Model dependency and anomolous scaling in polymer critical phenomena

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

†MASCOS and Department of Mathematics and Statistics, The University of Melbourne

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

June, 2012

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

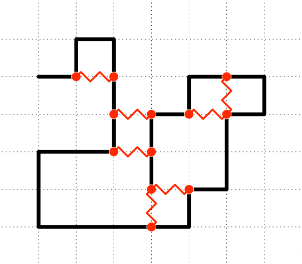
AUSTRALIAN RESEARCH COUNCIL
Centre of Excellence for Mathematics and Statistics of Complex Systems

THE UNIVERSITY OF MELBOURNE

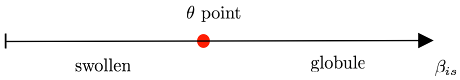
The Canonical Collapsing Polymer Lattice Model

Interacting Self-Avoiding Walk (ISAW)

- *Start with a 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

- 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

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

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

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

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

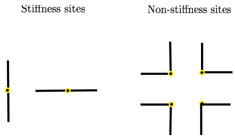
Note that this implies that the specific heat does *not* diverge at the transition (exponent $\alpha\phi$). However, the third derivative of the free energy with respect to temperature will diverge with exponent

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

Adding stiffness to ISAW

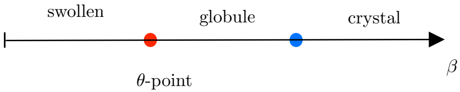
Adding stiffness

- 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

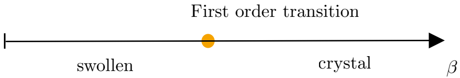


SEMI-FLEXIBLE ISAW

- 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

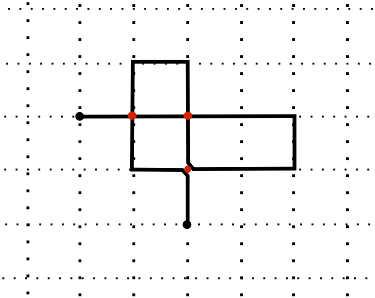
Second order in two dimensions with estimated $\alpha \approx 0.6(2)$

Meeting point

Unknown

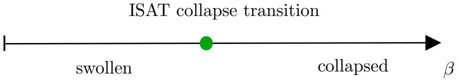
ISAT on the square lattice— different model of polymer collapse

- 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

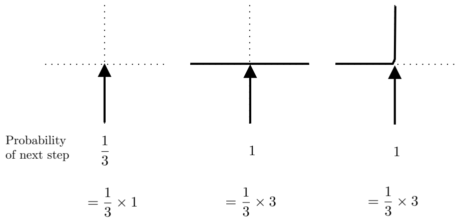
A single phase transition on varying temperature.



- 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 tranistion

Kinetic SAT (KSAT)

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 KSAT scaling

Owczarek and Prellberg (1995) studied KSAT. 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

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

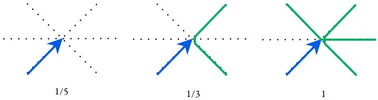
Square lattice ISAT Collapse transition

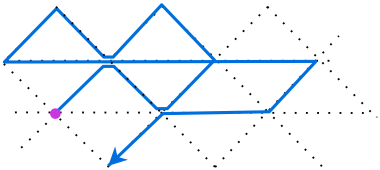
Transfer matrix calculations

- 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!

KINETIC GROWTH TRAILS ON THE TRIANGULAR LATTICE

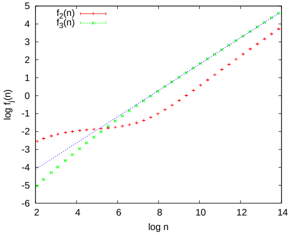




An example of a trail with 13 steps on the triangular lattice. This trail has six singly visited sites, two doubly-visited sites and one triply-visited site (with probability $\frac{1}{5}\frac{1}{3}1$).
This trail is produced by the growth process with probability $(\frac{1}{6})(\frac{1}{5})(\frac{1}{5})(\frac{1}{5})(\frac{1}{5})(\frac{1}{3})(\frac{1}{5})(\frac{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

FLUCTUATIONS IN TRIANGULAR KSAT

Fluctuations demonstrate divergent behaviour



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

Canonical 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

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

Collapse transition for tri-ISAT

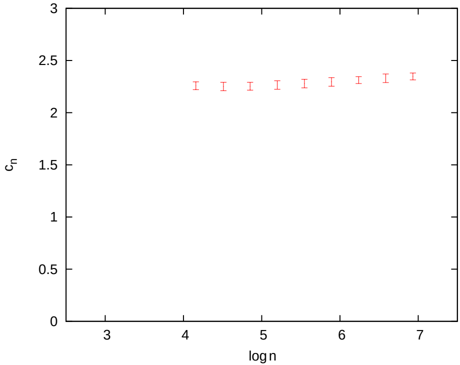


Figure: Plot of the value of the maximum of the specific heat $c_n = \max_\omega c_n^{(2)}$ against $\log n$. This suggests that the specific heat does not diverge as the polymer length is increased.

Free Energy Third Derivative

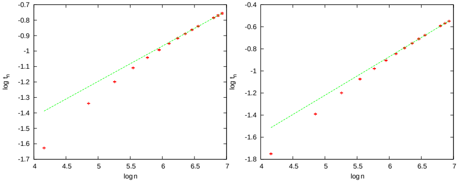


Figure: Plot of the height of the peaks of $t_n^{(2)}(\omega)$, the third derivative of the free energy with respect to temperature against n. The third derivative has two peaks: one positive and one negative in value.

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

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

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 $k = k_{KGT}$

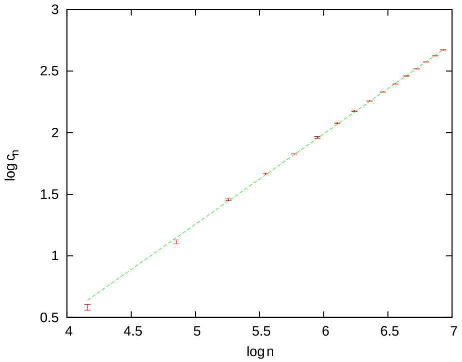


Figure: Plot of the logarithm of $c_n = \max_\omega c_n^{(k_G)}$, the value of the maximum of the specific heat, against $\log n$. The straight line has slope $\alpha\phi = 0.734$.

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

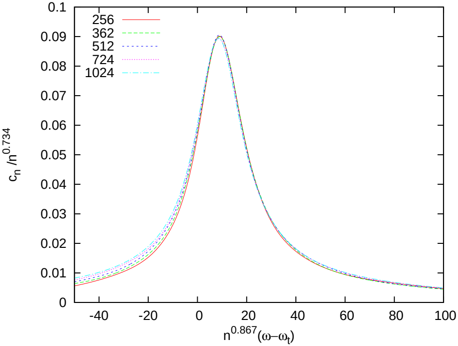


Figure: Scaling plot of the specific heat around the transition temperature, using the exponents from the growth process.

$k = \infty$ – 'TRIPLE' MODEL

Let us now only weight triply visited sites ($\omega_2 = 1, \omega_3 > 1$)

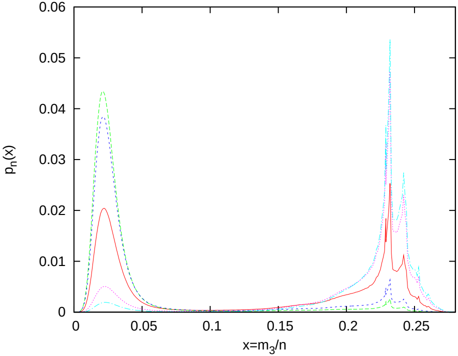


Figure: Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the *Triple* model at temperatures near, and at, the temperature at which the specific heat attains its maximum for length $n = 1024$.

$k = 6$

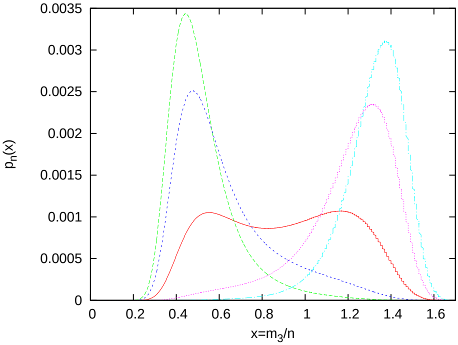


Figure: Plot of the distribution $p_n(m_3/n)$ of triply-visited sites for the $k = 6$ model at temperatures near, and at, the temperature at which the specific heat attains its maximum for length $n = 1024$.

Collapsed phase for canonical model — globule

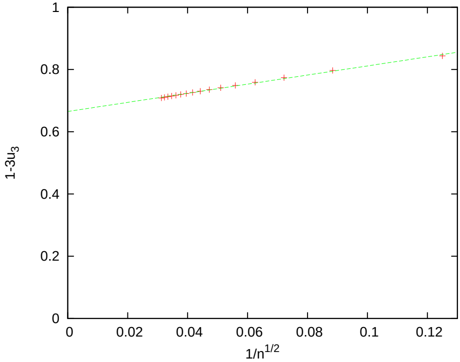


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(\omega_2, \omega_3) = (4, 16)$ in the collapsed liquid-drop-like globule phase. As the length increases this reaches a non-zero value.

A GLOBULE WHEN $k = 0$

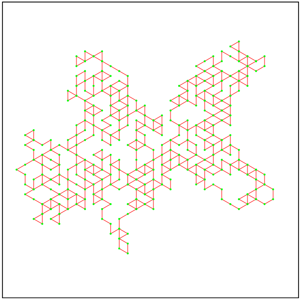


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (5, 1)$, which is in the globule phase: it looks disordered and rather more like a liquid-like globule than a crystal.

COLLAPSED PHASE WHEN $k = 6$

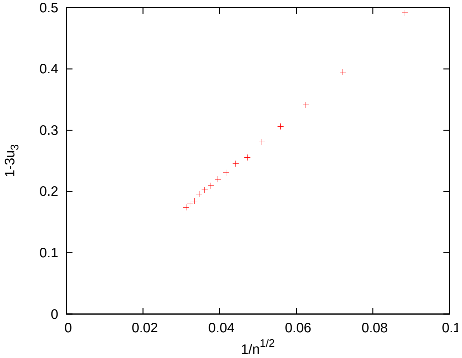


Figure: Plot of $1 - 3u_3(n)$, which measures the proportion of steps that are not involved with triply-visited sites per unit length, against $1/\sqrt{n}$ at a point $(1.58, 15.6)$ in the hypothesised frozen (crystal-like) phase. As the length increases this quantity vanishes.

A 'crystal' in the Triple model

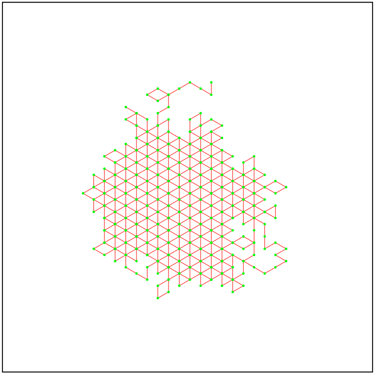


Figure: A typical configuration at length 512 produced at $(\omega_2, \omega_3) = (1, 10)$ which looks like an ordered crystal.

PHASE DIAGRAM

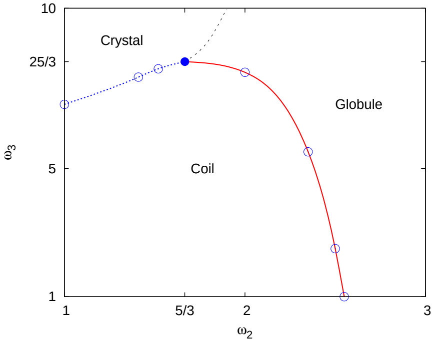


Figure: Schematic of the proposed phase diagram of the extended ISAT model on the triangular lattice. The filled circle is at the location of the kinetic growth point, and the open circles represent estimates of the collapse transition for various values of k.

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

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

Back to ISAW: 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 walk process gives

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

with

$$\zeta = 1.0 \pm 0.5$$

cf. the Edwards model has $\zeta = 3/16$.

eISAT on the Cubic lattice

- *But what about the eISAT model on the cubic lattice ...*
- *The coordination number of the cubic lattice is the same as the triangular lattice*
- *Hence for the cubic lattice the "kinetic growth trail point" in the eISAT model maps to the same location on* $k = k_G = 4.15...$

Cubic lattice k-eISAT with $k > k_G$

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

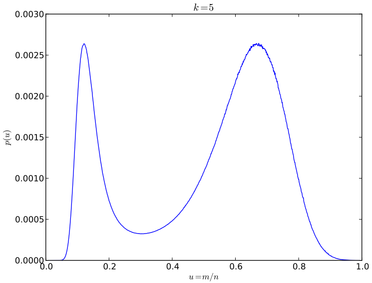


Figure: Energy distribution ($k > k_G$).

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

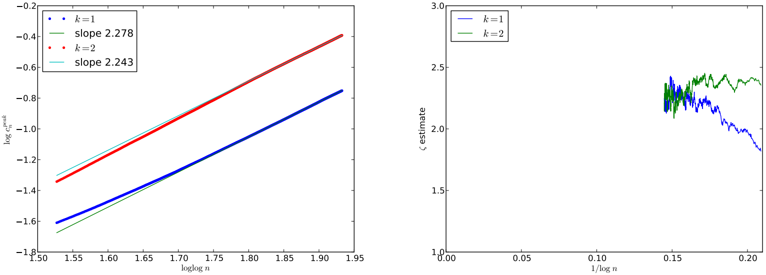


Figure: Specific heat peak scaling (left) and ζ estimates as local derivative (right) for small k.

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 $k = k_G$

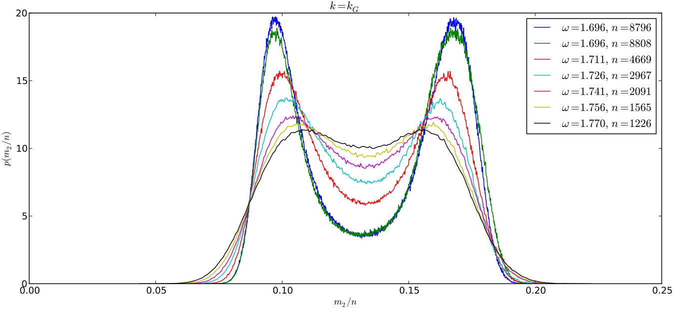


Figure: Energy distribution near the kinetic-growth point

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.

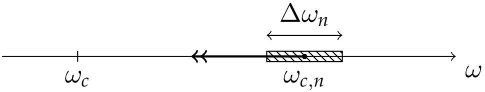


Figure: The observed scaling at $k = k_G$ is such that $(\omega_{c,n} - \omega_c) \gg \Delta\omega_n$.

Specific heat / Fluctuations

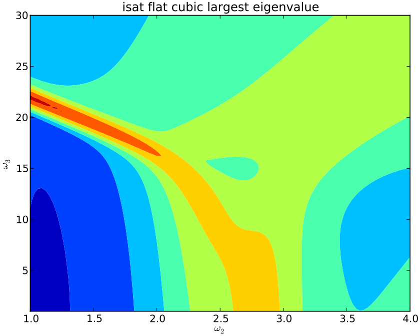
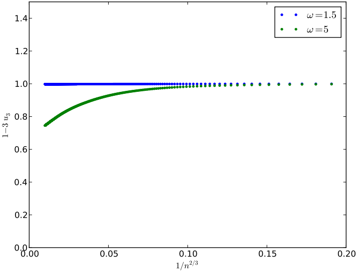
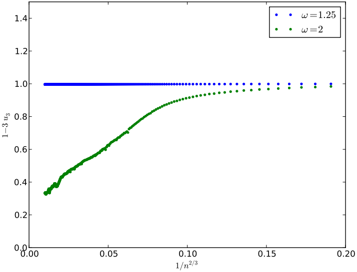


Figure: Density plot of the logarithm of the largest eigenvalue λ_{max} of the matrix of second derivatives of the free energy with respect to ω_2 and ω_3 at length $n = 512$.

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.

Conjectured Phase Diagram

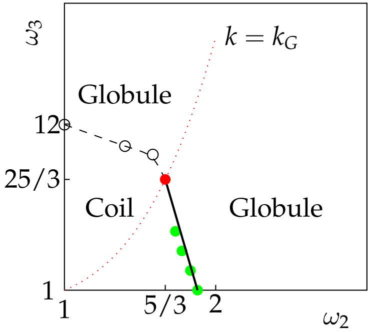


Figure: The conjectured phase diagrams for cubic lattice. Solid lines indicate phase transitions of the second order while the dashed indicates a first-order phase transition. The red dotted line only indicates the *k*-eISAT model which passes through the KGT point.

Cubic lattice eISAT Conclusions

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

- two phases, swollen and globule, as opposed to triangular lattice
- First and second order transitions between swollen and globule phases dependent on the amount of weight given to triply visited sites
- the meeting point of first and second order transition is given by the kinetic growth point
- Anomalous scaling for $k = k_G = 4.15...$ model: with width and shift scaling differently
- the $k = k_G$ model actually exhibits a first order transition

Our results are in press at *Phys. Rev. E*