Topological signatures of the thermodynamics of swollen and globular polymer rings

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collaborators

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Questions

- Up to what extent does the constraint of fixed topology affect the thermodynamics of a knotted polymer ring?
- Which are the relevant topological invariants?
- Are the effects of fixed topology different in different regimes (good solvent, globular, ...)?
- Does topology reveal in/determine peculiar physical phenomena?

Questions related to

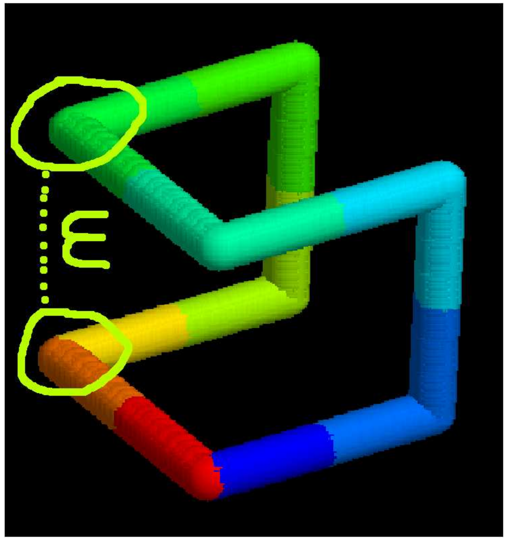
- knot localization/delocalization
- probabilities of realization of specific knots
- behavior in the presence of geometrical constraints (slip-links, walls with holes, etc.)

Overview

- Introduction
- Results for the swollen, good solvent regime
- Results for the globular, bad solvent regime
- Theta-collapsed polymer rings under various geometrical constraints. Novel, remarkable effects of topology

Model and simulations

N-step self-avoiding polygon (SAP) on the cubic lattice, with energy $\epsilon = -1$ between each pair of n.n. vertices

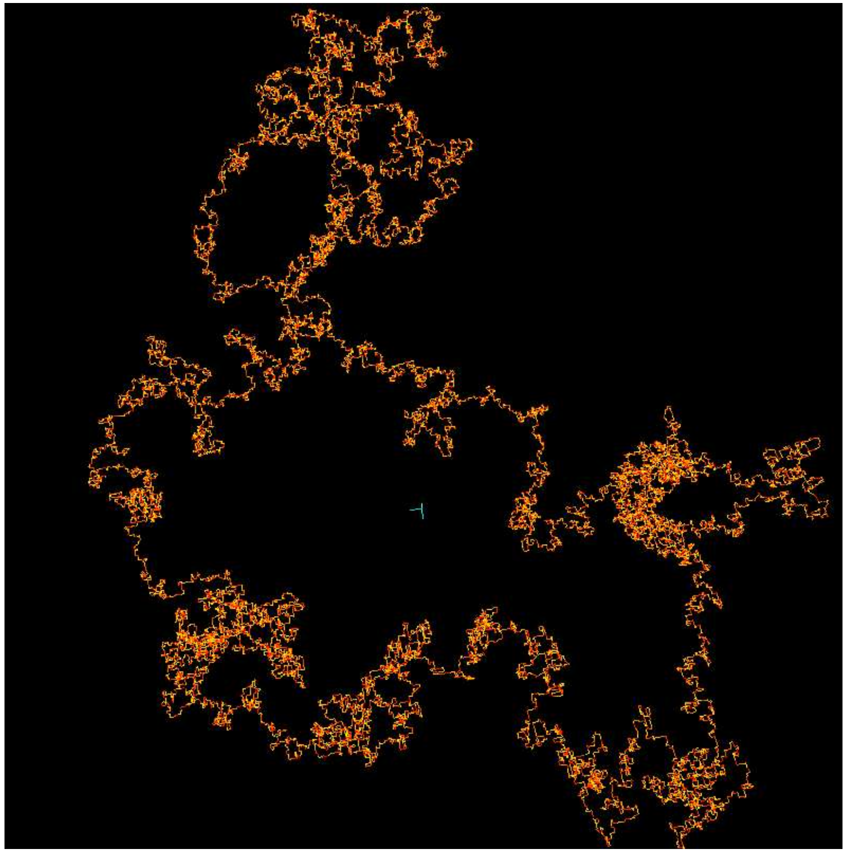


- Reference model for polymers
- Self-avoiding!

- Temperature $T = \infty \leftrightarrow \frac{\epsilon}{T} = 0$: **Swollen phase**
  - Pivot algorithm, no Metropolis $\rightarrow$ long chains
- Temperature $T = 2.5 < T_\theta$: **Collapsed phase**
  - pruned enriched Rosenbluth method (PERM) = Growth of linear walks + reweighting
  - Configurations with far ends (i.e. not n.n.) $\rightarrow$ not SAP: discarded

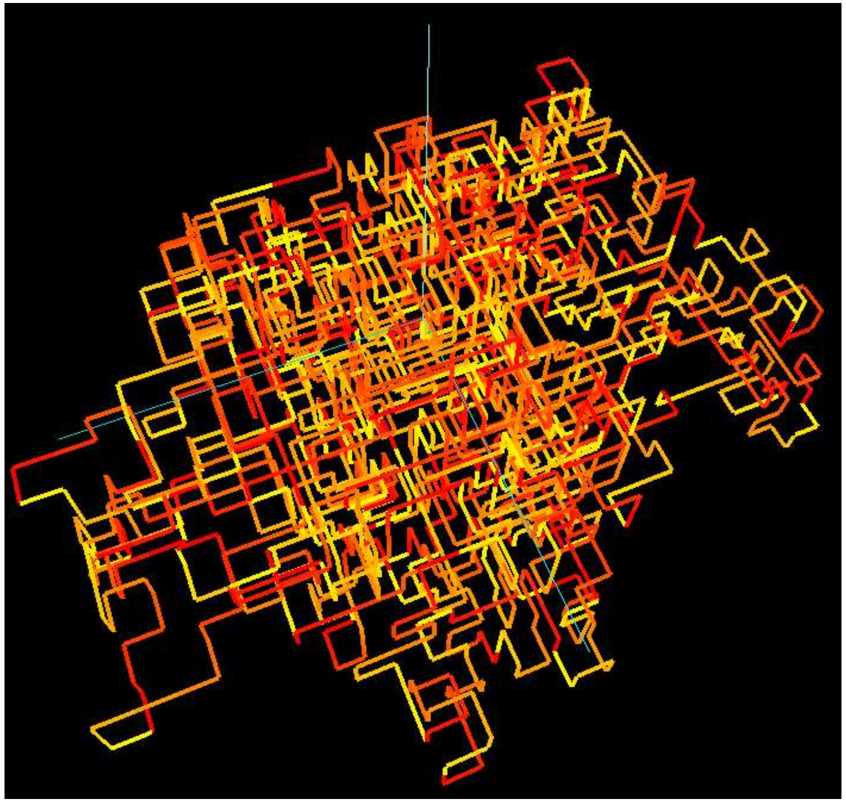
Swollen vs Collapsed

Swollen phase



chain length $N = 50000$

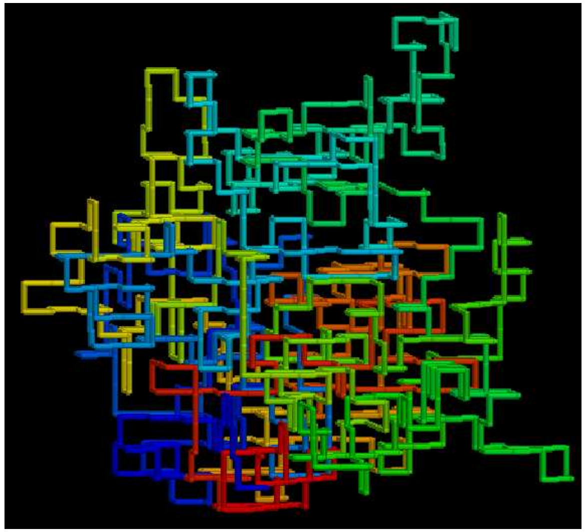
Collapsed phase

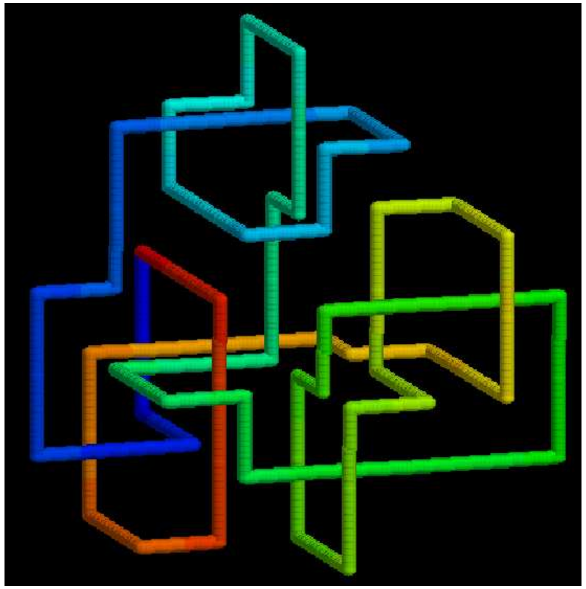


chain length $N = 1800$

Different knotting probabilities and knot spectra expected in the two phases

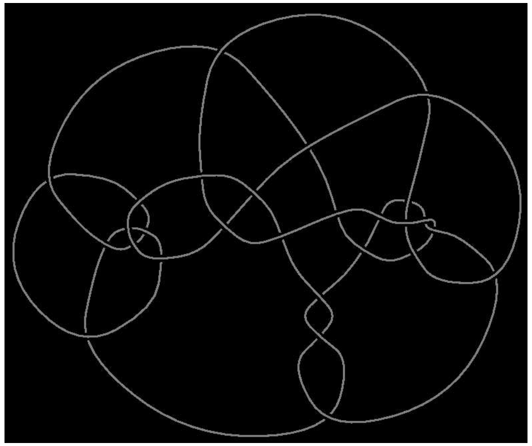
Knot identification





Steps:

- BFACF algorithm shrinks the configurations without changing knot
- Projection (now less crossings!)
- Dowker-Thistlethwaite code
- $\rightarrow$ *Knotscape* software
- HOMFLY polynomial
(prime knots up to 11 crossings)



Swollen Polymers

$$(T = \infty)$$

Knot probability

The number of polygons of length N scales as

$$Z_N \simeq A\,\mu^N\,N^{\alpha-2}$$

- α : universal exponent ($\simeq 0.236$)
- $\log(\mu)$: entropy per step ($\simeq 4.684$ for cubic lattice)
- A : Amplitude

Assumption: Number of chains with given (prime or composite) knot k:

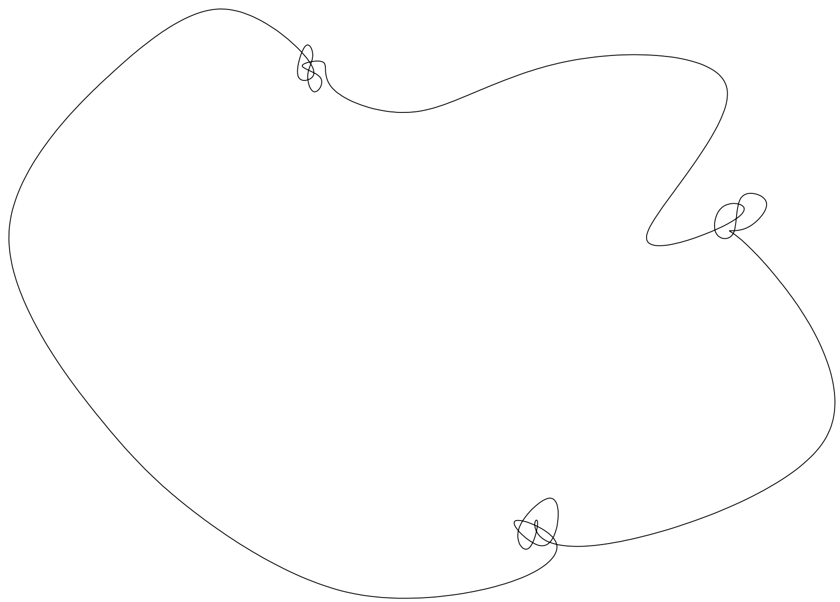
$$Z_{k,N} \simeq A_k\,\mu_k^N\,N^{\alpha_k-2}$$

- A_k, μ_k and α_k may depend on k; $\mu_\emptyset < \mu$, (Sumners, Whittington, 1988)

Probability of knot k:

$$p_{k,N} = \frac{Z_{k,N}}{Z_N} \simeq \frac{A_k}{A}\left(\frac{\mu_k}{\mu}\right)^N N^{\alpha_k-\alpha}$$

Knot localization



Prime knots localized in swollen polymers

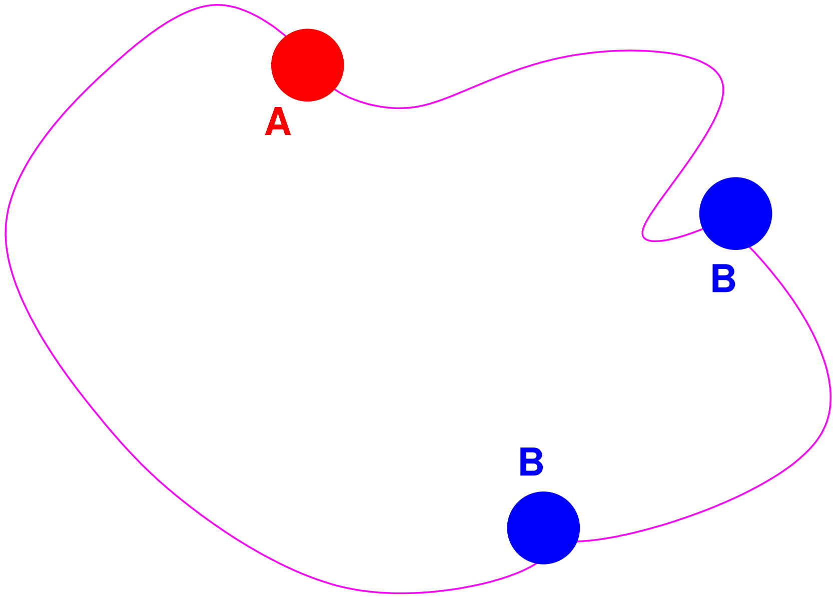
[Katritch, Olson, Vologodskii, Dubochet, Stasiak (2000)]

[Orlandini, Stella, Vanderzande (2003)]

[Hanke, Metzler, Dommersnes, Kantor, Kardar (2003)]

[Marcone, Orlandini, Stella, Zonta (2005)]

Prime components as sliding beads



$$k = A \# B \# B$$

knot component $\rightarrow$ bead

entropy contribution of each component k $\sim [log(N) - log(C)]$

$$Z_{k,N} = Z_{\emptyset,N} \times \frac{N}{C_A} \times \frac{N}{C_B} \times \frac{N}{C_B} \times \frac{1}{2}$$

$Z_{\emptyset,N}$: Partition function of the unknot

"$1/2$" : B components indistinguishable

NOTE: $\mu_k = \mu_\emptyset$

Relative frequencies: general formula

$$\frac{p_{k,N}}{p_{\emptyset,N}} = \frac{Z_{k,N}}{Z_{\emptyset,N}} \simeq \frac{1}{(\pi_1)!}\left(\frac{N}{C_{k_1}}\right)^{\pi_1} \cdots \frac{1}{(\pi_m)!}\left(\frac{N}{C_{k_m}}\right)^{\pi_m}$$

k = composite knot with m different kinds of primes:

π_1 knots of kind k_1

$\ldots$

π_m knots of kind k_m

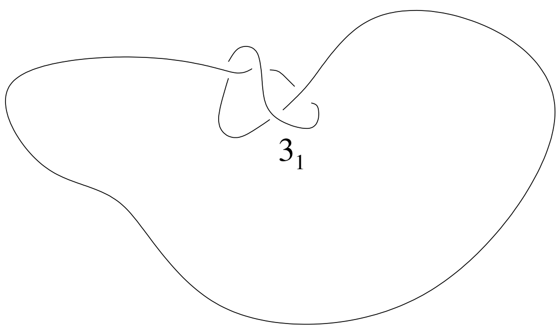
The exponent

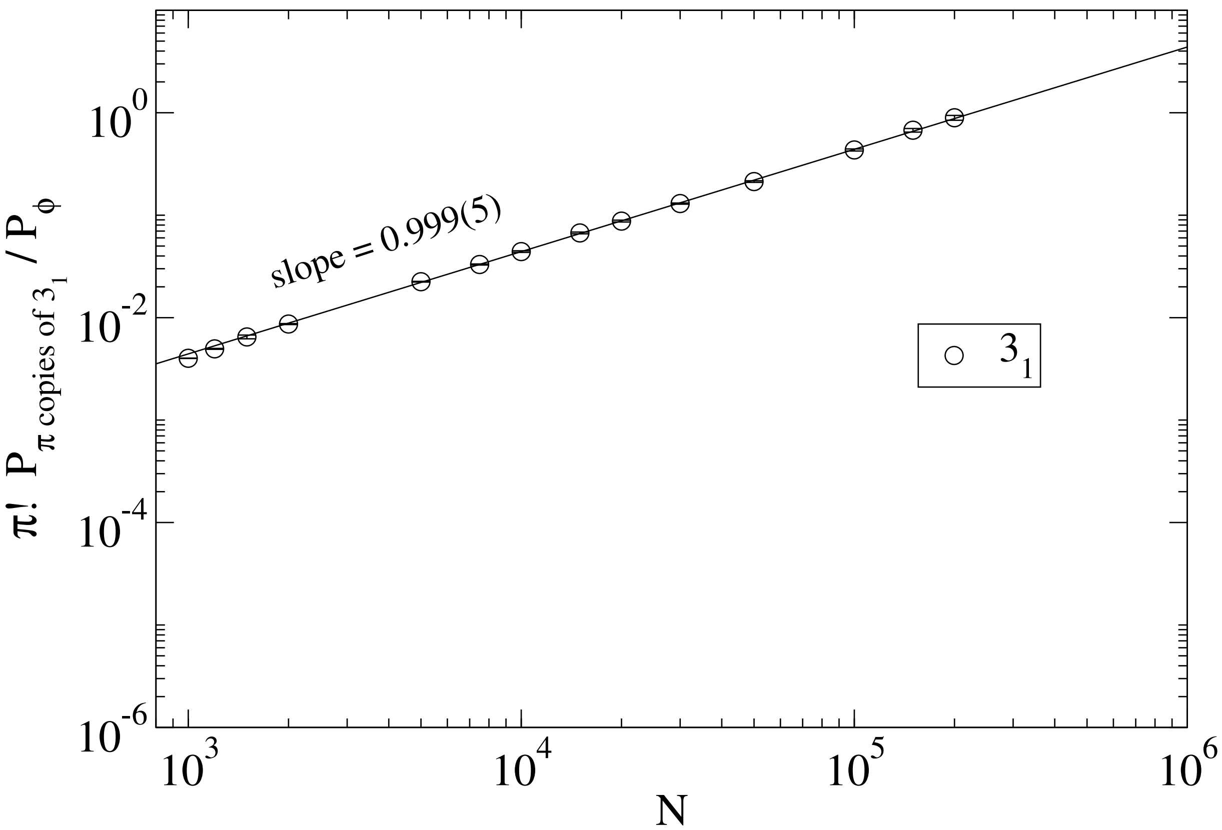
$$\alpha_k = \alpha_\emptyset + \pi_k$$

[Orlandini, Tesi, Janse van Rensburg, Whittington (1998)]

π_k = number of primes $= \pi_1 + \pi_2 + \cdots + \pi_m$

Multiple 3_1's: 1

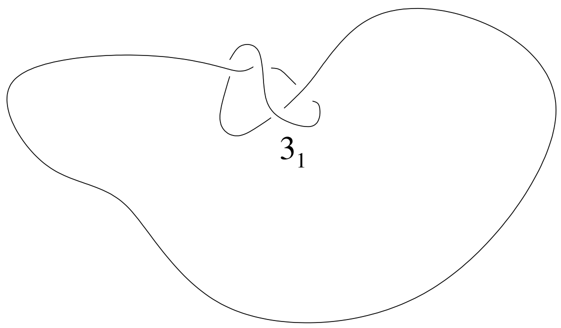




- slope $\simeq 1$
- $C_{3_1} \simeq 228000$

$$\frac{p_{3_1}}{p_\emptyset} \simeq \frac{N}{C_{3_1}}$$

Multiple 3_1's: 1



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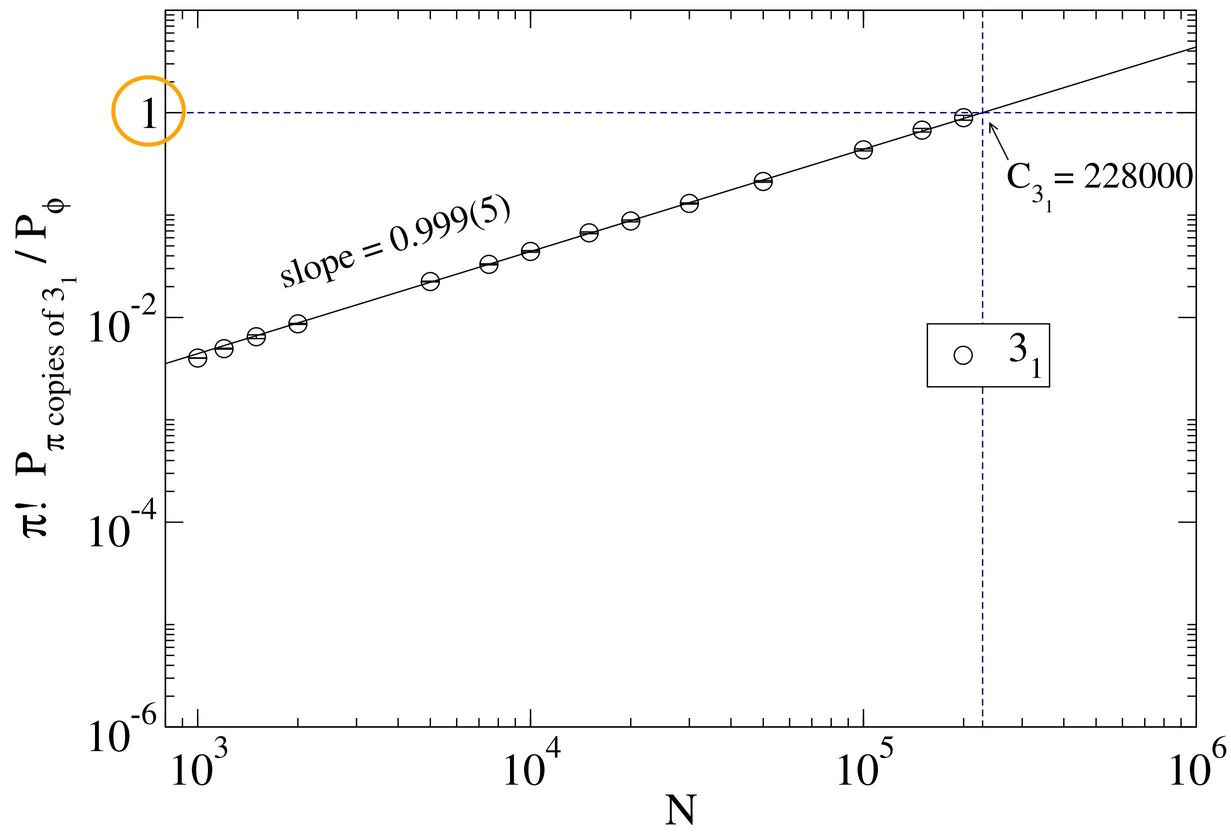
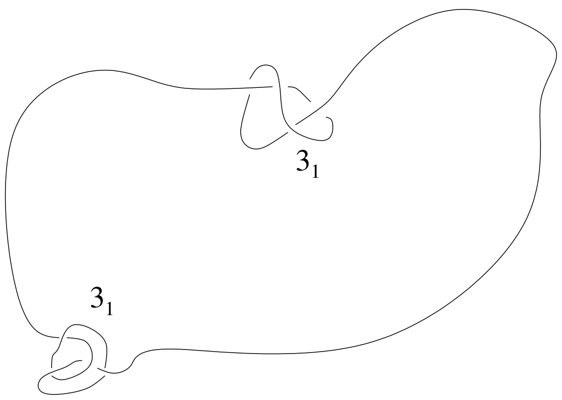
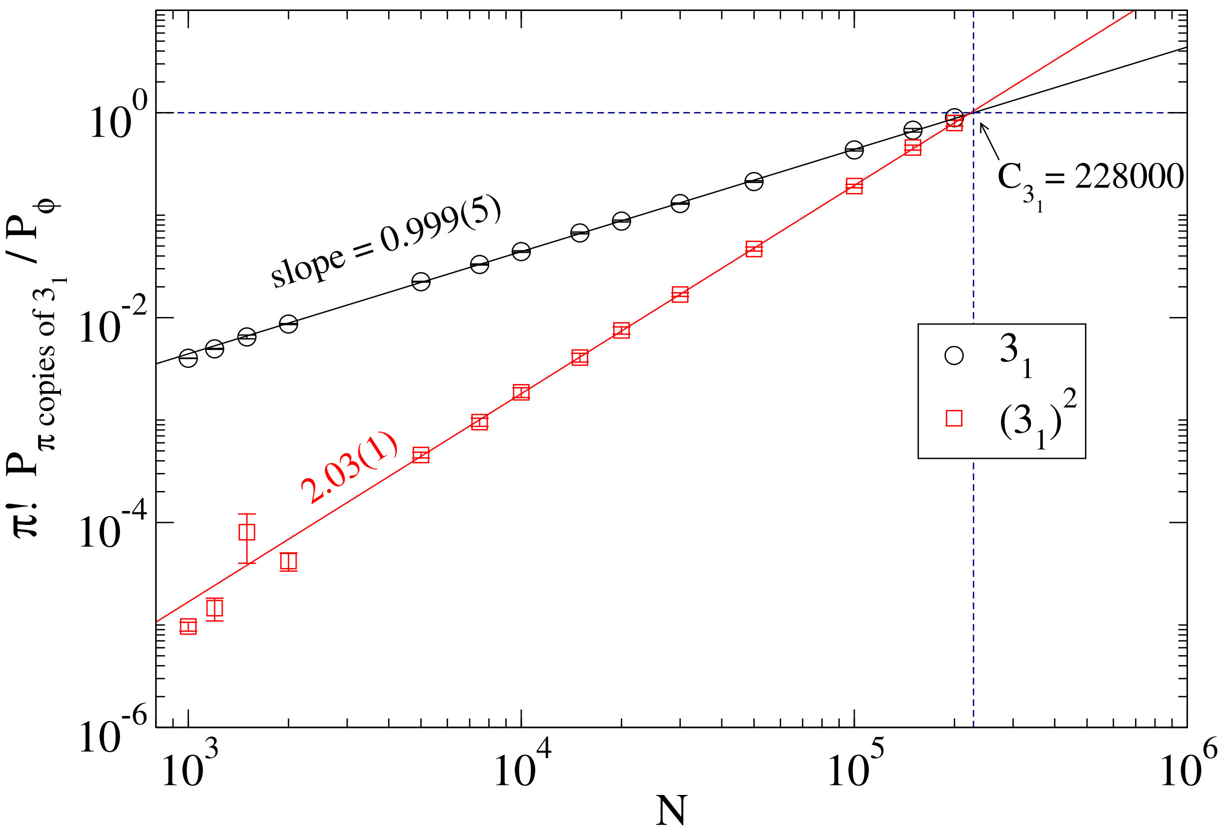


$$\frac{p_{3_1}}{p_\emptyset} \simeq \frac{N}{C_{3_1}}$$

Multiple 3_1's: 2

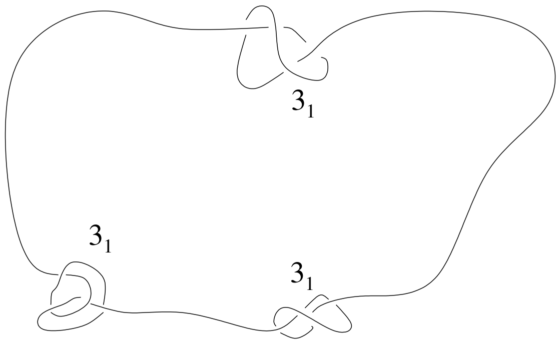


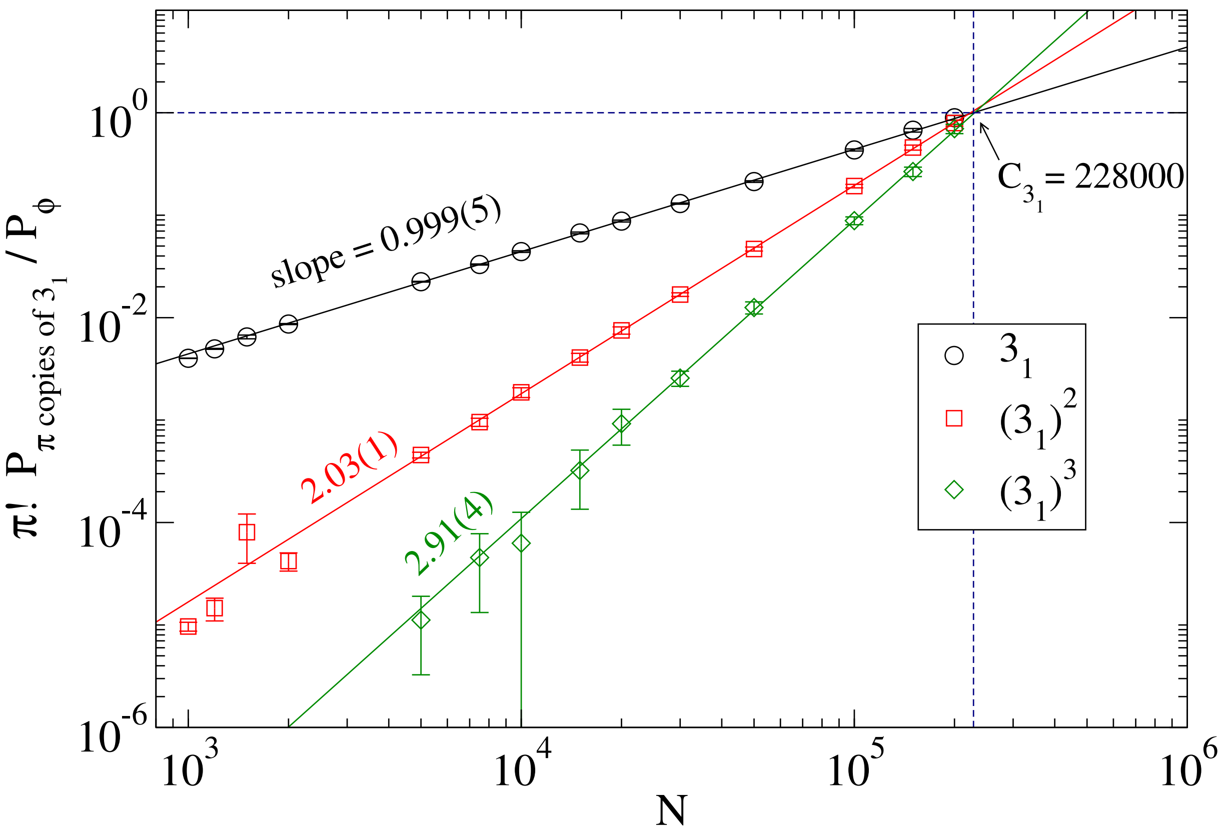


- slope $\simeq 2$
- $C_{3_1} \simeq 228000$

$$2 \times \frac{p_{3_1\#3_1}}{p_\emptyset} \simeq \left(\frac{N}{C_{3_1}}\right)^2$$

Multiple 3_1's: 3

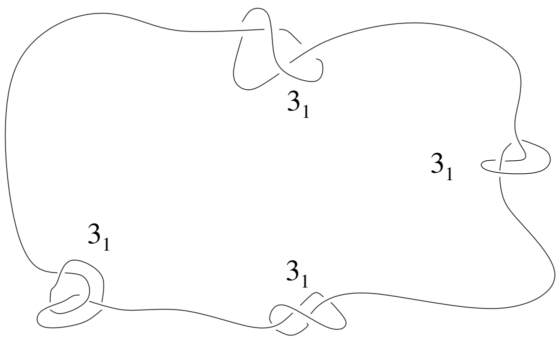


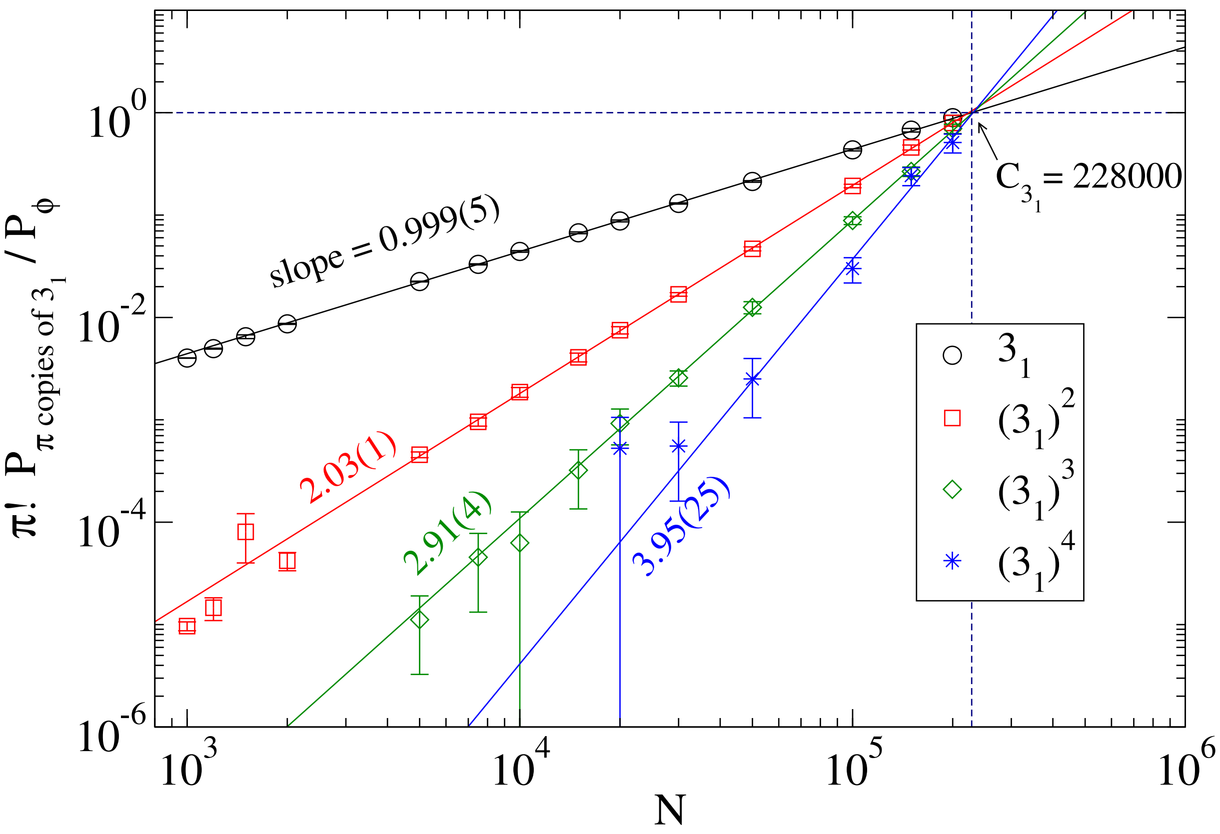


- slope $\simeq 3$
- $C_{3_1} \simeq 228000$

$$3! \times \frac{p_{3_1\#3_1\#3_1}}{p_\emptyset} \simeq \left(\frac{N}{C_{3_1}}\right)^3$$

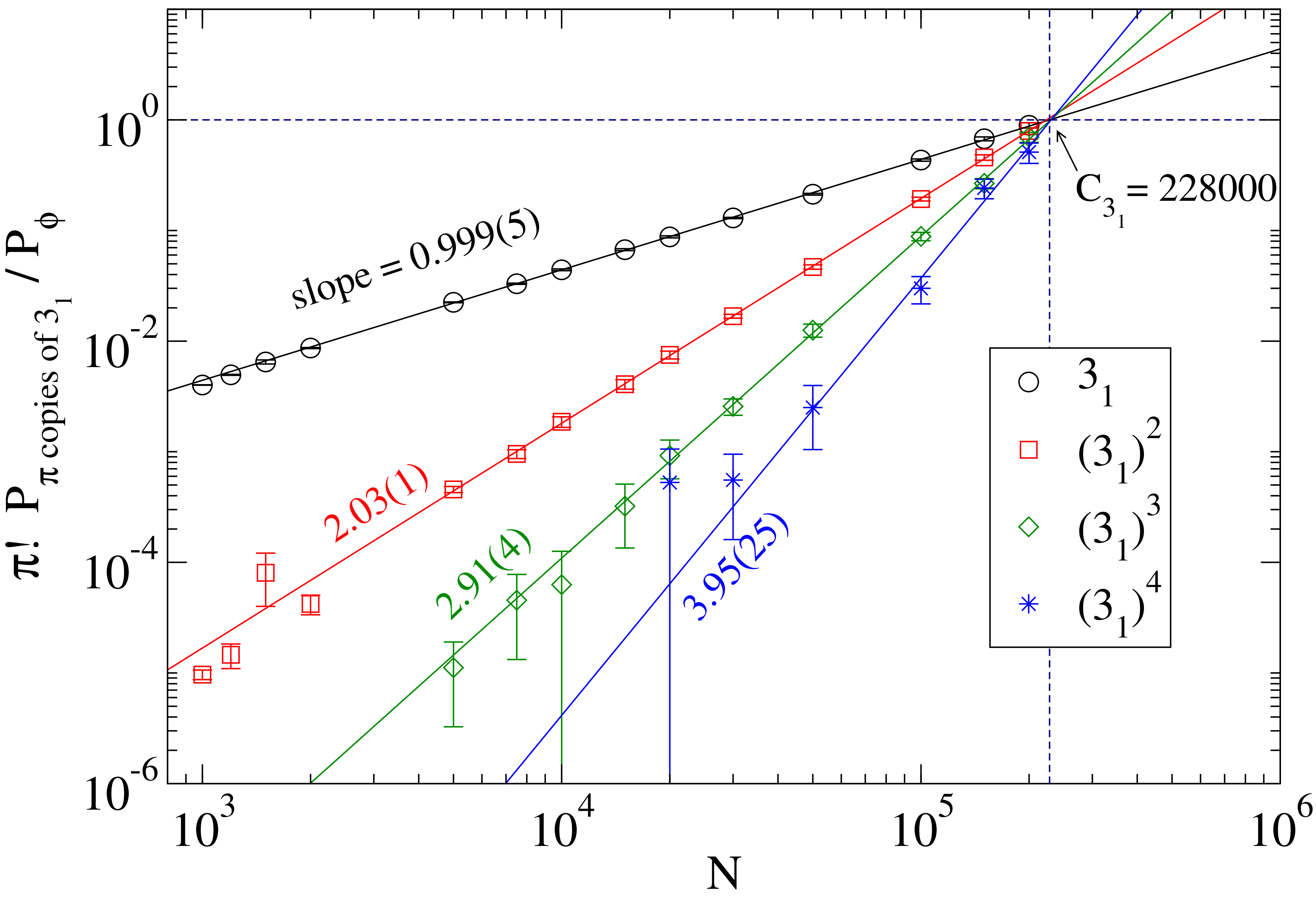
Multiple 3_1's: 4





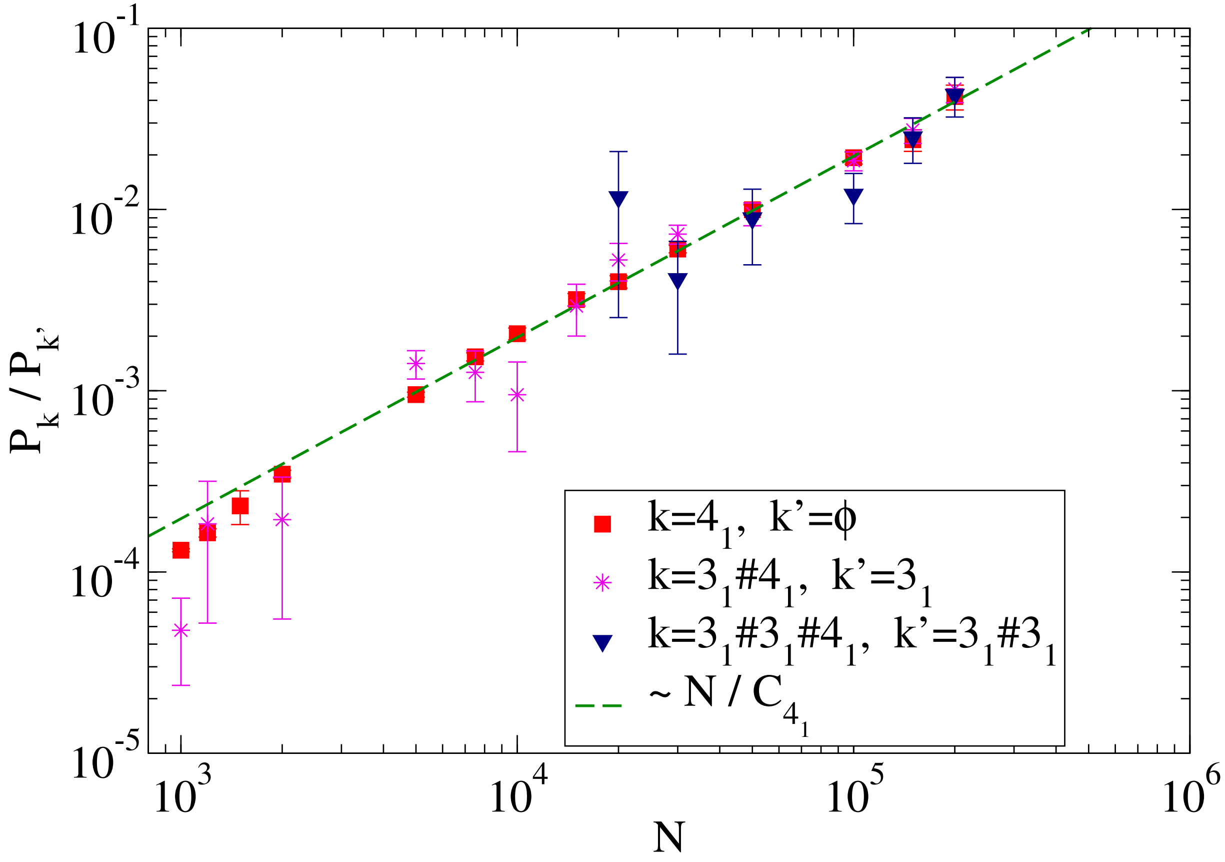
- slope $\simeq 4$
- $C_{3_1} \simeq 228000$

$$4! \times \frac{p_{3_1\#3_1\#3_1\#3_1}}{p_{\emptyset}} \simeq \left(\frac{N}{C_{3_1}}\right)^4$$



slope = 0.999(5)
2.03(1)
2.91(4)
3.95(25)
C_{3_1} = 228000
$\pi!\ P_{\pi \text{ copies of } 3_1} / P_\phi$
N
10^0
10^{-2}
10^{-4}
10^{-6}
10^3
10^4
10^5
10^6
3_1
$(3_1)^2$
$(3_1)^3$
$(3_1)^4$

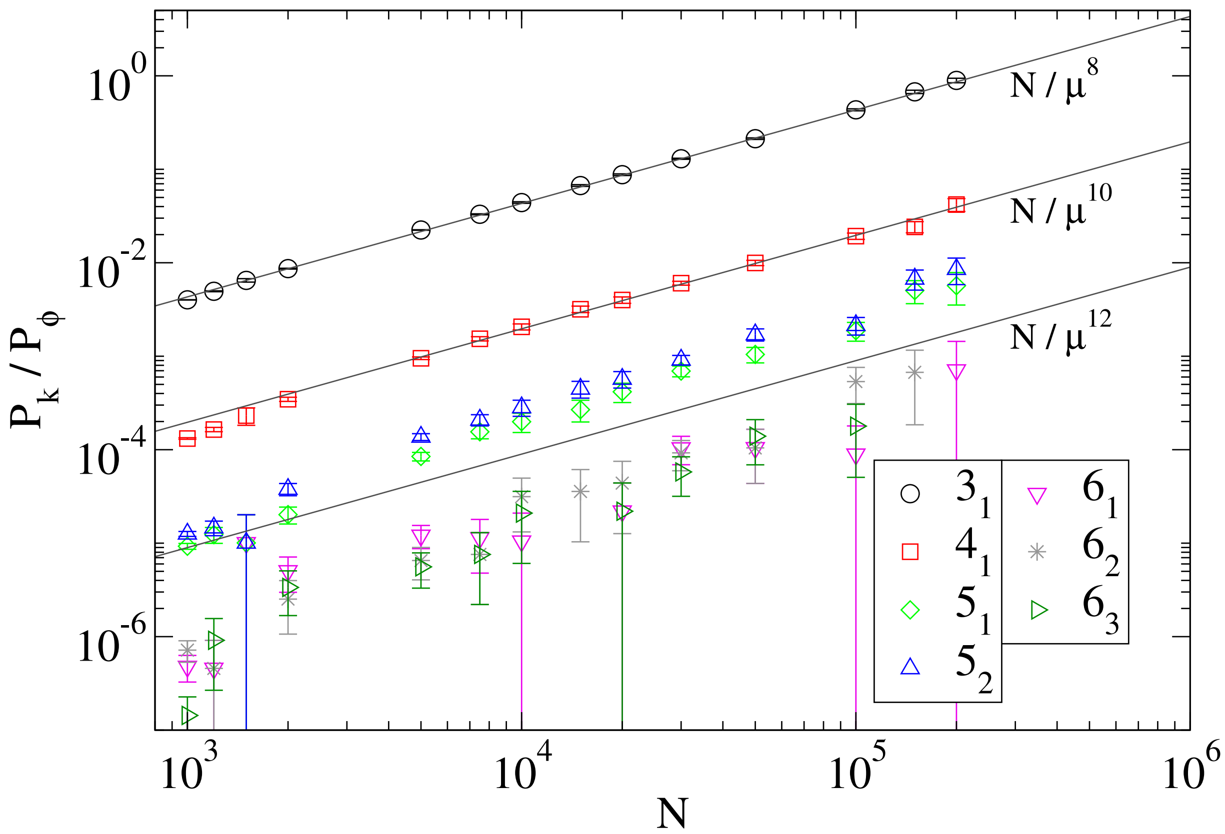
With or without 4_1



$C_{4_1} \simeq 5 \times 10^6$

$$\frac{p_{k\#4_1}}{p_k} \simeq \frac{N}{C_{4_1}} \qquad \rightarrow \text{ do not depend on } k$$

Simple prime knots



Cost ∼ complexity

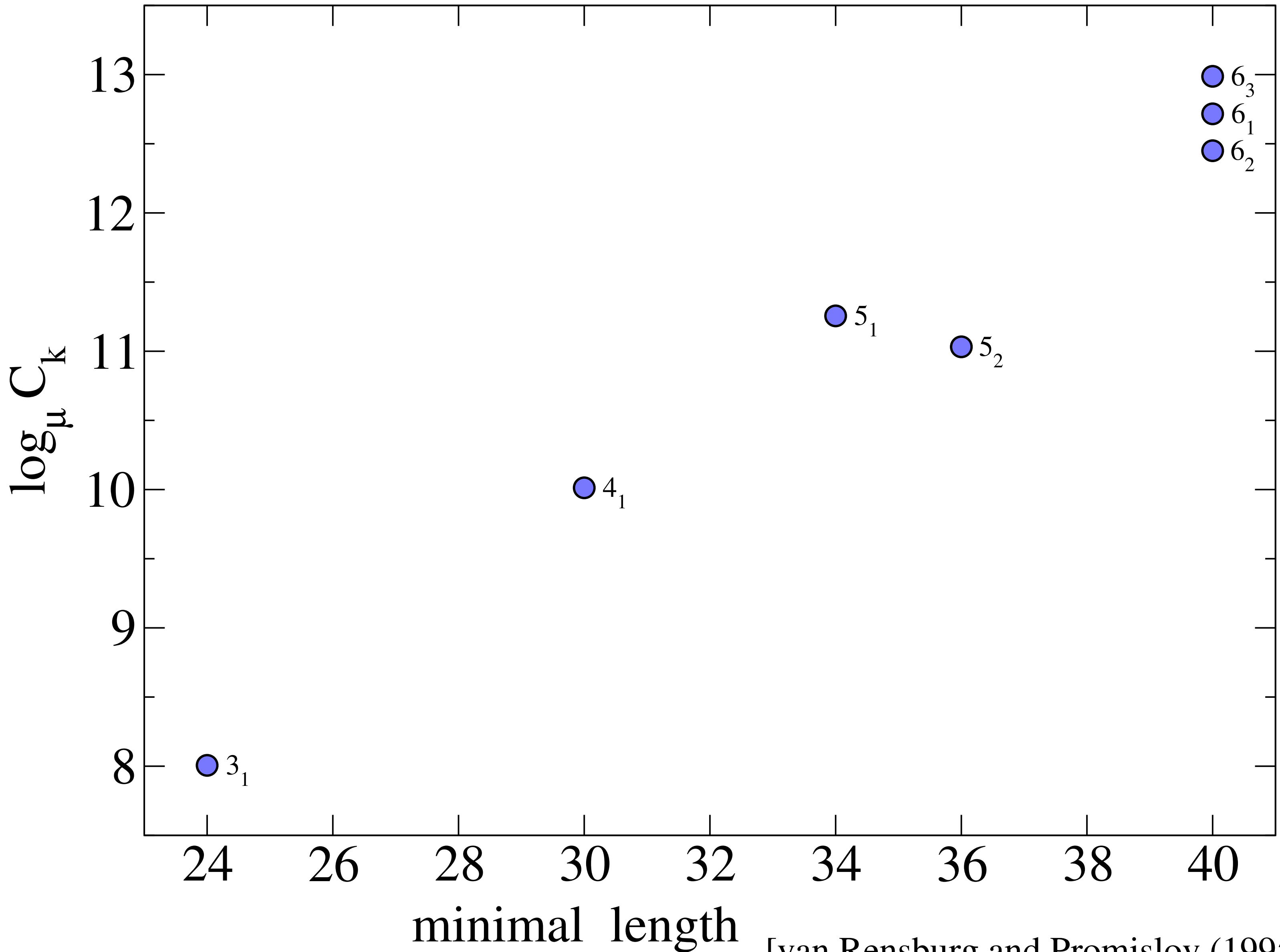
$$C_{3_1} \simeq \mu^8$$

$$C_{4_1} \simeq \mu^{10}$$

$$\frac{p_{\text{prime}}}{p_{\emptyset}} \simeq \frac{N}{C_{\text{prime}}}$$

- $C_k \sim \mu^{l(k)}$ with $l(k)$ giving the number of SAP steps which completely loose freedom in order to form the knot k

- Asymptotic localization suggests that in general $l(k)$ could be proportional to minimal length needed to realize knot k on lattice



[van Rensburg and Promislov (1995)]

Possible scenario:

The asymptotic correction $\propto const./N$ to the ring entropy per step depends on the topology of the knot. Each prime component contributes to $const.$ with a term proportional to its minimal length on cubic lattice.

Swollen Polymers: Conclusions

- $\mu_k = \mu_\emptyset < \mu$
- $\alpha_k = \alpha_\emptyset + \pi_k$
- knot relative frequencies:

$$\frac{p_{k,N}}{p_{\emptyset,N}} = \frac{Z_{k,N}}{Z_{\emptyset,N}} \simeq \frac{1}{(\pi_1)!}\left(\frac{N}{C_{k_1}}\right)^{\pi_1} \cdots \frac{1}{(\pi_m)!}\left(\frac{N}{C_{k_m}}\right)^{\pi_m}$$

- knot frequencies:

$$p_{k,N} \simeq \frac{A_\emptyset}{A}\left(\frac{\mu_\emptyset}{\mu}\right)^N N^{\alpha_\emptyset - \alpha}\frac{1}{(\pi_1)!}\left(\frac{N}{C_{k_1}}\right)^{\pi_1} \cdots \frac{1}{(\pi_m)!}\left(\frac{N}{C_{k_m}}\right)^{\pi_m}$$

- cost $C_k \sim \mu^{l(k)}$, with $l(k) \propto$ minimal length of component
- description "knot $\simeq$ sliding beads" works

Collapsed Polymers

$$(T < T_\theta)$$

Interacting SAP partition function

Globule has surface S:

$$Z_N(T) \simeq A\mu^N \mu_S^{N^{2/3}} N^{\alpha-2}$$

- $\ln \mu_S$: free energy correction per step on the surface (< 0)
- for specific knot k:

$$Z_{k,N} \sim A_k \, \mu_k \, \mu_{kS}^{N^{2/3}} N^{\alpha_k - 2}$$

The unknot $\emptyset$ case

Probability to find an unknot:

$$p_\emptyset \simeq \frac{A_\emptyset}{A}\left(\frac{\mu_\emptyset}{\mu}\right)^N \left(\frac{\mu_{kS}}{\mu_S}\right)^{N^{2/3}} N^{\alpha_\emptyset - \alpha}$$

one finds:

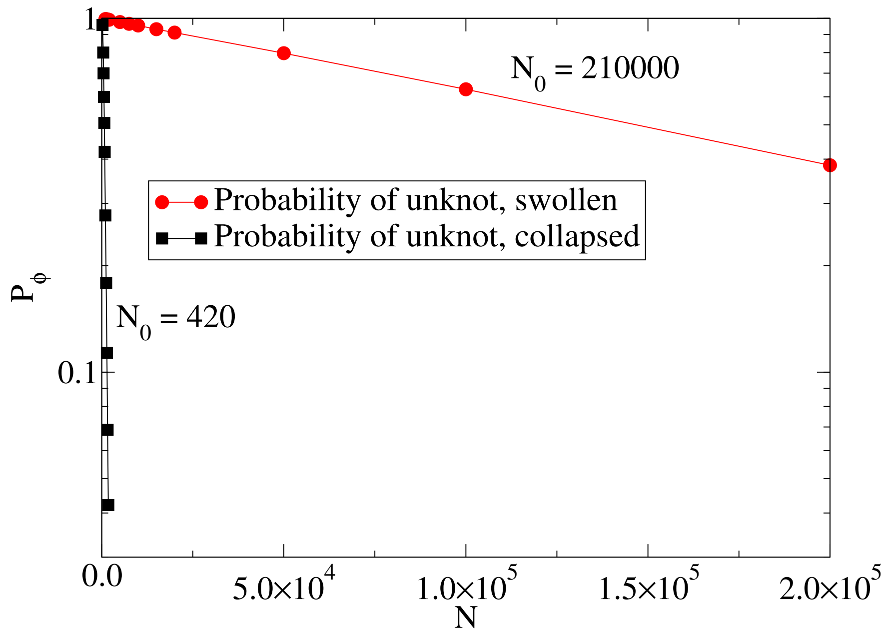
$$p_\emptyset \sim e^{-N/N_0}$$

with

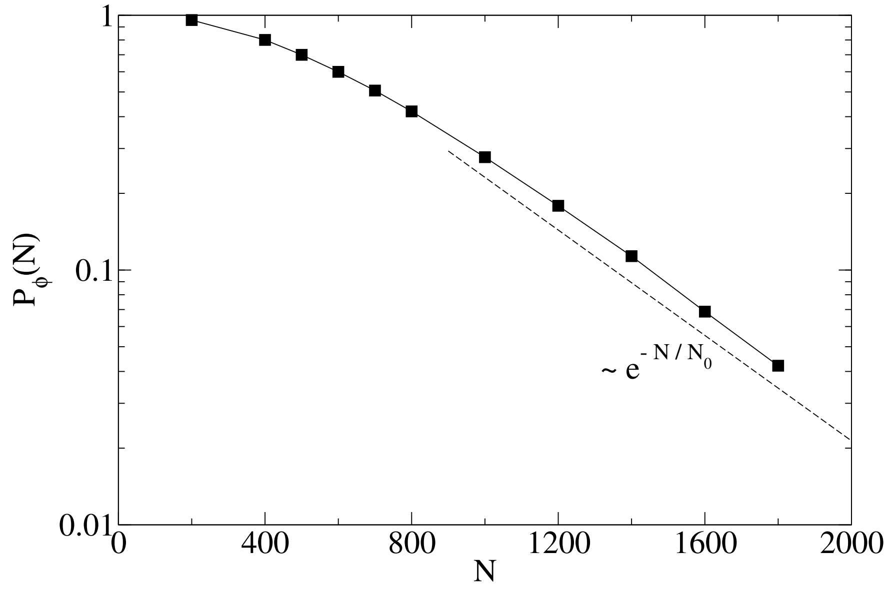
$$\left(\frac{\mu_\emptyset}{\mu}\right) = e^{-1/N_0}$$

- Swollen phase: N_0 large ($\mu_\emptyset \lesssim \mu$)
- Collapsed: N_0 not so large

Probability of unknot

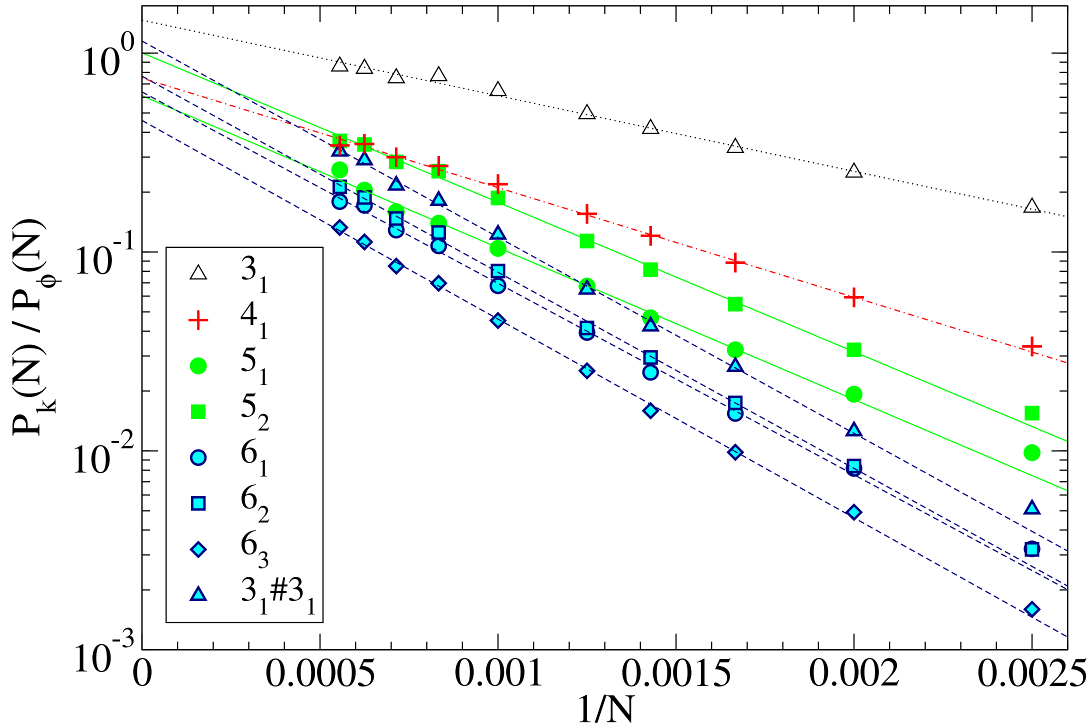


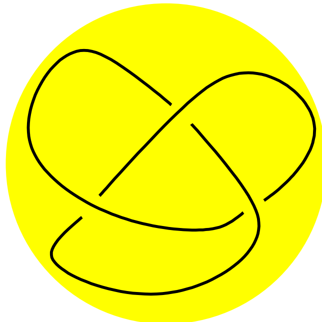
Swollen $(T = \infty)$: $N_0 = 210000$



Collapsed $(T = 2.5)$: $N_0 = 420$

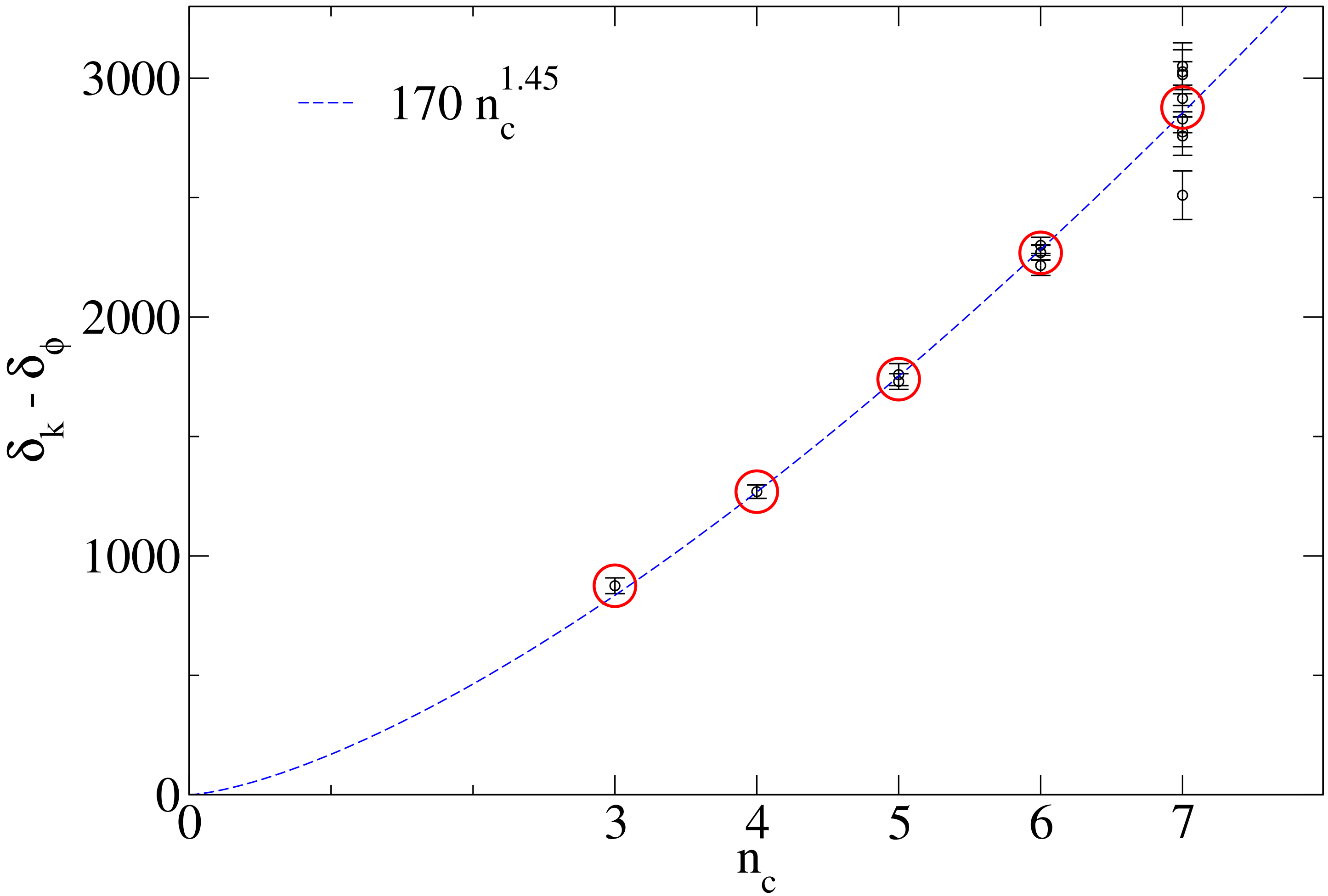
Collapsed phase: only one α and one μ_s!



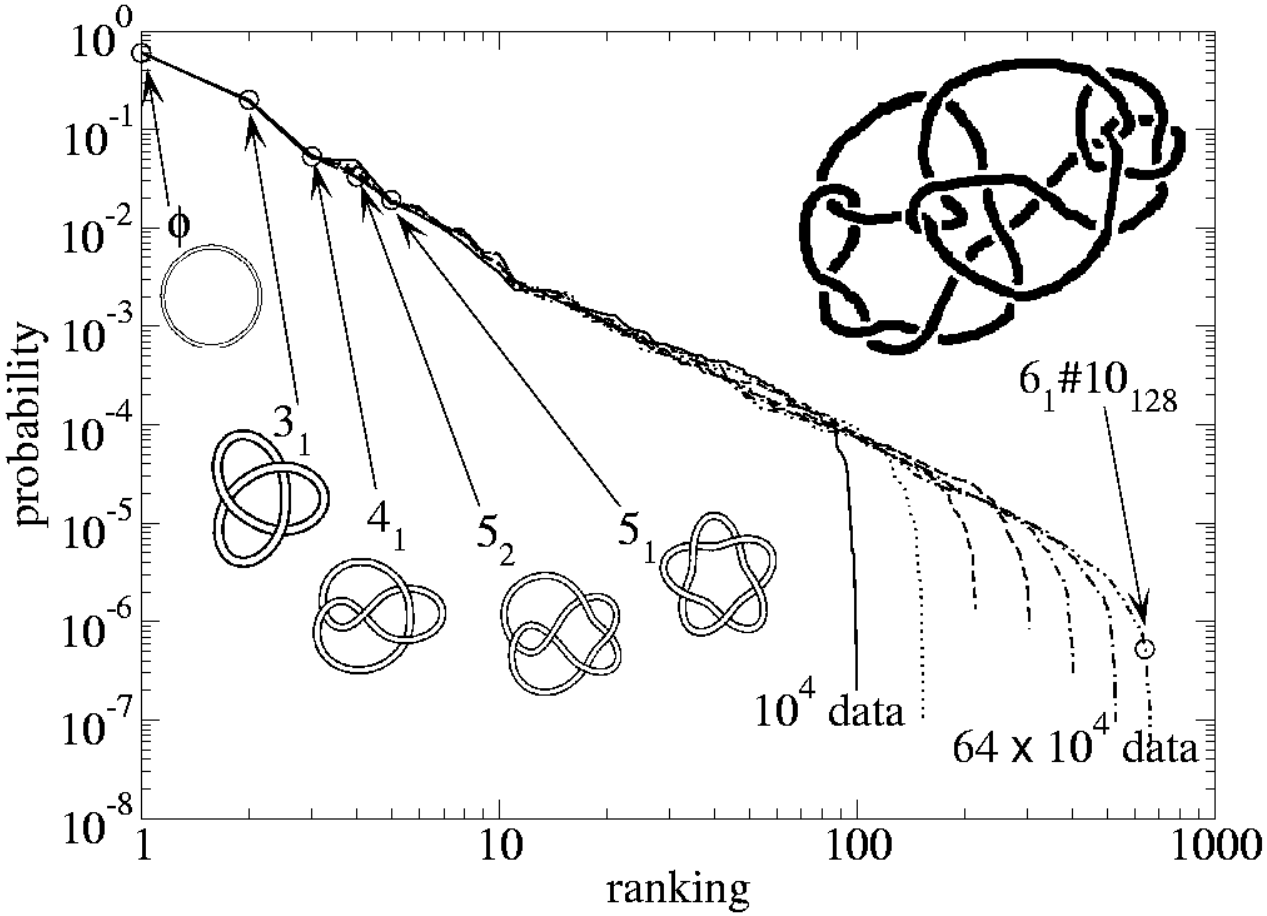


- $p_k/p_\emptyset$ does not diverge $\rightarrow T = \infty$ picture ruled out
  $\longrightarrow$ Delocalization is the only option
- Put a term $\exp(-\delta_k/N)$ in the partition function of a knot k
- δ_k seems to depend only on the minimal number of crossings of k

δ_k vs Nr. of crossings



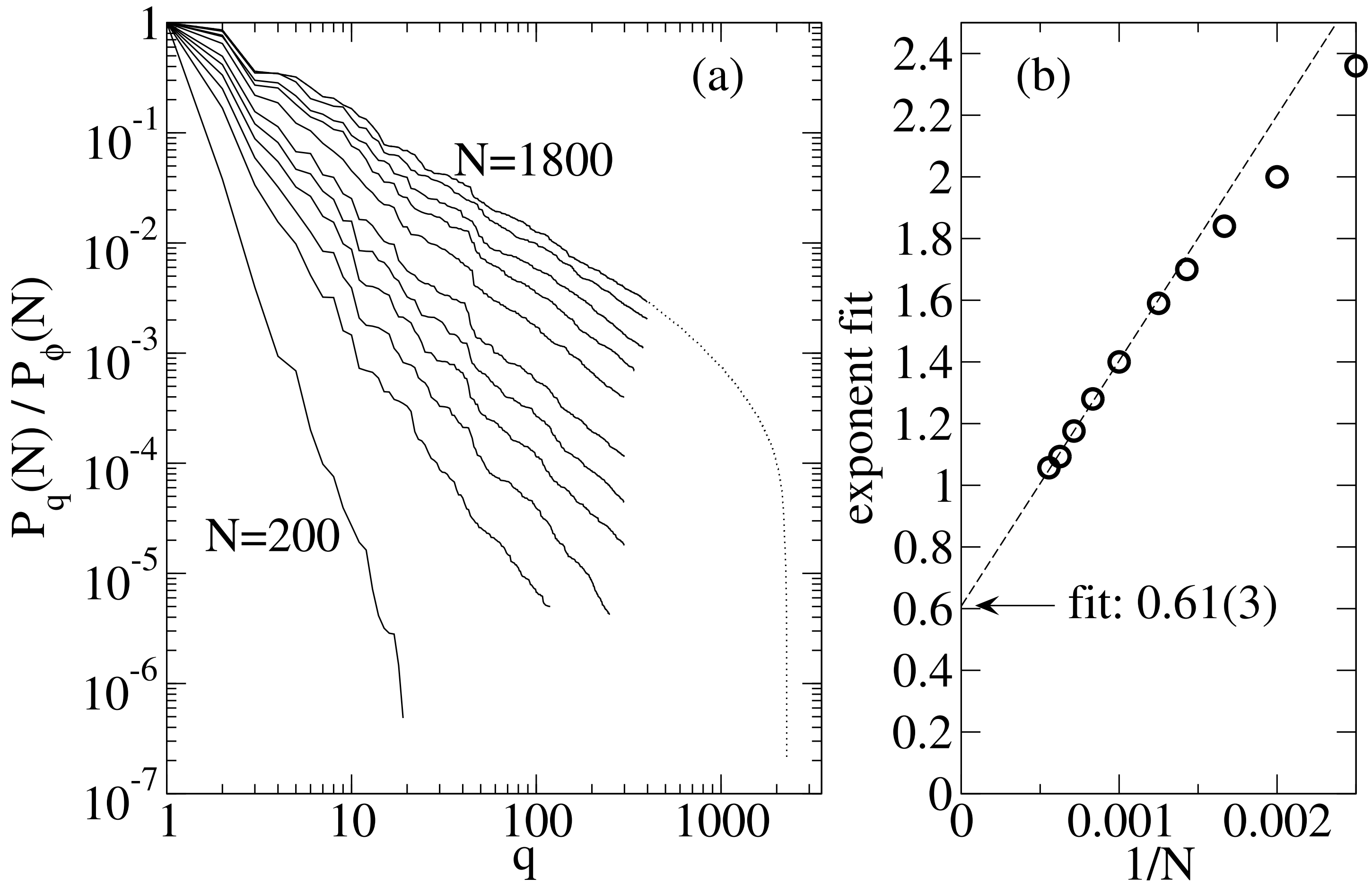
Ranking of knots: Zipf Law



$$P(\text{rank} = q) \sim q^{-r}$$

First discussed in linguistics by Zipf (1949)

Asymptotic Zipf Law



$$P(\text{rank} = q) \sim q^{-r}$$

$$r \to 0.6 \qquad \text{for} \quad N \to \infty$$

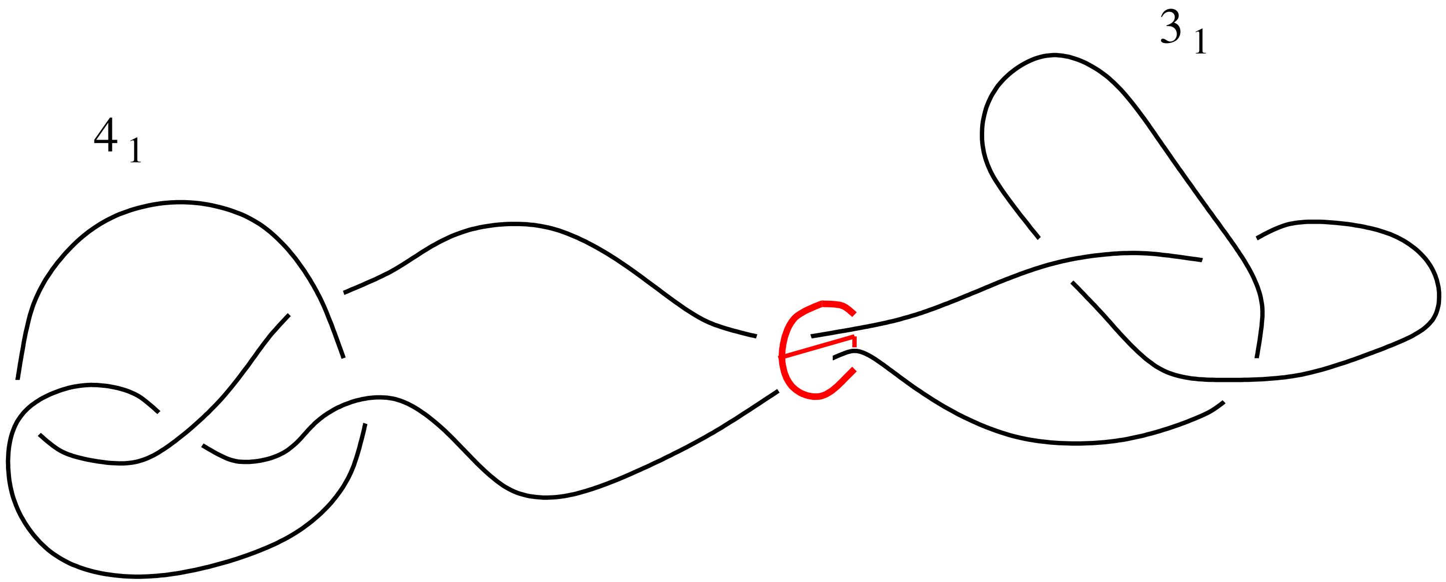
- In the collapsed phase rich knot spectrum
- Since:
  - each specific knot probability decays exponentially
  - the knot probability distribution is described by an exponent $r < 1$
  - the knot probability distribution needs to be normalized

  $\rightarrow$ The cutoff in the Zipf law scales exponentially with N
- Number of possible different knots in a chain of length N

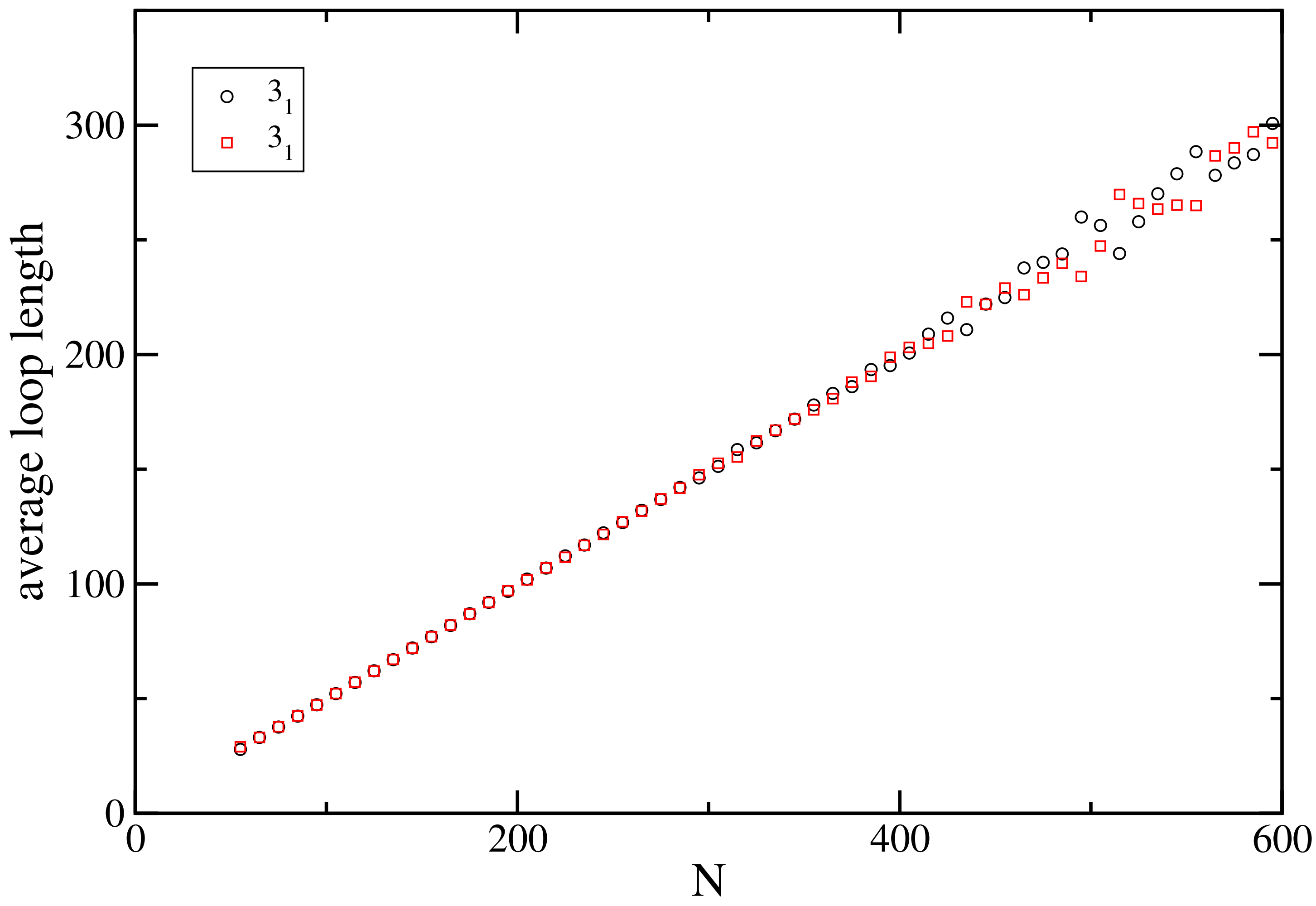
$$\sim \mathrm{const}^N$$

- Minimal number of crossings only relevant topological invariant in globular phase.
- Both minimal crossing number and correction $-\frac{\delta_k}{N^2}$ to free energy per step play major role in the physics of globule.

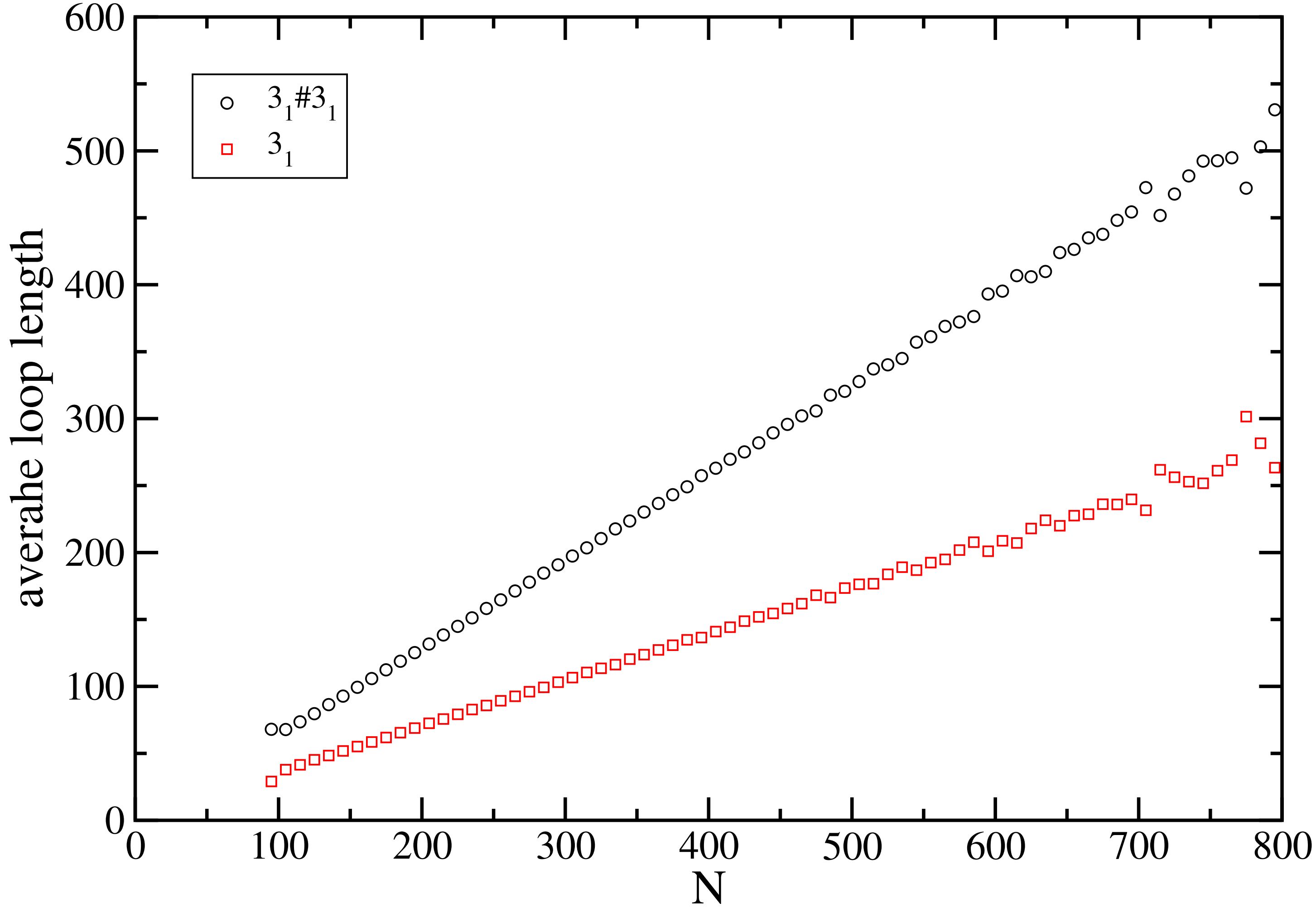
Slip-link divides globule into two knotted loops.



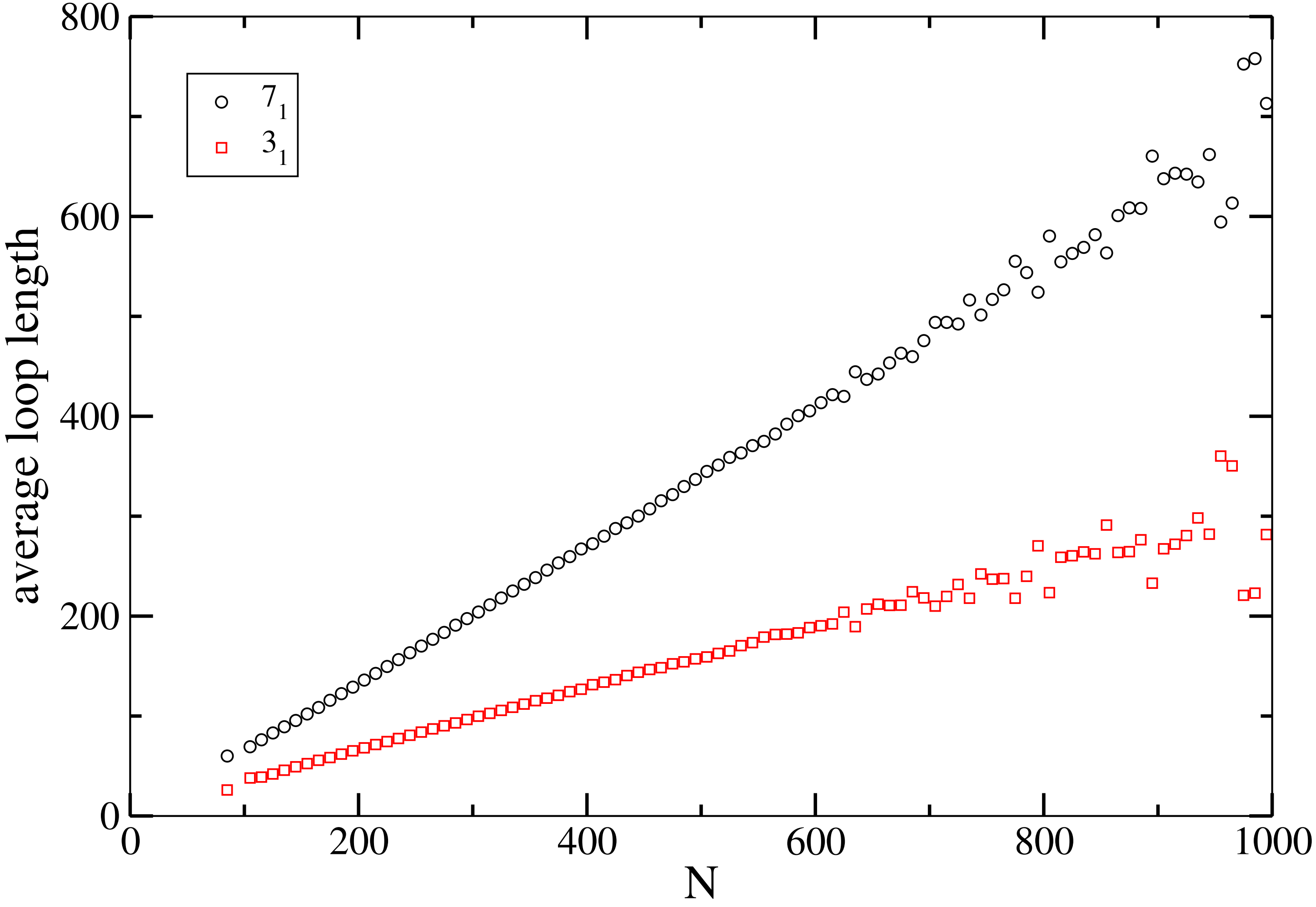
3_1 vs 3_1



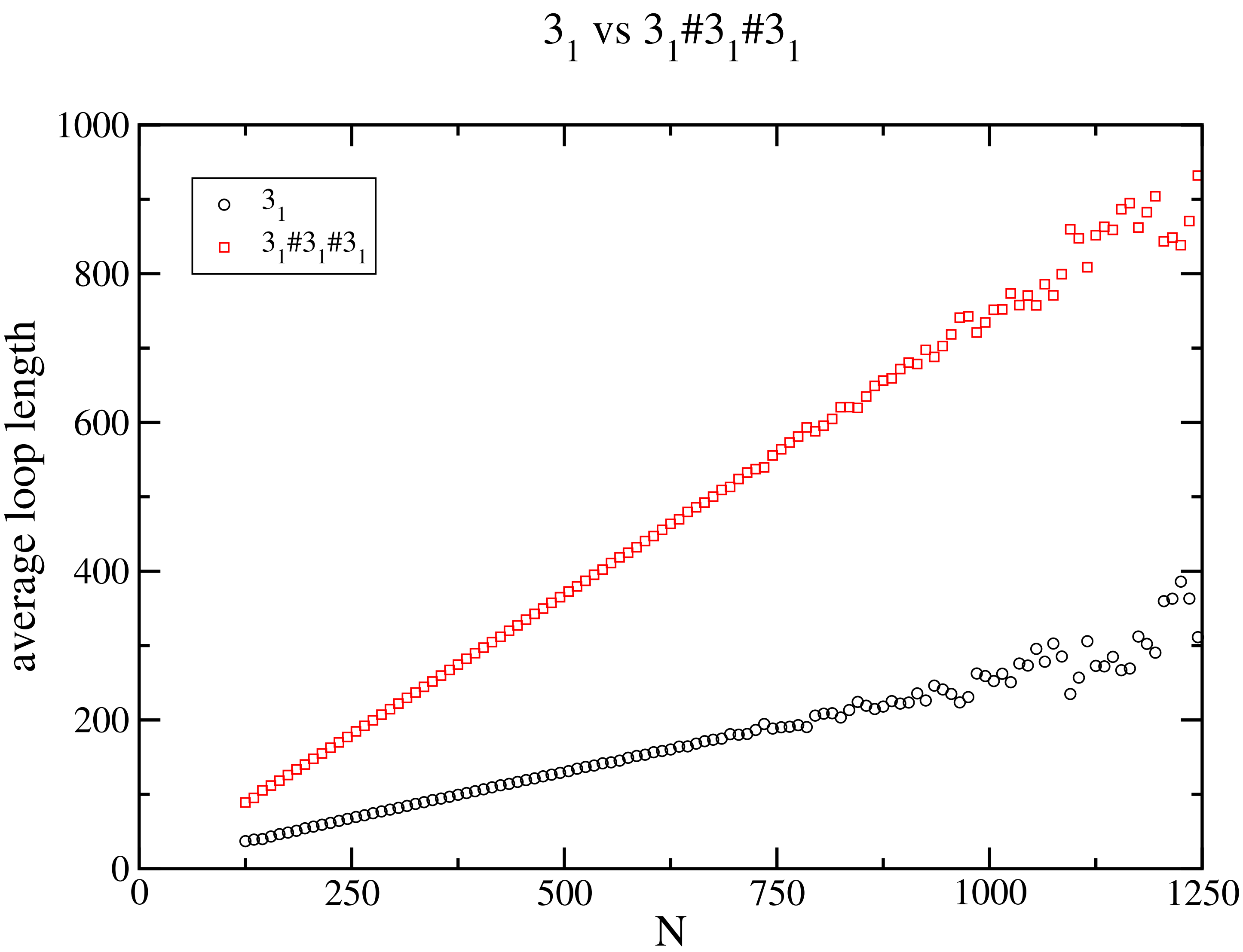
$3_1\#3_1$ vs 3_1

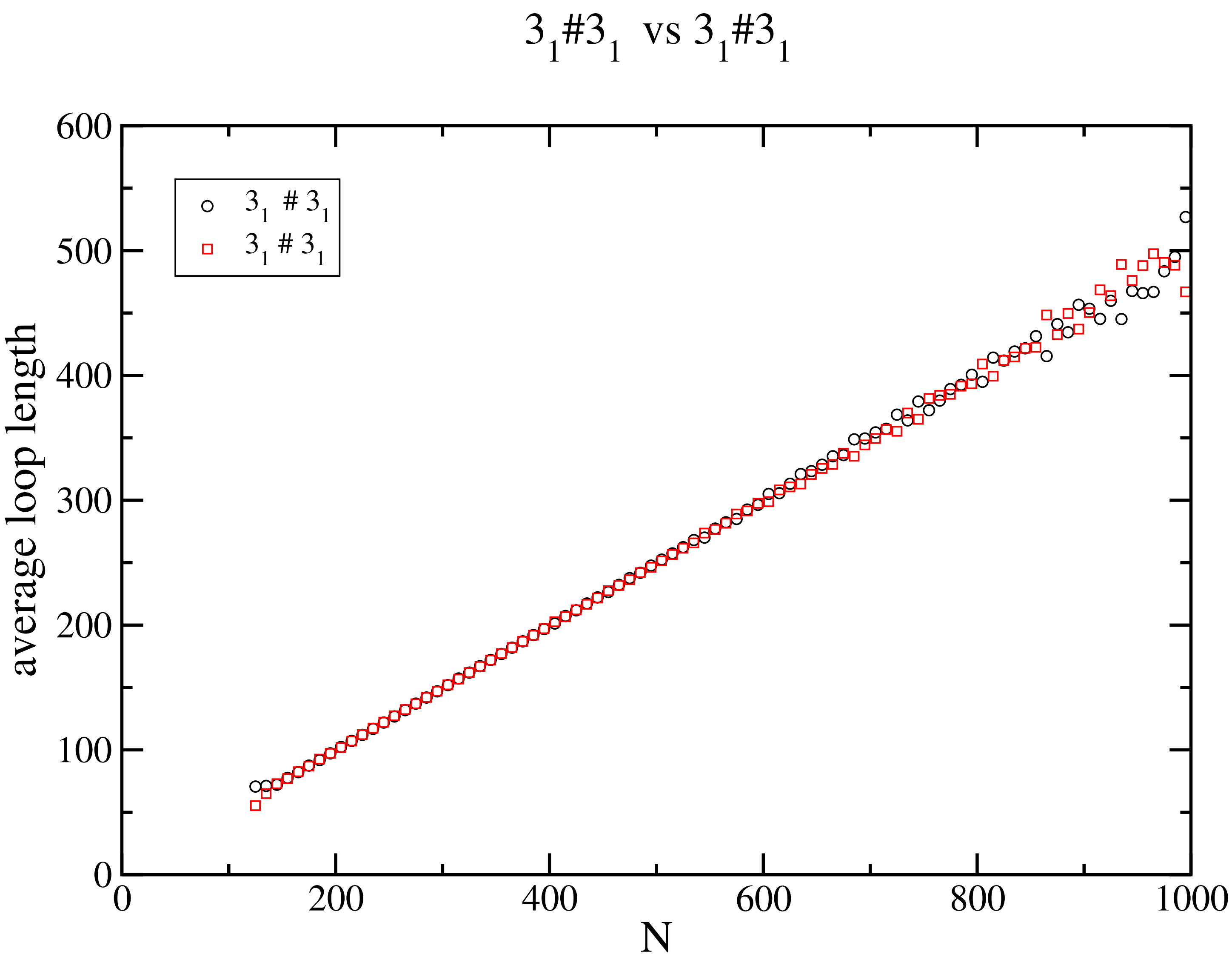


7_1 vs 3_1

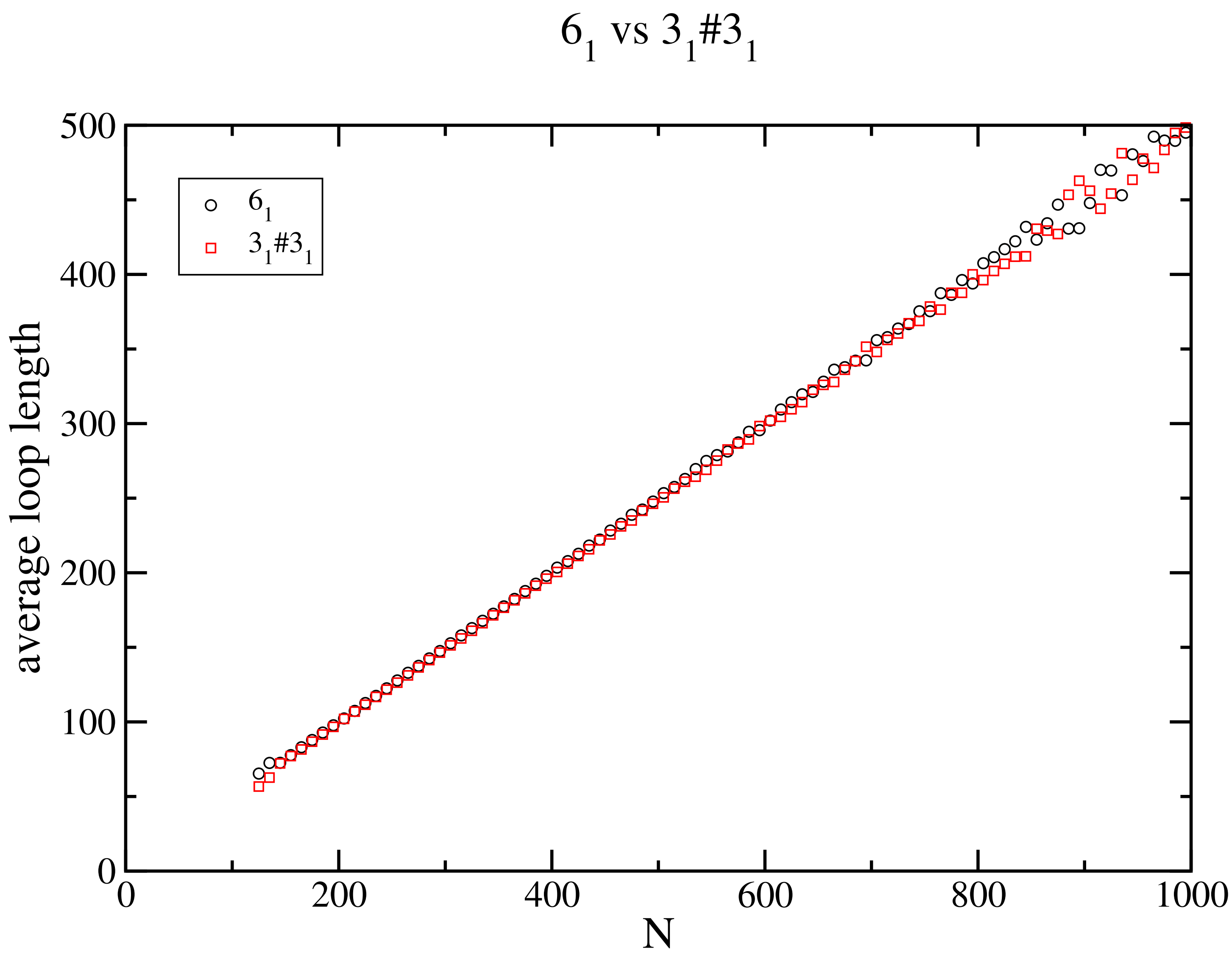


7
1
3
1
800
600
400
200
0
0
200
400
600
800
1000
average loop length
N


3_1 vs $3_1\#3_1\#3_1$
1000
800
600
400
200
0
0
250
500
750
1000
1250
N
average loop length
3_1
$3_1\#3_1\#3_1$



$3_1\#3_1$ vs $3_1\#3_1$
$3_1\ \#\ 3_1$
$3_1\ \#\ 3_1$
average loop length
N
0
100
200
300
400
500
600
0
200
400
600
800
1000



6_1 vs $3_1\#3_1$
6_1
$3_1\#3_1$
average loop length
N
0
100
200
300
400
500
0
200
400
600
800
1000

Strong evidence that

$$\langle l_i \rangle \sim A_i \, N \qquad (i = 1, 2)$$

with

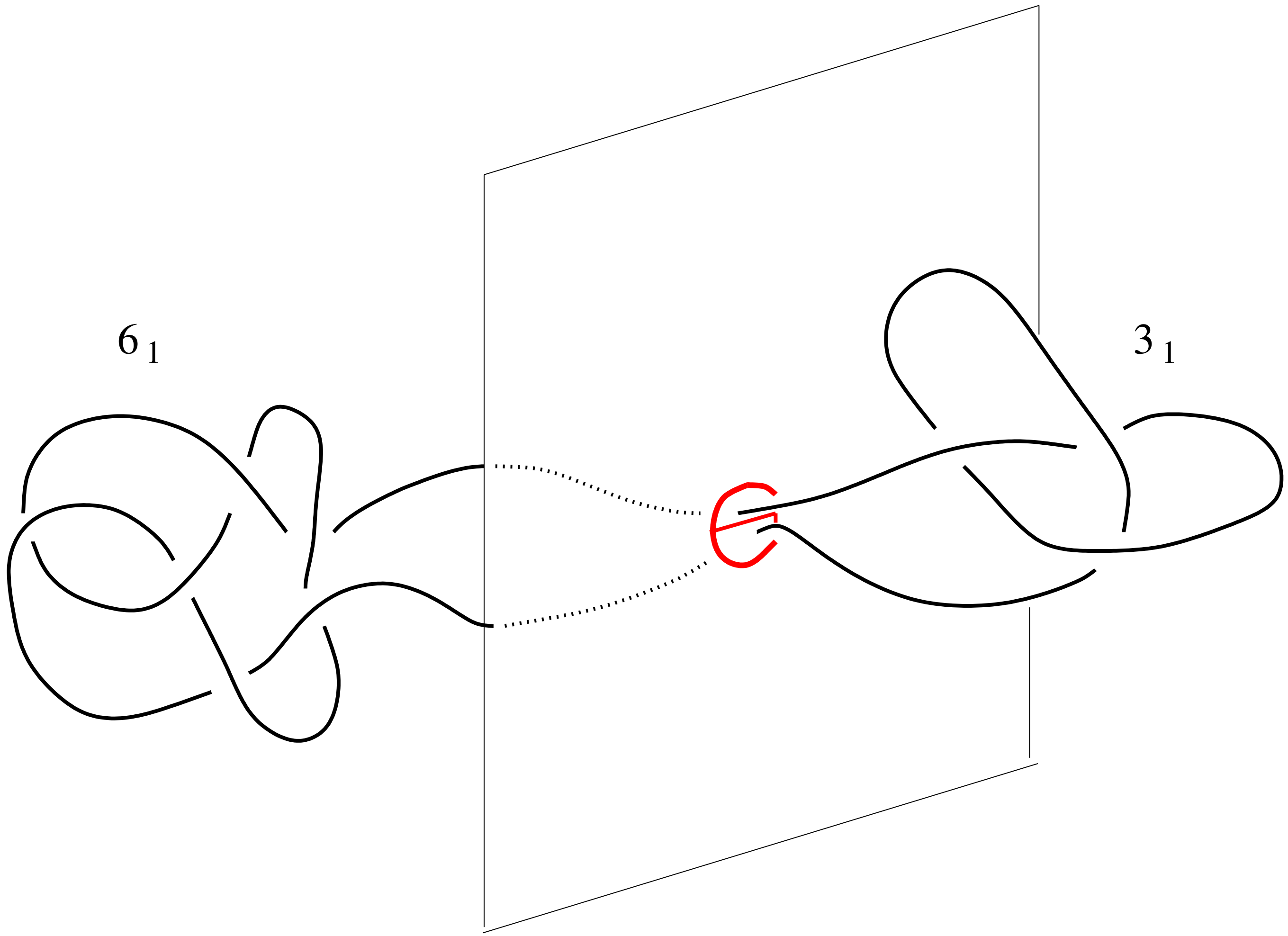
$$A_i = \frac{n_{ci}}{n_{c1} + n_{c2}}$$

The loops have av. lengths $\propto n_c$ of their knot!

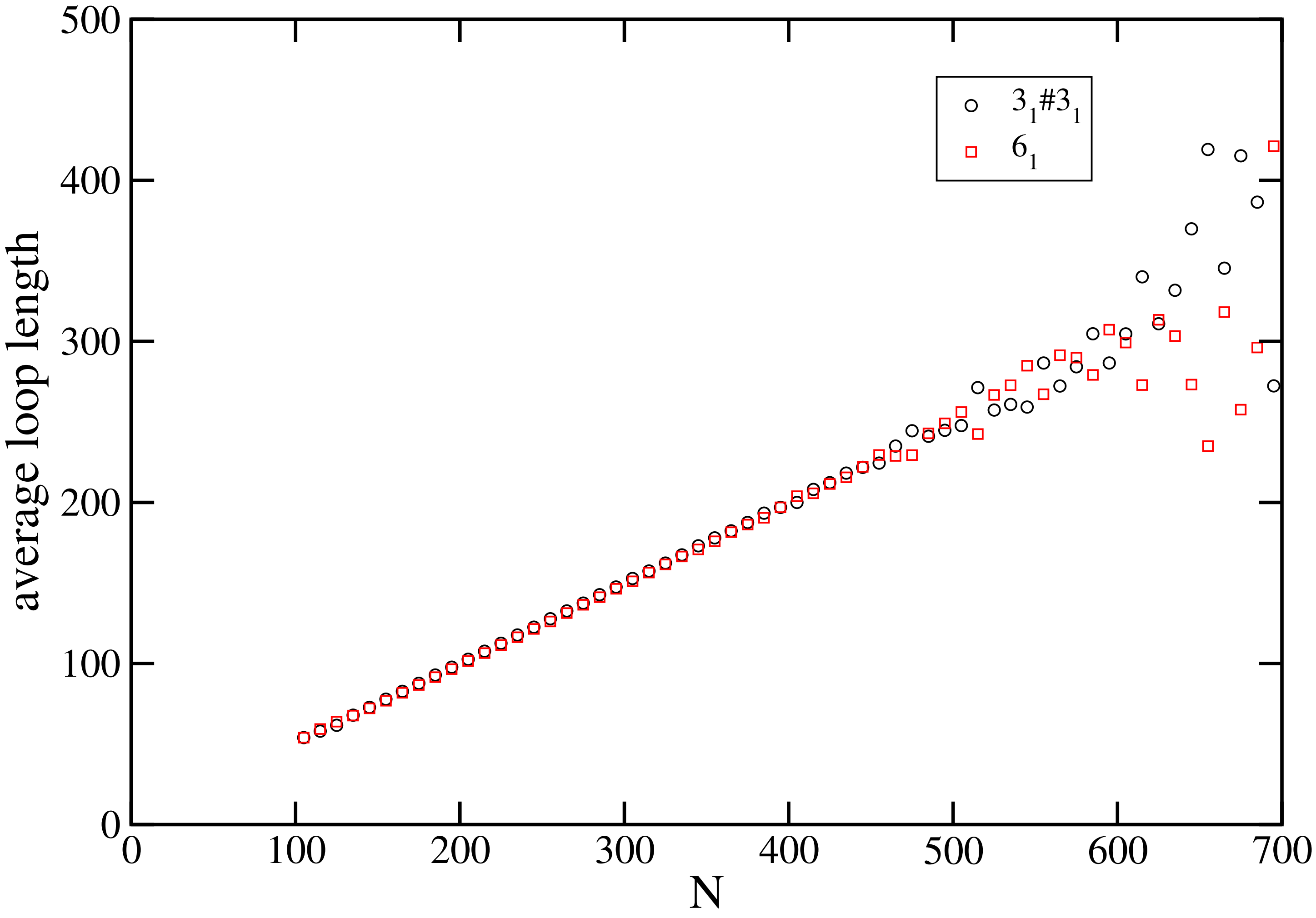
Consistent with delocalization: each crossing gets an equal share of the total length!

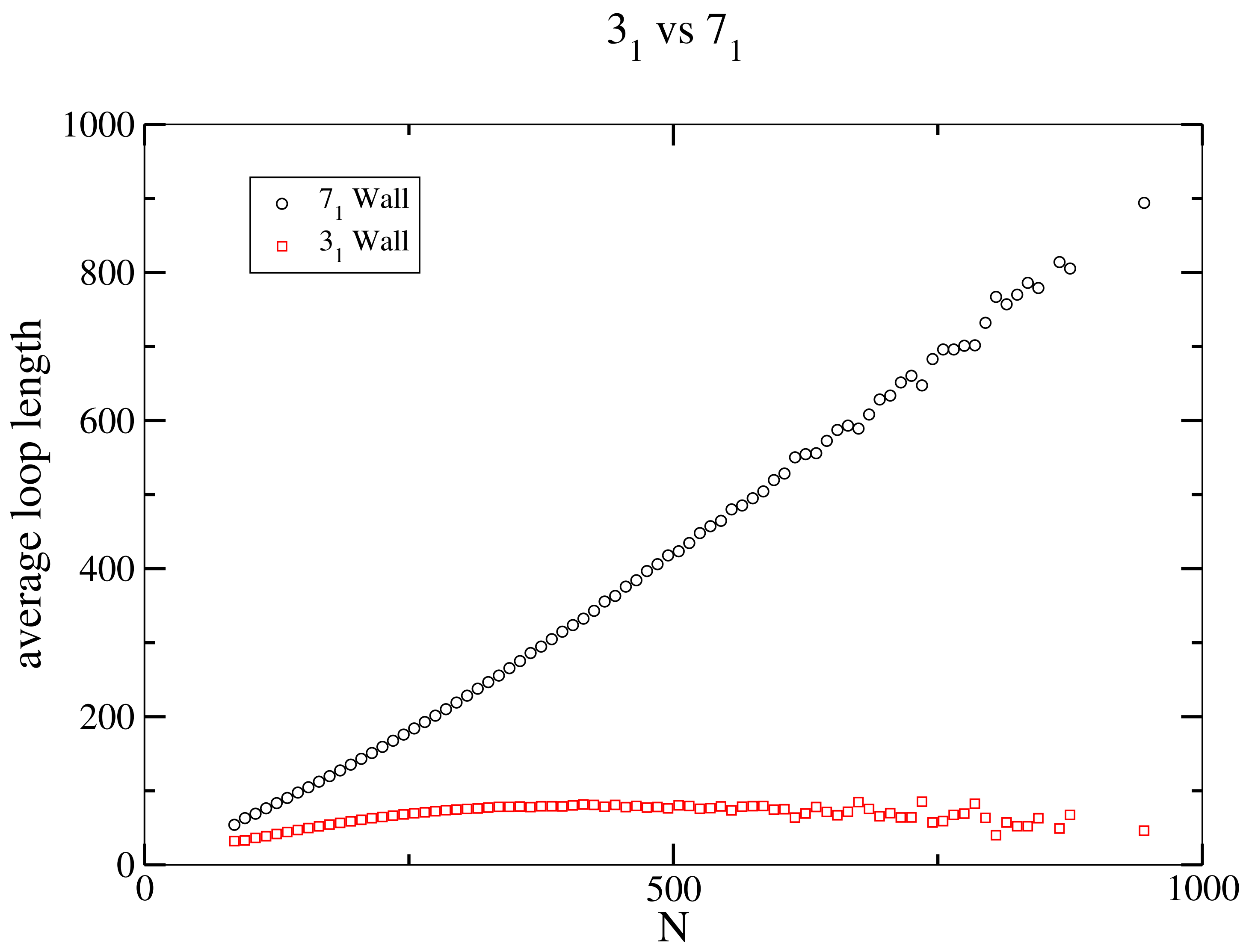
Topological correction to free energy plays major role when the slip-link is replaced by hole in an impenetrable wall.

The two loops become noninteracting globules.

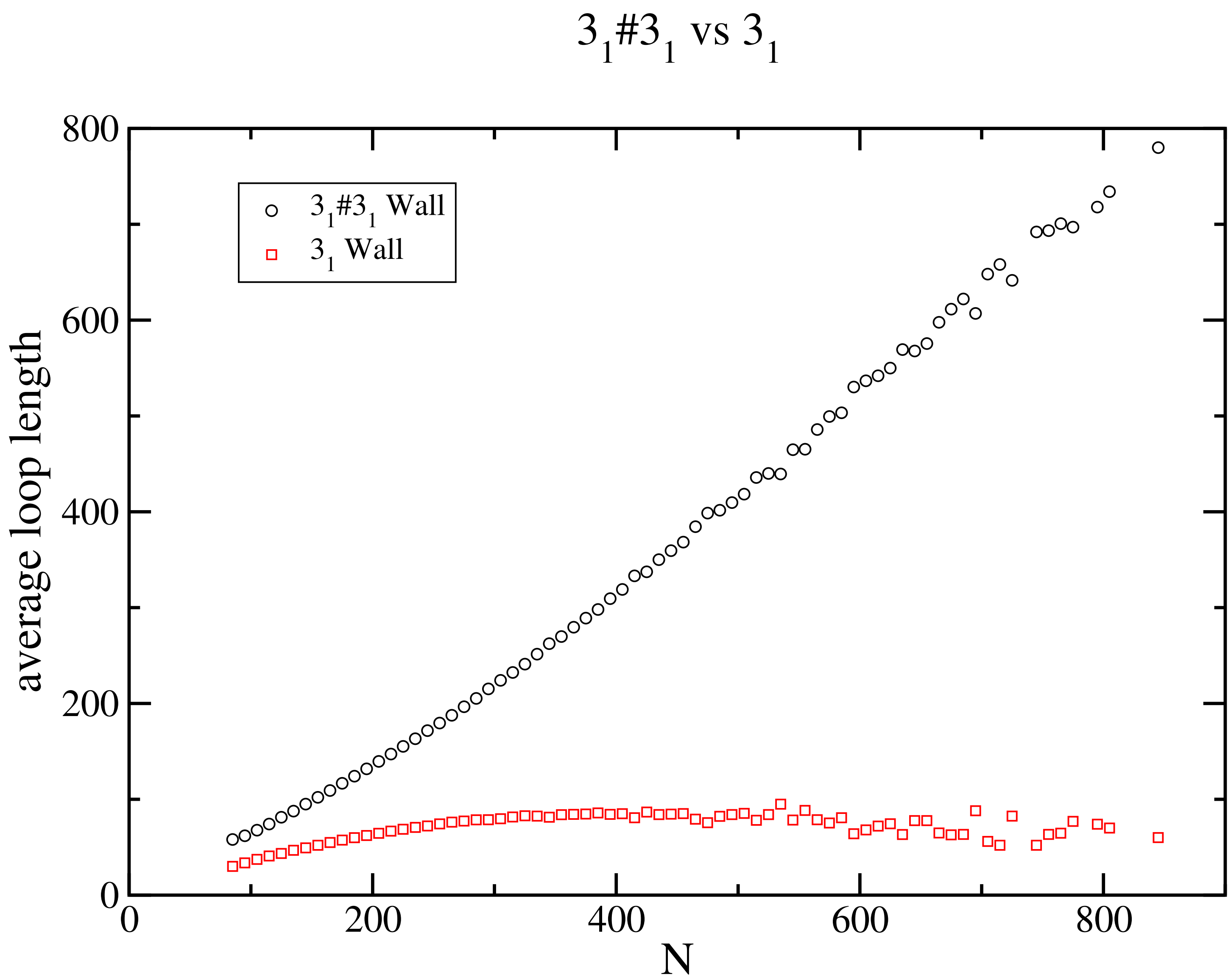


Wall: 3_1 # 3_1 vs 6_1





3_1 vs 7_1
7_1 Wall
3_1 Wall
average loop length
N
0
200
400
600
800
1000
0
500
1000


$3_1\#3_1$ vs 3_1
$3_1\#3_1$ Wall
3_1 Wall
average loop length
N
0
200
400
600
800

Explanation in terms of topological correction:

$$\begin{aligned}
\frac{P(l_1 = N - l_{min2})}{P(l_1 = l_{min1})} &= \frac{Z_{k_1, N-l_{min2}} \;\; Z_{k_2, l_{min2}}}{Z_{k_1, l_{min1}} \;\; Z_{k_2, N-l_{min1}}} \\
&\sim \exp\left(-\frac{\delta_{k_2}}{l_{min2}} + \frac{\delta_{k_1}}{l_{min1}}\right) \\
&\sim \exp\left[170\left(-\frac{n_{c2}^{1.45}}{l_{min2}} + \frac{n_{c1}^{1.45}}{l_{min1}}\right)\right] \\
&\gg 1 \qquad \text{if } n_{c1} > n_{c2}
\end{aligned}$$

- Baiesi, Orlandini, Stella, Phys. Rev. Lett. 99, 058301 (2007)
- Baiesi, Orlandini, Stella, Zonta, in preparation