Theoretical formation of carbon nanomembranes under realistic conditions using classical molecular dynamics

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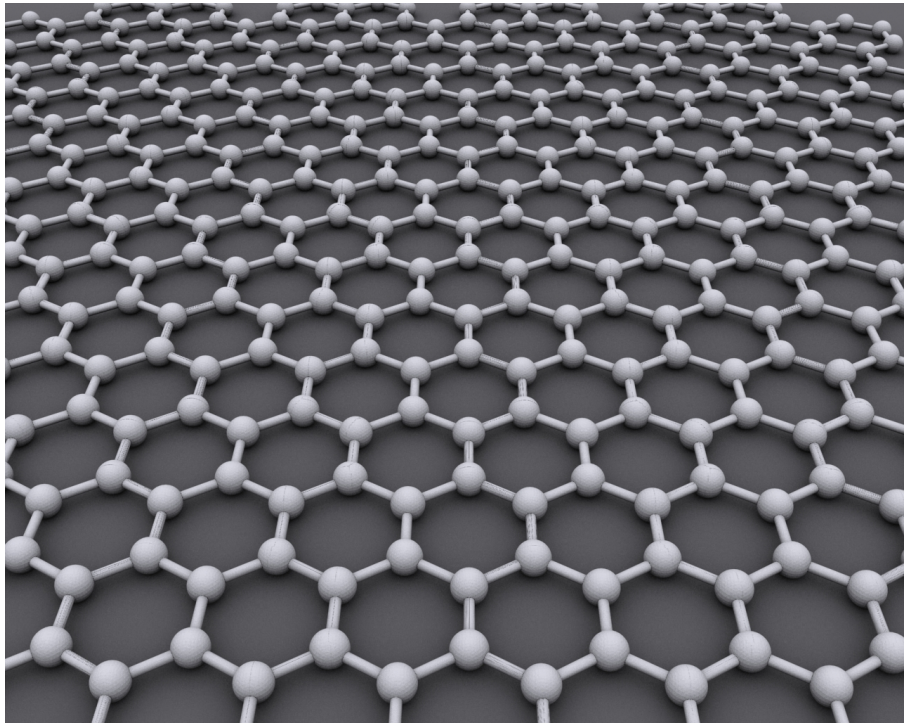
Disclaimer

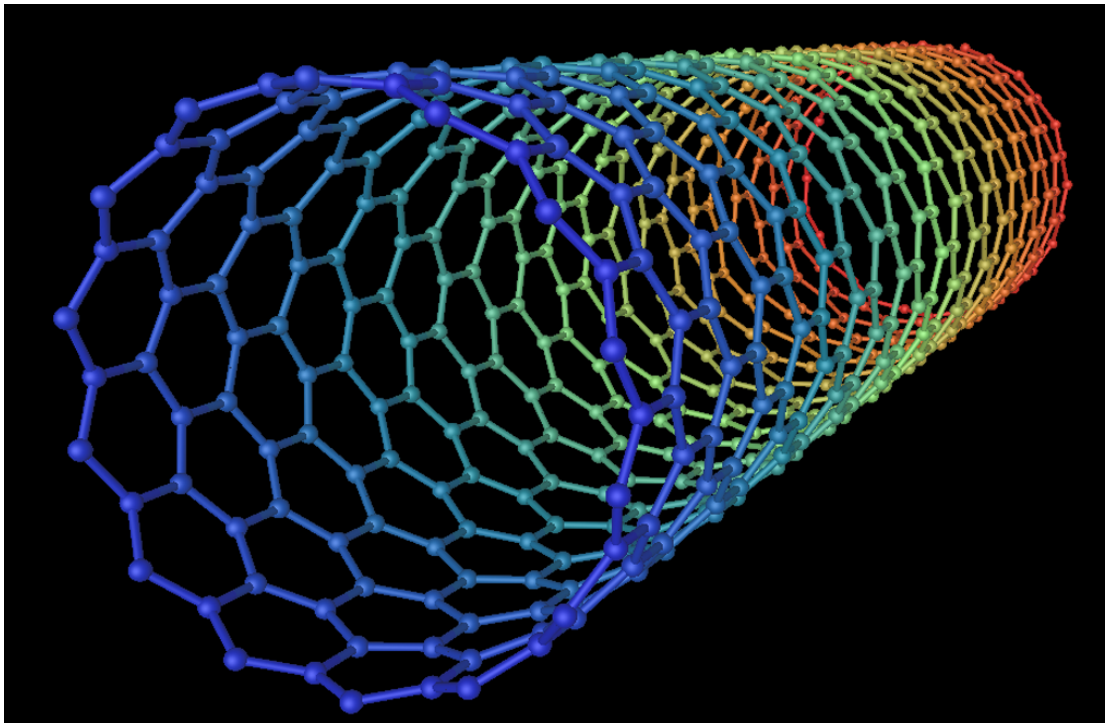
This talk may contain parts of an earlier talk “What we do **not** understand about carbon nanomembranes”.

⇒ Wien IX, Berggasse 19

Introduction

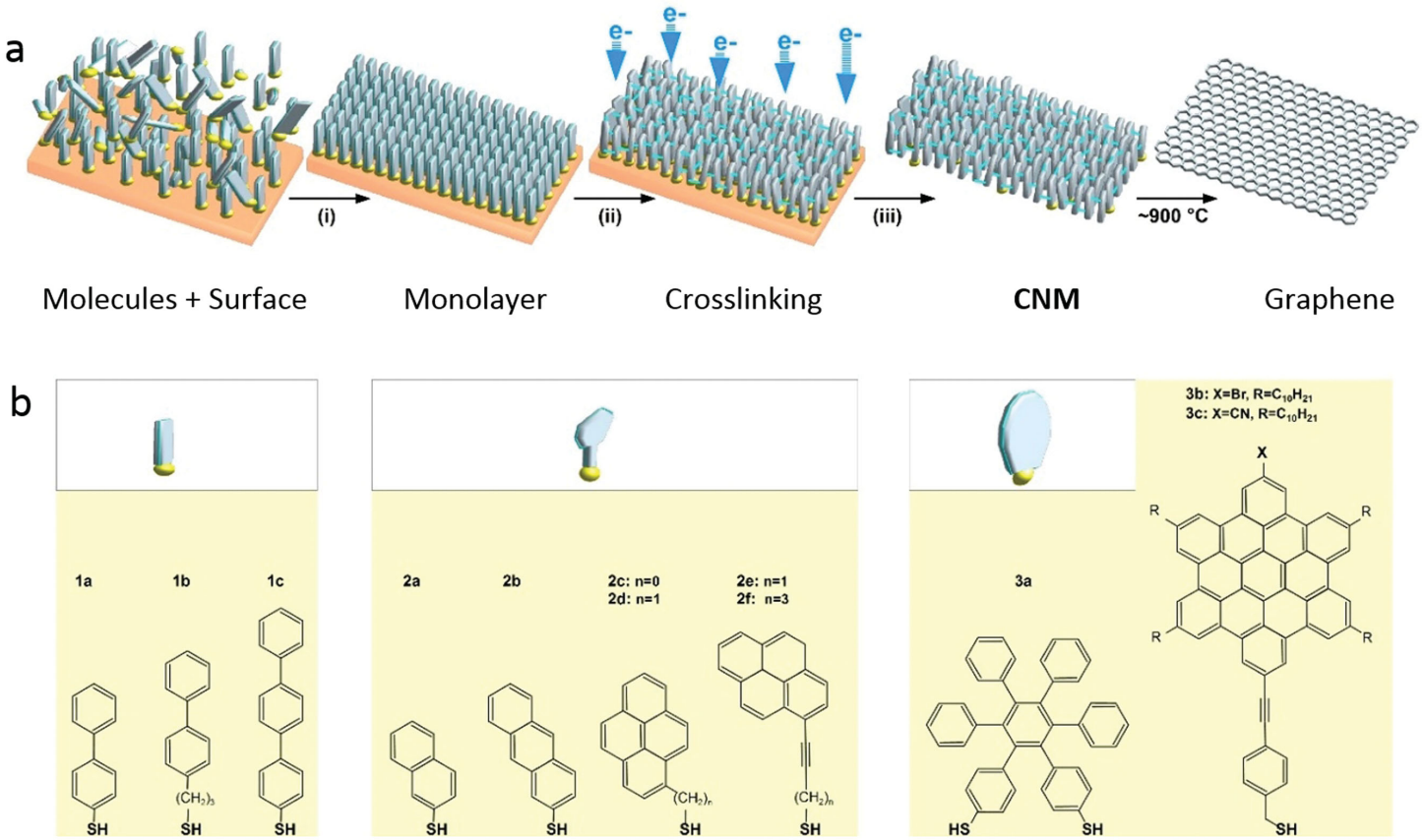
There are various well-known carbon-based nanostructures . . .





Regular, crystalline, sp^2 carbon.

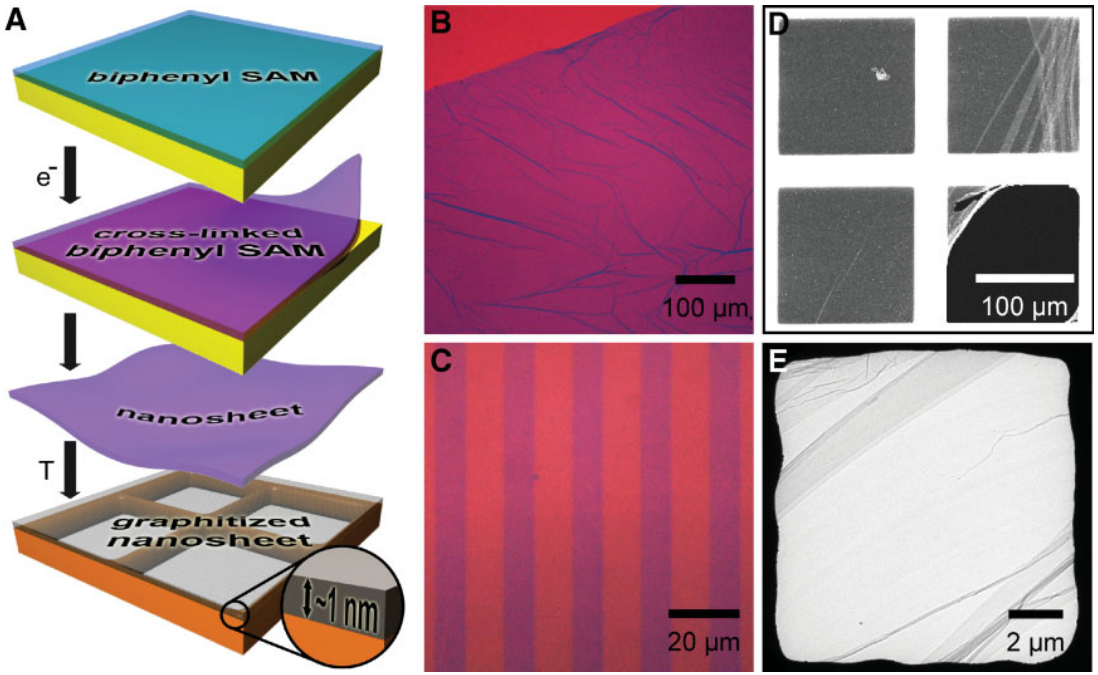
. . . and carbon-based cross-linked SAMs = CNM (I)

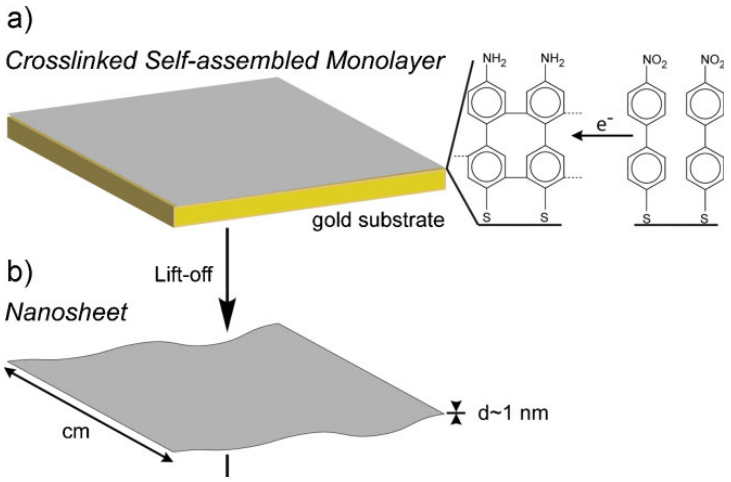


A. Turchanin, A. Gölzhäuser, Advanced Materials **28**, 6075-6103 (2016).

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

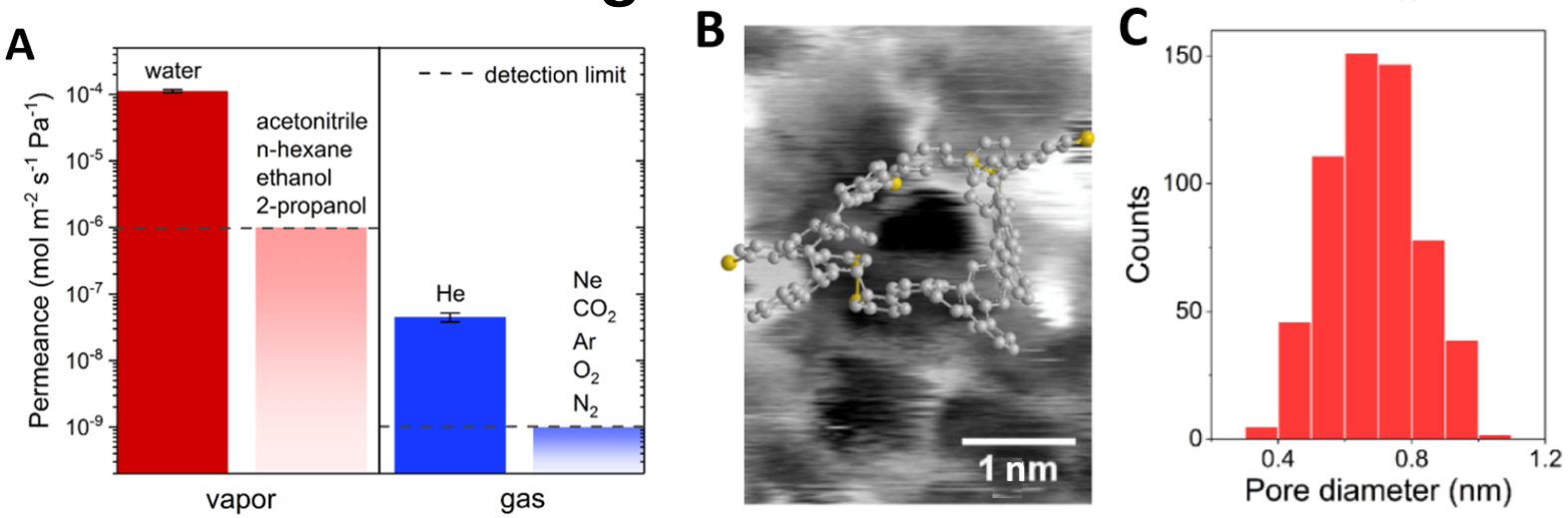
ADVANCED MATERIALS





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

. . . with amazing water filtration properties



- (A) Whereas water translocates through CNMs with extraordinary performance, other small molecules or gases are practically blocked.
- (B) Topographical closeup to a nanopore with an artistic overlay drawing of the pore by laterally crosslinking seven TPT molecules.
- (C) Statistical analysis of the nanopore diameter distributions (0.7 nm with 0.1 nm standard deviation) extracted from the acquired AFM images.

Y. Yang *et al.*, ACS Nano **12**, 4695 (2018).

Problems for theory

Problems for theory

- Systems contain very many carbon atoms.
- Structure very likely irregular. Holes! Huge holes!
- CNMs very soft: Young's module ca. 10 GPa, graphene 1000 GPa.
- Quantum methods, even DFT, cannot deal with such systems.
- Goal: realistic modelling of CNM formation with correct proeprties.
- Can we model water translocation?

Contents for you today

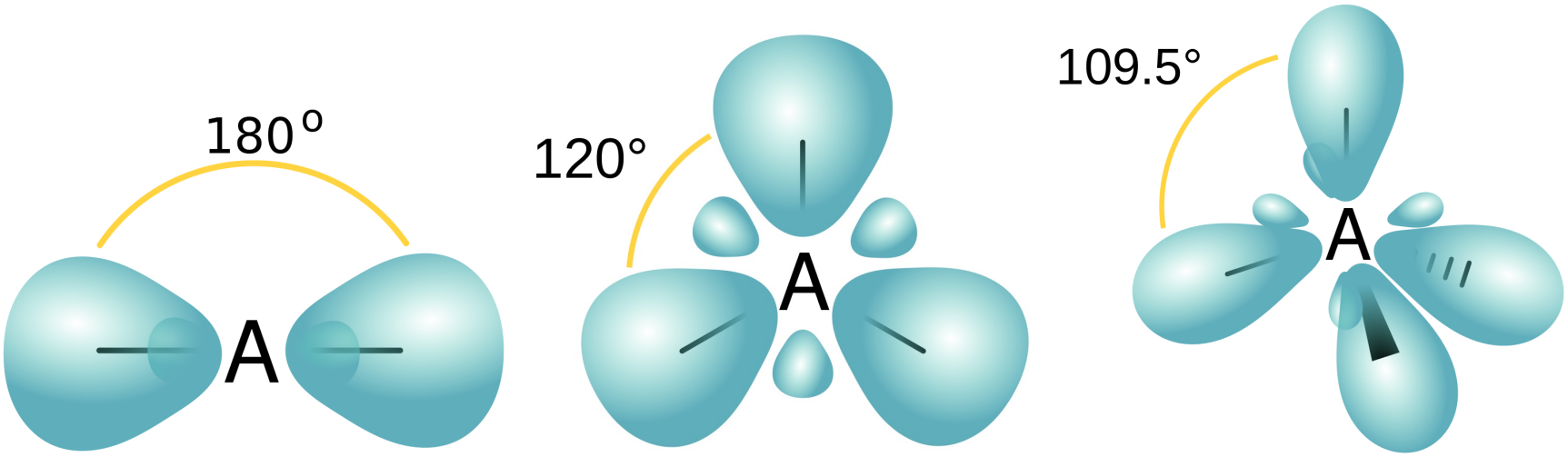
1. Carbon nanomembranes $\surd$
2. Classical molecular dynamics
3. Mechanical properties
4. Structure of CNMs
5. Open problems

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.
- 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 classical carbon potential

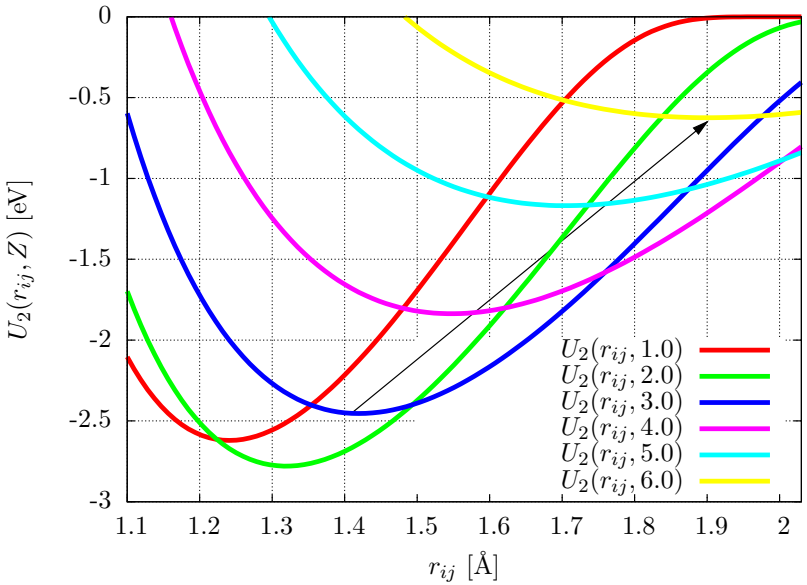
$$H(\vec{r}_1, \vec{p}_1; \vec{r}_2, \vec{p}_2; \dots) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_1, \vec{r}_2, \dots)$$

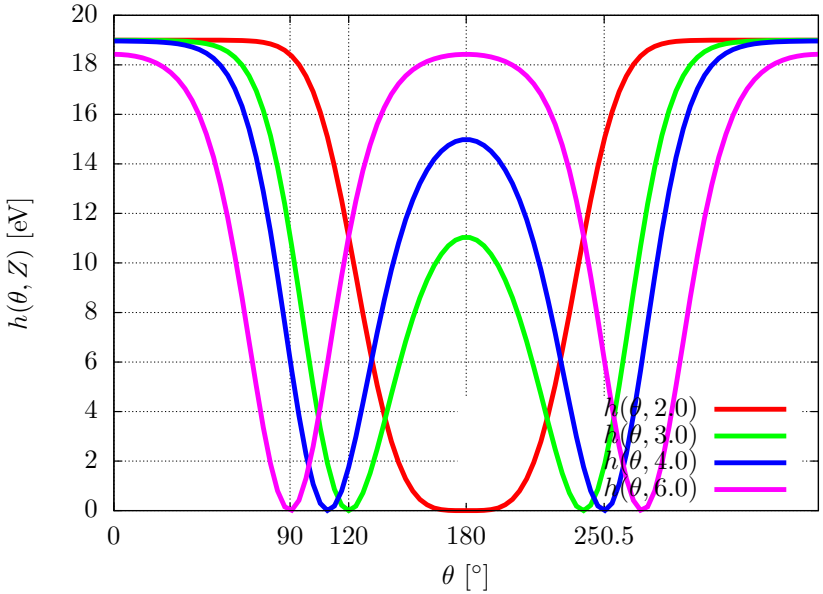
$$V(\vec{r}_1, \vec{r}_2, \dots) = \sum_{i \neq j}^{N} U_2(|\vec{r}_i - \vec{r}_j|, Z_i) + \sum_{i \neq (j<k)}^{N} U_3(|\vec{r}_i - \vec{r}_j|, |\vec{r}_i - \vec{r}_k|, \Theta_{ijk}, Z_i)$$

Θ_{ijk} – dehedral angles, Z_i continous coordination number.

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

Dependence on coordination number Z_i





Coordination influences strength and direction of bonding.
Mocks sp^n binding modes.

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 or XPS spectra.

(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!

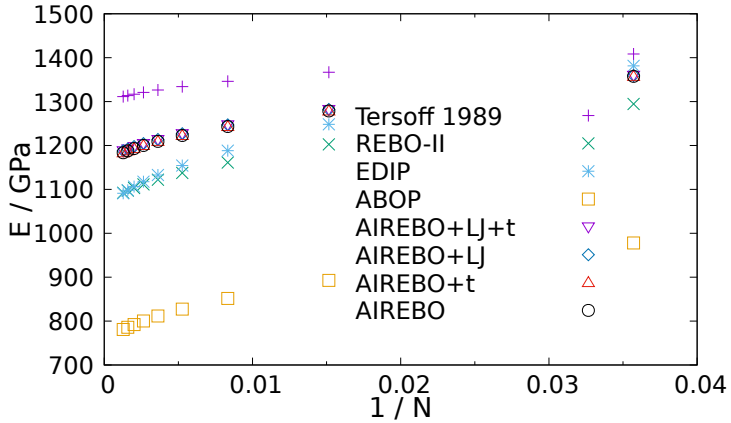
Ground state distances for graphene, CNT, and diamond

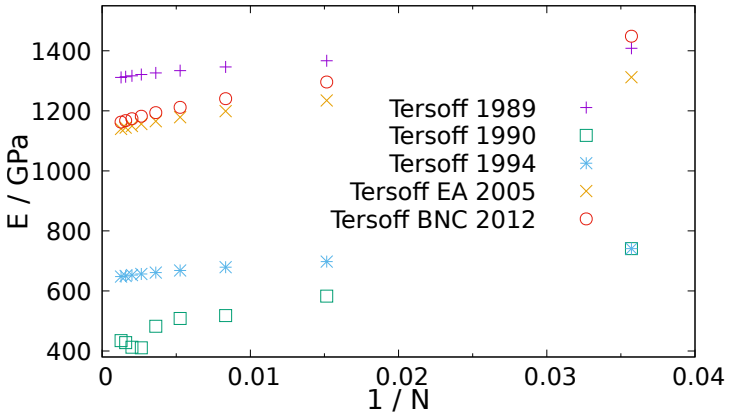
Table 1: Ground-state dimensions in Å of graphene, CNT, and diamond for the investigated potentials (LAMMPS).
(* No proper ground state structure found; † anisotropic.)

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

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

Young's modulus for graphene



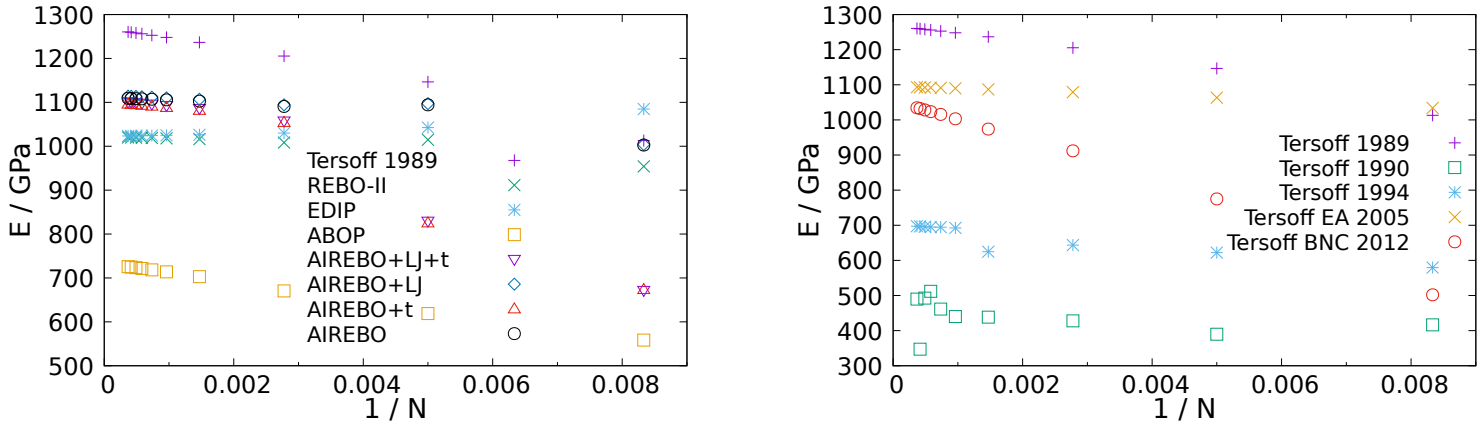


Young's modulus of graphene for various sizes and potentials. N denotes the number of atoms in the approximately square graphene sheets. Open boundary conditions are applied.

Experimental value: 1000 GPa.

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

Young's modulus for CNT

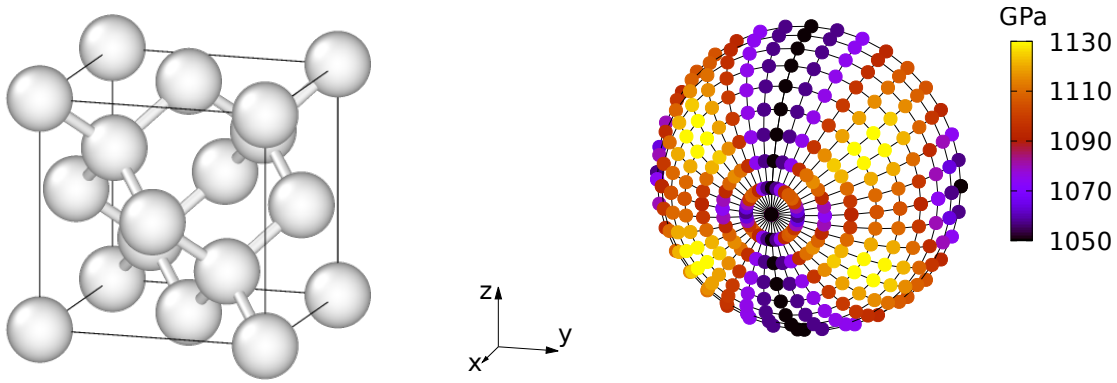


Young's modulus of a (20,20) CNT with armchair geometry along the tube, taken as x-direction, for various sizes and potentials. N denotes the number of atoms of the tube. Open boundary conditions are applied.

Experimental value: 1000 GPa.

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

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

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

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).

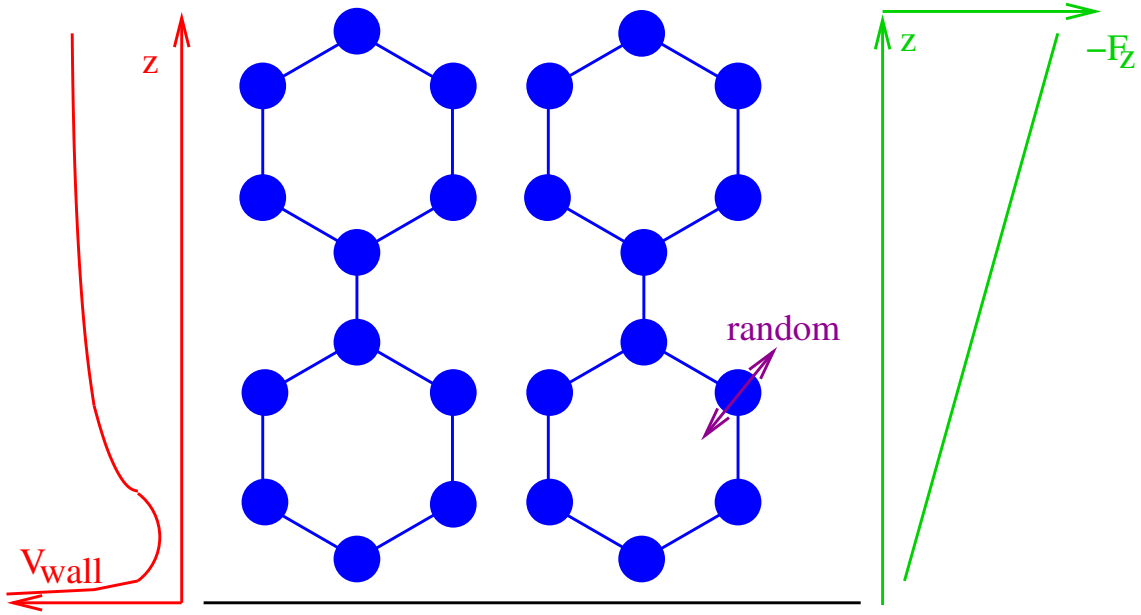
How to find the

Structure of CNMs?

Questions

- **The** structure or **a** structure?
- Structure very likely a metastable state, a local energy minimum. Many equivalent structures possible.
- How to model? Initial conditions, cooling, role of initial correlations, . . . ?
- Which structures are correct? Observables?
- X-ray structure determination impossible!
- Two approaches so far: Bielefeld and Australia.

Bielefeld approach: Initialization with initial molecular correlations



Model: includes only carbon atoms (+ surface potential);

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

Cooling: Nose-Hoover or alike;

LAMMPS: EDIP and analytical forces included in our local version.

Examples of CMNs 1

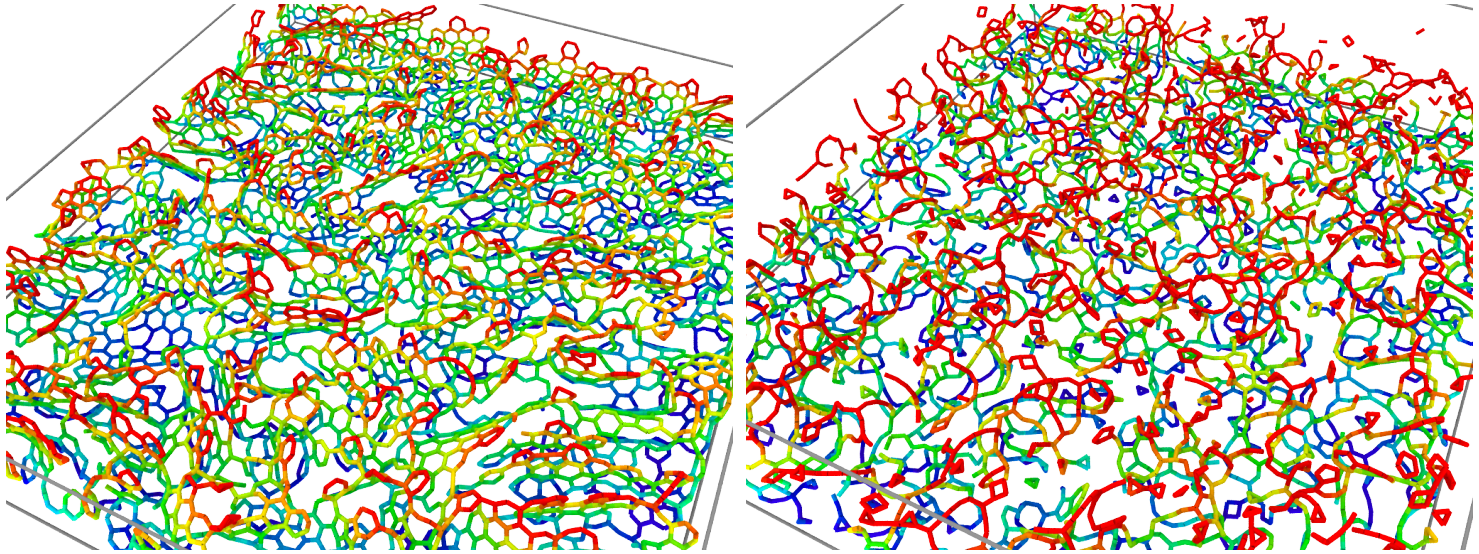


Abbildung 17: TPT, $T = 700$ K; $k = 30$ $\frac{\text{eV}}{\text{Å}}$ (links) und $k = 200$ $\frac{\text{eV}}{\text{Å}}$ (rechts)

J. Ehrens, F. Gayk, P. Vorndamme, T. Heitmann, N. Biere, D. Anselmetti, Xianghui Zhang, A. Gölzhäuser, J. Schnack, Phys. Rev. B **103** (2021) 115416

Examples of CMNs 2

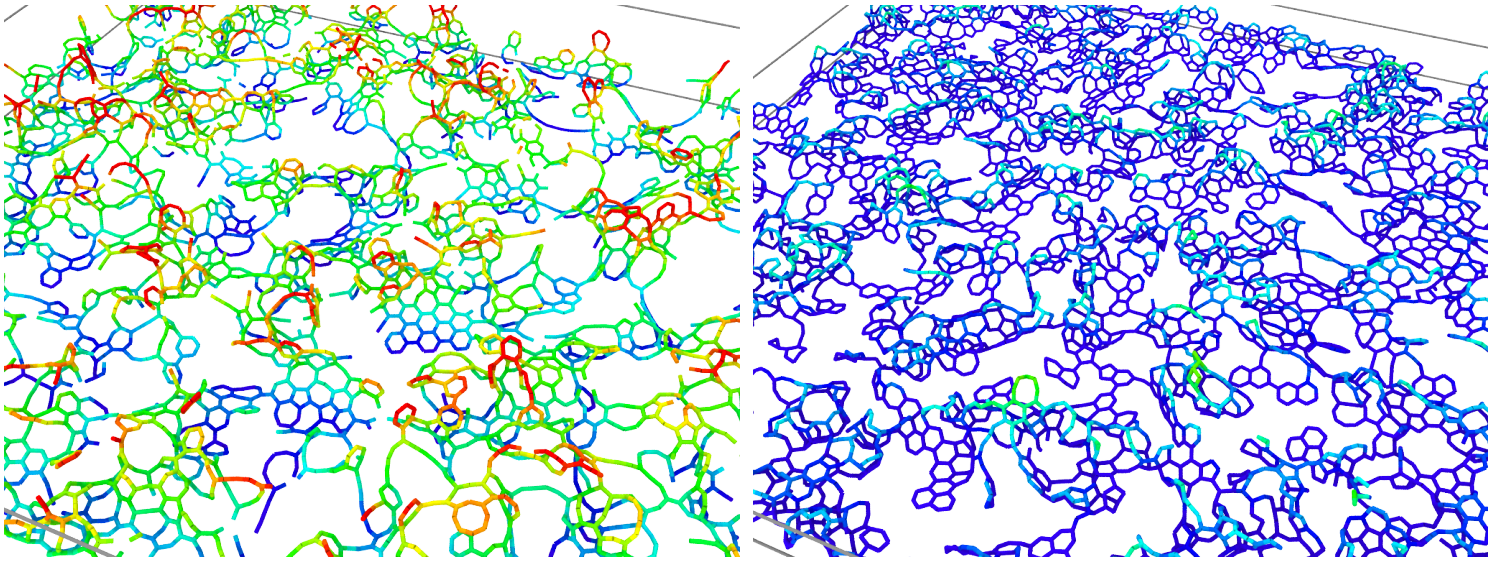


Abbildung 21: $k = 60\ \frac{\mathrm{eV}}{\mathrm{Å}}$, $T = 300$ K, $v = 35\ \frac{\mathrm{Å}}{\mathrm{ps}}$; BPT, $N = 4900$ (links) und NPTH, $N = 2500$ (rechts)

J. Ehrens, F. Gayk, P. Vorndamme, T. Heitmann, N. Biere, D. Anselmetti, Xianghui Zhang, A. Gölzhäuser, J. Schnack, Phys. Rev. B **103** (2021) 115416

Examples of CMNs 3

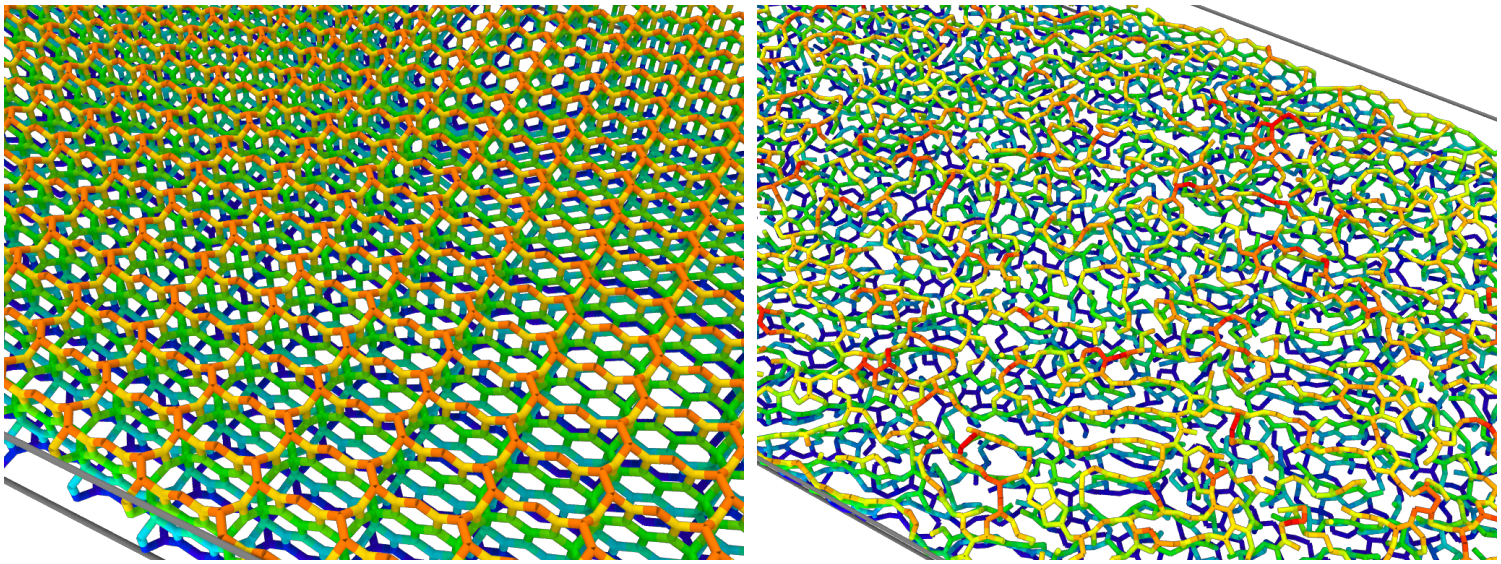
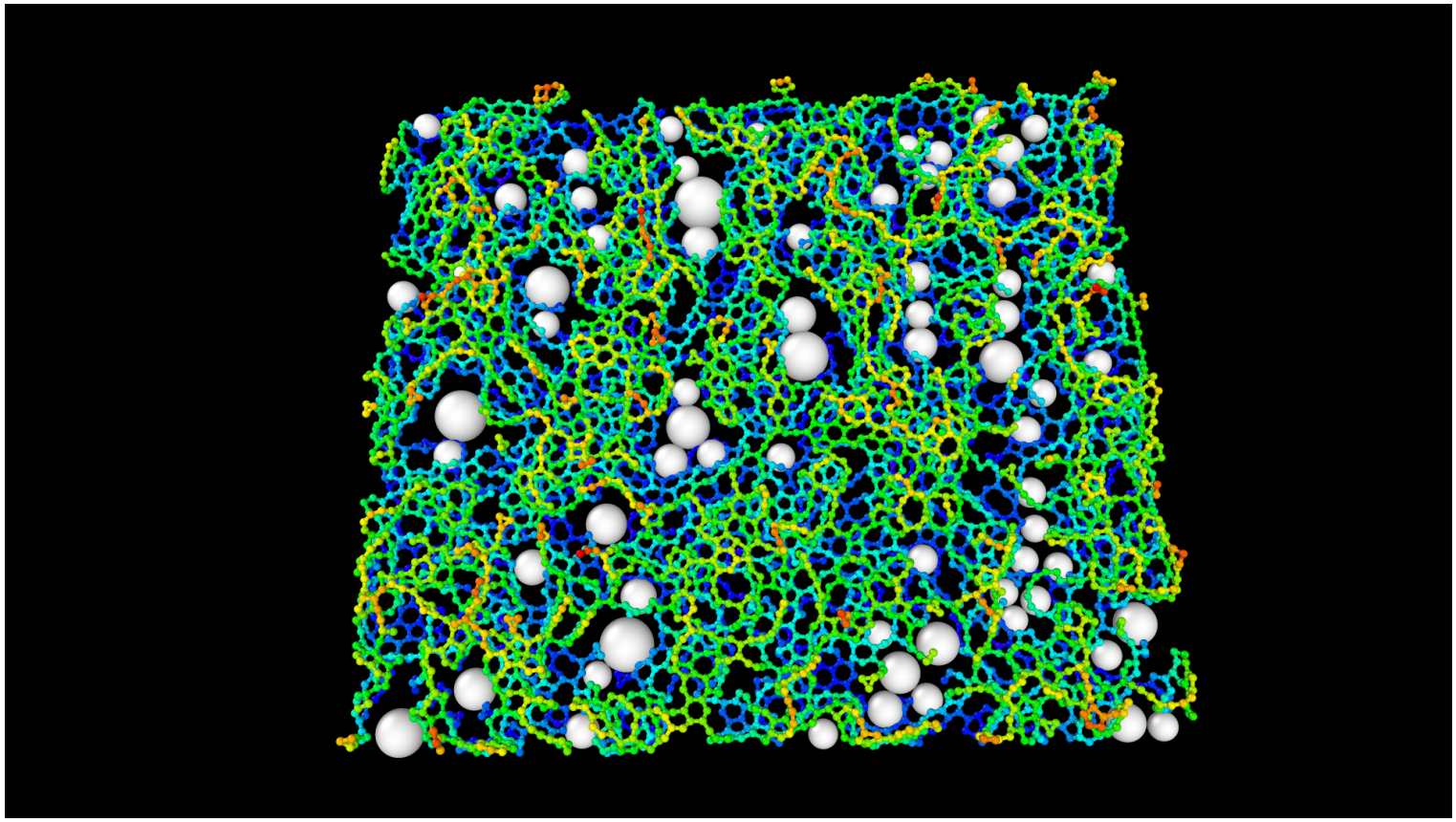


Abbildung 26: DFT Struktur (links); $k = 60\ \frac{\mathrm{eV}}{\mathrm{\AA}}$, $T = 300$ K auf DFT Struktur (rechts)

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

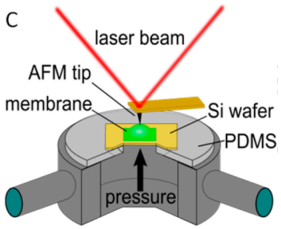


Abbildung 13: Aufbau des Beulentests [44]

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

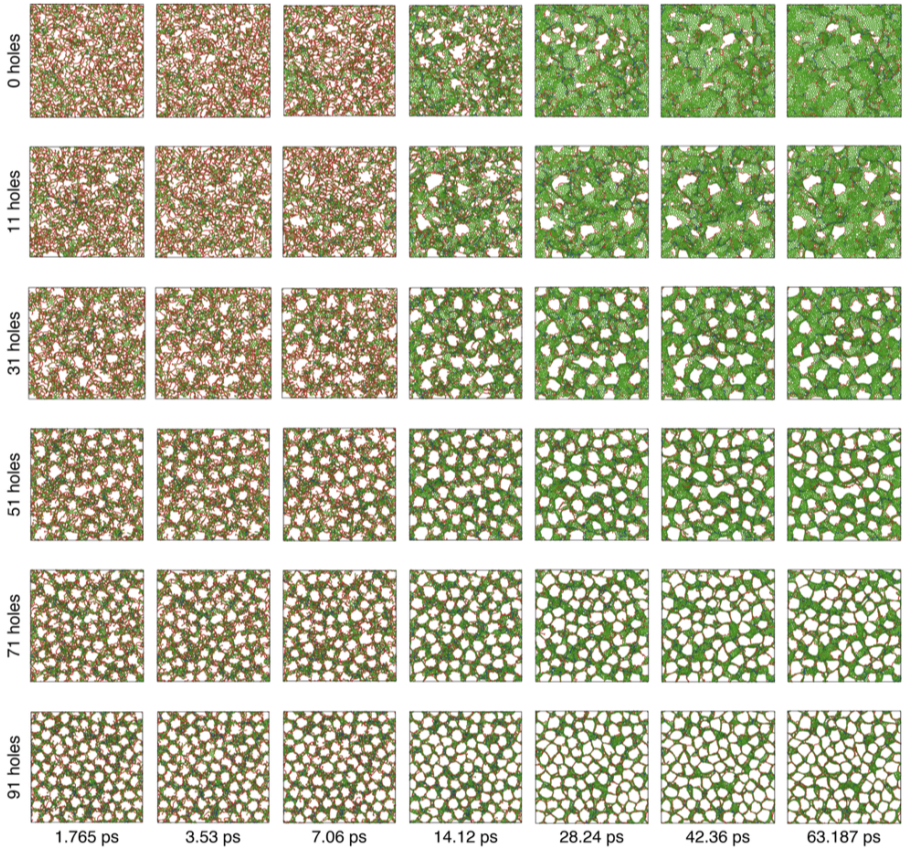
precursor molecules	thickness of SAM [Å]	structure of SAM	area per molecule [Å^2]	carbon density [nm^{-3}]	Young's modulus [GPa]
BPT	10	2×2	28.7	42	9.9
TPT	12	$\sqrt{3} \times \sqrt{3}$	21.6	64	9.0
NPTH	6	$\sqrt{3} \times \sqrt{3}$	21.6	77	18.6

Abbildung 14: E-Module aus Beulentest [44]

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

J. Ehrens, F. Gayk, P. Vorndamme, T. Heitmann, N. Biere, D. Anselmetti, Xianghui Zhang, A. Gölzhäuser, J. Schnack, Phys. Rev. B **103** (2021) 115416
X. Zhang, C. Neumann, P. Angelova, A. Beyer, and A. Gölzhäuser, Langmuir **30**, 8221 (2014).

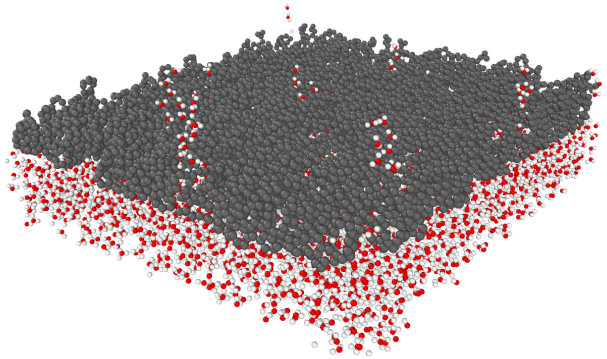
Australian approach: random carbon gas with excluded volume

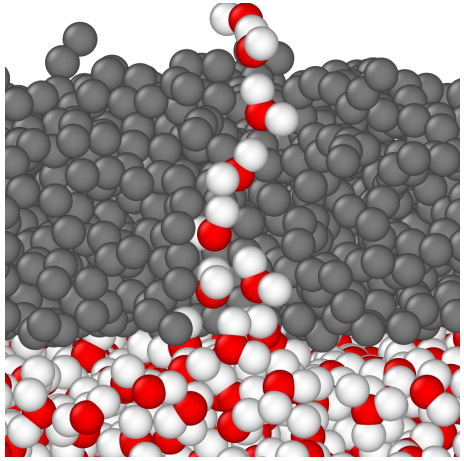


- Initial excluded volumes at random future hole positions; number of carbons preserved.
- No initial molecular correlations.
- Cooling and dynamical self-organization.
- Realistic Young's moduli! Holes.

(1) F. Vukovic, N. Marks, private communication.

Outlook: Water permeation

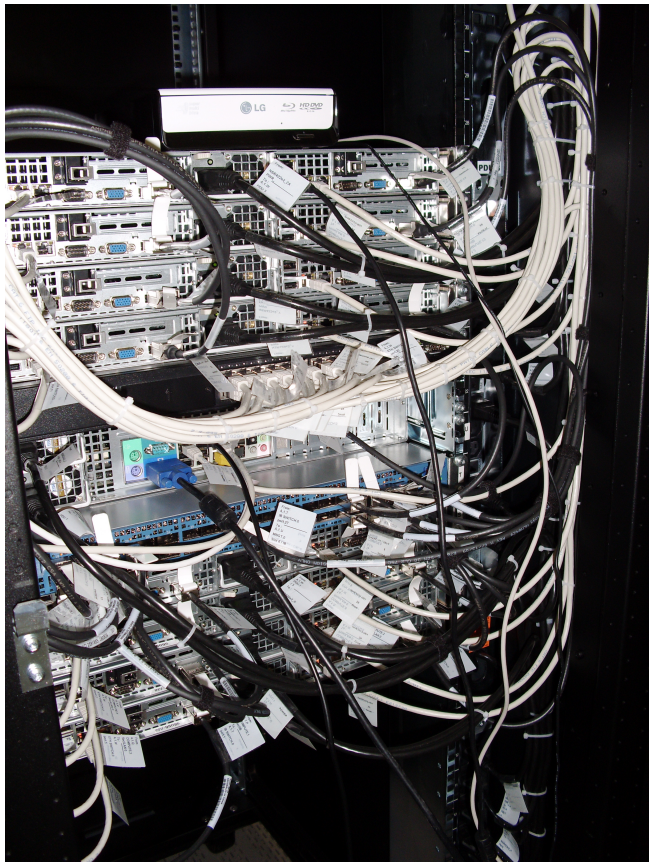




- Frozen CNM, TIP3P water.
- Single file motion? Preorganization?
- Problem: Time scales!
- Large pressure necessary.

J. Ehrens, Ph.D. Thesis, Bielefeld University (2022).

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).
- CNMs with reasonable characteristics can be achieved when a holes are introduced *a priori.*
- Can we understand and model the formation of holes?
- Just to remember: electronic properties cannot be modeled.

Many thanks to

Professor Nigel Marks, Curtin University, Australia

Thank you very much for your attention.