

Monte Carlo Calculation of Average Extension of Polymers

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Abstract

We investigate the scaling behaviour of linear polymer chains by simulating them as random walks on 2D and 3D lattices. Two models are examined: the ideal chain, which allows self-intersection, and the excluded volume chain, which enforces self-avoidance. For ideal chains, we confirm the theoretical prediction $\nu = 0.5$ relating polymer size to monomer count N through $R \sim N^\nu$, using 10,000 Monte Carlo realizations. For self-avoiding walks, we demonstrate that bare averaging produces artificially low exponents ($\nu \approx 0.64$ in 2D, $\nu \approx 0.52$ in 3D) due to sampling bias toward compact configurations. Implementing the Rosenbluth weighted sampling method corrects this bias, yielding $\nu \approx 0.75 - 0.78$ in 2D and $\nu \approx 0.61$ in 3D, in reasonably good agreement with theory predictions (0.75 and 0.588, respectively).

1 Introduction

The goal of this work is to determine the relation between the number of monomers of a polymer (N), and its size. We will only consider linear unbranched polymers, we also neglect interactions between polymers, effectively considering that the physics of the polymer collection can be described by the physics of a single polymer.

To model these polymers, we will consider their structure as a random walk in a lattice. We will take two possibilities for this lattice, either a square lattice (2D), or a cubic lattice (3D). Each step of the random walk, located at $\{\mathbf{R}_i\}$ with $i = 1, 2, \dots, N$, represents a given monomer of the chain, and the rods between them the bonds they form. We can take the lattice spacing $a = 1$ to simplify the calculations. We consider two models; first, an 'ideal chain' model; and then an 'excluded volume chain'.

The difference between the two models is very simple. The ideal chain, analogous to a random walk, allows the polymer to loop back onto itself. This occurrence is obviously unphysical, so we develop the excluded volume chain model to fix that. In this new model, we forbid the chain from crossing itself, generating an 'excluded volume effect' as the chain grows. To implement this restriction in the random walk, we make it so, that if a lattice node has already been visited once, it can not be visited again by our random walk.

1.1 Characterization of the size of the polymer

In order to characterize the polymers we generate, we must first define some quantities.

The first we define is the *end-to-end vector* \mathbf{R} , which joins the start and the end of the polymer.

$$\mathbf{R} = \mathbf{R}_N - \mathbf{R}_1 = \sum_{n=1}^{N-1} \mathbf{r}_n, \quad (1)$$

where $\mathbf{r}_n = \mathbf{R}_{n+1} - \mathbf{R}_n$. The square root of the average *end-to-end vector* squared can be used as a measure for the size of the polymer,

$$R_p \sim \sqrt{\langle \mathbf{R}^2 \rangle}. \quad (2)$$

We can also define the centre of mass of the polymer chain, \mathbf{R}_{CM} as

$$\mathbf{R}_{CM} = \frac{1}{N} \sum_{n=1}^N \mathbf{R}_n. \quad (3)$$

Which we will use for another measure of the polymer size, the *radius of gyration* R_g , which we define as

$$R_g^2 = \frac{1}{N} \sum_{n=1}^N \langle (\mathbf{R}_n - \mathbf{R}_{CM})^2 \rangle. \quad (4)$$

For this two magnitudes, we are not really interested on the particular values they may adopt for a given value of N , but on how they scale with the monomer count. So, we are interested in characterizing the exponent ν such as

$$R_g \sim N^\nu \quad R_p \sim N^\nu.$$

It is a well known result, that for a freely jointed chain in any dimension, we obtain a behaviour of $\nu = 0.5$ [2].

On the other hand, the calculation of these quantities for a self avoiding random walk is a lot more complex, we must resort to Flory. The result of the calculation, for the exponent, yields $\nu = 3/(d+2)$. In $d = 1$ this says $\nu = 1$, which is exactly correct because a SAW in $d = 1$ has no option but to keep going in the same direction. In $d = 2$, Flory theory predicts $\nu = 3/4$, which is also exact. In $d = 3$, we have $\nu = 3/5$, which is extremely close to the numerical value $\nu = 0.5880$ of the best models. Moreover, the theory also predicts an upper critical dimension $d = 4$, where we recover the random walk model with an exponent $\nu = 0.5$ [1].

1.2 Sampling algorithm of self-avoiding walk model

Computing these metrics for self-avoiding random walks appears simple in theory, but growing all possible polymers becomes computationally prohibitive as the number of possible walks grows exponentially. A Monte Carlo approach that samples only a subset of valid walks would be more practical for estimating polymer properties.

We will sample according to the **Rosenbluth method**. In this method, we generate M different self avoiding random walks (SARW) step by step. At each step, the SARW chooses randomly the position of its new monomer from all the unoccupied lattice sites adjacent to its growing end. We will call m_i at the number of available empty spaces at each step i . Which we will use to record the statistical weight of the parameter.

For each polymer (k) grown, we record the positions of each monomer $\mathbf{R}_i^{(k)}$, and the statistical weight of the parameter

$$\omega_k^{(N)} = \prod_{i=1}^N m_{k,i}, \quad (5)$$

where $m_{k,i}$ is the number of unoccupied lattice sites encountered in the growing process. The averaged end-to-end distance or radius of gyration can be calculated by the weighted average

$$R_P^2 = \frac{\sum_{k=1}^M w_k^{(N)} \left(\mathbf{R}_N^{(k)} - \mathbf{R}_1^{(k)} \right)^2}{\sum_{k=1}^M w_k^{(N)}}, \quad R_g^2 = \frac{\sum_{k=1}^M w_k^{(N)} \left[\frac{1}{N} \sum_{n=1}^N \left(\mathbf{R}_n^{(k)} - \mathbf{R}_{CM} \right)^2 \right]}{\sum_{k=1}^M w_k^{(N)}}. \quad (6)$$

2 Results

2.1 Ideal polymer

We begin by analysing the ideal chain model in two and three dimensions. We simulated up to $N = 100$, for $M = 10000$ independent realizations, the resulting scaling behaviour is shown in Fig. 1. We fitted this data to a power law of the form $\langle R^2 \rangle \sim N^{2\nu}$, the resulting coefficients are displayed in Table 1.

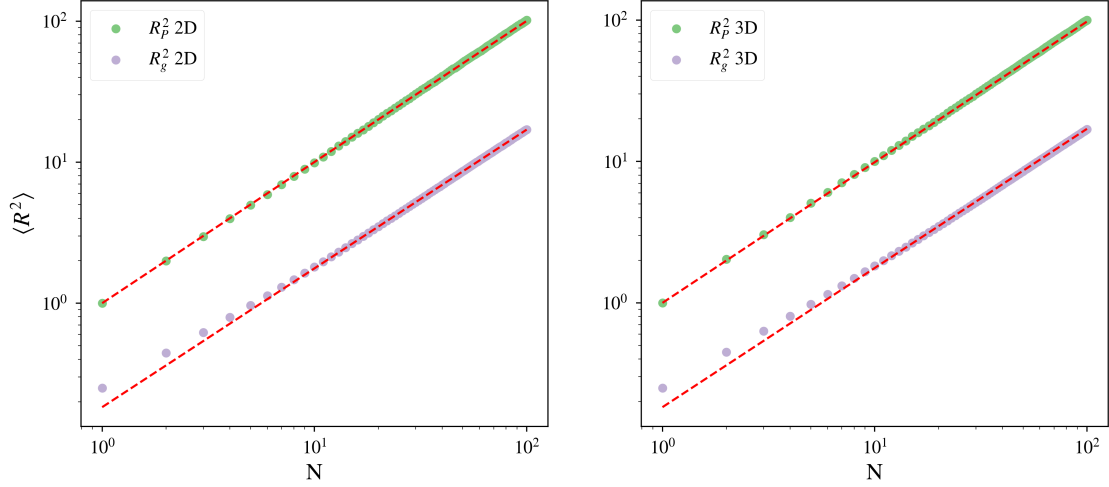


Figure 1: $\langle R_p^2 \rangle$ and $\langle R_g^2 \rangle$ sampled over $M=10000$ polymers of size $N \leq N_{max} = 100$, in a log-log scale, for polymers represented as random walks in 2 and 3 dimensions. Red dotted lines correspond to the fit to a power law.

Table 1: Exponents from power law fit in Fig. 1, an ideal polymer modelled as a random walk.

Dimension	Observable	ν
2D	$\langle R_p \rangle$	0.5024 ± 0.0002
	$\langle R_g \rangle$	0.4923 ± 0.0002
3D	$\langle R_p \rangle$	0.4992 ± 0.0002
	$\langle R_g \rangle$	0.4906 ± 0.0002

2.2 Excluded volume polymer

We now move on to a more realistic scenario, in which we model our polymer as self avoiding random walks. For this, we simulated polymer chains of up to $N = 100$ monomers, and sampled across $M = 10000$ realizations. We sampled these polymers using two methods, a *bare average*, or following the Rosenbluth method as we described it in Sec. 1.2. We show the results for two and three dimensions in Figs. 2 and 3, as well as a power law fit of the data, the resulting coefficients are displayed in Table 2.

3 Conclusion

In this work, we investigated the scaling behaviour of linear polymer chains by modelling them as random walks on 2D and 3D lattices. We examined two distinct models: the ideal chain, which permits self-intersection, and the more realistic excluded volume chain, which enforces self-avoidance.

For the ideal chain model, our simulations with $M = 10000$ realizations confirmed the theoretical prediction of $\nu = 0.5$ in both dimensions. The fitted exponents (Table 1) closely match this value, with $\nu \approx 0.50$ for the end-to-end distance and $\nu \approx 0.49$ for the radius of gyration, validating the freely

Table 2: Exponents from power law fit in Figs. 2 and 3, for polymers modelled as self avoiding random walks.

Dimension	Observable	ν	
		Bare	Rosenbluth
2D	$\langle R_p \rangle$	0.6430 ± 0.0016	0.753 ± 0.004
	$\langle R_g \rangle$	0.6522 ± 0.0005	0.776 ± 0.002
3D	$\langle R_p \rangle$	0.5228 ± 0.0004	0.6095 ± 0.0010
	$\langle R_g \rangle$	0.5263 ± 0.0001	0.6117 ± 0.007

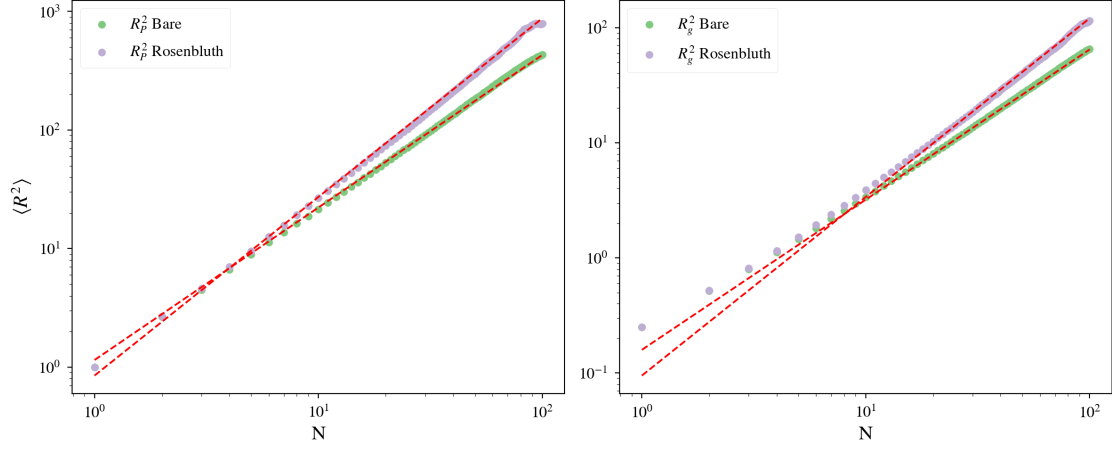


Figure 2: Comparison of $\langle R_p^2 \rangle$ and $\langle R_g^2 \rangle$ sampled over $M=10000$ polymers of size $N \leq N_{max} = 100$, computed both as a *bare average*, or using the Rosenbluth sampling method described in Sec. 1.2. In log-log scale, for polymers represented as self avoiding random walks in 2 dimensions. Red dotted lines correspond to the fit to a power law.

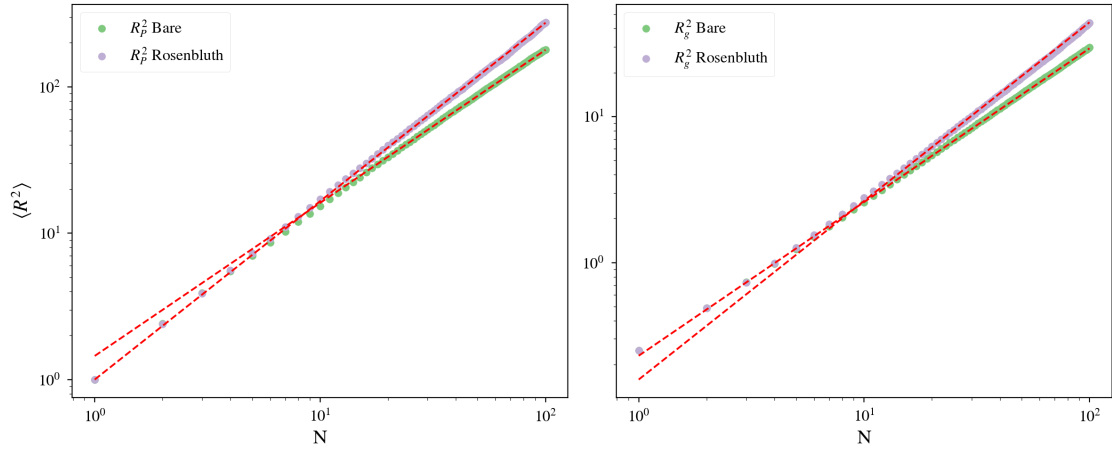


Figure 3: Comparison of $\langle R_p^2 \rangle$ and $\langle R_g^2 \rangle$ sampled over $M=10000$ polymers of size $N \leq N_{max} = 100$, computed both as a *bare average*, or using the Rosenbluth sampling method described in Sec. 1.2. In log-log scale, for polymers represented as self avoiding random walks in 3 dimensions. Red dotted lines correspond to the fit to a power law.

jointed chain model.

The excluded volume model revealed the importance of proper sampling methods. Bare averaging resulted in exponents of $\nu \approx 0.64$ in 2D and $\nu \approx 0.52$ in 3D, which significantly underestimate the polymer size due to sampling bias toward compact, unsuccessful configurations. The Rosenbluth weighted sampling method corrected this bias, producing exponents much closer to theoretical predictions: $\nu \approx 0.75 - 0.78$ in 2D (compared to the exact Flory prediction of 0.75) and $\nu \approx 0.61$ in 3D (approaching the numerical value of 0.588).

These results demonstrate that self-avoiding constraints heavily alter polymer scaling. The agreement between our Rosenbluth-weighted simulations and Flory theory validates both the computational approach and the theoretical framework. The consistent difference between bare and weighted averaging highlights the role of proper statistical weighting in polymer Monte Carlo simulations.

References

- [1] AROVAS, D. *Thermodynamics and Statistical Mechanics*. USC San Diego, 2025.
- [2] DOI, M. *Introduction to polymer physics*. Oxford University Press, 1995.

A Code availability

Code is available in the following GitHub repository [Project 2 Francesc Bagur](#)