Monte Carlo Investigation of Lattice Models of Polymer Collapse in Four and Five Dimensions

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- Polymer collapse above the upper critical dimension ($d_u = 3$) is a weak thermodynamic second-order phase transition.
- One finds an apparent first-order phase transition in finite systems due to strong finite-size corrections to scaling.
- We propose to call this scenario a

pseudo-first-order transition.

Int. J. Mod. Phys. **14** (2003), Comp. Phys. Commun. **147** (2002) 629, Physica A **297** (2001) 275, Europhys. Lett. **51** (2000) 602, Phys. Rev. E **62** (2000) 3780, Physica A **260** (1998) 20

Modeling of Polymers in Solution

Polymers = long chains consisting out of smaller units (monomers)

"Coarse-Graining": beads on a chain

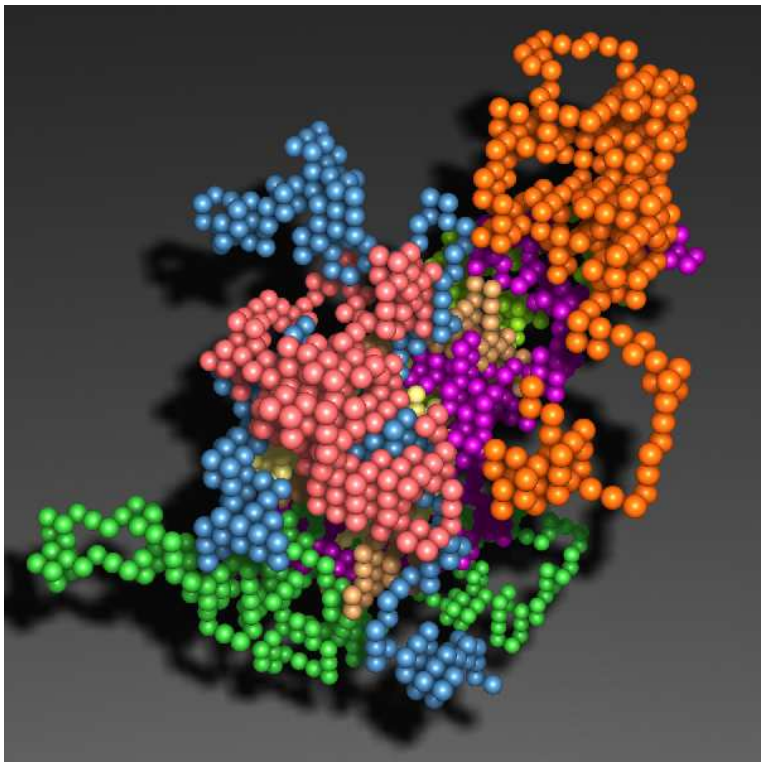
"Excluded Volume": minimal distance between monomers

Contact of monomers with solvent molecules

$\Rightarrow$ effective monomer-monomer-interaction

Good/bad solvent $\Rightarrow$ repelling/attracting interaction

Consequence: chains clump together



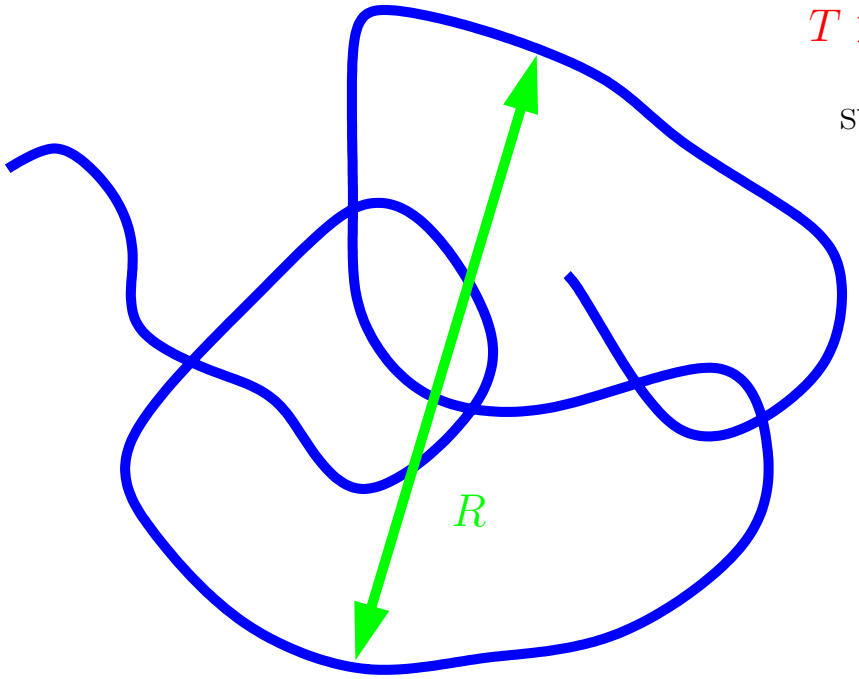
Eight linear polymer chains with 128 monomers each in a bad solvent

(Grassberger, FZ Jülich)

Polymer collapse in a dilute solvent

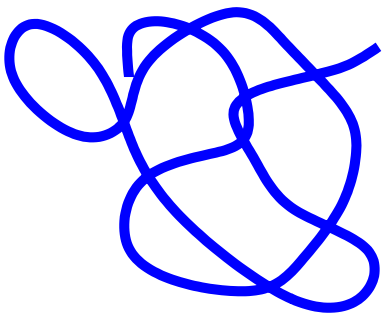
(Coil-Globule Transition, Θ-Point)

length N, spatial extension $R \sim N^{\nu}$



$T > T_c$: good solvent

swollen phase (coil)



$T = T_c$:

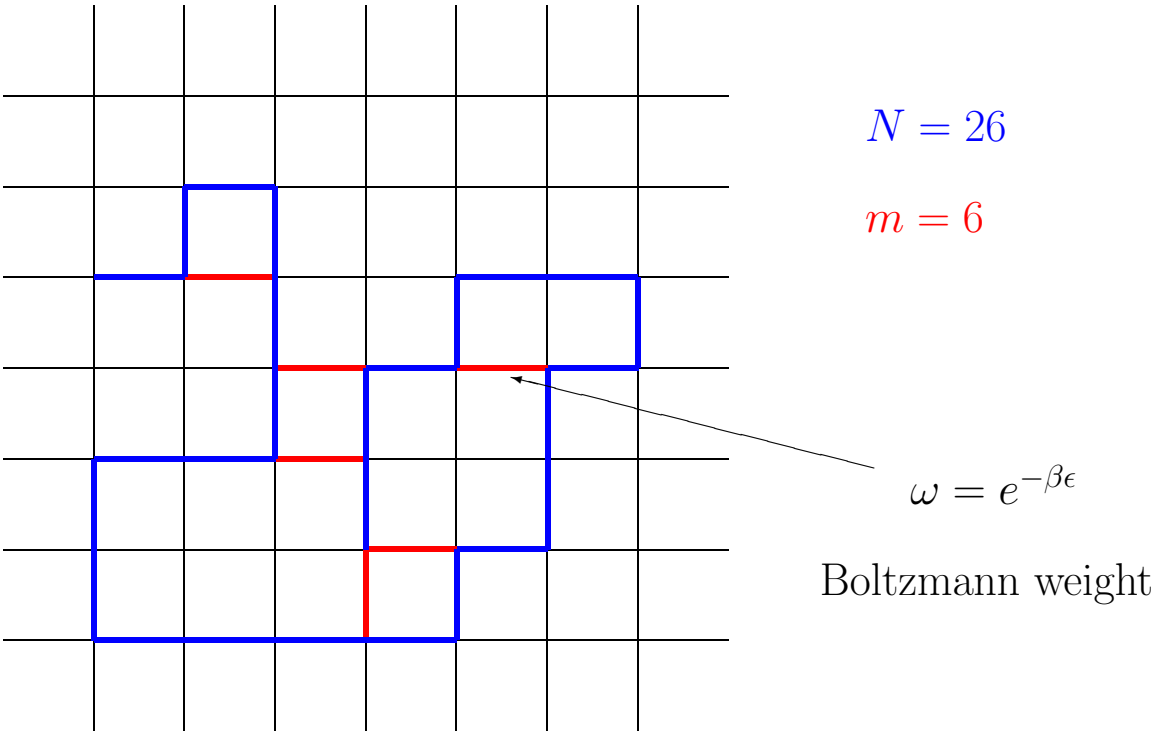
Θ-polymer

$T < T_c$: bad solvent

collapsed phase (globule)

Lattice Model: Interacting Self-Avoiding Walk (ISAW)

- Physical space $\Leftrightarrow$ lattice $\mathbb{Z}^3$ (or $\mathbb{Z}^d$)
- Polymer in solution $\Leftrightarrow$ Self-Avoiding Walk (SAW)
- Quality of solvent $\Leftrightarrow$ nearest-neighbor interactions



Partition function: $Z_N(\omega) = \sum_m C_{N,m}\omega^m$

$C_{N,m}$ number of SAW with length N and m interactions

Thermodynamic limit: $V = \infty$ and $N \to \infty$

Critical Exponents

1. Length scale exponent ν: $R_N \sim N^{\nu}$

d	Coil	Θ	Globule
2	3/4	4/7	1/2
3	0.587 . . . †*	1/2(log)	1/3
4	1/2(log)	1/2	1/4
> 4	1/2	1/2	1/d

* Belohorec and Nickel (1997): 0.58758(7), TP (2001): 0.5874(2)

† Irene Hueter (2002): lower bound $7/12 = 0.58\overline{3}$

2. Entropic exponent γ: $Z_N \sim \mu^N N^{\gamma-1}$

d	Coil	Θ	Globule
2	43/32	8/7	different scaling form
3	1.15 . . .	1(log)	$Z_N \sim \mu^N {\mu_s}^{N^\sigma} N^{\gamma-1}$
4	1(log)	1	$\sigma = (d-1)/d$ (surface)
> 4	1	1	[ALO, TP, PRL **70** (1993) 951]

Surface term: $\kappa_N = \frac{1}{N} \log Z_N \sim \kappa + \kappa_s N^{\sigma-1} + \ldots$

Crossover Scaling at the Θ-Point

$R_N \sim N^{\nu} \mathcal{R}(\Delta T\, N^{\phi})$

ϕ crossover exponent

$Z_N \sim \mu^N N^{\gamma-1} \mathcal{Z}(\Delta T\, N^{\phi})$

specific heat of Z_N: $C_N \sim N^{\alpha}$

$2 - \alpha = 1/\phi$ tri-critical scaling form

Mean Field Theory of the Θ-Point

Balance between "Excluded Volume"–repulsion

and attractive interaction

$\Rightarrow$ polymer behaves like random walk: $\nu = 1/2$, $\gamma = 1$

One expects a weak thermodynamic phase transition

$\Rightarrow$ $\alpha = 0$, i.e. $\phi = 1/2$

($d = 2$: $\phi = 3/7$, $d = 3$: $\phi = 1/2(\log)$, $d > 3$: $\phi = 1/2$)

Why look at $d \geq 4$?

Theoretical predictions for ϕ:

- Mean field theory: $\phi = 1/2$ for $d > 3$

  $(= 1/2$ in $d = 4)$

- Continuous Edwards model (equivalent with field-theoretic formulation): $\phi_E = 2 - d/2$ for $d > 3$

  - Edwards model = Brownian motion

    + suppression of self-intersections + attractive interactions

  - field theory is $\phi^4 - \phi^6$ $O(n)$-model for $n \to 0$

  $(= 0$ in $d = 4)$

- Edwards model predicts a **shift** of the Θ-point by $N^{-\Psi_E}$:

  $$\Psi_E = d/2 - 1 \quad \text{for } d > 3$$

  $(= 1$ in $d = 4)$

- Matching of scaling form for R_N: $\phi = d/2 - 1$

  $(= 1$ in $d = 4)$

Further Motivations ...

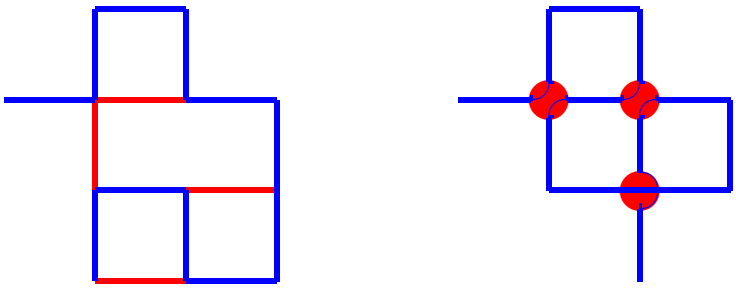
- silent assumption: Θ-point exists.

  But this is not obvious for $d > 3$ ...

  M.A. Moore, J Phys A **10** (1976) 305

- There are indications that the way self-avoidance and interaction enters the modeling influences the critical behavior of the respective Θ-point

vertex avoidance (Walks) $\Leftrightarrow$ edge avoidance (Trails)



nearest-neighbor interaction $\Leftrightarrow$ contact interaction

open questions, unclear theory $\Rightarrow$ simulations of lattice models for polymer collapse, ISAW and ISAT, on $\mathbb{Z}^4$ and $\mathbb{Z}^5$

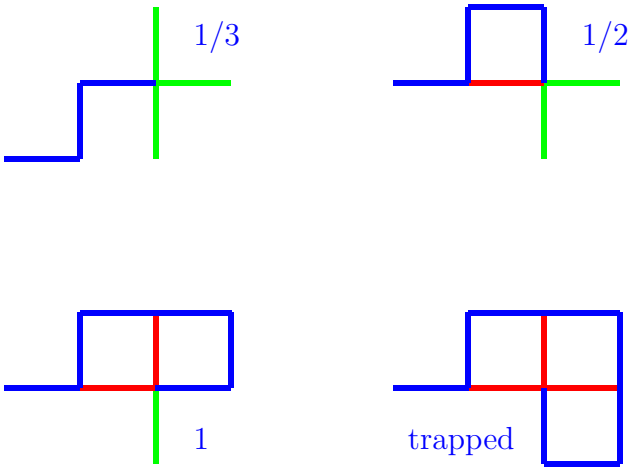
PERM – "Go with the Winners" Monte-Carlo

PERM = Pruned and Enriched Rosenbluth Method

Grassberger, Phys Rev E **56** (1997) 3682

(improvements possible, see e.g. Hsu *et. al.*, `cond-mat/0209363`)

Rosenbluth Method: kinetic growth



Observation: kinetic growth weights and interactions balance each other at suitable temperatures (near the Θ-point?)

Enrichment: too large weight

→ make copies of configuration (and adjust weight)

Pruning: too small weight

→ remove configuration occasionally (and adjust weight)

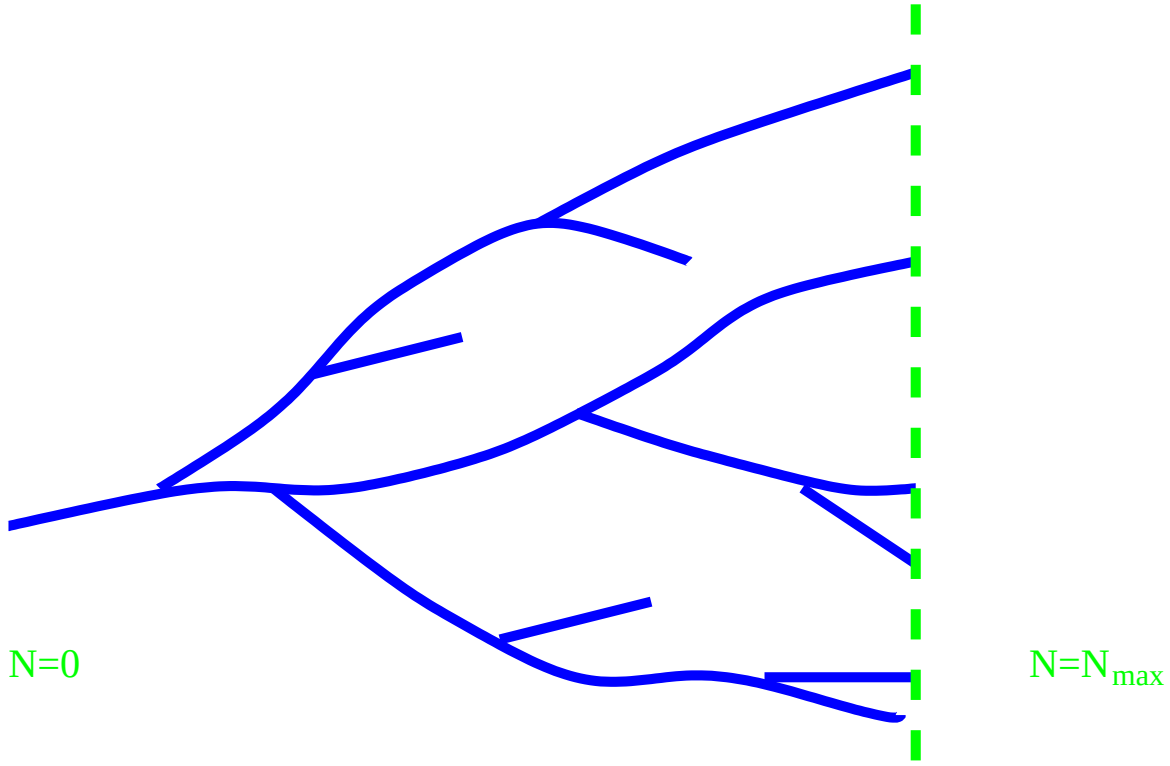
PERM – CONTINUED

Kinetic growth is close to the Θ-point (for d large)

$\longrightarrow$ PERM well suited for simulation of polymer collapse

Disadvantage: enrichment creates correlated configurations

$\longrightarrow$ error estimation *a priori* impossible, *a posteriori* difficult



All configurations in a tour are correlated

Cost of simulation for 4d ISAW (600MHz Dec Alpha):

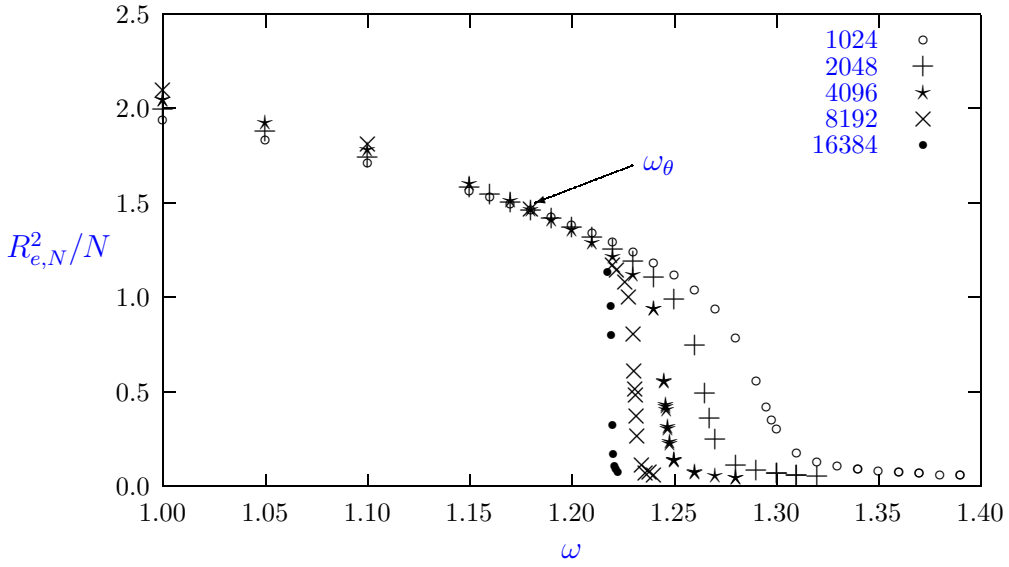
10^7 configurations with $N_{max} = 16384$ in 2 weeks

Further applications for PERM:

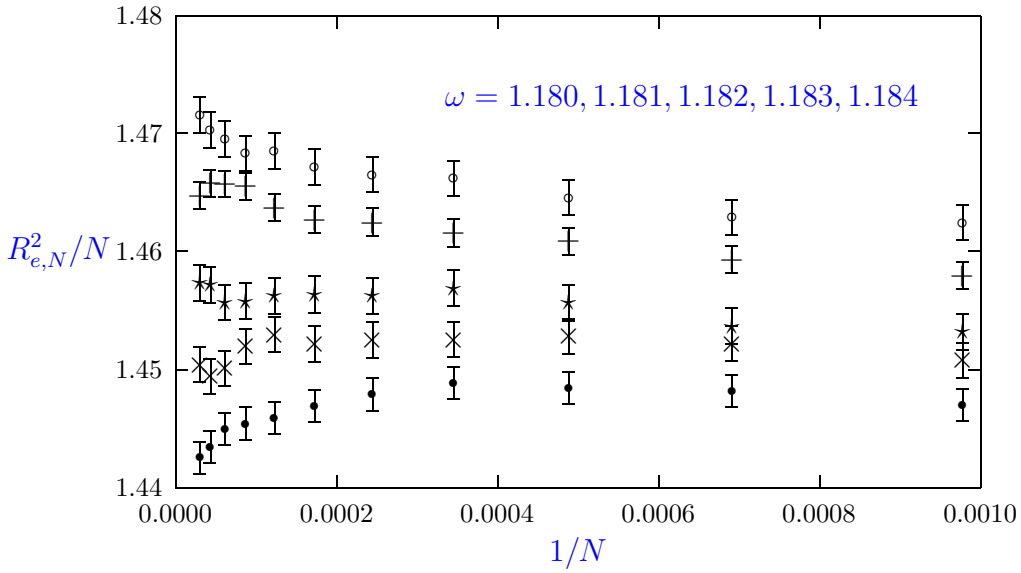
branched polymers, DNA, proteins, percolation, ...

4D ISAW Simulations: End-to-End Distance $R^2_{e,N}$

$R^2_{e,N}/N$ as function of the temperature variable ω



- One finds a Θ-point with $R^2_{e,N}/N$ constant
- Collapse region and Θ-region are well separated!

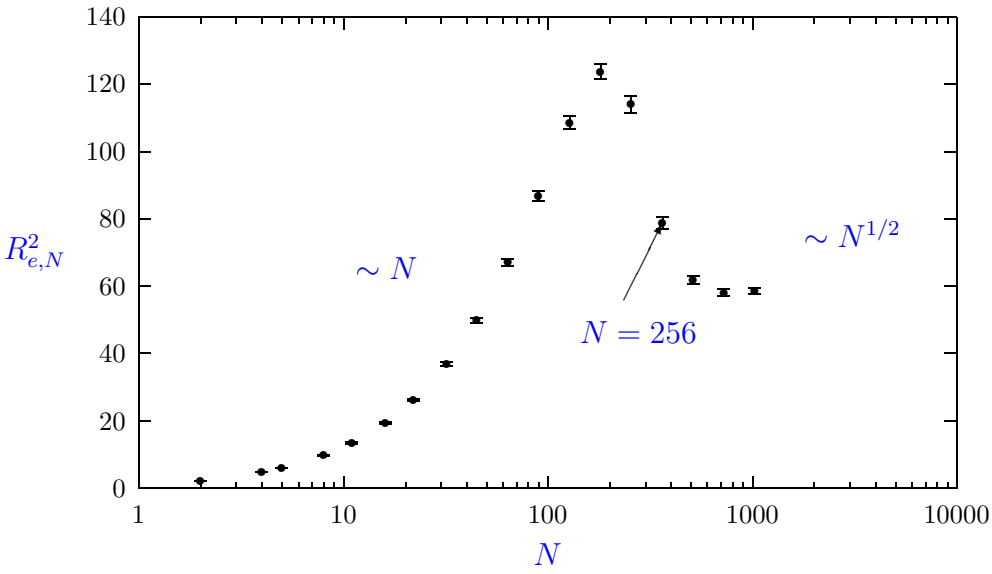


Θ-point determination: $\omega_\theta = 1.182(1)$

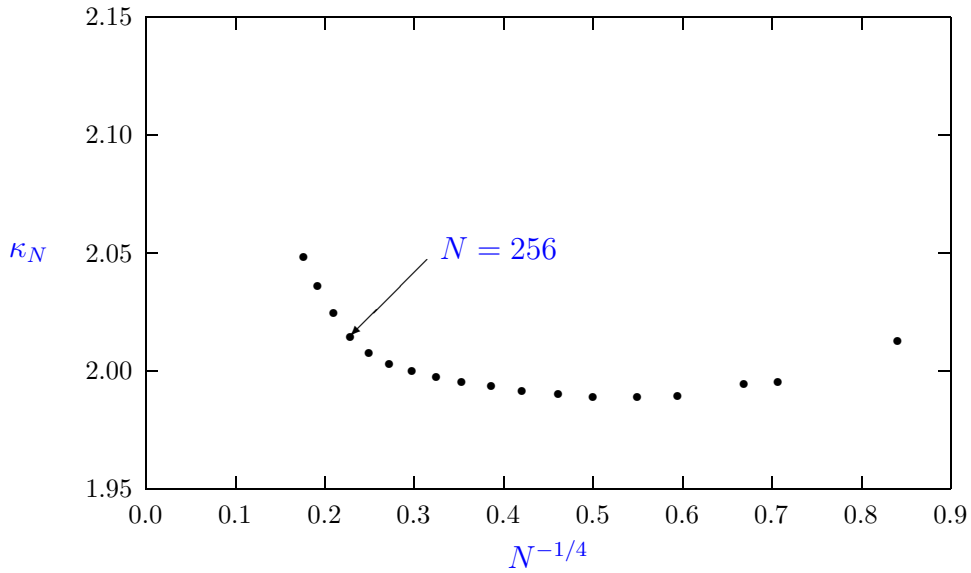
4D ISAW Simulations: The Collapsed Phase

$\omega = 1.40 > \omega_\theta$ fixed:

- Change of $R^2_{e,N}$ in N is not monotone

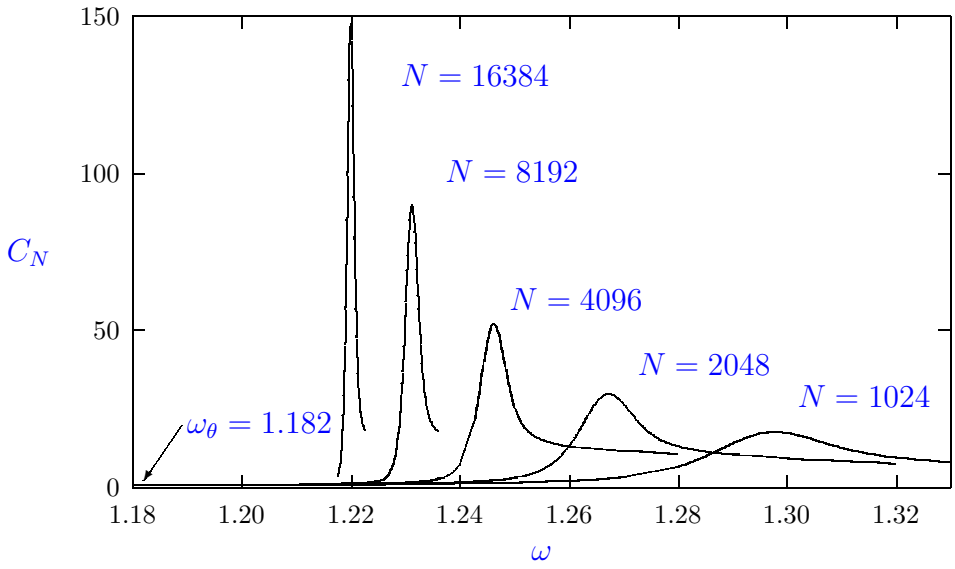


- Surface correction term $\kappa \sim \kappa + \kappa_s N^{-1/4}$?

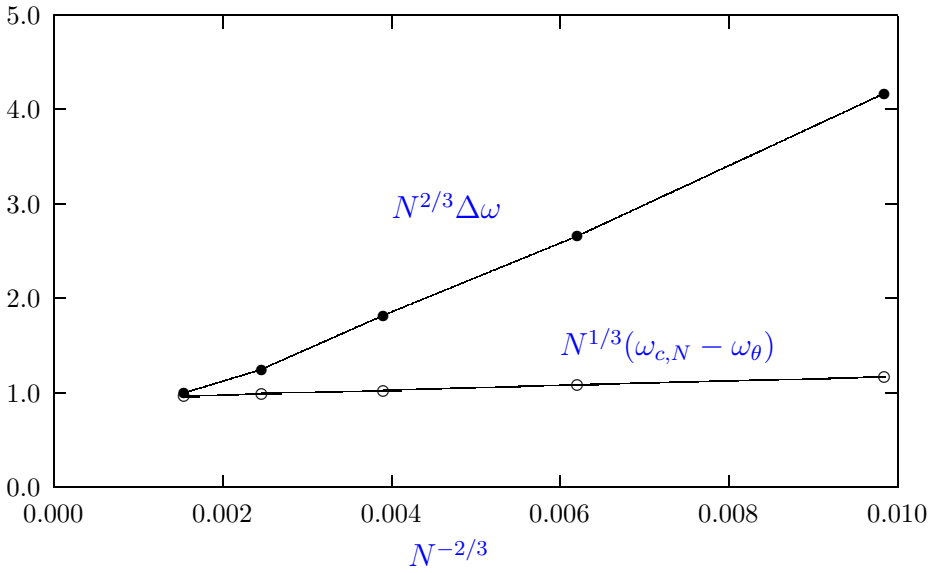


4D ISAW Simulations: the Specific Heat

- Collapse region and Θ-region are well separated!



- Scaling behavior of the transition: width $\neq$ shift



$$\omega_{c,N} - \omega_\theta \sim N^{-1/3} \qquad \Delta\omega \sim N^{-2/3} \ (?)$$

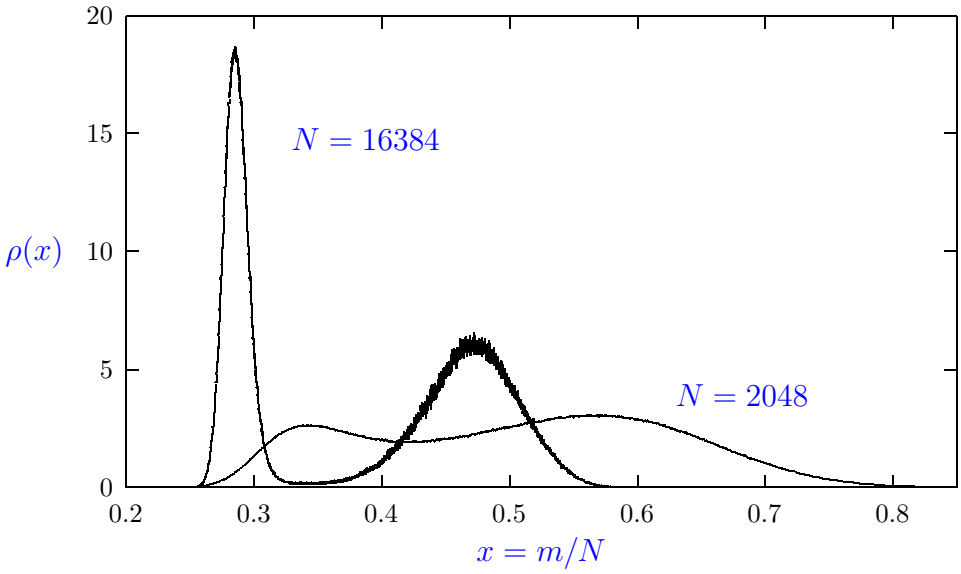
Cannot be explained by conventional tri-critical scaling form!

4D ISAW Simulations: Internal Energy Distribution

A surprising, unexpected result:

- The internal energy histogram near the collapse shows a bimodal distribution!

  ($\Rightarrow$ First-Order Phase Transition?!?)



- The bimodality becomes stronger with increasing system size

  $\Rightarrow$ no disappearing finite-size crossover effect

Mean Field Theory of Khokhlov

(Based on works of Lifshitz and Grosberg in $d = 3$)

Khokhlov, Physica A **105** (1981) 357

- Consider effect of a surface term in the free energy

$$F_N = F_{bulk} + F_{surface}$$

- classical mean field theory predicts

$$F_{bulk} \sim -N(\Delta T)^2$$

- extended self-consistent mean field theory predicts

$$F_{surface} \sim R^{d-1}\sigma$$

  - globule radius $R \sim (N/|\Delta T|)^{1/d}$
  - surface tension $\sigma \sim (\Delta T)^2$

Conclusion:

$$F_N \sim -N(\Delta T)^2 \left[1 - |\Delta T_c/\Delta T|^{(d-1)/d}\right]$$

with $\Delta T_c \sim N^{-1/(d-1)}$

Predictions of the Khokhlov Theory

- Shift of the transition

$$\omega_{c,N} - \omega_\theta \sim N^{-1/(d-1)} \qquad (-1/3 \text{ in } d = 4)$$

- Width of the transition

$$\Delta\omega \sim N^{-(d-2)/(d-1)} \qquad (-2/3 \text{ in } d = 4)$$

- Heat of the transition

$$\Delta U \sim N^{-1/(d-1)} \qquad (-1/3 \text{ in } d = 4)$$

- Height of specific heat peak

$$C_{max} \sim N^{(d-3)/(d-1)} \qquad (1/3 \text{ in } d = 4)$$

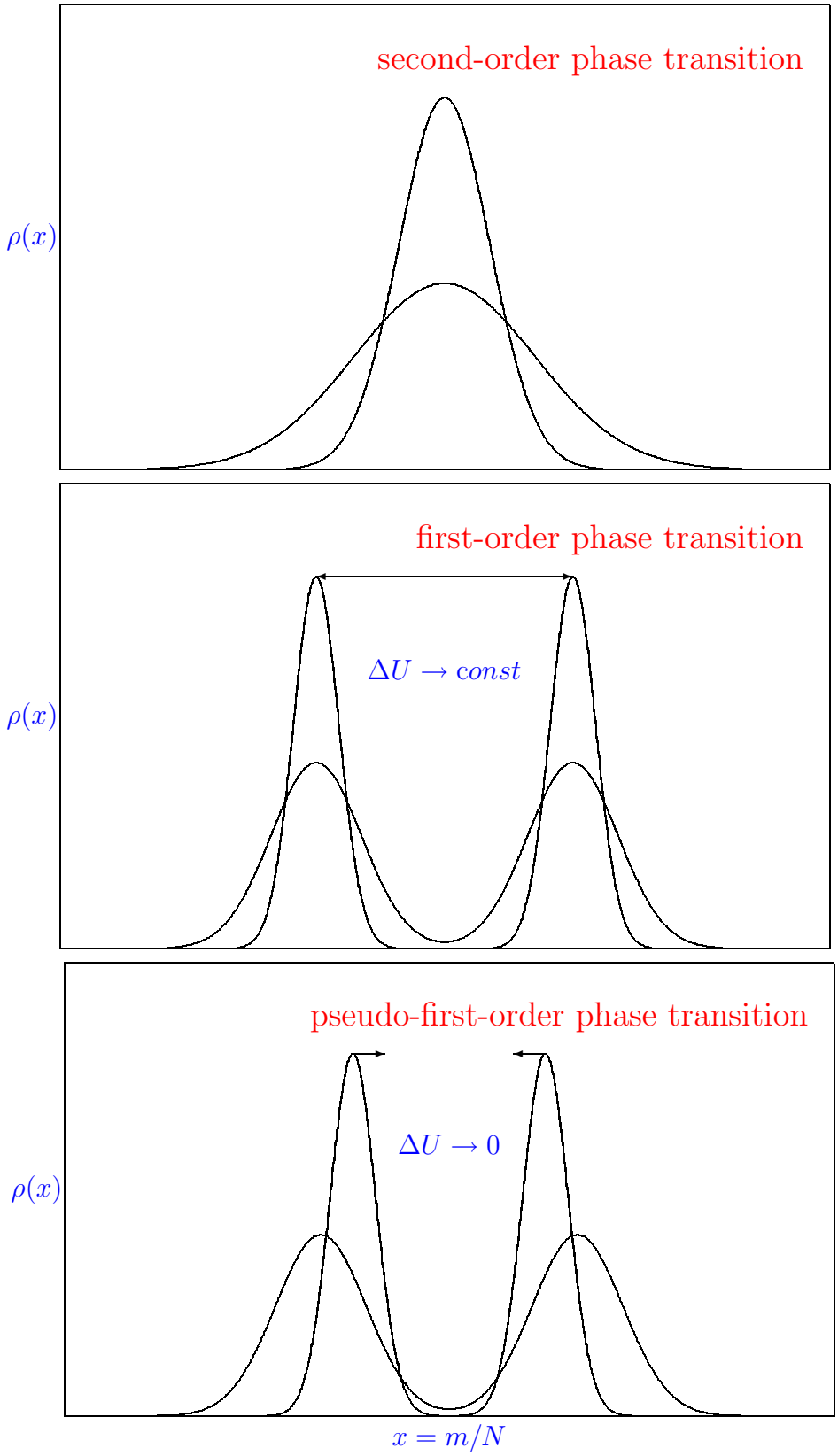
Conclusion:

Pseudo-First Order Transition

- A sharp transition with aspects of a first-order phase transition (e.g. the heat of the transition ΔU is released in a relatively small temperature range $\Delta\omega$)

- We find a classical second-order phase transition in the thermodynamic limit.

Alternative Interpretation: Internal Energy Distribution



Implications for Scaling

- Conventional scaling breaks down:

  one needs an extended scaling form

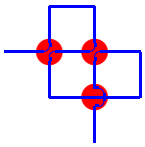
$$R_N(T) \sim N^{\nu} \overbrace{\mathcal{R}((T_\theta - T)\, N^{\phi})}^{\Theta\text{-point}} \overbrace{\mathcal{S}((T_{c,N} - T)\, N^{\phi_c})}^{\text{collapse}}$$

  with

$$T_\theta - T_{c,N} \sim N^{-\psi}$$

  i.e. two further exponents for the collapse

- Relevance for three-dimensional models:

  Consider trails with contact interactions  on the diamond lattice

  Conflicting results:

  – existence of a Θ-point (second-order transition)

  Prellberg, Owczarek, Phys Rev E **51** (1995) 2142

  – bimodal energy distribution (first-order transition)

  Grassberger, Hegger, J Phys A **29** (1996) 279

  This work opens up a possible new scenario

Comparison ISAW $\leftrightarrow$ ISAT

Motivation:

- Physically relevant open questions in d=3
- Testing of validity of theoretical approaches

Mean field theory predictions:

- An important parameter is

$$\frac{v}{a^d}$$

  v effective volume of a monomer

  a distance between two monomers on the chain

- influence on scaling behavior:

$$\omega_{c,N} - \omega_\theta \sim \left(\frac{a^d}{Nv}\right)^{1/(d-1)}$$

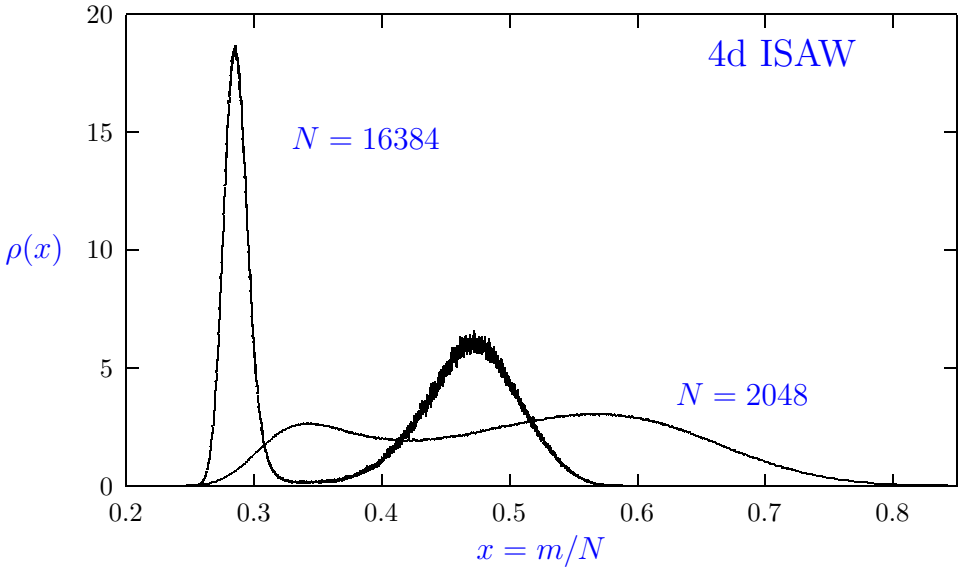
Interpretation for ISAW $\leftrightarrow$ ISAT:

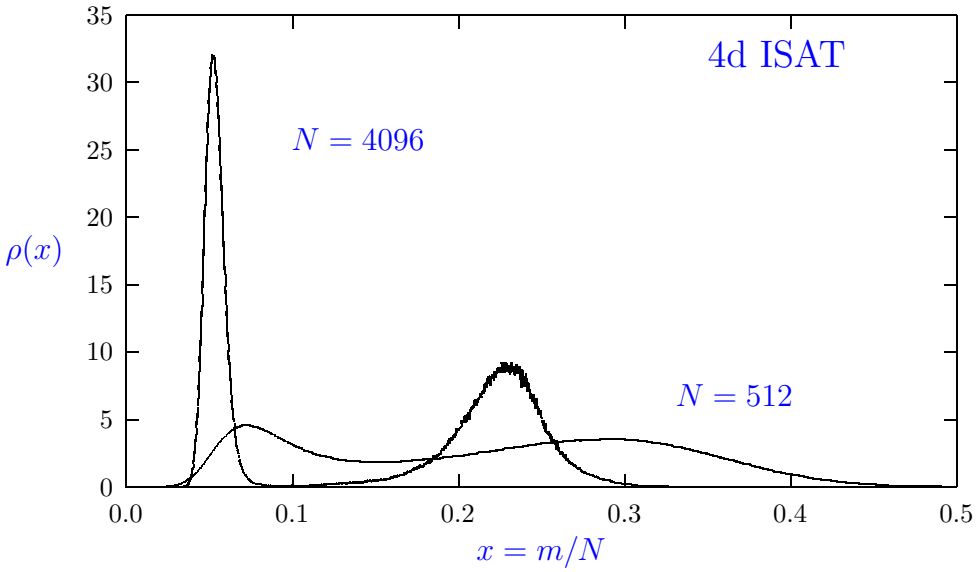
- a lattice constant
- Nearest neighbor interaction $\leftrightarrow$ contact interaction:

$$v_{SAW} >> v_{SAT}$$

Simulations: 4d ISAW ↔ 4d ISAT

- Bimodality in ISAT at much smaller system sizes





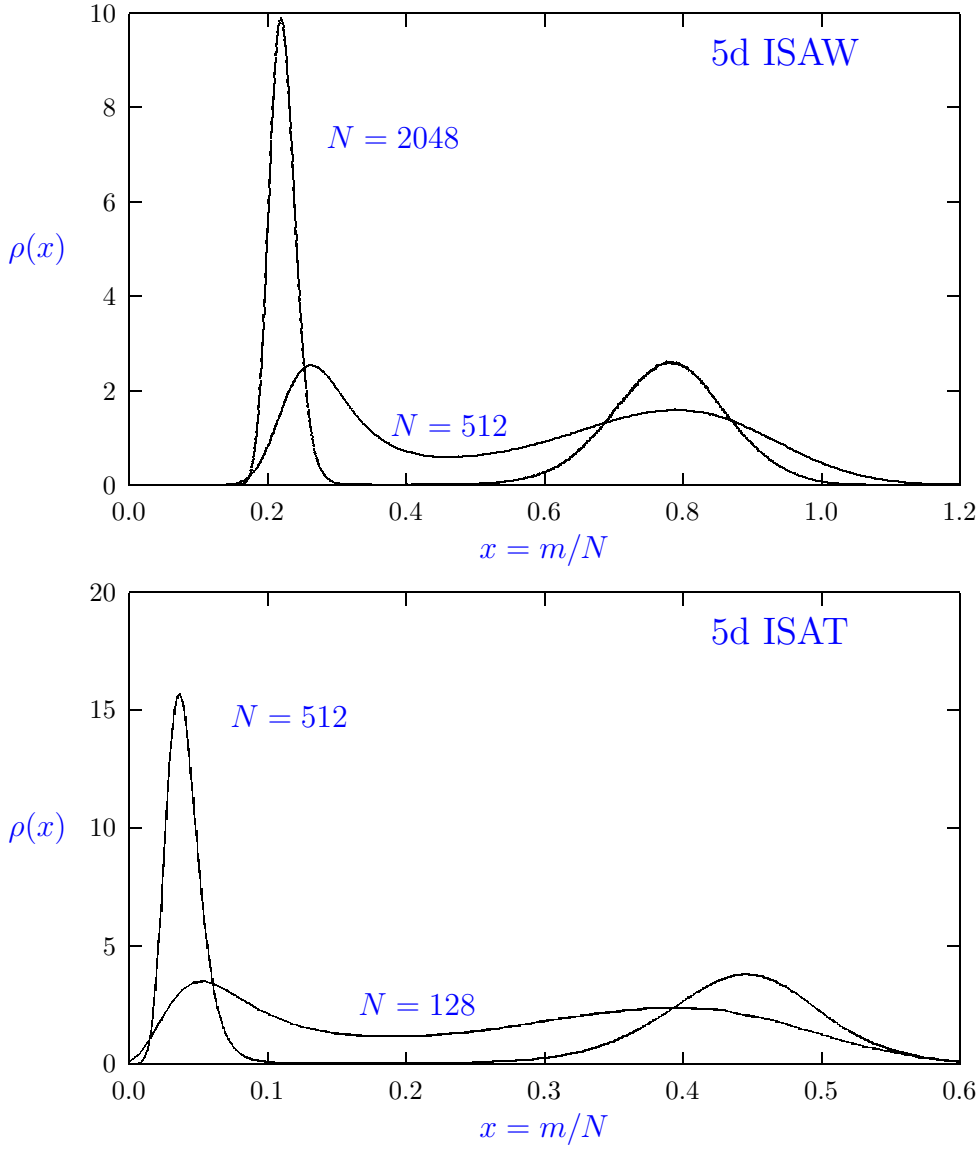
- A comparison shows

$$\frac{v_{SAT}}{v_{SAW}} \approx 0.03$$

Simulations: 4 Dimensions $\leftrightarrow$ 5 Dimensions

- Surface effects more pronounced:

  bimodality appears at even smaller system sizes



- Peak distance does not (yet?) decrease as $N^{-1/4}$

  Need $R >>$ lattice spacing for true asymptotics ($4^5 = 1024$)

Summary

- Existence of a collapse transition in $d \geq 4$
- Θ-point has Gaussian statistics
- Collapse transition is well separated from Θ-point
- Khokhlov mean field theory applies:
  - second-order phase transition with strong finite-size corrections
  - At fixed system size, the phase transition appears to be of first-order

Suggestion:

Pseudo-First Order Transition

Are there other systems which show this kind of behavior?