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Partition function zeros and finite size scaling for polymer adsorption

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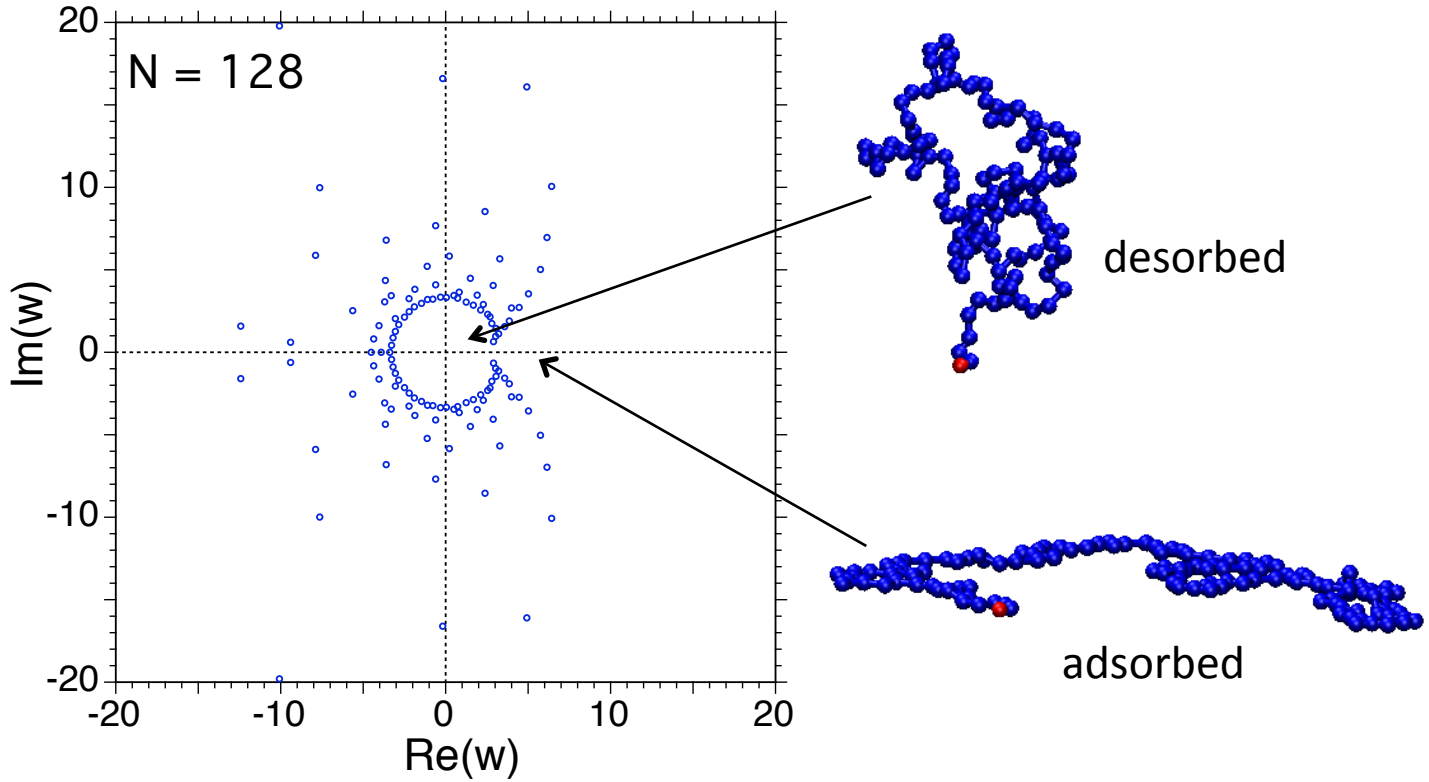
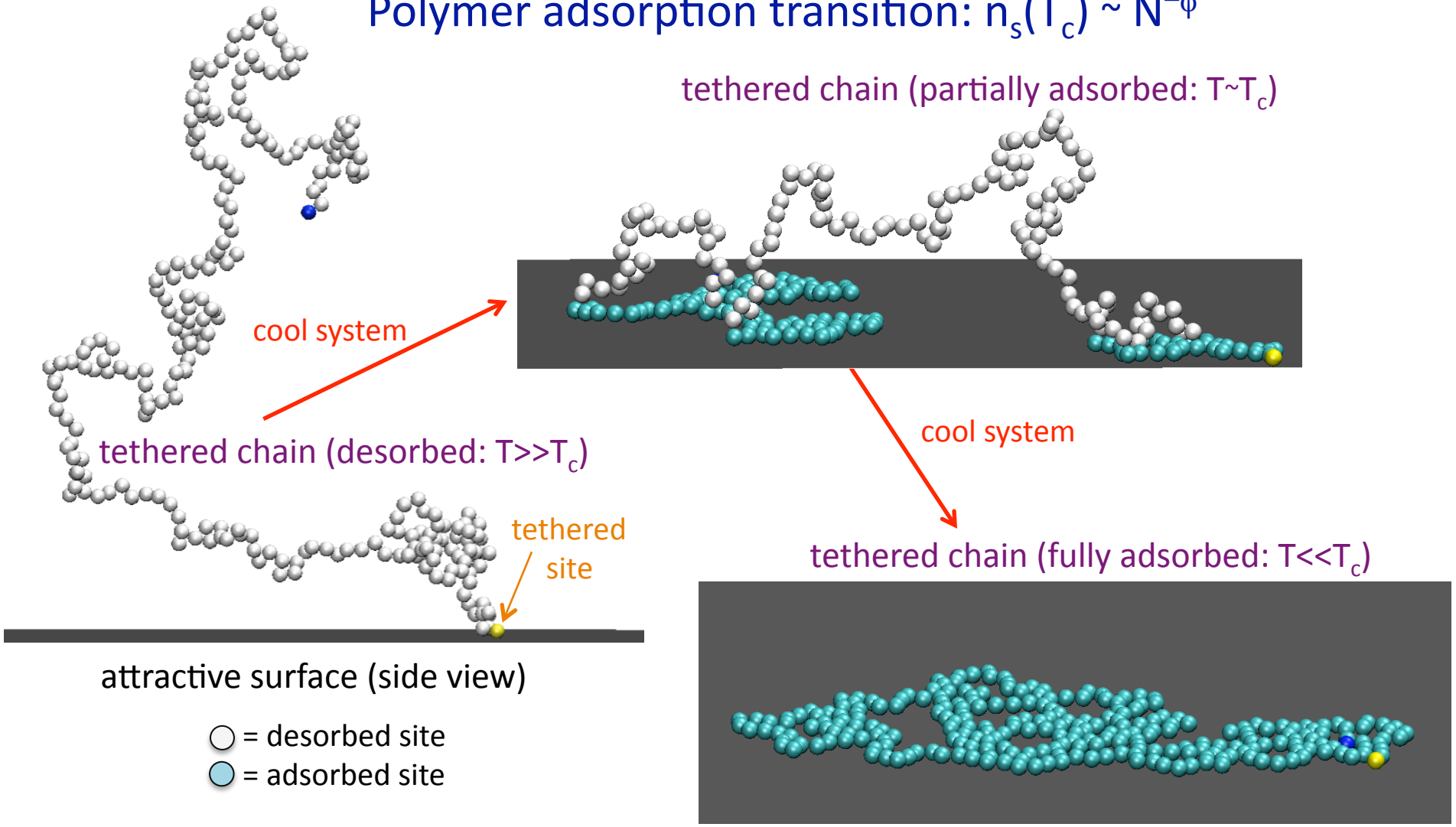


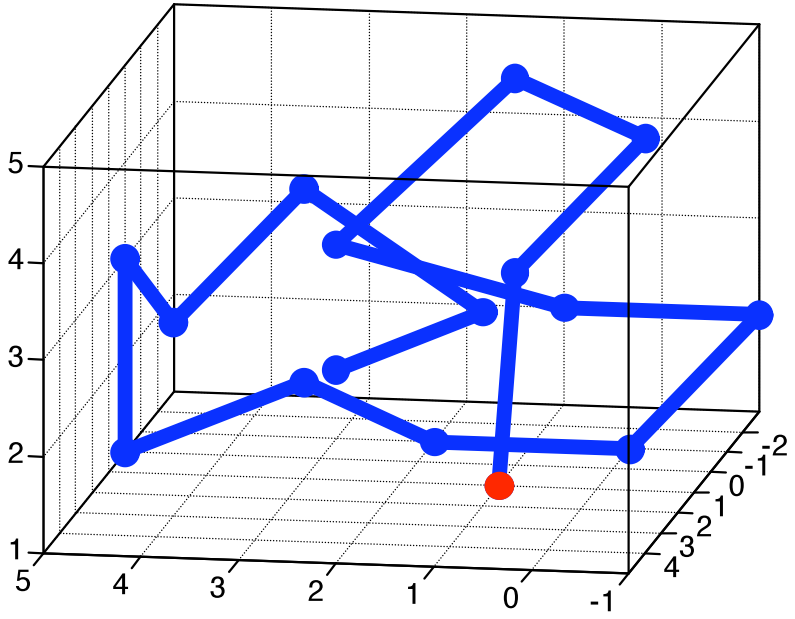
Polymer adsorption transition: $n_s(T_c) \sim N^{-\phi}$



Eisenriegler, Kremer, Binder, JCP **77**, 6296 (1982) [$\phi = 0.58$]
Metzger, Muller, Binder, Bashnagel, Macromol Theory Sim **11**, 985 (2002) [lit. review: $\phi = 0.40\text{-}0.67$; $\phi = 0.50$]
Grassberger, J Phys A: Math Gen **38**, 323 (2005) [$\phi = 0.48$]
Decas, Sommer, Blumen, Macromol Theory Sim **17**, 429 (2008) [$\phi = 0.50\text{-}0.59$]
Klushin, Polotsky, Hsu, Markelov, Binder, Skvortsov, PRE **87** 022604 (2013) [$\phi = 0.48$]

Bond fluctuation model for tethered chains

- Simple cubic lattice (a = 1)
- Bond lengths: $\sqrt{4}$ to $\sqrt{10}$
- Bead 1 fixed at (1,1,1)
- 108 bond vectors



- Interactions between beads i and j with distance r_{ij}:
  - hard core repulsion for $r_{ij}^2 < 4$
- Interactions with the surface:
  - contribution to the internal energy of $-\varepsilon_s$ for $z_i = 1$

Total energy:

$$E = -n_s\varepsilon$$

n_s = number of surface contacts

$T = k_BT/\varepsilon$ = reduced temperature

Density of States and Wang-Landau Sampling I

Density of States:

$g(E_n)$ = volume of configurational phase space for energy state E_n

Thermodynamics:

microcanonical entropy:

$S(E) = k_B \ln g(E)$

canonical partition function:

$Z(T) = \sum g(E) \exp(-E/k_B T)$

Wang-Landau algorithm* ... an iterative simulation method to compute $g(E_n)$:

Starting w/ $g(E_n)=1$, $H(E_n)=0$ $\forall$ n, $f_0 = e$

Generate sequence of chain conformations using acceptance criteria:

$$P_{acc}(a \to b) = \min\left(1, \frac{g(E_a)}{g(E_b)}\right)$$

Update DOS: $g(E_n) \to f_m\, g(E_n)$

Update visitation histogram: $H(E_n) \to H(E_n)+1$

When histogram ~flat ...

reduce modification factor: $f_{m+1} = (f_m)^{1/2}$

reset histogram to zero: $H(E_n) = 0$ $\forall$ n

iterate m levels

m=20 is standard

we need m>25

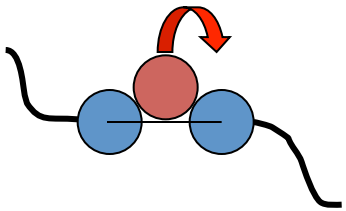
*Wang & Landau, PRL 86, 2050 (2001); PRE 64, 056101 (2001).

Wang-Landau Sampling II

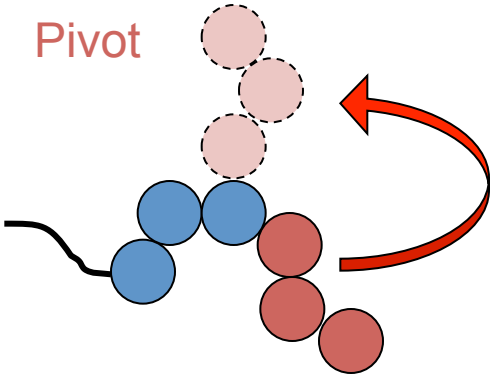
Success of the WL methods depends on underlying MC move set

These "standard" moves easily sample most of configuration space:

Single bead displacement

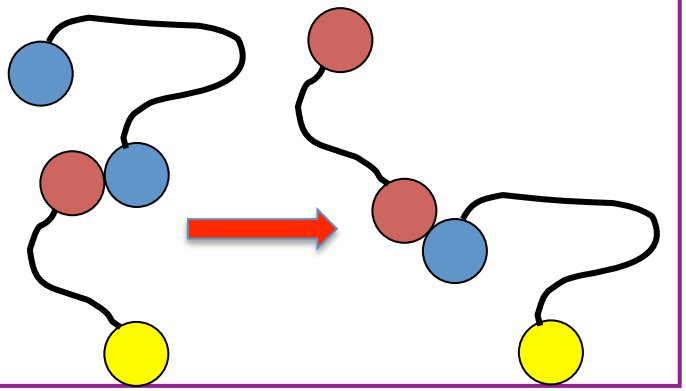


Pivot



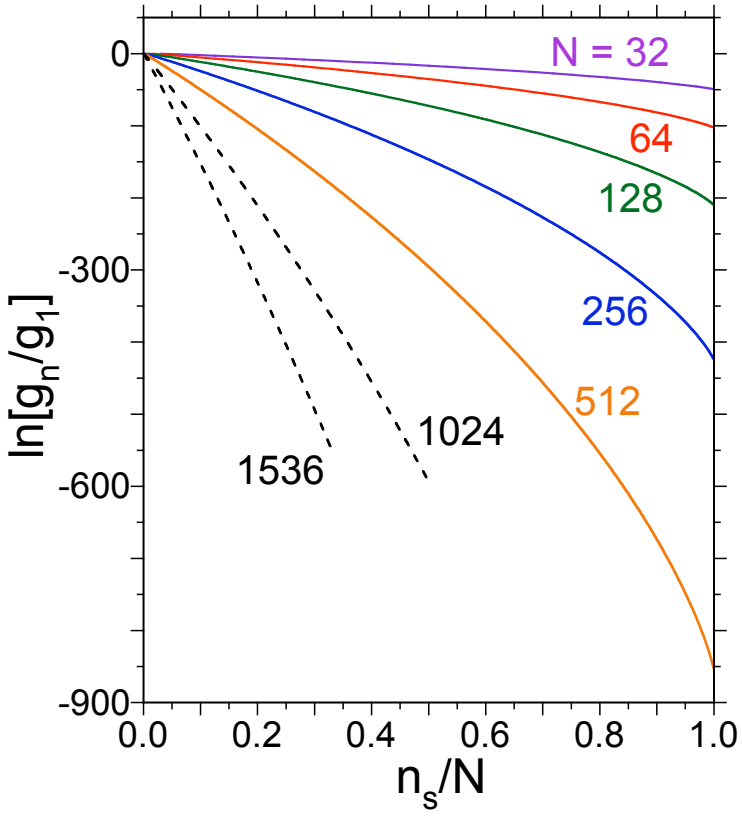
But for good sampling of chain configurations near the grafting point we also use:

Cut and Permute



Causo, J. Stat. Phys. **108**, 247 (2002)

Polymer Adsorption: Single Chain DOS and Specific Heat



n_s = number of surface contacts

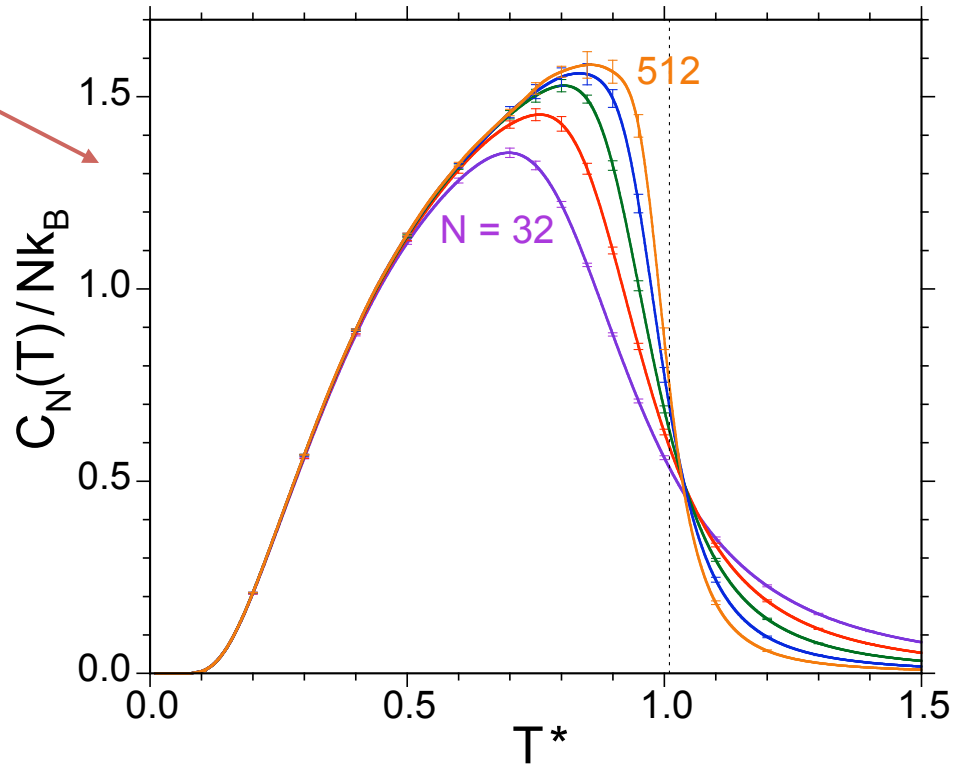
Canonical Analysis

Partition Function: $Z = \sum g(E)\, e^{-E/kT}$

Probability: $P(E,T) = g(E)\, e^{-E/kT} / Z$

Average Energy: $\langle E(T) \rangle = \sum EP(E,T)$

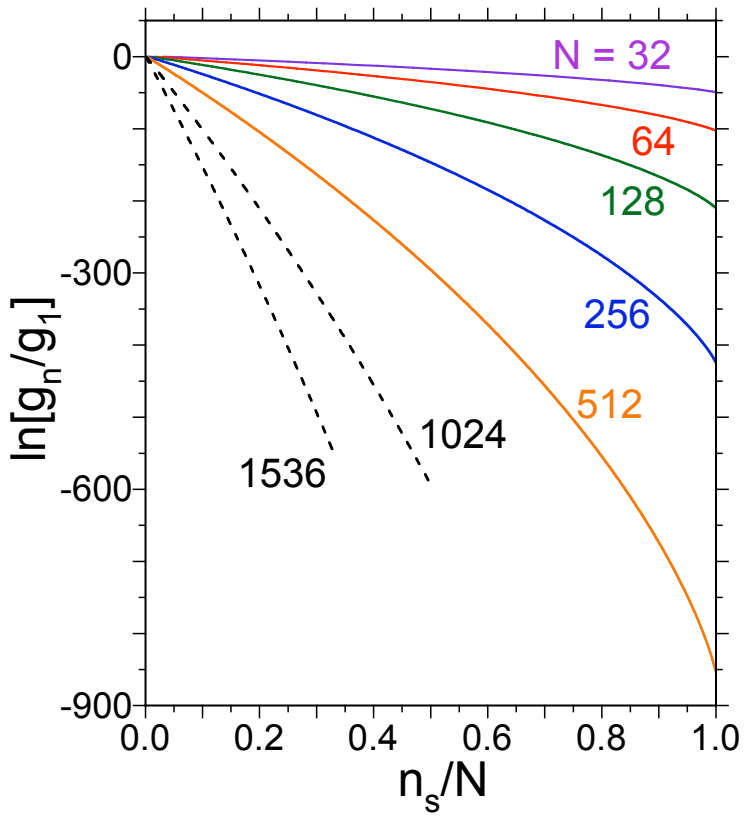
Specific Heat: $C(T) = d\langle E(T) \rangle / dT$



expected behavior:

$$C_{inf}/Nk_B \sim |T - T_c|^{-\alpha}$$

Polymer Adsorption: Single Chain DOS and Fraction Adsorbed



n_s = number of surface contacts

Canonical Analysis

Partition Function: $Z = \sum g(E)\, e^{-E/kT}$

Probability: $P(E,T) = g(E)\, e^{-E/kT} / Z$

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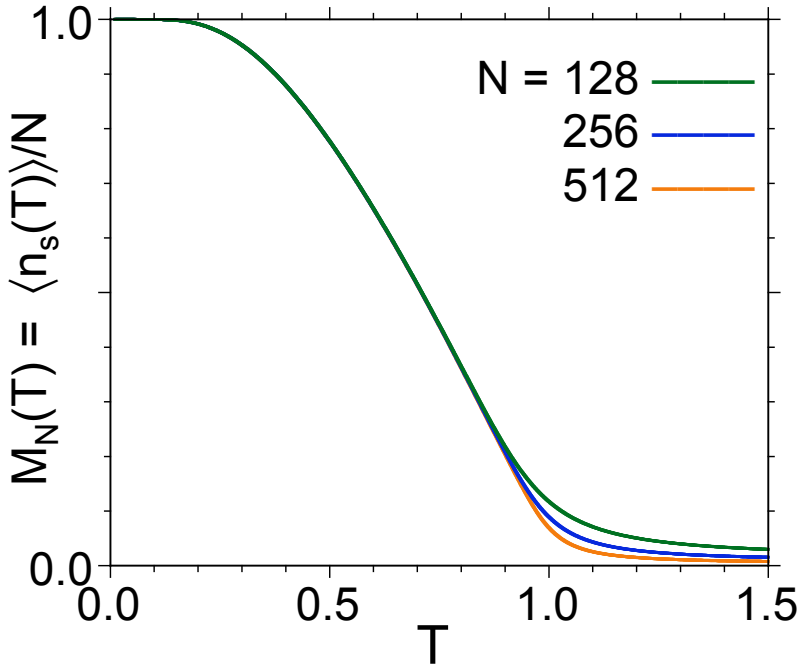
Order Parameter: $M(T) = \langle n_s(T) \rangle / N = \langle E(T) \rangle / N\varepsilon$



expected behavior:

$$M_{inf}(T) \sim |T - T_c|^{\beta}$$

Polymer Adsorption: Partition Function Zeros

Model has discrete energy spectrum: $-\varepsilon, -2\varepsilon, \ldots, -N\varepsilon$

Partition function is a polynomial in $y=e^{\varepsilon/kT}$:

$Z(T) = \sum g(E)\, e^{-E/kT} = \sum_n g_n\, y^n$

or

$Z(T) = \Pi_k\, (y-w_k)$ where $w_k = a_k + ib_k$ are the complex zeros of Z(T)

Properties: complex zeros come in pairs $a \pm ib$
any real zeros must be negative
sum of $\mathrm{Re}(w_k)$ is negative, i.e., $\sum_k a_k < 0$

All thermodynamics can be expressed in terms of the zeros $\{w_k\}$

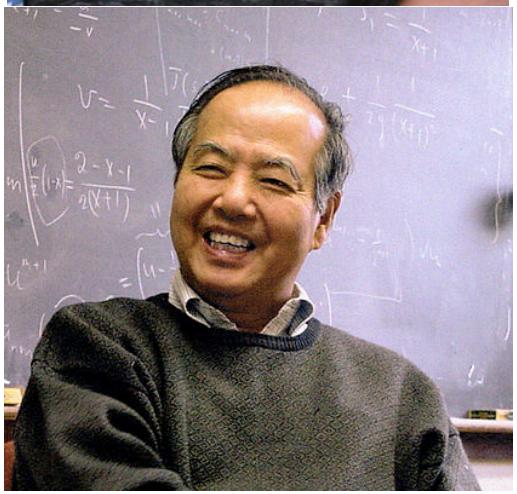
Example: Heat Capacity (physical temp. range: $y > 1$)

$$\frac{C(y)}{k_B} = \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} = (\ln y)^2 \sum_{k=0}^{k_{\max}} \frac{-y w_k}{(y - w_k)^2}$$

Zeros near real axis contribute most

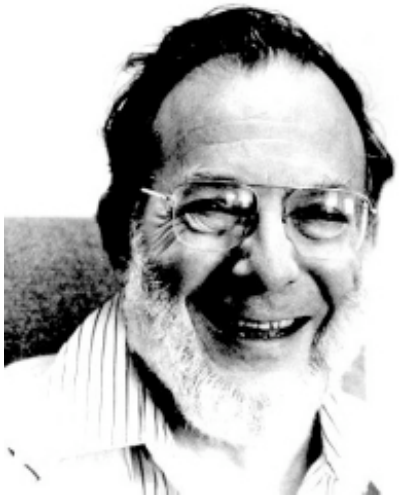
Partition Function Zeros: Yang-Lee theory

In 1952 C. N. Yang and T. D. Lee proposed a very general theory for phase transitions based on the distribution of the zeros of the grand canonical partition function in the complex plane.



Non-analytic behavior of thermodynamic functions arises when some zeros move onto the positive real axis in the thermodynamic limit.

Yang & Lee, Phys. Rev. 87, 404, 410 (1952).

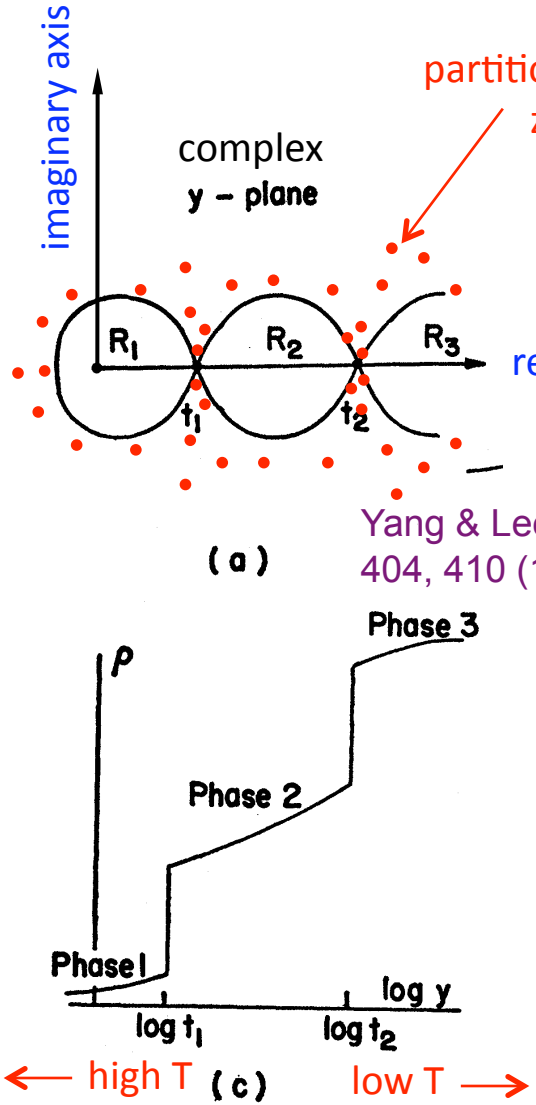


In 1965 M. Fisher extended the approach to the canonical partition function and zeros in the complex temperature plane.

Fisher, in Lecture Notes in Theoretical Physics (U. of Colorado Press, 1965).

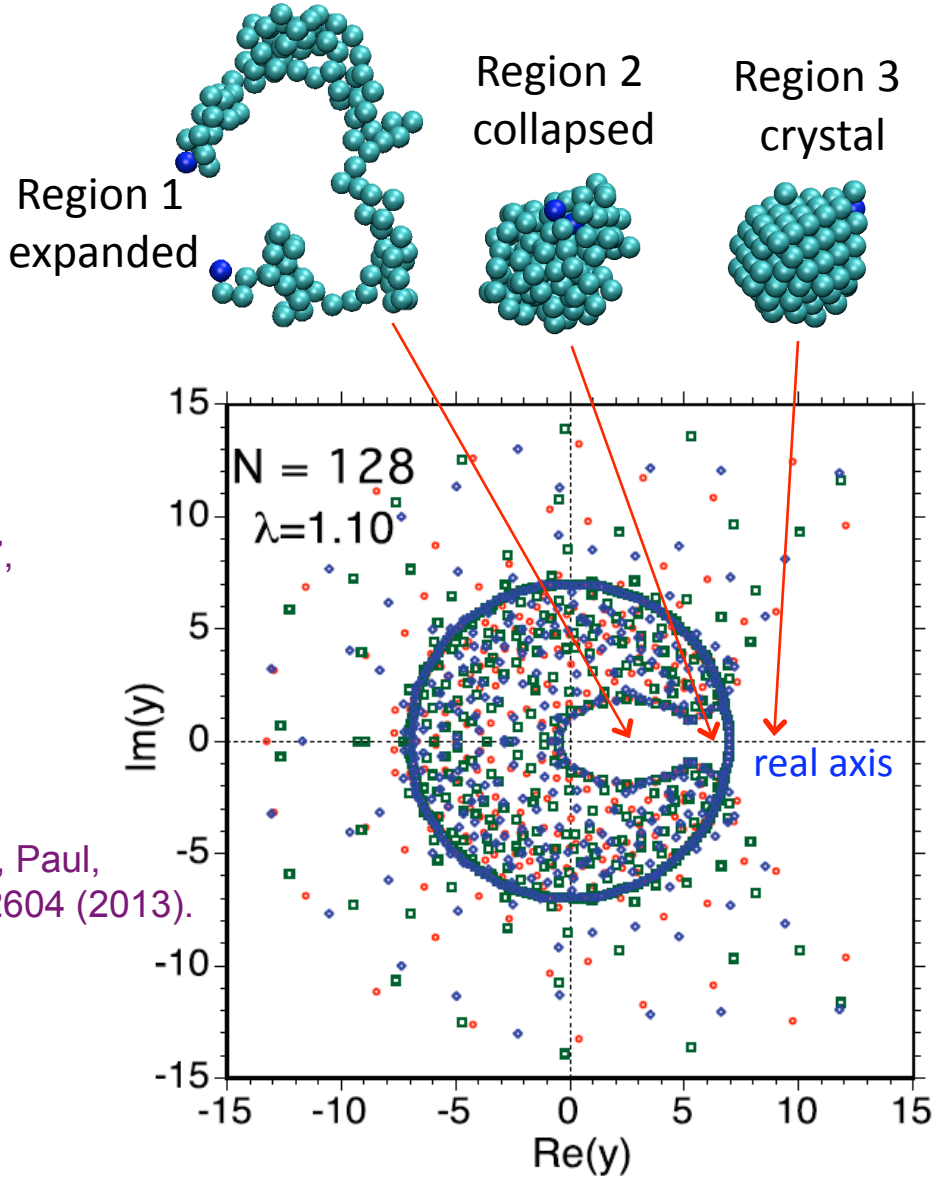
Yang-Lee theory of phase transitions

System with two phase transitions



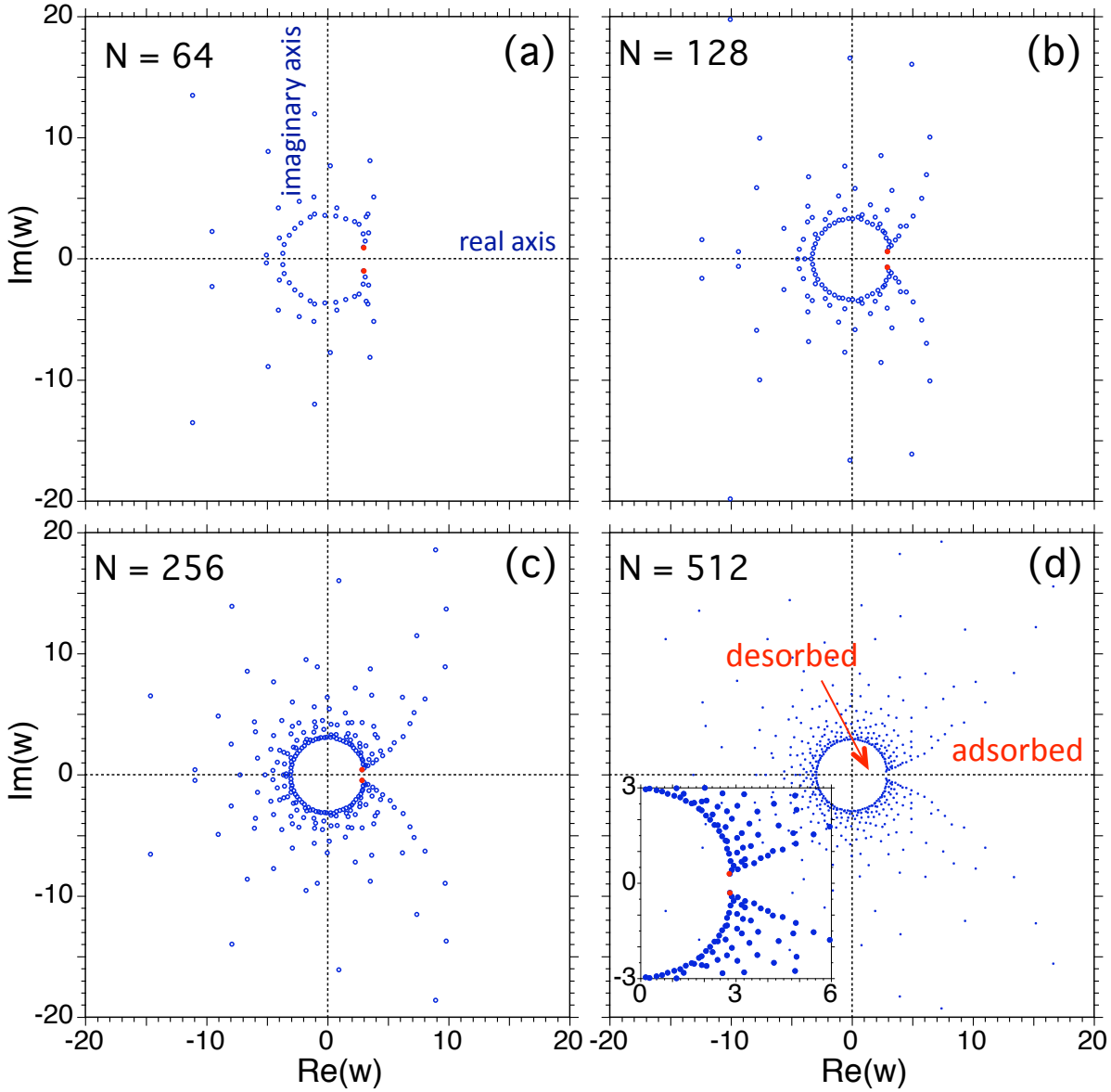
Yang & Lee, Phys. Rev. **87**, 404, 410 (1952).

Collapse and freezing of a SW-chain

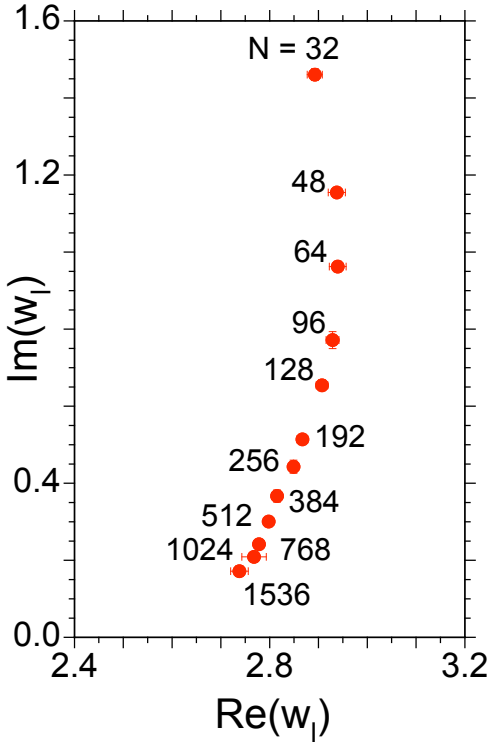


Taylor, Aung, Paul, PRE **88**, 012604 (2013).

Roots maps for polymer adsorption follow Yang-Lee behavior ...
leading zeros pinch down onto positive real axis:



Approach of the leading zeros towards the real axis:



Finite size scaling of the leading zeros

Expected scaling form: $w_1 - y_c \sim DN^{-\phi}$

critical point (real: $y=e^{\beta}=e^{1/T}$)

crossover exponent

leading root (complex)

complex constant ($D=d_a+id_b$)

Itzykson, Pearson, Zuber, Nucl. Phys. B **220**, 415 (1983)

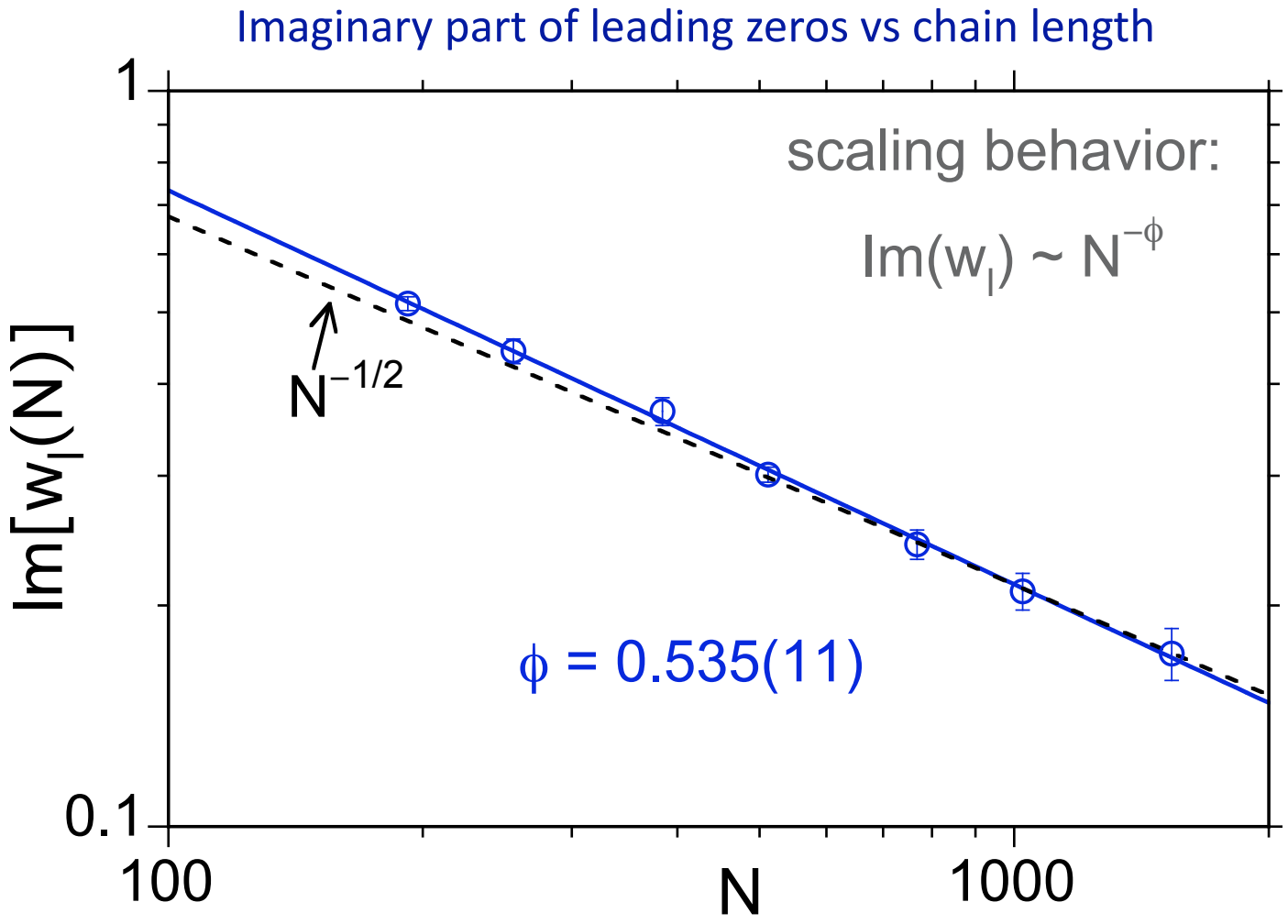
Scaling of $\mathrm{Im}[w_1]$ gives ϕ: $\mathrm{Im}[w_1] \sim d_b N^{-\phi}$

Linear correlation between $\mathrm{Im}[w_1]$ and $\mathrm{Re}[w_1]$ gives $\mathbf{y_c}$: $\mathrm{Im}[w_1] \sim (\mathrm{Re}[w_1] - y_c) d_b / d_a$

Alternately, linear correlation between $\mathrm{Im}[w_1]$ and β_1 gives $\boldsymbol{\beta_c}$: $\mathrm{Im}[w_1] \sim (\beta_1 - \beta_c) y_c d_b / d_a$

Complex inverse temperature: $\ln(w_1) = \beta_1 + i\tau_1$

Adsorption transition: The crossover exponent ϕ

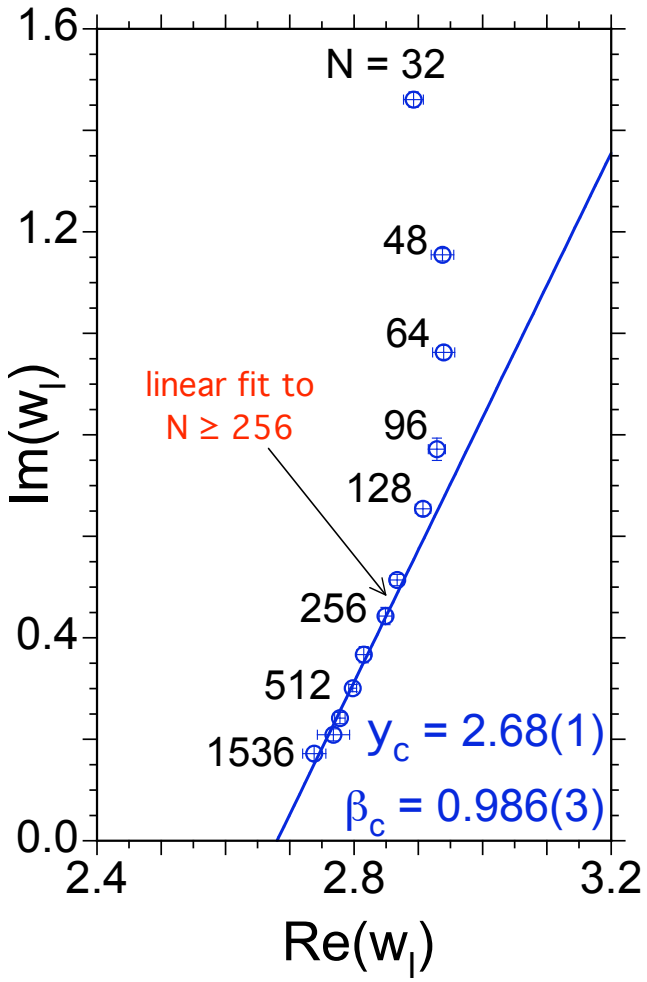


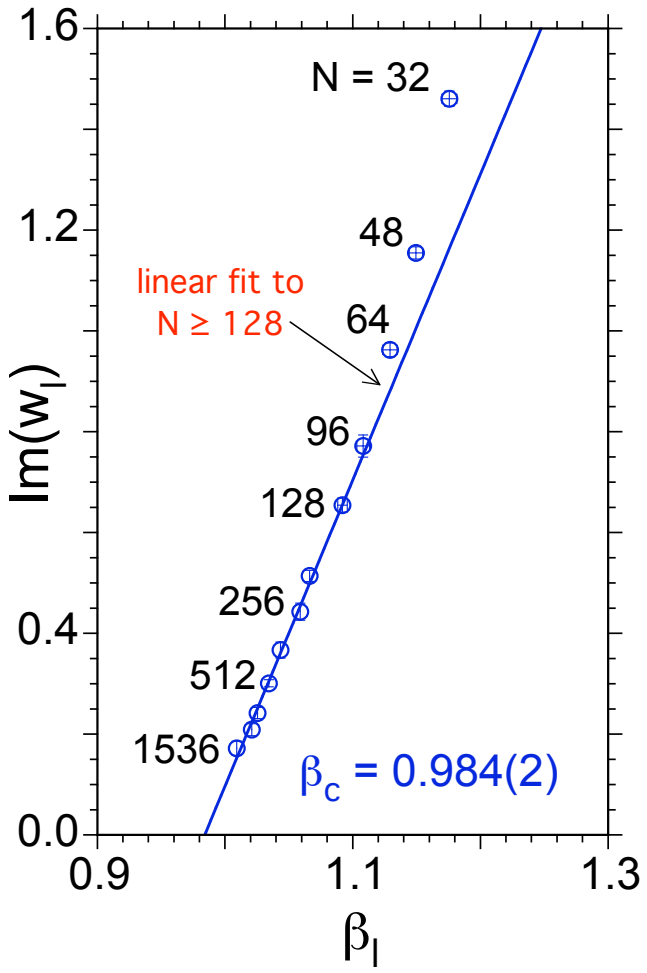
Adsorption transition: The transition temperature T_c

For long chains the leading zeros are expected to show a linear approach the Re(w)-axis (or the β-axis)

$y = \mathrm{Re}(w) = e^{1/T}$

$\beta = 1/T$





Result for transition temperature:

$T_c = 1.016(2)$

Finite size scaling for thermodynamics

PFZ scaling form in complex temperature plane: $\ln(w_1) - \beta_c \sim (D/y_c)N^{-\phi}$

critical point (real)

crossover exponent

leading root (complex: $w=\beta+i\tau$)

complex constant ($D=d_a+id_b$)

Real part gives: $\beta_1 - \beta_c \sim N^{-\phi} \longrightarrow \boxed{\left|1 - T_c/T_1\right| \sim N^{-\phi}}$

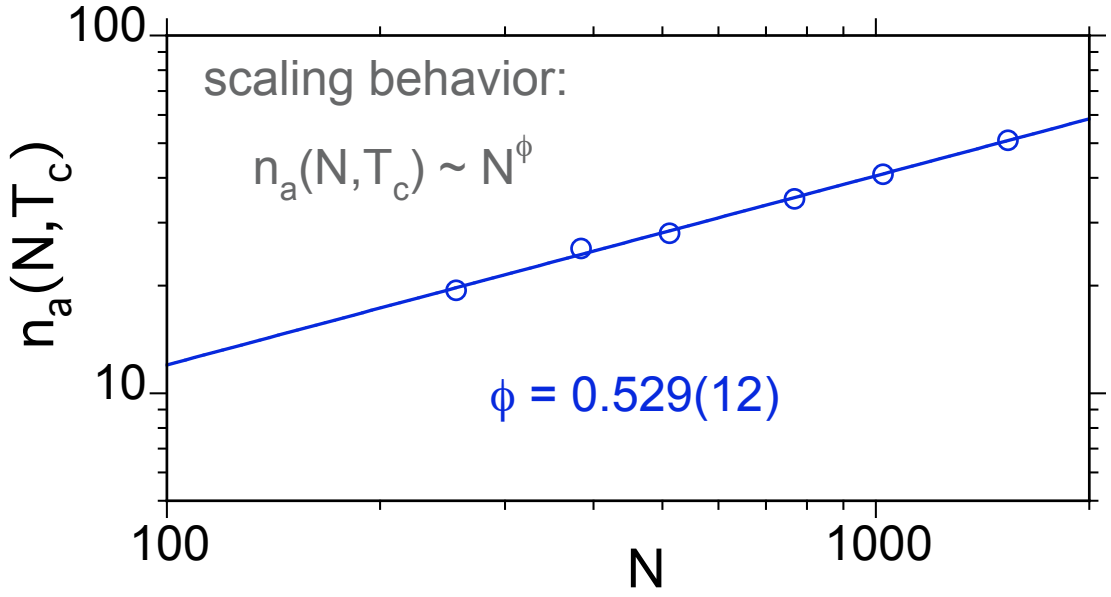
Leads to scaling relations:

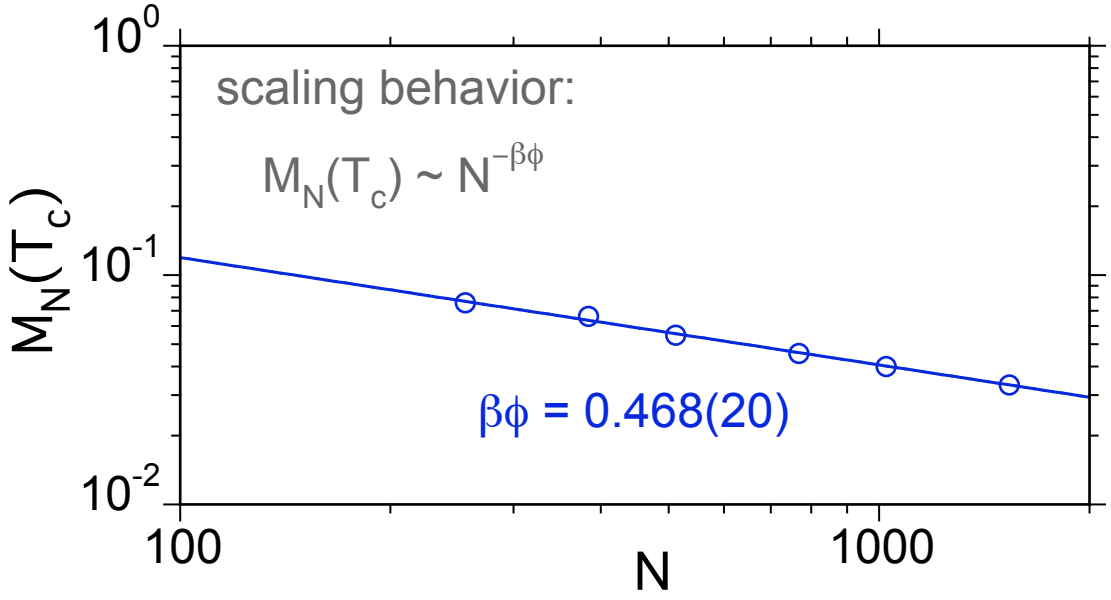
$$\begin{cases} M_N(T_c) \sim N^{-\tilde{\beta}\phi} & \text{order parameter} \\ n_s(T_c) = NM_N(T_c) \sim N^{\phi} & \text{number adsorbed} \\ C_N(T_c)/Nk_B \sim N^{\alpha\phi} & \text{specific heat} \end{cases}$$

And exponent identities:

$$\begin{cases} \tilde{\beta} = -1 + 1/\phi \\ \alpha = 2 - 1/\phi \end{cases}$$

Finite size scaling at T_c: Number absorbed and order parameter

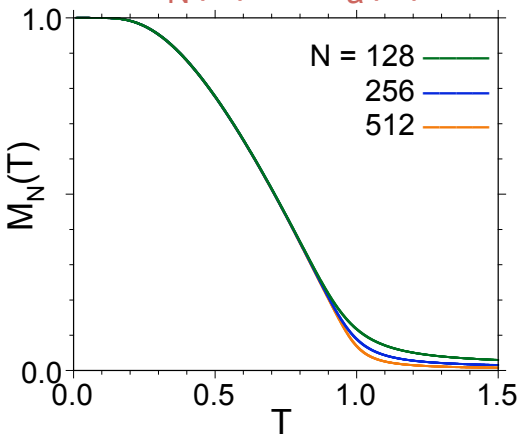




Agrees with Result from Im(w_1):

ϕ = 0.535(11)

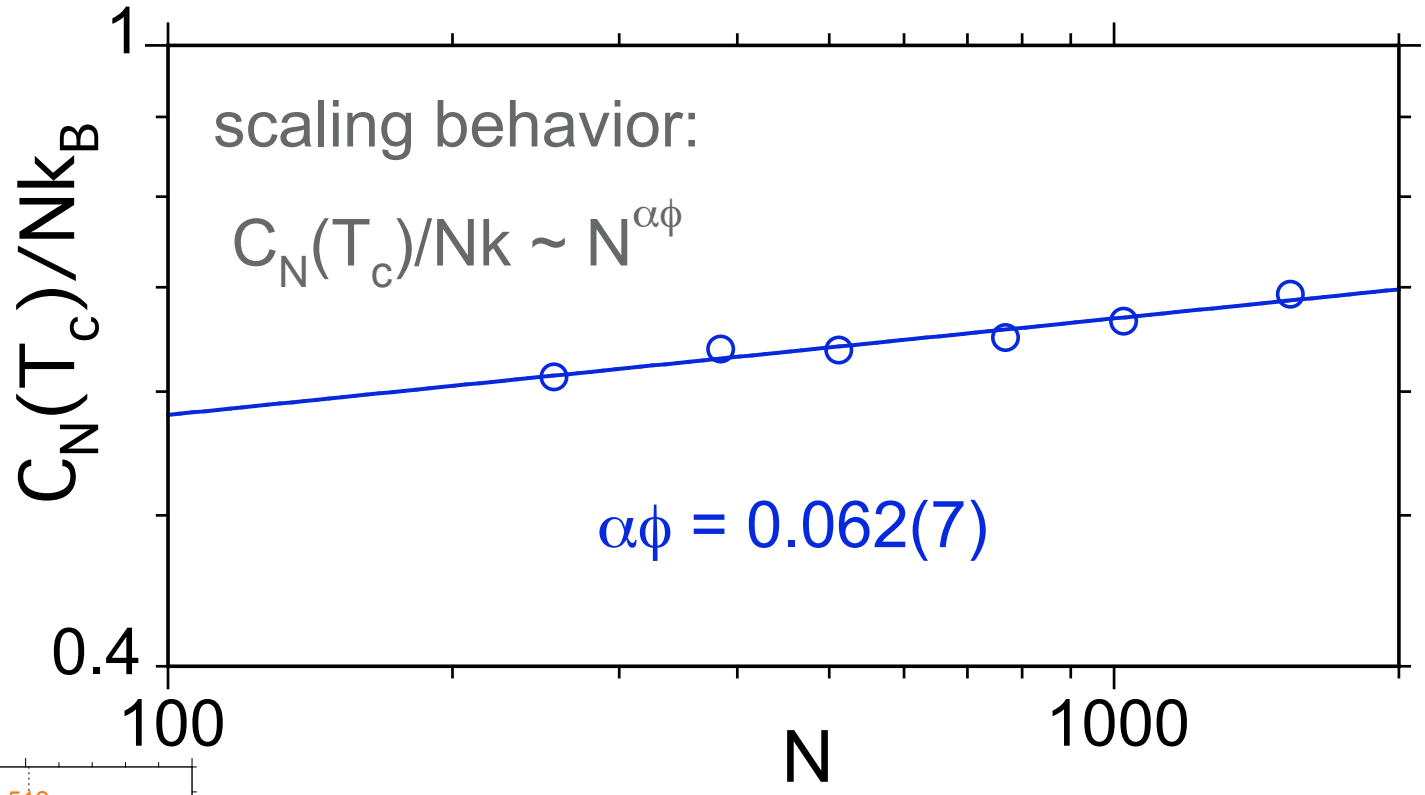
$M_N(T) = n_a(T)/N$

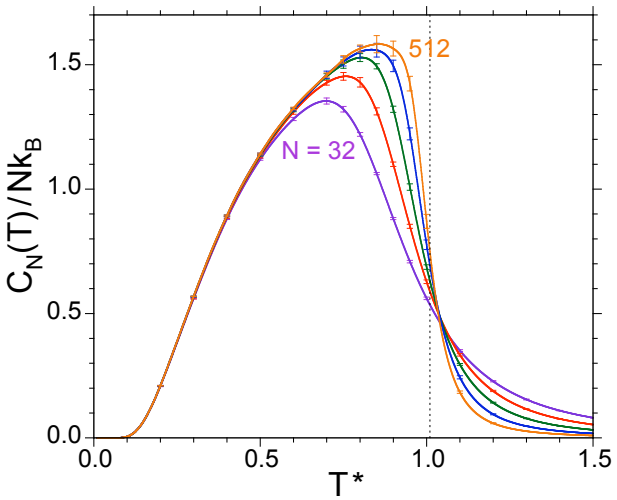


Result for order parameter exponent: **β = 0.875(41)**

Agrees with: $\beta = -1 + 1/\phi$

Finite size scaling at T_c: Specific Heat





Result for specific heat exponent: $\alpha = 0.116(13)$

Agrees with exponent identity: $\alpha = 2 - 1/\phi$

Polymer Adsorption: Summary of Results

Transition temperature: $T_c = 1.016(2)$

Crossover exponent: $\phi = 0.535(11)$
Specific heat exponent: $\alpha = 0.116(13)$
Order Parameter exponent: $\beta = 0.875(41)$

Satisfy exponent identities: $\alpha = 2 - 1/\phi$
$\beta = -1 + 1/\phi$

Caveat: Grassberger and Hsu et al. find $\phi = 0.48$ studying very long lattice chains via the PERM algorithm. They suggest larger values of ϕ are caused by strong corrections to scaling. Note that $\phi = 0.48$ gives a negative α, indicating a non-diverging specific heat.

Grassberger, J Phys A: Math Gen **38**, 323 (2005).
Klushin, Polotsky, Hsu, Markelov, Binder, Skvortsov, PRE **87** 022604 (2013).

Summary and Outlook

Adsorption transition for a tethered polymer chain

Findings: Partition function zeros display Lee-Yang behavior.
Finite size scaling (FSS) of zeros locates T_c and determines ϕ.
FSS determines specific heat and order parameter exponents.

To do: Include correction to scaling terms in this analysis.
Carry out same analysis for a continuum chain model.

Funding: NSF (DMR-1204747)

Special thanks to Wolfgang Paul's group for their hospitality!

Happy "American" Thanksgiving