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

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UNIVERSITÄT BIELEFELD
Fakultät für Physik

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Irz

Disclaimer

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

Solution in 2022:

Wien IX, Berggasse 19

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Solution in 2022:

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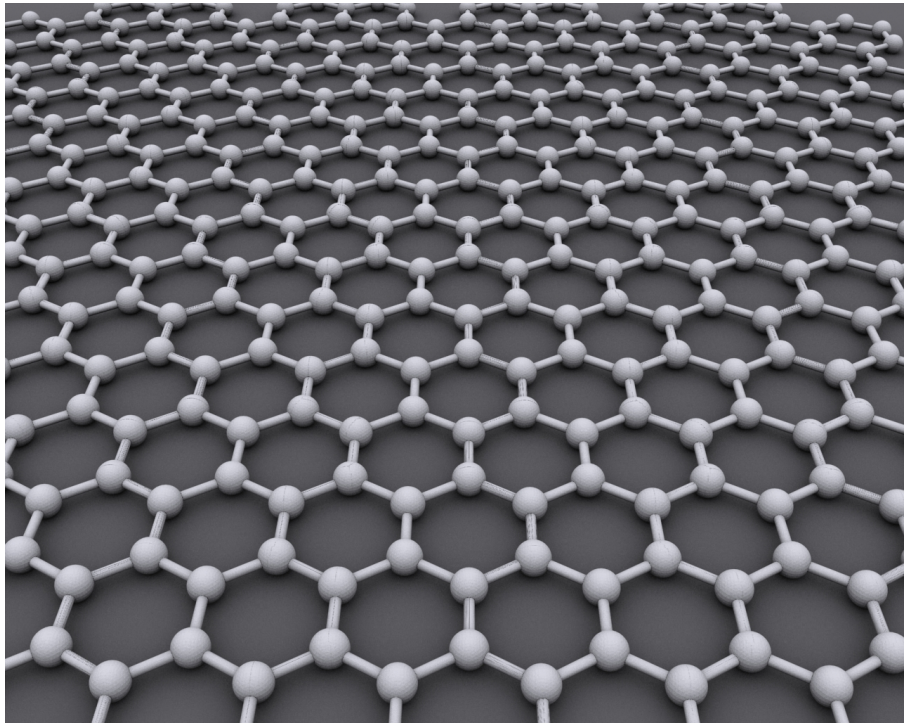
Solution in 2024 (Christmas!):

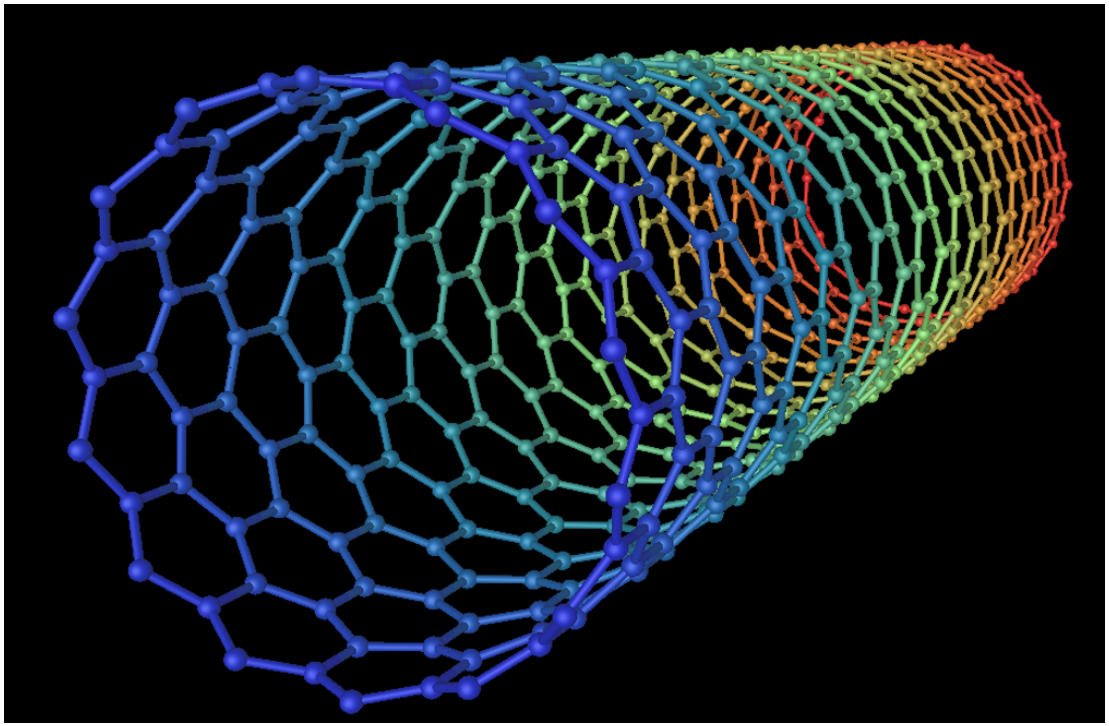
DFG

Chexdyn

Introduction

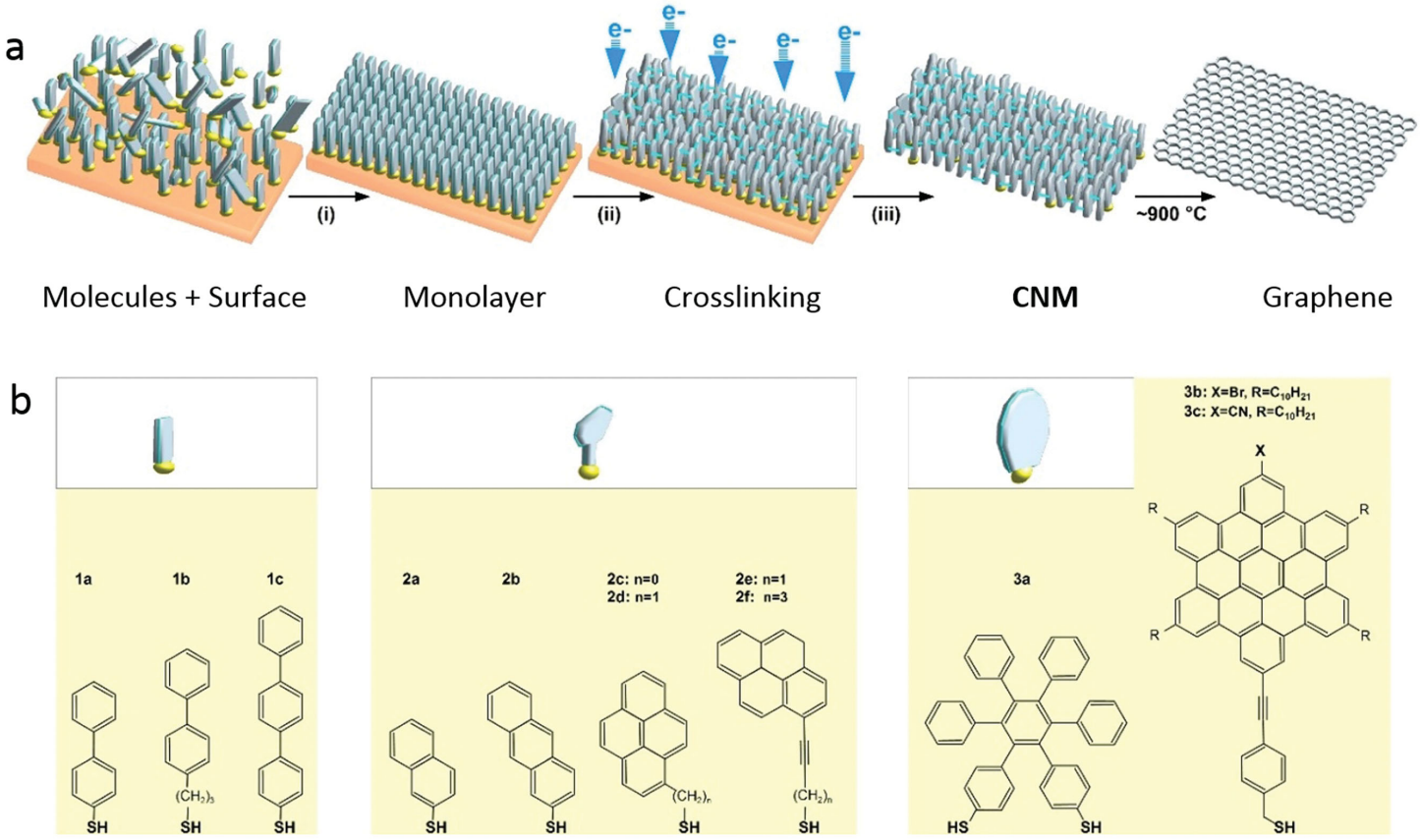
There are various well-known carbon-based nanostructures . . .





Regular, crystalline, sp^2 carbon.

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

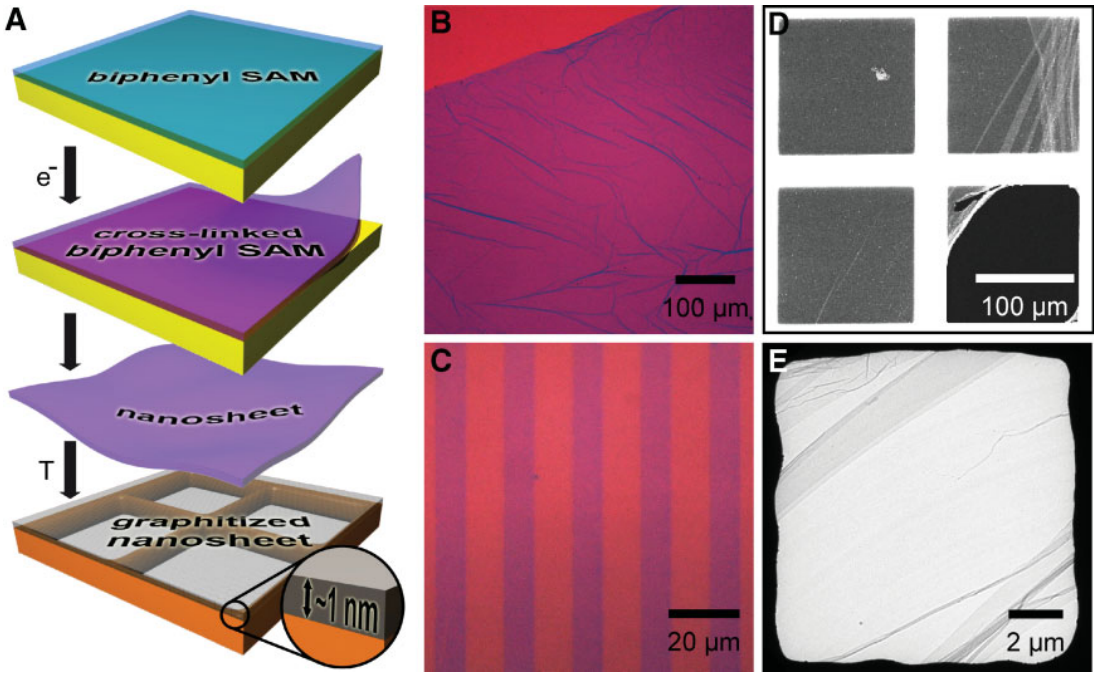


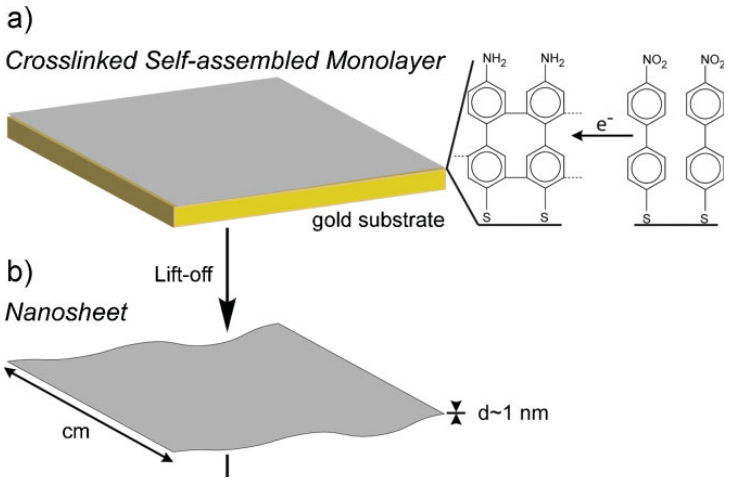
A. Turchanin, A. Gölzhäuser, Advanced Materials **28**, 6075-6103 (2016).

W. Geyer, V. Stadler, W. Eck, M. Zharnikov, A. Gölzhäuser, and M. Grunze, Appl. Phys. Lett. **75**, 2401 (1999).

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

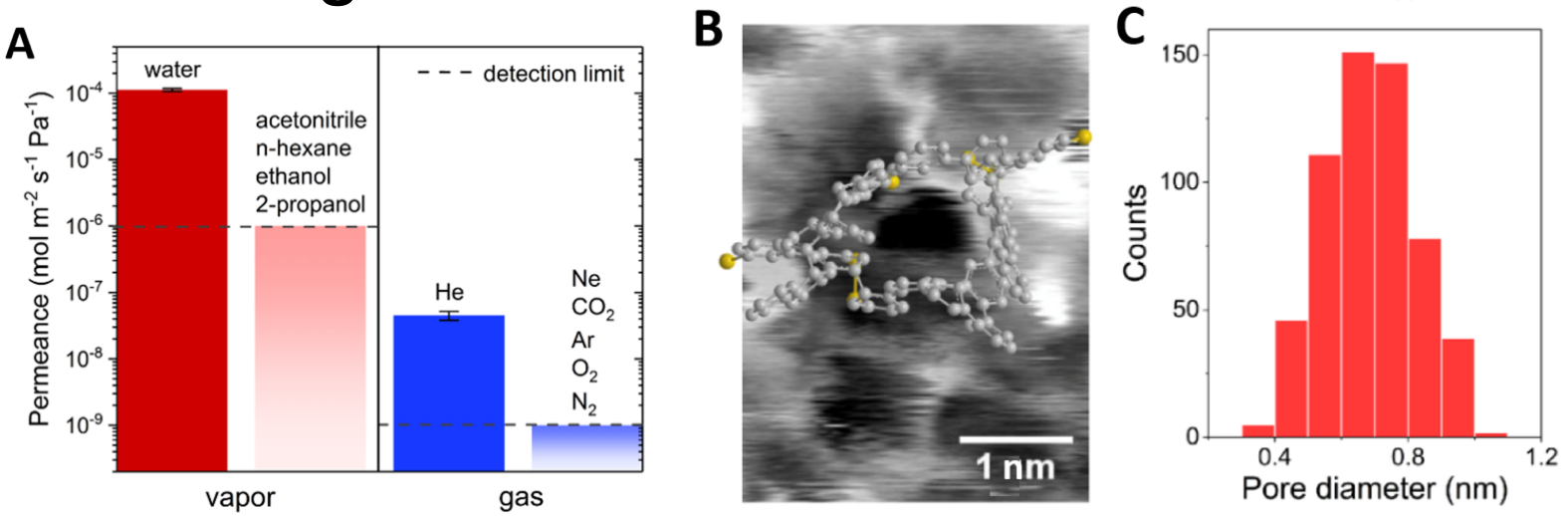
ADVANCED MATERIALS





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

. . . with amazing water filtration properties (to be discussed)



- (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 disordered/irregular. Holes! Holes? Huge holes! Huge?
- CNMs very soft: Young's module ca. 10 GPa, graphene 1000 GPa.
- Quantum methods, even DFT, cannot deal with such big systems.
- Goal: realistic modelling of CNM structure and even formation with correct properties.
- Can we model water translocation? Time scales!!!

Contents for you today

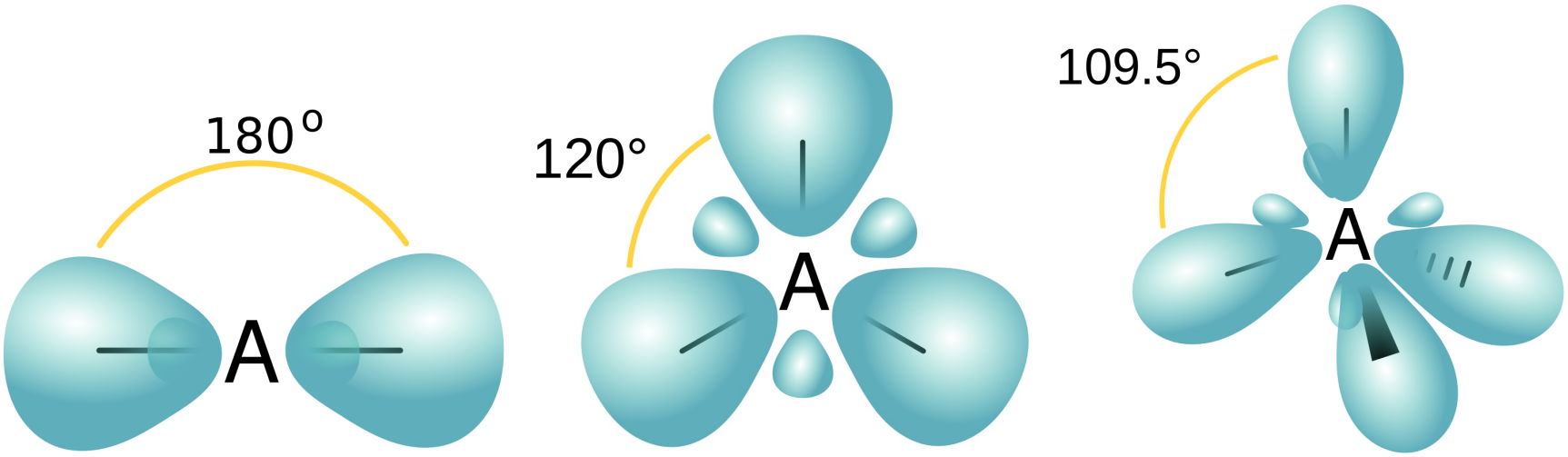
1. Carbon nanomembranes $\surd$
2. Classical molecular dynamics
3. Mechanical properties
4. Structure of CNMs $\Rightarrow$ Levin & Fil
5. Open problems $\Rightarrow$ Levin & Fil

Classical Molecular Dynamics

Classical Molecular Dynamics

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

sp hybridization modes



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

wikipedia: orbital hybridization

Very sophisticated classical carbon potential

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

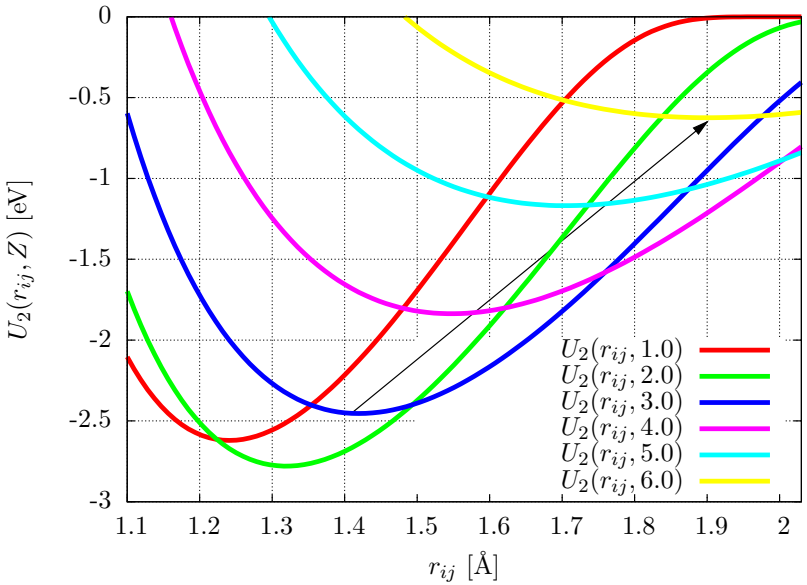
$$V(\vec{r}_1, \vec{r}_2, \dots) = \sum_{i \neq j}^{N} U_2(|\vec{r}_i - \vec{r}_j|, Z_i) + \sum_{i \neq (j<k)}^{N} U_3(|\vec{r}_i - \vec{r}_j|, |\vec{r}_i - \vec{r}_k|, \Theta_{ijk}, Z_i)$$

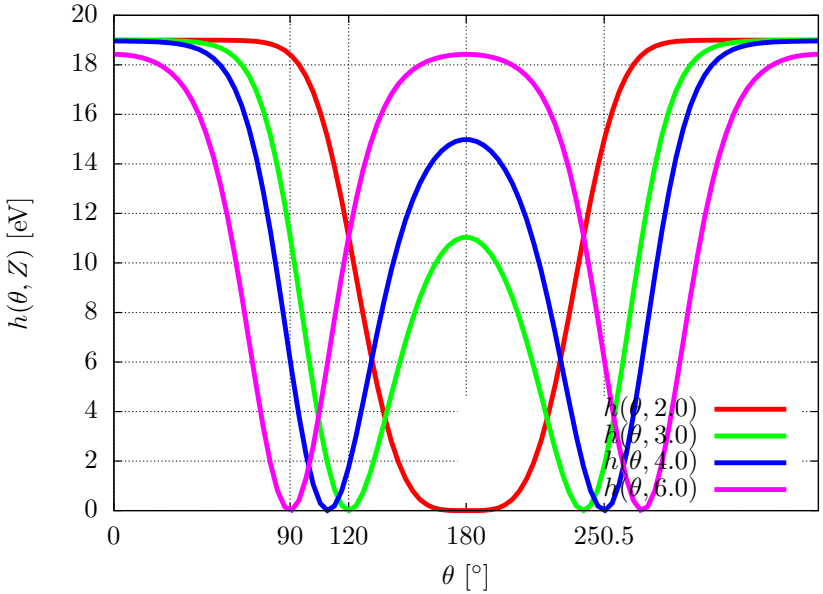
Θ_{ijk} – dehedral angles, Z_i continous coordination number.

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. Irregular = many structures correct!
- 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 UPS spectra.

  $\Rightarrow$ Might be possible soon! Levin! + Andrei Postnikov

(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).

L. Mihlan, J. Ehrens, and J. Schnack, Physica E **167**, 116170 (2025).

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!

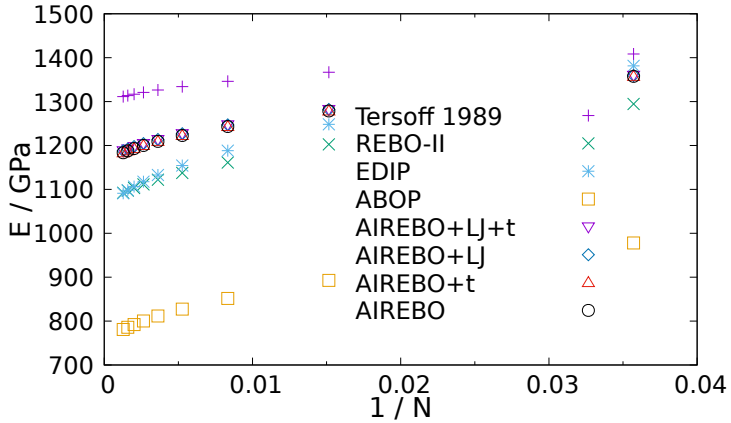
Ground state distances for graphene, CNT, and diamond

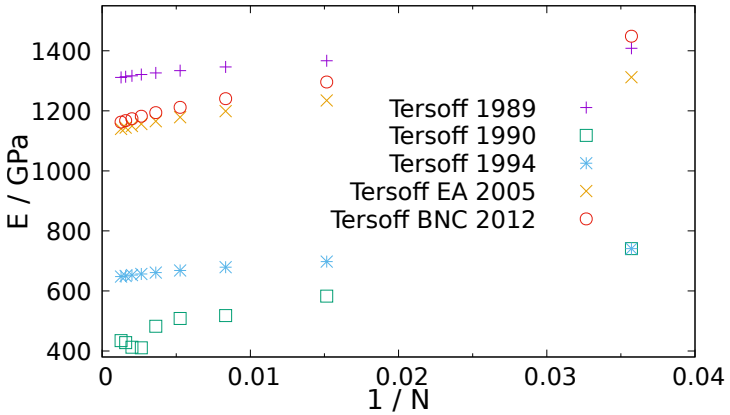
Table 1: Ground-state dimensions in Å of graphene, CNT, and diamond for the investigated potentials (LAMMPS).
(* No proper ground state structure found; † anisotropic.)

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



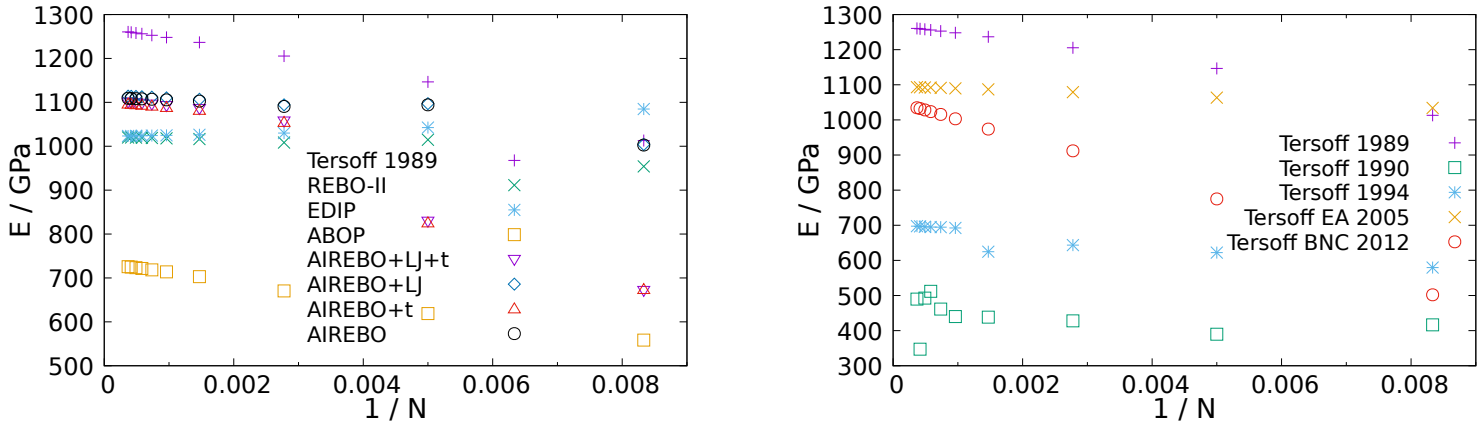


Young's modulus of graphene for various sizes and potentials. N denotes the number of atoms in the approximately square graphene sheets. Open boundary conditions are applied.

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

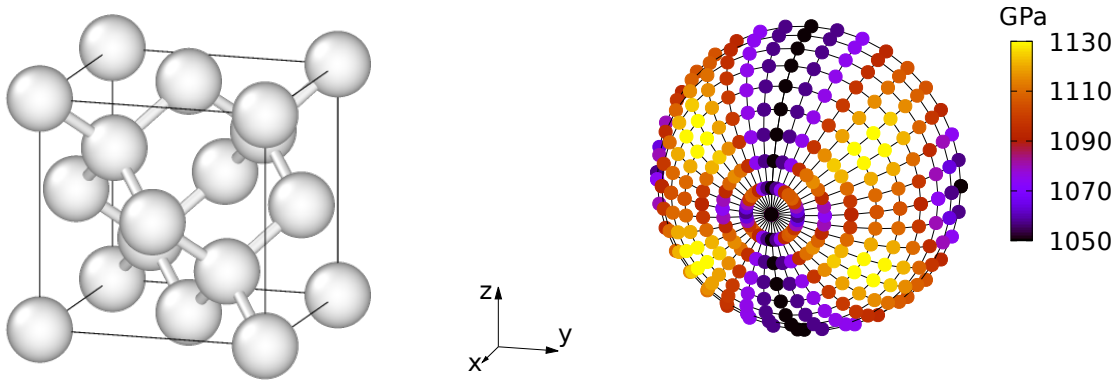


Young's modulus of a (20,20) CNT with armchair geometry along the tube, taken as x-direction, for various sizes and potentials. N denotes the number of atoms of the tube. Open boundary conditions are applied.

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

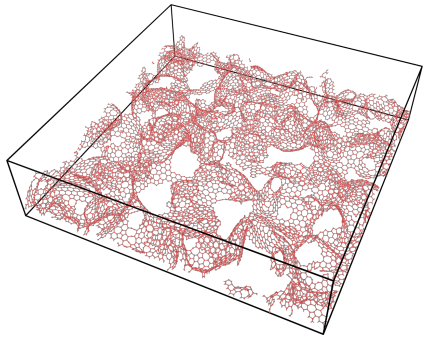


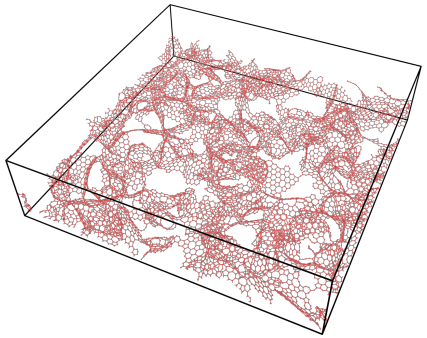
Structure and directions as well as Young's modulus of diamond taken in various directions on the northern hemisphere around the positive x-direction for $N = 8631$ and the EDIP potential. Open boundary conditions are applied.

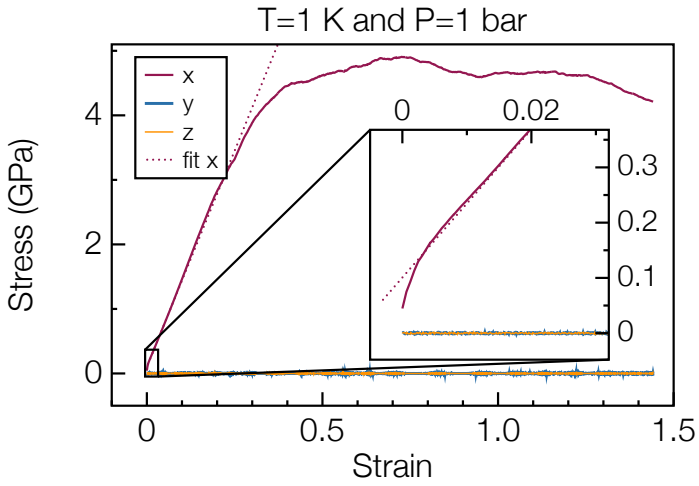
Experimental values: 1.05 TPa . . . 1.21 TPa

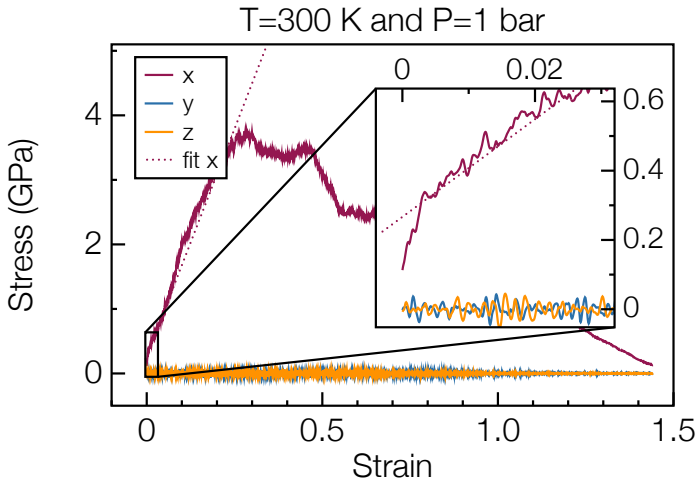
F. Gayk, J. Ehrens, T. Heitmann, P. Vorndamme, A. Mrugalla, and J. Schnack, Physica E **99**, 215 (2018).

Young's modulus for CNMs – Howto?





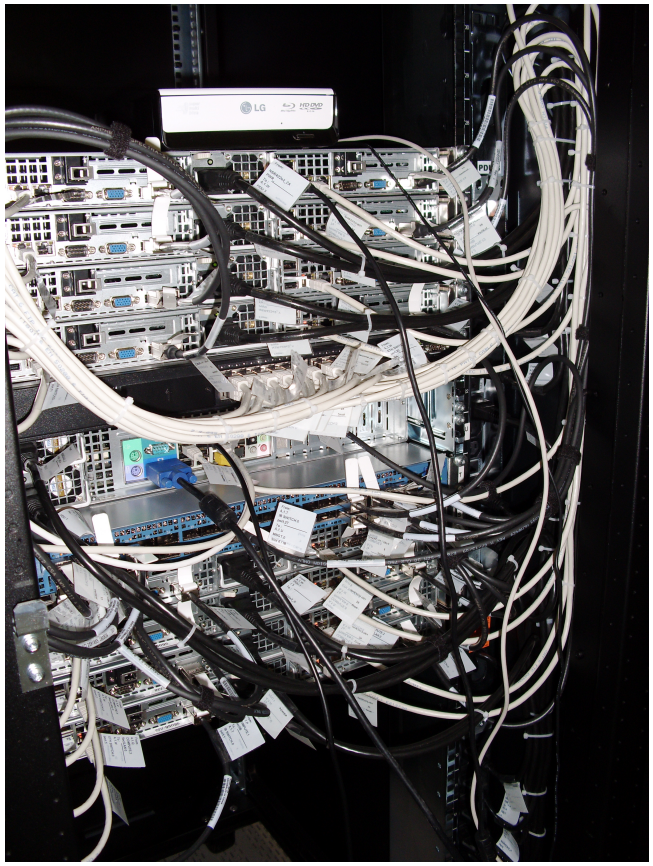




Simulation method matters a lot! How would you do it?

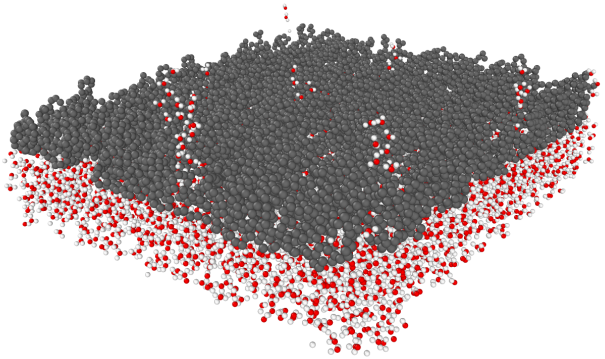
L. Mihlan, J. Ehrens, and J. Schnack, Physica E **167**, 116170 (2025).

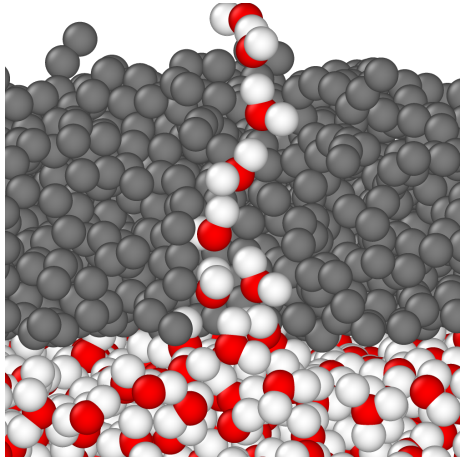
Summary



- Classical Molecular Dynamics can be set up for carbon systems using effective many-body carbon potentials.
- Ground-state geometries and Young's moduli can be determined with great accuracy (exception graphite).
- CNMs are not carbon ground states! Disordered carbon systems constitute local energy minima. There are *zillions.*
- Levin and Fil can understand and model the formation CNMs including holes!

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).

Thank you very much for your attention.