Application of Third-Generation Charge-Optimized Many-Body Potentials (COMB3) in LAMMPS

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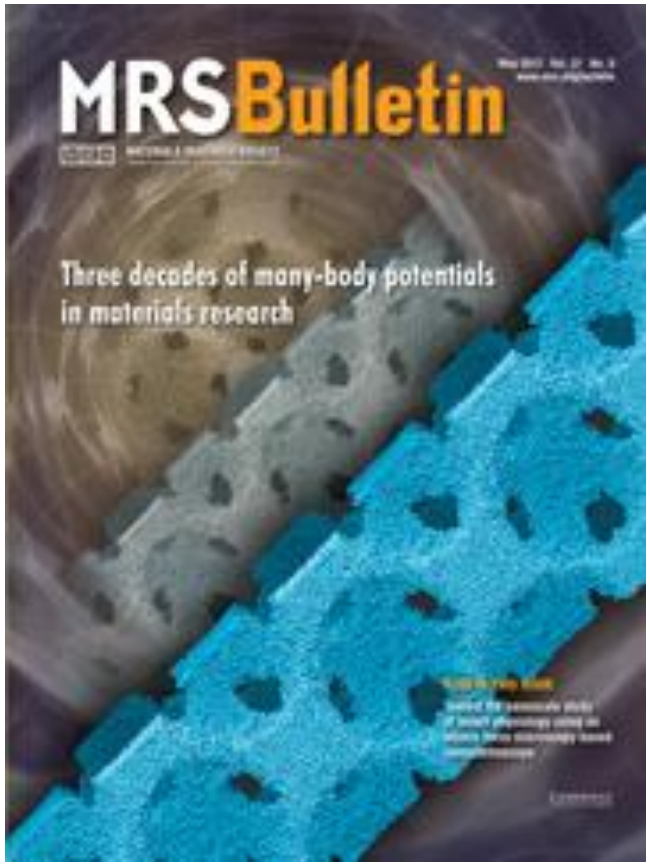
Reactive many-body empirical potentials in materials science



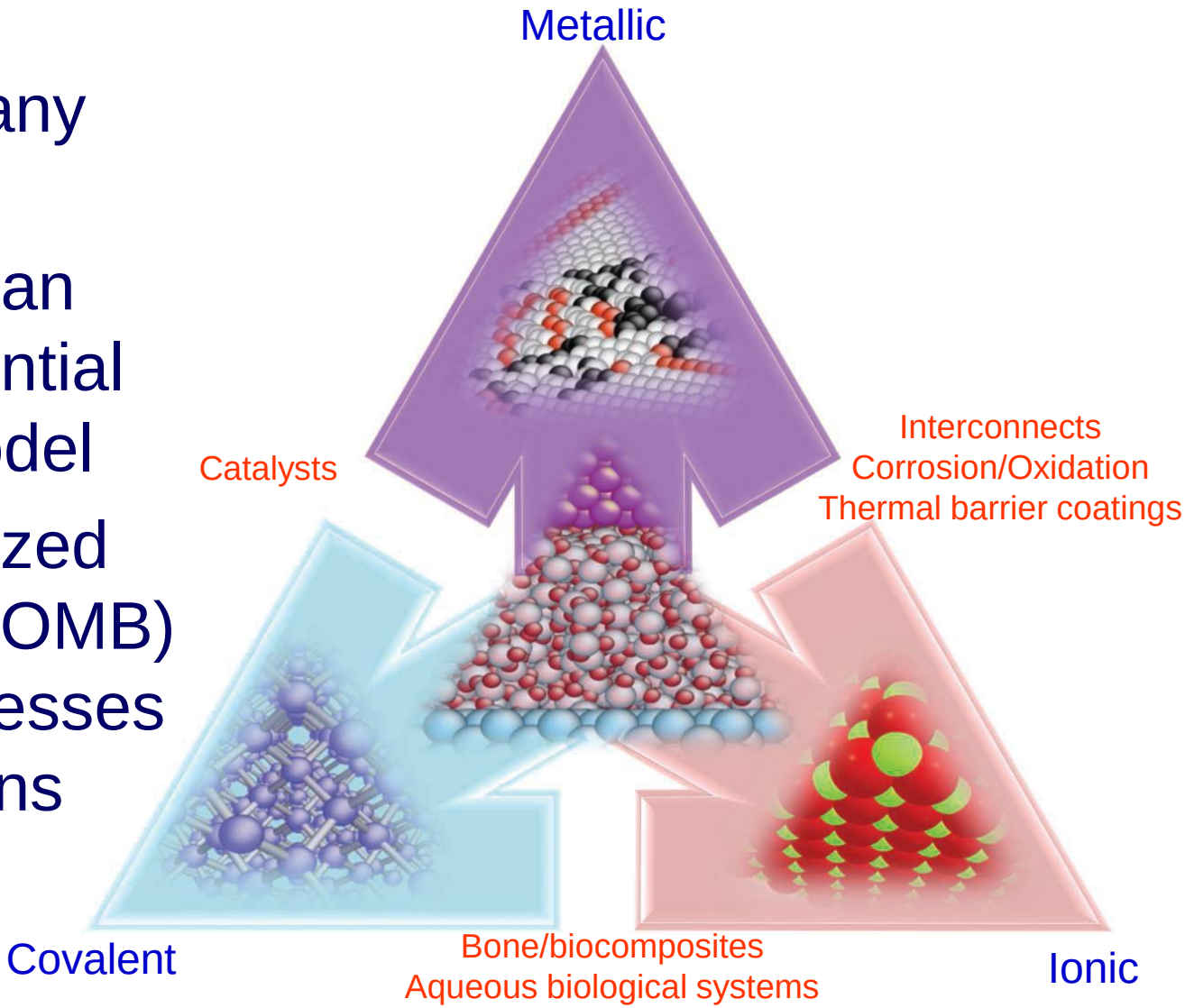
May 2012 issue

Historically developed for materials with specific types of chemical bonds

- Tersoff potentials for Si
  - Brenner or REBO potential for C,H + O,F,S,….
  - AIREBO
- EAM potentials for metals
  - MEAM for metals and oxides
  - EAM+ES for metals and oxides
- Buckingham potentials for ionically bound materials

Modeling heterogeneous interfaces

- Inherent to many applications
- Challenge for an empirical potential function to model
- Charge optimized many body (COMB) potential addresses these limitations



S. R. Phillpot, S. B. Sinnott, ***Science*** 325, 1634 (2009).

Functional form of COMB3 potential

$$E_T = \sum_i \left\{ \begin{array}{l} E_i^{Self}(q_i) + \frac{1}{2}\sum_{j\neq i}\left[V_{ij}^{short}(r_{ij}, q_i, q_j) + V_{ij}^{Coul}(r_{ij}, q_i, q_j)\right] \\ +B_i(q_i) + C_i(r_{ij}, \theta_{ijk}) + E^{polar}(q_i, r_{ij}) + E^{vdW}(r_{ij}) \end{array} \right\}$$

- Self energy: ionization energies and electron affinities; includes penalty function to capture change in self-energy due to the field from the ionic lattice
- Short-range interactions: bond-order REBO potential
- Coulomb interactions: Streitz & Mintmire QeQ scheme
- Angular correction terms
- Polarization: Atomic polarizabililty for organic systems
- van der Waals energy: Lennard Jones

S.R. Phillpot and S.B. Sinnott, Science (2009)
T. Liang et al., Materials Science and Engineering R (2013)

Dynamic Variable Charge

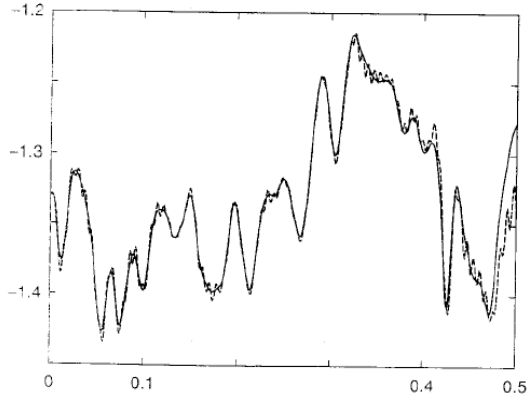
- The electronegativity (-∂E/∂q) is equal at all sites

$$L = \sum_{i=1}^{N} \tfrac{1}{2} m \dot{r}_i^2 + \sum_{i=1}^{N} \tfrac{1}{2} m_q \dot{q}_i^2 - U(r,q) - \lambda \sum_{i=1}^{N} q_i$$

Extended Lagrangian Dynamics:

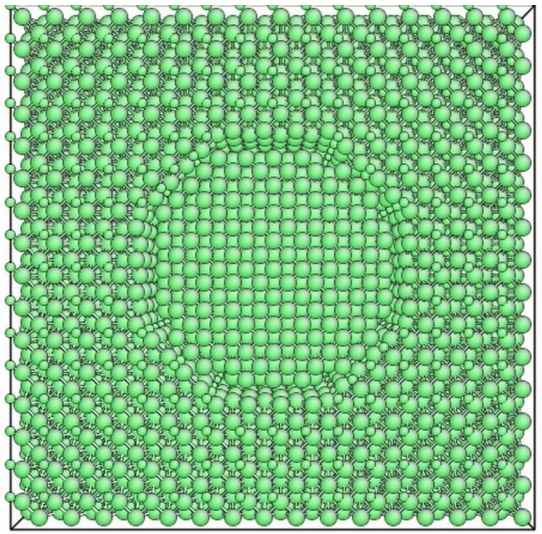
$$m_i \ddot{\vec{r}} = -\vec{\nabla}_i V$$

$$\mu_i \ddot{q}_i = -\frac{\partial V}{\partial q_i}$$



- Avoids matrix inversion or optimization
- Low computational cost
- requires smaller time step
- Damped dynamics

$$-m_q \ddot{q}_i = \mu_{Ti} - \bar{\mu}_T + \eta_D \dot{q}_i$$



Cu_2O with a Cu core

Rick & Stuart *Rev Comp Chem* 18, 89 (2002)
A. K. Rappe, W. A. Goddard, *J Phys Chem* 95, 3358 (1991)
J. Yu, S. Sinnott, S. Phillpot *Phys. Rev. B* 75 085311 (2007)

Cost of Potentials in LAMMPS

Potential	System	# Atoms	Memory	LJ Ratio
Lennard-Jones	LJ liquid	32000	12 Mb	1.0x
EAM	**bulk Cu**	**32000**	**13 Mb**	**2.4x**
Tersoff	**bulk Si**	**32000**	**9.2 Mb**	**4.1x**
Stillinger-Weber	bulk Si	32000	11 Mb	4.1x
EIM	crystalline NaCl	32000	14 Mb	6.5x
CHARMM + PPPM	solvated protein	32000	124 Mb	13.6x
MEAM	bulk Ni	32000	54 Mb	15.6x
AIREBO	polyethylene	32640	101 Mb	54.7x
ReaxFF/C	PETN crystal	32480	976 Mb	185x
COMB2 (fixed q) QEq	Ti crystalline SiO_2	32400 32400	31 Mb 85 Mb	55x 284x
eFF	H plasma	32000	365 Mb	306x
ReaxFF	PETN crystal	16240	425 Mb	337x
VASP/small*	water	192 ($512e^-$)	320 procs	17.7×10^6

Intel Xeon 2.66 GHz, single processor
*Not from LAMMPS

Courtesy of Steve Plimpton, Sandia
http://lammps.sandia.gov/bench.html

Current status of COMB3

- **Semiconductors**
  - Si
- **Metals**
  - Cu, Zn, Al, Zr, Ti, U
- **Compounds**
  - Cu_2O, ZnO, UO_2, NO_X, NH_3, Al_2O_3, TiO_2
  - TiN, AlN

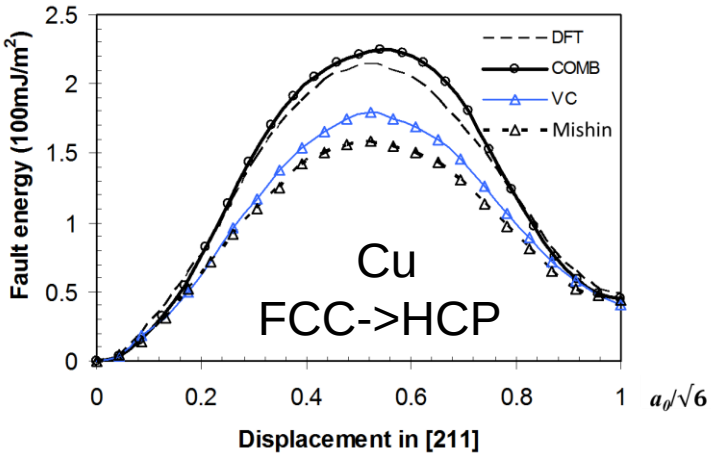
- Carbon based systems
  - CHO systems
  - H_2O and O_2
  - C/H/Cu/O/Zn
  - CN
  - CHON

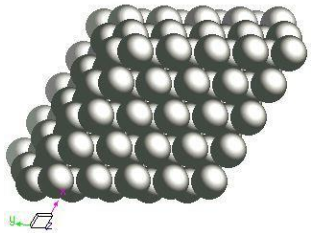
Applications

- **Tensile test of polycrystalline Zr**
- Graphene/Cu_2O interfaces
- Cu metallization on PS surfaces

Stacking fault map of Zr

COMB -> Tersoff-type





Zr:

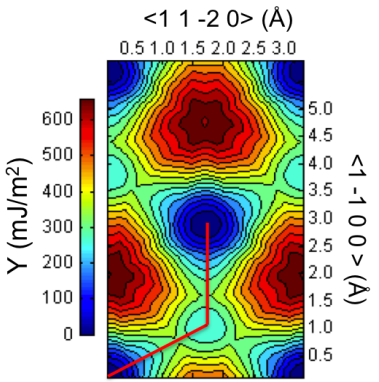
- hcp
- a=3.23
- c=5.15
- **c/a=1.59 < 1.633**

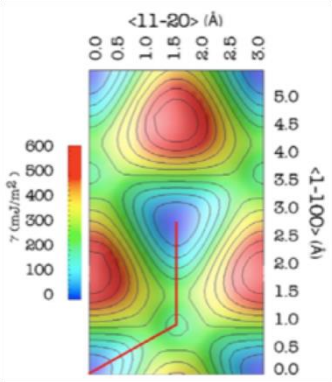
Yu et al., Phil. Mag. Lett., 89 (2009)
Noordhoek et al., J. Nucl. Mat., 441 (2013)

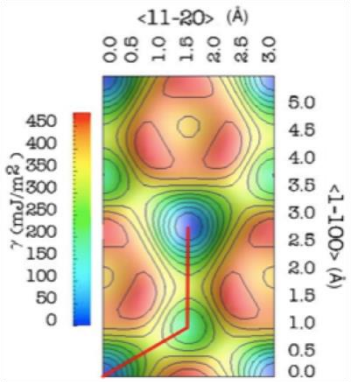
COMB: 267
saddle 367

DFT: 213
saddle 260

EAM: 199
saddle 314







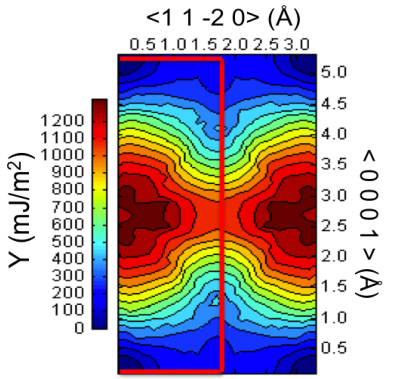
HCP-> FCC:

Basal {0001} stacking fault map

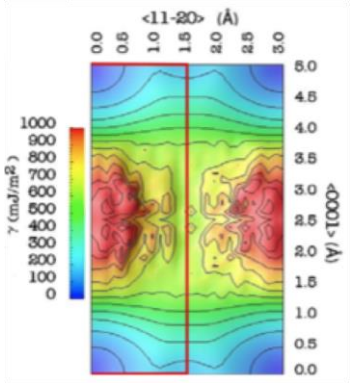
- $\{0001\} < 11\bar{2}0 >$

Tensile test on polycrystalline Zr

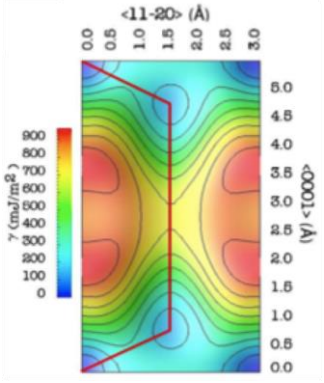
COMB: 215
Saddle 247



DFT: 166
saddle 194



EAM: 145
saddle 190

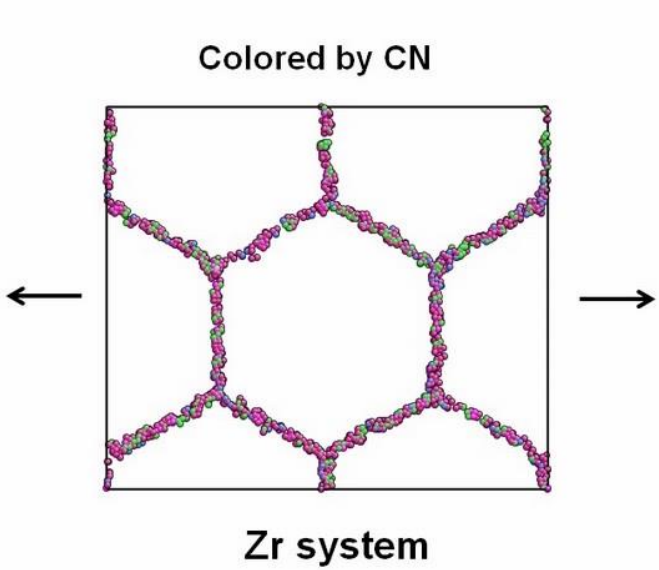


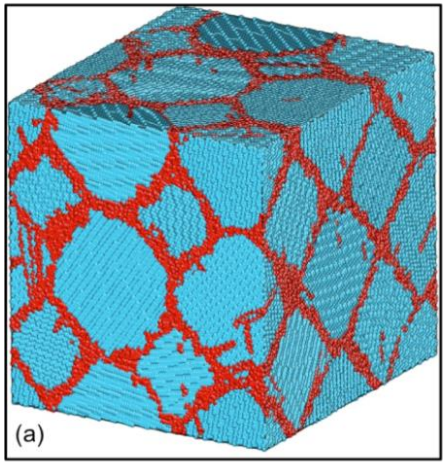
c/a << 1.633

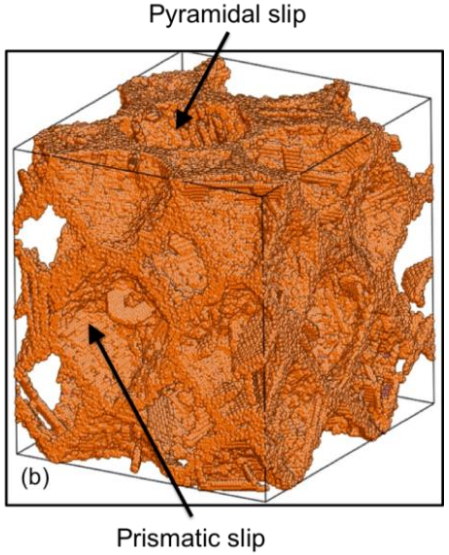
Prism $\{10\bar{1}0\}$ stacking fault map

- $\{10\bar{1}0\} < 11\bar{2}0 >$

$\{11\bar{2}2\} < 11\bar{2}3 >$







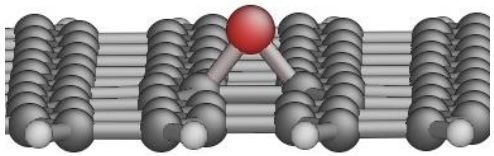
~3 million atoms

$\{10\bar{1}0\} < 11\bar{2}0 >$

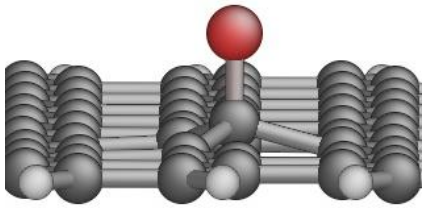
Applications

- Tensile test of polycrystalline Zr
- **Graphene/Cu_2O interfaces**
- Cu metallization on PS surfaces

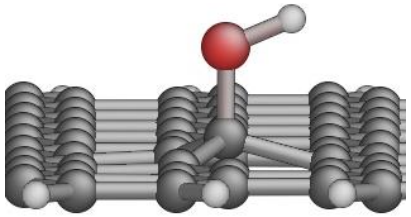
Graphene oxides



GO-bridge



GO-atop



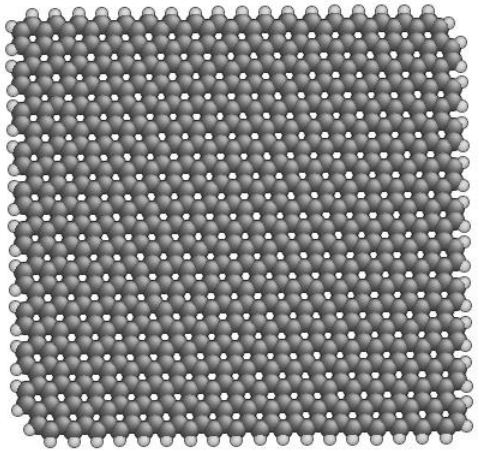
GO-Hydroxyl

O site	Properties	DFT[a]	COMB
GO-brige	C-O length (Å)	1.44	1.40
	E_ads (eV @ 0.1 ML)	-3.18	-3.18
GO-atop	C-O length (Å)	1.40	1.30
	E_ads (eV @ 0.1 ML)	-2.43	-2.40
GO-hydroxyl	C-O length (Å)	1.48	1.44
	E_ads (eV @ 0.1 ML)	-1.48	-1.48

a: A. F. Fonseca et al, Phy. Rev. B 84, 075460 (2011)

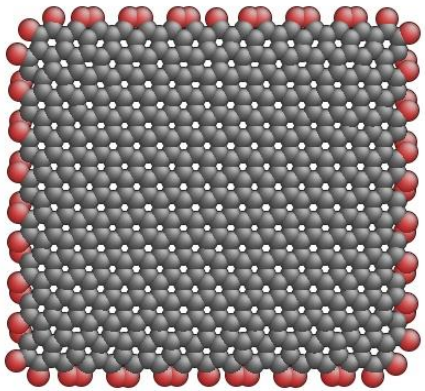
Graphene adhesion on Cu_2O

4114 C atoms



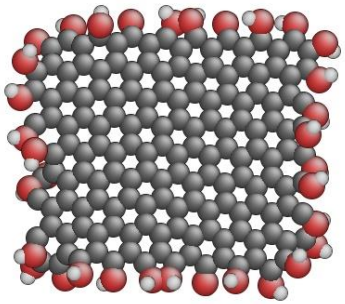
H-Terminated

796 C atoms

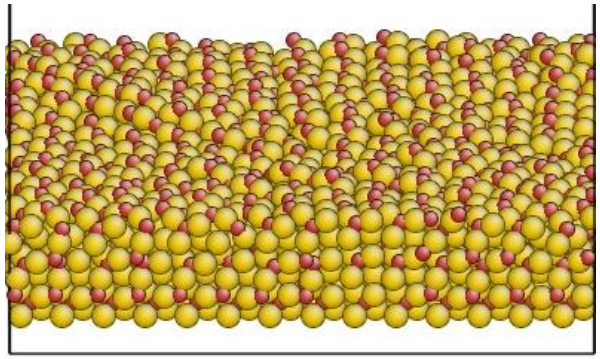


O Terminated

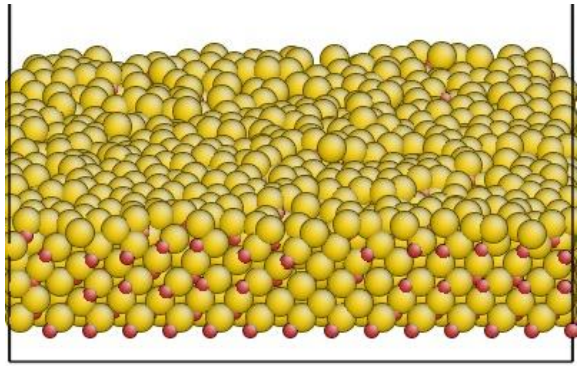
542 C atoms



OH Terminated

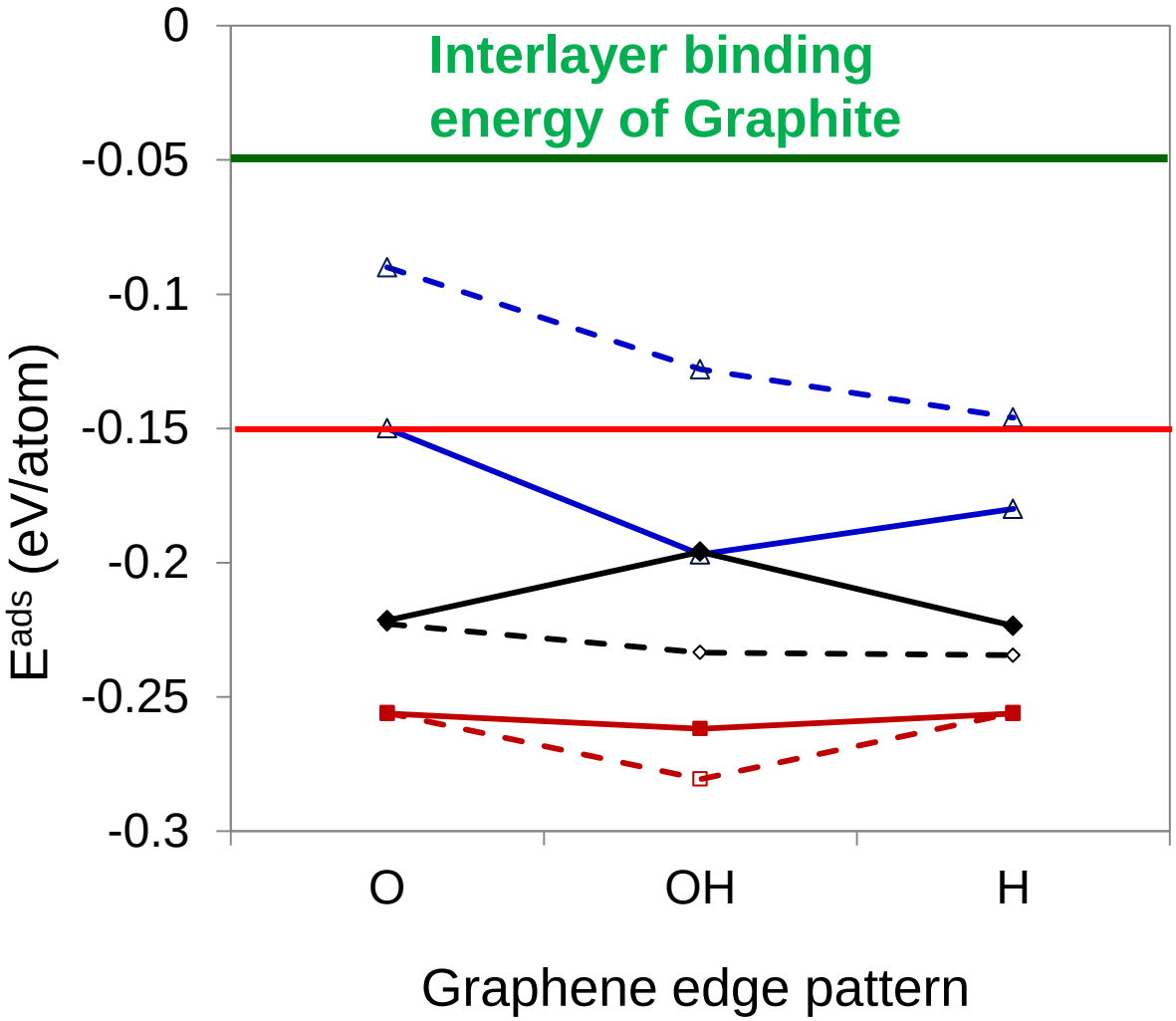


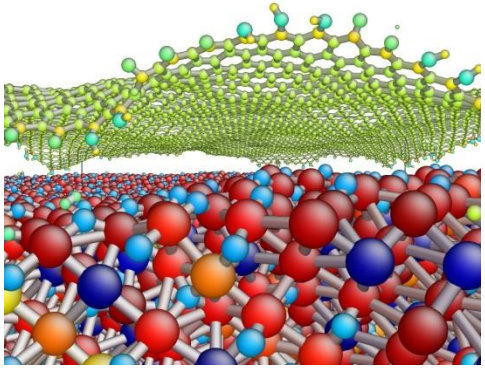
CuO-Termination



Cu-Termination

Graphene adhesion on Cu_2O





Exp. E^{ads} on SiO_2

Solid line CuO terminated and dash line Cu terminated Cu_2O substrate

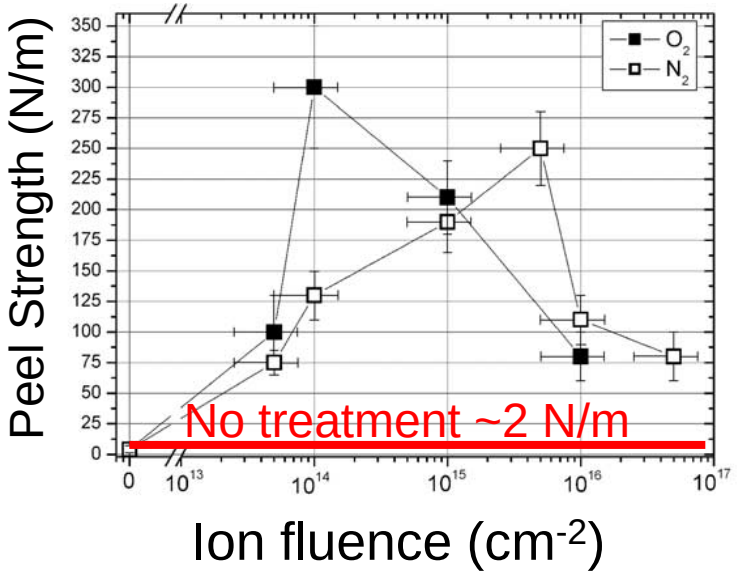
Koenig et al. Nature Nano, 6 (2011)

Applications

- Tensile test of polycrystalline Zr
- Graphene/Cu_2O interfaces
- **Cu metallization on PS surfaces**

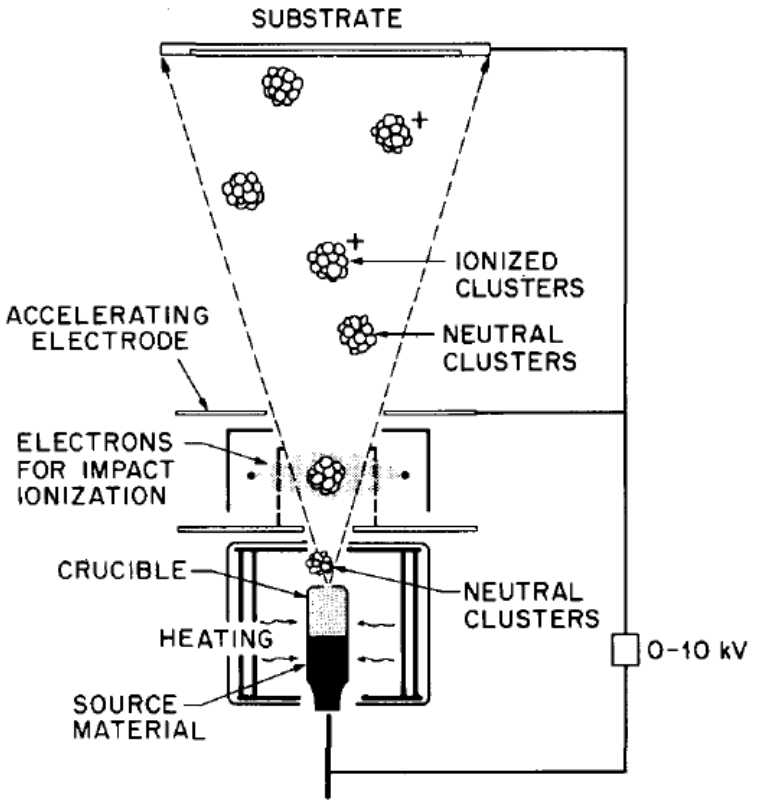
Electroless metallization of polymers

- Poor wettability and adhesion
- Pre-treatments needed
  - Surface modification
  - Metal seeds
- Metal deposition



McEachern et al. J. Vac. Sci. Tech. A 9 (1991)
Zaporojtchenko et al. Nucl. Instrum Meth. B, 236 (2005)

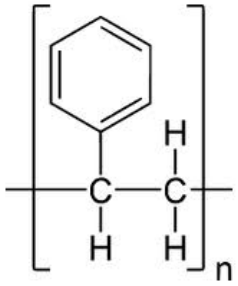
ion cluster beam deposition



Incident beam energy: several eV/atom
Complex surface chemistry: adhesion, diffusion, nucleation, sputtering ….

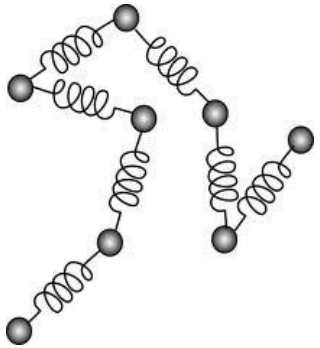
Build amorphous polystyrene

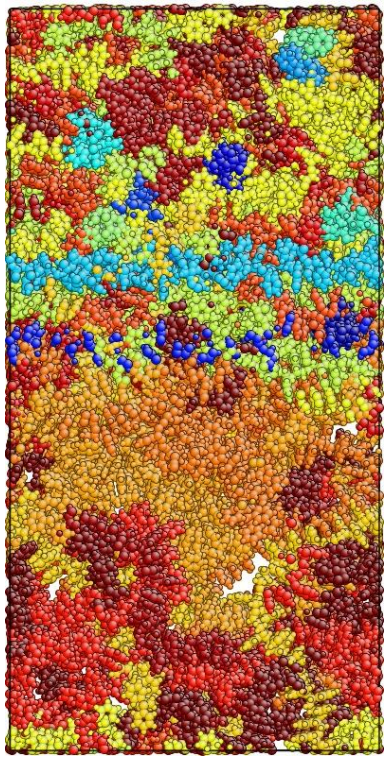
Monomer



C_8H_8

Bead-spring





PS: Colored by chain ID

Summary

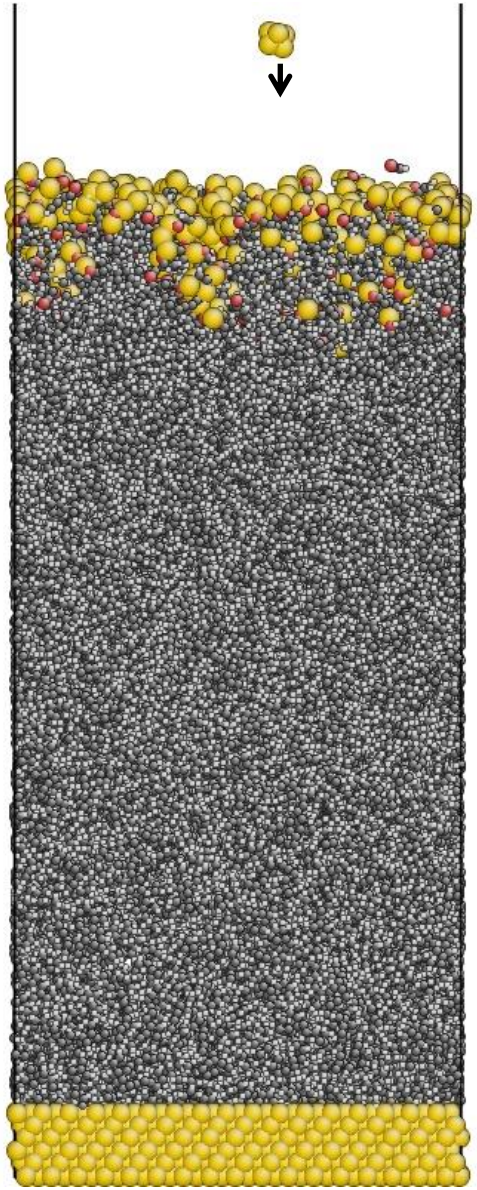
Density: 1.05 g/cm^3

Molecular weight: ~23,000

# of atoms: ~83000

# of C atoms: ~41300

As-build PS is relaxed and then built PS-O, PS-Cu, PS-OCu systems

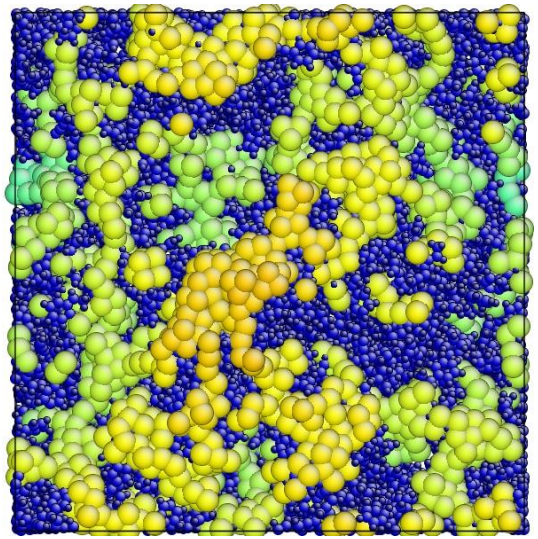


Metallization on PS surfaces – Effects of surface modification and seeds

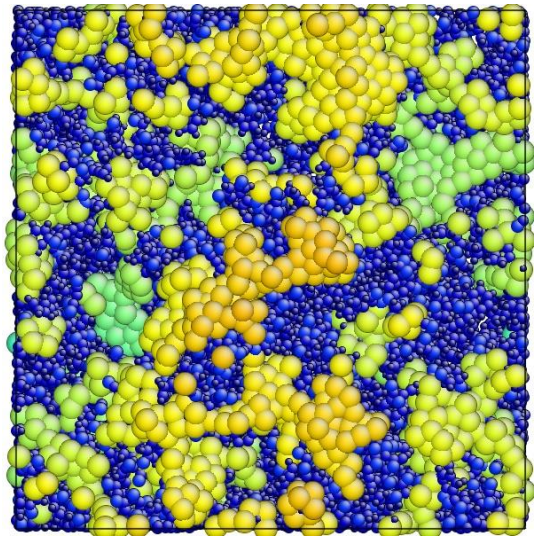
Summary:

- PS built by bead-spring model
- PS, PS-O, PS-Cu and PS-OCu
- Incident molecules are 200 x Cu_6
- Incident energies are 5 eV/atom
- Molecules are randomly distributed
- Relaxation time between deposition events is 0.5 ps
- Surface temperature is 300 K
- Total atoms ~90,000

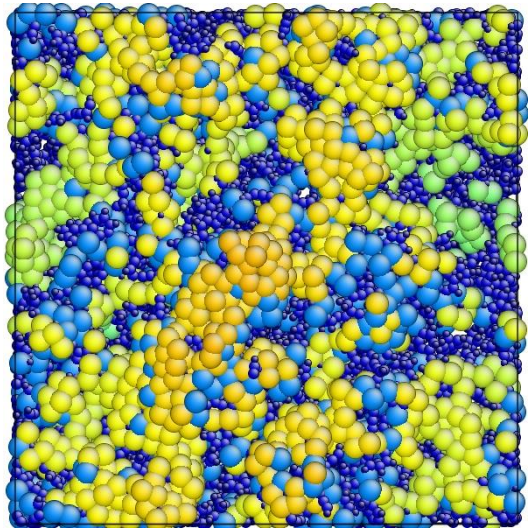
2 ML Cu on PS surfaces



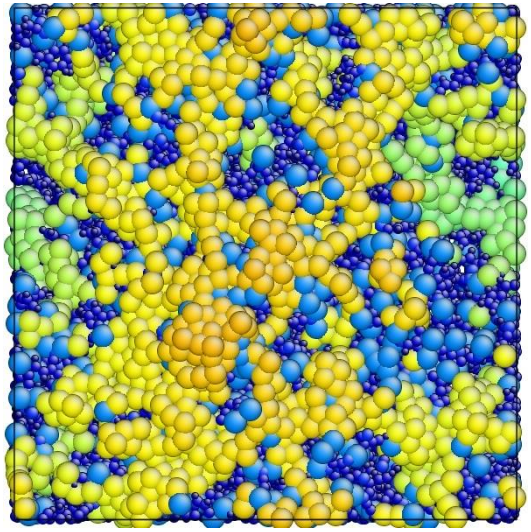
PS



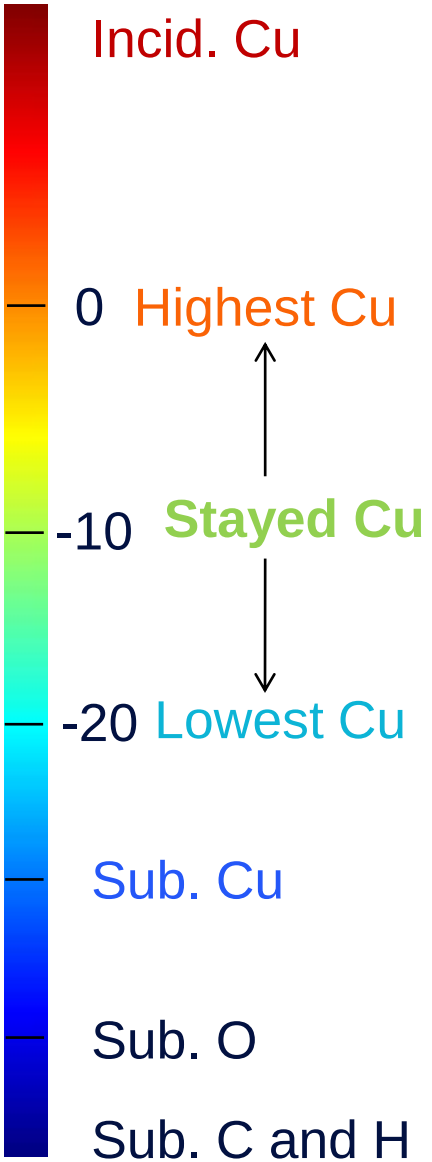
PS-O



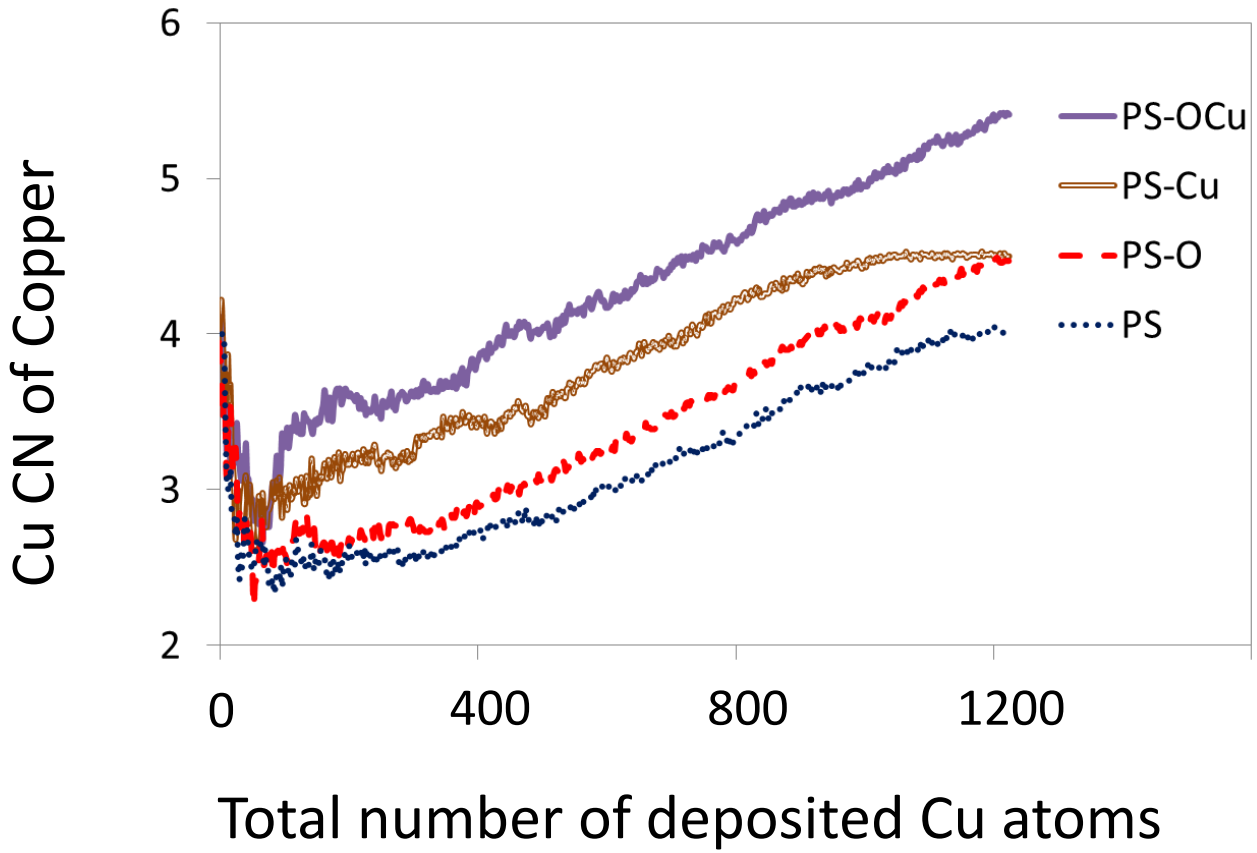
PS-Cu



PS-OCu



Cu Coordination Number of Cu



Conclusions

- Have developed an empirical, variable charge many body (COMB3) potential for modeling heterogeneous interfaces
- Successfully applied to atomic-scale simulations of systems consisting of discrete bonding types

Work with Steve Plimpton to disseminate COMB3 in LAMMPS

Acknowledgement

U.S. DEPARTMENT OF ENERGY | Office of Science

Center for Atomic-Level Catalyst Design

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Consortium for Advanced Simulation of Light Water Reactors