Molecular Dynamics: *High Energy-Density Physics*

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Today's Itinerary

I. High Energy-Density Physics: Defined and Quantified
   A. high energy-density physics regimes
   B. dimensionless parameters
   C. ionization and plasma physics

II. Long Range Forces
   A. Ewald
   B. other methods: PME, PPPM, tree, multipole

III. Models of HED Matter: Forces
   A. One Component Plasma (OCP)
      ✓ Example: kinetic theory of stopping
   B. Yukawa model
      ✓ Example: mixing at an interface
   C. Quantum Statistical Potentials (QSPs)
      ✓ Example: temperature relaxation

IV. Integrators
   A. r-RESPA formulation
   B. MTS and NAPA methods
      ✓ Example: hard collisions associated with fusion

High Energy-Density Physics: Definitions

The total energy density in a material is the sum of three terms:

$$E = E_{radiation} + E_{electrons} + E_{ions}$$

How do these scale with temperature and density?

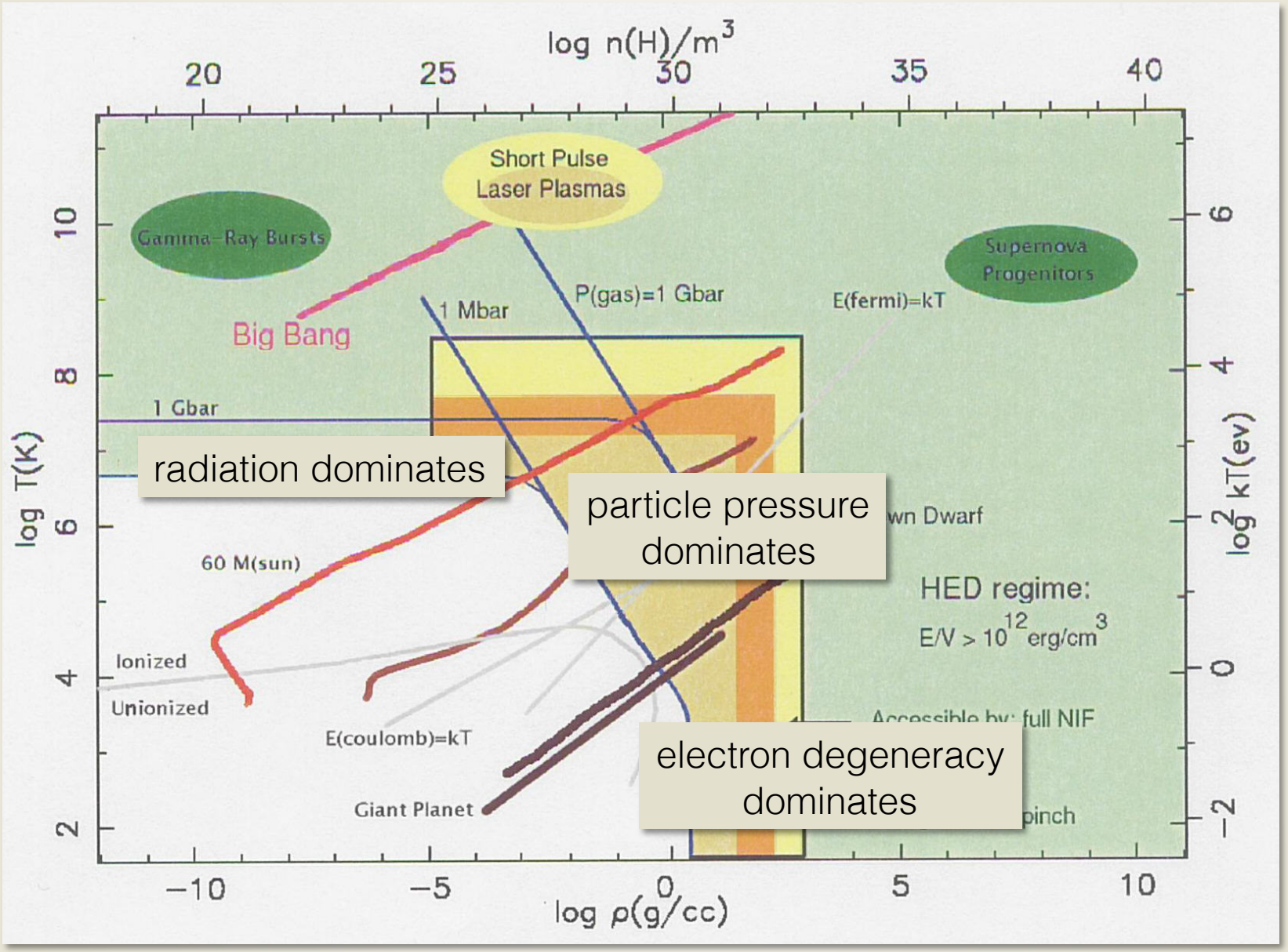
$$\begin{aligned} E_{radiation} &\sim T^4 \\ E_{electrons} &\sim n\sqrt{T^2 + \left(\frac{3}{5}E_F\right)^2} \\ E_{ions} &\sim nT \end{aligned}$$

$$E_F \sim n^{2/3}$$

High energy density *defined* as:

$$\begin{aligned} P &= 1\,\mathrm{Mbar} \\ &\rightarrow 10^{11}\,\mathrm{J/m^3} \end{aligned}$$

Regimes of High Energy-Density Physics



Important Physical Parameters For MD

Coulomb coupling parameter:

$$\Gamma = \frac{\langle \text{potential energy} \rangle}{\langle \text{kinetic energy} \rangle} = \frac{Z^2 e^2}{a_{WS} T}$$

average spacing estimated by the Wigner-Seitz radius:

$$\frac{4}{3}\pi n a_{WS}^3 = 1$$

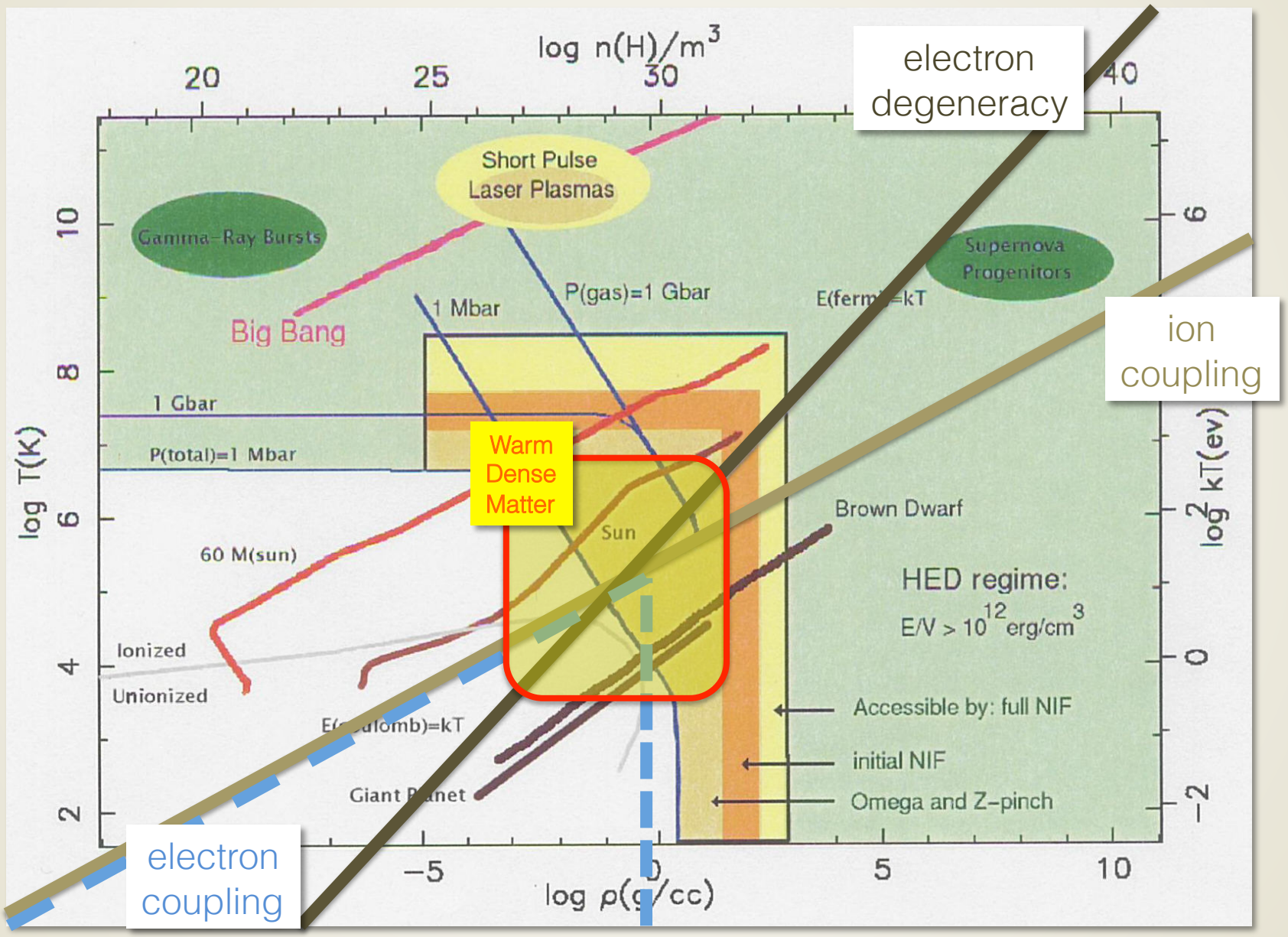
Degeneracy parameter:

$$\theta = \frac{T}{E_F}$$

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

$$\Gamma_{ee} = \frac{e^2}{a_e \sqrt{T^2 + (\frac{3}{5}E_F)^2}}$$

Regimes of High Energy Density Physics



One-Slide Primer on Plasma Physics

Time Scales:

1. plasma frequency
2. collision rate

$$\omega_p = \sqrt{\frac{4\pi n Z^2 e^2}{m}} = 5.6 \cdot 10^4 Z \sqrt{\frac{n[1/cc]}{\mu[m_e]}}\ 1/sec$$

$$\nu_e = 3 \cdot 10^{-6} n_e[1/cc] \ln(\Lambda) T_e^{-3/2}[eV]\ 1/sec$$

$$\nu_i = 5 \cdot 10^{-8} Z^4 n_e[1/cc] \ln(\Lambda) T_e^{-3/2}[eV] \sqrt{\frac{m_p}{m}}\ 1/sec$$

Length Scales:

1. interparticle spacing
2. screening length (e.g., Debye length)

$$a = \left(\frac{3}{4\pi n}\right)^{1/3}$$

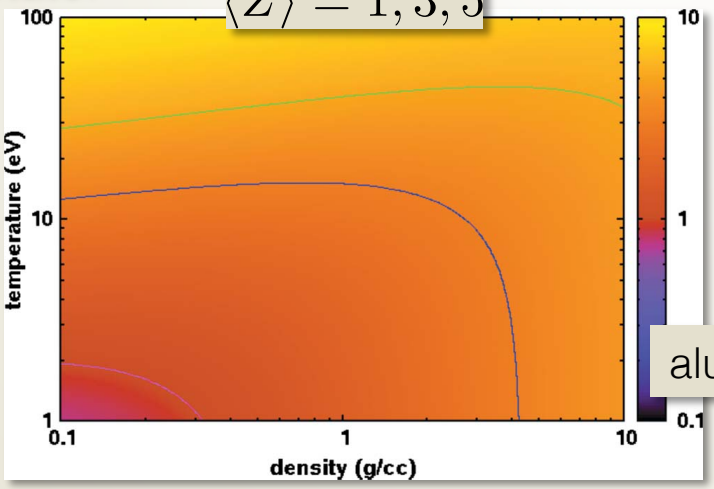
$$\frac{a}{\lambda_D} = \sqrt{3\Gamma}$$

$$N_D = (3\Gamma)^{-3/2}$$

$$\lambda_D = \sqrt{\frac{T}{4\pi n Z^2 e^2}} = \frac{740}{Z}\sqrt{\frac{T[eV]}{n[1/cc]}}\ cm$$

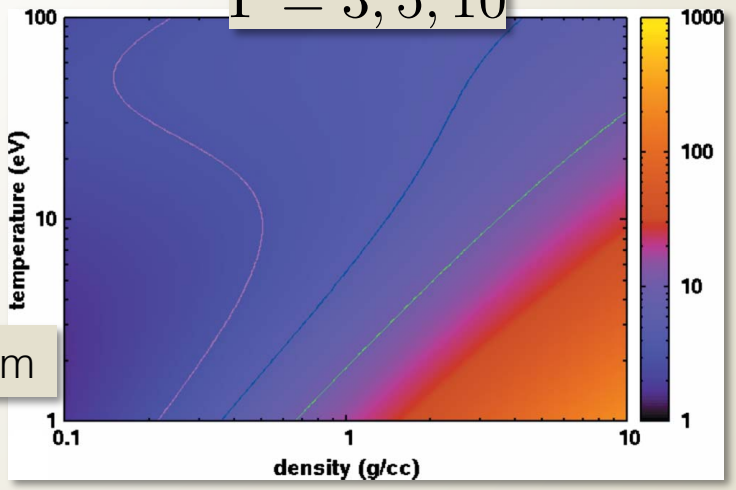
Ionization State:

$\langle Z \rangle = 1, 3, 5$



aluminum

$\Gamma = 3, 5, 10$



Long Range Potentials in MD

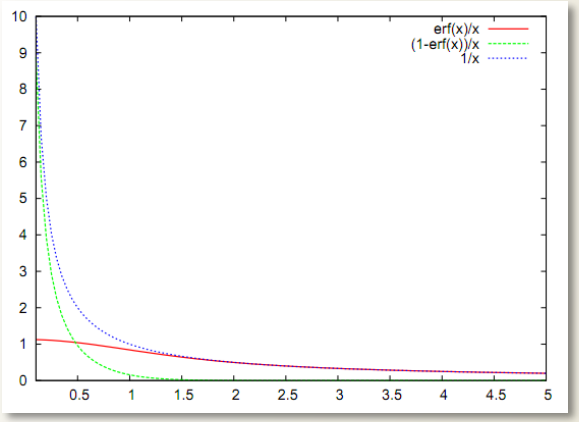
Forces that have a long range are deadly for MD. Not only do they scale as $O(N^2)$, because there is no appropriate cutoff radius, the forces also extend far beyond the edge of the simulation box.

The total energy for a Coulomb system is:

$$U = \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mathbf{n}\in\mathbb{Z}^3}^{\dagger} \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|} \qquad \Longrightarrow \mathcal{O}(N^2)\ !!!$$

We can separate the Coulomb potential into short and long-range components

$$\begin{aligned} \frac{1}{r} &= \frac{1}{r}\left(1 + f(r) - f(r)\right) \\ &= \frac{1}{r} f(r) + \frac{1}{r}\left(1 - f(r)\right) \end{aligned}$$



Typically, one chooses the complementary error function:

$$f(r) = \operatorname{erfc}(\alpha r)$$

Note that this is entirely independent of the the parameter **α**. Now the potential has a "hard" portion and a "soft" portion.

Sum Smooth Portion In Fourier Space: Ewald

Electrostatic energy of the box can be written as:

$$U = U^{(r)} + U^{(k)} + U^{(s)} + U^{(d)}$$

The long range portion is summed in Fourier space:

$$U^{(r)} = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{n} \in \mathbb{Z}^3}^{\dagger} q_i q_j \frac{\operatorname{erfc}\left(\alpha \left|\mathbf{r}_{ij} + \mathbf{n}L\right|\right)}{\left|\mathbf{r}_{ij} + \mathbf{n}L\right|}$$

This portion scales as $O(N^2)$.

$$U^{(k)} = \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \frac{4\pi}{k^2} \left|\tilde{\rho}(\mathbf{k})\right|^2 \exp\left[-\frac{k^2}{4\alpha^2}\right]$$

$$U^{(s)} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2$$

$$U^{(d)} = \frac{2\pi}{(1+2\epsilon)\Omega} \left(\sum_i q_i \mathbf{r}_i\right)^2$$

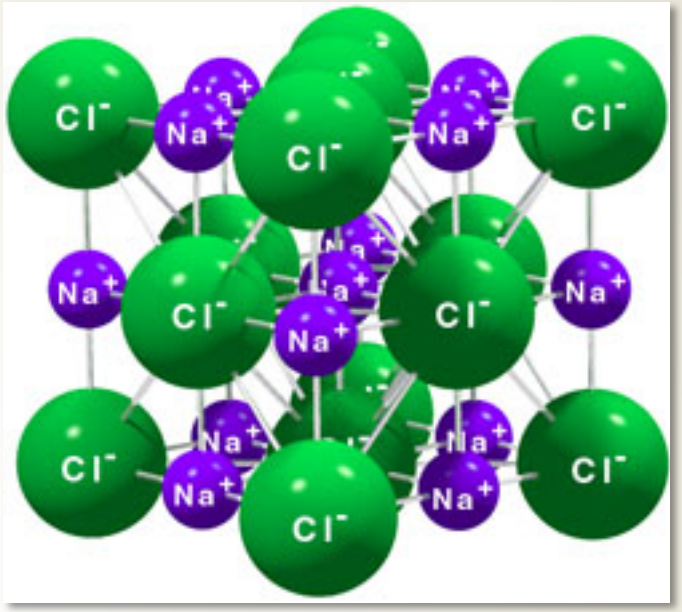
$$\tilde{\rho}(\mathbf{k}) = \int_\Omega d^3 r \rho(\mathbf{r}) \exp\left[-i\mathbf{k}\cdot\mathbf{r}\right] = \sum_j q_j \exp\left[-i\mathbf{k}\cdot\mathbf{r}_j\right]$$

This portion scales as $O(N)$.

Test: Madelung Energy

$$E = \frac{\mathcal{M}Q^2}{d}$$

$$\mathcal{M} = \sum_{ij} \frac{\mathrm{sign}(Q_i Q_j) d}{r_{ij}}$$



$$\mathcal{M} = -1.747564594633182190636212035544397403485161436624741758152825350 7$$

Advanced Methods For Long Range Potentials

Optimally implemented, the Ewald summation techniques scale as $\mathcal{O}(N^{3/2})$

This is a substantial improvement over the direct-summation method, but one can improve upon this scaling using more advanced methods:

1. Particle-Mesh methods $\mathcal{O}(N \log N)$
   a) Particle-Mesh Ewald
   b) Smoothed Particle-Mesh Ewald
   c) Particle-Particle-Particle-Mesh (P^3M)
2. Heirarchical methods $\mathcal{O}(N)$
   a) Tree methods (e.g., Barnes-Hut)
3. Multipole methods $\mathcal{O}(N)$
   a) Fast Multipole Method
4. Multigrid methods $\mathcal{O}(N)$

Periodic systems.

Non-periodic systems.

There Are Three Categories of MD Models for HEDP

HEDP encompasses enormous ranges in material properties (temperature, density, composition, kinetic state); *which forces are appropriate?*

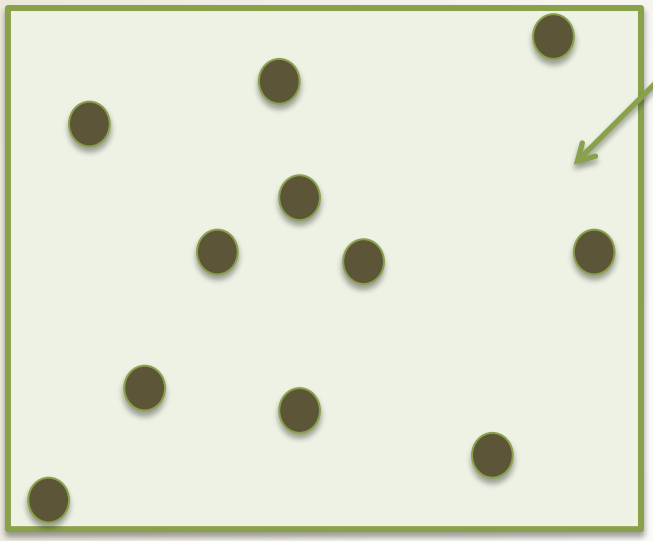
1. Model/Toy problems: Simplify the problem of interest so that it is amenable to MD methods; validate theory and/or provide insight.

2. Ionic physics problems: Find a good ion-ion interaction and simulate ion dynamics; understand structural and transport properties.

3. Electronic physics problems: Electron dynamics is crucial to the problem of interest; reveal realistic properties of high energy density matter.

The One Component Plasma (OCP)

The OCP model is the prototypical model of dense plasma molecular dynamics.



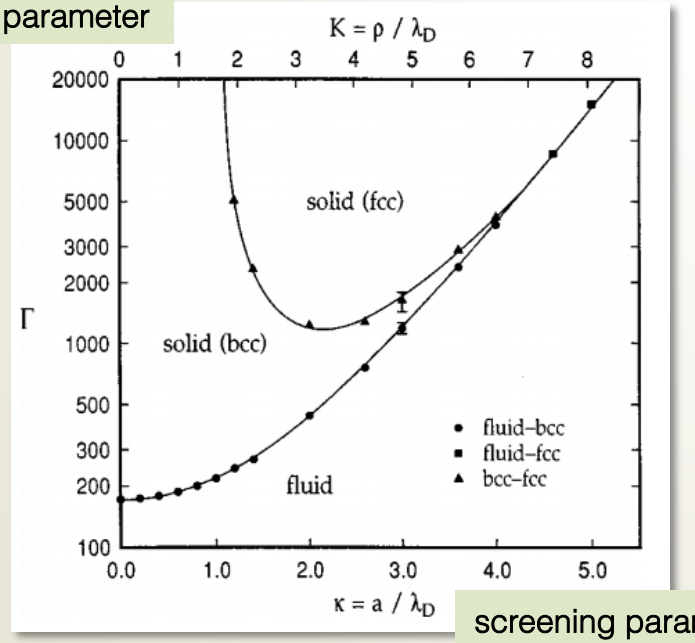
1. ion OCP
2. classical electron OCP
3. quantum electron OCP ("jellium")

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N} \frac{Q^2}{r_{ij}} + \sum_{i=1}^{N} \int_{\Omega} d^3r \, \frac{Q\rho}{|\mathbf{r} - \mathbf{r}_i|}$$

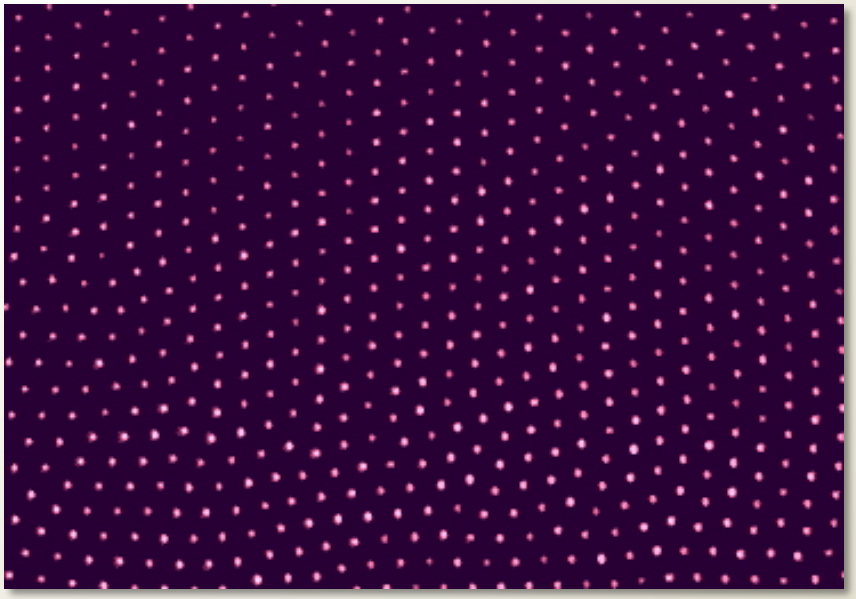
Some Important Facts About The OCP

- A great deal can be learned from the OCP; use as a starting point.
- In some cases, the OCP does describe the real system:
  - white dwarf interiors
  - very hot plasmas
  - charged particles in traps
- The OCP crystallizes at Γ=178.
- Has simple generalizations: binary ionic mixture (BIM).

coupling parameter



screening parameter



Example: Stopping of Fast Particles

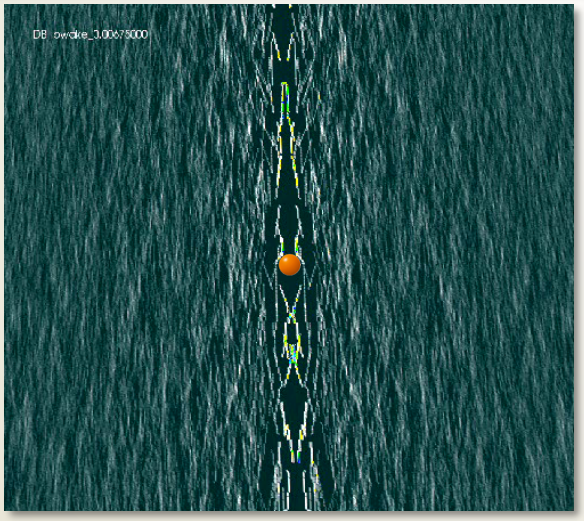
Stopping is a ubiquitous problem:

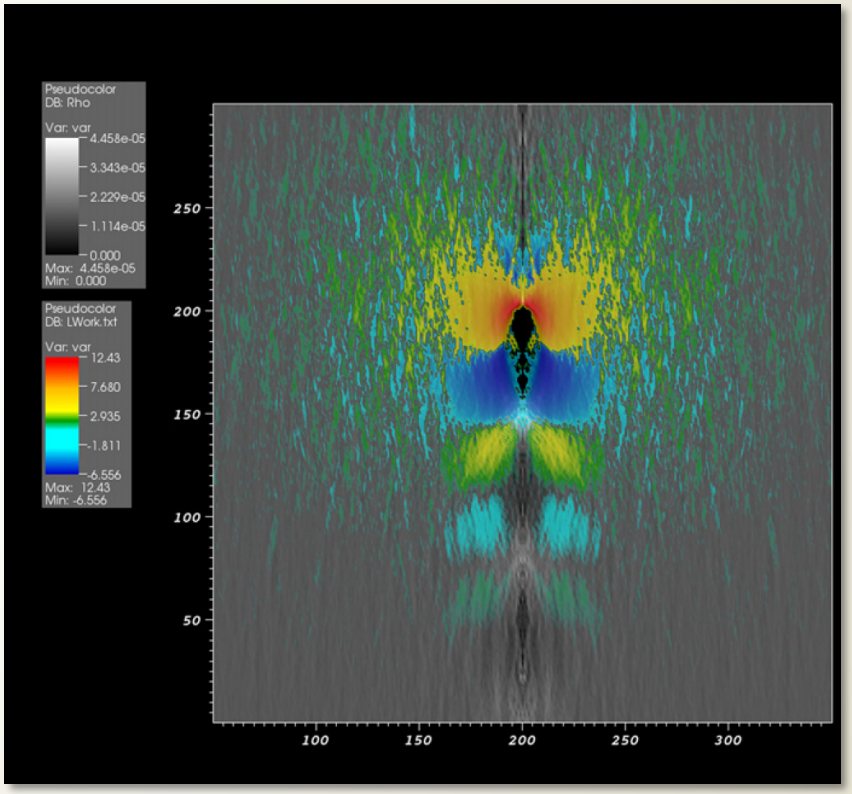
- cosmic rays
- proton cancer therapy
- ion beam deposition in materials
- particle tracking
- fusion-generated alpha particles
- etc.

Problem:
In high energy density physics environments, how accurate are our stopping models?

Solution:

- Equilibrate an OCP to chosen (T,n) point.
- Choose the charge of the projectile.
- Insert fast particle into simulation.
- Record energy loss per unit time/length during NEMD simulation.

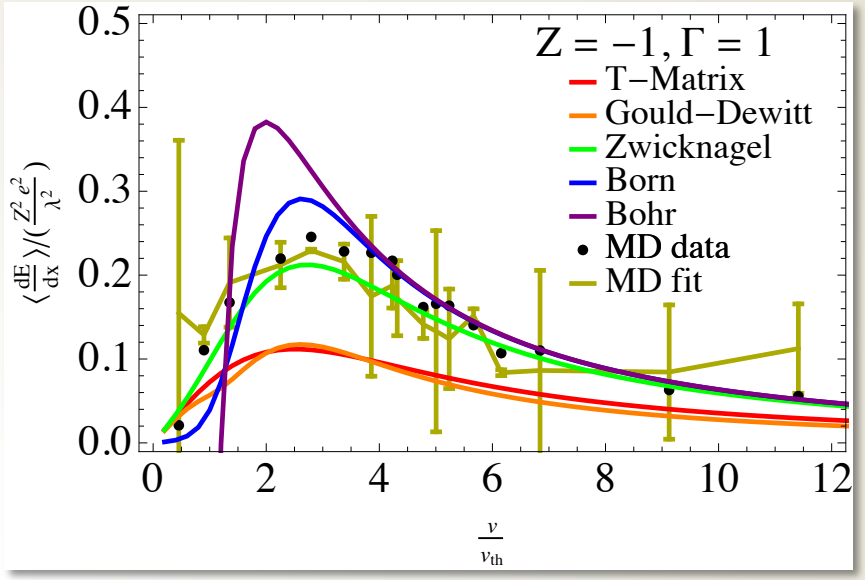


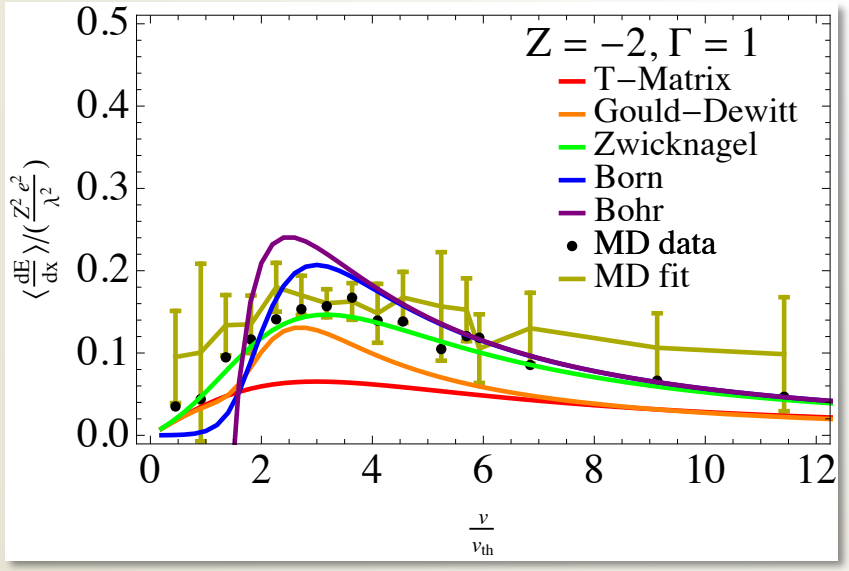


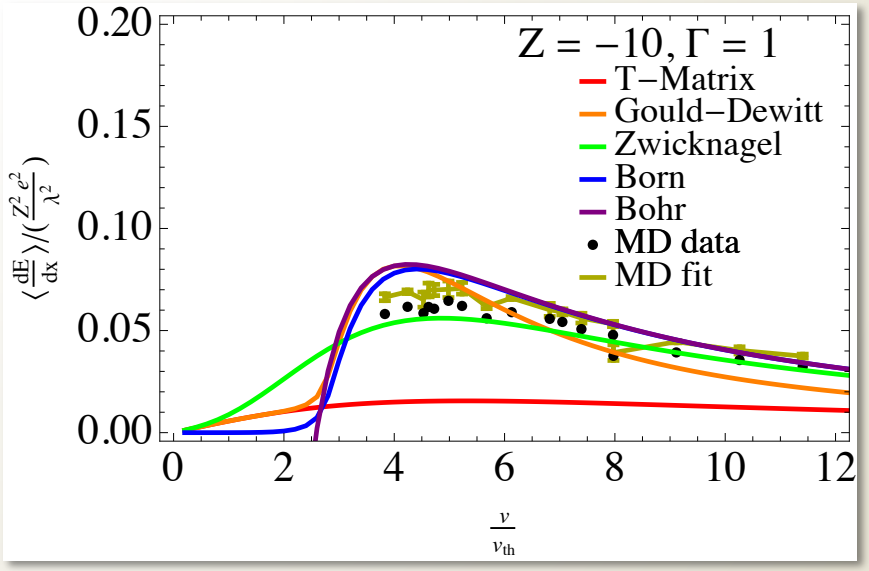
Kudos, kudos, kudos: Mike Surh (LLNL)

Stopping of Fast Particles: Theory Validation

- ✓ Detailed simulations of charged particle energy loss are producing "data" for model validation.





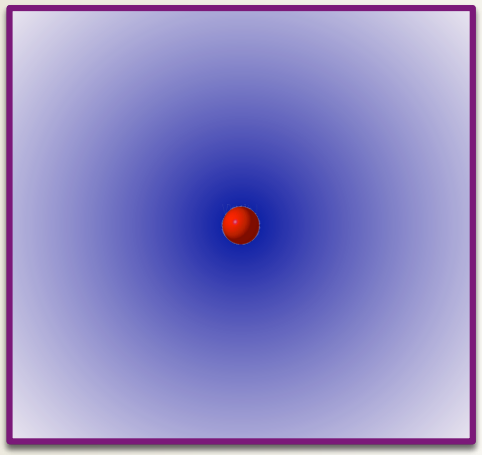


Kudos, kudos, kudos: Paul Grabowski (LANL)

(paper *in preparation*)

Linear Polarization Correction to OCP: Yukawa

Except under very high temperature and/or density HED conditions, particles *do not* have uniform densities.



The response of the background (here, electrons) can be obtained using linear response functions, such as the dielectric response function.

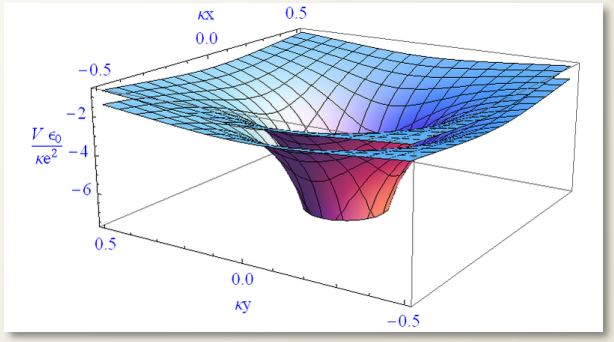
$$\begin{aligned} u_{eff}(k) &= \frac{u_c(k)}{\epsilon(k)} \\ &= \frac{4\pi(Ze)^2/k^2}{1+k_s^2/k^2} \end{aligned}$$

$$\begin{aligned} k_s^2 &= 4\pi e^2 \frac{\partial n}{\partial \mu} \\ &= \frac{4\pi n e^2}{T} \frac{F_{-1/2}(\mu/T)}{F_{1/2}(\mu/T)} \end{aligned}$$

"Fermi integrals" give screening at arbitrary degeneracy.

Yukawa Potential

$$u_Y(r) = \frac{(Ze)^2}{r} e^{-k_s r}$$

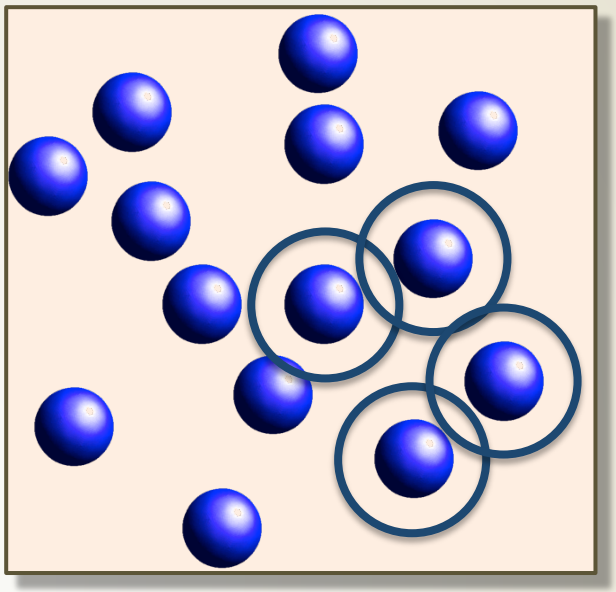


en.wikipedia.org/wiki/Thomas-Fermi_screening

Yukawa Model: Linear Model?

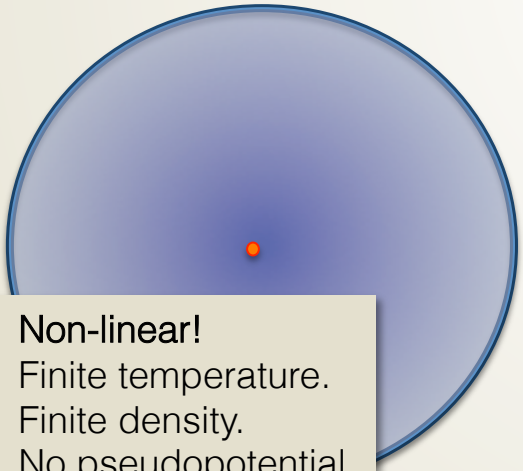
But wait, you have a dense plasma and you are using a *linear theory*?

$$a = \left(\frac{3}{4\pi n}\right)^{1/3}$$



Assume that the electronic structure is a superposition of overlapping spheres.

Compute electronic structure within an average atom.



- Non-linear!
- Finite temperature.
- Finite density.
- No pseudopotential.

Separate:

1. Strongly interacting states: “bound”.
2. Weakly interacting states: “free”.

“Ahhh…this is where you put the rabbit *into* the hat!” Sam Trickey

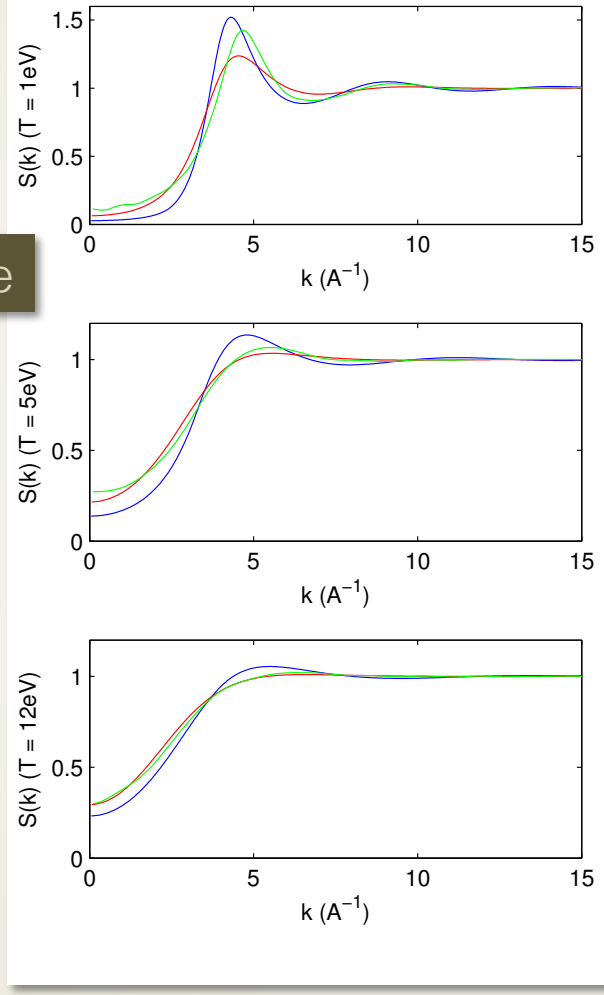
$$u_Y(r) = \frac{\langle Z \rangle^2 e^2}{r} e^{-r/\lambda}$$

The Yukawa Model Has Been Validated

$$S(k) - 1 = n \int d^3r \; [g(r) - 1] \, e^{i\mathbf{k}\cdot\mathbf{r}}$$

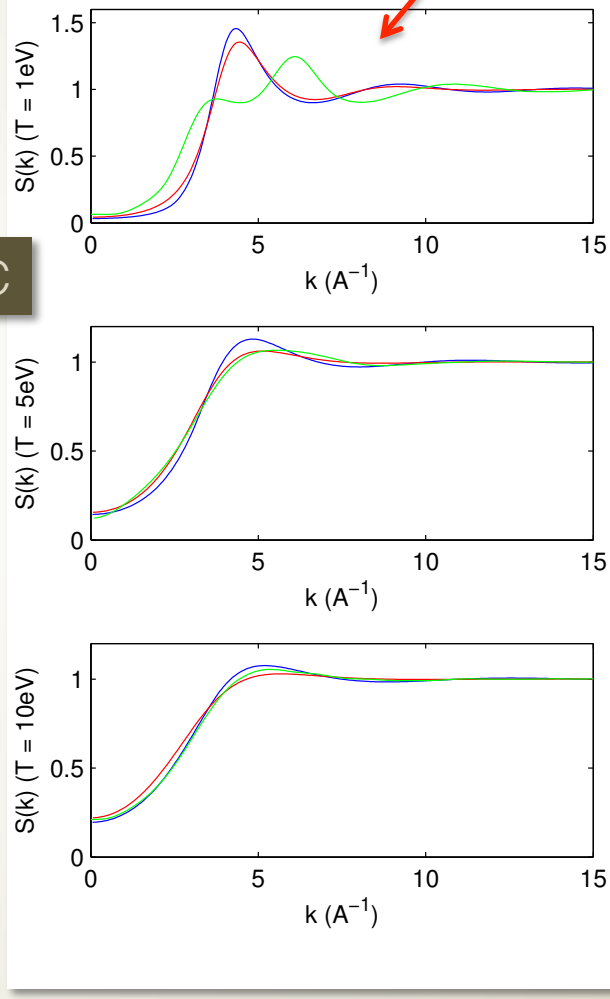
- QMD
- Yukawa
- SOCP

Be



C

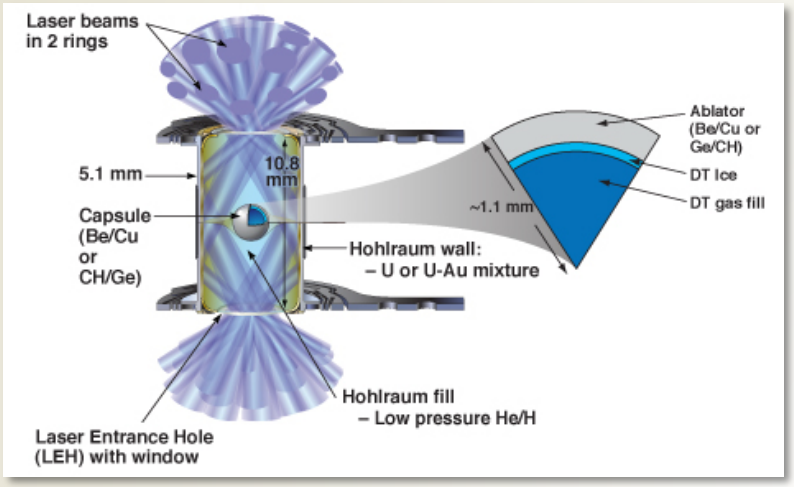
Yukawa qualitatively fails!



With: John Benage (LANL), Liam Stanton (LLNL), Mike Desjarlais (SNL) (*in preparation*)

Interface Mixing Example: Fuel-Pusher Interface

Mixing of ablator material into fusion fuel spoils ignition and burn.



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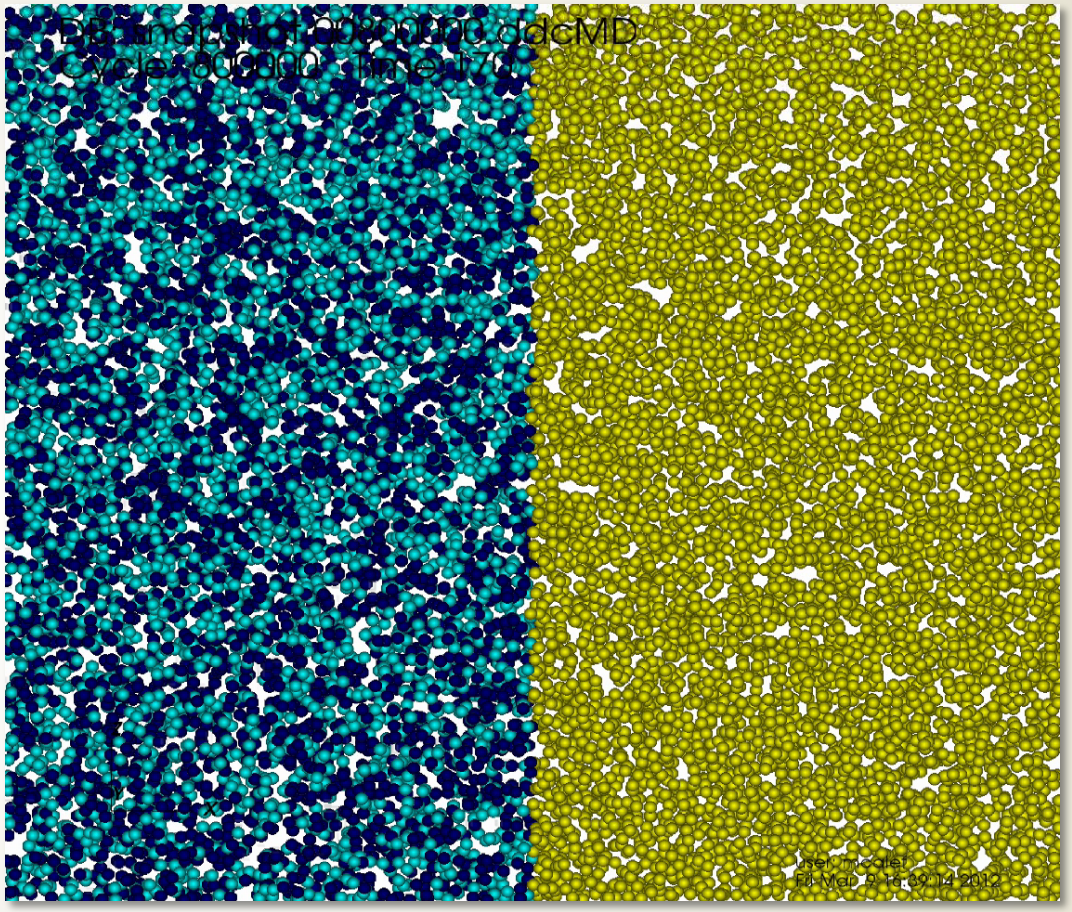


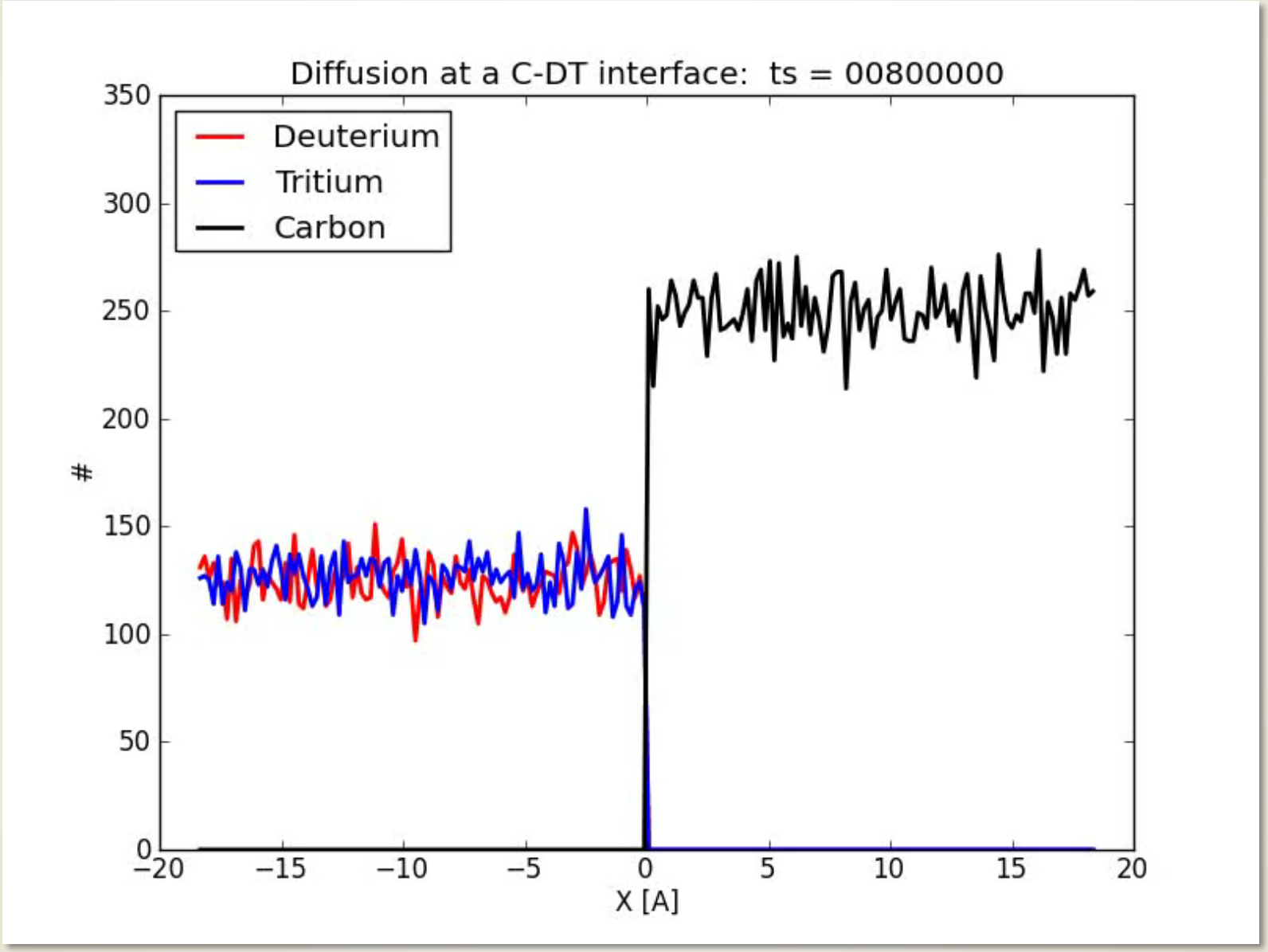
- All species at 300eV; n=1e24/cc
- C=gold, T=cyan, D=blue
- 50,000 total particles

Kudos: Chris Fichtl and Matt Calef (LANL)!

A Yukawa model:

- Mixing takes place on ion time scales.
- Assume fuel is fully ionized.
- Assume a carbon ablator stripped to He-like core.
- Is Fick's Law valid? (Knudsen gas?)

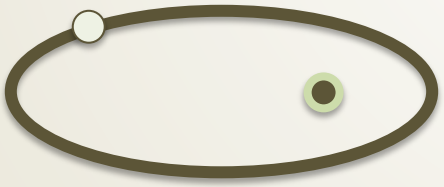
Diffusion Profiles Near Fuel-Pusher Interface



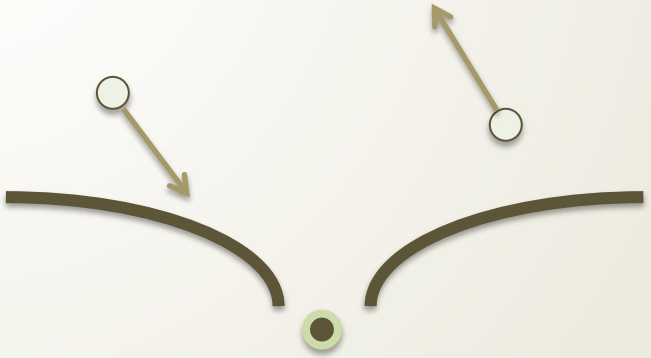
Dynamic Electrons

When dynamical processes occur on electron time scales, we must directly simulate the electrons.

1. **Easy:** treat electrons as one component plasma (OCP).
2. **Very, very hard:** need to treat electrons and ions.
   - External fields (laser absorption, stopping of fast particles)
   - Transport (electrical and thermal conduction, diffusion)
   - Relaxation to equilibrium



Two-body: simple Kepler orbits



Three-body: atomic recombination

Options For Forces: Dynamic Electrons

There are very few options today.

1. Soften electron-ion interaction to prevent collapse. Choose some application-specific cutoff; for example, to get the ground-state energy correct.

2. Wave Packet Molecular Dynamics (WPMD). Evolve Gaussian wavepacket according to the time dependent Schrodinger equation. (*See Grabowski talk….*)

3. Momentum-dependent potentials. Form potentials that depend on separations in coordinate and momentum spaces to exclude phase space occupation according to Heisenberg uncertainty.

4. Quantum Statistical Potentials. Derive effective potentials by rewriting quantum partition function to have a classical form.

Quantum Statistical Potentials (QSPs)

$$
\begin{aligned}
e^{-\beta F} &= Tr\left[e^{-\beta \hat{H}}\right] \\
&= \int d\mathcal{R}\left\langle \mathcal{R}\left|\exp\left(-\beta\hat{H}\right)\right|\mathcal{R}\right\rangle \\
&= \mathcal{C}\int d^{3N}p\, e^{-\beta T}\int d\mathcal{R}\left\langle \mathcal{R}\left|\exp\left(-\beta\hat{H}\right)\right|\mathcal{R}\right\rangle \\
&\equiv \mathcal{C}\int d^{3N}p\int d\mathcal{R}\, e^{-\beta(T+U(\mathcal{R}))}
\end{aligned}
$$

Now, approximations must be made…..

Diffraction:

$$
\begin{aligned}
U(r) &= \frac{Z_1 Z_2 e^2}{r}\left(1-\exp(-r/\lambda)\right) \\
&\rightarrow \frac{Z_1 Z_2 e^2}{\lambda}
\end{aligned}
$$

Pauli:

$$U_P(r) = -\beta^{-1}\ln\left(1-\frac{1}{2}e^{-r^2/\lambda^2}\right)$$

$$\lambda = \frac{\hbar}{\sqrt{\pi m_e T}}$$

Temperature Relaxation In Dense Mixtures

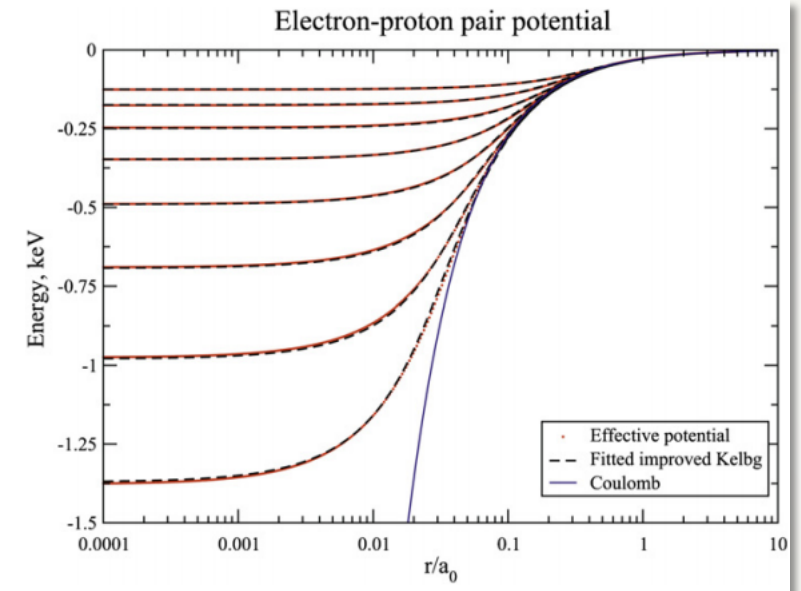


Fig. 2. Comparison of effective potentials for an electron-proton pair calculated from Eq. (14) (red) using the matrix squaring method. The fitted potential from Eq. (15) is shown as black dashed lines. The dashed blue curve is the Coulomb potential. The effective potential is shown for eight different temperatures (from top to bottom: T = 86 eV, 172 eV, 345 eV, 689 eV, 1.4 keV, 2.8 keV, 5.5 keV, 11 keV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

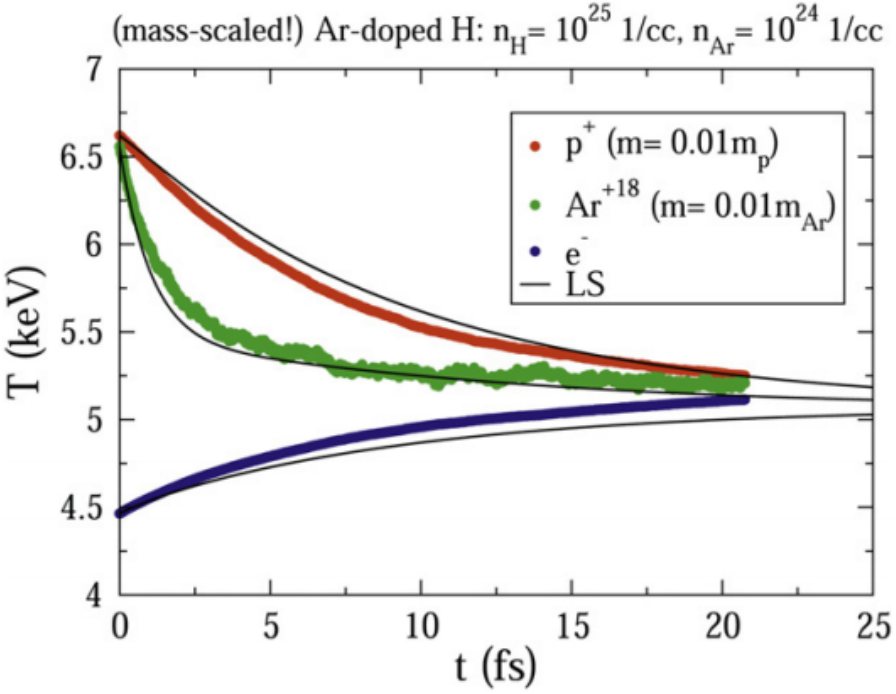
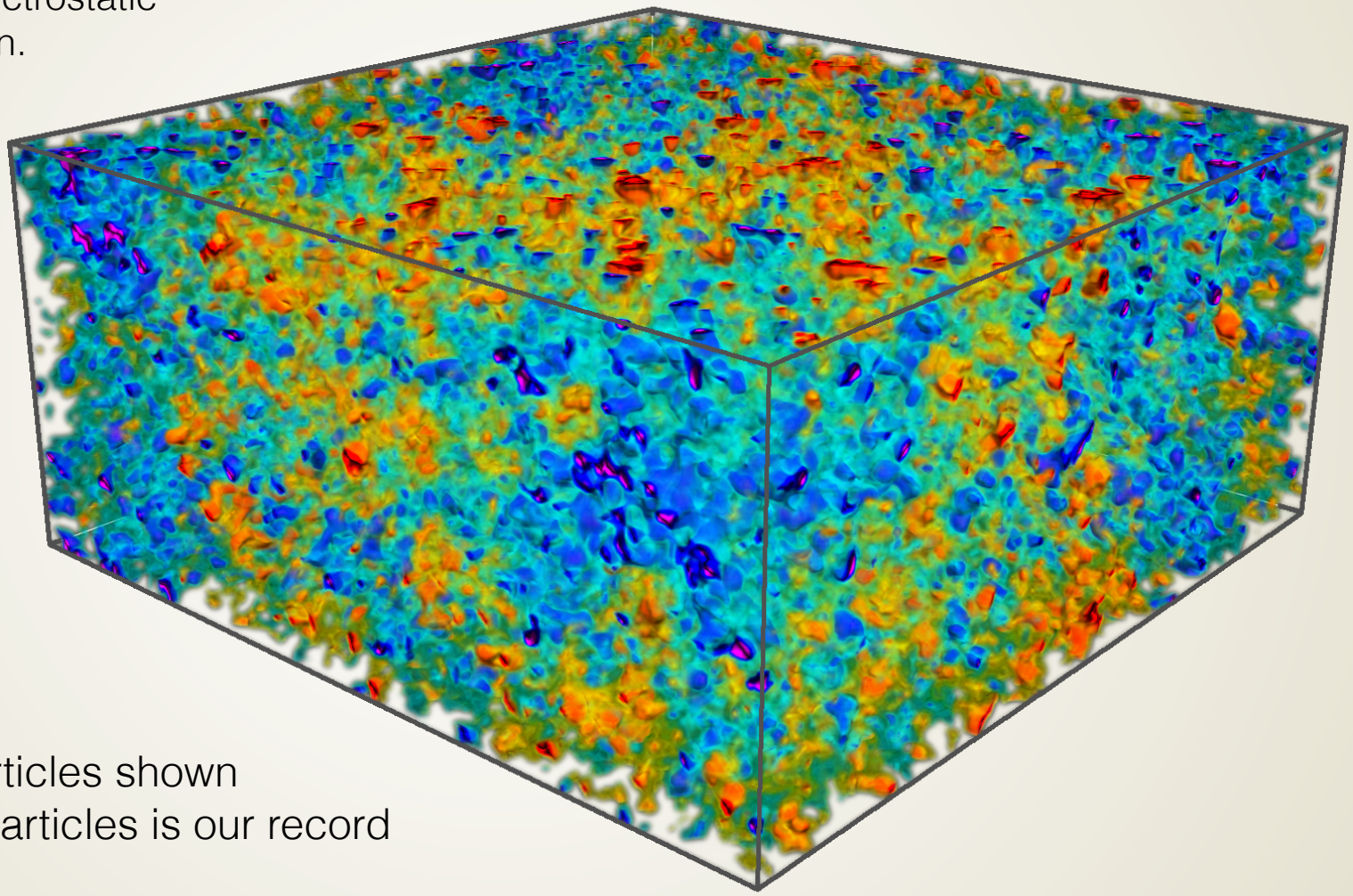


Fig. 7. Time-dependent temperatures of the (mass-scaled!) Ar-doped H plasma (see text) as computed by MD with the Dunn-Broyles potentials. Also plotted are the results of Landau-Spitzer with judiciously chosen Coulomb-logarithms.

F.R. Graziani et al. / High Energy Density Physics 8 (2012) 105–131

Mesoscale Plasma MD I: ddcMD

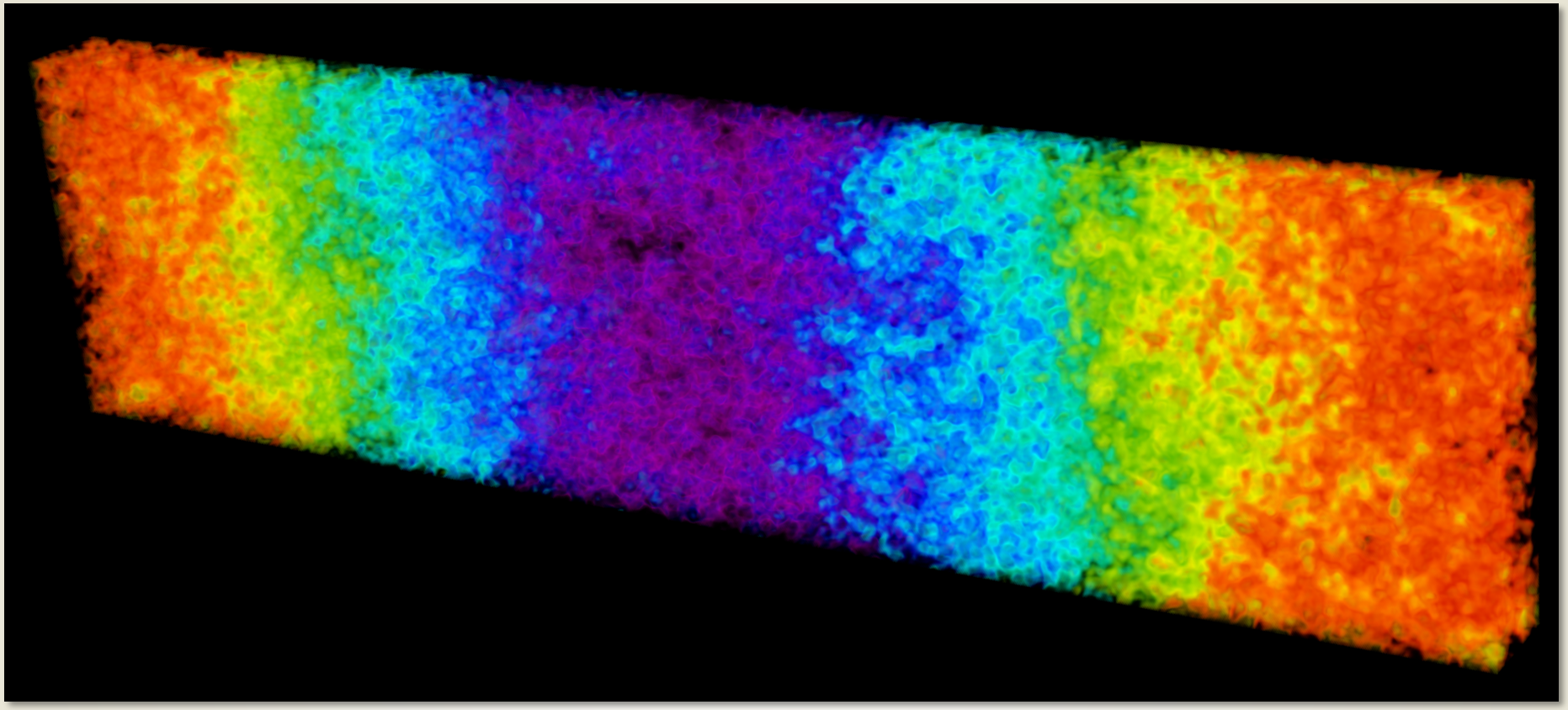
Instantaneous electrostatic potential is shown.



- D, T, e, Ar, α

140,000,000 particles shown
2,800,000,000 particles is our record

Mesoscale Plasma MD II: ddcMD



- 400,000,000 particles.
- Dense proton beam in dense hydrogen.

HEDP Problems Encourage Advanced Integrators

Returning to Hamilton…

$$\begin{aligned}
\frac{d}{dt}A\left(q(t),p(t)\right) &= \sum_i \frac{\partial A}{\partial p_i}\frac{dp_i}{dt} + \frac{\partial A}{\partial q_i}\frac{dq_i}{dt} \\
&= \sum_i \frac{\partial A}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial H}{\partial q_i} \\
&\equiv [A,H]_{PB} \\
&= \sum_i \left[\frac{p_i}{m}\frac{\partial}{\partial q_i} - \frac{\partial U}{\partial q_i}\frac{\partial}{\partial p_i}\right] A \\
&\equiv i\hat{L}A
\end{aligned}$$

Hamilton equations.

Poisson bracket.

Liouville operator.

We now have an *exact* solution to classical mechanics:

$$\begin{aligned}
A(t) &= e^{i\hat{L}t}A(0) \\
&= \hat{U}(t)A(0)
\end{aligned}$$

In this form:

- classical mechanics is time reversible
- new *(q(t),p(t))* are canonical transformations of *(q(0),p(0))*
  - ✓ *flow map is symplectic; Liouville theorem*
- propagator built from exponentials of derivatives

Three Useful Theorems

The Poisson bracket is linear:

$$\begin{aligned} [A, H_1 + H_2]_{PB} &= [A, H_1]_{PB} + [A, H_2]_{PB} \\ i\hat{L}A &= i\hat{L}_1 A + i\hat{L}_2 A \end{aligned}$$

Exponentials of derivatives are translations:

$$e^{a\frac{d}{dx}} f(x) = f(x + a)$$

Baker-Campbell-Hausdorff/Trotter/Strang:

$$e^{A+B} = \lim_{P\to\infty} \left[e^{B/2P} e^{A/P} e^{B/2P} \right]^P$$

Reversible multiple time scale molecular dynamics

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Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Semi-Implicit Euler and Velocity-Verlet

Because we usually have separable Hamiltonians, it often makes sense to define separate Liouville operators for the kinetic and potential energies.

$$\begin{aligned} \hat{L} &= \hat{L}_T + \hat{L}_U \\ \hat{U}_{SIE}(t) &\approx e^{i\hat{L}_T t} e^{i\hat{L}_U t} \\ \hat{U}_{VV}(t) &\approx e^{i\hat{L}_U t/2} e^{i\hat{L}_T t} e^{i\hat{L}_U t/2} \end{aligned}$$

Construction of higher order symplectic integrators

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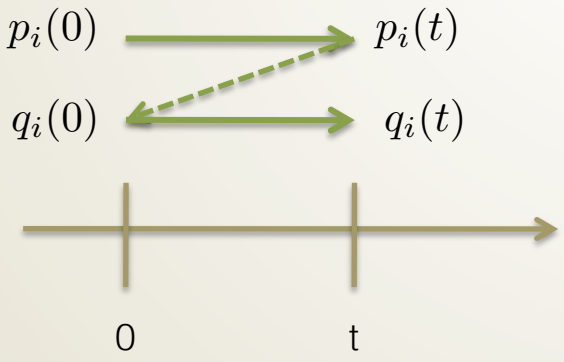
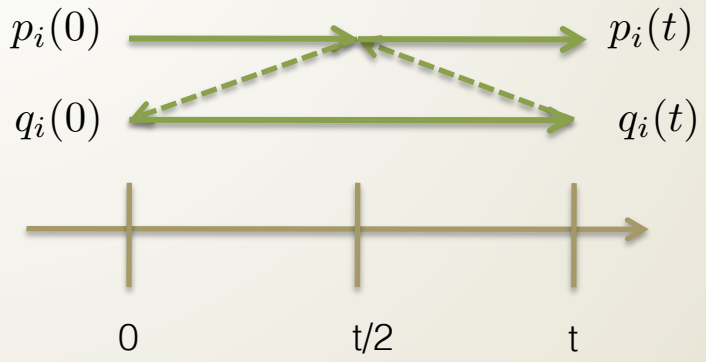
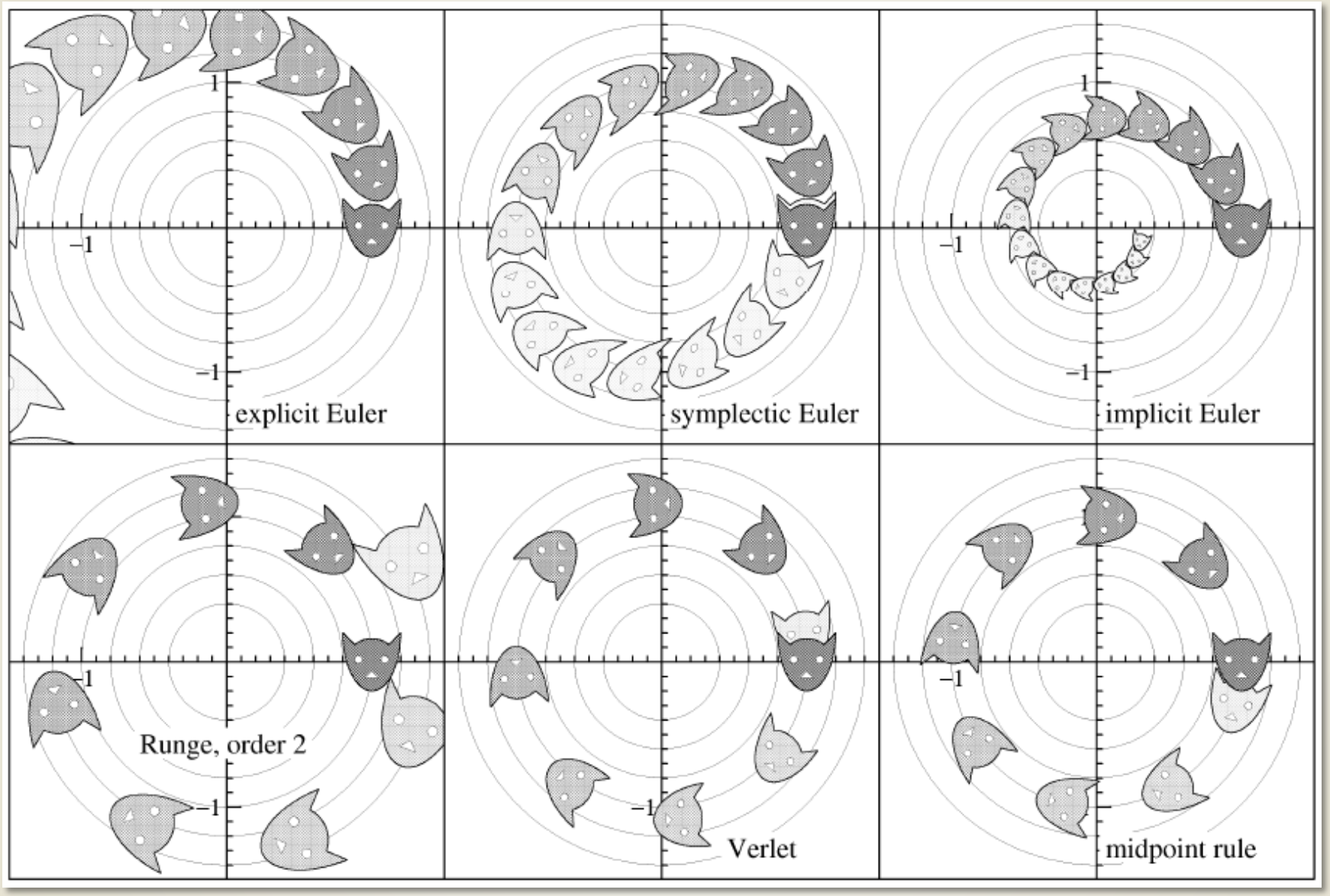
first step:

$$\begin{aligned} \begin{pmatrix} p_i(t) \\ q_i(t) \end{pmatrix} &= \exp\left(-\frac{\partial U}{\partial q_i} t \frac{\partial}{\partial p_i} \right) \begin{pmatrix} p_i(0) \\ q_i(0) \end{pmatrix} \\ &= \begin{pmatrix} p_i(0) - \frac{\partial U}{\partial q_i} t \\ q_i(0) \end{pmatrix} \end{aligned}$$





Integrator Comparison



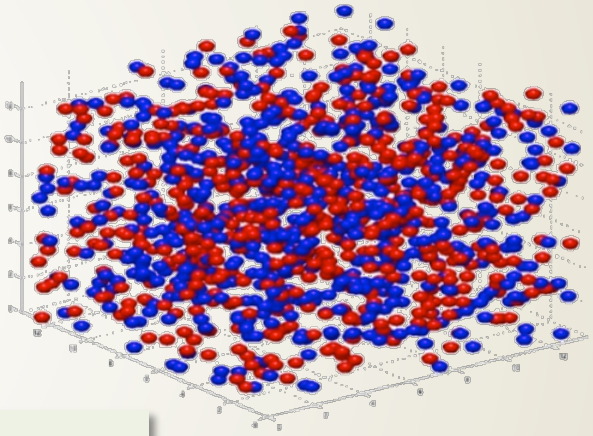
Multiple Time-Step (MTS) Methods

A general class of integrators can be constructed that are known as RESPA (*reference system propagator algorithms*) methods. There are essentially two types: MTS and NAPA (next slide).

Here, we will only consider reversible methods, or r-RESPA methods.

For HED applications, consider the case in which we perform MD with dynamical electrons and ions.

1. Lighter electrons control time step.
2. Long range forces change more slowly.



$$\begin{aligned} \hat{L} &= \hat{L}_e + \hat{L}_i \\ U_{mass}(t) &\approx \exp\left(i\hat{L}_i\Delta t/2\right)\exp\left(i\hat{L}_e\Delta t\right)\exp\left(i\hat{L}_i\Delta t/2\right) \end{aligned}$$

$$\exp\left(i\hat{L}_e\Delta t\right) \approx \left[\exp\left(i\hat{L}_{U,e}\Delta t/(2P)\right)\exp\left(i\hat{L}_{T,e}\Delta t/P\right)\exp\left(i\hat{L}_{U,e}\Delta t/(2P)\right)\right]^P$$

An analogous separation can be made by rearranging the Hamiltonian into short and long-range forces.

Numerical Analytic Propagator Algorithms (NAPA)

If you are lucky, the fastest time scales are associated with components of the model that have analytic solutions. These components can be "split" and solved exactly with a large time step.

- In biology, some bonds are treated as harmonic.
- For 1/r potentials, the Kepler solution is available.

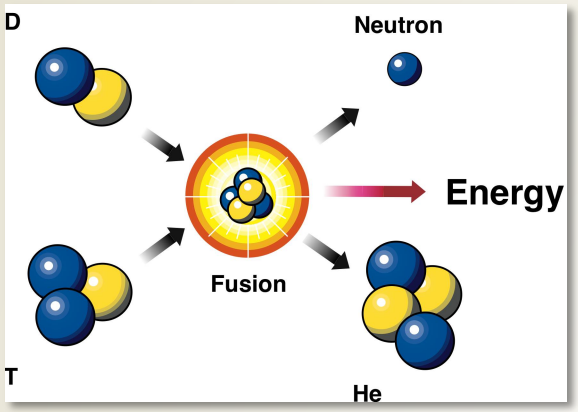
Johannes Kepler

$$
\begin{aligned}
\hat{L} &= \hat{L}_{simple} + \hat{L}_{complicated} \\
\hat{L}_{simple} &= \hat{L}_T + \hat{L}_{U,known} \\
U_{NAPA}(t) &\approx \exp\left(i\hat{L}_{complicated}\Delta t/2\right) \exp\left(i\hat{L}_{simple}\Delta t\right) \exp\left(i\hat{L}_{complicated}\Delta t/2\right)
\end{aligned}
$$

propagate exactly

If the "simple" part is stiff, this can potentially save an "order of magnitude" of run time.
However, actual scaling is problem dependent.

A Worked Example: MD At Kilovolt Temperatures



At high temperature there are very close collisions; the Coulomb barrier can be overcome by very fast particles.

This is, in fact, important and physical since these rare events can lead to fusion events that produce useful energy.

This suggests a "triggered" MTS/NAPA method.

$$\hat{U}(t) = \hat{U}_{VV}(t) \cdot \hat{U}_{VV}(t) \cdots \hat{U}_{MTS/NAPA}(t) \cdots \hat{U}_{VV}(t) \cdot \hat{U}_{VV}(t)$$

trigger

Algorithm:

1. Close collision?
2. If 'no', use Velocity Verlet, as usual.
3. If 'yes', temporarily insert modified propagator.
4. Repeat

Choices:

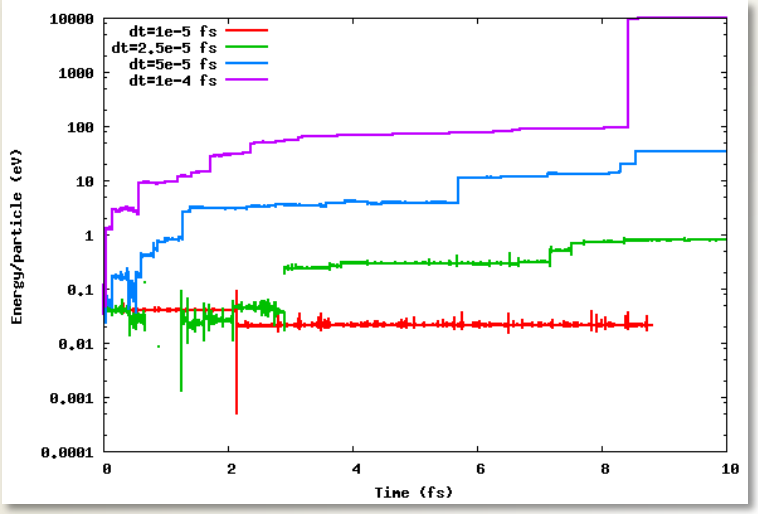
1. "Very-Binary" events: Kepler orbit
2. "Cluster" events: MTS with thousands of steps

exact *Velocity Verlet*

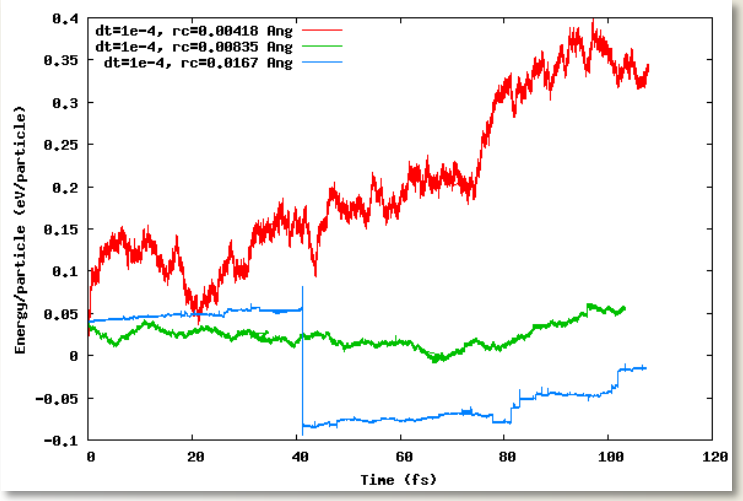
$$\begin{aligned} H &= H_{pair} + H_{background} + U_{coupling} \\ \hat{U}_{background}(t) \cdot V_{pair} &= 1 \\ \hat{U}_{pair}(t) \cdot V_{background} &= 1 \\ \hat{U}(t) &\approx \exp\left(i\hat{L}_{coupling}t/2\right) \cdot \exp\left(i\hat{L}_{pair}t\right) \exp\left(i\hat{L}_{background}t\right) \cdot \exp\left(i\hat{L}_{coupling}t/2\right) \end{aligned}$$

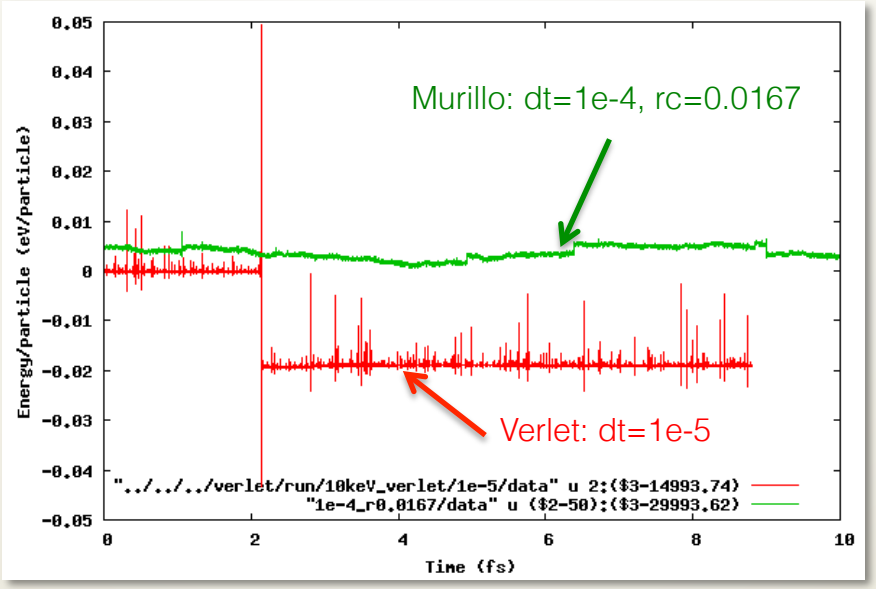
Triggered NAPA Results

32768 Ions (50/50 DT mix); 1e26/cm^3;
T=10keV, Velocity Verlet integrator



32768 Ions (50/50 DT mix); 1e26/cm^3;
T=10keV, new Murillo integrator





Numerical tests by Dave Richards (LLNL).

(paper *in preparation*)

Summary and Outlook

- High energy-density environments span a very large range of physical conditions.
- Molecular dynamics can address many important questions across this range. A major challenge is high temperature MD.
- Choosing the forces is a key issue. Many are understood (OCP, Yukawa, QSPs).
  - *Time-dependent, attractive forces are an open problem.*
  - *We would like to not refer to the ionization state: OF-DFT, etc.*
- Many problems of interest involve disparate time and length scales.
  - *Brute force HPC has made very large strides.*
  - *An open area is multi-scale simulations that couple MD to larger scales.*

Thank You!