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Self-Avoiding Rotating Walks as Models of Crystals Made of Freely-Rotating Polymers in Two Dimensions

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OBJECTIVE

Calculate the thermodynamic stability of crystals made of freely-rotating polymers in extremely confined thin films (monolayers).

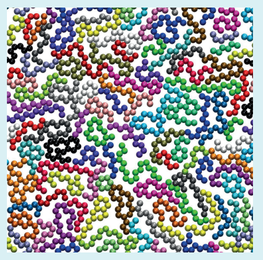
Calculate the number of possible polymer configurations, c_N, compatible to a reference crystal and thus the configurational entropy since: $S = k_b \log(c_N)$.

Introduction of the concept of "Self-Avoiding Rotating Walks" (SARWs) to map isolated polymer chains of specific bending stiffness.

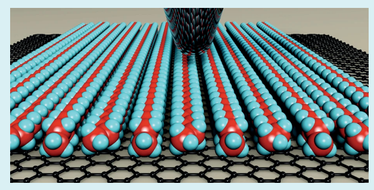
Compare the results with the ones of crystals made of freely-jointed chains

Parreño, O. *et al., Polymers* **12**, 799 (2020).
Benito, J. *et al., Crystals* **13**, 1316 (2023).

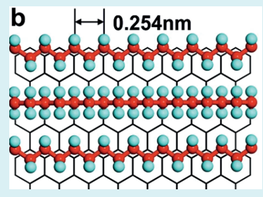
APPLICATIONS



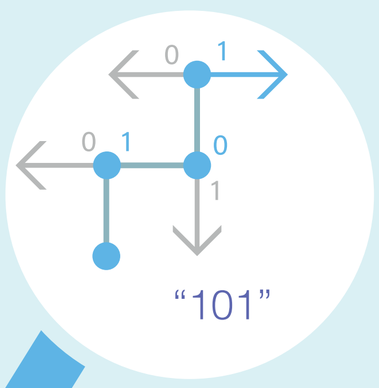
D. Martinez-Fernandez *et al., J. Chem. Phys.* **161,** 034902 (2024)



Zhang, R., Fall, W.S., Hall, K.W. *et al., Nat Commun* **12**, 1710 (2021).



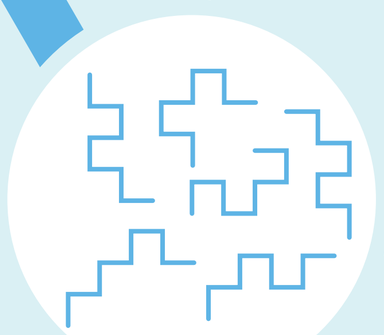
METHODOLOGY



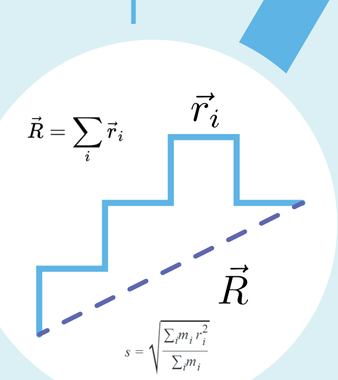
Encode the possible paths into a binary string.

Eliminate all possible string patterns that close upon themselves.

Calculate all possible paths for a single angle and N steps.



Calculate the average end-to-end distance and radius of gyration.



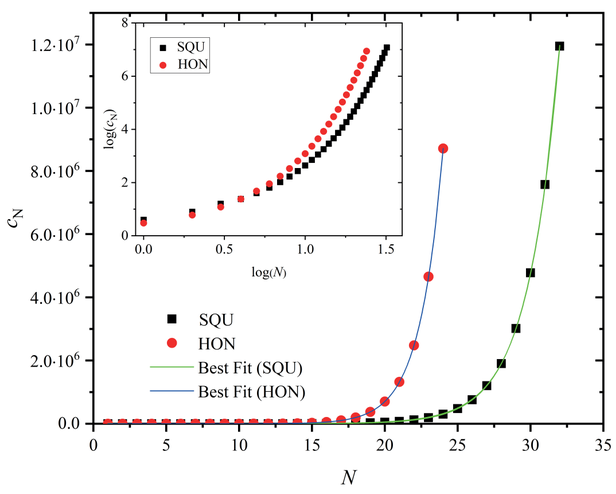
The model is developed using three methods: Fortran, Pythonand analytic calculations (for small N). Results from each approach are analyzed to assess consistency.

RESULTS

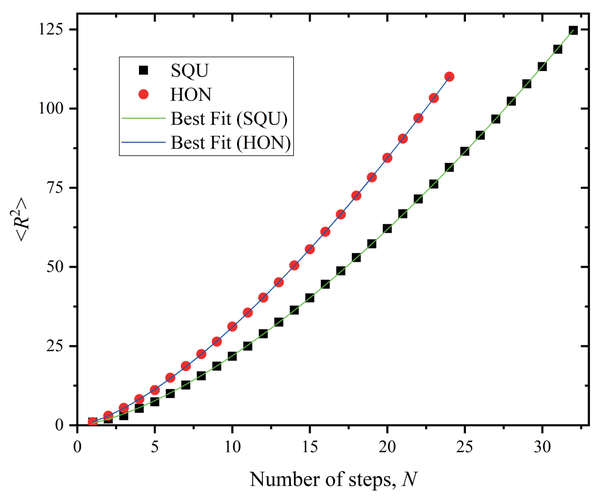
SQUARE

For square lattice we have calculated SARWs up to $N = 32$ (5 days of wall-clock time).

$c_n(X) \sim A\mu^N N^{\gamma-1}$



$< R^2 > \sim DN^{2v}$



HONEYCOMB

For honeycomb lattice we have calculated SARWs up to $N = 24$ (30 minutes of wall-clock time).

Parameters fitting and calculation tables:

	A	μ	γ
SQU	1.033	1.548	1.658
HON	0.920	1.469	1.469
	D	v	
SQU	0.704	0.747	
HON	1.107	0.724	

TRIANGULAR

For the triangular lattice there is no need for enumeration of SARWs because:

- **120°:** The result is the one of HON by multiplying with the ratio of the coordination numbers of the crystals (ncoord*(TRI)* / ncoord*(HON)* = 6 / 3 = 2)
- **60°:** The number of paths remains constant and equal to 12 for all N

CONCLUSIONS

We have developed an algorithm (written in Python and Fortran) to tackle the SARW enumeration problem whose computational difficulty increases exponentially with the number of steps.

Results can be directly compared against the ones obtained for fully flexible polymers (corresponding to conventional self-avoiding random walks).

The freely-rotating chain on the honeycomb crystal has more SARWs than the one on the square lattice even if the coordination number of the latter is higher than the former.

The SARW methodology is currently generalized to tackle crystals in three dimensions.

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