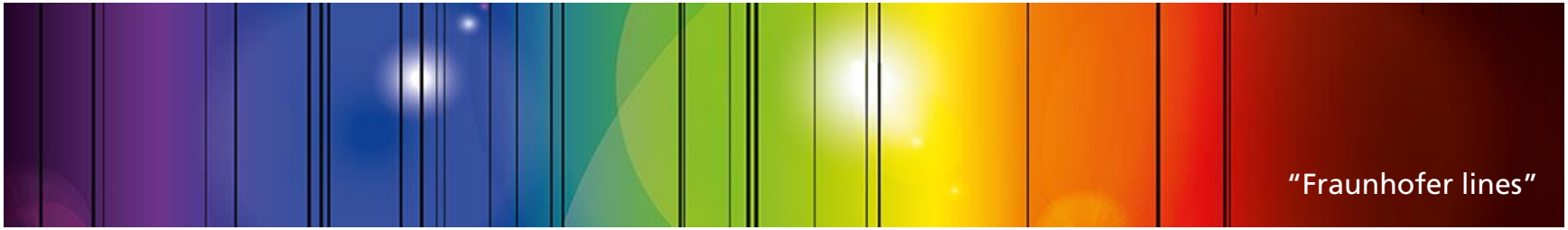
# Tribology of Diamond and Silicon

## atomic-scale insights from computer simulations

University of Warwick – WCPM Seminars – 19.02.2018

Gianpietro Moras




Fraunhofer KIT Karlsruher Institut für Technologie
MIKROTRIBOLOGIE CENTRUM µTC

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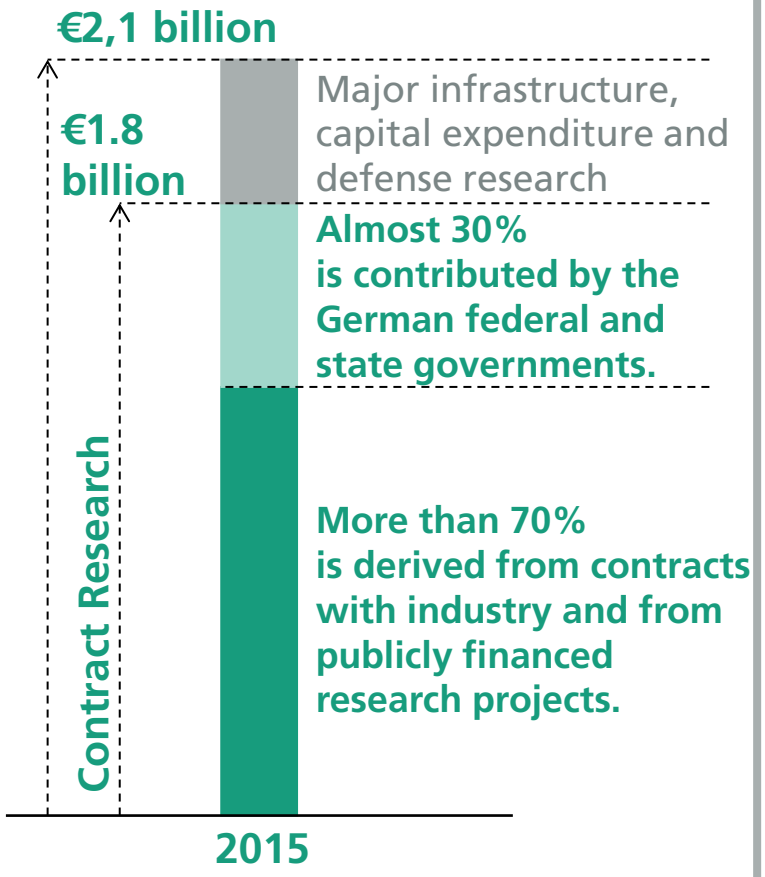
# The Fraunhofer-Gesellschaft at a glance

## The Fraunhofer-Gesellschaft undertakes applied research of direct benefit to private and public enterprise and of wide benefit to society.

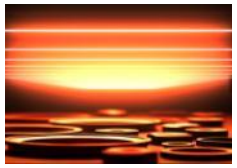
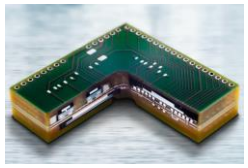
Nearly **24,000** staff

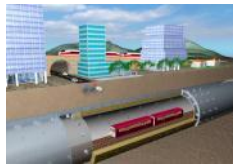

**67** institutes and research units



# Pooling expertise
## Fraunhofer Groups



Institutes working in related subject areas cooperate in Fraunhofer Groups and foster a joint presence on the R&D market. They help to define the Fraunhofer-Gesellschaft's business policy and act to implement the organizational and funding principles of the Fraunhofer model.

- ICT
- Life Sciences
- Light & Surfaces
- Microelectronics
- Production
- Materials and Components – MATERIALS
- Defense and Security VVS

# FRAUNHOFER INSTITUTE FOR MECHANICS OF MATERIALS IWM

Fraunhofer

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www.mikrotribologiecentrum.de

# Fraunhofer Institute for Mechanics of Materials IWM

- Directors
  - Prof. Dr. Peter Gumbsch
  - Dr. Rainer Kübler (Deputy director)
  - Prof. Dr. Chris Eberl (Deputy director)
- 20,1 Mio.€ budget – 290 employees – 47% from industry (12.2017)



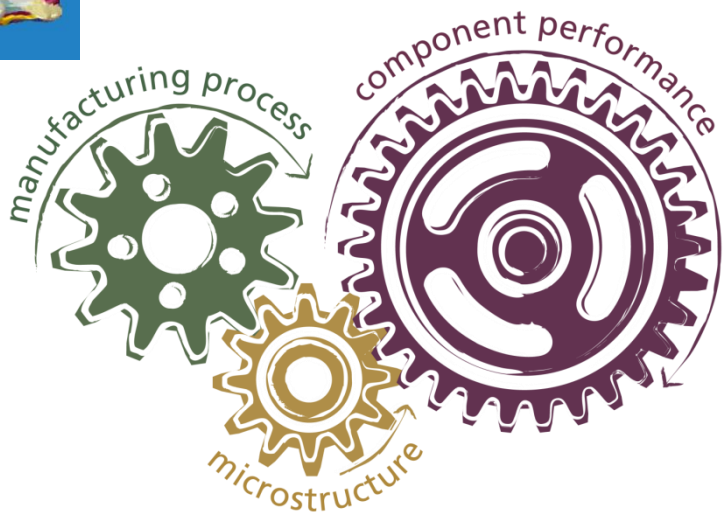
Freiburg


Karlsruhe

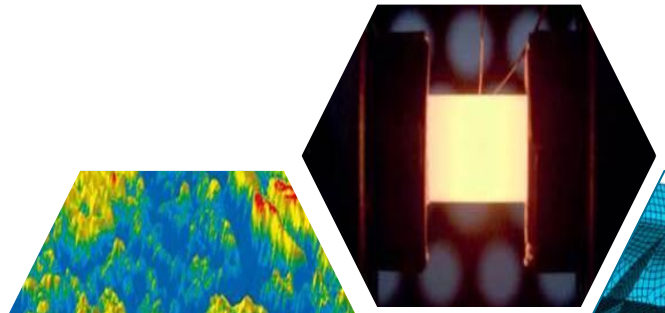
# Mechanics of Materials

- How do materials behave in components?
- How do material properties evolve during the manufacturing process?
- How can material properties be accurately adjusted?

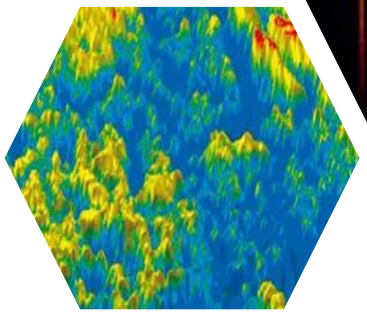
- Integrated examination of materials, manufacturing and components
- Identifying and adjusting critical parameters for material properties and component functions



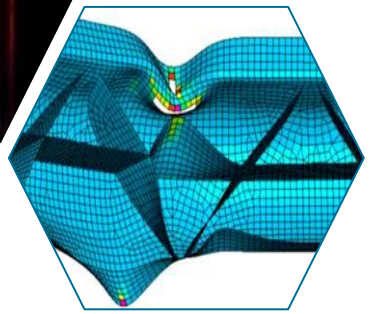
# Virtual and experimental assessment of materials and components under a wide range of manufacturing and service induced loads



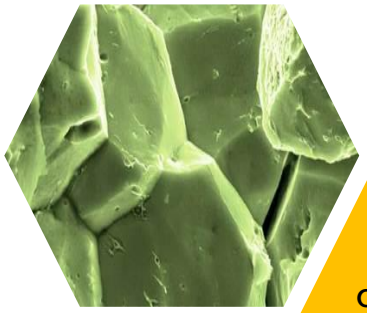
thermal and mechanical loads



tribological loads



dynamical loads



structural and chemomechanical loads

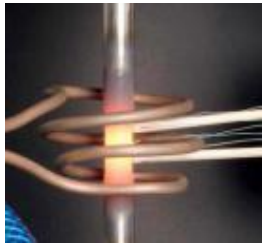
corrosive loads

metals, polymers, ceramics, glass, composites, semi-conductors

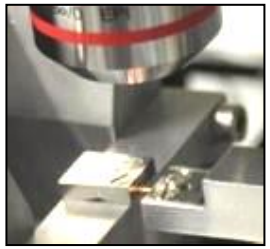
# Multiscale approach – experimental and numerical

For the virtual development and assessment of materials and components, the institute works with advanced multiscale simulations on the nano, micro and macro levels and/or develops the appropriate models.

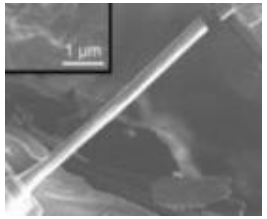
Macroscopic Assessment



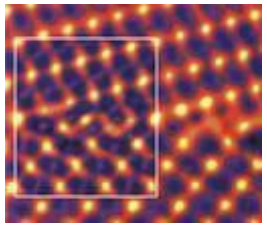
Microscopic Assessment

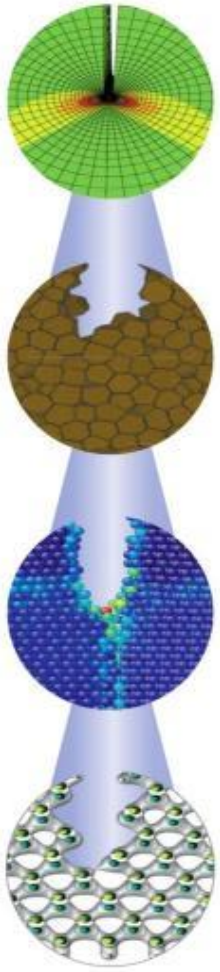


In situ SEM




TEM





Continuum

Micro-structure

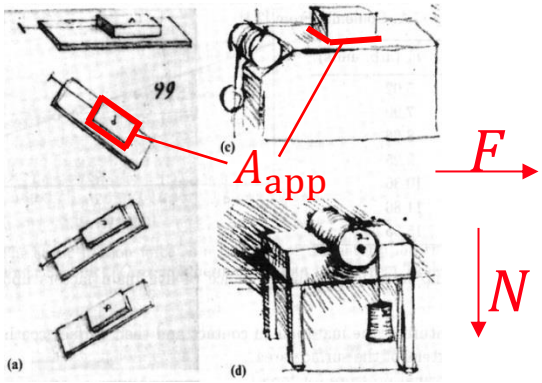
Atoms

Quantum Mechanics

# Tribology

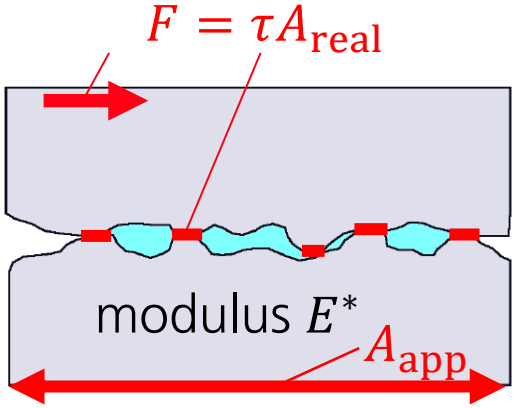
*Tribology is the science and engineering of interactive surfaces in relative motion. It includes the study and application of principles of friction, lubrication and wear.*

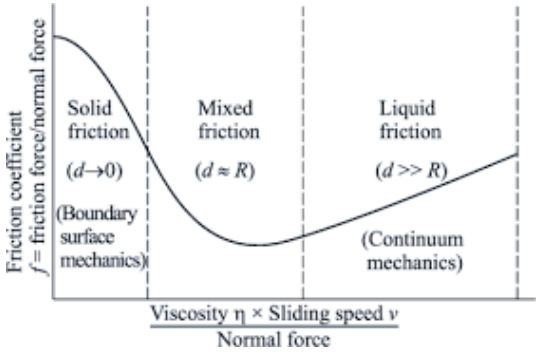
wikipedia.org




- Leonardo Da Vinci (1452-1519), Guillaume Amontons (1663-1705)
  - **Independence of the area of contact**. *Friction is independent of the apparent area of contact.*
  - **Amontons' law**. *Friction is proportional to the applied load:* $F = \mu N$ (μ is the friction coefficient and is larger for static than for kinetic friction).

- **Bowden & Tabor** (1950)
  - Surfaces are rough (fractal): contact between asperities.
  - The real contact area is a few order of magnitudes smaller than the apparent area
  - More generally $\tau = \tau_0 + \alpha P$

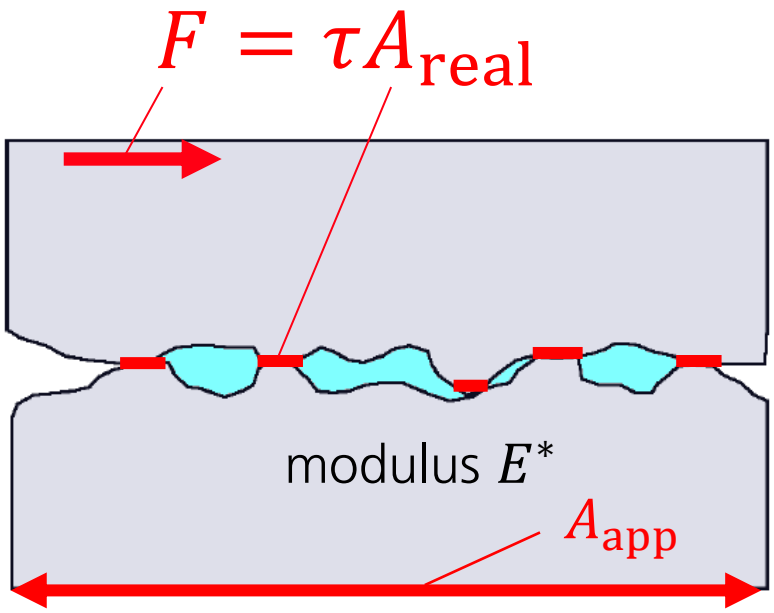


# Tribology
## (Macroscopic) Friction

- Is $F = \tau A_{real}$ ?

- Problems:
  - What determines $\tau$?
  - Why $\mu$ ~constant for given materials?
  - Macroscale: $A_{\mathrm{real}}/\mathrm{N}$ is not a material property $(\sim 1/h'_{\mathrm{rms}})$
  - Nanoscale: $A_{\mathrm{real}}$ hard to define, $\tau$ often zero, depends on pressure, variables not controlled in experiment



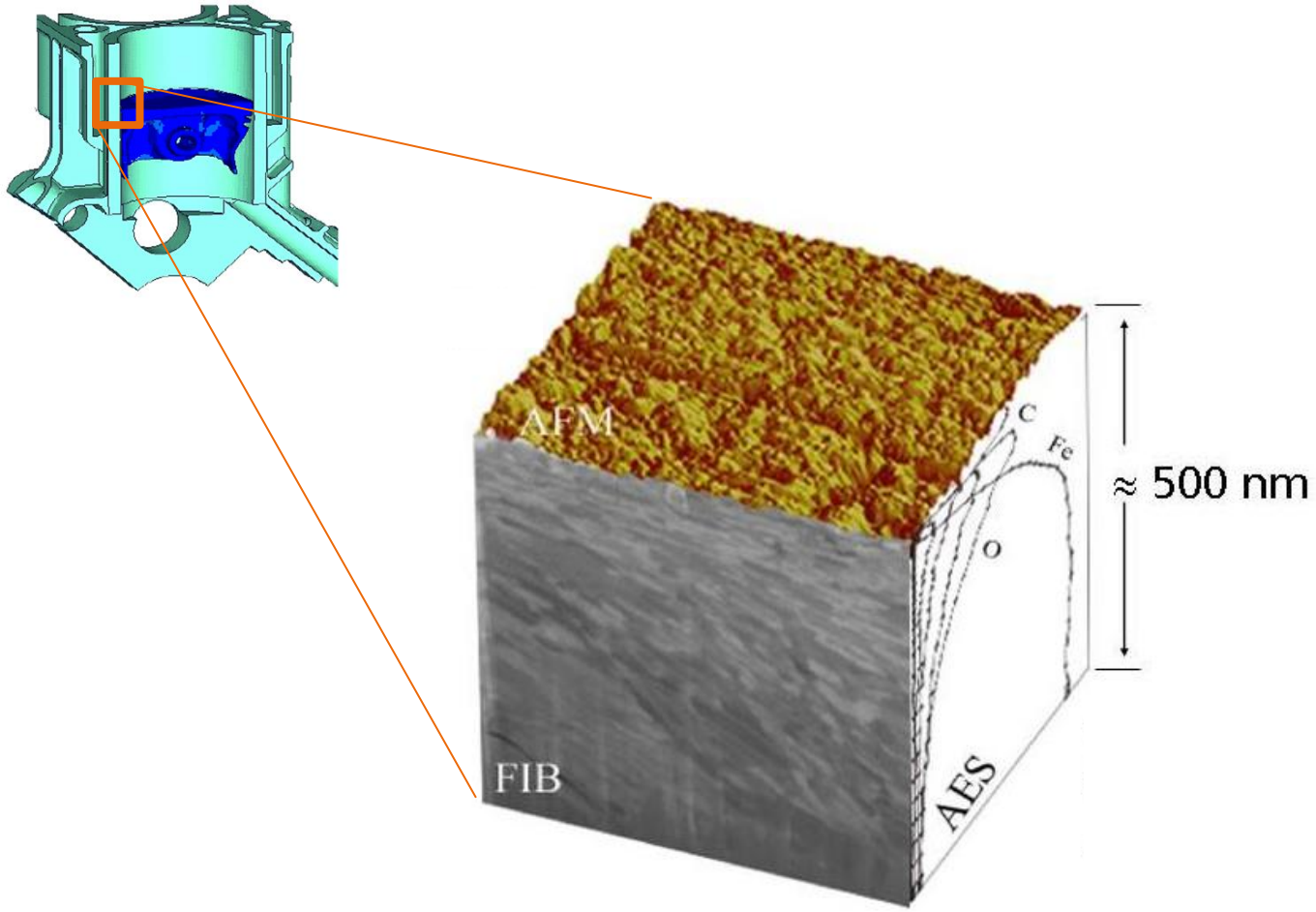

$A_{\mathrm{real}}$ is a fraction of the apparent contact area $A_{\mathrm{app}}$

$$A_{\mathrm{real}} = \kappa \frac{N}{h'_{\mathrm{rms}} E^*}$$

Hyun, Pei, Molinari, Robbins, Phys. Rev. E 70, 026117 (2004) $\kappa \approx 2$

Pastewka, Robbins, PNAS 111, 3298 (2014) $\kappa \geq 2$

# Structure evolution in tribological systems




Scherge et al., Wear (2006)

# Structure evolution in tribological systems

## Questions

**Surface structure**

Evolution of the topography

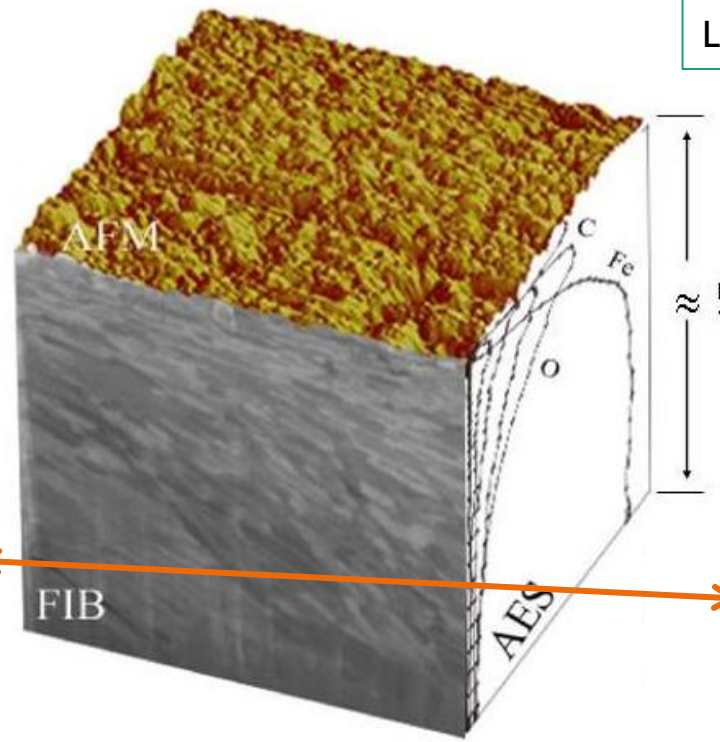
Plasticity / fracture / wear

**Lubricant structure**

Adsorption / wetting

Slip length

Layering




**Atomic structure and microstructure**

Amorphization

Grain structure

Plasticity

**Chemical structure**

Tribochemistry

Surface termination

SAMs

Oxidation

Diffusion

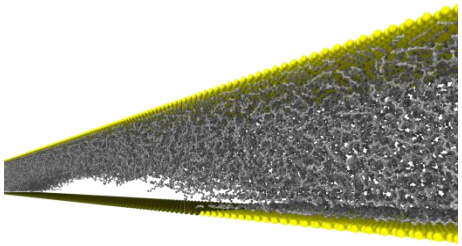
**Effects of the tribo-structure on friction, wear and lubrication?**

# Structure evolution in tribological systems

## A multiscale problem

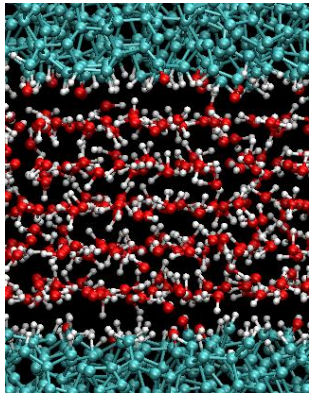
Coasre graining

Continuums methods
„Coarse grained“ methods



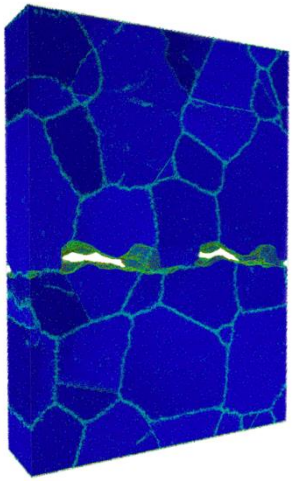
Hydrodynamic lubrication
Surface structuring
Contact mechanics

Non-reactive potentials



Liquid layers
Wetting
Friction coefficient

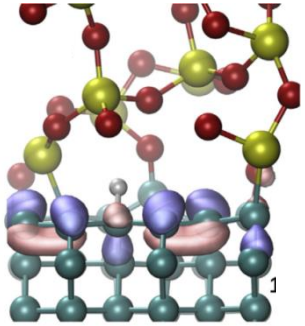
Reactive potentials
(BOP, MEAM,…)



Nanostructure
Phase transitions
Third body

TB

DFT



Interface chemistry
Tribochemistry

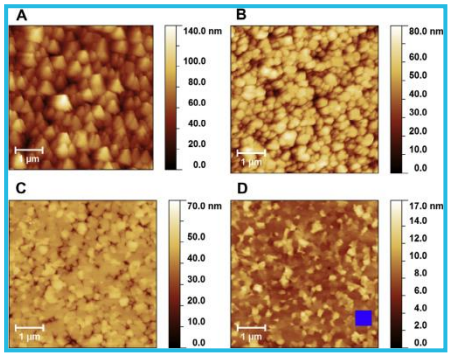
| | | | |
|---|---|---|---|
| Length | 1 nm | 10-100 nm | 1 μm |
| Time | 0.1-1 ns | 100 ns | 1 μs |

# Tribology of diamond and silicon

## Some examples

Mechanical polishing

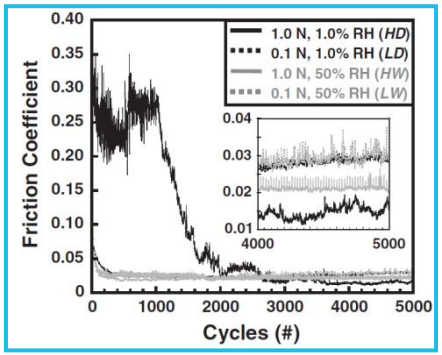
CMP




Thomas et al., Carbon (2014)

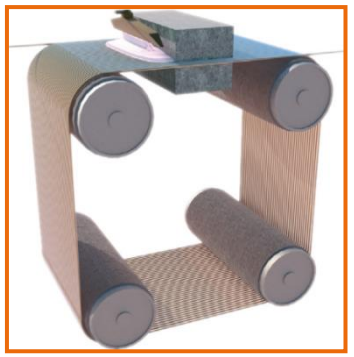
Wear of diamond films

Ultralow friction of UNCD

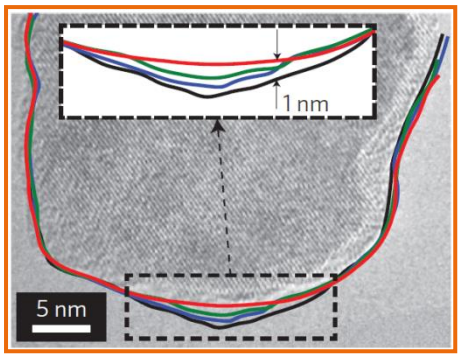



Konicek et al., Phys. Rev. Lett (2008)

Multi-wire sawing

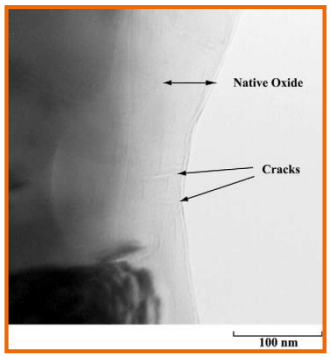


Wear of AFM tips



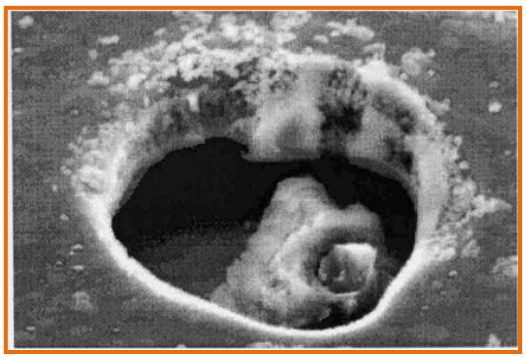

Jacobs et al., Nat. Nanotech. (2013)

SCC of MEMS




Muhlstein et al., Acta Mat. (2002)

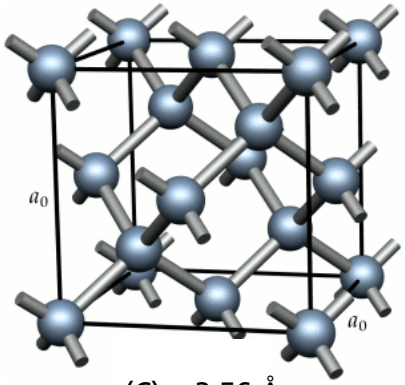
Wear of MEMS



Williams et al., J. Phys. D: Appl. Phys. (2002)

# Diamond and silicon

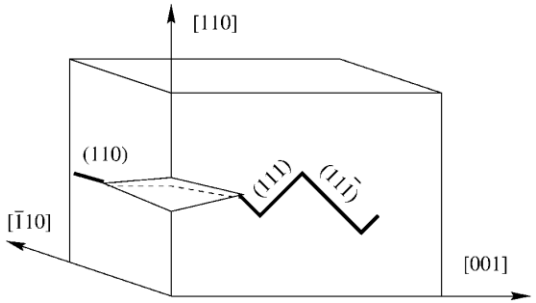
## Analogies

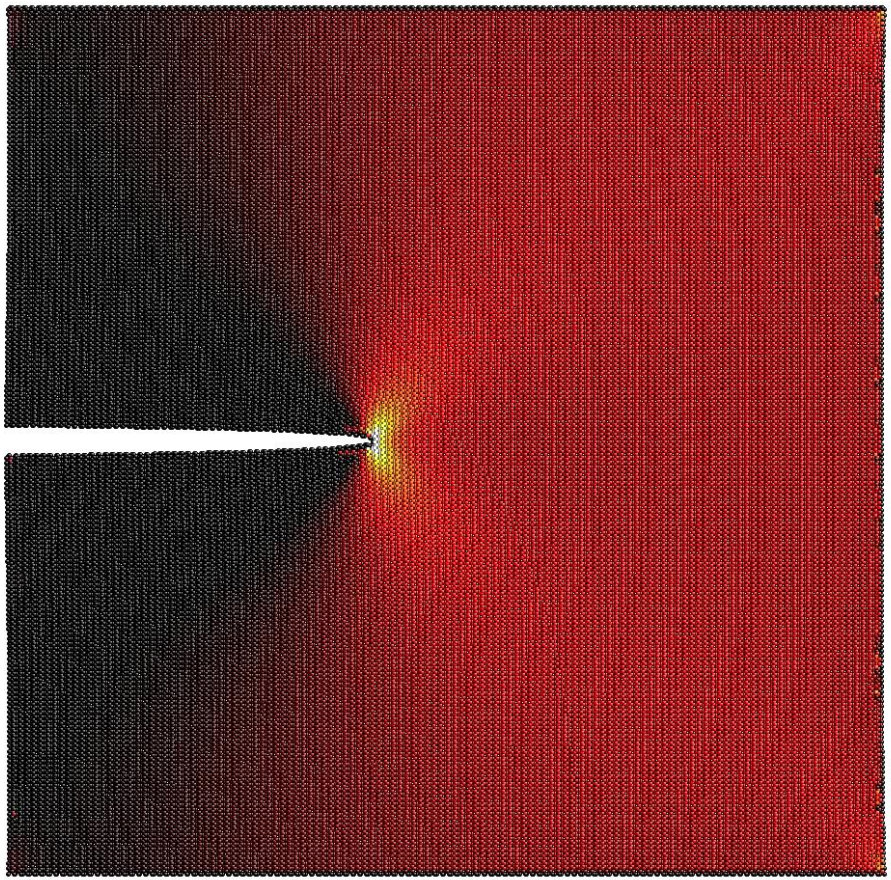



$a_0$(C) = 3.56 Å

$a_0$(Si) = 5.43 Å

- Brittle materials
  - low dislocation mobility
  - (100) is not a stable cleavage plane

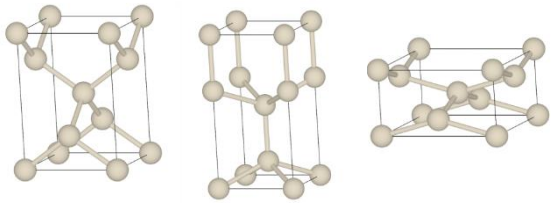


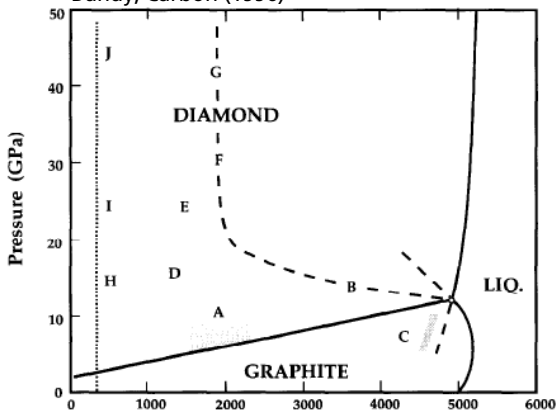
Perez et al., Phys. Rev. Lett. (2000)

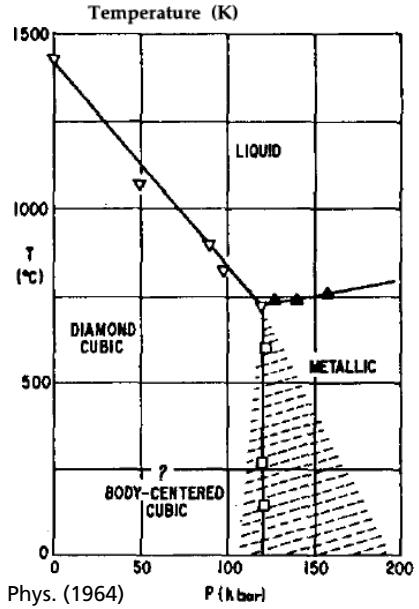
# Diamond and silicon

## Differences: phase diagrams and oxides



Bundy, Carbon (1996)



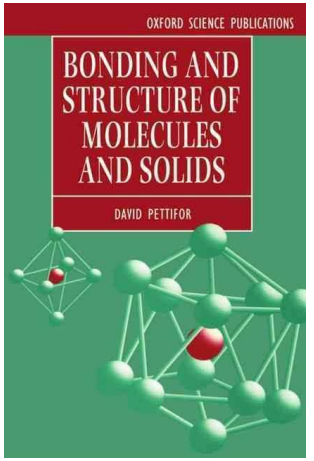

Bundy, J. Chem. Phys. (1964)

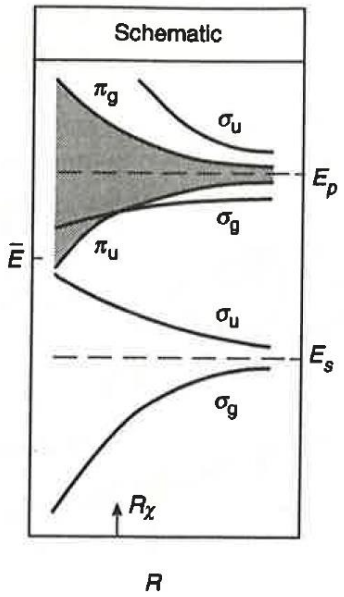
- Diamond is metastable at low P
- Si-I is stable at low P
  - Many high-pressure phases: Si-II, bct-5
  - Si-II (ß-tin Si) is metallic
- Clausius-Clapeyron $\frac{dT_m}{dP} = T_m \frac{\Delta V}{\Delta H}$
  - C: $dT_m/dP > 0 \rightarrow \rho(\text{liquid}) < \rho(\text{crystal})$
  - Si: $dT_m/dP < 0 \rightarrow \rho(\text{liquid}) > \rho(\text{crystal})$
- Polyamorphysm in Si (LDA and HDA Si)
- Oxides:
  - CO, $CO_2$: gas
  - $SiO_2$: solid, prone to SCC in water

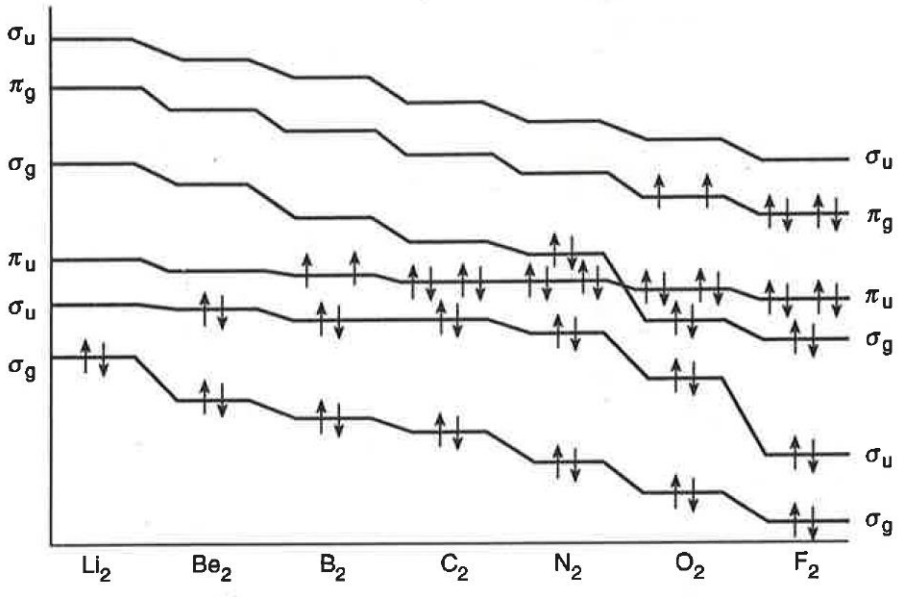
# Diamond and silicon

## Differences: π-bonding and aromaticity

David Pettifor



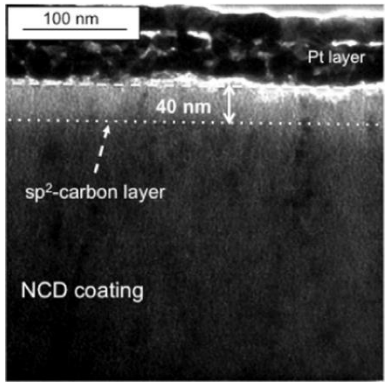



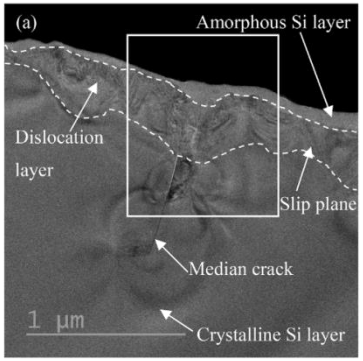

- Equilibrium inter-nuclear separation: $R_{C2} < R_\chi < R_{Si2}$
- This is due to the anomalously small core size of the C atom (→ short bonds)
- C: $\pi_u^4$ more stable than $\pi_u^2\sigma_g^2$ → favours π-bonded configurations
- Si: $\pi_u^4$ 1.5 eV less stable than $\pi_u^2\sigma_g^2$ → prefers σ-bonded configurations

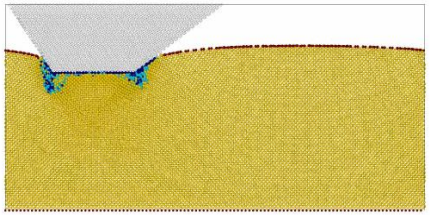
# Tribology of diamond and silicon

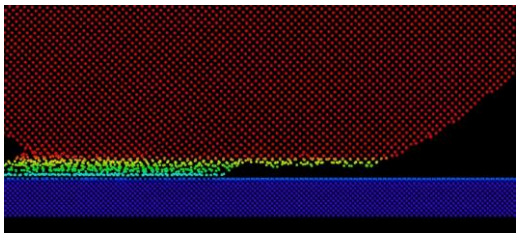
## Case studies

### Phase diagram and amorphous structures



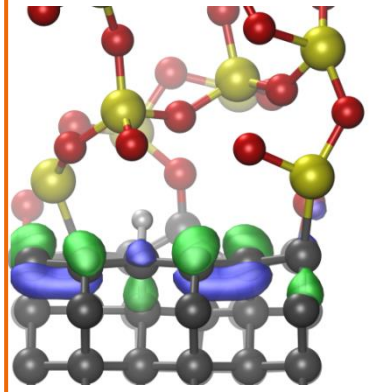



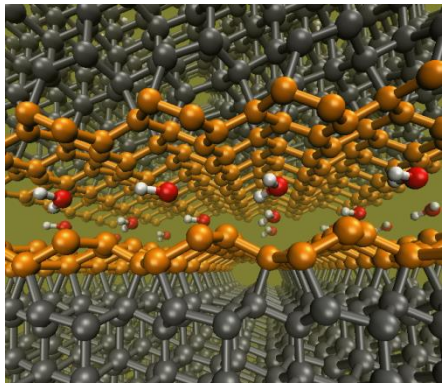


De Barros Bouchet et al., Carbon (2015)  T. Suzuki et al., Precision Engineering (2017)

### Aromatic reconstructions and oxides

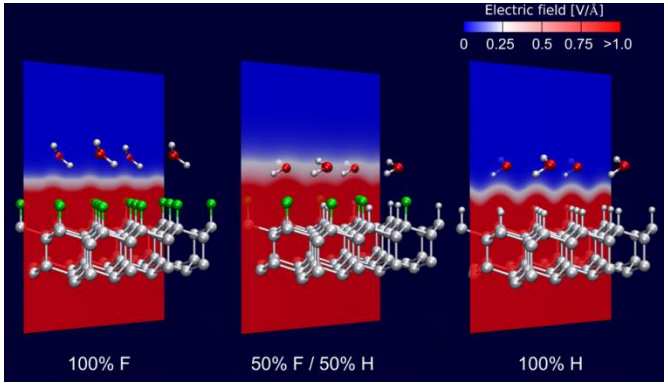


Peguiron et al., Carbon (2016)



Kuwahara et al., Phys. Rev. Lett. (2017)

### Bond length

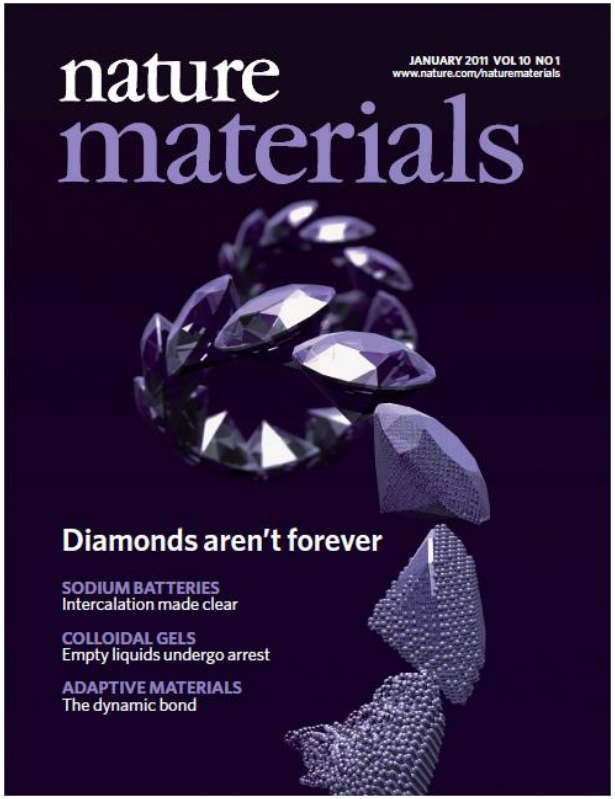


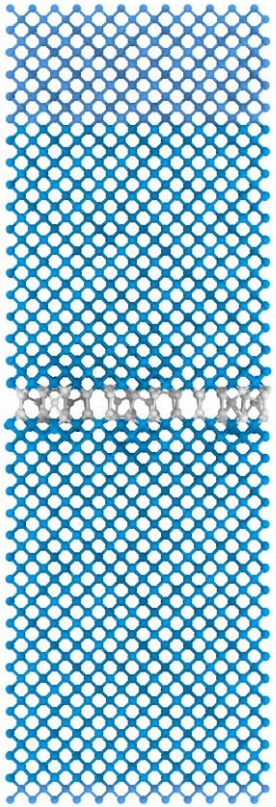

Mayrhofer et al., J. Am. Chem. Soc. (2016)

# Mechanical polishing diamond

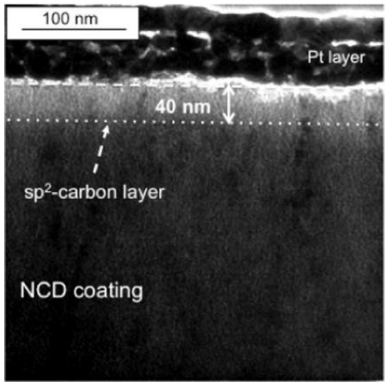
## Severe wear conditions

P = 10 GPa



v = 10 $ms^{-1}$

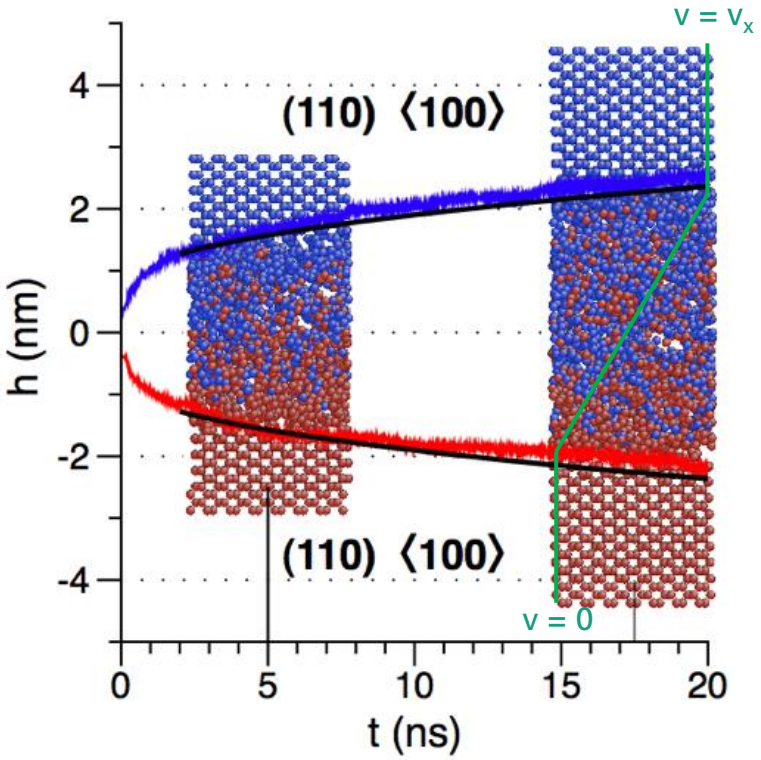



De Barros Bouchet et al., Carbon (2015)

L. Pastewka, S. Moser, P. Gumbsch, M. Moseler, Nat. Mater. 10, 34 (2011)

# Mechanical polishing of diamond

## Anisotropic mechanical amorphization




- Mechanical process
  - Amorphization rate depends on local shear rate
  - $\frac{dh}{dt} = \lambda(P)\frac{v}{h}$ $(shear\ rate\colon \dot{\gamma} = \frac{v}{h})$
  - $h(t) = A + \sqrt{2\lambda v t}$
- h depends on the sliding distance *x=vt*
- h does not depend on temperature (if T < ~$T_m$/2)

BOP of the Tersoff-Brenner type + modified cutoff scheme: REBO2/Tersoff (C), Kumagai *et al.* (Si)

L. Pastewka, S. Moser, P. Gumbsch, M. Moseler, Nat. Mater. 10, 34 (2011)

Pastewka et al. Phys. Rev. B 87, 205410 (2013)

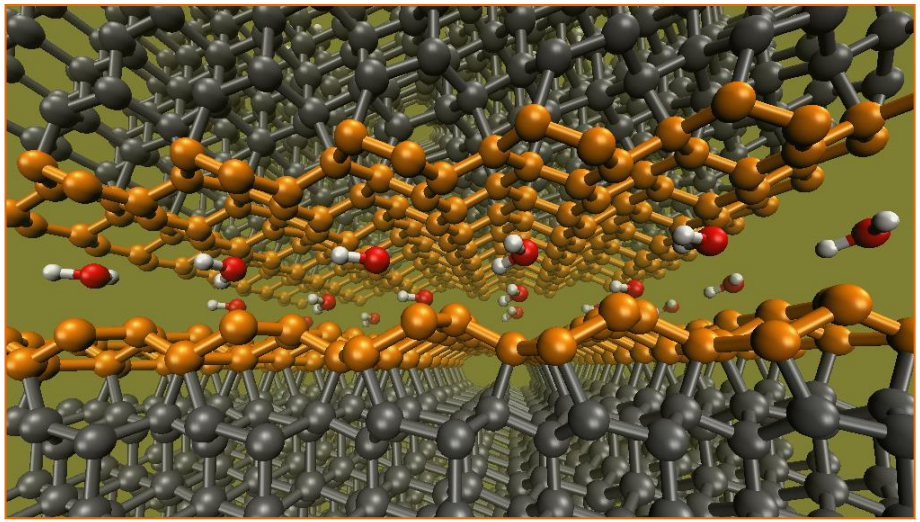
# TRIBOCHEMISTRY AND FRICTION REGIMES IN WATER-LUBRICATED DIAMOND

Kuwahara, Moras, Moseler, Phys. Rev. Lett. 119, 096101 (2017)

Takuya Kuwahara

Michael Moseler

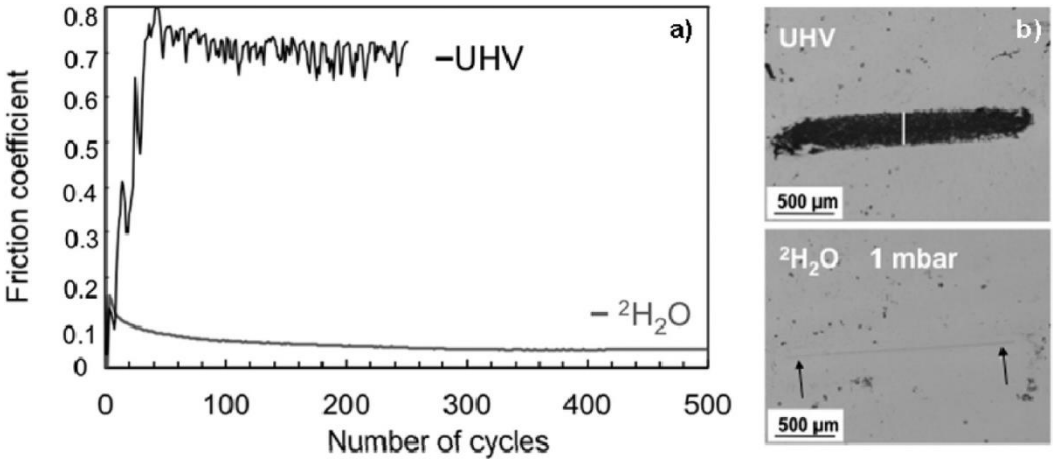
Fraunhofer IWM, Freiburg



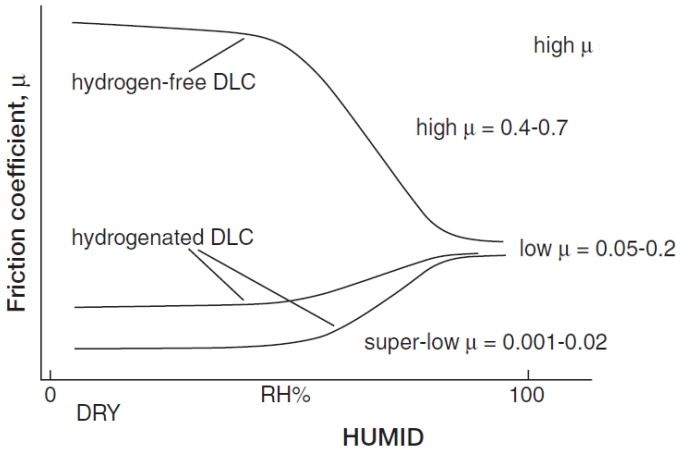
# Water-lubricated diamond

## Very low friction coefficients with low RH

H.Ronkainen, K.Holmberg, in "Tribology of Diamond-Like Carbon Films" (Springer, 2008)

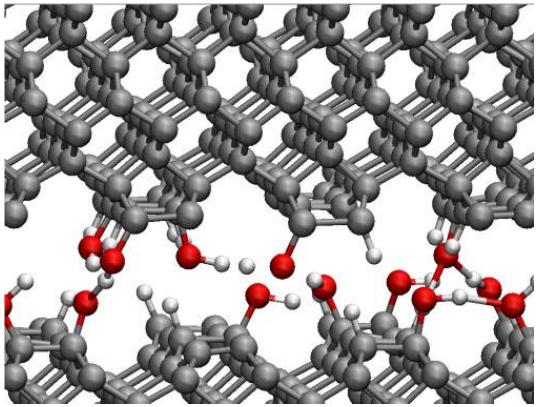



M.-I. De Barros Bouchet et al., J. Phys. Chem. C 116, 6966 (2012)




| Contact conditions | $\mu_{ss}$ | No. of run-in cycles |
|---|---|---|
| 1.0 N load 1.0% RH | 0.015 ± 0.002 | 2000 |
| 0.1 N load 1.0% RH | 0.028 ± 0.001 | <500 |
| 1.0 N load 50% RH | 0.0212 ± 0.0008 | <250 |
| 0.1 N load 50% RH | 0.029 ± 0.002 | <250 |

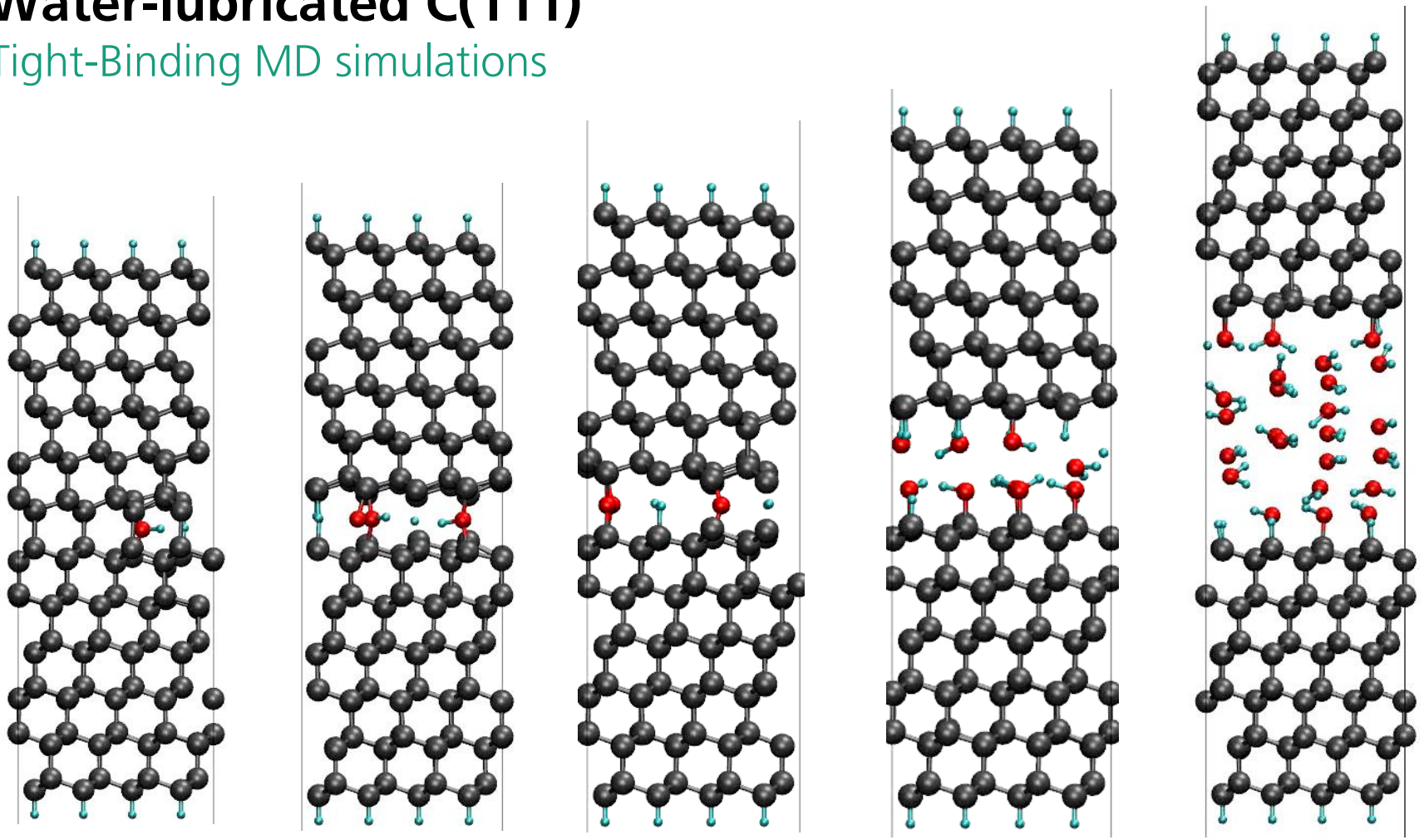
A. R. Konicek et al., Phys. Rev. Lett. 100, 235502 (2008)



G. Zilibotti et al., Phys. Rev. Lett. 111, 146101 (2013)

# Water-lubricated C(111)

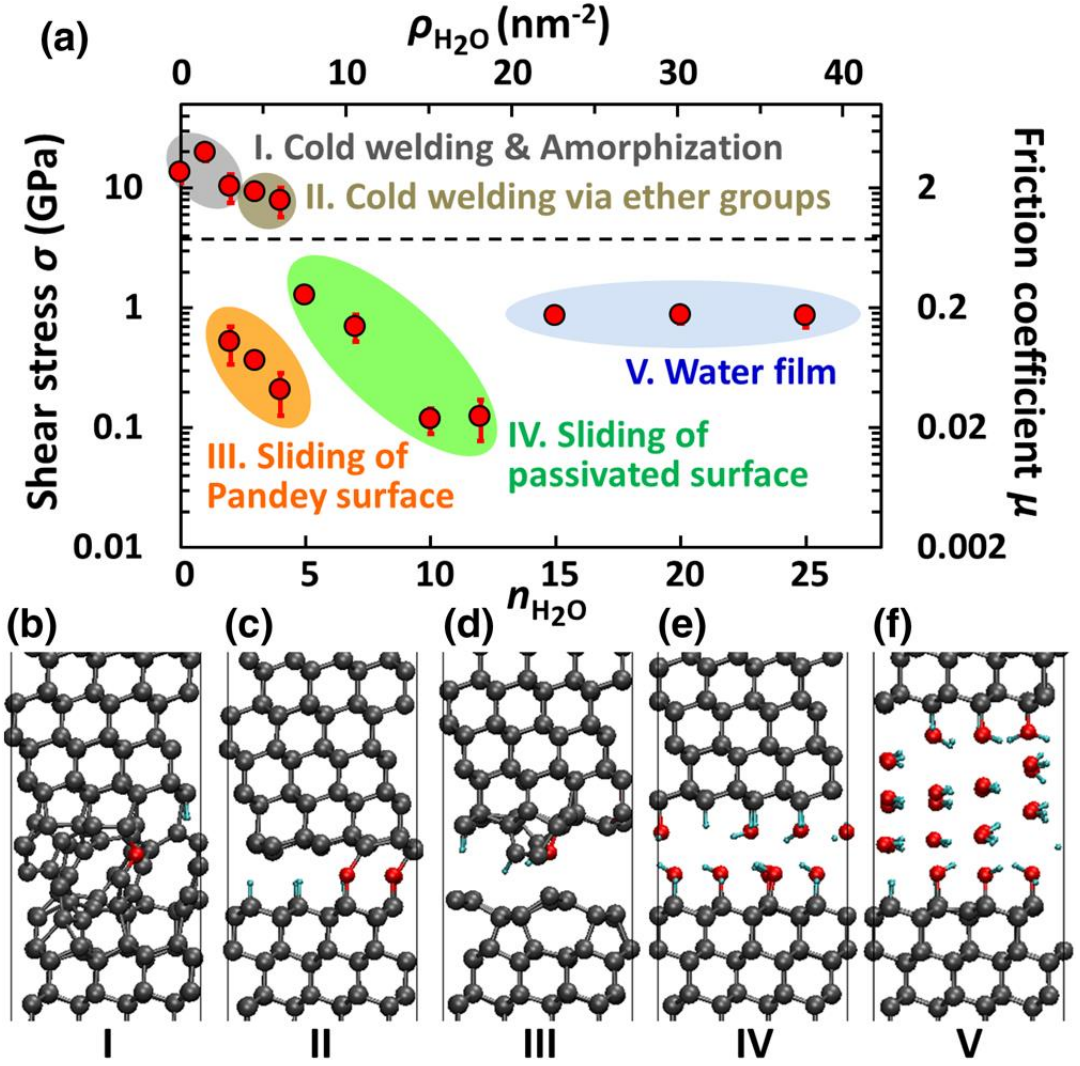
## Tight-Binding MD simulations



$n_{H_2O} = 1$ $n_{H_2O} = 3$ $n_{H_2O} = 3$ $n_{H_2O} = 10$ $n_{H_2O} = 25$

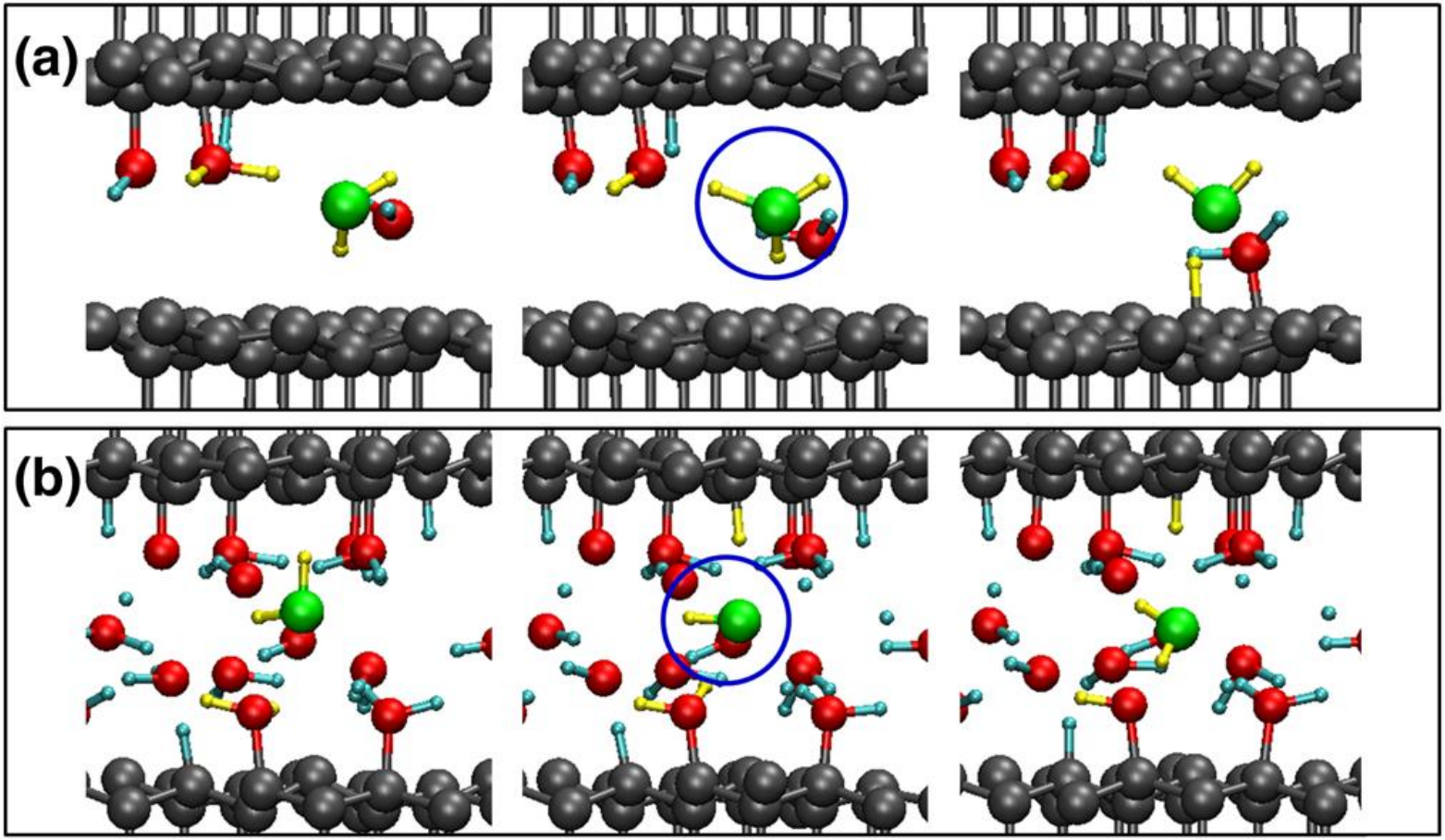
# Water-lubricated C(111)

## Friction regimes



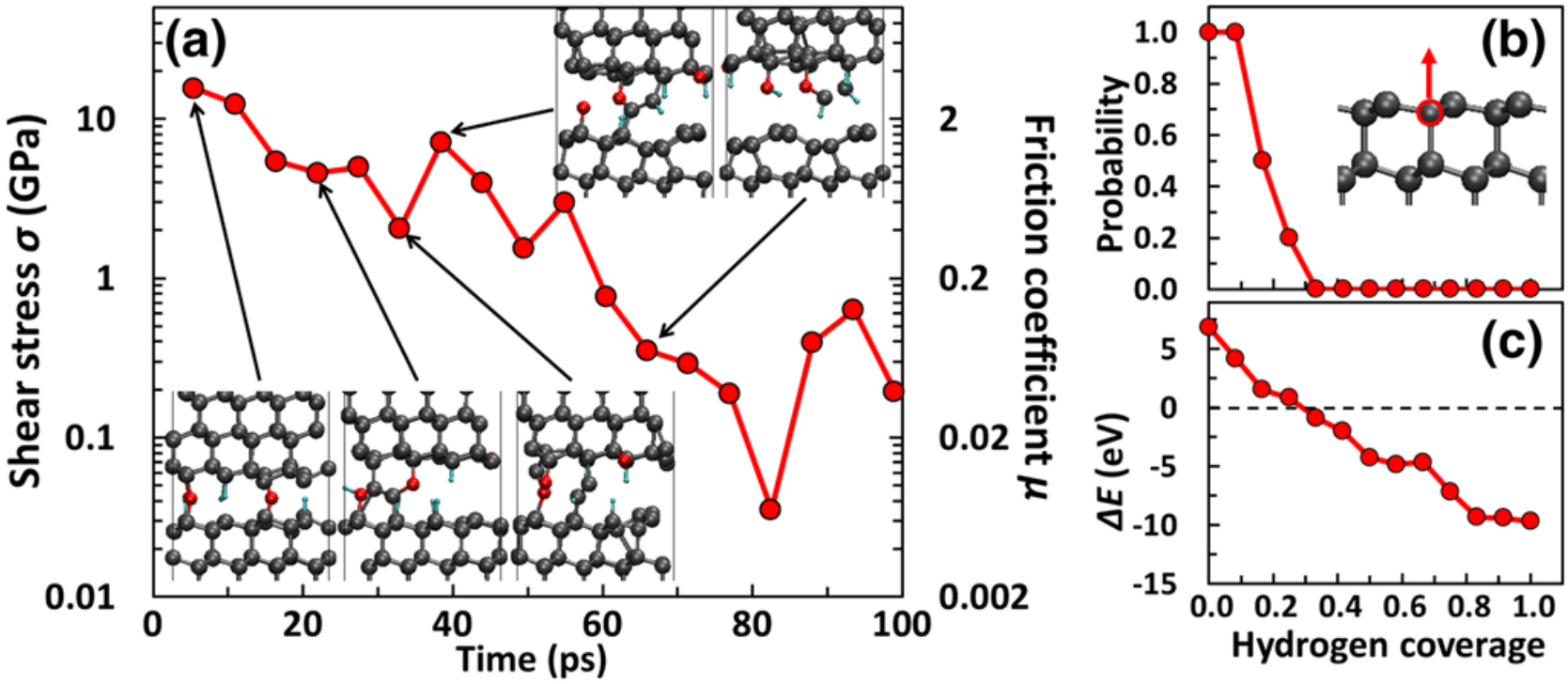
# Water-lubricated diamond

## Grotthus mechanism



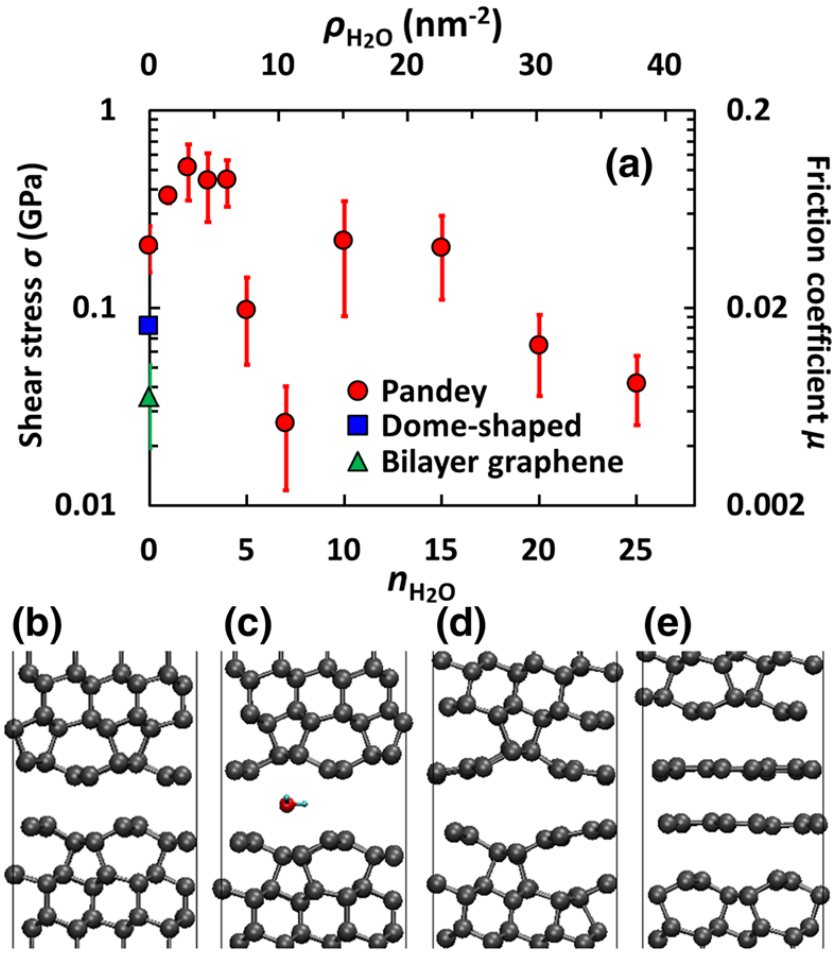
# Water-lubricated diamond

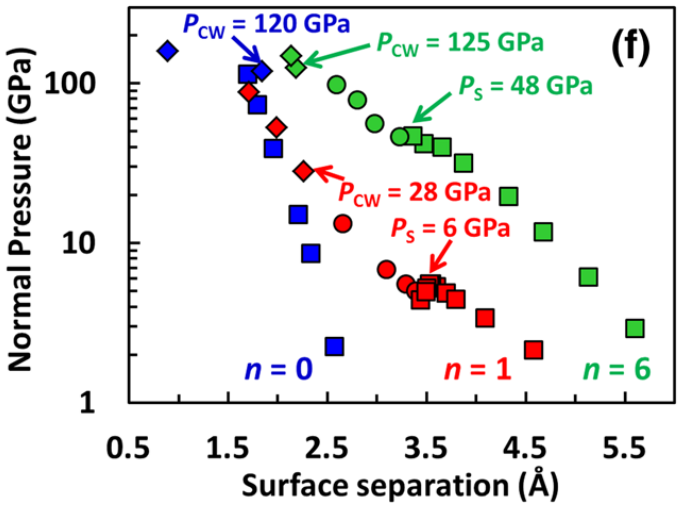
## Tribo-induced Pandey reconstruction



# Water-lubricated diamond

## Stability of Pandey reconstruction and other aromatic terminations



# FLUORINE-TERMINATED DIAMOND SURFACES POLAR HYDROPHONICITY & FRICTION

Mayrhofer et al., JACS 138, 4018 (2016)

Leonhard Mayrhofer

Narasimham Mulakaluri

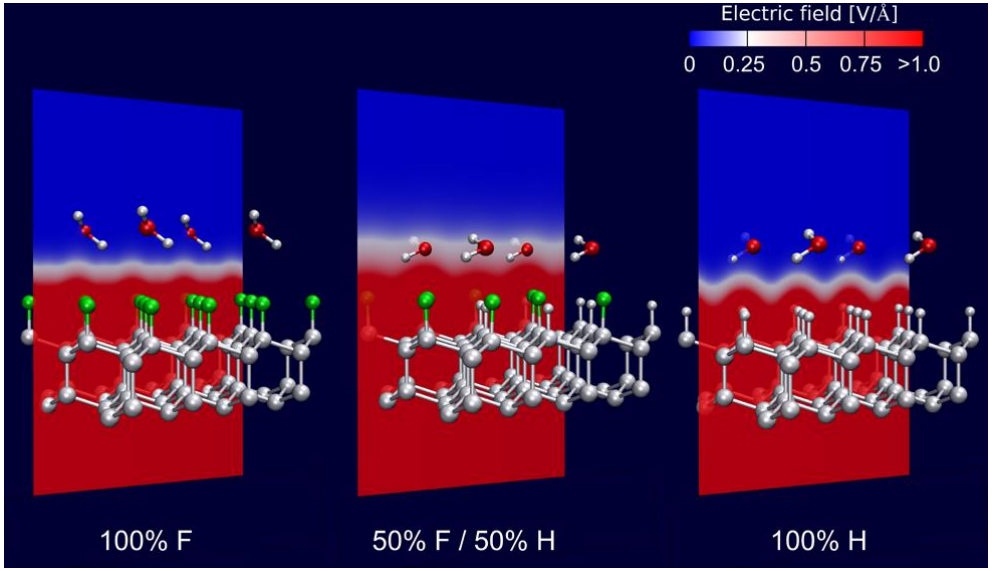
Michael Moseler

Fraunhofer IWM, Freiburg

Srinivasan Rajagopalan

Paul Stevens

ExxonMobil Research and Engineering Company, Annandale, NJ, USA

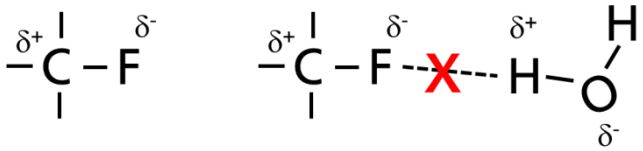


# Motivation

## CF compounds

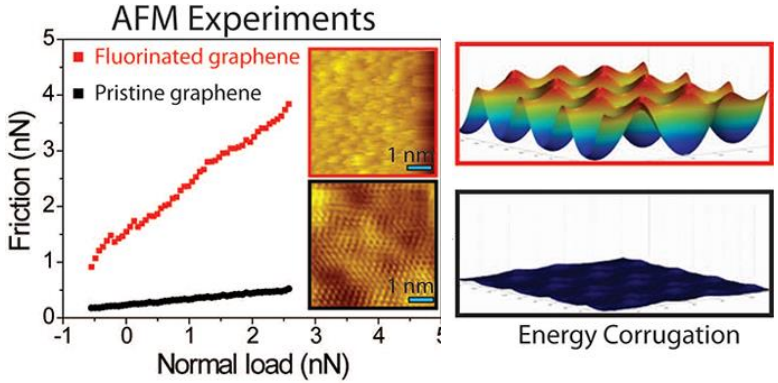

## The C–F bond

## Polar hydrophobicity



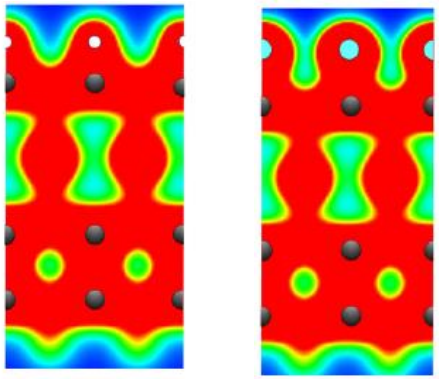

O'Hagan, Chem. Soc. Rev. (2007)

## Friction on F-graphene




Li et al., Nano Lett. (2014)

## Friction and energy corrugation

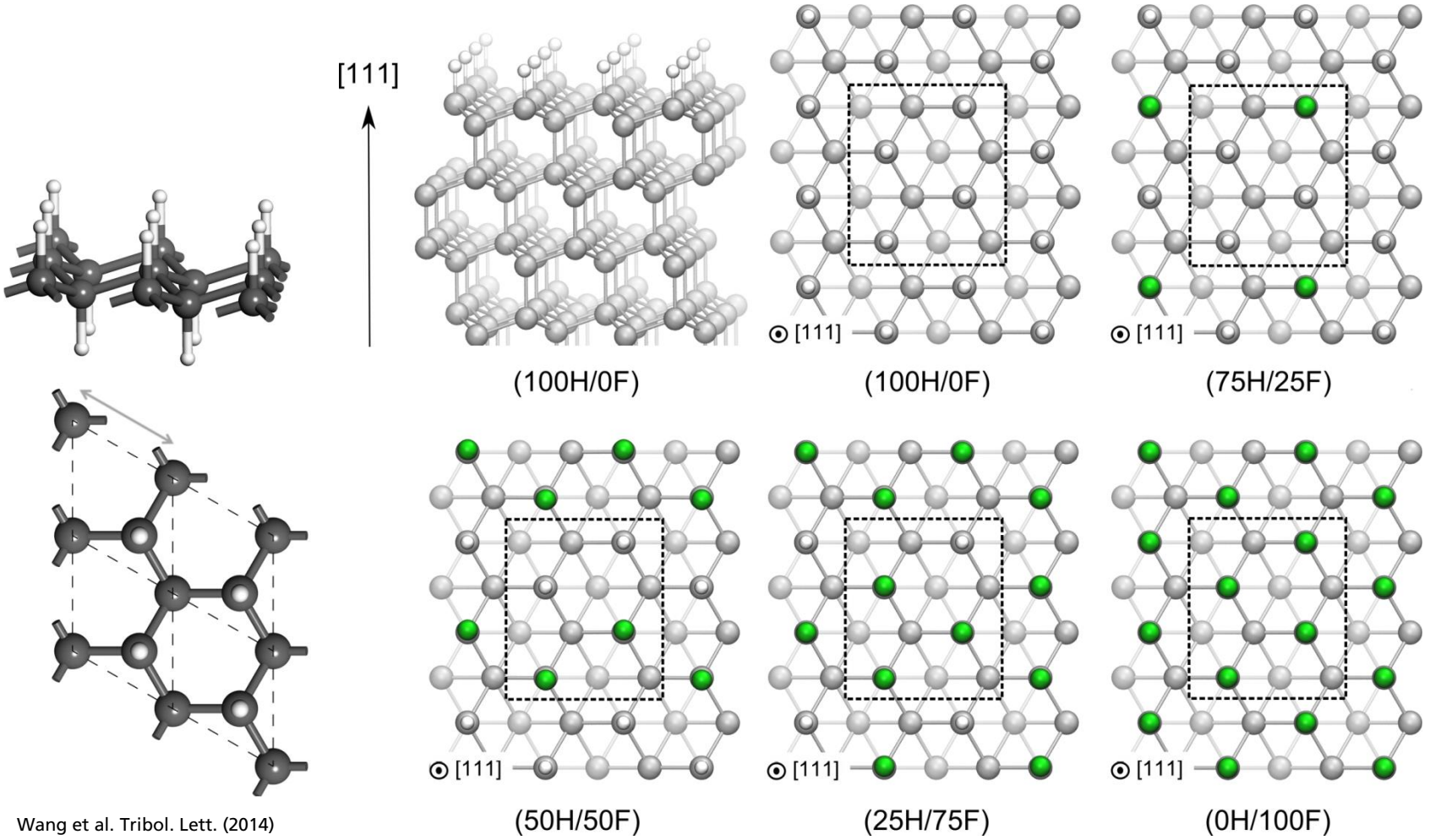


Wang et al., Surf. Sci. (2013)

# Model system

## H/F-terminated C(111)

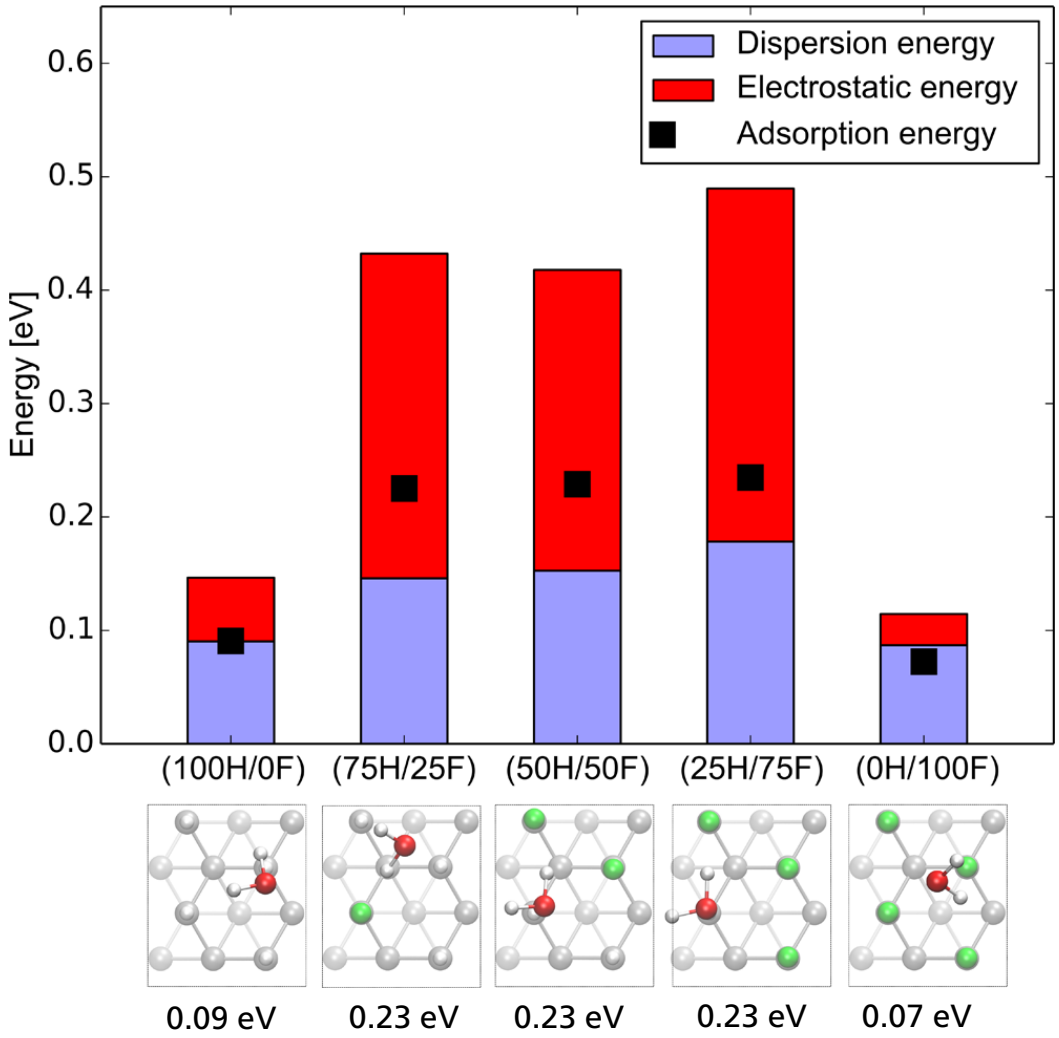
Mayrhofer et al. JACS 138, 4018 (2016)




Wang et al. Tribol. Lett. (2014)

# Water adsorption

## Single $H_2O$ on F/H-terminated C(111): DFT + vdW




DFT

=

PBE

+

Grimme's D2 vdW correction

# Water adsorption

## Single $H_2O$ on F/H-terminated C(111): DFT + vdW

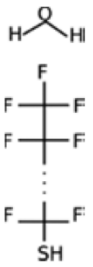
DFT

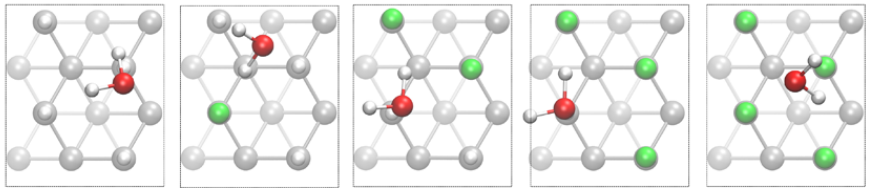
=

PBE

+

Grimme's D2 vdW correction

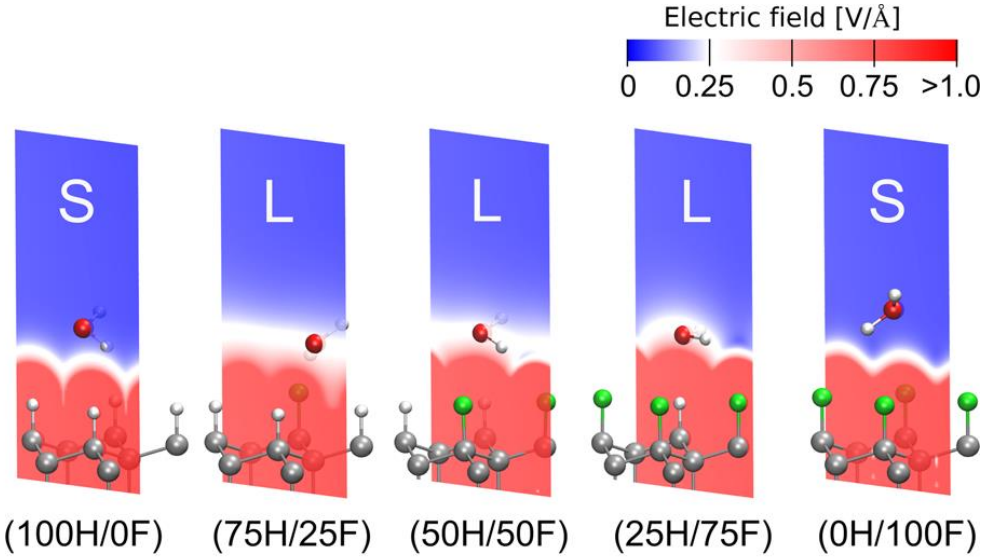
| | $C_{12}H_{25}SH$ | $C_{12}H_{24}FSH$ | $C_{12}F_{24}HSH$ | $C_{12}F_{25}SH$ |
|---|---|---|---|---|
| |  |  |  |  |
| $E_{ad}$ | 0.06 eV | 0.21 eV | 0.18 eV | 0.05 eV |
| $E_{disp}$ | 0.05 eV | 0.05 eV | 0.07 eV | 0.05 eV |
| $E_{elst}$ | 0.05 eV | 0.26 eV | 0.25 eV | 0.03 eV |

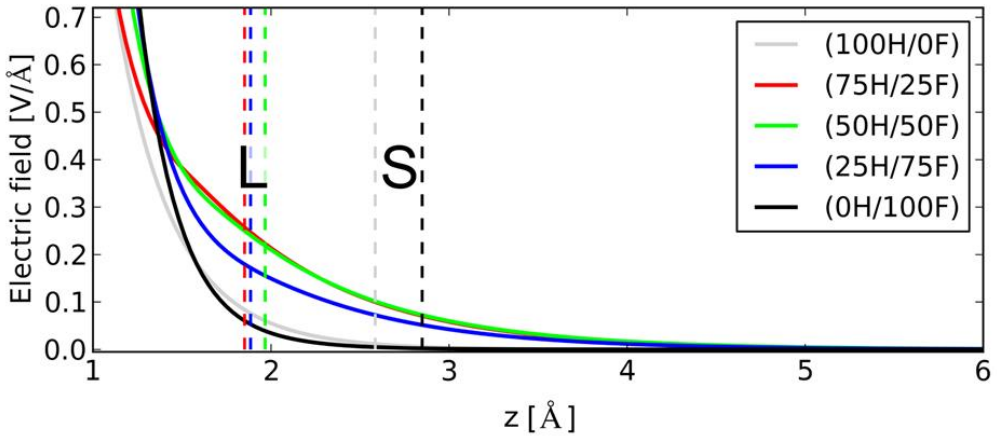


0.09 eV 0.23 eV 0.23 eV 0.23 eV 0.07 eV

# Water adsorption

## Near-surface electric field



# Polar hydrophobicity

## A dipole lattice model for the electric field

F$^{-0.2}$ H$^{+0.09}$

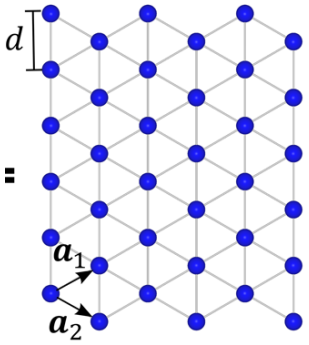
C$^{+0.2}$ C$^{-0.09}$

$$\boldsymbol{E} = \frac{\sigma}{2\varepsilon_0} \sum_{l,m\neq 0} \frac{e^{-|\boldsymbol{G}_{l,m}||z-z_{up}|} - e^{-|\boldsymbol{G}_{l,m}||z-z_{low}|}}{\boldsymbol{G}_{l,m}} \times \begin{pmatrix} -sin(\boldsymbol{G}_{l,m}\boldsymbol{r})G_{l,mx} \\ -sin(\boldsymbol{G}_{l,m}\boldsymbol{r})G_{l,my} \\ +cos(\boldsymbol{G}_{l,m}\boldsymbol{r})|\boldsymbol{G}_{l,m}| \end{pmatrix}$$

Lennard-Jones & Dent, Trans. Faraday. Soc. 24, 92 (1928)

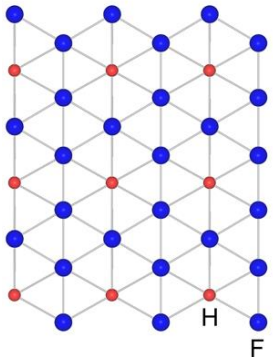
- E decay length along z: $\lambda_{max}=1/|G_{min}|$
- If decay is shorter than core-core repulsion: no electrostatic interaction

100% case




$$\lambda = \frac{\sqrt{3}}{4}\frac{d}{\pi} \approx 0.14\, d$$

Mixed case

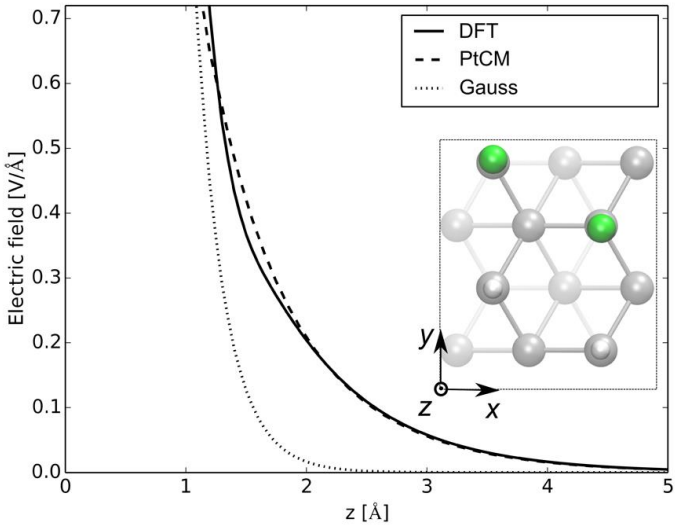


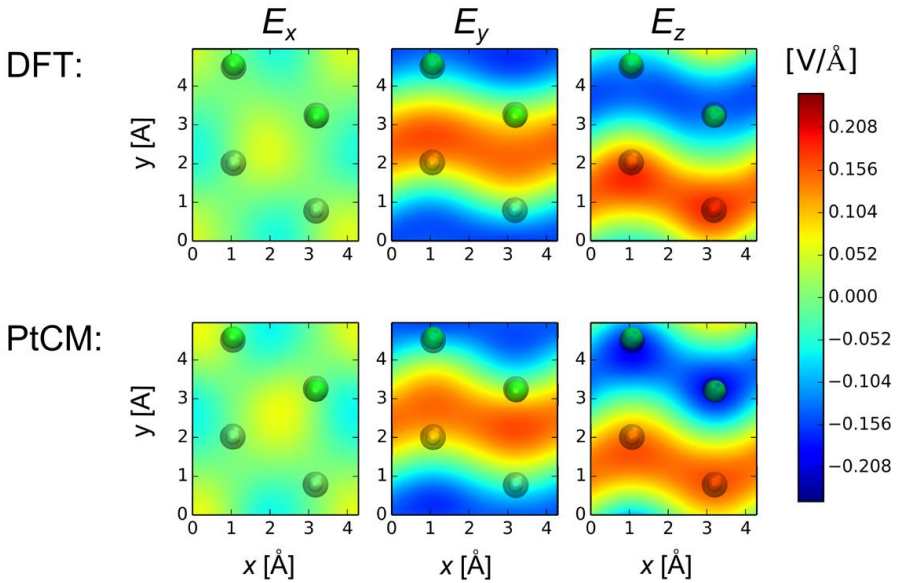

$$\lambda = \frac{d}{\pi} \approx 0.32\, d$$

# Polar hydrophobicity
## A point-charge model

- Charges that best fit the electrostatic field
- $q_{C(x)} = -q_x$ (x = H, F)
- Only $q_H$-$q_F$ matters: we choose $q_F$ = -0.2 e (as in many force fields) → $q_H$ = 0.09 e

(50H/50F)



# MD simulations
## Classical force field

Jorgensen et al. JACS (1996)

**Form of the Force Field**

Bond stretching: $E_{bond} = \sum_{bonds} K_r (r - r_{eq})^2$

Angle bending: $E_{angle} = \sum_{angles} K_\theta (\theta - \theta_{eq})^2$

→ Diamond structure
→ Elastic constants
→ C-H and C-F bonds

Torsion: $E(\phi) = \frac{V_1}{2}[1 + \cos(\phi + f1)] + \frac{V_2}{2}[1 - \cos(2\phi + f2)] + \frac{V_3}{2}[1 + \cos(3\phi + f3)]$

Non-bonded: $E_{ab} = \sum_{i}^{on\,a} \sum_{j}^{on\,b} [q_i q_j e^2 / r_{ij} + 4\varepsilon_{ij}(\sigma_{ij}^{12} / r_{ij}^{12} - \sigma_{ij}^{6} / r_{ij}^{6})] f_{ij}$

$f_{ij}$ = 0.5 if i, j are 1,4; otherwise, $f_{ij}$ = 1.0

→ $H_2O$ adsorption energy (50H/50F)

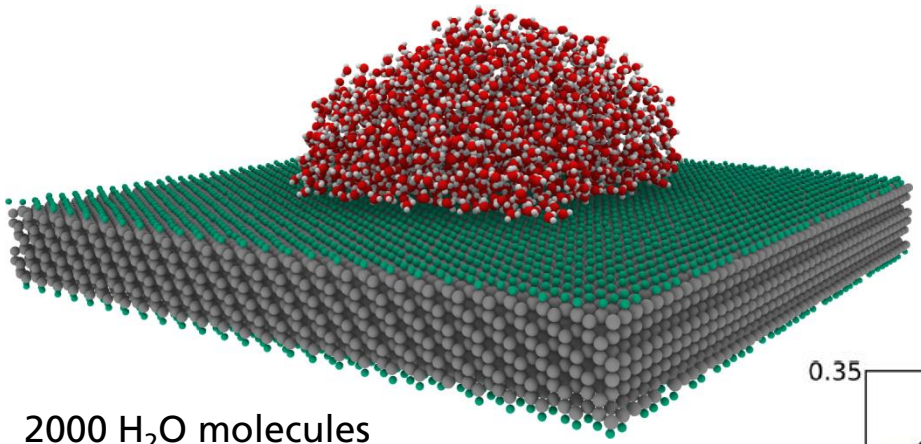
Electrostatic field

| termination | $E_{ad}$(DFT) | $E_{ad}$(OPLS) | $E_{elst}$(OPLS) |
|---|---|---|---|
| (100H/0F) | 0.09 | 0.08 | 0.01 |
| (75H/25F) | 0.23 | 0.24 | 0.21 |
| (50H/50F) | 0.23 | 0.23 | 0.19 |
| (25H/75F) | 0.23 | 0.20 | 0.14 |
| (0H/100F) | 0.07 | 0.06 | 0.00 |

Mayrhofer et al. JACS 138, 4018 (2016)

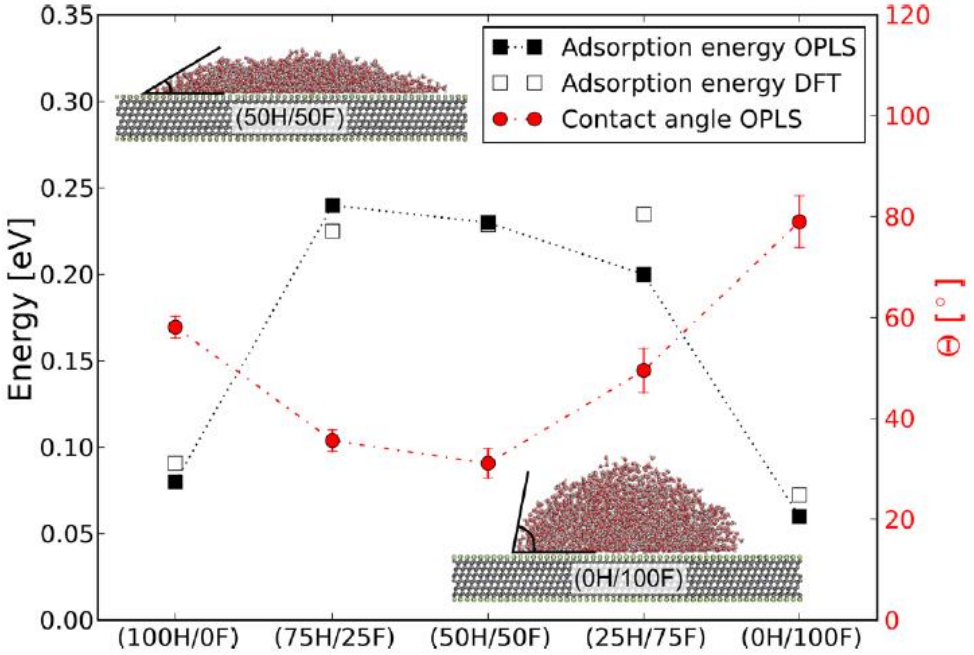
# MD simulations

## Contact angle



2000 $H_2O$ molecules

11.2 x 11.4 x 12.2 $nm^3$



# THANK YOU FOR YOUR ATTENTION!