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Partition function zeros and phase transitions of a homopolymer chain

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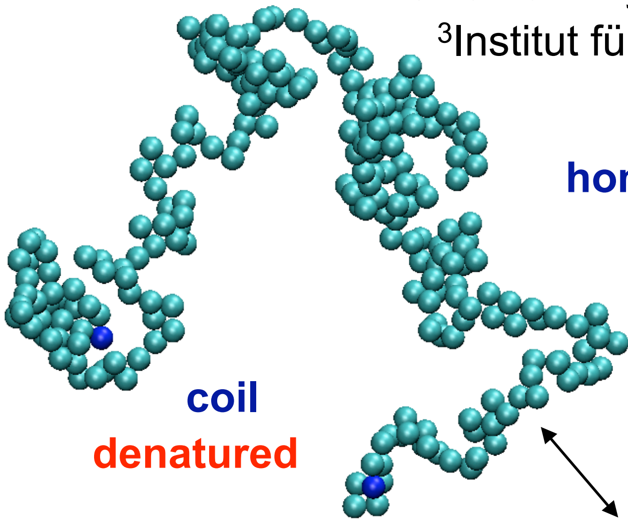
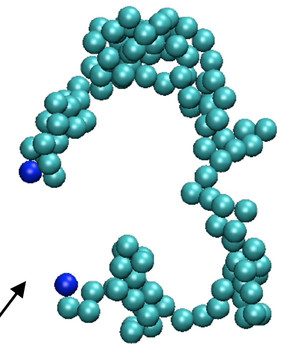
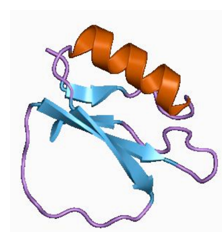


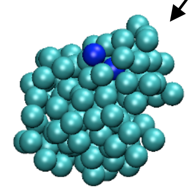
coil
denatured



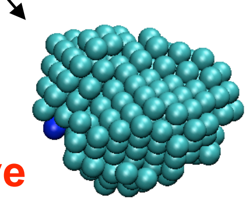
coil
denatured

homopolymer vs bulk fluid transitions

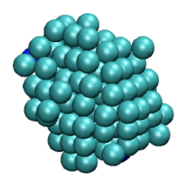




molten
globule



native
crystallite



native
crystallite

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homopolymer freezing vs protein "folding"


OHIO
ONTARIO
CANADA
Lake Erie
MICHIGAN
NY
PENNSYLVANIA
INDIANA
KENTUCKY
WEST VIRGINIA
Pymatuning Reservoir
Grand Lake
Scioto
Campbell Hill 1549
Muskingum R
Ohio River
Toledo
Bowling Green
Defiance
Sandusky
Fremont
Norwalk
Lorain
Elyria
Strongsville
Euclid
Cleveland
Parma
★ Hiram
Ashtabula
Warren
Kent
Youngstown
Cuyahoga Falls
Akron
Barberton
Fostoria
Findlay
Van Wert
Lima
Bucyrus
Ashland
Wooster
Mansfield
Massillon
Canton
Alliance
East Liverpool
Marion
New Philadelphia
Mt Vernon
Steubenville
Coshocton
Bellefontaine
Sidney
Greenville
Westerville
Gahanna
Newark
Cambridge
Upper Arlington
Springfield
Columbus
Zanesville
Dayton
Kettering
Beavercreek
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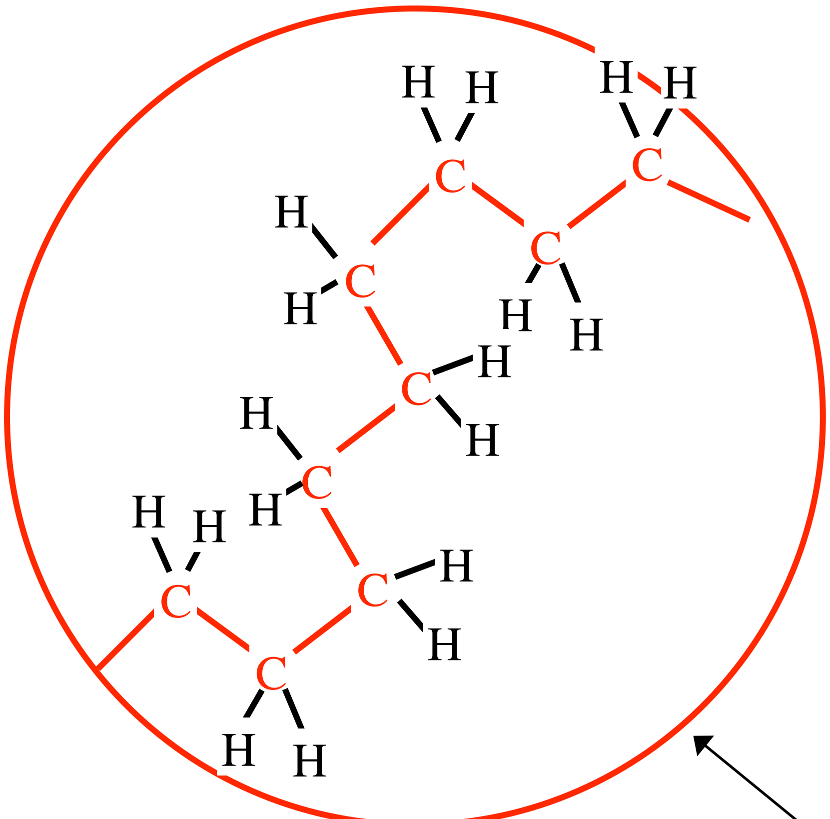
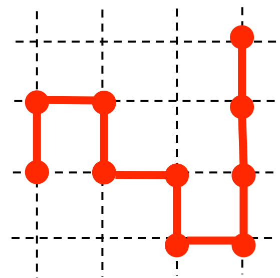
Coarse-Grained Models of Polymers

The "real" world



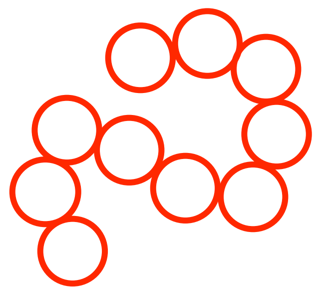
poly(ethylene)

The theorist's world



Study via combinatorics

Lattice Self Avoiding Walk

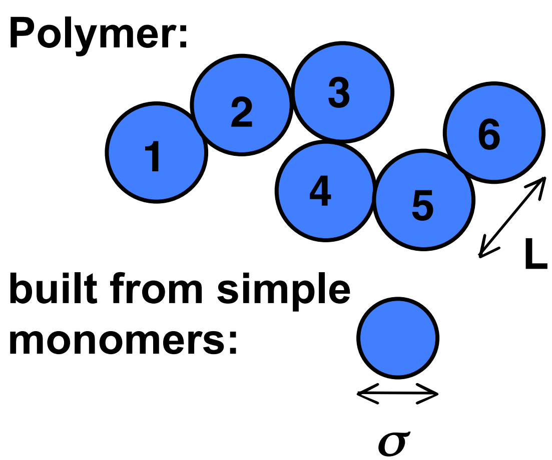


Study via methods of liquid-state physics

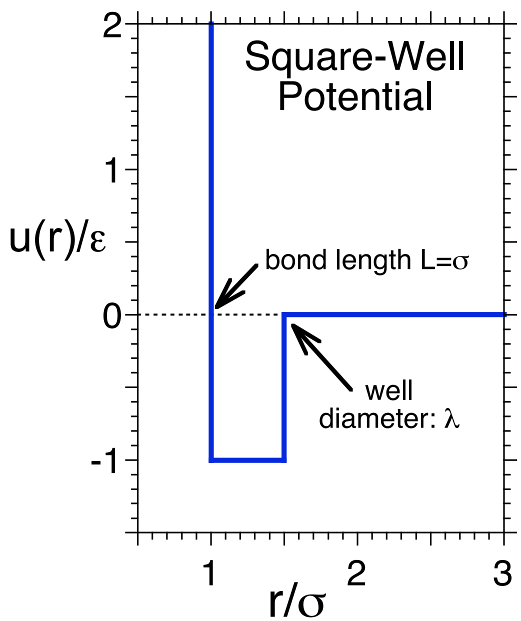
Continuum "pearl neaklace"

Each site or bead = many chemical repeat units

SW Chain Model



monomer-monomer interaction



Model Parameters:

- ε = well depth (sets energy scale)
- σ = hard-sphere diameter
- L = fixed bond length ($L = \sigma$)
- **λ = interaction range/σ**
- $T^* = k_B T/\varepsilon$ = reduced temperature

Can study this model for a continuous range of λ

Model has a discrete energy spectrum: $\mathbf{E_n = n\varepsilon}$
(**n** = number of monomer-monomer interactions)

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

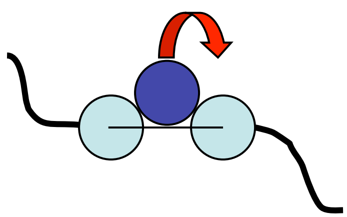
***Wang & Landau, PRL 86, 2050 (2001); PRE 64, 056101 (2001).**

Wang-Landau Sampling II

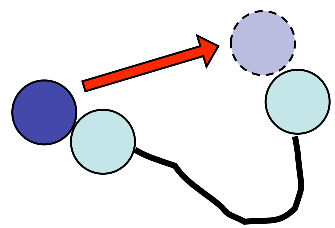
Success of the WL methods depends critically on underlying MC move set

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

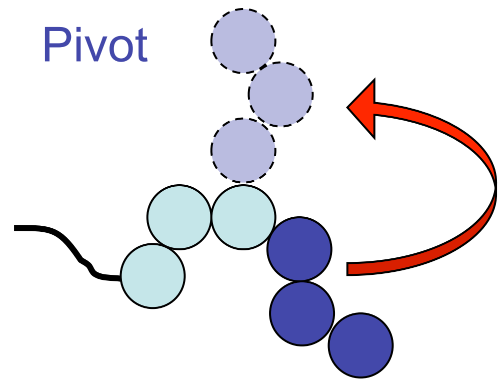
Single bead crankshaft



Reptation

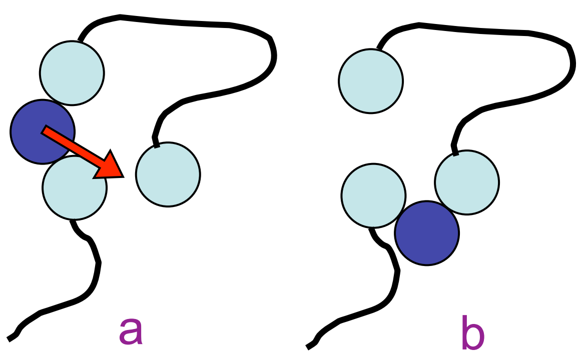


Pivot



... However, we need **this move** to access the lowest energy regions of phase space:

End-bridging



This move requires weight factors in the acceptance criteria:

$$w_b = n_a J_b$$

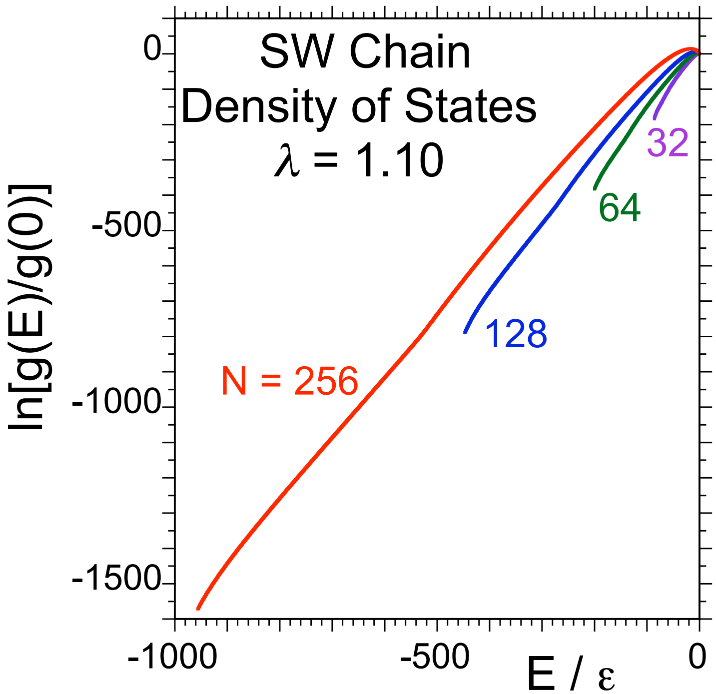
# of bridgable sites in state a

Jacobian factor for state b

Escobedo & de Pablo, JCP **102**, 2636 (1995)

Single Chain DOS and Canonical Analysis I

Algorithm validated via comparison with exact DOS results for short (n≤6) SW chains.



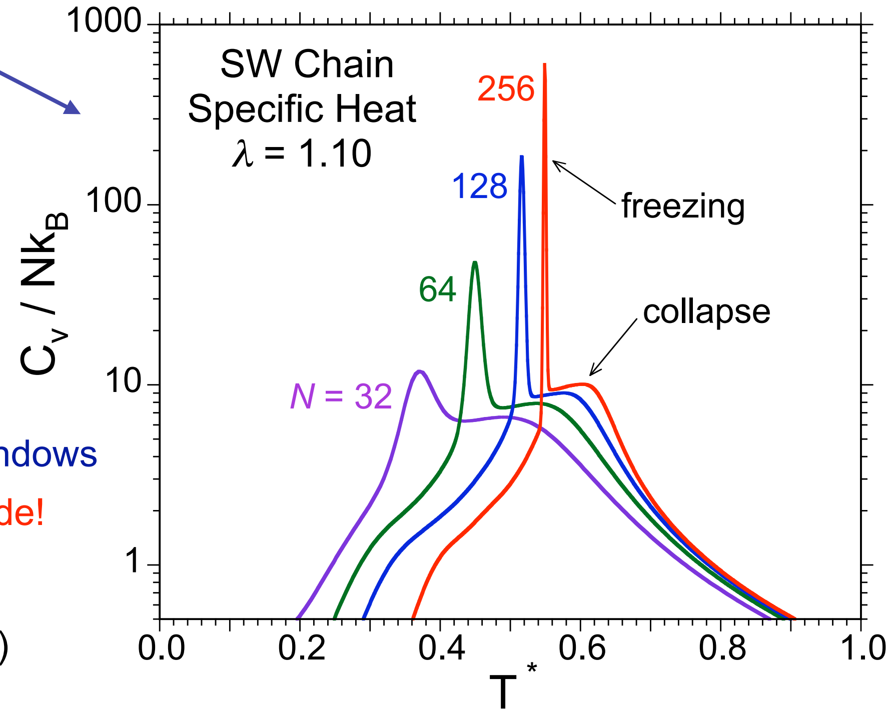
Canonical Analysis

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

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

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

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



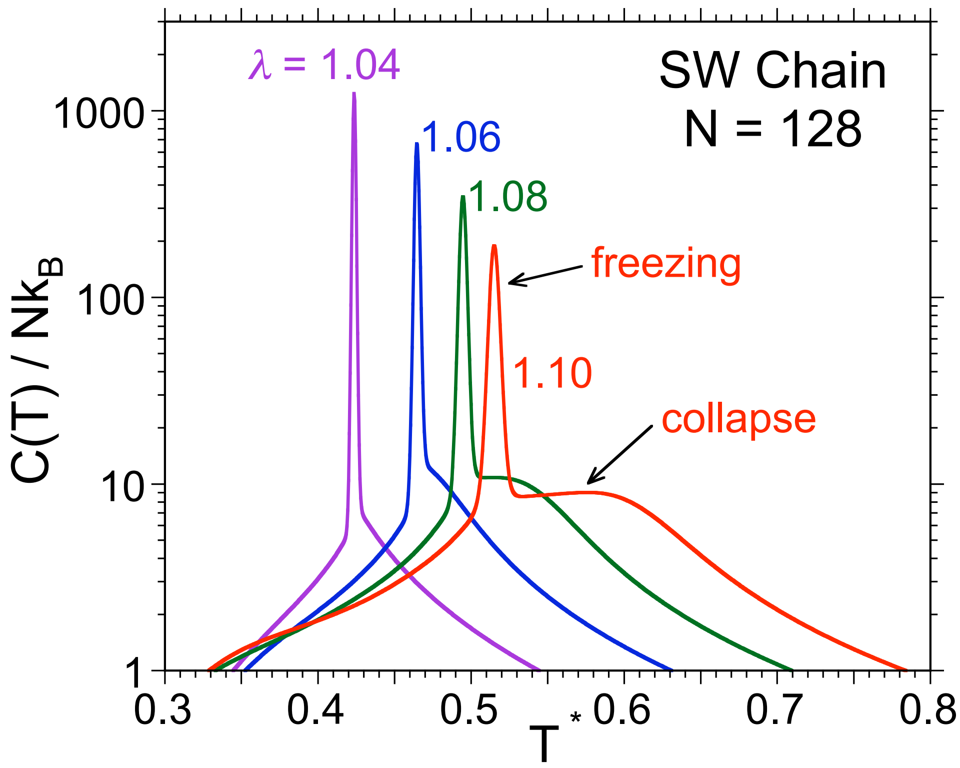
For N≥128 sampling done in overlapping energy windows

For N = 256: g(E) spans ~700 orders of magnitude!

Taylor, Paul, & Binder, PRE **79**, 050801(R) (2009)

Canonical Analysis II

In the "canonical analysis", collapse and freezing specific heat peaks merge for small λ ...

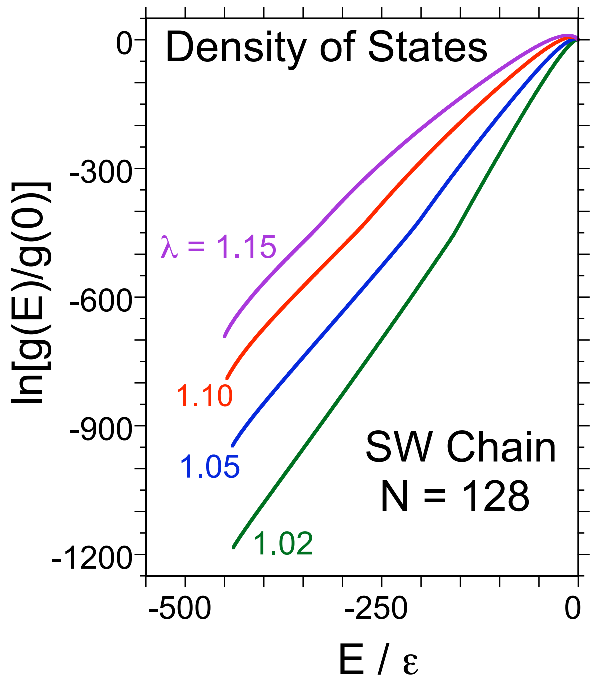


... a "microcanonical analysis" can be used to distinguish these transitions

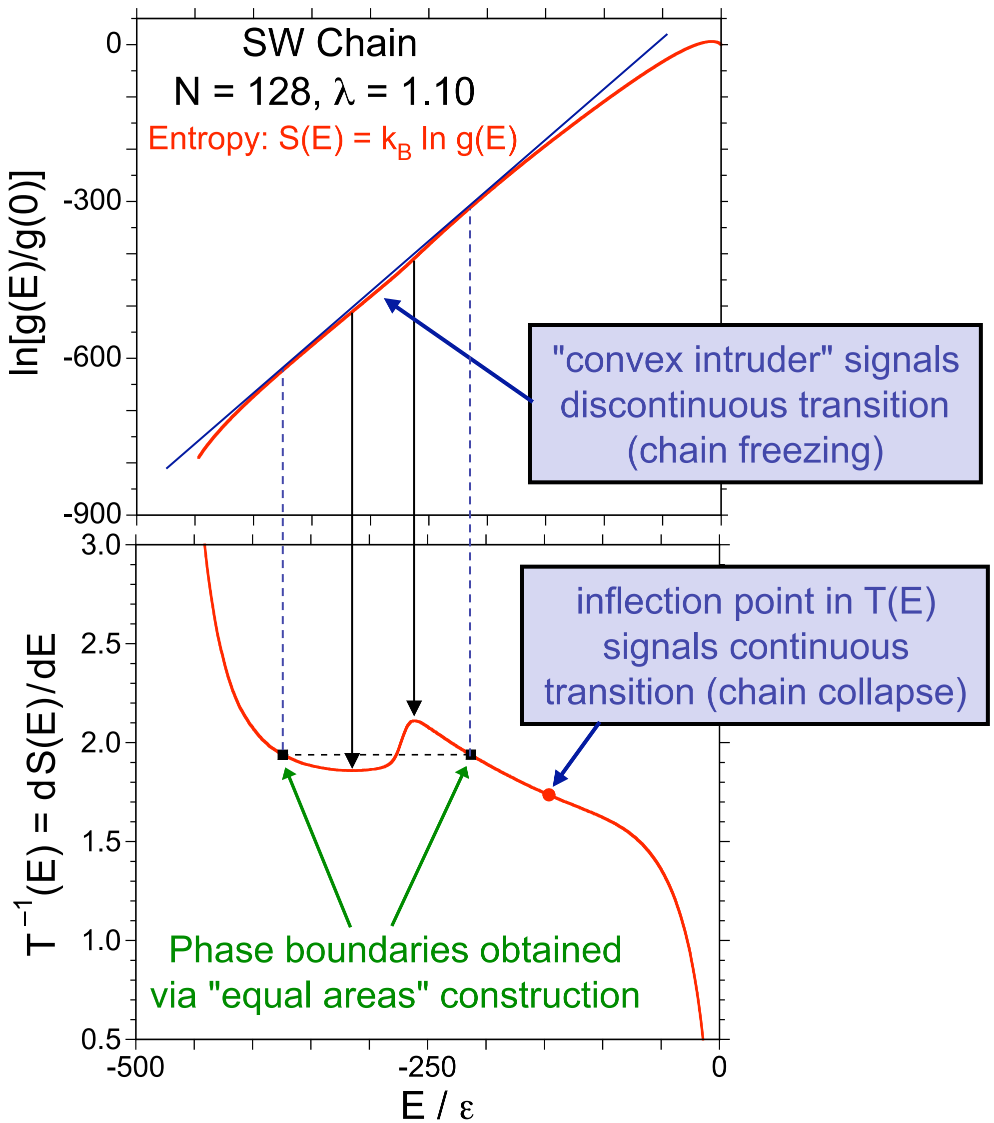
Microcanonical Analysis I

Phase transitions in a finite system determined from **curvature** of the microcaonical entropy:

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

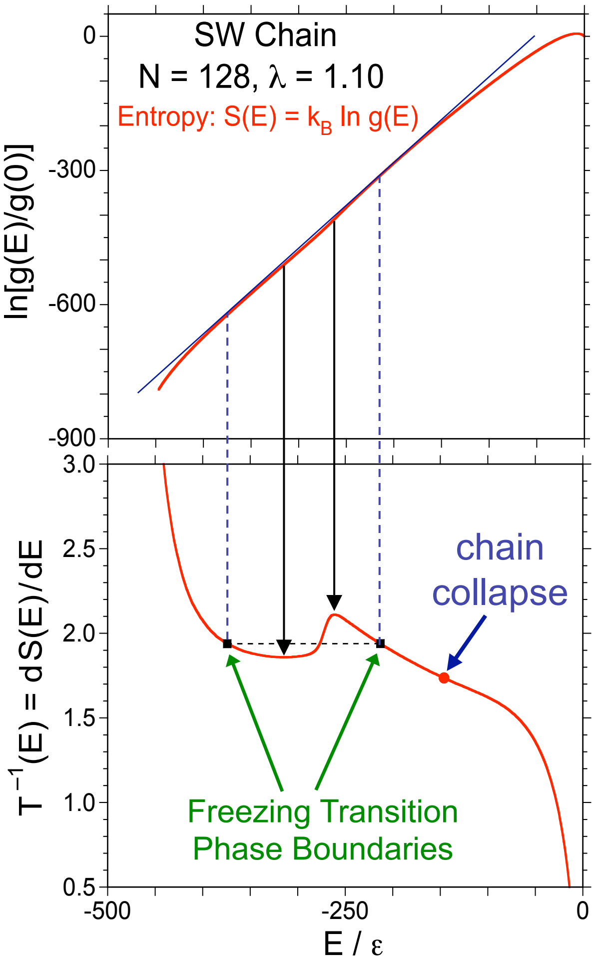


Gross, "Microcanonical Thermodynamics" (2001)
Behringer, Pleimling, & Huller, JPA **38**, 973 (2005)
Junghans, Bachmann, & Janke, PRL **97**, 218103 (2006)
Taylor, Paul, & Binder, PRE **79**, 050801(R) (2009)

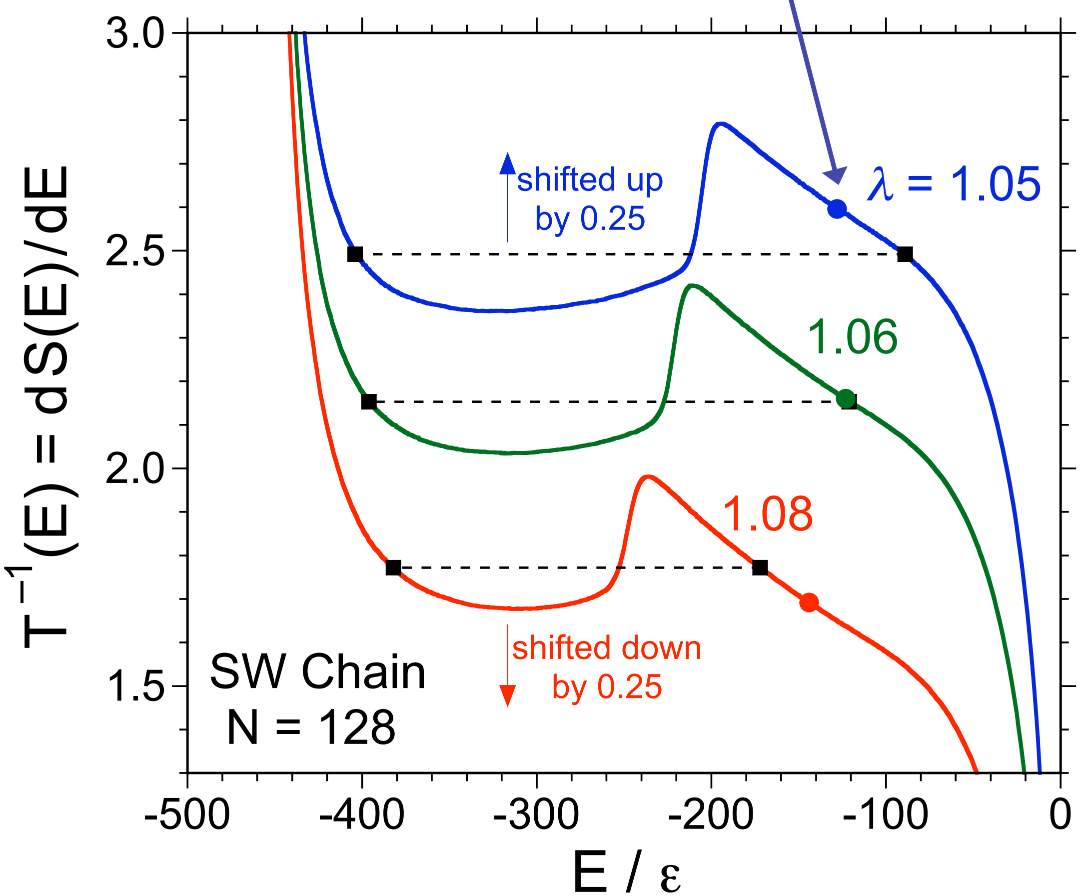


Microcanonical Analysis II

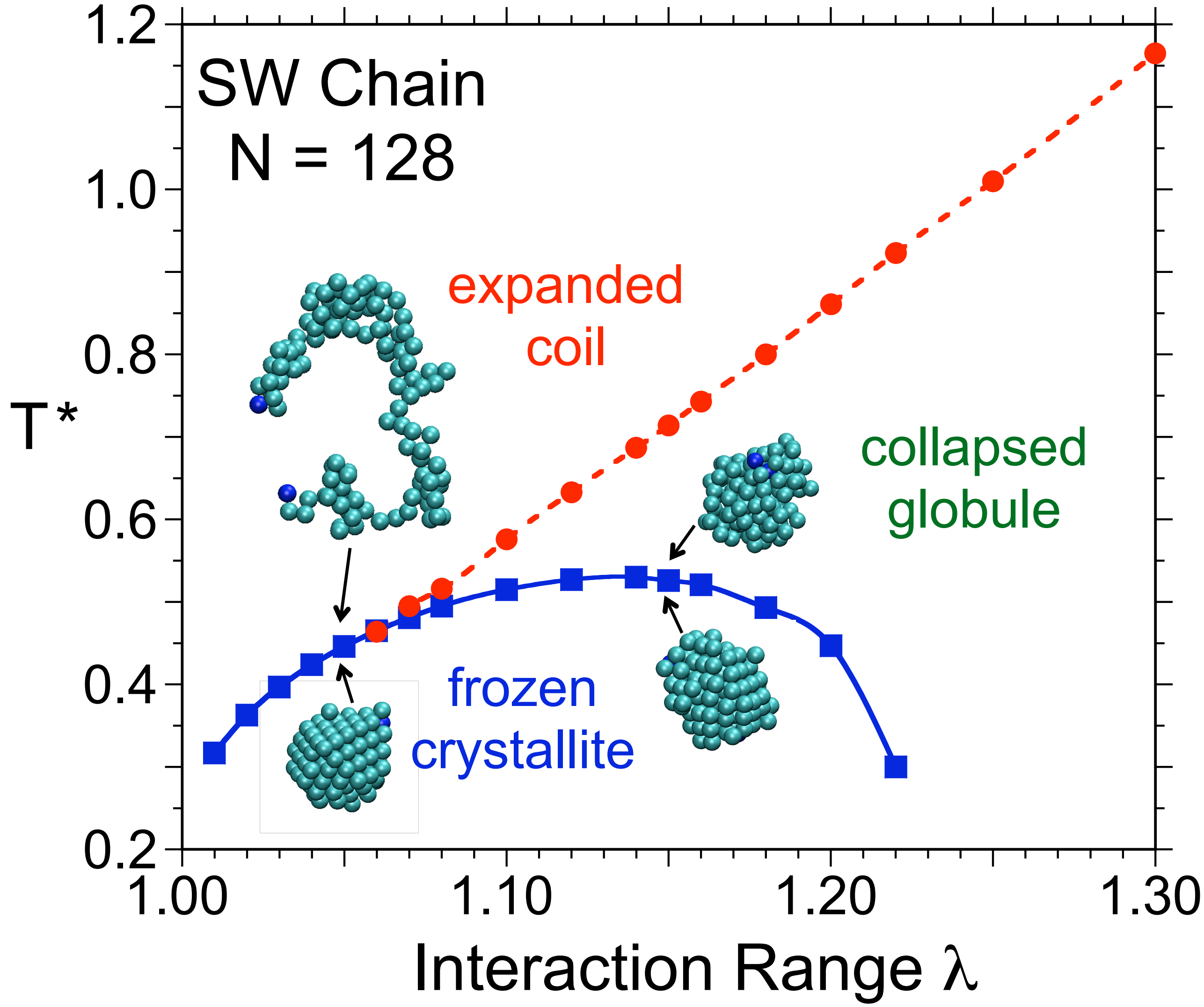
Phase transitions in a finite system determined from **curvature** of S(E)



Collapse transition is preempted by freezing for short-range interaction!



Single Chain Phase Diagram: T-λ Version



Taylor, Paul, & Binder, J. Chem. Phys. **131**, 114907 (2009)

Partition Function Zeros

Energy states for the SW chain: 0, $-\varepsilon$, -2ε, ..., $-n_{max}\varepsilon$

SW chain partition function is a polynomial in $y=\exp(1/T^*)$:

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

or

$Z(T) = \prod (y-y_k)$

where $y_k = a_k + ib_k$ are the complex roots of $Z(T)$

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

All thermodynamics can be written in terms of roots $\{y_k\}$

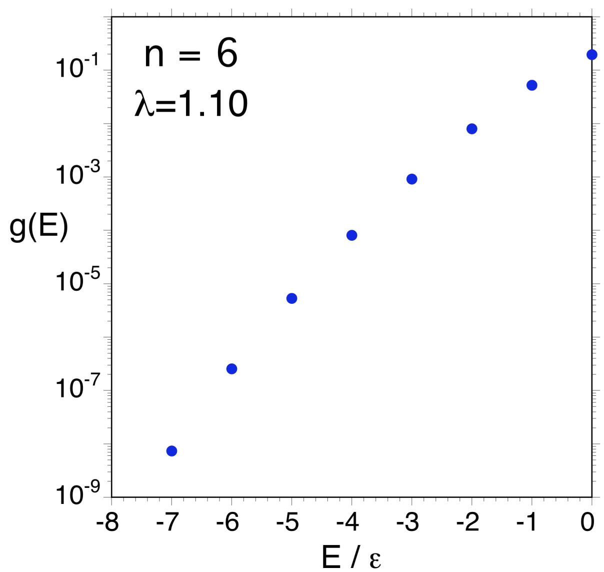
Example: Heat Capacity (physical temp. range: $y > 1$)

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

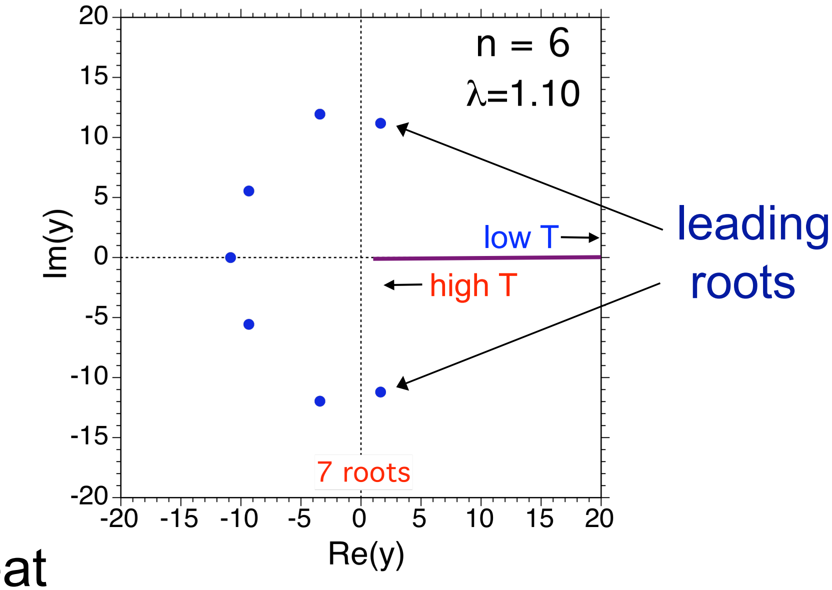
Roots near real axis contribute most

Thermodynamics from Partition Function Zeros I

Exact Density of States*

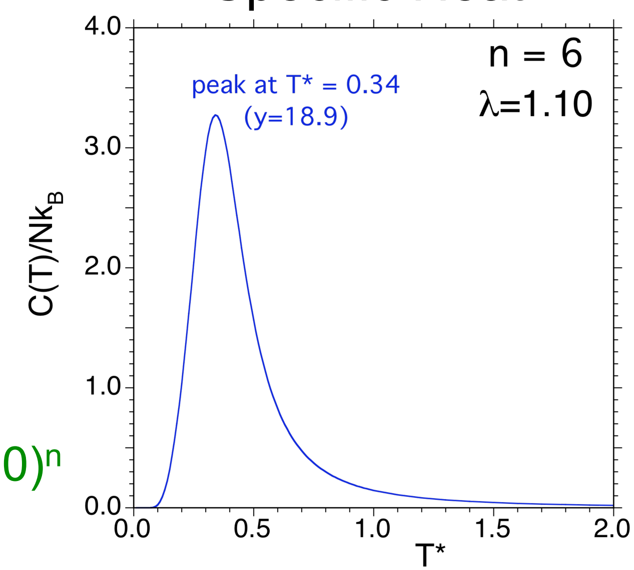


Partition Function Zeros



$Z(T) = \sum_n g_n y^n$

Specific Heat



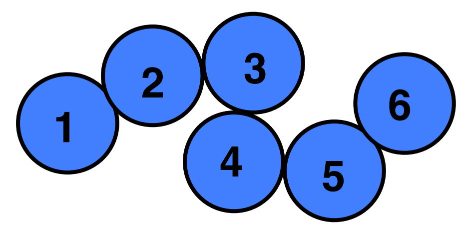
$Z(T) = \Pi_k (y-y_k)$

Technical note:

since $g_n \sim 10^{-n}$

can compute roots of

$Z(T) = \sum_n (10^n g_n)(y/10)^n$



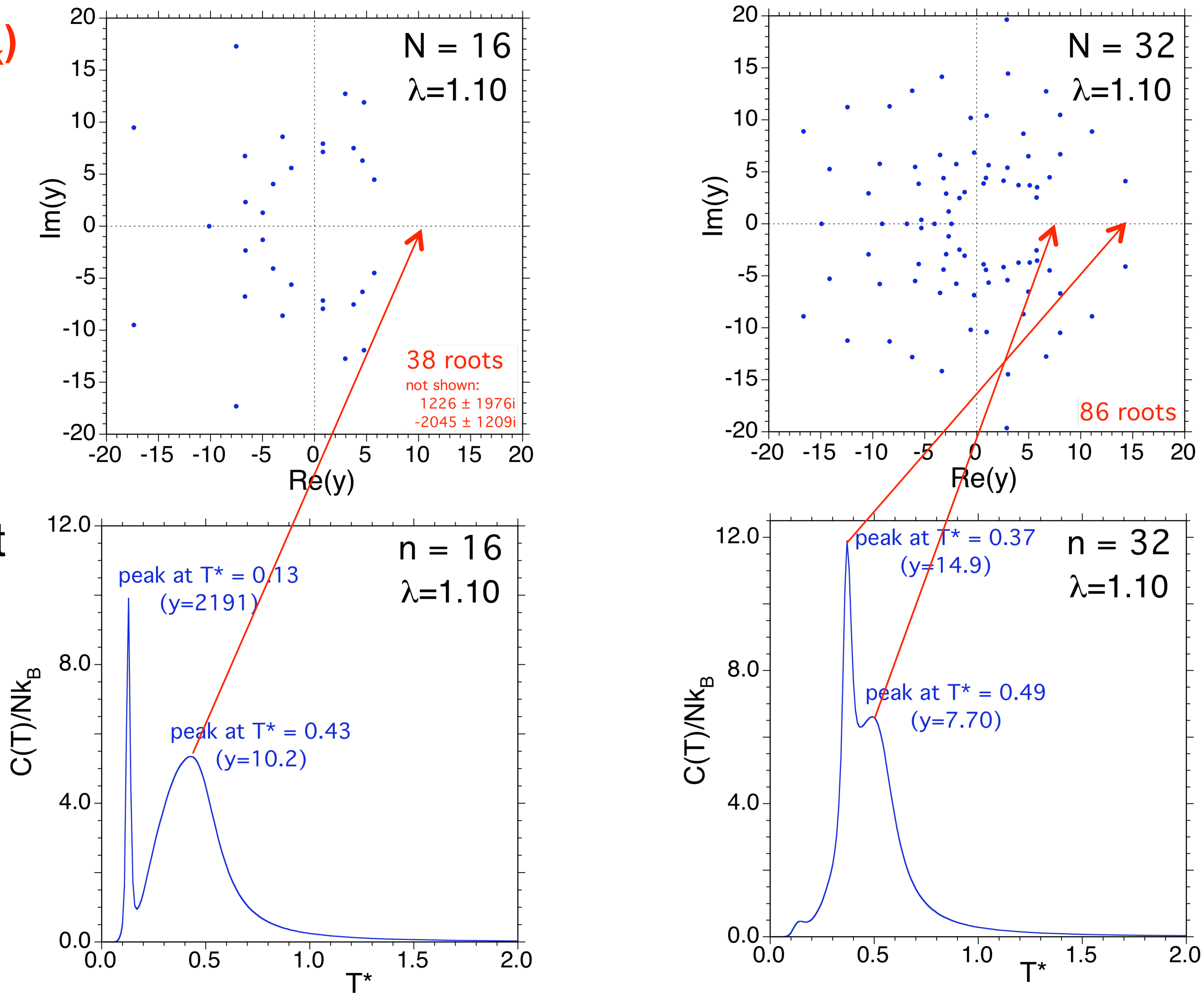
*J. Chem Phys. **118**, 883 (2003)

Thermodynamics from Partition Function Zeros II

Partition Function Zeros

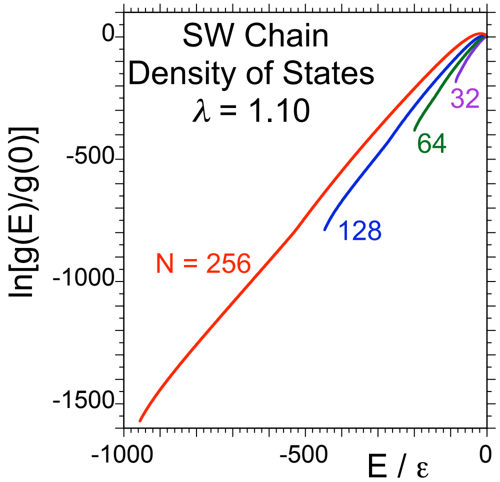
$Z(T) = \Pi_k\ (y-y_k)$

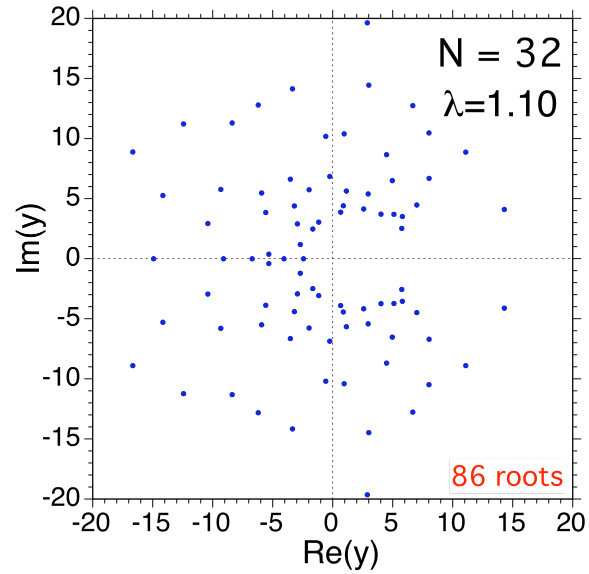
Specific Heat

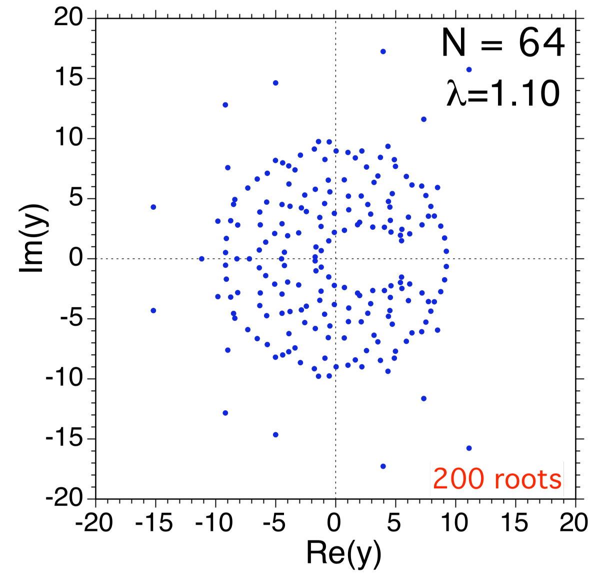


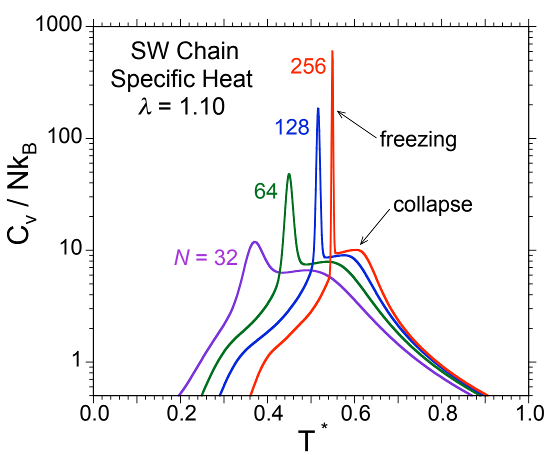
Phase Behavior from Partition Function Zeros I

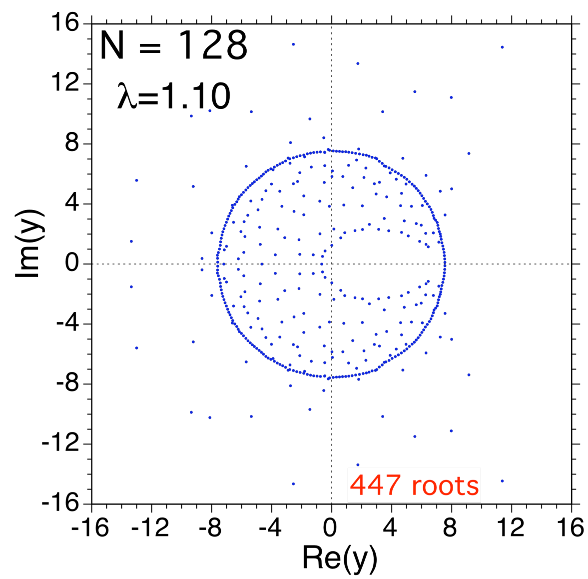
With increasing N "root maps" develop distinctive structure:

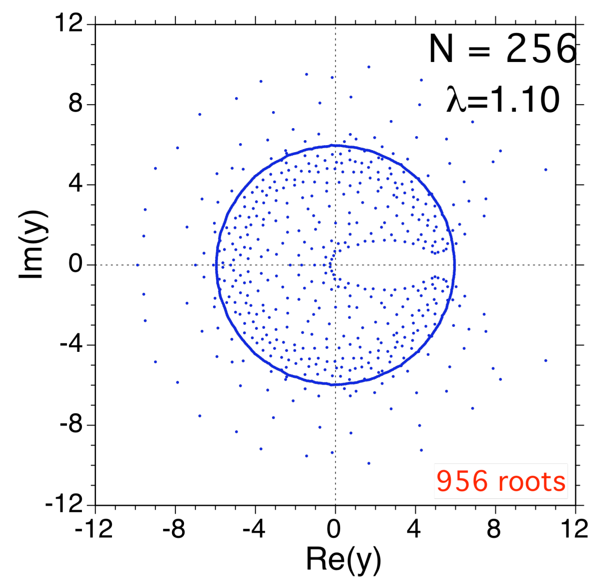












Phase Behavior from Partition Function Zeros II

For the SW chain: root maps show distinctive signatures for transitions ...

collapse = elliptical horseshoe ring

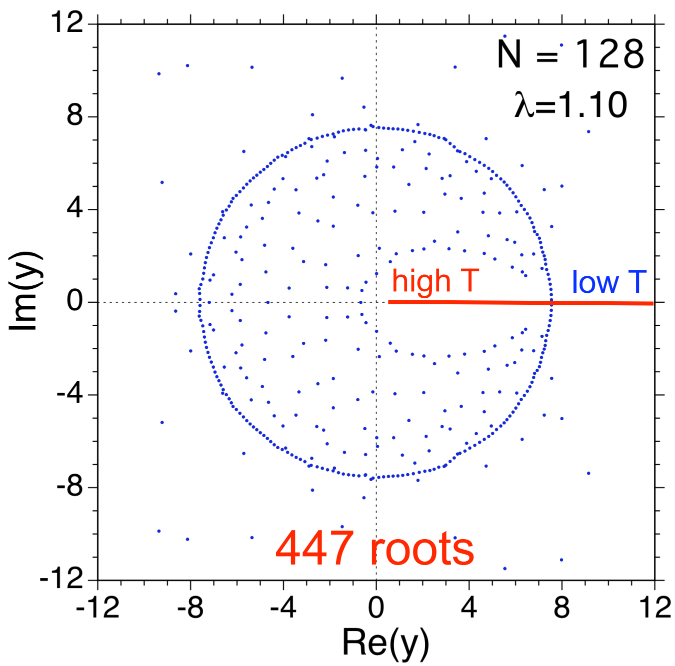
freezing = circle of roots

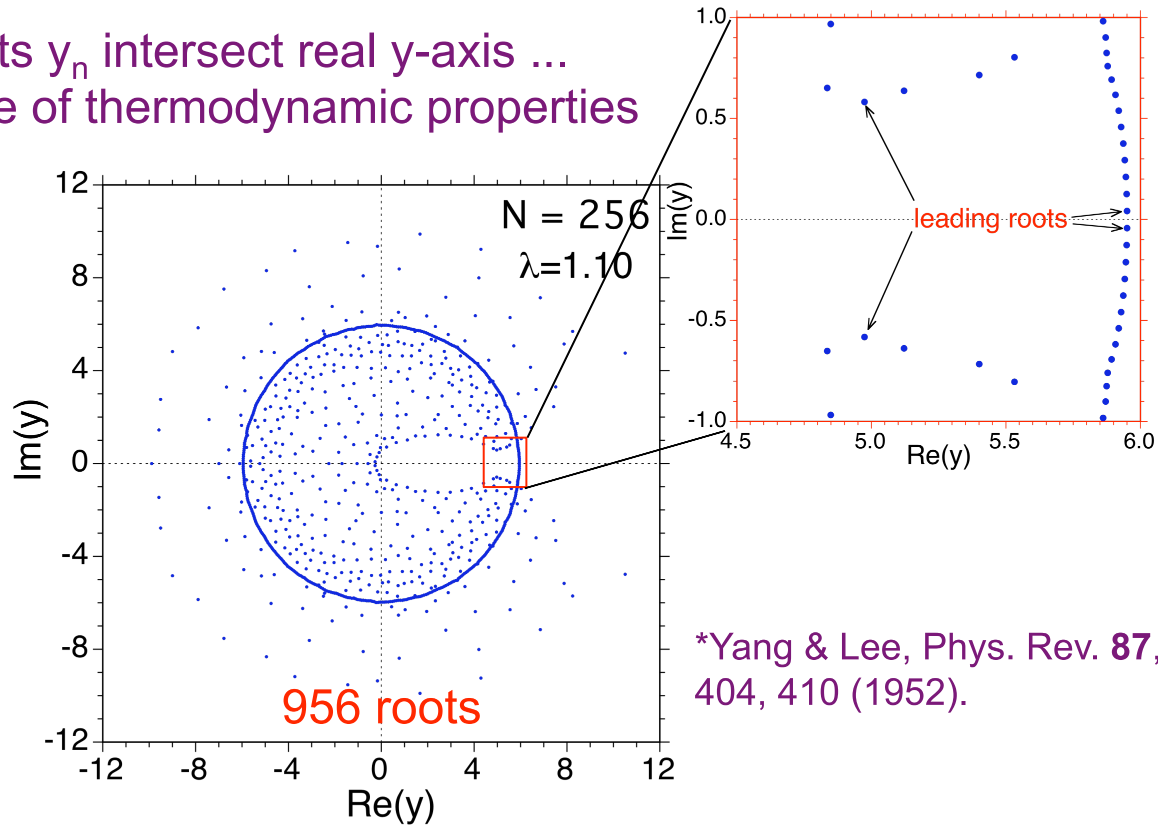
With increasing N, leading roots approach the real axis

Follows Yang-Lee behavior*:

In the thermodynamic limit roots y_n intersect real y-axis ...

gives rise to divergence of thermodynamic properties



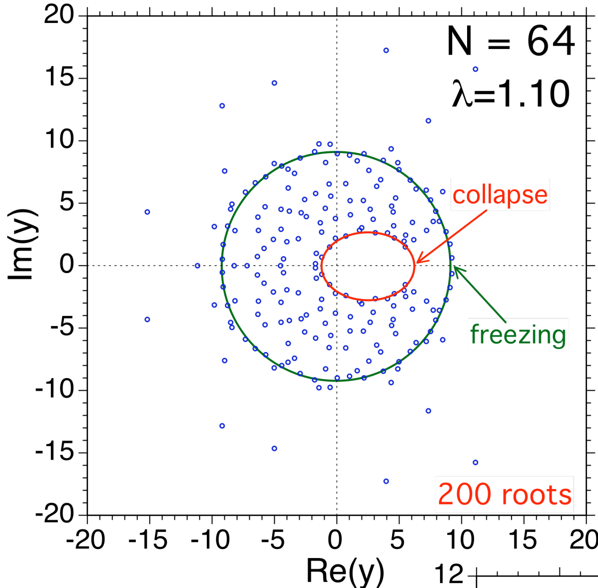


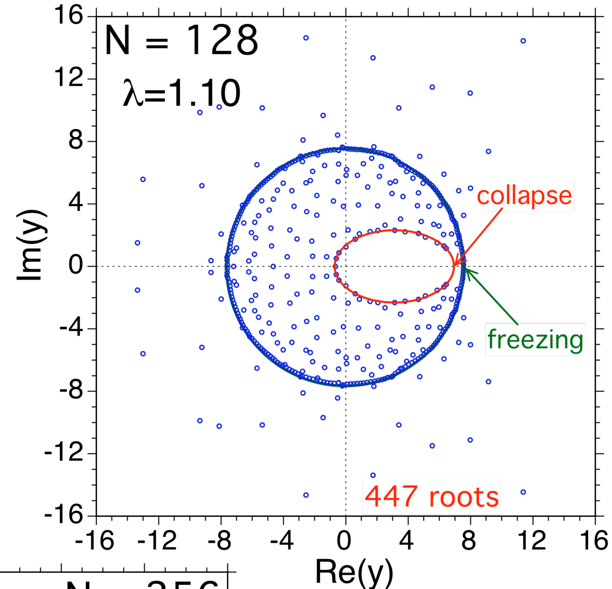
*Yang & Lee, Phys. Rev. **87**, 404, 410 (1952).

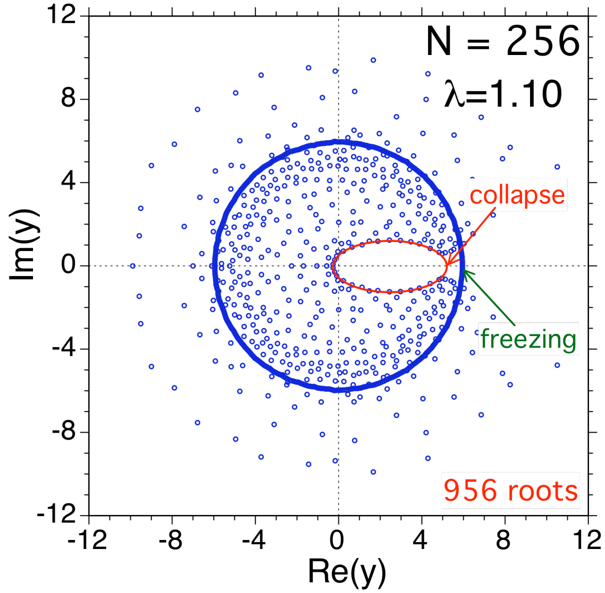
Using Partition Function Roots Maps I

Transition temperatures for finite chains can be obtained by:

fitting ellipse and circle to root maps







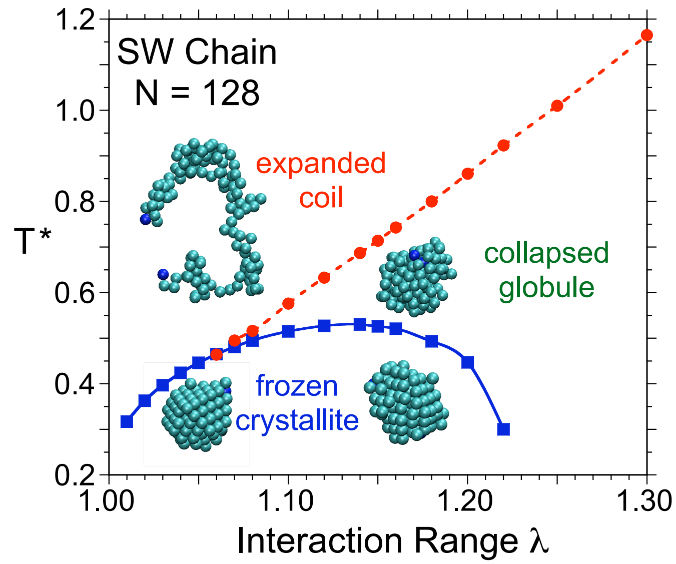
With increasing N, root density on rings increase

... scaling of the root density can be used to determine transition strength.

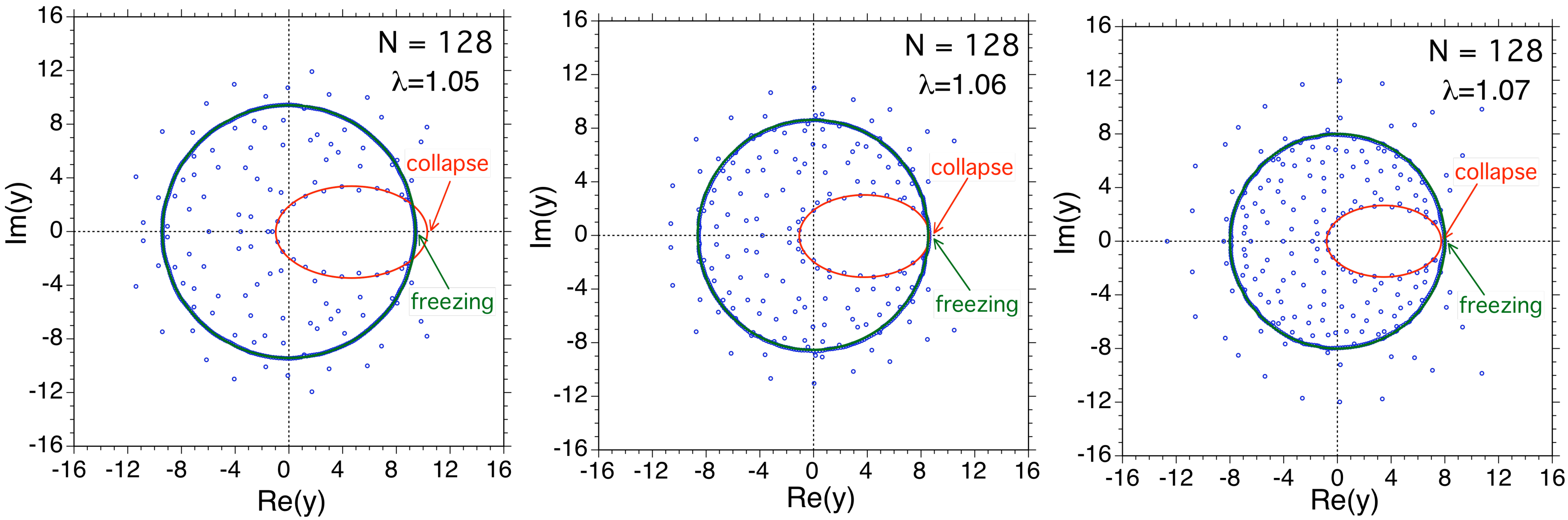
Janke & Kenna, J. Stat. Phys. **102**, 1211 (2001)

Using Partition Function Roots Maps II

Roots maps clearly show disappearance of chain collapse for short range interactions



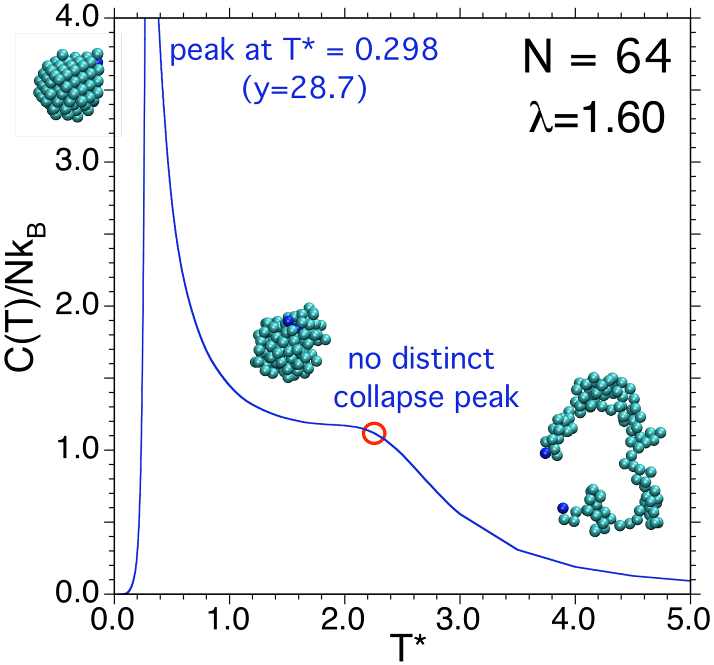
decreasing T

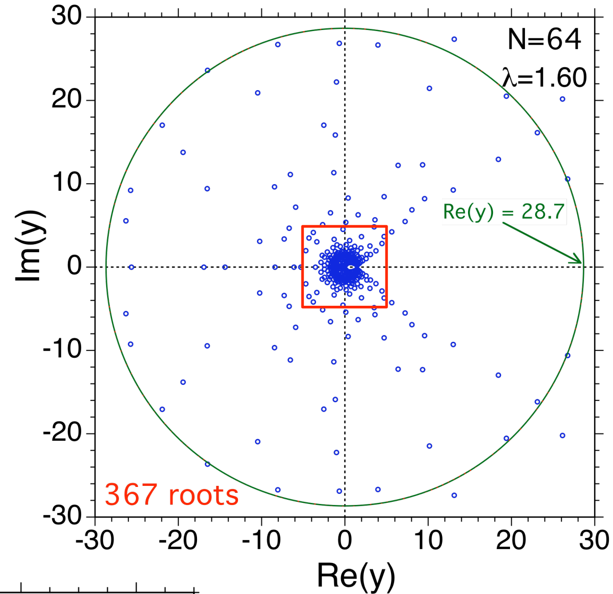


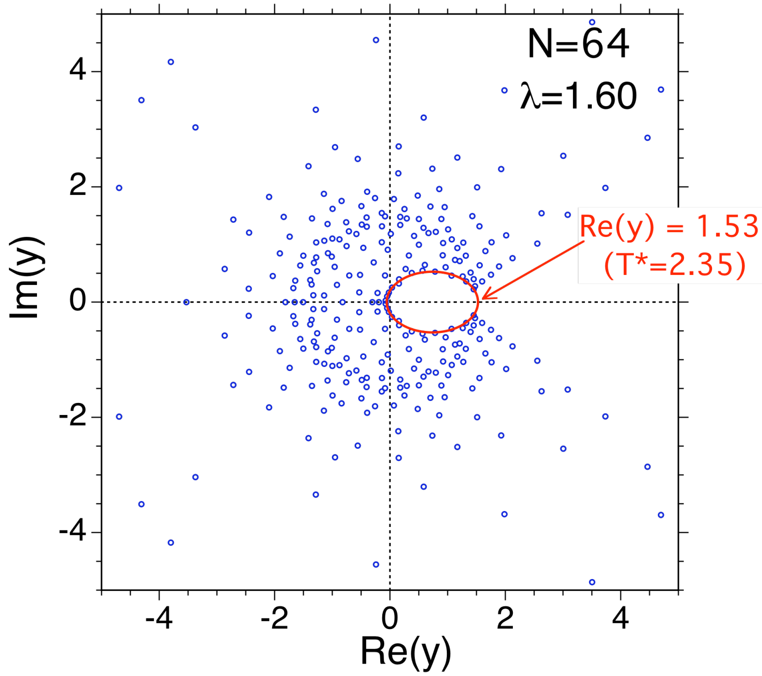
Using Partition Function Roots Maps III

Collapse transitions often have very weak C(T) or c(E) peaks

Root maps can precisely locate these weak transitions







Properties of the Partition Function Zeros

Origin of the circle:

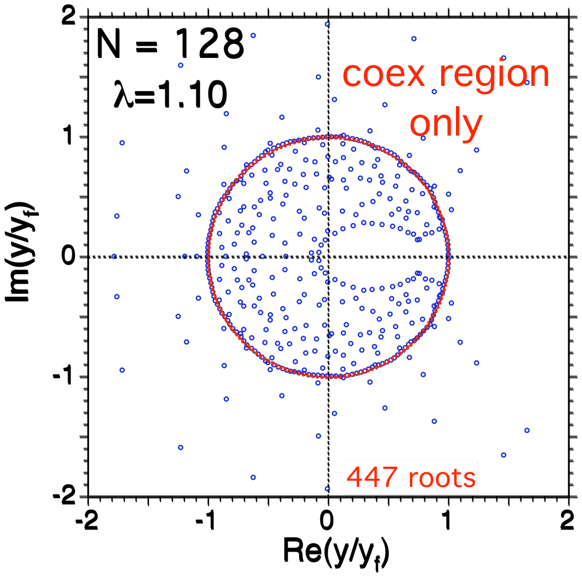
Number of roots forming circle equals number of energy states in "coexistence" region of S(E)

This portion of the Z(T) polynomial can be approx. mapped onto a polynomial of the form:

$$Z = 1 + c_1 y + c_2 y^2 + \ldots + c_{n-1} y^{n-1} + y^n$$

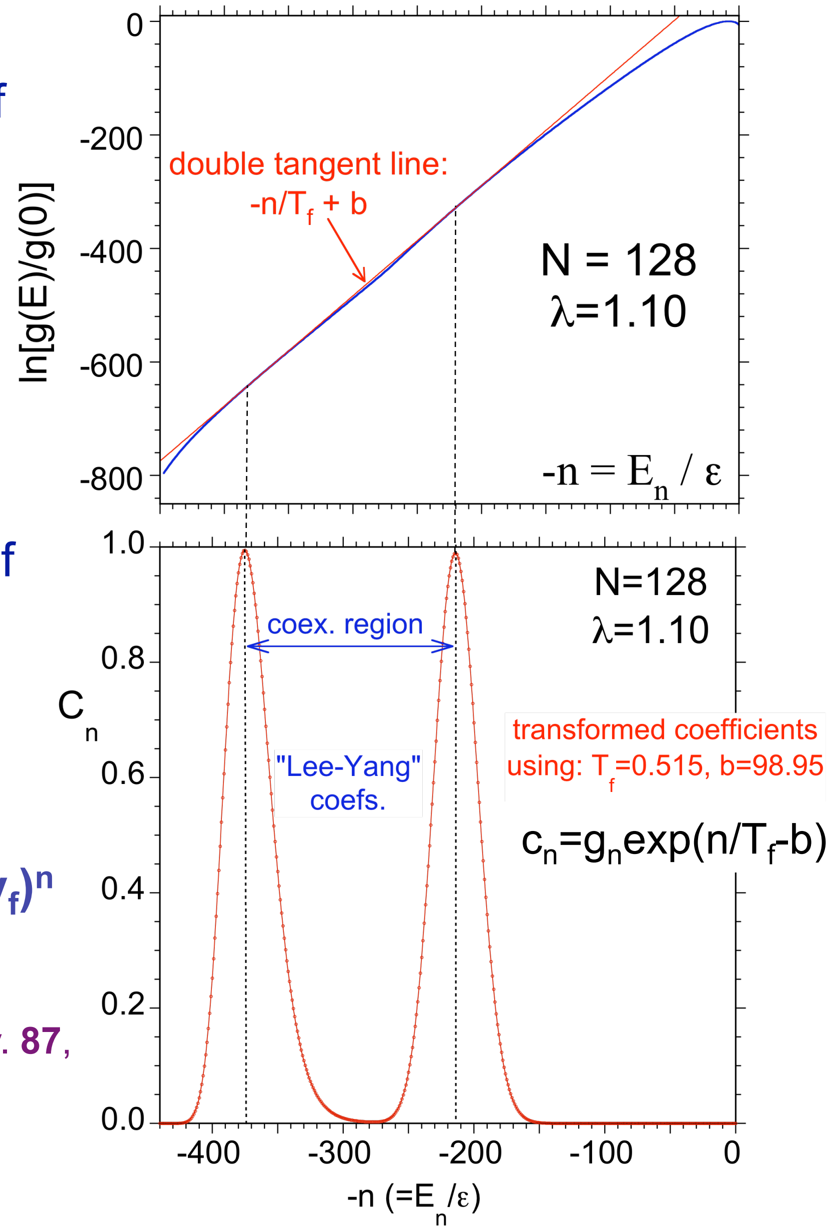
where $c_i < 1$ and $c_i = c_{n-i}$

Yang and Lee have shown that any polynomial of this form has roots confined to the unit circle*



$$Z(T) = e^b \sum_n c_n \, (y/y_f)^n$$

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



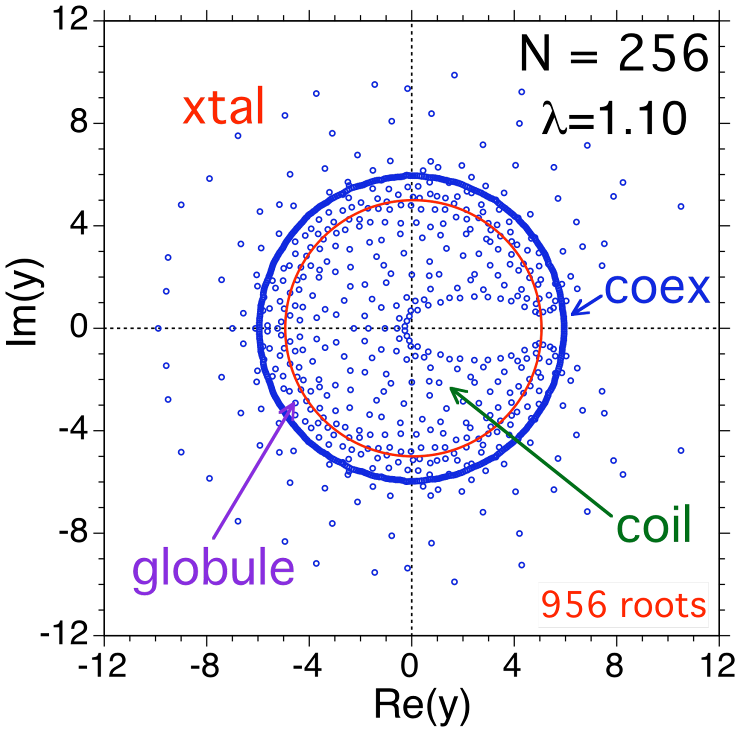
Properties of the Partition Function Zeros

$$Z(T) = \sum g(E)\, e^{-E/kT} = \sum g_n\, y^n \quad \text{where } y=\exp(1/T^*)$$

Transitions divide the complex y-plane into circular regions

Z(T) can be divided into "sub-polynomials"
that span the energy range for each phase:

$$Z(y) = Z_{coil} + Z_{globule} + Z_{coex} + Z_{crystal}$$



Summary and Outlook

Flexible SW Chain Model

Findings: Partition function zeros provide clear signatures for chain freezing and collapse transitions.

Chain collapse located more robustly than from C(T) or c(E).

To do: Study more fully relation between curvature properties of S(E) and distribution of zeros in the complex plane.

Carry out finite size scaling analysis with these roots.

Funding: DFG (SFB 625-A3)

NSF (DMR-0804370)

Hiram College

Special thanks to the Binder and Paul groups for their hospitality!

Happy "American" Thanksgiving