Partition function zeros and finite size scaling for polymer adsorption

Mark P. Taylor¹ and Jutta Luettmer-Strathmann²

¹Dept. of Physics, Hiram College, Hiram, OH  USA
²Dept. of Physics, University of Akron, Akron, OH  USA

\[ N = 128 \]
Polymer adsorption transition: \( n_s(T_c) \sim N^{-\phi} \)

- tethered chain (desorbed: \( T>>T_c \))
- tethered chain (partially adsorbed: \( T\sim T_c \))
- tethered chain (fully adsorbed: \( T<<T_c \))
- cool system

attractive surface (side view)

\[ \phi = 0.58 \]
\[ \phi = 0.48 \]
\[ \phi = 0.50-0.59 \]

Eisenriegler, Kremer, Binder, JCP 77, 6296 (1982) [\( \phi = 0.58 \)]
Metzger, Muller, Binder, Bashnagel, Macromol Theory Sim 11, 985 (2002) [lit. review: \( \phi = 0.40-0.67; \phi=0.50 \)]
Grassberger, J Phys A: Math Gen 38, 323 (2005) [\( \phi = 0.48 \)]
Decas, Sommer, Blumen, Macromol Theory Sim 17, 429 (2008) [\( \phi = 0.50-0.59 \)]
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: \(\sqrt{4} \text{ to } \sqrt{10}\)
- 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:

\[ E = -n_s \varepsilon \]

\(n_s = \text{number of surface contacts}\)

\(T = k_B T / \varepsilon = \text{reduced temperature}\)
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 with \( g(E_n) = 1, \) \( H(E_n) = 0 \) \( \forall n, \) \( f_0 = e \)

Generate sequence of chain conformations using acceptance criteria:

\[
P_{acc}(a \rightarrow b) = \min \left(1, \frac{g(E_a)}{g(E_b)}\right)
\]

Update DOS:
\( g(E_n) \rightarrow f_m g(E_n) \)

Update visitation histogram:
\( H(E_n) \rightarrow H(E_n) + 1 \)

When histogram \( \sim \) flat ...
- reduce modification factor: \( f_{m+1} = (f_m)^{1/2} \)
- reset histogram to zero: \( H(E_n) = 0 \) \( \forall n \)

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

Polymer Adsorption: Single Chain DOS and Specific Heat

Canonical Analysis

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

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

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

Specific Heat: $C(T) = \frac{d\langle E(T) \rangle}{dT}$

$n_s = \text{number of surface contacts}$

expected behavior:

$C_{\text{inf}}/Nk_B \sim |T - T_c|^{-\alpha}$
Polymer Adsorption: Single Chain DOS and Fraction Adsorbed

Canonical Analysis

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

Probability: $P(E,T) = \frac{g(E)}{Z}$

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

Order Parameter: $M(T) = \frac{\langle n_s(T) \rangle}{N} = \frac{\langle E(T) \rangle}{N \epsilon}$

expected behavior:

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

$n_s = \text{number of surface contacts}$

$n_s/N$ vs. $\ln[g_n/g_1]$ (for different $N$ values: 128, 256, 512, 1024, 1536)
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

\[ Z(T) = \prod_k (y-w_k) \quad \text{where } w_k = a_k + ib_k \text{ are the complex zeros of } Z(T) \]

Properties: complex zeros come in pairs \(a \pm ib\)
- any real zeros must be negative
- sum of \(Re(w_k)\) 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: \(y > 1\))

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

Zeros near real axis contribute most
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.

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

Yang-Lee theory of phase transitions

System with two phase transitions

Collapse and freezing of a SW-chain


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: \( y = e^{\beta} = e^{1/T} \))
- Leading root (complex)
- Crossover exponent
- Complex constant \( (D = d_a + id_b) \)


Scaling of \( \text{Im}[w_1] \) gives \( \phi \):

\[ \text{Im}[w_1] \sim d_b N^{-\phi} \]

Linear correlation between \( \text{Im}[w_1] \) and \( \text{Re}[w_1] \) gives \( y_c \):

\[ \text{Im}[w_1] \sim (\text{Re}[w_1] - y_c) d_b / d_a \]

Alternately, linear correlation between \( \text{Im}[w_1] \) and \( \beta_1 \) gives \( \beta_c \):

\[ \text{Im}[w_1] \sim (\beta_1 - \beta_c) y_c d_b / d_a \]

Complex inverse temperature:

\[ \ln(w_1) = \beta_1 + i\tau_1 \]
Adsorption transition: The crossover exponent $\phi$

Imaginary part of leading zeros vs chain length

scaling behavior:

$$\text{Im}(w_l) \sim N^{-\phi}$$

$\phi = 0.535(11)$
Adsorption transition: The transition temperature $T_c$

For long chains the leading zeros are expected to show a linear approach the $\text{Re}(w)$-axis (or the $\beta$-axis).

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

Result for transition temperature:

$T_c = 1.016(2)$
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:

$$\beta_1 - \beta_c \sim N^{-\phi}$$

$$|1 - T_c / T_1| \sim N^{-\phi}$$

Leads to scaling relations:

$$M_N(T_c) \sim N^{-\tilde{\beta} \phi}$$

Order parameter

$$n_s(T_c) = NM_N(T_c) \sim N^{\phi}$$

Number adsorbed

$$C_N(T_c) / Nk_B \sim N^{\alpha \phi}$$

Specific heat

And exponent identities:

$$\tilde{\beta} = -1 + 1/\phi$$

$$\alpha = 2 - 1/\phi$$
Finite size scaling at $T_c$: Number absorbed and order parameter

**Scaling Behavior for Number Absorbed**

$n_a(N, T_c) \sim N^\phi$

$\phi = 0.529(12)$

**Result from $\text{Im}(w_1)$**

$\phi = 0.535(11)$

**Scaling Behavior for Order Parameter**

$M_N(T_c) \sim N^{-\beta \phi}$

$\beta \phi = 0.468(20)$

**Result for Order Parameter Exponent**

$\beta = 0.875(41)$

Agrees with: $\beta = -1 + 1/\phi$
Finite size scaling at $T_c$: Specific Heat

Scaling behavior:

$$C_N(T_c)/Nk \sim N^{\alpha_\phi}$$

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 \( \phi \) are caused by strong corrections to scaling. Note that \( \phi = 0.48 \) gives a negative \( \alpha \), indicating a non-diverging specific heat.

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 $\phi$.
    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.

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Happy "American" Thanksgiving