A model of Warm Dense Matter for small computers

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• Motivation

• Theoretical approach
  Average atom model
  Interacting fluids: Integral equations

• The model

• Some results

• Numerical challenges

• Summary
Motivation

Ab initio ("brute force") methods are computationally very expensive

Often limits the number of states that can be calculated in practice
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
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
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Average Atom model of dense matter

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
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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
**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

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

**Closure relation**

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

**Bridge function (beyond 2-body correlations)**

\[
B(r) = 0 \quad \text{Hypernetted chain approximation (HNC)}
\]

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

\[ \frac{U}{NkT} = \frac{3}{2} + \frac{n_0}{2kT} \int V(r)g(r)d^3r \]

\[ \frac{P}{n_0kT} = 1 - \frac{n_0}{6kT} \int r \frac{dV}{dr}g(r)d^3r \]
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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)
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):

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

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

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

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

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 $\varepsilon_{kl}$)
Key equations and assumptions

Bound states:

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

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

$w_{nl}(T, \rho)$ 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 $\bar{Z} = Z - N_{ion}$
Key equations and assumptions

Free states:

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

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

Charge neutrality of average atom:

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

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

(i.e. neutral ion sphere)
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

\[ n_{\text{screen}}(r) = n_{PA}(r) - n_{\text{ion}}(r) \]

From the integral fluid equations,

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

This effectively couples the average atom model \([n_{\text{screen}}(r)]\) to the fluid equations \([C_{ei}(r)]\)
2) The ion-ion problem

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

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

Direct ion-ion Coulomb term  Screening from electron fluid

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![Graph showing the screened Coulomb potential for Aluminum with specified energy and density.](LosAlamos)
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 $\rho$

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: $\bar{Z}$
- 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 ($Z, T, \rho$)
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
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

\[ n_{\text{screen}}(r) = n_f(Z, \mu_e, r) - n_f(0, \mu_e, r) \]

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

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

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

QHNC

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

A minimization principle?
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Application to a liquid metal: Mg

- Limit of very strong ion-ion coupling: $\Gamma_{\text{Mg}} = 400$
- Strong degeneracy: $T/T_F \sim 0.006$

- Our model is in excellent agreement with data
- Structure of $g(r)$ slightly too pronounced
Application to WDM: Aluminum

Aluminum $\ 2.7 \text{g/cm}^3 \quad T=0.5$ to $10\text{eV}$

- Agreement between model and QMD-DFT is excellent
- Improves at larger $T$ (weaker ion-ion coupling)
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 $T<10^2$eV

OFMD calculation from Lambert et al. (2006)
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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
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

\[
\chi'' = 4\pi r n(r) \quad \text{where} \quad \chi = r V_{ie}(r)
\]

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

**Ion-electron problem**

**Coulomb tails**

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

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

\( \frac{1}{\kappa} \) 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 \( V_{ie}(r) \)

\( \rightarrow \) Convergence is slow (oscillatory)
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

\( \Rightarrow \) BUT may converge on a bad solution when coupling is very strong
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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