
Part 1: Tartarus

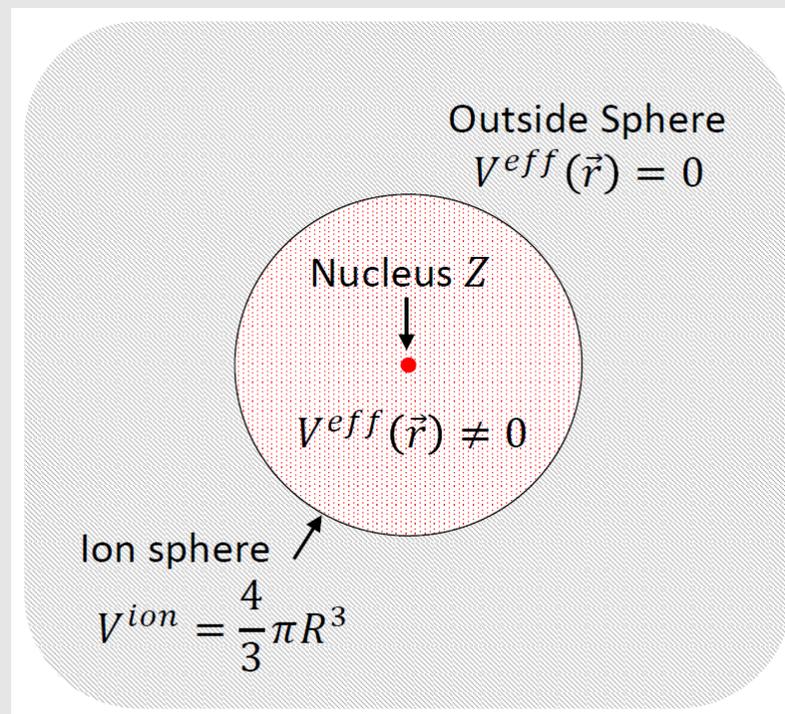
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Tartarus: hybrid AA model

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 over a huge range of conditions, for all elements
- This is a tremendous numerical challenge with a long history



Greens Function Method

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

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

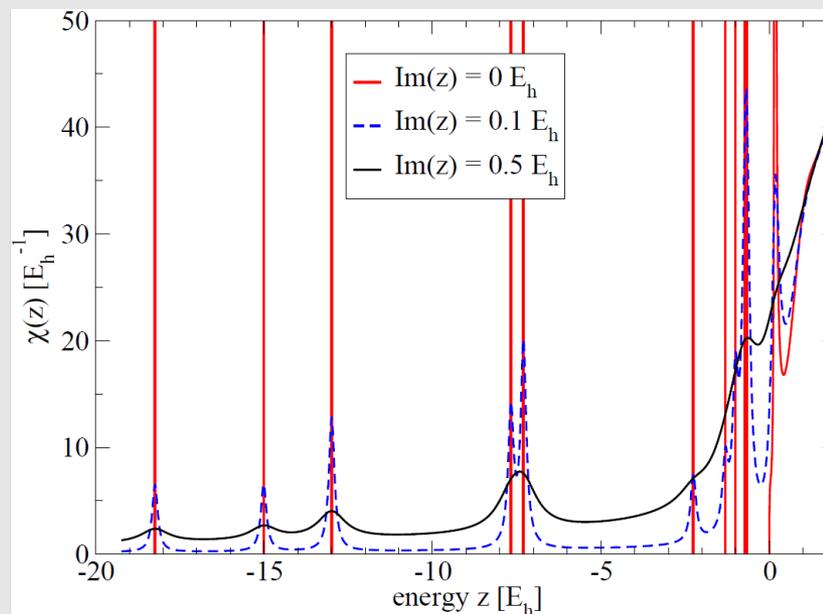
The GF is analytic in the complex plane → All energy integrals can be deformed using Cauchy's integral theorem!

Greens Function Method

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

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

In the complex plane
the DOS is guaranteed
to be smooth!! Easy to
integrate over.



Hybrid Approach

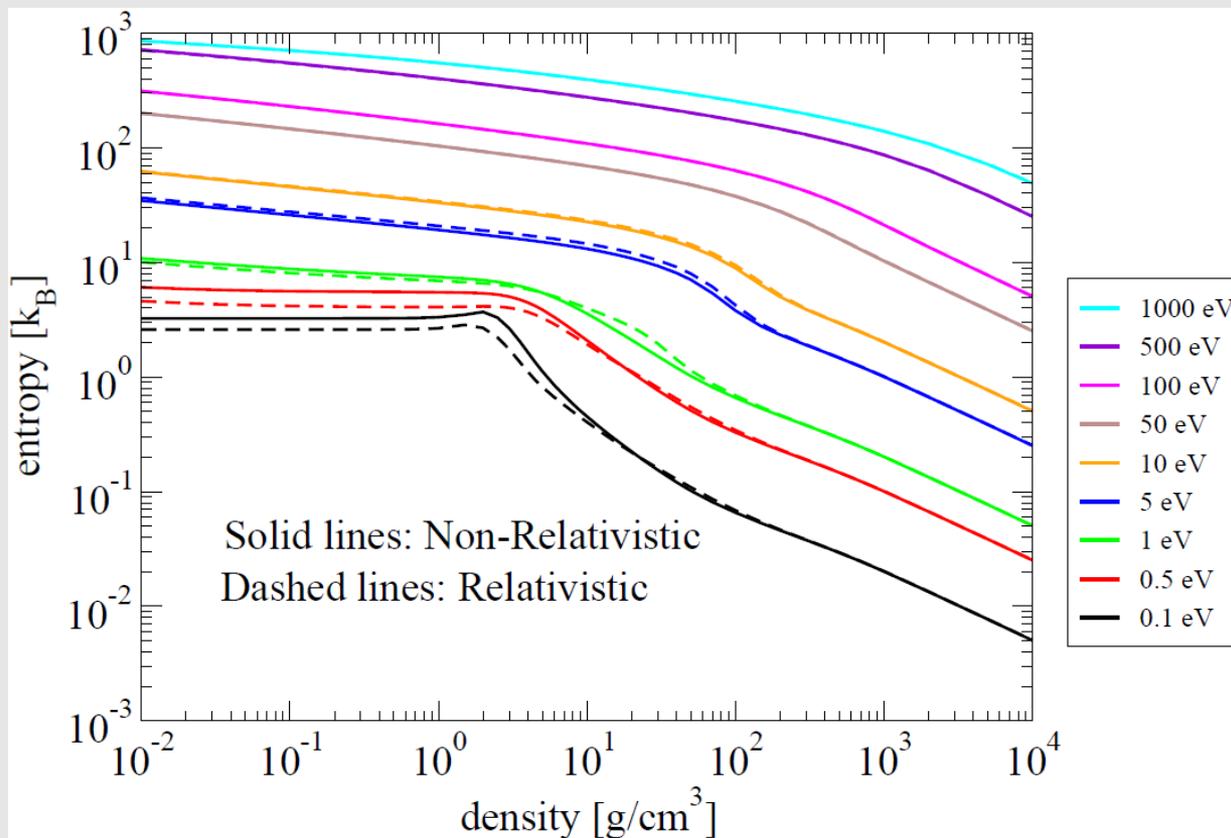
GF is 2 times solved to evaluate per energy than orbital

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.

This gives stability and accuracy

Entropy of Lu:



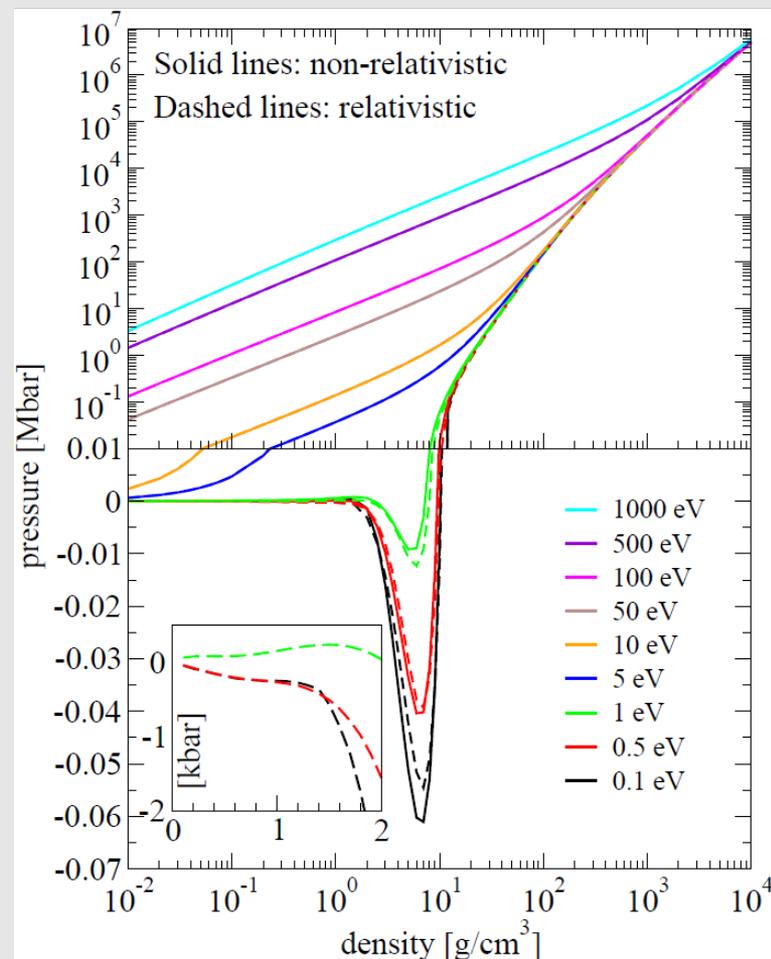
This gives stability and accuracy

Pressure of Lu:

Unsavory feature of model:

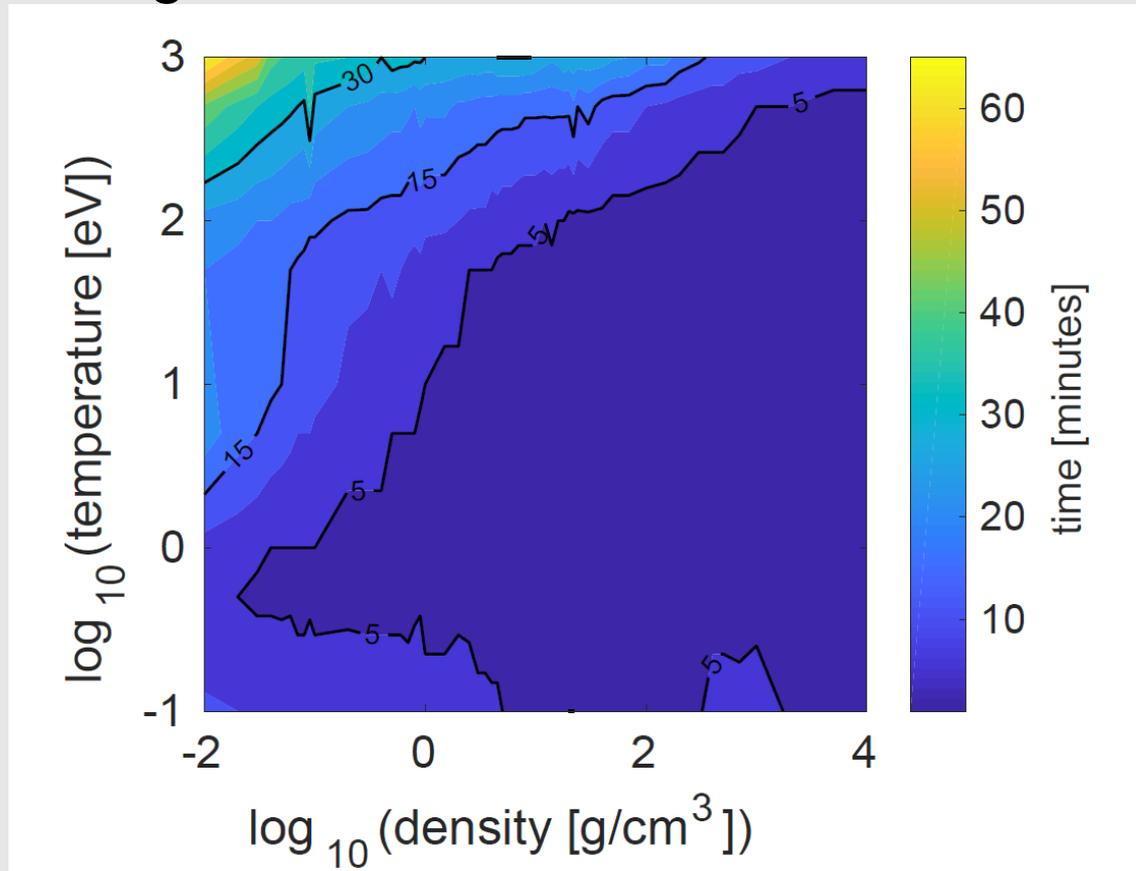
For small region near liquid/gas transition, pressure decreases as T increases along isocore

Not numerical, but due to physical model

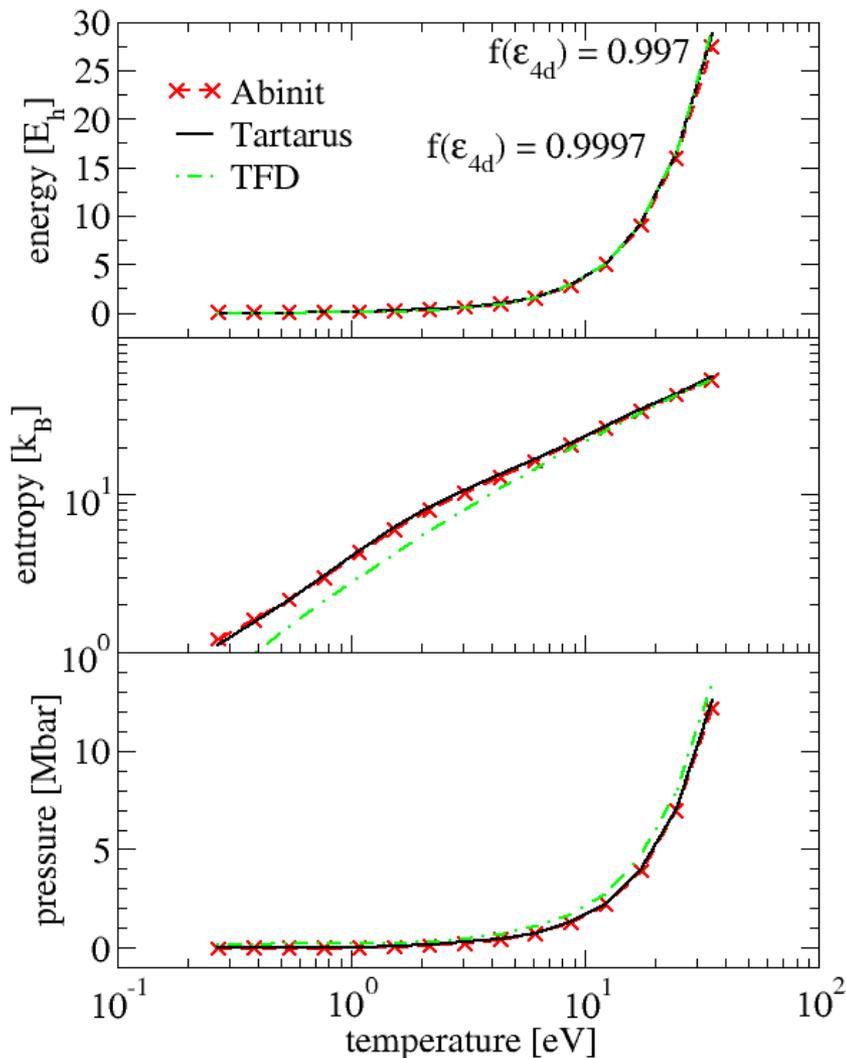


It is also fast

Time for Lu grid



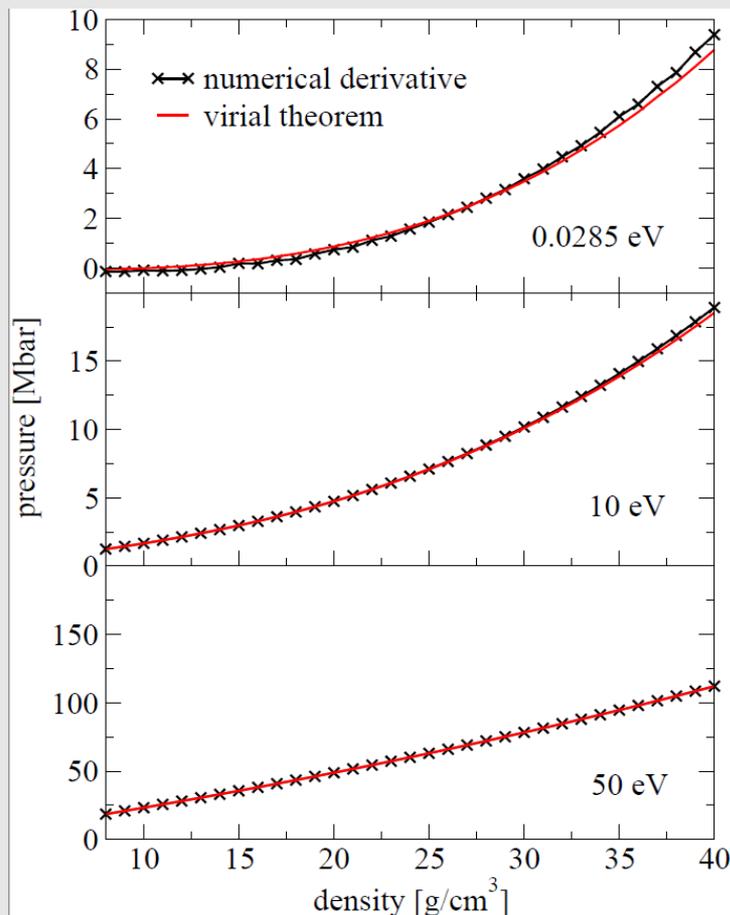
Example for Lutetium (Z=71) @ solid density



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

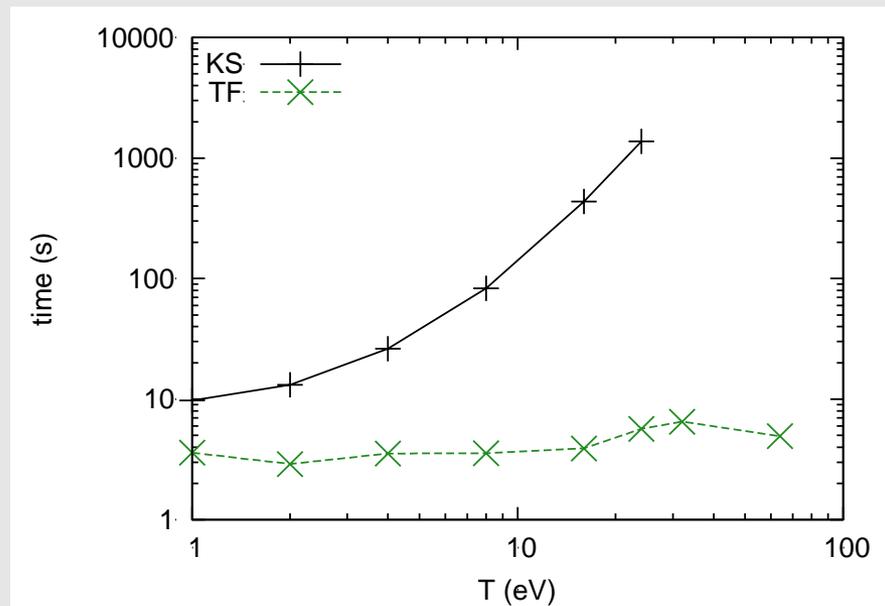
- Hybrid GF/Orbtial approach gives good stability and can be used for tables automatically
- Physical model imperfect and has unsavory features (thermo-inconsistency, entropy increases with density along isotherm (low T))
- Reasonable agreement with plane wave code, but far from perfect.

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

Improve electronic structure with KKR-GF

KKR-GF (Korringa-Kohn-Rostoker Greens-Function)

Divide space into non-overlapping polyhedra (Voronoi)

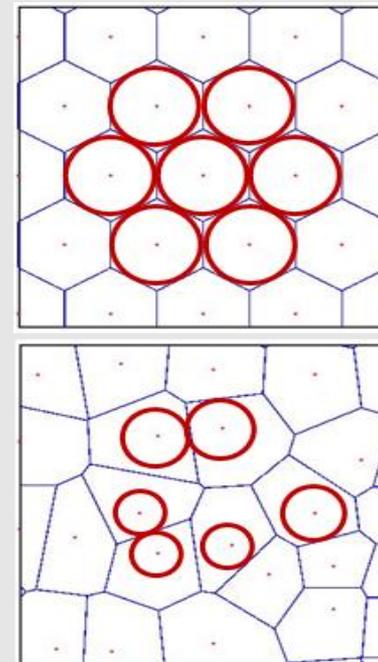
Solve single site problem for each polyhedron (using DFT)

→ t-matrix $t(\epsilon)$

→ 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

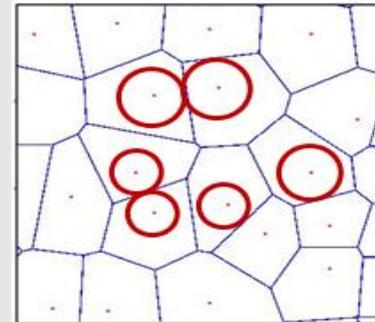
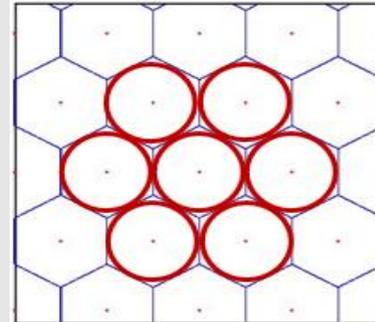


Improve electronic structure with KKR-GF

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.

Improve electronic structure with KKR-GF

The Green's function

$$G(\vec{r}, \varepsilon) = R(\vec{r}, \varepsilon)H(\vec{r}, \varepsilon) + R(\vec{r}, \varepsilon)^2 G^S(\varepsilon)$$

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

$$G^{SS}(\vec{r}, \varepsilon) = R(\vec{r}, \varepsilon)H(\vec{r}, \varepsilon)$$

and a multi-center (**multiple scattering**) part:

$$G^{ms}(\vec{r}, \varepsilon) = R(\vec{r}, \varepsilon)^2 G^S(\varepsilon)$$

Calculation of observables

The electron density:

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

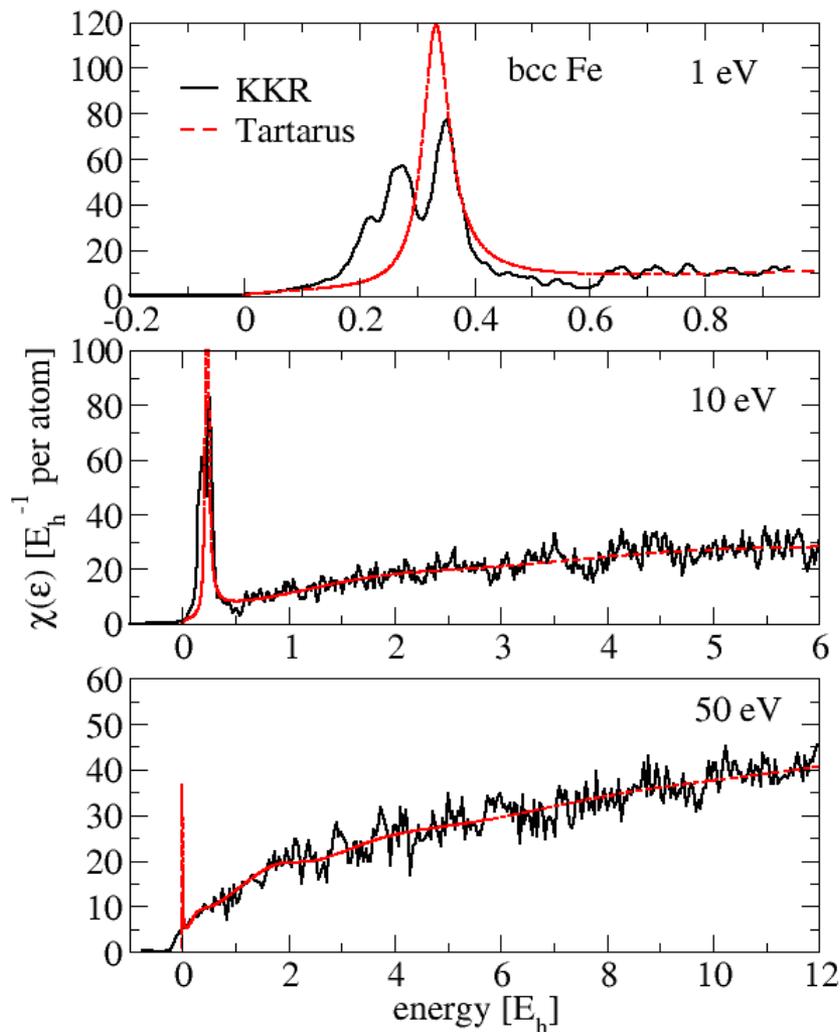
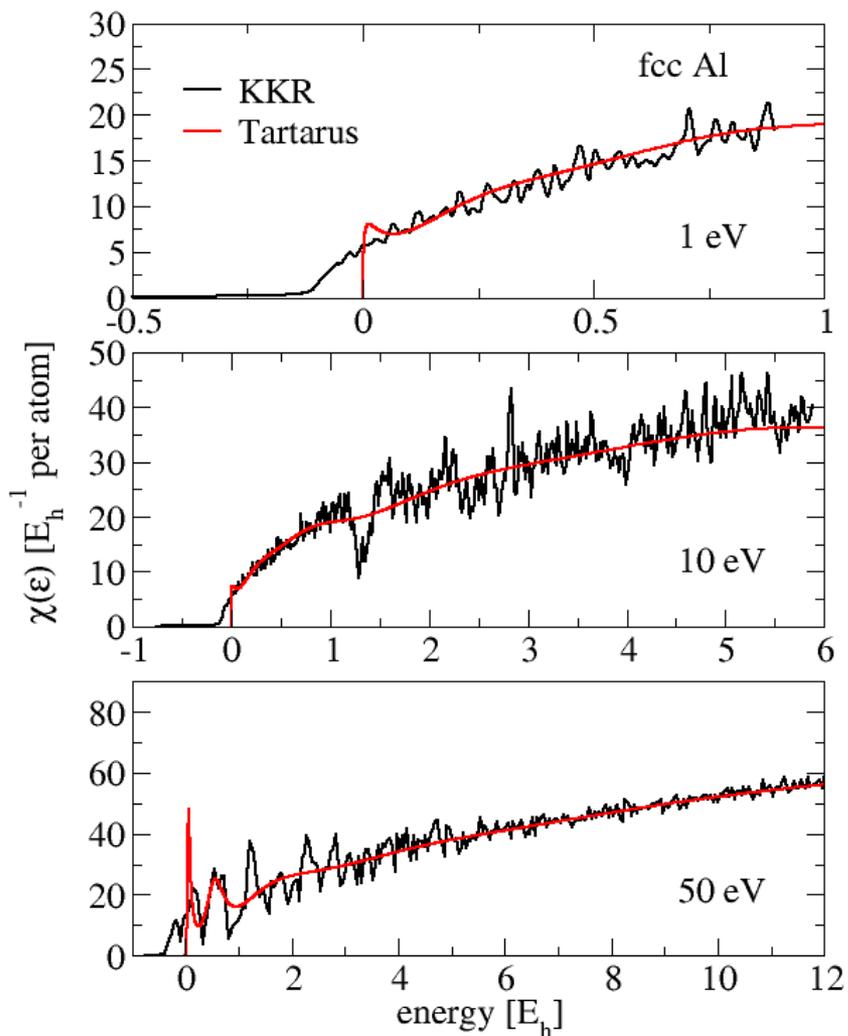
Electron kinetic energy-like term

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

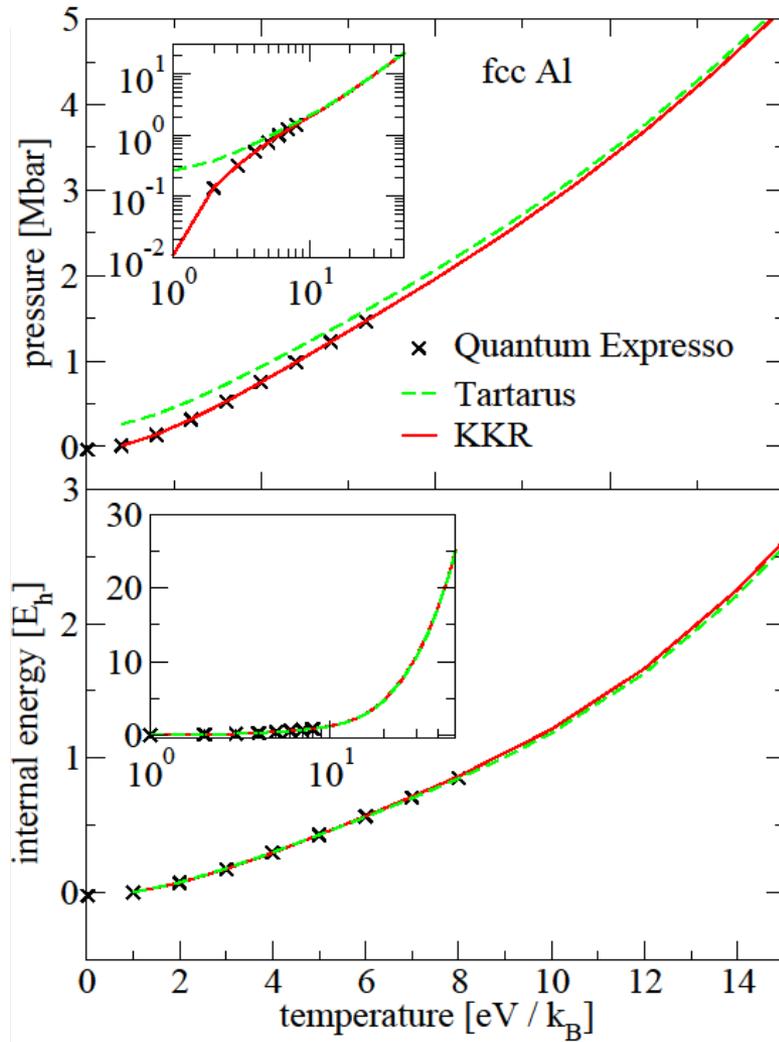
z is the electron energy

$f(z)$ is the Fermi-Dirac occupation factor

Example : Density of states

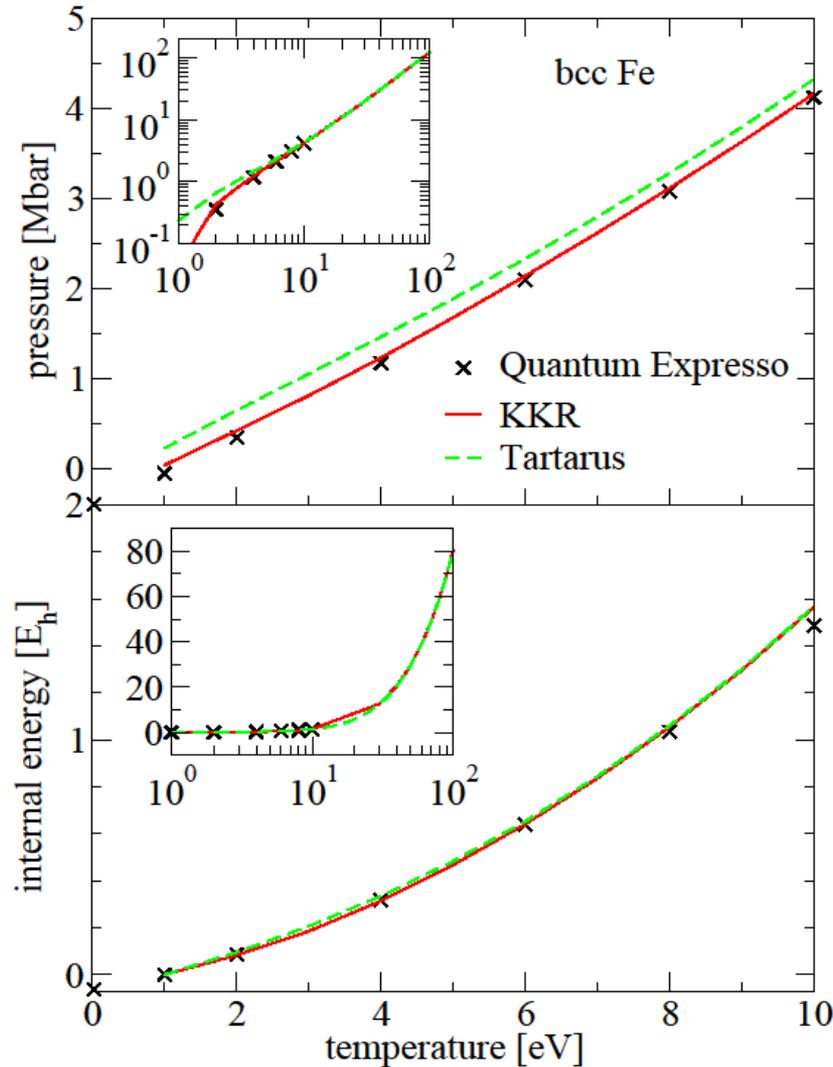


fcc aluminum pressure (isocore, 2.7 g/cm³)



KKR matches Average Atom at high temperature and plane wave code at low T

bcc iron excess pressure (isocore, 7.87 g/cm³)



Small differences between plane wave code and KKR are probably due to Muffin-Tin approximation

Summary

KKR-GF in principle works from low to high T and low to high ρ , 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 τ_ε is the relaxation time. This model assumes all scattering centers are identical.

τ_ε is related to the momentum transport cross section

$$\tau_\varepsilon = \frac{1}{n_i^0 v \sigma_{TR}(\varepsilon)}$$

Relaxation Time approximation for Conductivity

$$\sigma_{TR}(\varepsilon) = \frac{4\pi}{p^2} \sum_{l=0}^{\infty} (l+1) [\sin(\eta_{l+1} - \eta_l)]^2$$

The phase shifts η_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?

Obviously, the AA potential, right?

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

$$\rightarrow V^{AA}(r)$$

Obviously, the AA potential, right?

You can then derive an expression for σ_{TR}

The result has the ion-ion structure factor appearing explicitly

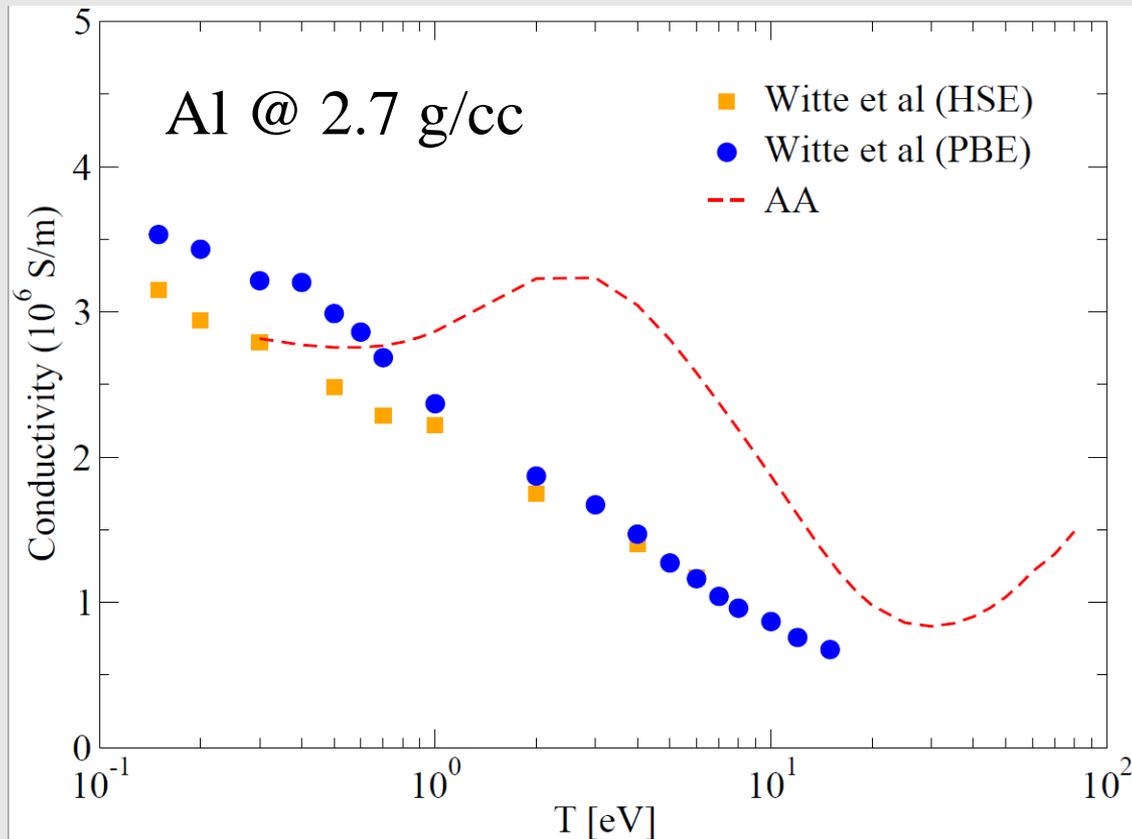
$$\frac{d\sigma}{d\theta}(\varepsilon, \theta) = S(q) |\mathcal{F}(\varepsilon, \theta)|^2$$

(This differential cross section is related to σ_{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

Born Limit can be recovered by PseudoAtoms

Instead of combining superposition approximation with muffin-tin, just use superposition

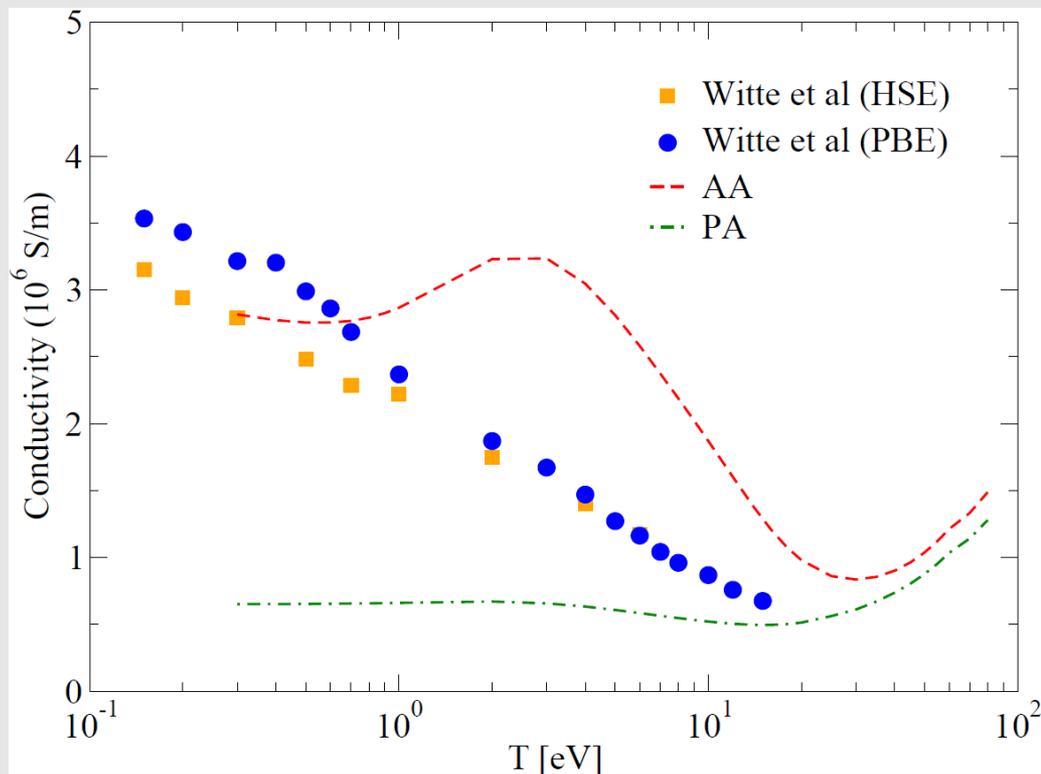
$$V(\vec{r}) = \sum_{atoms, i} V^{PA}(|\vec{r} - \vec{R}_i|)$$

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

What is missing? Correlations with other ions

From classical physics we have the concept of the “potential of mean force”

$$g(r) = e^{-\beta V^{MF}(r)}$$

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

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

This potential has proved very successful in predicting ion transport coefficients (Dalgault, 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)

$$V^{MF}(r) = V^{PA}(r) + \int d^3r' \frac{n_i^0 \bar{Z} h_{ii}(r') + n_e^x(r')}{|\vec{r} - \vec{r}'|}$$

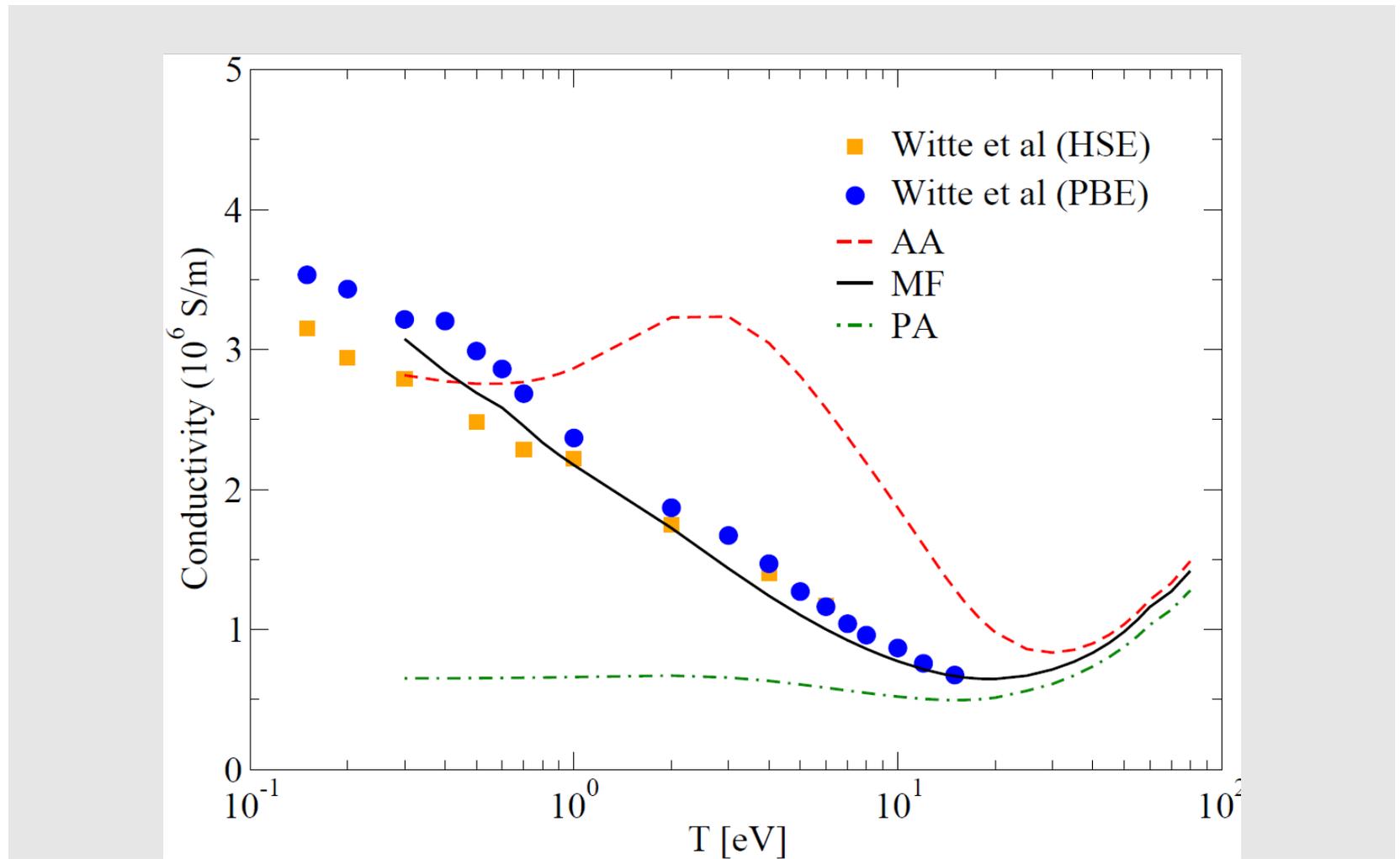
+ electron-electron correlations

+ electron-ion correlations

All these terms are calculated in our AA+ion correlation models (Starrett + Saumon PRE 2013)

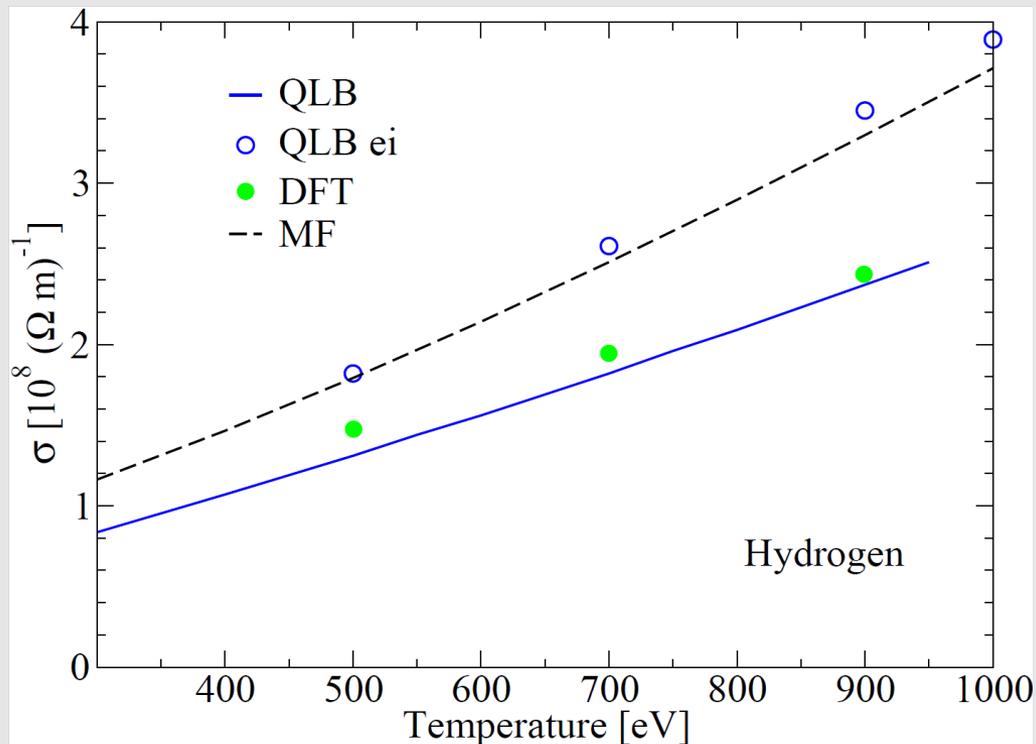
This corrects $V^{PA}(r)$ to include Coulombic interactions and correlations with other ions.

Potential of Mean Force – its works!



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?

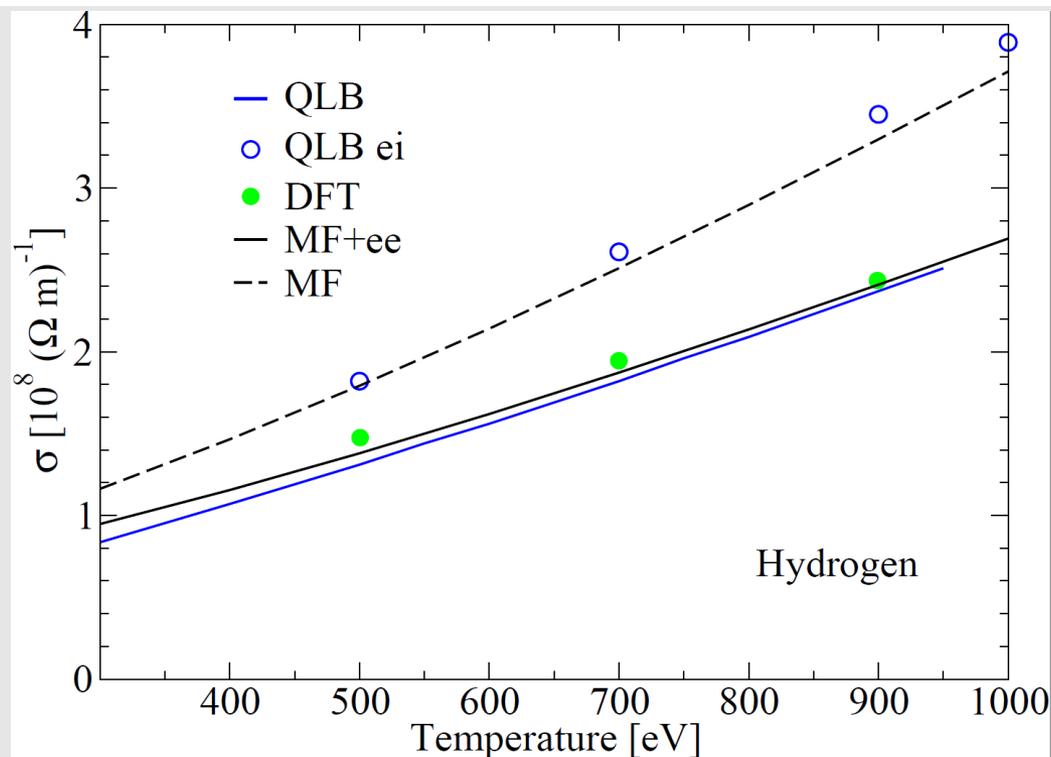
Could use effective e-e potential and calculate the same way, but...

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

$$\sigma_{dc} = R \sigma_{dc}^{ei}$$

R depends on T , average ionization and density \leftarrow AA model

Include electron-electron collisions



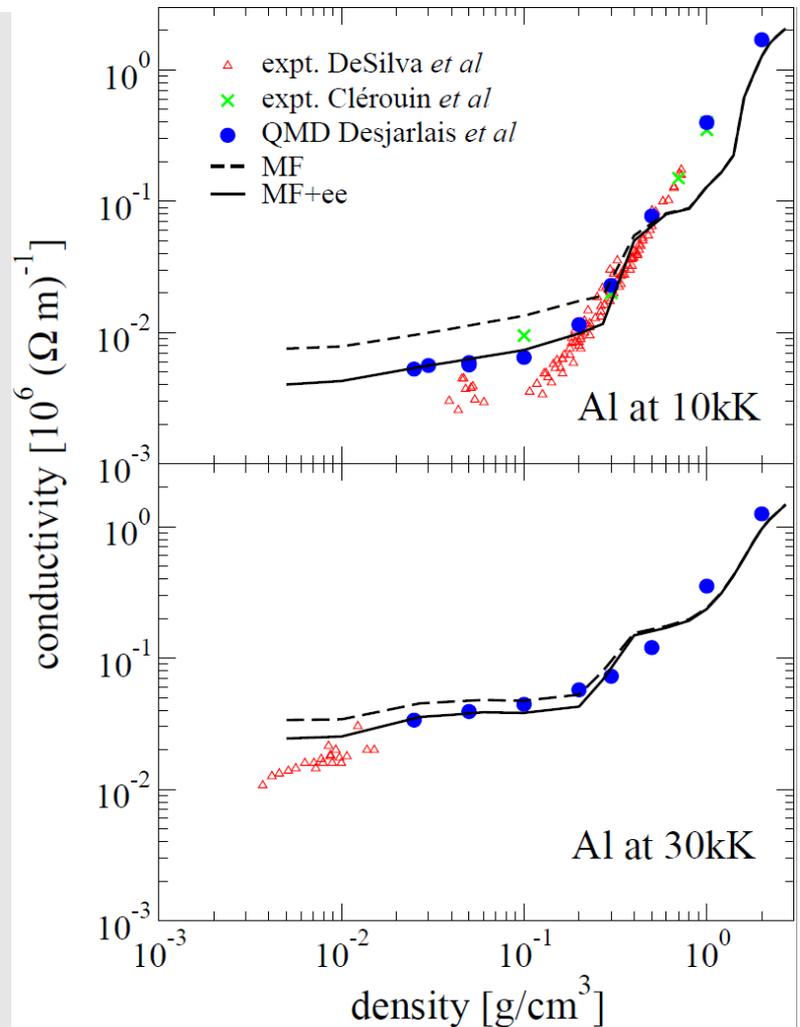
QLB from Desjarlais et al PRE 2017

ee factor from Reinholz et al PRE 2015

Important for low Z @ high T or low density

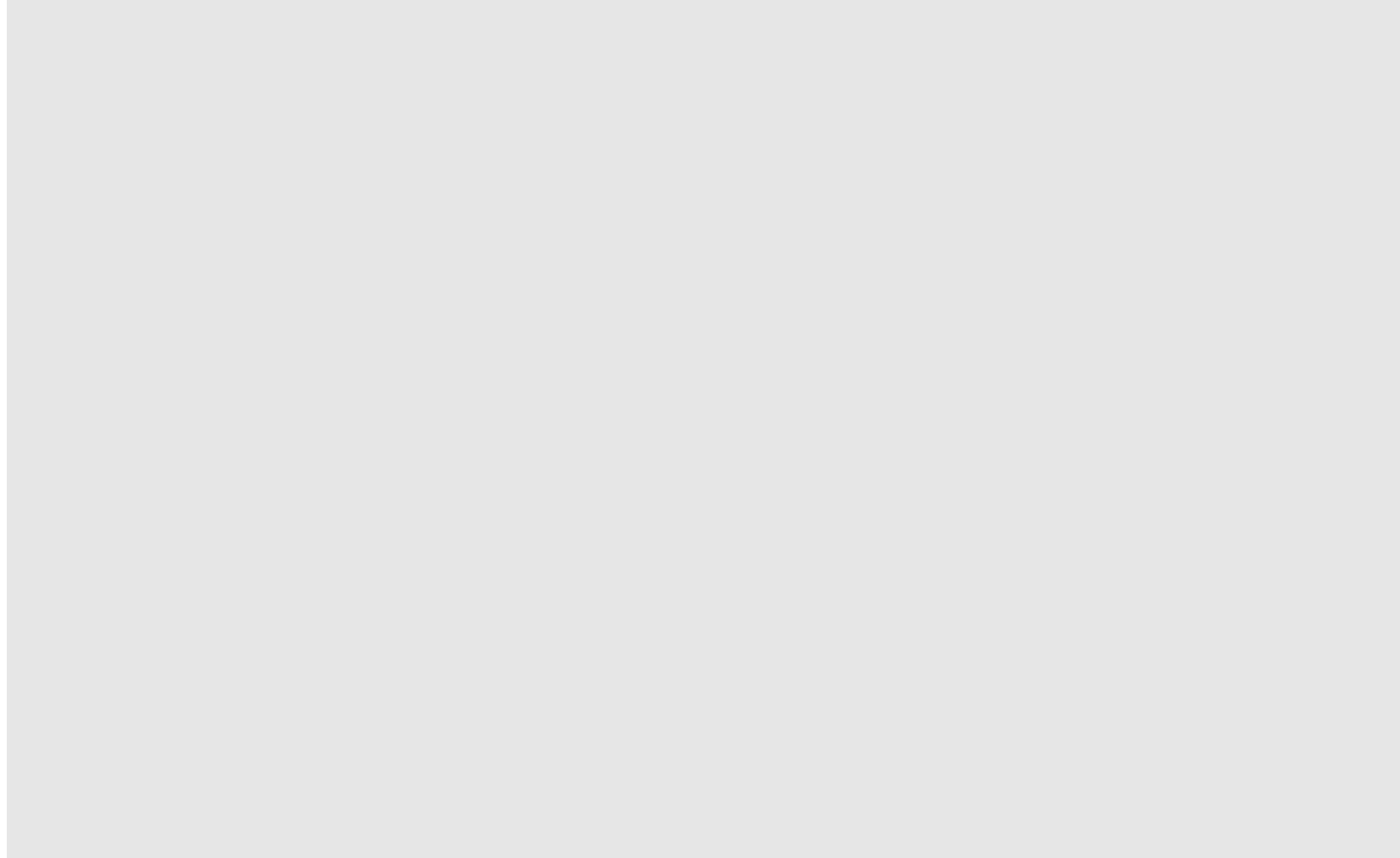
But model isn't perfect

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, its hard to really say definitively how well we are doing → **experiments are needed!**
- Other electron transport properties possible (eg. 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.

