Some Properties of Polymers with Tube Constraint

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[a] common work with M. Bachmann, W. Janke and T. Vogel; on knots : work with P. Virnau

Introduction

- we study low temperature and ground state configurations of homopolymers
- tube model of J.R.Banavar, A.Flammini, D.Marenduzzo, A.Maritan and A.Trovato, J.Phys.:Cond.Matt.**15**:1787(2003)

  - statistical ensemble

  - 3d flexible tubes with volume exclusion through thickness

  - attractive homopolymer interaction at some distance scale

  $\longrightarrow$ volume exclusion and potential attraction compete within a compact polymer with a compactness that can be tuned, which gives rise to secondary structure

  - the global radius of curvature is a 3-point function, different from the standard two point approach of hard sphere volume exclusion, we are studying effective theories

  - the global radius of curvature favors helices as low temperature configurations in the homopolymer in $3d$

  - the global radius of curvature favors an ”asymmetric” and parallel alignment of close polymer sections, there is a possible analogy to the condensation of non-spherical atoms, that show liquid crystal phases

The Model

- $2d$ and $3d$ continuum chains of N monomers at fixed bond $\mid \vec{x}_i, ..., \vec{x}_j \mid = 1$

$$conf = [\vec{x}_1, ..., \vec{x}_N]$$

- Lennard Jones homopolymer Hamiltonian

$$H_{pot} = \sum_{i<j} V_{int}(r_{ij})$$

$$V_{int}(r) = 4([\frac{R_{LJ}}{2^{1/6}r}]^{12} - [\frac{R_{LJ}}{2^{1/6}r}]^{6})$$

with scales $R_{LJ} = 1$ or $R_{LJ} = 2^{1/6} = 1.1225$

- with the thick polymer partition function at T and thickness D

$$Z(\beta = 1/T, D) \; = \; \sum_{conf} \; e^{-\beta H} \; \Theta(2R_{grc} - D)$$

- Monte Carlo evaluation of Z in $0.001 \leq T \leq \mathcal{O}(1)$

The Thickness

- any 3 nondegenerate points $\vec{x}, \vec{y}, \vec{z}$ define a unique circle through these points with a radius of curvature: R_{rc}
- which can be calculated easily

$$R_{rc}(\vec{x},\vec{y},\vec{z}) = \frac{|\,\vec{x}-\vec{y}\,| \quad |\,\vec{x}-\vec{z}\,| \quad |\,\vec{y}-\vec{z}\,|}{4A_{Triangle}(\vec{x},\vec{y},\vec{z})}$$

$$A_{Triangle}(\vec{x},\vec{y},\vec{z}) = \sqrt{s(s-a)(s-b)(s-c)}$$

$$s = \frac{a+b+c}{2} \quad \text{with} \quad a = |\,\vec{x}-\vec{y}\,| \;\; ; \;\; b = |\,\vec{x}-\vec{z}\,| \;\; ; \;\; c = |\,\vec{y}-\vec{z}\,|$$

- the global radius of curvature R_{grc} is defined as the minimum

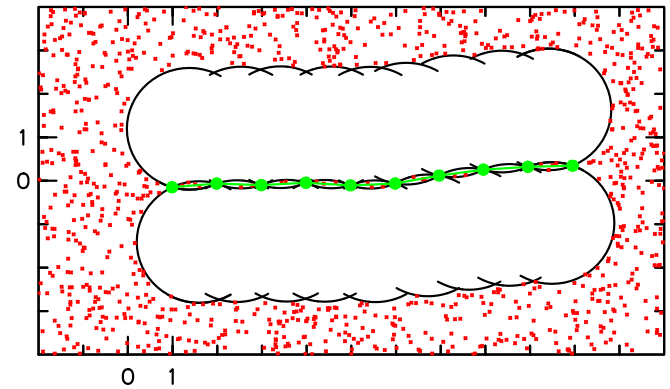
$$R_{grc} = \min\{R_{rc}(\vec{x}_1,\vec{x}_2,\vec{x}_3), R_{rc}(\vec{x}_1,\vec{x}_2,\vec{x}_4), ..., R_{rc}(\vec{x}_{N-2},\vec{x}_{N-1},\vec{x}_N)\}$$

  on the set of all radii of curvature
- providing a regularization of thick polymers with thickness $D = 2R_{grc}$
- which formally is a 3-point function

A Thick Polymer Example

- at $D = 2.8$ and we consider a $N = 10$ polymer, which satisfies

$$\Theta(2R_{grc} - D) = 1 \quad \text{or} \quad R_{grc} \geq 1.4$$



- any single red dot of the figure then also solves $\Theta(2R_{grc} - D) = 1$, now for the "$N + 1$ body" problem
- O.Gonzalez and H.Maddocks, PNAS **96**:4769 (1999), a numerical calculation of the length of perfect knot shapes

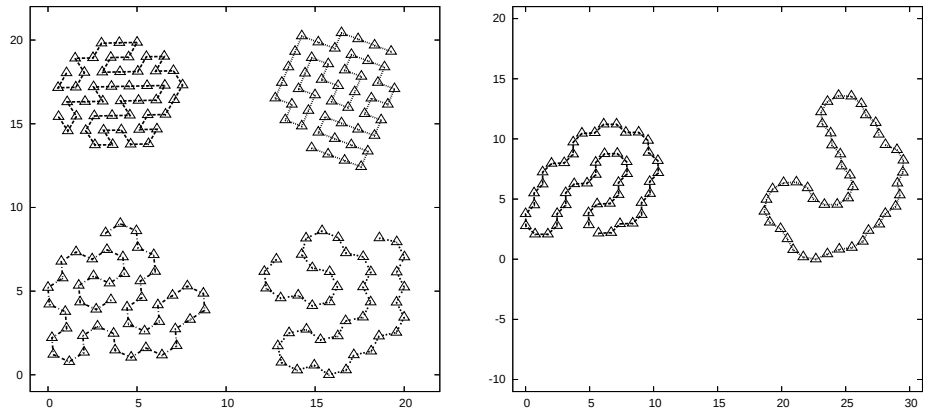
Polymers on Circles

there are periodic molecules, one of them is a circle

R_{grc}	$N_{\mathrm{mon}}(2\pi)$
0.6774	3
0.7071	4
0.8507	5
1.0000	6
1.1524	7
1.3066	8
1.4619	9
1.6180	10

$2d$ Homopolymer

- we have calculated low temperature configurations at $T = 1/1000$ with $R_{LJ} = 1$ as a function of D at values $N_{\rm mon}(2\pi) = 3, 4, 6, 7, 8, 10$ for the number of monomers on circular shaped polymers



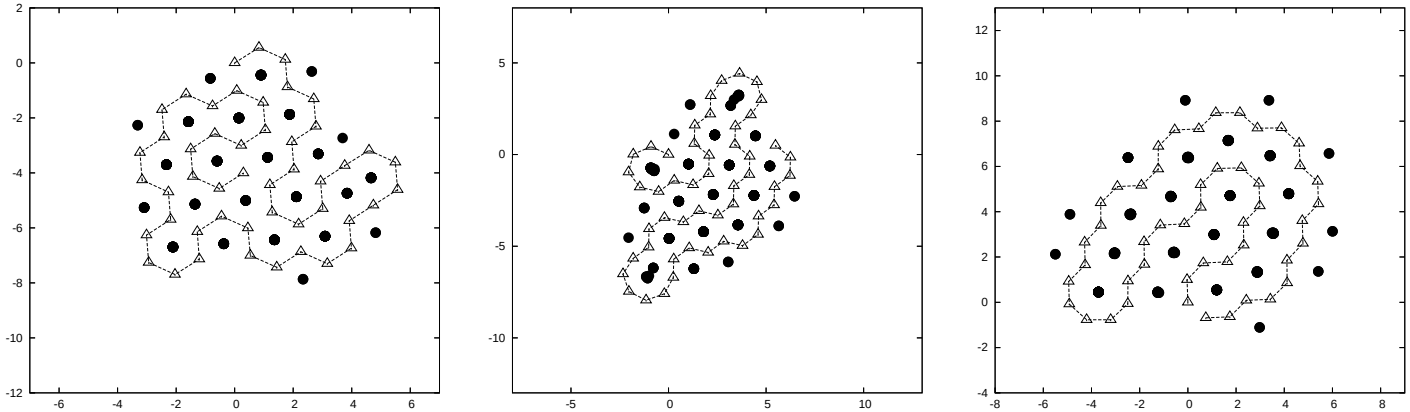
- the continuum of thickness values is punctured by a finite set of thickness values R_{grc}, that correspond to regular lattices (crystals) either in the polymers point set, or its radius-dual

  - for $N_{\rm mon}(2\pi) = 3, 4, 6$ ($R_{grc} = 0.6774, 0.7071, 1.0$) we observe triangular,simple cubic and honeycomb lattices in the polymers point set

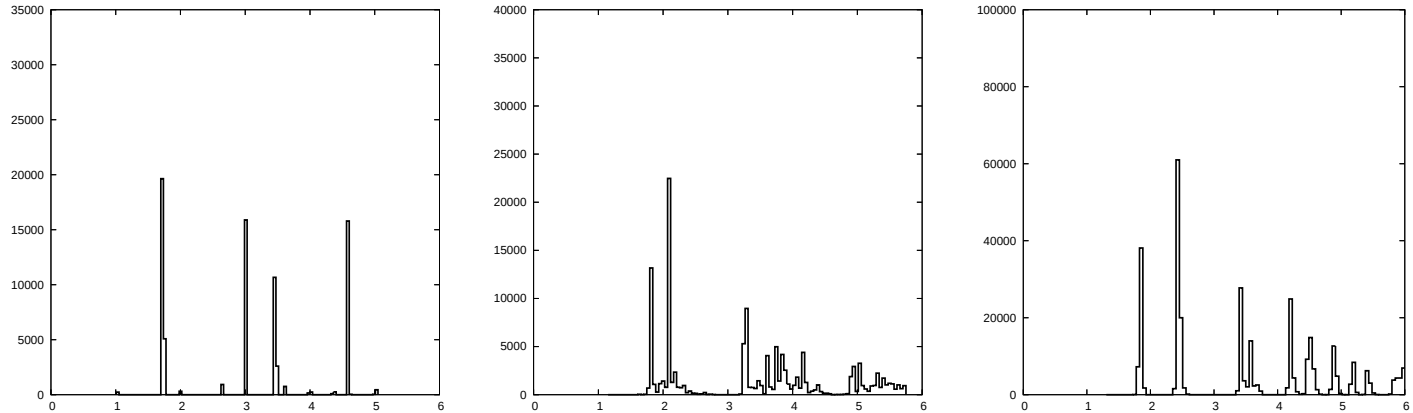
  - at $N_{\rm mon}(2\pi) = 3, 4, 5, 6, 7, 8$ we find sharp peaks in inter-distance distributions on the dual point set

Crystals in $2d$

dual lattices at $N_{\rm mon}(2\pi) = 6, 7, 8$ ($R_{grc} = 1.0, 1.1524, 1.3066$):



inter-distance distributions on the dual point set:



$3d$ Homopolymer

Maritan et. al. in “Optimal shapes of compact strings “, Nature 2000 , upon imposing compactness of the helix along its z-direction proposed the Maritan helix

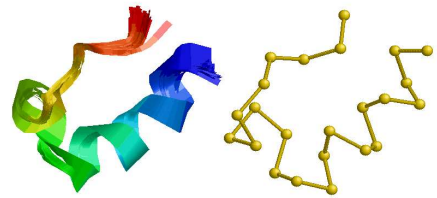
$$x = R_{cyl}\,\sin(\phi) \qquad y = R_{cyl}\,\cos(\phi) \qquad z = p\,\frac{\phi}{2\pi},$$

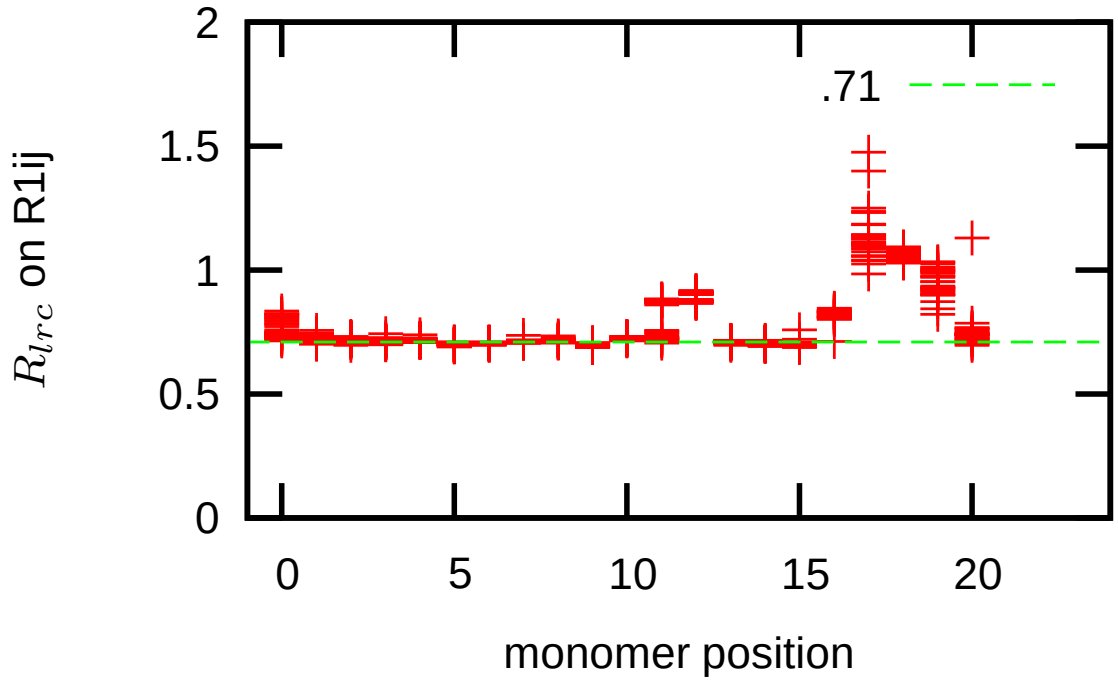
reducing the 2 parametric class of helix configurations into a 1 parametric one, we choose R_{grc} as a parameter

R_{grc}	$N_{\mathrm{mon}}(2\pi)$	p	R_{cyl}	p/R_{grc}	p/R_{cyl}
0.7070	3.7050	1.2323	0.6288	1.7430	1.9599
0.8500	4.6640	1.5522	0.7559	1.8261	2.0536
0.9990	5.5458	2.0015	0.8689	2.0035	2.3035
1.1520	6.4750	2.3694	0.9977	2.0568	2.3748
1.3060	7.4139	2.7042	1.1323	2.0706	2.3883
1.4610	8.3589	3.0217	1.2701	2.0682	2.3745
...	...	...	...	...	...
3.9890	23.2052	8.6060	3.4404	2.1574	2.5015

PDB's R1ij molecule

α-helices are Maritan helices with $R_{grc} \approx 0.71$ and $N_{\mathrm{mon}}(2\pi) \approx 3.6 - 3.8$ at a pitch $p \approx 1.25$





Secondary Structure.

- large scale simulation of ground states and thermodynamic properties on $N = 8, ..., 13$ with ELP, WL, MUCA, PATE methods at a multitude of R_{grc} values in $.0.01 \leq T \leq \mathcal{O}(1)$: T. Vogel, M. Bachmann, W. Janke and T.N., "Thickness-Dependent Secondary Structure Formation of Tubelike Polymers", accepted at EPL, at

$$R_{LJ} = 2^{1/6} = 1.1225... \quad (\mathrm{CHARM})$$

Findings:

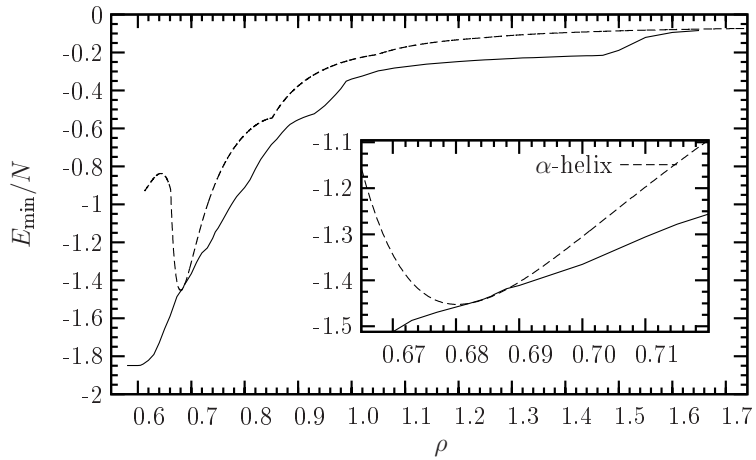
- the dominance of crystalline structure in $2d$ is not repeated in $3d$, we find one particular point in parameter space $R_{grc} = 0.7071 = 1/\sqrt{(2)}$ and $R_{LJ} = 1$, where the polymers point set for $N < 48$ is that of a simple hyper cubic lattice
- we find 4 pseudophases, which with increasing R_{grc} can be characterized as follows
- PHASE 1: in $0.5 \leq R_{grc} \leq 0.92$ polymers are of helical structure. This phase contains at $R_{grc}(\alpha) = 0.684$ natures α-helix with

$$N_{\mathrm{mon}}(2\pi) = 3.6 \quad \Theta_{\mathrm{Torsion}} = 41.6$$

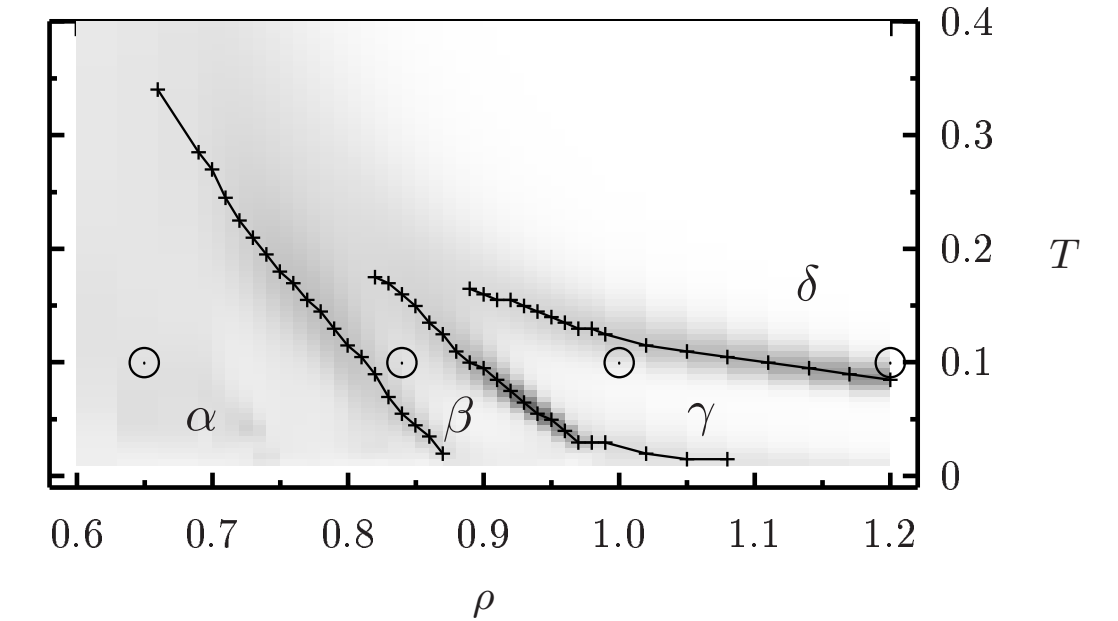
which for $N \leq 9$ is an exact ground state

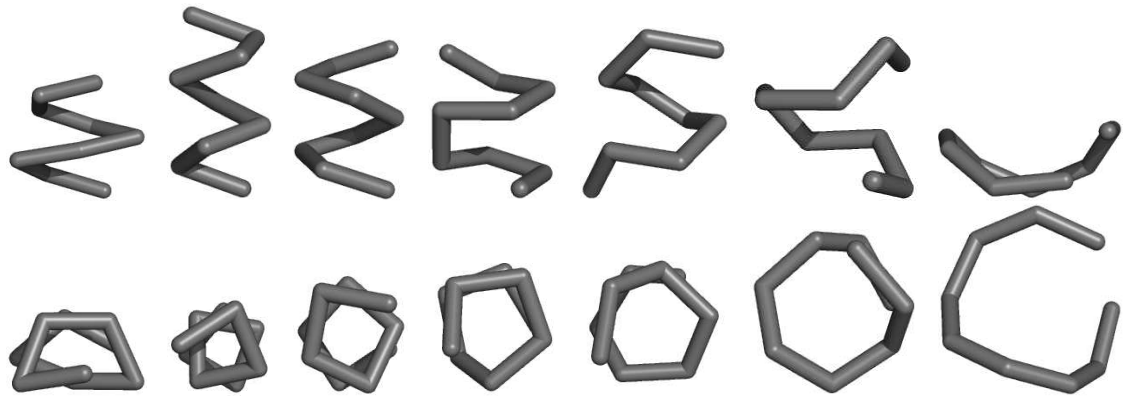
Secondary Structure..

- PHASE 2: in $0.92 \leq R_{grc} \leq 1.1 - 1.2$ the helices open up and planar conformations like β-hairpins become dominant, this phase contains the point $R_{grc} = 1$ at $T = 0$, which in $2d$ gave rise to the honeycomb lattice. In the $3d$ theory for $N = 8$ there is a ground state, that is an exact planar hairpin at $R_{grc} = 1$.
- PHASE 3: in $1.1 - 1.2 \leq R_{grc} \leq N/2\pi$ we find ringlike polymers. A subset of these be classified as twisted circles. The existence of this phase is caused by he non-vanishing potential at large distances and is bounded from above by a ground state, that is an circle.
- PHASE 4: in $R_{grc} > N/2\pi$ we find rodlike structures
- some data at $N = 9$:



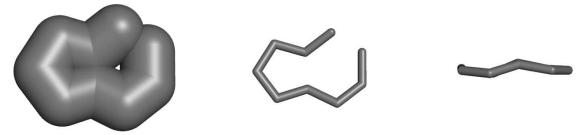
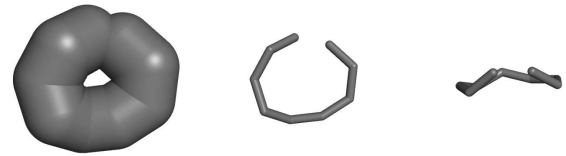
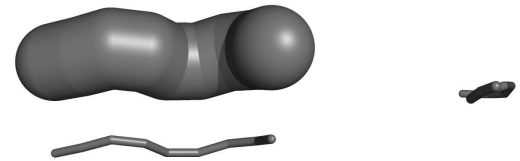
Secondary Structure...





$\rho = 0.60$ 0.69 0.73 0.78 0.88 0.92 1.20

Secondary Structure....

phase	type	views of representative example
α	helix	
β	sheet	
γ	ring	
δ	rod	

Conclusion

- for homopolymers and given a class of potential functions: LJ 6-12, non-vanishing at large distance
- with scales: $R_{LJ} = 2^{1/6}$ and $-1 = V_{int}|_{min} = V_{int}(R_{LJ})$
- and in the statistical ensemble of chains
- we find a "primitive" hierarchy of secondary structures as a function of the thickness
- which with increasing R_{grc} exhibits: helices, sheets, rings and rods
- there is the non-trivial information on the location of the pseudophases. The pseudo critical values R_{grc} that bound the four pseudophases are geometric scales ! At temperature $T = 0$ we have $0.92, 1.2 - 1.3, N/2\pi$.

  the four pseudophases
- avoid a crystal
- allow for α-helices and β sheets
- and as far nature is concerned: we hope for the design of nano-sized molecular machines, that exhibit similar structures, proteins exhibit similar structures

Outlook

- The abundances of knots in polymers with secondary structure. Knots in proteins are very rare /Virnau, Mirny, Kadar, PLoS Comput Biol. 2006 September; 2(9): e122/ , while knots in polymers without secondary structure are frequent /Virnau, Kantor, Kadar, J. A. CHEM. SOC., 2005, **127** 15102./.

  probabilities to find any knot in a polymer model with grc and left (less), right (more) helical secondary structure as a function of the inverse temperature for $N = 100, 200, 300$. The model does not contain a polymer stiffness term.