pEFF: Large-scale Excited Electron Mechanics/Dynamics over LAMMPS

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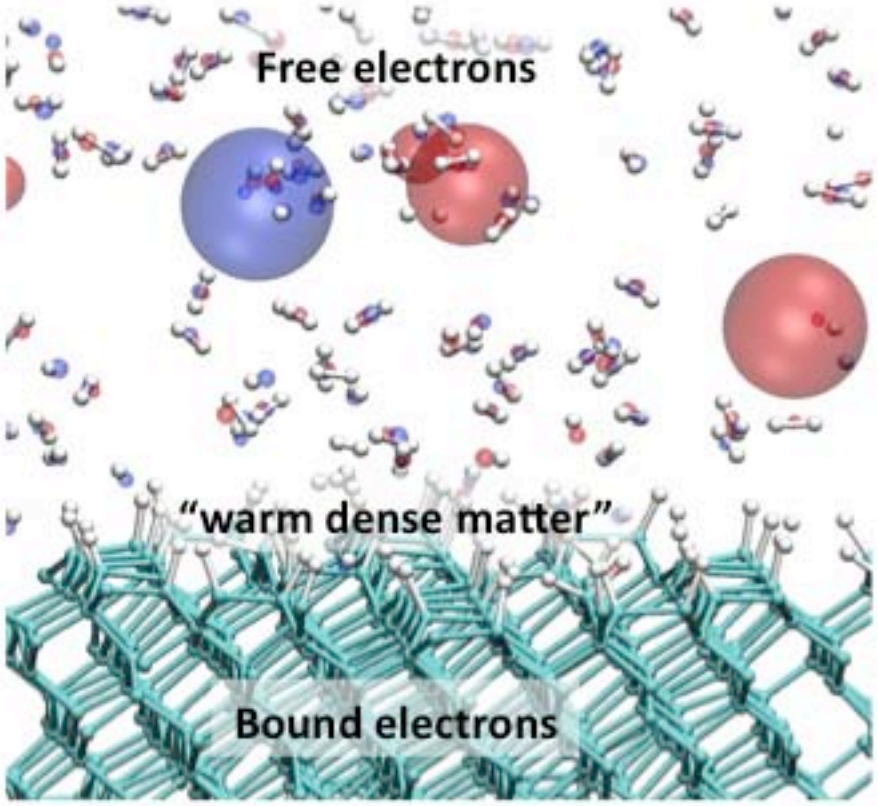
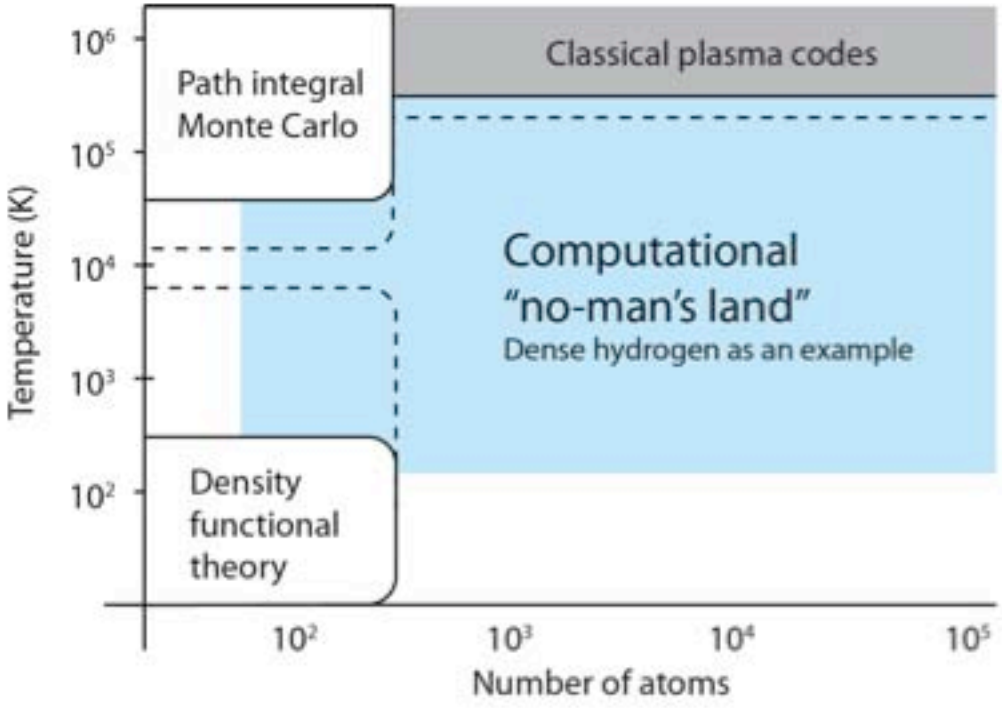
1. Significance
2. The Electron Force Field method
3. Parallel-EFF (pEFF) on LAMMPS
   - Implementation/extension details and validation
   - Sample Applications
   - Performance
4. Acknowledgements

OUTLINE

SIGNIFICANCE

Interfaces between materials and excited phases





Important to understand but challenging to model

Bridges electronic structure and plasma physics methods

Significance

- Enables large-scale, long-term molecular simulations with explicit non-adiabatic electronic contributions
- Enables study of challenging problems beyond current QM and classical-MD capabilities, for example,

Material properties and phenomena under extreme (equilibrium and non-equilibrium) conditions:

- Electronic effects during hypervelocity shock and interfacial instabilities (RMI, RTI)
- Warm-dense-matter (shock and laser induced plasmas, ionization, emission)
- Molecular, transitional and turbulent flows (reactive flow, radiative heating)
- Semiconductor Electron Etching (versus ion etching)
- Radiation damage, and other systems with a high number of electronically excited states

- Extends original eFF capabilities and leverages from existing/future LAMMPS functionality

Fundamentals on the Electron Force Field

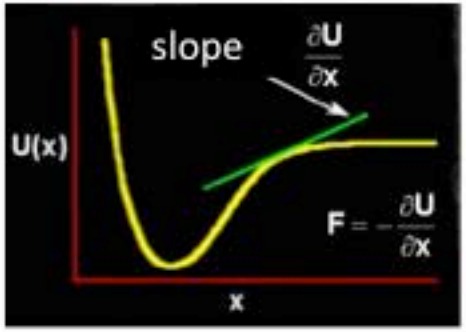
BACKGROUND

A. Jaramillo-Botero
LAMMPS Workshop (Sandia, Feb-2010)

From Schrödinger's equation to the Electron Force Field Approx.

1. **FSGO wave-functions used to describe electrons**
   - QM effects: Electron size-dependent KE pressure and spin-dependent Pauli (no explicit anti-symmetrization). FSGO, Frost, J. Chem. Phys. 47 (1967) 3707, 3714.
2. **Nuclei point charges + electrons** (*r* and *s*) **move as classical particles on PES**
3. **Approximate PES with analytical potentials**

$$U = E_{KE}(r,s) + E_{NN}(R) + E_{Ne}(R,r,s) + E_{ee}(r,s) + E_{Pauli}(\uparrow\downarrow,S)$$



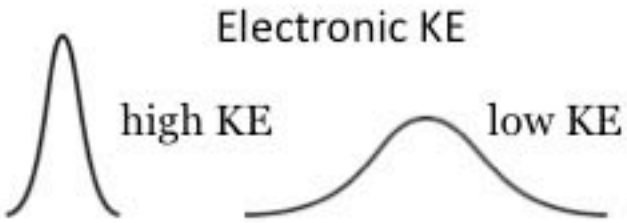
$$\frac{\partial^2(R,r,s)}{\partial t^2} = -M^{-1}\frac{\partial U}{\partial(R,r,s)}$$

TRANSFERABLE, ~AB-INITIO, AND NOT LIMITED TO GROUND STATE

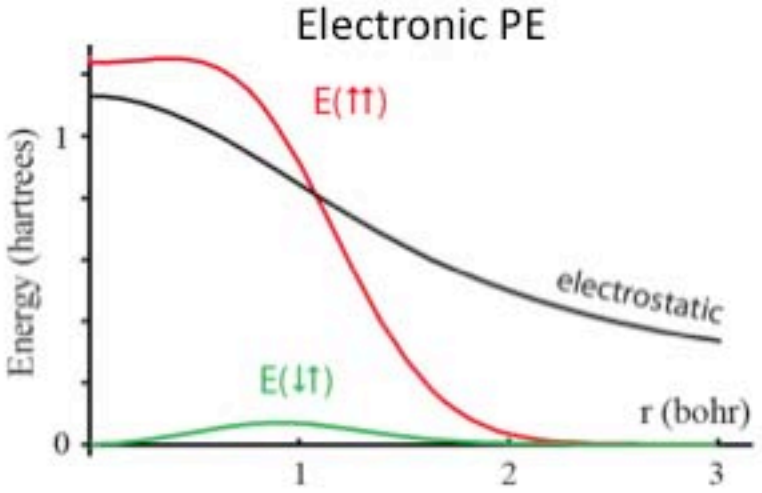
Pairwise Interactions in eFF

(1) Classical electrostatics plus (2) **quantum potentials**:

Kinetic energy pressure
Heisenberg principle



Pauli repulsion
Spin-dependent, 3 parameters



Similar formulations

Boal and Glosli, nuclear reactions
Phys Rev C **1988** 38(4):1870-1878

Klakow et al, hydrogen plasma
J. Chem. Phys **1994** 101(12):10766-10774

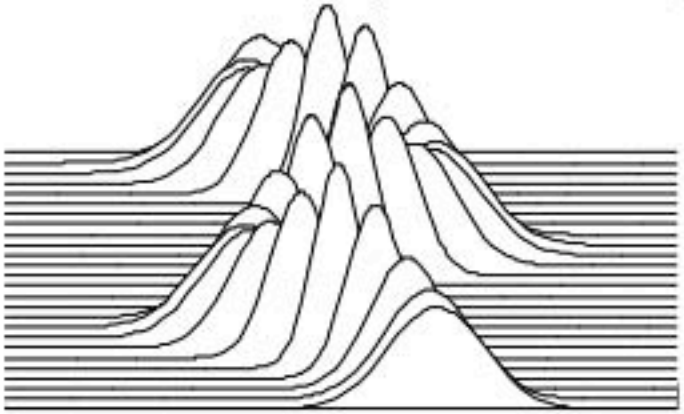
Our expression is the first applicable to a wide range of molecules

Dynamics of Floating Spherical Gaussian wave packets

Wave packet whose **size and position varies with time**:

$$\Psi(\mathbf{x}) \propto \exp\left[-\left(\frac{1}{s^2} - \frac{2p_s}{s}\frac{i}{\hbar}\right)(\mathbf{x}-\mathbf{r})^2\right] \cdot \exp\left[\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}\right]$$

Assume a *locally harmonic* potential, stays Gaussian over time:



$$\frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}}{m} \qquad \frac{d\mathbf{p}}{dt} = -\nabla E$$

$$\frac{ds}{dt} = \frac{p_s}{(3/4)m} \qquad \frac{dp_s}{dt} = -\frac{\partial E}{\partial s}$$

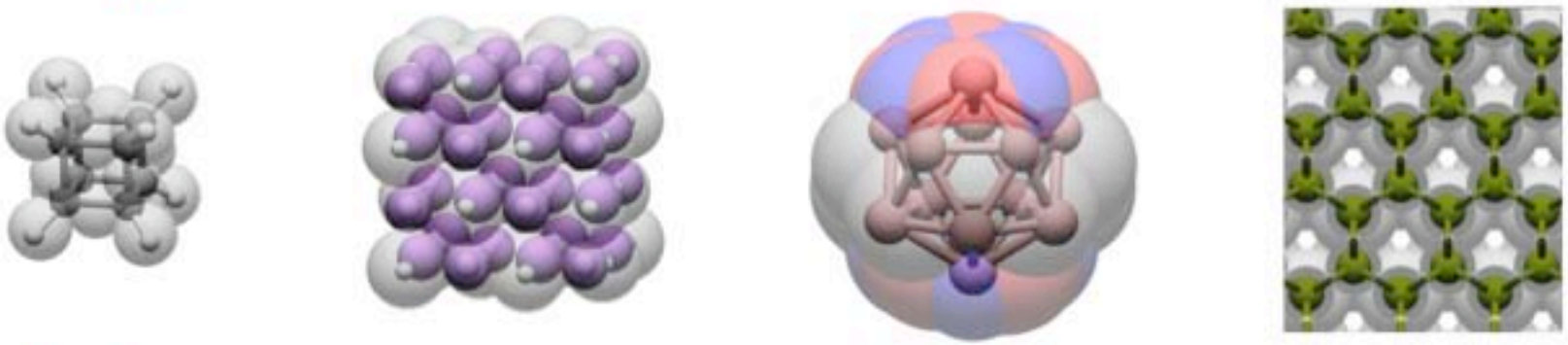
Schrodinger's equation gives simple equations of motion

Heller, semiclassical dynamics – J. Chem. Phys **1975** 62(4) 1544-1555

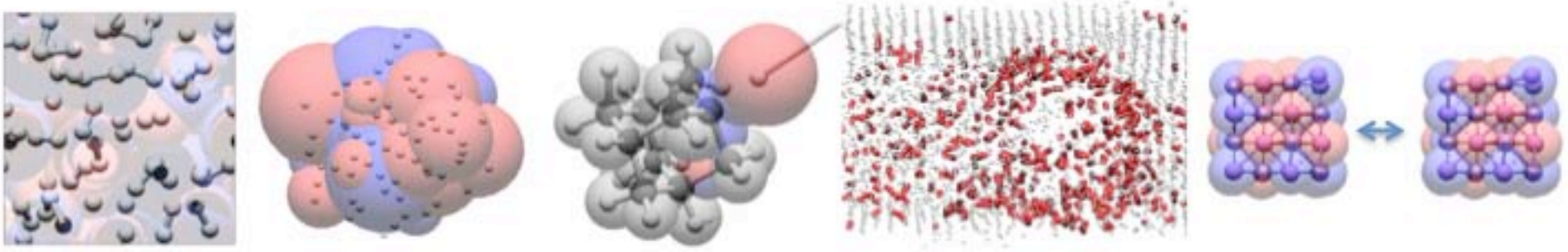
Fermionic molecular dynamics – Rev. Mod. Phys. **2000** 72 655-688

eFF Describes Many Materials and Excitations Consistently

Bonding: covalent, ionic, multicenter, metallic



Excitation: thermal, laser, core ionization, proton impact, hypervelocity impact



Makes it feasible to study large heterogeneous excited systems

CALTECH
PSAAP

NNSA
National Nuclear Security Administration

MSC

Extensions and tools

Energy expressions, temperature, pressure

SPE, Min, NVE, NVT, and NPT dynamics (Applications)

Single and Multiprocessor Performance

pEFF-LAMMPS

A. Jaramillo-Botero

LAMMPS Workshop (Sandia, Feb-2010)

pEFF LAMMPS Extensions and Tools

- **Included as a LAMMPS USER-EFF package:**
  - pair_eff_cut.cpp/h, atom_vec_electron.cpp/h, compute_ke_eff.cpp/h, compute_ke_atom_eff.cpp/h, compute_temp_eff.cpp/h, fix_nve_eff.cpp/h, fix_nvt_eff.cpp/h, fix_npt_eff.cpp/h, Install.sh
  - atom.cpp/h, compute_ke.cpp, compute_temp.cpp, dump_custom.cpp, pair.cpp/h, min.cpp, min_cg.cpp, verlet.cpp, update.cpp, Makefile

  Note: full atom style implemented as a hybrid pair_style
- **Style and syntax of core, installs/uninstalls as user package:**
  - make yes/no-user-eff.
- **Includes data/script/post processing tools and examples:**
  - Perl scripts to generate LAMMPS input files (e.g. data files for uniform gas, Li-solid, Li-hydride, Be-solid, Diamond, and scripts for MM/MD),
  - TCL code and Python scripts to enable VMD visualization of pEFF trajectories,
  - cfg2lammps translator, plus nd other analysis tools.

pEFF LAMMPS Extensions and Tools

- **Included as a LAMMPS USER-EFF package:**
  - fix ID group-ID nve/eff
  - fix ID group-ID nvt/eff Tstart Tstop Tdamp keyword value
  - fix ID group-ID npt/eff Tstart Tstop Tdamp p-style args keyword value
  - compute ID group-ID temp/eff
  - compute ID group-ID ke/eff
  - compute ID group-ID ke/atom/eff

  - units electron
  - atom_style electron or atom_style hybrid charge electron
  - pair_style eff/cut cutoff
  - pair_coeff I J cutoff

  - dump_custom supports electron-specific quantities (i.e. radius, rf, vr, etc.)
  - restarts include all electron-specific quantities
  - minimization includes radial changes (extra quantity)

Example LAMMPS data and input files

data.Li-solid

```
16000 atoms
2 atom types

0.0 83.52 xlo xhi
0.0 83.52 ylo yhi
0.0 83.52 zlo zhi

Masses

1 6.941
2 1.000

Atoms

1     1     4.176   4.176   4.176   3.00   0    0.00
2     1     8.352   8.352   4.176   3.00   0    0.00
3     1     4.176   8.352   8.352   3.00   0    0.00
|
4001  2     4.176   4.176   4.176   0.0    1    0.70
4002  2     4.176   4.176   4.176   0.00   -1   0.70
4003  2     8.352   8.352   4.176   0.00   1    0.70
4004  2     8.352   8.352   4.176   0.00   -1   0.70
```

```
variable        sname index Li-solid
log             ${sname}.nvt.log

units           electron
newton          on
boundary        p p p

atom_style      hybrid charge electron

read_data       data.${sname}

pair_style      eff/cut 41.76
pair_coeff      * *

thermo          100
thermo_style    multi
neigh_modify    one 10000 page 100000

timestep        0.005
fix             1 all nvt/eff 300.0 300.0 1.0
dump    1 all custom 100 ${sname}.nvt.lammpstrj id type x y z spin radius
dump    2 all xyz 100 ${sname}.nvt.xyz
restart ${sname}.npt.restart1  ${sname}.npt.restart2

run             1000000

unfix           1
undump          1
undump          2
```

Energy Expressions

$$U = E_{KE}(r,s) + E_{NN}(R) + E_{Ne}(R,r,s) + E_{ee}(r,s) + E_{Pauli}(\uparrow\downarrow, S)$$

$$E_{NN} = \frac{1}{4\pi\varepsilon_0} \sum_{i<j} \frac{Z_i Z_j}{R_{ij}}$$

$$E_{Ne} = -\frac{1}{4\pi\varepsilon_0} \sum_{i,j} \frac{Z_i}{R_{ij}} Erf\left(\frac{\sqrt{2}R_{ij}}{s_j}\right)$$

$$E_{ee} = \frac{1}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{r_{ij}} Erf\left(\frac{\sqrt{2}r_{ij}}{\sqrt{s_i^2 + s_j^2}}\right)$$

$$E_{Pauli} = \sum_{\sigma_i = \sigma_j} E(\uparrow\uparrow) + \sum_{\sigma_i \neq \sigma_j} E(\uparrow\downarrow)$$

$$E_{KE} = \frac{\hbar}{m_e} \sum_i \frac{3}{2} \frac{1}{s_i^2}$$

Temperature and Pressure

Temperature:

$$T = \frac{2}{3 K_B N_{nuc}} \left\langle \sum_i \frac{1}{2} m_i v_i^2 \right\rangle$$

compute temp/eff

Pressure:

$$P = \frac{1}{V}\left[N_{Nuc} K_B T + \frac{1}{3} \left\langle \sum_i x_i \cdot \frac{\partial E}{\partial x_i} \right\rangle \right]$$

Both T and P Include electron dependent contributions (i.e. radius, spin, *vr, rf,* etc)

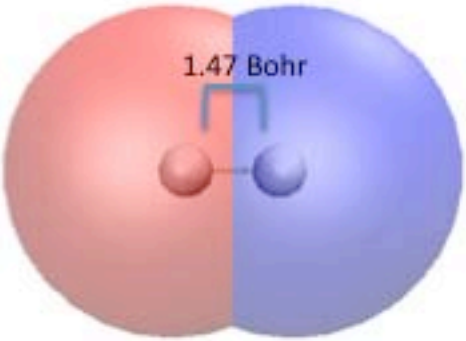
Note:

- pEFF-LAMMPS includes tally functions to handle "flexible" pressure

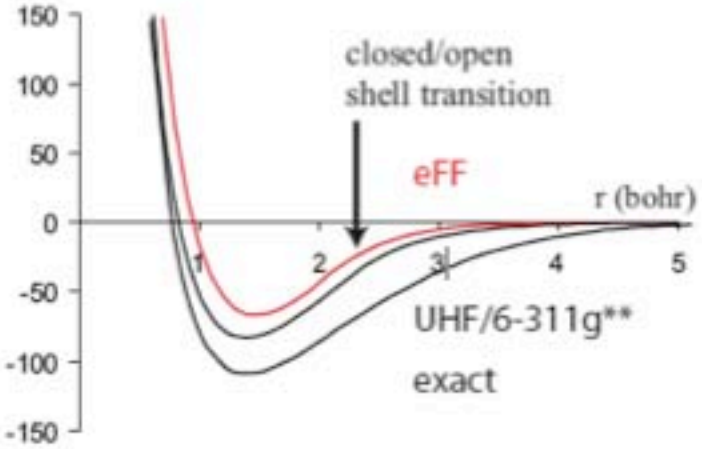
Energy Minimization
(H, H2 structure optimization)

Case	MIN (Hartrees)	Rigid P (GPa)	Flex P (GPa)	Iter/Force (Back)Quad
H atom	-0.424413	0	0	2/5:(18/18)5/12
H molecule	-0.95594	-2.48984	-0.639163	10/21: (15/26)14/27
H bulk	-29.4027	5.80948e10	5.8095e10	12/30: (37/41)19/37

Criteria: 0.01e-5

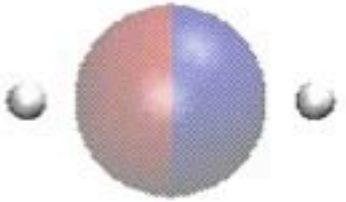


H bond energy: 0.95594−2(0.424413)=0.107109H=67 kcal/mol



LAMMPS: Required hooks to extra (r) quantities

Bond-centered electrons

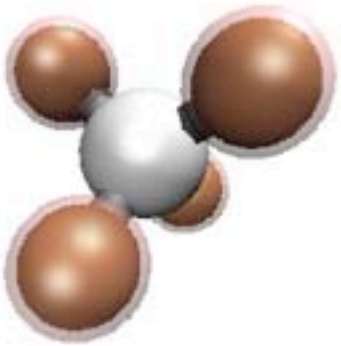


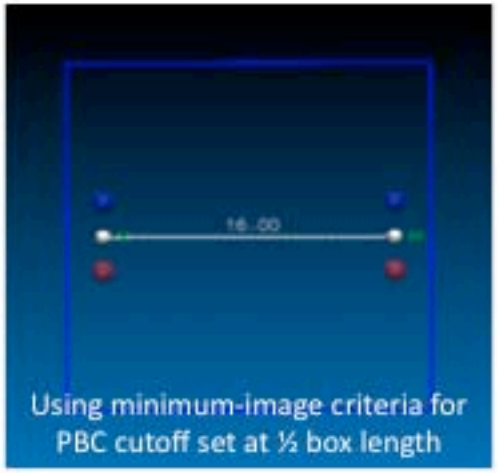
Platform: PowerBook, Intel Mac OS 10.5.8

SPE and Structure Optimization in Hydrocarbons

Case	MIN (Hartrees)	Rigid Press (GPa)	Flex Press (GPa)
CH4 (SPE)	-27.3141	-56.5889	-31.5171
CH4 (MIN)	-34.07446	2.6114e-6	-5.7980e-6
Adamantane (SPE)	-326.0969	341.1104	7.8565e4
Adamantane (MIN)	-329.0982	6.12e-3	6.91e-3

Min Criteria: 0.0 1e-5

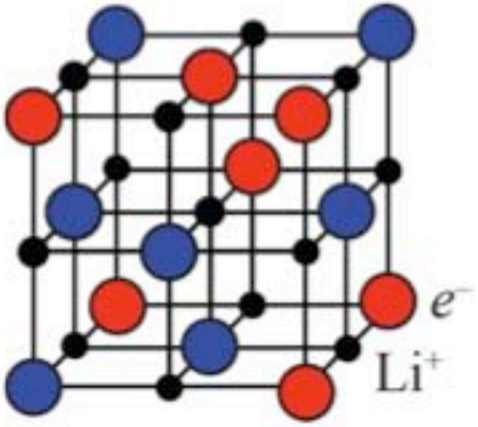


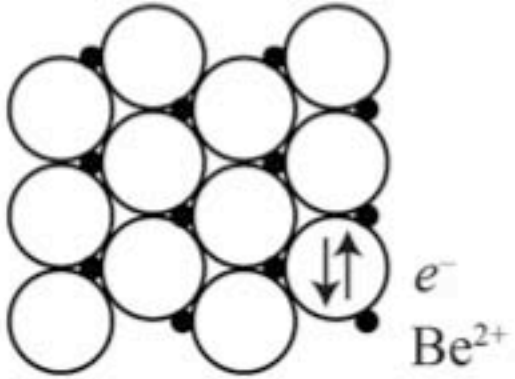


Using minimum-image criteria for PBC cutoff set at ½ box length

Platform: PowerBook, Intel Mac OS 10.5.8

Metal bonds are diffuse interstitial electrons in eFF





Lithium (fcc)
NaCl-like bonds

a = 4.42 (4.40) Å
E = 60.3 (37.7) kcal/mol/atom
Y = 12.2 (13.0) GPa

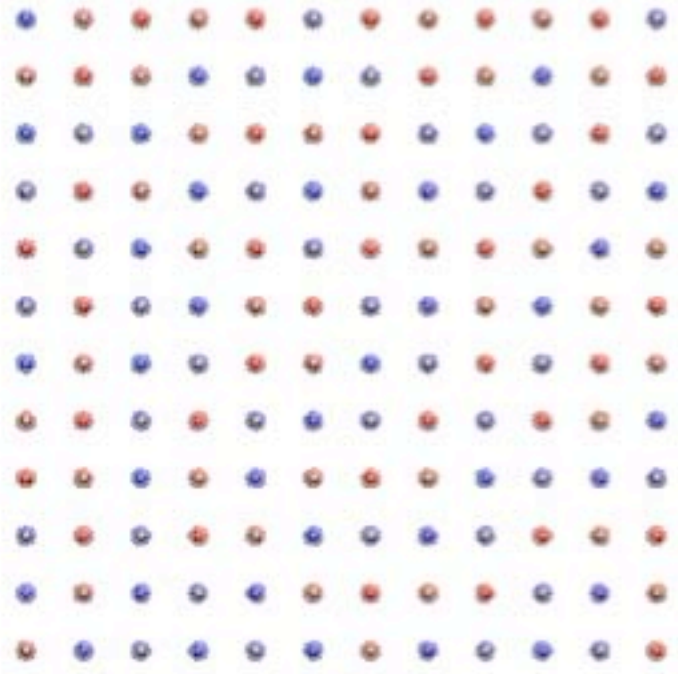
Beryllium (hcp),
strong layer bonds

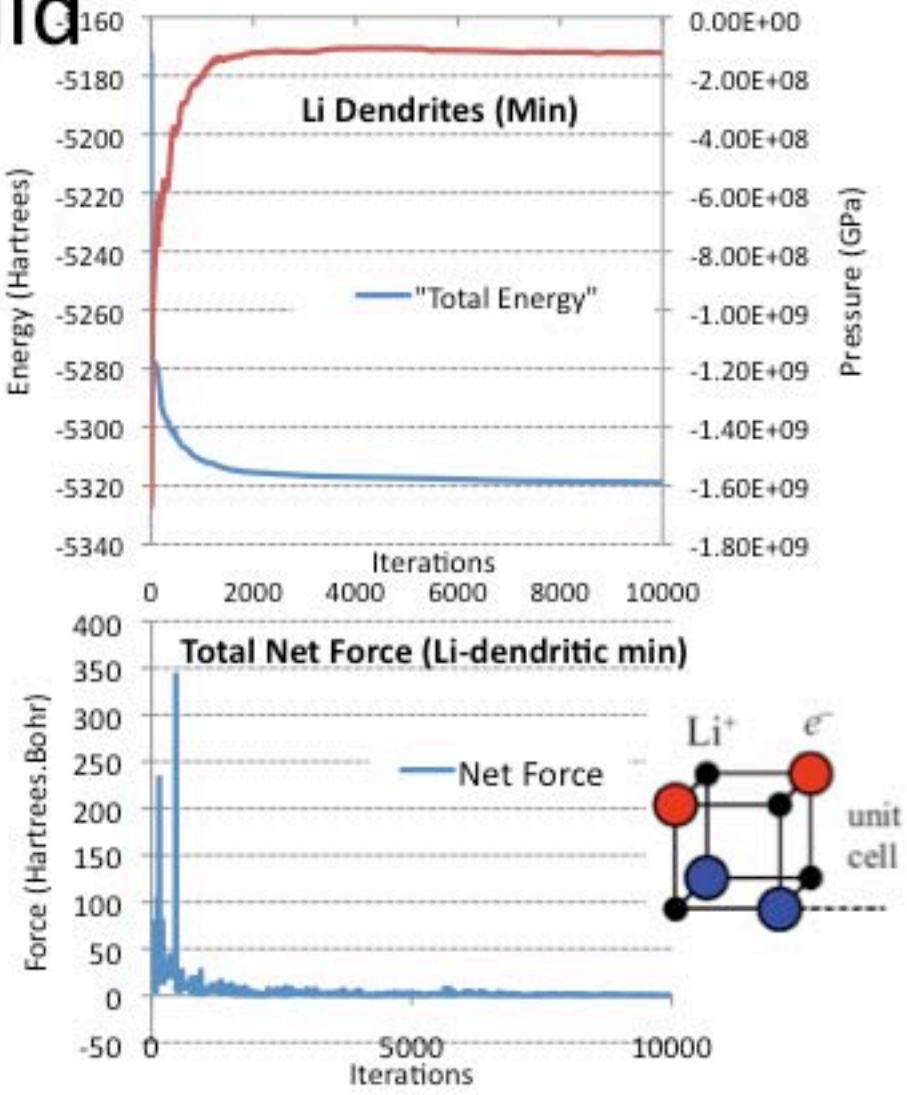
a = 2.43 (2.29) Å
c = 3.72 (3.59) Å
E = 138.4 (76.6) kcal/mol/atom
Y = 122.9 (110-127) GPa

Bonding too strong, but elastic constants are correct

Structure Optimization in Expanded Li solid

- Li dendrite formation





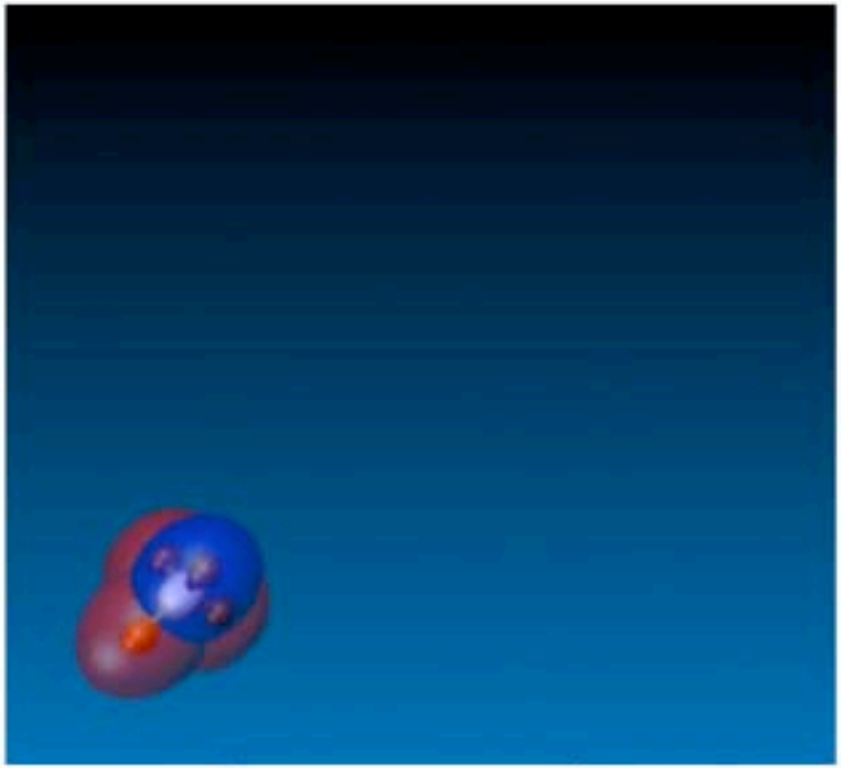
Platform: PowerBook, Intel Mac OS 10.5.8

Dynamics NVE

Methane valence electron ionization

Ionizing a valence electron can cause the bond it is participating in to break.

For methane, the energy input is 20 eV.



$\Delta t = 0.005$, T=9,000K

CH4 dissociates into CH3 and H and that after 50 fs these fragments are separated by 8.17A.

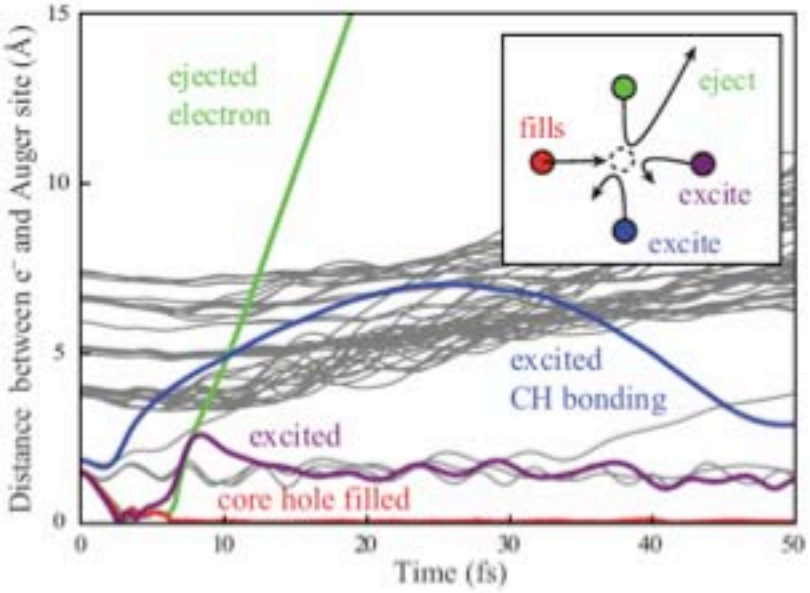
Platform: PowerBook, Intel Mac OS 10.5.8

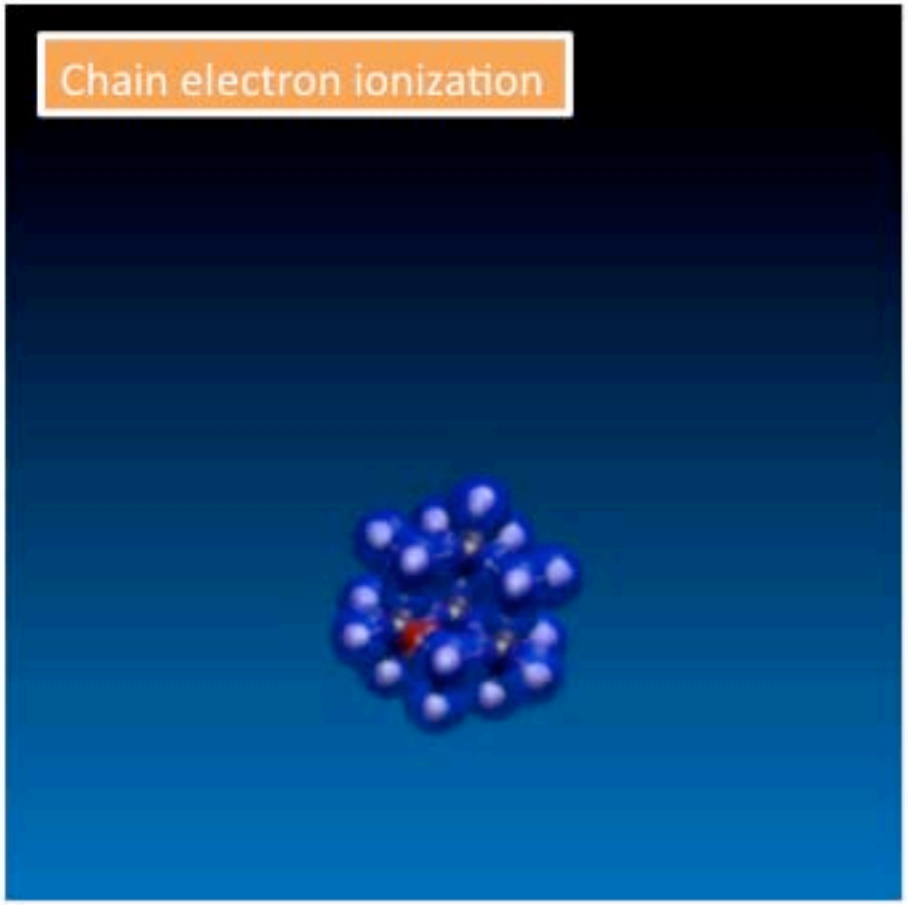
Dynamics – NVE

Core electron-ionization

Auger dynamics in Adamantane

- Larger energy input needed (290eV)
- Additional electrons may be ionized, and several bonds may be broken



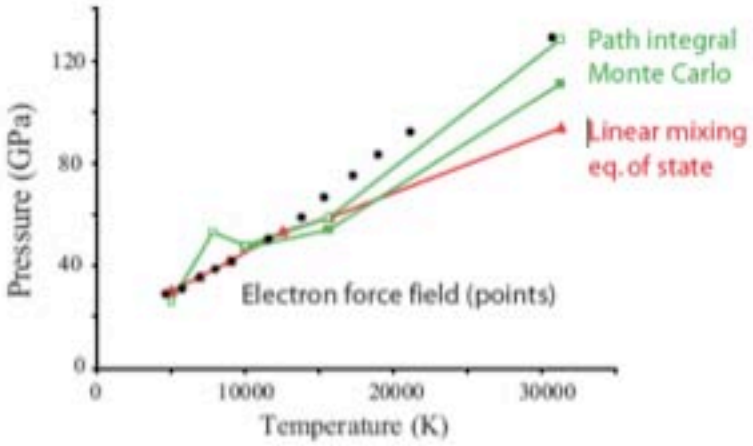


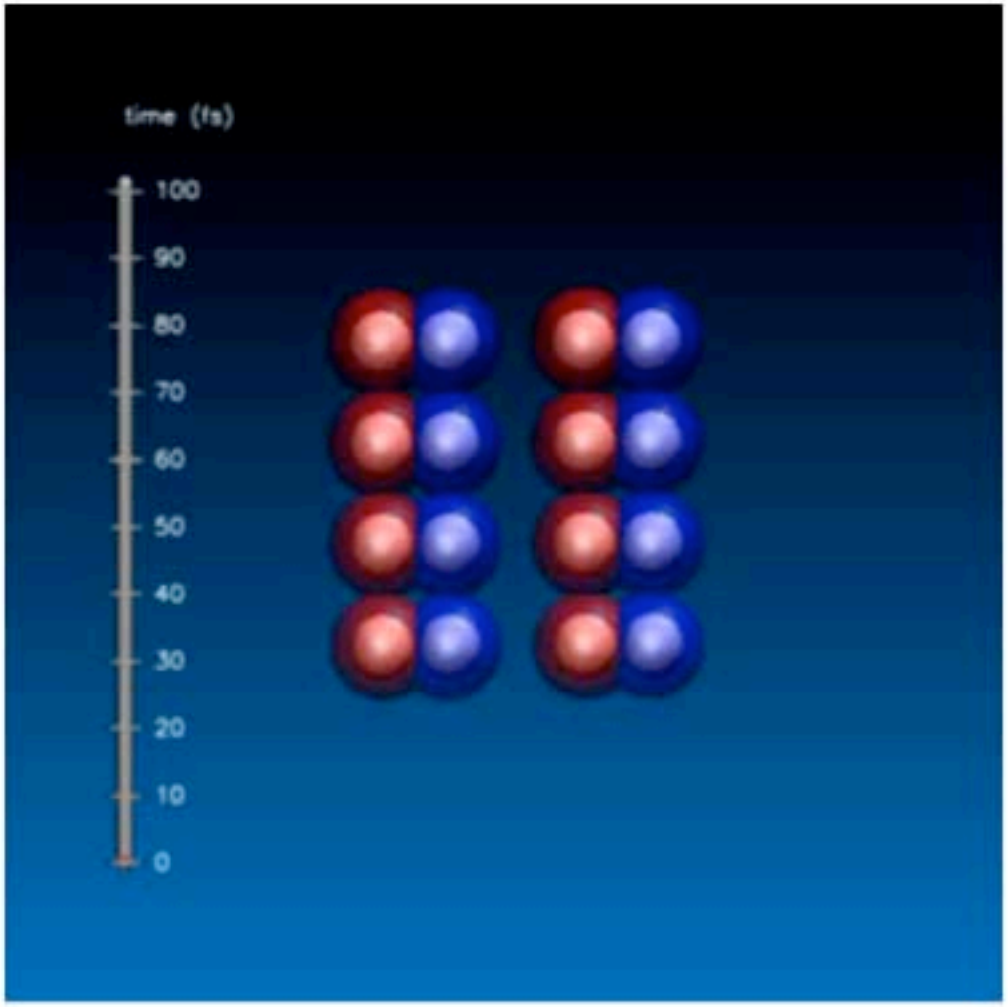
Platform: PowerBook, Intel Mac OS 10.5.8

Dynamics - NVE

Pressure of warm dense hydrogen

- The behavior of H at extreme P and moderate T has relevance to phase partitioning of planetary interiors, as well as in the design of ICF systems.
- EOS under these conditions, as it is sensitive to the electron dynamics of the system





Platform: PowerBook, Intel Mac OS 10.5.8

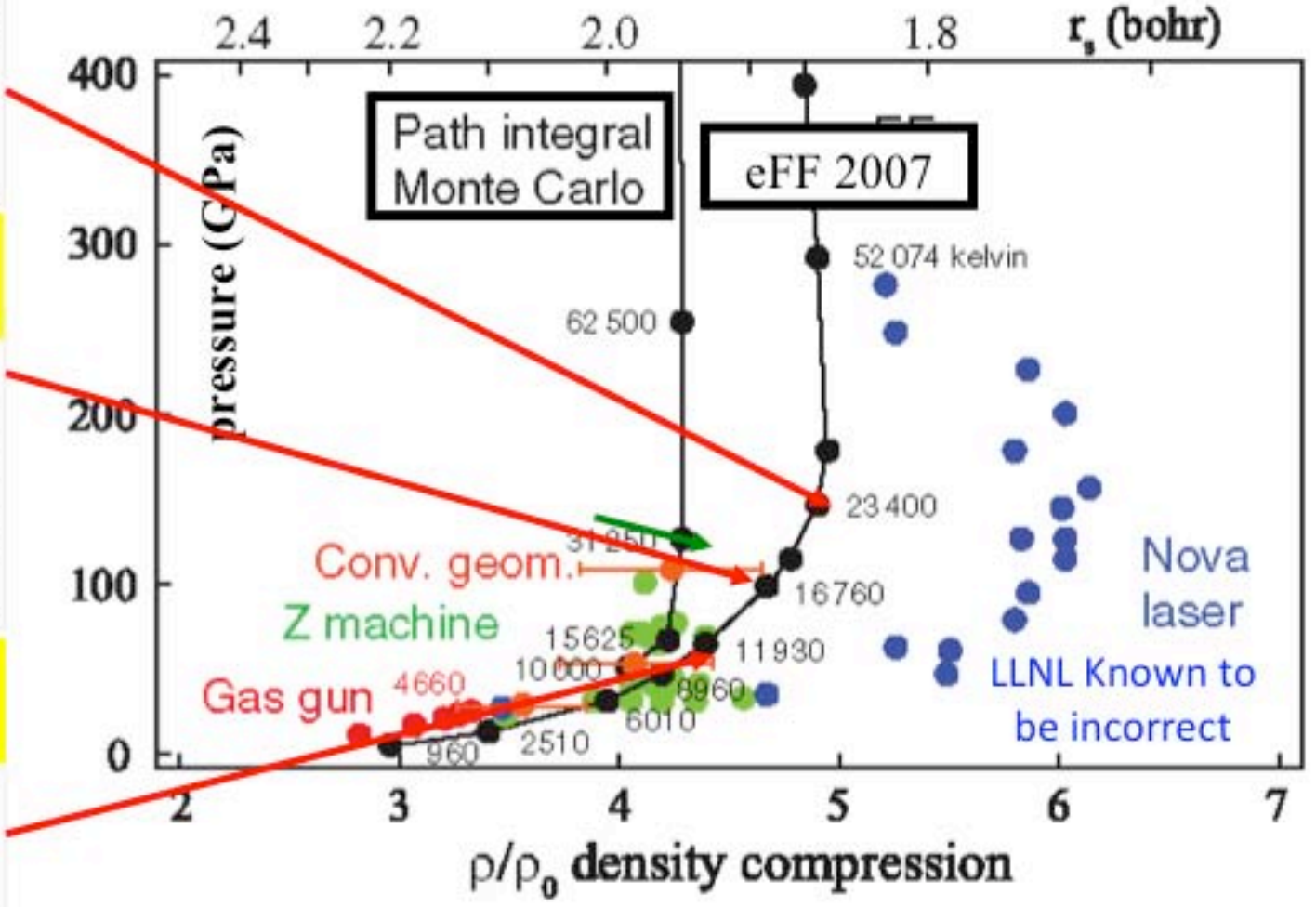
Dynamics – NVE

Shock Hugoniot for D2

21100 K Mostly atoms

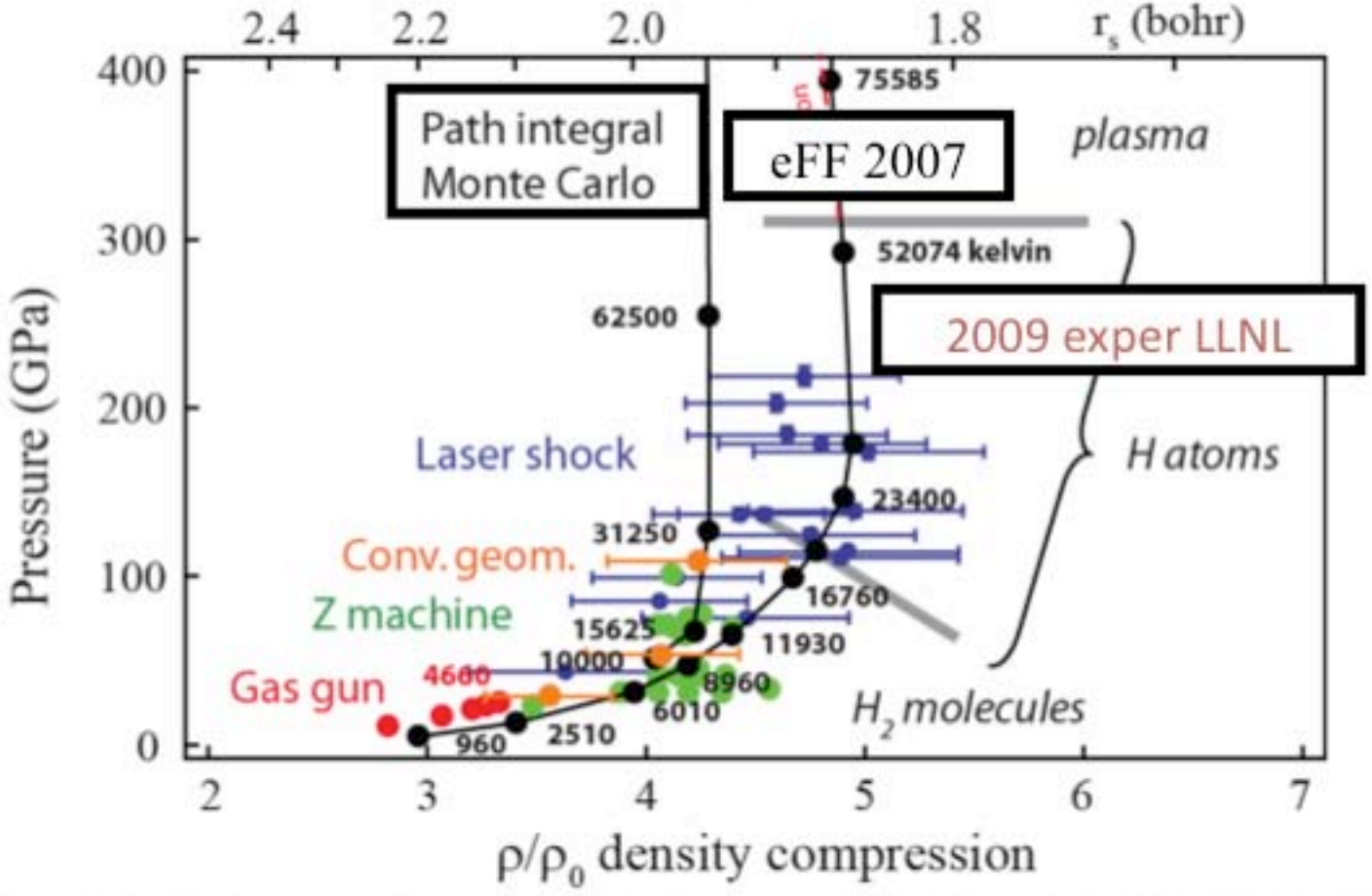
Transition 15400 K

9100 K Mostly molecules



Excited Electron Dynamics Modeling of Warm Dense Matter PRL 99, 185003 (2007) J. Su and WAG

2009 LLNL experiments confirm 2007 eFF predictions

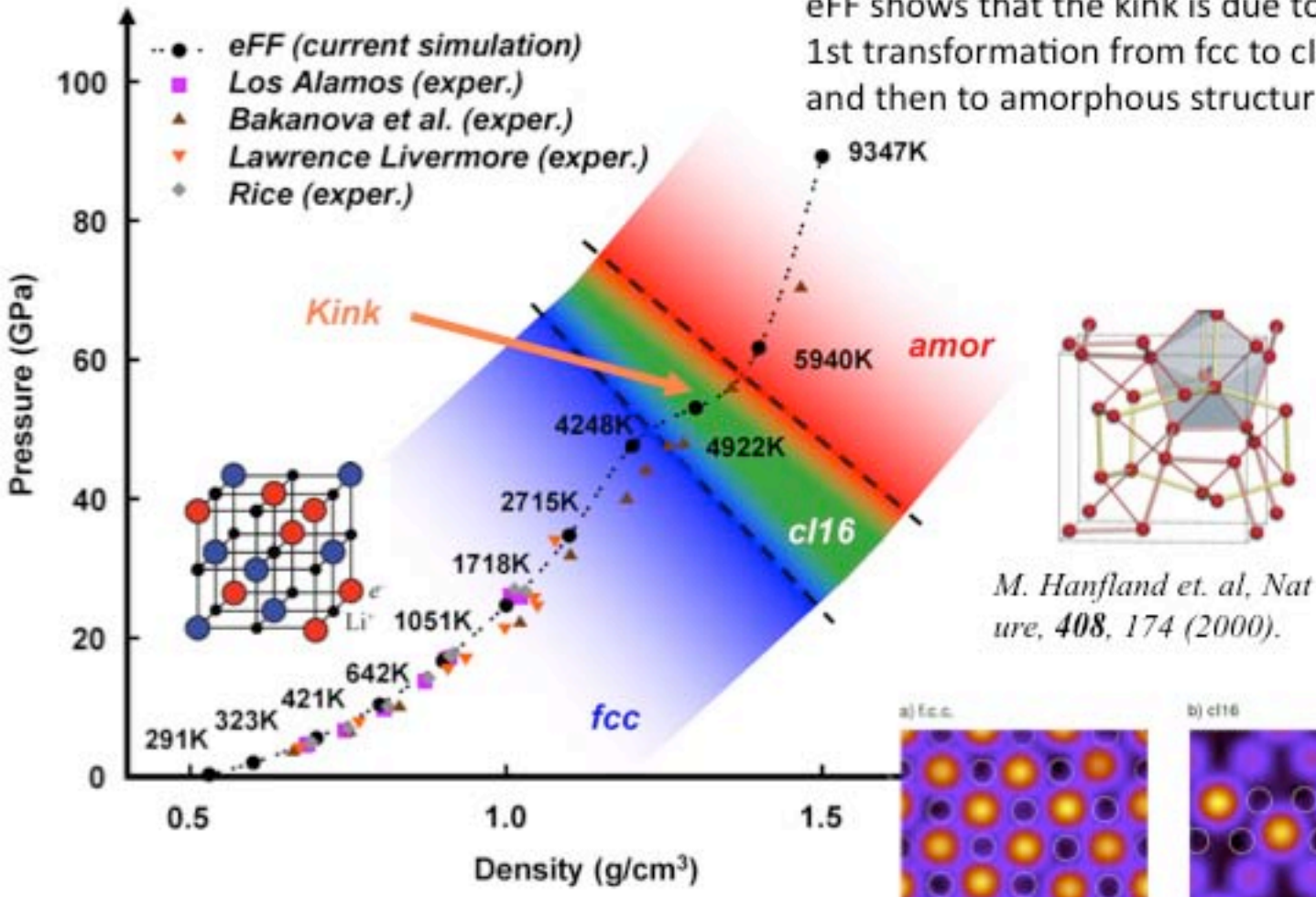


Laser-driven single shock compression of fluid deuterium from 45 to 220 Gpa D. G. Hicks, T. R. Boehly,P. M. Celliers,J. H. Eggert,S. J. Moon,D. D. Meyerhofer, and G. W. Collins; PHYSICAL REVIEW B **79**, 014112 2009

Dynamics – NVE

eFF Shock Hugoniot for Li

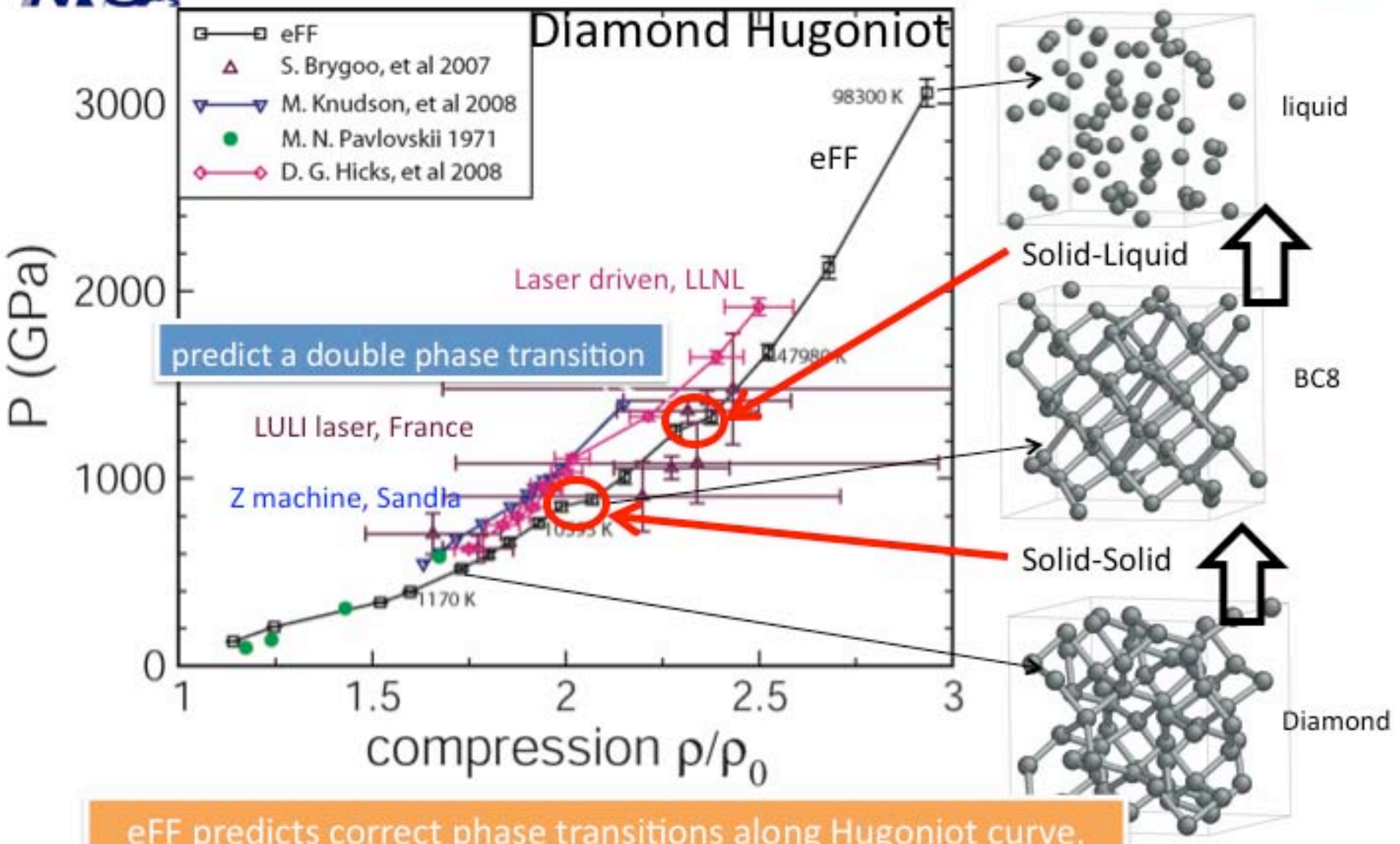
eFF shows that the kink is due to:
1st transformation from fcc to cI16
and then to amorphous structure



*M. Hanfland et. al, Nature, **408**, 174 (2000).*

Kim, su, wag, subm publ

Dynamics – NVE



eFF predicts correct phase transitions along Hugoniot curve.

Qi et al, 2010

Dynamics – NVE

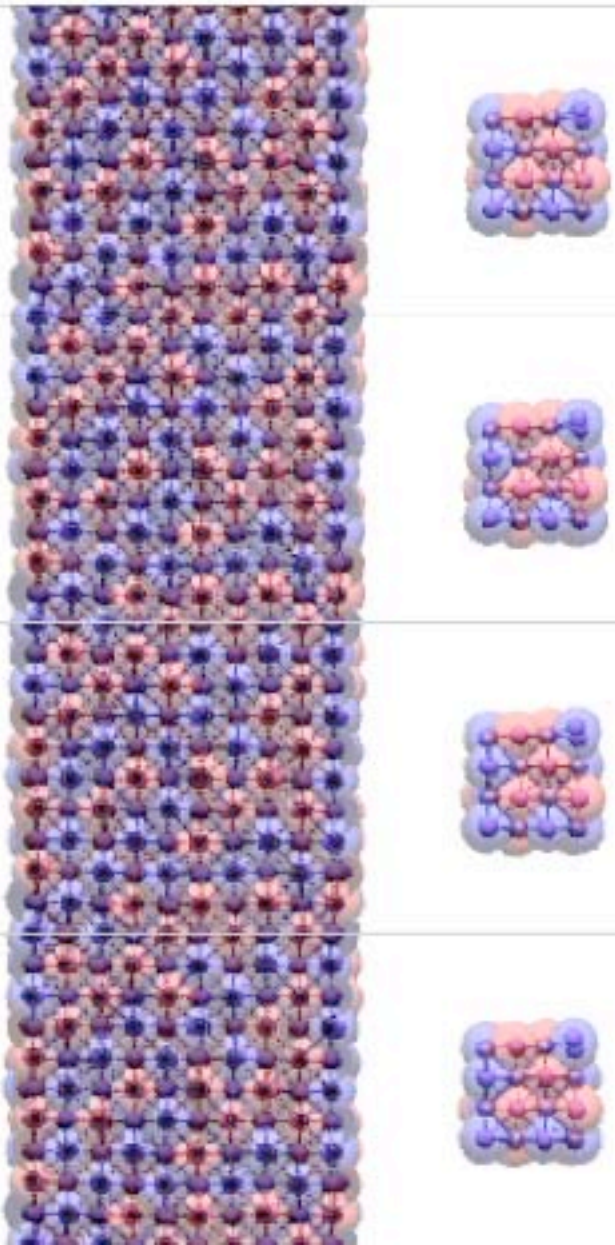
Li-Li hypervelocity impact: eFF1

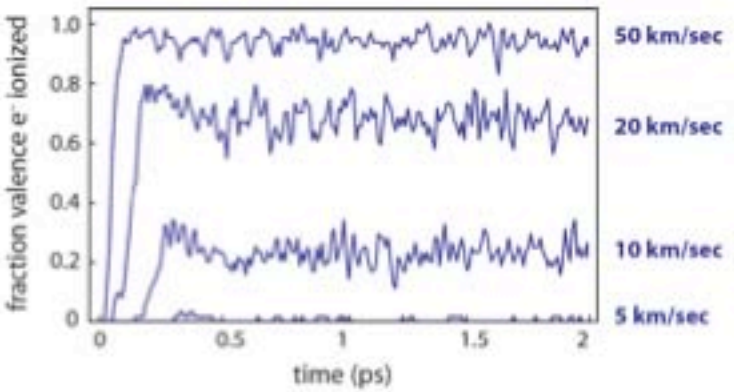
2 km/sec,
welding

5 km/sec,
melting

10 km/sec,
fluid layer

20 km/sec,
plasma





Progression from solid to liquid to plasma as impact velocity increases

Hyungjun Kim et al

Dynamics – NVE

Li-Li hypervelocity impact

LANL-Lobo

- Shock simulation (Li-Li impact at 15Km/sec)
  - Plasma characterization

97,200 particles
- 24,300 nuclei
- 72,900 electrons

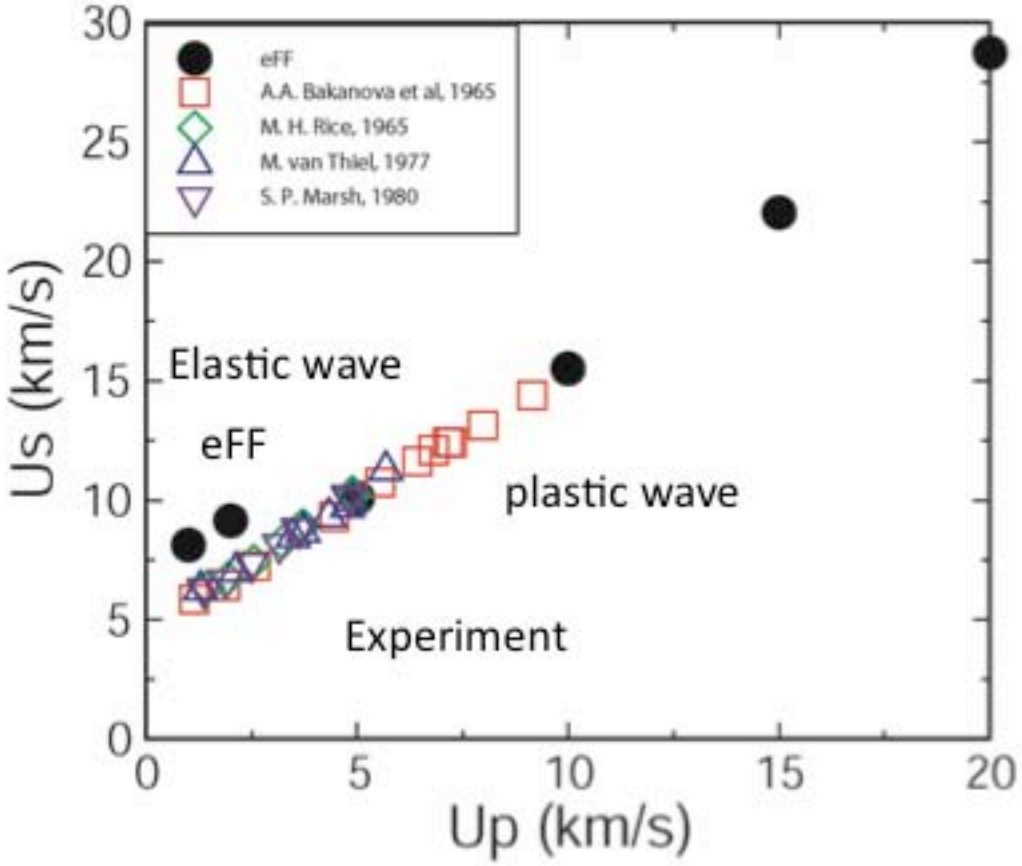
With Qi An

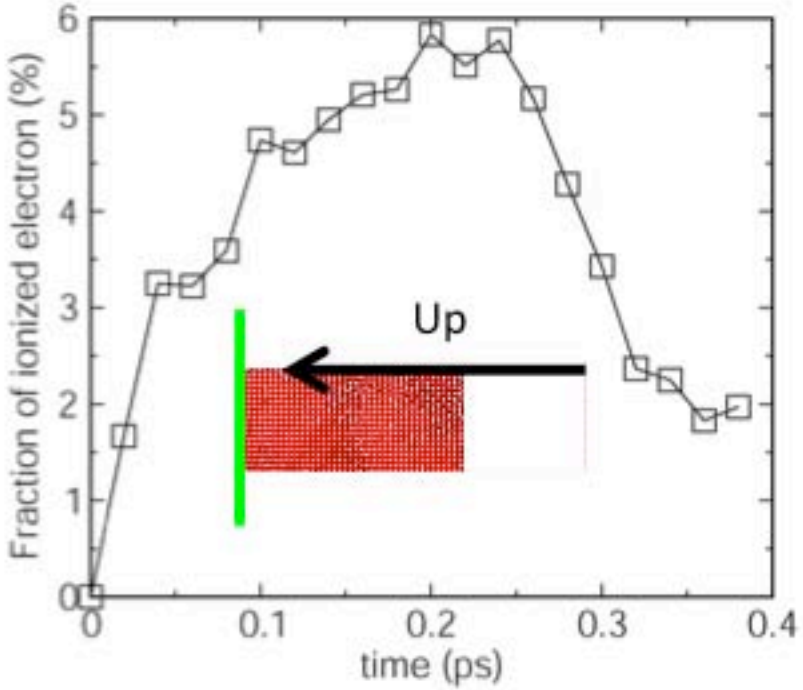
Dynamics – NVE

Li-wall hypervelocity impact

LANL-Lobo

- Shock simulation (Li-wall impact: 2-20Km/sec)





Ionization

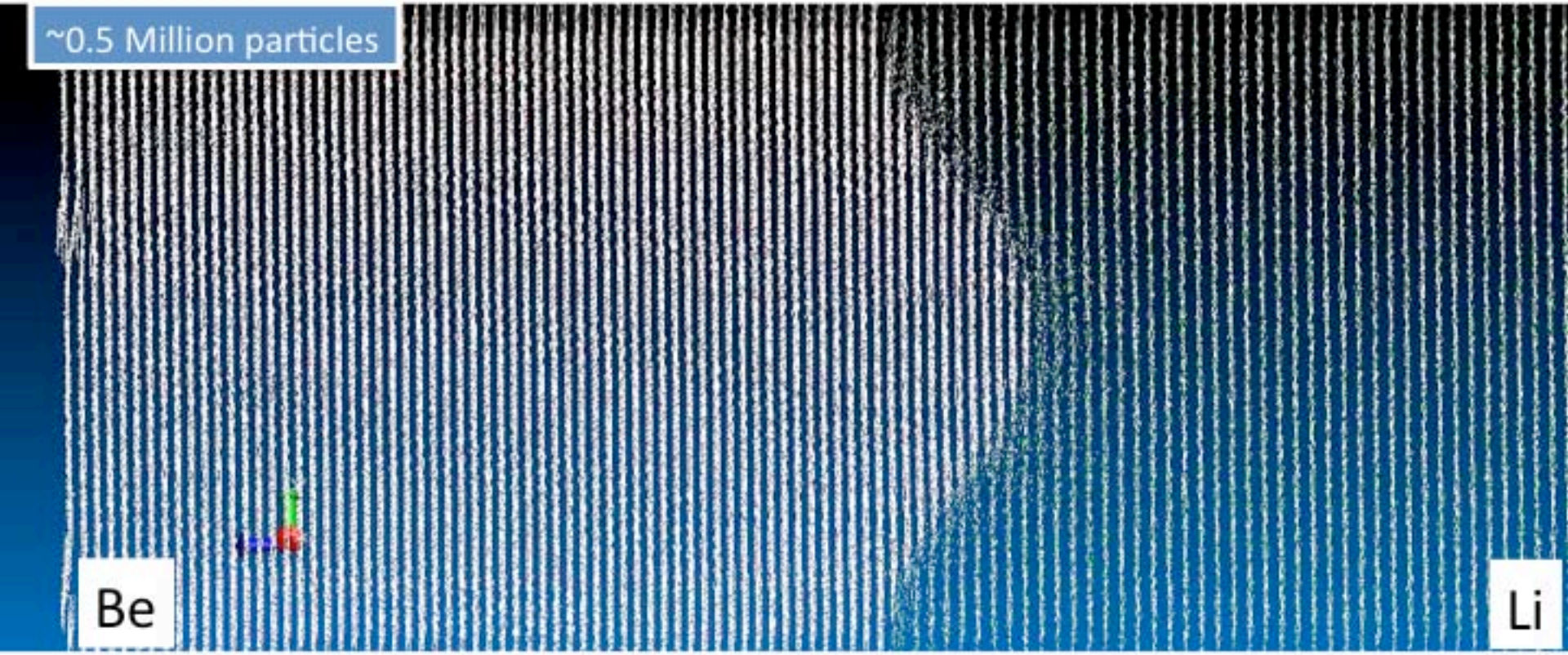
With Qi An

Dynamics - NVE

Li-Be Interfacial Instabilities (RMI/RTI)

LANL-Lobo

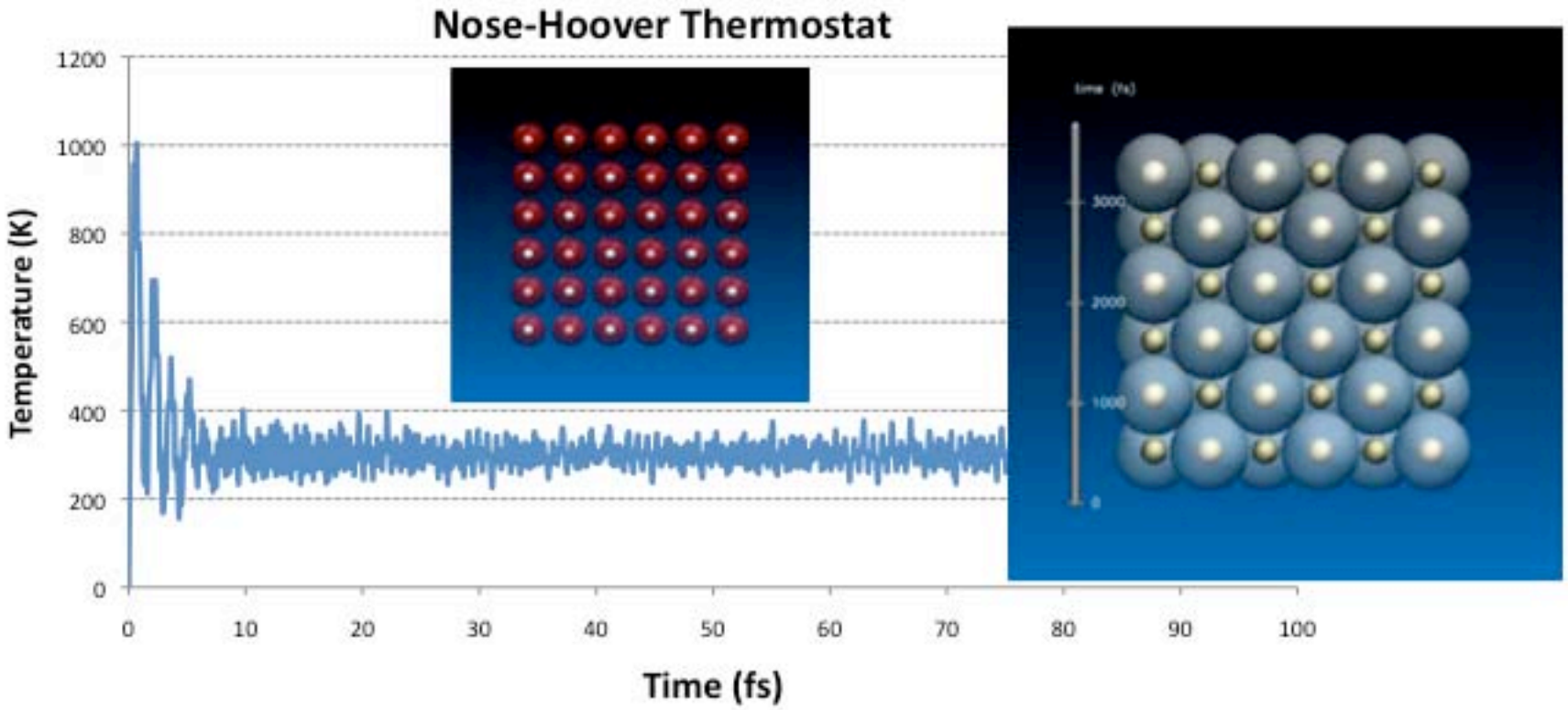
- Electronic Effects on Interfacial Instabilities



With Hai Xiao

Dynamics – NVT

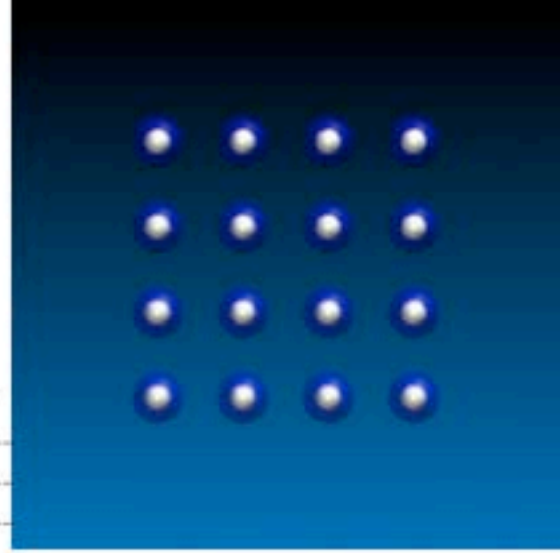
Bulk Li @ 300K and ramped 0-10,000K

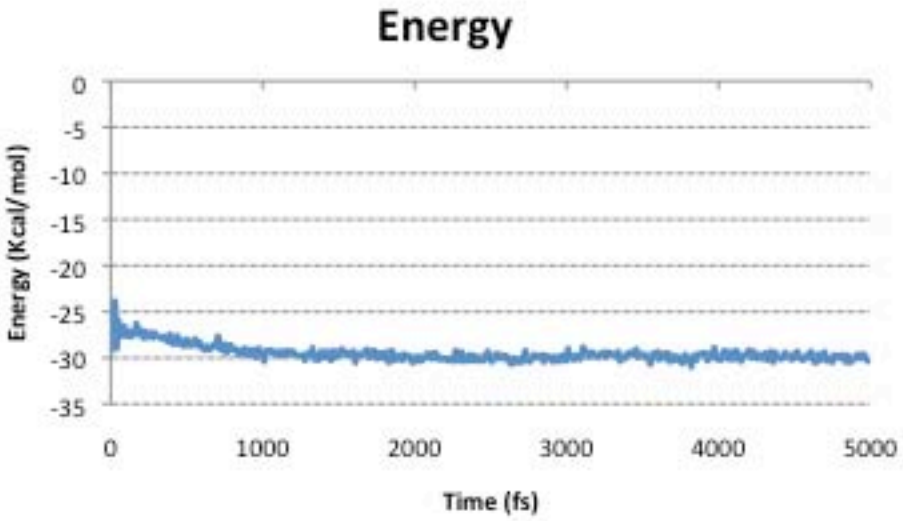


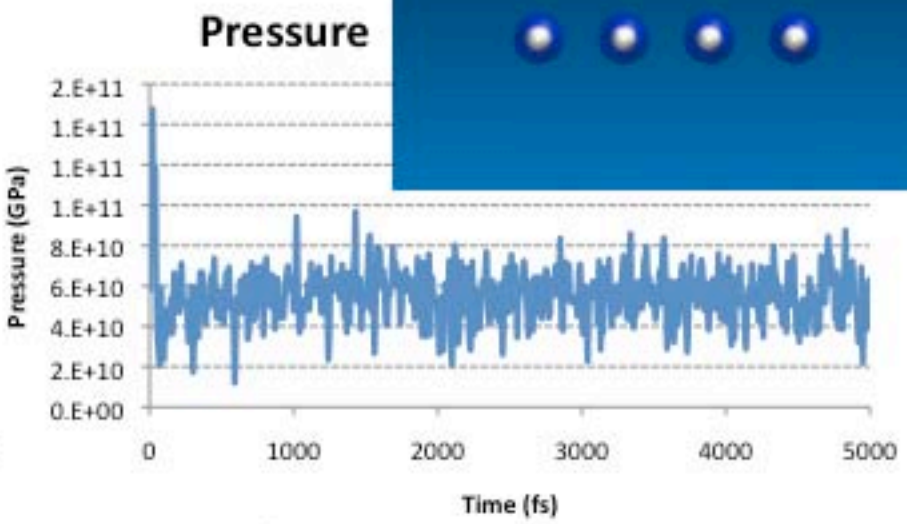
Platform: PowerBook, Intel Mac OS 10.5.8

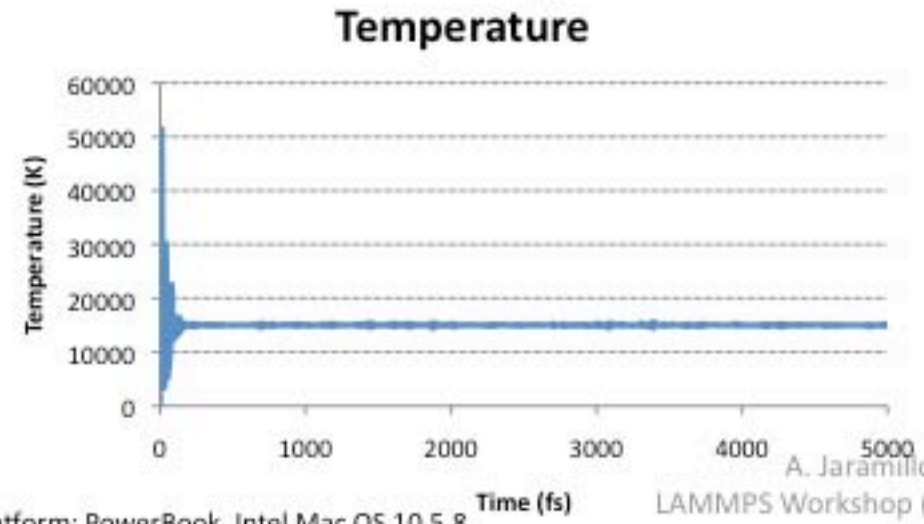
Dynamics – NPT

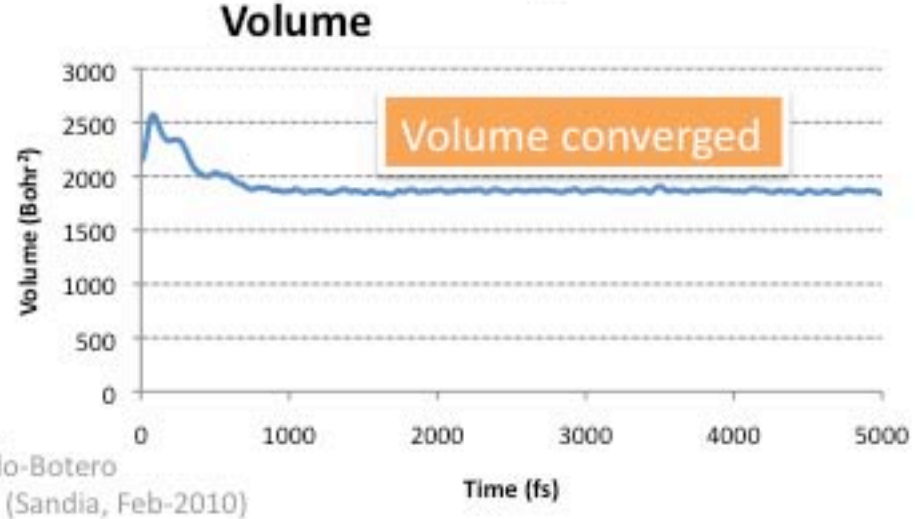
Dense H -> 5 ps @15,000K, @5.5GPa











Platform: PowerBook, Intel Mac OS 10.5.8

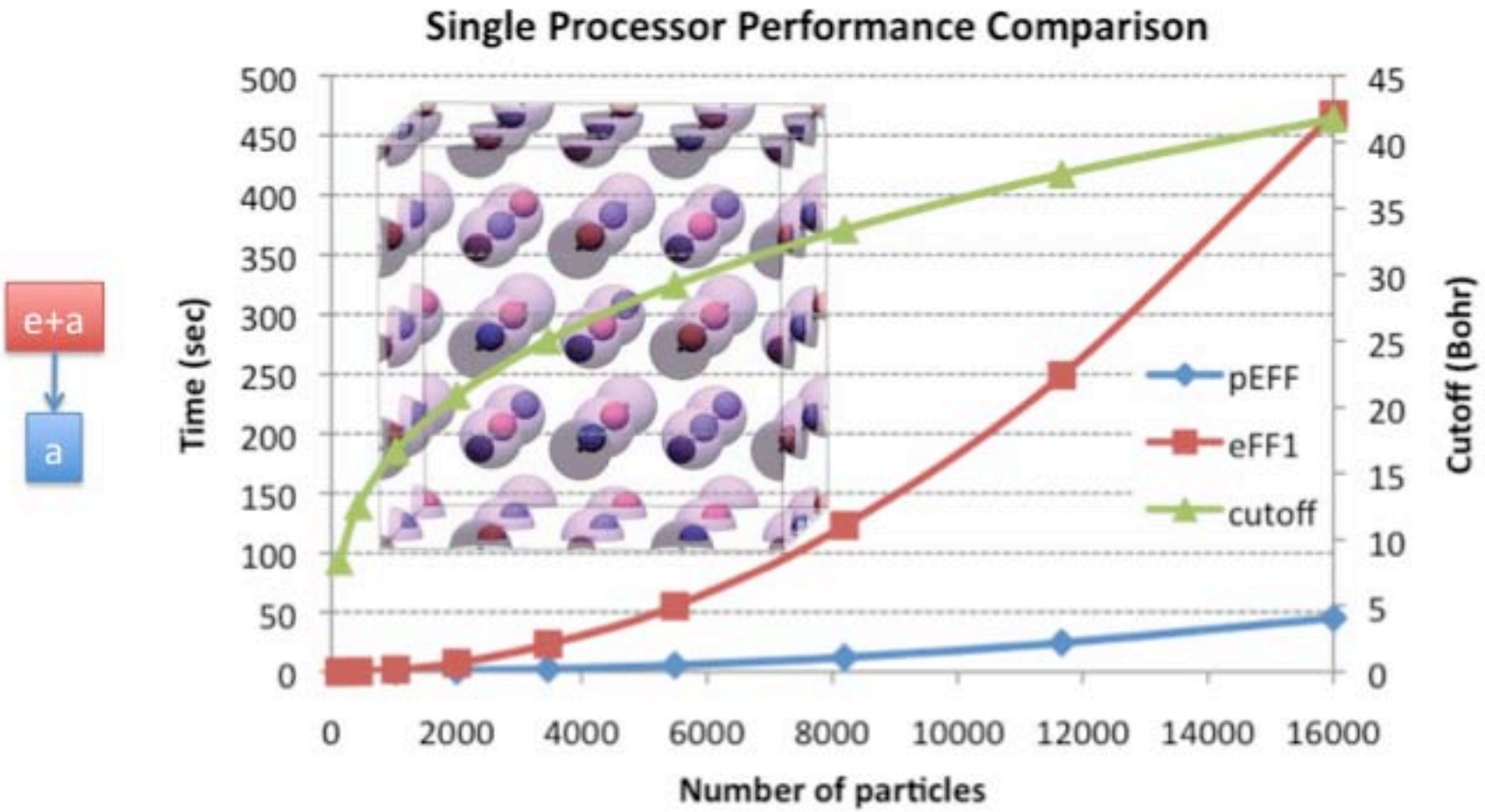
Single Processor

Multiple Processors

PERFORMANCE

Performance

eFF1 versus pEFF-LAMMPS (single processor, Li solid)



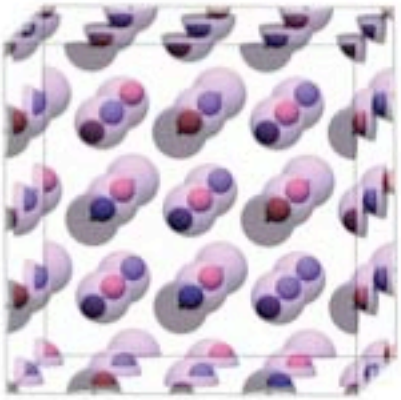
Platform: PowerBook, Intel Mac OS 10.5.8

Performance

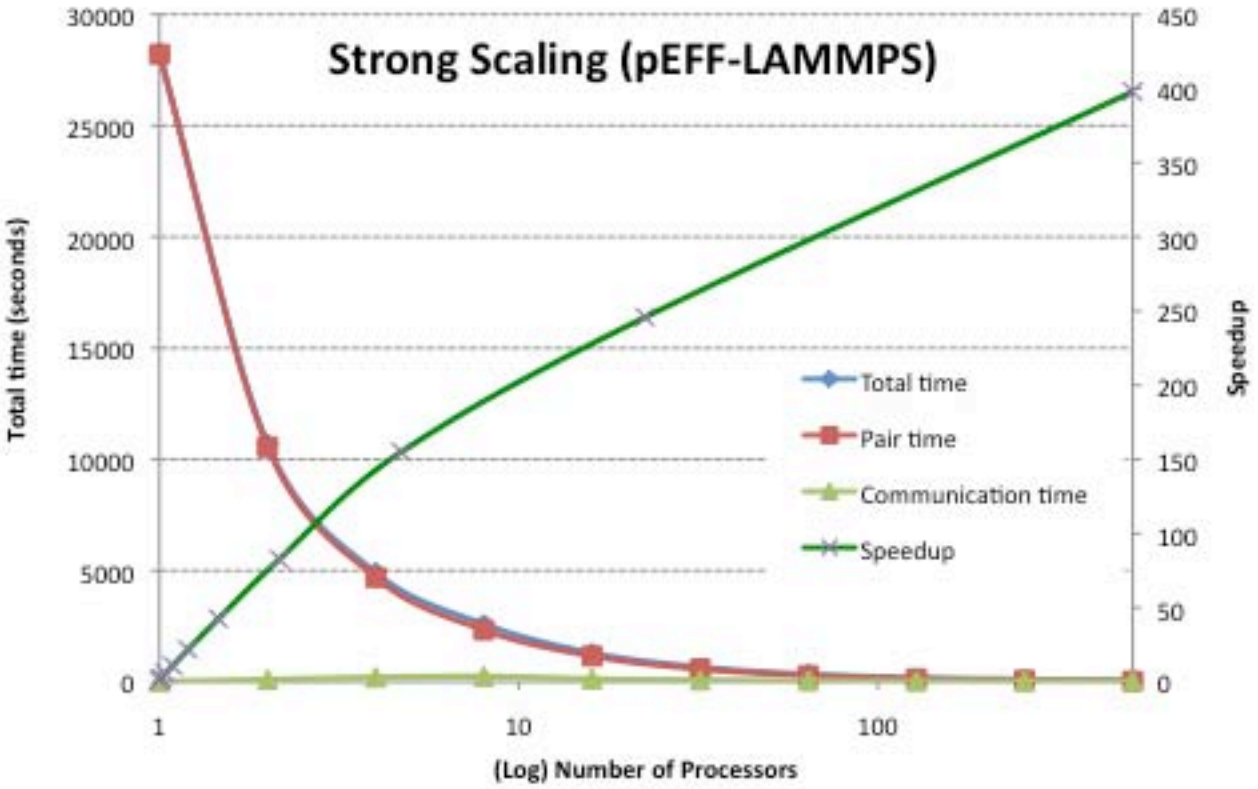
(Strong Scaling)

Over 1K steps of NVE

32,000 particles
- 8,000 nuclei
- 24,000 electrons



System: Li bulk

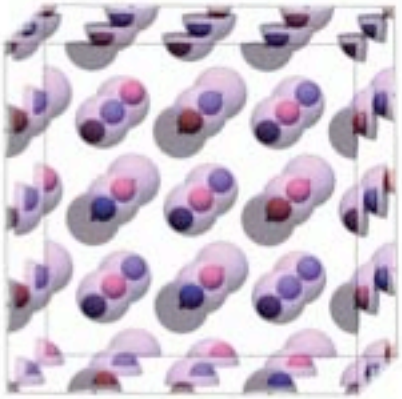


Platform: LANL's-Lobo: Quad-core AMD Opteron with infiniband (38TFLOPS)

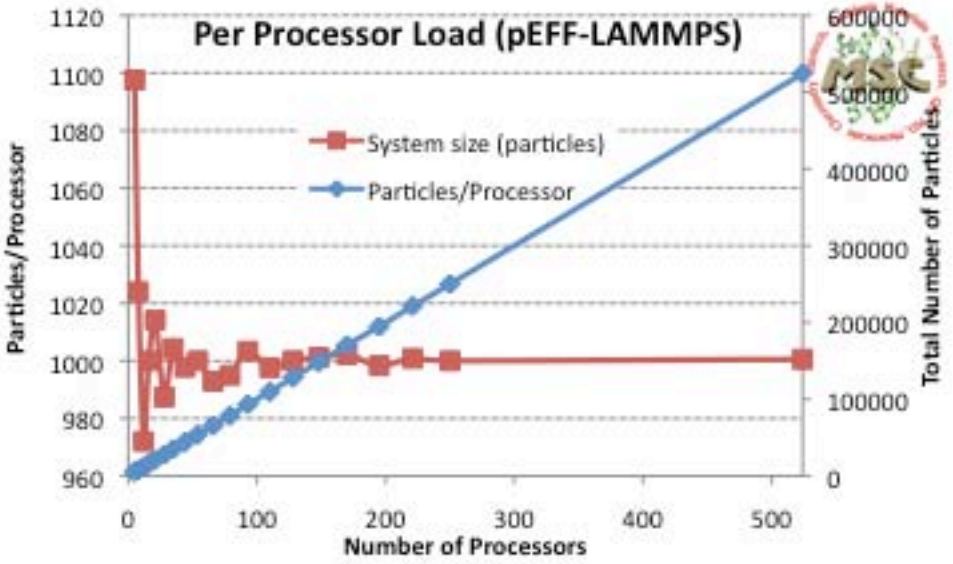
Performance

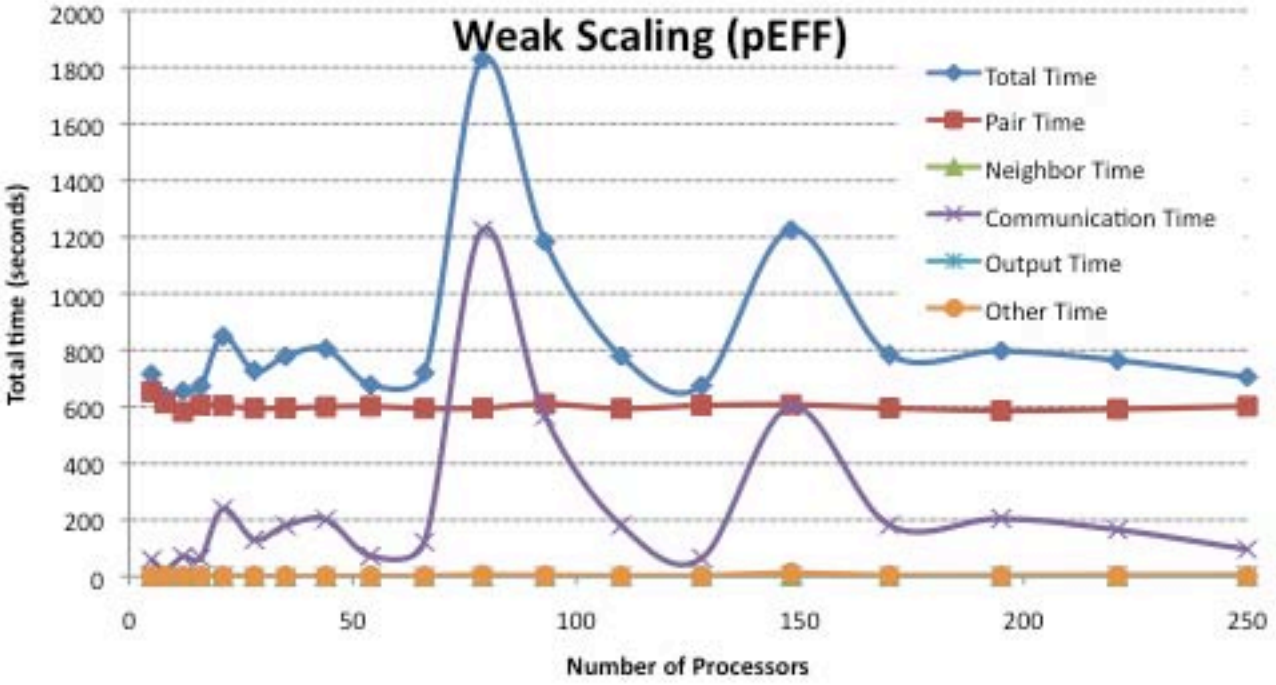
(Weak Scaling)

Over 1K steps of NVE



System: Li bulk



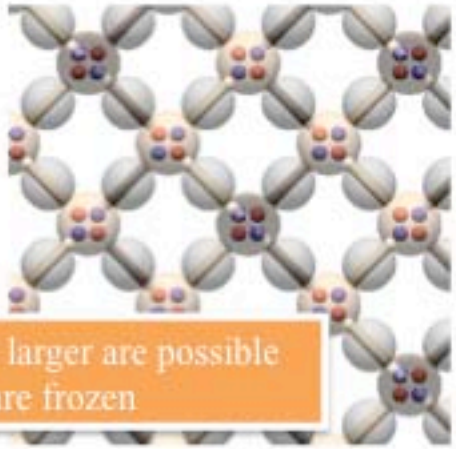


Platform: LANL's-Lobo: Quad-core AMD Opteron with infiniband (38TFLOPS)

Current Work

- Core approximation and PP for higher Z atoms (Si)
- Floating Elliptical Gaussian wavefunctions (p-block)
- Electron correlation, Electron conductivity, E levels
- Long-range electrostatics (Ewald)
- New 'fix'es and computes (as needed)

Si^{4+} core ~ Ne
frozen rigid body



Time steps of ~20x larger are possible when *1s* electrons are frozen

	SiH4	Si2H6	
	Si-H bond	Si-Si bond	Si-H bond
frozen core	1.47	2.32	1.45
pseudopotential	1.48	2.33	1.49
full eFF	1.48	2.40	1.47
experimental	1.48	2.32	1.47

Table 1. Bond length of SiH4 and Si2H6

With Song D.

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- Paul Crozier and other LAMMPS developers

- My wife and sons