Part 1: Tartarus

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Tartarus: hybrid AA model

A numerically stable hybrid Green’s function / orbital based average atom code for EOS

- DFT, nucleus in a spherical cavity in jellium
- Same model as INFERNO, PURGATORIO
- Code needs to work of over huge range of conditions, for all elements
- This is a tremendous numerical challenge with a long history
Schrödinger's (Dirac’s) equation is usually solved for orbitals to give the electron density

\[ n(r) = \int_{-\infty}^{+\infty} d\varepsilon \, f(\varepsilon, \mu) \, |\varphi_\varepsilon(r)|^2 \]

In the GF approach we solve for the GF

\[ n(r) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{+\infty} d\varepsilon \, f(\varepsilon, \mu) \text{Tr} G(r, \varepsilon) \]

The GF is analytic in the complex plane \(\rightarrow\) All energy integrals can be deformed using Cauchy’s integral theorem!
Greens Function Method

Example: Density of states of Lu at 10 eV / 10 g/cc

\[ \chi(\varepsilon) = \frac{-1}{\pi} \text{Im} \int dr \ Tr \ G(r, \varepsilon) \]

In the complex plane the DOS is guaranteed to be smooth!! Easy to integrate over.
GF is 2 times solved to evaluate per energy than orbital

GF is hard to evaluate accurately near origin for high orbital angular momentum $l$.

So we use the usual orbital expression for high $l$, where no bound states or resonances are expected.

Gill & Starrett, HEDP 2017
This gives stability and accuracy

Entropy of Lu:

Solid lines: Non-Relativistic
Dashed lines: Relativistic
This gives stability and accuracy

Pressure of Lu:

Unsavory feature of model:
For small region near liquid/gas transition, pressure decreases as T increases along isocore

Not numerical, but due to physical model
It is also fast

Time for Lu grid

-2 0 2 4
log_{10} (density [g/cm^3])

0 1 2 3
log_{10} (temperature [eV])

10 20 30 40 50 60
time [minutes]

Los Alamos
Example for lutetium (Z=71) @ solid density

TFD gets trends, but has large errors.

Tartarus (KS-DFT) is in much better agreement with plane wave code, relatively small differences persist.
Another unsavory feature of model

Pressure from Virial expression is not guaranteed to be equal to

\[ P = -\left. \frac{\partial F}{\partial V} \right|_T \]

Agreement is at its worse in highly degenerate electron regime.
Summary of Tartarus

- Hybrid GF/Orbital approach gives good stability and can be used for tables automatically
- Physical model imperfect and has unsavory features (thermo-inconsistency, entropy increases with density along isotherm (low T))
- Reasonable agreement with plane wave code, but far from perfect.
Part 2: KKR-GF

Inspired by Brian Wilson’s work

HEDP 2011
Plane wave KS-DFT scales poorly with $T$

Plane wave Kohn-Sham calculations become prohibitively expensive as temperature increases.

Figure credit: Sjostrom and Daligault
KKR-GF (Korringa-Kohn-Rostoker Greens-Function)

Divide space into non-overlapping polyhedra (Voronoi)

Solve single site problem for each polyhedron (using DFT)

→ t-matrix \( t(\varepsilon) \)

→ local wavefunctions \( R \) and \( H \)

As a first step we assume spherical symmetry in each polyhedron (the Muffin Tin approximation).

This is like an Average Atom calculation
Construct structure constants from ion positions and periodic cell \( \rightarrow G_0(\varepsilon) \)

Step 4: Calculate structural GF by matrix inversion
\[
G^s(\varepsilon) = [t(\varepsilon)^{-1} - G_0(\varepsilon)]^{-1}
\]

This modifies the boundary condition from free-electron, to the matching of incoming and outgoing waves.
The Green’s function

\[ G(\mathbf{r}, \varepsilon) = R(\mathbf{r}, \varepsilon)H(\mathbf{r}, \varepsilon) + R(\mathbf{r}, \varepsilon)^2 G^S(\varepsilon) \]

This is composed of an Average-Atom like single site part:

\[ G^{ss}(\mathbf{r}, \varepsilon) = R(\mathbf{r}, \varepsilon)H(\mathbf{r}, \varepsilon) \]

and a multi-center (multiple scattering) part:

\[ G^{ms}(\mathbf{r}, \varepsilon) = R(\mathbf{r}, \varepsilon)^2 G^S(\varepsilon) \]
Calculation of observables

The electron density:

\[ n(\vec{r}) = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{+\infty} dz \ f(z) G(\vec{r}, z) \]

Electron kinetic energy-like term

\[ K = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{+\infty} dz \ f(z) zG(\vec{r}, z) \]

\( z \) is the electron energy

\( f(z) \) is the Fermi-Dirac occupation factor
Example: Density of states
fcc aluminum pressure (isocore, 2.7 g/cm$^3$)

KKR matches Average Atom at high temperature and plane wave code at low T
bcc iron excess pressure (isocore, 7.87 g/cm$^3$)

Small differences between plane wave code and KKR are probably due to Muffin-Tin approximation.
KKR-GF in principle works from low to high $T$ and low to high $\rho$, and *should* be cheap enough for tables …

Disordered systems (not crystals) will be more difficult to handle

Preliminary results are encouraging, but much work remains.
Part 3: Potential of Mean Force for Electrical Conductivity

HEDP 2017
Relaxation Time approximation for Conductivity

\[ \sigma_{dc} = \frac{1}{3\pi^2} \int_0^\infty d\varepsilon \left( -\frac{\partial f}{\partial \varepsilon} \right) v^3 \tau_\varepsilon \]

where \( \tau_\varepsilon \) is the relaxation time. This model assumes all scattering centers are identical.

\( \tau_\varepsilon \) is related to the momentum transport cross section

\[ \tau_\varepsilon = \frac{1}{n_i^0 v \sigma_{TR}(\varepsilon)} \]
The phase shifts \( \eta_l \) (relative to a plane wave) are calculated by solving the Schrödinger equation for a given scattering potential.

But what is the scattering potential of one center in the plasma?
Physical interpretation of $V^{AA}(r)$:

Plasma is made up of identical PseudoAtoms. Total potential is then

$$V(\vec{r}) = \sum_{\text{atoms, } i} V^{PA}(|\vec{r} - \vec{R}_i|)$$

AA potential is then a muffin-tin-ization of this:

In a sphere surrounding a nucleus, spherically average $V(\vec{r})$, and average over all nuclei

$\Rightarrow V^{AA}(r)$
You can then derive an expression for $\sigma_{TR}$

The result has the ion-ion structure factor appearing explicitly

$$\frac{d\sigma}{d\theta}(\varepsilon, \theta) = S(q) |F(\varepsilon, \theta)|^2$$

(This differential cross section is related to $\sigma_{TR}$)

However, this does not recover the Born Limit (valid at high $T$) due to muffin-tin-ization, which is worrying…

$$\frac{d\sigma}{d\theta}(\varepsilon, \theta) = S(q) \left| \frac{V^{PA}(q)}{2\pi} \right|^2$$
Wrong! AA potential leads to weird results

Witte et al, Pop 2018. DFT-MD calculations.
AA model from Starrett & Saumon PRE 2013
Instead of combining superposition approximation with muffin-tin, just use superpostion

\[ V(\vec{r}) = \sum_{\text{atoms, } i} V^{PA}(|\vec{r} - \vec{R}_i|) \]

The result also has the ion-ion structure factor appearing explicitly

\[ \frac{d\sigma}{d\theta}(\varepsilon, \theta) = S(q)|\mathcal{F}(\varepsilon, \theta)|^2 \]

But now \( \mathcal{F}(\varepsilon, \theta) \) is calculated for \( V^{PA}(r) \), so the Born limit is recovered
Great, problem solved, right?

Wrong! PA potential does not improve results where Born is not valid.
From classical physics we have the concept of the “potential of mean force”

\[ g(r) = e^{-\beta V_{MF}(r)} \]

\[ V_{MF}(r) = \frac{Z^2}{r} + n^0 \int d^3r' \frac{C(|\vec{r} - \vec{r}'|)}{-\beta} h(r') \]

which uses the HNC approximation to the Ornstein-Zernike equations.

This potential has proved very successful in predicting ion transport coefficients (Daligault, Baalrud PRL 2017)
Potential of Mean Force

For a mixture of quantal electrons and classical ions, the analogue is the Quantum Ornstein-Zernike equations and the Quantum HNC approximation (Chihara)

\[ V^{MF}(r) = V^{PA}(r) + \int d^3r' \frac{n_i^0 Z_h_{ii}(r') + n_e^x(r')}{|\vec{r} - \vec{r}'|} \]

+ electron-electron correlations
+ electron-ion correlations

All these terms are calculated in our AA+ion correlation models (Starrett + Saumon PRE 2013)
This corrects \( V^{PA}(r) \) to include Coulombic interactions and correlations with other ions.
Potential of Mean Force – its works!

Starrett, HEDP 2017
Include electron-electron collisions

Hydrogen @ 40 g/cc: without e-e collisions

QLB from Desjarlais et al PRE 2017
Include electron-electron collisions

Our relaxation time approach only includes electron-ion collisions.

What about electron-electron collisions?

Could use effective e-e potential and calculate the same way, but…

Reinholz et al (PRE 2015) came up with a simple correction factor (0 ≤ R ≤ 1)

\[ \sigma_{dc} = R \sigma_{dc}^{ei} \]

R depends on T, average ionization and density \( \leftrightarrow \) AA model
Include electron-electron collisions

QLB from Desjarlais et al PRE 2017
ee factor from Reinholz et al PRE 2015
Important for low Z @ high T or low density
But model isn’t perfect

At low T, metal to non-metal transition is not well modeled by AA leading to bad conductivities.
Summary

• Potential of Mean Force gives better conductivities than widely used AA potential
• It consistently includes the effects of correlations with surrounding ions
• Due to lack of experiments, it’s hard to really say definitively how well we are doing → experiments are needed!
• Other electron transport properties possible (e.g., thermal conductivity).
But model isn’t perfect

At low T, metal to non-metal transition is not well modeled by AA leading to bad conductivities.