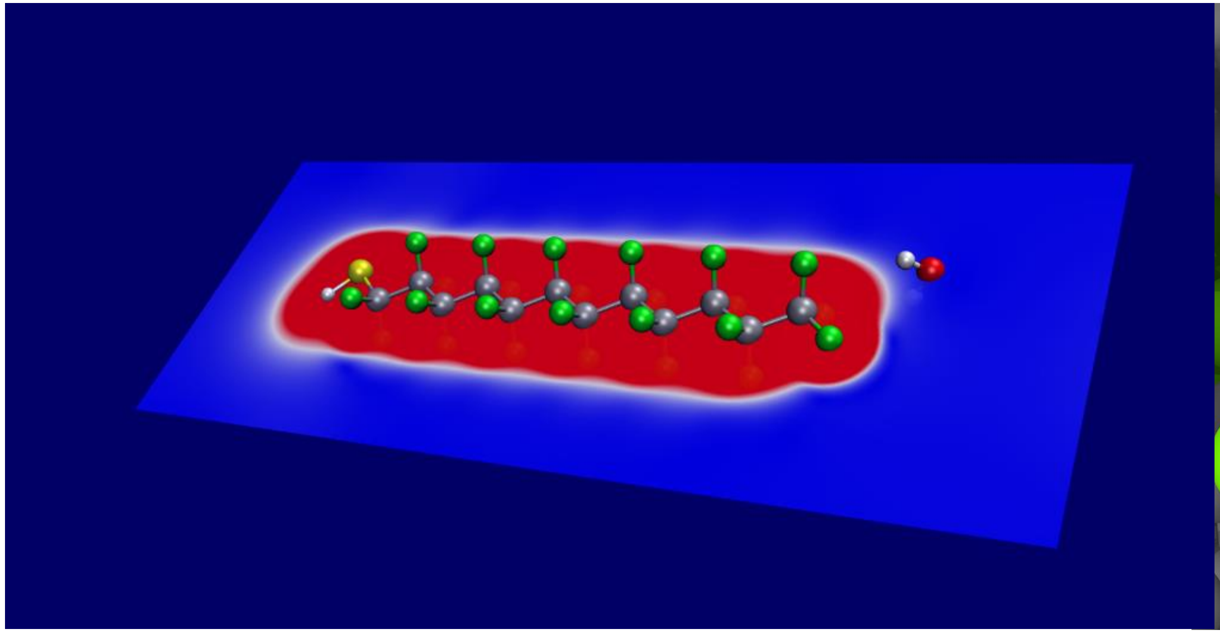
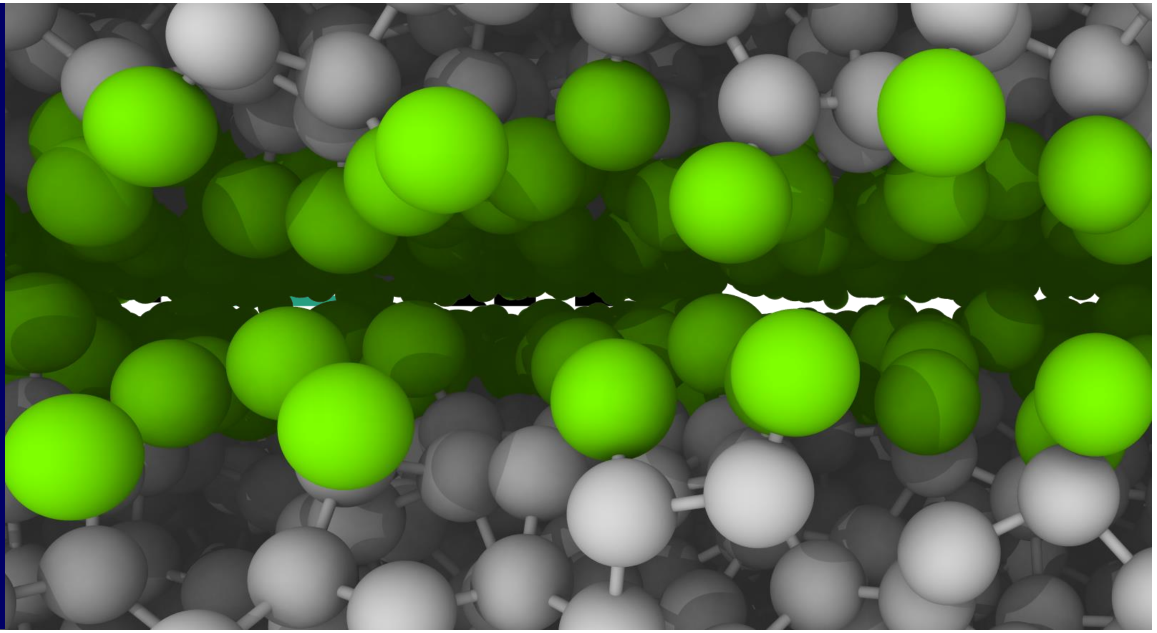
ATOMIC-SCALE INSIGHTS INTO FLUORINATED CARBON COMPOUNDS

Leonhard Mayrhofer, Takuya Kuwahara, Gianpietro Moras, Michael Moseler, Thomas Reichenbach



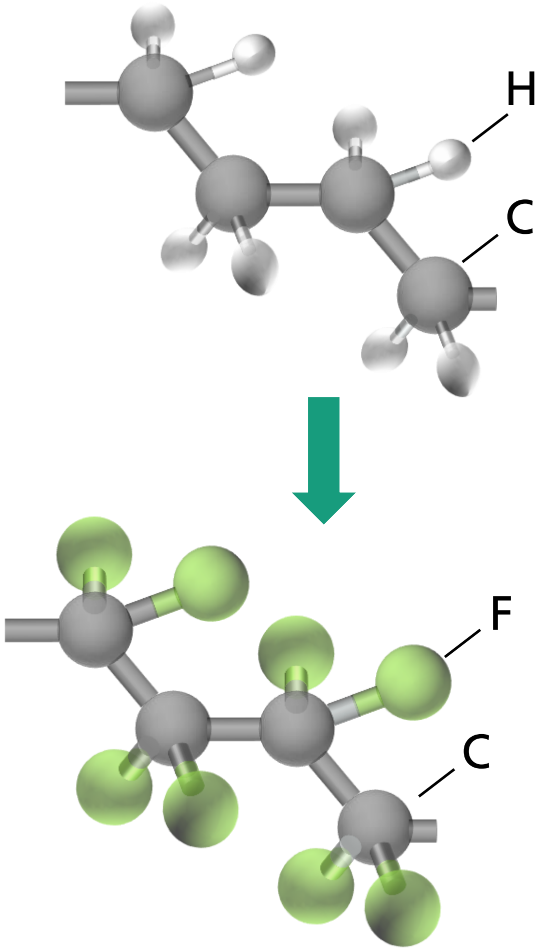
Polar Hydrophobicity



Friction

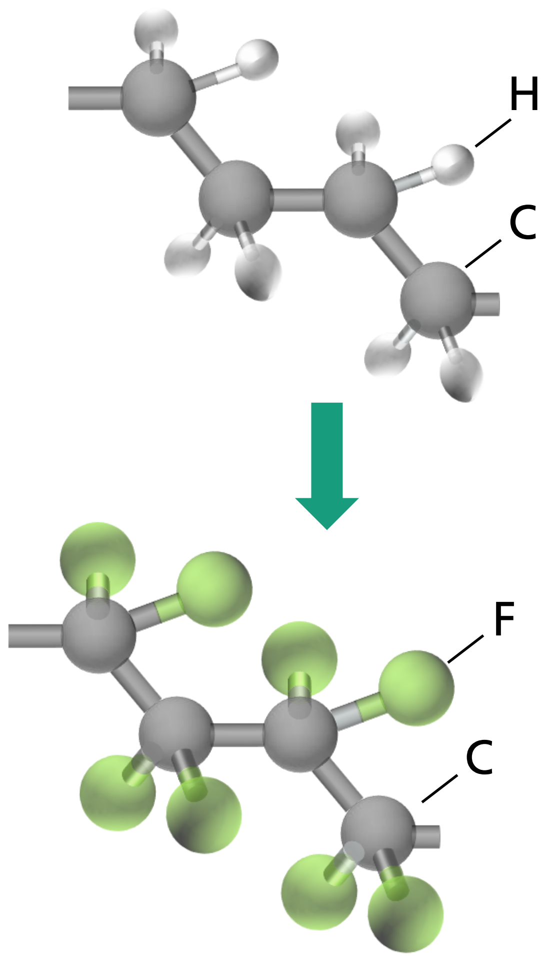
Per- and Polyfluorinated carbon substances

Extremely versatile but …



https://echa.europa.eu/documents/10162/2082415/pfas_infographic_en.pdf

Per- and Polyfluorinated carbon substances
Extremely versatile but …



Industry branches	
Aerospace (7)	Mining (3)
Biotechnology (2)	Nuclear industry
Building and construction (5)	Oil & gas industry (7)
Chemical industry (8)	Pharmaceutical industry
Electroless plating	Photographic industry (2)
Electroplating (2)	Production of plastic and rubber (7)
Electronic industry (5)	Semiconductor industry (12)
Energy sector (10)	Textile production (2)
Food production industry	Watchmaking industry
Machinery and equipment	Wood industry (3)
Manufacture of metal products (6)	
Other use categories	
Aerosol propellants	Metallic and ceramic surfaces
Air conditioning	Music instruments (3)
Antifoaming agent	Optical devices (3)
Ammunition	Paper and packaging (2)
Apparel	Particle physics
Automotive (12)	Personal care products
Cleaning compositions (6)	Pesticides (2)
Coatings, paints and varnishes (3)	Pharmaceuticals (2)
Conservation of books and manuscripts	Pipes, pumps, fittings and liners
Cook- and bakingware	Plastic, rubber and resins (4)
Dispersions	Printing (4)
Electronic devices (7)	Refrigerant systems
Fingerprint development	Sealants and adhesives (2)
Fire-fighting foam (5)	Soldering (2)
Flame retardants	Soil remediation
Floor covering including carpets and floor polish (4)	Sport article (7)
Glass (3)	Stone, concrete and tile
Household applications	Textile and upholstery (2)
Laboratory supplies, equipment and instrumentation (4)	Tracing and tagging (5)
Leather (4)	Water and effluent treatment
Lubricants and greases (2)	Wire and cable insulation, gaskets and hoses
Medical utensils (14)	

https://echa.europa.eu/documents/10162/2082415/pfas_infographic_en.pdf

Environ. Sci.: Processes Impacts 22, 2345-2373 (2020), DOI: 10.1039/D0EM00291G

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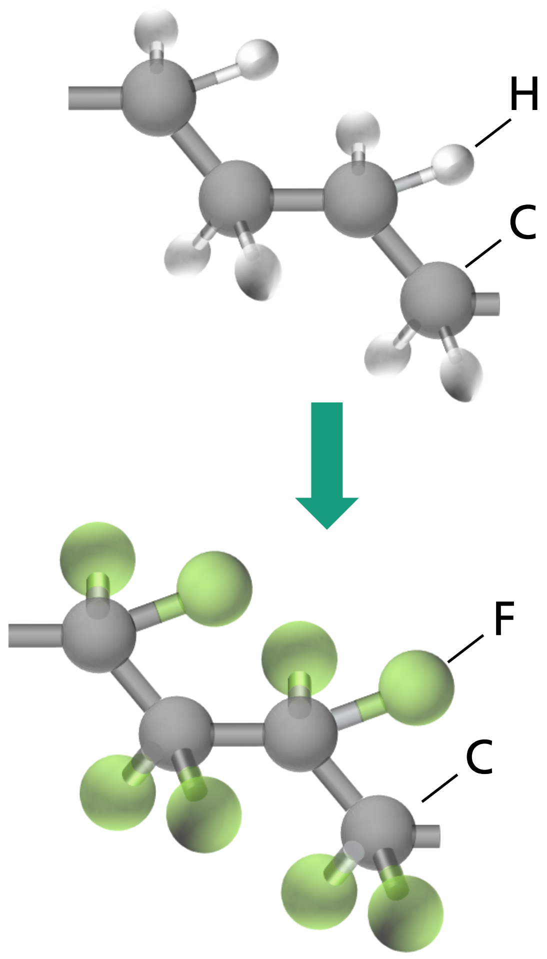
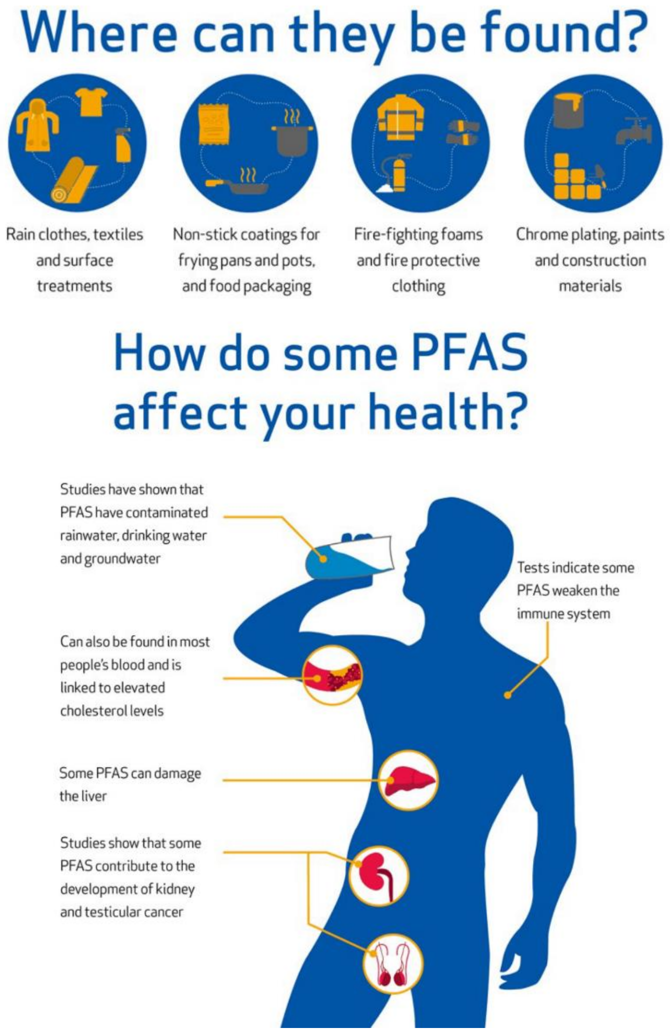
Per- and Polyfluorinated carbon substances

Extremely versatile but often harmful to the environment and health





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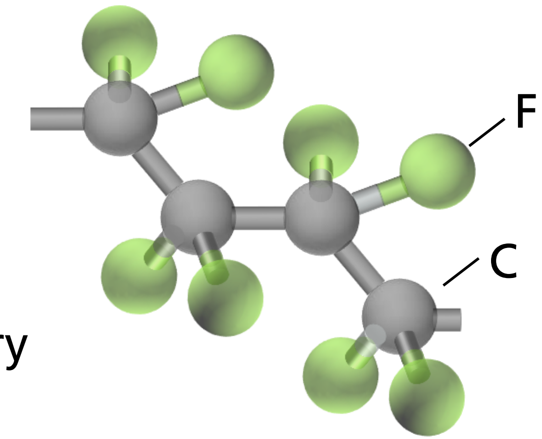
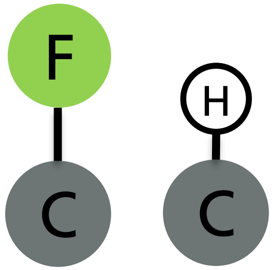
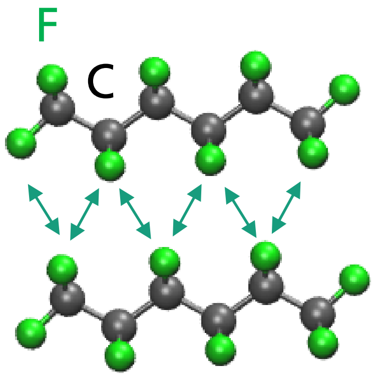
Per- and Polyfluorinated carbon substances
What is so special? Some basics

- F: The most electronegative element
- F: Low Polarizability → small dispersion forces
- C-F: Highly polar bond
- C-F: The strongest single bond of organic chemistry
  → „Forever Chemicals“

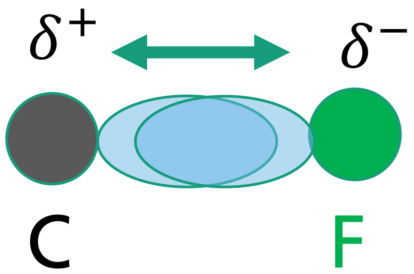




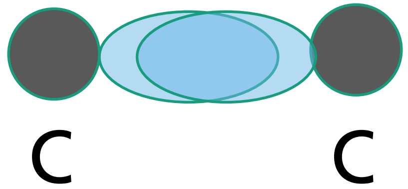
- $|q_F| > |q_H|$
- $m_F > m_H$
- $r_F > r_H$
- $d_{CF} > d_{CH}$
- $k_{CF} > k_{CH}$



$E_{vdW,FF} \approx 0.02\ eV$



$E_{CF} = 4.4\ eV$



$E_{CC} = 3.5\ eV$

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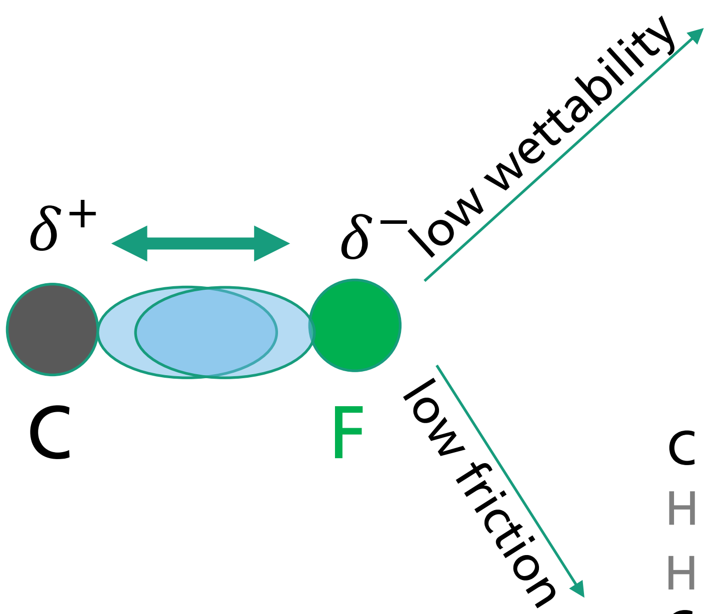
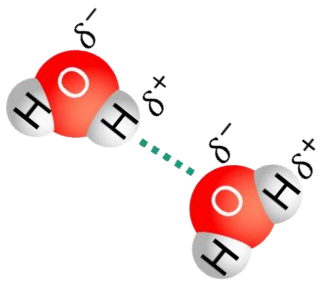
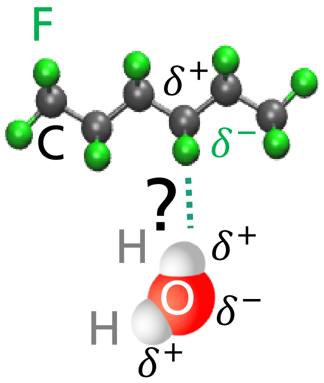
Why are perfluorinated carbons non-wettable and slippery?

What is the role of the C-F bond?



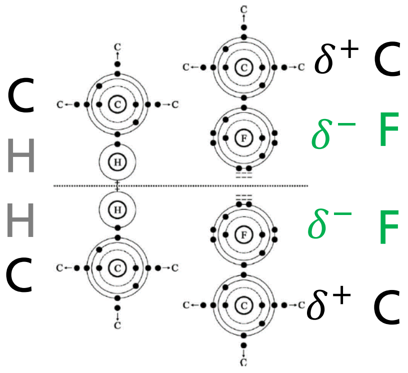


$$E_{\mathrm{H-bond}} \approx 0.2\ eV$$



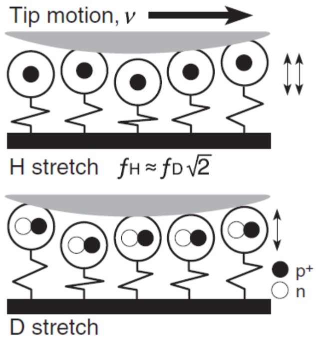
Polar Hydrophobicity

?



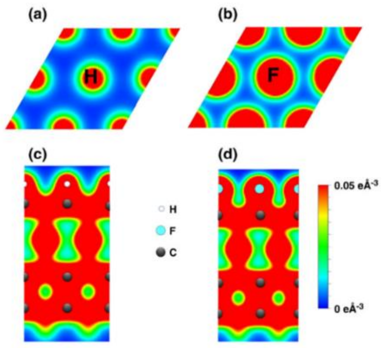
Electrostatic repulsion?

Sung, Int. Journal of Refractory Metals & Hard Materials, 2009



Mass → Frequencies?

Cannara, Carpick, Science 2007



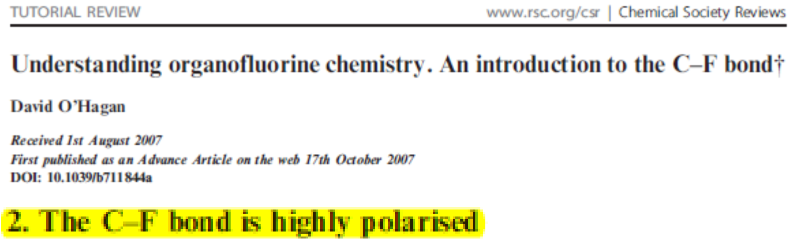
Pauli repulsion → Corrugation?

Wang et al. Surface Science 2013

?

Why are perfluorinated carbons hydrophobic and polar?

The origin of polar hydrophobicity

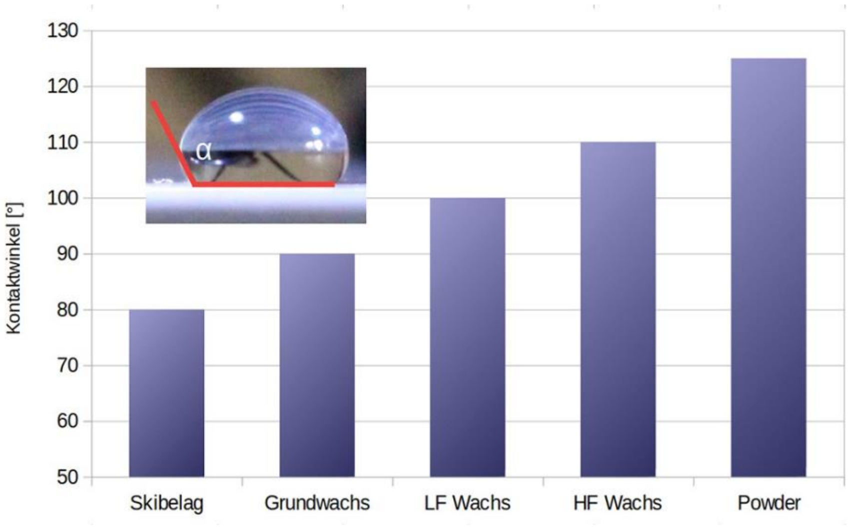


Understanding organofluorine chemistry. An introduction to the C–F bond†

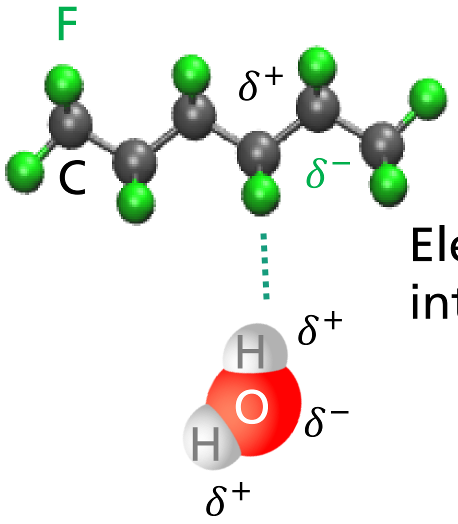
David O'Hagan

Received 1st August 2007
First published as an Advance Article on the web 17th October 2007
DOI: 10.1039/b711844a

2. The C–F bond is highly polarised



© Team Snowstorm



Electrostatic interaction?

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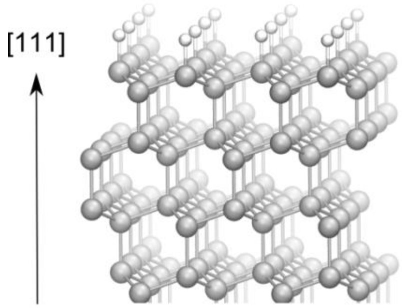
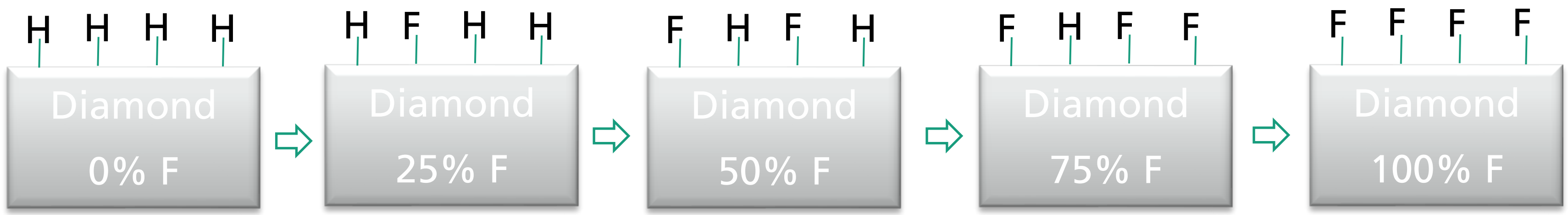
Polar Hydrophobicity – An atomistic investigation

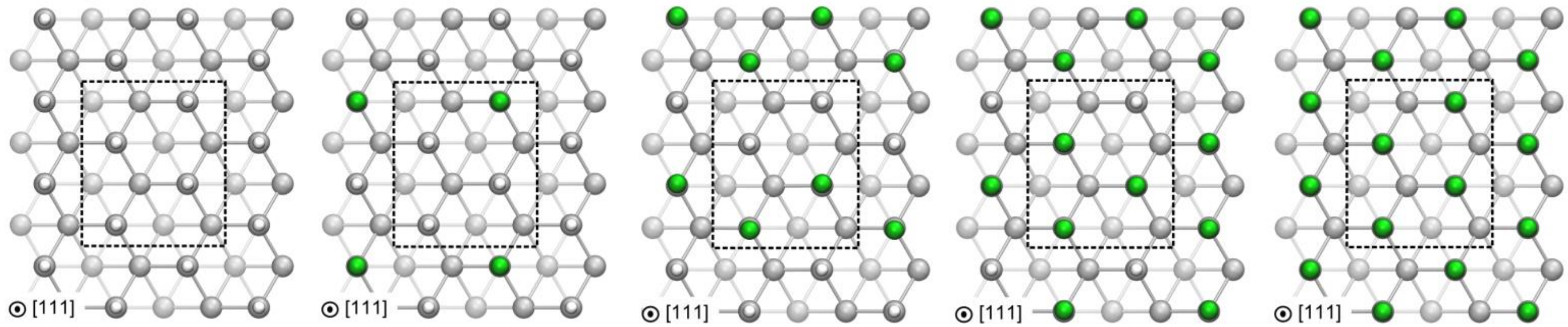
Diamond C(111) as model surface



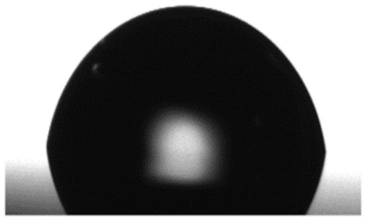
(100H/0F)

- How does an increasing fluorination change the wettability?





(100H/0F) (75H/25F) (50H/50F) (25H/75F) (0H/100F)



or

?

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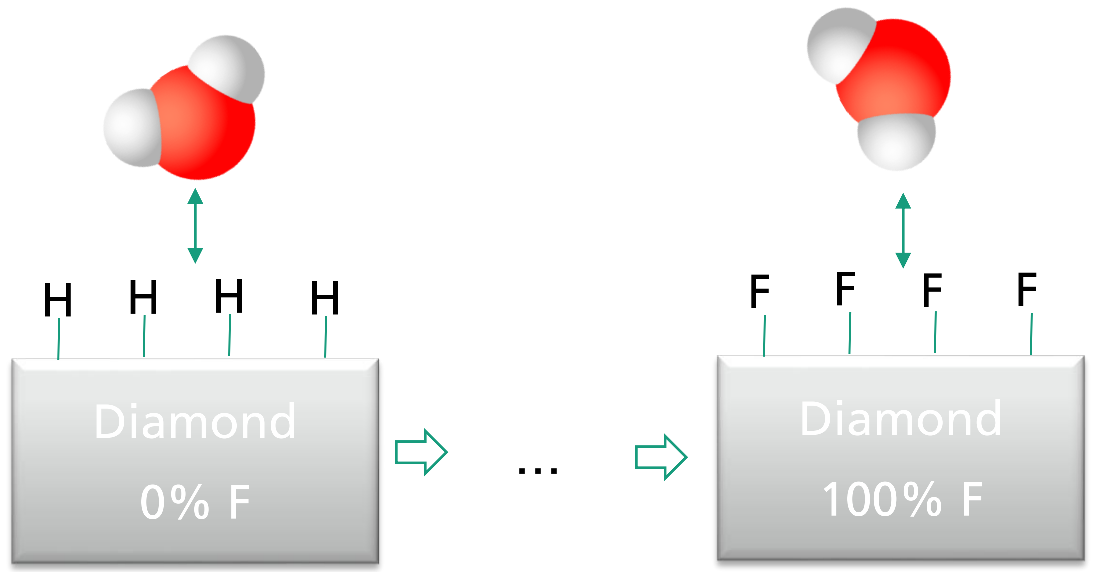
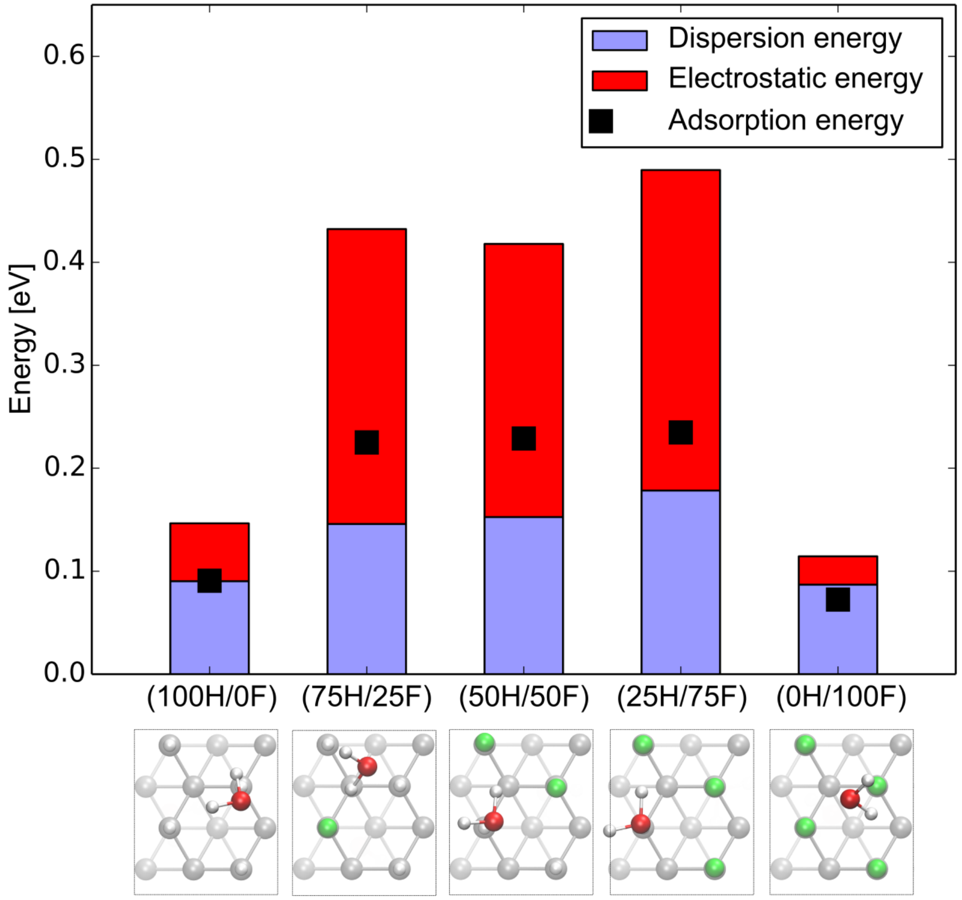
Adsorption of a single water molecule

A surprising result from DFT calculations (PBE + Grimme's D2 correction)





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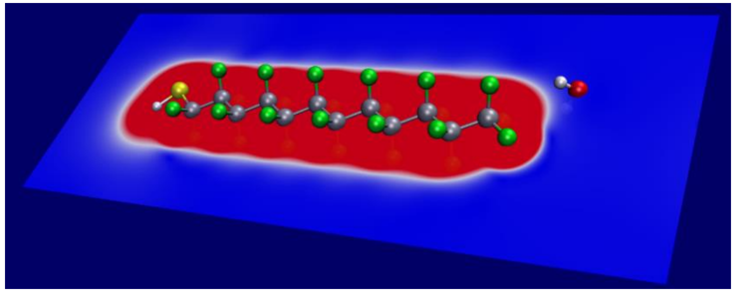
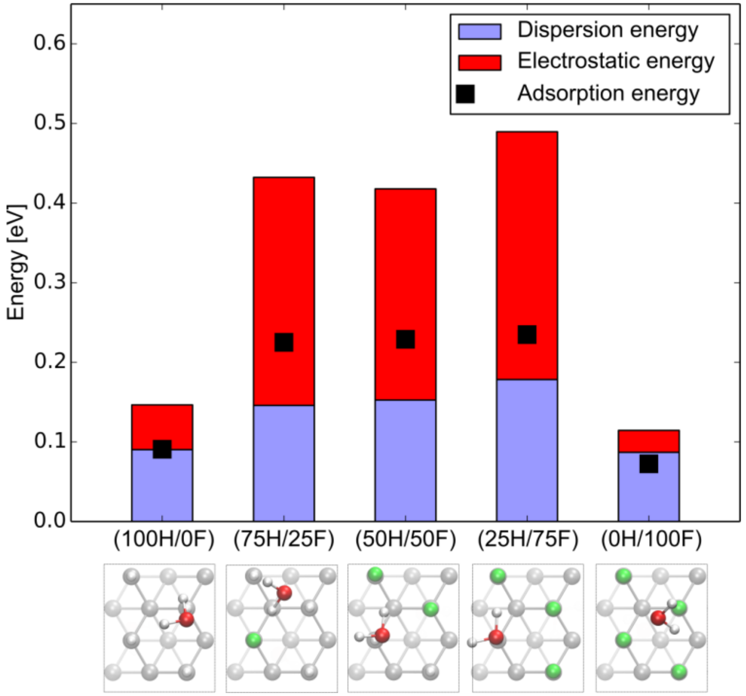
Why partial fluorination increases wettability

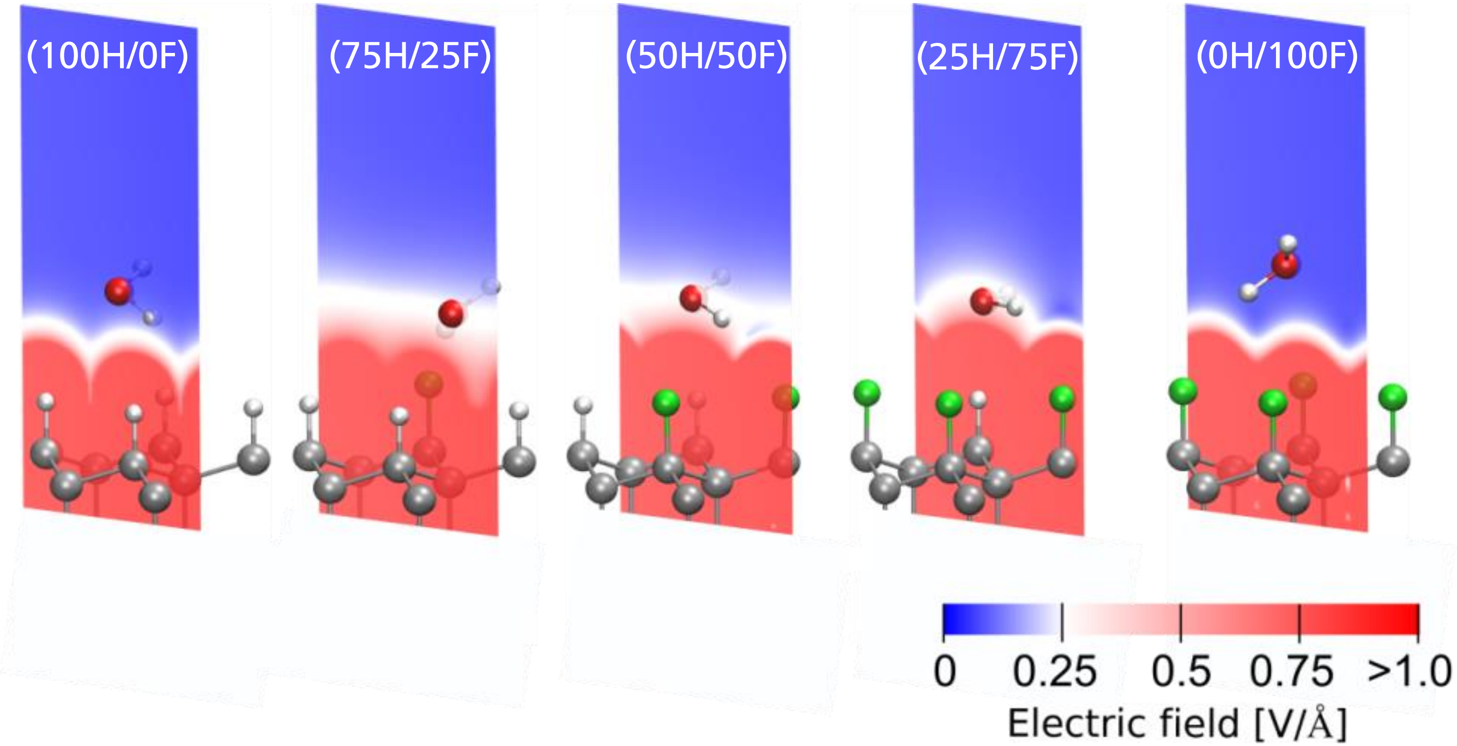
It is all about the range of the surface electric field



Adsorption energy



Electric field strength



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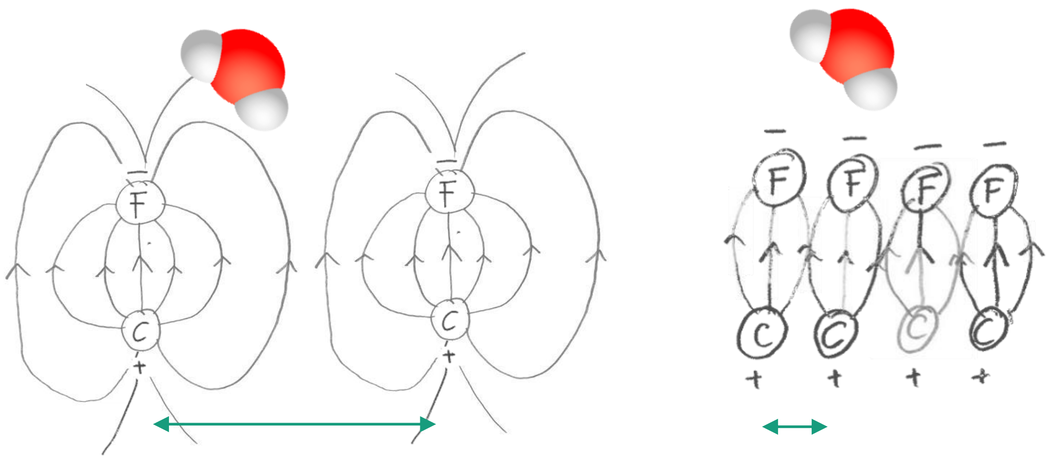
Why the electric field of polar perfluorinated surfaces is confined

It is classical electrostatics

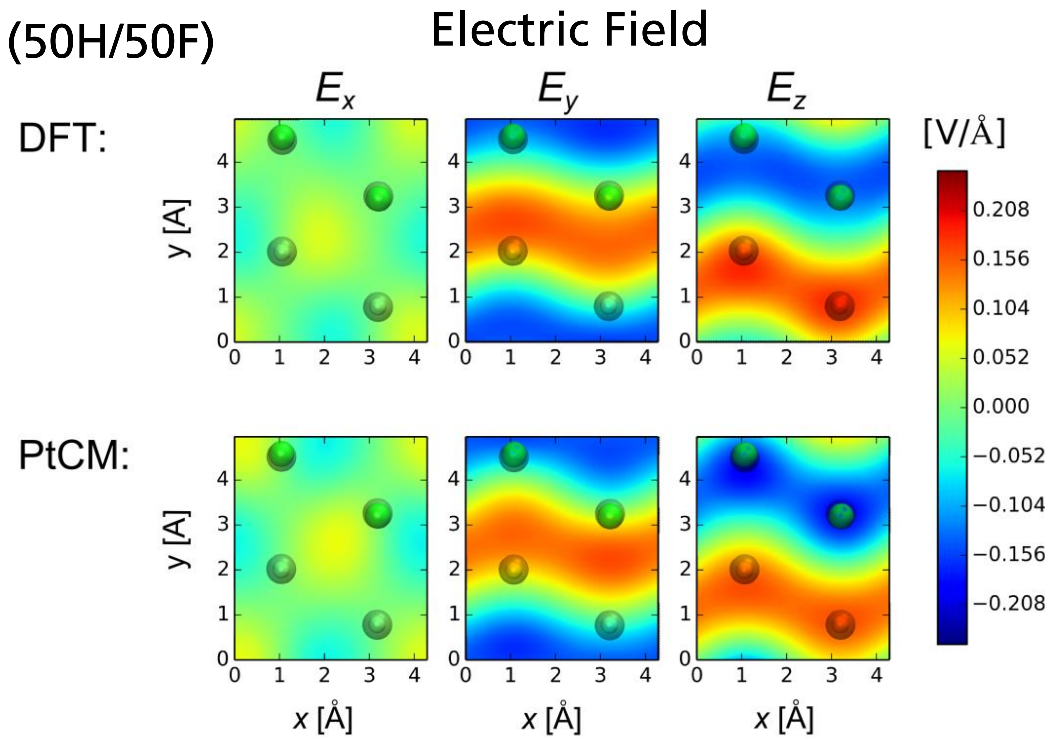
$$\mathbf{E} = \frac{\sigma}{2\varepsilon_0} \sum_{l,m\neq 0} \frac{\boxed{\mathrm{e}^{-|\mathbf{G}_{l,m}||z-z_{\mathrm{up}}|}} - \boxed{\mathrm{e}^{-|\mathbf{G}_{l,m}||z-z_{\mathrm{low}}|}}}{|\mathbf{G}_{l,m}|} \begin{pmatrix} -\sin(\mathbf{G}_{l,m}\mathbf{r})G_{l,mx} \\ -\sin(\mathbf{G}_{l,m}\mathbf{r})G_{l,my}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

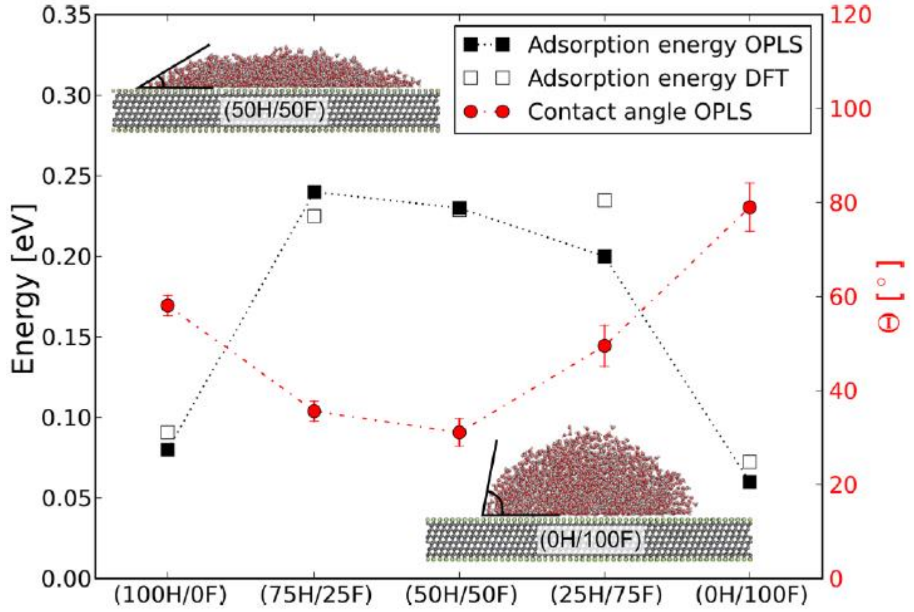


$$|G_{\mathrm{sparse,\,min}}| \sim \frac{1}{a_{\mathrm{sparse}}} \ll |G_{\mathrm{dense,\,min}}| \sim \frac{1}{a_{\mathrm{dense}}}$$

Lennard-Jones, J. E.; Dent, B. M. Trans. Faraday Soc. 24, 92–108 (1928)

From DFT to classical MD
From adsorption energies to contact angles





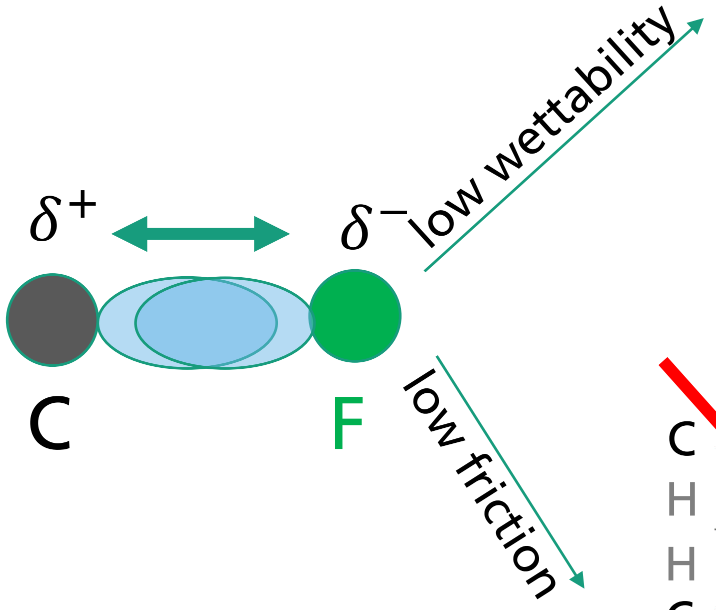
Parametrization of classical OPLS force field with point charges fitted to DFT electrostatics

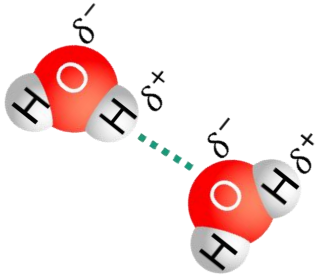
Contact angle directly correlated with water adsorption energy

Mayrhofer, Moras, Mulakaluri, Rajagopalan, Stevens, Moseler, J. Am. Chem. Soc. 138, 4018 (2016)
Fluorine-Terminated Diamond Surfaces as Dense Dipole Lattices: The Electrostatic Origin of Polar Hydrophybicity

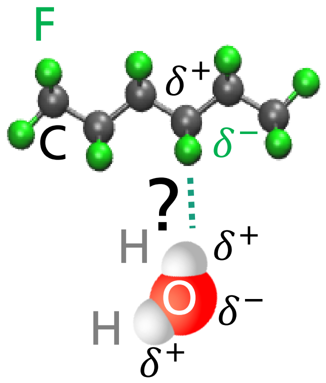
Why are perfluorinated carbons non-wettable and slippery?

What is the role of the C-F bond?





$E_{\mathrm{H-bond}} \approx 0.2\ eV$



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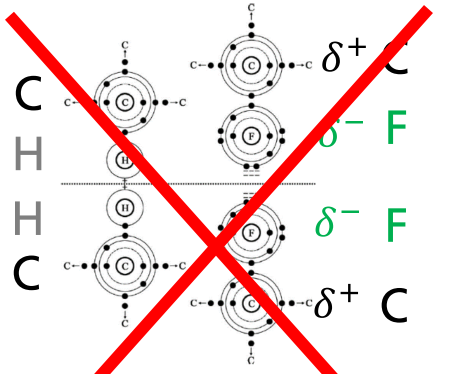

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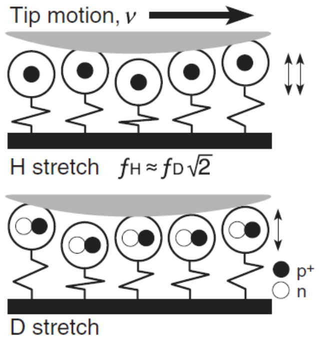
~~Sung, Int. Journal of Refractory Metals & Hard Materials, 2009~~



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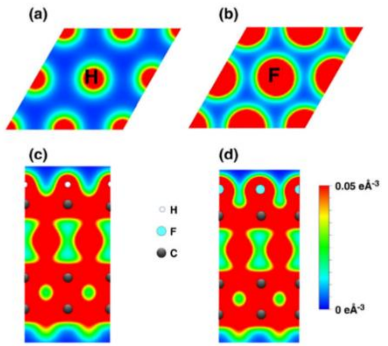
Cannara, Carpick, Science 2007



Pauli repulsion → atom size?

Wang et al. Surface Science 2013

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Non-reactive simulations of H/F-terminated carbon surfaces

Optimized Potential for Liquid Simulations (OPLS)

Jorgensen et al. J. Am. Chem. Soc. (1996)

$$E = E_{\mathrm{bonded}} + E_{\mathrm{nonbonded}} = \mathrm{E_{bonds}} + \mathrm{E_{angles}} + \mathrm{E_{Coulomb}} + \mathrm{E_{Lennard-Jones}}$$

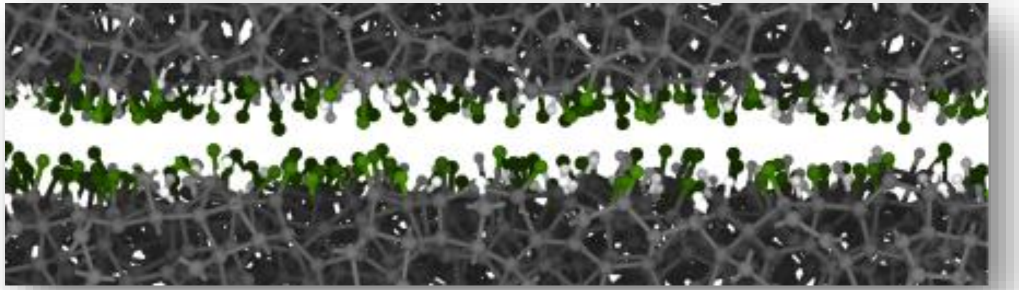
$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

- Diamond/DLC structure
  - Elastic constants
  - C-H and C-F lengths
- C-H and C-F bending and stretching

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

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



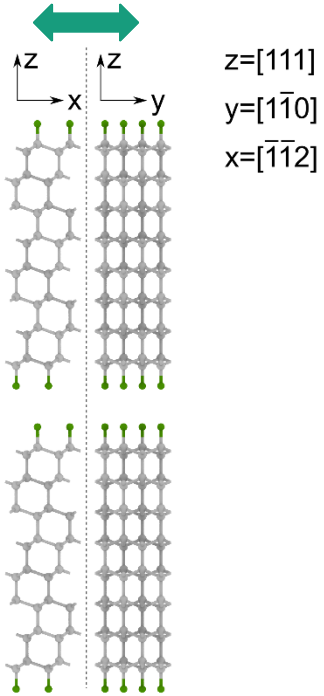
- Contact potential energy surface CPES (Pauli repulsion, vdW interactions)

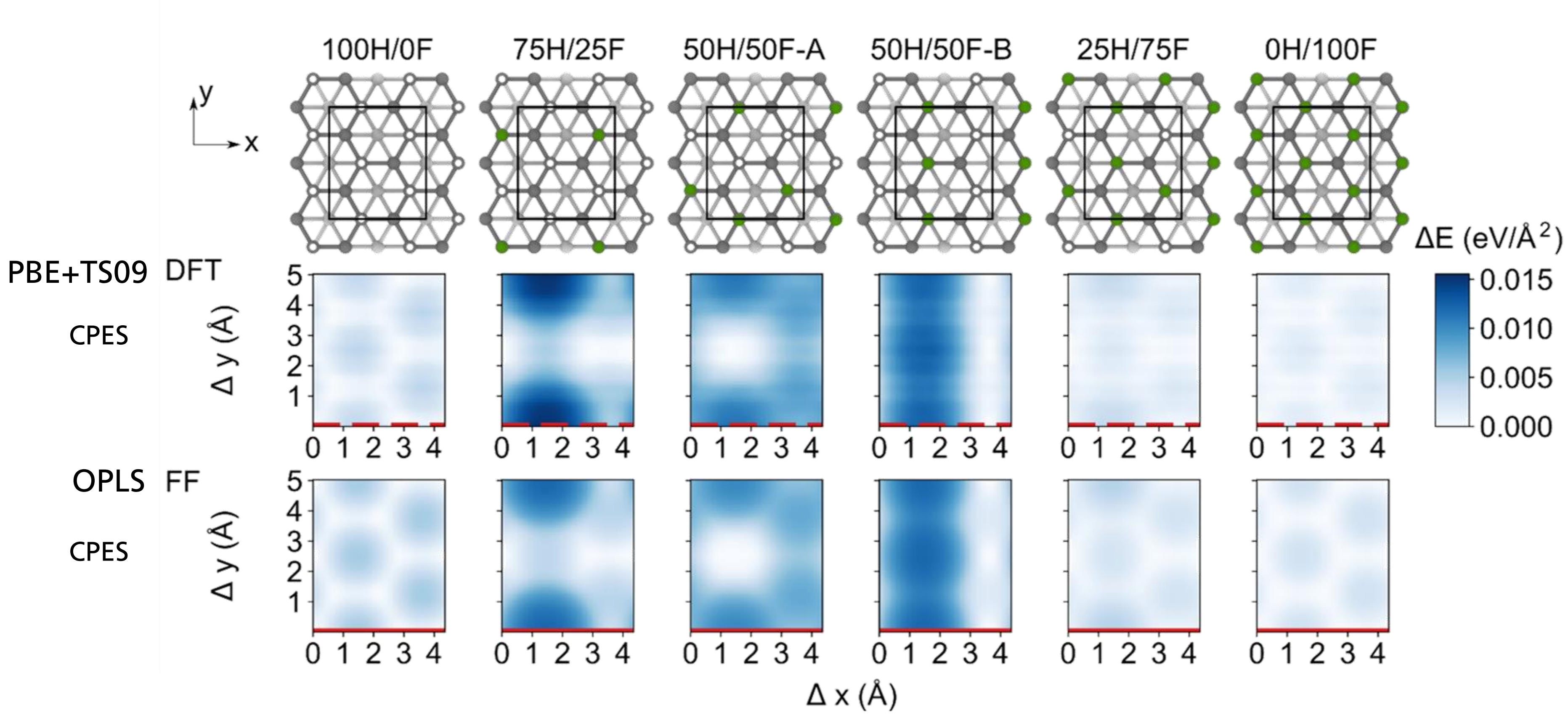
$$E_{ab} = \sum_{i}^{on\,a} \sum_{j}^{on\,b} \left[\boxed{q_i q_j e^2 / r_{ij}} + \boxed{4\varepsilon_{ij} (\sigma_{ij}^{12} / r_{ij}^{12} - \sigma_{ij}^6 / r_{ij}^6)} \right]$$

- Electrostatic field produced by the surface

Non-reactive simulations of H/F-terminated carbon surfaces

Validating the force field: potential energy landscapes for diamond C(111) surfaces





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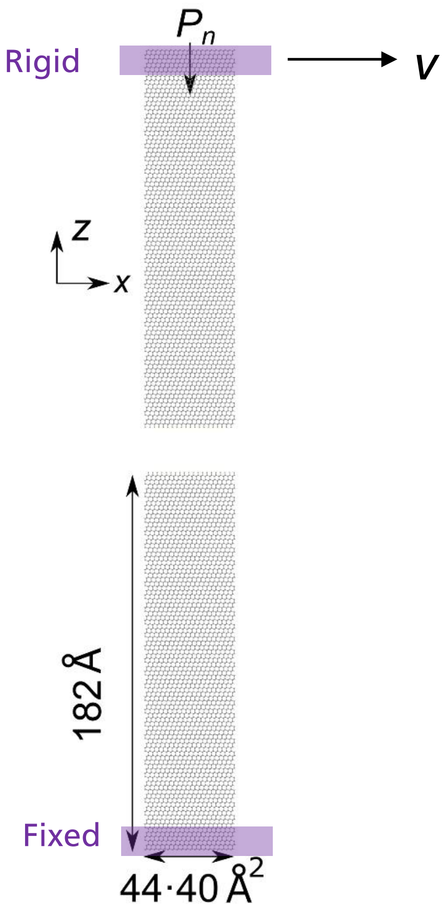
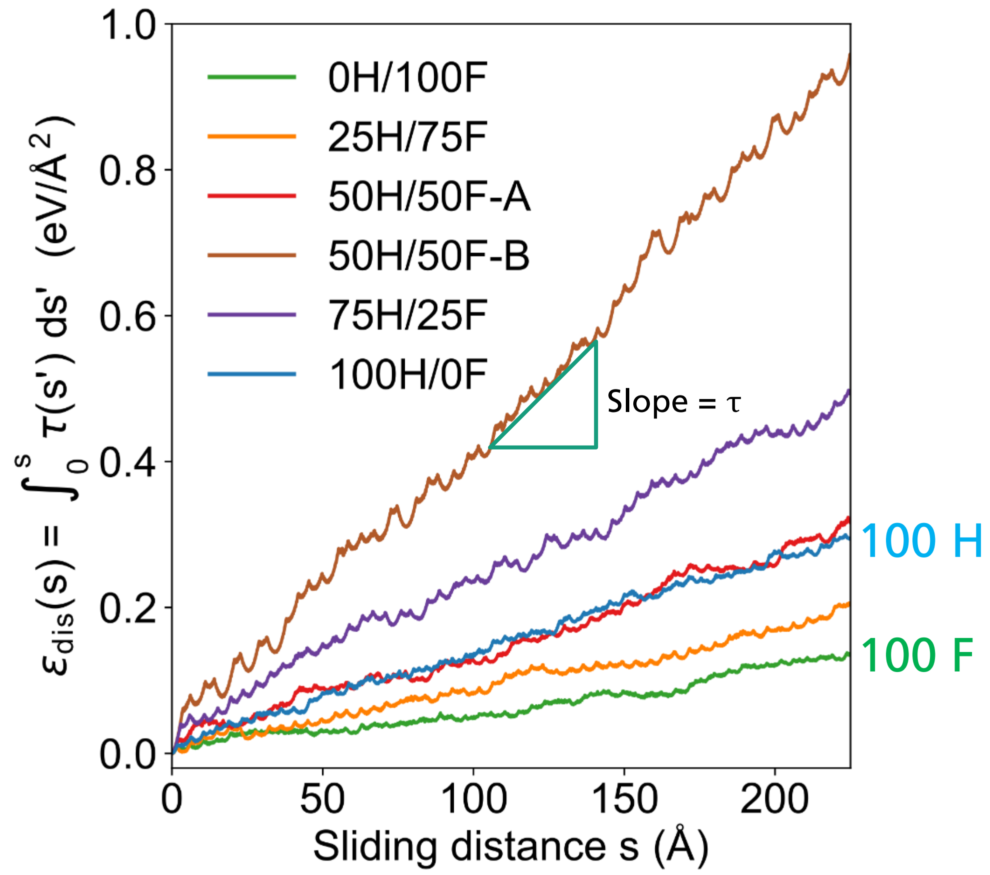
Non-reactive MD simulations

Measuring shear stress



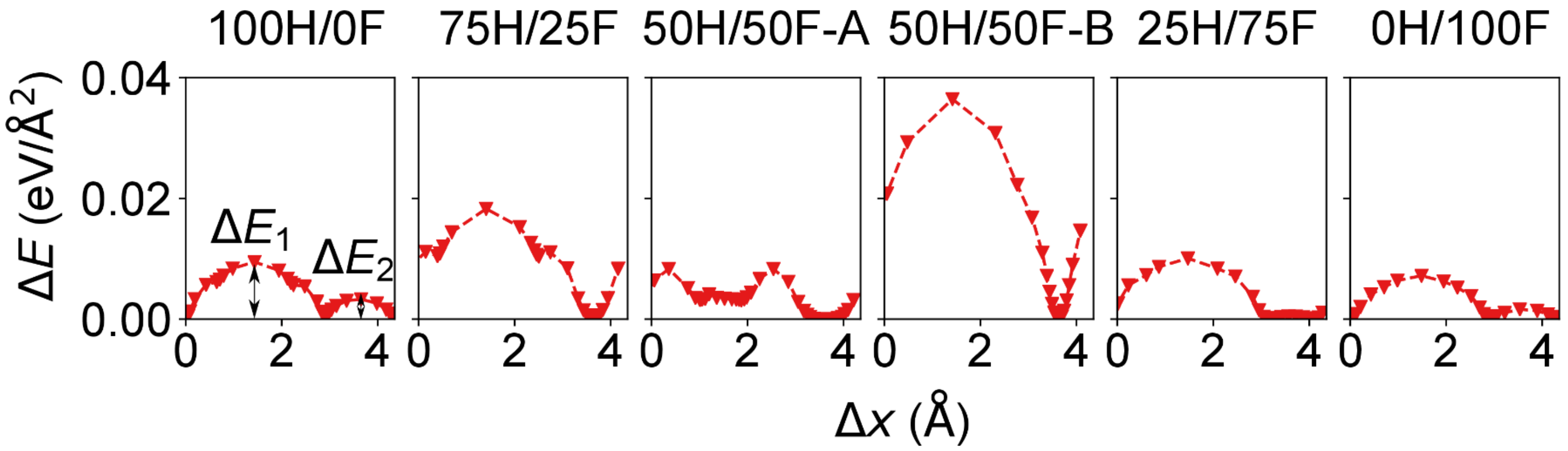


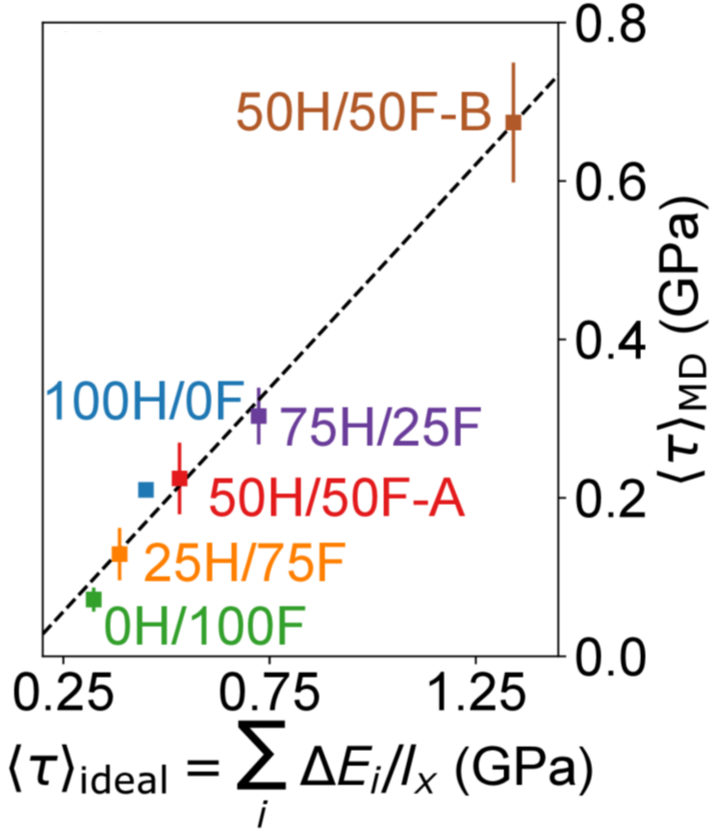
~ 120.000 atoms; $P_N = 5$ GPa; $T = 300\ K$; $v = 10\ m/s$

MD: The system is thermalized before sliding. No thermostat while measuring friction. T is stable

Non-reactive NEB simulations

CPES corrugation under a normal load of 5 GPa versus shear stress





What determines the smoothness of the CPES corrugation?

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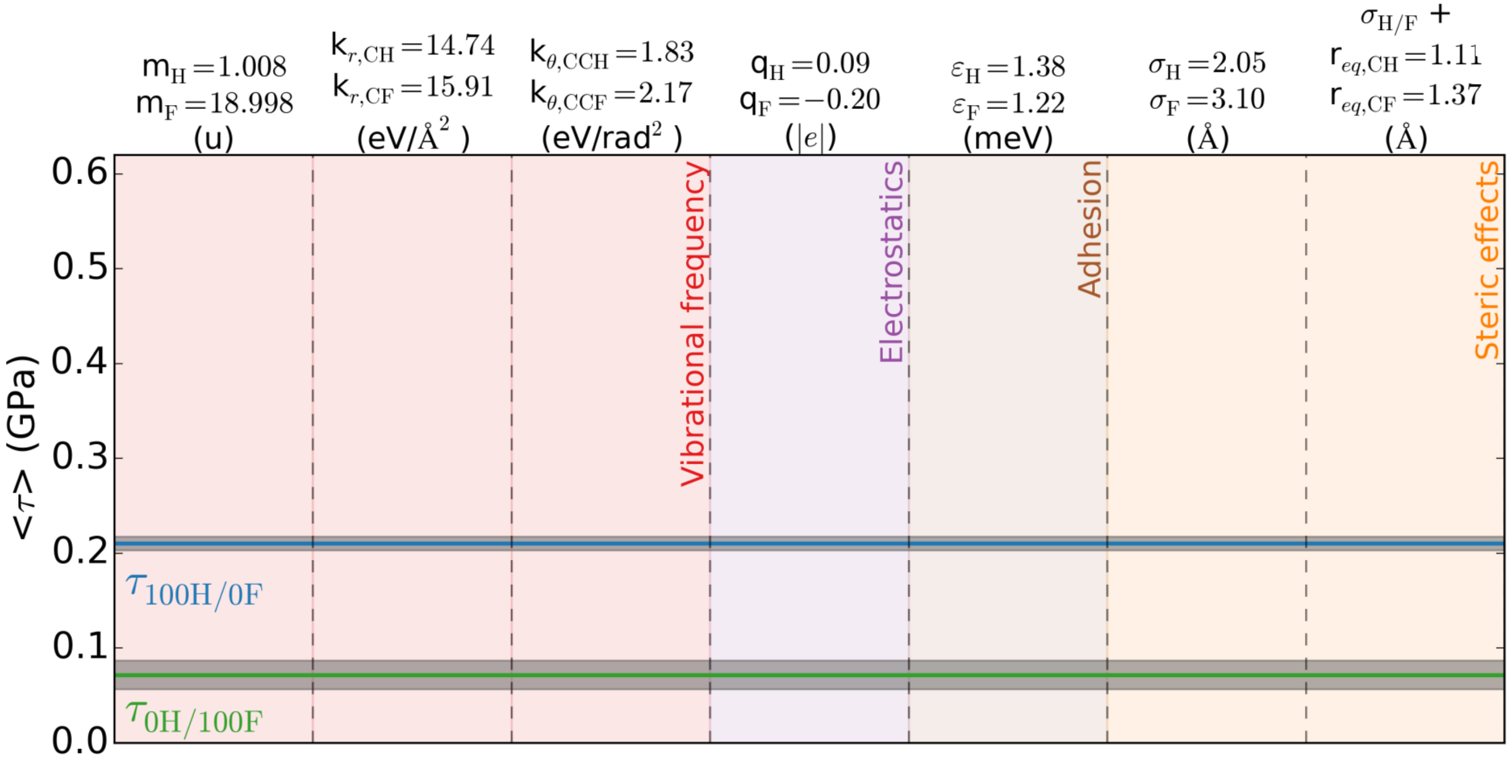
Non-reactive MD simulations

Disentangling vibrational, electrostatic and steric effects

100H/0F vs. 0H/100F



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

$$E_{ab} = \sum_i^{on\,a} \sum_i^{on\,b} [q_i q_j e^2 / r_{ij} + 4\varepsilon_{ij}(\sigma_{ij}^{12} / r_{ij}^{12} - \sigma_{ij}^6 / r_{ij}^6)]$$

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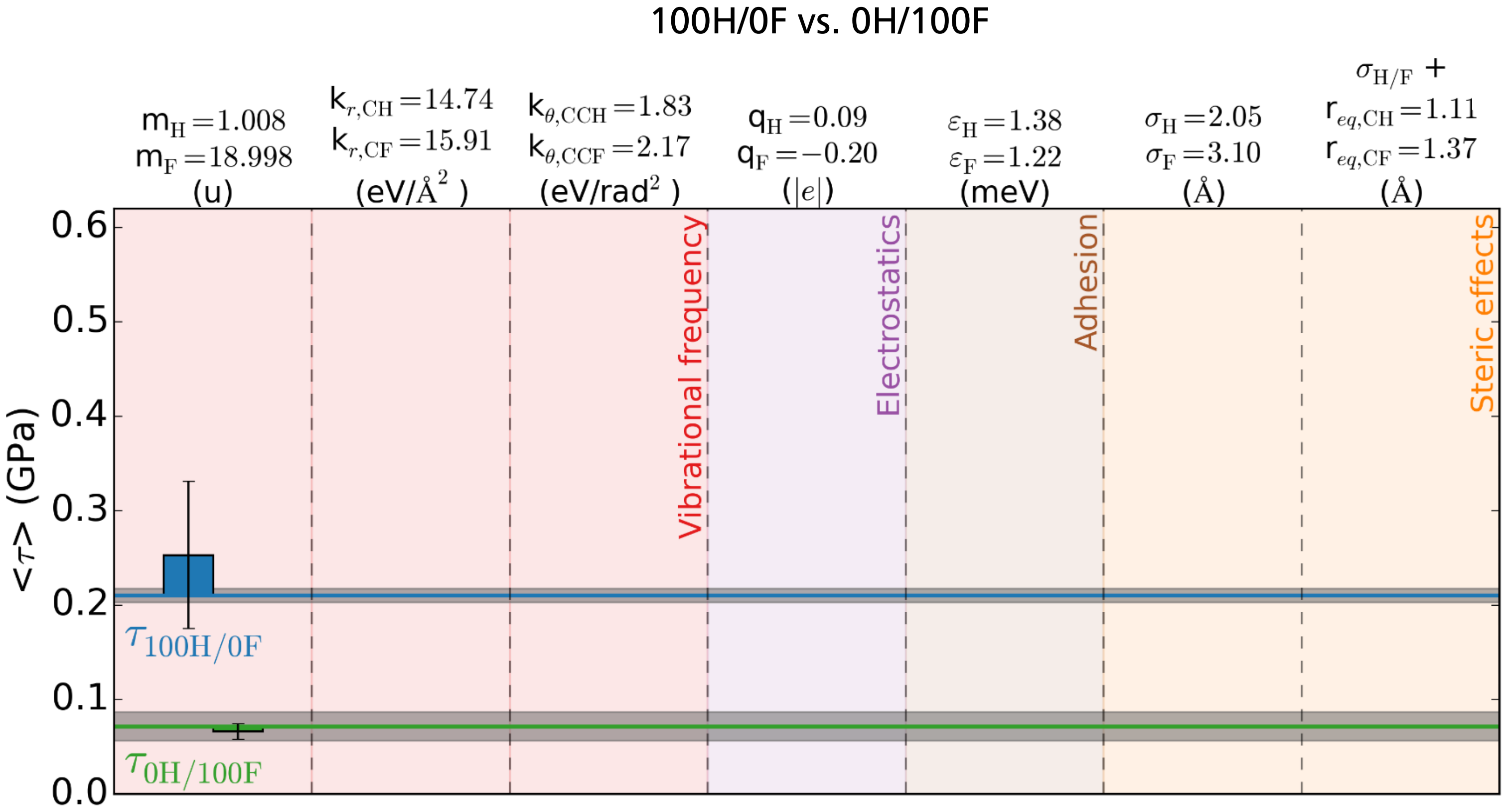
Non-reactive MD simulations

Disentangling vibrational, electrostatic and steric effects



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

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

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

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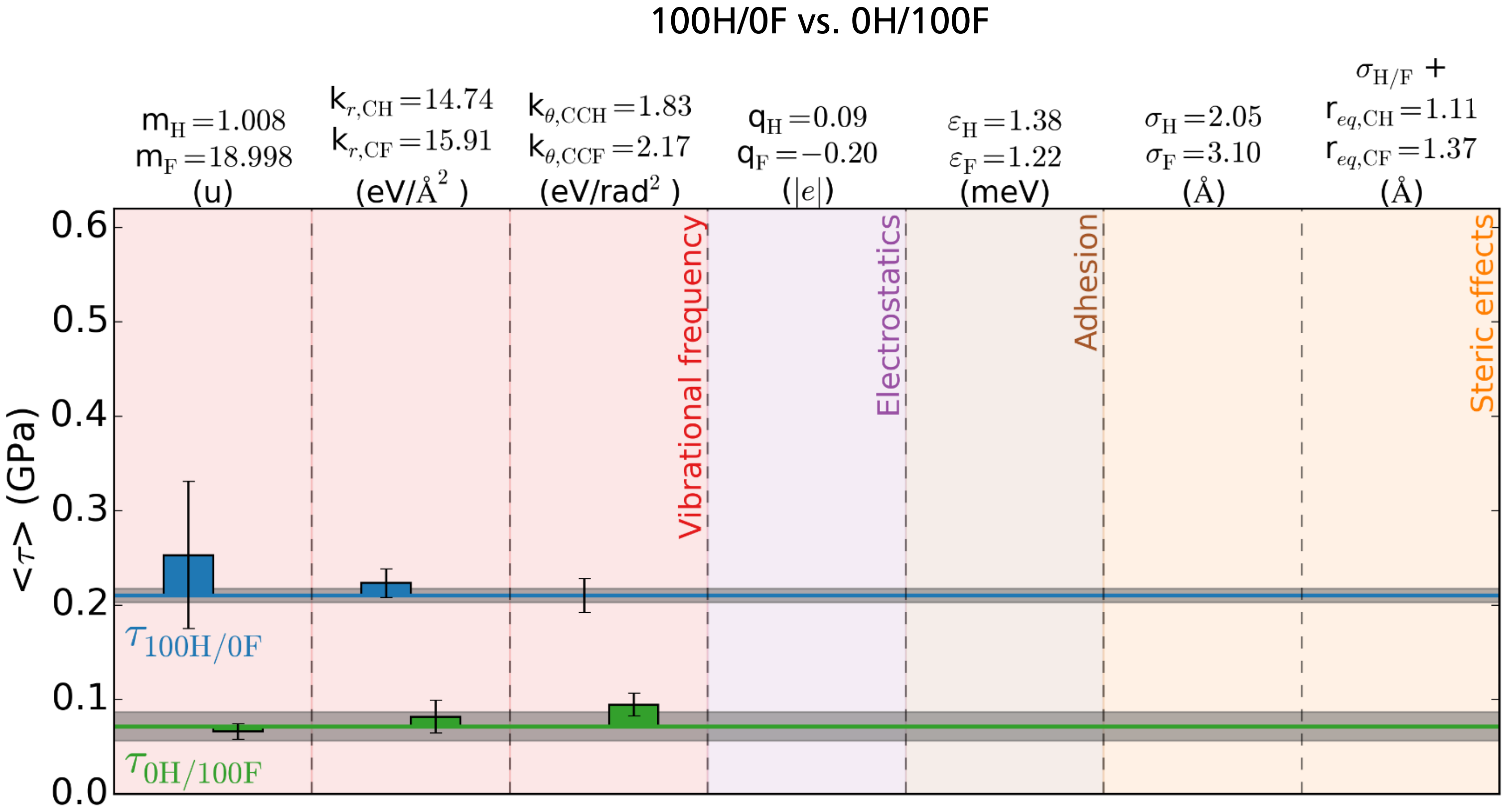

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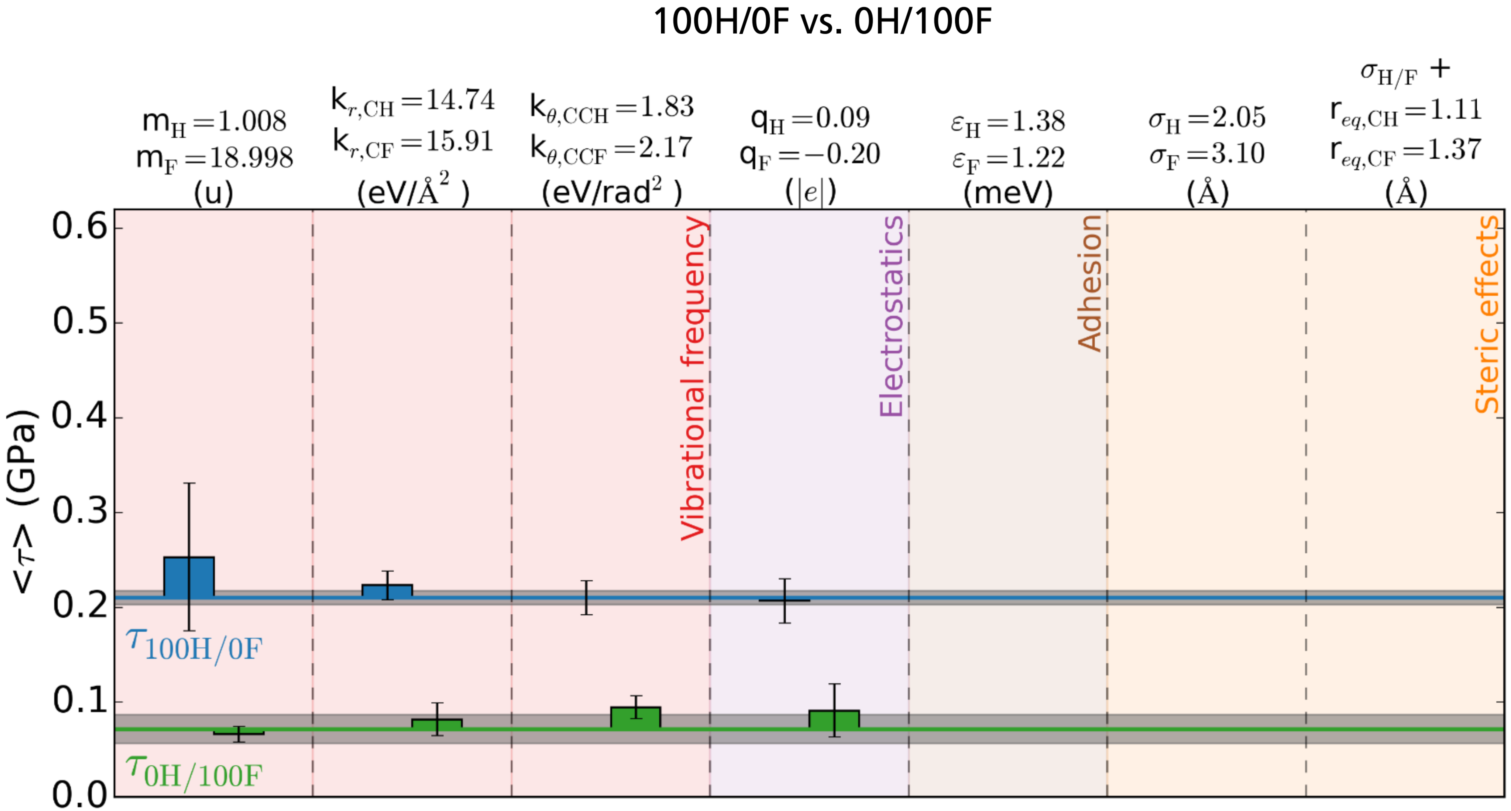

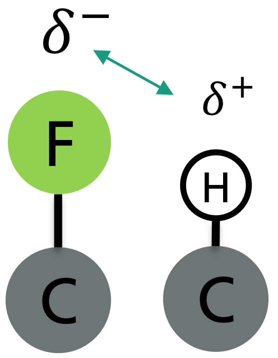

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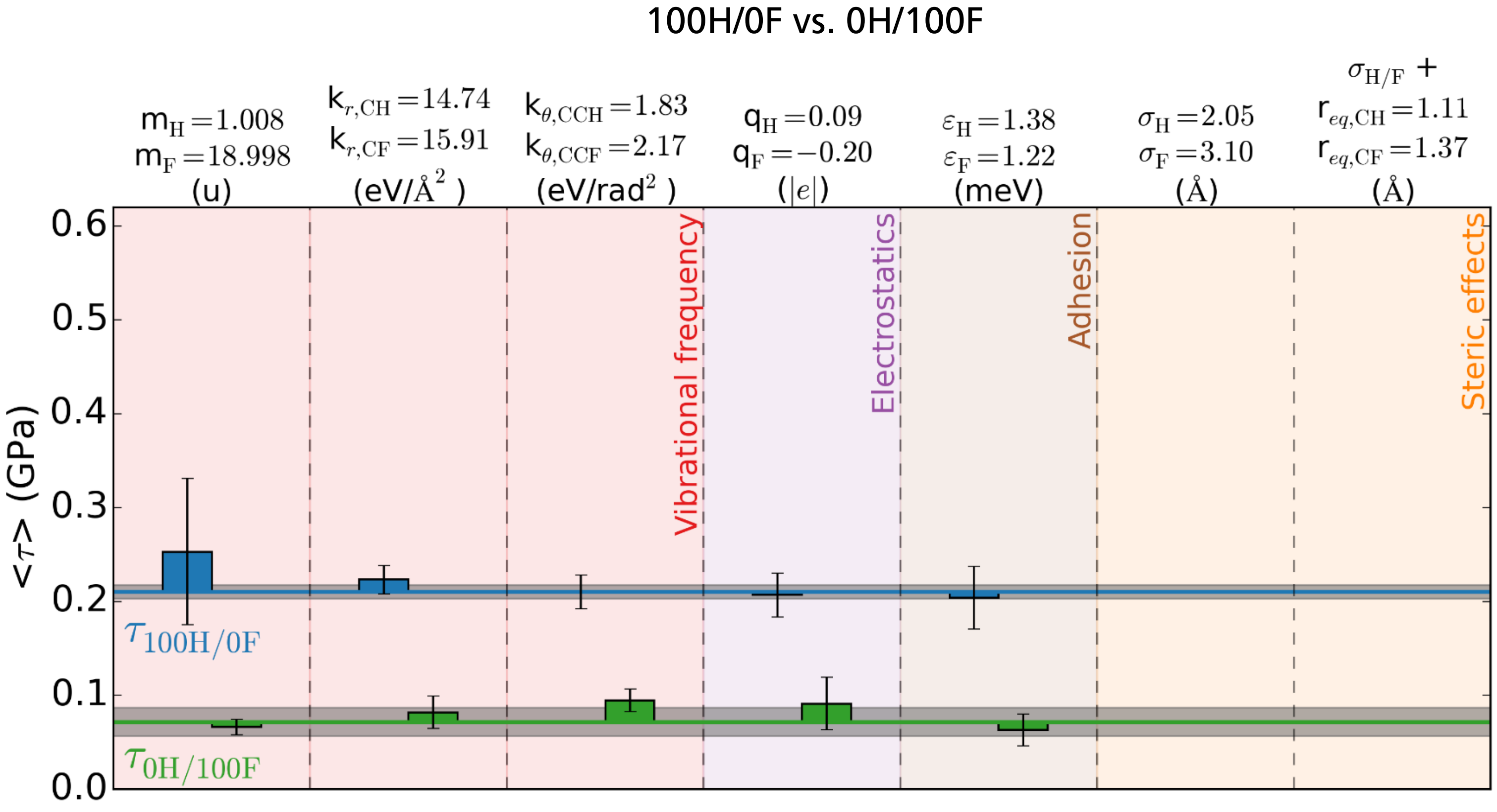

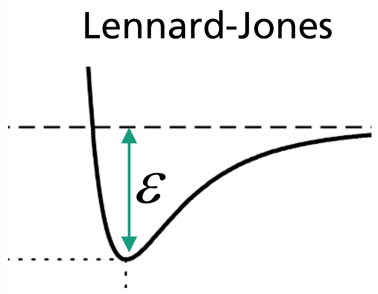

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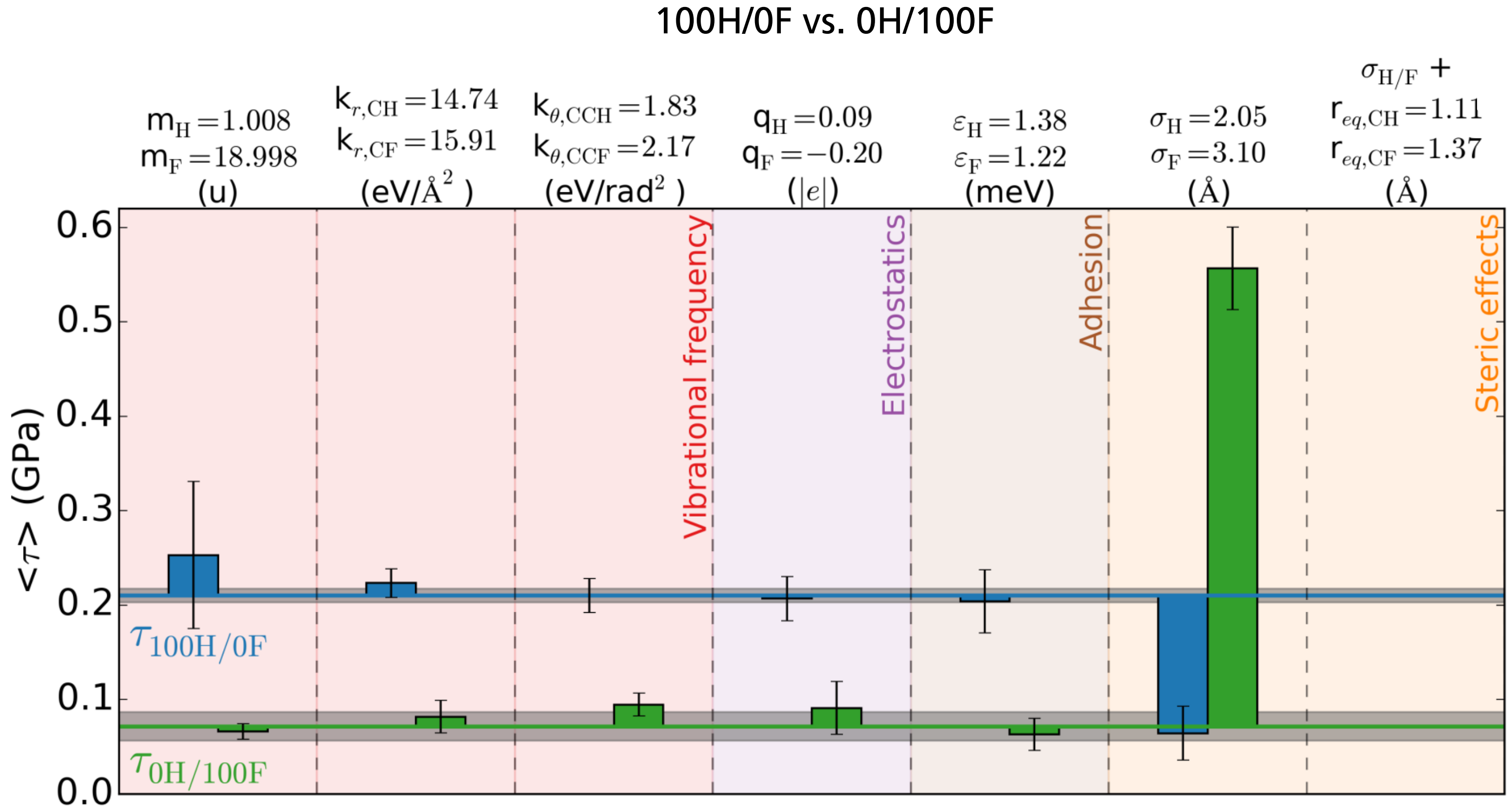

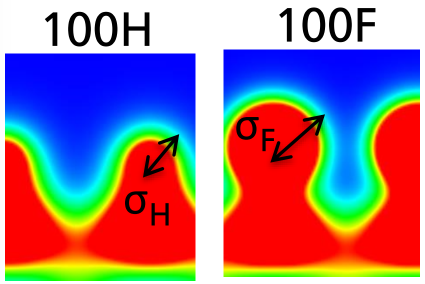

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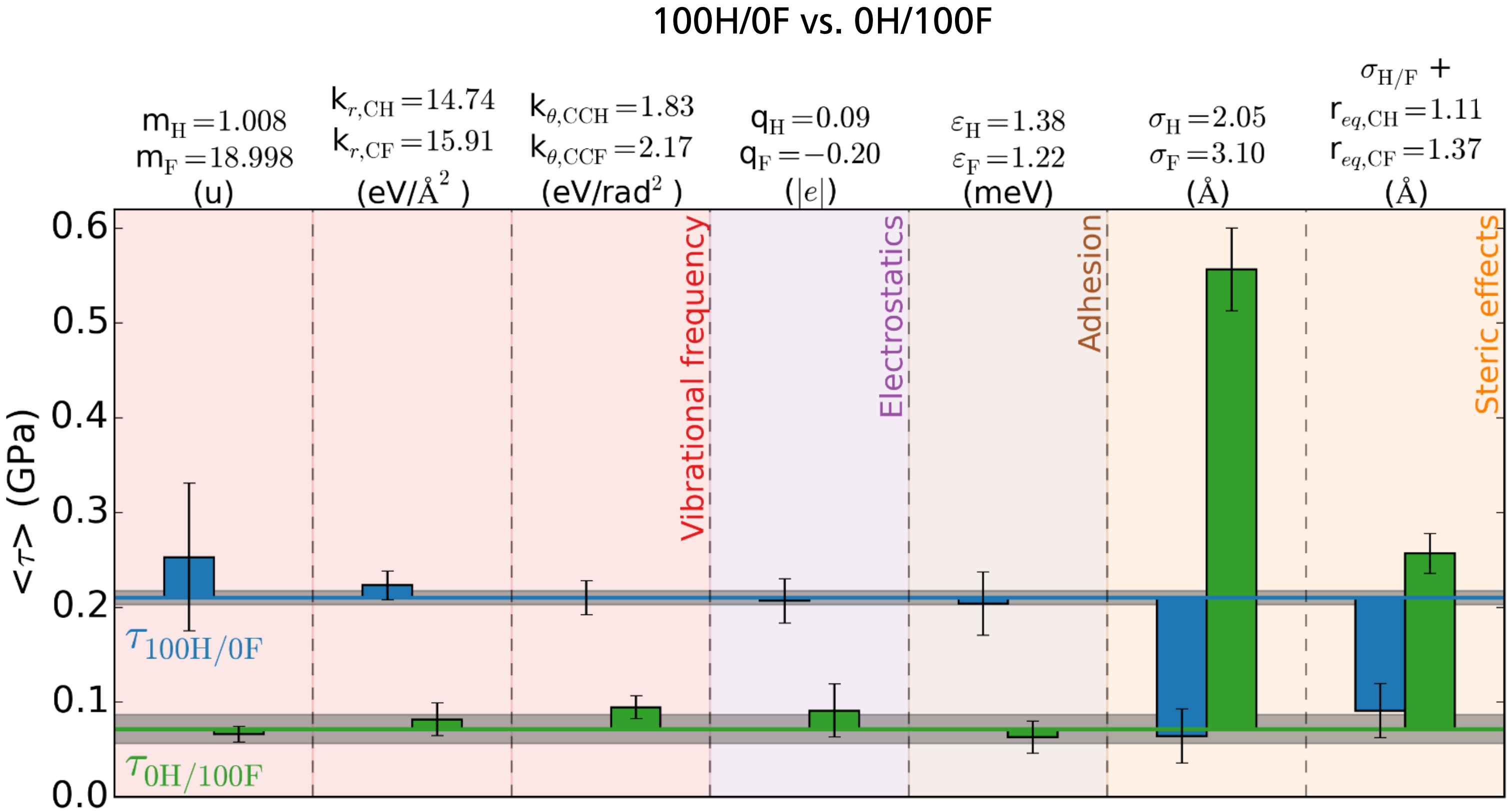

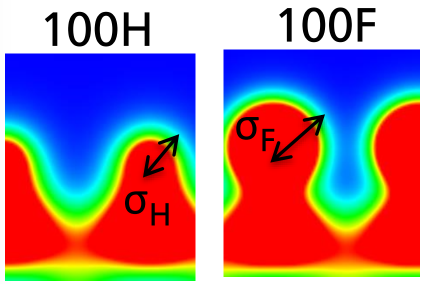

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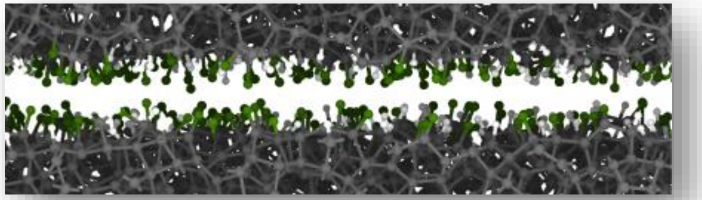
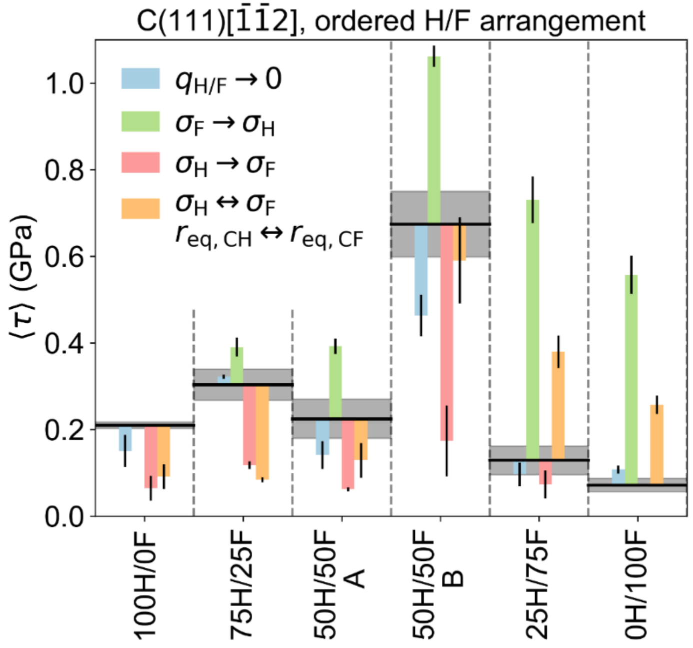
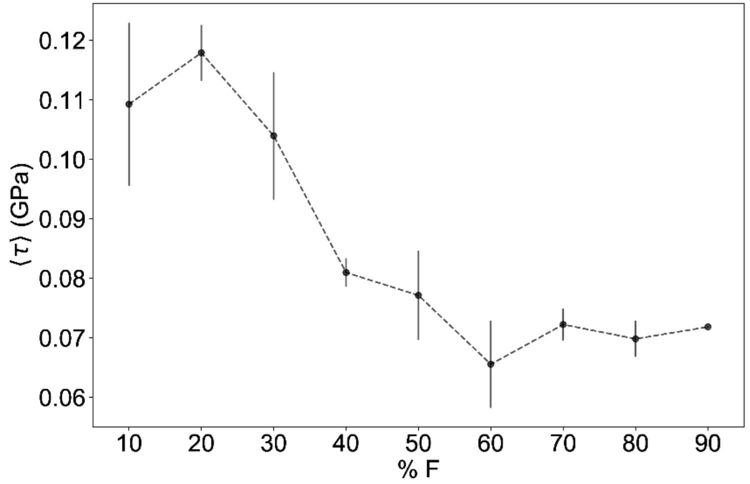


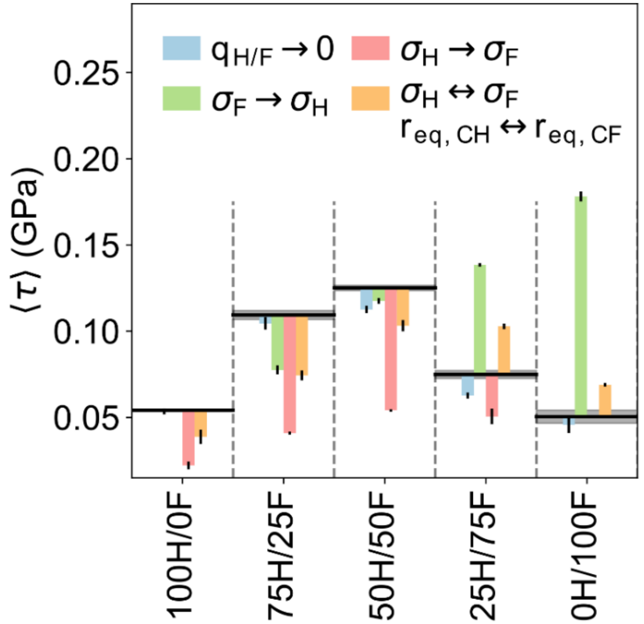
Commensurate mixed H/F-terminated diamond contacts



Incommensurate H/F-terminated diamond contacts



H/F-terminated ta-C contacts



Reichenbach, Mayrhofer, Kuwahara, Moseler, Moras, ACS Appl. Mater. Interfaces 12, 8805-8816 (2020)

Steric Effects Control Dry Friction of H- and F-Terminated Carbon Surfaces

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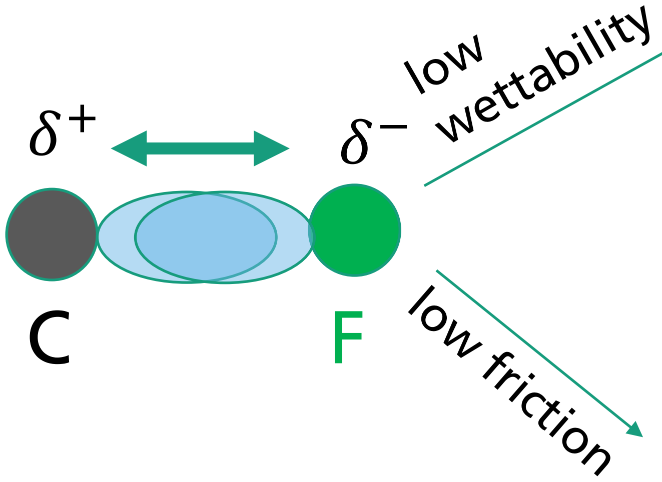
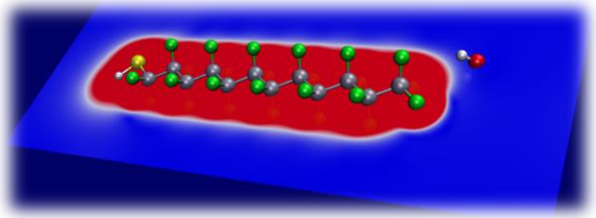
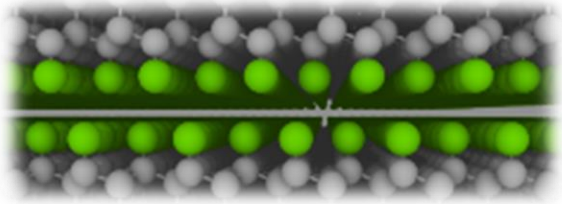
Conclusions

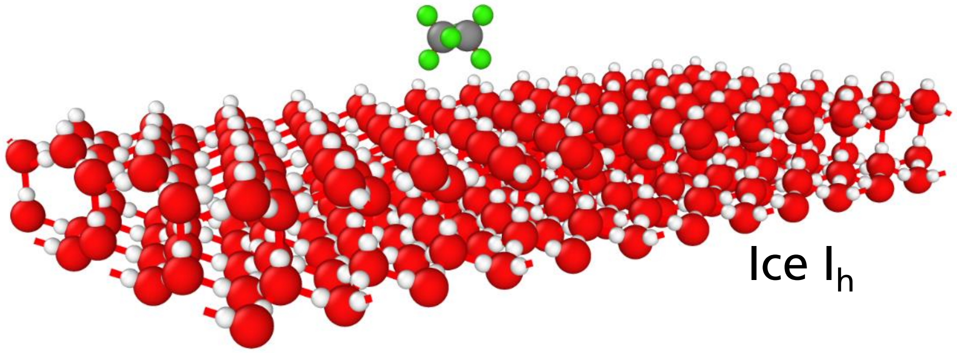




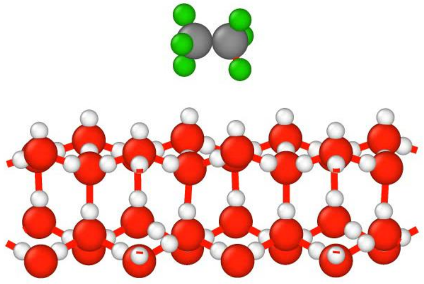
High density of C-F dipoles
(Polar Hydrophobicity)



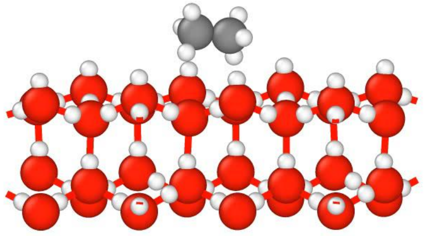
Large size of F atom
(Geometrically smooth surfaces)



Ice I_h



C_2F_6



C_2H_6

THANK YOU FOR YOUR ATTENTION!

Further Reading

J. Am. Chem. Soc. 138, 4018 (2016)

ACS Appl. Mater. Interfaces 12, 8805-8816 (2020)

Tribol. Lett. 69, 136 (2021)

Funding

Federal Ministry for Economic Affairs and Energy

DFG Deutsche Forschungsgemeinschaft

ExxonMobil

Poseidon II

SPP 2074 – MO 879/22-1

Computing time

NIC

JÜLICH FORSCHUNGSZENTRUM

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