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Density Functional Theory of Extreme Environments

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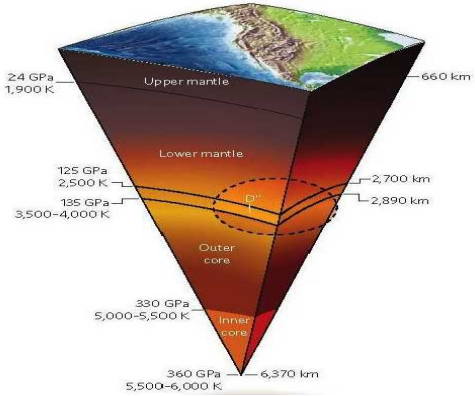
Materials Properties are Needed to Model Complex Phenomena through Equations of State

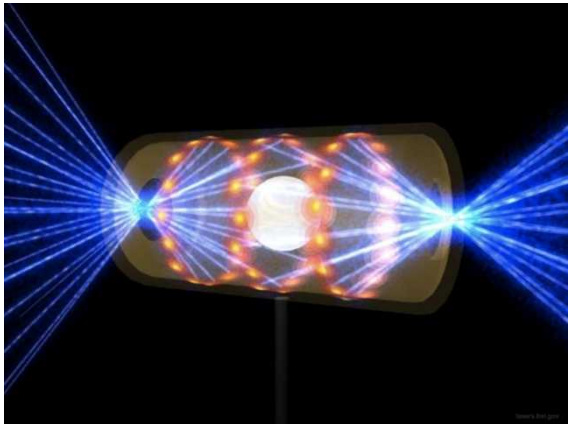
Pressure, density, temperature, phase….

- Materials science
- Planetary collision science
- Geoscience
- Inertial confinement fusion

Information to build equations of state

- Low temperature experiments diamond anvil cell
  < a few kK
- High temperature plasma physics where degeneracies are negligible





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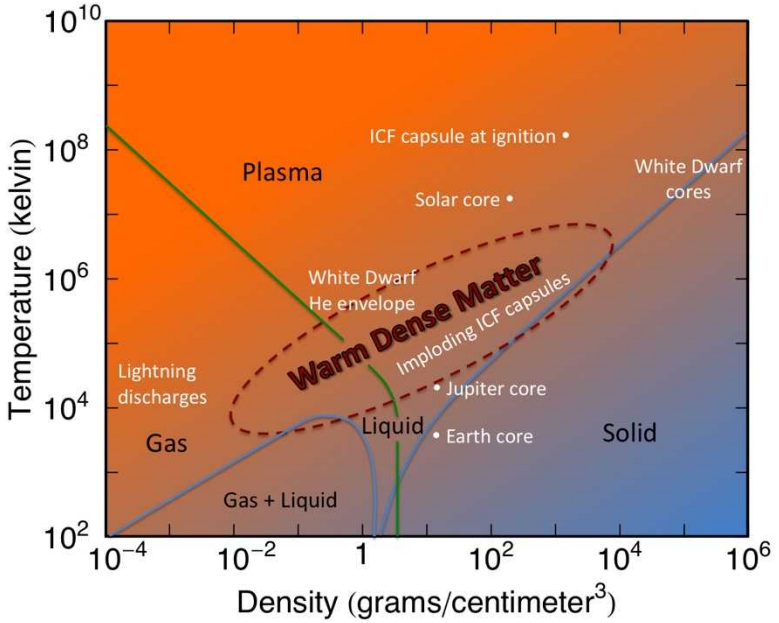
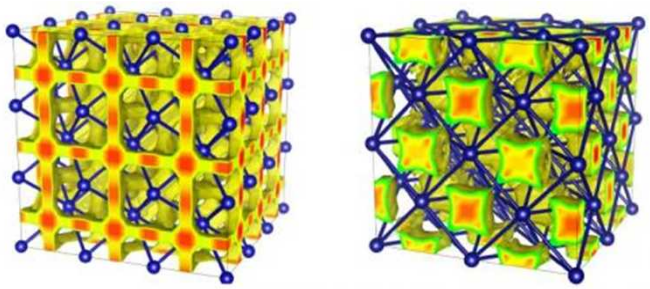
A Difficult Region of Phase Space to Access is the Warm Dense Matter Region

- Highly compressed matter with electron densities of 10^{21}-10^{26} electrons / cm^3
- Temperature on the order of several eVs, 10s of kK
- Electron degeneracy significant
- Bound-free electron correlations significant
- Accessible to experiment and theory - Warm dense matter near-solid (2-4x) density
- Mbars of pressure
- The plasmon energy, ω_P ~1-4 eV



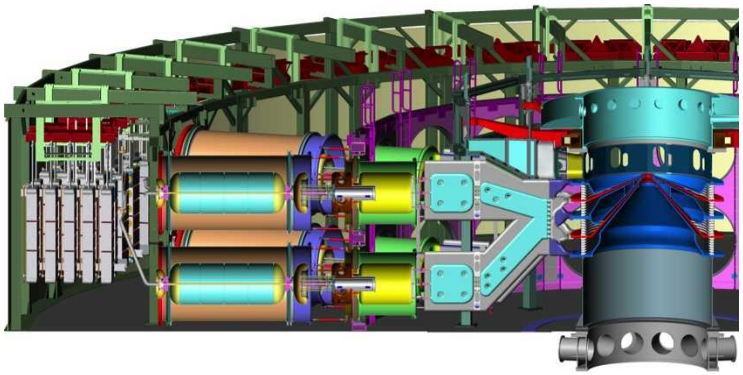


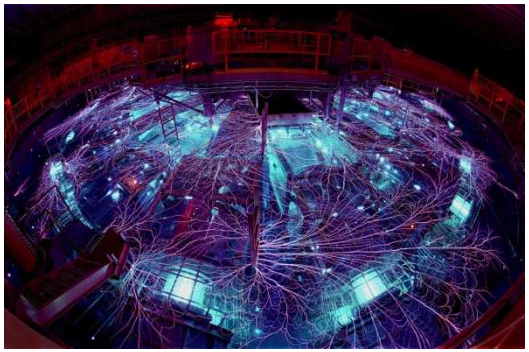
Super ionic water

The Z-Machine can Probe this Region

- The world's most powerful pulsed power machine
- Accelerates aluminum flyer plates to 40 km/sec.
- Delivers 27 MegaAmps in 95 nanoseconds.
- Achieves Pressures greater than 10 Mbar (1 TPa).
- Recent work on Xenon reached a state 840 GPa and 149kK
- Compare to diamond Anvil cell – up to 300 GPa and several kK

Indirectly but Accurately Measures **Pressures and Densities**





First Principles Probes

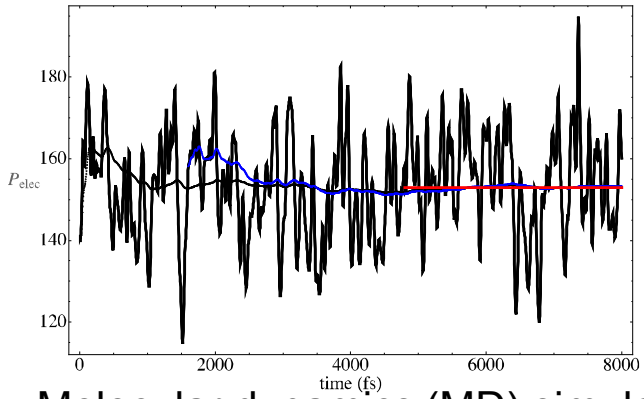
- First principles approach to simulations of total energies, pressures, and other physical quantities
- Unbiased as to elemental species
- **First-principles simulations using DFT**
  - **VASP – plane-wave code with PAW core-functions**
  - **Great care in convergence**
    - *A. E. Mattsson et. al. Modelling and Simulation in Material Science and Engineering **13**, R1 (2005)*
  - **Importance of exchange-correlation functional**
    - *A. E. Mattsson et al. JCP **128**, 084714 (2008)*

TOP500 SUPERCOMPUTER SITES

TOP10 November 2013

1. **Tianhe-2 (MilkyWay-2)** - TH-IVB-FEP Cluster, Intel Xeon E5-2692 12C 2.200GHz, TH Express-2, Intel Xeon Phi 31S1P
   NUDT
2. **Titan** - Cray XK7 , Opteron 6274 16C 2.200GHz, Cray Gemini interconnect, NVIDIA K20x
   Cray Inc.
3. **Sequoia** - BlueGene/Q, Power BQC 16C 1.60 GHz, Custom
   IBM

b-initio VASP ackage ienna imulation



Molecular dynamics (MD) simulations give thermo-physical properties

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DFT, DFT-MD, and TDDFT

DFT:

--Electron degeneracy/correlation treated exactly .

--Many-body Schrodinger equation from $R^{3N} \rightarrow R^{3}$.

--Ground state or equilibrium thermal state.

DFT-MD:

--DFT electronic state → forces on ions.

--Typically within BO approximation.

TDDFT:

--Exact treatment of electron dynamics.

--Excited states.

--Ehrenfest-TDDFT → forces including excited electronic states.

--Electrons and ions do not have to be in equilibrium.

Approximations in DFT are not material specific.

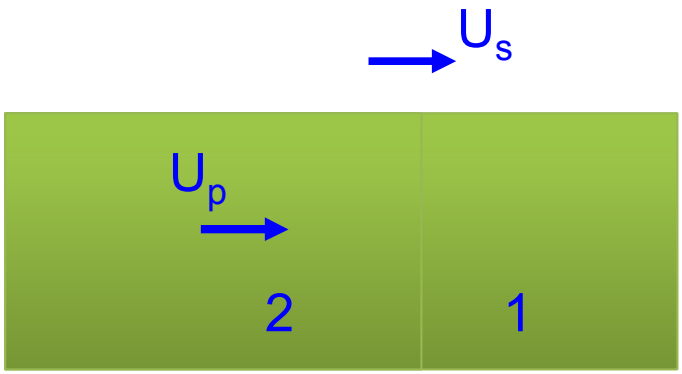
We are implementing Ehrenfest-TDDFT in an existing PAW code.

(Plane wave basis with a soft cutoff)

'Most accurate' treatment of electron-ion interaction

Validation of the DFT-MD Simulations

- Compare simulation results to Z-data
- Convenient –especially in the warm dense matter regime – connection through the Hugoniot
- Example successes Xe and Ethane
- Note the dissociation of the latter

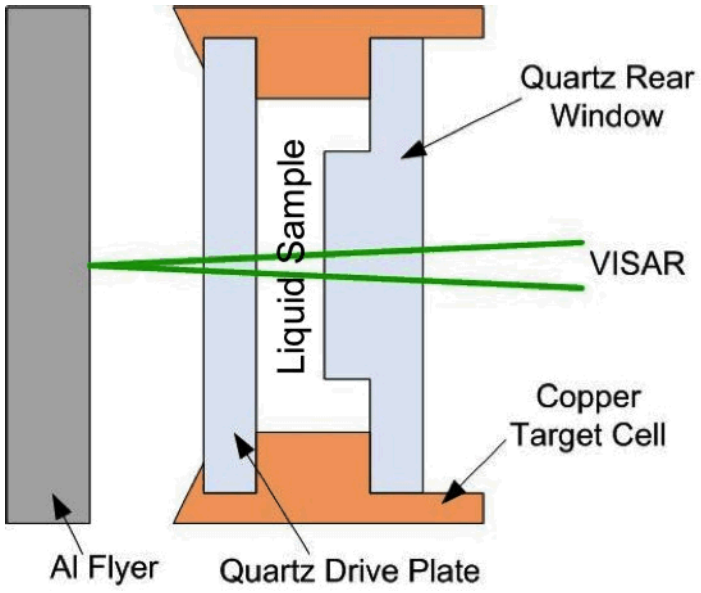


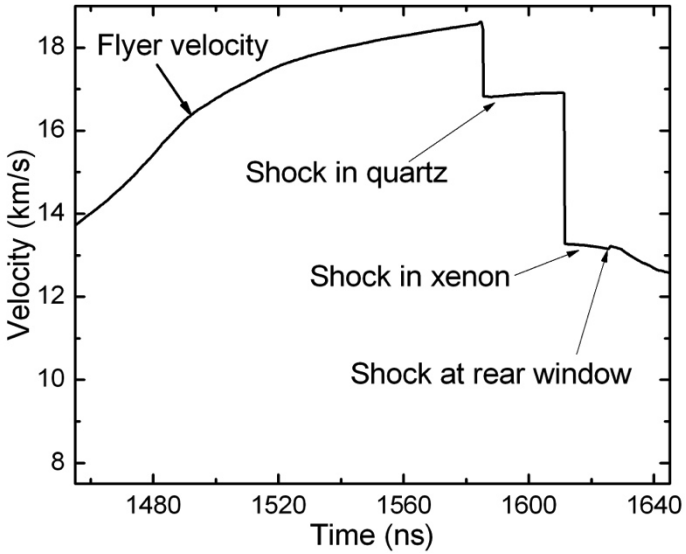
- *Conservation of mass, energy, and momentum* lead to the **Rankine-Hugoniot condition** for the initial (1) and final state (2).
  - E - internal energy
  - P - pressure
  - v – specific volume

$$2(E_2 - E_1) = (P_2 + P_1)(\upsilon_1 - \upsilon_2)$$

- *High accuracy measurement and/ or calculations of thermo-physical properties* can be compared to validate understanding.

We Measure Shock Velocities in Materials with Sub-Percent Accuracy





Precision Accuracy and Reproducibility

VISAR main diagnostics

- Flyer velocity, time of impact
- Arrival at interfaces and breakout
- Shock velocity in samples

Monte-Carlo error analysis

- Accuracy of shock standards
- Correlation among parameters
- Error propagation

VISAR trace from a xenon experiment with 18.5 km/s impact velocity

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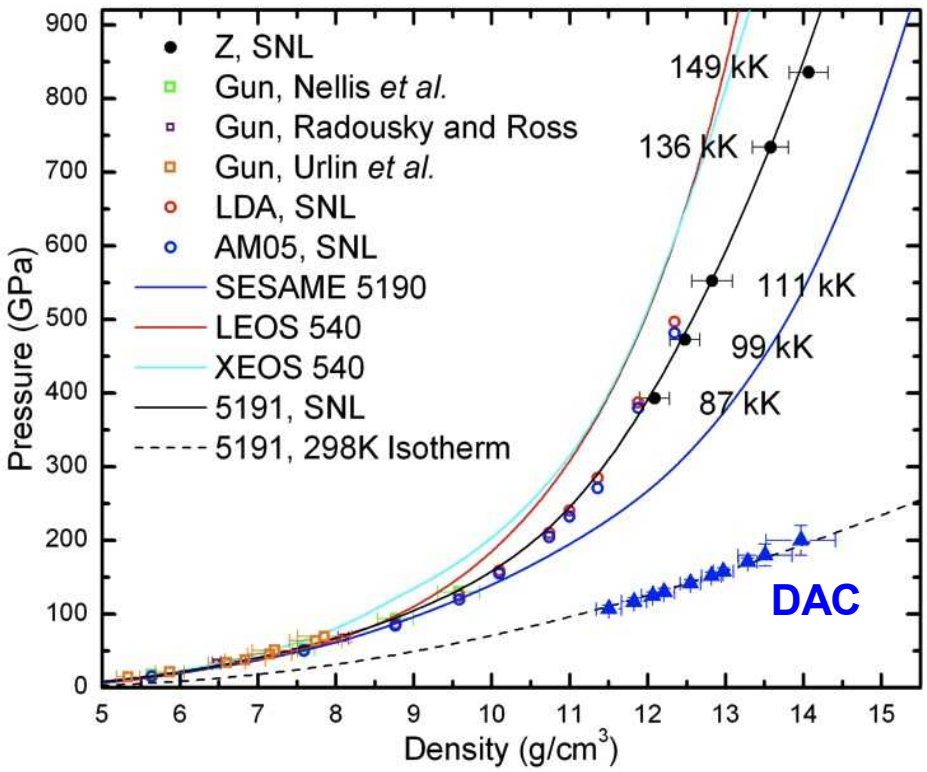
Experiments on Sandia's Z Machine Obtained High-Precision Data for Xenon to 840 GPa/ 14 g/cm^3



Seth Root et al Phys. Rev. Lett. **105**, 085501 (2010)

Neither LEOS 540 nor SESAME 5190 captures the behavior of xenon above 100 GPa

Demonstrated the need for validating EOS tables to enable high-fidelity simulations

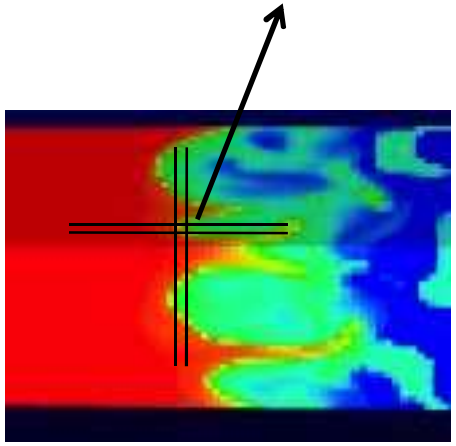
Developed a new multi-phase wide-range EOS table: 5191 in the LANL database

AM05 GGA developed by Ann Mattsson (SNL) is highly accurate for WDM.

Hydrocodes, Materials, and Mixtures

A cell in a hydro simulations with two materials “mixed cell”

Material 1 | Material 2



Tom Haill
Al Liner impacting on foam

- High-fidelity hydrodynamics simulations to solve solid dynamics problems
- Require high fidelity equation of state (EOS) models to describe the response of materials to external stimuli e.g. P[ρ,T]
- Materials can mix.
- Dynamic mixing can occur for example through Rayleigh Taylor instabilities.
- For practical reasons, a rule must be used to combine EOS models of pure materials to EOS of mixtures.

Classical Mixing Rules for Binary Mixtures Developed for Nineteenth Century Engineering Problems

$$x = \frac{\rho_L}{\rho_L + \rho_H} = \frac{\rho_L}{\rho}$$

- Ideal (Ideal gas law astrophysics)

$$P = x P_L\left[\rho, T\right] + \left(1 - x\right) P_H\left[\rho, T\right]$$

- Volume (Dalton's law 1801 related to cell approaches)

$$P = P_L\left[x\rho, T\right] + P_H\left[\left(1 - x\right)\rho, T\right]$$

- Pressure (Amagat's 1880 law of partial volumes some hydro-codes)

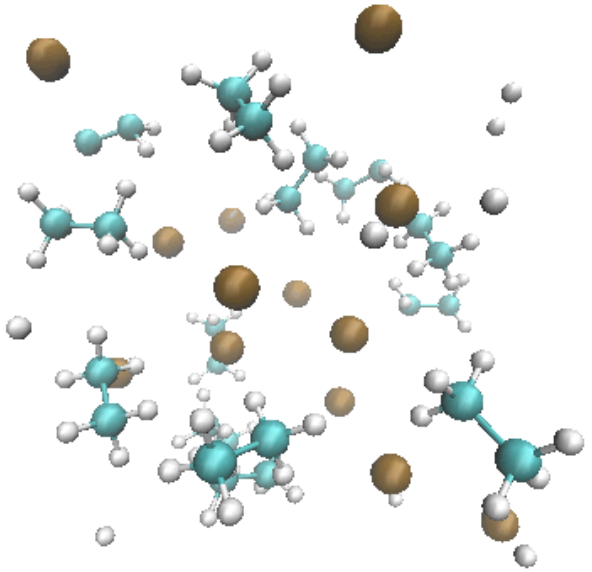
$$P_{MIX} = P_L\left[\tilde{\rho}_L, T\right] = P_H\left[\tilde{\rho}_H, T\right], \quad x/\tilde{\rho}_L + (1-x)/\tilde{\rho}_H = 1/\rho,$$

$$f_L \tilde{\rho}_L = \rho_L, \quad f_H \tilde{\rho}_H = \rho_H$$

- Relates total pressure of the mixture to equation of state models of the pure states

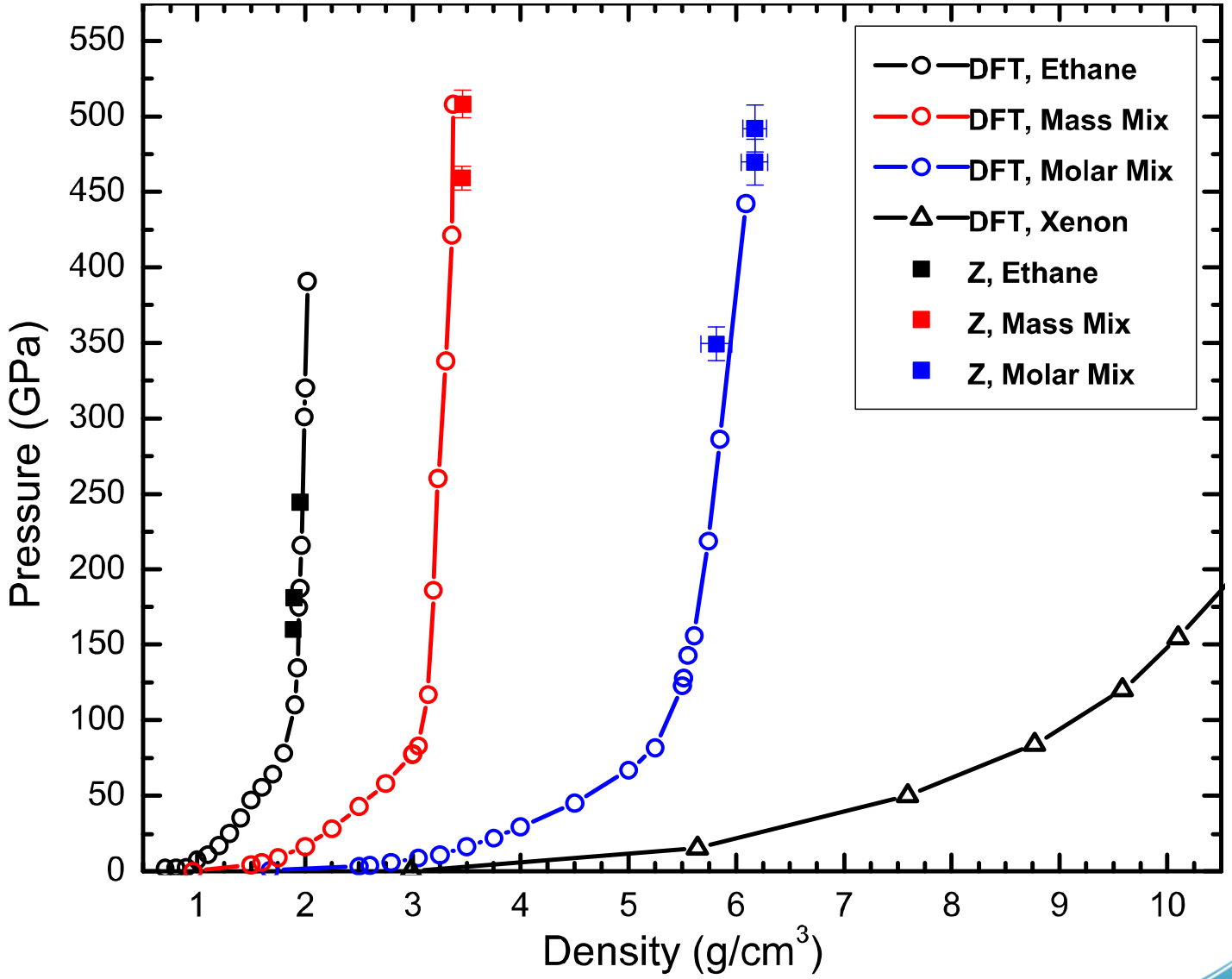
Xe-Ethane (C_2H_6) Mix Hugoniot Reference State

- T=163.5 K
- Rho=1.5 and 1.7 gcc
- P=16.8 psi
- Molar mix ratios 42% and 50%
- Mass mix 5 Xe:18 Ethane (159 atoms per simulation) x=0.5
- Molar mix 13 Xe:13 Ethane (117 atoms per simulation) x=0.19
- Plane-wave energy cut off 900 eV
- Time steps 0.8-0.04 fs
- 8000 time steps
- Mean value point
- AM05 exchange-correlation results shown

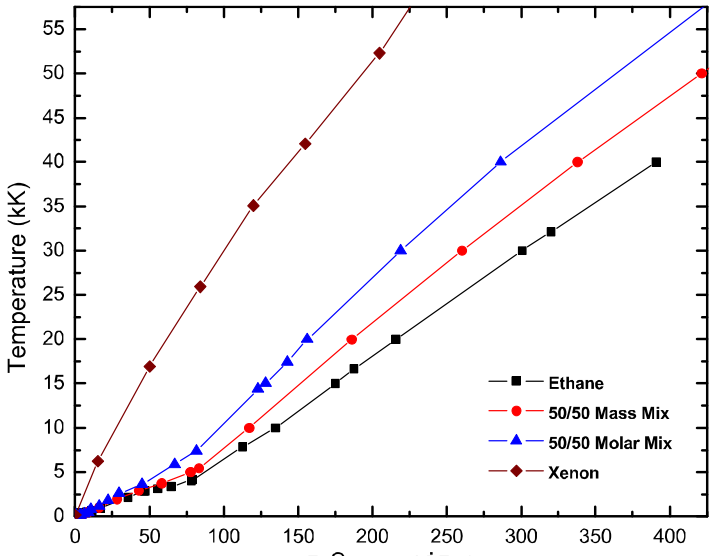


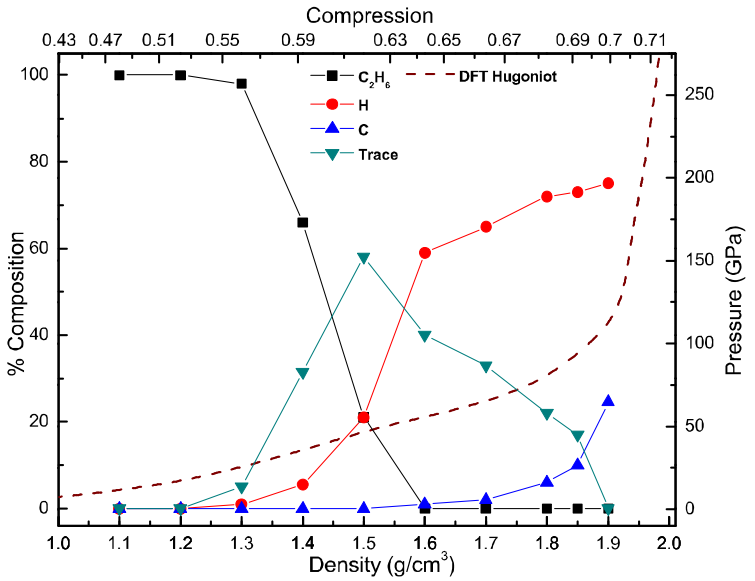
$$x = \frac{Ethane\ mass}{Xenon\ and\ Ethane\ mass}$$

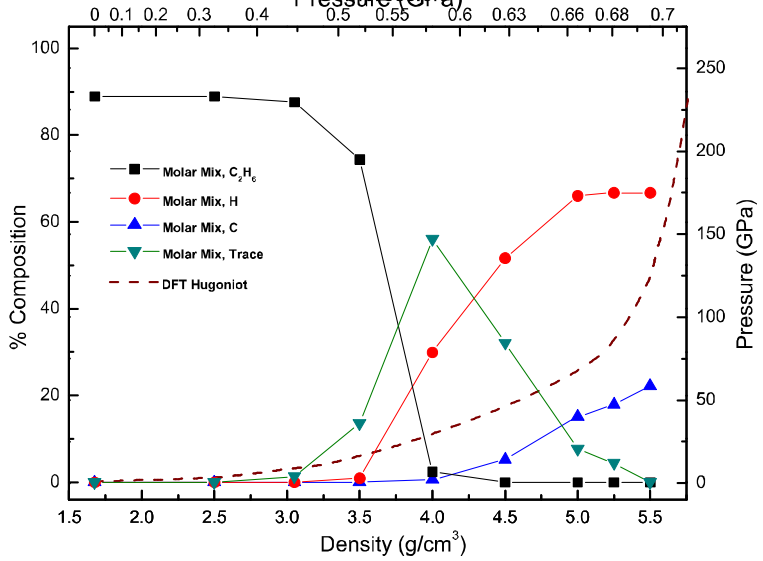
Xe-Ethane Mix Hugoniot

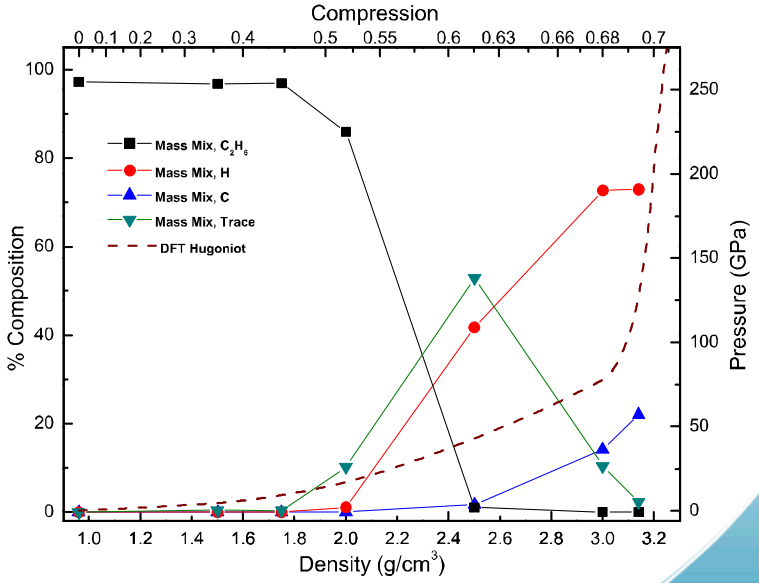


Decomposition Along the Hugoniot

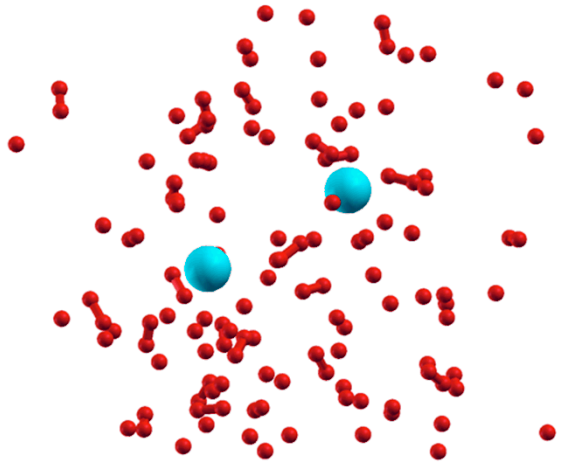








Mixing Ratio for Binary Mixtur



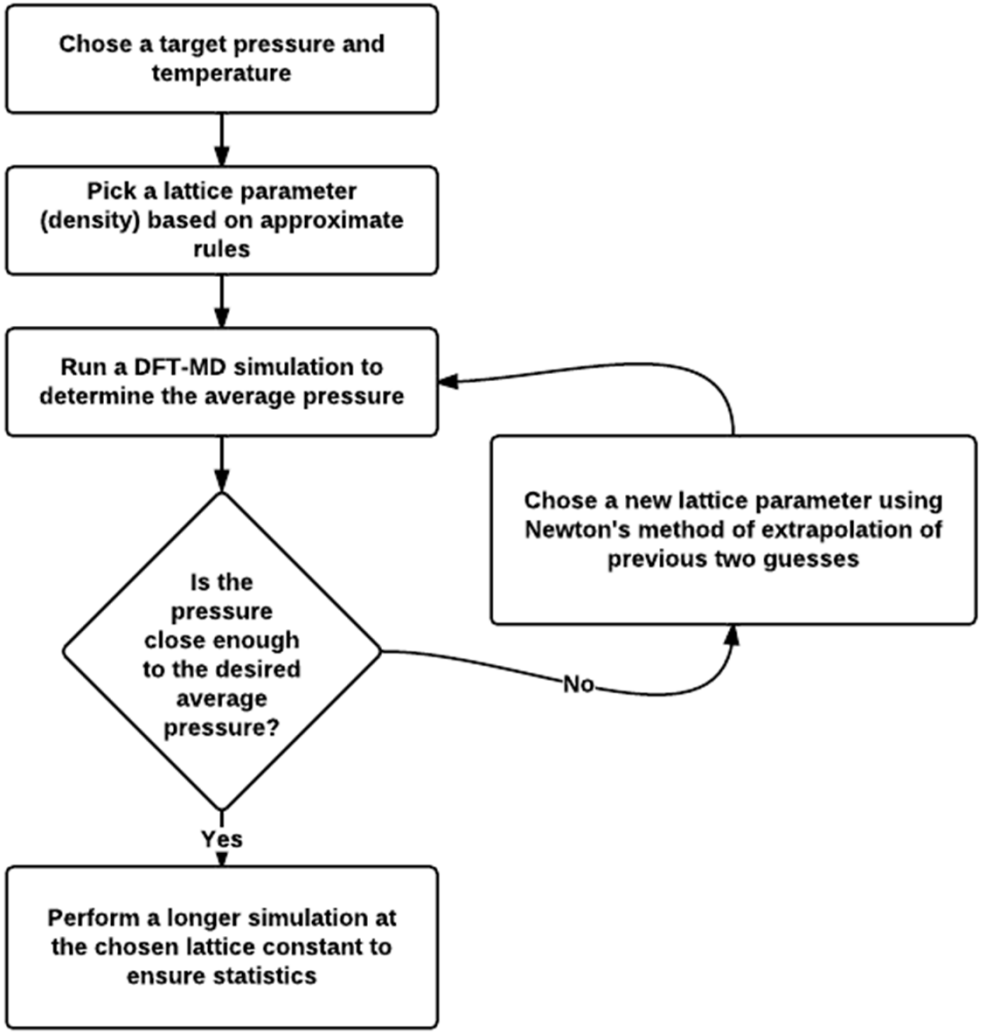
High Z- low Z mixture used in gas puff experiments
Difficult to mix experimentally

$$x = \frac{Deuterium\ mass}{Xenon\ and\ Deuterium\ mass}$$

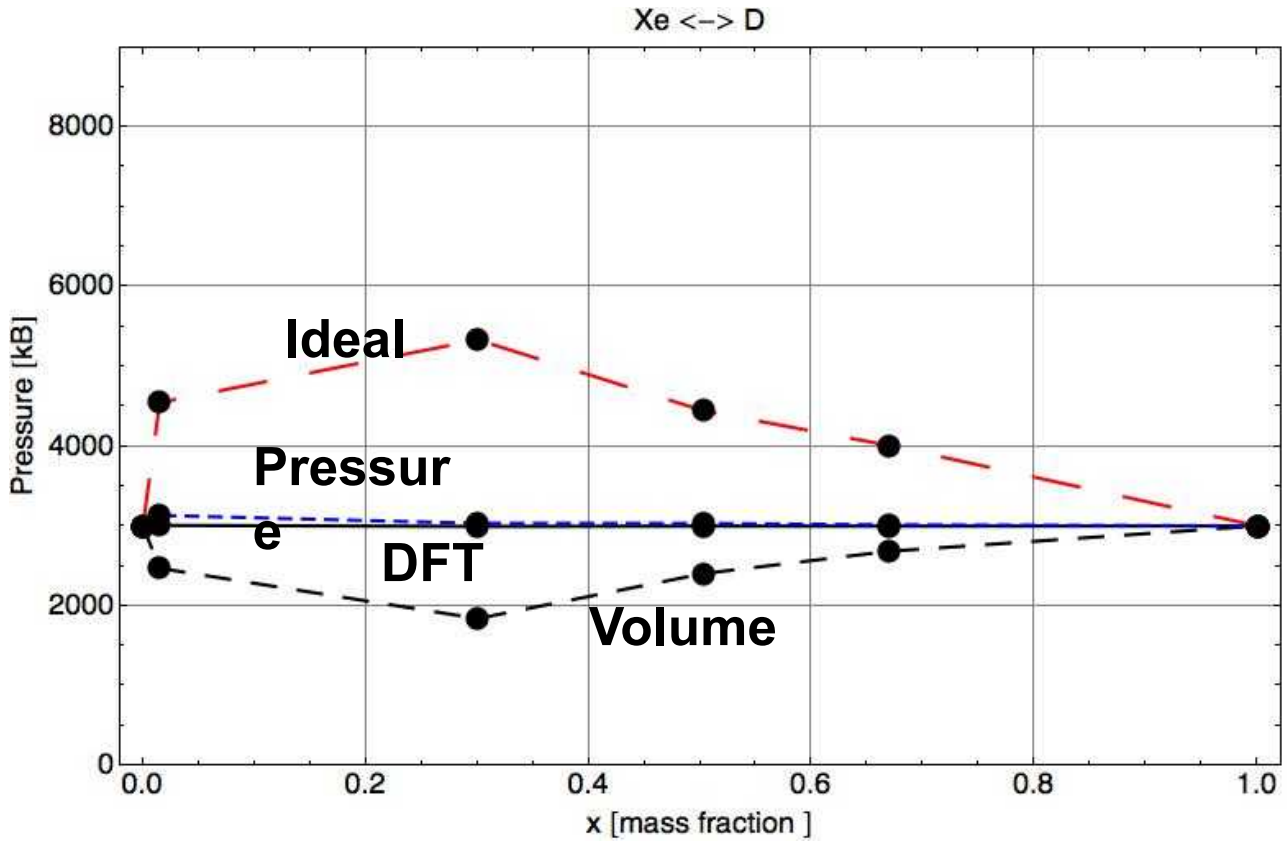
Mix Ratio	# of Xe Atoms / Cell	# of D Atoms / Cell
0.0	32	0
0.3	3	84
0.5	2	132
0.67	1	132
1.0	0	200

Note: Deuterium mass / Xenon mass ≈ 0.015
According to the ideal gas law: P is proportional to n the number density
To achieve similar pressures the mass densities are related $\rho_{Xe} \approx 100\ \rho_D$

Constant Pressure Calculations Implementation at First Principles Simulations



Xe-D with fixed pressure: DFT/AM05, SESAME 5365 for D

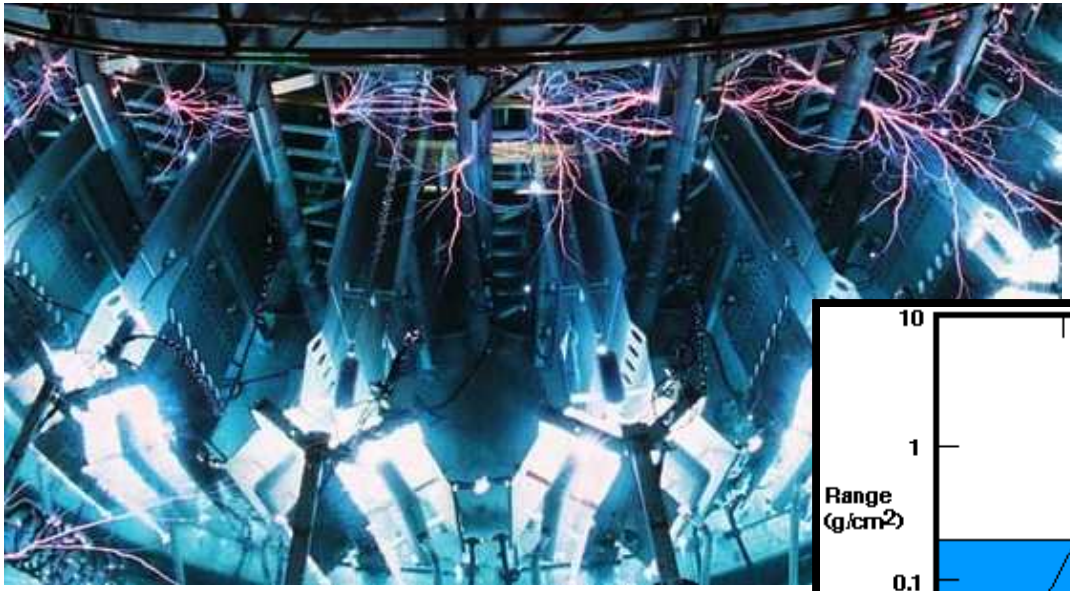


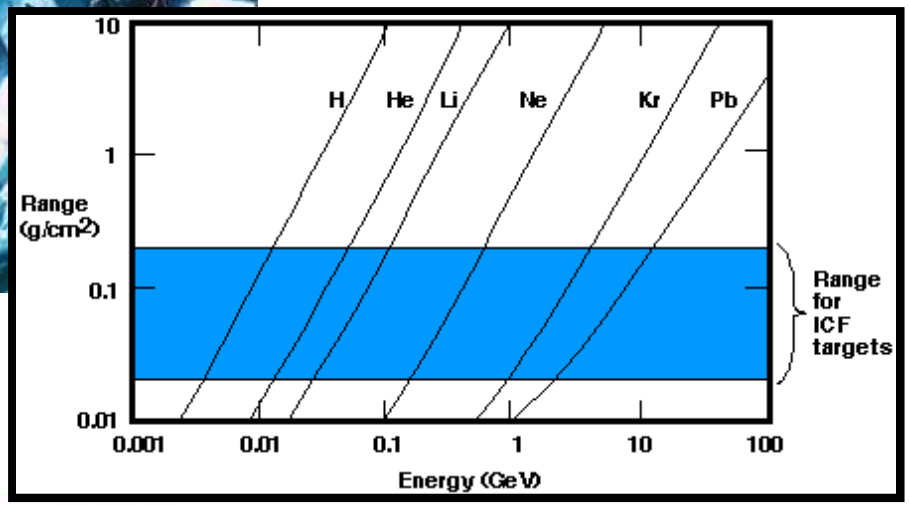
- **T = 10 kK**

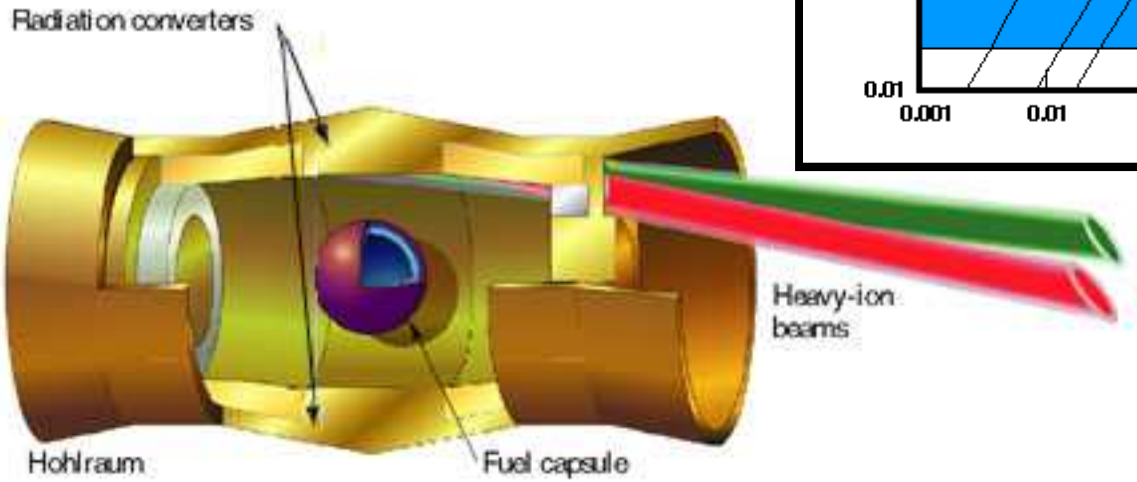
Pressure: blue short-dashed
Ideal: red long-dashed
DFT: solid black
Volume: black medium-dashed
ρ_{Xe}= 15.9 g/cc

Magyar and Mattsson, Phys. Plasmas **20**, 032701 (2013)
Notes: Ideal mixing rule is clearly flawed especially for small x.
Volume mixing predicts lower pressures than DFT-MD.

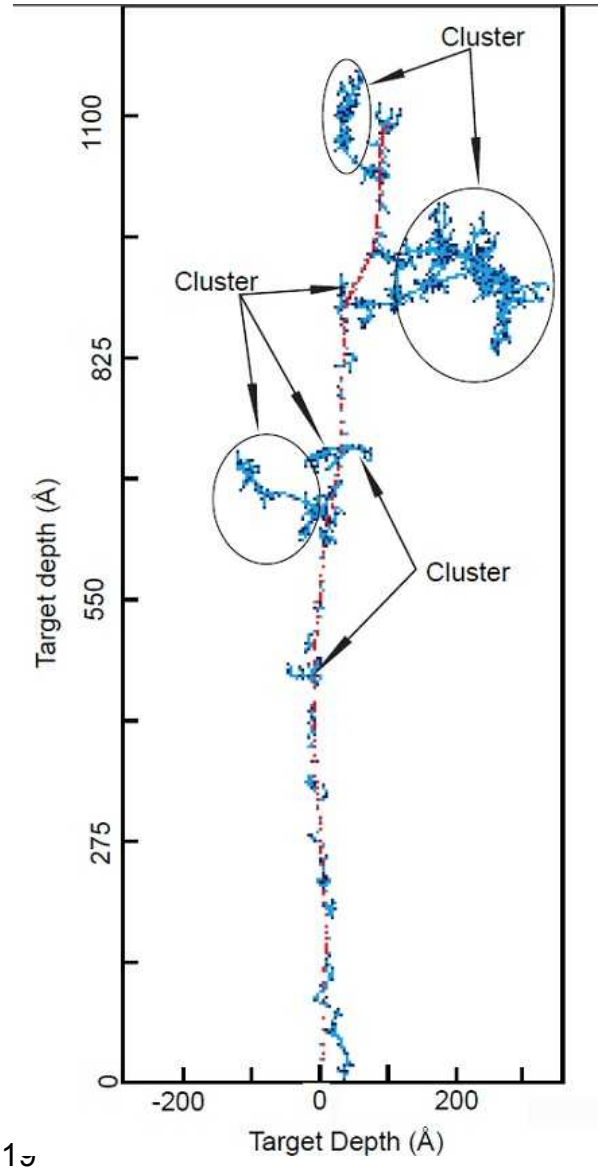
Stopping Powers for Inertial Confinement Fusion and Warm Dense Matter

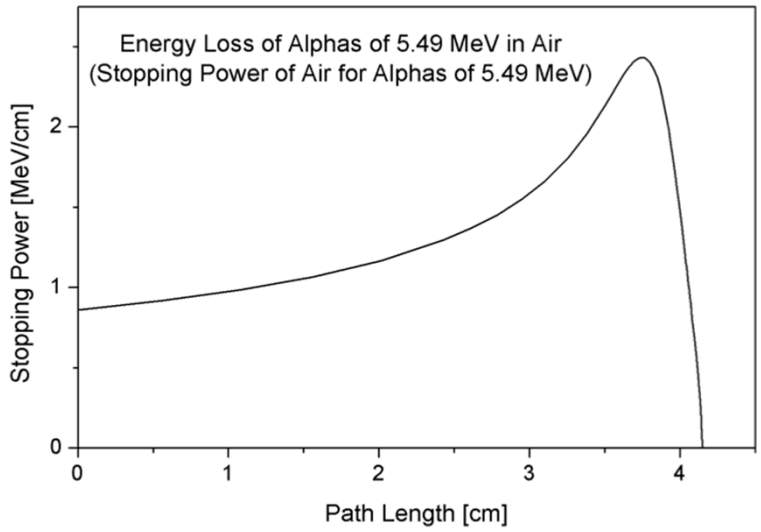






Stopping Power





$$S(E) = -dE_{\text{Projectile}} / dx$$

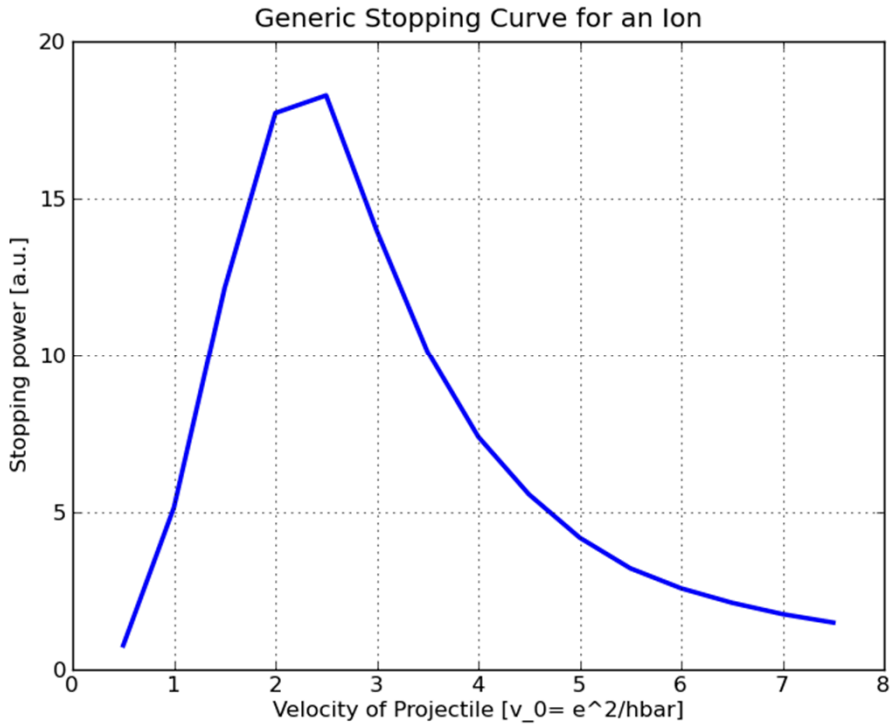
Penetration Depth :

$$\Delta x = \int_0^{E_0} dE \frac{1}{S(E)}$$

Common Materials Monte Carlo Data Tabulated:
www.srim.org

Energy Regimes in Stopping Power

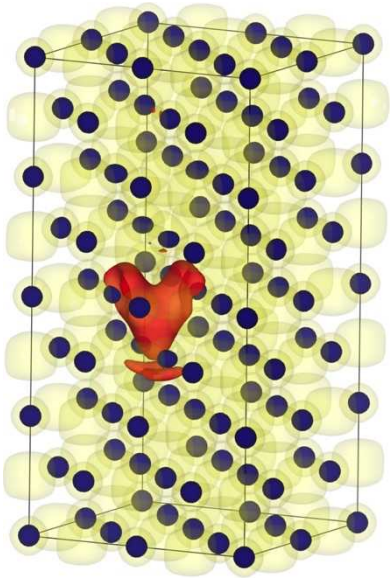
- Low energy v<0.1 a.u. ground-state or thermal electrons / adiabatic regime
- High energy v>>0.1 a.u. electron dynamics
- Intermediate regime: combined electron-nuclear dynamics, electron capture and ionization

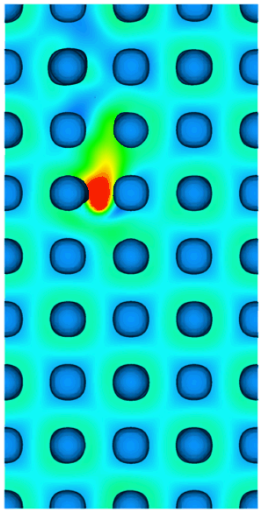


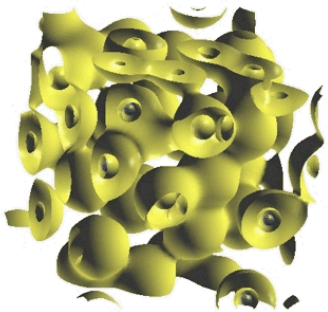
Developments Required for TDDFT of WDM

- Extended system for dense disordered materials
- Real-time evolution to allow non-harmonic nuclear motion to couple
- Extended system optical or small q response
- Finite temperature theory
- Coupled-electron-ion motion
- Electron-ion energy transfer

$$i\frac{\partial}{\partial t}\phi_i(r,t) = \left[-\tfrac{1}{2}\nabla^2 + v_{KS}\left[\Psi_0,\Phi_0,n\right](r,t)\right]\phi_i(r,t)$$

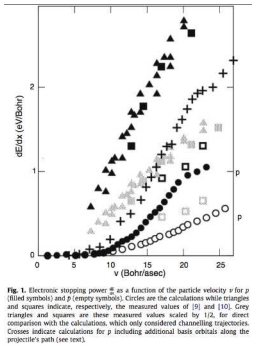




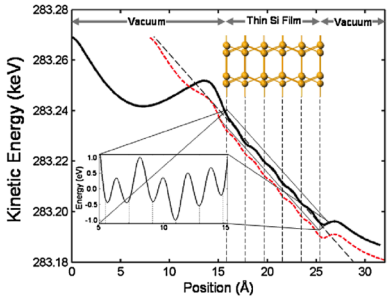


Approaches to Stopping in Real-Time Electron Dynamics Simulations

1. Total energy – Constant velocity projectile, increasing total energy of system
2. Forces on nuclei – Direct solution of forces of projectile
3. Perturbative – Relationship to dielectric response of system



J.M. Pruneda et al. Nuclear Instruments and Methods in Physics Research B 267 (2009) 590–593



R. Hatcher, M. Beck, A. Tackett, and S.T. Pantelides, Phys. Rev. Lett. 100, 103201 (2008).

J. M. Pruneda, D. Sánchez-Portal, A. Arnau, J. I. Juaristi, and E. Artacho, Electronic stopping power in LiF from first principles, Phys. Rev. Lett. **99**, 235501 (2007).

Electron-Dynamics through TDDFT

Time-dependent KS Scheme Builds Upon the Highly Successful Ground-state Theory

$$i\frac{\partial}{\partial t}\phi_i(r,t) = \left[-\tfrac{1}{2}\nabla^2 + v_{KS}\left[\Psi_0,\Phi_0,n\right](r,t)\right]\phi_i(r,t)$$

$$\phi_i(\mathrm{r},0) = \phi_i^T(r) \qquad \int d^3r\,\phi_i(r,t)\phi_j(r,t) = \delta_{ij}$$

$$n(r,t) = \sum_i^{occ.} \left|\phi_i(r,t)\right|^2$$

In the spirit of KS DFT, we postulate that a non-interacting system with a judiciously chosen potential can reproduce the time dependent density.

Non-linear and complex

$t_{electron} << t_{nuclei}$ for long simulations 50000 time steps typical > 5000 in DFT-MD

Elevated-Temperature Time-Dependent Density Functional Theory (ET-TDDFT)

$$n(r,t) = Tr\left[\hat{n}(r)\,\hat{\rho}(t)\right] = \sum_{norbs} w_i(t)\left|\phi_i(r,t)\right|^2$$

$$w_{N,i} = f\left[\beta\left(\varepsilon_{N,i} - \mu N\right)\right]$$

- Mermin formulation
- Ground-state exchange-correlation Functionals (local density and gradient approximations)
- Chemical bonds
- Thermostats
- Molecular dynamics of the nuclei

$$n(r,t) = \sum_{i}^{occ.} w_i \left|\phi_i(r,t)\right|^2 , f_i \le 1$$

Electron-Ion Equilibration

Hot ions and cold electrons or Hot electrons and cold ions

Often modeled in terms of a 2 temperature model

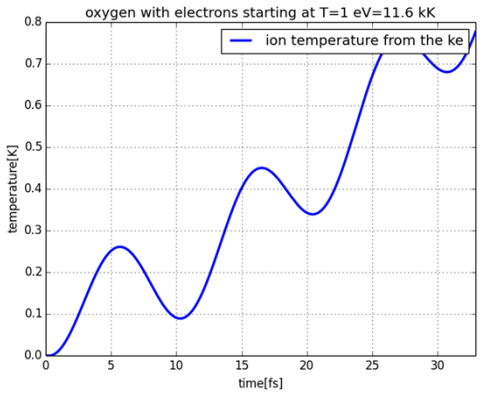
$T_{equilibration}$ = 0.33 -10 ps

Runge-Gross Leaves the Question of Weights Open

- Different representations of TDDFT ensemble densities
- NVT thermal density but NVE propagation?!

$$\hat{\rho}^{Exact} = \sum_i W_{i,\beta} \left|\Psi_i\right\rangle\left\langle\Psi_i\right|$$

$$\hat{\rho}^{Mermin} = \sum_i w_{i,\beta} \left|\phi_i(w_{i,\beta})\right\rangle\left\langle\phi_i(w_{i,\beta})\right|$$



Trouble with Von Neumann and Mermin States

- Assume for example non-interacting Fermions.
- Try to connect 2 different Mermin states trough unitary propagation alone.
- Some mechanism to change occupations is required.

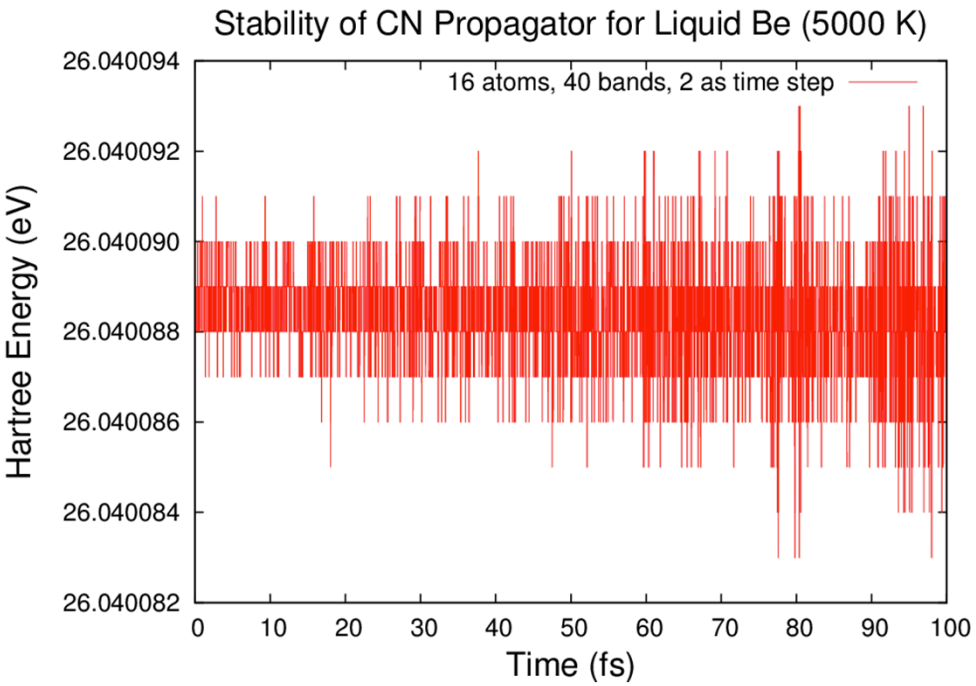
$$\hat{\rho}_1 = \sum_i w_i^{(1)} \left|\Phi_i\right\rangle\left\langle\Phi_i\right| \quad \hat{\rho}_2 = \sum_i w_i^{(2)} \left|\Phi_i\right\rangle\left\langle\Phi_i\right|$$

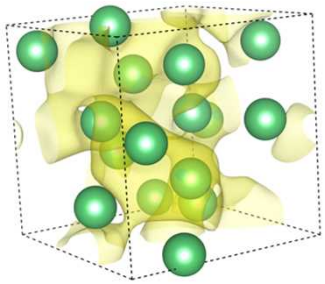
$$\hat{\rho}_2 = \sum_i w_i^{(1)} U(T) \left|\Phi_i\right\rangle\left\langle\Phi_i\right| U(T)$$

$$U(t) = \sqrt{w_i^{(2)} / w_i^{(1)}}$$

Time-integration and Stability

- Highly nonlinear equations
- Sources of trouble:
- Iterative solve at each step
- Hartree/XC ← $n(\mathrm{r}, t)$ ← $|\psi_m(\mathrm{r}, t)|^2$
- Accumulation of floating-point error
- Validation: Does Mermin state stay in Mermin state?
- Crank-Nicolson proves robust : Exact unitary propagation
- Orbitals orthogonal for 50k+ steps
- Hartree energy conserved ± 10μeV!

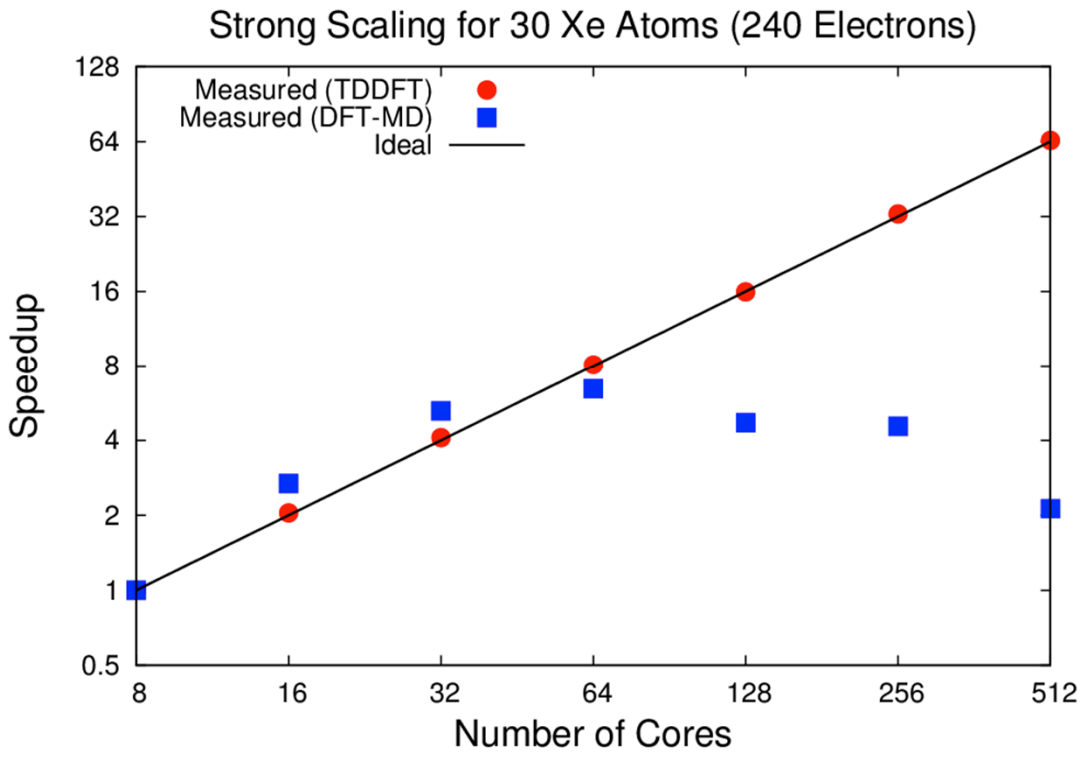




$$\left[S(t)+\tfrac{i\Delta}{2}H_{smooth}(t+\tfrac{\Delta}{2})\right]\psi_{n,smooth}(t+\Delta$$
$$=\left[S(t)-\tfrac{i\Delta}{2}H_{smooth}(t+\tfrac{\Delta}{2})\right]\psi_{n,smooth}(t)$$

Parallel Scalability

- Ehrenfest TDDFT: 'more parallel' than DFT-MD.
- Primary cost/step is iterative linear solve
- No orthogonalization
- Hierarchical parallelism
- The catch: time step in attoseconds
- Of course, we also capture influence of electronic excited states. . .



Coupled Electrons and Moving Nuclei

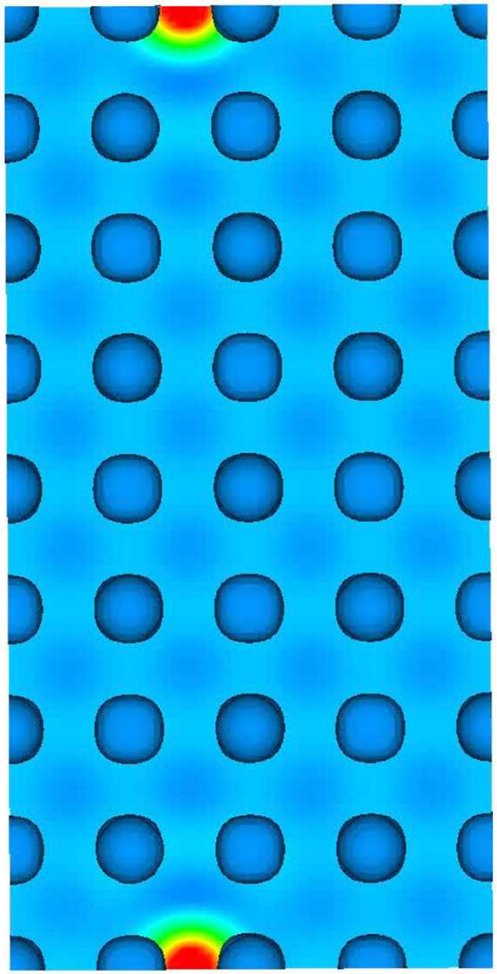
$$H\left[\left\{R_I\right\}\right]\phi = \varepsilon\phi \quad \text{Vs.} \quad H\left[\left\{R_I\right\}\right]\phi = i\frac{d}{dt}\phi$$

$$F_I = -\left\langle \nabla_I V\left(\left\{R_I\right\}\right)\right\rangle$$

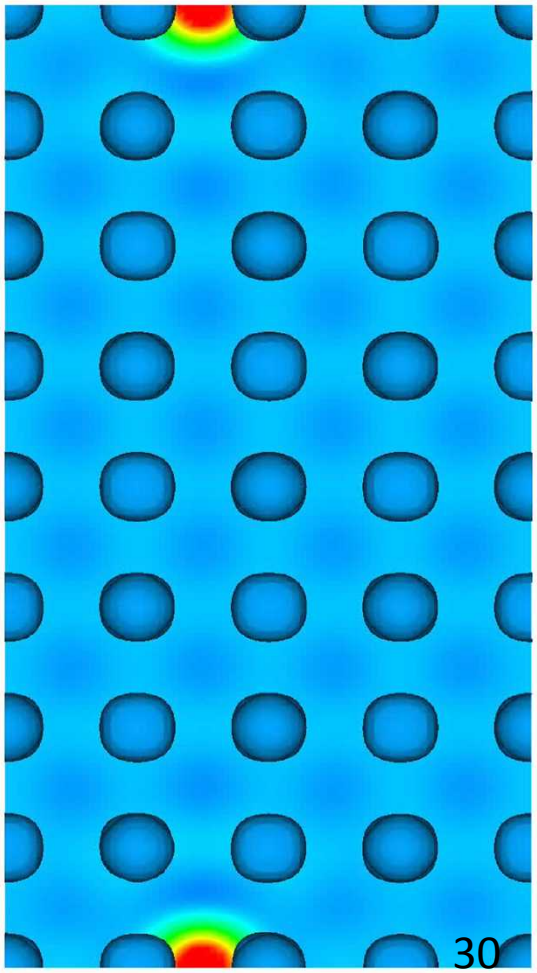
- **Separate model for coupled electron ion dynamics**
- No uncoupled electron dynamics Born-Oppenheimer
- Electron-dynamics in Ehrenfest
- Certain processes not described by even Ehrenfest such as photochemistry, discrete electron relaxation

Born-Oppenheimer vs. Ehrenfest

Born-Oppenheimer



Ehrenfest



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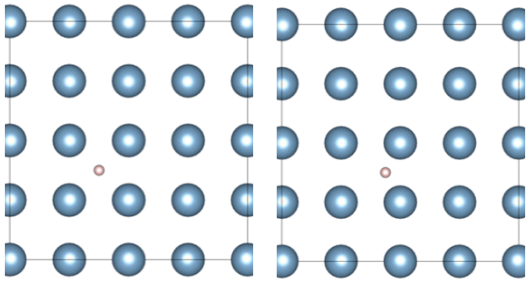
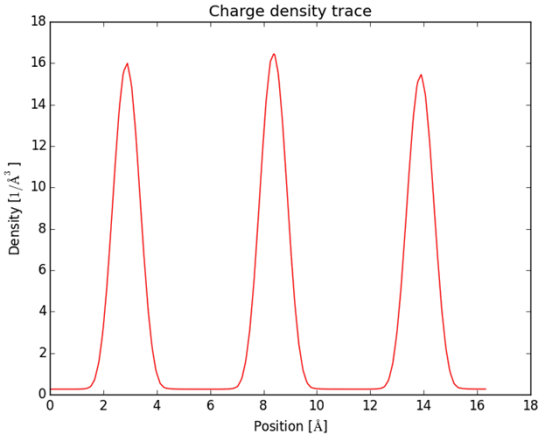
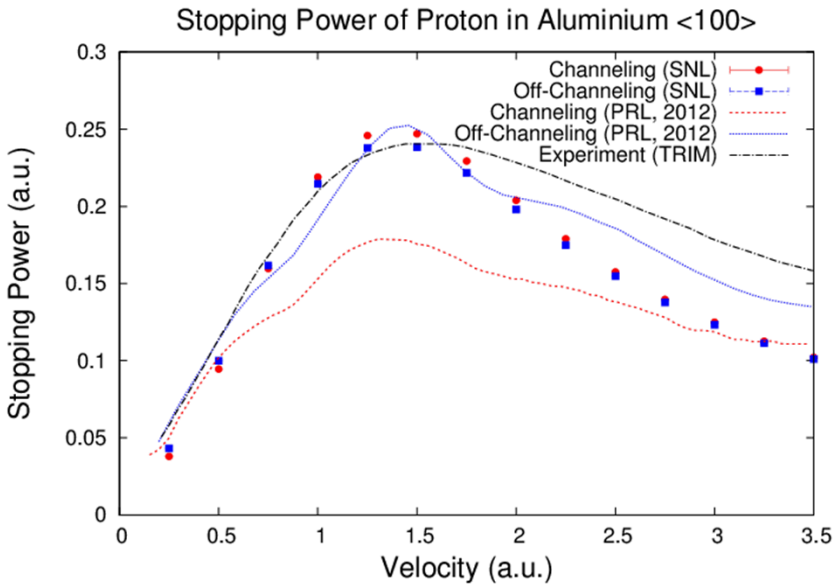
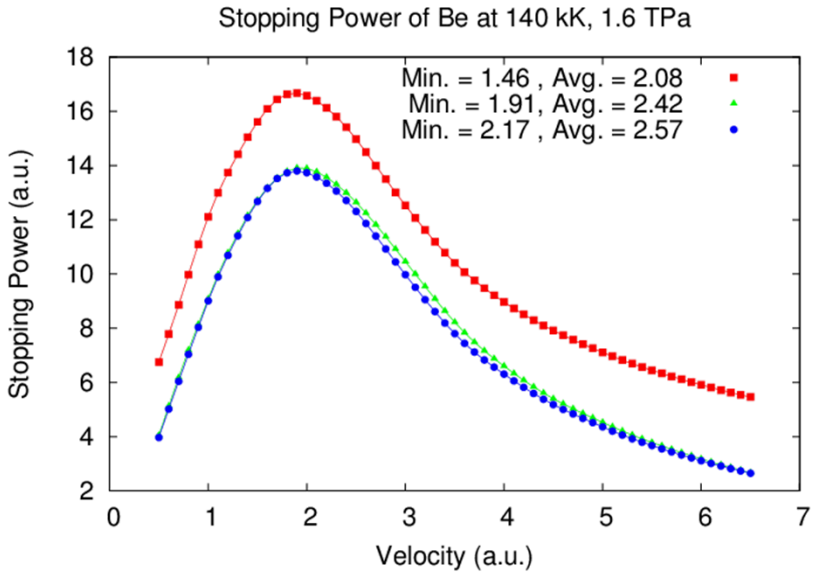
Stopping Power Calculations Extended to WDM

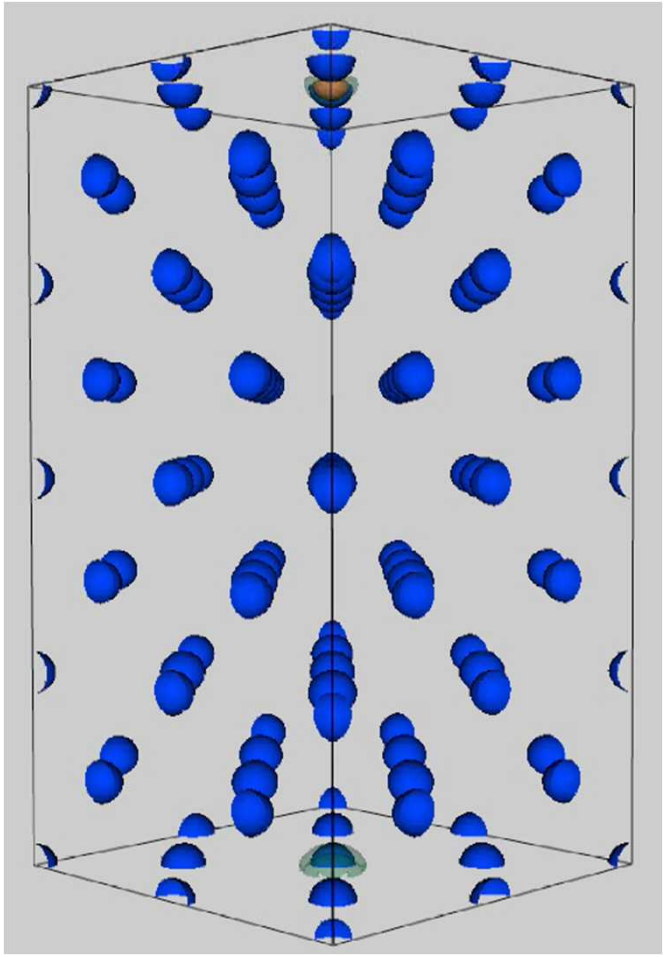






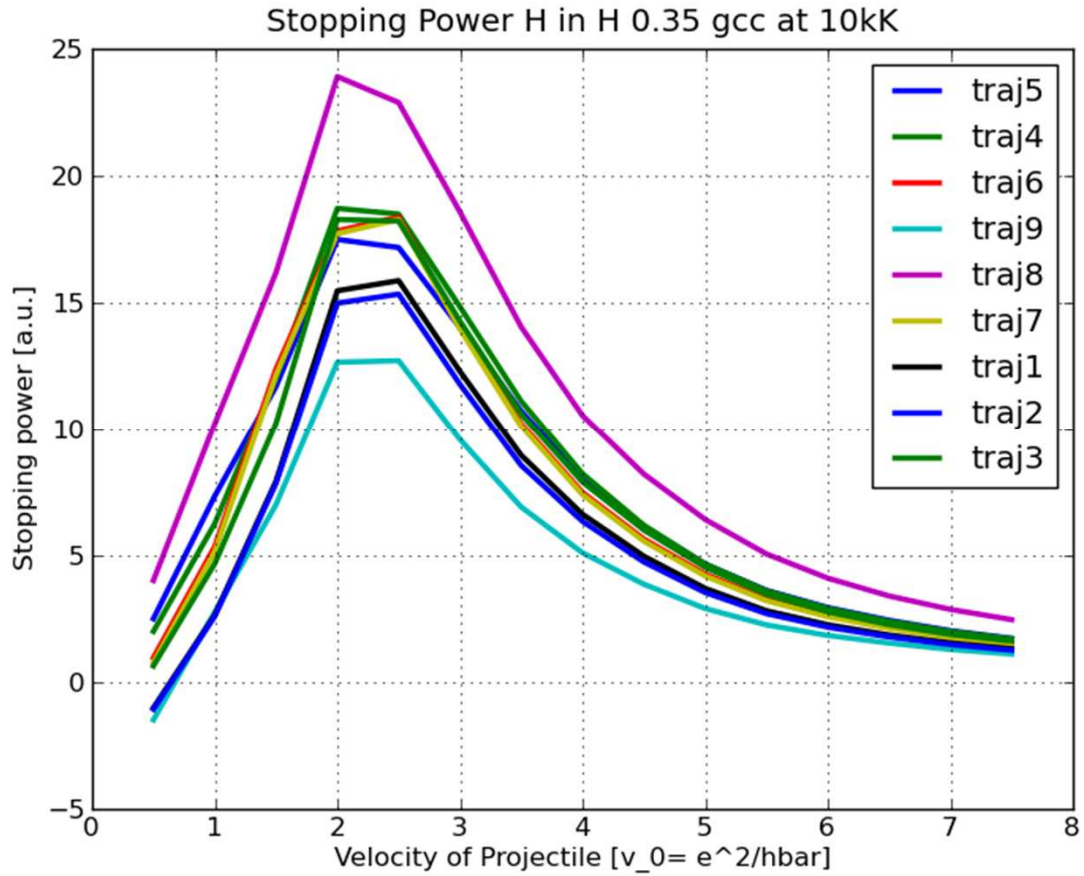


Plasmons are Formed in the Wake.



H in H at 1000 K

- **Liquid density at ambient 0.07 gcc**

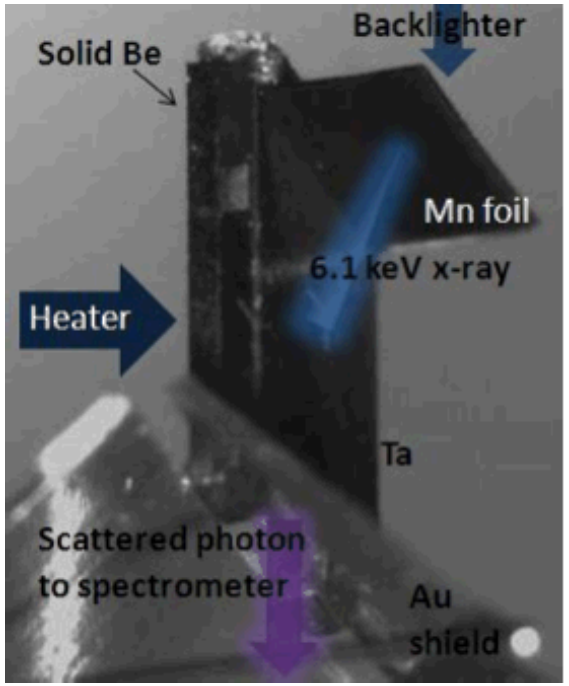


X-Ray Thomson Scattering, a New Diagnostic, in Warm Dense Matter

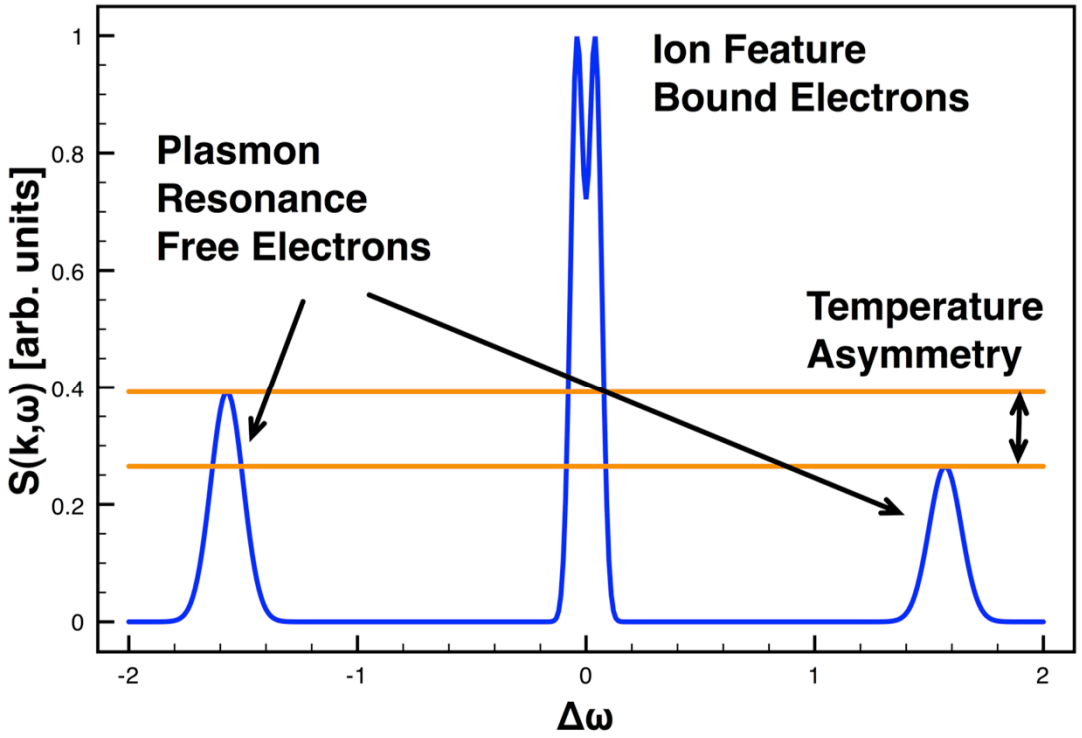
- Diagnosing Warm Dense Matter

- X-Ray Thomson scattering can test EOS by providing a measure of bulk **temperature**, density, and ionization state (not surface limited)

- Used (or soon to be used) at several facilities:
- Z-Machine, Omega, DESY , Tsinghua, and many more



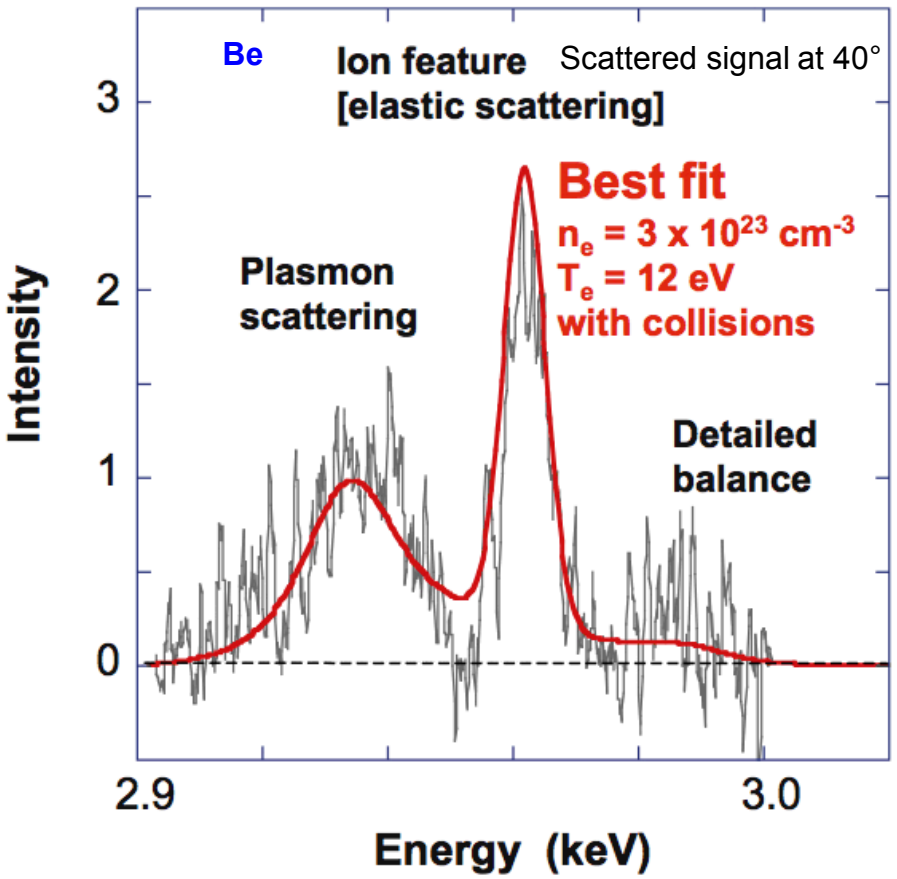
Temperature Diagnostic X-Ray Thompson Scattering



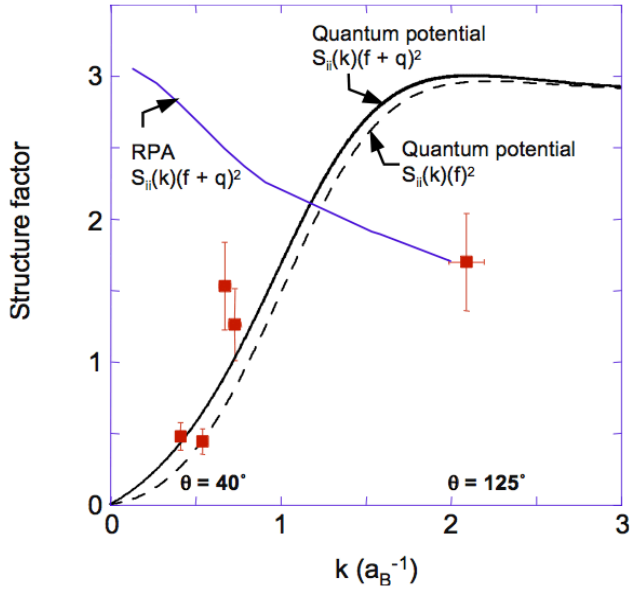
$$S^{tot}(k,-\omega) = Exp\left(-\hbar\omega / k_B T\right) S^{tot}(k,\omega)$$

- Based on fundamental principle of detailed balance
- Temperature diagnostic for warm dense matter
- Structural information about a material
- *Works* at low k based on models (Chihara) that use unphysical ion structure factors from classical plasma simulations with *effective quantum potentials*

X-Ray Thomson scattering has delivered temperature measurements and questions



Beryllium data from Glenzer, *et al*., Phys. Rev. Lett. 98 (2007)



$$S(k,\omega) = \left(f(k) + q(k)\right) S_{ii}(k)\delta(\omega) + Z_C S_{ee}(k,\omega) + S_{cv}(k,\omega)$$

The Chihara models that "work" at low k use unphysical ion structure factors from classical plasma simulations w effective "quantum potentials".

Core-valence separation; frequency domains of validity

Most Direct Simulation through the Dynamic Structure Factor

- Time-domain quantum mechanics simulations allows a direct calculation of the structure factor S(k,ω) that

-Includes quantum degeneracy

-Correlations

-Electrons and nuclei out of thermal equilibrium

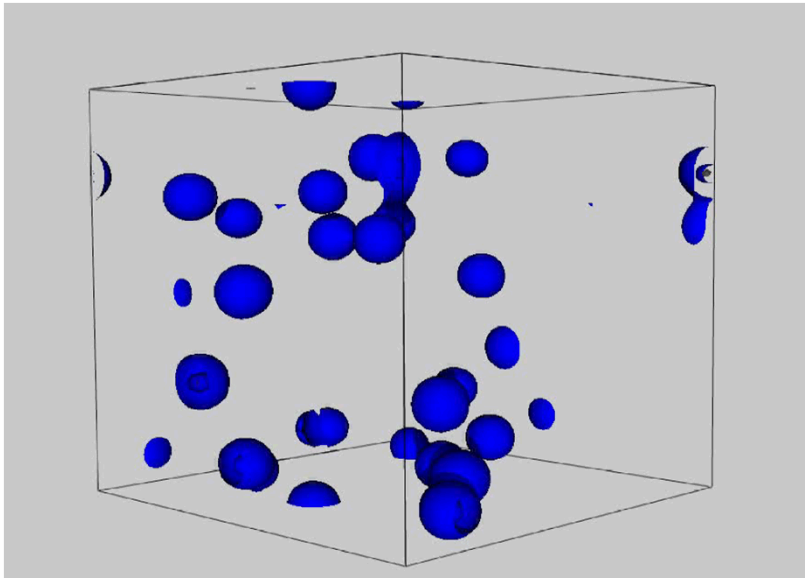
-Non Fermi-Dirac distributions

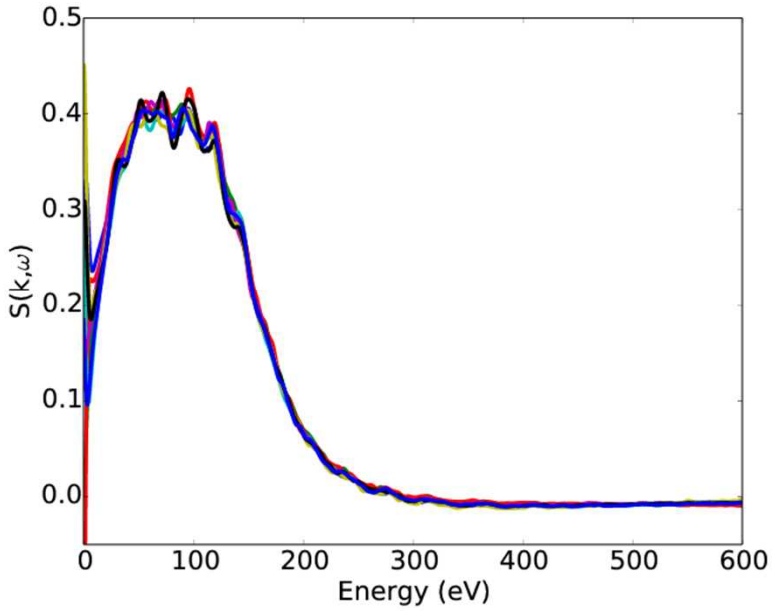
-Collective excitations

$$\frac{d\sigma}{d\omega\, d\Omega} = \sigma_T S^{tot}(k,\omega) \qquad S_{ee}^{tot}(k,\omega) = \frac{1}{N_{\text{ion}}}\left\langle \left| \rho_e^{\text{tot}}(\mathbf{k},\omega) \right|^2 \right\rangle$$

Movie:
X-Ray Thomson Scattering Calculation

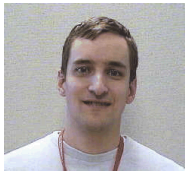
$$\delta v_{pert.}(r,t) = v_0 e^{iq\cdot r} f(t) \qquad \delta\rho(k,\omega)/v_0 f(\omega) = \chi(k,-k,\omega) \qquad S(k,\omega) = -\tfrac{1}{\pi}\frac{\mathrm{Im}[\chi(q,-q,\omega)]}{1-e^{-\omega/kT}}$$





The LDRD Team

BACZEWSKI, ANDREW



SHULENBURGER, LUKE

DESJARLAIS, MICHAEL P.

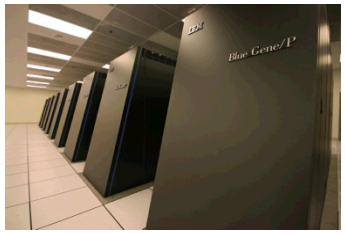
- The Z team
- Thomas Mattsson
- Dawn Flicker
- Seth Root
- Kyle Cochrane
- Programmatic leadership
- The Cryogenic Team – D. L. Hanson
- Sandia High-Performing Computing (HPC) – S. Corwell
- Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
- And you for listening

Summary and Future Work

- DFT based MD simulations to model shock compression of mixtures under WDM conditions
- Experimental validation through shots on the Z-machine
- New tools for TDDFT of WDM:
  - Ehrenfest-TDDFT for coupled electron-ion motion in bulk systems
  - Stable, accurate, and scalable PAW implementation
  - XRTS/DSF is primary goal
- Immediately: dielectric function of interesting WDM systems (SEQUOIA).
- Near term: direct calculation of dynamic structure factor.
- Challenge: Identify surface hopping model that gets non-adiabatic electron-ion energy transfer ‘right’.

Sandia National Laboratories

NNSA National Nuclear Security Administration



LDRD

Some considerations

- **Translational invariance**

$$\Psi_n(x,t) = \exp(-i\varepsilon_n t + i\upsilon x)\,\Psi_n(x+\upsilon t, t)$$