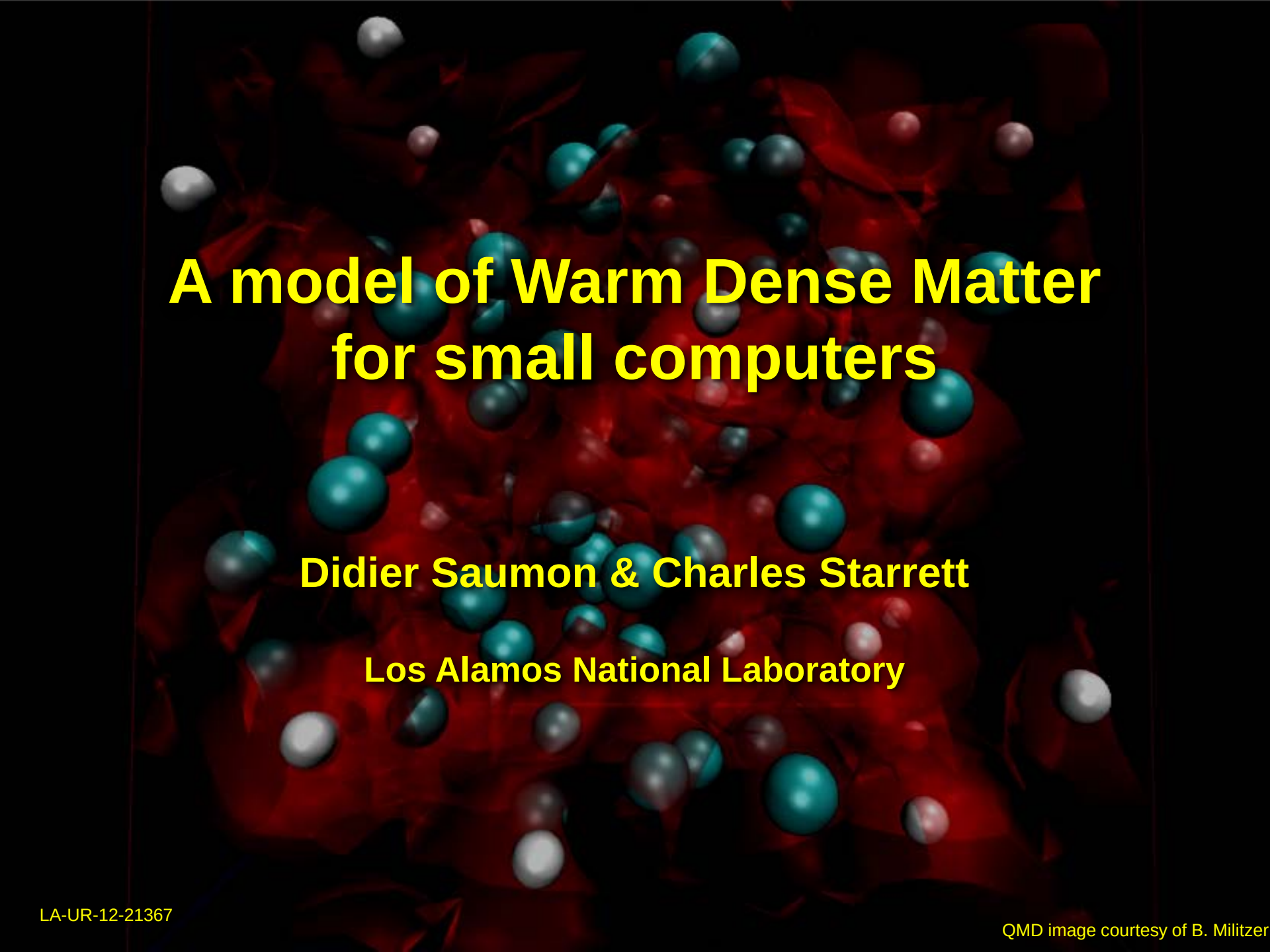


A model of Warm Dense Matter for small computers

Didier Saumon & Charles Starrett

Los Alamos National Laboratory

LA-UR-12-21367

QMD image courtesy of B. Militzer

- **Motivation**
- Theoretical approach
  - Average atom model
  - Interacting fluids: Integral equations
- The model
- Some results
- Numerical challenges
- Summary

Los Alamos

Motivation

Ab initio (“brute force”) methods are computationally very expensive

Often limits the number of states that can be calculated in practice

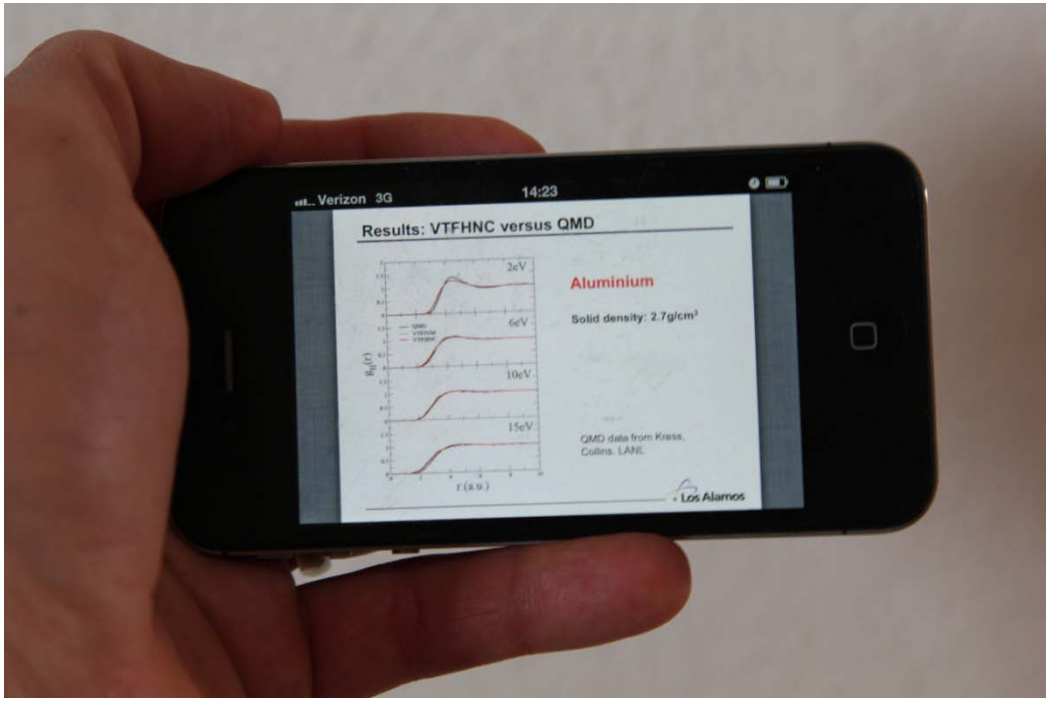
Los Alamos

Goal

To develop a model of Warm Dense Matter

- **Computationally tractable**
- **Captures the essential physics**
- **Can be turned into a production tool**

a WDM app



Los Alamos

General outline of model

A model of Warm Dense Matter

Main features:

- Assume spherical symmetry
- Ion-ion interactions self-consistent with ion-electron screening

Combines:

- Average atom model
- Integral equations of fluid theory

Not a new concept. Earlier models by

- Chihara (QHNC)
- Dharma-wardana & Perrot
- Faussurier (SCAALP)

Bring a fresh look to this approach and go beyond existing models

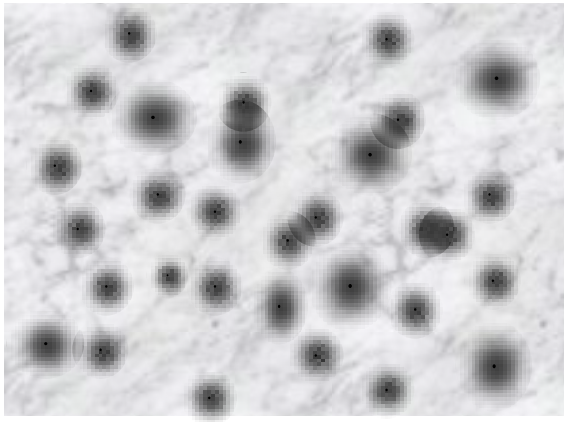
- Motivation
- **Theoretical approach**
  - **Average atom model**
  - Interacting fluids: Integral equations
- The model
- Some results
- Numerical challenges
- Summary

Los Alamos

Average Atom model of dense matter

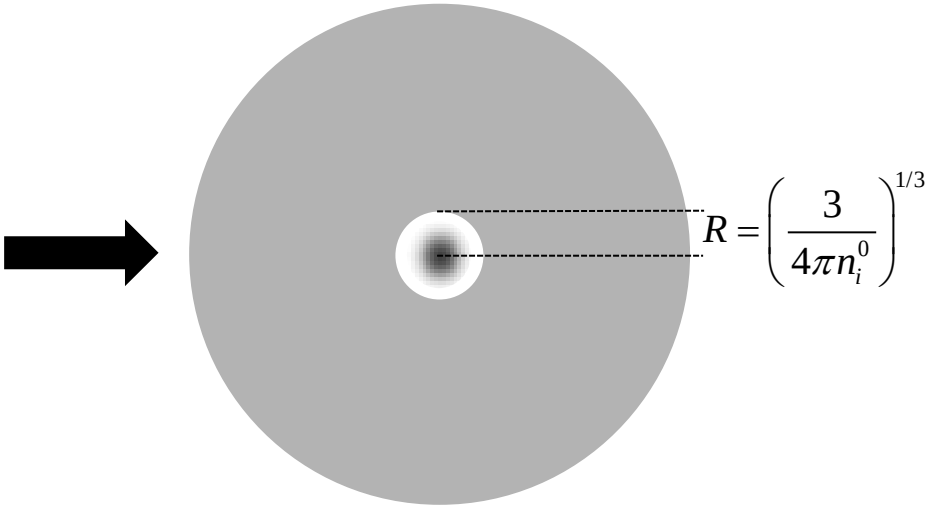
Real plasma

Multi-center system



N-body quantum problem

Average atom model



1 atom/ion at the center of a cavity (ion sphere)

Surrounding (neutral) plasma is smeared out
effectively replaced by a boundary condition:
Charge neutrality of the ion sphere

Solve for the quantum states of the central ion in the cavity

Beyond average atom models

Such 1-ion average atom models are nevertheless very useful

- All-electron models
- Account for temperature excitation and density effects

- Electronic properties of the ion
- Basis for the calculation of electronic transport properties

Limitations

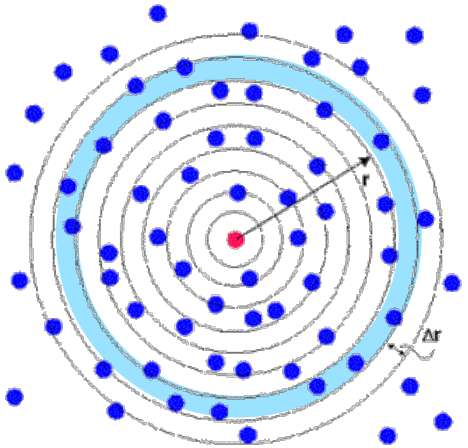
- Poor description of interactions of electrons with plasma
- Ion-ion interactions are missing

- Motivation
- **Theoretical approach**
  - Average atom model
  - **Interacting fluids: Integral equations**
- The model
- Some results
- Numerical challenges
- Summary

Los Alamos

Interacting fluids

Fluid of classical point particles interacting with a pair potential *V(r)*



The fluid is fully characterized by

temperature *T*
average particle density n_0
pair potential *V(r)*

Compute thermodynamics of the interactions

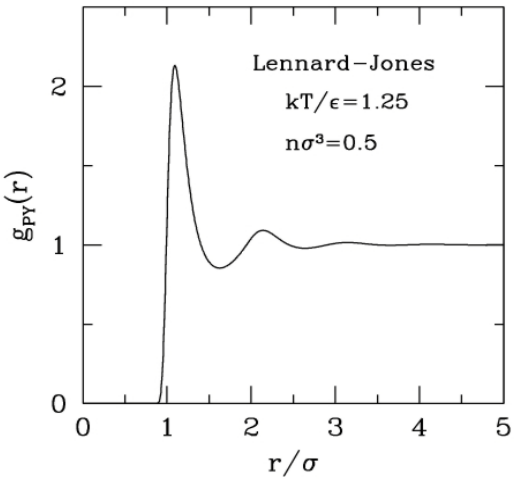
Molecular Dynamics / Monte Carlo
Perturbation theory
Integral equations

Particle positions are correlated

radial distribution function *g(r)*

$$N(r \to r + dr) = g(r) n_0 4\pi r^2 \Delta r$$

g(r) can be measured with X-ray or neutron diffraction



Los Alamos

Interacting fluids: Integral equations

Integral equations of fluid theory (1-component system)

define $h(r) = g(r) - 1$ pair correlation function

Ornstein-Zernike equation

$$h(r) = c(r) + n_0 \int h(|\vec{r} - \vec{r}'|) c(r') d\vec{r}'$$

defines *c(r)*, the direct correlation function

$$\hat{h}(k) = \hat{c}(k) + n_0 \hat{h}(k)\hat{c}(k)$$

Fourier transform

Closure relation

$$g(r) = h(r) + 1 = \exp[-V(r)/kT + h(r) - c(r) + B(r)]$$

Bridge function (beyond 2-body correlations)

$B(r) = 0$ Hypernetted chain approximation (HNC)
Other (better) approximations to *B(r)* exist

Given *V(r)*, n_0, *T* : 2 equations in 2 unknowns: *h(r),c(r)*

Interacting fluids: Integral equations

Thermodynamics follows from the distribution functions

$$\frac{U}{NkT} = \frac{3}{2} + \frac{n_0}{2kT}\int V(r)g(r)d^3r \qquad \frac{P}{n_0kT} = 1 - \frac{n_0}{6kT}\int r\frac{dV}{dr}g(r)d^3r$$

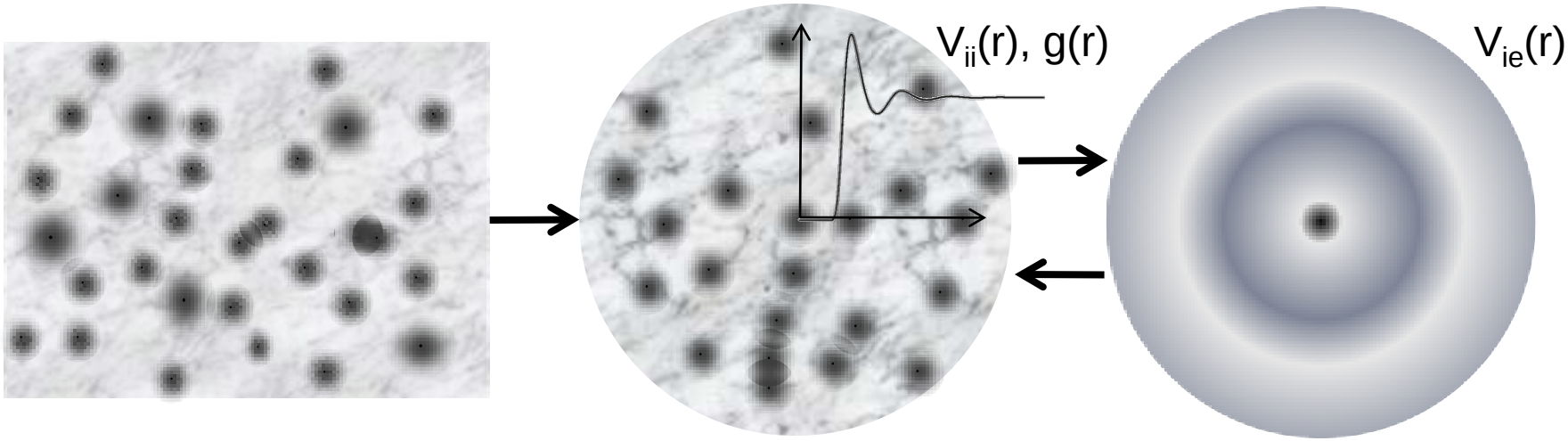
- Motivation
- Theoretical approach

  Average atom model
  Interacting fluids: Integral equations

- **The model**
- Numerical challenges
- Some results
- Summary

Los Alamos

General concept



Multi-center system
Multiple ion configurations

Single center system
Average ion (Z*)
Classical ions + qm electrons
"ion-ion problem"

Central average ion (Z*)
Spherically symmetric potential
"electron-ion problem"

Integral fluid equations

- **2–component fluid: classical ions + quantum electrons**
- **Closure relations**

All-electron average atom model

Self-consistency

Chihara (1991); Anta & Louis (2000)

Los Alamos

Key equations and assumptions

1) The ion-electron problem

The electrons' response to the presence of a nucleus is given by the solution to the Schrödinger equation for bound ($\varepsilon_{nl}<0$) and free ($\varepsilon_{kl}>0$) states (over all space):

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2}-\frac{l(l+1)}{r^2}\right)+V_{ie}(r)\right]u_{nl}(r)=\varepsilon_{nl}u_{nl}(r) \qquad u_{nl}(r)=r\psi_{nl}(r)$$

The spherically symmetric, effective, one-electron electron-ion potential (in the DFT framework) is

$$V_{ie}(r)=-\frac{Z}{r}+\int\frac{n_b(r')}{|\vec{r}-\vec{r}'|}d^3r'+V_{xc}(n_b(r)+n_e^0)-V_{xc}(n_e^0)]$$

$$-n_e^0\int C_{ee}(|\vec{r}-\vec{r}'|)h_{ie}(r')d^3r'$$

$$-n_i^0\int C_{ie}(|\vec{r}-\vec{r}'|)h_{ii}(r')d^3r'$$

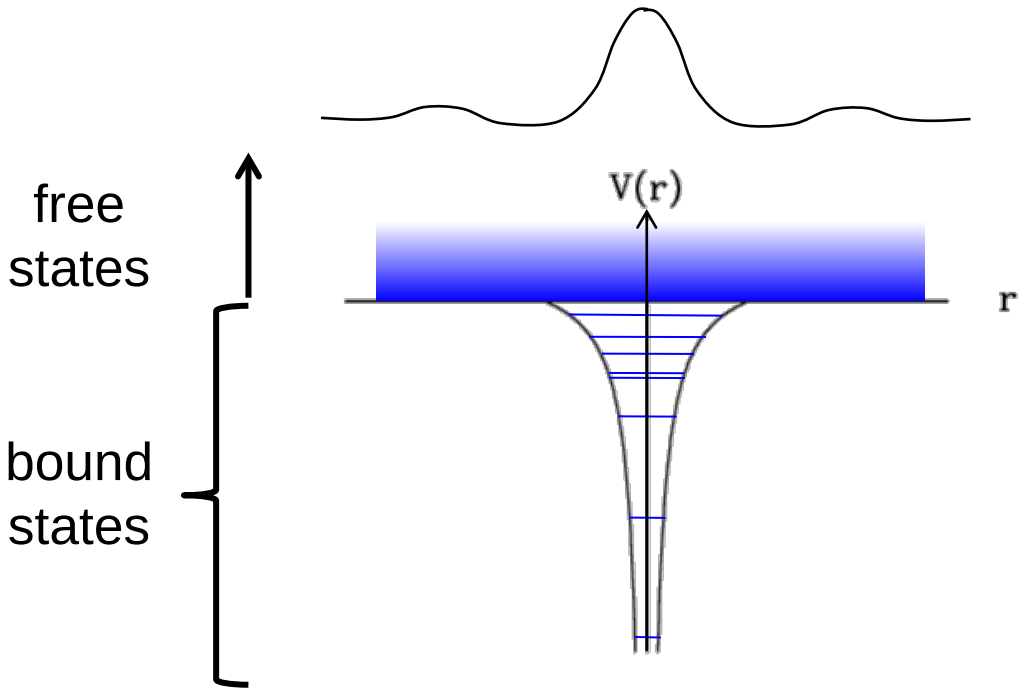
"external" potential

"ionic" potential

Note that $V_{ie}(r)$ depends on the wave functions and thus requires the solution of a self-consistent field problem

Key equations and assumptions

The solution gives a spectrum of discrete bound states with $\varepsilon_{nl}<0$ and a continuum of solutions with $\varepsilon_{kl}=k^2/2>0$



The continuum solutions may include resonances (wave functions that peak near the nucleus for a narrow range of ε_{kl})

Key equations and assumptions

Bound states:

The ion is *defined* as a nucleus plus the electron charge cloud from bound states ($\varepsilon_{nl}<0$)

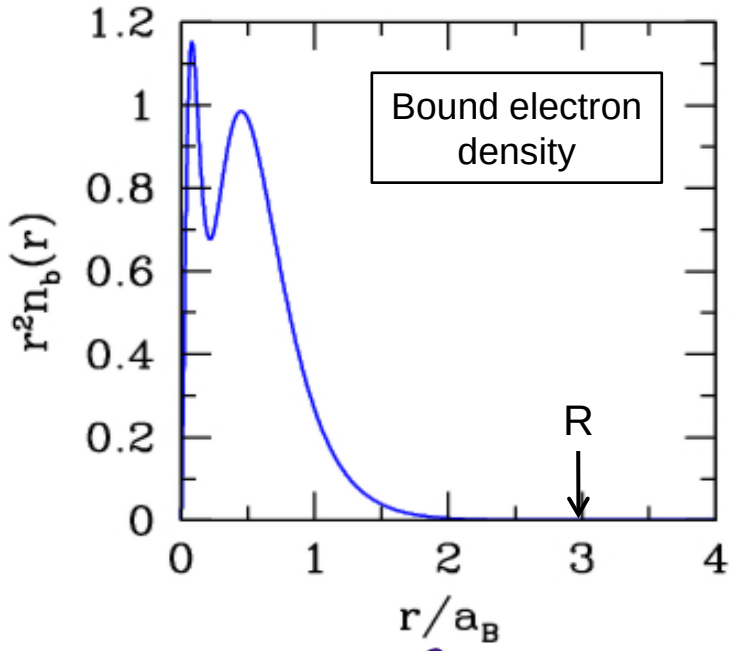
$$n_{ion}(r) = n_b(r) = \frac{1}{4\pi} \sum_{n,l} \frac{2(2l+1)}{e^{\beta(\varepsilon_{nl}-\mu_e)}+1} \psi_{nl}^2(r) w_{nl}(T,\rho)$$

$w_{nl}(T,\rho)$ is a weighting factor that ensures continuity of $n_{ion}(r)$ across the pressure ionization of a bound state

The number of electrons bound to the nucleus is

$$N_{ion} = \int_0^\infty n_{ion}(r) d^3r$$

and the ion charge is $\bar{Z} = Z - N_{ion}$



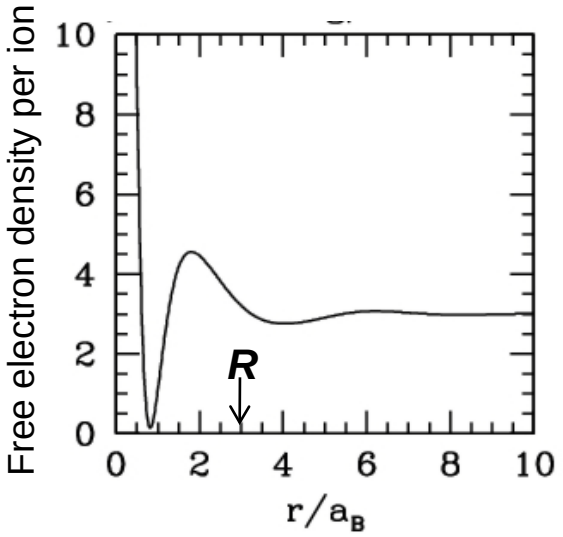
Los Alamos

Key equations and assumptions

Free states:

The charge density from the "free" electrons ($\varepsilon_{kl}=k^2/2>0$) is

$$n_f(r)+n_e^0=\frac{1}{4\pi}\int_0^\infty \frac{d\varepsilon}{e^{\beta(\varepsilon-\mu_e)}+1}\sum_{l=0}2(2l+1)\ \psi_{\varepsilon l}^2(r)$$



Charge neutrality of average atom:

The electron chemical potential μ_e and the uniform electron density n_e^0 are given by the charge neutrality condition

$$\int_0^R [n_b(r)+n_f(r)]\,d^3r\ +\ \frac{n_e^0}{n_i^0}=Z$$

(i.e. neutral ion sphere)

Los Alamos

Key equations and assumptions

Coupling the average atom to the fluid equations

Consider the plasma as a superposition of neutral pseudo-atoms.
Define the pseudo-atom charge density as (Perrot 1990)

$$n_{PA}(r) = n_b(Z,r) + n_f(Z,r) - [n_b(0,r) + n_f(0,r)]$$

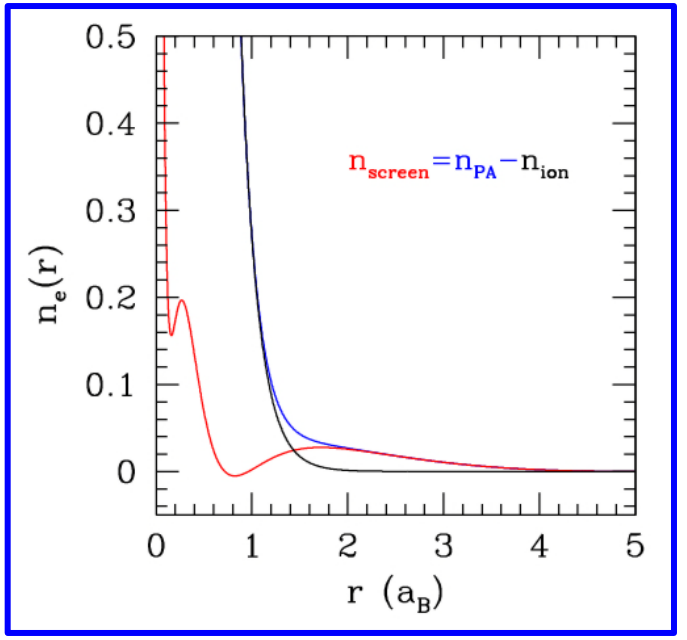
and the cloud of screening electrons as

$$n_{screen}(r) = n_{PA}(r) - n_{ion}(r)$$

From the integral fluid equations,

$$C_{ie}(k) = \frac{-n_{screen}(k)[1 + \chi_0(k) C_{ee}(k)/\beta]}{\chi_0(k)}$$

This effectively couples the average atom model [$n_{screen}(r)$] to the fluid equations [$C_{ei}(r)$]



Los Alamos

Key equations and assumptions

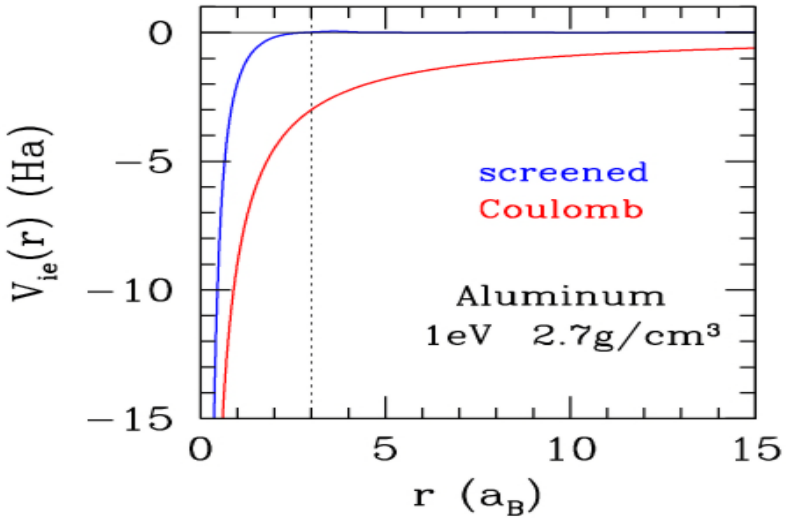
2) The ion-ion problem

The spherically symmetric effective ion-ion potential is (in Fourier space)

$$V_{ii}(k) = \frac{4\pi(\bar{Z})^2}{k^2} + n_{screen}(k)C_{ie}(k)/\beta$$

Direct ion-ion Coulomb term

Screening from electron fluid



Los Alamos

Key equations and assumptions

The pair correlation functions $h_{ij}(r)$ and the direct correlation functions $C_{ij}(r)$ are related by the quantum fluid equations (in Fourier space),

$$h_{ii}(k) = C_{ii}(k)[1 + n_i^0 h_{ii}(k)]$$

For the ions, the closure relation is

$$h_{ii}(r) = e^{-\beta V_{ii}(r) + h_{ii}(r) - C_{ii}(r) + B_{ii}(r)} - 1$$

Where the bridge function $B_{ii}(r)$ is obtained with Variational Modified HNC (Rosenfeld 1986)

- Perturbation approach based on hard sphere system
- Closed form for free energy
- Thermodynamic consistency follows
- Very accurate (Faussurier 2004)

Equations are solved over all space

The model: inputs and outputs

The 13 coupled, highly non-linear equations are solved numerically.

INPUTS

- Atomic number *Z*
- Atomic weight *A*
- Temperature *T*
- Density ρ
- THERE ARE NO FREE PARAMETERS

OUTPUTS

- Structure of the fluid: $g(r)=h_{ii}(r)-1, C_{ii}(r), h_{ei}(r), C_{ei}(r), V_{ei}(r), V_{ii}(r)$
- Average ion charge: $\overline{Z}$
- Wave functions (bound and free states) and energy levels
- Density of states, phase shifts, resonances

FROM THESE OUTPUTS, CALCULATE

- Thermodynamics
- Transport coefficients
  - conductivity, XRTS, XANES, diffusion coefficient, viscosity

The model: Appraisal

The good

- 100-1000 times faster than QMD
- No statistical noise (smooth solutions)
- Not limited to relatively low temperatures
- All-electron model (no pseudo potential)
- Average atom: quantum or Thomas-Fermi model

The model: Appraisal

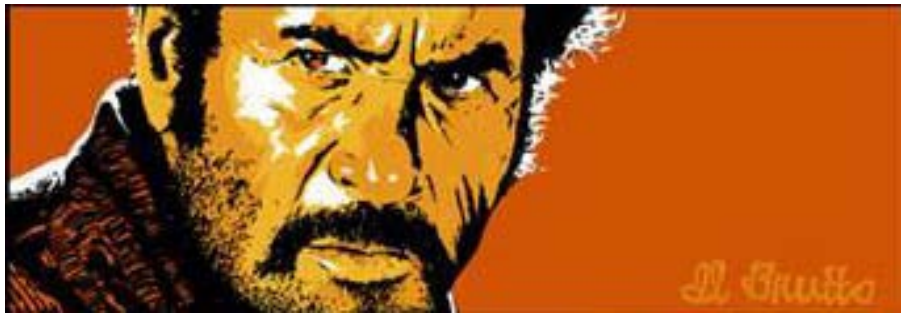
The bad

- More approximate than ab initio
- Pair interactions only
- Limited to spherical symmetry
- No chemical bonding
- Range and degree of reliability yet to be determined (*Z*, *T*, ρ)

The model: Appraisal

The ugly

- **Some degree of arbitrariness in model**
  - **coupling of average atom and fluid equations**
  - **charge neutrality condition**
  - **definition of ion charge cloud**



Los Alamos

The model: Subtleties

Coupling of average atom with the fluid equations

What part of the solution of the Schrödinger equation contributes to the electron fluid?

Perrot's neutral pseudo-atom

$$n_{screen}(r) = n_f(Z, \mu_e, r) - n_f(0, \mu_e, r)$$

$$C_{ie}(k) = \frac{-n_{screen}(k)[1 + \chi_0(k) C_{ee}(k)/\beta]}{\chi_0(k)}$$

QHNC

$$h_{ie}(r) = \frac{n_f(Z, \mu_e, r)}{n_e^0} - 1$$

Charge neutrality (see poster by Charles Starrett)

Neutral ion sphere

$$\int_0^R [n_b(r) + n_f(r)]\, d^3r + \frac{n_e^0}{n_i^0} = Z$$

QHNC

$$\int_0^\infty n_b(r)\, d^3r + \frac{n_e^0}{n_i^0} = Z$$

A minimization principle?

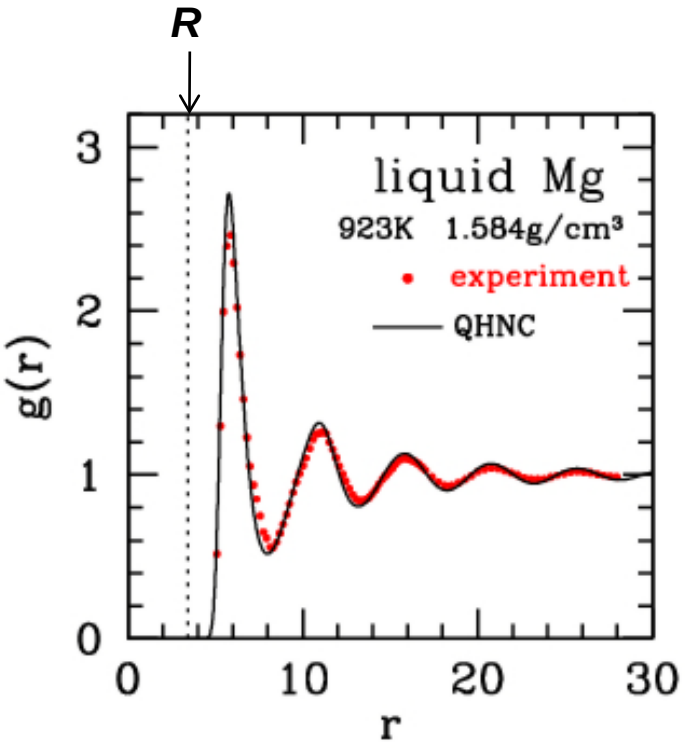
Los Alamos

- Motivation
- Theoretical approach

  Average atom model
  Interacting fluids: Integral equations
- The model
- **Some results**
- Numerical challenges
- Summary

Los Alamos

Application to a liquid metal: Mg



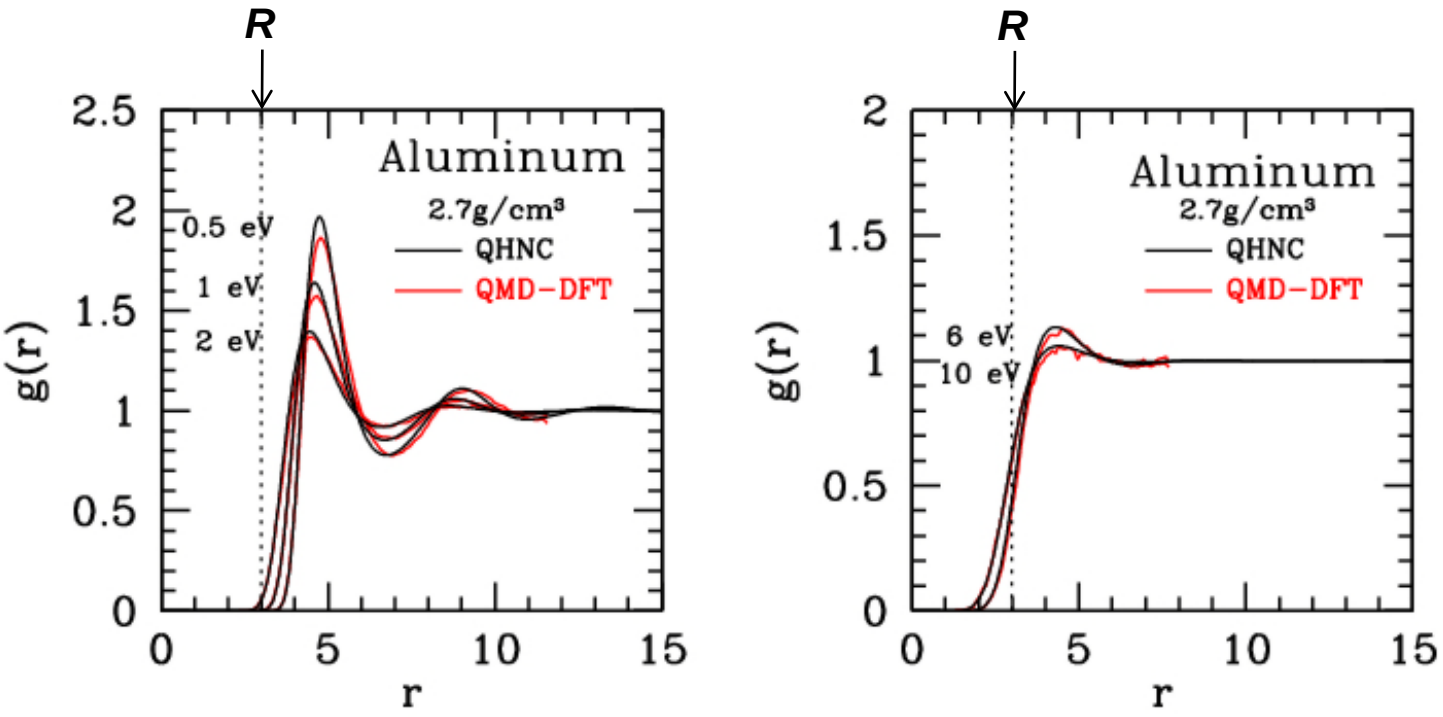
- Limit of very strong ion-ion coupling: Γ_{Mg}=400
- Strong degeneracy: T/T_F~0.006

- Our model is in excellent agreement with data
- Structure of *g(r)* slightly too pronounced

Los Alamos

Application to WDM: Aluminum

Aluminum 2.7g/cm^3 T=0.5 to 10eV

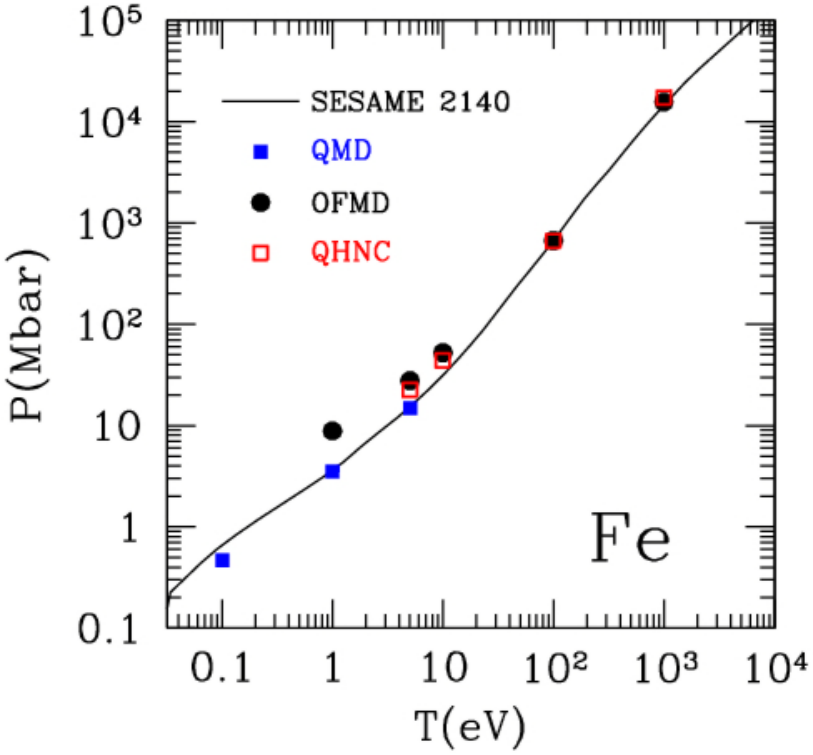


- **Agreement between model and QMD-DFT is excellent**
- **Improves at larger *T* (weaker ion-ion coupling)**

Los Alamos

Application to WDM: Iron

Pressure along the Hugoniot of iron

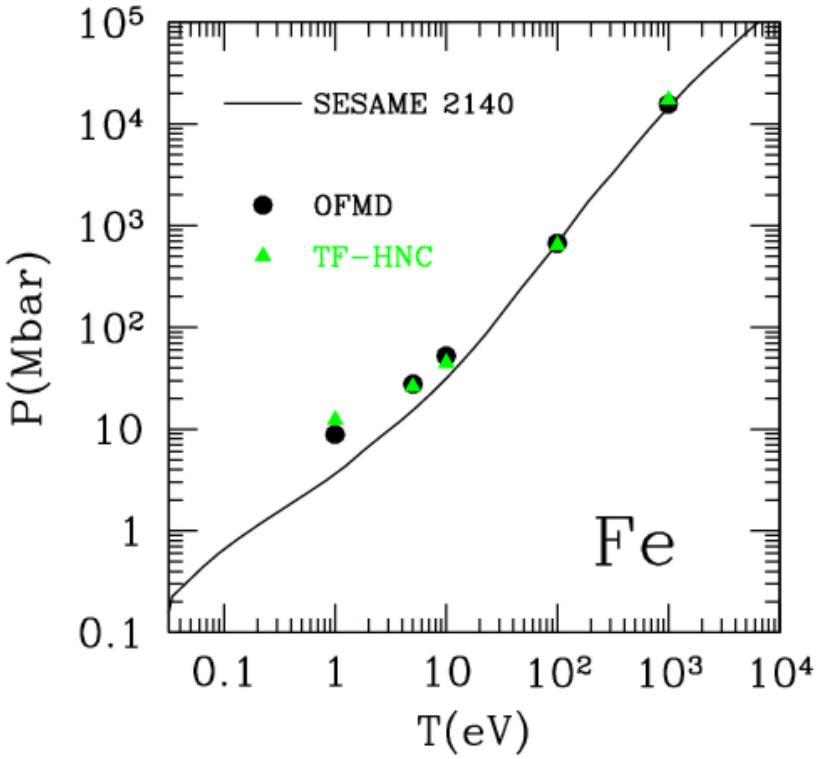


Very good agreement with Orbital Free MD at high T
Passable agreement with QMD at 5eV (but no bridge function here)

OFMD and QMD calculations from Lambert et al. (2006)

Application to WDM: Iron

Pressure along the Hugoniot of iron



TF version does work

Ofer et al. (1988) couldn't find solutions for T< 10^2eV

OFMD calculation from Lambert et al. (2006)

Los Alamos

- Motivation
- Theoretical approach

  Average atom model
  Interacting fluids: Integral equations
- The model
- Some results
- **Numerical challenges**
- Summary

Los Alamos

Numerical solution

Primary difficulty

Coupled integral equations of the ion-ion and ion-electron problems

- need a very robust scheme
- sensitive to details of numerical precision
- need a good initial guess

Widely recognized as a difficult numerical problem

Numerical solution

Ion-electron problem

Self-consistent field (SCF) problem

The potential $V_{ie}(r)$ depends on the solutions (wave functions)

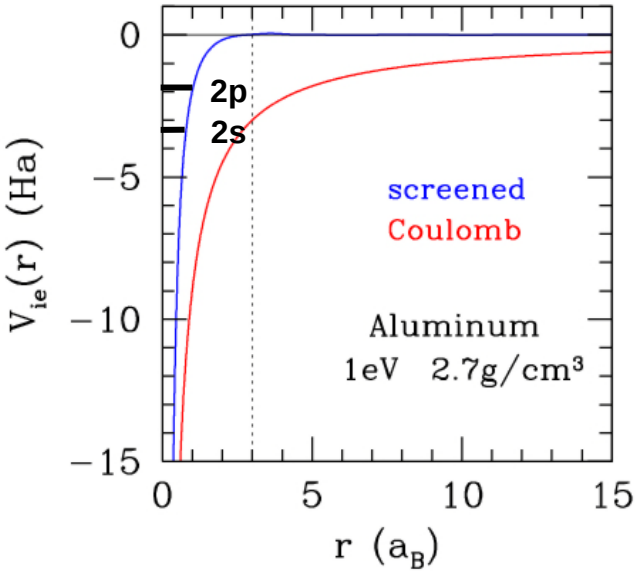
→ Iterative solution not robust enough

The calculation of $V_{ie}(r)$ involves Fourier transforms of 1/r functions

Coulomb tails

Physics ensures that $V_{ie}(r)$ is short-ranged in the converged solution

1/r tails in $V_{ie}(r)$ can develop during SCF iterations but MUST be avoided!



Parts of $V_{ie}(r)$ are obtained by solving Poisson's equation for the charge distribution

$$\chi'' = 4\pi r n(r) \quad \text{where} \quad \chi = rV_{ie}(r)$$

If $n(r)$ contains a net charge, $V_{ie}(r) \sim 1/r$ for large r

Los Alamos

Numerical solution

Ion-electron problem

Coulomb tails

Trick (e.g. Kerker 1981): Introduce numerical screening of the potential

$$\chi'' - \kappa^2 \chi = 4\pi r n(r) - \kappa^2 \chi$$

1/κ is a screening length

In terms of the iterative procedure:

$$\chi''_{n+1} - \kappa^2 \chi_{n+1} = 4\pi r n(r) - \kappa^2 \chi_n$$

This effectively controls (damps) Coulomb tails in $V_{ie}(r)$

→ Convergence is slow (oscillatory)

Numerical solution

Ion-ion problem

Given $V_{ii}(r)$, solve the fluid equation for $g(r)$

$$g(r) = h(r) + 1 = \exp[-V_{ii}(r)/kT + h(r) - c(r) + B(r)]$$

$$\hat{h}(k) = \hat{c}(k) + n_0 \hat{h}(k)\hat{c}(k)$$

More Fast Fourier Transforms

Coulomb tails in $V_{ii}(r)$ to be avoided

- Not as problematic as in $V_{ie}(r)$
- No safeguard yet

Iterative Newton solver (NITSOL package) is fairly robust

→ BUT may converge on a bad solution when coupling is very strong

- Motivation
- Theoretical approach
  - Average atom model
  - Interacting fluids: Integral equations
- The model
- Some results
- Numerical challenges
- **Summary**

Los Alamos

Summary

The model

- Extended the QHNC model of Chihara to include WDM physics
- Explored the “arbitrary” aspects of the model
  - unresolved issue: charge neutrality condition
- A broad range of applications is possible

Numerics

- Developed a package of algorithms that widens the domain of convergence
  - more robust algorithms with stronger convergence are desirable
- Runs fast compared to ab initio methods

Validation

- Calculated radial distribution functions and pressures
  - liquid metals to WDM (H, Li, B, C, Mg, Al, Fe)
- Results good to excellent (compared to QMD and experiments)

See poster by Charles Starrett