Dynamical Electron Models in Molecular Dynamics

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CIMARRON

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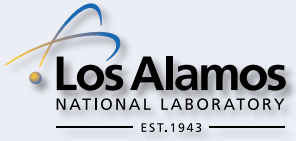
The Cimarron Team



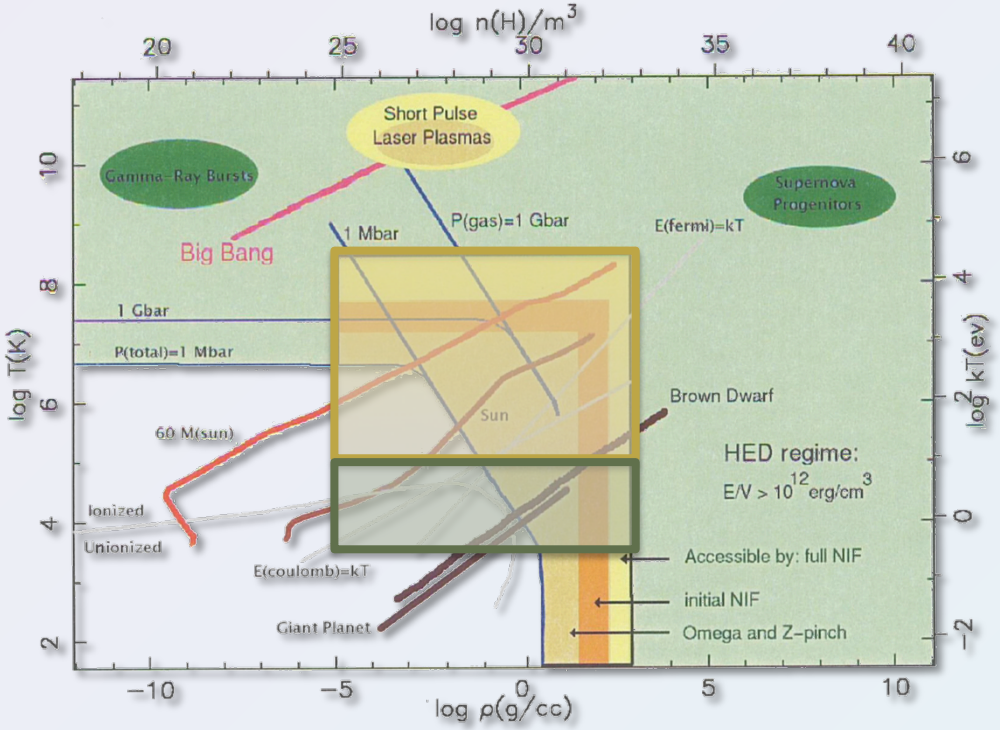



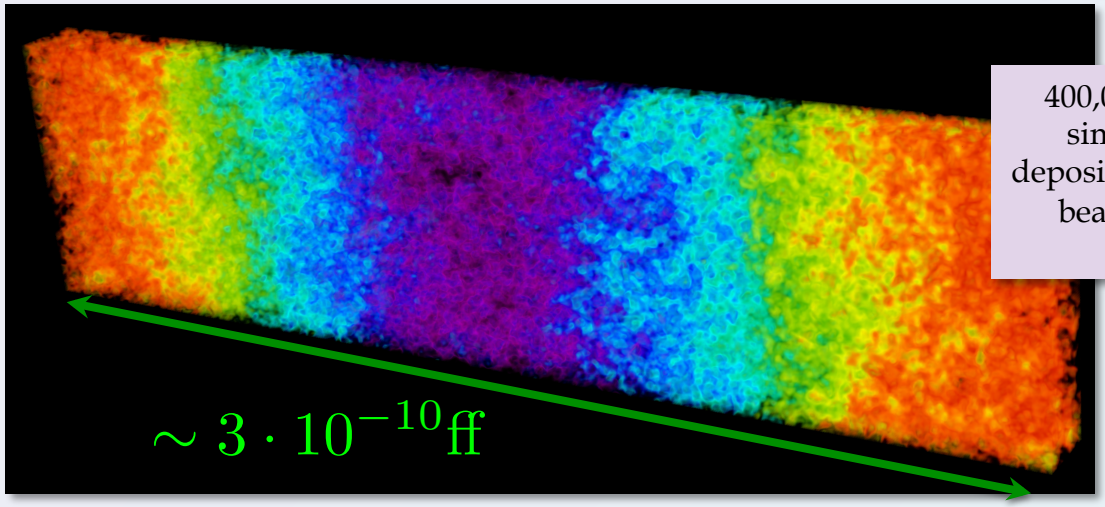
V. Batista, J. Bauer, L. Benedict, M. Calef, J. Castor, S. Chen, M. Desjarlais, I. Ellis, **C. Fichtl**, **J. Glosli**, **P. Grabowski**, A. Graf, **F. Graziani**, S. Hau-Riege, T. Haxhimali, A. Hazi, S. Khairallah, L. Krauss, B. Langdon, R. London, **A. Markmann**, R. More, **M. S. Murillo**, D. Richards, R. Rudd, H. Scott, R. Shepherd, L. Stanton, F. Streitz, M. Surh, J. Weisheit, **H. Whitley**

Regimes and Problems of Interest

Goal: Create a virtual laboratory for the study of hot dense matter with a focus on collisional processes that control fusion.

- dense plasma physics (coupling and degeneracy)
- non-equilibrium processes
- finite mean free path physics
- microscopic self-consistency
- *warm dense matter (experiments)*





400,000,000 particle MD simulation of energy deposition of a dense proton beam into a hydrogen plasma (QSPs)

Cimarron's Tool is Molecular Dynamics

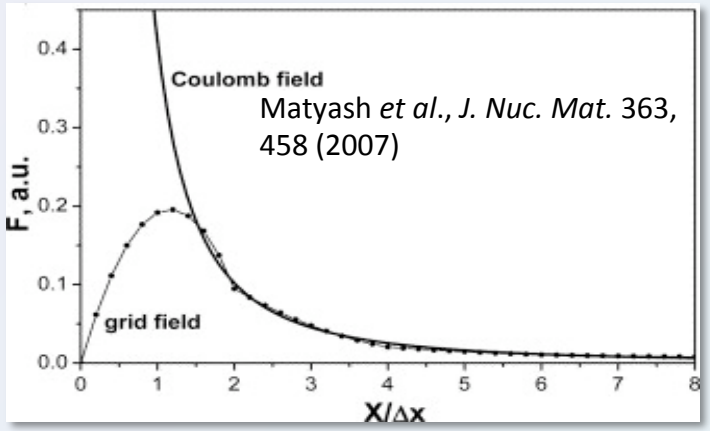
1) MD simulates *real* particles to yield an understanding of how many-body interactions determine *time-dependent* material properties.

2) Particles are treated as discrete objects and forces are computed to high precision ("exactly"). That is, a premium is placed on details of **particle-particle interactions**.

3) Typically, MD is implemented as an atomistic method. The particles are electrons and/or ions.

We solve:

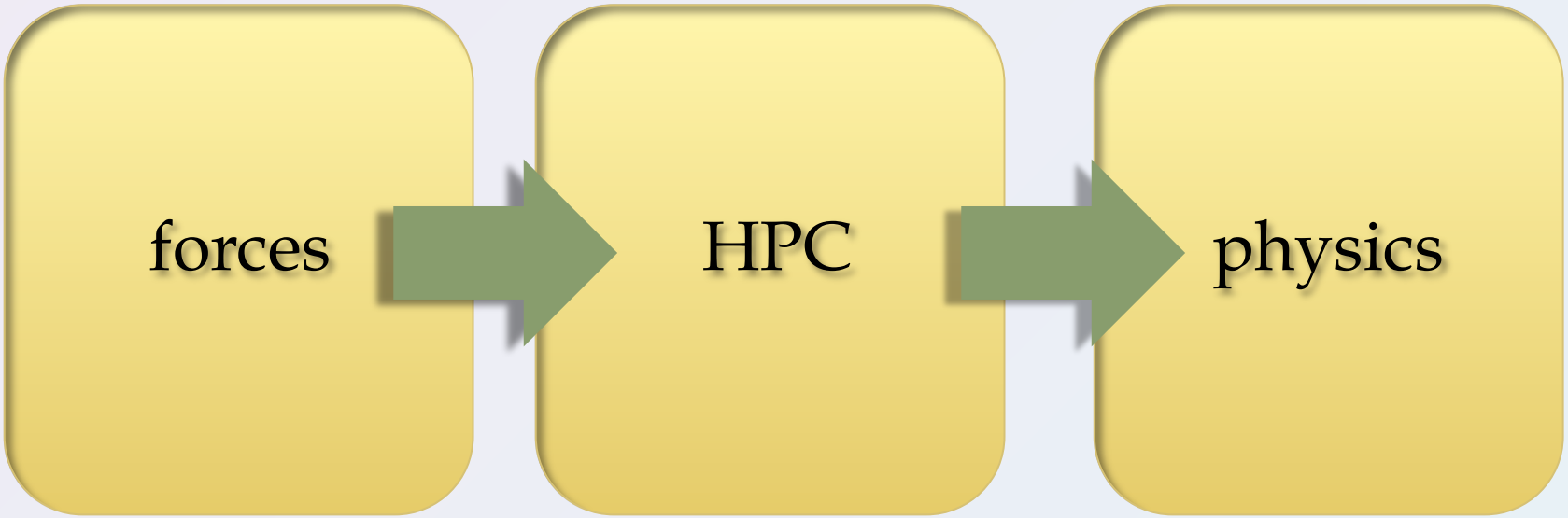
$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{i<j} \mathbf{F}_{ij}$$



Matyash *et al.*, *J. Nuc. Mat.* 363, 458 (2007)

Because MD's strength is the particle-particle interaction, getting the force right is absolutely essential.

Garbage In, Garbage Out



Forces in Hot Dense Matter

- A hard problem is choosing ion-ion potentials.
  - ✓ pure Coulomb (OCP)
  - ✓ screened Coulomb (Yukawa)
  - ✓ OF-DFT (Thomas-Fermi-like models)
  - ✓ DFT ("QMD")
- A much harder problem is *dynamic* electrons in the presence of the ions.

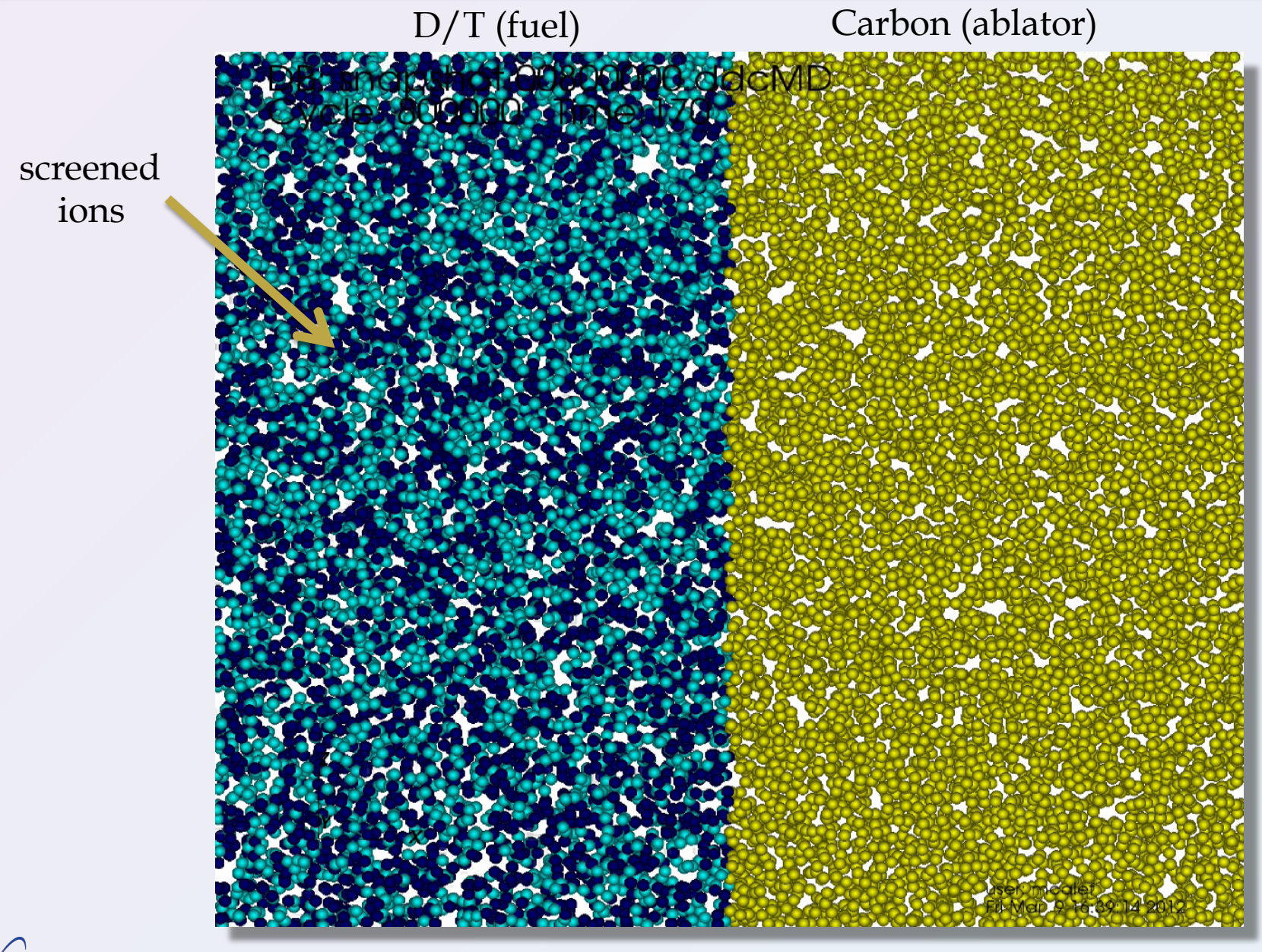
Why?

1. Time-dependent quantum mechanics is harder and less developed.
2. Electrons form bound atomic states.

Who cares?

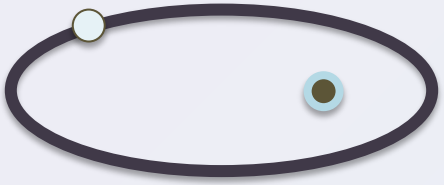
1. Thermal, electrical conduction
2. Fast particle stopping
3. Temperature relaxation
4. Inverse bremsstrahlung
5. Etc.

Some Ion-Physics Problems Require Dynamical Electrons

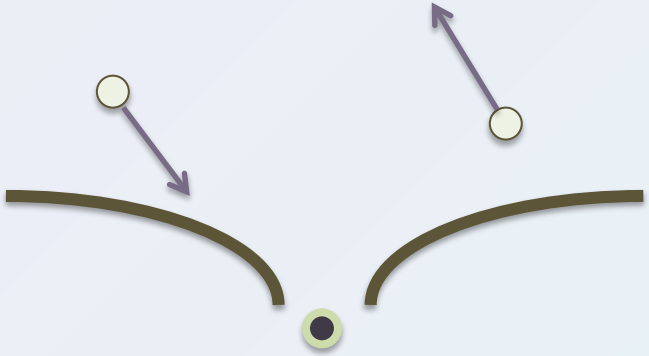


What Physical Properties Do We Wish To Capture?

1. Prevent the Coulomb Catastrophe.
2. ICF plasmas are mildly degenerate.
3. Fast ignition plasmas even more degenerate.
4. Minimum impact parameter set by deBroglie wavelength.
5. Validation by experiments often in WDM regime.



Two-body: simple Kepler orbits



Three-body: atomic recombination

Cimarron Is Exploring Several Methods Simultaneously

- Different problems require different solutions
- Cross comparison among competing methods

1. **Quantum Statistical Potentials (QSP) (Whitley)**

2. **Wave Packet Molecular Dynamics (WPMD) (Grabowski)**

3. **Kinetic Theory Molecular Dynamics (KTMD) (Fichtl)**

Quantum Statistical Potentials

(QSPs)

Quantum Statistical Potentials (QSPs)

MD codes are designed to solve a classical problem. Can we make quantum mechanics look like classical mechanics?

Utilize well-known properties of the quantum partition function.

$$\beta = (k_B T)^{-1}$$

$$\hat{H} = \hat{T} + \hat{U}$$

$$|\mathcal{R}\rangle = |\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\rangle$$

$$\begin{aligned} Z &= \sum_s e^{-\beta E_s} \\ &= \sum_s \langle s| e^{-\beta \hat{H}} |s\rangle \\ &= Tr\left[e^{-\beta \hat{H}}\right] \\ &= \int d\mathcal{R} \langle \mathcal{R}| e^{-\beta \hat{H}} |\mathcal{R}\rangle \end{aligned}$$

Classical mechanics looks similar….

$$Z_{CM} = \frac{1}{N!(2\pi\hbar)^{3N}} \int d^{3N}p \, d^{3N}r \exp\left[-\beta\left(\sum_i \frac{p_i^2}{2m_i} + \sum_{i<j} U(r_{ij})\right)\right]$$

Defining the QSP Formally

Key observations:

1. Gaussian integrals in classical form are trivially done.
2. Expectation of density operator is positive.

$$
\begin{aligned}
Z &= \int d\mathcal{R}\, \langle \mathcal{R}|\, e^{-\beta \hat{H}}\, |\mathcal{R}\rangle \\
&= \mathcal{C} \int d^{3N}p\, d\mathcal{R}\, e^{-\beta T_{CM}}\, \langle \mathcal{R}|\, e^{-\beta \hat{H}}\, |\mathcal{R}\rangle \\
&= \mathcal{C}' \int d^{3N}p\, d\mathcal{R}\, e^{-\beta T_{CM}}\, \frac{\mathcal{C}}{\mathcal{C}'}\, \langle \mathcal{R}|\, e^{-\beta \hat{H}}\, |\mathcal{R}\rangle \\
&\equiv \mathcal{C}' \int d^{3N}p\, d\mathcal{R}\, e^{-\beta (T_{CM} + \mathcal{U}(\mathcal{R}))} \\
\mathcal{C}' &= \frac{1}{N!(2\pi\hbar)^{3N}}
\end{aligned}
$$

$$
\frac{\mathcal{C}}{\mathcal{C}'}\, \langle \mathcal{R}|\, e^{-\beta \hat{H}}\, |\mathcal{R}\rangle \equiv e^{-\beta \mathcal{U}(\mathcal{R})}
$$

Nothing has been done, yet. But, we have identified the object we need to work with.

Two approximations:

1. Assume antisymmetry is additive: *Pauli potential*
2. Assume that total interaction is sum over pairs: *diffractive potential*

Density Dependent Pauli Potentials

- For a finite temperature and density *ideal* Fermi gas, the effective potential can be explicitly written down.
- In a pair approximation, the effective interaction results from the solution of a non-linear integral equation.
- We solved that equation and we fit the result.
- *Important point*: we fit to a density-dependent pair potential.

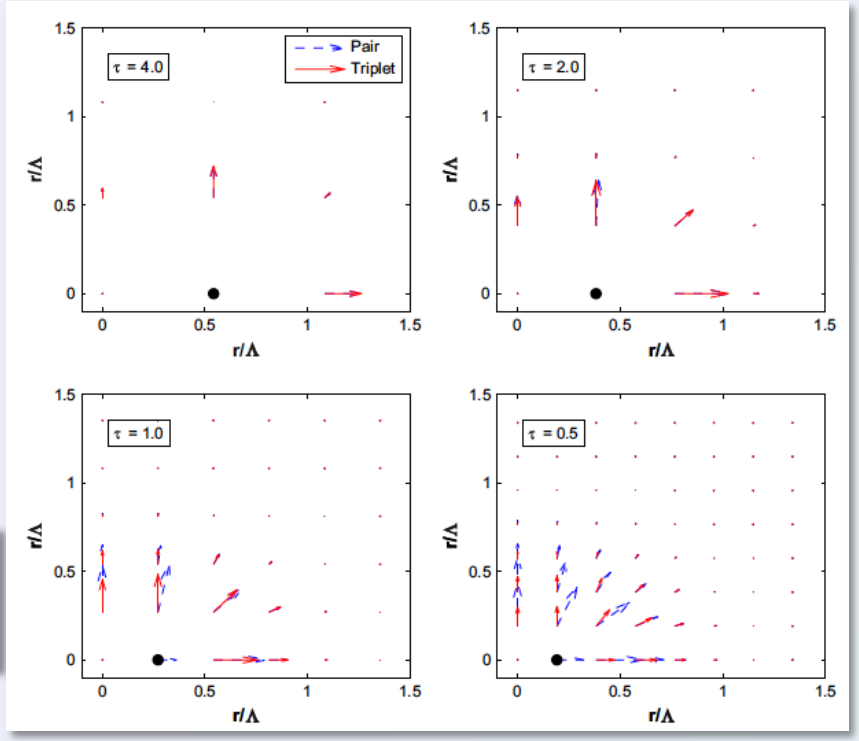
Pauli potential:

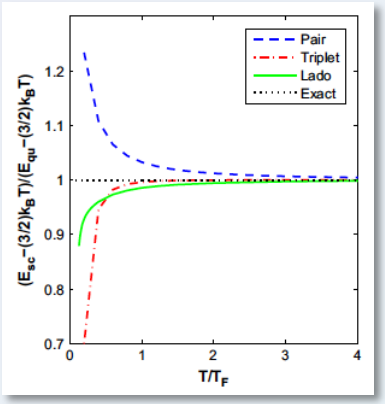
$$u_2(r) = -k_B T \ln\left[1 - \frac{1}{2}A(\tau)\exp\left(-2\pi B(\tau) r^2/\Lambda^2\right)\right]$$

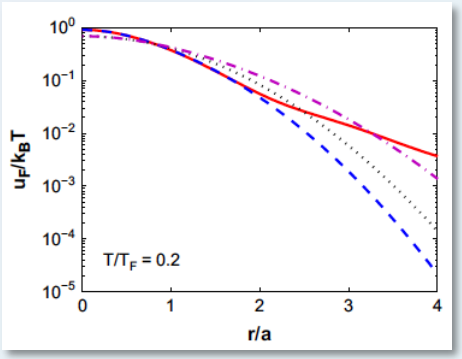
Definitions used:

$$A(\tau) = 1 + \frac{a_1}{1 + a_2 \tau^{a_3}}, \quad B(\tau) = 1 + b_1 \exp\left(-b_2 \tau^{b_3}\right)/\tau^{b_4}$$

$$\Lambda = \sqrt{2\pi\hbar^2/k_B T m} \qquad \tau = \frac{T}{T_F} \propto \left(\frac{a}{\Lambda}\right)^2$$







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Analysis of semi-classical potentials for molecular dynamics and Monte Carlo simulations of warm dense matter

Christopher S. Jones [a,*], Michael S. Murillo [b]

Pair Diffraction Potentials

Solve the Bloch equation perturbatively:

$$\begin{aligned} \hat{\rho} &= e^{-\beta \hat{H}} \\ \frac{\partial \hat{\rho}}{\partial \beta} &= -\hat{H}\hat{\rho} \\ &= -\left(\hat{T}+\hat{U}\right)\hat{\rho} \end{aligned}$$

→ Kelbg potential

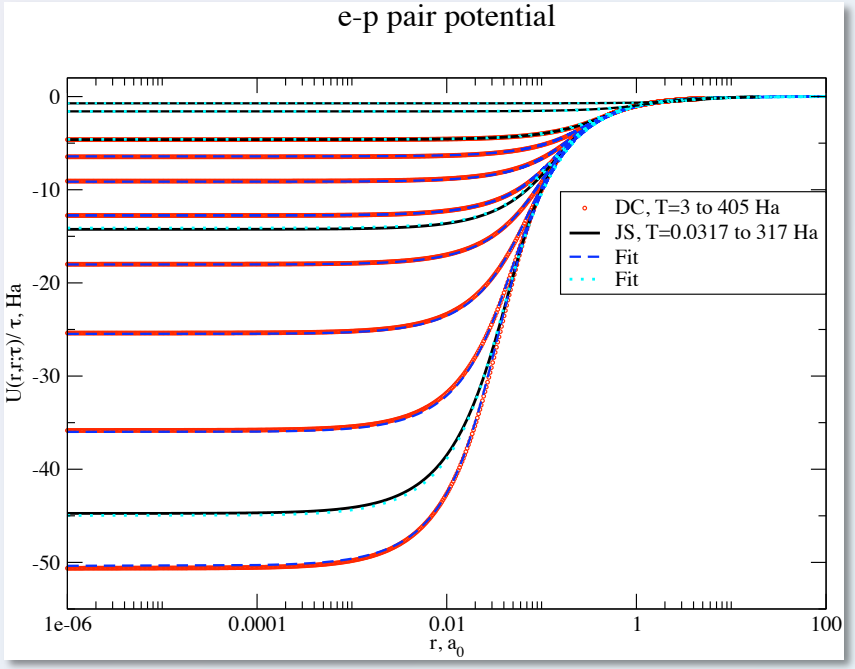
There is no reason not to simply solve this exactly, using solutions of the two-body Schrodinger equation:

$$\rho_2(r,r';\beta) \equiv \sum_s \psi_s(r) e^{-\beta E_s} \psi_s^*(r')$$

$$V_{eff}(r,\beta) = -\frac{1}{\beta}\ln\left(\frac{\rho_2(r,r;\beta)}{\rho_1(r,r;\beta)}\right)$$

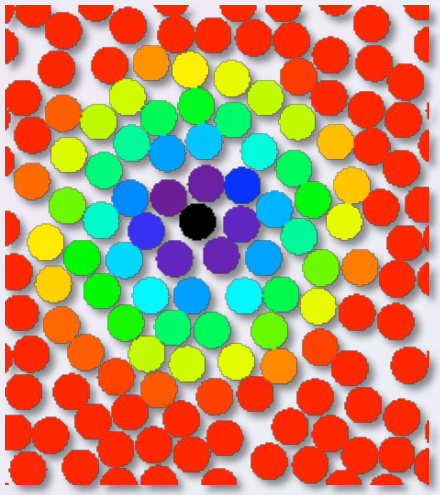
$$V_{eff}(r) = \frac{q_1 q_2}{r}\left[1 - e^{-\left(\frac{r}{\lambda}\right)^2} + \frac{r}{\lambda\gamma}\sqrt{\pi}\left(1 - erf\left(\gamma\frac{r}{\lambda}\right)\right)\right]$$

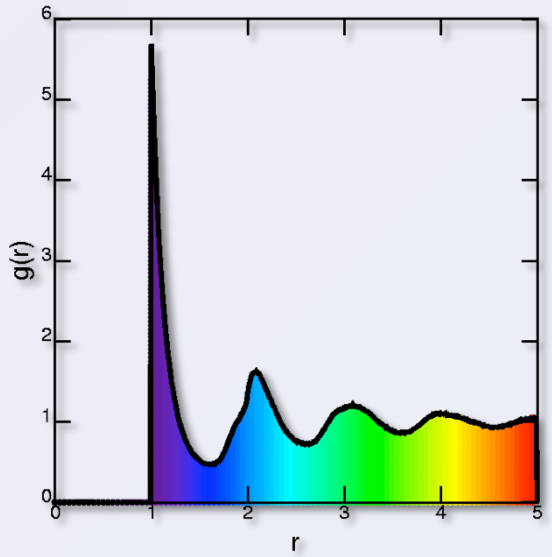
We include contributions from the discrete and continuous spectrum (i.e., bound states are included).



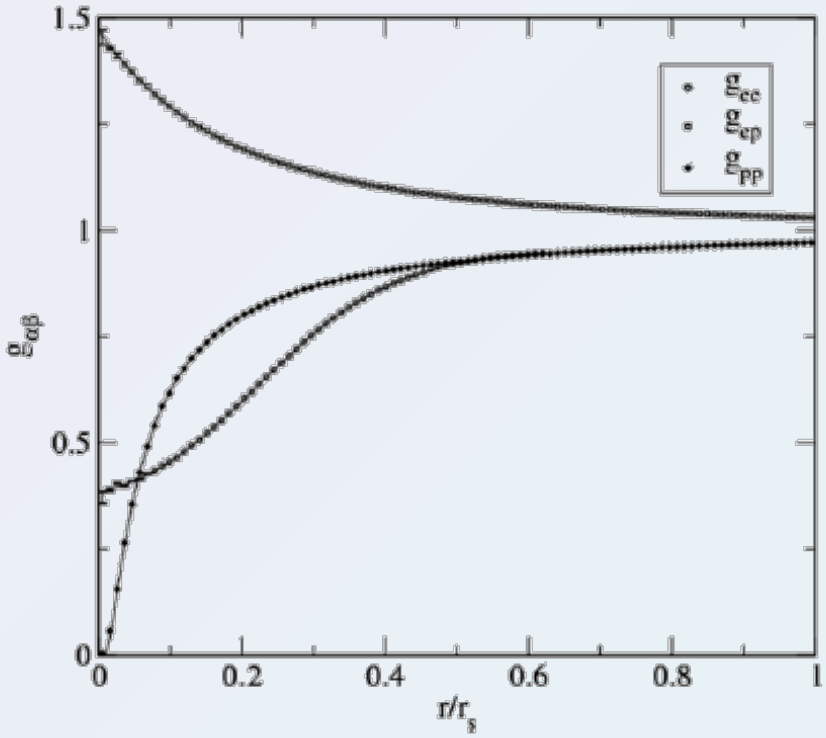
How Well Does This Procedure Work?

Examine the radial distribution functions.





$$P = nT - \frac{1}{6}\sum_{i \neq j} n_i n_j \int d^3 r \, \frac{\partial u_{ij}(r)}{\partial r} g_{ij}(r)$$

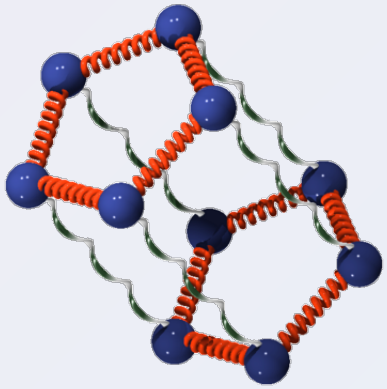


Path Integral Monte Carlo "Gold Standard"

Feynman suggested another way to treat this problem.

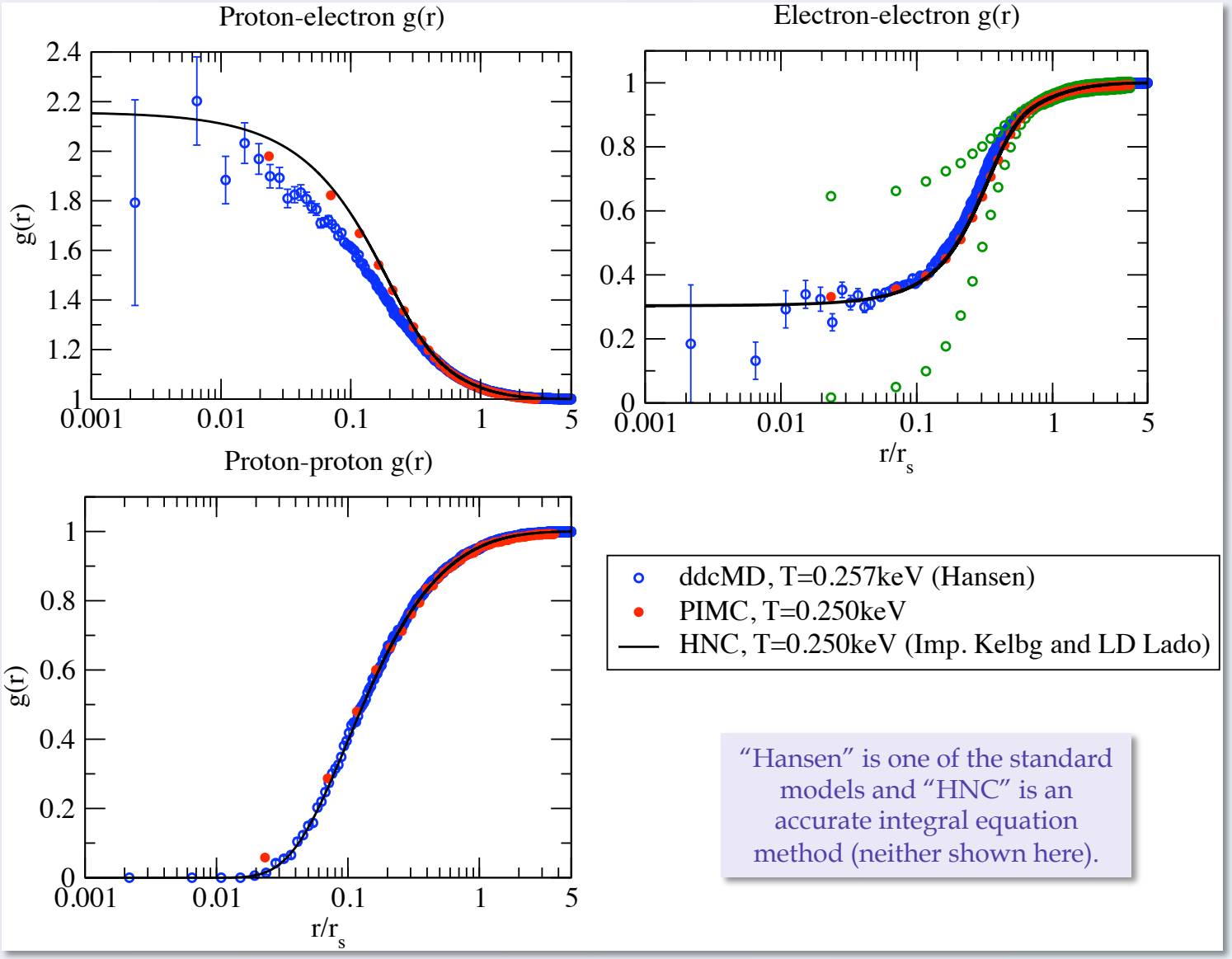
$$
\begin{aligned}
Z &= \int d\mathcal{R} \, \langle \mathcal{R} | \, e^{-\beta \hat{H}} \, | \mathcal{R} \rangle \\
e^{-\beta \hat{H}} &= (e^{-\beta \hat{H}/P})^P \\
Z &= \int d\mathcal{R} \, \langle \mathcal{R} | \, (e^{-\beta \hat{H}/P})^P \, | \mathcal{R} \rangle \\
&= \int d\mathcal{R} ... \, d\mathcal{R}_{P-1} \, \langle \mathcal{R} | \, ... \, (e^{-\beta \hat{H}/P}) \, | \mathcal{R}_1 \rangle \, \langle \mathcal{R}_1 | \, (e^{-\beta \hat{H}/P}) \, | \mathcal{R} \rangle
\end{aligned}
$$

This leads to the "polymer ring isomorphism":



Most difficult for us is the Fermion Sign Problem.

Results for Hot Dense Hydrogen I

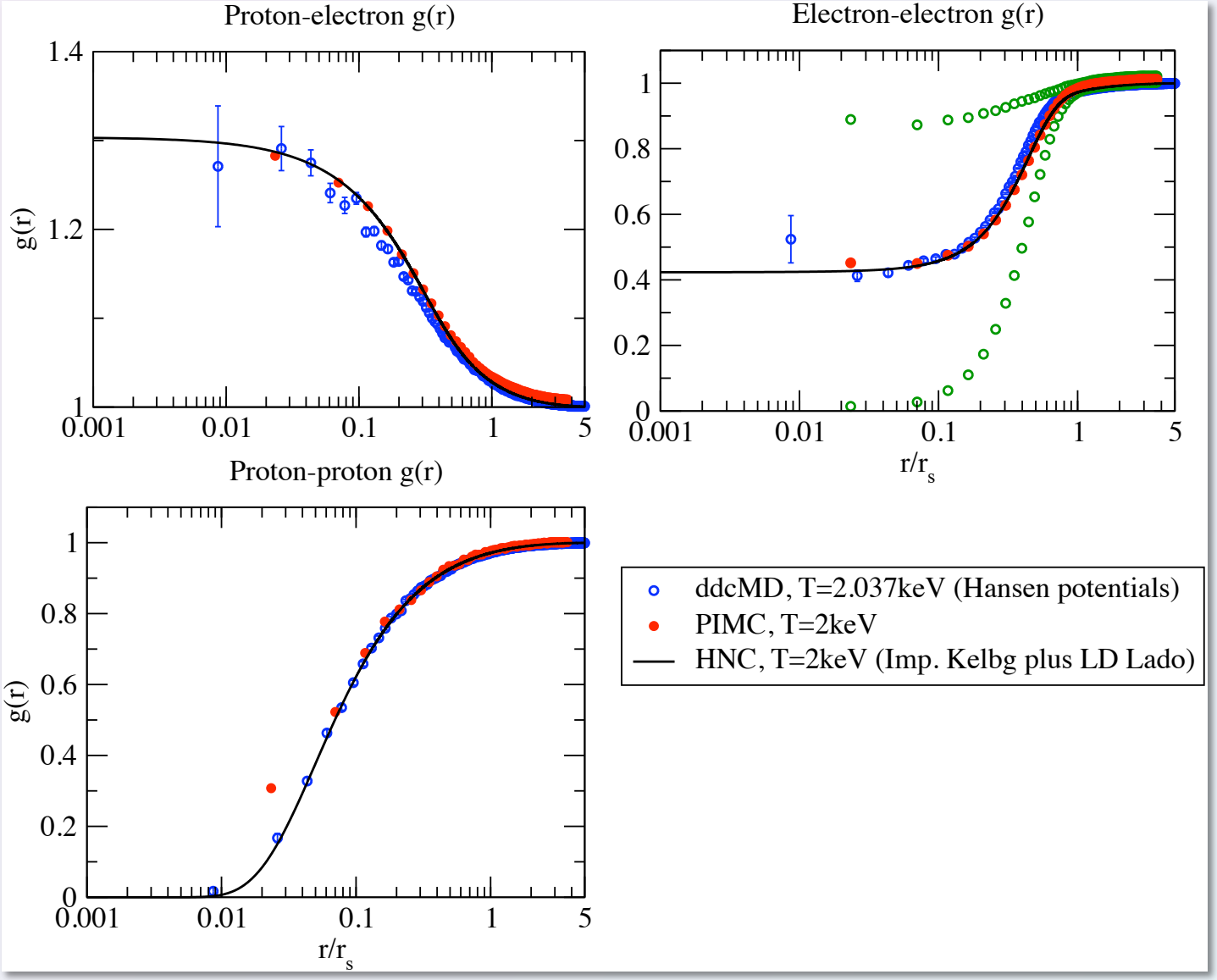


$$\Gamma_{ei} = 0.01$$

$$\theta = \frac{T}{T_F} = 6.05$$

"Hansen" is one of the standard models and "HNC" is an accurate integral equation method (neither shown here).

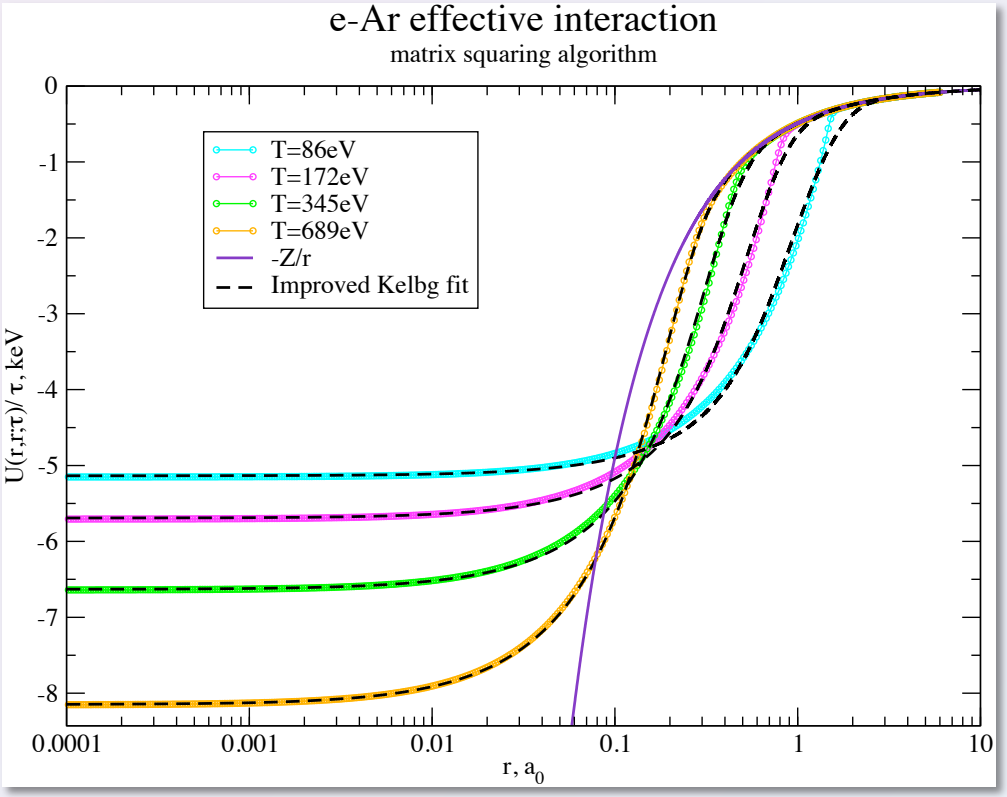
Results for Hot Dense Hydrogen II

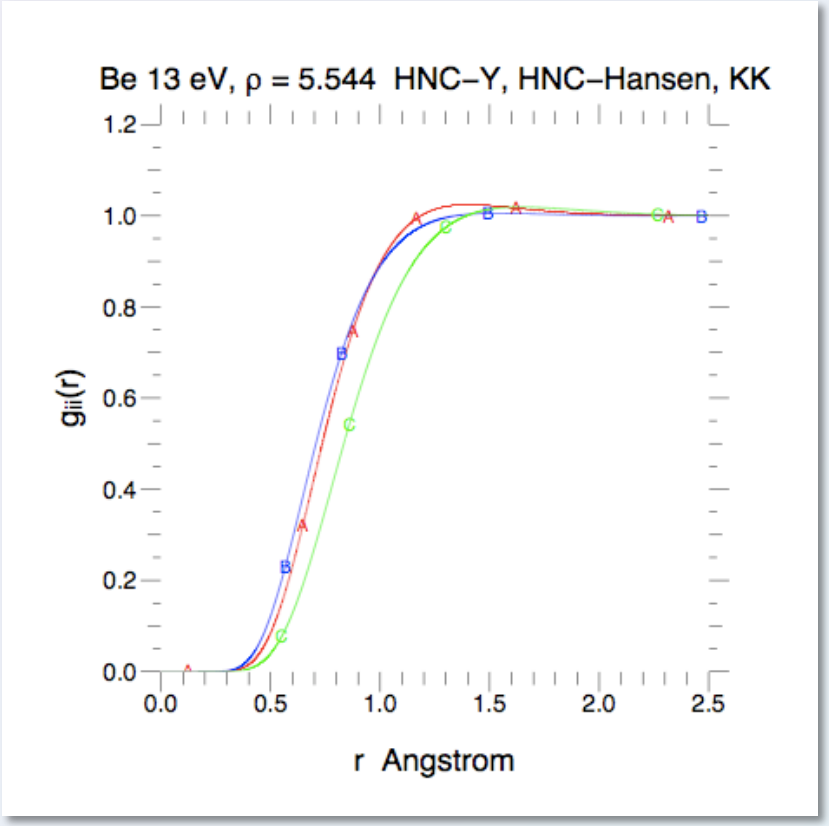


$$\Gamma_{ei} = 0.05$$

$$\theta = \frac{T}{T_F} = 2.95$$

We Consider A Wide Range Of Elements

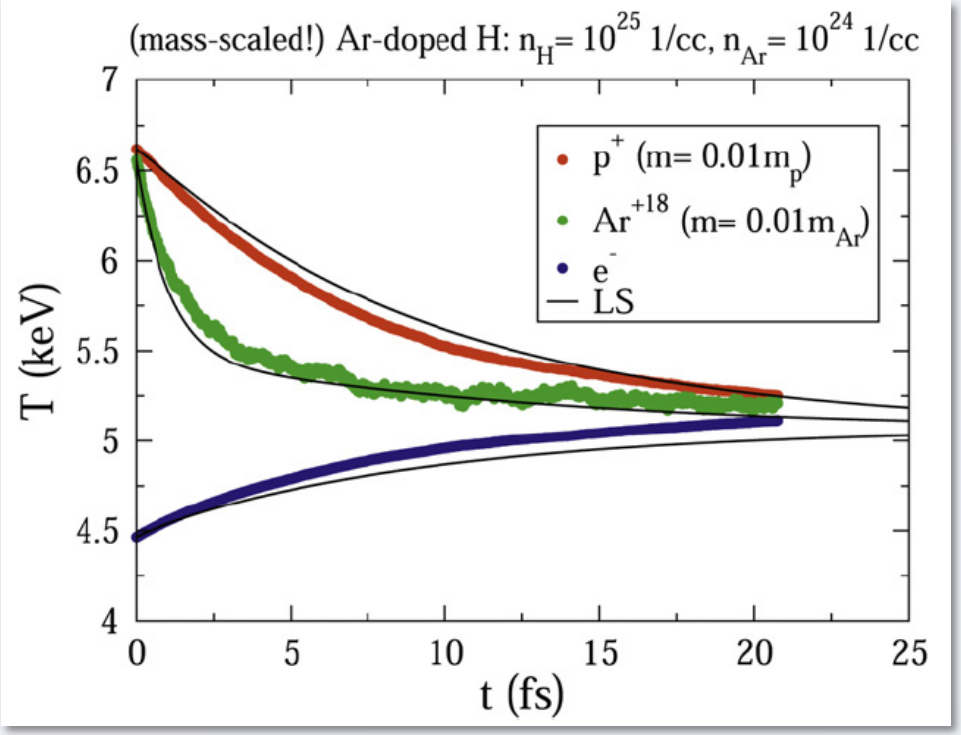


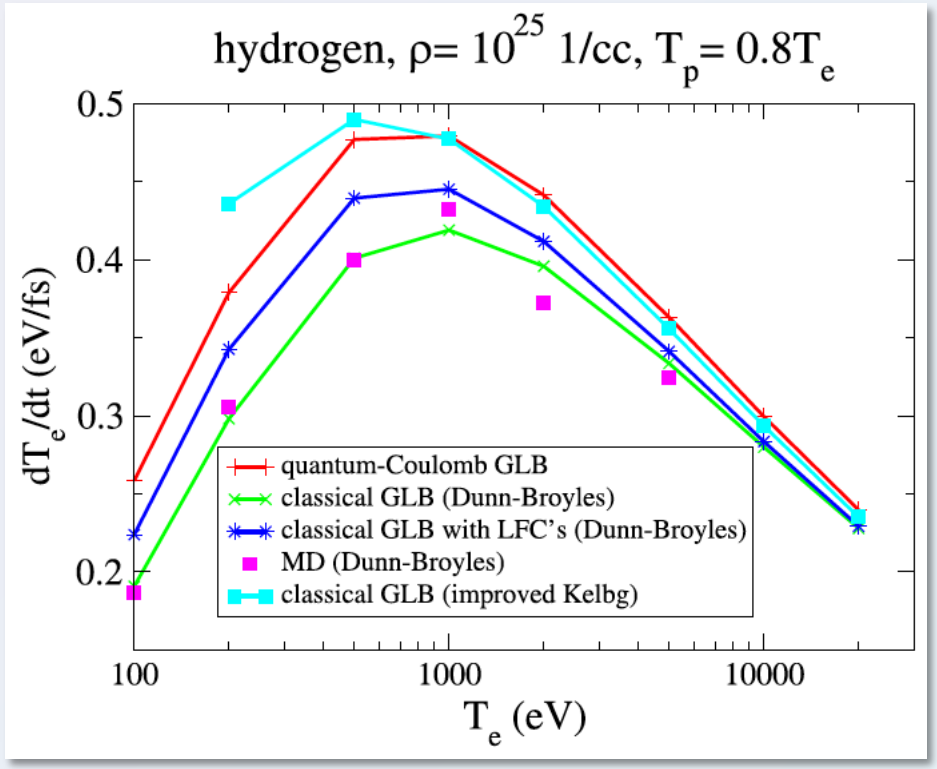


Time-Dependent Phenomena With QSPs

$$\frac{dT_e}{dt} = \frac{T_i - T_e}{\tau_{ei}}$$

$$\frac{1}{\tau_{ei}} = \frac{8\sqrt{2\pi}\rho_i Z_i^2 e^4}{3 m_e m_i c^3}\left[\frac{T_e}{m_e c^2} + \frac{T_i}{m_i c^2}\right]^{-3/2} \ln\lambda_{ei},$$





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

Successes and Failures of QSPs

Why QSPs work.

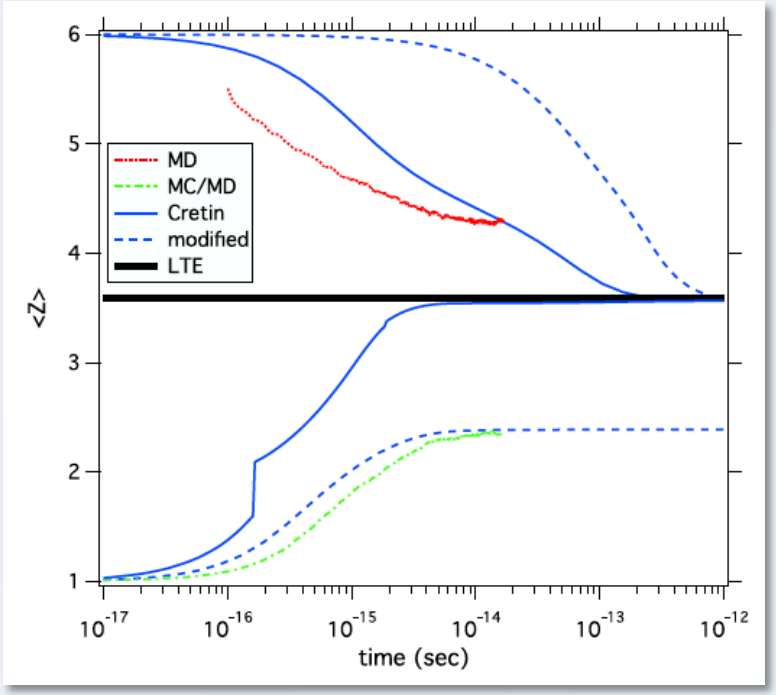
$$S(k,\omega) = \mathcal{C} \int_{-\infty}^{\infty} dt \ \langle n(k,t) n(-k,0) \rangle \, e^{i\omega t}$$

$$S_{ee}(k,\omega) = -\frac{\hbar\omega_{pe}}{\pi n_e \left(1 - \exp\left(-\frac{\hbar\omega}{T_e}\right)\right)} \mathrm{Im}\left[\frac{\chi_0^{\mathrm{HT}}(k,\omega)}{1 - v(k)\,\chi_0^{\mathrm{HT}}(k,\omega)}\right]$$

$$\mathrm{Im}\left[\chi_0^{\mathrm{HT}}(k,\omega)\right] = -\frac{2n_e\beta\omega}{k}\sqrt{\frac{\pi\beta m_e}{2}} \exp\left(-\frac{\beta m_e\omega^2}{2k^2} - \frac{\beta\hbar^2k^2}{8m_e}\right) \frac{\sinh\left(\frac{\beta\hbar\omega}{2}\right)}{\beta\hbar\omega}$$

This term acts to suppress unphysical density fluctuations (Heisenberg).

Why QSPs don't work.



Atomic recombination in carbon.

What's this?

Wave-Packet and Plane-Wave Molecular Dynamics

(WPMD & PWMD)

Wave-Packet Molecular Dynamics (WPMD)

- Fundamentally, we want to solve the time-dependent Schrodinger equation (TDSE).
- For large systems, this will always be out of reach.
- For HDM physics, we are not interested in "chemical accuracy".
  - ✓ Develop simple quantum models with as few parameters as possible.

The basic classical variables are position and momentum (x,p). Heisenberg forbids us from knowing these simultaneously. *Rethink what we mean by these variables*.

Ehrenfest Theorem reveals challenge:

$$\begin{aligned} \frac{d\langle\hat{x}\rangle}{dt} &= \langle\hat{p}\rangle \\ \frac{d\langle\hat{p}\rangle}{dt} &= (i\hbar)^{-1}\left\langle[\hat{p},\hat{H}]\right\rangle \\ &= \langle F(\hat{x})\rangle \end{aligned}$$

- It makes sense to think about expectation values.
- Except for the SHO, this is an infinite hierarchy.
- We need to keep more variables.
- Best to choose truncation wisely.

Standard: Gaussian Wavepackets

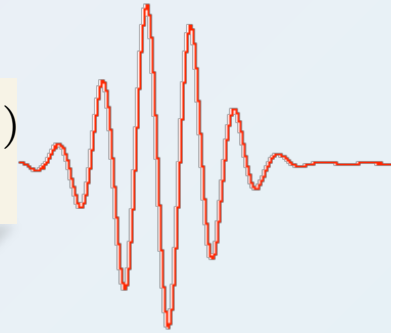
Begin with a time-dependent variational principle:

$$\begin{aligned} S[\{\alpha_i(t), \dot{\alpha}_i(t)\}] &= \int_{t_1}^{t_2} dt\, \mathcal{L}\left(\{\alpha_i(t), \dot{\alpha}_i(t)\}\right) \\ \mathcal{L} &= \langle \psi\{\alpha_i(t)\}| \, i\hbar \frac{d}{dt} - \hat{H} \, |\psi\{\alpha_i(t)\}\rangle \end{aligned}$$

This yields a set of coupled ODEs that is suitable for implementation into an MD framework. In fact, one obtains the Euler-Lagrange equations for the parameters.

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\alpha}_i} = \frac{\partial \mathcal{L}}{\partial \alpha_i}$$

$$\psi(R,t) = \frac{1}{w^{3/2}(t)} e^{-(R-r(t))^2\left(\frac{1}{2w(t)} + \frac{m\dot{w}(t)}{2w(t)}\right)} e^{i\frac{m}{\hbar}\dot{r}(t)\cdot(R-r(t))}$$



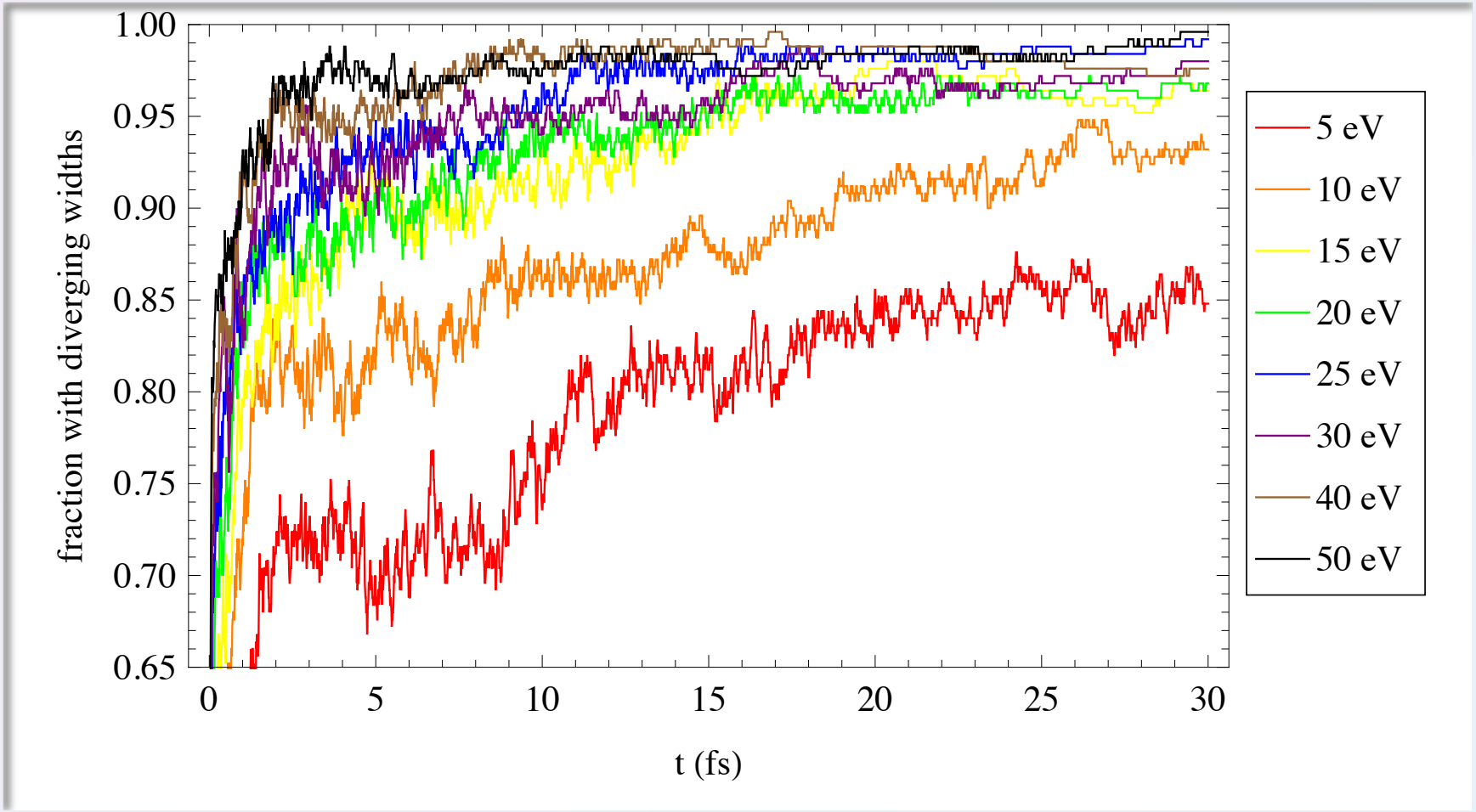
This is a closure for the Ehrenfest hierachy.

$$\begin{aligned} E_H^{GWP} &= \frac{8}{3\pi} E_H \\ E_{He}^{GWP}/E_{He} &= 0.79 \end{aligned}$$

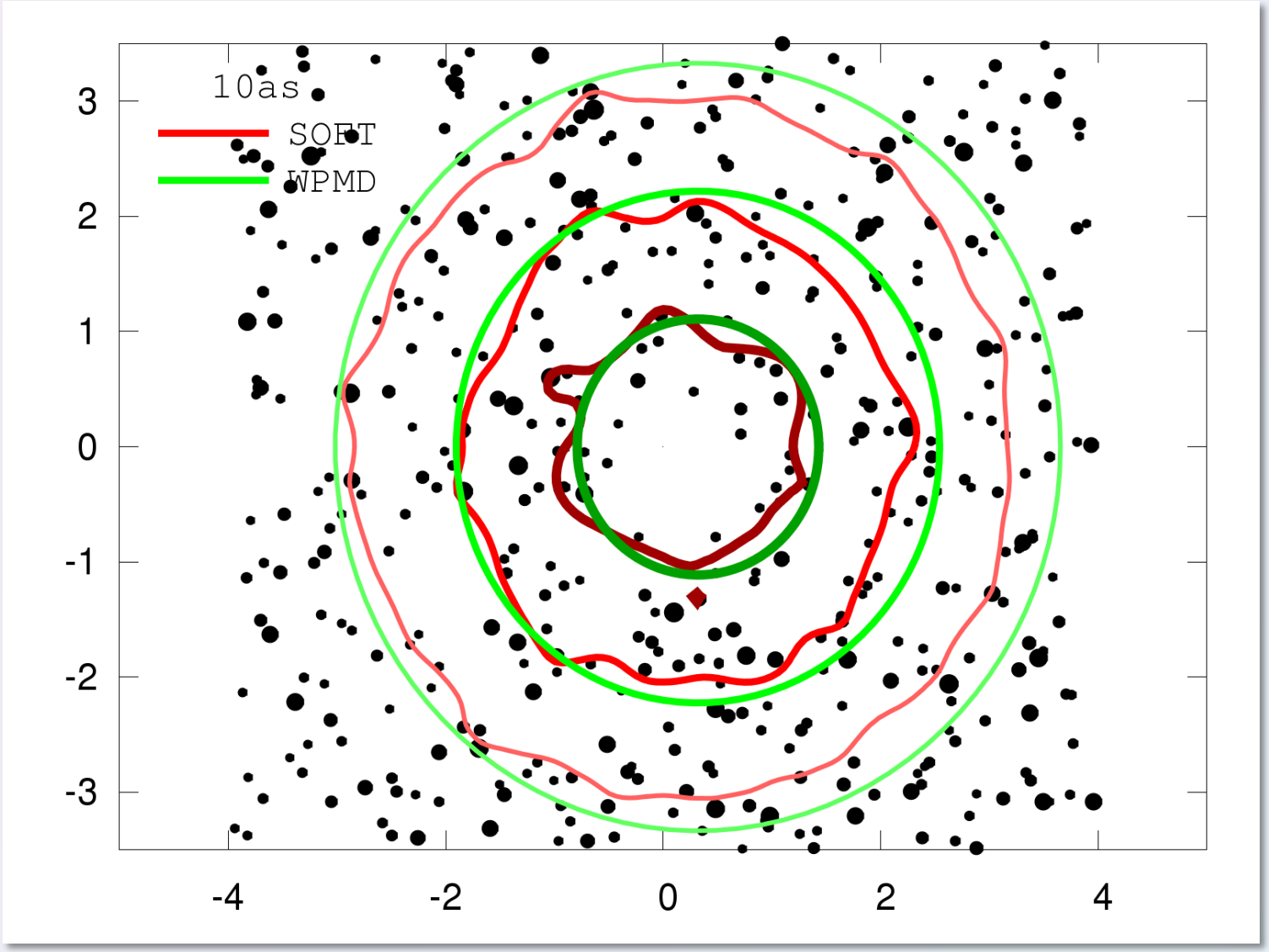
M. S. Murillo and E. Timmermans, Contrib. Plasma Phys. 43, 333 (2003).

It Doesn't Work

WPMD for dense hydrogen. (electron-proton plasma n=1e24/cc)



Compare With Accurate Results For Single Particle Motion



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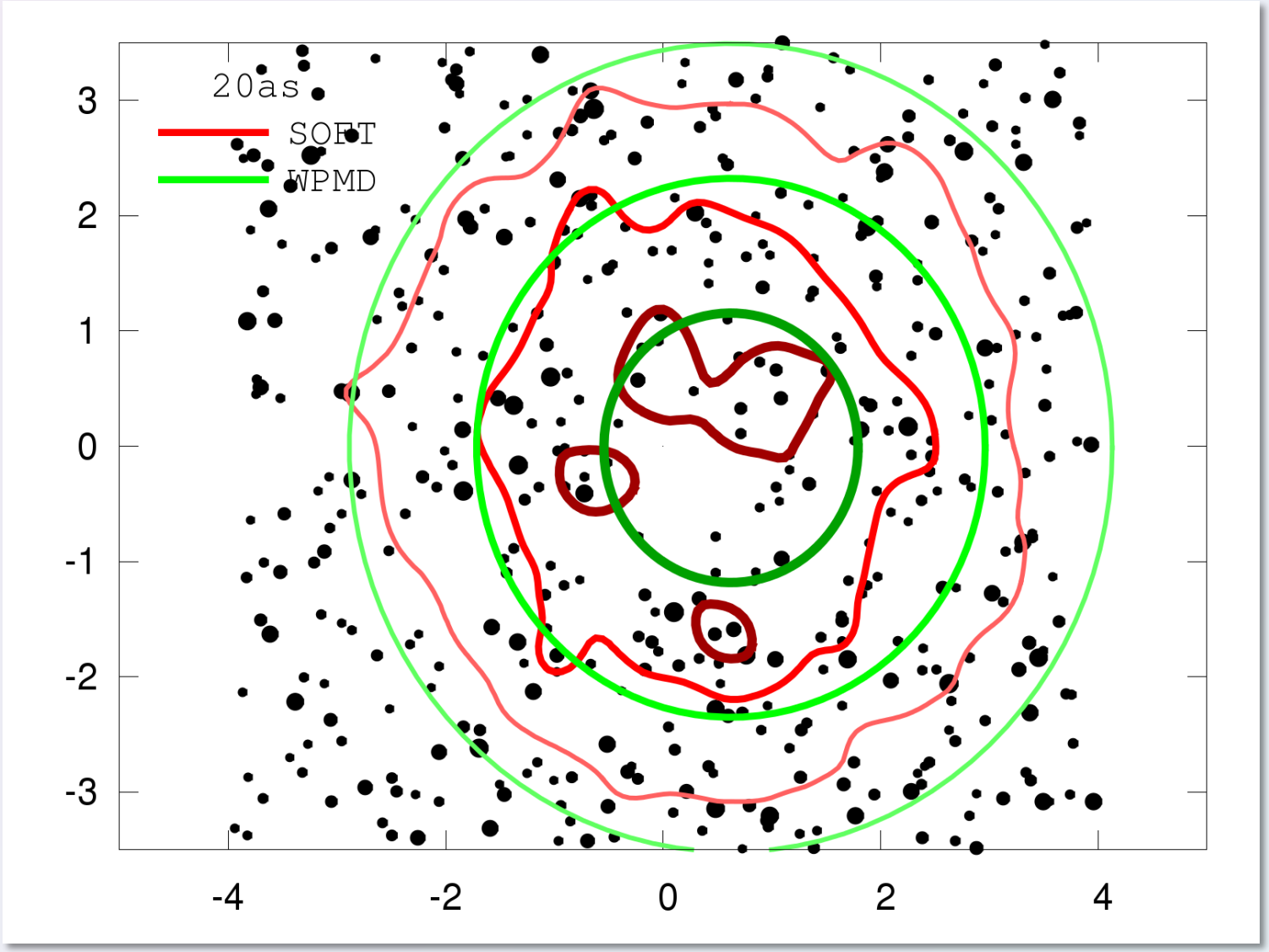

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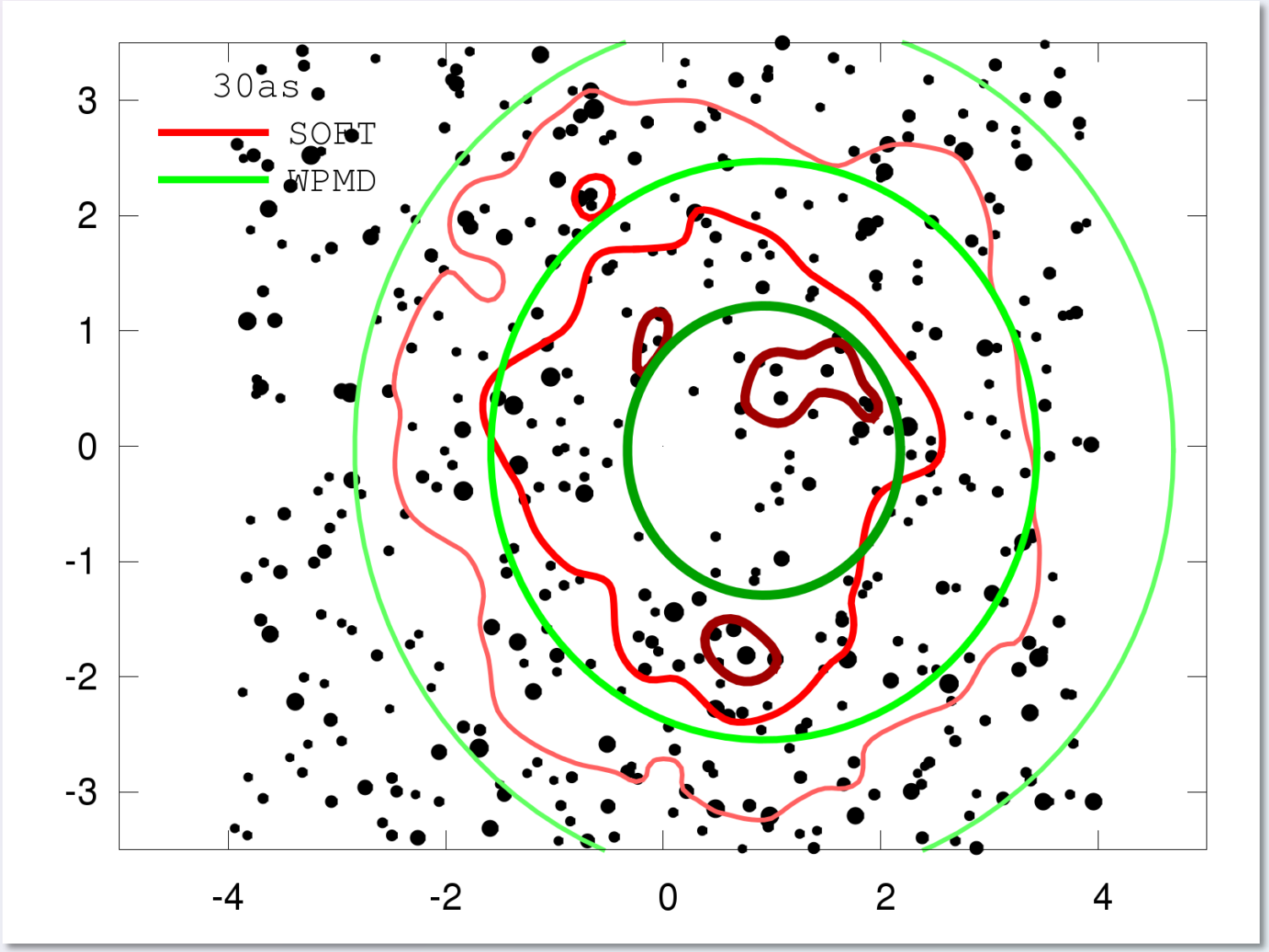

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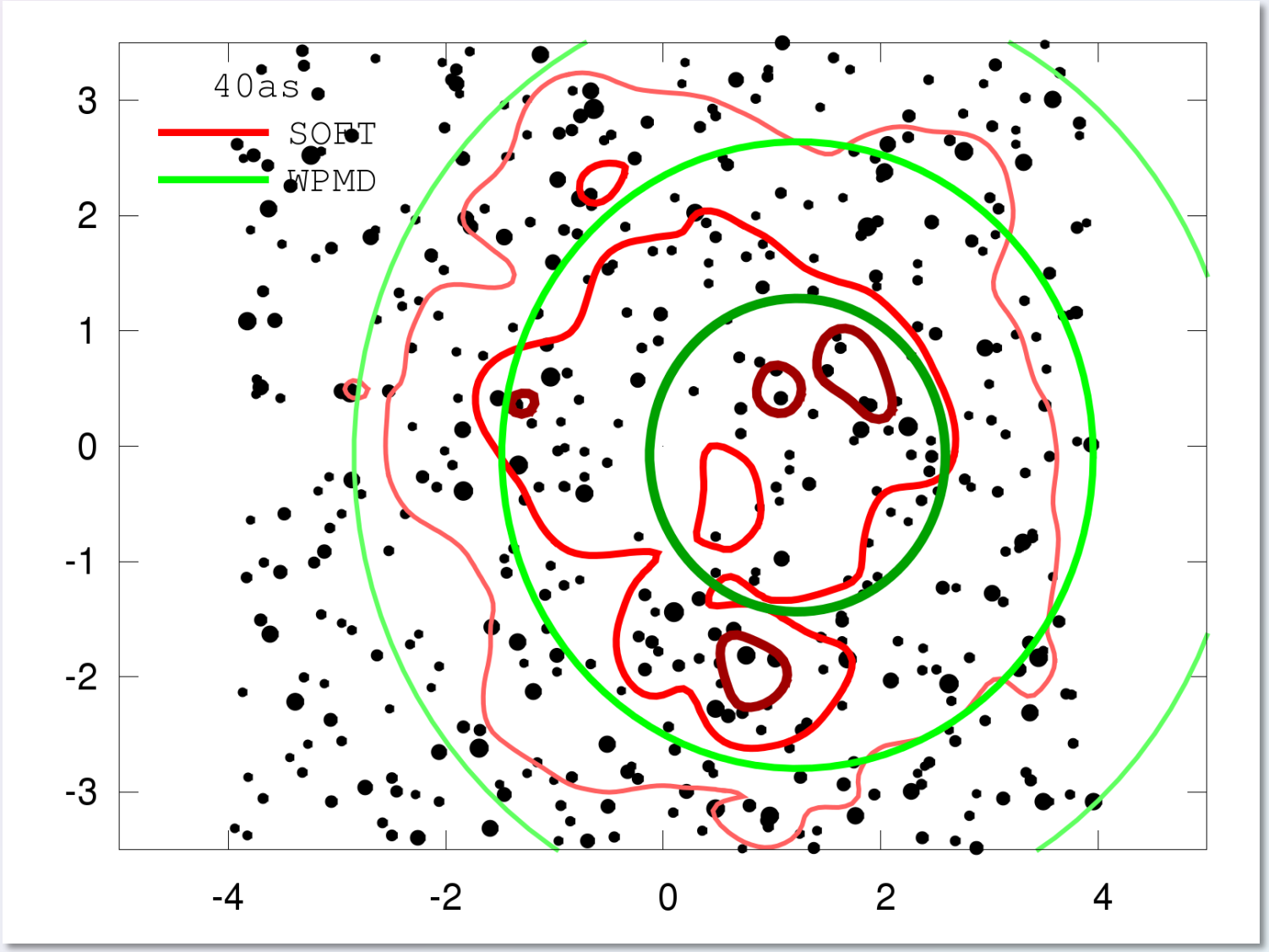

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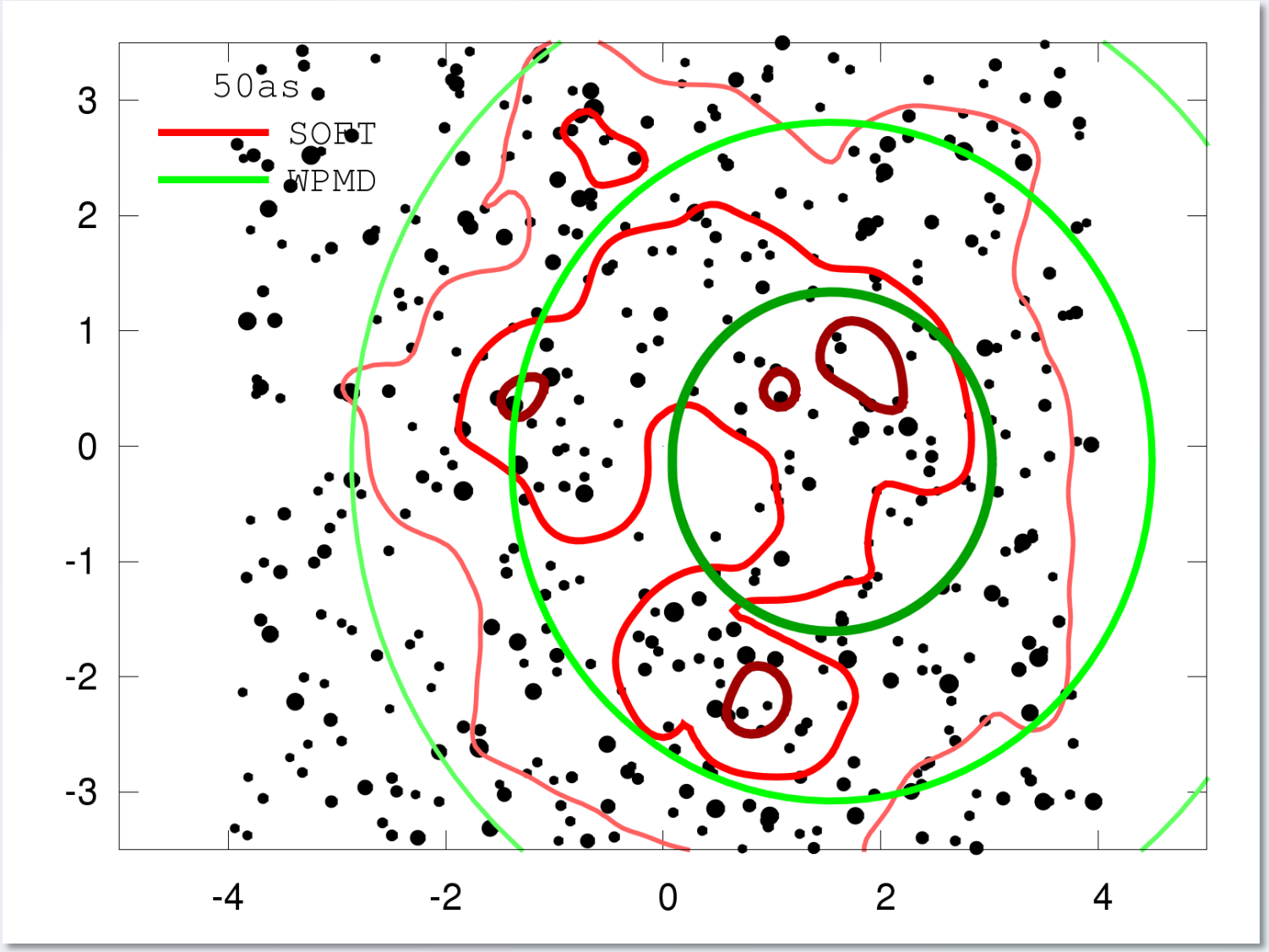
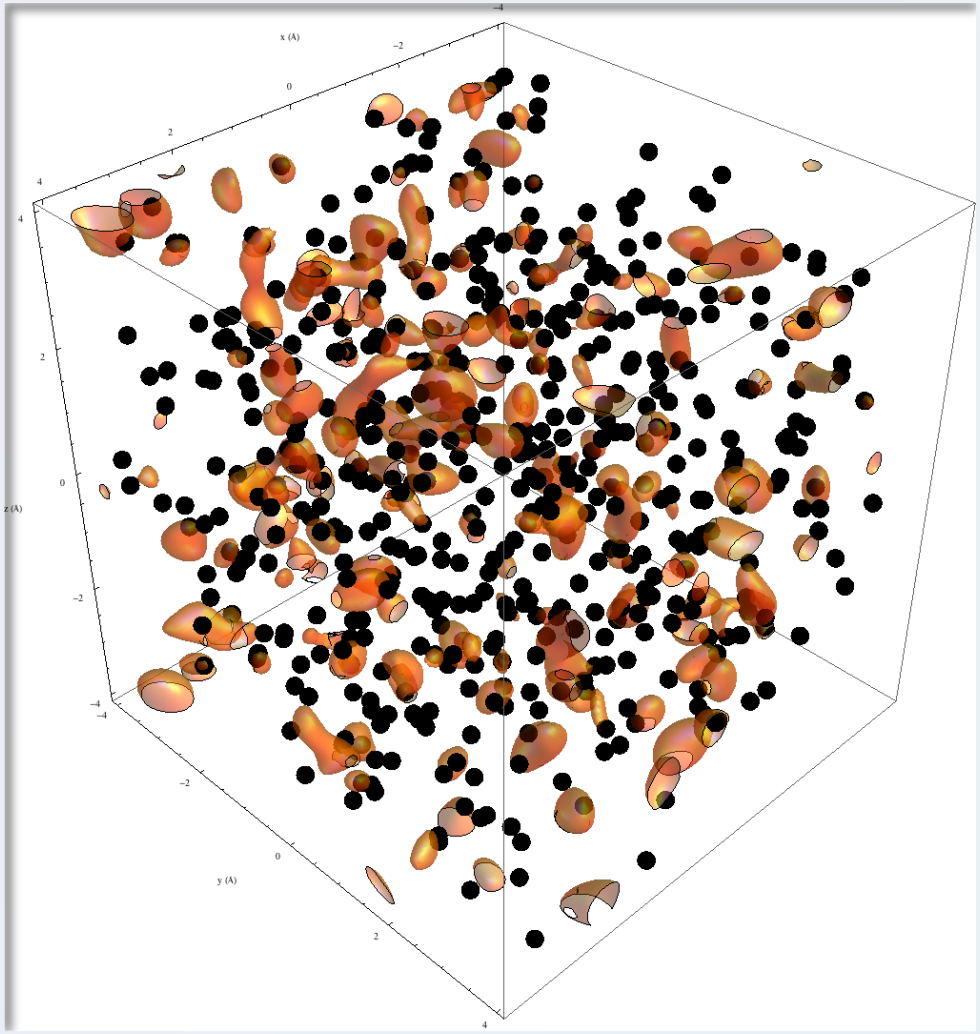


Examine Wavepacket Breakup

- Our numerically exact solver SOFT is used to simulate the localization of a wave function.
- The initial condition is a travelling plane wave with kinetic energy = 85 eV.
- This shows how a wave packet of infinite width can still produce non-trivial contributions to g(r).



A New Method: Plane Wave Molecular Dynamics (PWMD)

Write single electron states as:

$$\phi_n(\vec{r}) = \sum_{\vec{k}} \phi_{n\vec{k}}\, e^{2\pi i \vec{k}\cdot\vec{r}/L}$$

- N = number of particles
- M = Fourier modes (per dimension)
- Computational Scaling = $O(NM^3 \ln M)$
- Memory Scaling = $O(NM^3)$

Define canonical positions and momenta:

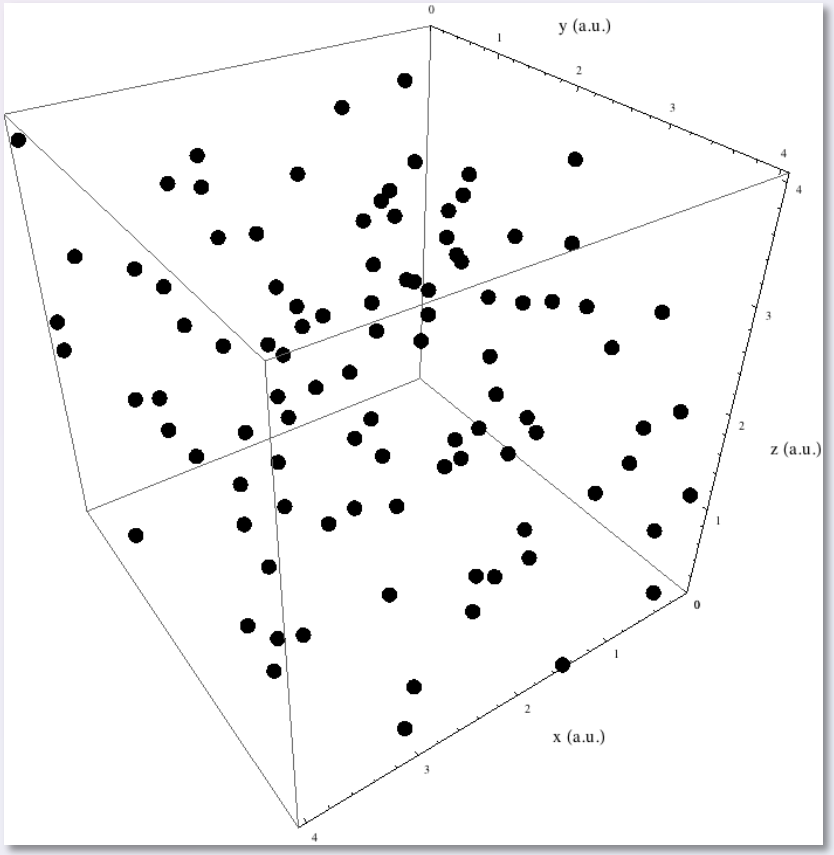
$$\phi_{n\vec{k}} = q_{n\vec{k}} + ip_{n\vec{k}}$$

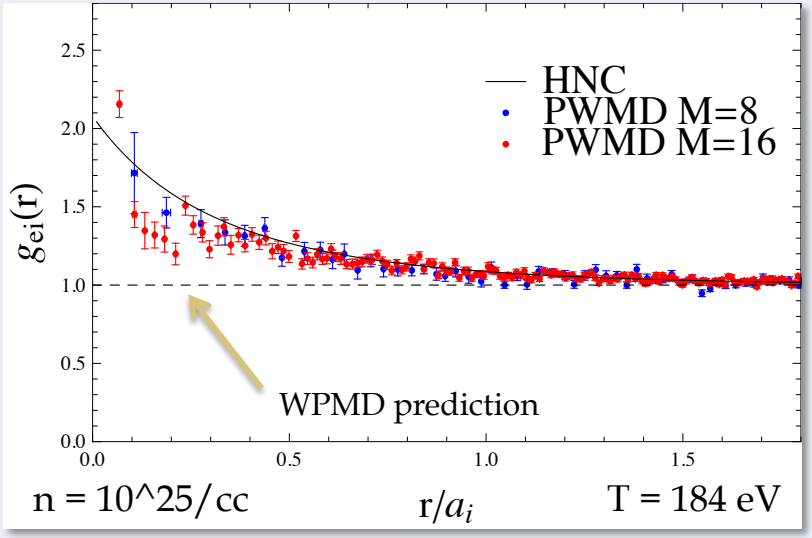
The equations of motion are :

$$\dot{q}_{n\vec{k}} = \frac{1}{2\hbar}\frac{\partial\langle\hat{H}\rangle}{\partial p_{n\vec{k}}}$$

$$\dot{p}_{n\vec{k}} = -\frac{1}{2\hbar}\frac{\partial\langle\hat{H}\rangle}{\partial q_{n\vec{k}}}$$

Good Results So Far With PWMD





- Hydrogen Plasma
- T = 184 eV
- n = 10^{25} cm^{-3}
- 100 *fixed* protons and 100 *dynamic* electrons
- Black dots are protons
- Colors are electron density (Red = Twice average density, Blue = Half average density)

Kinetic Theory Molecular Dynamics

(KTMD)

For Hot Dense Matter, Are We Trying Too Hard?

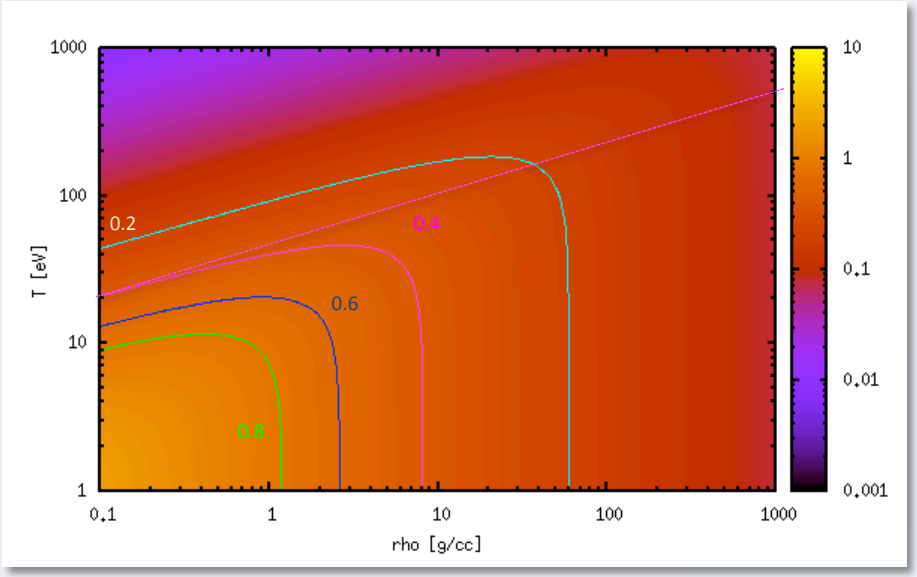
$$\Gamma = \frac{\langle \text{potential energy} \rangle}{\langle \text{kinetic energy} \rangle} = \frac{Z^2 e^2}{a_{WS} T}$$

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

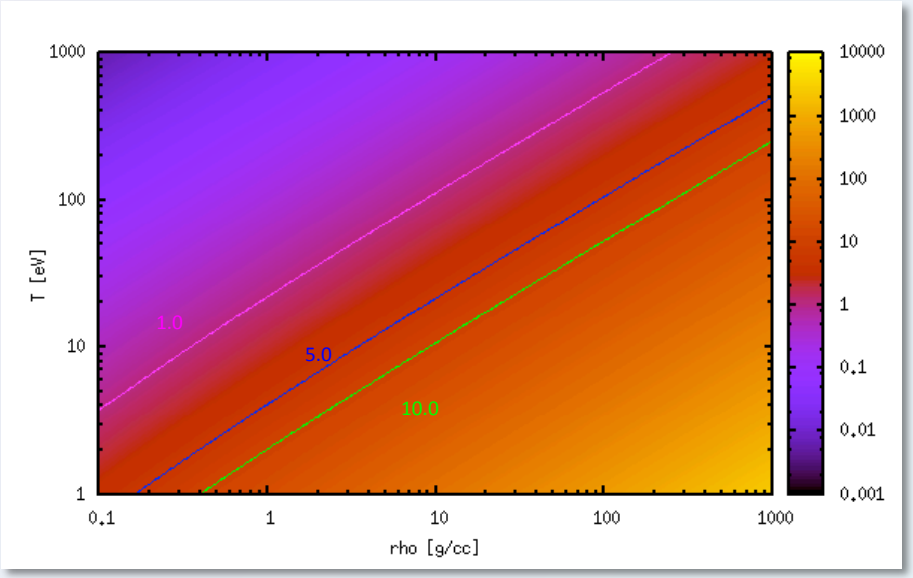
$$\Gamma_{ee} = \frac{e^2}{a_e \sqrt{T^2 + (\frac{3}{5}E_F)^2}}$$

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

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



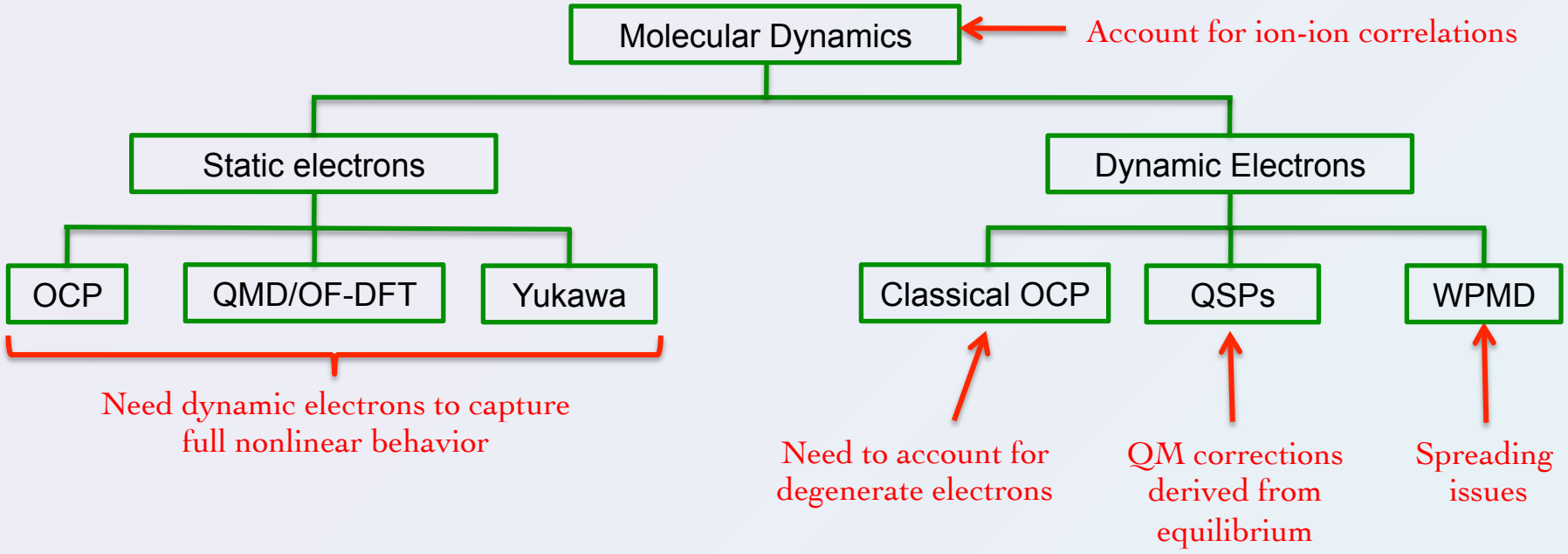
Coulomb coupling. Ion couplings are extrapolations (straight lines from lower left; only one is shown) of the electron couplings. Electron couplings are the bent lines, and are slightly smaller.



Electron degeneracy.

Where Does This Leave Us?

Molecular Dynamics (MD) is the obvious choice to accurately follow ion dynamics; modeling the associated electron dynamics accurately requires more thought.



Kinetic Theory Molecular Dynamics (KTMD)

- Treat ions with classical MD techniques:

$$\dot{\mathbf{r}}_j = \mathbf{p}_j$$
$$\dot{\mathbf{p}}_j = -\nabla \left(U_{ii} + U_{ei}\right)_j$$

- For now, treat electrons with appropriate QM single-particle mean-field evolution equation:

Non-equilibrium Wigner distribution

$$\frac{\partial f_e\left(\mathbf{r},\mathbf{p},t\right)}{\partial t} + \frac{\mathbf{p}}{m_e}\cdot\nabla f_e\left(\mathbf{r},\mathbf{p},t\right) + \int d^3p' K\left(\mathbf{r},\mathbf{p}'-\mathbf{p},t\right) f_e\left(\mathbf{r},\mathbf{p}',t\right) = 0$$

Nonlinear!

where

$$K\left(\mathbf{r},\mathbf{p}'-\mathbf{p},t\right) \equiv \frac{ie}{\hbar}\left(\frac{m_e}{2\pi\hbar}\right)\int d^3s \exp\left[i\left(\mathbf{p}-\mathbf{p}'\right)\cdot\frac{\mathbf{s}}{\hbar}\right]\times\left[\phi\left(\mathbf{r}+\frac{\mathbf{s}}{2},t\right)-\phi\left(\mathbf{r}-\frac{\mathbf{s}}{2},t\right)\right]$$

QM smearing of potential

and

$$f_e\left(\mathbf{r},\mathbf{p},0\right) = \frac{1}{\left(\pi\hbar\right)^3}\int d^3s \left\langle \mathbf{r}-\mathbf{s}\right| \hat{\rho} \left|\mathbf{r}+\mathbf{s}\right\rangle$$

with

$$\hat{\rho} \equiv \frac{\exp\left(-\beta\left(\hat{H}-\mu\hat{N}\right)\right)}{\mathrm{Tr}\left[\exp\left(-\beta\left(\hat{H}-\mu\hat{N}\right)\right)\right]}$$

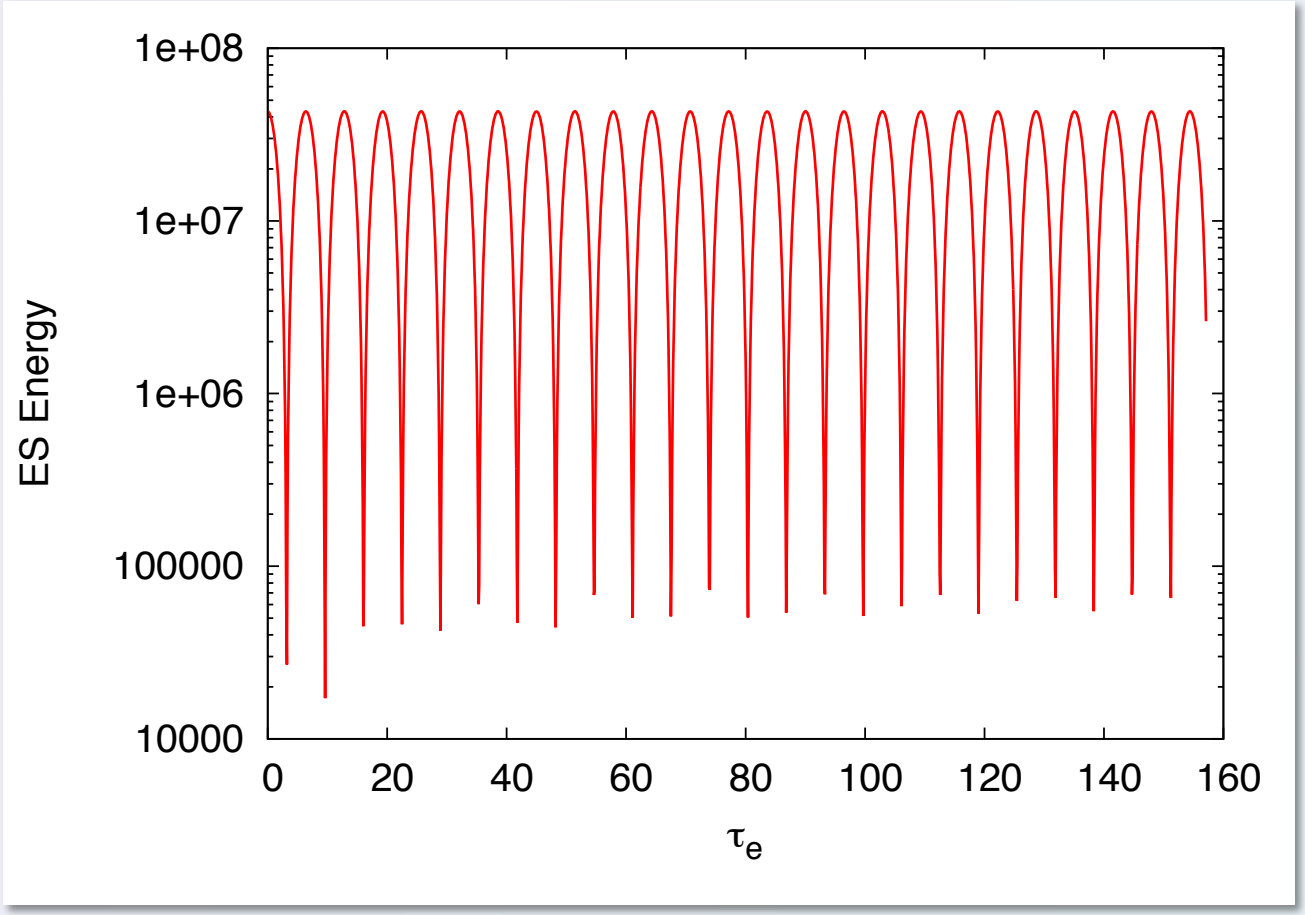
Retains Fermi-Dirac Statistics

$$\nabla^2\phi = 4\pi e\left[2\int\frac{d^3p}{\left(2\pi\hbar\right)^3} f_e\left(\mathbf{r},\mathbf{p},t\right) - \sum_{j=1}^{N_{\mathrm{ions}}} Z_j\delta\left(\mathbf{r}-\mathbf{r}_j(t)\right)\right]$$

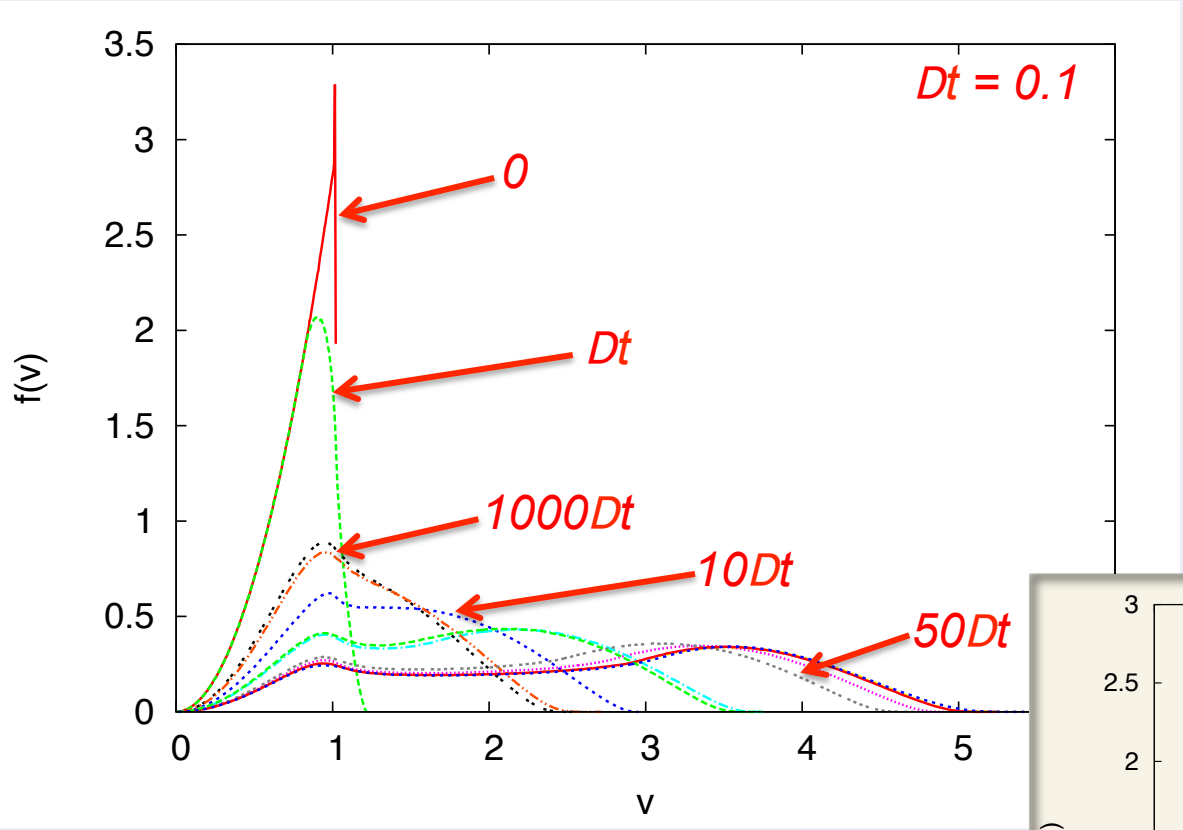
First Step: KTMD As QPIC

$$\frac{\omega(q)}{\omega_p} = \lim_{T_e \to 0} \left[1 + \frac{\sqrt{2m_e}\, k^2 T_e^{5/2}}{\pi^2 \omega_p^2 n_e \hbar^3} I_{3/2}(\beta\mu) \right] = \left[1 + \frac{3}{10} \left(\frac{q p_F}{\hbar m_e \omega_p} \right)^2 \right]$$

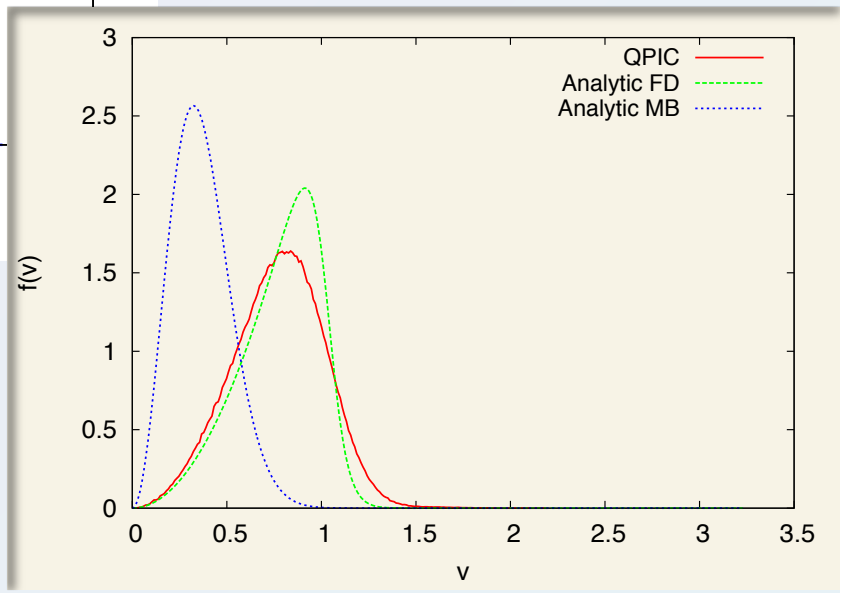
Landau damping test.



Guess What? Numerical Issues!



Introduce Langevin thermostat with FDT tuned to corrrect Fermi-Dirac second moment.



Outlook: A Score Card

- QSPs are quite useful for MD simulations of HDM.
  - Enforce self-consistency between diffractive and Pauli contributions.
  - Steer toward path integral molecular dynamics (PIMD)
  - Steer toward path integral centroid dynamics (PICD)
  - Extend to include momentum dependence.
- WPMD/PWMD is a promising model, but issues remain.
  - Improve computational scaling.
  - Develop intermediate model (between WP and PW).
- KTMD looks promising, so far.
  - Develop better collision models.
  - Understand Wigner smearing computationally.
  - Retain Fermi-Dirac distribution.
  - Develop computationally and validate further.