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Streitz-Mintmire Potential, Variable Charge Equilibration, and Chemical Species Analysis for ReaxFF

Ray Shan

Sandia National Laboratories, New Mexico

3rd LAMMPS Users' Workshop and Symposium

Albuquerque, NM August 6-8, 2013

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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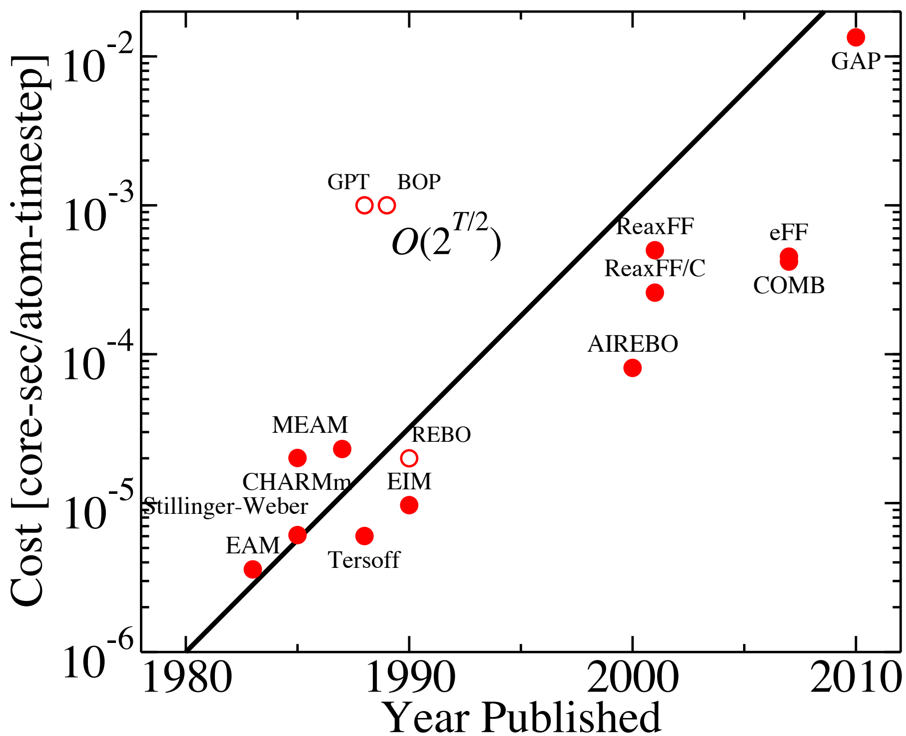
Explosive Growth in Complexity of Interatomic Potentials

- **Driver: Availability of Accurate QM data**
  - Exposes limitations of existing potentials
  - Provides more data for fitting



Moore’s Law for Interatomic Potentials
Plimpton and Thompson, MRS Bulletin (2012).

Aidan Thompson’s talk, Session II, 10:35, Thursday

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STREITZ-MINTMIRE POTENTIAL

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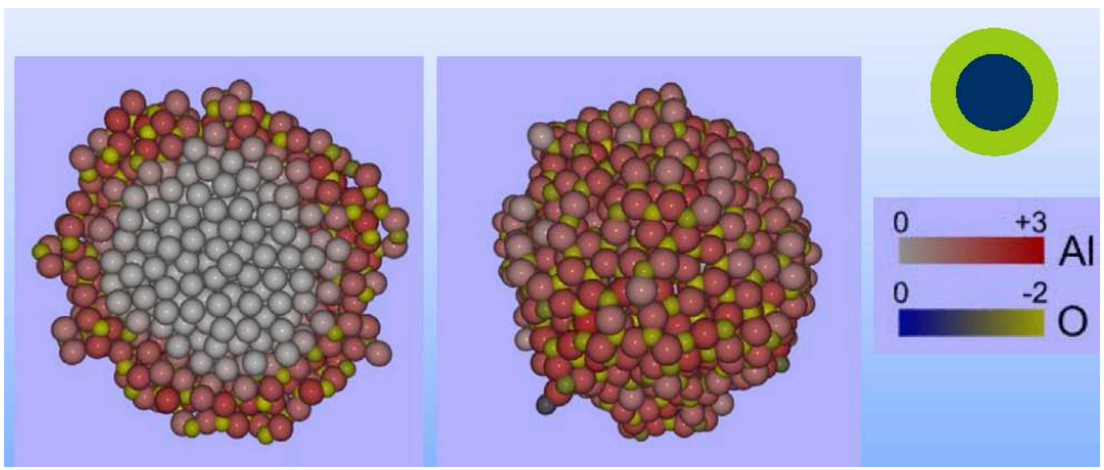
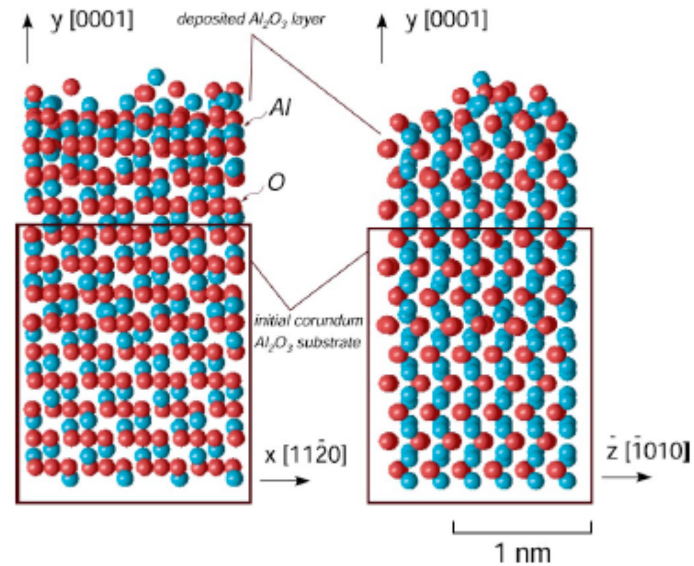
Streitz-Mintmire Potential

F. H. **Streitz** and J. W. **Mintmire**, Phys. Rev. B 50, 11996 (1994)

- Developed in 1994 for Al/Al_2O_3
- First variable charge potentials
  - Along with *fluc*-q force field by Rick, Stewart and Berne[1]
- Application to Al/Al_2O_3 core-shell nanoparticle[2] and vapor deposition of Al_2O_3 [3]





[1] S. W. **Rick**, S. J. **Stuart**, and B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)
[2] T. **Hawa** and M. R. **Zachaeriah,** *Phys Rev. B.*, 2005
[3] X. W. **Zhou**, H. N. G. **Wadley**, J.-S. **Fillhol**, and M. N. **Neurock**, Phys. Rev. B 69, 035402 (2004)

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Streitz-Mintmire Potential

- Long range electrostatics potential **(with Ewald Sum)**
- Variable charge **(via electronegativity equalization method)**
- Couples to short-range potential **(with embedded atom method)**
- Electrostatics potential formalism:
  - $$E_{es} = \sum_i E_i(q) + \frac{1}{2}\sum_{i \neq j} V_{ij}(r_{ij}, q_i, q_j)$$
    - $$E_i(q_i) = E_i(0) + \chi_i q_i + {}^1\!/_2\, \eta_i q_i^2$$
    - $$V_{ij}(r_{ij}, q_i, q_j) = \int d^3 r_i \int d^3 r_j \cdot \rho_i(r_i, q_i) \cdot \rho_j(r_j, q_j) / r_{ij}$$
      - $$\rho_i(r_i, q_i) = Z_i \delta(r - r_i) + (q_i - Z_i) f_i(r - r_i)$$

F. H. **Streitz** and J. W. **Mintmire**, Phys. Rev. B 50, 11996 (1994)

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Implementation in LAMMPS

- Long range electrostatics potential
  - Implemented with Ewald Sum or Wolf Sum
- Variable charge
  - EEM method; Implemented as fix qeq/sm
- Couples to short-range potential
  - Via pair_style hybrid/overlay
  - Default to EAM
  - Once supplied with self energy parameters, can be coupled to any short-range, charge independent pair styles, e.g. Tersoff, SW
    - $E_i(q_i) = E_i(0) + \chi_i q_i + \frac{1}{2}\eta_i q_i^2$

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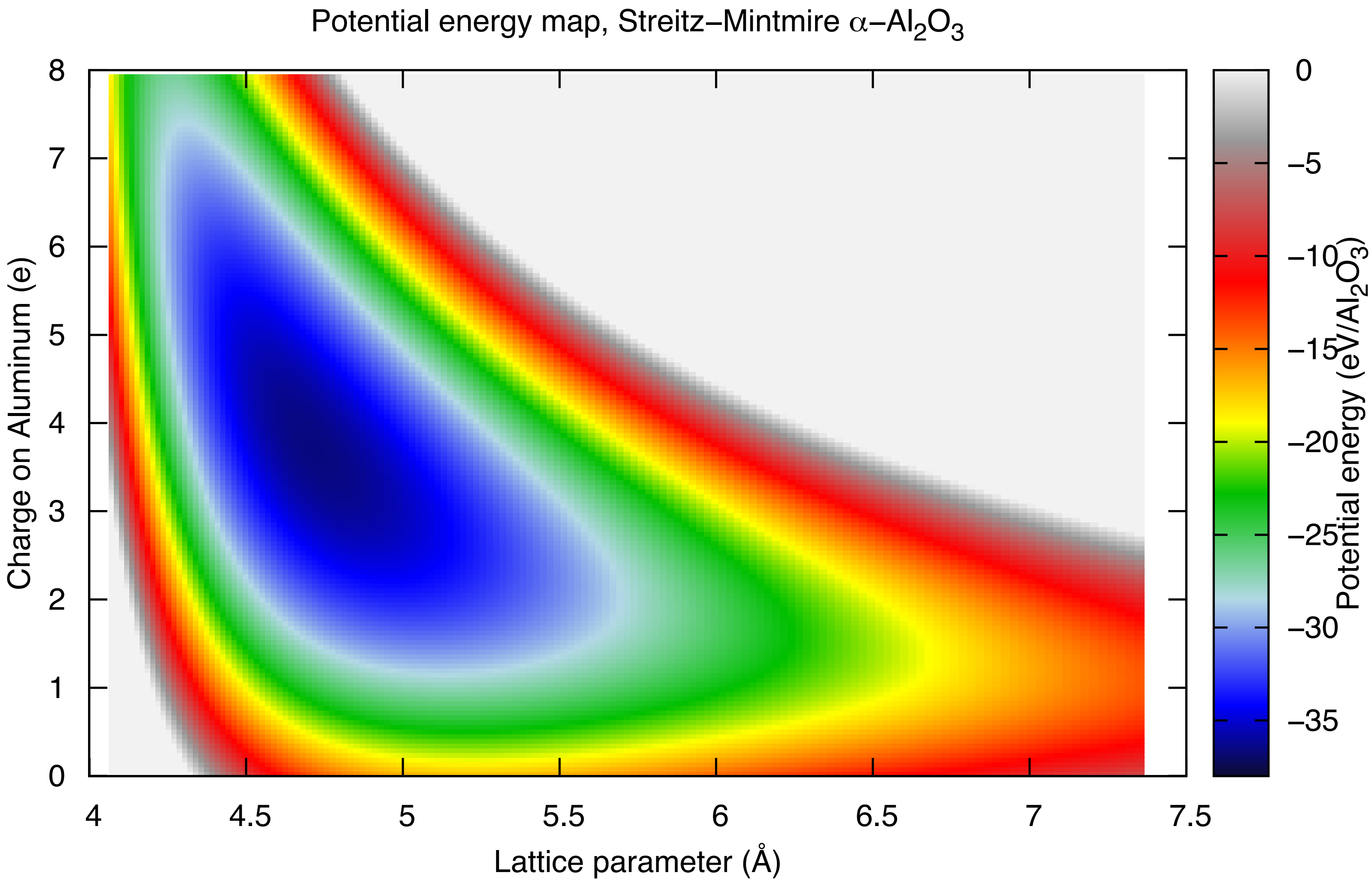
Potential energy map, α-Al_2O_3

-



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Summary and Outlooks

- Original Streitz-Mintmire Potential for Al/Al_2O_3 will be released soon
  - Long range, electrostatic, variable charge potential
  - Does not yet include modifications by Zhou et al (PRB 2004)
- Implementation allows coupling with all pair styles via hybrid/overlay
  - Can be applied to a wide range of pair styles
  - Supply self energy parameters
  - Done with Tersoff for SiO_2

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VARIABLE CHARGE EQUILIBRATION

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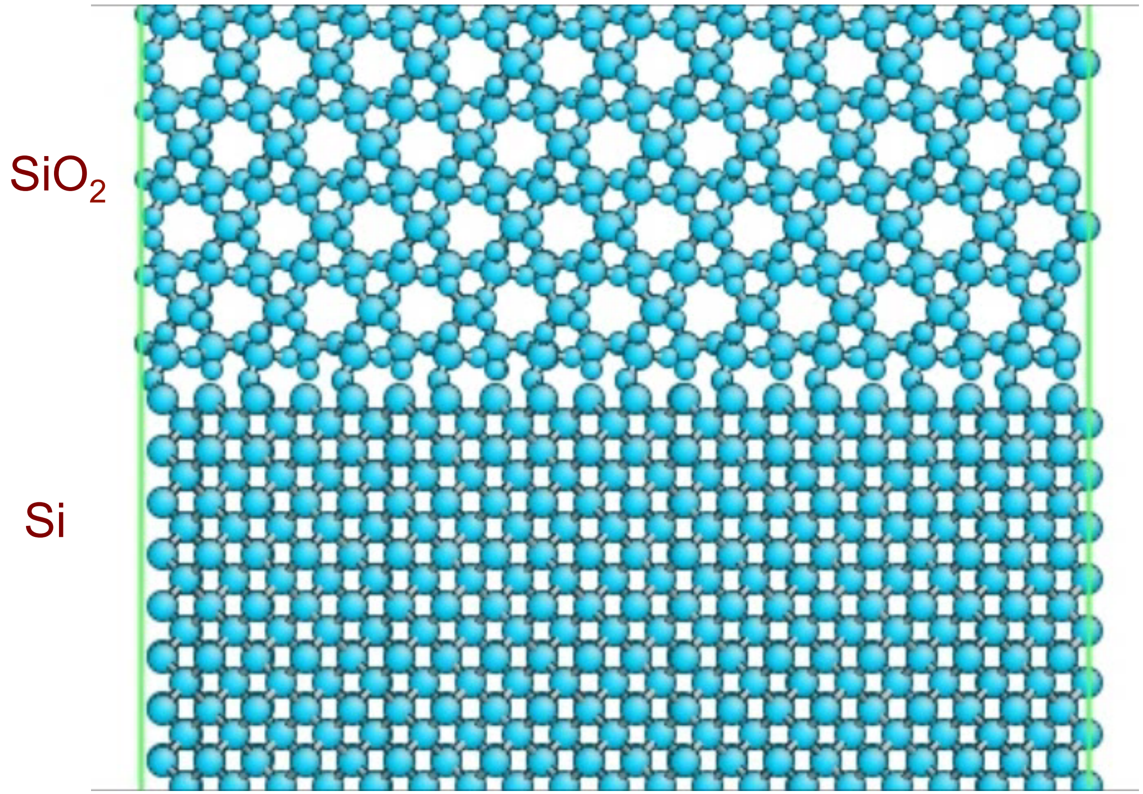
Charge equilibration

- Si/α-quartz SiO_2 interface with COMB (pair_style comb)



Fang-Yin Lin's talk, B2, 2:45, Today

- Variable charge potentials in LAMMPS include:
  - COMB (**comb**, **comb3**), ReaxFF (**reax**, **reax/c**), embedded ion method (**eim**), and Streitz-Mintmire (**coul/sm**)

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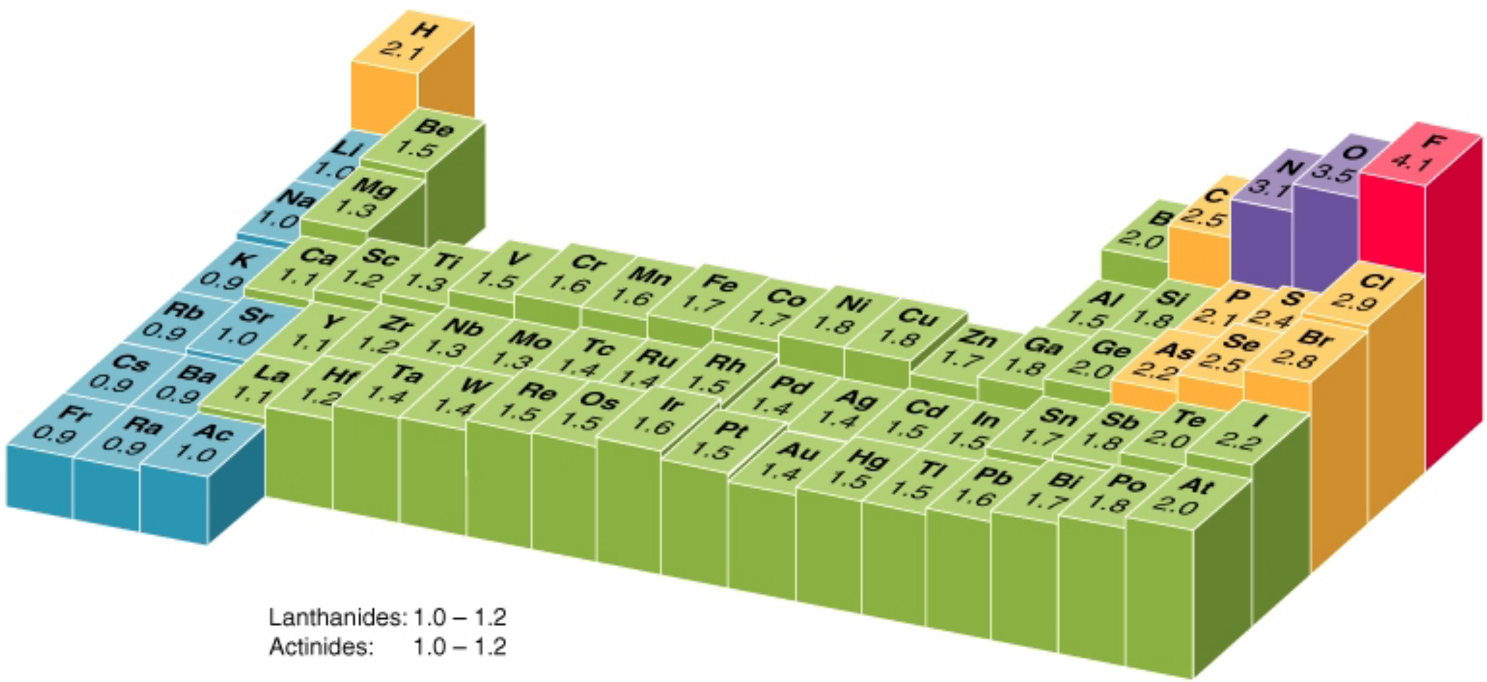
Electronegativity

- First proposed by Linus Pauling in 1932
- A chemical property that describes the tendency of an atom to attract electrons (or electron density) towards itself



Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

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Electronegativity

- When two or more atoms combine to form a molecule, their electronegativities are equalized – Sanderson's postulate [a]
- Electronegativity, X, of any chemical species is the negative of its chemical potential, μ [b]
  - $$\mathrm{X}_i = -\mu_i = -\frac{\partial E(\rho)}{\partial \rho} = e\frac{\partial E(q_i)}{\partial q_i}$$
- At equilibrium, electron density will transfer between atoms so that chemical potential (electronegativity) at all atomic sites are equal

Electronegativity equalizaton ➔ charge transfer

[a] R. T. **Sanderson**, *Chemical Bonds and Bond Energy*; Academic, New York (1976)
[b] R. G. **Parr**, R. A. **Donnelly**, M. **Levy**, W. E. **Palke**, *J. Chem. Phys.* 68, 3801 (1978)

Electronegativity

- Since electronegativity is the derivative of energy with respect to electron density (charges), it is useful to express electronegativity through expressing energy as a function of charge

- Most basic expression is the sum of atomic polarization energy and electrostatics

  - $$E(q_i) = \chi \cdot q_i + \tfrac{1}{2} \cdot \eta \cdot q_i^2 + \sum_{i<j} q_i \cdot J_{ij} \cdot q_j$$
  - $$\mu(q_i) = q_i + \eta \cdot q_i + \sum_{i<j} J_{ij} \cdot q_j$$
  - Used in ReaxFF and Streitz-Mintmire potentials

A. K. **Rappe**, W. A. **Goddard** III, *J. Phys. Chem.* 95 8 (1991)
A. C. T. **van Duin**, S. **Dasgupta**, F. **Lorant**, W. A. **Goddard** III, *J. Phys. Chem. A* 105 9396 (2001)
F. H. **Streitz** and J. W. **Mintmire**, Phys. Rev. B 50, 11996 (1994)

Electronegativity Equalization Method

- Solving equilibrium charges for a system of *N* atoms
  - A problem of *N* variables
- Based on electronegativity equalization principle
  - $\mu_i = \mu_{i+1} = \cdots = \mu_N$
  - *N – 1* conditions
  - Adding the condition of conservation on total charge
    - $q_{tot} = \sum_i q_i$
- The charge equilibration equations become
  - CD = -D

Rappe, A. K., Goddard III, W. A, *J. Phys. Chem.* 95 8 (1991)

Electronegativity Equalization Method

- Solving charges with CD = -D

$$\begin{bmatrix} J_{i,j}-J_{1,j} & J_{i+1,j}-J_{1,j} & \cdots & J_{N,j}-J_{1,j} & 1 \\ J_{i,j+1}-J_{1,j+1} & J_{i+1,j+1}-J_{1,j+1} & \cdots & J_{N,j+1}-J_{1,j+1} & 1 \\ \vdots & \vdots & \vdots & \vdots & 1 \\ J_{i,N}-J_{1,N} & J_{i+1,N}-J_{1,N} & \ddots & J_{N,N}-J_{1,N} & 1 \\ q_i & q_{i+1} & \cdots & q_N & 1 \end{bmatrix} \begin{bmatrix} \eta_i-\eta_1 \\ \eta_{i+1}-\eta_1 \\ \vdots \\ \eta_N-\eta_1 \\ -q_{tot} \end{bmatrix} = - \begin{bmatrix} \eta_i-\eta_1 \\ \eta_{i+1}-\eta_1 \\ \vdots \\ \eta_N-\eta_1 \\ -q_{tot} \end{bmatrix}$$

- Solve the sparse matrix problem with a linear conjugate gradient minimization method
  - Fast converging method for solving *q*, but only applicable to linear equations
  - $$\mu(q_i) = q_i + \eta \cdot q_i + \sum_{i<j} J_{ij} \cdot q_j$$

Electronegativity Equalization Method

- More complicated expression of energy as a function of charge
  - COMB
  - $$E(q_i) = E^p(q_i) + \sum_{i<j} q_i \cdot J_{ij} \cdot q_j + \sum_{i<j} V_{ij}\left(r_{ij}, q_i, q_j\right)$$

$$E^p(q_i) = \chi \cdot q_i + \tfrac{1}{2} \cdot \eta_1 \cdot q_i^2 + \tfrac{1}{3} \cdot \eta_2 \cdot q_i^3 + \tfrac{1}{4} \cdot \eta_3 \cdot q_i^4$$

$$V_{ij} = A(q) \cdot Ae^{-\lambda \cdot r_{ij}} + B(q) \cdot Be^{-\alpha(q) \cdot r_{ij}}$$

- Solving charges with EEM requires iterative, damped dynamics

Yu J., Sinnott S. B., Phillpot, S. R., *Phys. Rev. B* 75 085311 (2007)
Shan T.-R., Devine B. D., Kemper T. W., Sinnott S. B., Phillpot S. R., *Phys. Rev. B* 81 125328 (2010)

EEM with Damped Dynamics

- Analogous to classical Newtonian dynamics
  - $$m_i \ddot{r}_i = -\frac{\partial}{\partial r_i} E(\{r_i\},\{q_i\})$$
  - $$s_i \ddot{q}_i = -\frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\})$$

$$q_{tot} = \sum_i q_i$$

S. W. **Rick**, S. J. **Stuart**, B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)

EEM with Damped Dynamics

- Analogous to classical Newtonian dynamics
  - $$m_i \ddot{r}_i = -\frac{\partial}{\partial r_i} E(\{r_i\},\{q_i\})$$
  - $$s_i \ddot{q}_i = -\left(\frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\}) - \frac{1}{N} \sum_i \frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\})\right)$$

S. W. **Rick**, S. J. **Stuart**, B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)

EEM with Damped Dynamics

- Analogous to classical Newtonian dynamics
  - $$m_i \ddot{r}_i = -\frac{\partial}{\partial r_i} E(\{r_i\},\{q_i\})$$
  - $$s_i \ddot{q}_i = -\left(\frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\}) - \frac{1}{N}\sum_i \frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\})\right)$$
  - $$s_i \ddot{q}_i = -\mu_i + \overline{\mu} - \eta_d \dot{q}_i$$
- Also know as the Extended Lagrangian method
  - Damped dynamics with fixed damping
  - Large damping facilitates convergence, but leads to instability more easily

S. W. **Rick**, S. J. **Stuart**, B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)

Summary and Outlooks

- Current variable charge fixes are implemented independently
  - fix qeq/reax
  - fix qeq/comb
  - fix qeq/sm
  - Pair_style eim has its own built-in variable charge routines
- These qeq fixes will be reorganized/modified into one fix
  - fix qeq
  - fix_modify qeq style *cg (conjugate gradient)* or *dd (damped dynamics)*
- Main advantage is easy to expand and include more qeq styles
  - E.g. SQE [1], QTPIE [2], etc

[1] D. **Mathieu**, J. Chem. Phys. 127 224103 (2007)
[2] J. **Chen** and T. J. **Martinez**, Chem. Phys. Lett. 438 315 (2007)

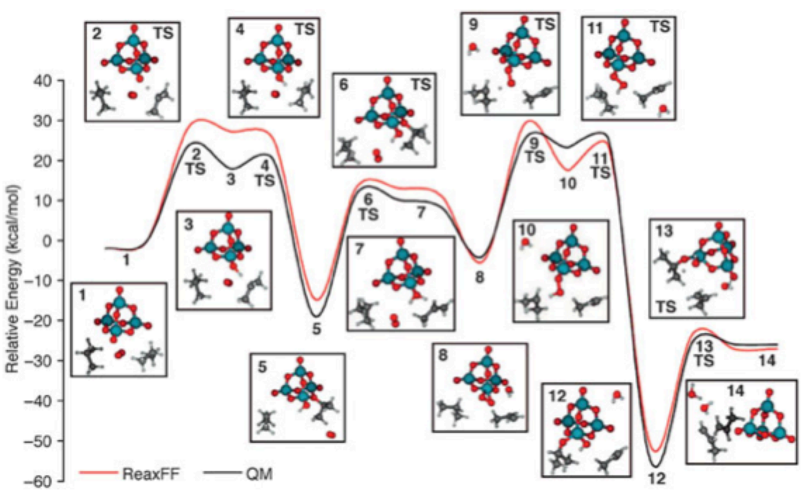
ON-THE-FLY CHEMICAL SPECIES ANALYSIS FOR REAXFF

Unclassified Unlimited Release

Reactive Force Field (ReaxFF)

- $$\begin{aligned} E^{ReaxFF} \;=\;& E^{self} + E^{Coul} + E^{vdW} + E^{bond} + E^{angle} + E^{torsion} \\ & + E^{conjugation} + E^{H-bond} + E^{lone-pair} + E^{over} + E^{under} \\ & + E^{others} \end{aligned}$$
  - Ability to model chemical reactions

- Trained against QM/QC data
  - Reproduces transition states, energy barriers



A. C. T. **van Duin**, S. **Dasgupta**, F. **Lorant**, W. **Goddard**, *J. Phys. Chem. A* 105 9396 (2001)

K. Chenoweth, A. C. T. **van Duin**, W. **Goddard**, *J. Phys. Chem. A* 112 1040 (2008)

Adri van Duin's talk, Session II, 11:00, Thursday

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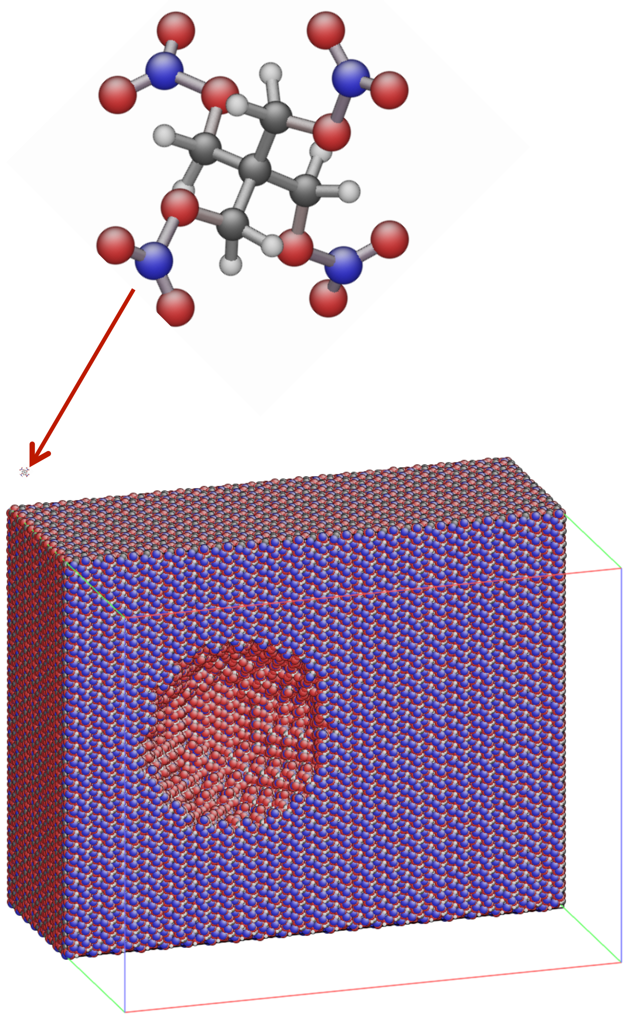
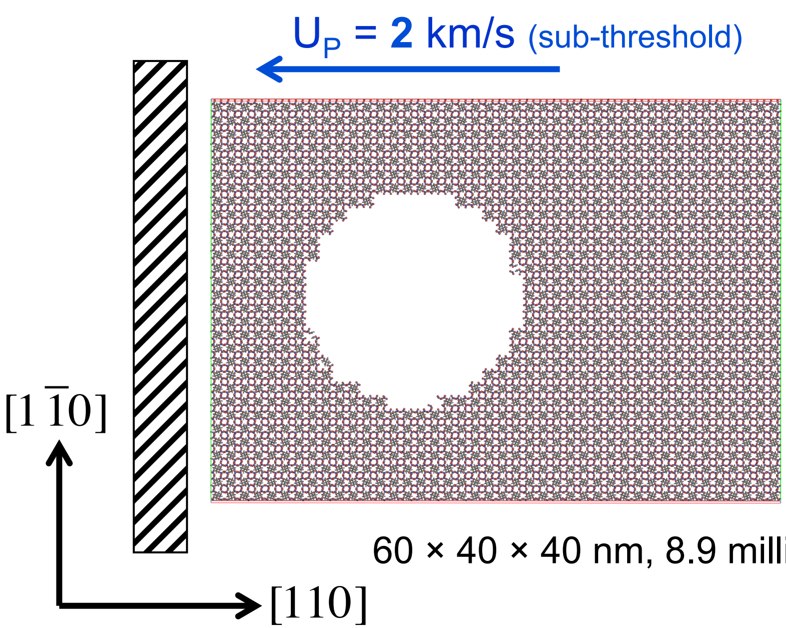
Large-Scale Explicit NEMD Simulation of Shockwave Interaction with Spherical Void



- DOE ASC TLCC2 Chama (Sandia)
  - 256 nodes/4096 MPI tasks
- LAMMPS software
- ReaxFF force field (reax/c)



60 × 40 × 40 nm, 8.9 million atoms

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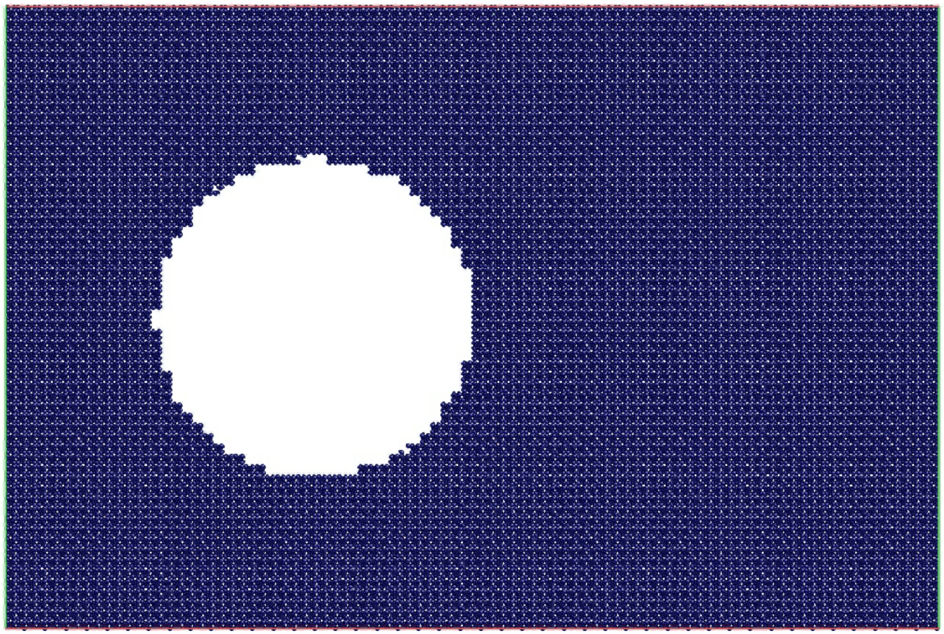
Large-Scale Explicit NEMD Simulation of Shockwave Interaction with Spherical Void

- Kinetic energy

U_P = **2** km/s



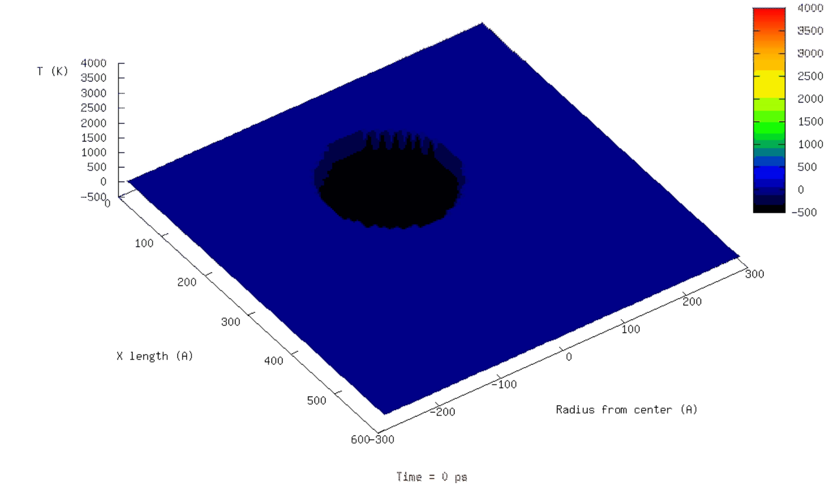
20 nm void
60 × 40 × 40 nm
8.9 million atoms

20 kcal/mol ≈ 10,000 K

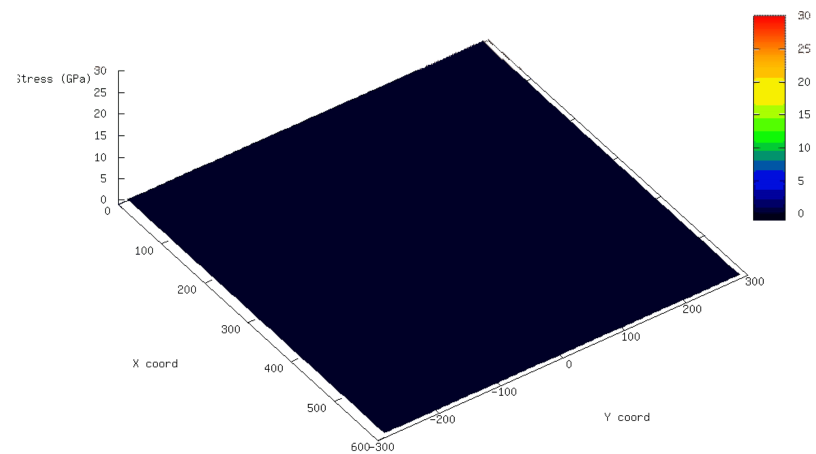
0 kcal/mol

10 nm

- Temperature



- Stress



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Identify Molecules & Species

- Current (and only) method: with pair_style reax/c:
  - Use “fix reax/c/bonds” to print a connection table
  - Post-process the table with a serial program
  - Drawbacks:
    - Massive storage required
      - One line per atom
    - Time consuming post-process
      - Single core program
    - No information on spatial distribution of molecules & species

```
# Timestep 2
#
# Number of particles 81983
#
# Max number of bonds per atom 5 with coarse bond order cutoff 0.300
# Particle connection table and bond orders
# id type nb id_1...id_nb mol bo_1...bo_nb abo nlp q
 576 1 3 577 581 582 0      0.885      1.216      1.704      3.807      0.000      0.510
 13445 1 2 13448 13470 0      2.640      0.764      3.436      0.000      0.289
 538 3 2 569 875 0      1.489      0.390      2.027      1.996      -0.493
 13466 2 1 528 0      0.801      0.857      0.000      0.398
 528 3 2 13466 526 0      0.801      1.054      1.907      2.000      -0.576
 577 3 2 576 584 0      0.885      0.609      1.705      2.000      -0.314
 589 3 2 13444 674 0      0.850      0.792      1.716      2.000      -0.610
 566 3 2 572 536 0      0.672      0.941      1.658      2.000      -0.489
 13448 3 1 13445 0      2.640      2.719      1.047      -0.404
 569 1 3 538 570 530 0      1.489      0.973      1.649      4.125      0.000      0.448
 1844 3 2 558 1869 0      0.483      0.952      1.713      2.000      -0.517
 570 2 1 569 0      0.973      1.041      0.000      0.191
 13447 2 1 13446 0      0.966      0.995      0.000      0.196
 530 3 1 569 0      1.649      1.864      2.000      -0.416
 526 4 3 528 13492 555 0      1.054      0.914      0.539      2.537      1.000      0.236
 1869 2 1 1844 0      0.952      0.981      0.000      0.432
 821 3 2 555 601 0      0.707      0.882      1.777      2.000      -0.615
 13658 2 1 585 0      0.855      0.930      0.000      0.409
 555 4 4 526 821 13710 561 0      0.539      0.707      1.132      0.373      2.754      1.000      0.266
 601 2 1 821 0      0.882      0.910      0.000      0.429
 536 2 1 566 0      0.941      0.943      0.000      0.365
 581 1 3 576 571 579 0      1.216      1.252      1.305      3.773      0.000      -0.058
 13444 2 1 589 0      0.850      0.927      0.000      0.407
 585 3 3 13658 13505 561 0      0.855      0.471      0.476      1.908      2.000      -0.446
 674 2 1 589 0      0.792      0.899      0.000      0.462
 584 4 4 577 561 846 541 0      0.609      0.770      0.878      0.744      3.049      0.986      -0.126
 13710 3 2 555 817 0      1.132      0.719      1.899      2.000      -0.469
 13470 1 3 13445 13713 13446 0      0.764      1.287      2.005      4.057      0.000      0.191
 817 2 1 13710 0      0.719      0.979      0.000      0.380
 561 4 3 555 585 584 0      0.373      0.476      0.770      1.877      1.011      0.105
 853 1 3 13777 599 828 0      1.306      1.249      0.968      3.543      0.000      0.432
…
```

Identify Molecules & Species

- Would not it be great if we can:
  - Avoid storing huge output files?
  - Avoid post-processing with serial programs?
  - Monitor molecules and species on-the-fly?
  - Know where and when specific molecules/species are formed?

- Solution is a new fix: "reax/c/species"
  - **fix ID group-ID reax/c/species Nevery Nrepeat Nfreq filename keyword value ...**
  - Analyzes chemical bonds, molecules, and species based on time-averaged or instantaneous bond order values
  - Currently limited to pair_style reax/c
    - But extension to other reactive potentials (**tersoff**, **rebo/airebo**, **bop**, **comb**, etc) is made as simple as possible

Species Analysis

Sandia National Laboratories

- Output type 1:

# Timestep	No_Moles	No_Specs	C5H8O12N4
2	2827	1	2827

# Timestep	No_Moles	No_Specs	H2O3N	H2O	HO	CH2O3	ON2	......
55002	6703	747	43	1557	1537	8	31	......

  - Terse list, know what and how many molecules right away

- Output type 2:

Timestep 55002 NSpec 747 NMole 6703 xlo 0.000000 xhi 121.397880 ylo 0.953317 yhi 79.582283 zlo -1.443159 zhi 57.372959

ID	Atom_Count	Type	Ave_q	CoM_x	CoM_y	CoM_z
1	6	H2O3N	-0.02388735	0.00604353	0.03255288	0.62153236
2	28	C4H8O9N7	0.02785239	0.01054783	0.27594189	0.55659111
3	296	C67H46O129N54	-0.01571570	0.06200146	0.85039233	0.44433890
4	3	H2O	0.07147703	0.02367206	0.10731024	0.41775836
5	38	C13H2O17N6	-0.03316714	0.04845567	0.21833137	0.58398634
6	2	HO	-0.14814854	0.02654568	0.04087529	0.62640116
7	25	C8H7O9N	0.00647330	0.03278529	0.05240849	0.48259218
8	2	HO	-0.00285301	0.03098041	0.08792044	0.58878768

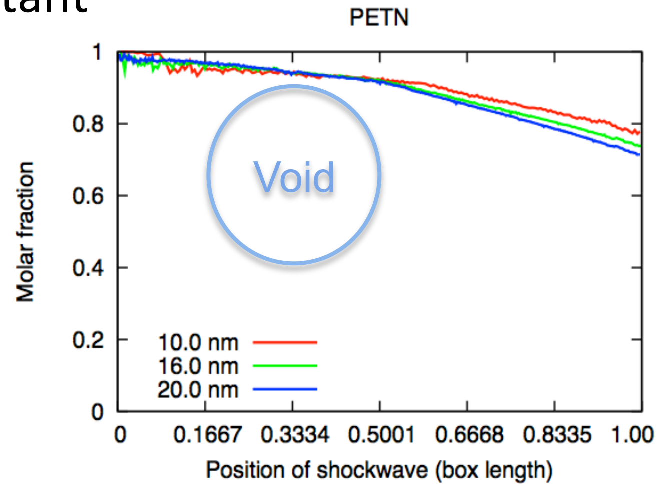
……

  - Generates cfg files with a small analysis program

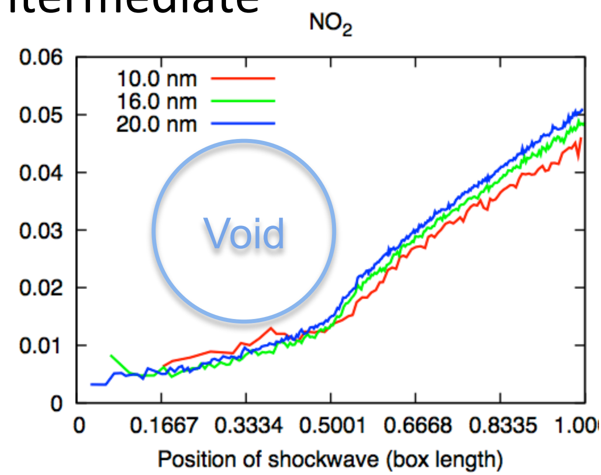
Chemical species analysis

U_P = **2** km/s

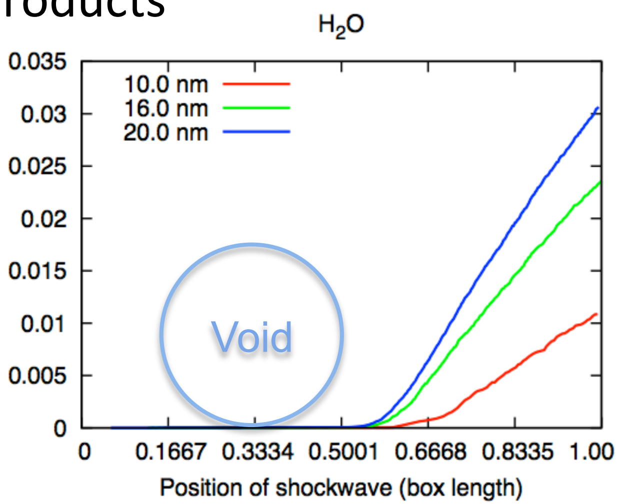
- Reactant

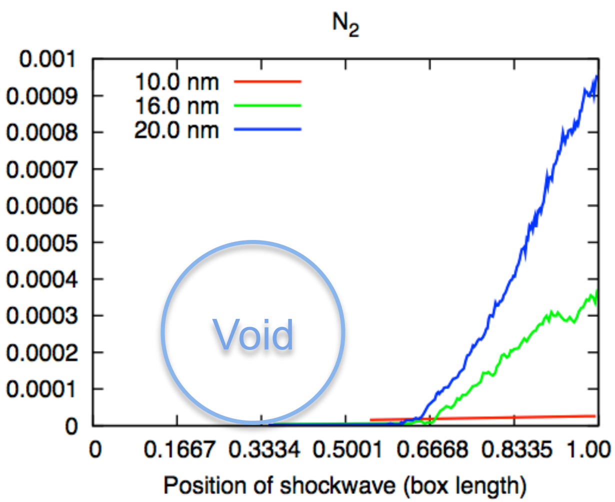


- Intermediate



- Final Products





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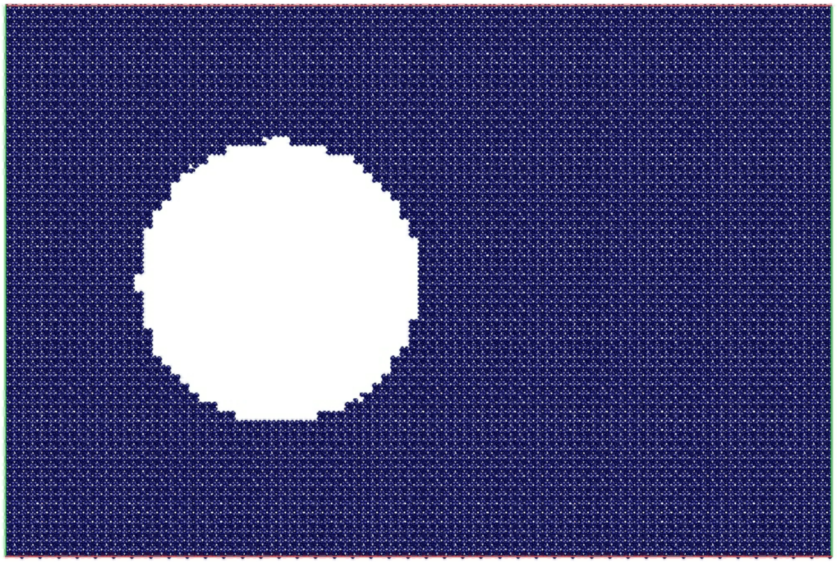
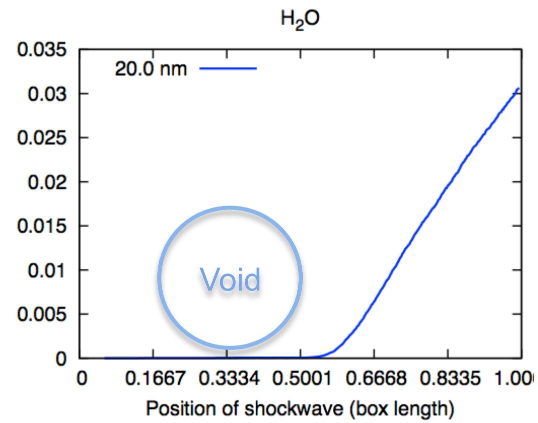
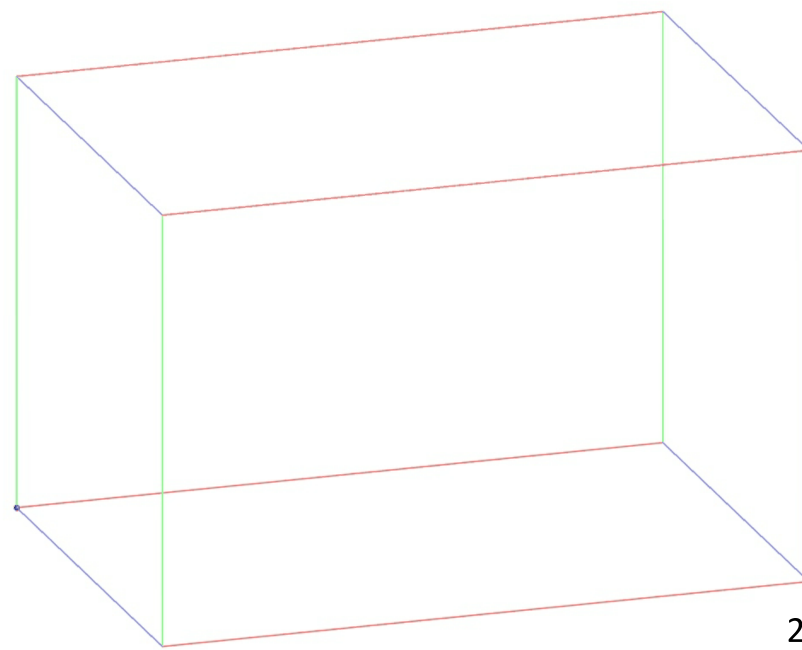
Formation of H_2O: 20 nm void, 2 km/s







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Summary and Outlooks

- On-the-fly, real-time chemical species analysis based on bond order values
- Currently limited to pair_style reax/c
  - Can be extended to other bond order pair styles

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Conclusions

- Advanced force fields
  - Reactive (bond order), Variable charge, and Others (electron orbitals, automated machine-learning)
  - Allow modeling of bond forming/breaking (chemical reactions), charge transfer, and more
- Streitz-Mintmire will be released
  - Applicable to all pair_styles via hybrid
- Variable charge fixes will be reorganized/modified
  - Allows easy extension to include more QEq styles
- Fix reax/c/species can be extended to more reactive potentials
  - Volunteers?

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