Modified Embedded Atom Method (MEAM) with Bond Order Implementation in LAMMPS

Presenter: **Sungkwang Mun**

Ric Carino, Michael Baskes

Center for Advanced Vehicular Systems (CAVS)

Mississippi State University

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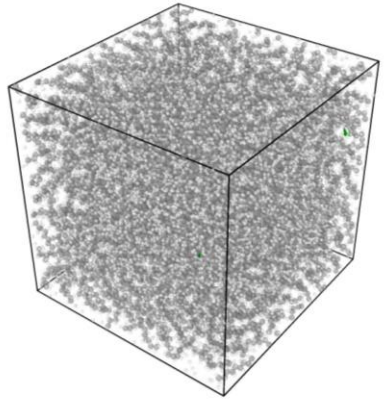
MISSISSIPPI STATE UNIVERSITY

Outline

1. Motivation
2. MEAM with bond order (MEAM-BO)
    1. Equations in detail
    2. Prediction comparison with other force-fields (REBO and ReaxFF)
3. Implementation of MEAM-BO in LAMMPS
4. Summary and future works

Fracture predicted in finite element analysis of notched tension specimen of high-density polyethylene (HDPE)



Damage Evolution (ϕ)

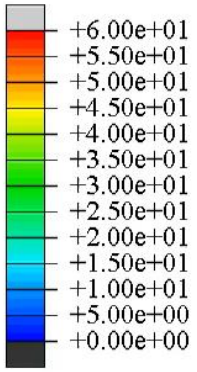
$$\phi = \eta \nu c$$

nucleation

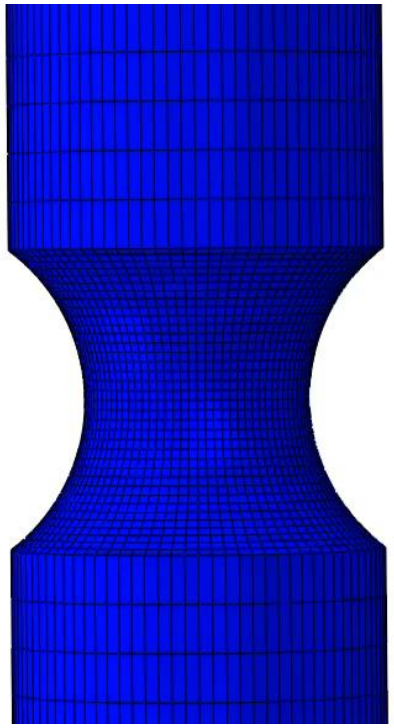
growth

coalescence

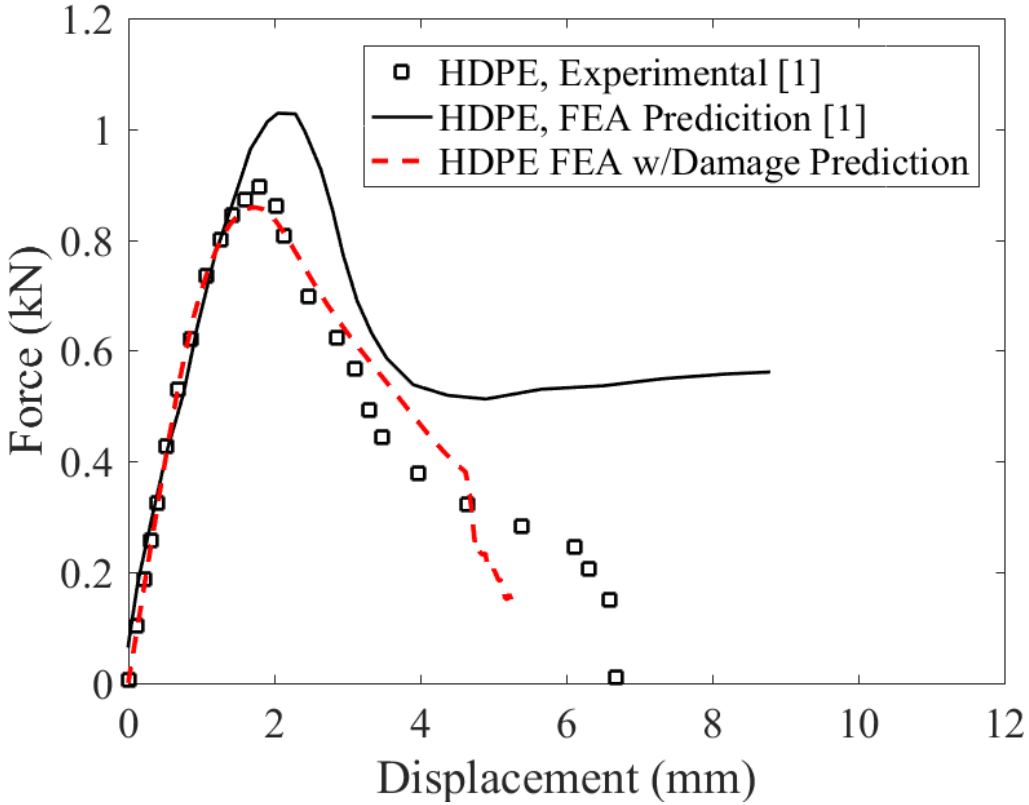
Von Mises Stress (MPa)



Velocity .04 mm/s



HDPE – Internal State Variable Plasticity Model with Multiscale Damage[2]



[1] Ognedal, A.S., Large-Deformation Behavior of Thermoplastics at Various Stress States , Ph.D. Thesis, Norwegian University of Science and Technology, (2012).
[2] A. L. Bowman, **S. Mun**, S. Nouranian, S. R. Gwaltney, **M. I. Baskes**, and M. F. Horstemeyer, "Multiscale Damage and Fracture Modeling Using Molecular Dynamics and Continuum Internal State Variable Theory for Polyethylene," in preparation.

Modified Embedded Atom Method (MEAM)

EAM(1984)
- Linear
- FCC structure

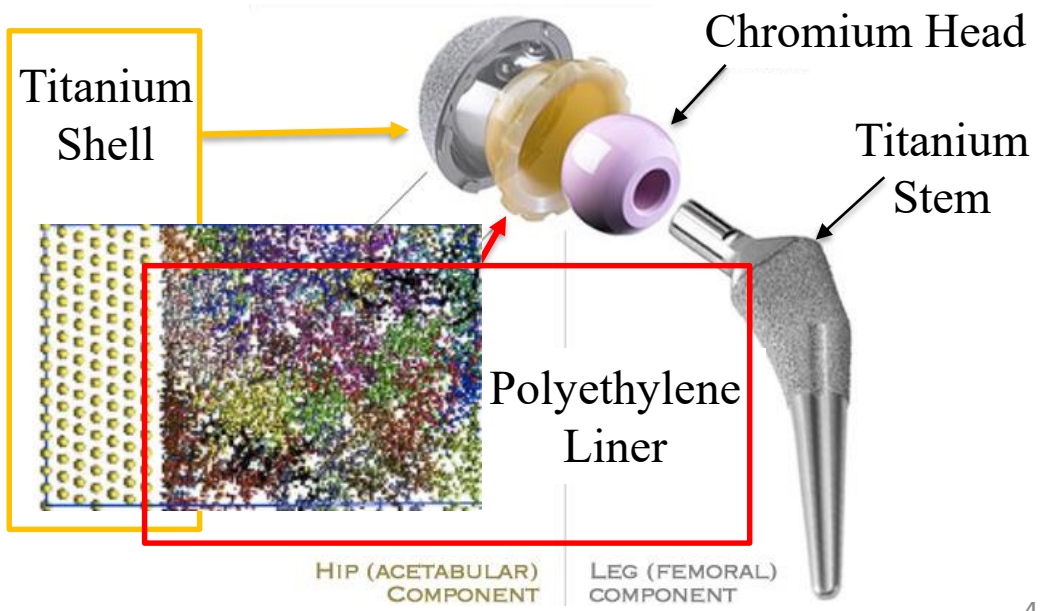
MEAM(1988)
- Angular
- Screening
- BCC, HCP, diamond structure

MEAM-BO (2017, 2018)
- Double/triple bond
- Van der Waals interaction [2]
- C/H (done) O/N (in progress)
- Polymer/metal interface

✓ Embedded Atom Method (EAM) is first developed by Daw and Baskes in 1984 based on density functional theory (DFT) later extended by Bakes to handle angular dependency (MEAM)

✓ EAM and MEAM are widely used for metallic system dealing with many problems such as point defects, melting, grain boundary, dislocations, fracture, surface, bulk and interface problems, etc

✓ Recently, MEAM is extended for hydrocarbon system; MEAM with bond order (MEAM-BO) [1]



[1] Mun, Baskes. et. al., J. Phys. Chem. A 2017 [2] Dickel, Mun, Baskes, J. Phys. Chem. A 2018

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2. **MEAM with bond order (MEAM-BO)**
    1. **Equations in detail**
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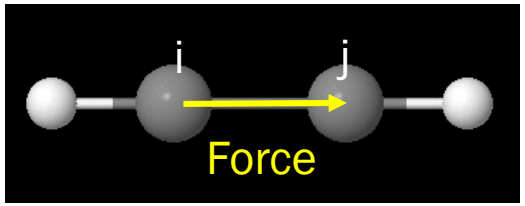
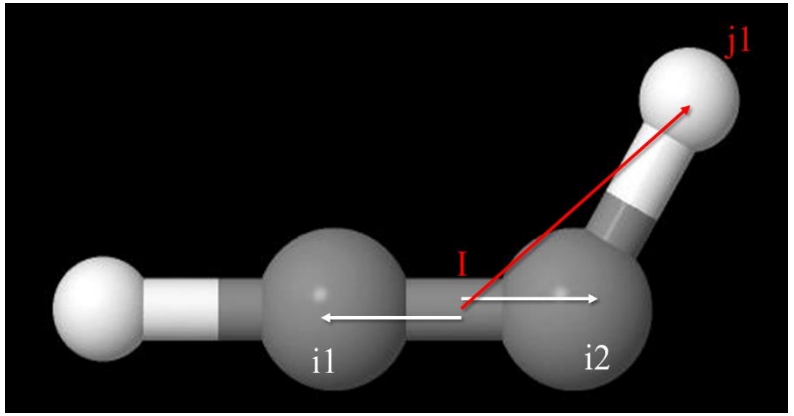
MEAM with bond order (MEAM-BO)

$$E_{\mathrm{MEAM-BO}} = E_{\mathrm{MEAM}} + \sum_I f_{I3} \cdot E_3(R_I) + \sum_I f_{I2} \cdot E_2(R_I, BO_I)$$

- $f_{I\mathrm{bond}}$: Energy fraction depends on electron density at each bond to satisfy geometrical condition
- $E_{\mathrm{bond}}(R_I, BO_I)$: Energy increment due to the bond unsaturation w.r.t bond order to shift MEAM energy to first principle (FP) energy
- If no bond characteristic, the two terms will be zero and return to the original MEAM
- New entity: bond center I which is a halfway between two atoms



MEAM force deals i-j atom pairs only



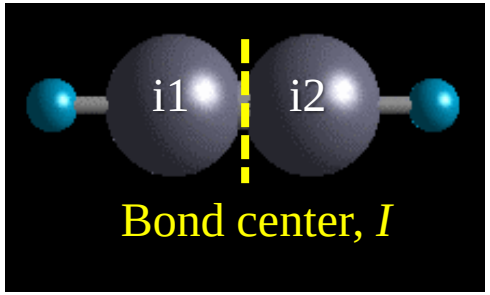
MEAM-BO requires additional force due to bond center, i.e. I-j where I=(i1+i2)/2

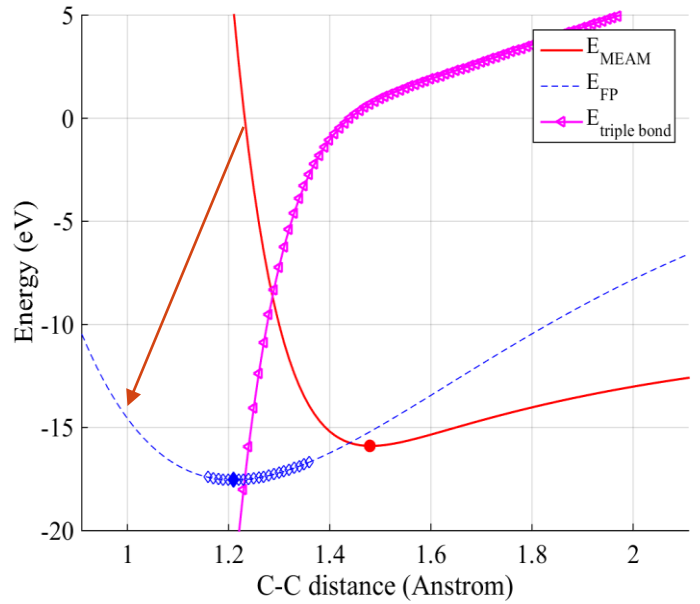
Bond order calculation in detail

- $E_{\mathrm{MEAM-BO}} = E_{\mathrm{MEAM}} + \sum_I f_{I3} \cdot \boldsymbol{E_3(R_I)} + \sum_I f_{I2} \cdot E_2(R_I, BO_I)$

- Triple bond (e.g. 2 neighbors per carbon)
  - $f_{I3} = S_{i_1 i_2} \cdot D_3^{(0)}\left(\left[Z_{i_1}^{(0)} - Z_3\right]^2\right) \cdot D_3^{(0)}\left(\left[Z_{i_2}^{(0)} - Z_3\right]^2\right) \cdot D_3^{(3)}\left(\left[Z_I^{(3)}\right]^2\right)$

    where $Z_i^{(0)}, Z_i^{(1)}, Z_I^{(3)}$: counting factors, $D_{\mathrm{bond}}^{(h)}$ is Gaussian type function
    - $D_{\mathrm{bond}}^{(h)}(Z) = \exp\left(-Z^{p_{\mathrm{bond}}^{(h)}} \cdot \beta_{\mathrm{bond}}^{(h)}\right), h = 0,1,\text{and } 3$
  - $\boldsymbol{E_3(R_I) = e_0 \cdot \left\{1 + \sum_{k=1}^{2} e_k \cdot \left[\frac{R_I}{R_3} - 1\right]^k\right\}}$





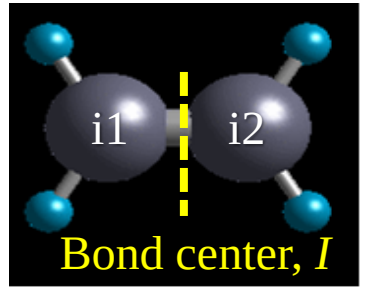
Bond order calculation in detail

- $E_{\mathrm{MEAM-BO}} = E_{\mathrm{MEAM}} + \sum_I f_{I3} \cdot E_3(R_I) + \sum_I f_{I2} \cdot \boldsymbol{E_2(R_I, BO_I)}$

- Double bond (e.g. 3 neighbors per carbon, planar, two parallel planes)
  - $f_{I2} = S_{i_1 i_2} \cdot D_2^{(0)}\left(\left[Z_{i_1}^{(0)} - Z_2\right]^2\right) \cdot D_2^{(0)}\left(\left[Z_{i_2}^{(0)} - Z_2\right]^2\right)$
    $\cdot D_2^{(1)}\left(\left[Z_{i_1}^{(1)}\right]^2\right) \cdot D_2^{(1)}\left(\left[Z_{i_2}^{(1)}\right]^2\right) \cdot D_2^{(3)}\left(\left[Z_I^{(3)}\right]^2\right) + f_{I3} \cdot \left(1 - D_3^{(3)}\left(\left[Z_I^{(3)}\right]^2\right)\right)$
  - $\boldsymbol{E_2(R_I, BO_I) = e_0(BO_I) \cdot \left\{1 + \sum_{k=1}^{2} e_k(BO_I) \cdot \left[\frac{R_I}{R_2(BO_I)} - 1\right]^k\right\}}$
    $\boldsymbol{\cdot \exp\left(-\beta_2^{(2)} \cdot \left[\frac{R_I}{R_2(BO_I)} - 1\right]\right) + \left[1 - S_{i_1 i_2}\right] \cdot E_{\mathrm{vdW}}(R_I)}$

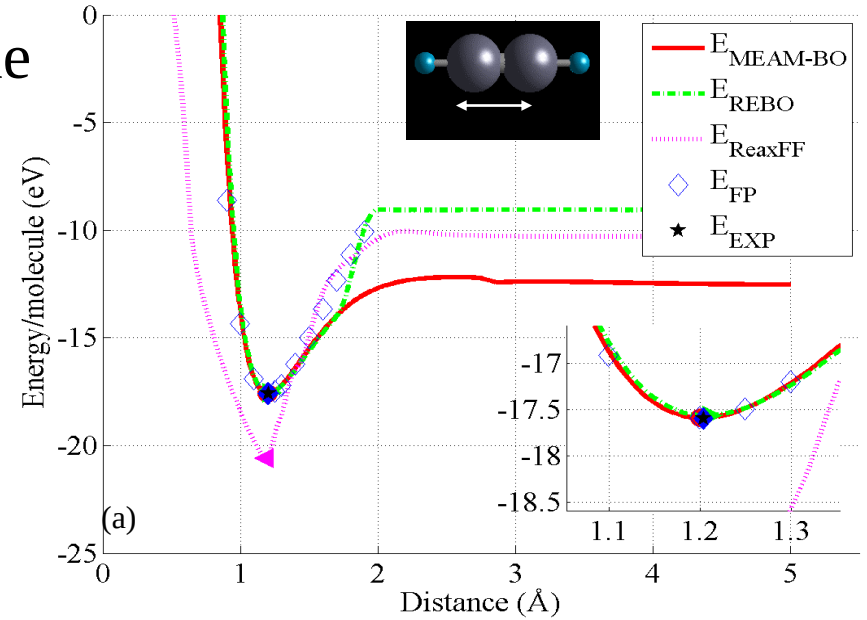
    Where bond order, $BO_I = \frac{2+n_I}{n_I}$

  - $n_I = \max\left(2, \begin{array}{c} \sum_{j \neq i_1} S_{i_1 j} \cdot D_2^{(0)}\left(\left[Z_j^{(0)} - Z_2\right]^2\right) \cdot D_2^{(1)}\left(\left[Z_j^{(1)}\right]^2\right) \\ + \sum_{j \neq i_2} S_{i_2 j} \cdot D_2^{(0)}\left(\left[Z_j^{(0)} - Z_2\right]^2\right) \cdot D_2^{(1)}\left(\left[Z_j^{(1)}\right]^2\right) \end{array}\right)$

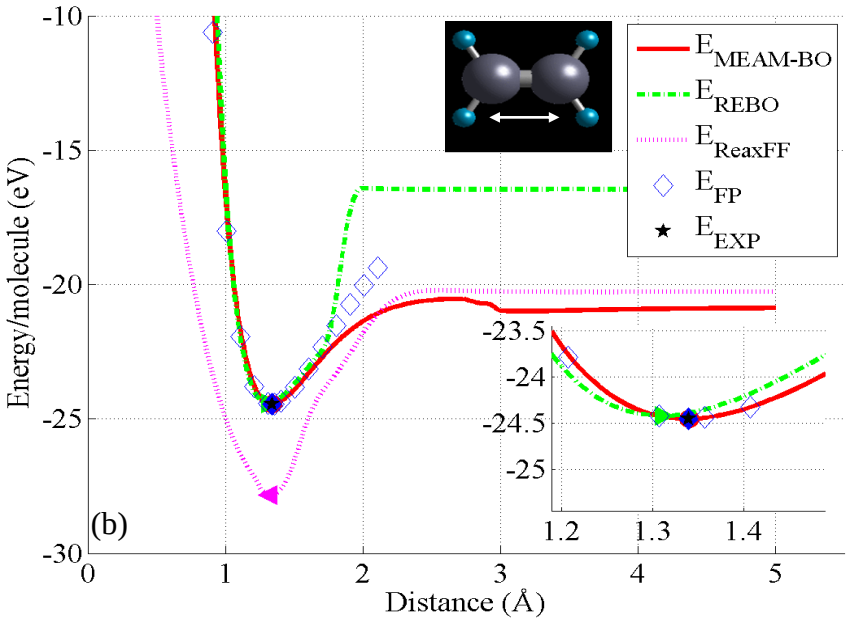


Reference structures for unsaturated hydrocarbon

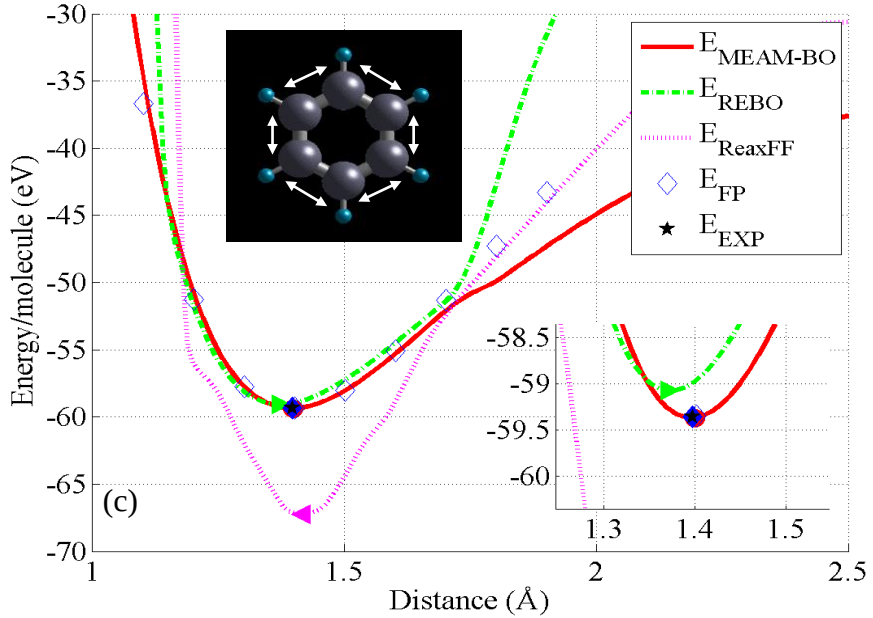
(a) Acetylene (C_2H_2)



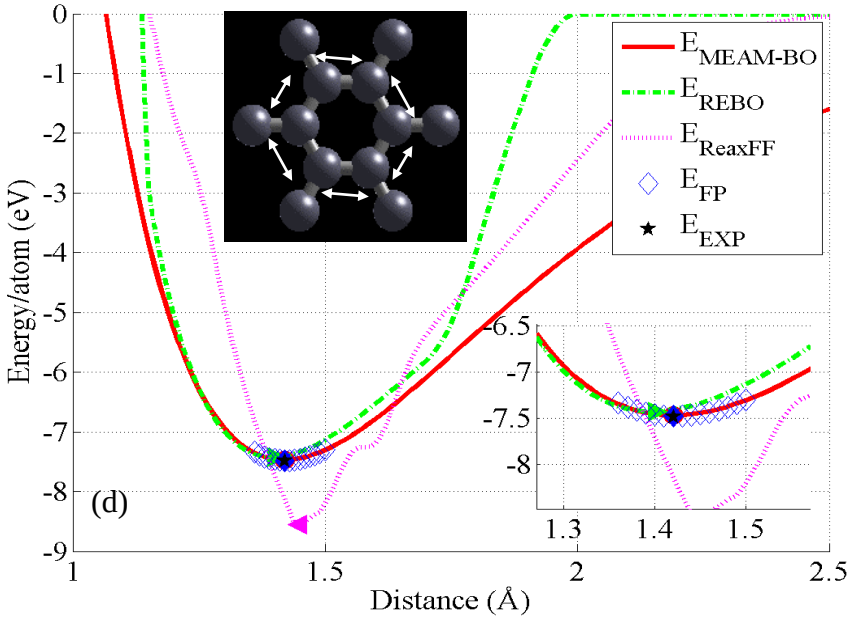
(b) Ethylene (C_2H_4)



(c) Benzene (C_6H_6)



(d) Graphene



Atomization energy comparison

				MEAM-BO		REBO		ReaxFF	
Molecule	**Expt. (eV)**	**ZPE (eV)**	**Heat inc. (eV)**	**Calc. (eV)**	**Corr. (eV)**	**Calc. (eV)**	**Corr. (eV)**	**Calc. (eV)**	**Corr. (eV)**
Methane	**17.018**	1.214	2.592	18.232	**17.018**	18.185	**16.971**	20.092	**17.499**
Ethane	**28.885**	2.023	4.515	30.941	**28.918**	30.846	**28.823**	34.453	**29.937**
Propane	**40.880**	2.803	6.439	43.723	**40.92**	43.593	**40.790**	48.732	**42.294**
n-Butane	**52.896**	3.578	8.362	56.503	**52.925**	56.347	**52.769**	63.020	**54.658**
Isobutane	**52.977**	3.564	8.362	56.559	**52.995**	56.340	**52.776**	63.030	**54.669**
n-Pentane	**64.915**	4.351	10.285	69.282	**64.931**	69.102	**64.751**	77.308	**67.023**
Isopentane	**64.964**	4.338	10.285	69.328	**64.99**	69.050	**64.712**	77.325	**67.040**
Neopentane	**65.123**	4.319	10.285	69.416	**65.097**	69.074	**64.755**	77.711	**67.426**
n-Hexane	**76.922**	5.123	12.208	82.062	**76.939**	81.858	**76.735**	91.593	**79.385**
Isohexane	**76.975**	5.113	12.208	82.072	**76.959**	81.677	**76.564**	91.541	**79.333**
3-Methylpentane	**76.946**	5.114	12.208	82.071	**76.957**	81.742	**76.628**	91.540	**79.332**
2,3-Dimethylbut..	**76.970**	5.101	12.208	82.119	**77.018**	81.701	**76.600**	91.532	**79.324**
Neohexane	**77.060**	5.098	12.208	82.145	**77.047**	81.723	**76.625**	91.955	**79.748**
n-Heptane	**88.957**	5.896	14.131	94.841	**88.945**	94.614	**88.718**	105.886	**91.755**
Isoheptane	**89.008**	5.881	14.131	94.81	**88.929**	94.370	**88.489**	105.874	**91.743**
n-Octane	**100.971**	6.668	16.054	107.62	**100.952**	107.369	**100.701**	120.174	**104.120**
Percent error:					**0.1**		**0.4**		**3.2**

Graphene and graphite properties

Species	Property	Expt.	MEAM-BO Calc.	MEAM-BO Diff.	REBO Calc.	REBO Diff.	ReaxFF Calc.	ReaxFF Diff.
Graphene	E_{Corr}(eV/atom)	7.315[f]	7.304	-0.011	7.243	-0.072	6.884	0.431
	Lattice const., a (Å)	2.462[g]	2.46	-0.002	2.419	-0.043	2.501	0.041
	$C_{11} + C_{12}$ (N/m)	358.1[h]	361.6	3.5	436.9	78.8	744787	744428
	C_{66} (N/m)	60.4[h]	132.3	71.9	194.0	133.6	193449	193388
	Young's modulus (GPa)	1020[i]	1022[k]	2.4	1279[k]	259	53704[k]	52684
	Poisson's ratio	0.165[i]	0.156	-0.009	0.126	-0.039	0.979	0.814
	Percent error			**21.0**		**49.2**		**88954**
Graphite	E_{Corr}(eV/atom)	7.371[a]	7.37	-0.001	7.311	-0.060	7.413	0.042
	Lattice const., a (Å)	2.462[g]	2.47	0.008	2.418	-0.042	2.501	0.041
	Lattice const., c (Å)	6.707[g]	6.707	0	6.713	0.008	6.319	-0.386
	$C_{11} + C_{12}$ (GPa)	1240[j]	1051	-189	1309	69	2434604	2433364
	C_{66}(GPa)	440[j]	401	-39	508	69	12822	12382
	C_{13}(GPa)	15[j]	28	13	0.3	-14.7	7.8	-7.2
	C_{33}(GPa)	36.5[j]	38.3	1.8	41.0	4.5	1082.5	1046.0
	C_{44}(GPa)	4.5[j]	293.4	288.9	0.1	-4.4	4.9	0.4
	Percent error	-	-	817.0	-	29.0	-	25247
	Percent error (except C_{44})			**16.6**		**19.1**		**28854**

Detail in Mun et. al., J. Phys. Chem. A 2017

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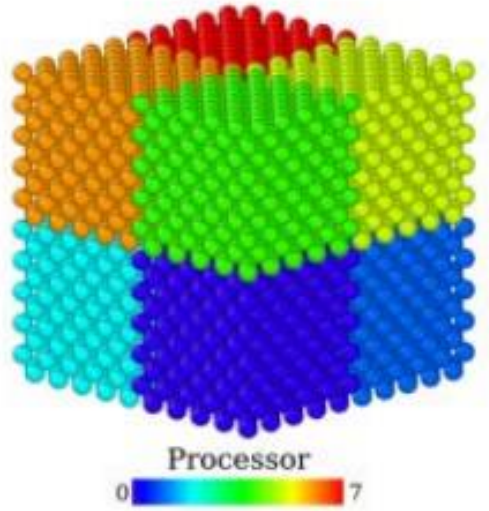
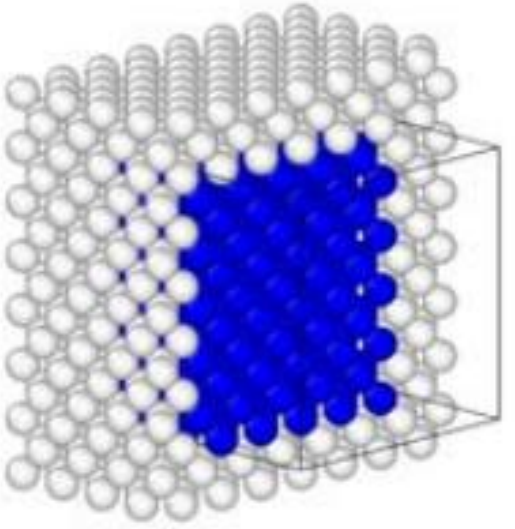
MEAM-BO in LAMMPS

- Written in C++ based on meam/c (5Jun2019 version)
- Can run in parallel through Message Passing Interface (MPI) thanks to LAMMPS communication functions
- New variables such as counting factors and their derivatives are added to the buffer array for the communication between the atoms in the local and the ghost region
- Challenges
  - Complex form of derivatives due to the bond center concept
  - Redundant calculations on ghost atoms due to the necessary pair terms between (local+ghost) atoms and their full neighbors

[1]ARL-TR-8213



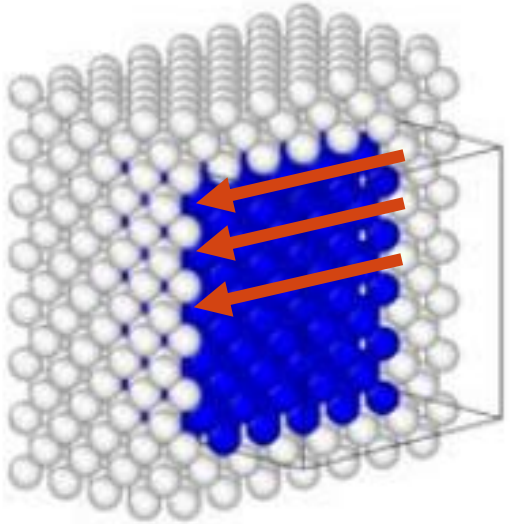
8 sub-domain



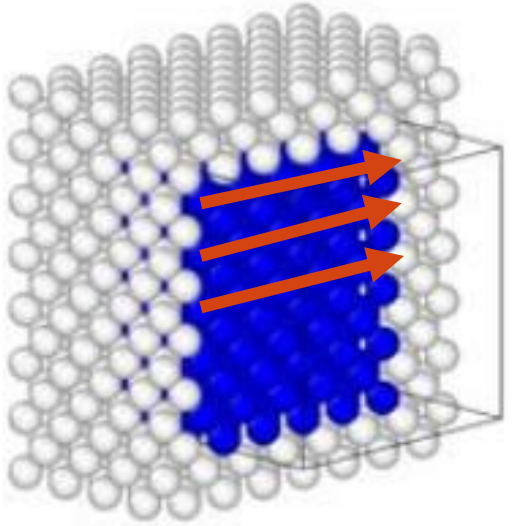
Blue: local atoms
White: ghost atoms

MEAM calculation procedure

1. Get screening between local atoms and their half neighbors
2. Get density terms
3. Reverse communication (ghost->local, sum)
4. Get derivatives for force calculation
5. Forward communication (local->ghost, copy)
6. Energy calculation
7. Force calculation



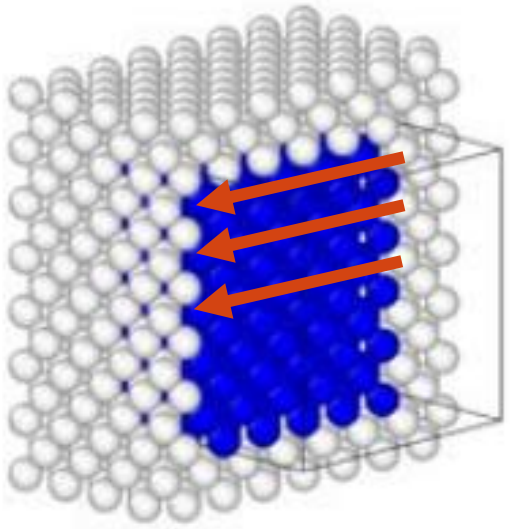
Reverse comm



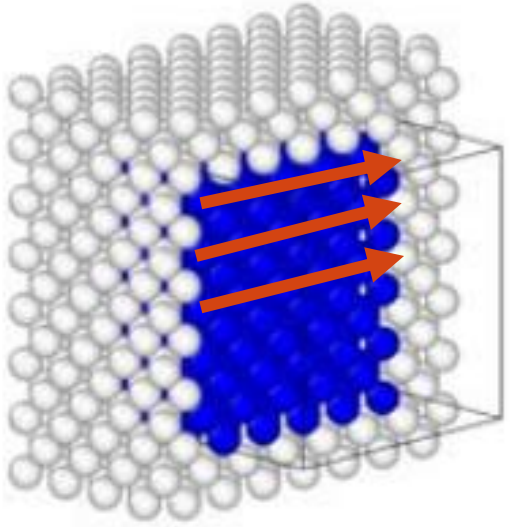
Forward comm

MEAM-BO calculation procedure

1. Get screening between local+ghost atoms and their full neighbors
2. Get density terms for local atoms
3. Determine bonds between local atoms and their full neighbors
4. If any bond exists
   - 4.1. Build a neighbor list of bonds by merging the neighbors
   - 4.2. Get screening for each bond
5. Reverse communication (ghost->local, sum)
6. Get derivatives for force calculation
7. If any bond exists
   - 7.1. Get counting factors for each atom and each bond
   - 7.2. Get derivatives for force due to bond order (local+ghost)
8. Forward communication (local->ghost, copy)
9. Energy calculation (Energy due to bond order)
10. Force calculation (Force due to bond order)



Reverse comm

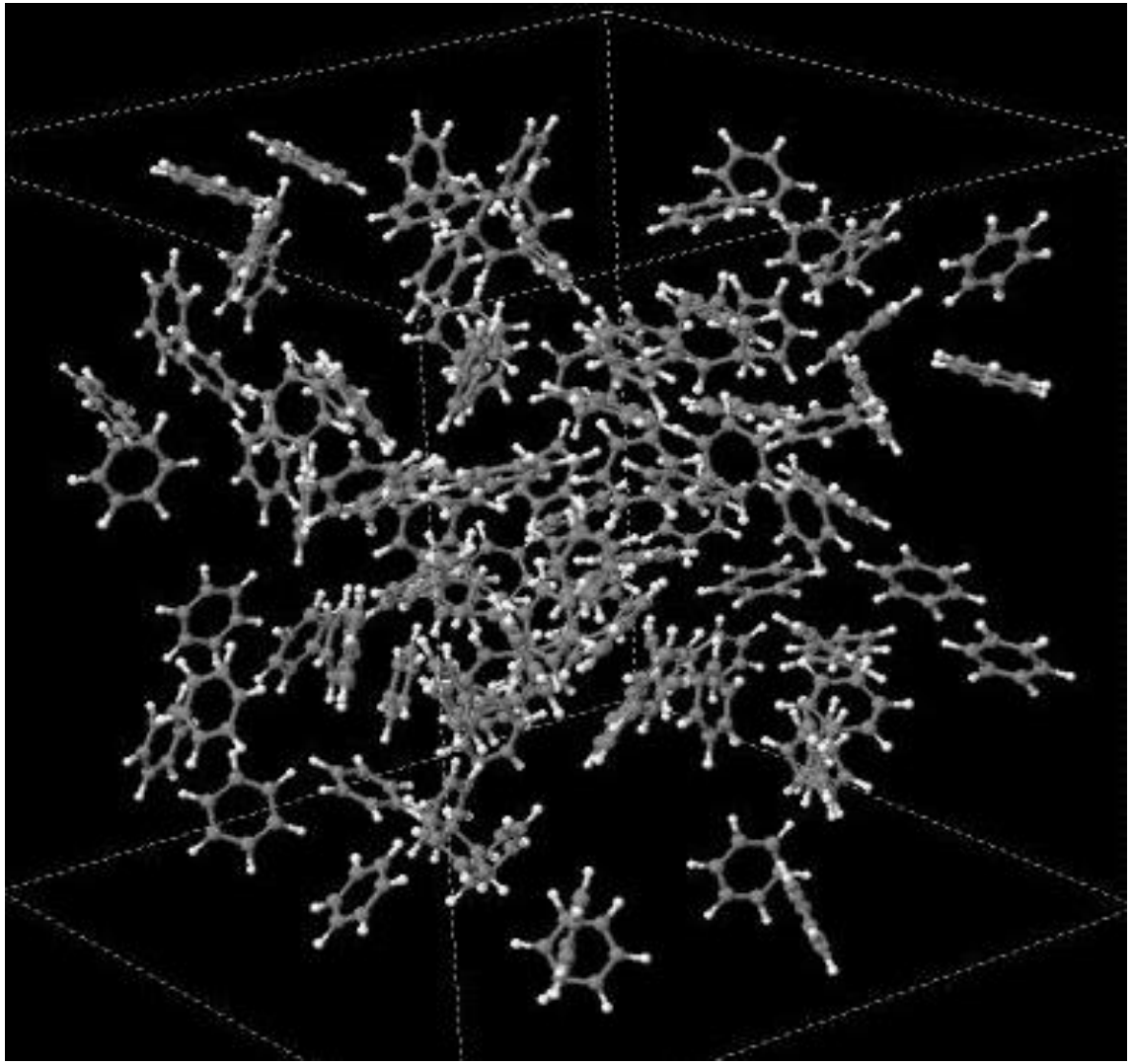


Forward comm

CPU cost of various force-field relative to MEAM/C

- Bulk benzene (1200 atoms)
- MEAM/C: 1.0
- MEAM/Fortran: 1.1
- AIREBO: 1.0
- MEAM-BO (no bond params): 1.01
- MEAM-BO*: 5.3
- ReaxFF/C: 8.6

* Can/will be improved up-to ~ 2.0 observed in the in-house serial code



How to use MEAM-BO in LAMMPS

- Input syntax is similar to MEAM/C

```
pair_style meambo
pair_coeff * * param1 C H param2 el1 C H bond_param
```

- New adjustable parameters
  - 3 per element in param2 file
  - 20/11 bond parameters per double/triple bond, respectively

- Can run original MEAM too!

```
pair_coeff * * param1 C H param2 el1 C H NULL
```

Summary and future work

- MEAM-BO: A new formalism for bond order has been added to the existing MEAM formalism to handle unsaturated bonds in hydrocarbons
- The results show that the properties of saturated and unsaturated hydrocarbons are comparable to those of the other reactive potentials and are reasonably close to the experimental data/first principles calculations.
- Can run in parallel
- Can run with the MEAM parameters in literatures with minimal modifications
- No bond parameters will run MEAM (with <1% extra computational cost)
- Future work
  - Performance optimization related to full neighbor operations
  - Generalized vdW interaction function (DFT-D3) implementation in LAMMPS
  - Improved bond order (*BO*) term calculation that consists of different element pair such as C-O and O-N
  - Parameterization tool for MEAM-BO parameters.

Question?

- Thank you for your attention!
- sungkwan@cavs.msstate.edu
- Code available at https://github.com/sungkwang/MEAM-BO