Universality of Crossover Scaling for the Adsorption Transition of Lattice Polymers

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Recent Developments in Computer Simulational Studies in Condensed Matter Physics, University of Georgia, February 2018

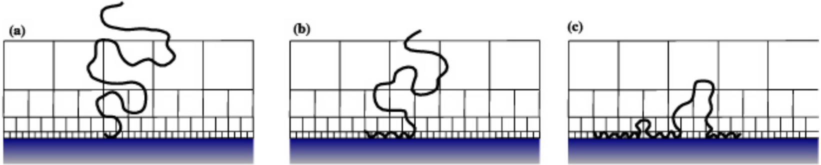
Adsorption of polymers

Examples:

- adhesion
- wetting
- surface coating
- adsorption chromatography

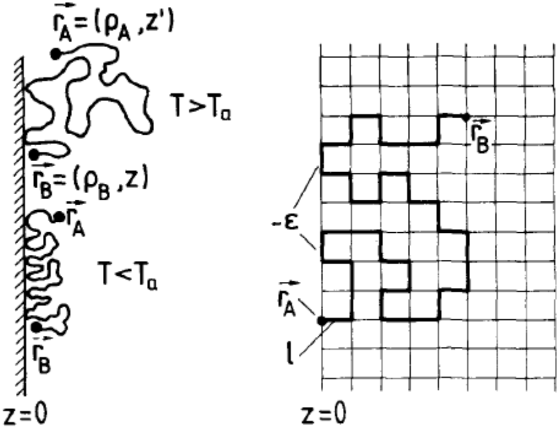
Motivation:

- numerical vs. field theory results
- universality classes and dimensions
- surface effects



O'Shaugnessy & Vavylonis, *J. Phys.*, 2004

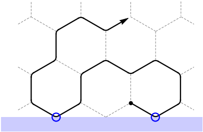
Adsorption of polymers



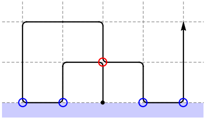
Eisenriegler, Kremer & Binder, *J. Chem. Phys.*, 1982

Lattice models - I

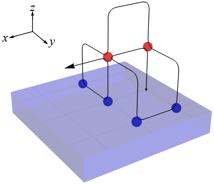
- SAWs are canonical model of lattice polymers - excluded volume of polymer
- R&R weighting for Monte-Carlo simulation
- extensions to interacting systems, SATs, grooves, directed walks etc.
- different universality classes for SAWs and SATs (?)



(a)



(b)

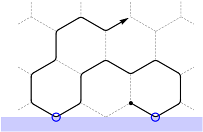


(c)

Lattice models - II

- single polymer; one end attached; dilute bulk solution
- R&R weighting for Monte-Carlo simulation
- microcanonical parameters: length n, energy m,...
- surface-monomer interaction energy ϵ
- weight $\kappa = \exp(\epsilon / k_B T)$

$$Z_n = \sum_{\text{walks}} \kappa^m$$



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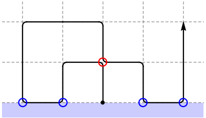

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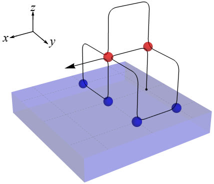

(c)

Finite-size scaling

- Thermodynamic limit: $u \equiv \partial F / \partial T \sim t^{1-\alpha}$
- Finite system at given temperature: $u_n \equiv \langle m \rangle / n \sim n^{\phi - 1}$
- ϕ: controls no. of contacts with surface

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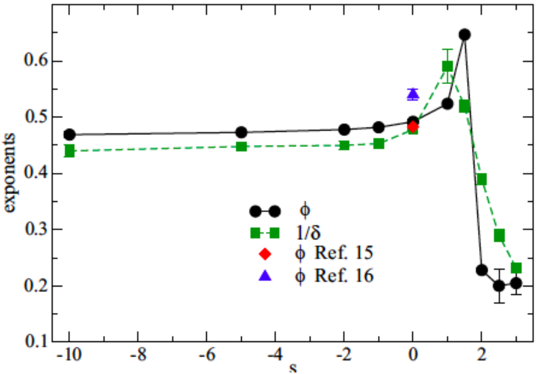
- Thus: $\phi = 1/\delta$
- no problem in 2D, debate in 3D
- universality with respect to interaction

Non-universality for 3d ISAW?

"... suggest that the critical line does not seem to be universal under general solvent conditions"



Plascak, Martins & Bachmann, PRE **95** 050501(R), 2017

FlatPERM algorithm

- Outputs estimated microcanonical density of states, $W_{n,m}$

$$Z_n(\kappa) = \sum_m \kappa^m W_{n,m} \quad , \quad \langle Q \rangle = \frac{1}{Z_n} \sum_m \hat{Q}(m) \kappa^m W_{n,m}$$

- R&R weighting: $W_{n,m} \propto$ no. available steps
- prune/enrich cycle (Grassberger 1997)
- flattening histogram to access all parts of energy space
- athermal; all lengths up to some N_{max}

Simulations

Table: Details of flatPERM simulations. In all cases the number of samples and effectively independent samples is the average of 10 independent runs.

Lattice	Walks/ trails	Max length	Iterations	Samples at max length	Ind. samples max length
hex	SAW	4096	1.8×10^7	2.3×10^9	1.0×10^7
hex	SAW	1024	5.5×10^5	2.0×10^{10}	2.6×10^8
squ	SAW	1024	3.7×10^5	3.9×10^{10}	3.2×10^8
squ	SAT	1024	3.7×10^5	3.9×10^{10}	3.1×10^8
sc	SAW	1024	4.4×10^5	3.5×10^{10}	5.4×10^8
sc	SAT	1024	4.4×10^5	3.4×10^{10}	5.9×10^8

Extracting exponents

FSS form: $u_n \sim n^{\phi-1} f_u^{(0)}(tn^{1/\delta})[1 + n^{-\Delta} f_u^{(1)}(tn^{1/\delta}) + \ldots]$

- **direct**: extract ϕ as leading order term; $\phi \sim 1 + \log(u_n/u_{n/2})$
- **Gamma**: extract $1/\delta$ from $\Gamma_n \equiv \partial \log u_n / \partial T \Rightarrow \max \Gamma_n \sim n^{1/\delta}$

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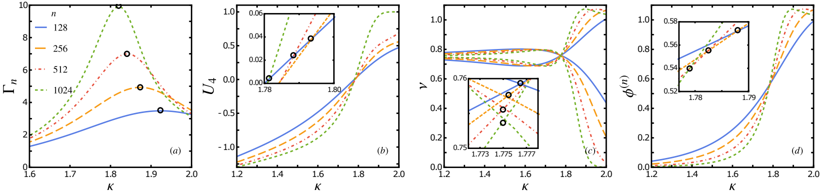
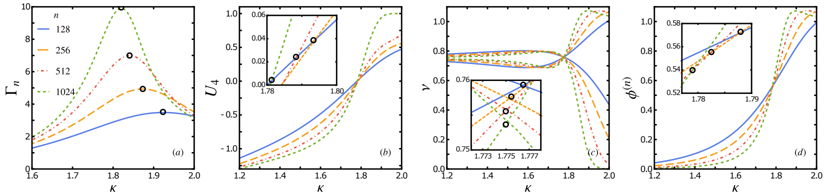
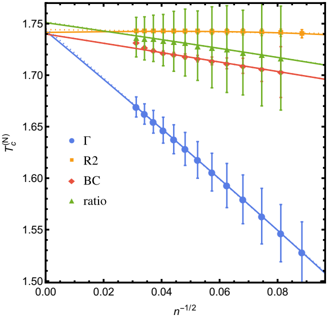
- **R2**: Universal value of Flory exponent ν of polymer size in each direction
- **BC**: Universal value of Binder cumulant $U_4 = 1 - \langle m^4\rangle/3\langle m^2\rangle^2$
- **ratio**: crossover of direct ϕ curves

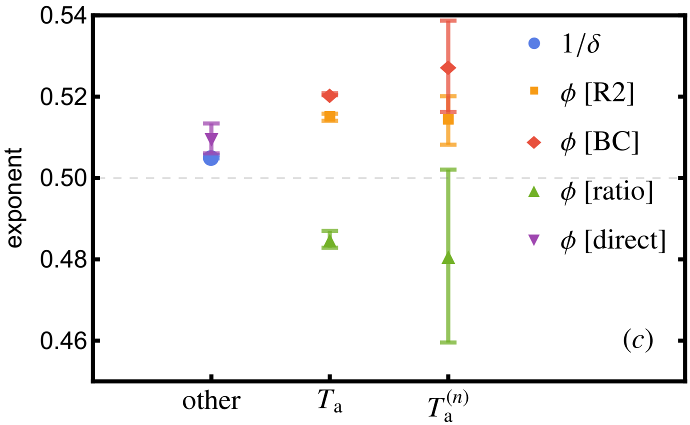


Square lattice SAWs: Critical temperatures





Square lattice SAWs: Exponent results



All 2D lattices: exponents

- hexagonal lattice SAW
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  at exact $T_c = 1/\log(1+\sqrt{2})$
- square lattice SAT
- square lattice repulsive ISAT
  (a. k. a. SAW)

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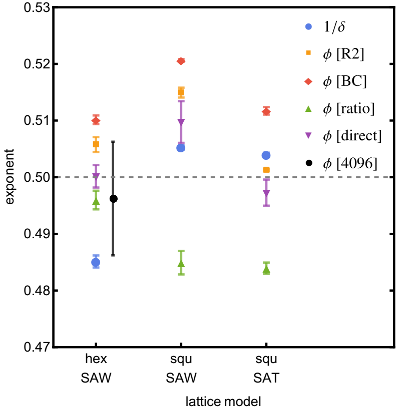

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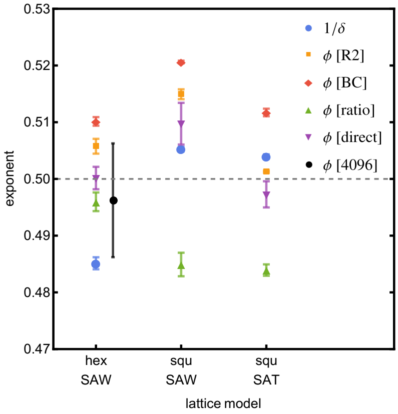
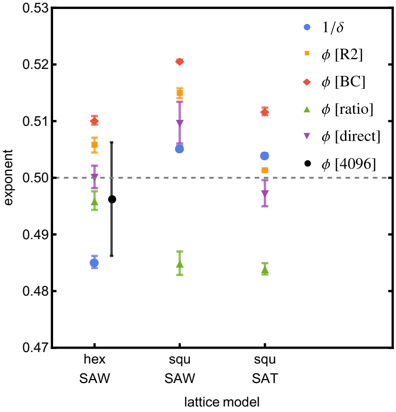


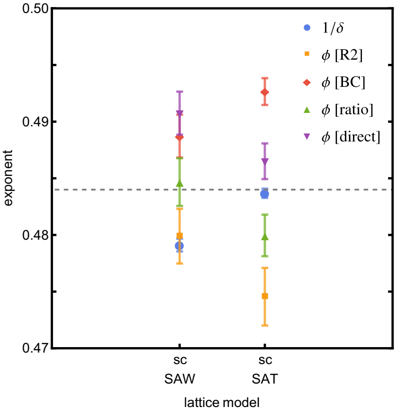
averaging of "independent estimates": $\phi_{2D}\ [= 1/\delta] = 0.501(2)$

All lattices: exponents

2D



3D



$\phi_{2D}\ [= 1/\delta] = 0.501(2)$

$\phi_{3D}\ [= 1/\delta] = 0.484(4)$

Summary & Outlook

Conclusion

- $\phi \neq 1/\delta$ not confirmed
- $\phi_{\mathrm{3D}} < 1/2$ confirmed; i.e. not superuniversal
- variation of ϕ with interaction not confirmed*
- statistical error $<$ systematic error
- flatPERM good for accessing enough parameter space for this problem; still has standard limitation of finite size

Future questions

- closer look at varying interaction strength but with trails*
- other interactions/lattices/models

Article: PRE **97** 022503, 16 Feb 2018