What we do (not) understand about carbon nanomembranes

Jürgen Schnack

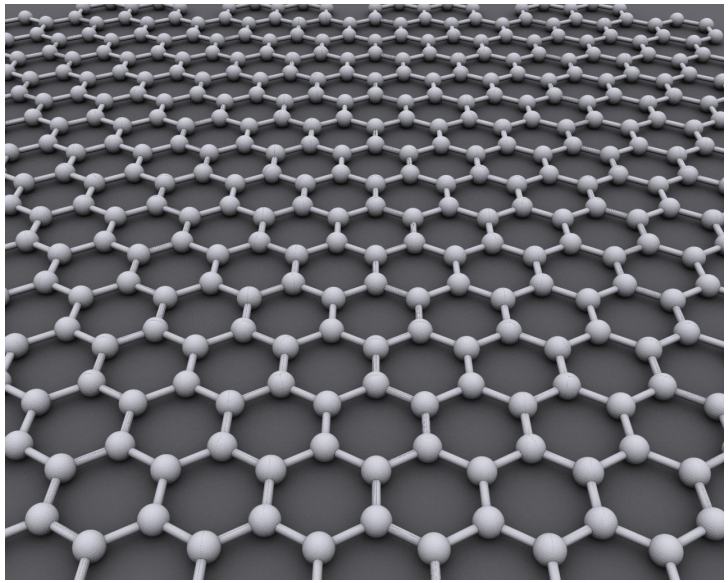
Department of Physics – University of Bielefeld – Germany

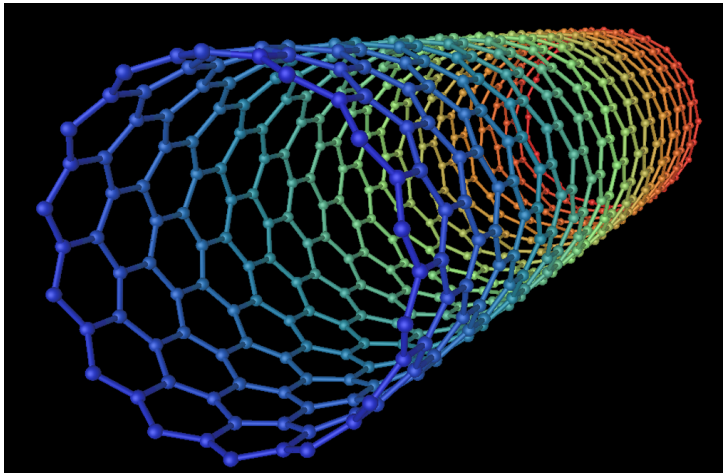
http://obelix.physik.uni-bielefeld.de/∼schnack/

Seminar, Bielefeld University, D0, 11 December 2020

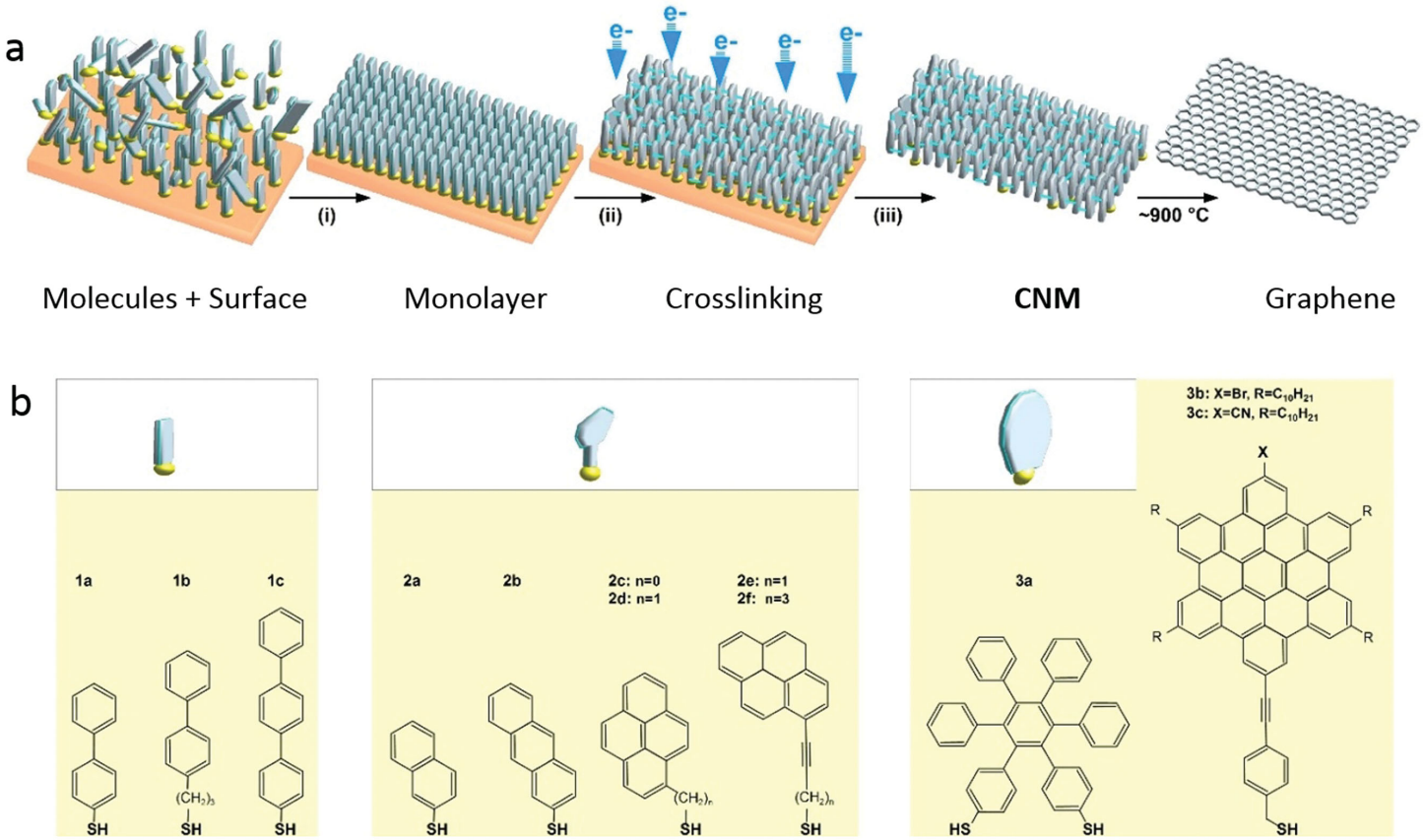
Introduction

There are various carbon-based nanostructures . . .





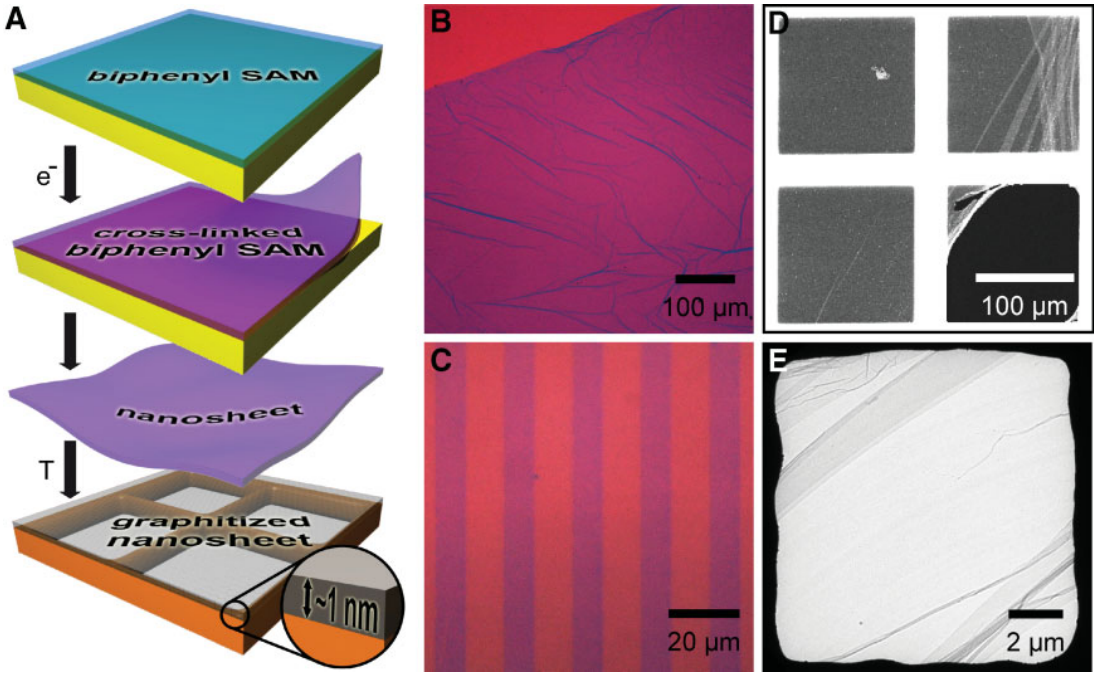
. . . and carbon-based cross-linked SAMs (I).

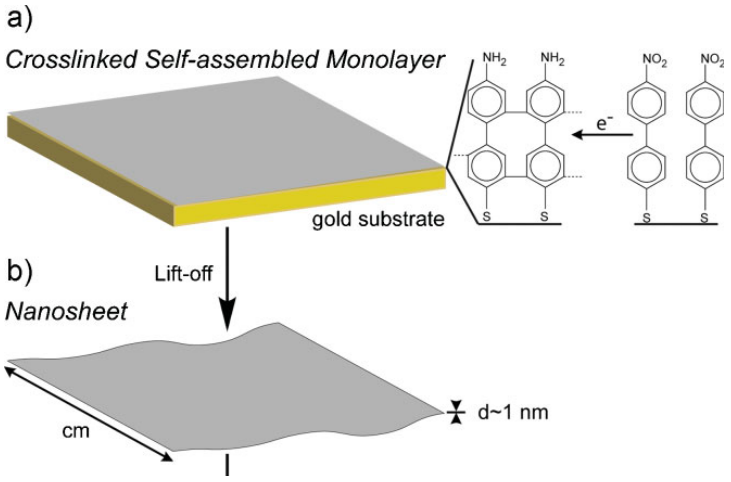


A. Turchanin, A. Gölzhäuser, Advanced Materials **28**, 6075-6103 (2016).

. . . and carbon-based cross-linked SAMs (II).

ADVANCED MATERIALS





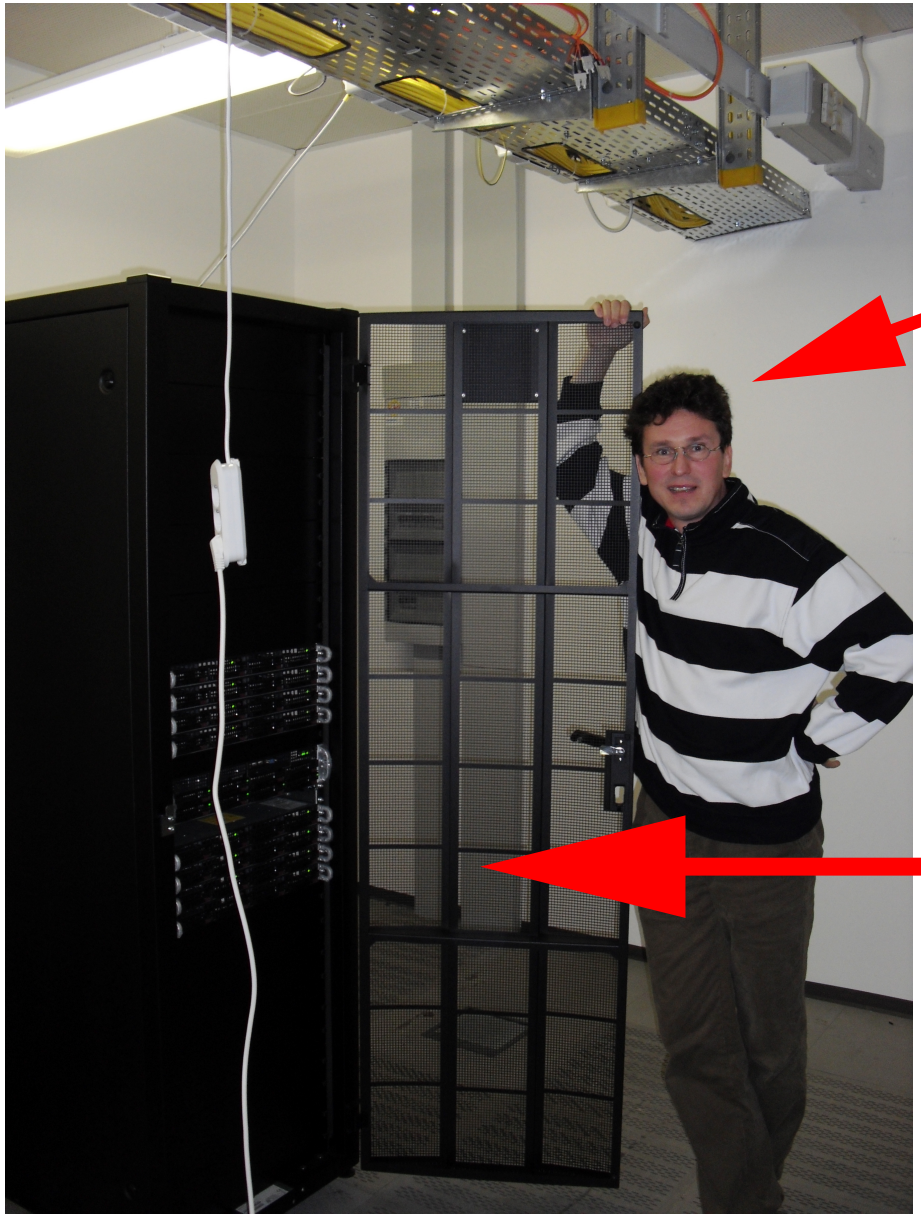
A. Turchanin *et al.*, Advanced Materials **21**, 1233 (2009); I. Amin *et al.*, Small **6**, 1623 (2010).

Problems for theory

- Systems contain very many carbon atoms.
- Structure very likely irregular. Defects?
- Quantum Methods, even DFT, cannot deal with such systems. No way!

. . . and there are more questions to come.

Thank God, we have computers



“Espresso-doped multi-core”

128 cores, 384 GB RAM

. . . but that’s not enough!

Contents for you today

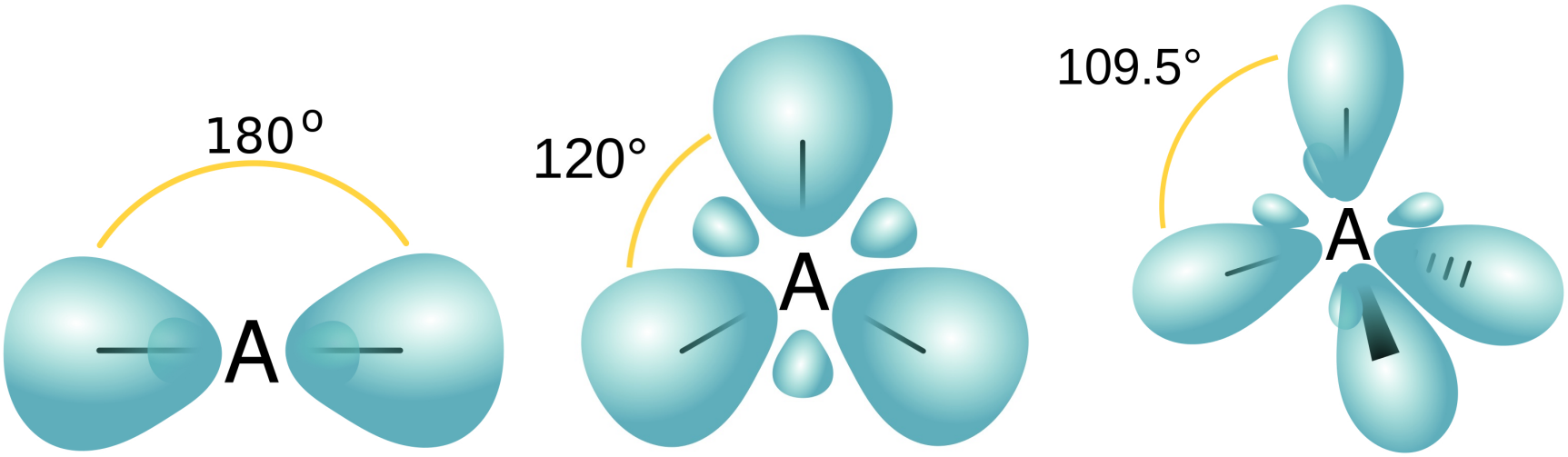
1. Carbon nanomembranes $\surd$
2. Classical molecular dynamics
3. Mechanical properties
4. Structure of CNMs
5. Open problems

Classical Molecular Dynamics

Classical Molecular Dynamics

- CMD can model very large systems ($\sim 10.000.000$ particles).
- CMD can find ground states and model dynamics.
- CMD can model thermal equilibrium and non-equilibrium.
- But how should this be realistic for carbon-based compounds, where the chemical bond is of quantum nature?

sp hybridization modes



sp, sp^2, and sp^3 hybridization modes.

wikipedia: orbital hybridization

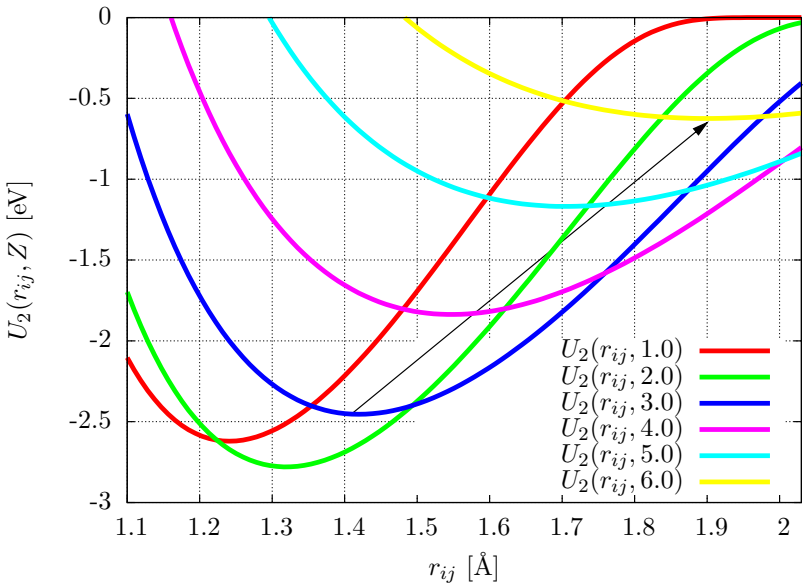
Very sophisticated carbon potential

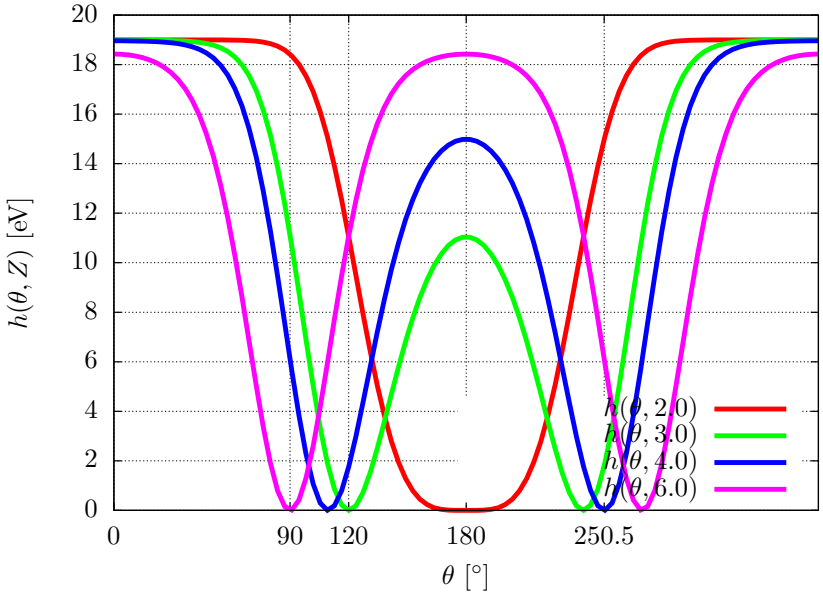
$$H(\vec{r}_1, \vec{p}_1; \vec{r}_2, \vec{p}_2; \dots) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_1, \vec{r}_2, \dots)$$

$$V(\vec{r}_1, \vec{r}_2, \dots) = \sum_{i \neq j}^{N} U_2(|\vec{r}_i - \vec{r}_j|, Z_i) + \sum_{i \neq (j<k)}^{N} U_3(|\vec{r}_i - \vec{r}_j|, |\vec{r}_i - \vec{r}_k|, \Theta_{ijk}, Z_i)$$

D. W. Brenner *et al.*, J. Phys.: Cond. Mat. **14**, 783 (2002).
N. A. Marks, Phys. Rev. B **63**, 035401 (2000).

Coordination dependence





Coordination influences strength and direction of bonding.

N. A. Marks, Phys. Rev. B **63**, 035401 (2000).
A. Mrugalla, Master thesis (2013)

What can be achieved realistically?

- Structure calculations.
- Dynamical self-organization (1).
- Mechanical properties, such as vibrational spectra and response to mechanical stress.
- Sorry, no electronic properties, such as conductance or heat conductance.

(1) R. C. Powles, N. A. Marks, and D. W. M. Lau, Phys. Rev. B **79**, 075430 (2009).

Mechanical properties (Young's modulus)

F. Gayk, J. Ehrens, T. Heitmann, P. Vorndamme, A. Mrugalla, and J. Schnack, Physica E **99**, 215 (2018).

Question

What is the predictive power
of classical carbon potentials
for structure and moduli
for known carbon materials?

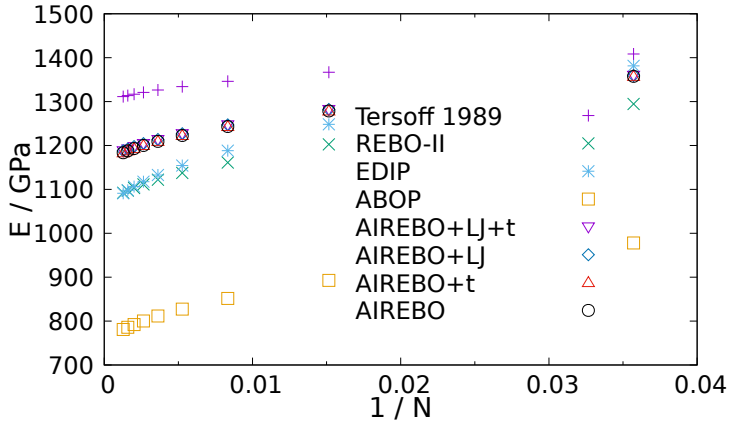
. . . before we start to investigate unknown materials!

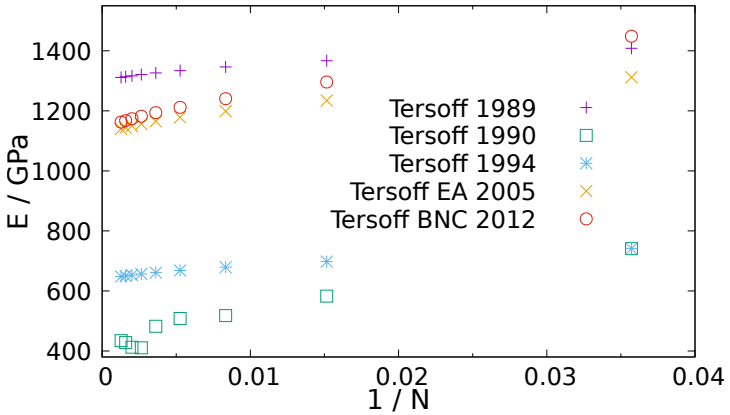
Ground state distances for graphene, CNT, and diamond

Table 1: Ground-state dimensions in Å of graphene, CNT, and diamond for the investigated potentials (LAMMPS).
(* No proper ground state structure found; † anisotropic.)

potential	graphene C-C distance	CNT C-C distance	diamond lattice const.
EDIP	1.42	1.42	3.56
REBO-II	1.42	1.42	3.58
ABOP	1.42	1.424, 1.417 †	3.46
Tersoff 89	1.46	1.46	3.57
Tersoff 90	*	*	3.56
Tersoff 94	1.55	*	3.56
Tersoff BNC	1.44	1.44	-
Tersoff EA	1.48	1.48	3.57
AIREBO+LJ+t	1.40	1.41	3.58
AIREBO+LJ	1.40	1.40	3.58
AIREBO+t	1.40	1.40	3.58
AIREBO	1.40	1.40	3.58
experimental	1.42	1.42	3.567

Young's modulus for graphene

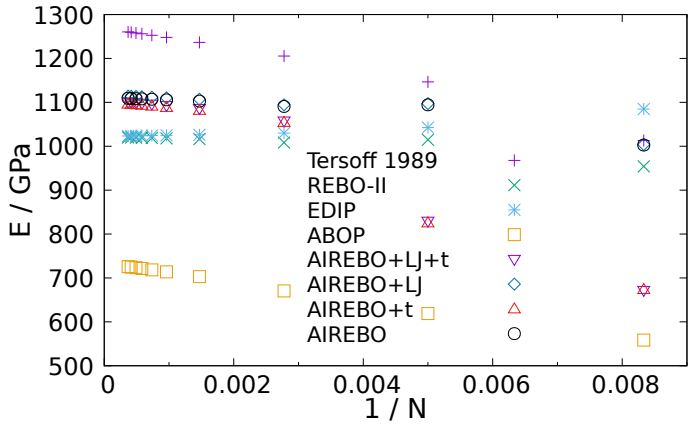


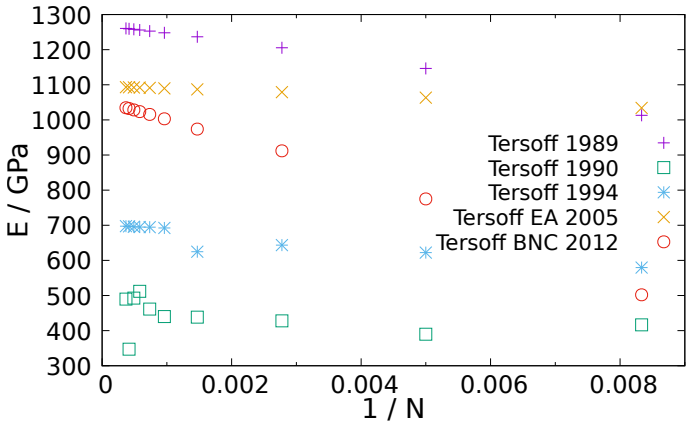


Young's modulus of graphene for various sizes and potentials. N denotes the number of atoms in the approximately square graphene sheets. Open boundary conditions are applied.

Experimental value: 1000 GPa.

Young's modulus for CNT

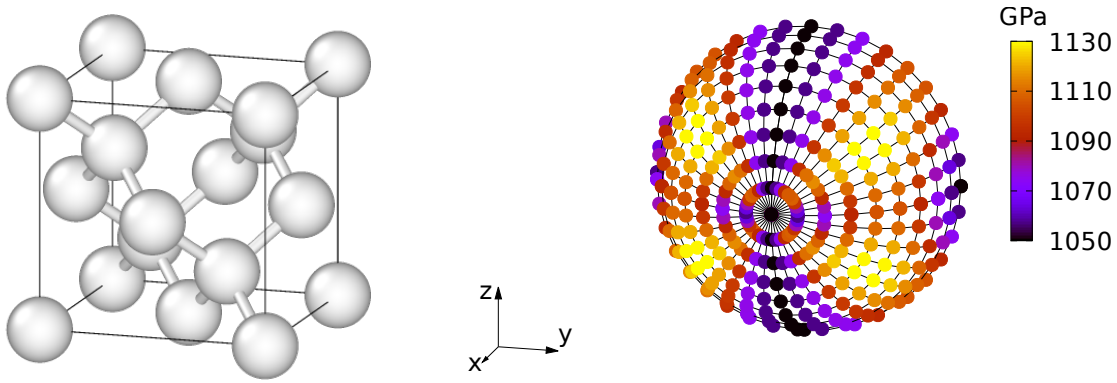




Young's modulus of a (20,20) CNT with armchair geometry along the tube, taken as x-direction, for various sizes and potentials. N denotes the number of atoms of the tube. Open boundary conditions are applied.

Experimental value: 1000 GPa.

Young's modulus for diamond



Structure and directions as well as Young's modulus of diamond taken in various directions on the northern hemisphere around the positive x-direction for $N = 8631$ and the EDIP potential. Open boundary conditions are applied.

Experimental values: 1.05 TPa . . . 1.21 TPa

Conclusion

For the investigated observables
(bond length & Young's modulus)
and the chosen carbon materials
EDIP and REBO-II
perform overall well.

F. Gayk, J. Ehrens, T. Heitmann, P. Vorndamme, A. Mrugalla, and J. Schnack, Physica E **99**, 215 (2018).

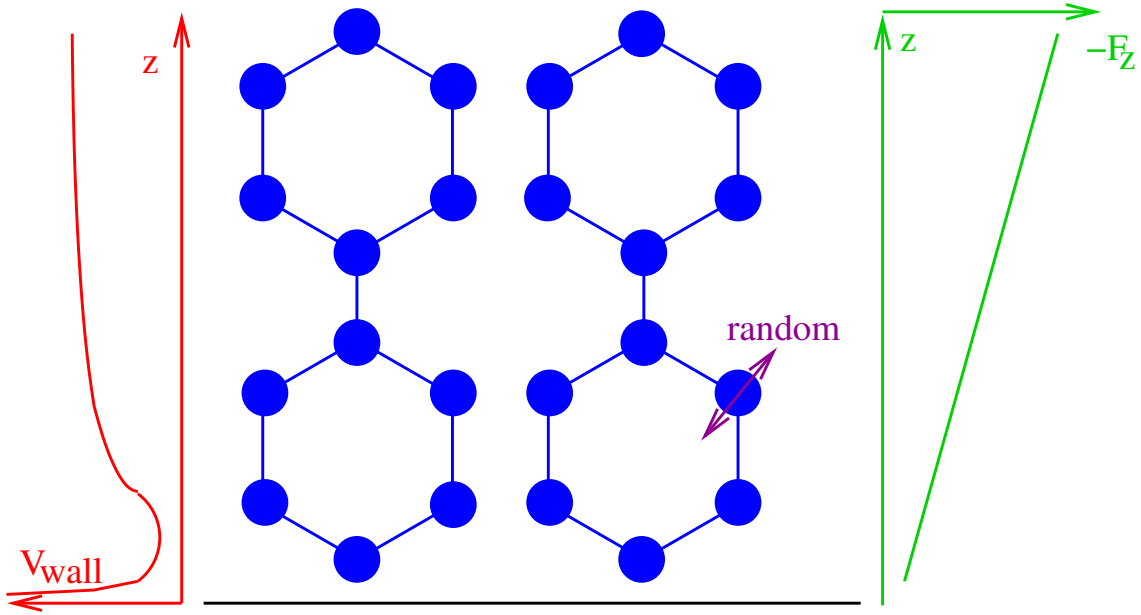
How to find the

Structure of CNMs?

Questions

- **The** structure or **a** structure?
- Structure very likely a metastable state, a local energy minimum. Glas-like?
- How to model? Initial conditions, cooling, . . . ?
- Which structures are correct? Observables?
- X-ray structure determination impossible!

That's how we do it



Model: includes only carbon atoms (+ surface);

Initial state: randomized carbon positions in SAM, vertical force field;

Cooling: Nose-Hoover or alike;

LAMMPS: EDIP and analytical forces included in our version.

Examples of CMNs

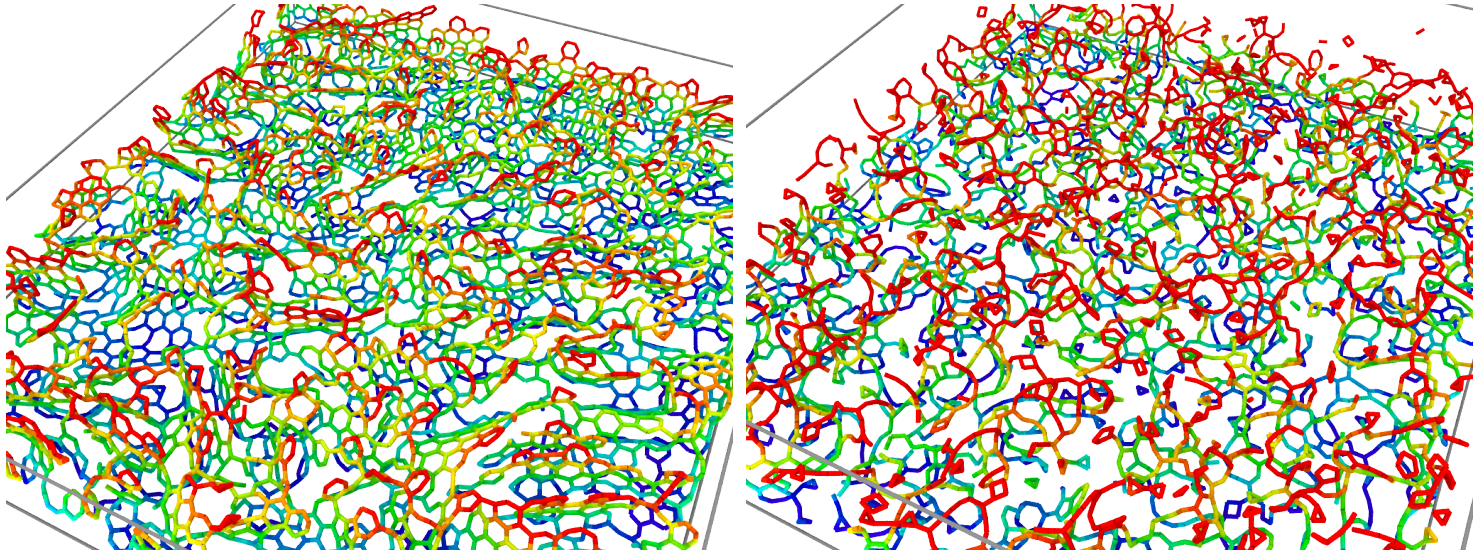


Abbildung 17: TPT, $T = 700$ K; $k = 30$ $\frac{\text{eV}}{\text{Å}}$ (links) und $k = 200$ $\frac{\text{eV}}{\text{Å}}$ (rechts)

F. Gayk, Master Thesis, Bielefeld University (2018)

J. Ehrens *et al.*, arXiv:2011.00880

Examples of CMNs

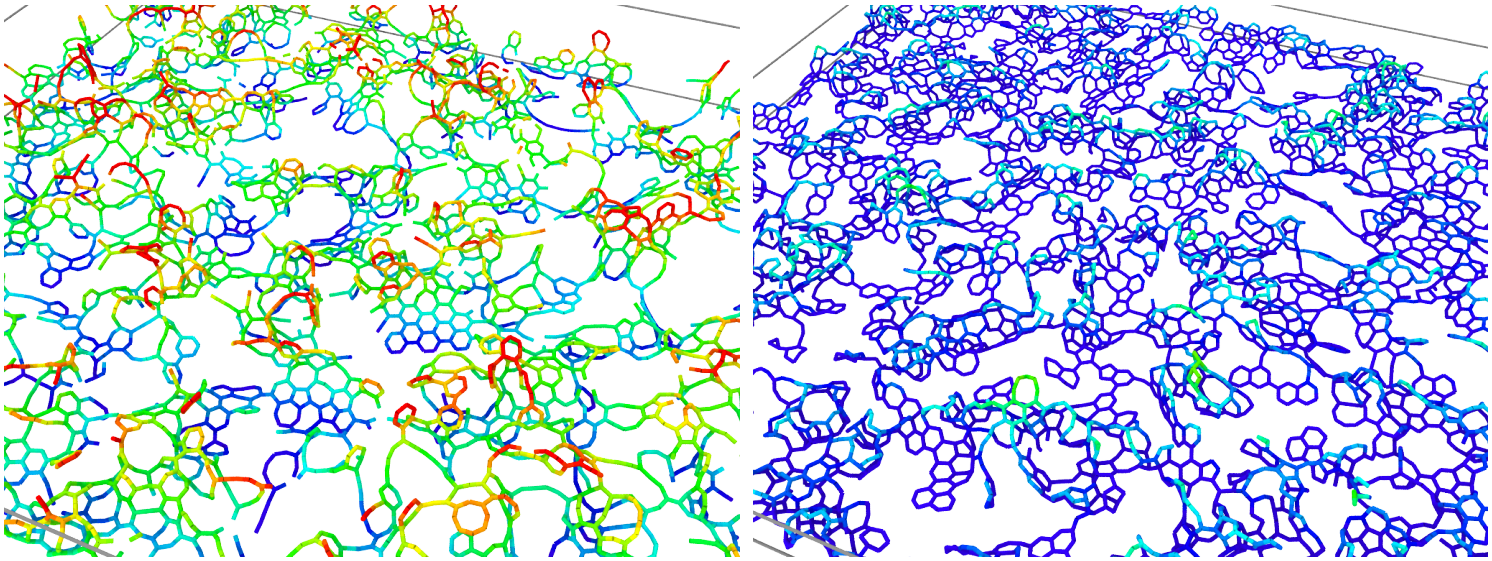


Abbildung 21: $k = 60\ \frac{\mathrm{eV}}{\mathrm{Å}}$, $T = 300$ K, $v = 35\ \frac{\mathrm{Å}}{\mathrm{ps}}$; BPT, $N = 4900$ (links) und NPTH, $N = 2500$ (rechts)

F. Gayk, Master Thesis, Bielefeld University (2018)

J. Ehrens *et al.*, arXiv:2011.00880

Examples of CMNs

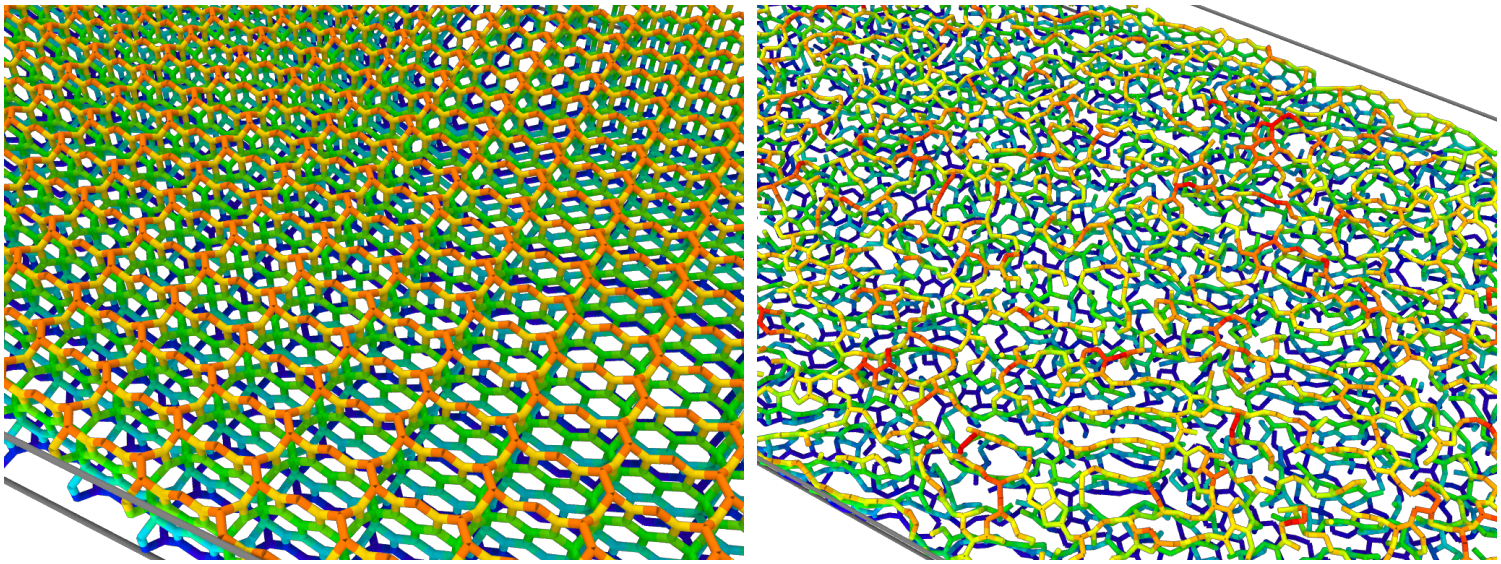
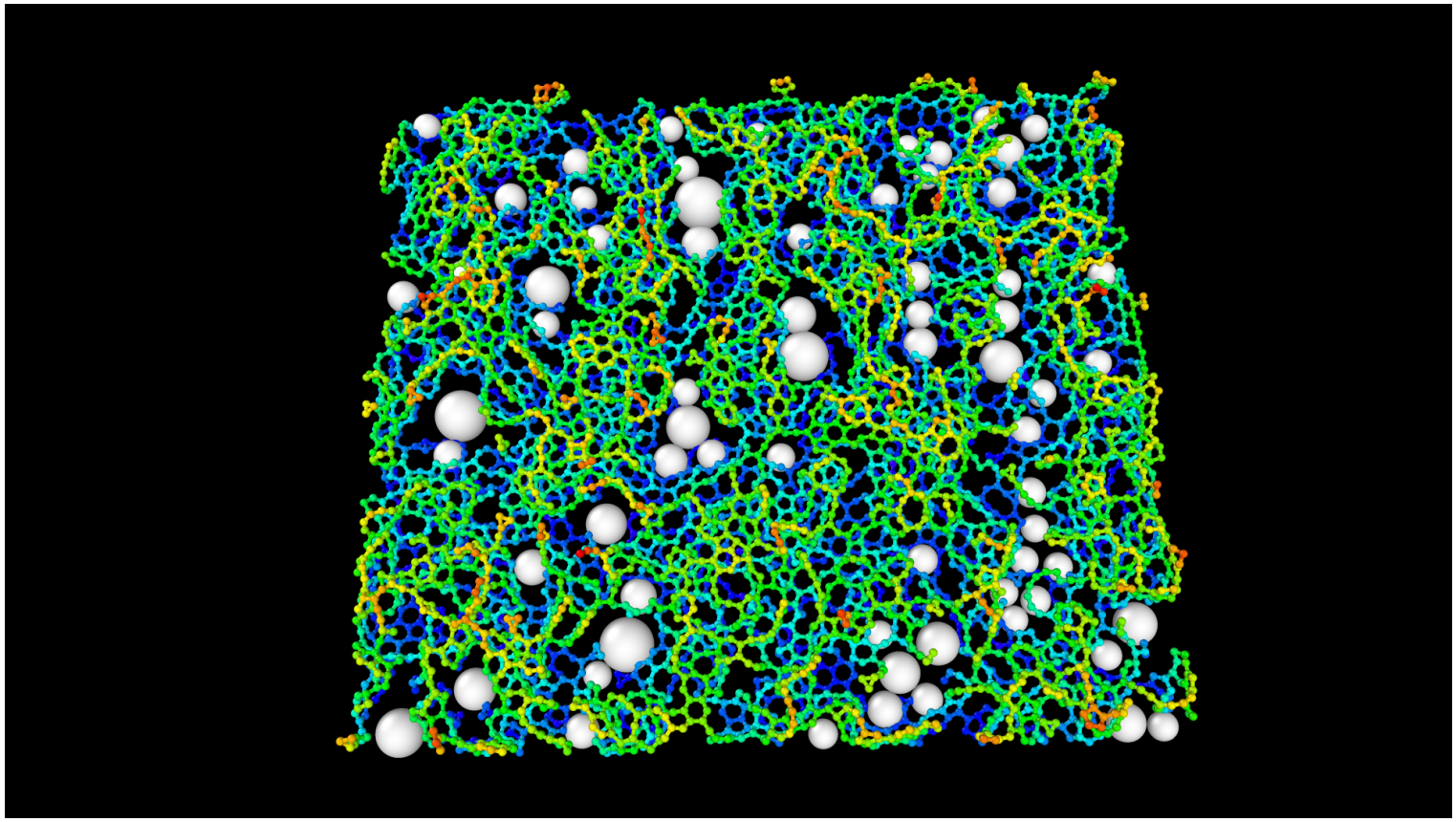


Abbildung 26: DFT Struktur (links); $k = 60\ \frac{\mathrm{eV}}{\mathrm{\AA}}$, $T = 300$ K auf DFT Struktur (rechts)

Randomized and cooled DFT structure (1).

(1) P. Cabrera-Sanfelix, A. Arnau, and D. Sanchez-Portal, Phys. Chem. Chem. Phys. **12**, 1578 (2010).
(2) F. Gayk, Master Thesis, Bielefeld University (2018)

Examples of CMNs



CNM have got holes (pores)! In simulations this depends on initial conditions: more violence $\Rightarrow$ more holes.

Young's modulus of CMNs

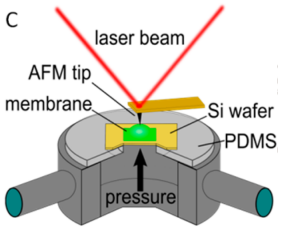


Abbildung 13: Aufbau des Beulentests [44]

Tabelle 7.2: E-Module (bezüglich: Boxvolumen|Oberflächennetzvolumen)

	E_x / GPa	E_y / GPa
TPT (T=700 K, $k = 30\ \frac{\text{eV}}{\text{Å}}$)	436| 847	334| 649
TPT (T=700 K, $k = 200\ \frac{\text{eV}}{\text{Å}}$)	215| 448	220| 457
TPT (T=300 K, $k = 60\ \frac{\text{eV}}{\text{Å}}$)	325| 987	316| 960
TPT (T=1100 K, $k = 60\ \frac{\text{eV}}{\text{Å}}$)	351| 866	339| 838
BPT (T=700 K, $k = 60\ \frac{\text{eV}}{\text{Å}}$)	202| 736	191| 695
NPTH (T=700 K, $k = 60\ \frac{\text{eV}}{\text{Å}}$)	536|1367	500|1277

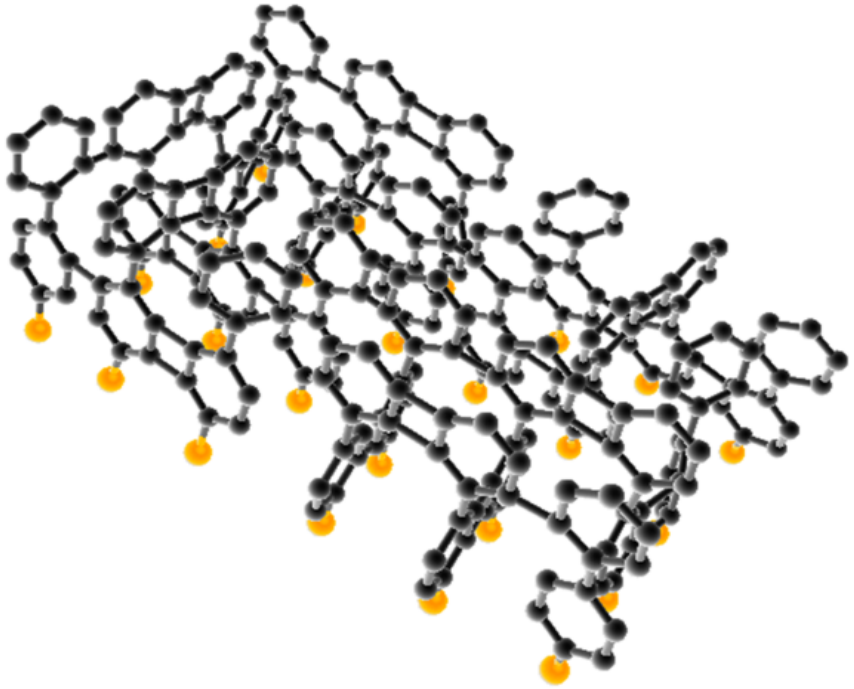
precursor molecules	thickness of SAM [Å]	structure of SAM	area per molecule [Å^2]	carbon density [nm^{-3}]	Young's modulus [GPa]
BPT	10	2×2	28.7	42	9.9
TPT	12	$\sqrt{3} \times \sqrt{3}$	21.6	64	9.0
NPTH	6	$\sqrt{3} \times \sqrt{3}$	21.6	77	18.6

Abbildung 14: E-Module aus Beulentest [44]

Theoretical Young's moduli closer to graphene;
factor 10 . . . 50 bigger than experiment.

F. Gayk, Master Thesis, Bielefeld University (2018)
X. Zhang, C. Neumann, P. Angelova, A. Beyer, and A. Gölzhäuser, Langmuir **30**, 8221 (2014).

Alternative structure



Possible configuration of a Biphenyl layer, ARGUS Lab (1).

Not realistic, since construction principle works only for BPT.
NEXAFS shows about 60 % aromaticity, i.e. 40 % of phenyl rings are broken.

(1) D. Rhinow, N.-E. Weber, A. Turchanin, J. Phys. Chem. C **116**, 12295 (2012).

CNMs from spaghetti?

Octadecanethiol

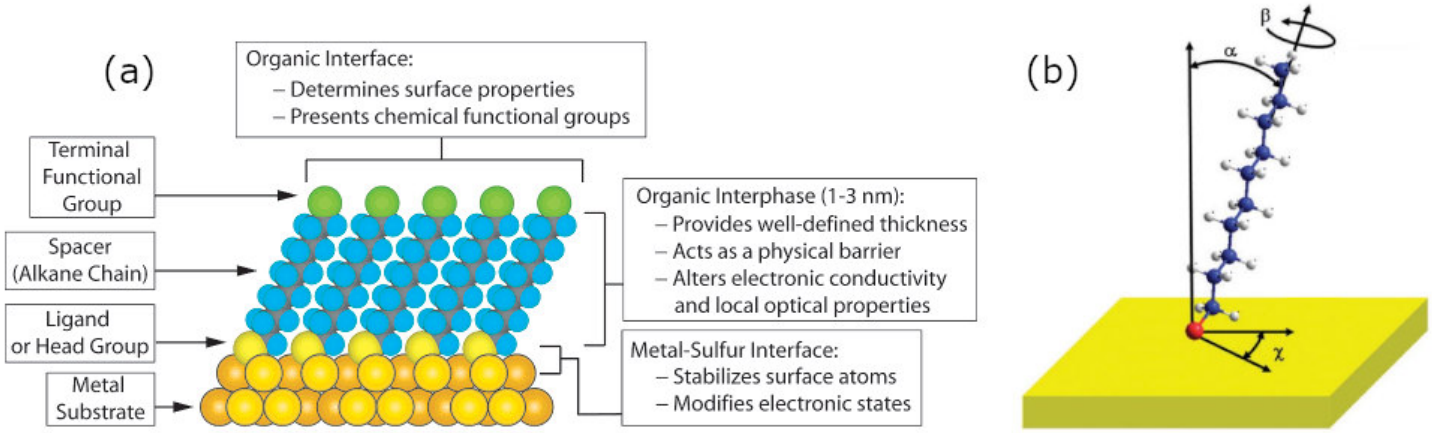
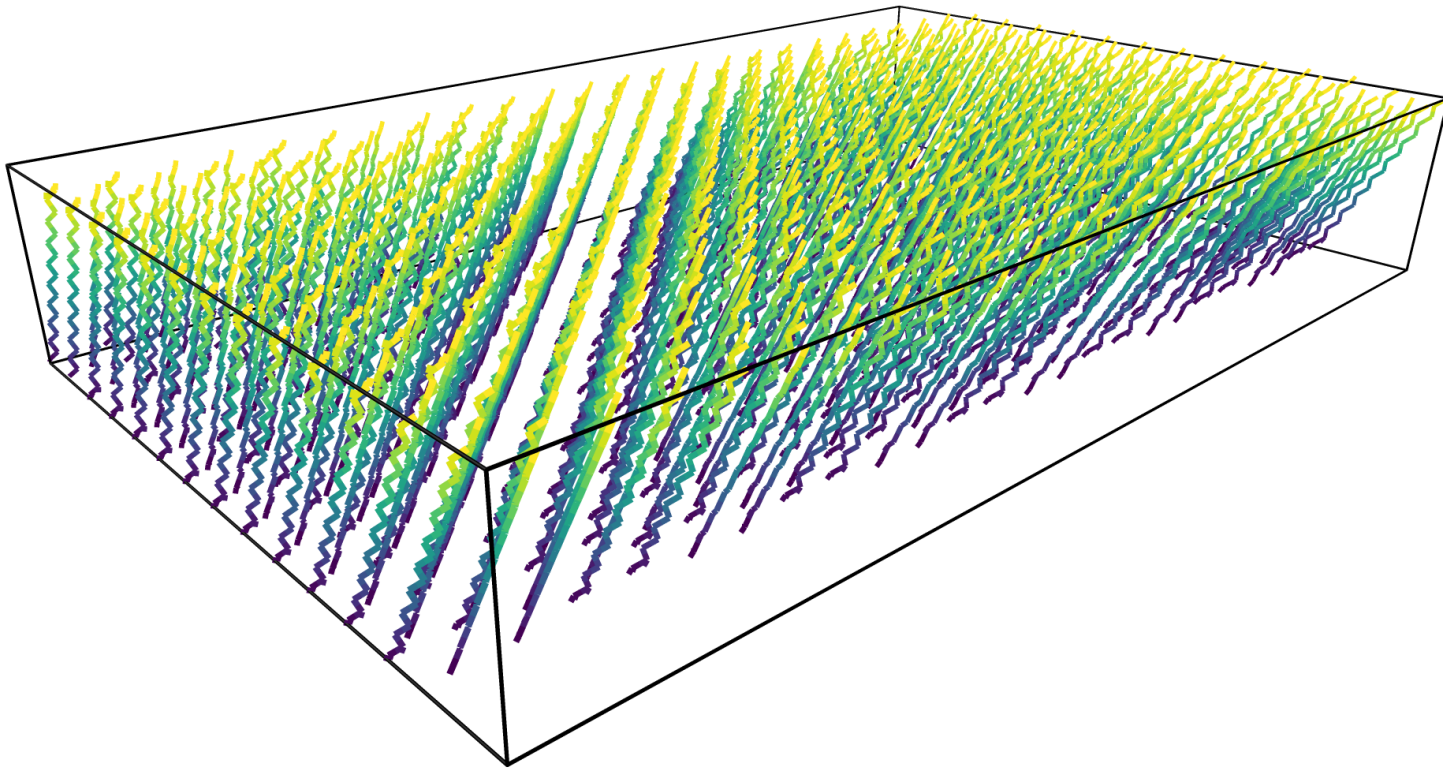


Figure 2.1: (a) Schematic diagram depicting a self-assembled monolayer (SAM) of alkanethiolates on a metal substrate. (b) Scheme of a decanethiol molecule adsorbed on a solid surface. The orientation of the molecule with respect to the substrate surface is defined by the tilt angle α, the twist angle β, and the precession angle χ. *Part a is reprinted with permission from ref 16. Copyright (2005) American Chemical Society. Part b is reprinted with permission from ref [20]. Copyright (2010) Royal Society of Chemistry (Great Britain).*

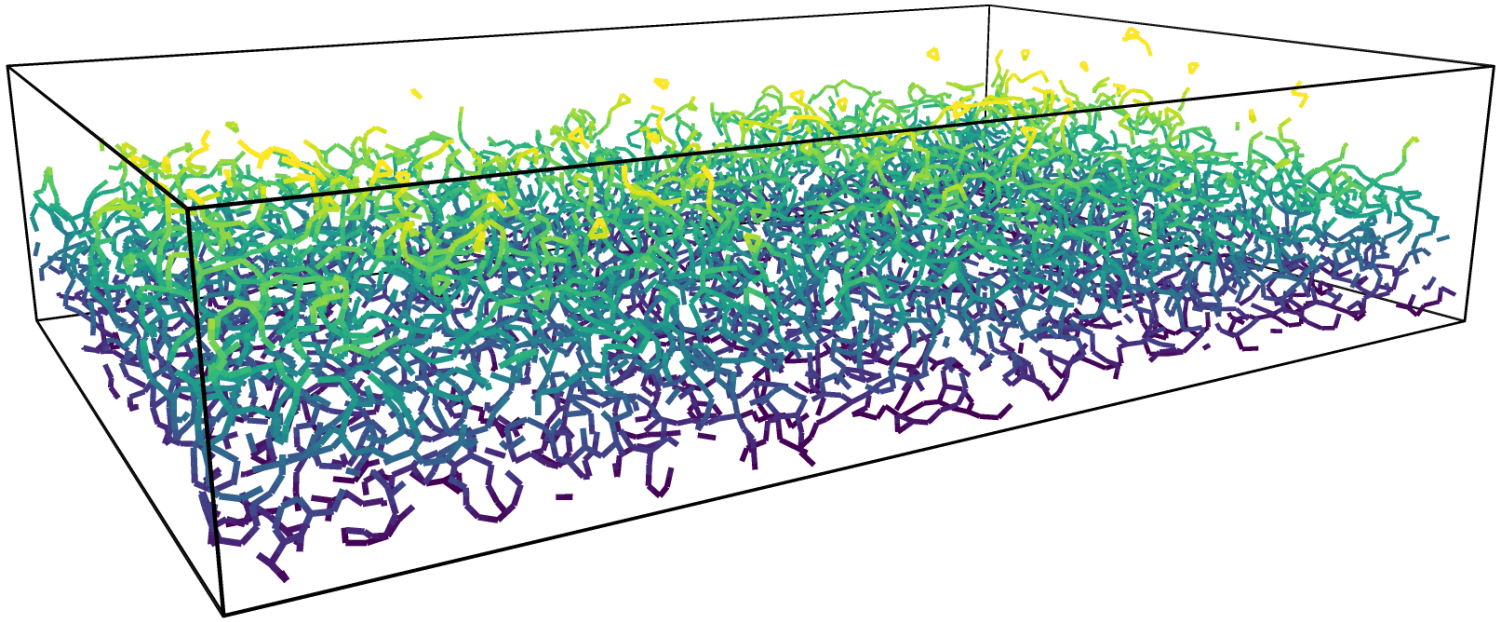
Patrick Stohmann, Dissertation, Bielefeld, 2020.

Octadecanethiol (ODT, C18) – initial SAM



J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides, Chem. Rev. **105**, 1103 (2005).

Octa-decane-thiol (ODT, C18) – first simulations



Structure is mechanically stable

Phenyls do not form

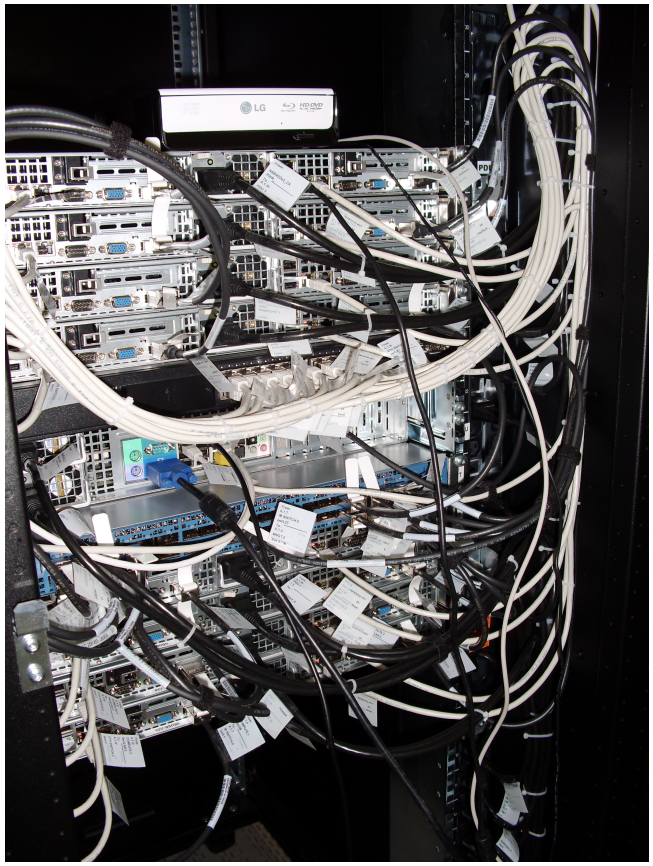
Theoretical Young's modulus much smaller than for BPT, TPT or NPT

J. Ehrens, private communication

Open questions

- Structure correct? Discrepancy w.r.t. Young's modulus!
- Compare to ion deflection studies (Richard Arthur Wilhelm (Wien))!
- How thick is a CNM?
- Precursor-CNM correlations? Which, if any?
- No thiols in decane-based CNMs?
- Systematic investigation of holes needed.
- Future: water permeation.

Summary



- Classical Molecular Dynamics can be set up for carbon systems using effective many-body carbon potentials.
- Ground-state geometries can be determined with great accuracy (exception graphite).
- Dynamical self-assembly can be simulated.
- Prospect to simulate nano sheets with realistic, i.e. probably irregular structure.
- Electronic properties CANNOT be modeled.

Thank you very much for your attention.