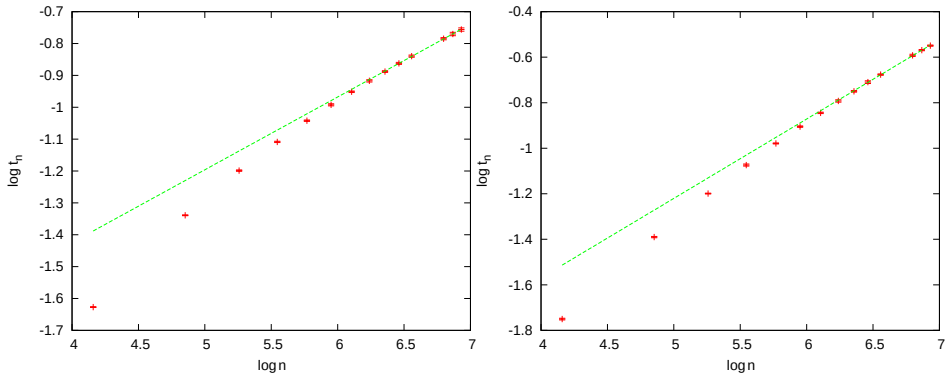


Figure: Plot of the height of the peaks of $t_n^{(2)}(\omega)$, the third derivative of the free energy with respect to temperature against n. The third derivative has two peaks: one positive and one negative in value.

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 $k = 2$

KGT mapping

The KGT 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 KGT process does not map to any temperature of the canonical ISAT on the triangular lattice.

Phase diagram

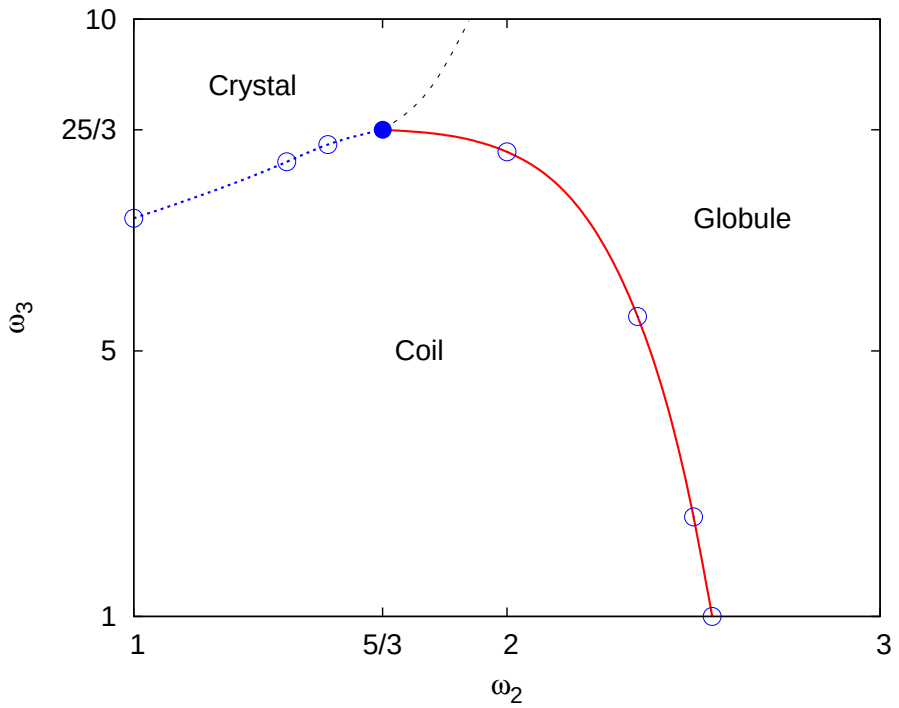


Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The filled circle is at the location of the kinetic growth point, and the open circles represent estimates of the collapse transition for various values of k.

A globule when $k = 0$

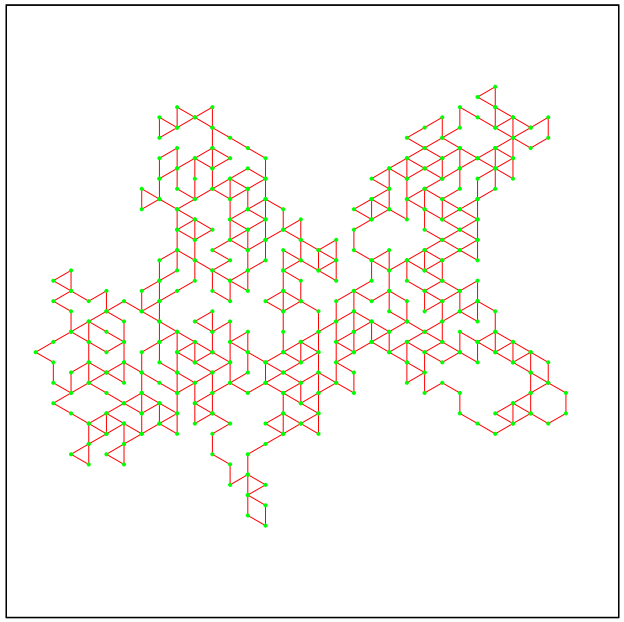


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (5, 1)$, which is in the globule phase: it looks disordered and rather more like a liquid-like globule than a crystal.

A 'crystal' in the Triple model

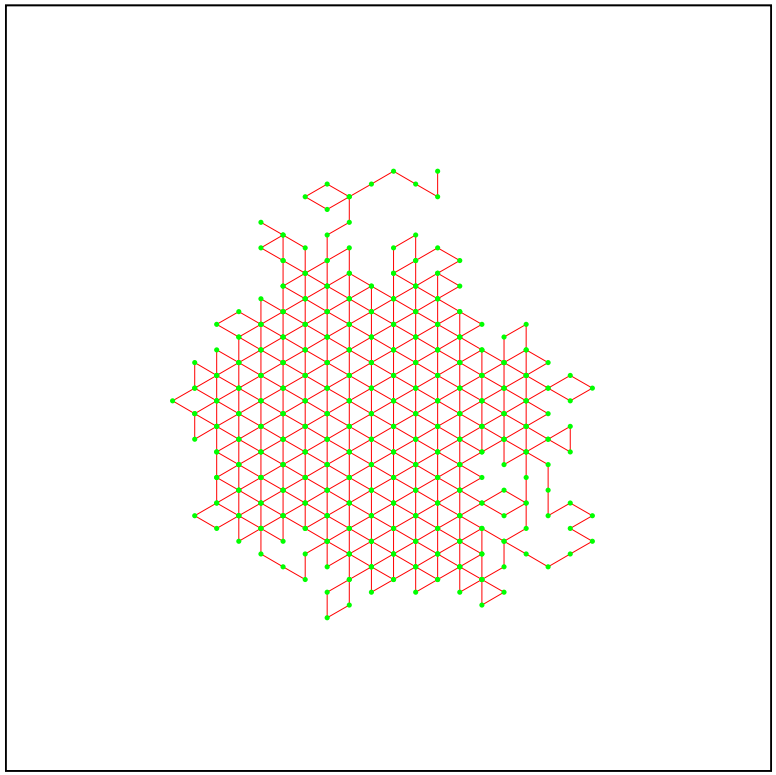


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

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

Our results are have appeared in J. Doukas, A. L. Owczarek and T. Prellberg, *Phys. Rev. E*, **82**, 031103 (12pp), 2010

Scaling around the θ point in three dimensions

For the ISAW model the tricritical field theory expects the width (crossover) exponent $\phi = 1/2$ and shift exponent $\psi = 1/2$ with logarithmic corrections present in the scaling forms because the system is at the upper critical dimension. The specific heat exponent $\alpha = 0$ with a logarithmically divergent specific heat

$$c_n(T_c) \sim C(\ln n)^{3/11} \tag{1}$$

The prediction for the shift is

$$T_{c,n} - T_c \sim D\, n^{-1/2}(\ln n)^{-7/11}. \tag{2}$$

Kinetic growth point in three dimensions

Simulation of the kinetic growth process was studied some time ago (see T. Prellberg and A. L. Owczarek, *Phys. Rev. E.* **51**, 2142 (1995)) and behavior similar to, but not quite that same as that predicted for the three-dimensional θ-point was found: for the cubic lattice it was conjectured that

$$c_n^* \sim C^* (\log n)^{\zeta}$$

with

$$\zeta = 1.0 \pm 0.5$$

cf. the Edwards model has $\zeta = 3/16$.
So perhaps again a difference between ISAW and ISAT?

Cubic lattice eISAT definition

Since the cubic lattice has the same coordination number as the triangular lattice we can define an extended ISAT model on the cubic lattice in exactly the same way as we did on the triangular lattice.

For each SAT we assign a Boltzmann weight $\omega_2^{m_2}\omega_3^{m_3}$, where $\omega_j = \exp(\beta\varepsilon_j)$, where ω_2 weights doubly visited sites while ω_3 weights triply visited sites.
The partition function of the eISAT model is then given by

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

Cubic lattice eISAT

- We again can define one temperature families paramerized by k, where
$$\omega_3 = \omega_2^k$$
- Once again the kinetic growth point lies in the $k \approx 4.15 \equiv k_G$ model with $\omega_2 = 5/3$.

Should we expect a similar behaviour? That is:

- For $k > k_G$ a first order transition
- For $k < k_G$ θ-like behaviour (albeit now three dimensional behavior)
- A KGT point separating the two lines of transition that is multicritical.

Cubic lattice k-eISAT with $k > k_G$

For $k > k_G$ a first-order collapse seems to occur like the triangular lattice

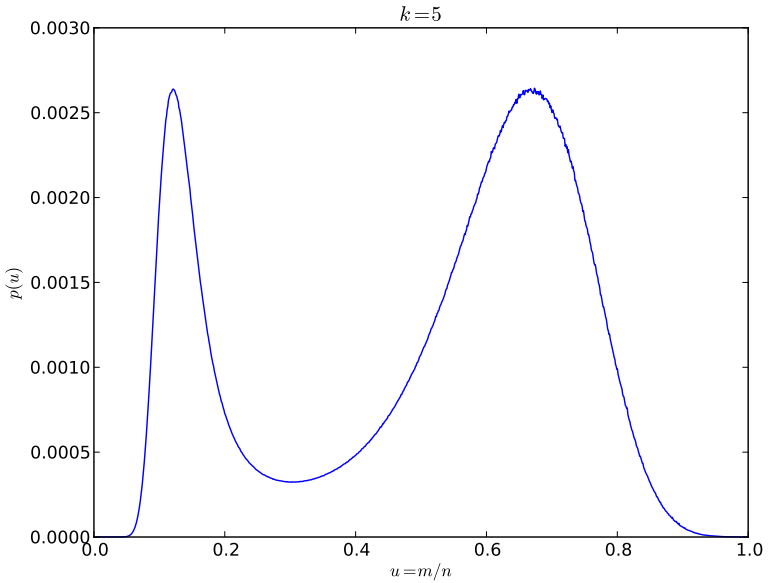


Figure: Energy distribution ($k > k_G$).

Cubic lattice k-eISAT with $k < k_G$

For $k < k_G$ a second order collapse (perhaps θ-like) seems to occur like the triangular lattice

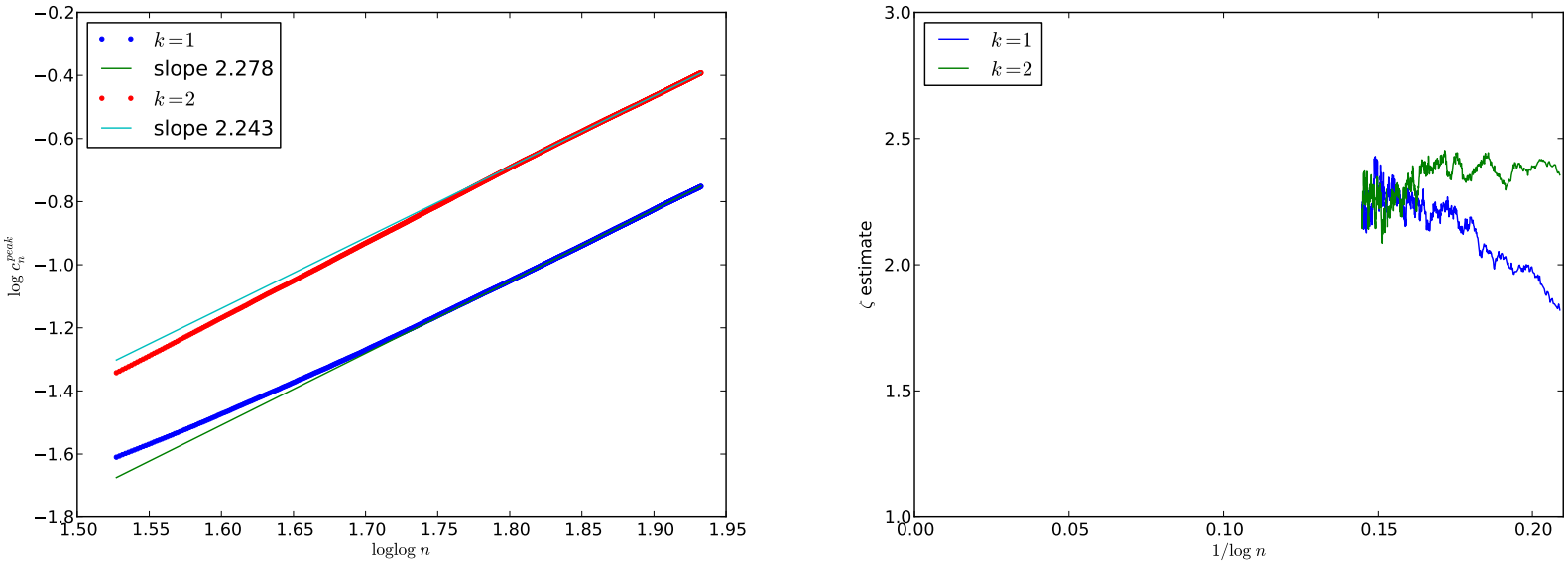


Figure: Specific heat peak scaling (left) and ζ estimates as local derivative (right) for small k. Note that our estimate for $\zeta = 2.25 \pm 0.25 \neq 3/11$

Cubic lattice k-eISAT with $k = k_G$

But the transition for $k = k_G$ does not appear to look like the KGT point even though that point has $k = k_G$

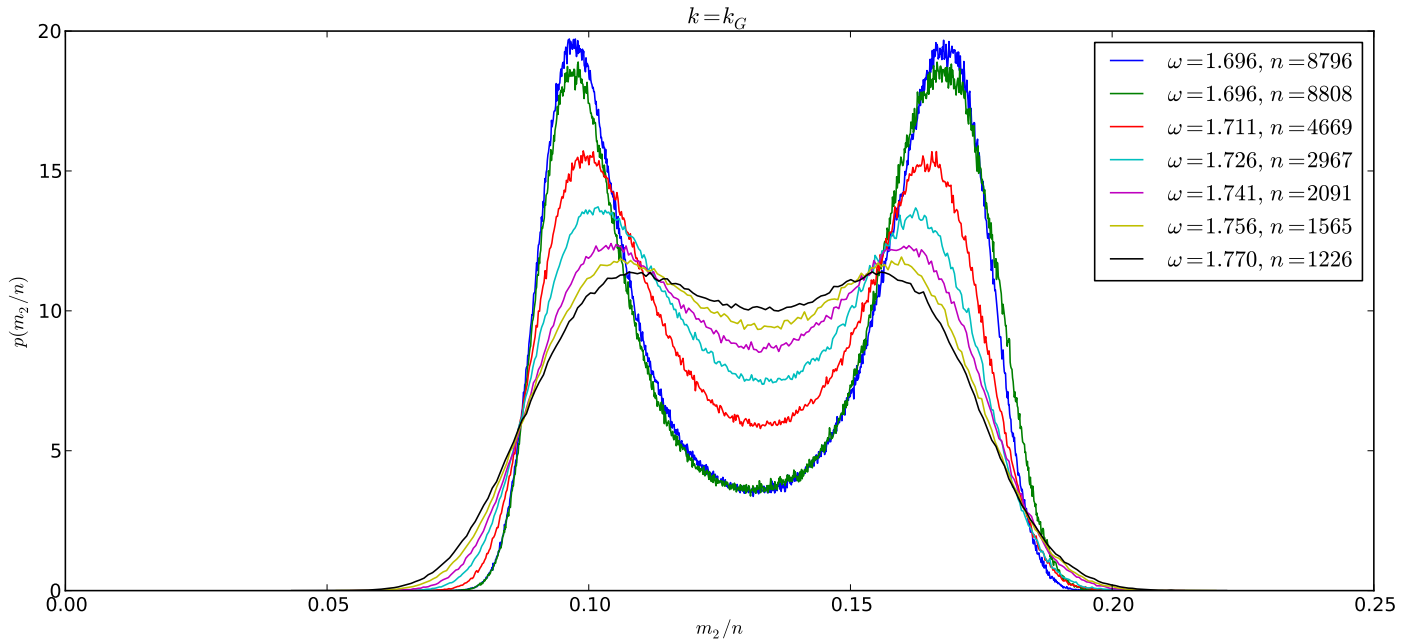


Figure: Energy distribution near the kinetic-growth point

Anomalous scaling

The temperature at which the two peaks are visible converges to the kinetic growth critical point ω_c with a shift exponent ψ, compatible with $1/2$ but the width of the critical region $\Delta\omega_n$ scales to zero and with an exponent $\phi \sim 1$.

$$\omega_{c,n} - \omega_c \sim D\, n^{-1/2}. \tag{3}$$

where $\omega_{c,n}$ is the location of the peak of the specific heat, and the width exponent by

$$\Delta\omega_n \sim E\, n^{-1}. \tag{4}$$

where $\Delta\omega_n$ is the width of the half-height of the specific heat peak.

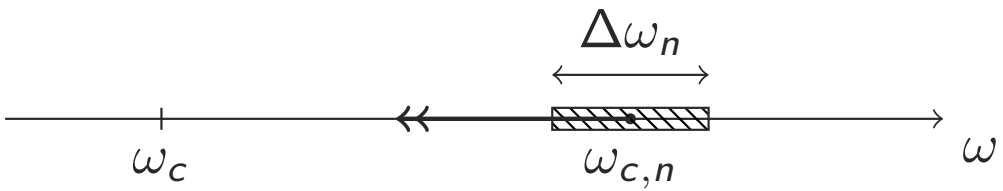


Figure: The observed scaling at $k = k_G$ is such that $(\omega_{c,n} - \omega_c) \gg \Delta\omega_n$.

Specific heat/Fluctuations

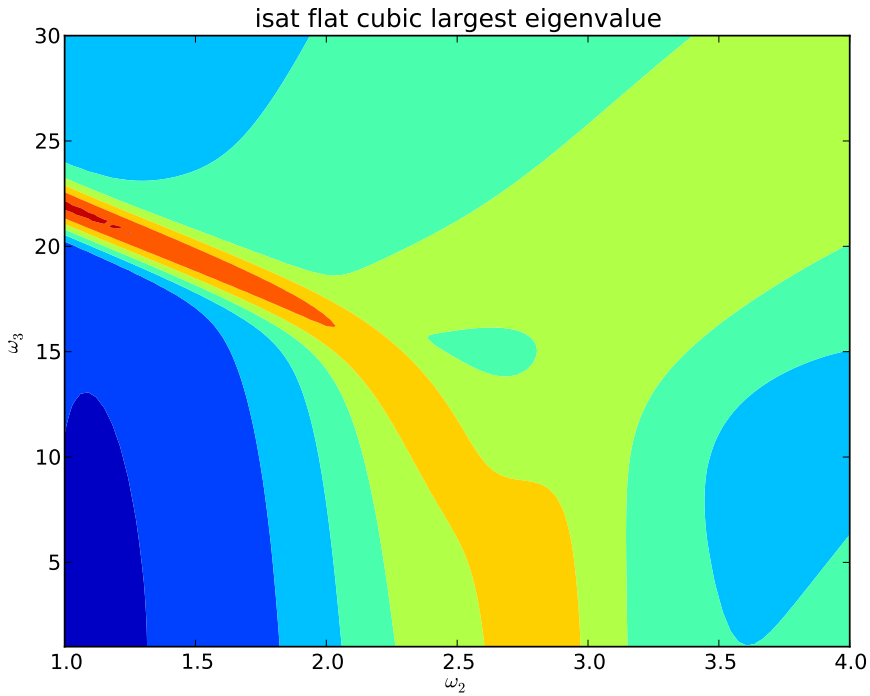
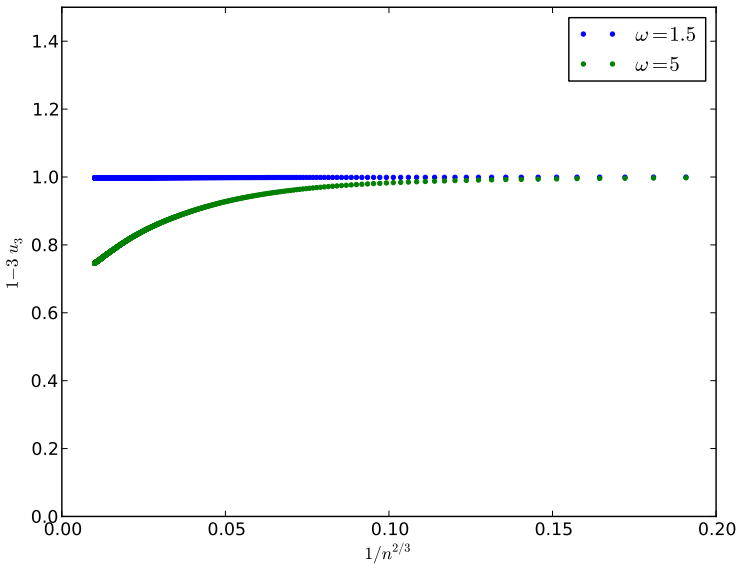
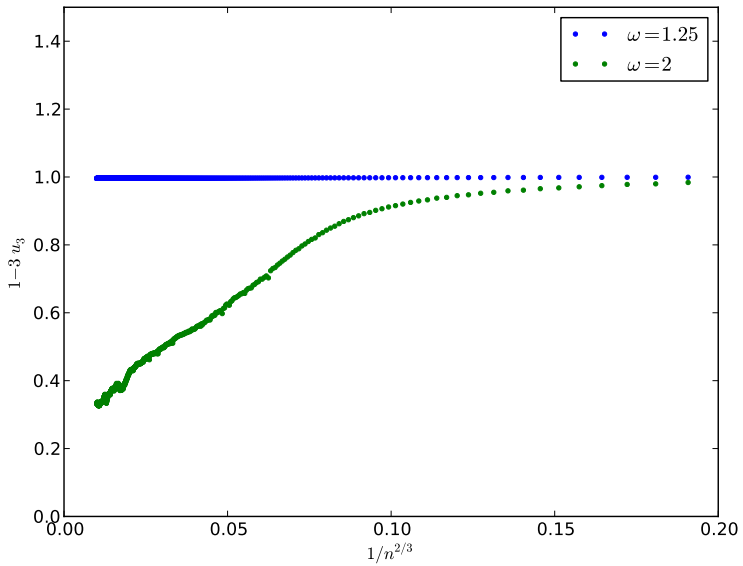


Figure: Density plot of the logarithm of the largest eigenvalue λ_{max} of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length $n = 512$.

Low temperatures



(a) $k = 2$, $\omega = 1.5$ and $\omega = 5$



(b) $k = 7$, $\omega = 1.25$ and $\omega = 2$

Figure: Proportion on steps not involved with triply-visited sites per unit length.

Phase diagram?

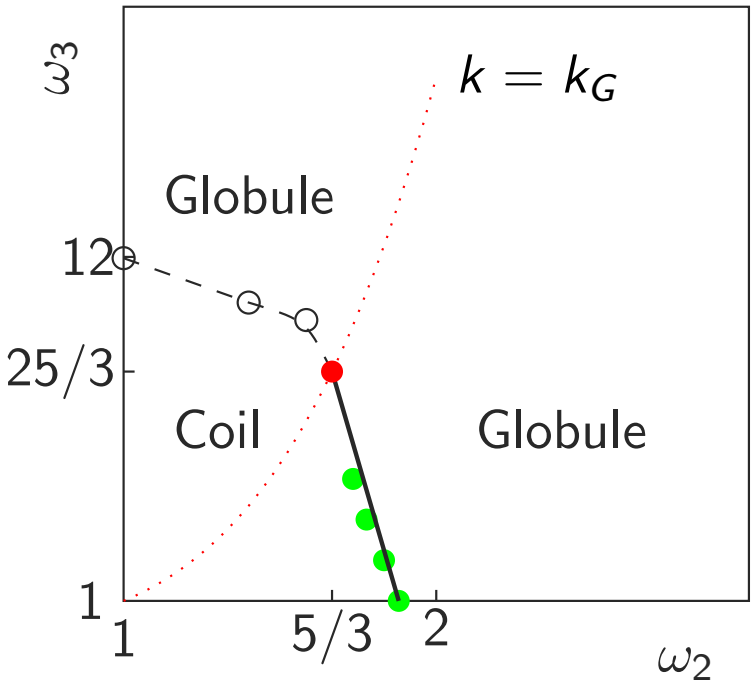


Figure: The conjectured phase diagrams for cubic lattice. Solid lines indicate phase transitions of the second order while the dashed indicates a first-order phase transition. The red dotted line only indicates the k-eISAT model which passes through the KGT point.

Cubic lattice eISAT Conclusions

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

- Two phases: swollen, and globule:
- No crystal-like fully dense phase
- Meeting point (at kinetic growth point) of two phase boundaries seems multi-critical but
- Simulations show over-riding first order behaviour will occur in thermodynamic limit
- Possible because of breakdown of full crossover scaling