

LA-UR-16-23282

Approved for public release; distribution is unlimited.

Title: Average Atom models

Author(s): Starrett, Charles Edward

Intended for: LANL EOS group website

Issued: 2016-05-09

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Average Atom models

Charlie Starrett (XCP-5)

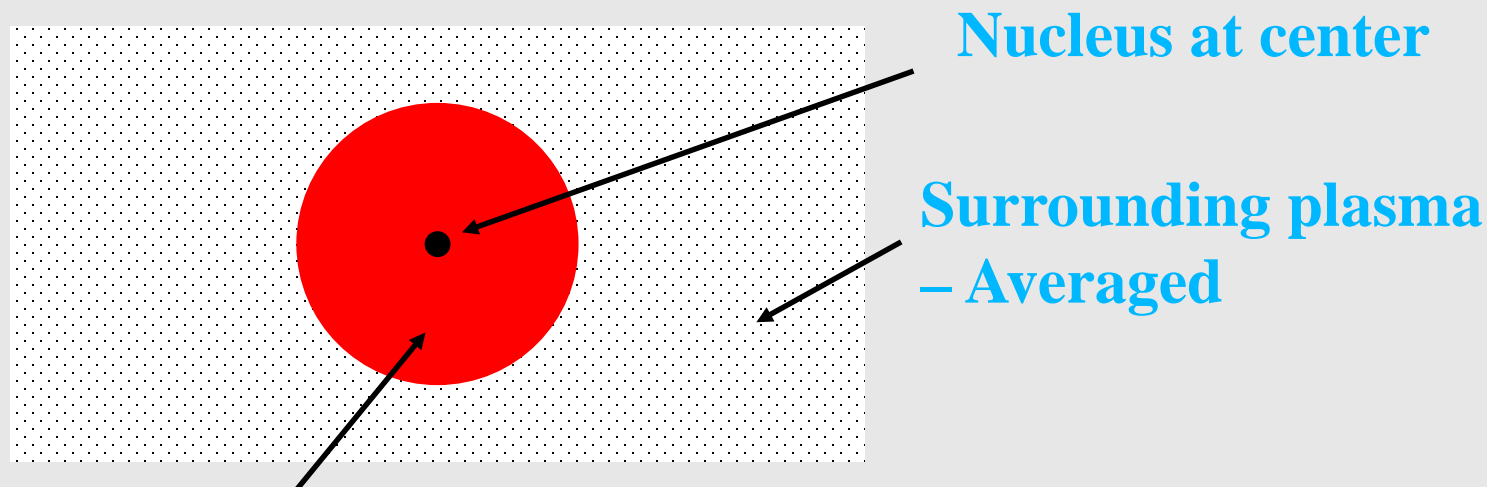
Relatively cheap EOS models based on DFT that can access any temperature or density point for any element (in principle!)

Basic physical model

There are a few ways to “derive” AA models:

- I'll stick to the **atom-in-jellium** concept

Imagine a sphere surrounding a nucleus in a plasma:



In red region we find electronic structure with density functional theory

Basic physical model

Density effects are modeled by sphere size:

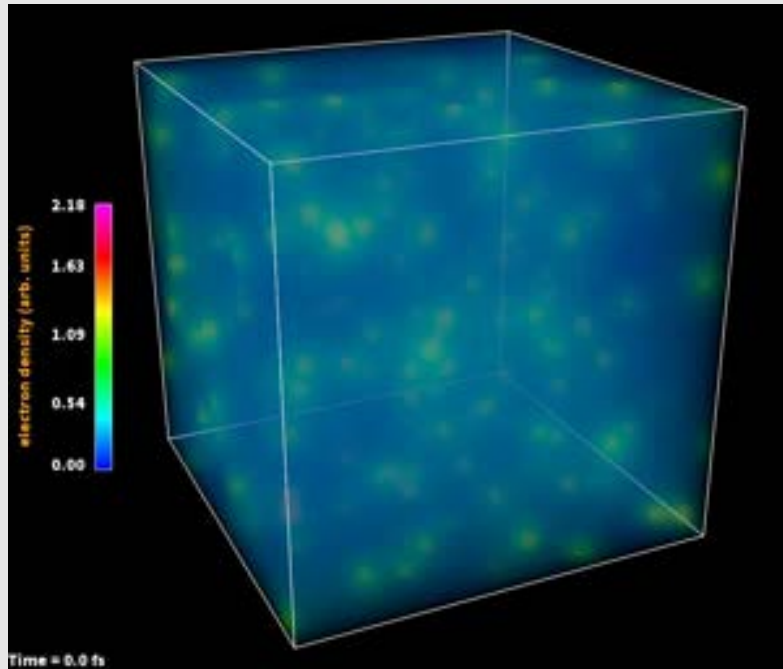
- Sphere size is ion-sphere (volume per ion)
- Charge neutral ion-sphere

$$Z = \int_0^R d^3r n(r)$$

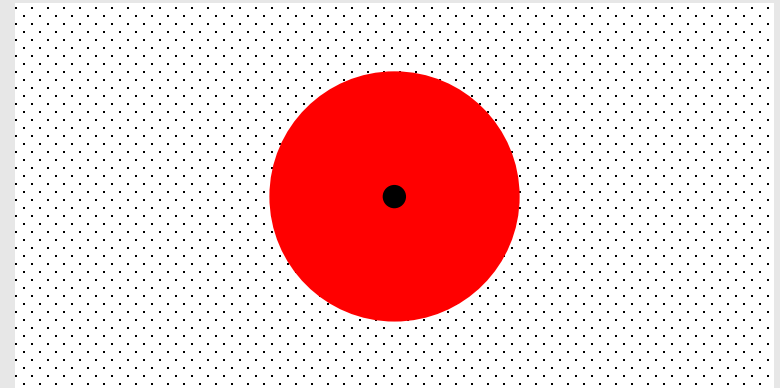
Nuclear charge

Electron density

How does this compare to reality?



**QMD, accurate but
expensive**



**AA, less accurate but
cheap**

Credit: J. Daligault, C. Levy, J. Schloss

Density Functional Theory (DFT)

DFT tells that to get the EOS we have to find the electron density that minimizes a free energy

$$F = F_S + F_{XC} + F_{el}$$

Electron kinetic
+ entropic
eg. KS or TF

Exchange and
correlation
eg. Dirac, KSDT,
PZ

Electrostatic
i.e. coulomb
energy between
ions and $n_{e(r)}$

DFT is exact if KS F_S is used with exact F_{XC} . But an exact F_{XC} is unknown

Thomas-Fermi (TF) model / TFD / TFcell

- Set : $F_{XC} = 0$
- Require : $\frac{\partial}{\partial n_e(r)} \left[F - \lambda \int_0^R d^3r n(r) \right] = 0$

$$V(r) = -\frac{Z}{r} + \int_0^R d^3r' \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|}$$

Effective potential

$$n(r) = c I_{\frac{1}{2}} \left[\frac{\mu - V(r)}{T} \right]$$

Electron density

T-dependent
constant

Fermi integral
(quick)

Chemical
potential

Temperature

Thomas-Fermi (TF) model: SCF algorithm

- Initial guess at $V(r), \mu$
- Do...
 - Get $n(r)$ subject to ion-sphere neutrality
 $Z = \int_0^R d^3r n(r)$ (determines μ)
 - Get new potential by solving Poisson equation $\nabla^2 V^{new}(r) = n(r)$ (easy and quick)
 - Generate new guess by mixing old and new potentials
- Done when $n(r)$ no longer changes between iterations

Thomas-Fermi-Dirac (TFD) model

- Including exchange effects with Dirac expression is easy

$$V^{xc,Dirac}(r) = - \left(\frac{3n(r)}{\pi} \right)^{1/3}$$

- Just add this to the potential at each iteration
- Other XC functionals can be used (eg the temperature dependent KSDT, where the S is for Sjöström)
- The inclusion of XC improves the model

Thomas-Fermi (TF) model

- Takes about 1 second on a computer per density, temperature and element
- Gives EOS
- Known limitations:
 - No shell structure due to bound states

$$\lim_{r \rightarrow 0} n(r) = \text{constant} \times r^{-3/2}$$

Kohn-Sham model: Inferno / Purgatorio / VAAQP

- This has the same structure as the TFD model, but we solve the Schrodinger equation to get $n(r)$

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

Fermi-Dirac
occupation factor

Wave function
from Schrodinger
equation

- $\varphi_\varepsilon(r)$ is expanded in spherical harmonics

Electron density

$$\left[-\frac{1}{2} \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} \right) + V(r) \right] y_{i,l}(r) = \varepsilon_i y_{i,l}(r)$$

$$n_b(r) = \sum_{n,l} f(\varepsilon, \mu) \frac{2(2l+1)}{4\pi} \left| \frac{y_{n,l}(r)}{r} \right|^2$$

$$n_c(r) = \int_0^\infty d\varepsilon f(\varepsilon, \mu) \frac{2(2l+1)}{4\pi} \left| \frac{y_{\varepsilon,l}(r)}{r} \right|^2$$

$$n(r) = n_b(r) + n_c(r)$$

Boundary condition

For $r > R$ require states to be free:

- Bound states

$$y_{n,l}(r) = C_{n,l} r I_l(-ikr)$$

- Continuum states

$$y_{\varepsilon,l}(r) = \left[\frac{2k}{\pi} \right]^{1/2} r \left[\cos \eta_{\varepsilon,l} j_l(kr) - \sin \eta_{\varepsilon,l} n_l(kr) \right]$$

- Normalization:

$$\int_0^{\infty} dr y_{\varepsilon_a,l}(r) y_{\varepsilon_b,l}(r) = \begin{cases} \delta_{a,b} & \text{for bound states} \\ \delta(\varepsilon_a - \varepsilon_b) & \text{for ctm states} \end{cases}$$

Connection to atomic physics

Single-Configuration State Functions (SCSFs) ϕ_v are constructed out of anti-symmetric sums of the products of N $y_{n,l}(r)$'s

Approximate fine structure wave function is then

$$\psi = \sum_{v=1}^{N_{SCSF}} b_v \phi_v$$

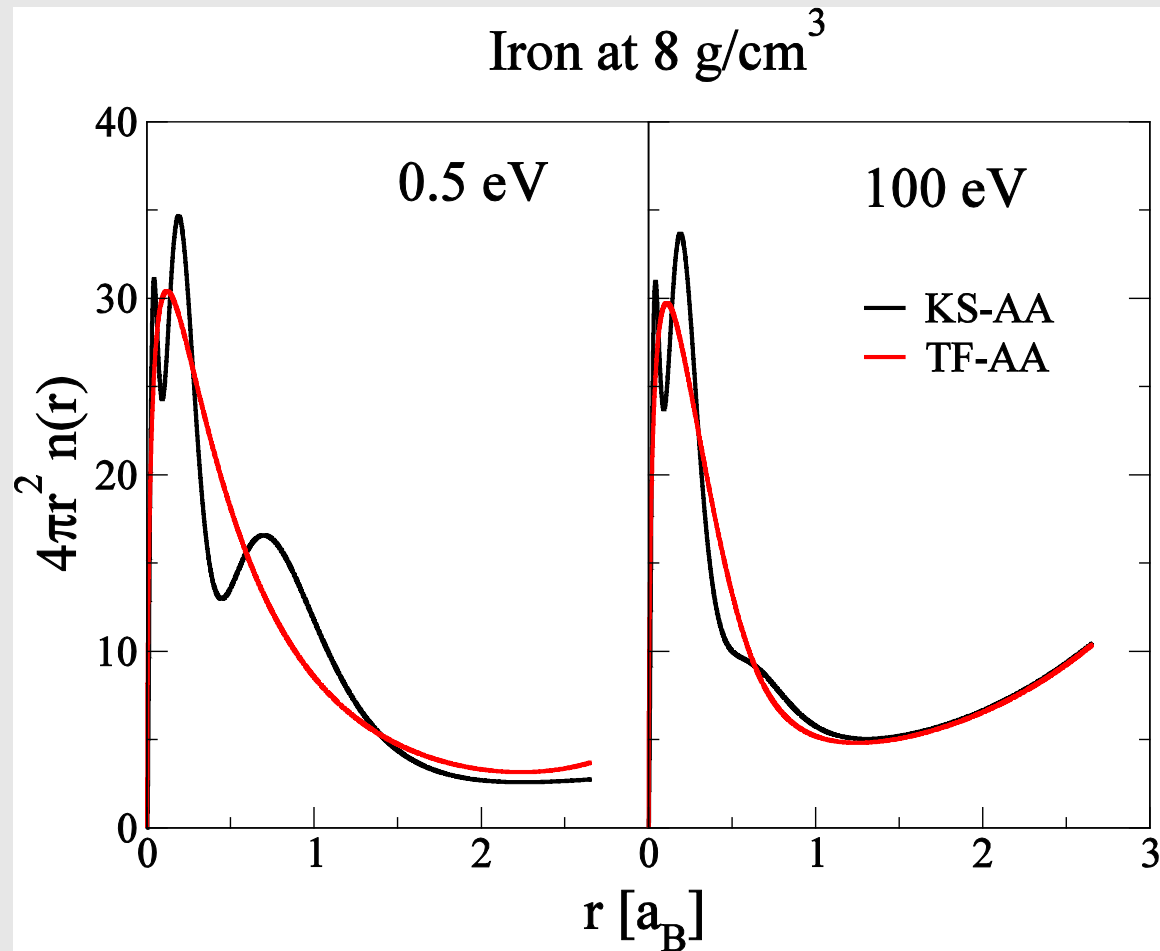
The coefficients are determined by diagonalizing the full Hamiltonian

See Sampson, Zhang and Fontes Physics Reports 2009

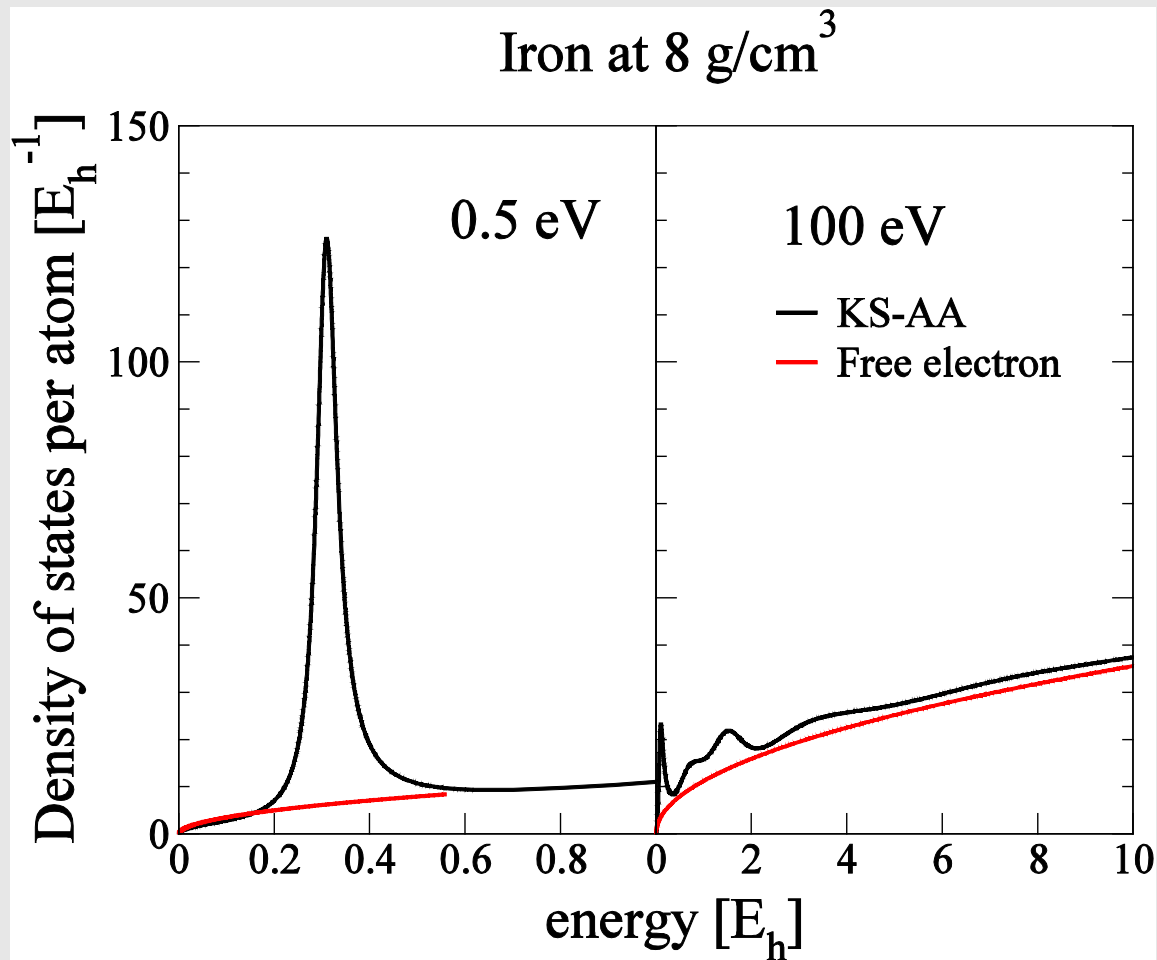
Kohn-Sham model

- Algorithm is the same as for TFD, except we now must solve the Schrodinger equation for one-electron wavefunctions in $V(r)$
- In atomic physics $V(r)$ would be called a central potential
- We get bound states and continuum states because the potential has “finite support”. i.e. it contains less bound electron states than there are electrons.

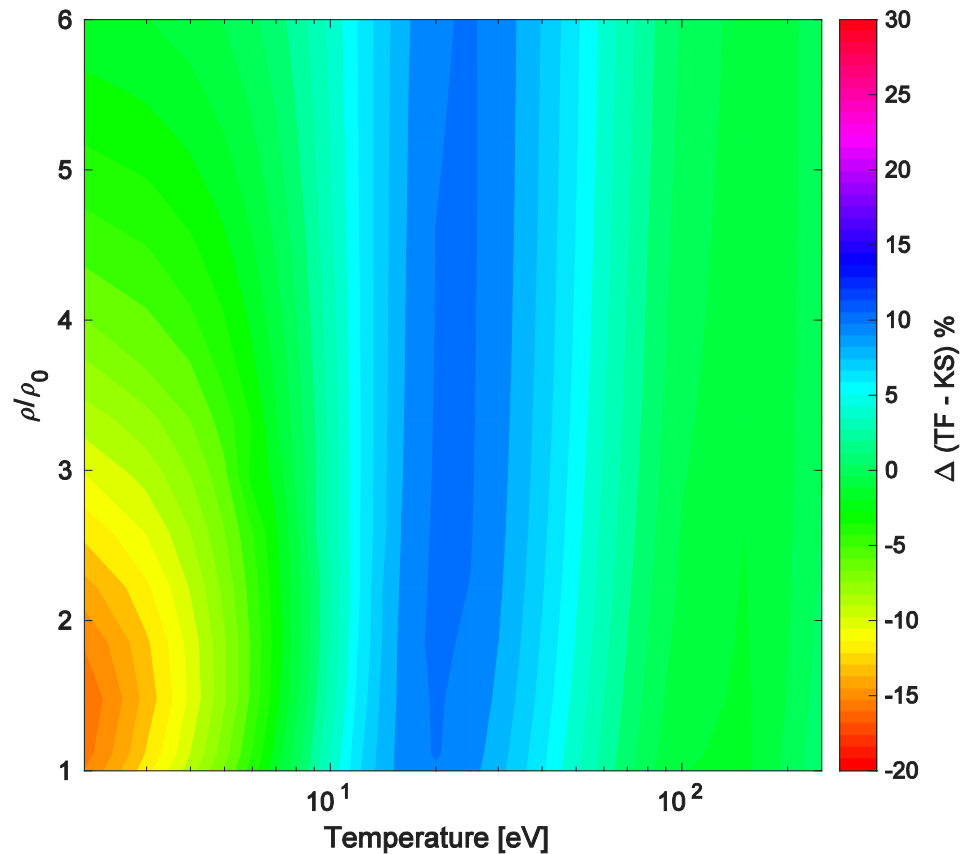
Example: Iron at 8 g/cc



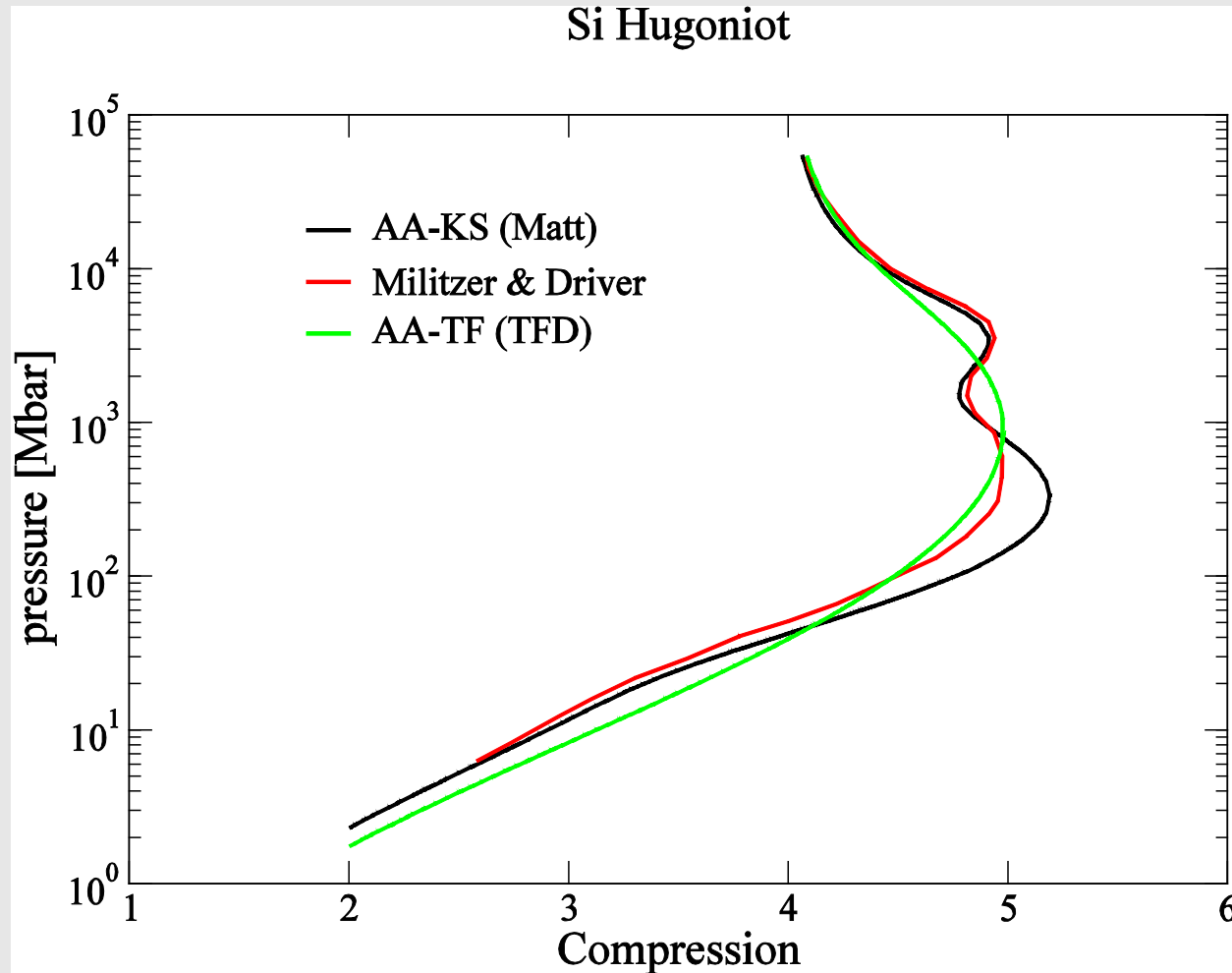
Example: Iron at 8 g/cc



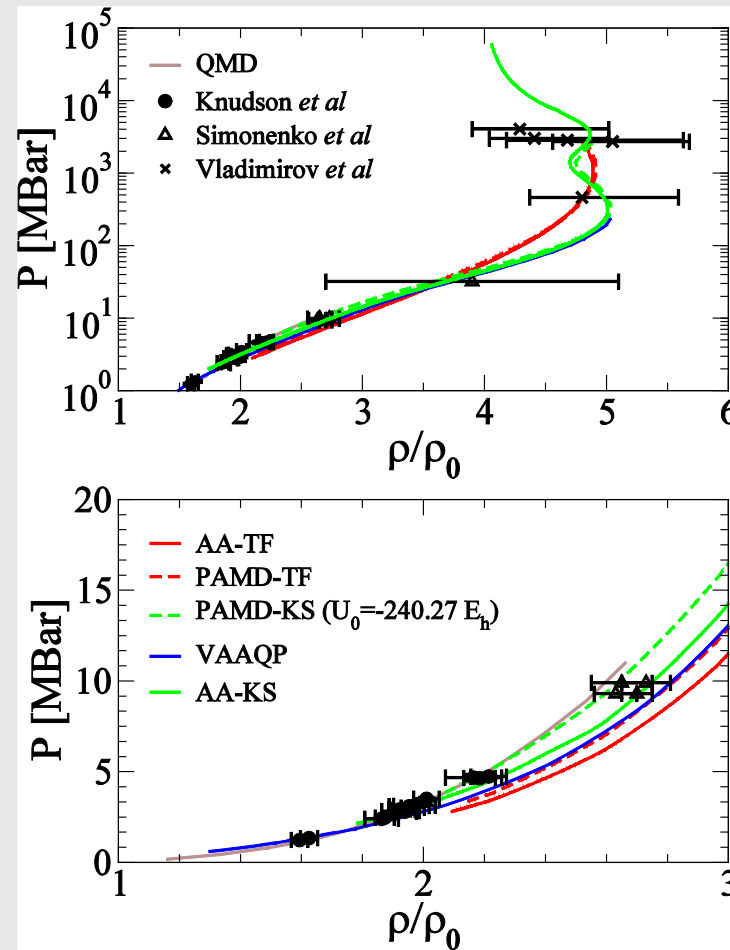
Example: Aluminum TF vs KS



Example: Silicon Hugoniot (0.8g/cc)



Example: Aluminum Hugoniot (2.7 g/cc)



Summary

- TF and KS are quick and useful models
- KS model is significantly better in terms of physics than TF
- Accuracy of EOS is still an open question, especially at high T where QMD can't be used
- Where QMD and KS-AA have been compared accuracy in pressure is at worst a few tens of percent.
- One expects KS-AA to be better at higher T where ion-correlations are less important

