ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Materials Modeling and Design: Tribology and Hydrogen production as case studies

www.tribchem.it

Maria Clelia Righi

Department of Physics and Astronomy Augusto Righi

- Designing Materials by High Throughput Calculations
- Modeling Materials Function by Molecular Dynamics
- What is tribology ?
- High throughput calculations to design solid interfaces
- Molecular dynamics to unravel mechanism of function of lubricants
- Simulating what happens in a reactor: H_2 and CNT production from CH_4

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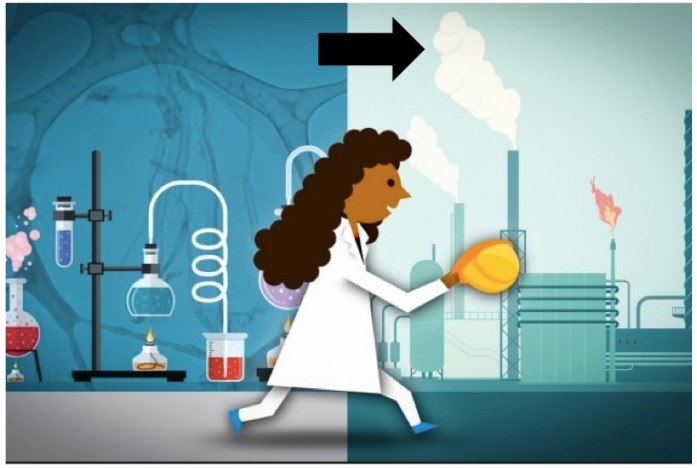
Advancing technologies by materials innovation

The advancement of many technologies important for our everyday life requires materials innovation.

Developing new materials is a difficult and time consuming task.

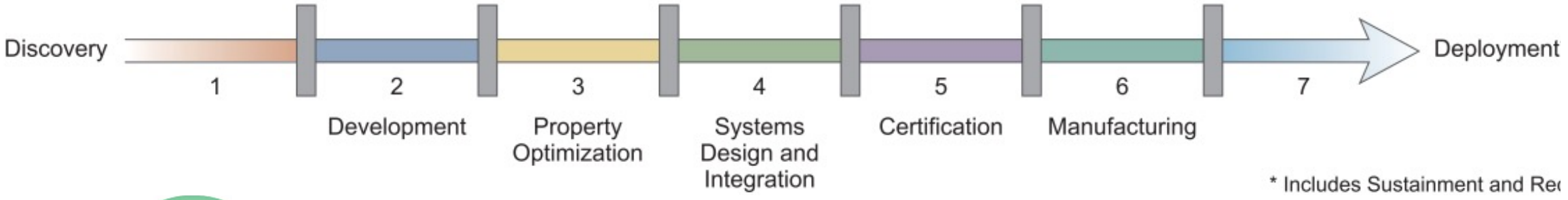


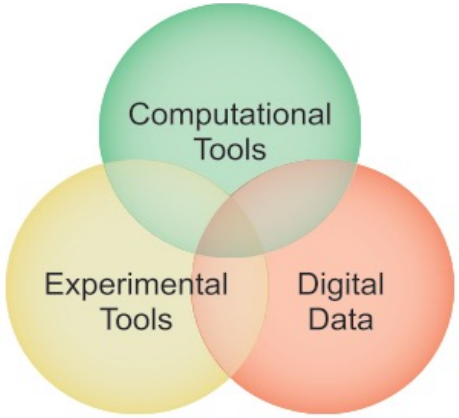
Identify new materials earlier on to begin the scale-up as soon as possible

Identify the strength and weakness of materials during the design process

Computational tools and digital data for accelerating materials innovation

20 years from the laboratory to the widespread adoption



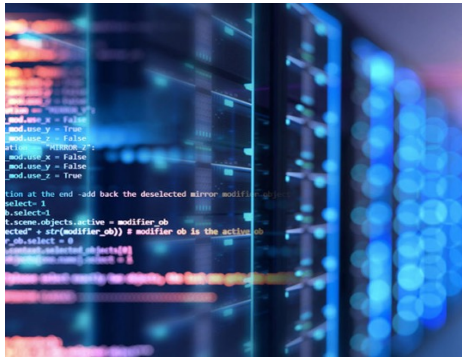


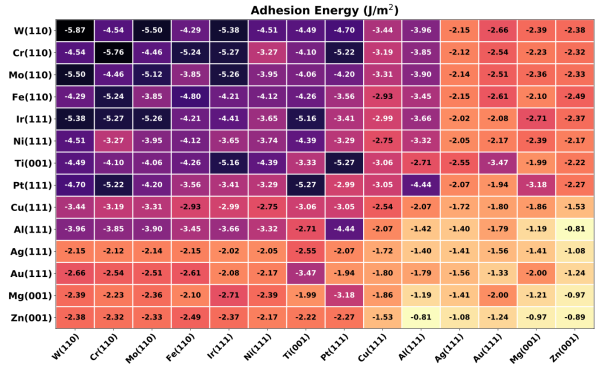
Reducing the time and the costs of material discovery and deployment by computational tools and digital data

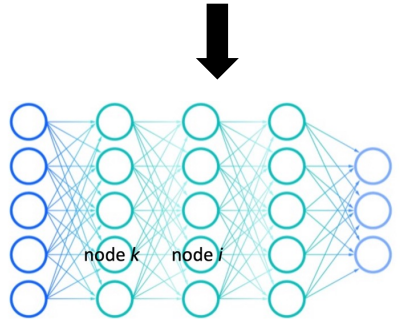
Materials design by high throughput calculations

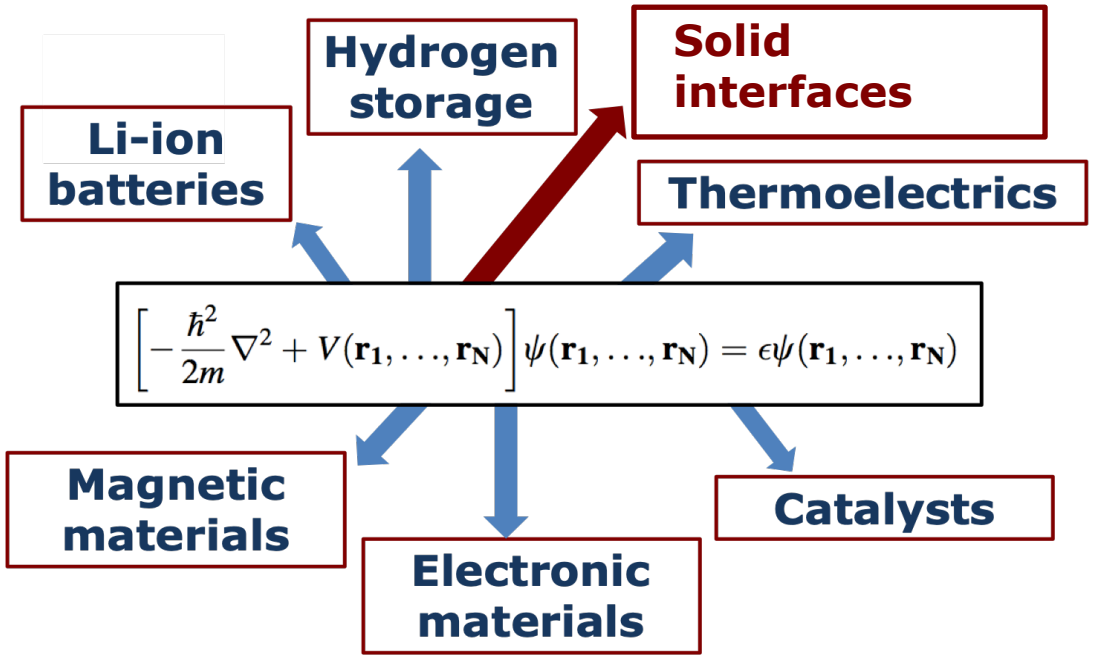
Ab initio **calculations have become ubiquitous in material science**

- ✓ availability of robust computer programs
- ✓ increase of high performance computing (HPC)
- ✓ appearance of curated materials databases









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Modeling materials function

To improve materials functioning

Trial and error approach

Understand the microscopic mechanisms that govern material functioning

Simulate materials with microscopic resolution *in operando* conditions

Modeling materials function

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Understand the microscopic mechanisms that govern material behavior

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atomistic

Molecular Dynamics

Molecular Dynamics (MD)

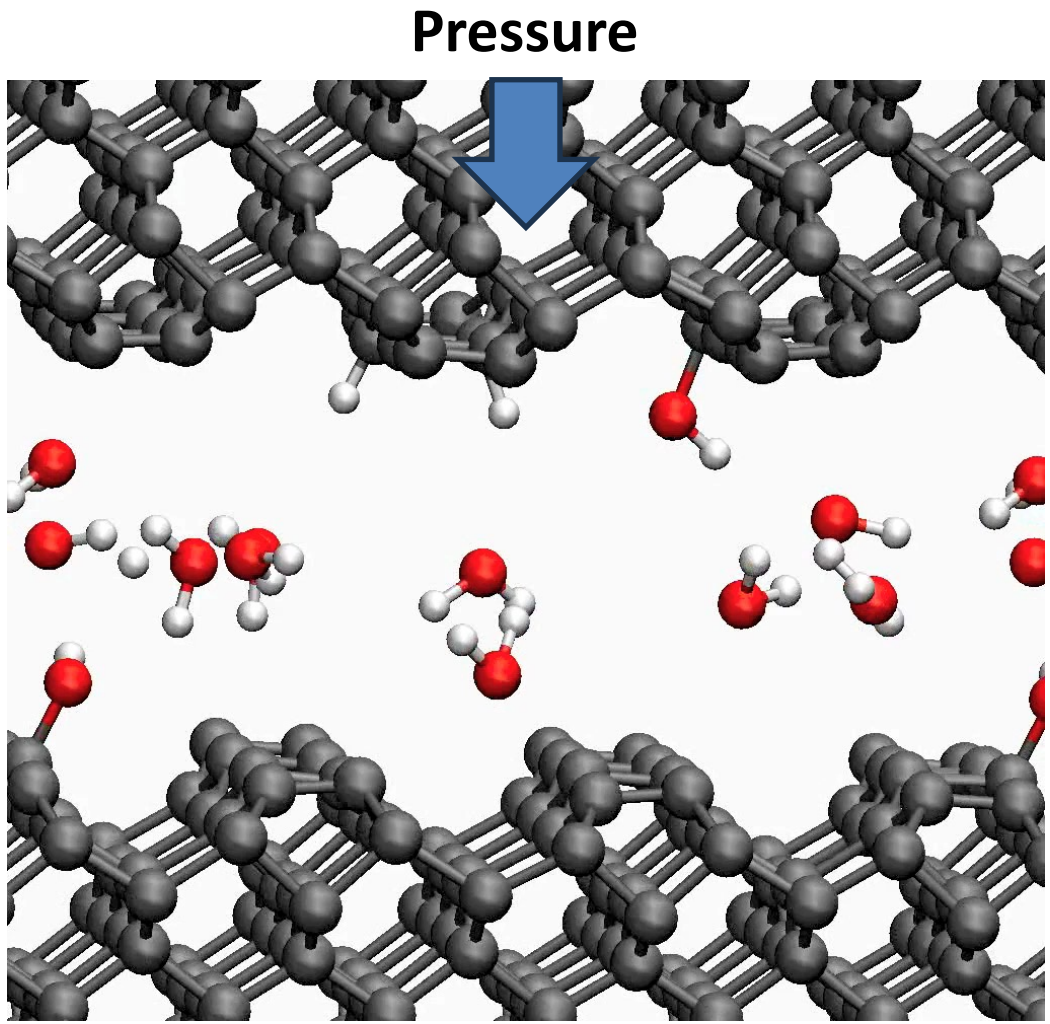
Impose the working conditions,
Temperature, Pressure, External forces..

Solve the equation of motion for each atom in the system

$$\mathbf{a} = \mathbf{F}/m$$

$$\mathbf{F} = -\nabla E(\mathbf{R})$$

$E(\mathbf{R}_1, \mathbf{R}_2, \ldots \mathbf{R}_N)$ interaction energy of the atoms



$E(R_1, R_2, \ldots R_N)$

Ab initio MD

$\mathbf{H}\,\Psi = \mathbf{E}\,\Psi$

solving the **quantum mechanical** equations for the system **electrons**

☺ High accuracy

☹ High computational cost

Classical MD

$\mathbf{E} = \Sigma_{ij}\, v(r_{ij})$

E sum of **parametric potentials** that **mimic the effects of electrons**

☺ High simulation efficiency

☹ Questionable accuracy

Machine Learning MD

E is the output layer of a **neural network** trained with *ab initio* data

☺ High accuracy

☺ High simulation efficiency

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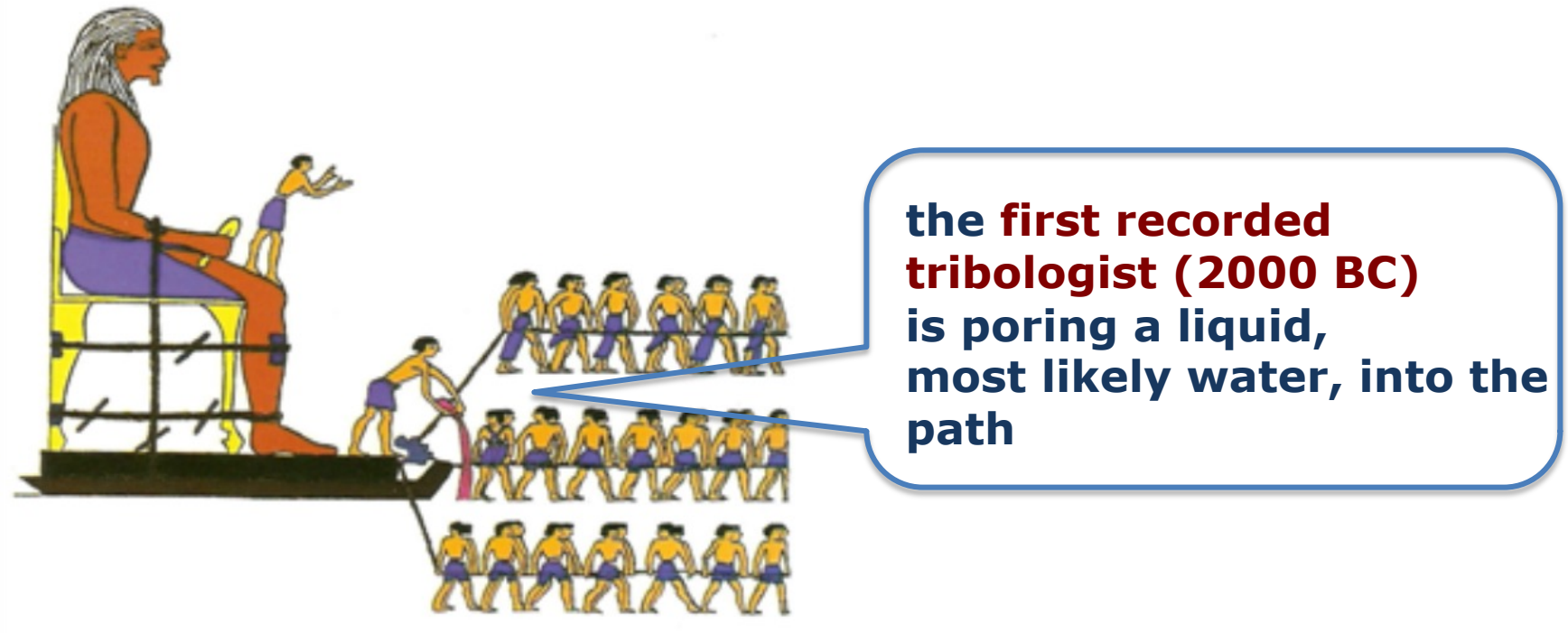
Tribology

- from the Greek word τρίβω meaning rubbing, literally tribology is the "science of rubbing"
- dictionaries define tribology as the science and technology of interacting surfaces in relative motion
- tribology includes the study of friction, wear and lubrication
- understanding these phenomena requires knowledge from physics, chemistry, mechanics, materials science. Tribology is a truly interdisciplinary science.
- the word tribology is recent, it was coined by the Jost committee in 1966, but the interest in tribology is much older

interest in tribology older than recorded hystory

records show the use wheel from 3500 BC: our ancestors were concerned with reducing friction in sliding motion



the first recorded tribologist (2000 BC) is poring a liquid, most likely water, into the path

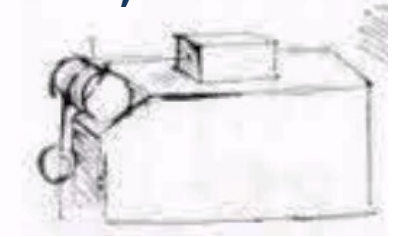
during and after the Roman empire tribology principles were mostly used to design war machinery and fortification

Leonardo da Vinci: a precursor

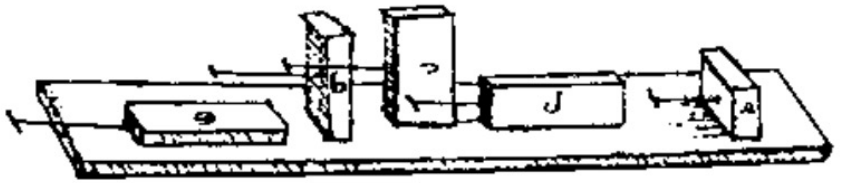
Da Vinci
1452-1519

Leonardo da Vinci was the first to study friction systematically
two phenomenological laws of friction:

1. **if the load of an object is doubled, its friction will also double**



2. **the areas in contact have no effect on friction**



- **Da Vinci laws 200 years before Newton even defined what a force is**
- **his work had no influence on subsequent studies, because his notes remained unpublished for hundred of years**

classical friction laws

in 1699 Amontons rediscovered the two basic rules of friction:

1. $F = \mu F_N$ Amontons' law
2. F independent from the contact area

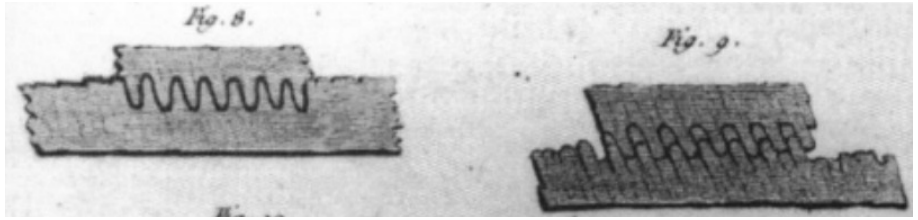
Amontons
1663-1705

Coulomb
1736-1806

Coulomb (1785) in the *Theorie des machines simples* made a distinction between static and kinetic friction

3. F=a+b·log(v) in the first hours of motion, then the friction force is independent from the sliding velocity

4. friction due to interlocking of asperities



real area of contact

For several centuries scientists believed that friction was due to the roughness. Geometrical hypothesis of friction.

Desanguliers (1734) first proposed that adhesion as a key element in the friction process. Tribologists rejected the idea as it appeared to contradict the independence on the contact area

Bowden 1903-1968

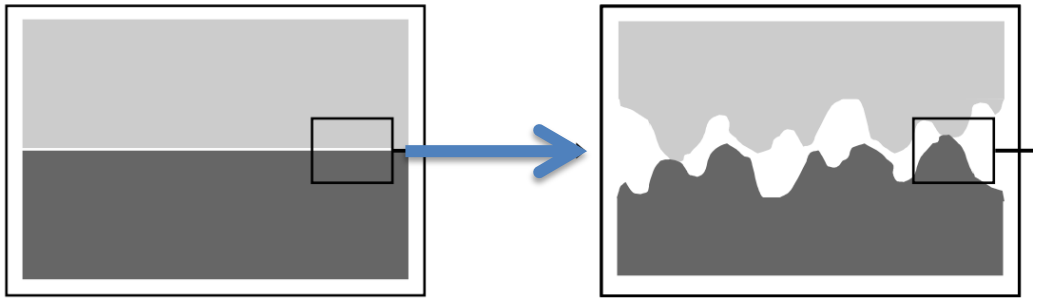
Tabor 1913-2005

Contradiction cleared up by the introduction of the concept of the real area of contact (1950)

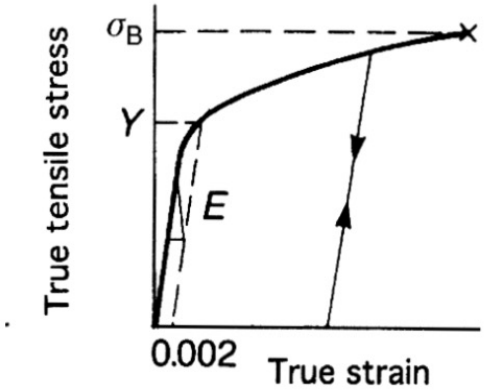
"putting two solids together is rather like turning Switzerland upside down and standing it on Austria – their area of intimate contact will be small"

asperity contact

real area of contact made up of a large number of small regions of contact, asperities or junctions



Strength of materials



$$A_r = \Sigma A_i$$

A_r increases with F_N until the real area of contact is just sufficient to support the load. For plastic contacts:

$$A_r = F_N/\tau_Y$$

τ_Y Yield strength: the maximum resistance to plastic deformation

adhesion theory of friction

Bowden and Tabor proposed that the friction force is necessary to overcome adhesion at asperity contacts

F due to adhesion $F = \tau_s A_r$

τ_s **shear strength: maximum resistance to sliding**

$F = \tau_s A_r = \tau_s/\tau_Y \; F_N, \quad \mu = \tau_s/\tau_Y$

consistent with the two Amontons laws…

…however things are more complicated:

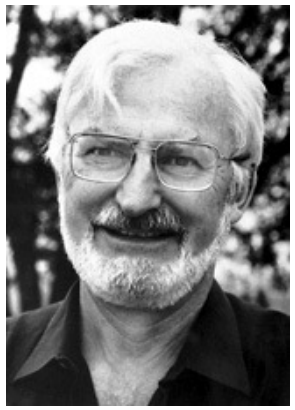
- τ_Y **reduced by the shear force**
- τ_s **can depend on the contact pressure** $\tau_s = \tau_0 + a\, p$
- **for elastic contacts** $F \sim (F_N)^{2/3}$
- **Archard (1953) load-dependent number of asperities in contact -> no contradiction with the Amontons 1st law**

nanotribology: the renaissance of friction

No progresses in the understanding of friction until ’80, when an exciting era of renewed interest in tribology has started. The fueling factors are:

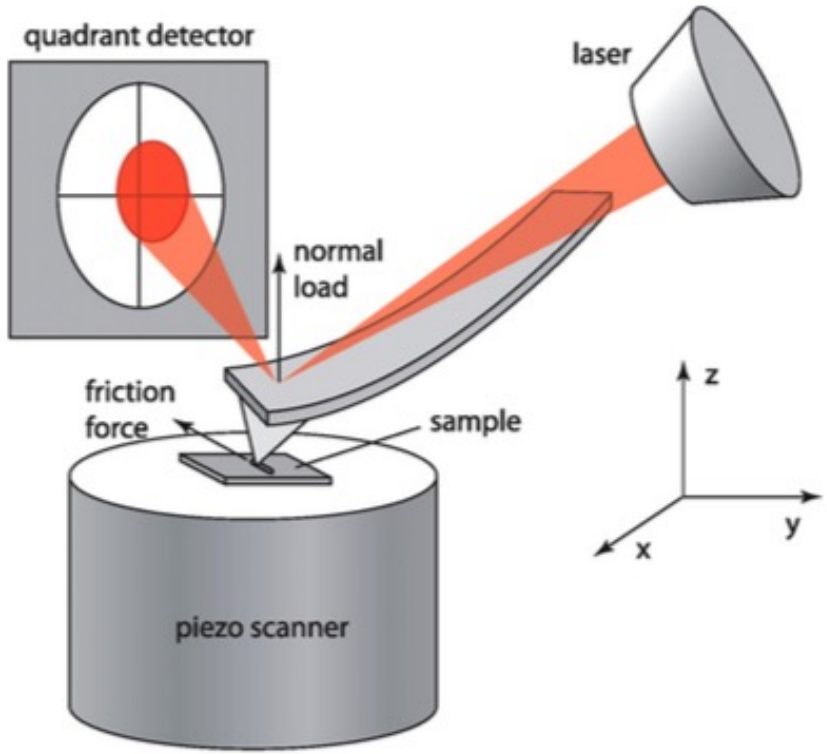
1. advent of new experimental techniques that allow to probe interfacial properties with atomic resolution

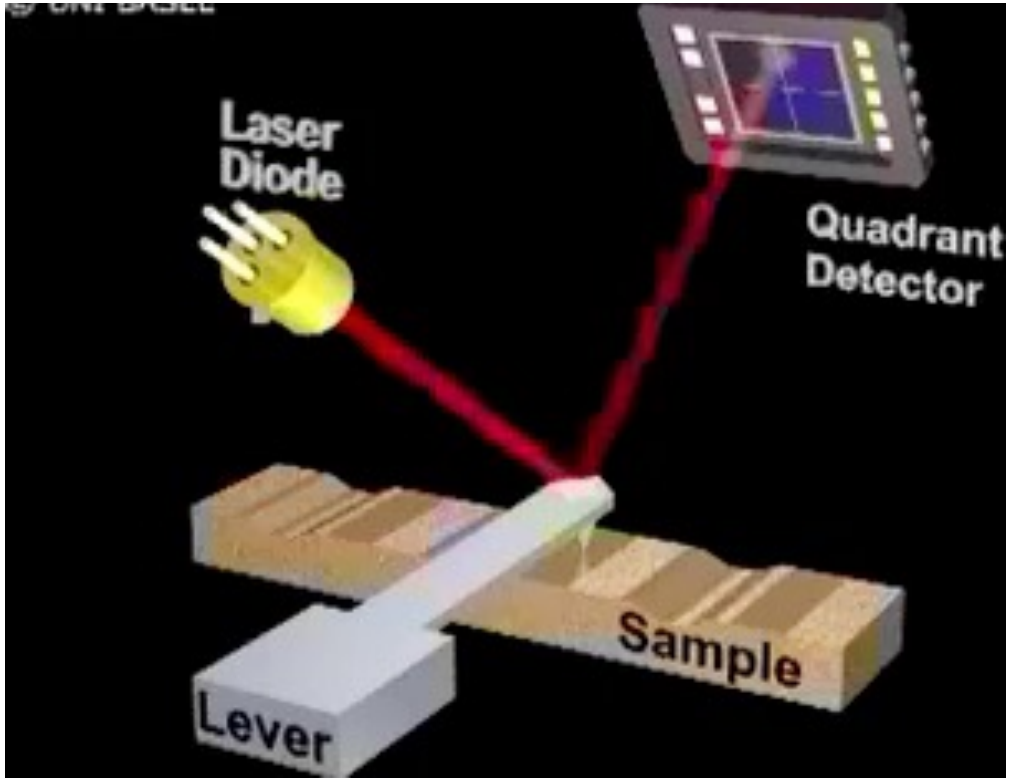
Gerd Binnig

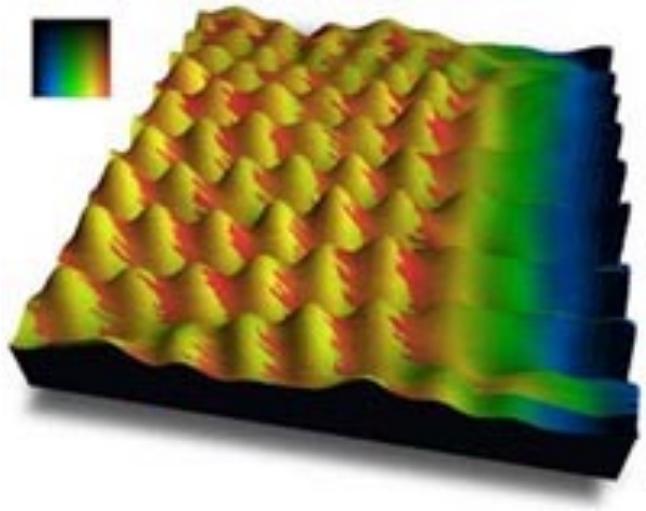


Heinrich Rohrer

1986, Nobel Prize in Physics for scanning tunneling microscopy (STM)

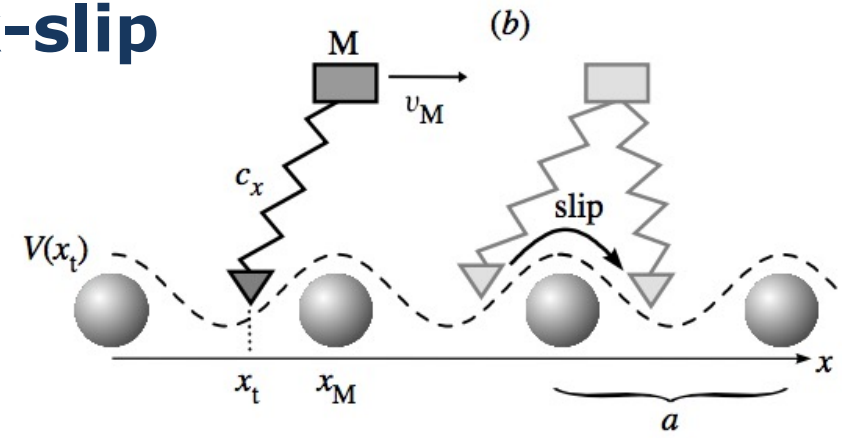


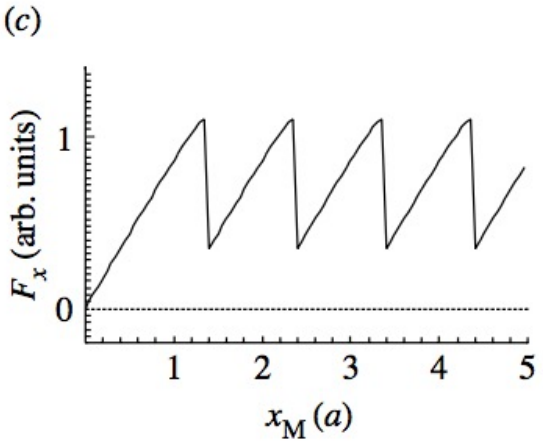




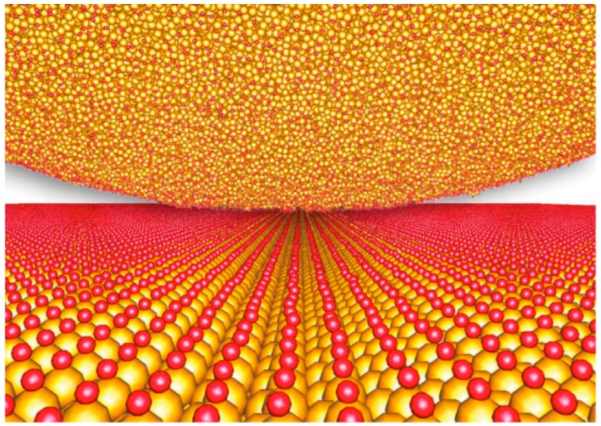
2.5 x 2.5 nm simultaneous topographic and friction image of HOPG.

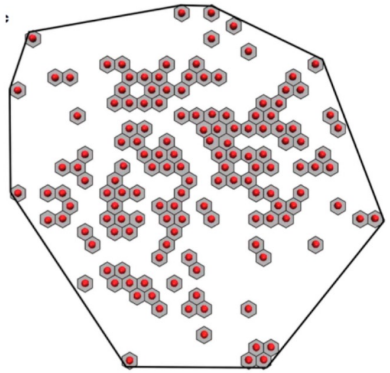
stick-slip





2. advances in computational methods and computer power.
Atomistic simulations, molecular dynamics, to model the asperity during sliding:



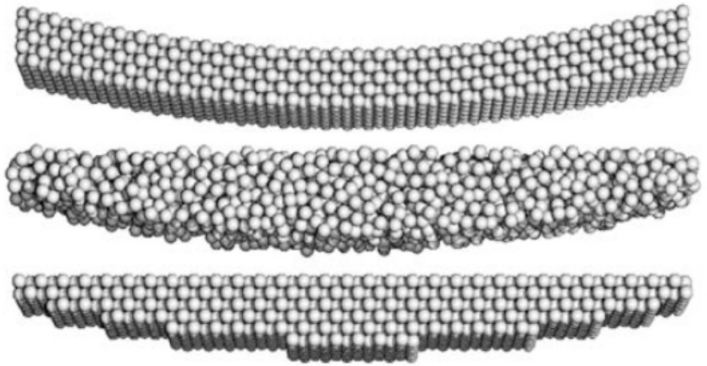


$$A_{real} = N_{at} A_{at}$$

Y. Mo, K. T. Turner and I. Szlufarska, Nature 457, 1116 (2009)

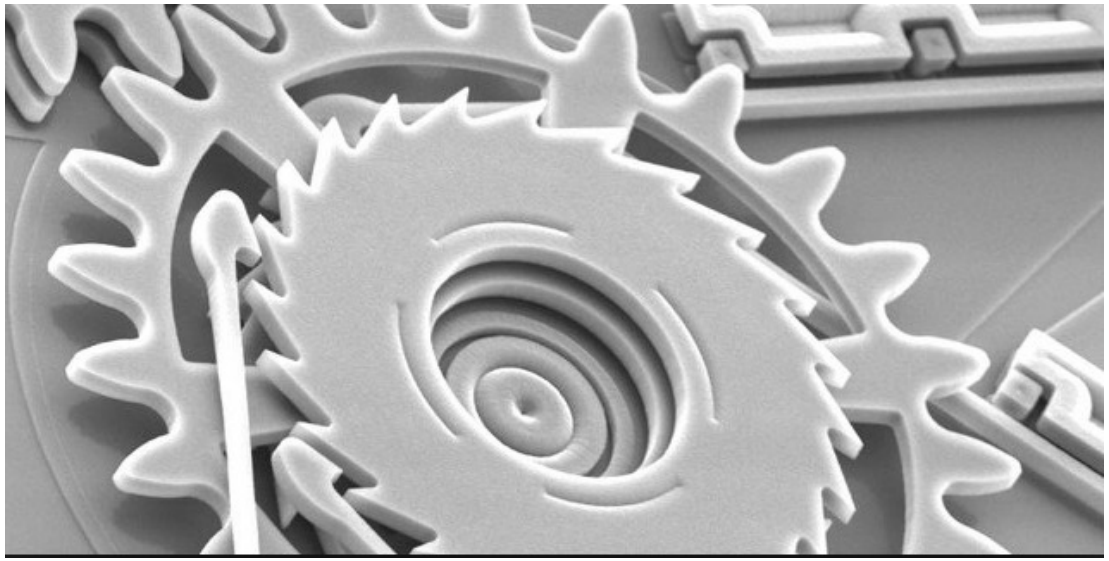
The surface roughness produced by discrete atoms leads to dramatic deviations from continuum theory.

B. Laun and M. O. Robbins, Nature 435, 929 (2005)



3. Nanotechnology

miniaturized devices with moving components, with high surface/volume ratio suffer problems of adhesion and friction



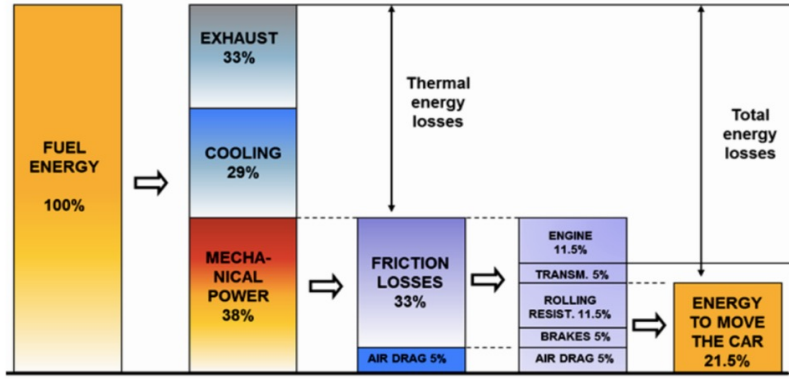
Micro-, nanoelectromechanical systems (MEMS & NEMS)

4. Energy saving

approximately 1/3 of the world's energy is lost in frictional processes

Impact of tribology on energy and environment

- **Friction and wear cause massive energy and environmental costs**

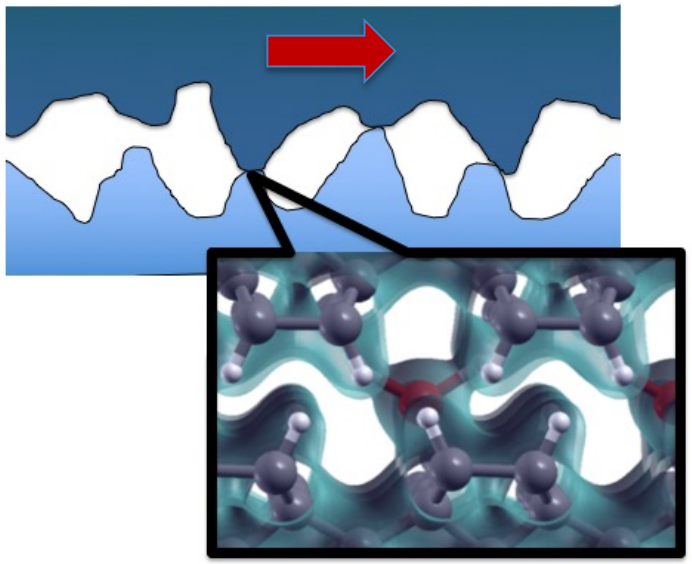


K. Holmberg and A. Erdemir, FME Transactions 43, 181 (2015)

10% less friction in cars = fuel saving (10^{11} lt/yr) & less CO_2 emissions (10^{11} Kg/yr)

Advancing the technologies to reduce friction: Materials

Ab initio MD to open a window on the buried sliding interface



- **Simulations can open a window on the sliding buried interface**
- **Quantum mechanics essential to accurately describe asperity adhesion and tribochemical reactions at nanosized contacts**

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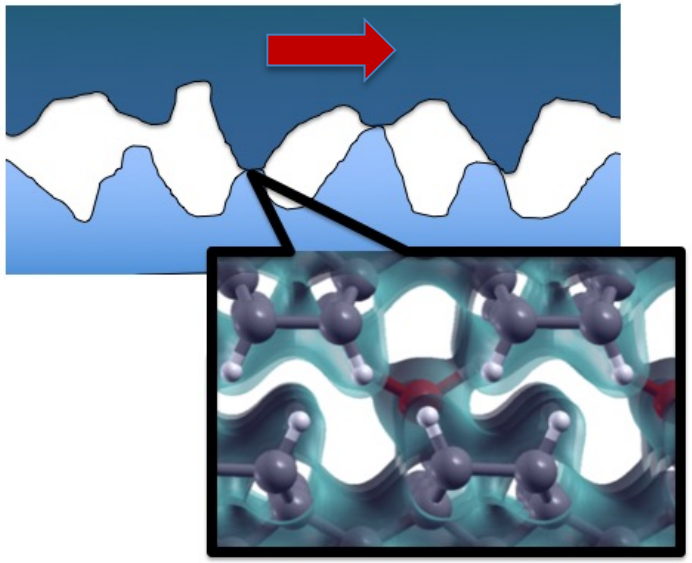

- **Simulations can open a window on the sliding buried interface**
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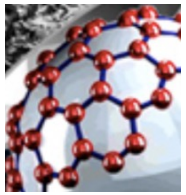
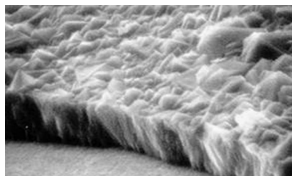
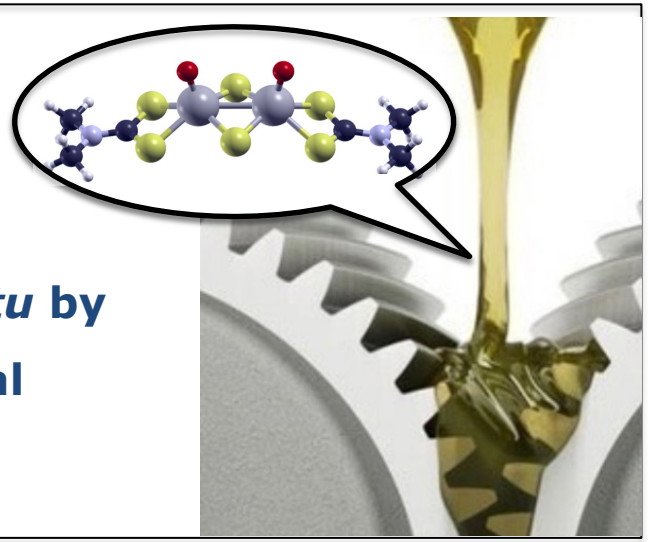
✓ **Solid lubrication: surface covered by inert layers or thin films**



DLC



✓ **Boundary lubrication: "tribofilms" formed *in situ* by tribochemical reactions**



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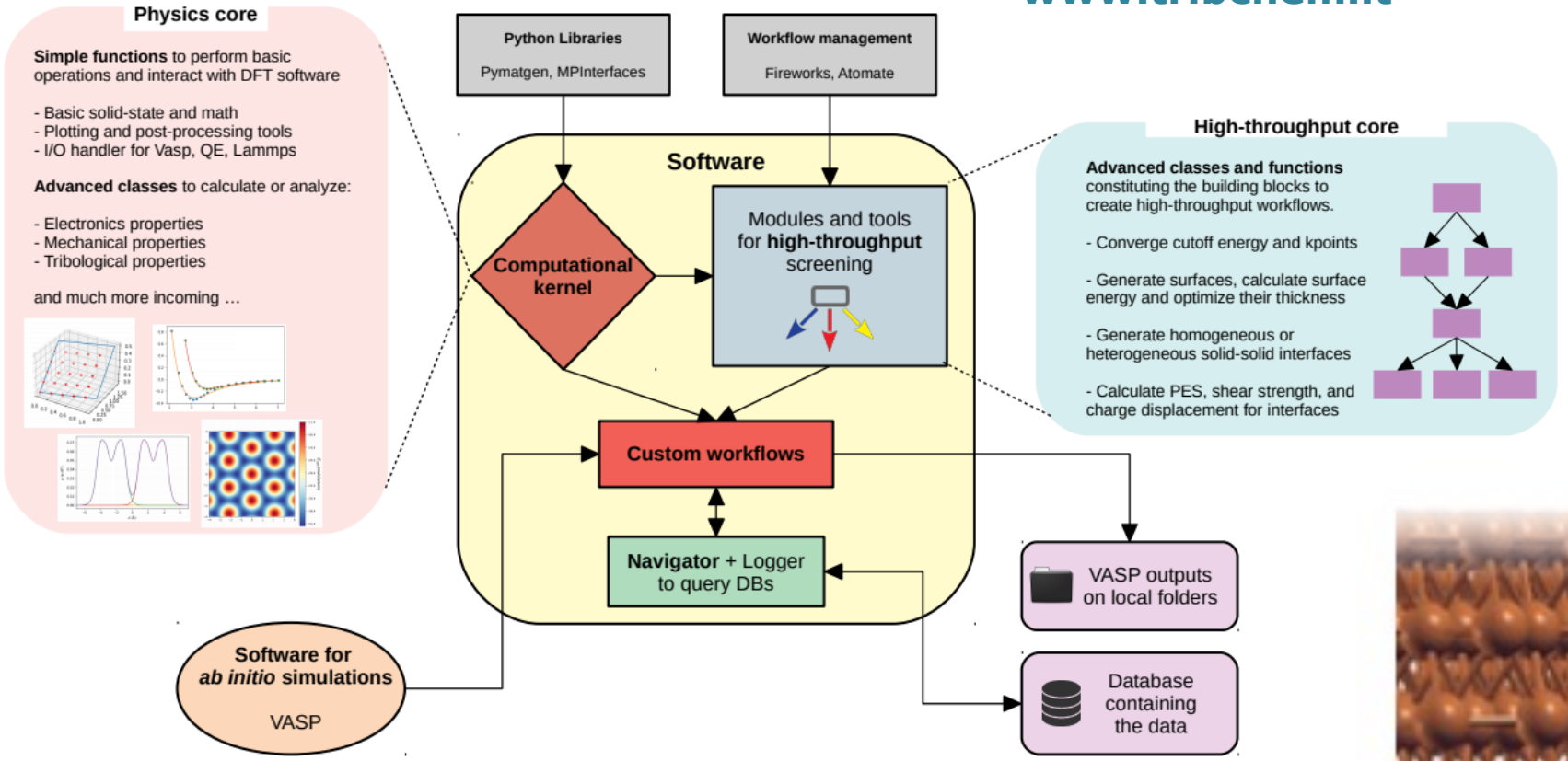
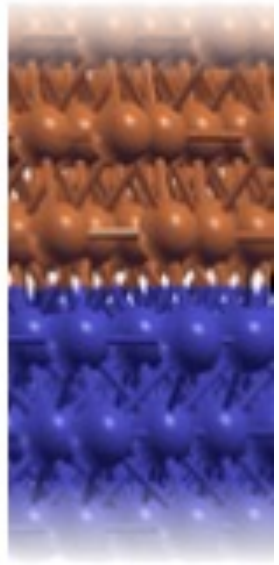
TRIBCHEM for high throughput calculations of solid interfaces

www.tribchem.it





G. Losi, O. Chehaimi, and M.C. Righi,
Journal of Chemical Theory and Computation (2023)

New release coming soon!

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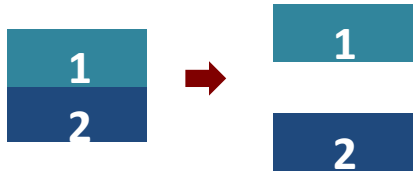
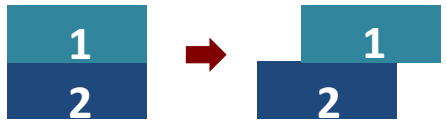
First principles calculation of adhesion and shear strength

work of adhesion

energy per unit area required to separate two surfaces from contact

$E_{adh} = (E_{12} - E_1 - E_2)/A$

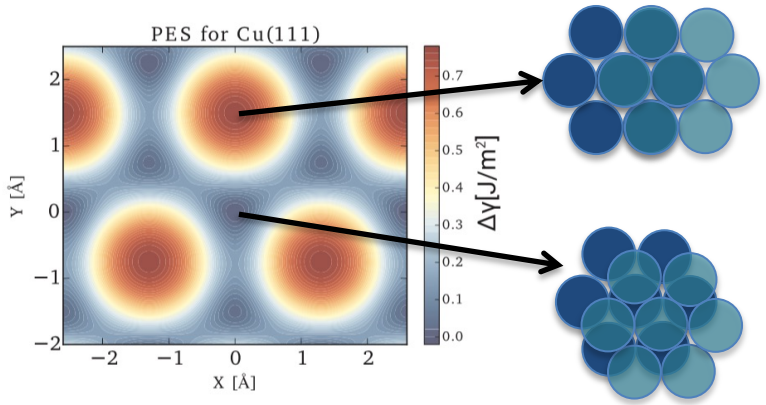




G. Zilibotti and M. C. Righi, Langmuir 27, 6862 (2011)

stacking fault energy surface

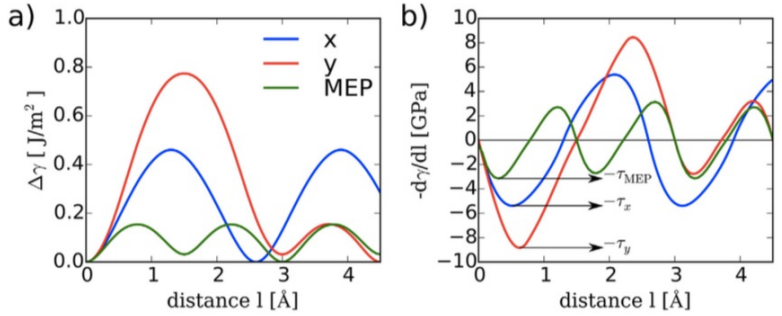
potential energy surface (PES) for the sliding interface $E_{adh}(x,y)$



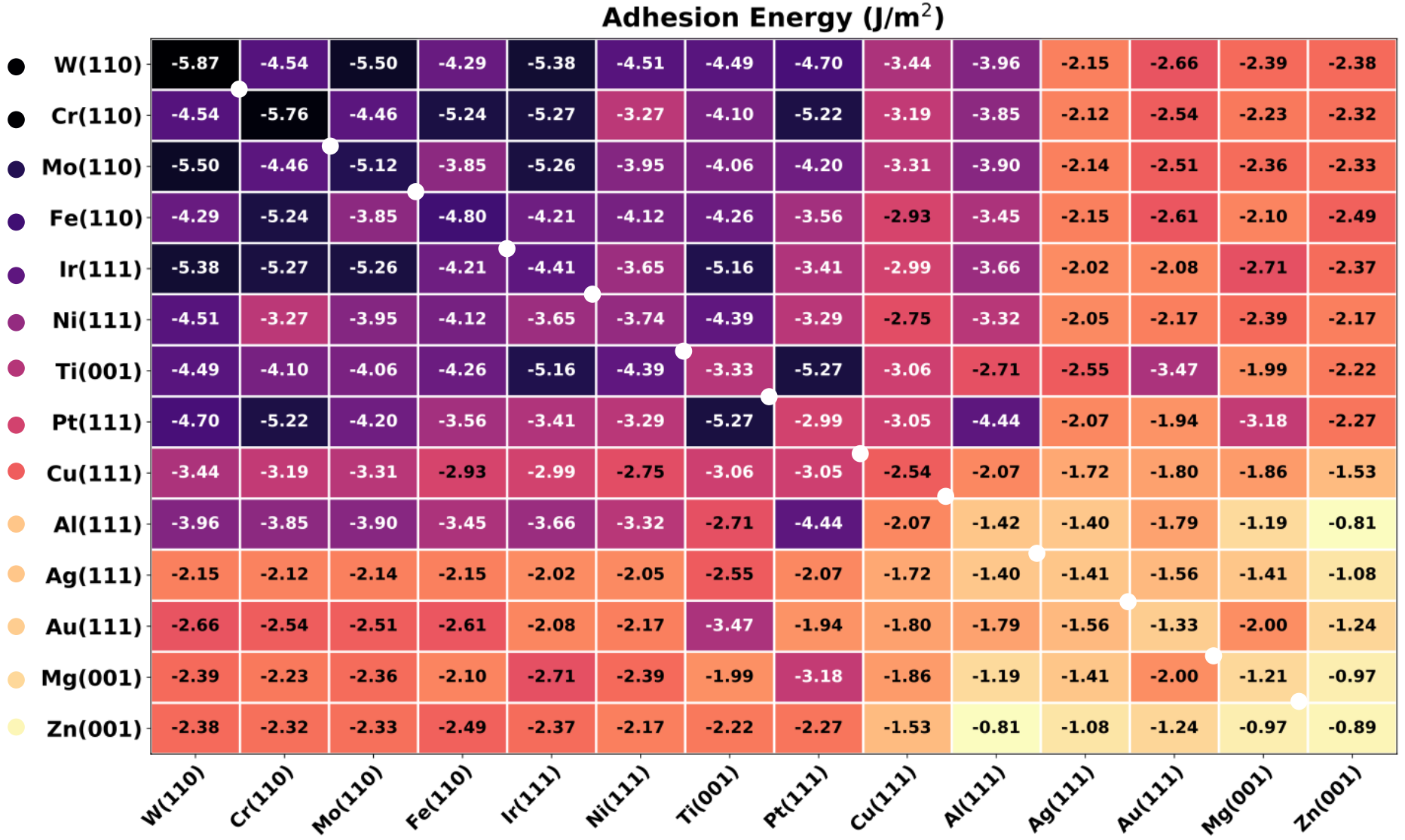
ideal shear strength

maximum restoring force

$\tau = \max | - \nabla E_{adh}(x,y) |$



Database for the adhesion of metallic interfaces



P. Restuccia, O. Chehaimi, G. Losi, M. Marsili and M.C. Righi
ACS Advanced Materials Interfaces 15, 19624 (2023)

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adhesion of metallic interfaces predicted by ML

The sure independent screening and sparsifying operator (SISSO):

- **extracts effective materials descriptors out of a number of possibly correlated features**
- **identifies an analytical equation able to describe the descriptor relationship**

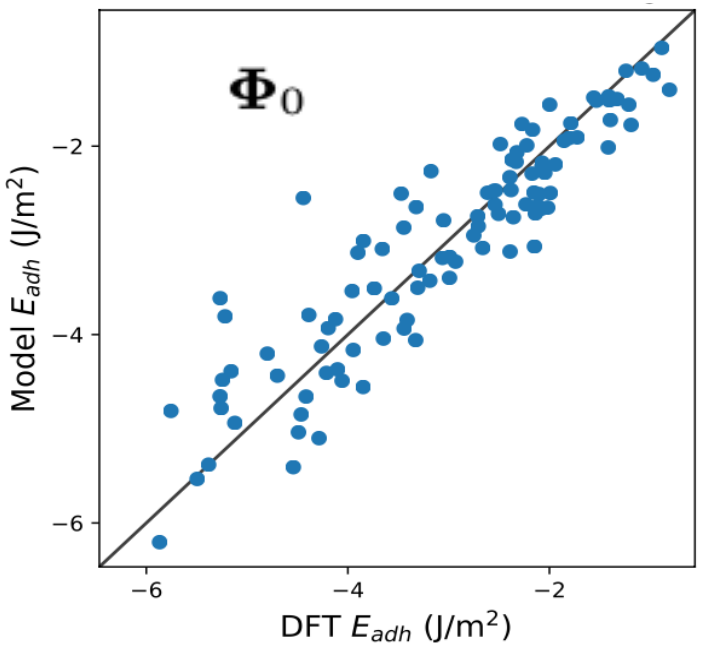
Ouyang, S. Curtarolo, E. Ahmetcik, M. Scheffler, and L. M. Ghiringhelli, Phys. Rev. Materials 2, 083802 (2018)

Screened descriptors:

$\varepsilon_{1,2}$ cohesive energy, $K_{1,2}$ bulk modulus, $\gamma_{1,2}$ surface energy, $\rho_{1,2}$ atom density at surf., $(e_1\text{-}e_2)$ electronegativity difference their arithmetic (AM) and geometric (GM) averages

$$\mathrm{E}_{adh} = A\sqrt{\gamma_1\gamma_2} + B\sqrt{\epsilon_1\epsilon_2} + C\sqrt{K_1K_2}$$

$$A = -1.13, B = -0.34; C = 0.0016$$



Model	R^2	RMSE (J/m^2)
$\mathbf{\Phi}_0$	0.83	0.52

P. Restuccia, O. Chehaimi, G. Losi, M. Marsili and M.C. Righi, ACS Advanced Materials Interfaces 15, 19624 (2023)

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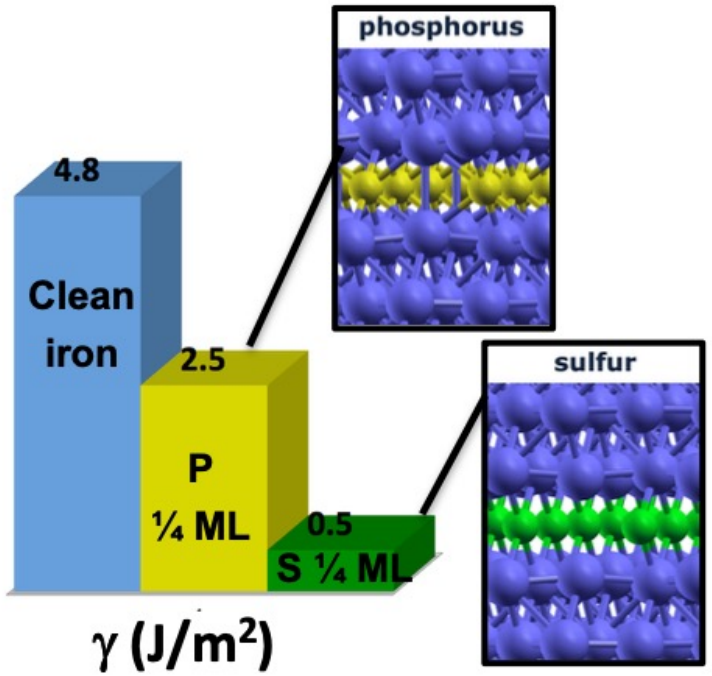
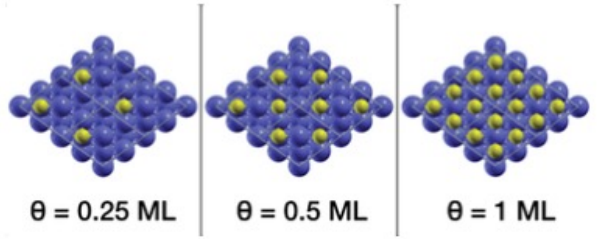
Effects of surface chemical modifications on interfacial adhesion



adhesion reduced by chemical surface modifications

screening intercalated species for selected levels of adhesion and friction



G. Fatti, P. Restuccia, C. Calandra and M. C. Righi
J. Phys. Chem. C 122, 28105 (2018)

Effects of surface chemical modifications on metal/metal

coverage

	25%								50%								100%								
Elem	B	C	F	H	N	O	P	S	B	C	F	H	N	O	P	S	B	C	F	H	N	O	P	S	Clean
W	-6.36	-6.48	-0.92	-6.20	-5.42	-4.42	-4.23	-3.20	-6.60	-7.09	-1.19	-4.86	-5.41	-2.63	-2.40	-1.94	-8.03	-9.58	-2.99	-3.43	-5.05	-2.17	-3.65	-1.86	-5.87
Cr	-5.43	-5.20	-2.59	-5.94	-5.88	-4.89	-3.13	-2.93	-6.06	-7.61	-0.95	-5.79	-6.39	-3.90	-2.85	-2.29	-8.59	-10.49	-2.07	-3.78	-1.23	-3.29	-4.11	-2.16	-5.76
Mo	-5.54	-5.84	-2.05	-5.20	-5.22	-4.09	-3.56	-3.13	-6.15	-6.67	-1.31	-4.40	-5.39	-2.51	-2.85	-2.14	-7.76	-9.34	-3.32	-3.40	-4.73	-2.45	-3.68	-1.90	-5.12
Fe	-5.05	-5.35	-2.20	-4.82	-4.71	-3.54	-3.22	-2.36	-2.32	-6.17	-0.66	-4.79	-4.81	-2.71	-2.91	-1.51	-8.00	-8.34	-1.98	-3.23	-3.80	-2.66	-3.18	-1.48	-4.80
Ir	-4.09	-3.64	-0.24	-3.53	-2.47	-1.89	-2.32	-0.71	-4.43	-3.60	-0.45	-2.81	-2.62	-0.04	-2.20	-0.95	-7.32	-5.06	-1.39	-1.70	-0.56	-0.67	-2.75	-1.24	-4.41
Ni	-4.29	-4.30	-0.98	-3.41	-3.46	-1.99	-4.38	-3.03	-5.99	-5.70	-2.67	-3.80	-3.99	-3.34	-3.88	-2.07	-7.43	-7.29	-2.65	-3.49	-5.22	-5.07	-3.87	-0.99	-3.47
Ti	-4.72	-5.54	-3.11	-4.37	-4.89	-4.79	-4.19	-3.49	-5.78	-6.93	-2.09	-3.55	-6.26	-5.16	-4.43	-3.20	-8.19	-12.02	-0.00	-2.80	-10.08	-7.05	-5.17	-4.03	-3.33
Pt	-3.19	-2.68	-0.32	-2.37	-1.55	-1.06	-1.92	-0.95	-4.01	-2.99	-0.52	-1.81	-2.20	-1.04	-2.29	-1.12	-6.99	-3.84	-1.76	-0.85	-0.42	-0.65	-2.12	-1.15	-2.99
Cu	-2.86	-2.11	-0.48	-2.08	-1.65	-1.40	-1.08	-0.56	-4.08	-2.53	-0.92	-1.61	-1.91	-1.43	-1.19	-0.81	-3.35	-4.08	-3.02	-0.93	-0.42	-3.24	-1.04	-0.85	-2.54
Al	-2.41	-2.17	-0.05	-1.37	-1.41	-0.88	-0.79	-0.18	-3.18	-3.54	-0.03	-1.13	-2.36	-1.17	-0.98	-0.30	-4.22	-7.31	-0.01	-0.68	-7.34	-0.04	-1.05	-0.42	-1.42
Ag	-1.63	-1.37	-0.81	-1.34	-1.31	-1.09	-0.75	-0.48	-2.45	-2.39	-0.87	-1.08	-1.54	-1.32	-1.31	-0.77	-2.75	-2.73	-2.67	-0.87	-1.75	-2.35	-1.08	-0.92	-1.41
Au	-1.65	-1.10	-0.29	-0.84	-0.58	-0.75	-0.63	-0.10	-2.58	-1.50	-0.74	-0.49	-0.99	-0.94	-0.84	-2.09	-3.66	-0.64	-2.19	-0.06	-1.83	-2.47	-0.58	-0.43	-1.33
Mg	-2.02		-0.82	-1.12		-1.63	-1.33	-0.95	-2.80		-0.45	-1.05		-2.55	-1.58	-1.36	-4.09	-5.96	-0.01	-0.85			-2.05	-2.73	-1.21
Zn	-1.65	-1.58	-0.18	-0.32	-1.37	-0.87	-0.83	-0.58	-2.31	-2.40	-0.57	-0.84	-2.23	-1.98	-0.83	-1.16	-2.57	-2.63	-0.58	-0.07	-3.15	-4.15	-0.58	-0.37	-0.89

$E_{adhesion}$ (J/m²)

- P, S and in particular F are the strongest adhesion reducers
- B and C and sometimes N are the adhesion enhancers

E. Poli, M. Cutini, M. A. Nosir, O. Chehaimi and M. C. Righi, Applied Surface Science (2024)

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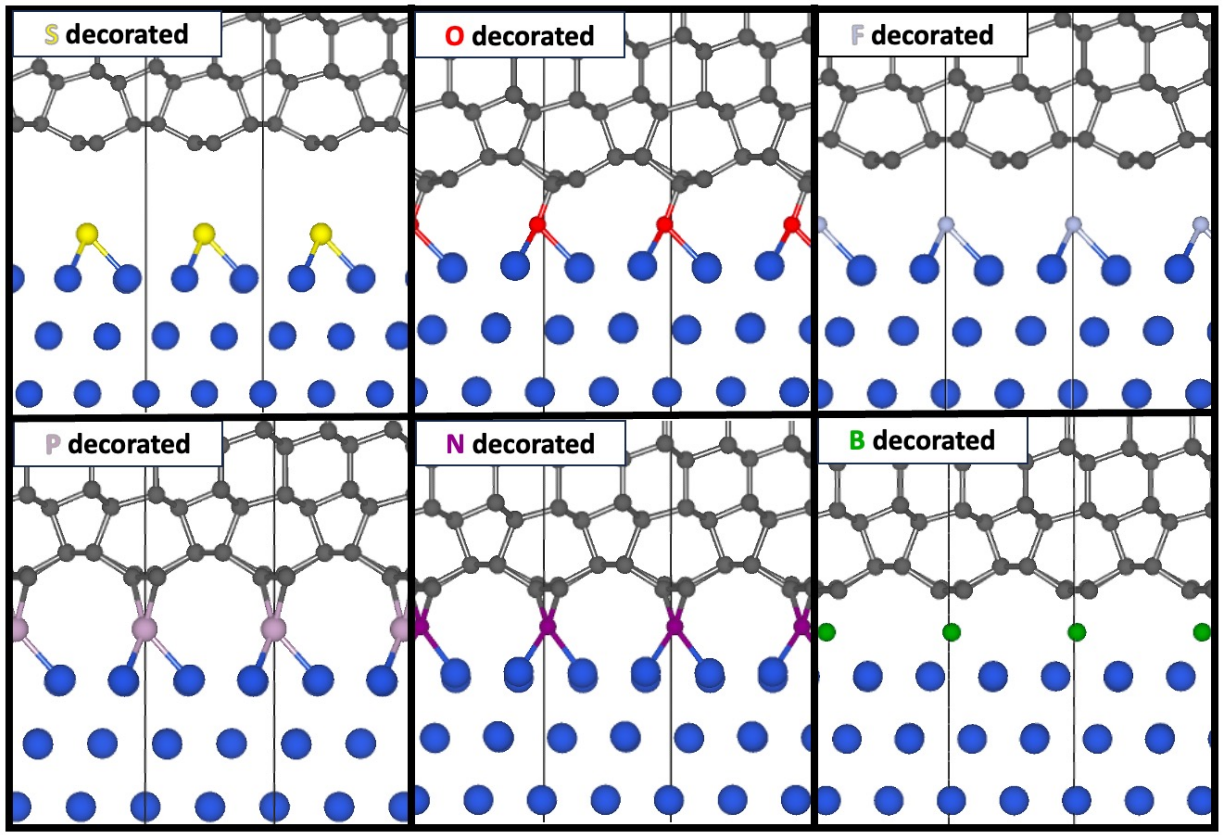
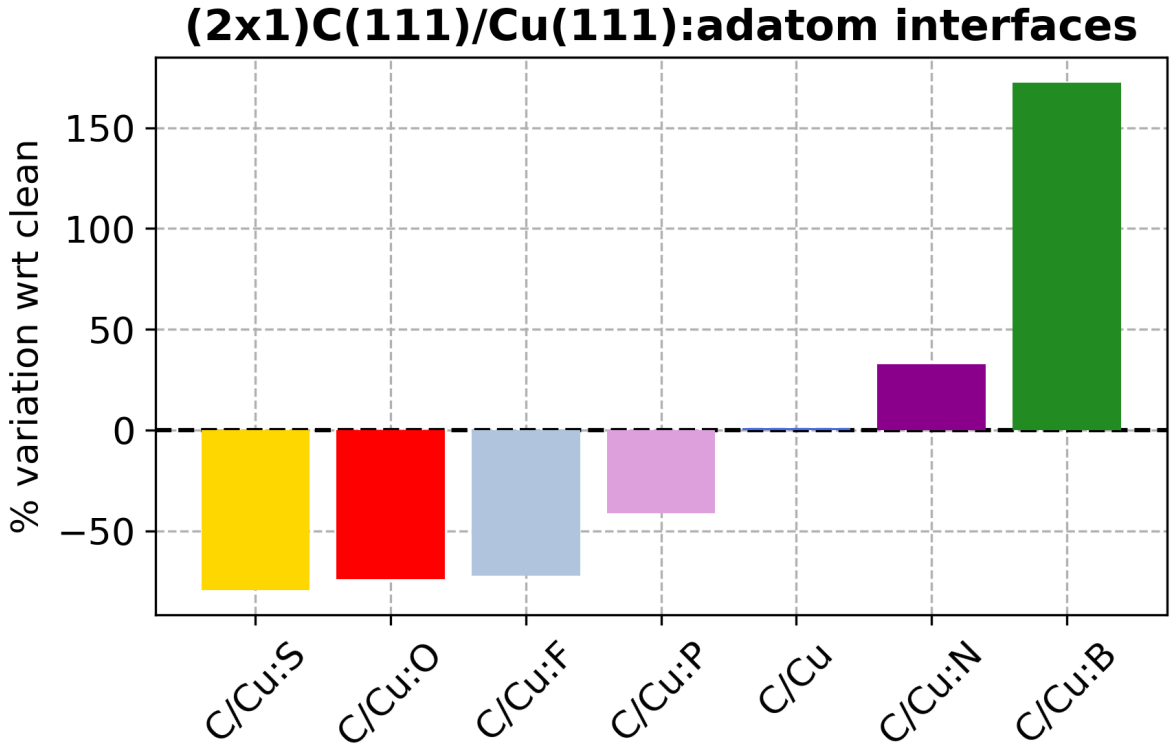
Effects of surface chemical modifications on covalent/metall





- **B** and **N** act as **adhesion enhancers** → adhesion increasing of 172% and 33%, respectively
- **S** makes the **Cu surface completely inert** → adhesion reduction of 80%

E. Damiani, M. Marsili and M. C. Righi, to be published (2024)

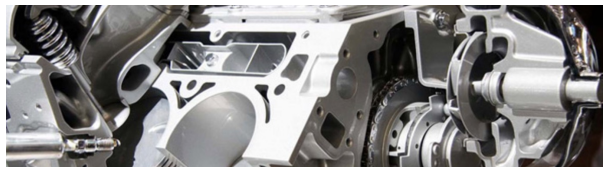
- Designing Materials by High Throughput Calculations
- Modeling Materials Function by Molecular Dynamics
- What is tribology ?
- High throughput calculations to design solid interfaces
- Molecular dynamics to unravel mechanism of function of lubricants
- Simulating what happens in a reactor: H_2 and CNT production from CH_4

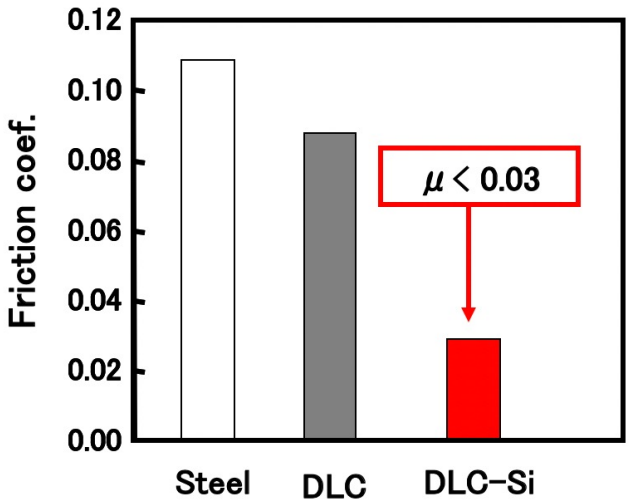
Designing coatings

TOYOTA CENTRAL R&D LABS

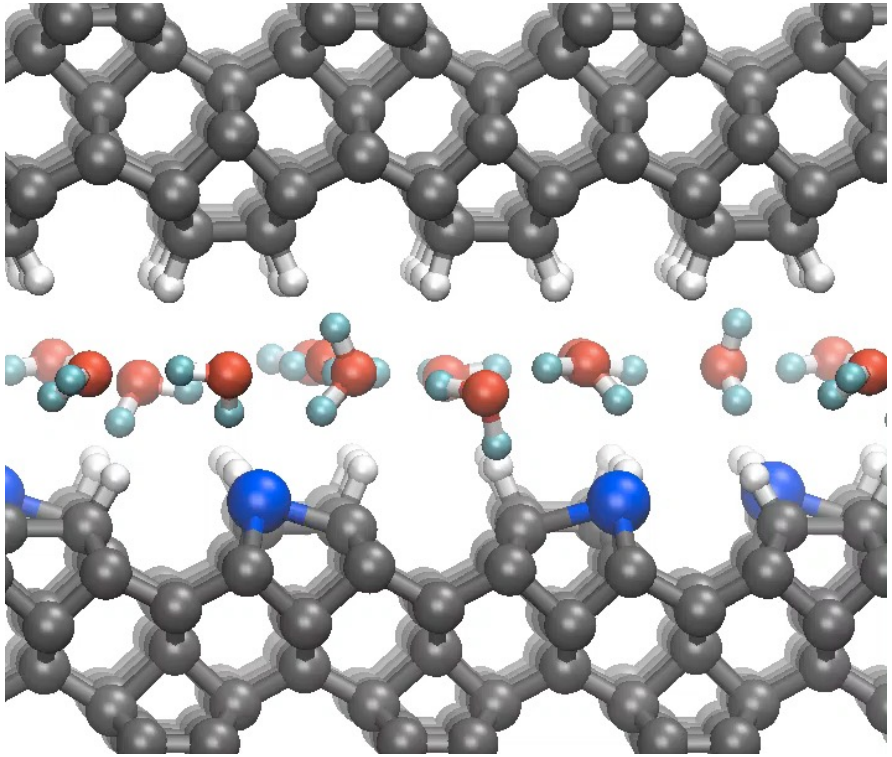
diamond like carbon (DLC)

used in automotive and racing to coat valves and part of the piston





Silicon dopants increase the surface hydrophilicity and reduce friction



2D materials formed in situ by mechanochemistry

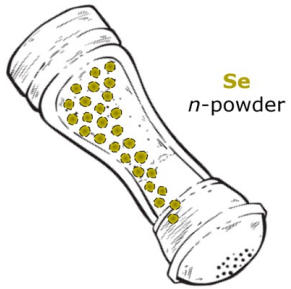
RESEARCH ARTICLE

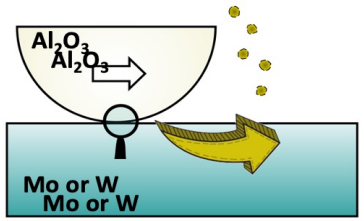
ADVANCED MATERIALS
www.advmat.de

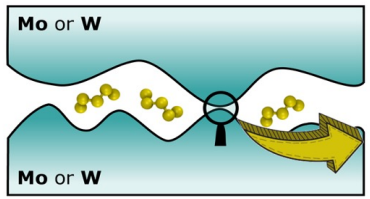
Se Nanopowder Conversion into Lubricious 2D Selenide Layers by Tribochemical Reactions

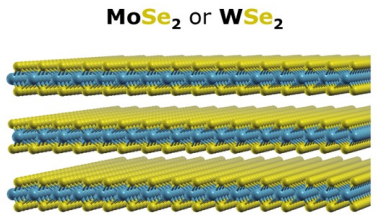
Philipp G. Grützmacher, Michele Cutini, Edoardo Marquis, Manel Rodríguez Ripoll, Helmut Riedl, Philip Kutrowatz, Stefan Bug, Chia-Jui Hsu, Johannes Bernardi, Carsten Gachot,* Ali Erdemir,* and Maria Clelia Righi**

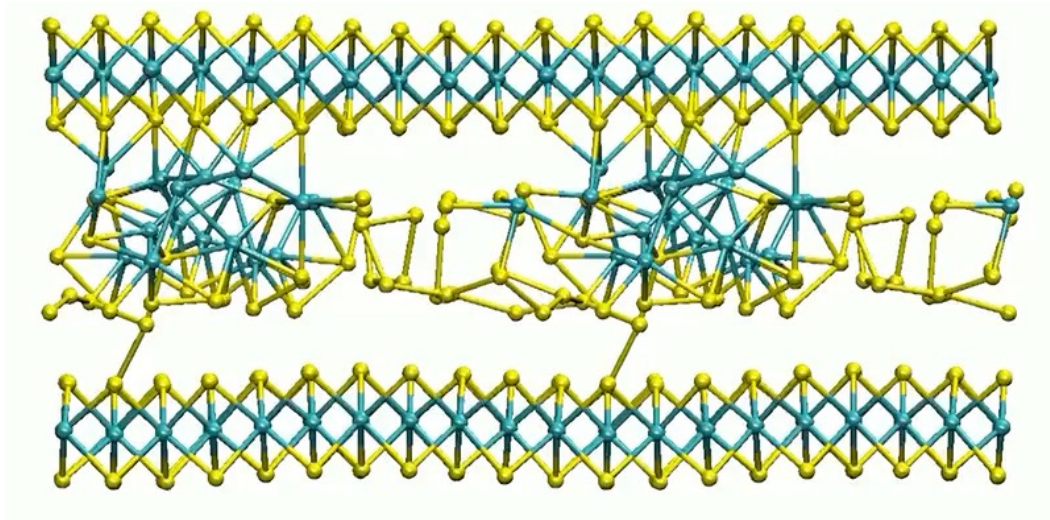
Adv. Mater. **2023**, 2302076

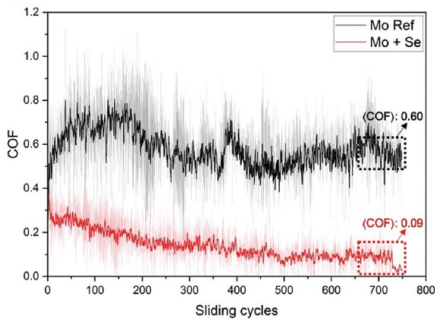


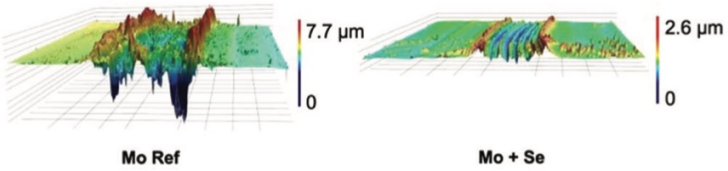












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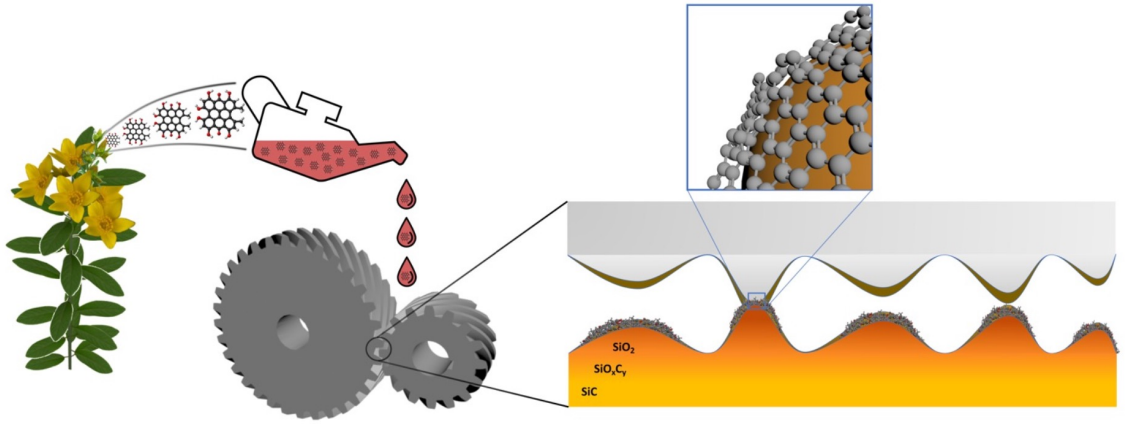
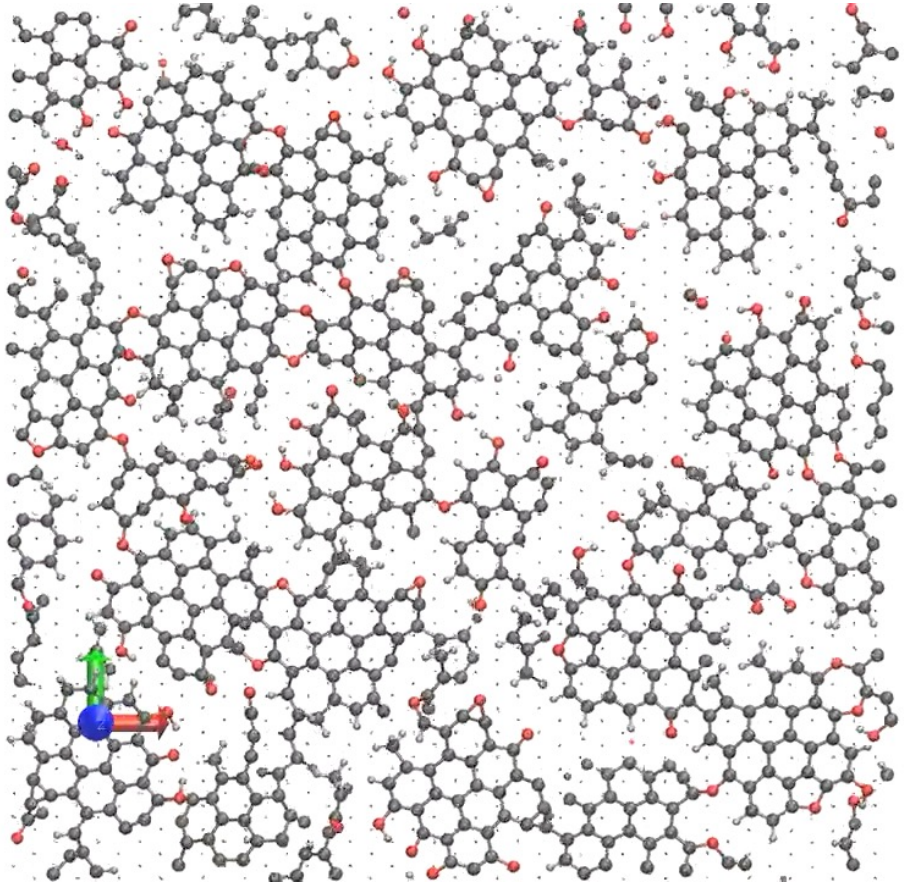
2D materials formed in situ by mechanochemistry





- Y. Long, A. Pacini, M. Ferrario, N. Van Tran, S. Peeters, B. Thiebaut, S. Loehlé, J.M. Martin, M.C. Righi, and M.I. De Barros Bouchet, *Graphene-induced superlubricity through antiviral hypericin in glycerol. A new concept for green lubrication*, **in printing Carbon (2024)**

- S. Peeters, G. Losi, S. Loehlé and M.C. Righi, *Aromatic molecules as sustainable lubricants explored by ab initio simulations*, **Carbon 203, 717 (2023).**

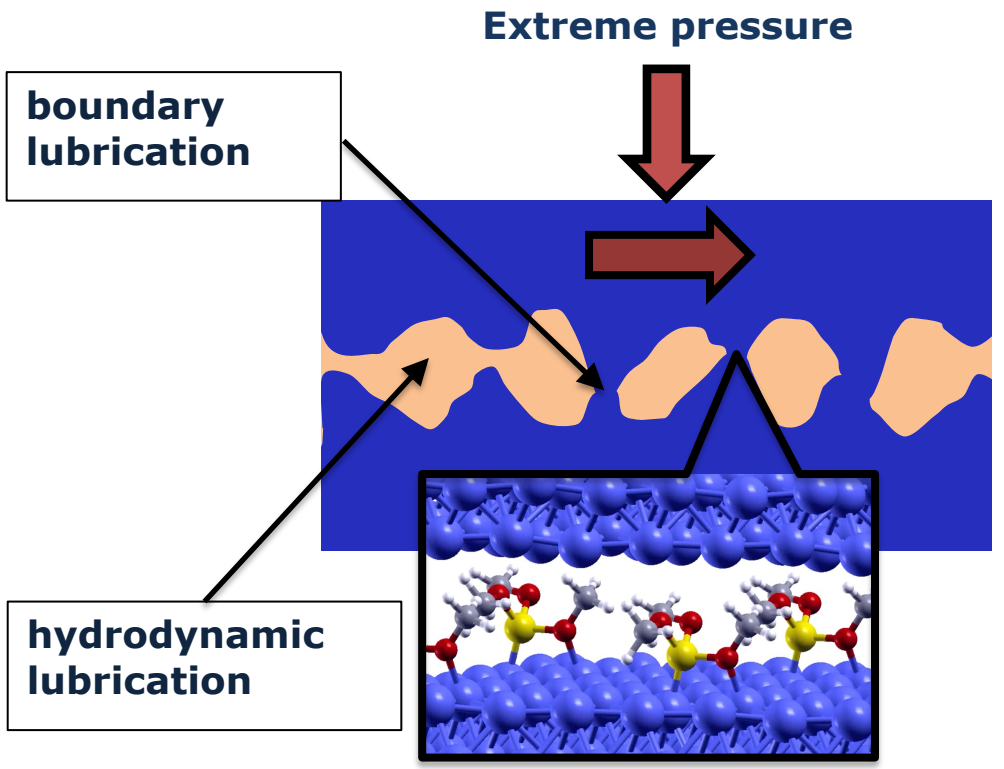
Designing lubricant additives

TotalEnergies

Key elements for extreme-pressure additives are **sulfur** and **phosphorus**

Limits have been imposed due to their **harmful effect on the environment**

Microscopic understanding is essential to design new compounds



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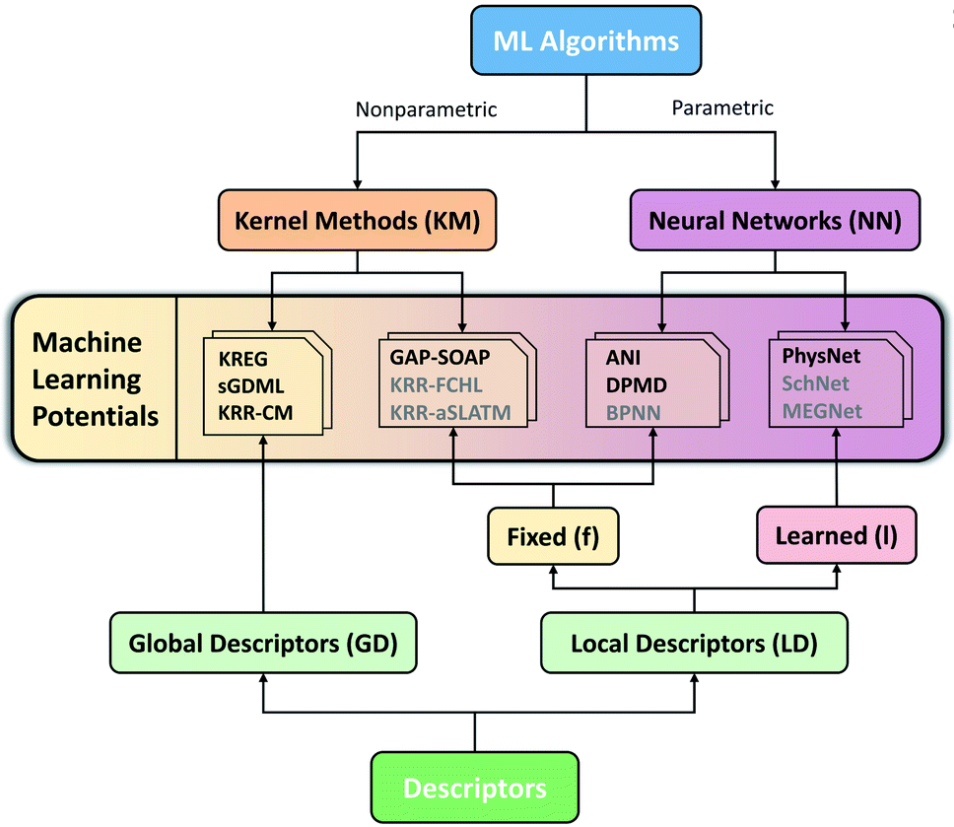
Machine learning (ML) interatomic potentials

Accuracy vs efficiency dilemma:

describe atomic interactions with the accuracy of *ab initio* MD;

simulate system evolution with the efficiency of classical MD;



Ab initio data are used to fit or to train the interatomic potentials used in MD

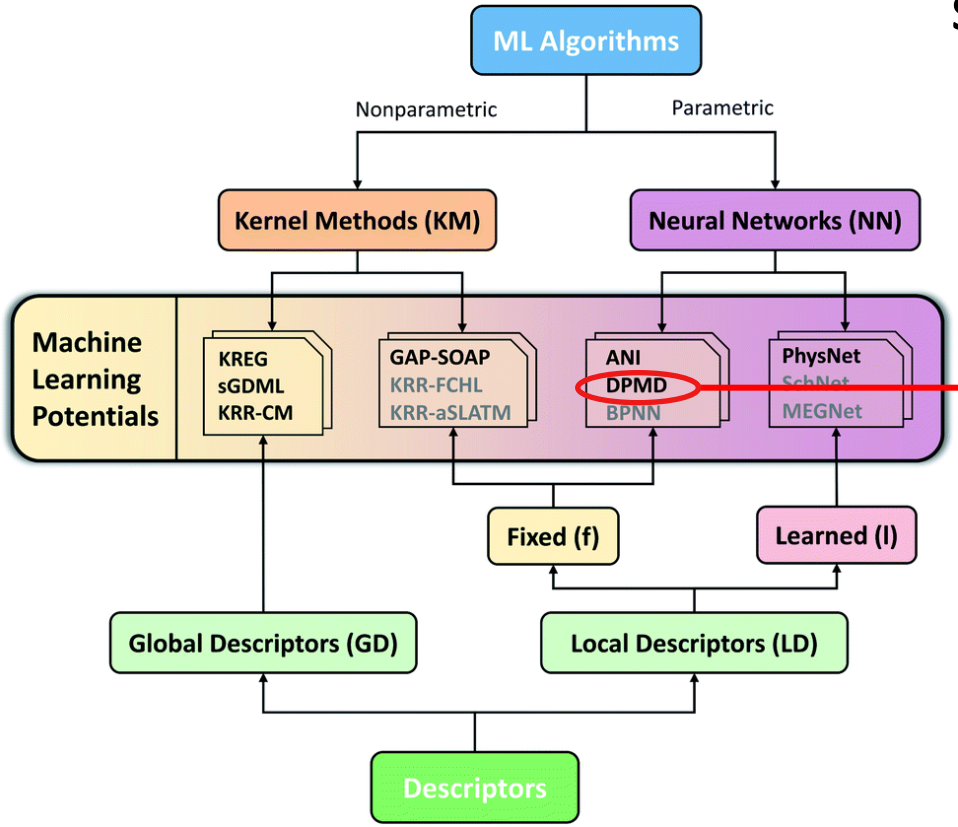
[M. Pinheiro, F. Ge, N. Ferré, P. O. Dral and M. Barbatti, Chem. Sci., 12, 14396 (2021)

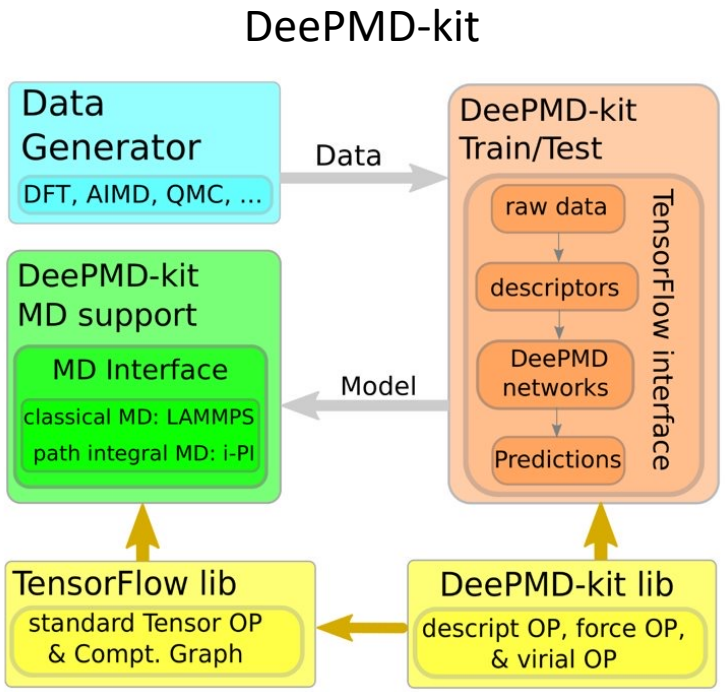
Machine learning (ML) interatomic potentials

accuracy vs efficiency dilemma:

Describe atomic interactions with the accuracy of ab initio MD;

Simulate system dynamics with the efficiency of classical MD;



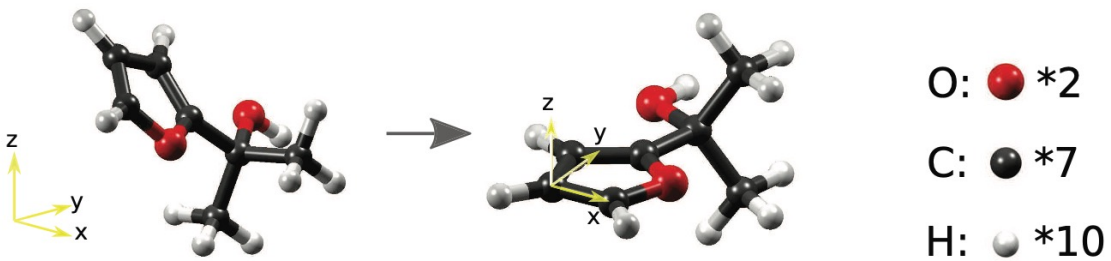


Deep learning models based on convolutional NN

- **L. Zhang, J. Han, H. Wang, R. Car, and W. E,**
  Phys. Rev. Lett. 120, 143001 (2018)
- **Han Wang, Linfeng Zhang, Jiequn Han, and Weinan E.**
  Comp. Phys. Com. 228, 178 (2018).
- **J. Zeng et al. J. Chem. Phys., 159, 054801 (2023).**

[M. Pinheiro, F. Ge, N. Ferré, P. O. Dral and M. Barbatti, Chem. Sci., 12, 14396 (2021)

DeePMD: method

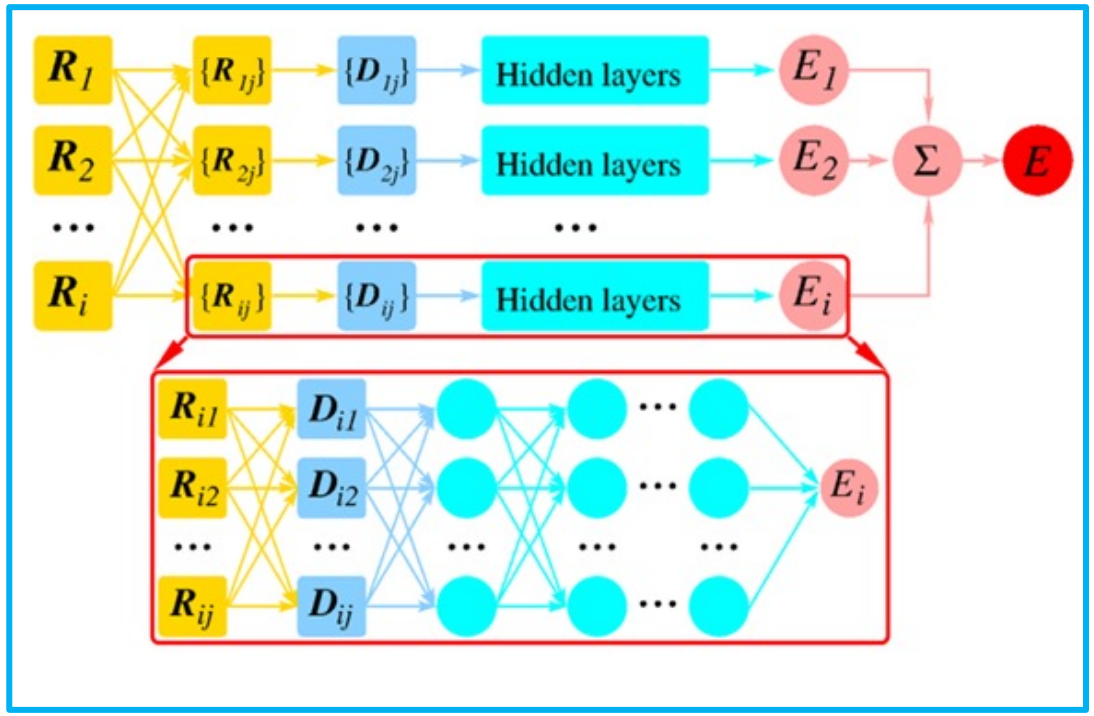


O: *2

C: *7

H: *10

Neural Network



Descriptors define the local atomic enviroment of each atom within a cutoff distance

Descriptors are in-layer of a NN which has as out-layer the local atomic energy.

The total energy of the system configuration then obtained by summing up all the local energies.

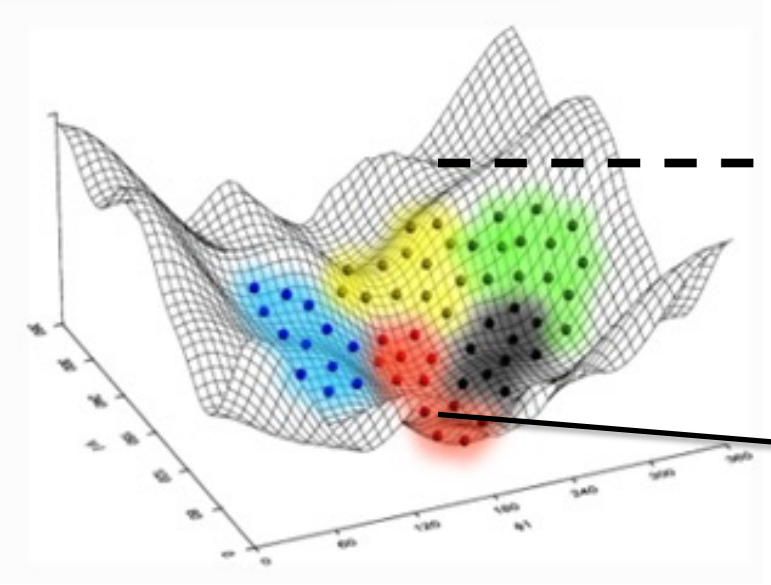
$$L \propto \sum |E_{ab\ initio} - E_{NN}|^2 + |F_{ab\ initio} - F_{NN}|^2$$

Minimize the loss function adjusting the NN parameters

Train the Neural Network with ab initio data

NN is an interpolator: unphysical results can be obtained if not well trained !

NN it produces a reliable dynamics when the systems evolves in regions of the configuration space sampled during the training



Unknown configuration space

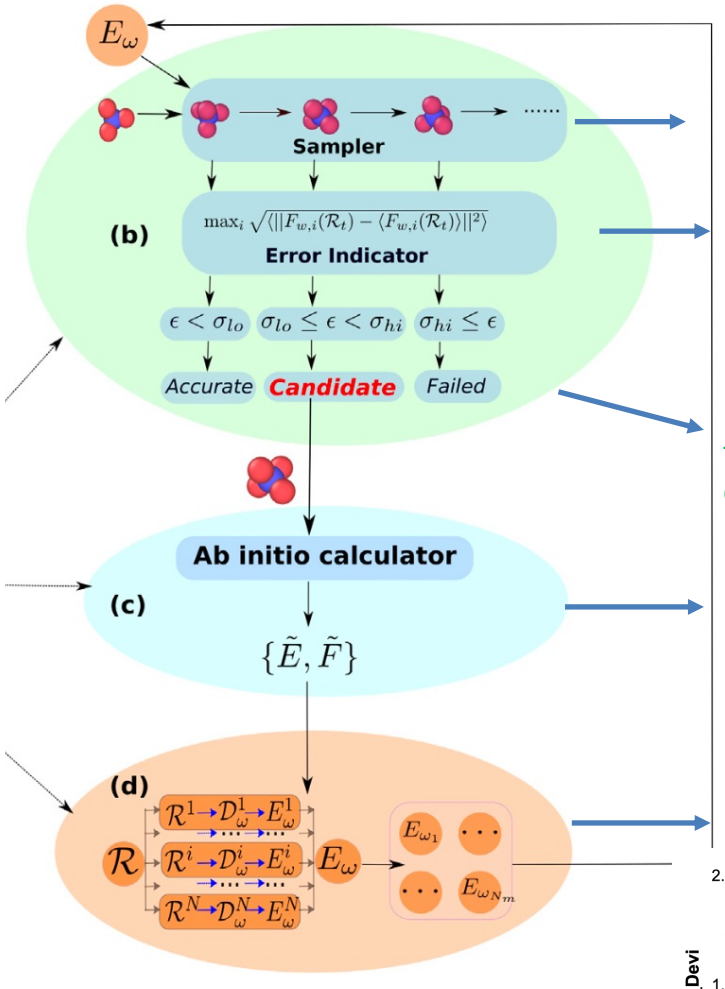
Known configuration space

in poorly explored regions ML-MD becomes unstable producing unphysical results

In the tribological systems the configuration space can vary a lot.
In these systems a straightforward use of AIMD is not not sufficient

Active learning

the atomic configurations used for the training are generated by the ML-MD itself, which reduces a lot the exploration time with respect to AIMD.



An initial dataset is used to train four NN

ML-MD with one NN to generate configurations, energy, forces

Calculate maximum force deviation produced by the four NN

$$\epsilon_t = \max_i \sqrt{\langle \|F_{w,i}(\mathcal{R}_t) - \langle F_{w,i}(\mathcal{R}_t)\rangle\|^2\rangle}$$

$$F_{w,i}(\mathcal{R}_t) = -\nabla_i E_w(\mathcal{R}_t)$$

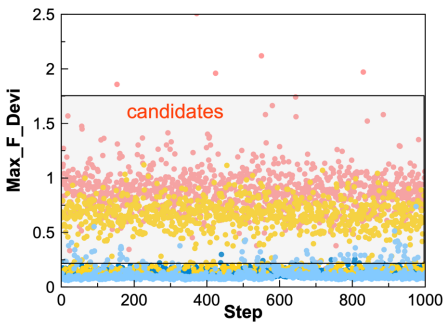
$$\langle F_{w,i}(\mathcal{R}_t)\rangle = \frac{1}{N_m}\sum_{\alpha=1}^{N_m} F_{w_\alpha,i}(\mathcal{R}_t)$$

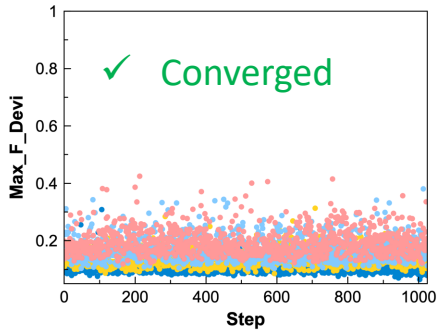
If the deviation is greater than a threshold the configuration is selected to enlarge the dataset

Ab initio calculations of energy and forces for selected candidates
Dataset enlarged

Train 4 NNs with the new dataset.
Repeat the procedure until no candidates are found

Train 4 models from the same data





Smart Configuration Sampling (SCS) software developed by our group and coupled with QE

A. Pacini, M. Ferrario, S. Loehlè, M.C. Righi, in printing The Eouropean Physical Journal Plus (2024)

Dp-gen package coupled with Vasp

Yuzhi Zhang, Haidi Wang, Weijie Chen, Jinzhe Zeng, Linfeng Zhang, Han Wang, and Weinan E, Computer Physics Communications, 107206 (2020).

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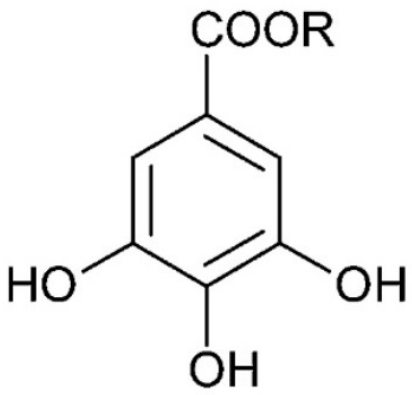
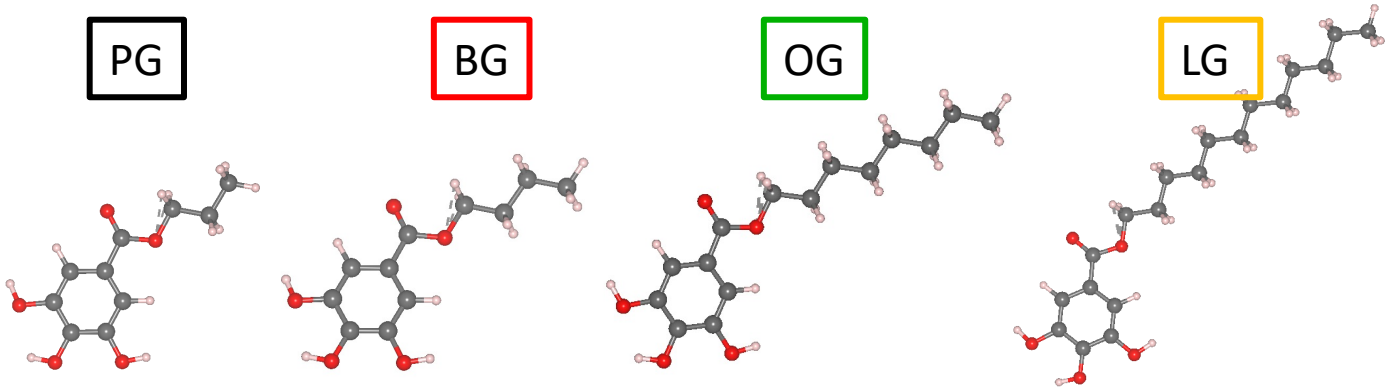
NN potential for Gallate molecules at sling iron interfaces



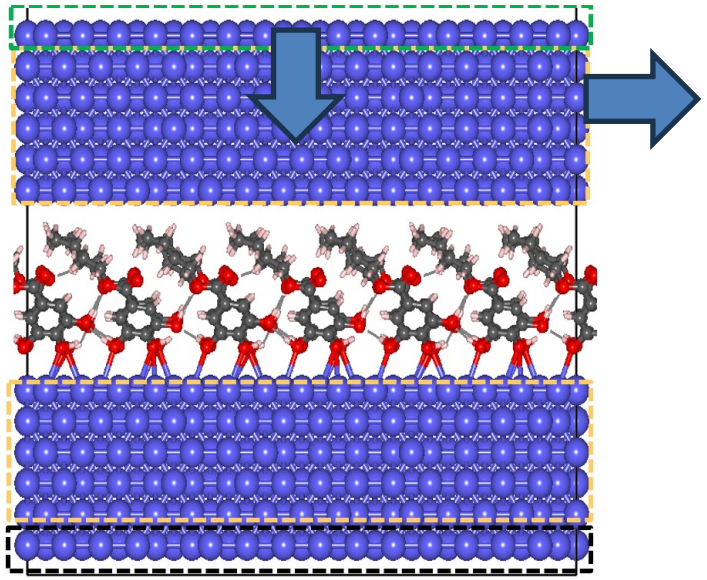
Easily accessible

Anti-Oxidant

Eco-friendly



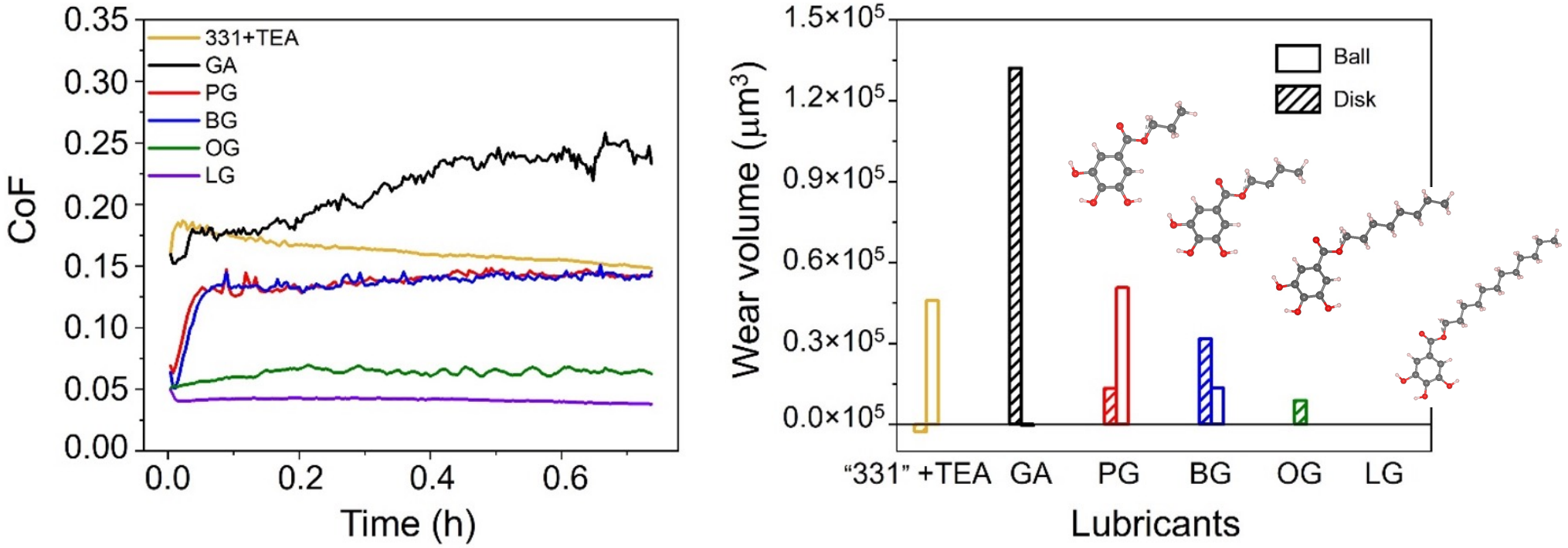
1. R = H – gallic acid (GA)
2. R = C_3H_7 – propyl gallate (PG)
3. R = C_4H_9 – butyl gallate (BG)
4. R = C_8H_{17} – octyl gallate (OG)
5. R = $C_{12}H_{25}$ – lauryl gallate (LG)



High accuracy needed in DFT for training NN involving **iron**

A. Pacini, M. Ferrario, S. Loehlè, M.C. Righi, Computational Materials Today 1, 100005 (2024)

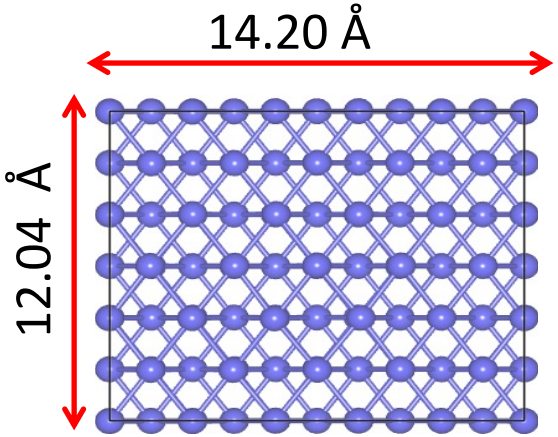
Measured friction and wear depend on the chain length



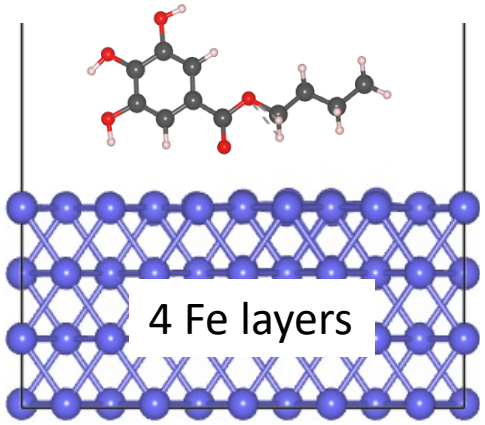
Tribological experiments by M. I. De Barros Bouchet and J. M. Martin and at LTDS

→ The longer the chain, the lower the COF and wear

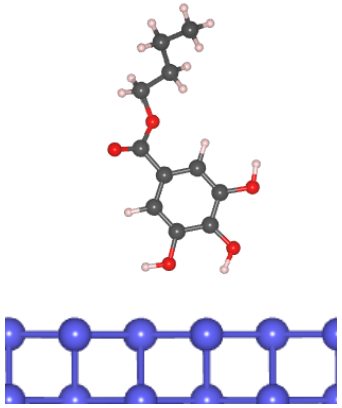
DFT calculations: Adsorption on Fe(110) surface



Fe(110) surface
30 atoms peer layer,
Slabs of 4 layers



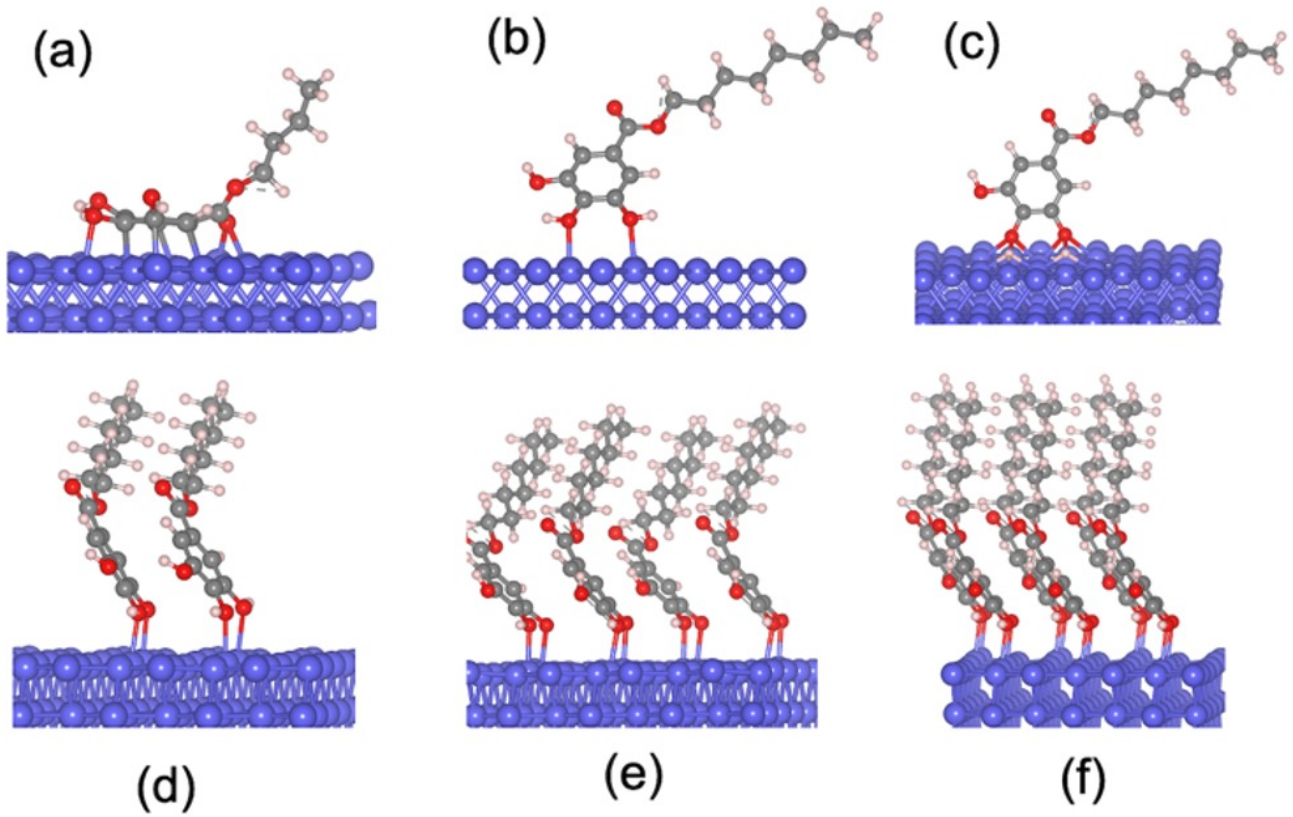
Parallel orientation
4 initial structures

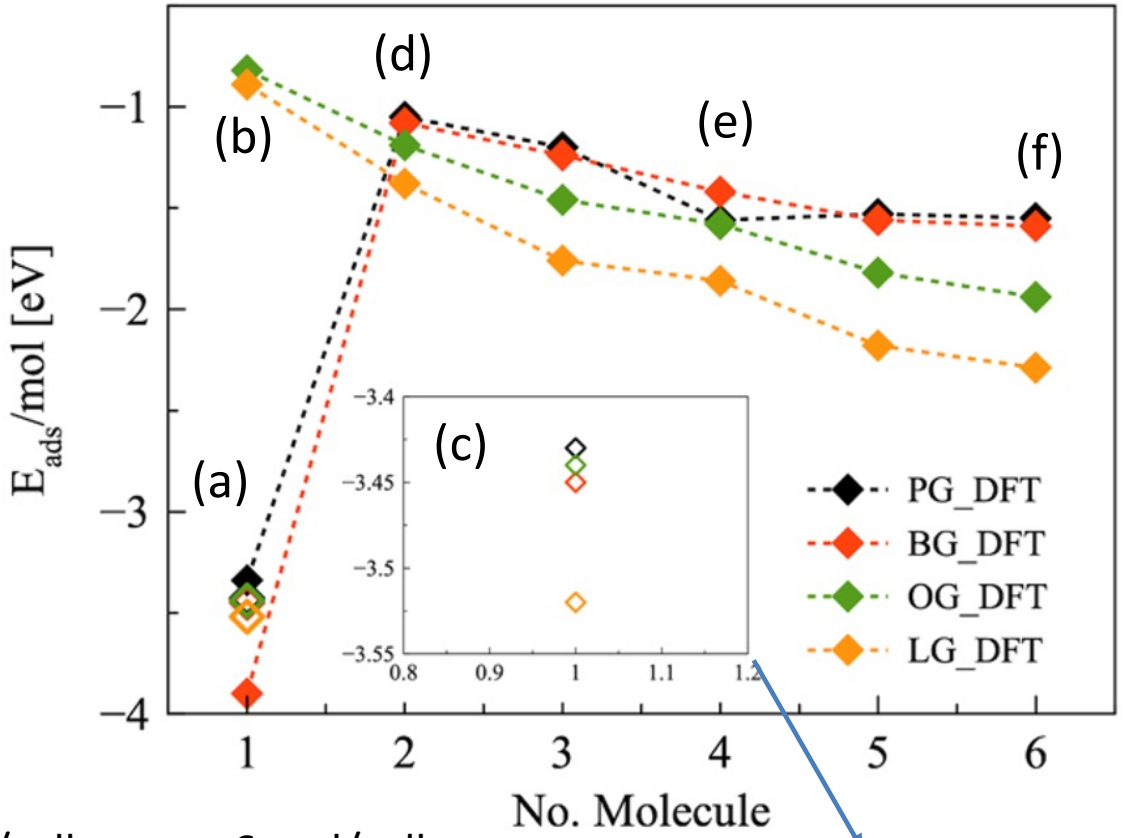


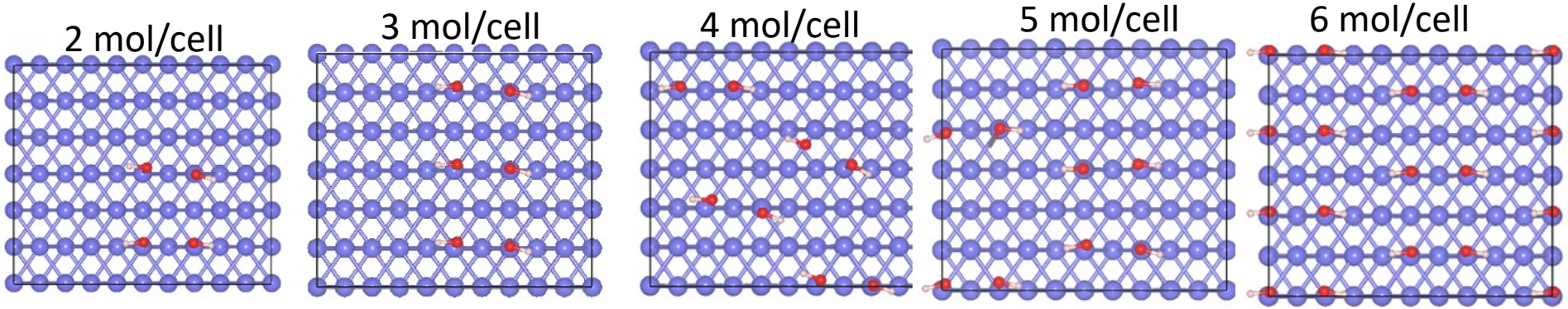
Perpendicular orientation
4 initial structures

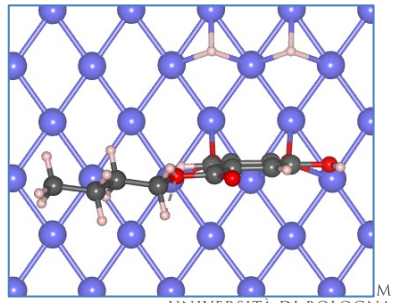
- Gallates adsorption considering different orientations and coverages.
- DFT calculations using VASP package, projector-augmented wave (PAW) method, spin-polarized calculations, cutoff energy to 450 eV, GGA-PBE functional, and vdw-D2 corrections.
- Adsorption energy: $E_{ads} = E_{total} - E_{BG} - E_{Fe}$

Results on molecular adsorption



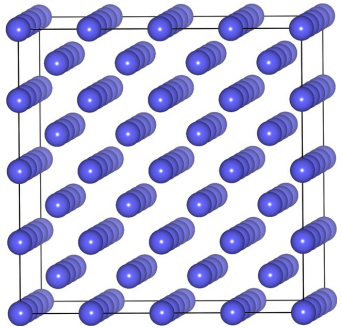




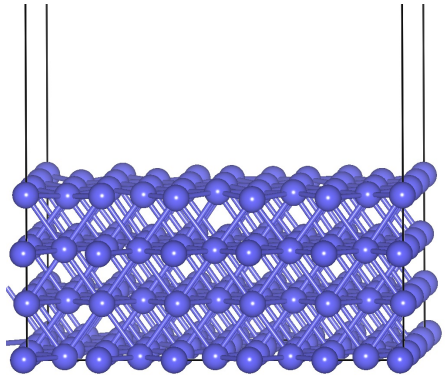


Data for training the initial NN

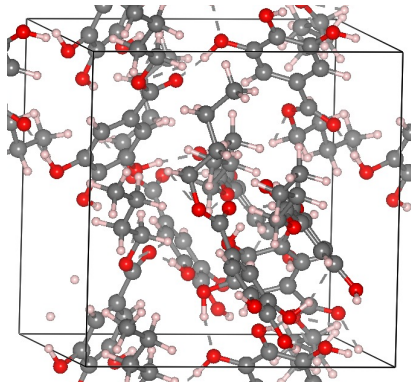
- Initial data: completely from AIMD
- 5 systems with different densities, chemical components, and temperatures
- AIMD simulations at 300, 500, 1000, and 3000 K



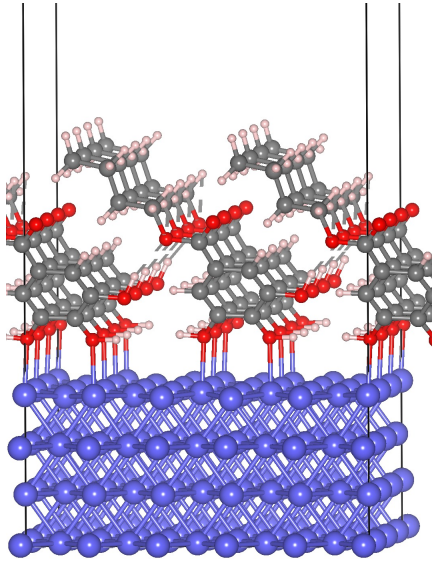
Bulk Fe



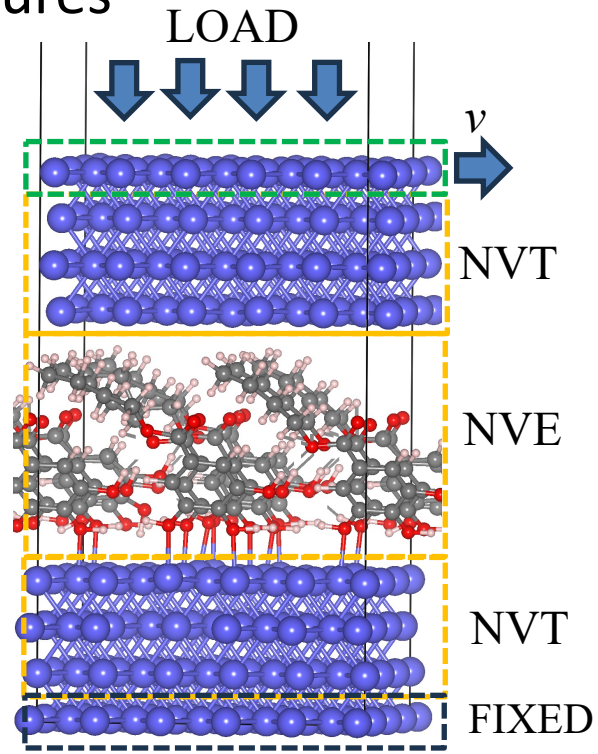
Fe surface



Gallate molecules



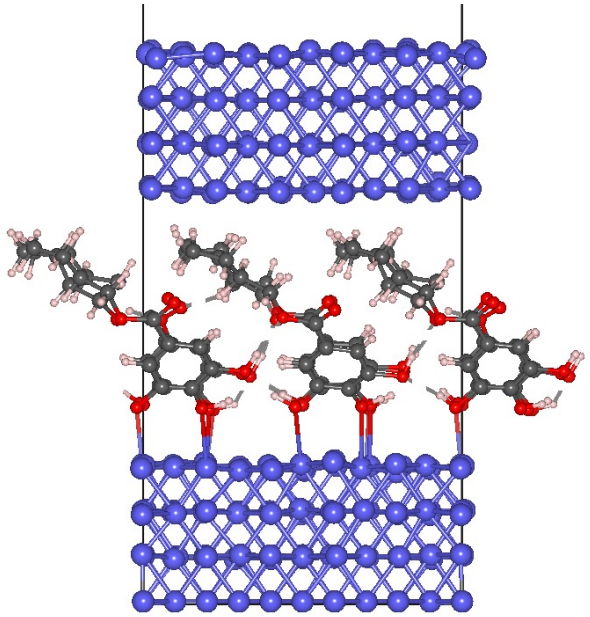
Molecules on surface



Molecules at the tribo interface

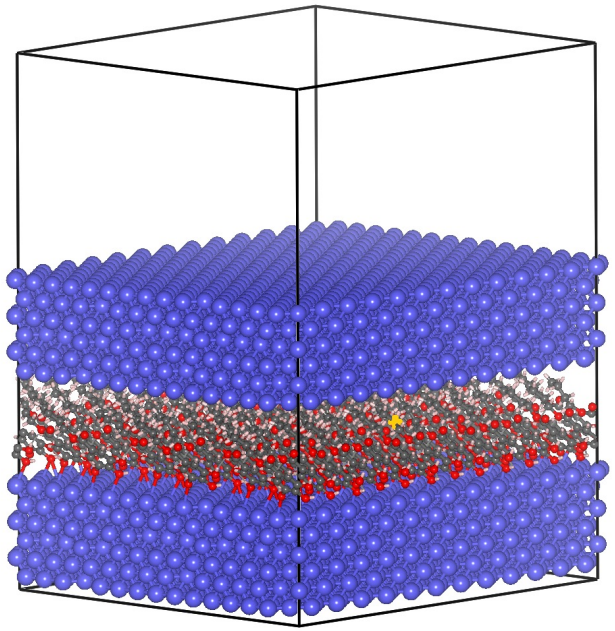
From DFT to NN and MD simulations

Active learning and Testing



Fe interf. + 6 molecules
(420 atoms)

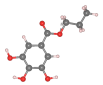
MD – production run



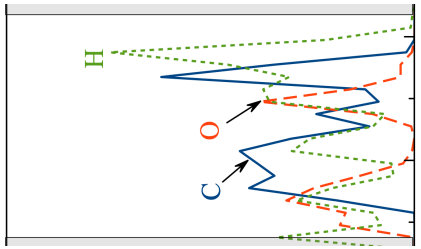
Fe interf. + 72 molecules
(6480 atoms)

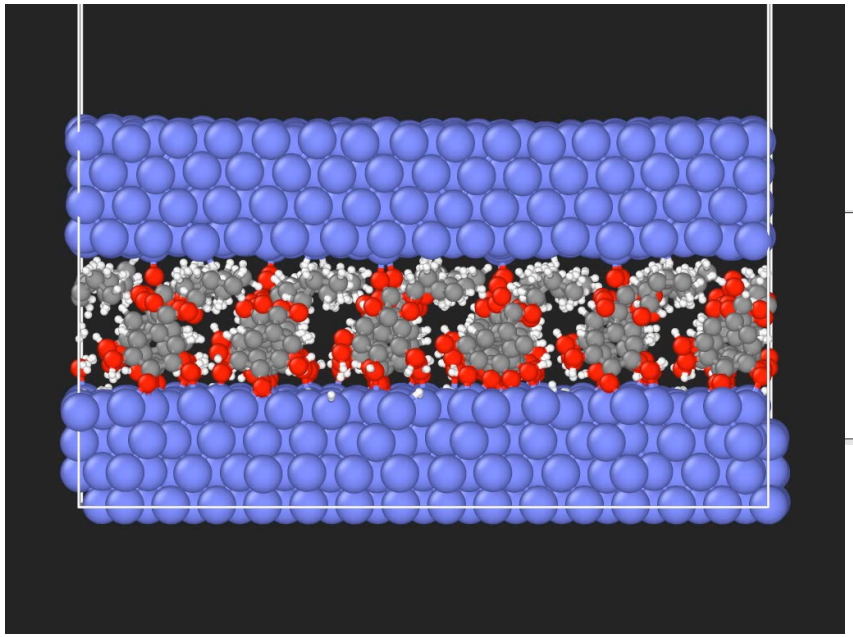
- 0.2 ns equilibration at T = 300 K followed by 1 ns of sliding
- Five different loads applied: 0.5 Gpa, 1.0 Gpa, 1.5 Gpa, 2.0 GPa, 2.5 Gpa
- Three different coverages: 100%, 66%, 50%
- Four different molecules: PG, BG, OG, LG

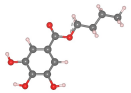
100% coverage, 2GPa



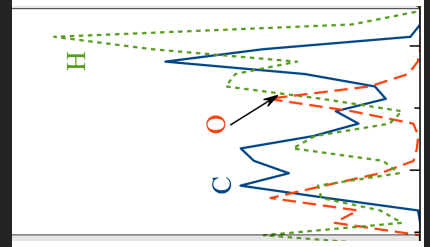
PG

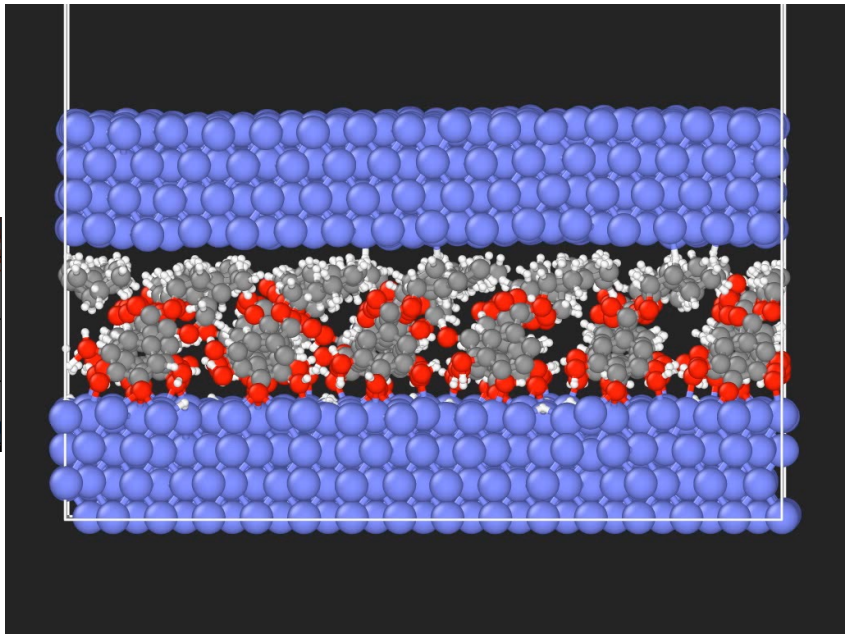


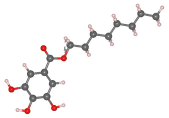




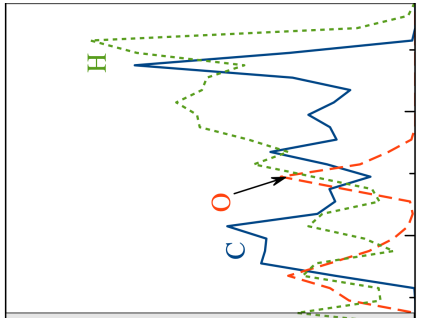
BG

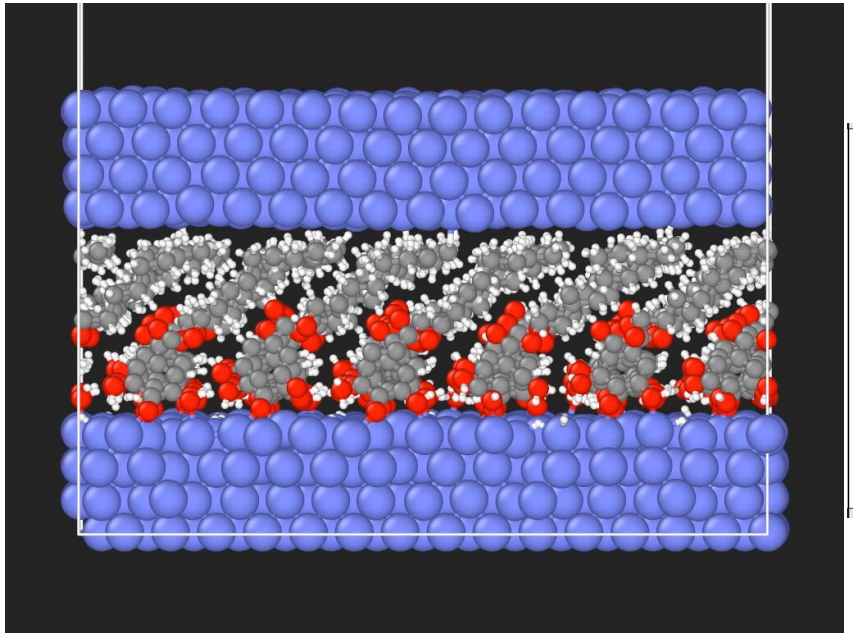


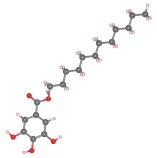




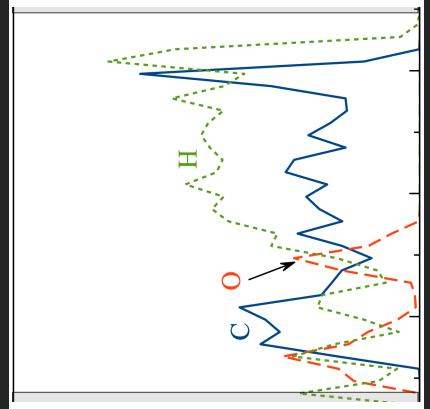
OG

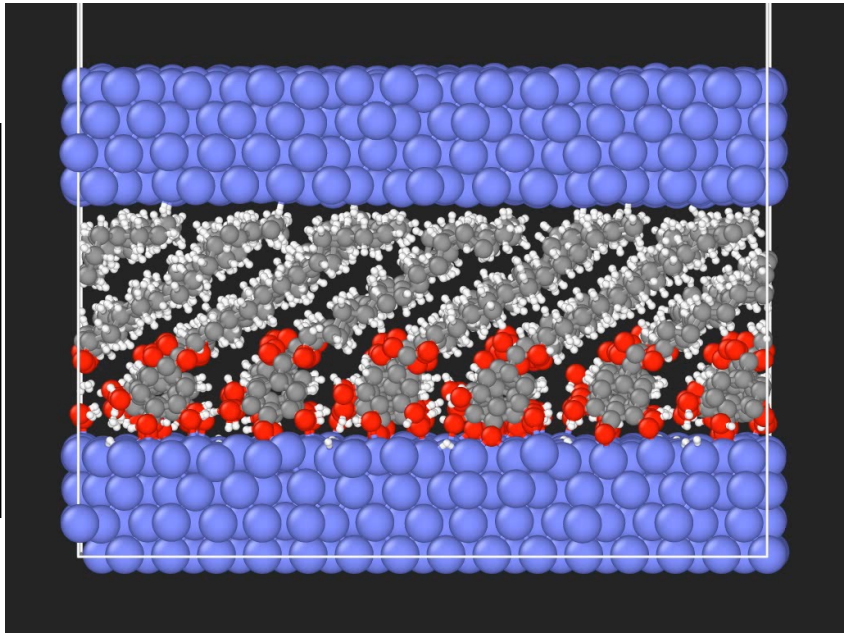






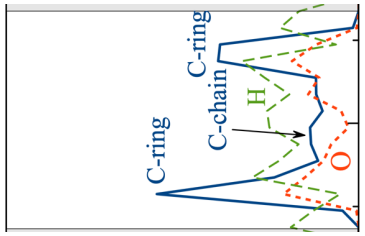
LG

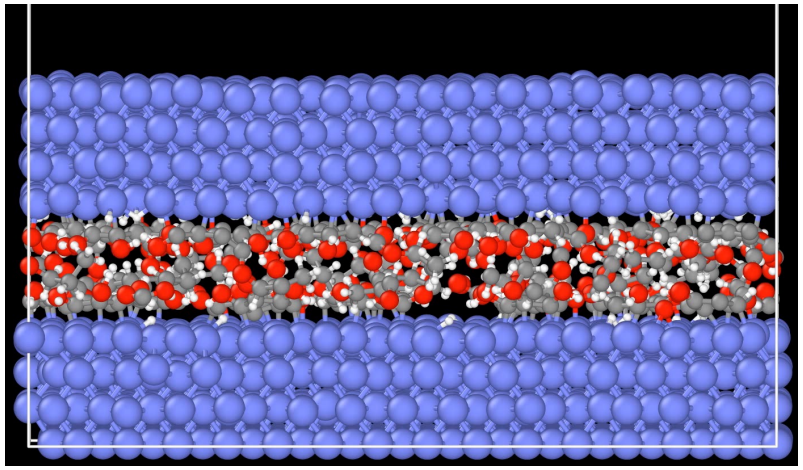




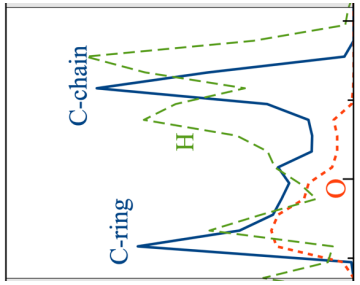
66% coverage

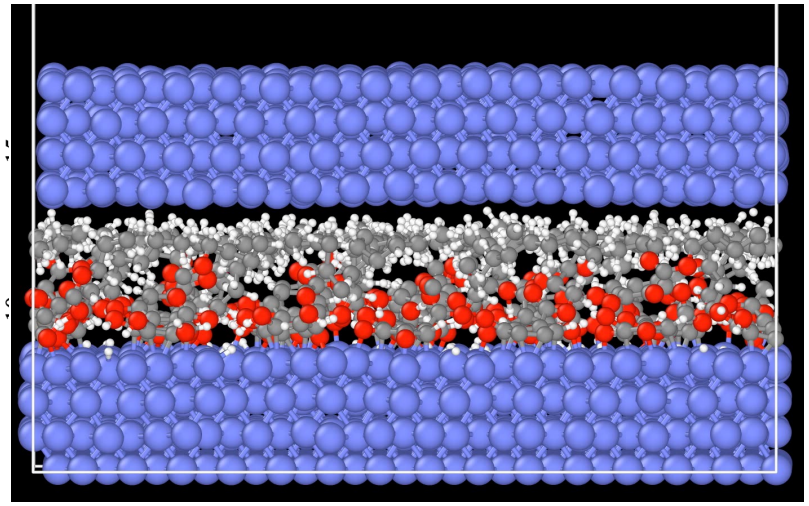
PG





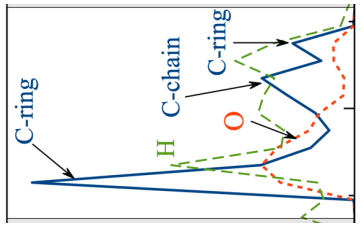
OG

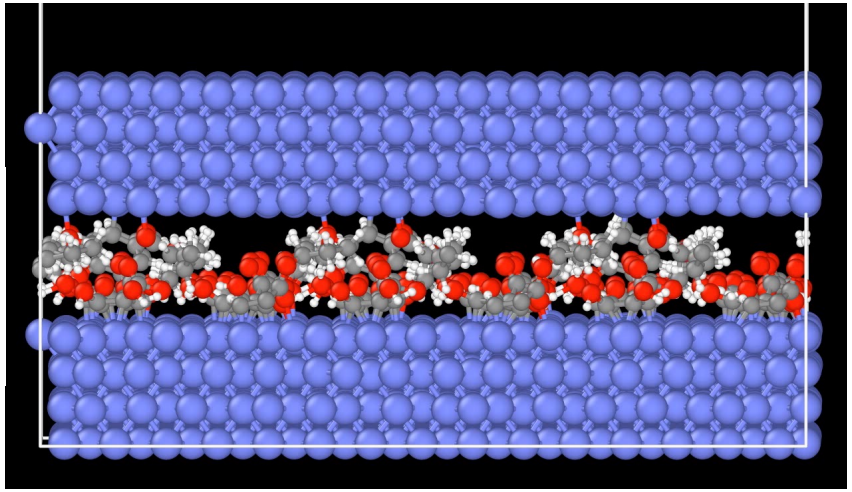




50% coverage

PG





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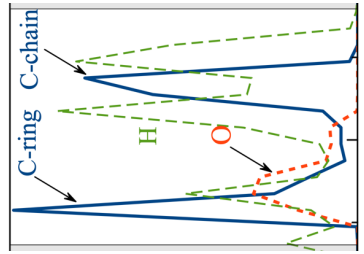
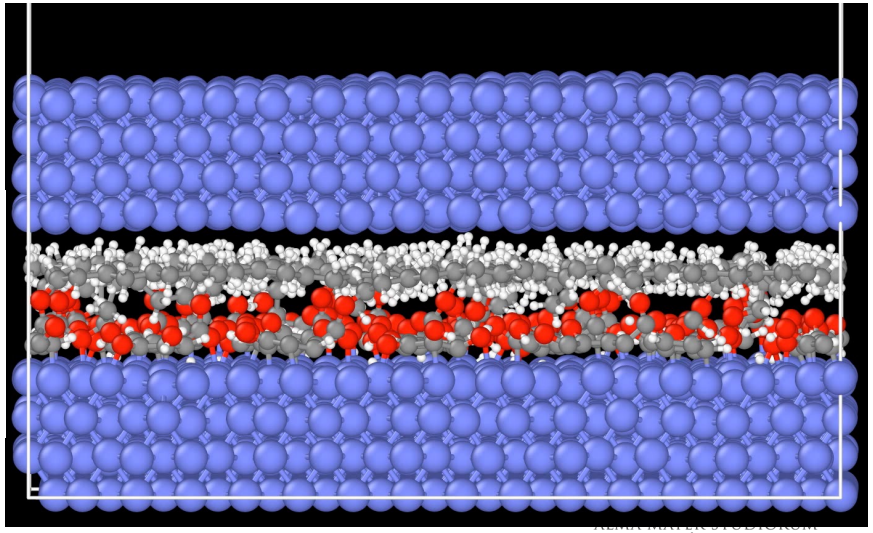
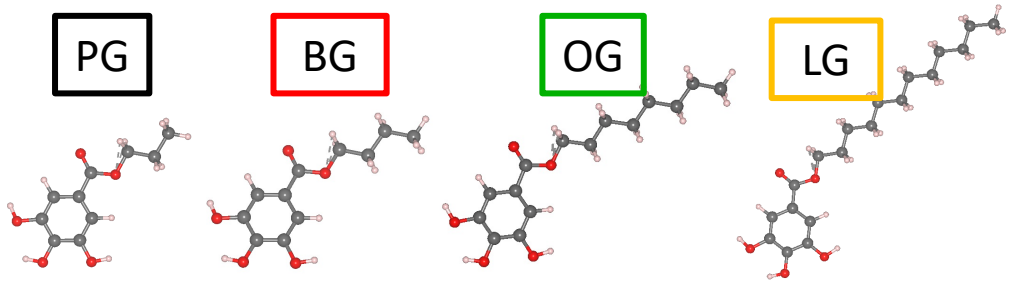
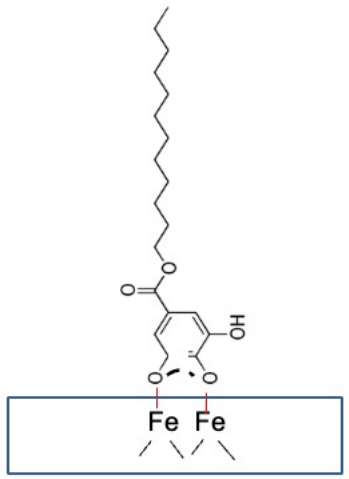


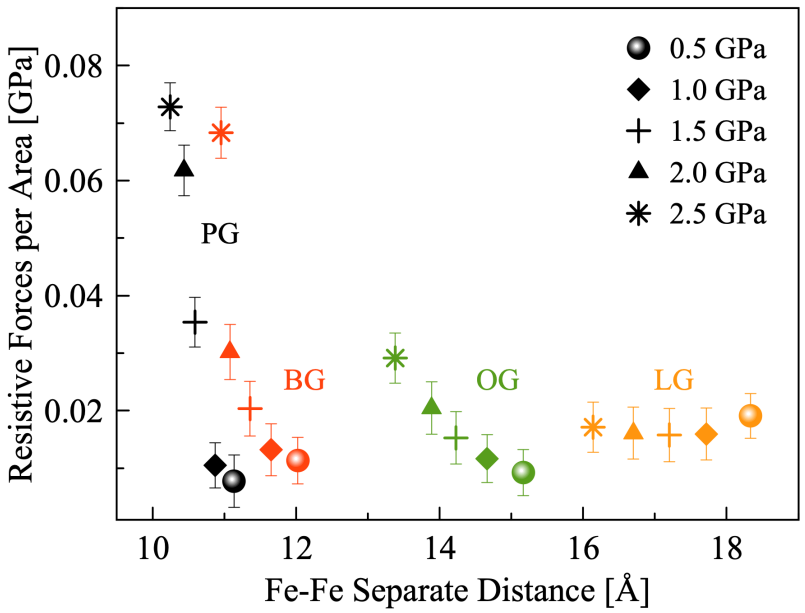


Effect of chain length explained

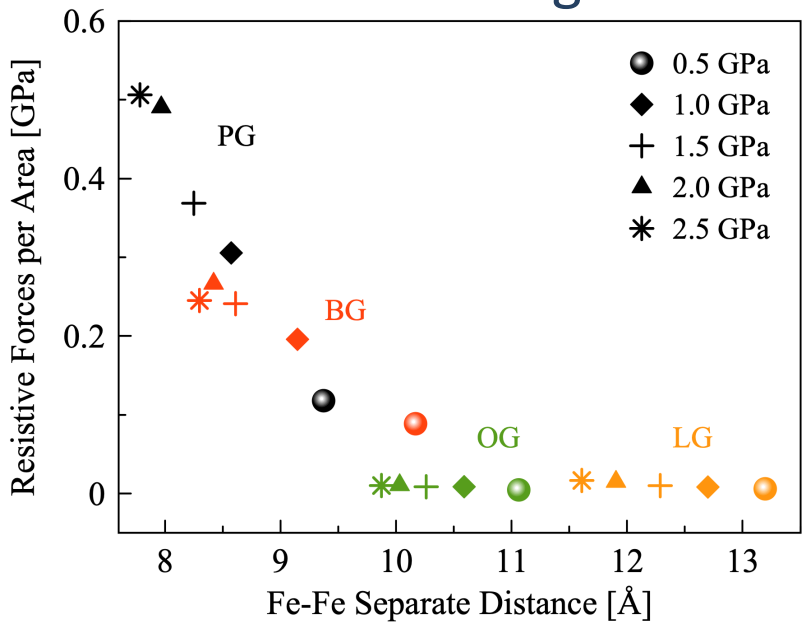


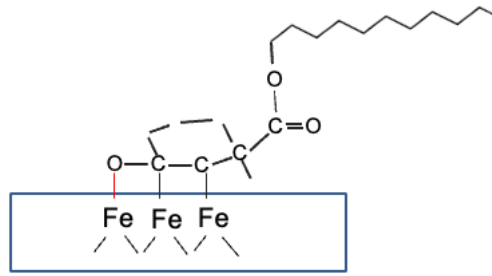


100% coverage



66% coverage



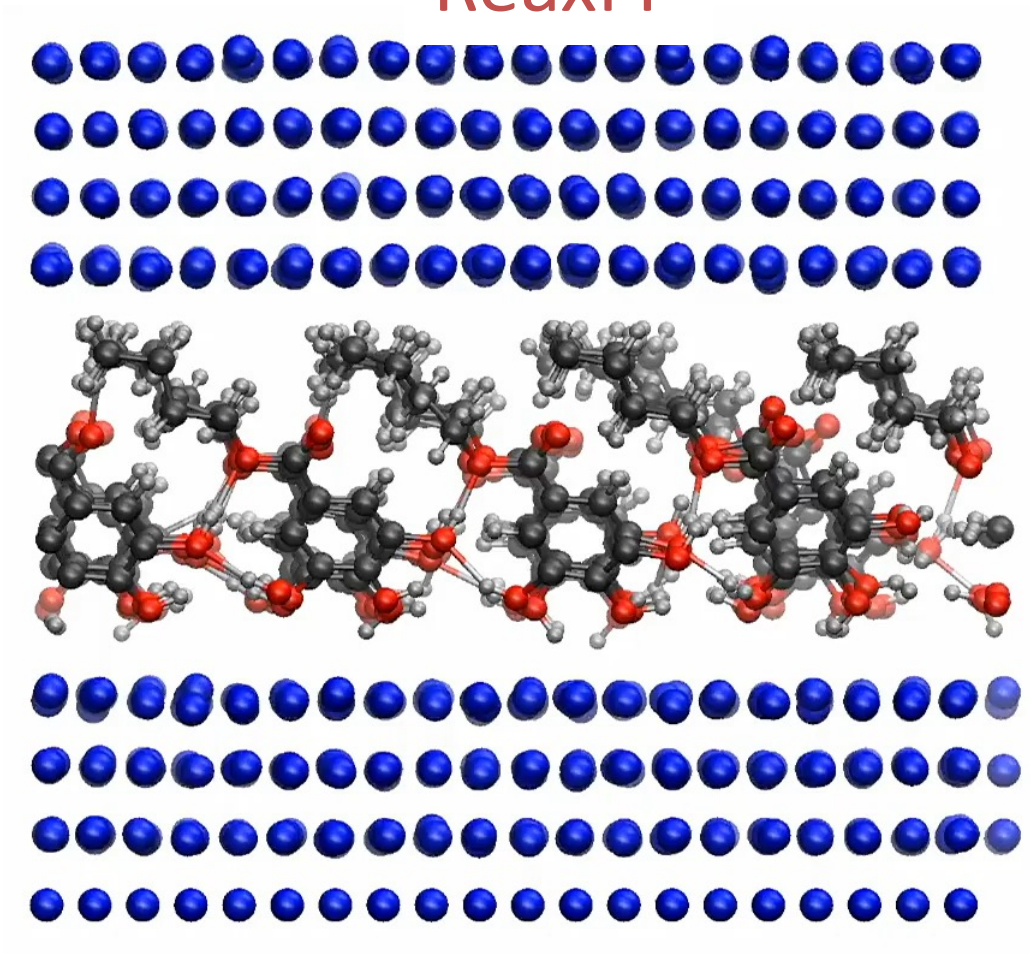


→ The longer the chain, the higher the interfacial separation, the lower the friction force.

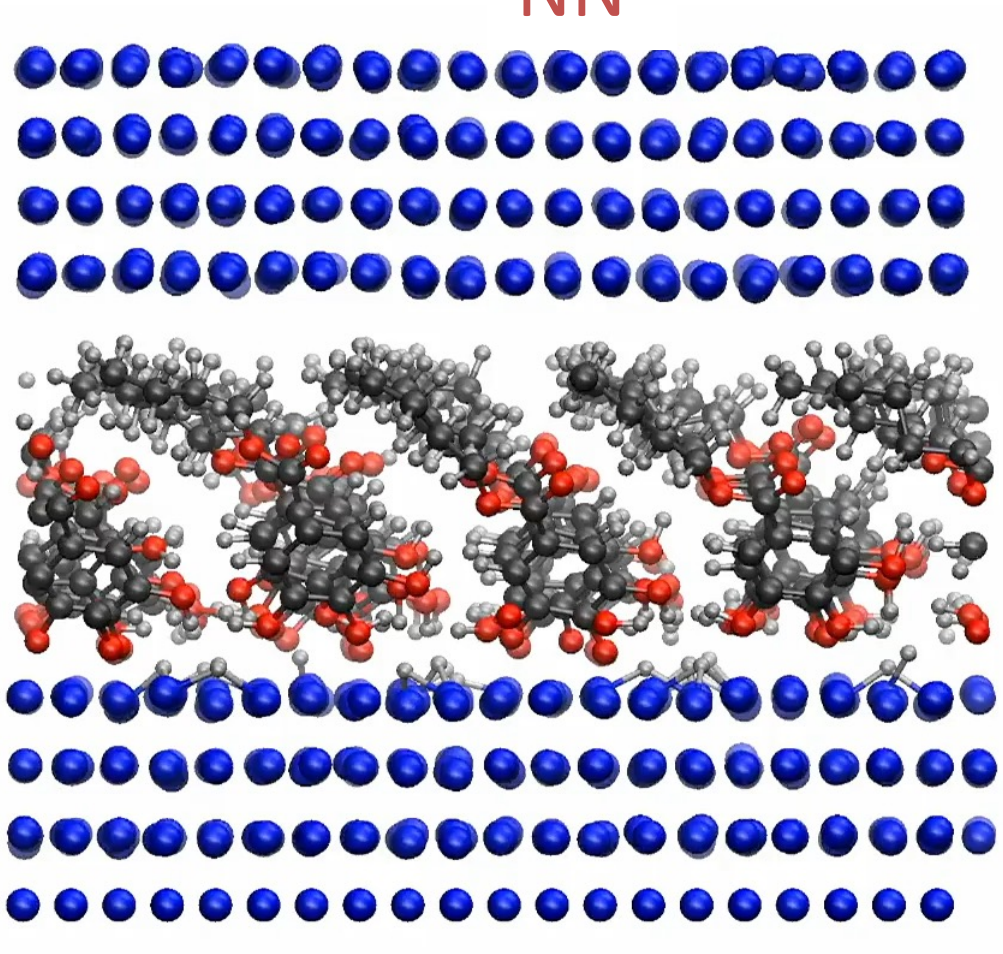
Comparison with ReaxFF

28BG at 0.5 GPa, 300 K

ReaxFF



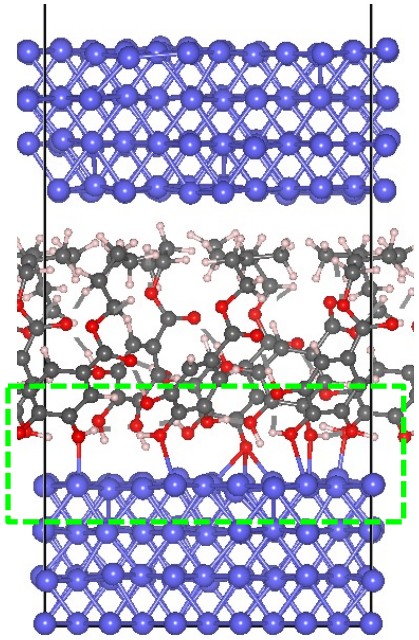
NN



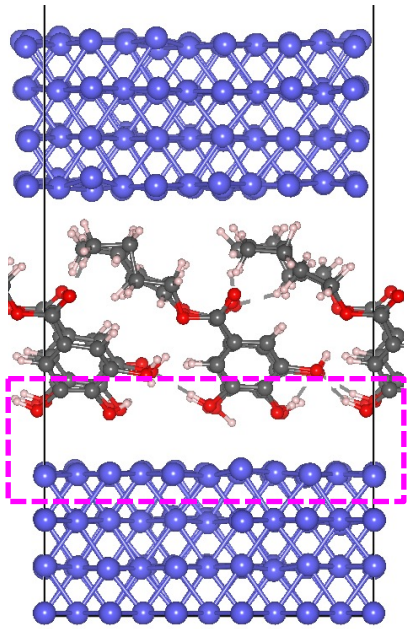
ReaxFF potential:

- Y.K. Shin, H. Kwak, A.V. Vasenkov, D. Sengupta and A.C.T. van Duin ACS Catalysis, 2015, 5 (12), pp 7226-7236
- (Fe parameters identical to M. Aryanpour, van Duin and Kubicki, J Phys Chem A, 2015, 114, 6298-6307)
- [QEQ charge equilibration (Rappe & Goddard) following Aktulga, Fogarty, Pandit, Grama, Parallel Computing, 2012, 38, 245-259]

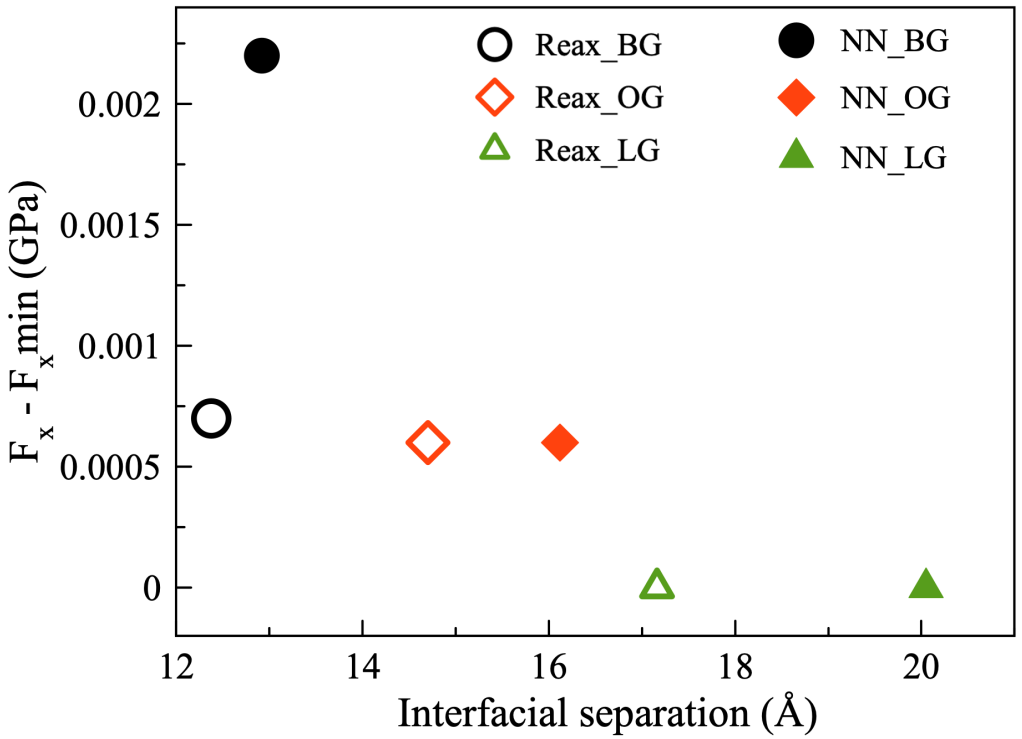
The effect of chain length not captured by ReaxFF



NN
Sliding, 1 Gpa, 100 ps

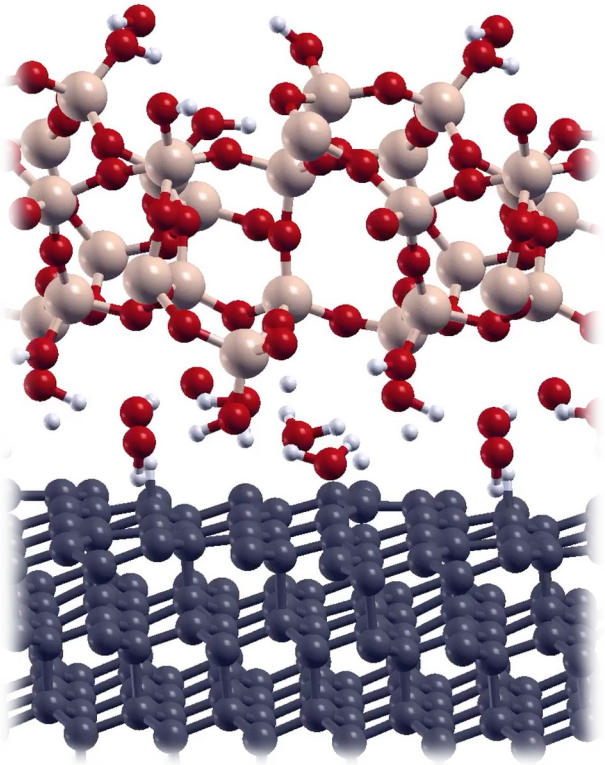


Reax FF
Sliding, 1 Gpa, 100 ps



- Reaxff does not allow H detachment and molecular docking to the substrate
- Relative motion of the molecules to the substrate
- No effect of chain length

Ab initio studies on diamond– silica interfaces



1. Tribochemistry of silica-diamond interface

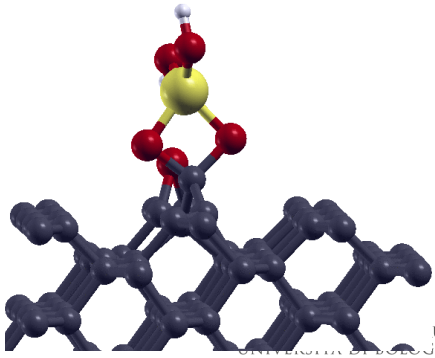
- ***Adhesion, Friction and Tribochemical reactions at the Diamond-Silica Interface*, Carbon 203, 601 (2023)**
- ***Nanotribological Properties of Oxidized Diamond/Silica Interfaces: Insights into the Atomistic Mechanisms of Wear and Friction by Ab Initio Molecular Dynamics Simulations*, ACS Applied Nano Materials 6, 16674 (2023)**

2. Atomistic mechanisms of diamond wear

- *Atomistic Wear Mechanisms in Diamond: Effects of Surface Orientation, Stress, and Interaction with Adsorbed Molecules,* **Langmuir 39, 14396 (2023)**

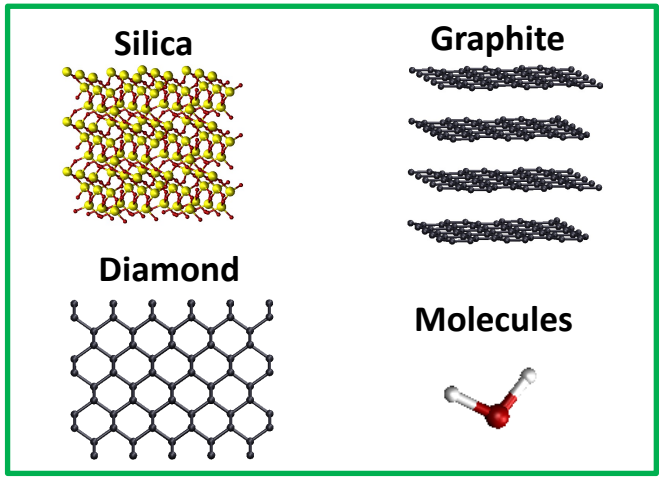
3. Adsorption and dissociation of H_2, H_2O and O_2 on diamond

- *Ab initio insights into the interaction mechanisms between H2, H2O, and O2 molecules with diamond surfaces,* **Carbon 199, 497 (2022)**
- Tuning the adsorption of H2O, H2 and O2 molecules on diamond surfaces by B-doping, **Surfaces and Interfaces 46, 104105 (2024)**



Active learning with SCS (ongoing)

We use our in-house developed workflow, *Smart Configuration Sampling (SCS)* to perform active learning



Starting dataset

~2000 *ab initio* configurations

SCS iterations

Ensamble Training

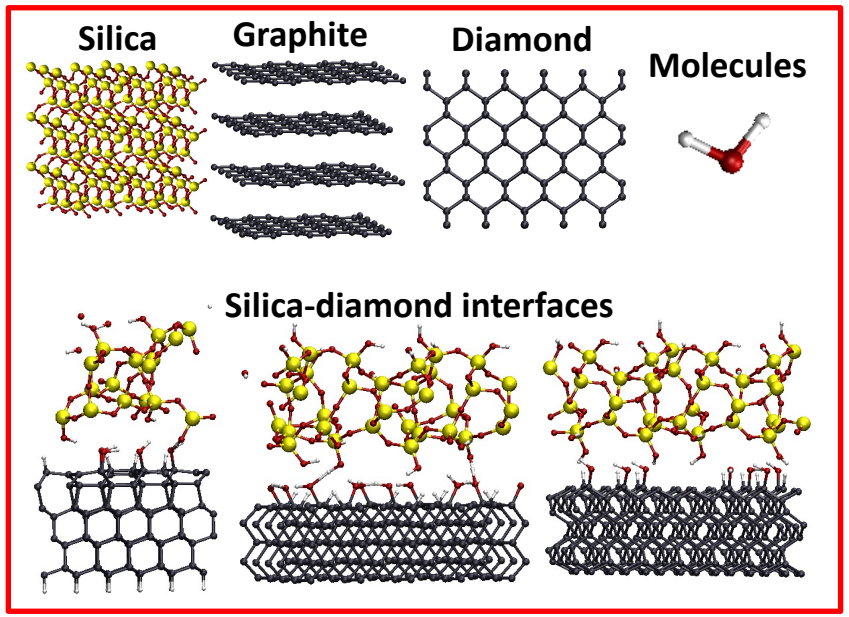
Exploration

ab initio sampling

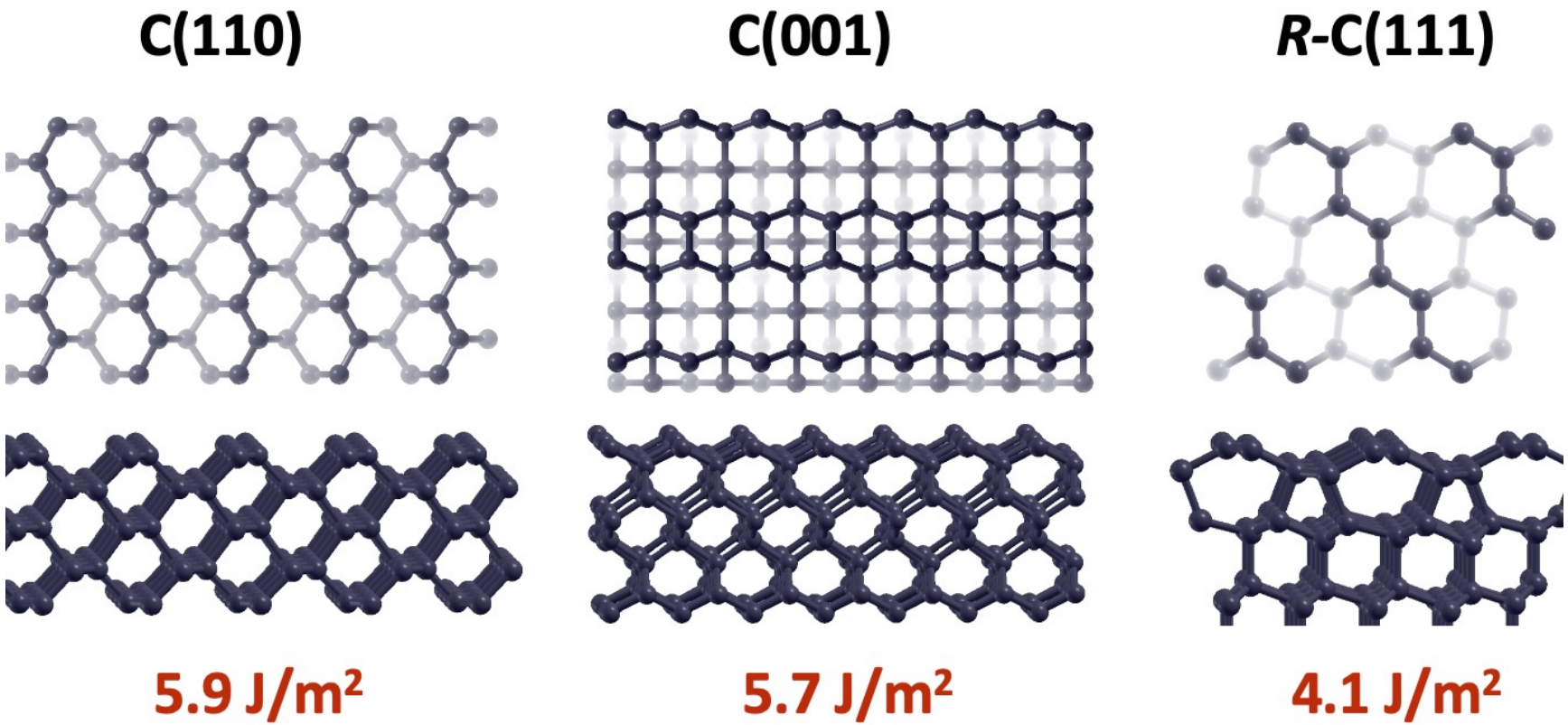
Enlarged dataset

Final dataset

~2500 *ab initio* configurations (**on-going**)



Effects of diamond orientation (on-going)

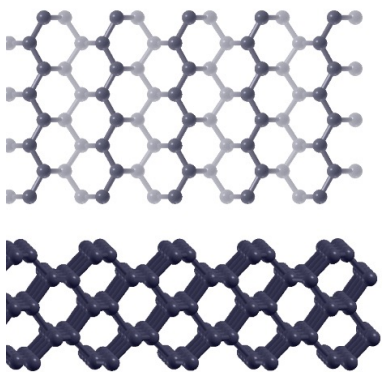


Calculated surface energies

ML-MD: effects of diamond orientation (on-going)

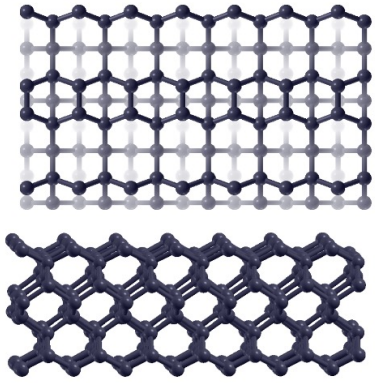
4800 atoms, surf area 0.25 nm²
Simulated time 1 ns
T= 300K, v= 50 m/s, Load 1 GPa

C(110)



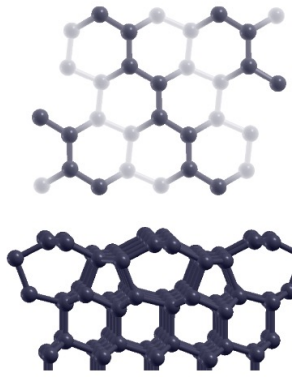
5.9 J/m²

C(001)



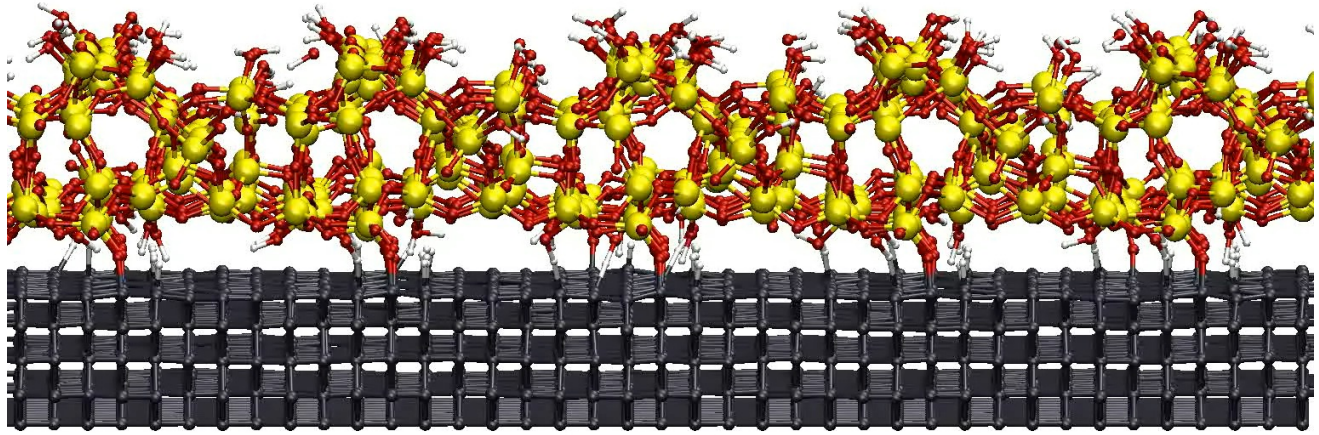
5.7 J/m²

***R*-C(111)**

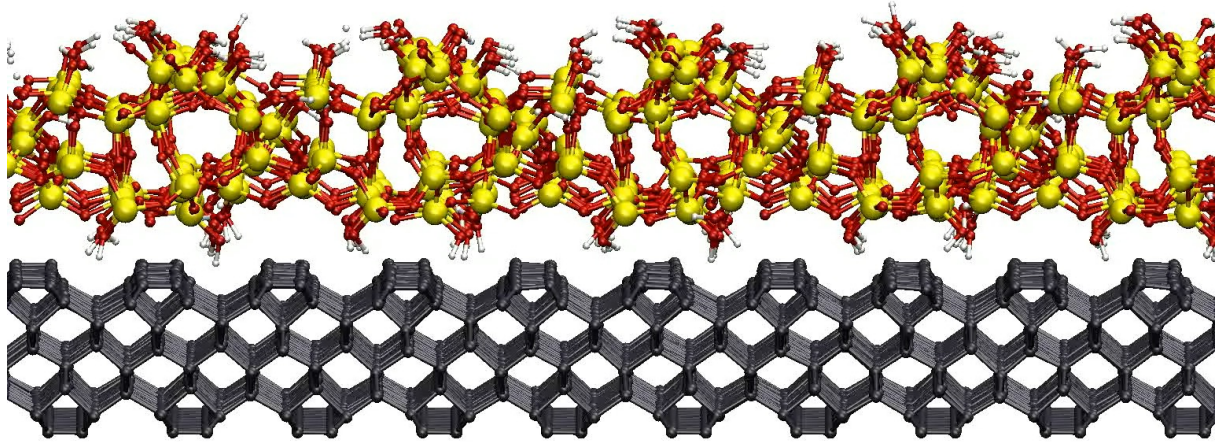


4.1 J/m²

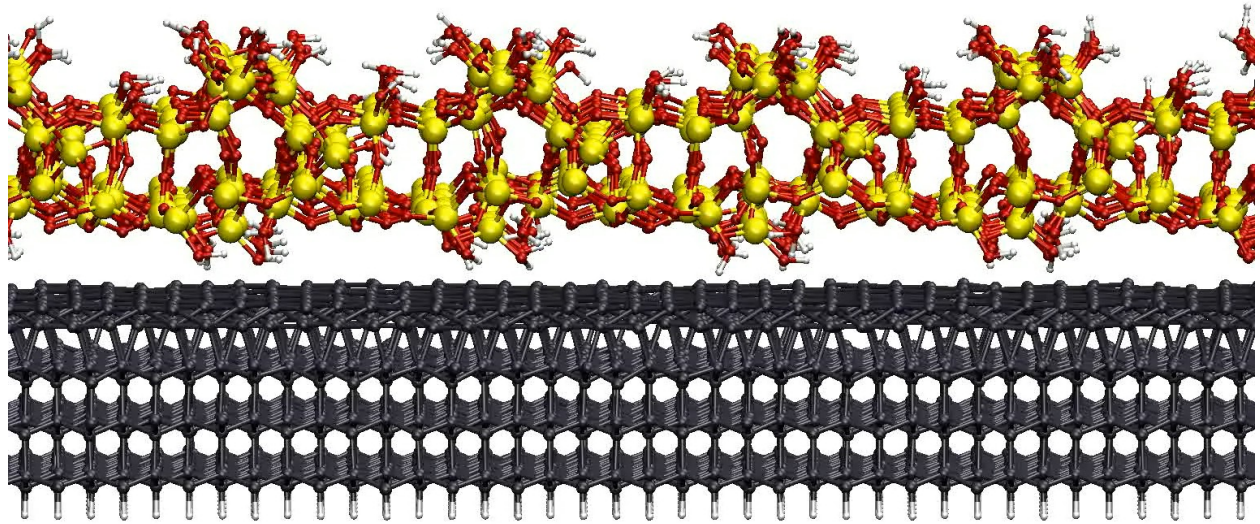
C(110)



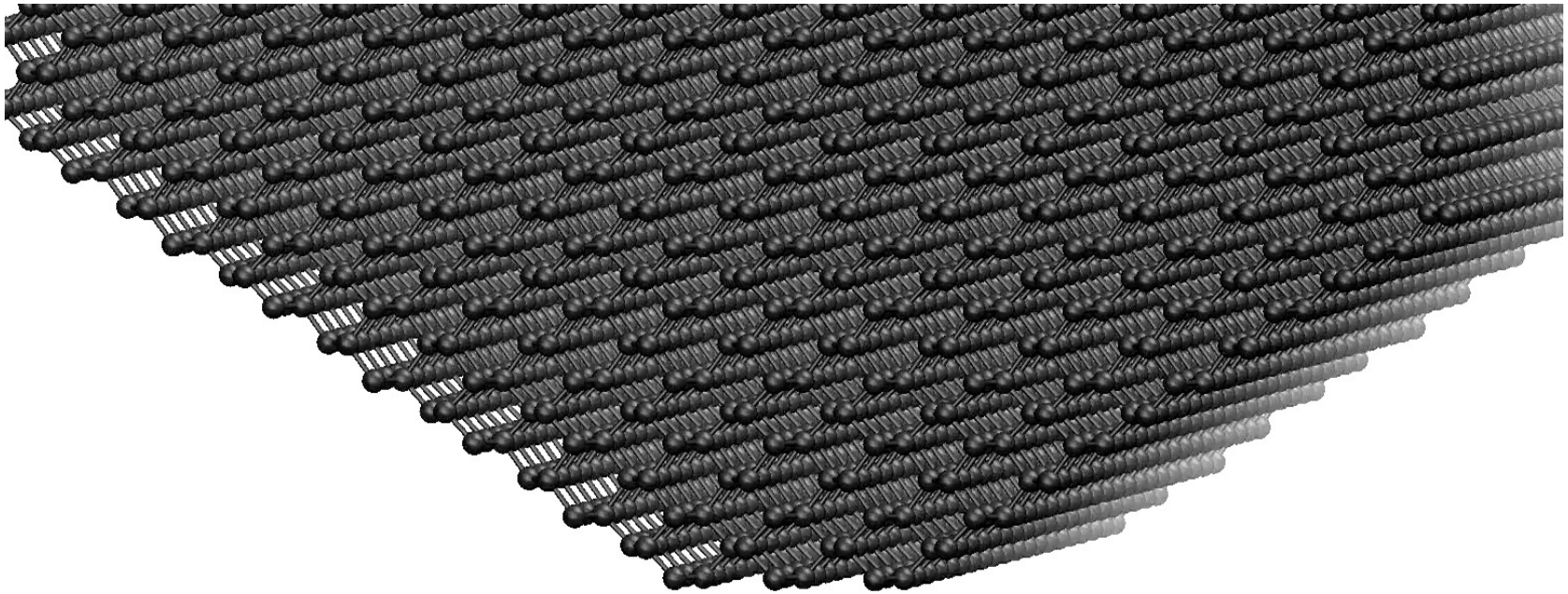
C(001)

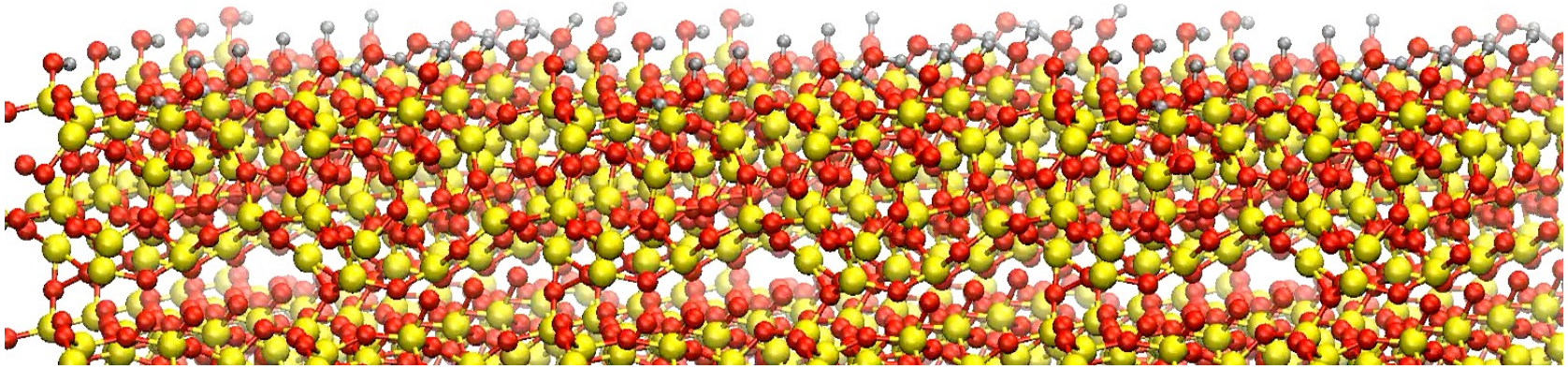


R-C(111)



ML-MD of a sliding asperity (on-going)





10850 atoms

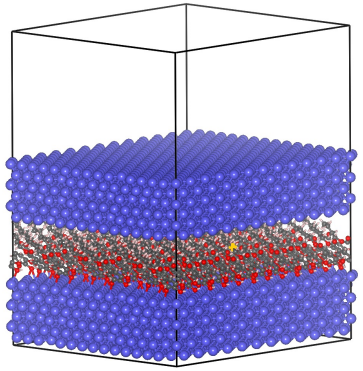
Simulated time 0, 5 ns/day

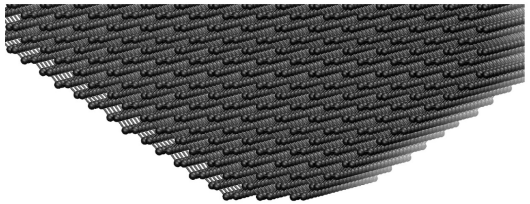
Tip surface C(110)

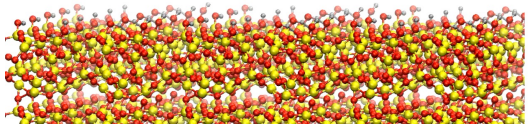
T= 300K, v= 1 m/s, Load 400 MPa

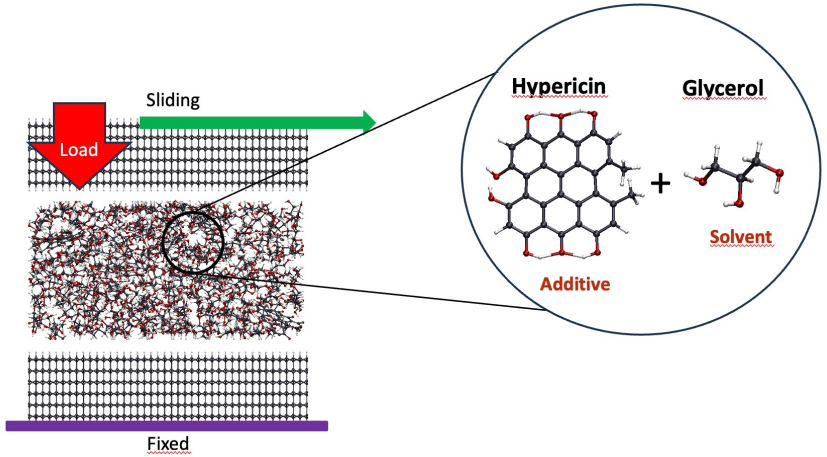
Conclusions

- Accurate Interatomic Potentials can be obtained by an Active Learning approach.
- We developed software, SCS, which couples DeeP-MD, LAMMPS and Quantum Espresso for the active learning training of Neural Networks
- By means of ML-MD we were able to simulate key tribological systems, which are impossible to simulate *ab initio*
- Self assembled monolayers of large molecules
- Additives included in liquid media
- *In silico* AFM experiments



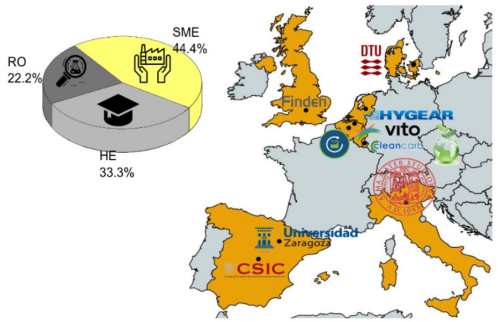


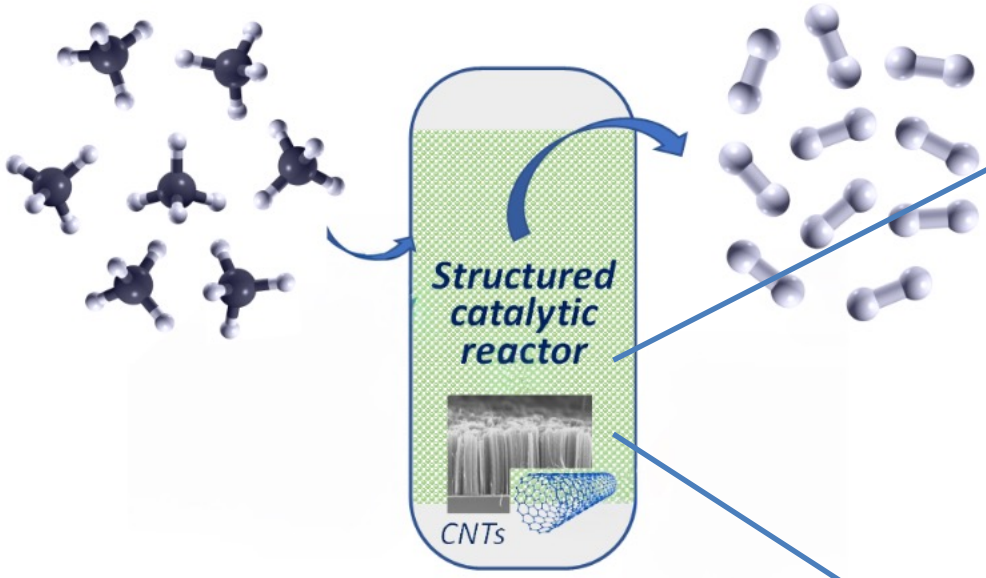


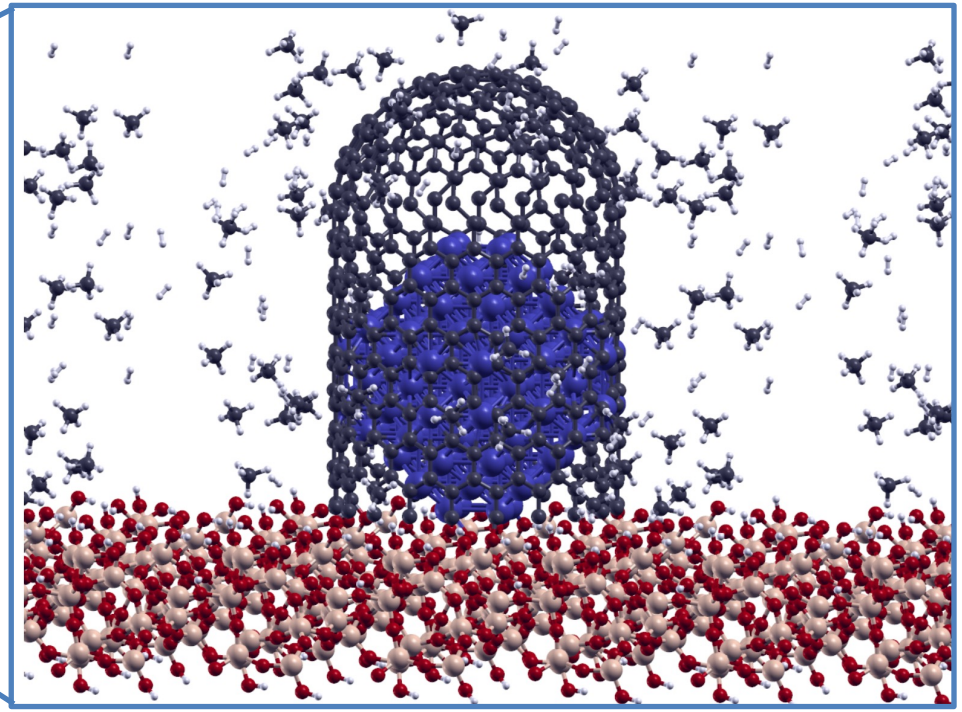


Simulating what happens in a reactor

EU Project "STructured unconventional reactors for CO2-free Methane catalytic cracking" (**STORMING**)







EUROHPC-JU 20 M core hours grant on Leonardo

erc

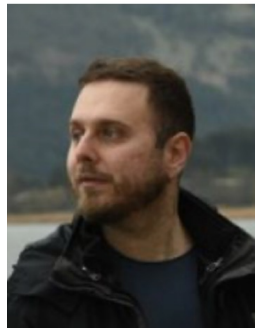
SLIDE

ADVANCING SOLID INTERFACES AND LUBRICANTS
BY FIRST PRINCIPLES MATERIALS DESIGN

Paolo Restuccia - Edoardo Marquis - Vito Foderà - Francesca Benini - Emiliano Poli - Enrico Pedretti - Elisa Damiani - Clelia Righi - Margherita Marsili - Alberto Pacini

Mauro Ferrario

Huong Ta Thi Thuy



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