Poly(3-hexylthiophene) adsorption on Au(001)

J. Gross[1]

(with S. Förster[2], E. Kohl[2], M. Ivanov[1], W. Widdra[2,3] and W. Janke[1])

[1] Institute for Theoretical Physics, University of Leipzig, Leipzig
[2] Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle
[3] Max-Planck-Institut für Mikrostrukturphysik, Halle

CQT
Computational Quantum Field Theory

Outline

1. Motivation
2. Experimental and simulational setup
3. Coarse-grained model of P3HT
4. Coarse-grained surface representation
5. Results and discussion

1. Motivation

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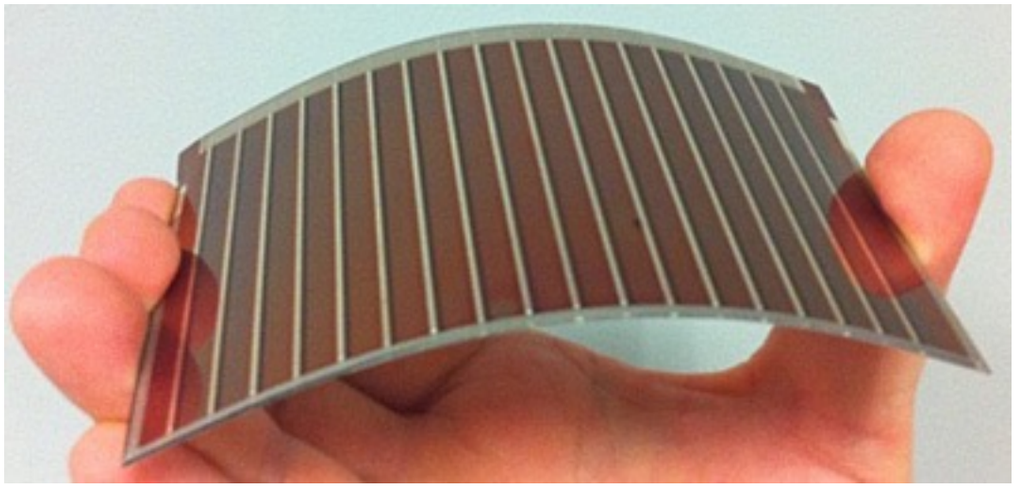

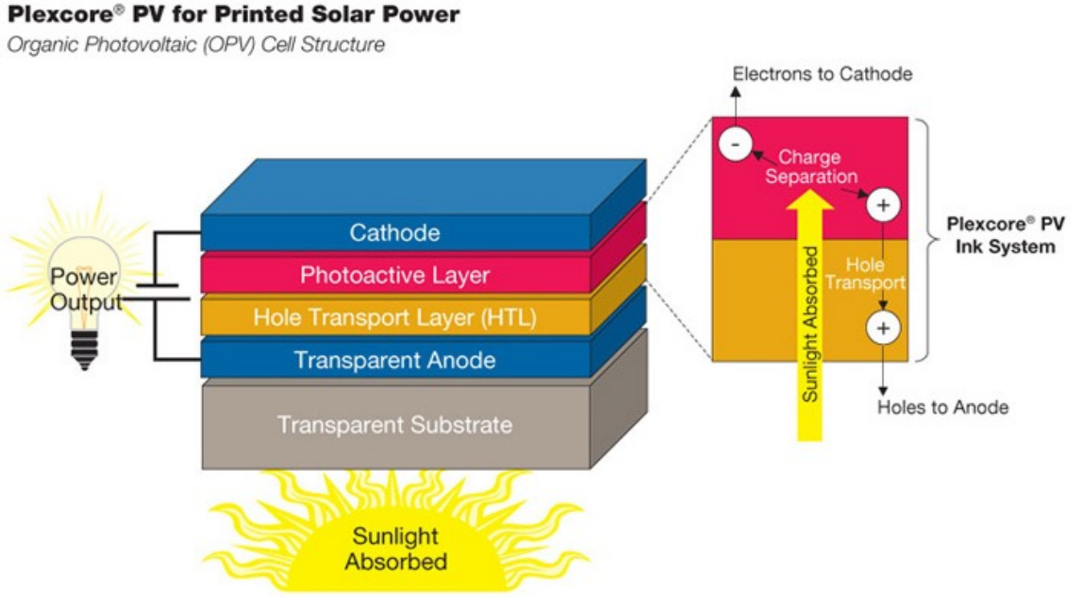

pictures taken from: www.sigmaaldrich.com

- building organic photovoltaics (OPVs)
- P3HT together with PCBM as photoactive layer

- studying adsorption behavior of P3HT on electrode surfaces is of fundamental interest

2. Experimental and simulational setup

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Experimental setup

- ultra-high vacuum custom-build high-temperature scanning tunnelling microscope
- Pt/Ir tips
- gold crystal was cleaned with Ar^+ ion spattering at T=550K
- electrospray deposition of P3HT on the surface at room temperature
- multiple STM pictures recorded

Simulational setup

- Metropolis Monte Carlo simulations at T=300K
- chain lengths between N=20 and 60 monomers in steps of 5

- single monomer displacement
- pivot chain rotation

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3. Coarse-grained model of P3HT

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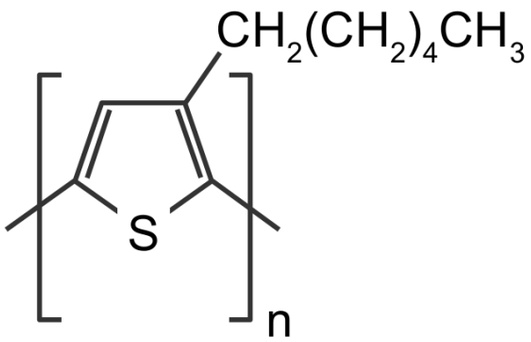

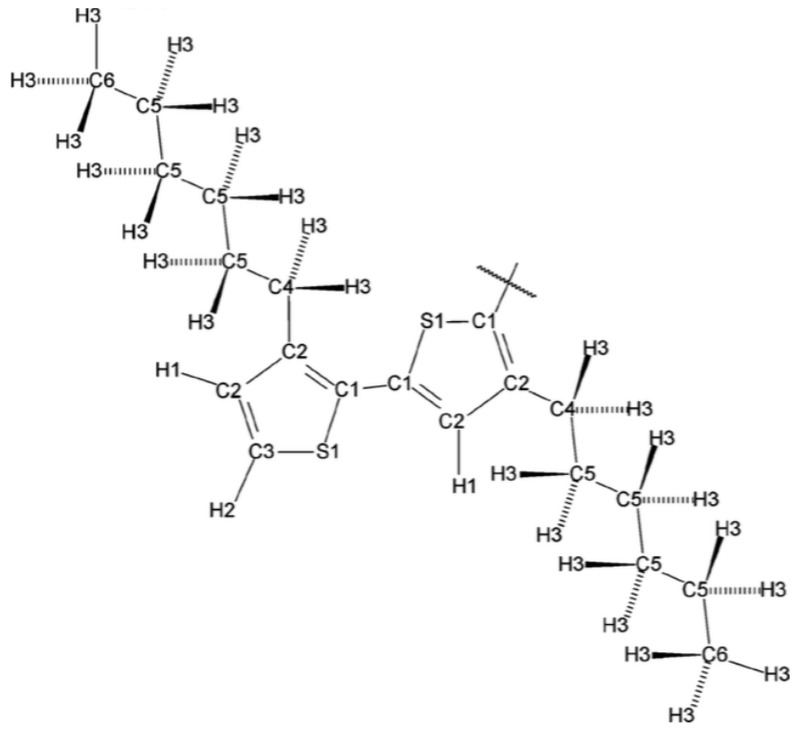

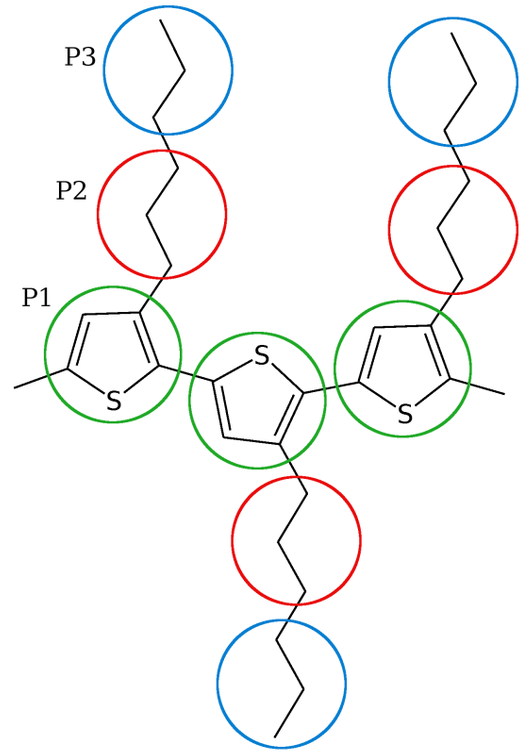

- fully atomistic model based on OPLS-AA force field
- coarse-grained model obtained by iterative Boltzmann inversion

D. M. Huang, R. Faller, K. Do, and A. J. Moule, J. Chem. Theory Comput. **6**, 526 (2010)

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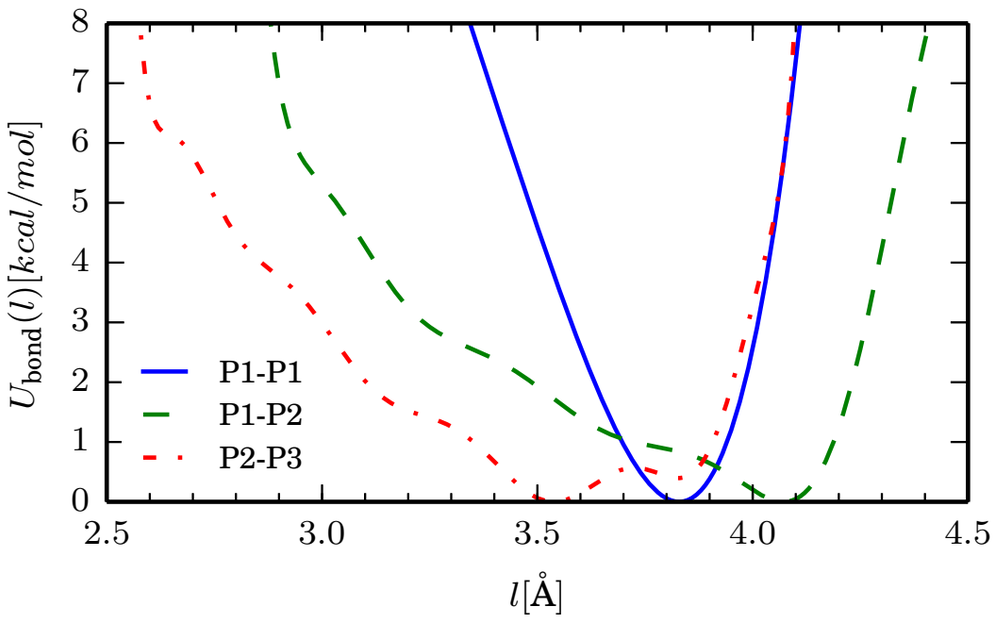
resulting coarse-grained potentials:

bond potential

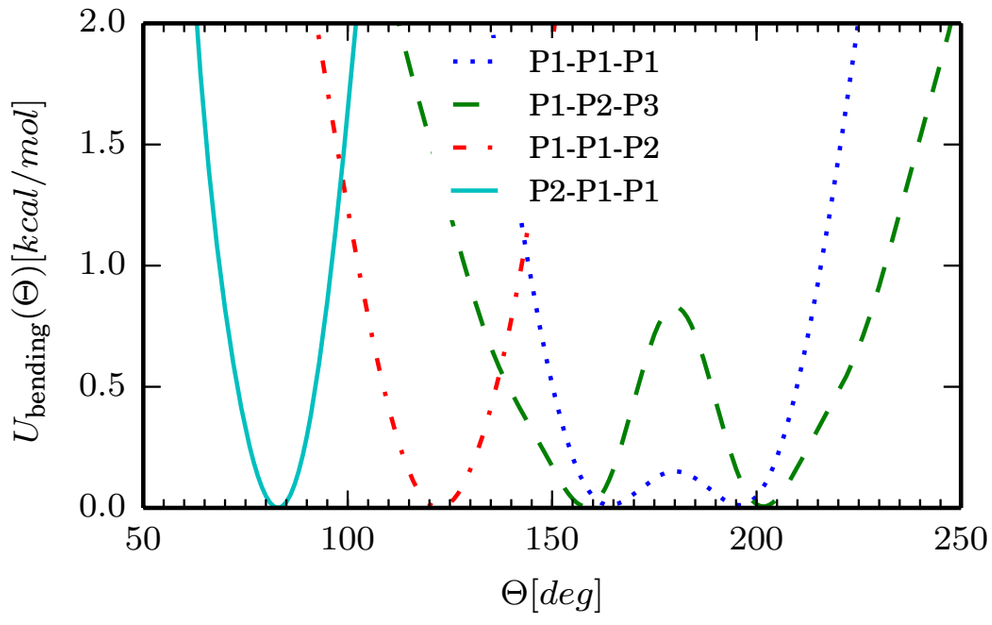
$$U_{\text{bond}}(l) = \sum_{i=2}^{n} c_i (l - l_0)^i$$



- different number of coefficients for each bond type
- 26 parameters in total

bending potential

$$U_{\text{bending}}(\Theta) = \sum_{i=0}^{n} c_i (\Theta - \Theta_0)^i$$



- 42 parameters for all bond angle potentials

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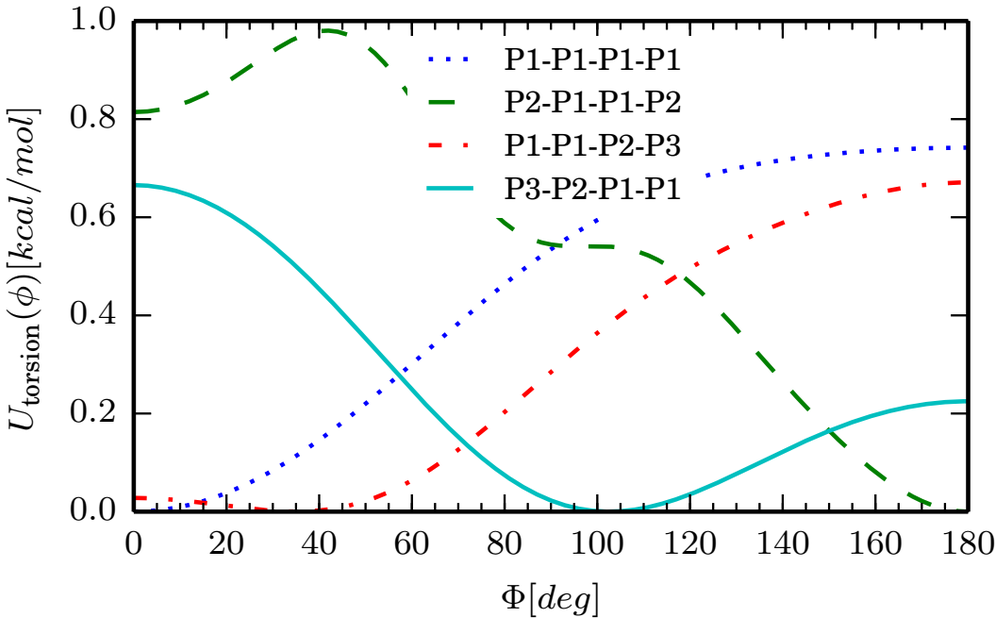
resulting coarse-grained potentials (cont'd):

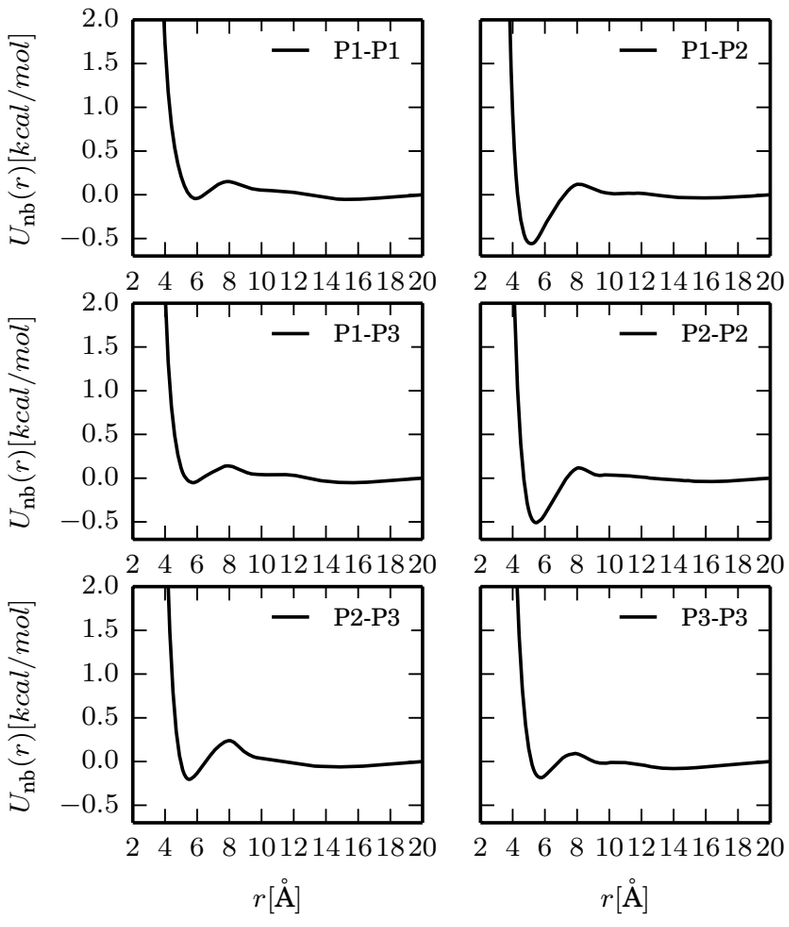
dihedrals and improper

$$U_{\text{torsion}}(\Phi) = \sum_{i=0}^{n} c_i \cos^i(\Phi)$$



- 26 parameters for torsion angle potential
- 5 for one improper between P1-P2-P1-P1

non-bonded potential



- numeric tables for Lennard-Jones like and Coulomb interactions

4. Coarse-grained surface representation

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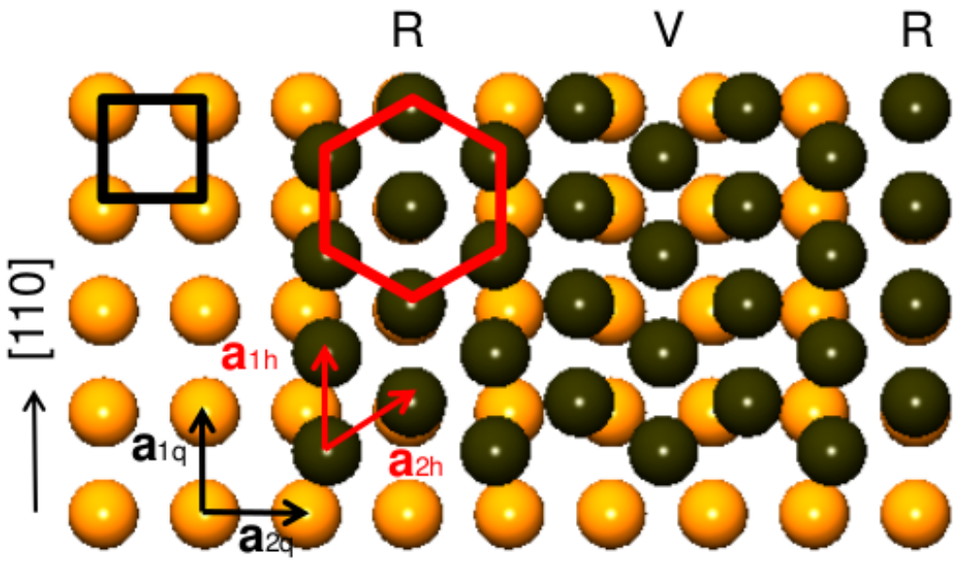
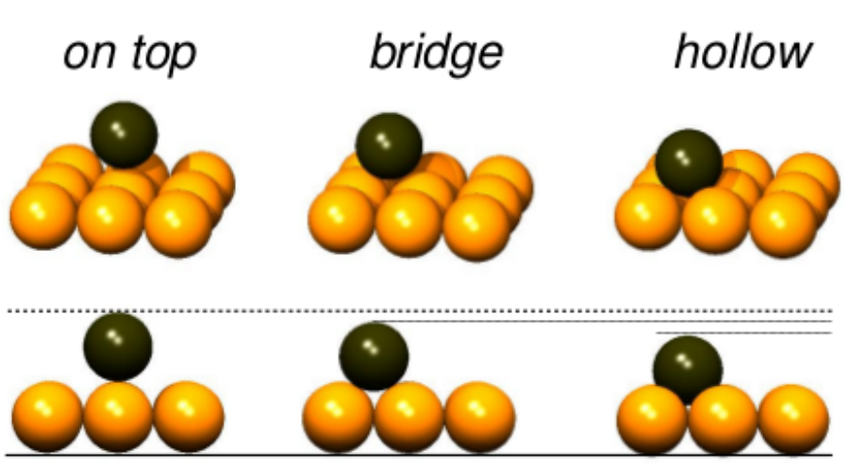


- gold usually is a FCC crystal

- surface of the crystal is reconstructed to a quasi-hexagonal top layer



- length mismatch leads to stripe-like pattern of different heights of the top layer

S. Förster and W. Widdra, J. Chem. Phys. **141**, 054713 (2014)

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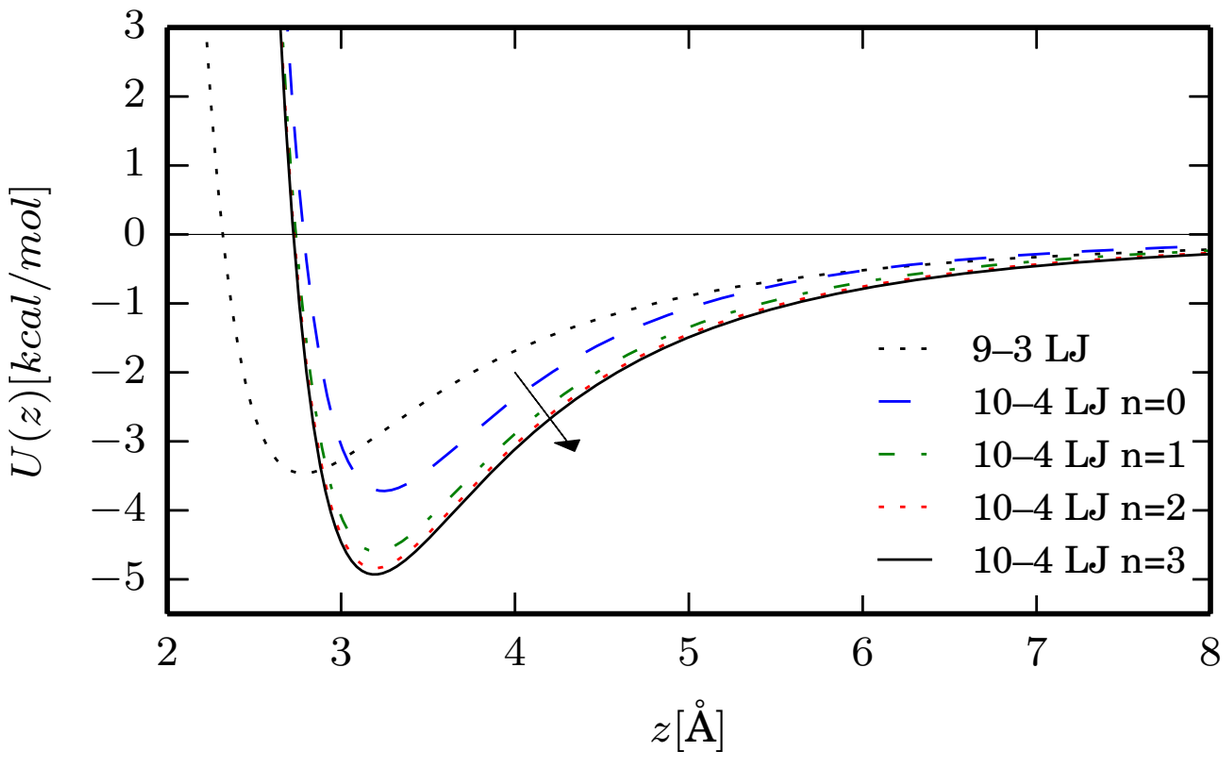
Surface interaction

R. Hentschke, Macromol. Theory Simul. **6**, 287 (1997)



- simples approach:
  - homogenous wall (9-3 LJ)

$$U_{\text{surf,9-3}}(z) = \frac{2\pi\epsilon\rho\sigma^3}{3}\left[\frac{2}{15}\left(\frac{\sigma}{z}\right)^9 - \left(\frac{\sigma}{z}\right)^3\right]$$

- underestimates minimum distance and potential

- better: layers that represent homogenous layers of the crystal (10-4 LJ)

$$U_{\text{surf,10-4}}(z,n) = 2\pi\epsilon\rho\Delta z\sigma^2 \times \left[\frac{2}{5}\left(\frac{\sigma}{z+n\Delta z}\right)^{10} - \left(\frac{\sigma}{z+n\Delta z}\right)^4\right]$$

- quickly converges to “real” potential
  (exact summation of 12-6 LJ interaction of a particle with every gold atom of a large crystal)

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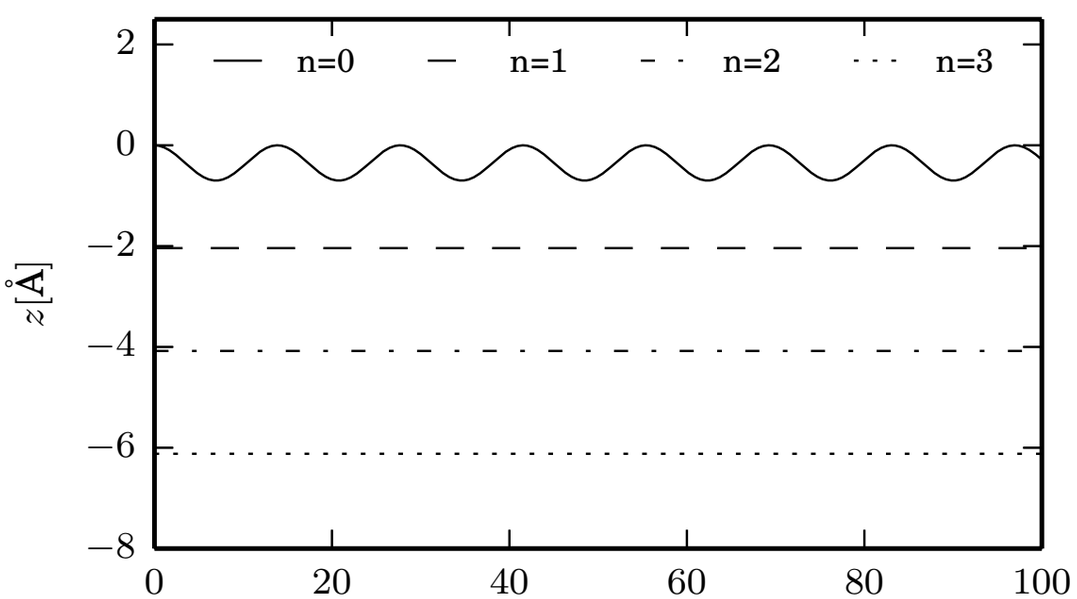

$$U_{\text{surf,10-4}}(z,n) = 2\pi\epsilon\rho\Delta z\sigma^2 \times \left[\frac{2}{5}\left(\frac{\sigma}{z+n\Delta z}\right)^{10} - \left(\frac{\sigma}{z+n\Delta z}\right)^{4}\right]$$

$$z(x) = z + \frac{\Delta h}{2}(1-\cos\theta), \quad \theta = 2\pi\frac{x}{\lambda}$$

$$U_{\text{surf}}(z) = U_{\text{surf,10-4}}(z(x),0) + \sum_{n=1}^{3} U_{\text{surf,10-4}}(z,n)$$

$$\lambda \approx 13.85\,\text{Å}$$

$$\Delta h \approx 0.7\,\text{Å}$$

S. Förster and W. Widdra, J. Chem. Phys. **141**, 054713 (2014)

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5. Results and discussion

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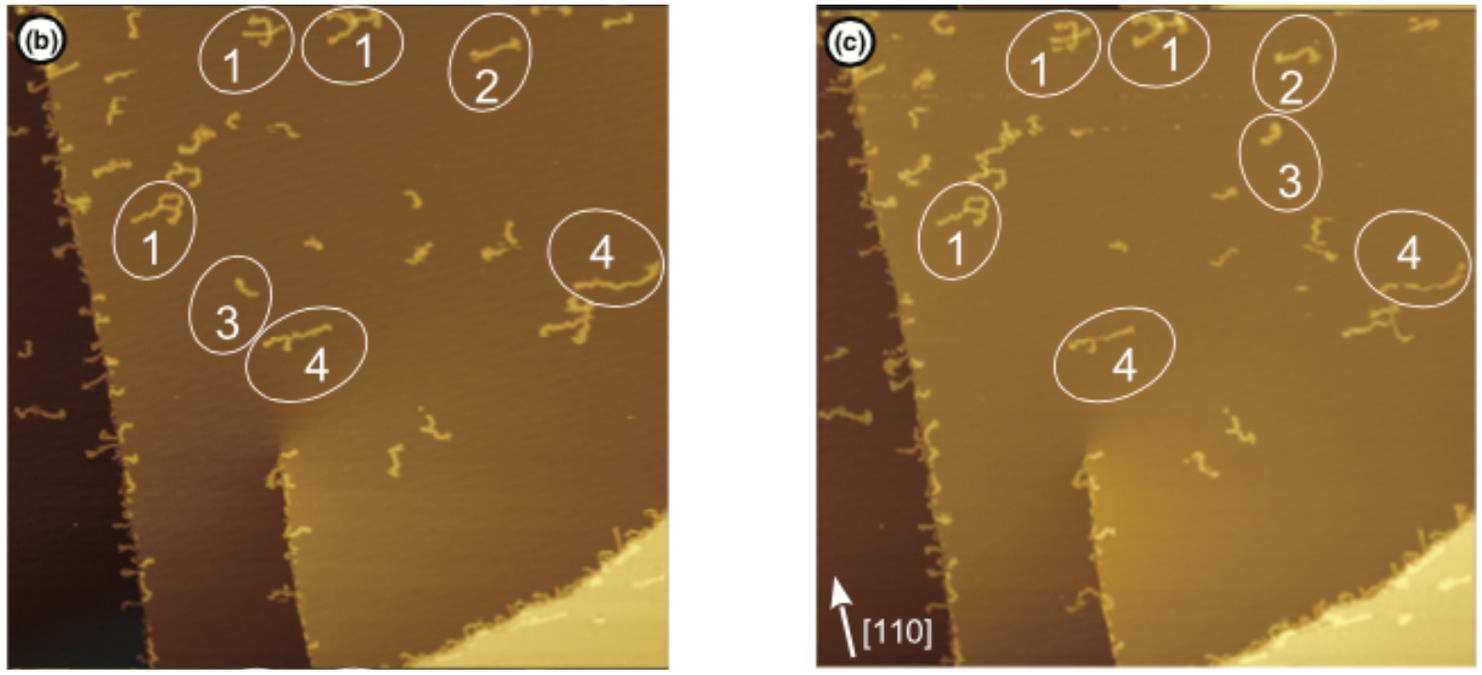
STM images and adsorption types

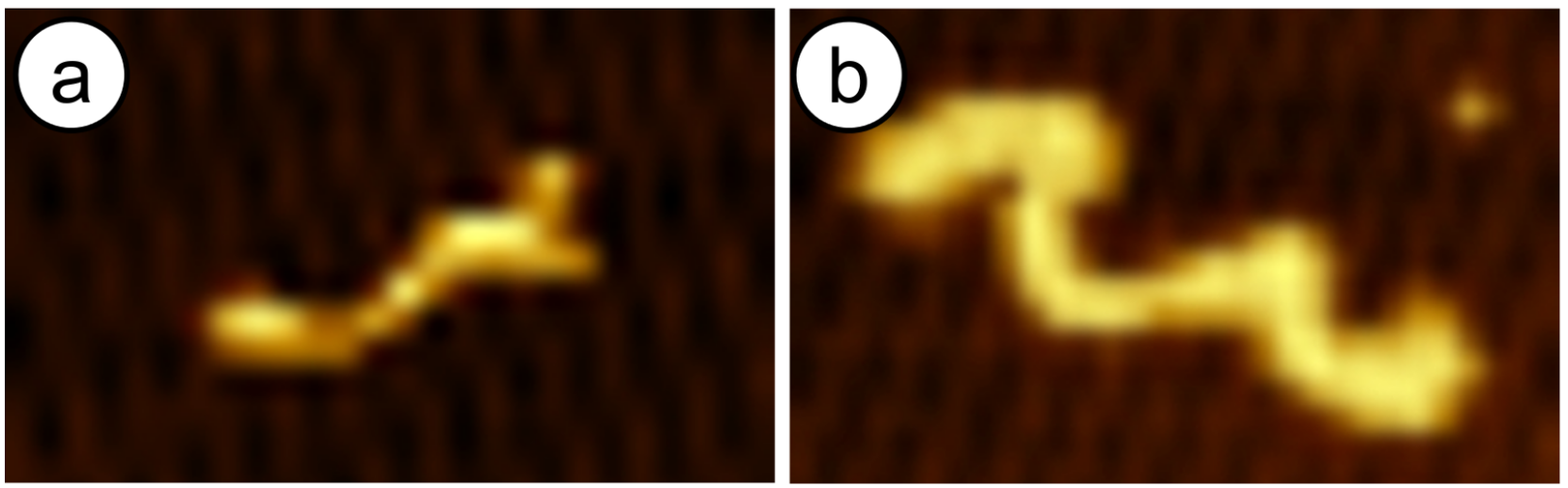


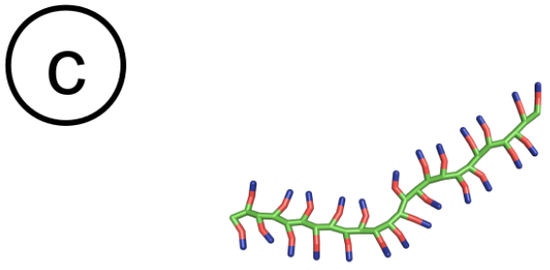
pictures taken 15 min apart

(1) few overlapping polymers parallel to the rows of the surface (immobile)
(2) single polymers, parallel (mobile, locally) *
(3) single polymers, perpendicular (mobile) *
(4) single polymers, parallel (immobile)

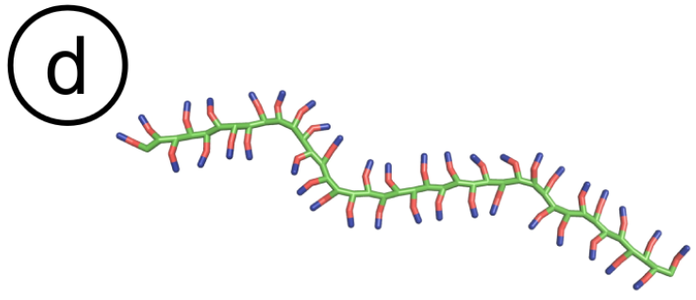
Poly(3-hexylthiophene) adsorption on Au(001)

Comparison of experimental and simulated structures





25 monomers



40 monomers

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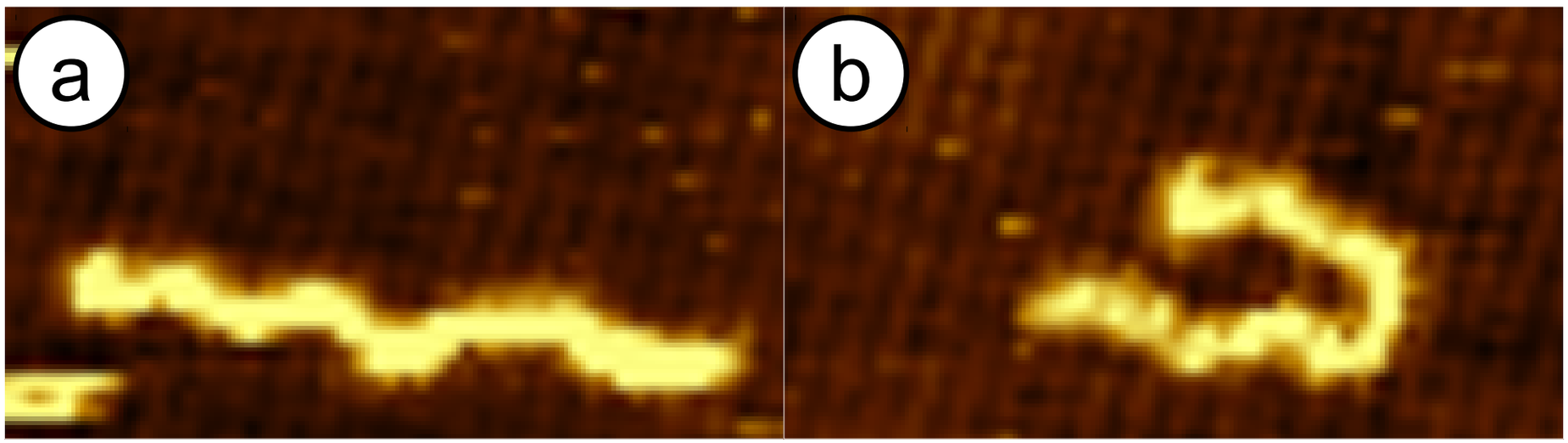
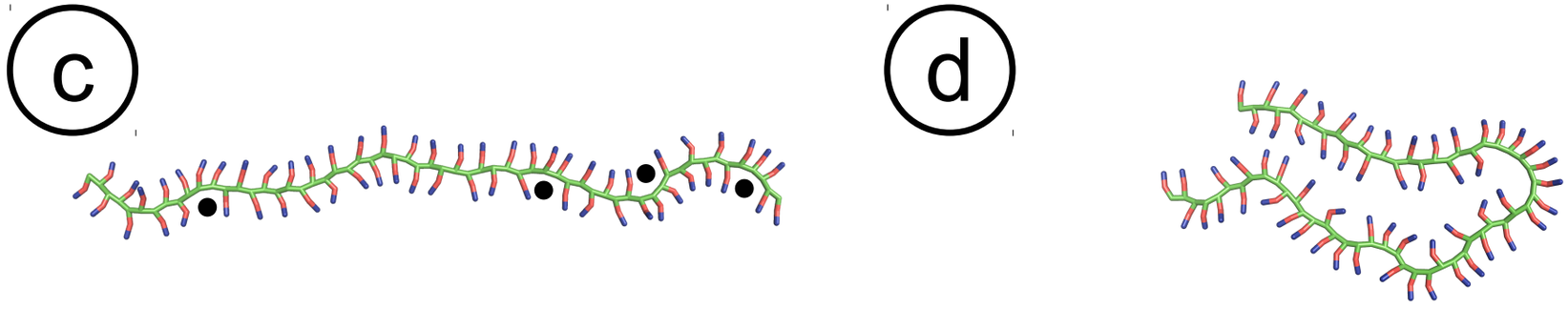
Comparison of experimental and simulated structures





- elongated coil (a) and (c) and collapsed hairpin (b) and (d) for a 60-mer
- bending of the backbone only possible, when side chains move out of the way

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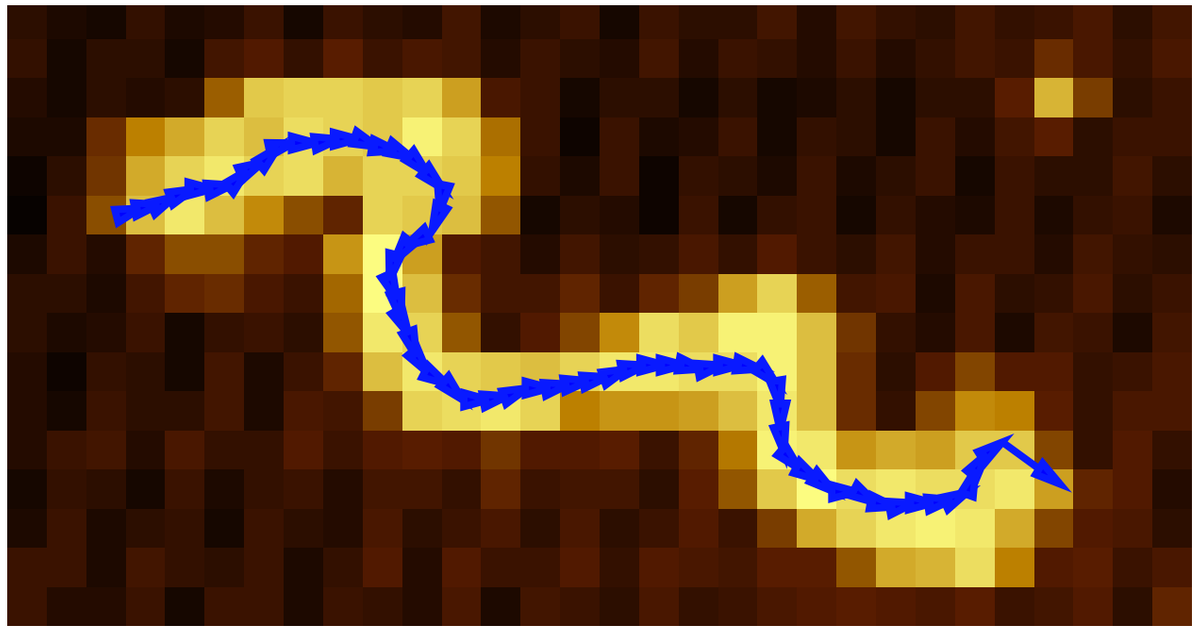
How do we know the length of the experimental structures?

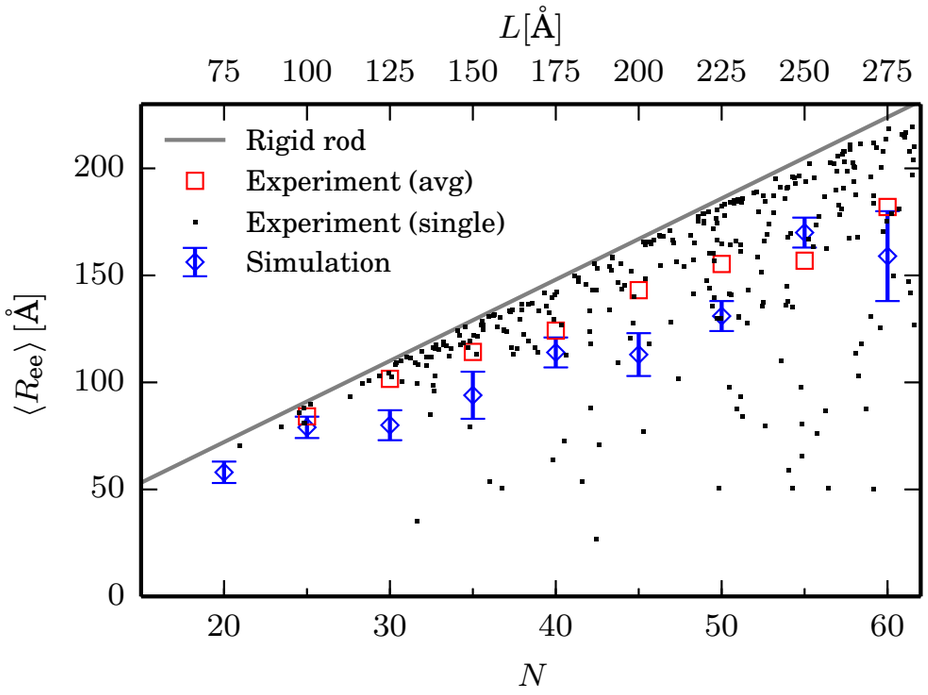
- computer aided tracing of chains in STM data
- cumbersome process
- between 700 and 1000 structures analysed so far

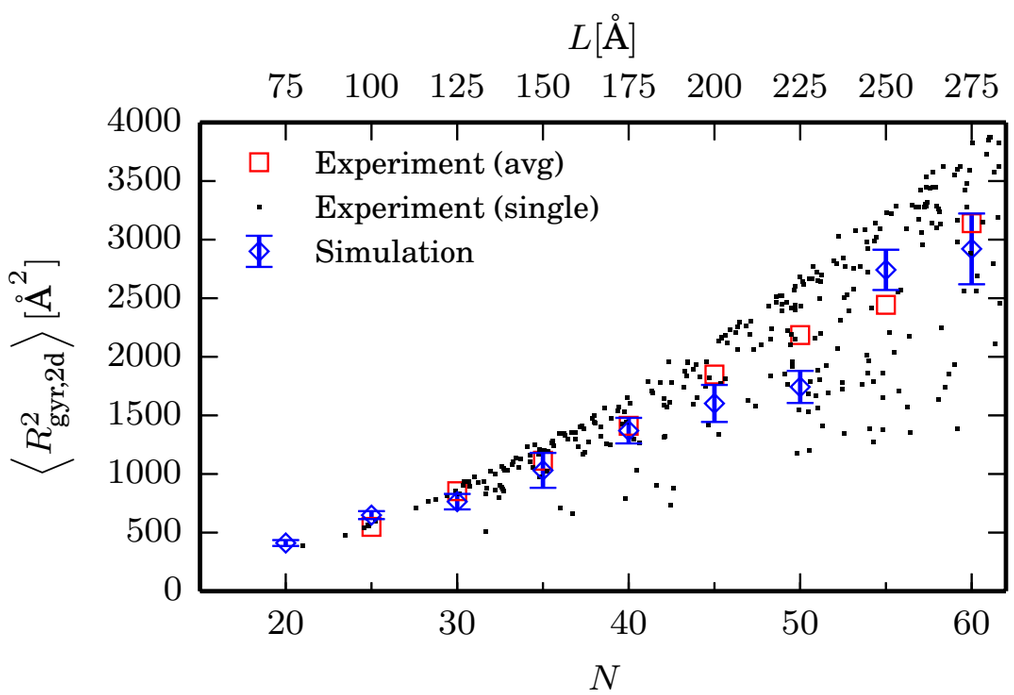


- allows us to calculate end-to-end distances and radii of gyration and thus a quantitative comparison with simulational data

Poly(3-hexylthiophene) adsorption on Au(001)

Numerical results





- black dots represent single experimental structure
- red squares are binned experimental averages (w/o error bars - see the distribution)
- blue diamonds are simulational averages
  using only single particle displacement (read: “realistic”) moves

- good agreement between experiment and simulation considering that this is a CG model and not a fully atomistic simulation

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THE JOURNAL OF CHEMICAL PHYSICS **141**, 164701 (2014)

Polymer adsorption on reconstructed Au(001): A statistical description of P3HT by scanning tunneling microscopy and coarse-grained Monte Carlo simulations

S. Förster,[1,a)] E. Kohl,[1] M. Ivanov,[2,b)] J. Gross,[2,c)] W. Widdra,[1,3,d)] and W. Janke[2,e)]
[1]*Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany*
[2]*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*
[3]*Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany*

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We report on a combined theoretical and experimental characterization of isolated Poly(3-hexylthiophene) (P3HT) chains weakly adsorbed on a reconstructed Au(001) surface. The local chain conformations of *in situ* deposited P3HT molecules were investigated by means of scanning tunneling microscopy. For comparison, Monte Carlo simulations of the system were performed up to a maximum chain length of 60 monomer units. The dependence of the end-to-end distance and the radius of gyration on the polymer chain length shows a good agreement between experiment and Monte Carlo simulations using simple updates for short chains. © *2014 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4898382]

Please visit Momchil Ivanov's poster in the Aula !

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Thank you for your attention.

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HALLE-WITTENBERG

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Dr. Stefan Förster
Erik Kohl

UNIVERSITÄT LEIPZIG

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Momchil Ivanov

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Polymers under multiple constraints

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