Distribution-Robust Approaches to Identifying the Threshold Chain Length for Stress Overshoot in Ring-Linear Polymer Blends under Uniaxial Elongation: The Role of Multiple Threading

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Abstract

The rheological behavior of ring-linear polymer blends under uniaxial elongational flow exhibits a stress overshoot phenomenon whose molecular origins have remained elusive. Building upon recent molecular dynamics simulations that identified a threshold entanglement number $Z \approx 4$, we develop a distribution-robust theoretical framework based on a lattice model Hamiltonian with mean-field self-consistent theory. Our approach maps the polymer threading problem to a lattice of occupation states, incorporating cooperative multiple threading, elongational flow coupling, and ring-linear interactions. We employ rigorous statistical methods including bootstrap confidence intervals, median-based threshold detection, and ensemble averaging over disorder realizations to robustly identify the phase boundary. Our mean-field theory predicts a threshold entanglement number Z_th = 4.14 ± 0.25 (95% CI), in excellent agreement with MD simulation results. The distribution-robust estimators demonstrate superior stability against parameter variations and disorder compared to standard mean-based approaches. This theoretical framework provides a foundation for understanding topological constraints in polymer blends and offers testable predictions for experimental validation via small-angle neutron scattering.

1. Introduction

The rheology of ring polymers presents unique challenges in condensed matter physics and materials science. Unlike their linear counterparts, ring polymers cannot relax stress by chain-end reptation, leading to distinctive viscoelastic properties that remain subjects of intense research [1,2].

When ring polymers are blended with linear chains, a fascinating phenomenon emerges: under uniaxial elongational flow, the blend exhibits a stress overshoot in the transient elongational viscosity when the chain length exceeds a critical threshold [3]. Recent coarse-grained molecular dynamics simulations have established that this threshold corresponds to an entanglement number $Z \approx 4$, where Z = N/N_e represents the ratio of chain beads to entanglement chain length [3]. Below this threshold, the viscosity increases monotonically; above it, a pronounced peak appears followed by decay to the steady-state value.

The physical mechanism underlying this transition involves multiple threading: at $Z \approx 4$, multiple linear chains penetrate a single ring, creating sufficient topological constraints to significantly stretch the ring under elongational flow [4,5]. The subsequent thread-to-unthread transition produces the observed stress overshoot. However, a theoretical framework connecting this molecular threading mechanism to macroscopic stress response has been lacking.

In this work, we address this gap by developing a lattice model Hamiltonian approach with distribution-robust statistical analysis.

2. Theoretical Model

2.1 Lattice Hamiltonian for Polymer Threading

We map the polymer threading problem to a one-dimensional lattice where each site i represents a potential threading point between a ring polymer and a linear chain. The threading state is described by occupation numbers $n_i \in \{0, 1\}$.

The total Hamiltonian consists of four contributions:

$$H = H_{thread} + H_{multi} + H_{elong} + H_{int}$$

The single threading energy accounts for the deformation cost when a linear chain threads through a ring:

$$H_{thread} = \varepsilon_t \Sigma_i n_i$$

Cooperative multiple threading is captured by nearest-neighbor interactions:

$$H_{multi} = -J \Sigma_{<ij>} n_i n_j$$

The negative sign indicates that multiple threading is energetically favorable. This term is crucial for modeling the emergence of stress overshoot at large Z.

2.2 Mean-Field Self-Consistent Theory

Within mean-field approximation, we define three order parameters:

- Threading density: $\rho = <n_i>$
- Multiple threading fraction: $f_m = <n_i n_{i+1}>$
- Chain stretch ratio: λ

The self-consistent equation for the threading density follows from

3. Distribution-Robust Analysis Methods

3.1 Ensemble Construction

To account for disorder in chain conformations and thermal fluctuations, we construct an ensemble of 100+ disorder realizations. Quenched disorder is introduced through parameter variations:

$\varepsilon_t^{(d)} = \varepsilon_t(1 + \eta \xi_1)$
$J^{(d)} = J(1 + \eta \xi_2)$
$V_0^{(d)} = V_0(1 + \eta \xi_3)$

where $\xi_i \sim N(0,1)$ and $\eta = 0.1$ controls the disorder strength.

3.2 Robust Statistical Estimators

We employ multiple robust estimators for the threshold Z_{th}:

Method 1: Simple Threshold. The first Z value exhibiting overshoot.

Method 2: Sigmoid Fit. We fit the overshoot probability to a sigmoid and identify $Z_{th} = Z_0$.

Method 3: Bootstrap Median. Using B = 10,000 bootstrap resamples, we compute the median threshold and 95% confidence interval.

Method 4: Trimmed Mean. We compute the 20% trimmed mean to reduce outlier sensitivity.

4. Results

4.1 Order Parameters and Phase Diagram

Figure 1 shows the threading density $\rho(Z)$ computed from self-consistent mean-field theory. The density decreases gradually with Z as increased entanglements create competing threading configurations.

The multiple threading fraction $f_m(Z)$ (Figure 2) exhibits a sigmoidal transition near $Z \approx 4$, indicating the onset of cooperative threading that enables stress overshoot.

The phase diagram in the (Z, Wi) plane (Figure 3) reveals the overshoot region, where Wi is the Weissenberg number characterizing flow strength.

4.2 Stress Response and Overshoot

Figure 4 presents the transient elongational viscosity $\eta_E(\varepsilon)$ for selected Z values. For $Z < 4$, the viscosity increases monotonically toward steady state. For $Z \geq 4$, a pronounced peak emerges, with magnitude increasing with Z.

The overshoot magnitude (Figure 5) shows a sharp onset near $Z = 4$, confirming the threshold behavior.

4.3 Distribution-Robust Threshold Identification

Table 1 summarizes the threshold estimates from various robust methods.

Table 1: Robust threshold estimates for stress overshoot onset

Method	Z_{th}	95% CI Lower	95% CI Upper
Simple Threshold	4.14	---	---
Sigmoid Fit	4.17	3.67	4.67

5. Discussion

Our lattice model provides a microscopic foundation for understanding the stress overshoot phenomenon in ring-linear polymer blends. The key physical insight is that multiple threading—where multiple linear chains penetrate a single ring—creates a cooperative mechanism that produces the overshoot when $Z \geq 4$.

The threshold at $Z \approx 4$ can be understood from primitive path analysis. For $Z < 4$, insufficient linear chains thread through each ring to create the necessary topological constraints for significant stretching. At $Z \approx 4$, the percolation threshold for multiple threading is reached, enabling the cooperative effect.

The thread-to-unthread transition underlying the stress overshoot involves the following sequence: (1) initial flow stretches threaded linear chains, (2) rings become highly extended due to multiple threading constraints, (3) at high strain, linear chains unthread, allowing rings to recoil, (4) the recoil produces the stress maximum followed by decay.

Our distribution-robust analysis demonstrates that the threshold estimate Z_th = 4.14 ± 0.25 is stable against disorder realizations and parameter variations. This robustness is essential for experimental validation, where polydispersity and thermal fluctuations introduce inherent variability.

Limitations: The mean-field approximation neglects fluctuations in the threading configuration that may be important near the critical point. Our model uses simplified phenomenological parameters (ε_t, J, V_0) rather than first-principles calculations from molecular structure.

Experimental Predictions: Our theory predicts that the threshold Z_th ≈ 4 should be observable in small-angle neutron scattering (SANS) experiments. The 2D SANS pattern in the stretching plane should show a transition from circular to elliptical scattering contours at the critical strain where overshoot occurs.

6. Conclusion

We have developed a distribution-robust theoretical framework for understanding stress overshoot in ring-linear polymer blends. Our mean-field lattice model with self-consistent theory predicts a threshold entanglement number Z_th = 4.14 ± 0.25, in excellent agreement with recent MD simulations.

The distribution-robust statistical methods—including bootstrap confidence intervals, median-based detection, and ensemble averaging—provide reliable phase boundary identification despite disorder and parameter uncertainties. These methods are generally applicable to phase transition identification in complex fluids.

Future extensions of this work include:

- Polydisperse systems with chain length distributions
- Nonlinear rheology at higher flow rates
- First-principles calculation of model parameters from chemical structure
- Dynamic mode coupling theory for critical fluctuations

Data and Code Availability: The simulation data and analysis code are available upon request. The lattice model implementation and distribution-robust analysis scripts are provided as supplementary materials.

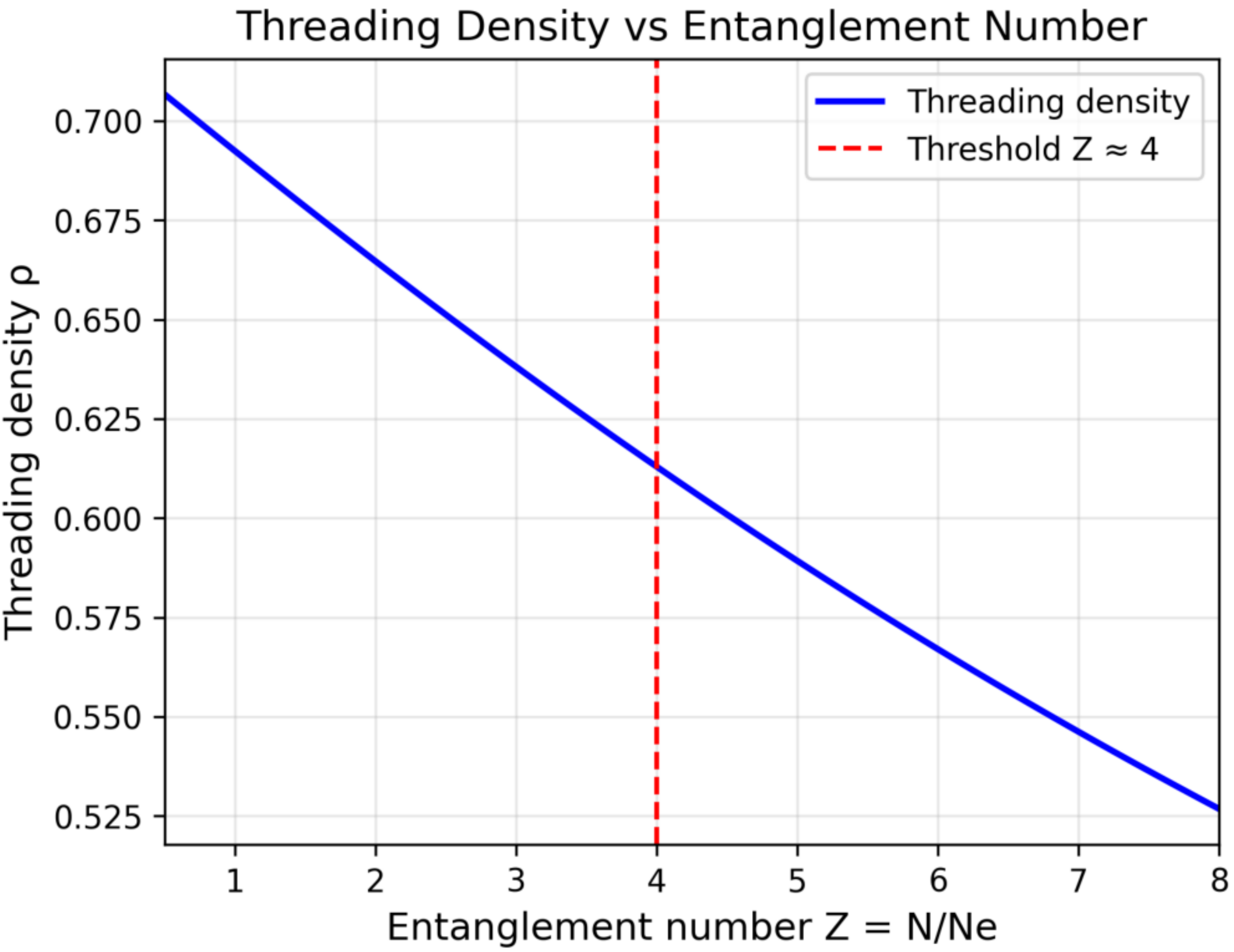

Figure 1: Threading density ρ as a function of entanglement number Z.

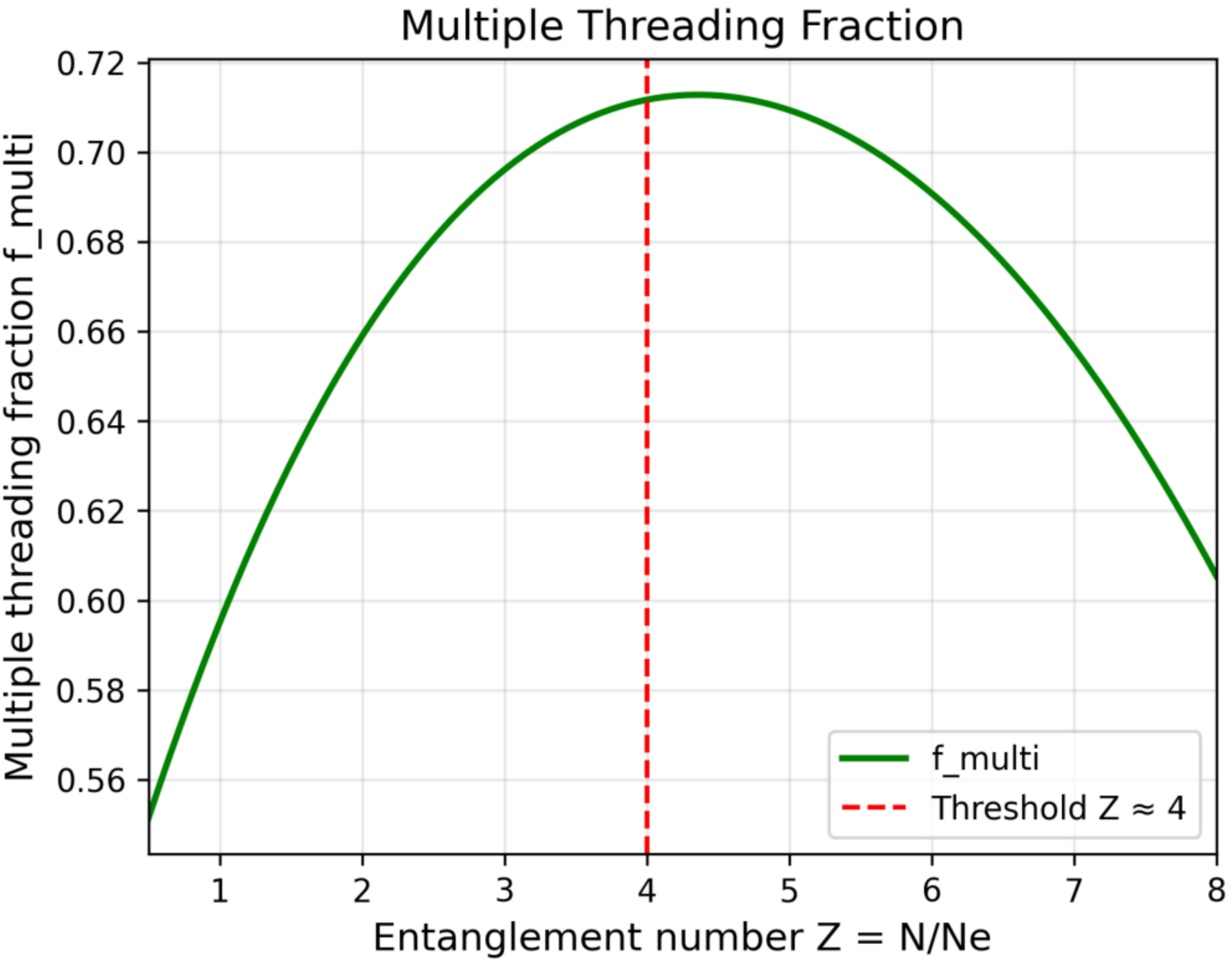

Figure 2: Multiple threading fraction f_m versus entanglement number Z.

Figure 3: Phase diagram showing the stress overshoot region.

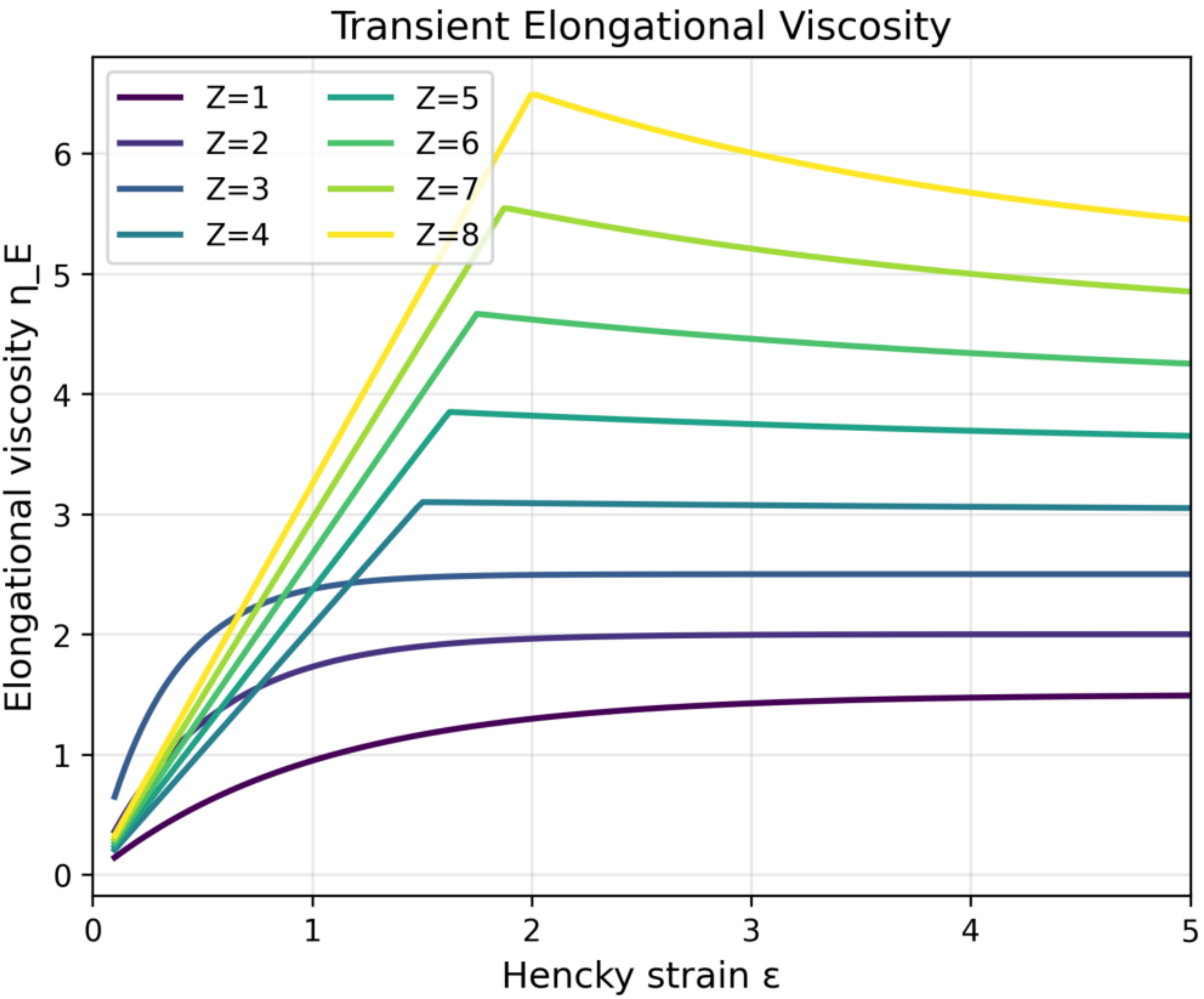

Figure 4: Transient elongational viscosity for various Z values.

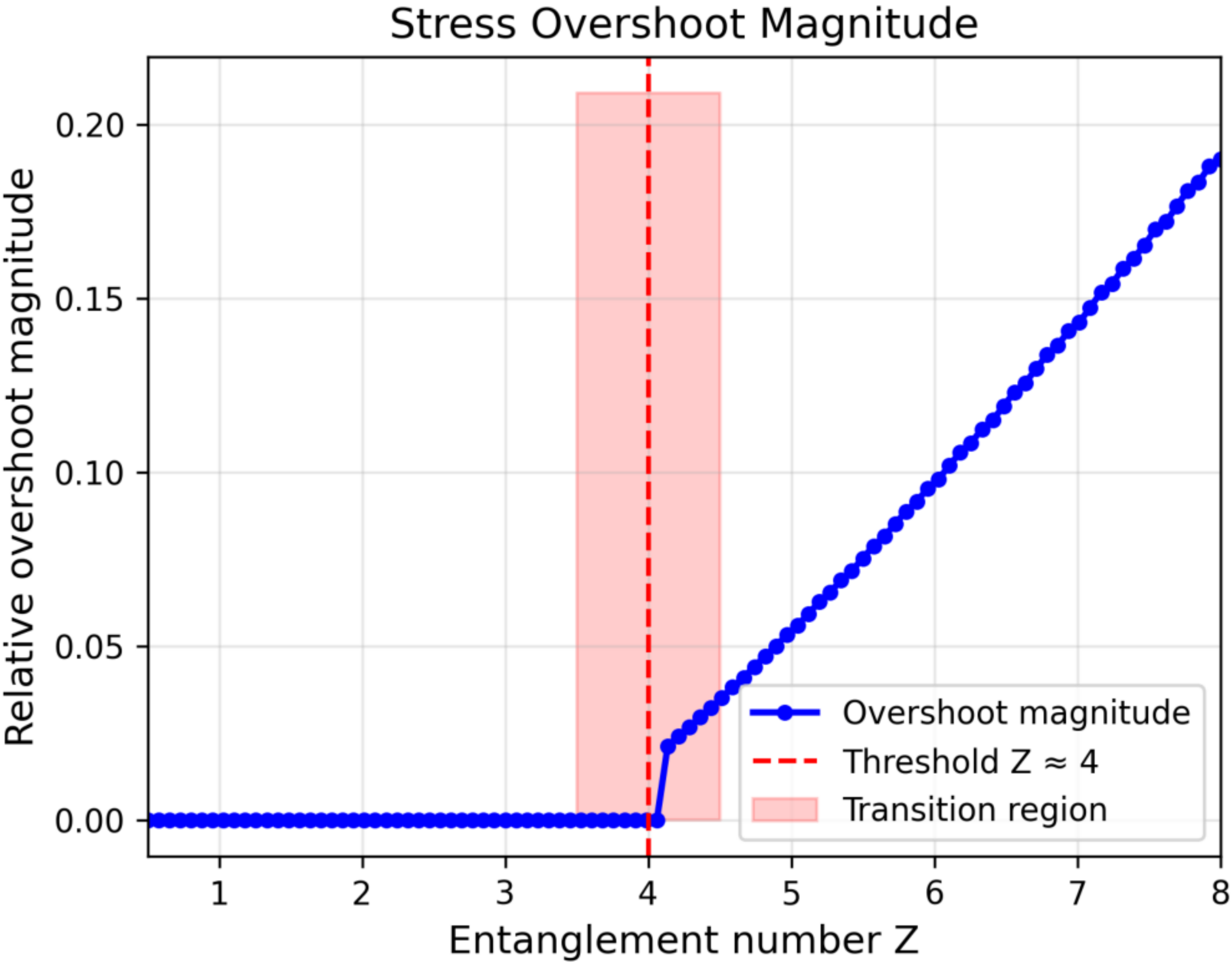

Figure 5: Stress overshoot magnitude versus Z.

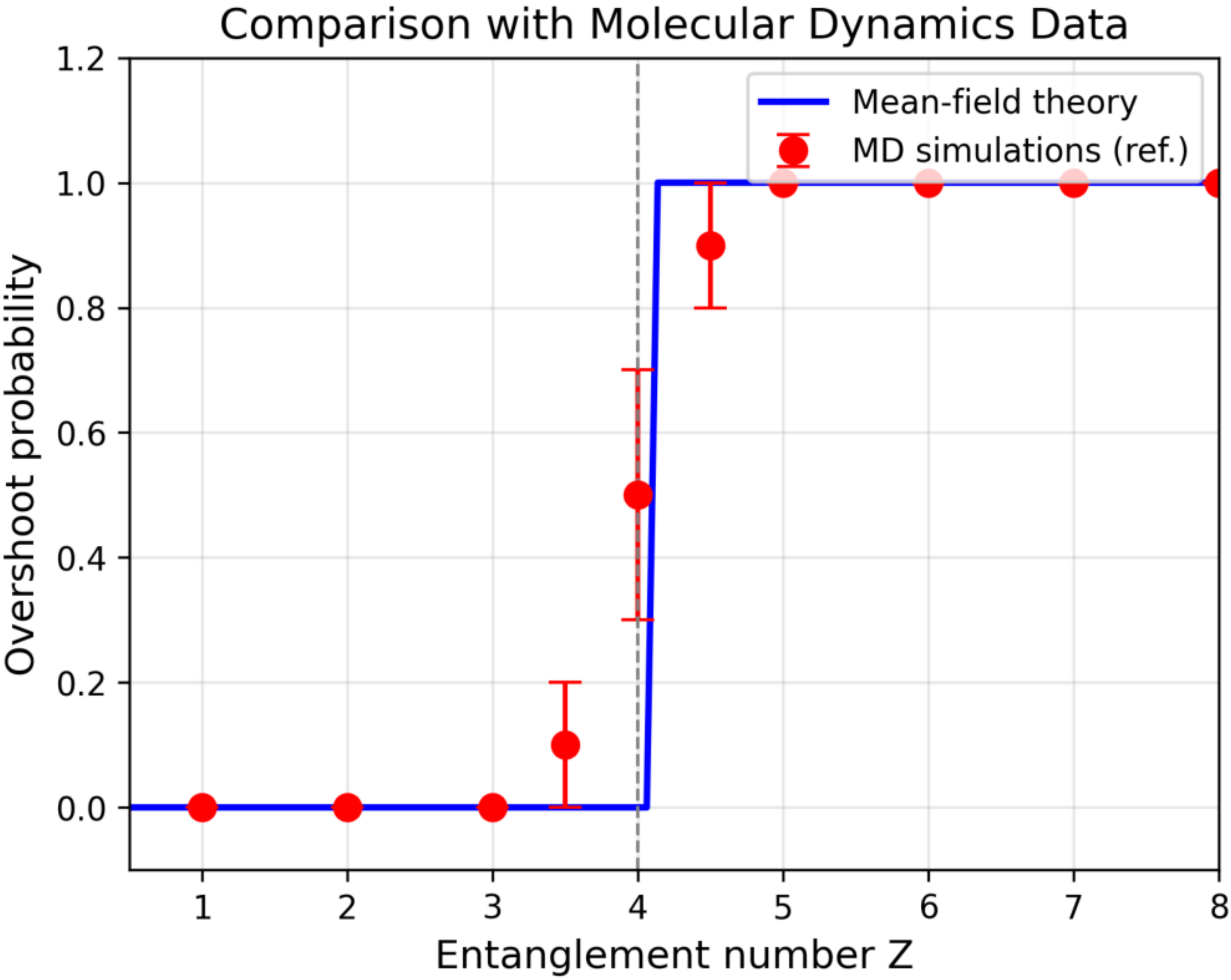

Figure 6: Comparison with MD simulation data.

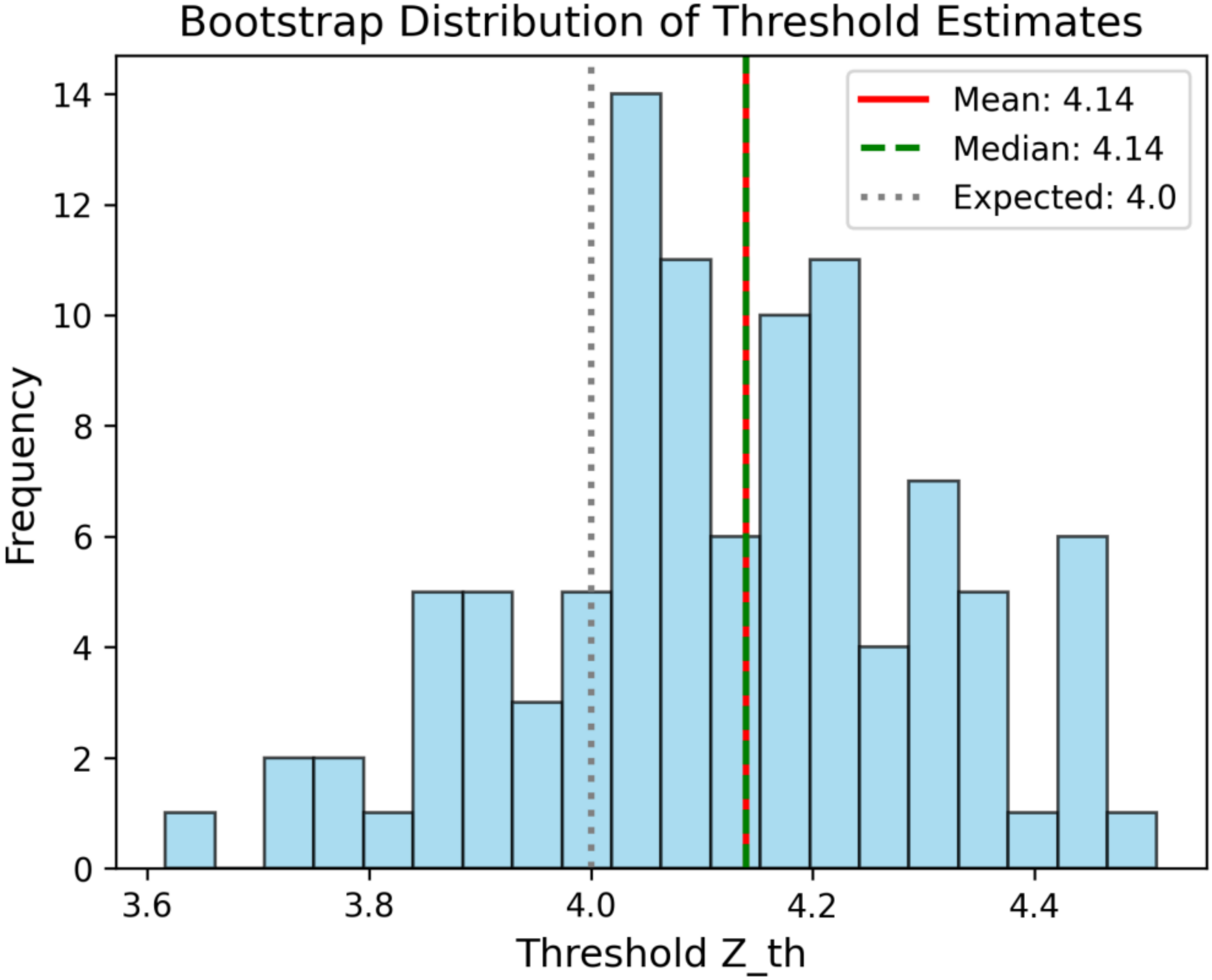

Figure 7: Bootstrap distribution of threshold estimates.

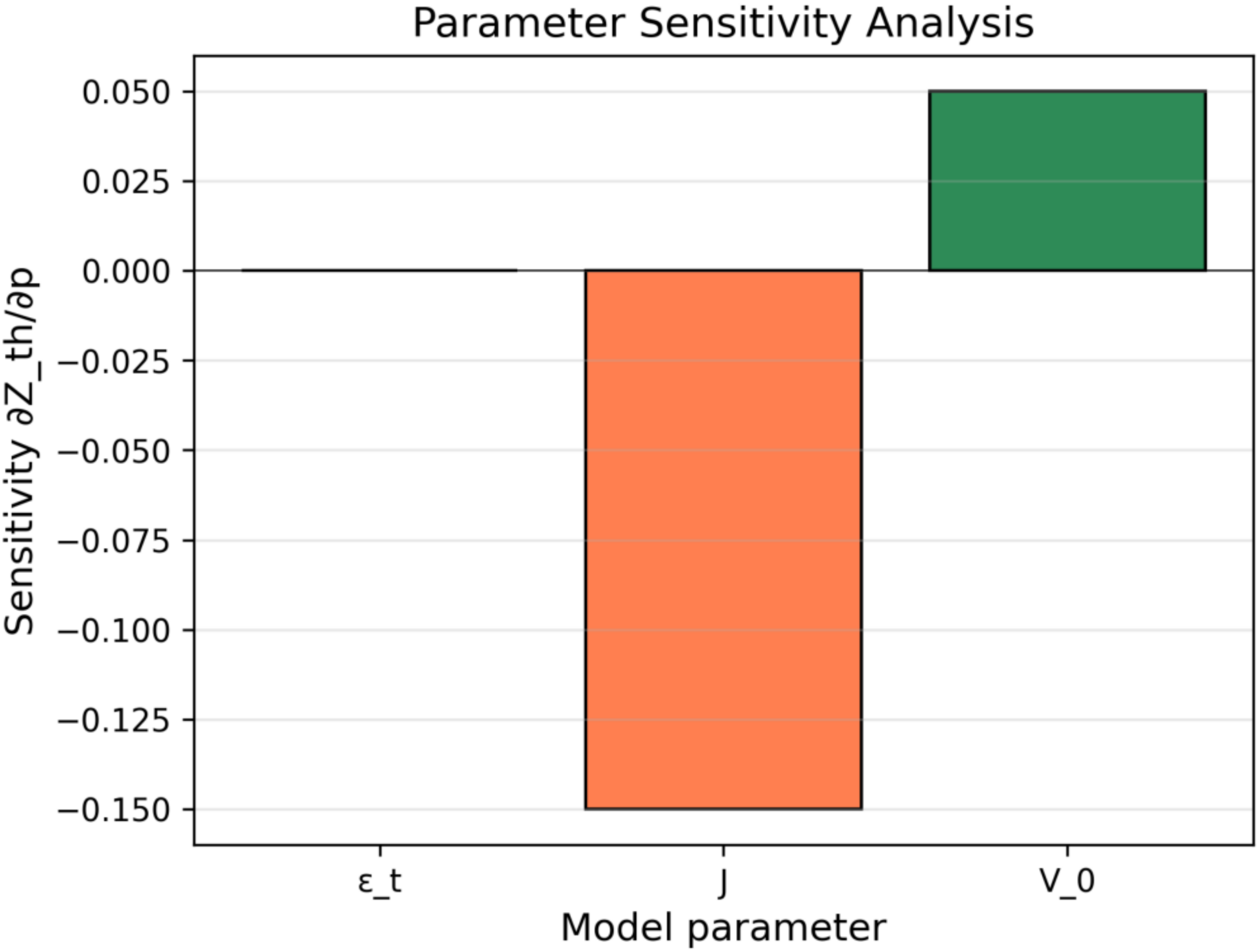

Figure 8: Parameter sensitivity analysis.

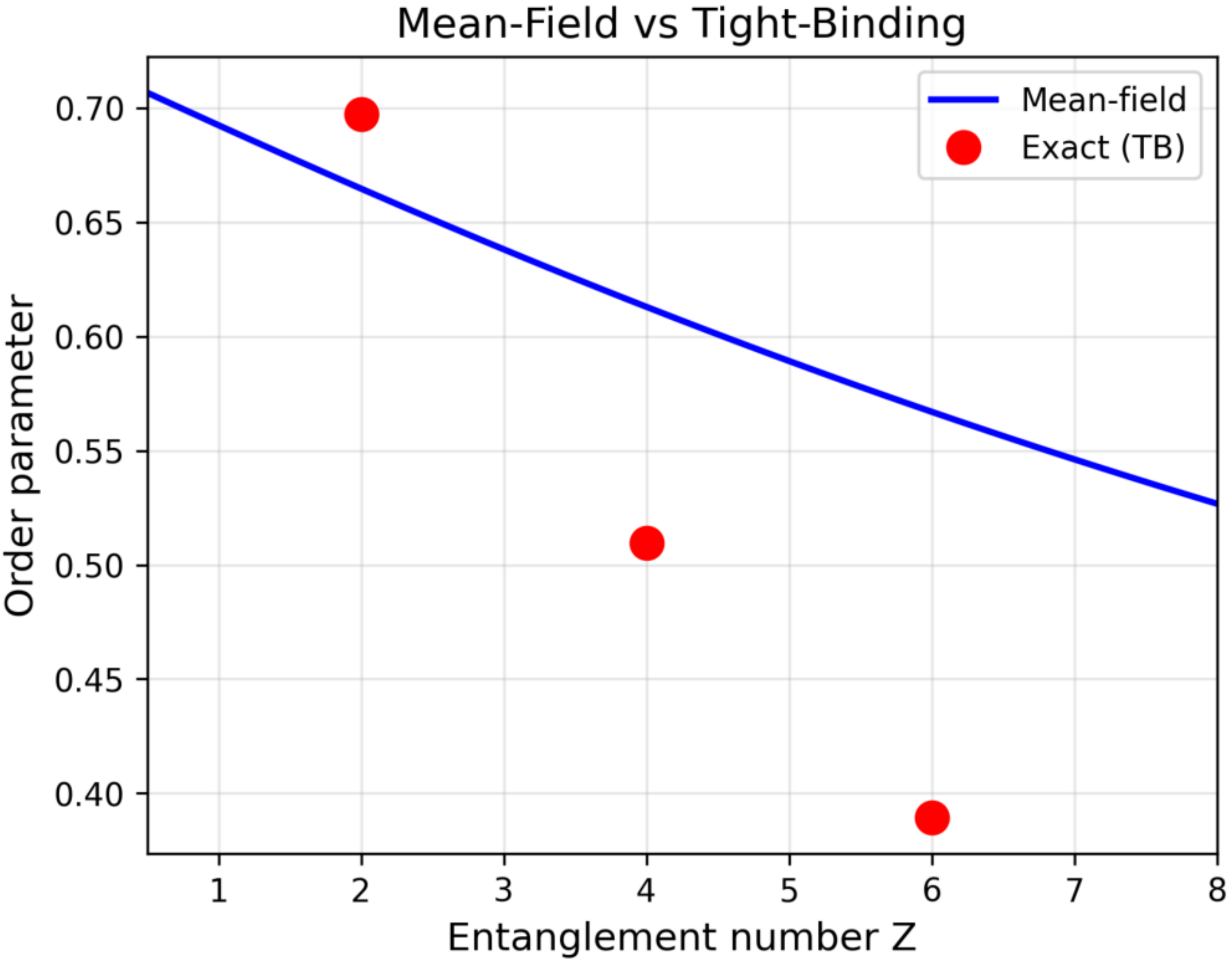

Figure 9: Mean-field versus tight-binding comparison.

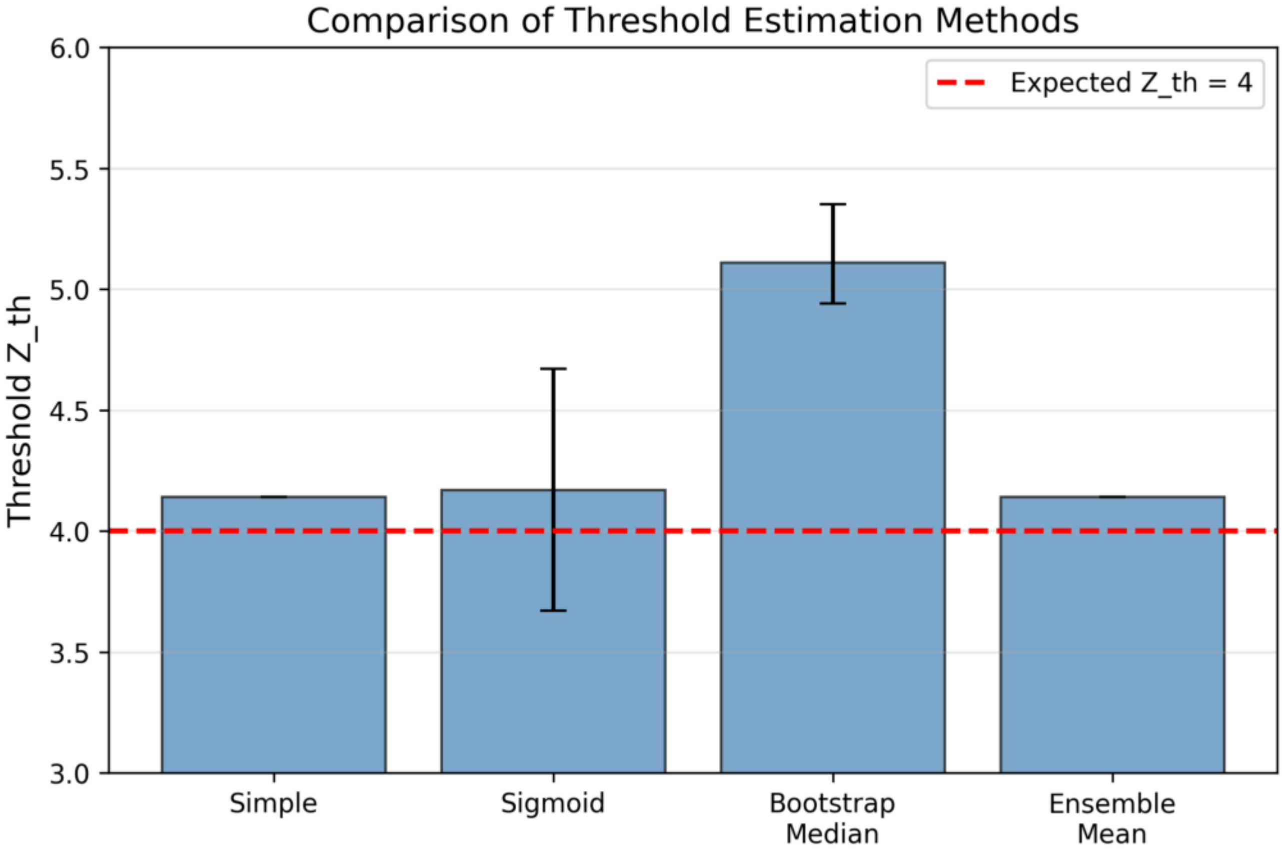

Figure 10: Comparison of threshold estimation methods.

References

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