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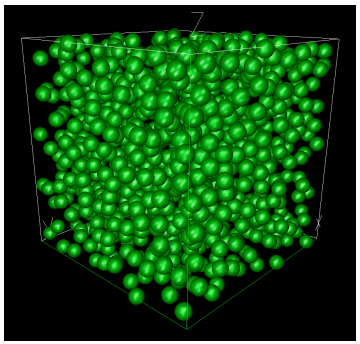

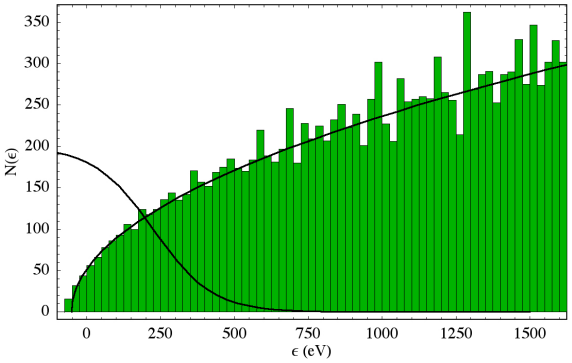

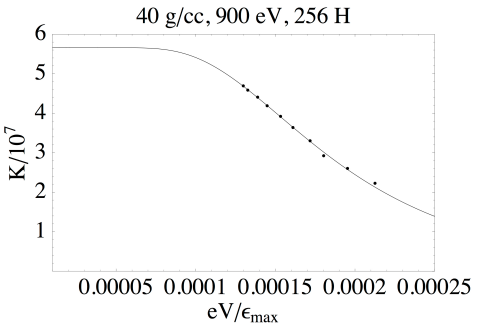

Electrical and thermal conductivities for warm dense hydrogen from DFT/Kubo-Greenwood calculations

Mike Desjarlais

Sandia National Laboratories, Albuquerque, NM, USA

in collaboration with Chris Scullard, Heather Whitely, Lorin Benedict and Frank Graziani (LLNL)

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Hubbard used the Kubo-Greenwood formalism to derive transport coefficients for dense matter

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Astrophysical Journal 146, 858 (1966)

STUDIES IN STELLAR EVOLUTION. V. TRANSPORT COEFFICIENTS OF DEGENERATE STELLAR MATTER

W. B. HUBBARD
Berkeley Astronomical Department, University of California
Received April 27, 1966; revised May 27, 1966

Assuming OCP (One Component Plasma) structure factors, degenerate non-interacting electrons and Born approximation electron-ion scattering, the thermal conductivity is given by

$$K = \frac{(2\pi\hbar)^3 k_B^2}{16 m_e^2 e^4 A m_H} G_\Gamma(\kappa_F)\rho T \qquad G_\Gamma(\kappa) = \left[2\int_0^{2\kappa} d\kappa' \phi(\kappa')/\kappa'\right]^{-1}$$

where the dimensionless Fermi wavenumber $\kappa_F = \left(\frac{9\pi Z}{4}\right)^{1/3} = 1.919$ for hydrogen

ϕ(k) : ion structure factor (OCP) Γ : ion-ion coupling parameter $\Gamma = \frac{e^2 Z^2}{a k_B T}$ $a = \left(\frac{3}{4\pi n_I}\right)^{1/3}$

The CEA group demonstrated the viability of *ab initio* thermal conductivity calculations for dense hydrogen

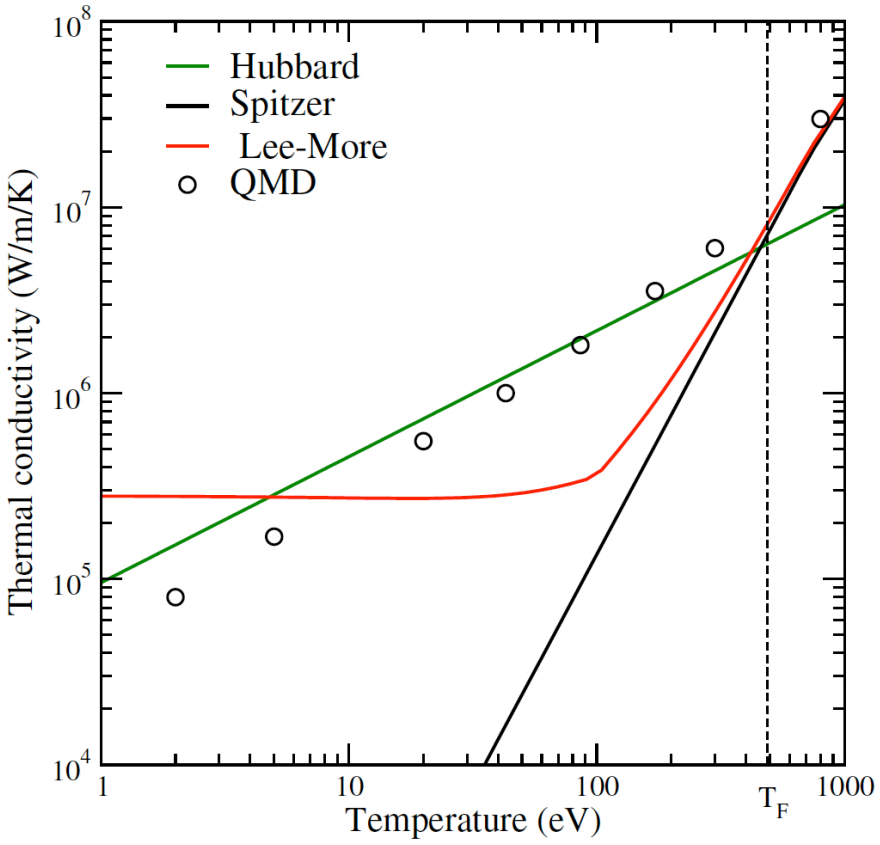
PRL 102, 075002 (2009) PHYSICAL REVIEW LETTERS week ending 20 FEBRUARY 2009

Ab Initio Determination of Thermal Conductivity of Dense Hydrogen Plasmas

Vanina Recoules, Flavien Lambert, Alain Decoster, Benoit Canaud, and Jean Clérouin
CEA, DAM, DIF, F-91297 Arpajon, France
(Received 4 November 2008; published 20 February 2009)

These earlier *ab initio* calculations gave thermal conductivities a factor of two below the Hubbard model in the degenerate limit, and a stronger scaling with T.

80 g/cc hydrogen
256 atoms L=1.75 Å



There is a problem:

$$\frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2 = 49.28\ eV!$$

Larger boxes (more atoms) are necessary to converge the degenerate limit

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1024 H atoms

0.0208 $Å^3$/atom

0.14 a_B^3 /atom

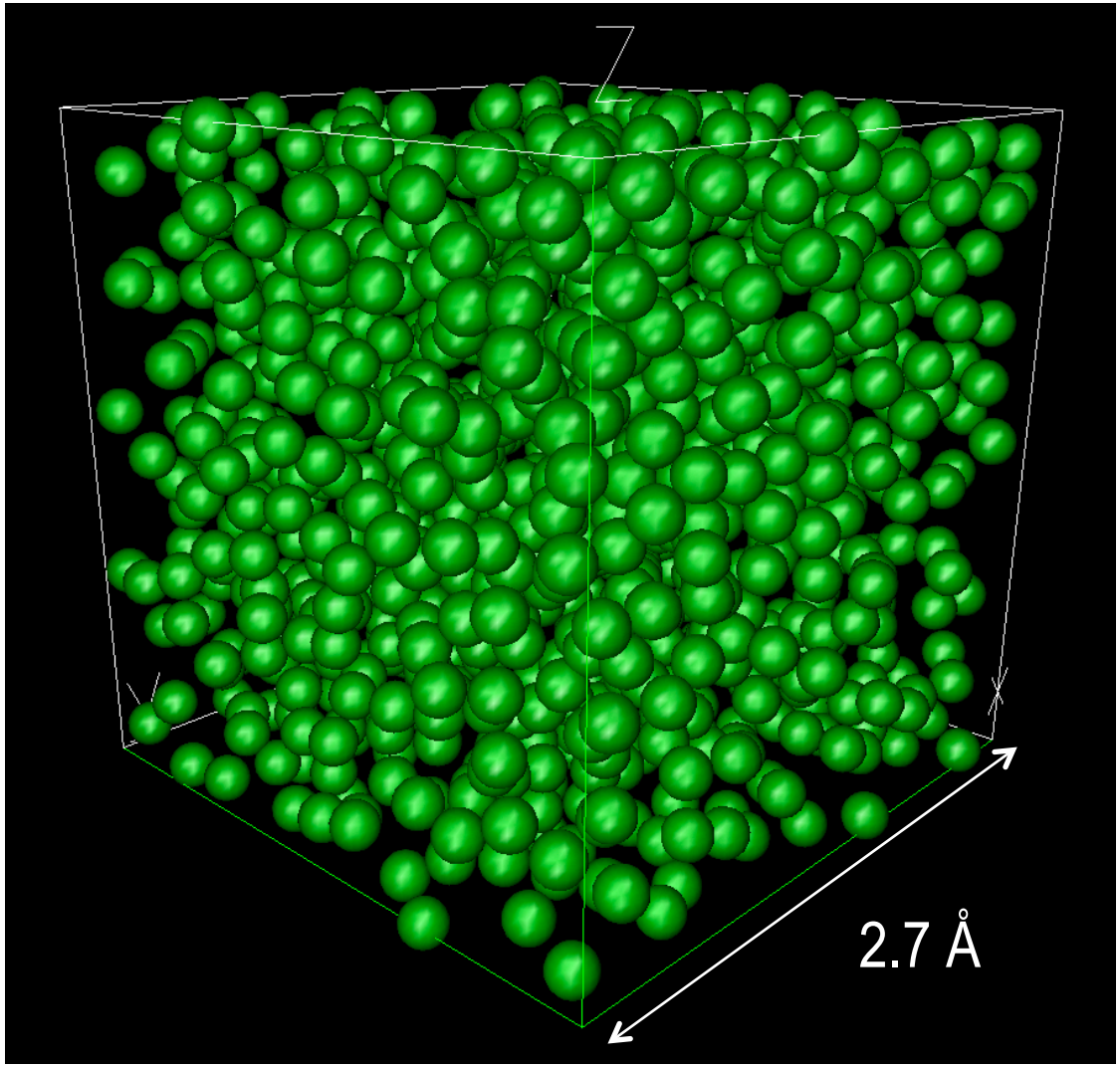
T = 10 eV

80 g/cc H

or

200 g/cc DT

P = 13 Gbar



First-principles calculations of transport quantities are carried out in the Kubo – Greenwood / Chester – Thellung formalism

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- For these dense conditions we abandon the pseudopotential approach and use a bare proton (this forces high plane wave cutoff energies)
- We calculate the full set of Onsager transport coefficients and calculate the thermal conductivity directly (no Wiedemann-Franz law assumptions)

Fermi weights

Dipole matrix elements

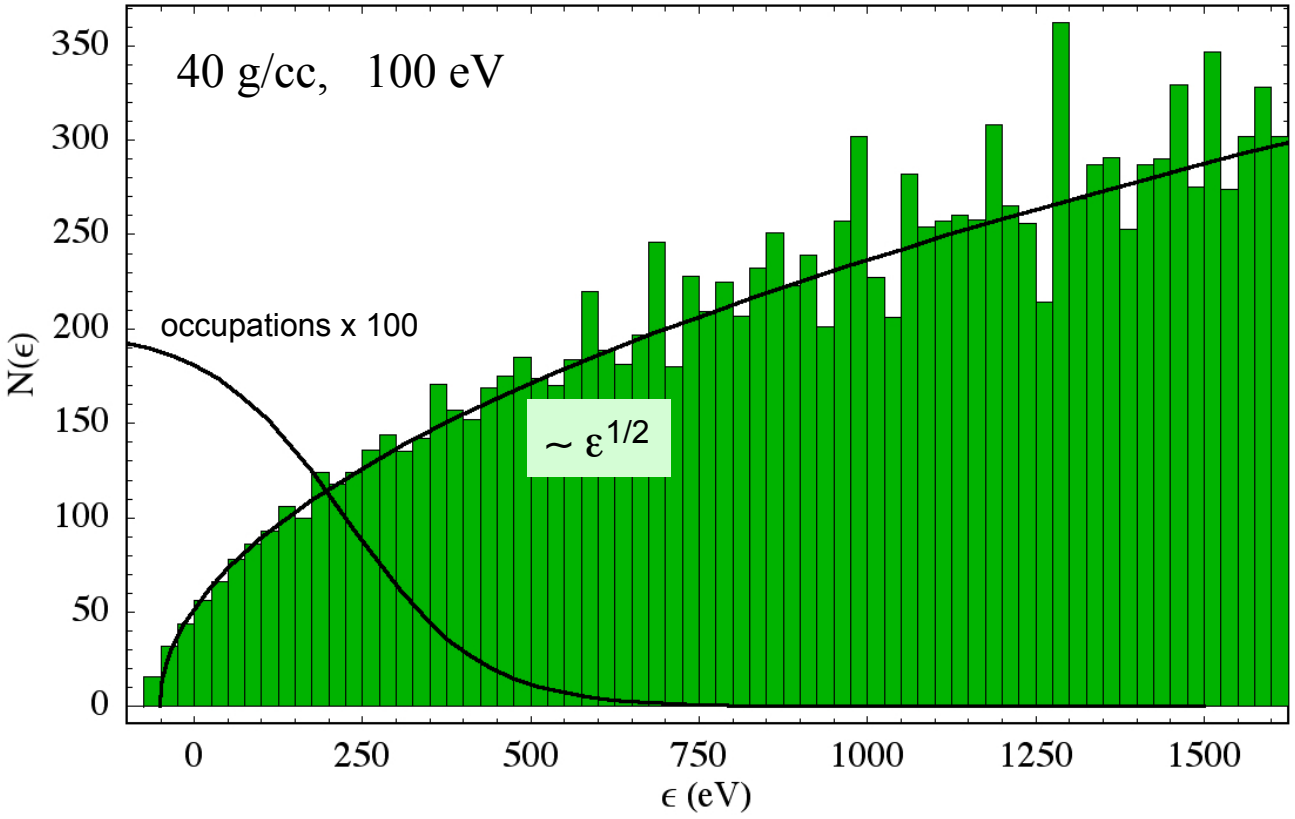
$$L_{mn}(\omega) = \frac{2\pi q^{4-m-n}}{3Vm_e^2\omega}\sum_{\mathbf{k}\nu\mu}(f_{\mathbf{k}\nu}-f_{\mathbf{k}\mu})\langle\mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle\langle\mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle \cdot\left(\frac{E_{\mathbf{k}\nu}+E_{\mathbf{k}\mu}}{2}-h\right)^{m+n-2}\delta(E_{\mathbf{k}\mu}-E_{\mathbf{k}\nu}-\hbar\omega) \quad .$$

Onsager weights

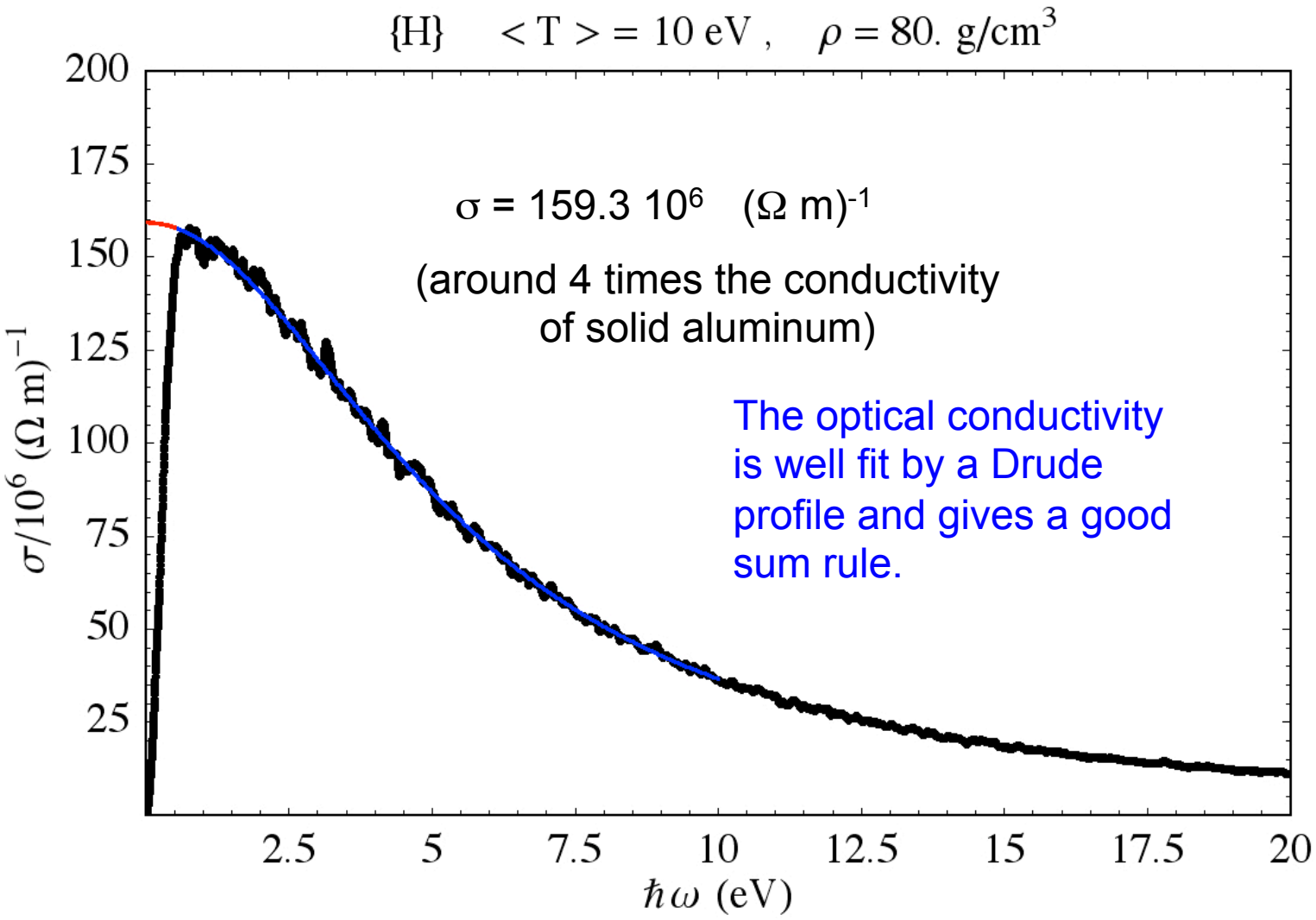
Energy conservation

$$\omega \to 0 \qquad K = \frac{1}{T}\left(\mathcal{L}_{22}-\frac{\mathcal{L}_{12}^2}{\mathcal{L}_{11}}\right),$$

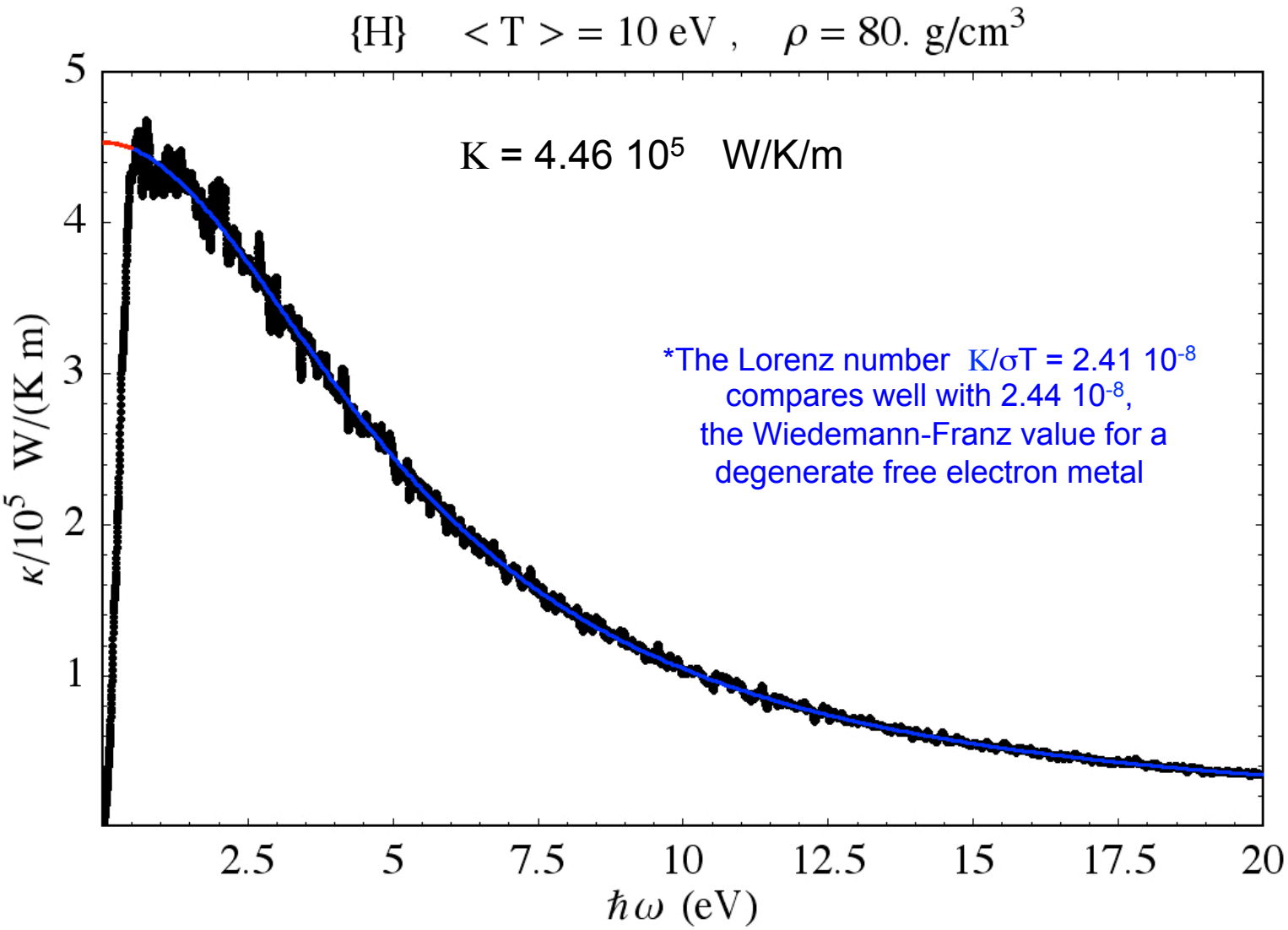
The electronic density of states with the bare potential is well behaved



For sufficiently large systems, calculations in the degenerate limit are well behaved



The thermal conductivity is equally well behaved in this limit



Careful attention to convergence in the low T limit brought agreement with Hubbard, and Ichimaru & Kitamura

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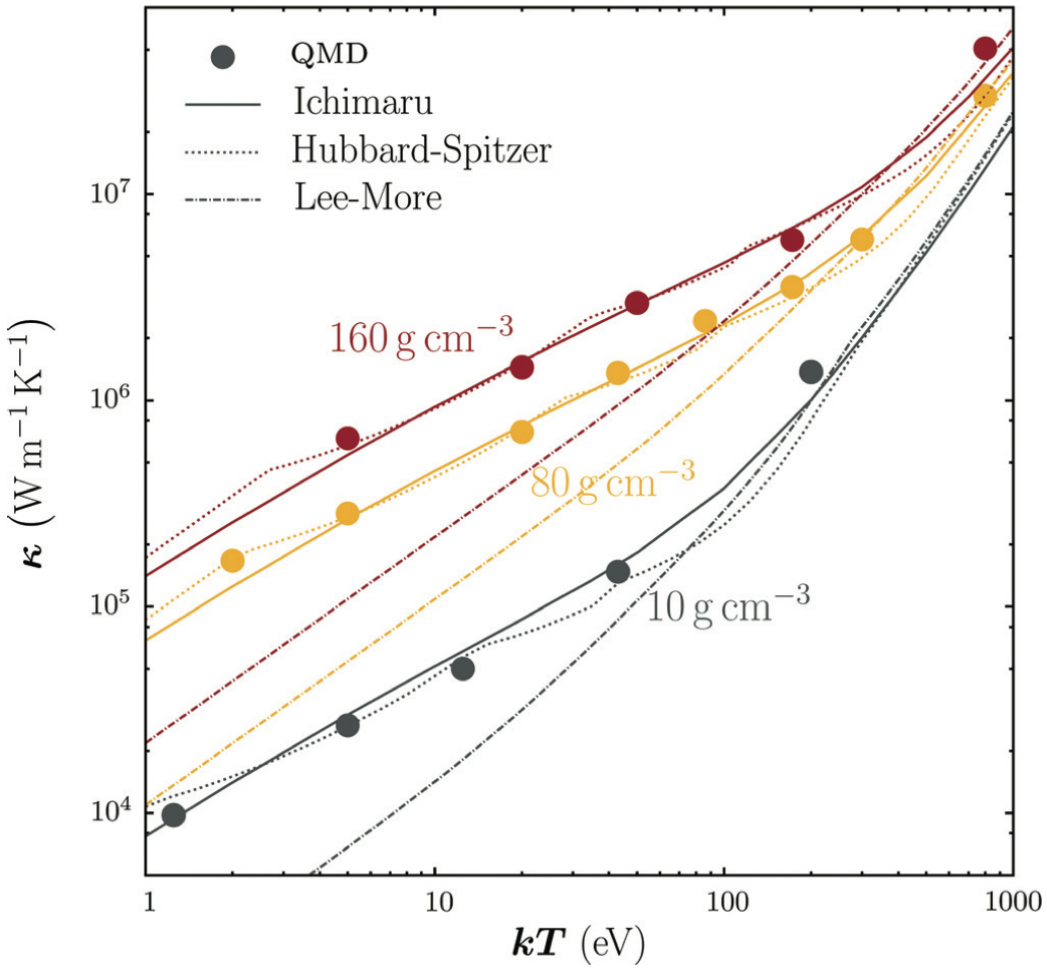
CEA/Sandia paper: Phys. Plasmas **18**, 056306 (2011)



Ichimaru-Kitamura is low by a factor of ~1.6 in this limit (approximate e-e treatment)

The high temperature CEA-Sandia results suggested a quick approach to the classical limit (for $\theta < 2$)

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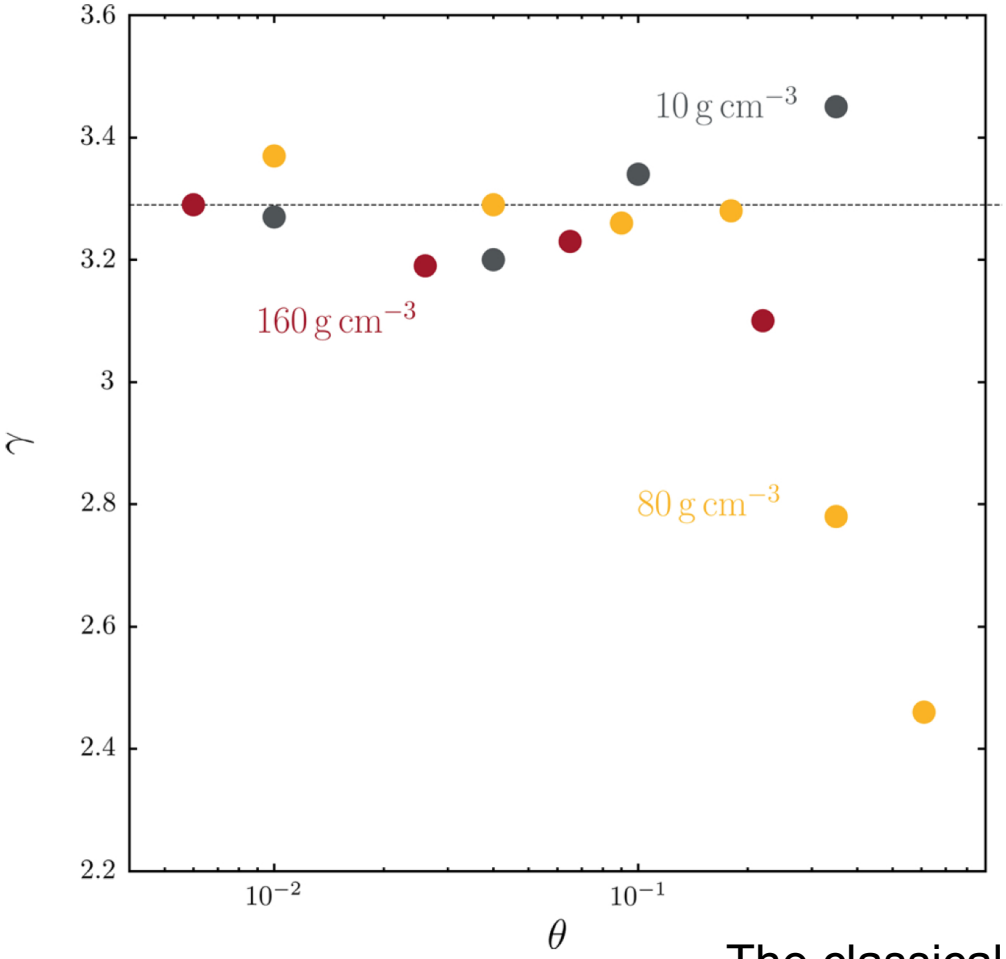
$$\gamma \equiv \frac{e^2}{k^2} L$$



The classical limit for γ is 1.597

Several issues were tackled in order to revisit the calculations in the high T limit

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- Very poor convergence for charge update algorithm in MD step. Explored various charge update algorithms for the MD portion; found one that was stable and fast.

- Frequent crashes due to running off the exchange-correlation table. Expanded the exchange-correlation tables to handle much smaller r_s values than typical condensed matter conditions.

- One-shot electronic minimization for very large band numbers proved unstable. Implemented block increases in band numbers, using prior converged wavefunctions for initialization.

Several issues remain

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- Scaling is very bad for dense conditions (high Fermi energy) – must have at least one plane wave that can represent the highest electronic energy. So as the band number goes up, so must the highest plane wave energy, to a much higher level than needed for simply resolving a 1s electron around the bare proton.

- This issue forces fewer atoms in the high T limit.

- At the temperatures explored here, complete convergence on K was not feasible. We develop a scheme to extrapolate to an infinite number of bands.

A power law *ansatz* for the dipole matrix elements in the high energy tail is used to extrapolate to infinity

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To extrapolate to the limit of infinite bands, we write the thermal conductivity for a given maximum Kohn-Sham eigenvalue in the DFT as an integral over the derivative of the Fermi function dF/dE, times E^2 (the leading Onsager term for thermal) and a power law model for the dipole matrix elements as a function of energy $g(E) \sim E^{\nu}$. This fits all the simulations quite well, with only very small (2 to 3%) changes in the power law exponent that gives the best fit.

$$K(\varepsilon_{\max}) \sim L_{22} \sim \int_{\varepsilon=0}^{\varepsilon_{\max}} E^2 g(E) \frac{dF}{dE} dE$$

The power law model for the high energy dipole matrix elements fits the calculations very well

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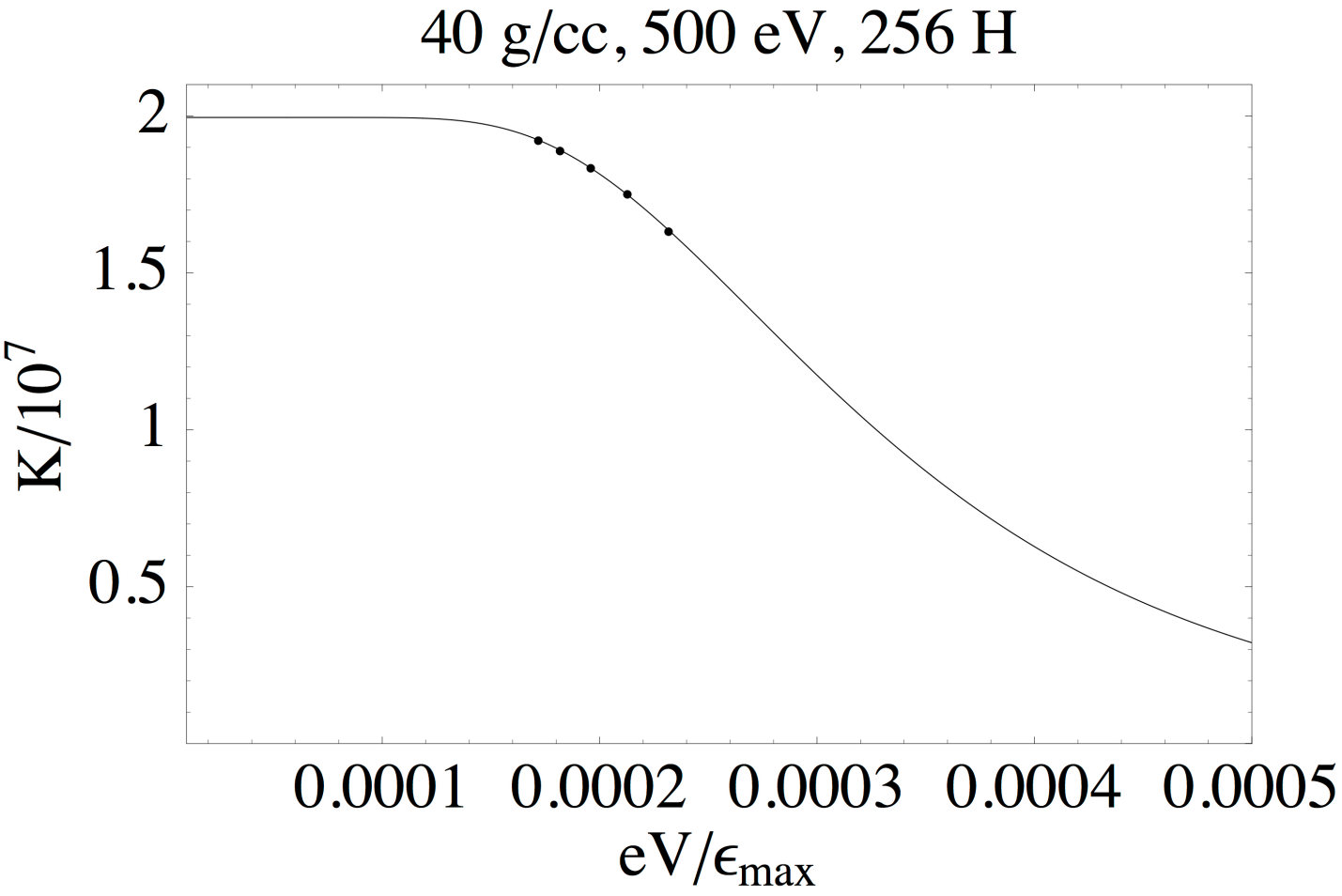

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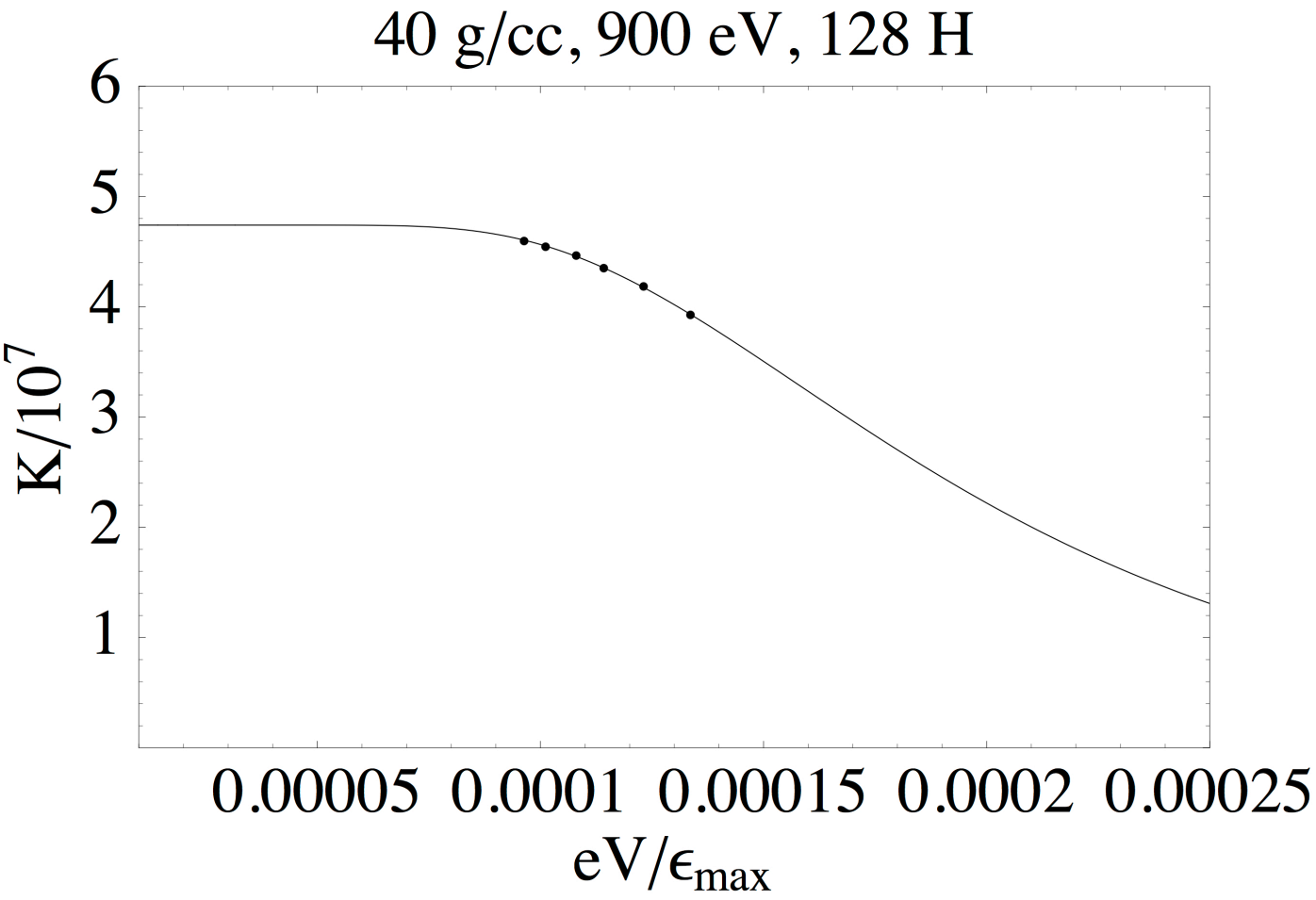

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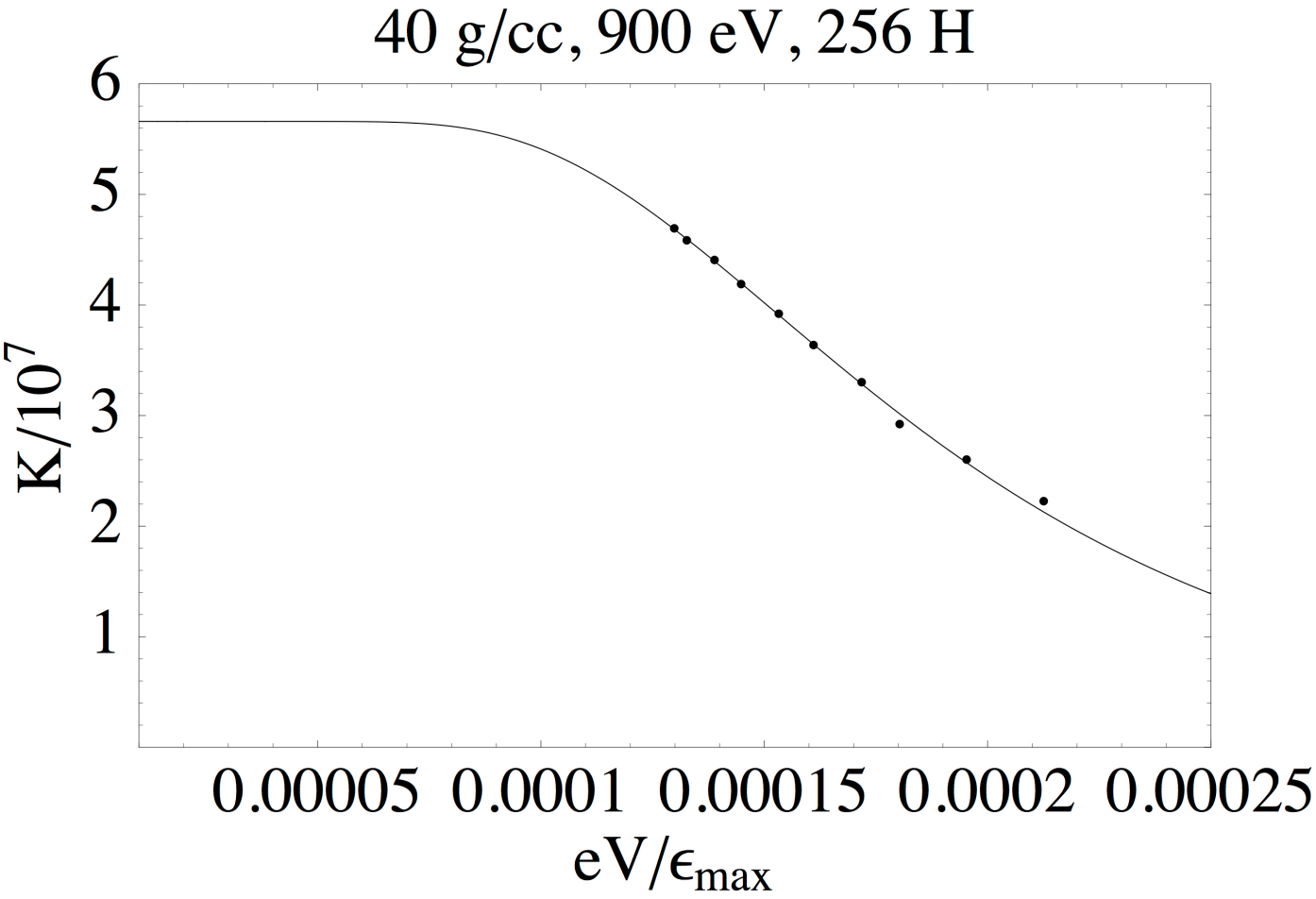
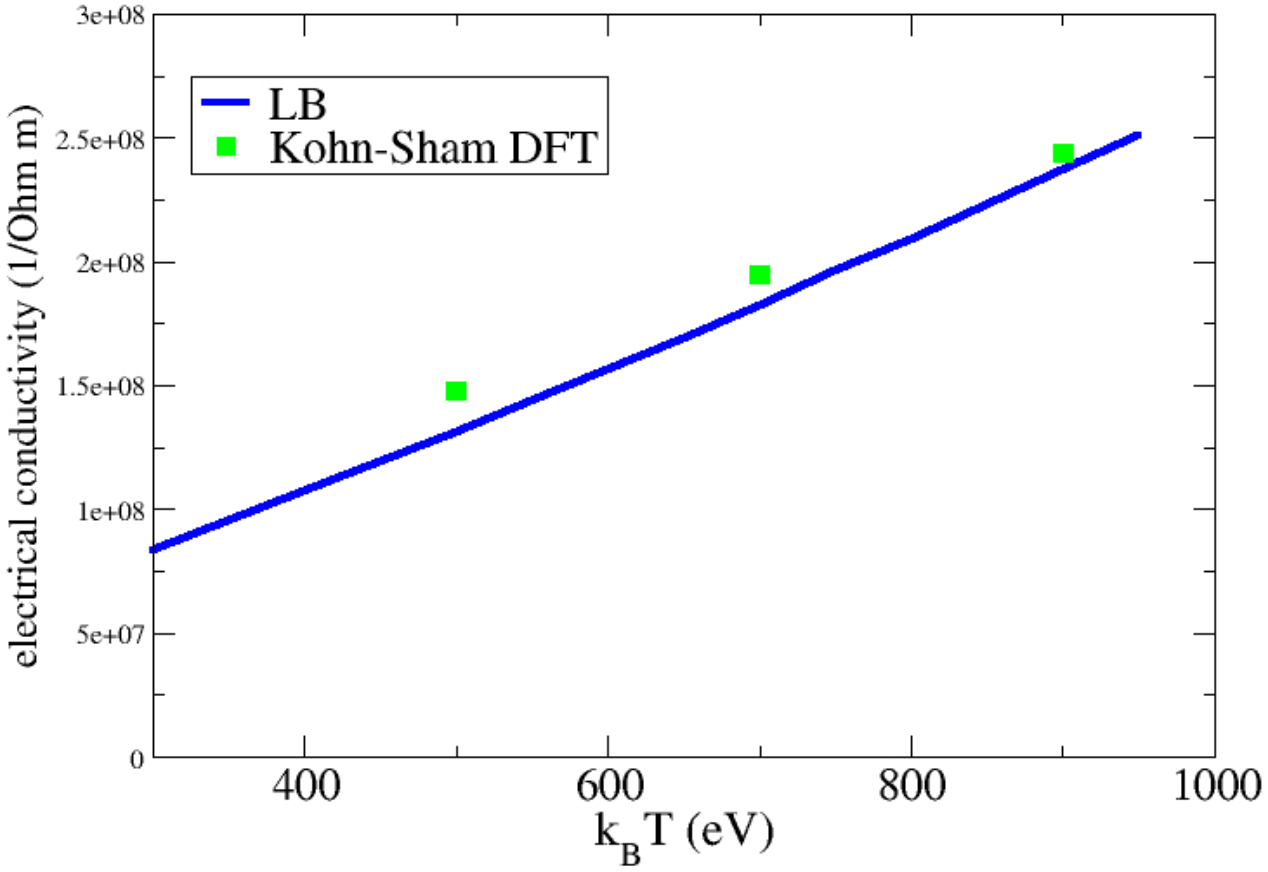


The electrical conductivity from the Kubo-Greenwood calculations agrees well with our quantum Lenard-Balescu results



Residual differences are due to small degeneracy effects included in the DFT
The sum rule on $\sigma(\omega)$ is well satisfied

The thermal conductivities from the Kubo-Greenwood calculations (▪) do not agree with our quantum Lenard-Balescu results

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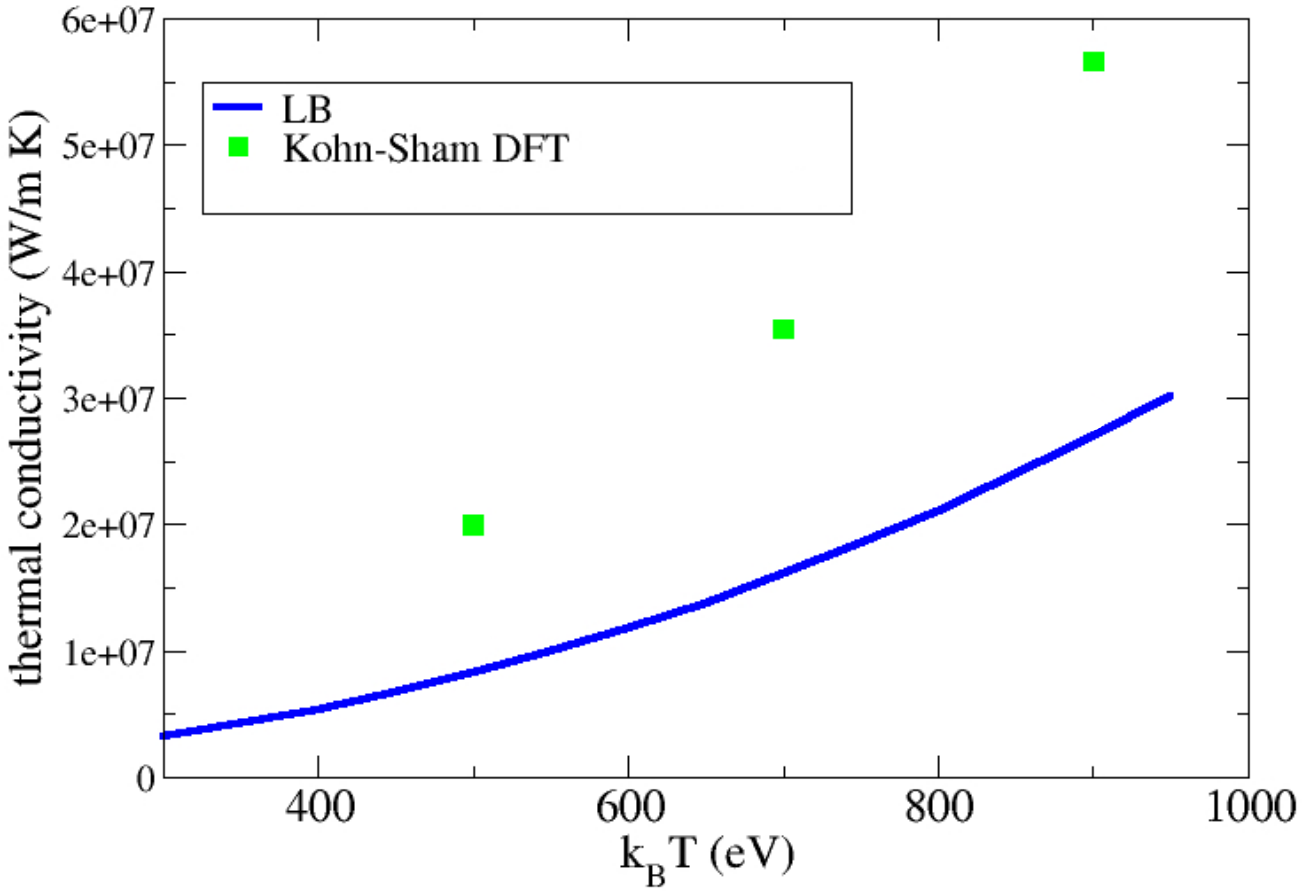

We explore the addition of an explicit e-e scattering term to the thermal conductivity only

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The total thermal conductivity with an e-e collision correction is obtained in the usual inverse addition

$$\frac{1}{K} = \frac{1}{K_{DFT}} + \frac{1}{K_{ee}}$$

K_{ee} is calculated within the Zubarev formalism with T-matrix cross sections and a Debye screened Coulomb potential

In the following we justify this decomposition and reconstruction

We write the total scattering as the usual inverse sum for two distinct scattering processes

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$$\frac{1}{\sigma} = \frac{1}{S_\sigma \sigma_{ei}} + \frac{1}{\sigma_{ee}}$$

$$\frac{1}{K} = \frac{1}{S_K K_{ei}} + \frac{1}{K_{ee}}$$

Note $\sigma_{ee} = \infty$

The subscripts *ei*, *ee* refer to quantities calculated in the limit that the other scattering (*ee*, *ei*, respectively) is excluded.

The pre-factors S_σ and S_K take into account the reshaping of the electron distribution function resulting from e-e scattering.
For example, S_σ is analogous to the usual Spitzer factor $\gamma_E = 0.5816$ in the weakly coupled, non-degenerate limit.

We test the decomposition with the Zubarev framework

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$$\frac{1}{\sigma} = \frac{1}{S_\sigma \sigma_{ei}} + \cancel{\frac{1}{\sigma_{ee}}}$$

Satisfied by definition

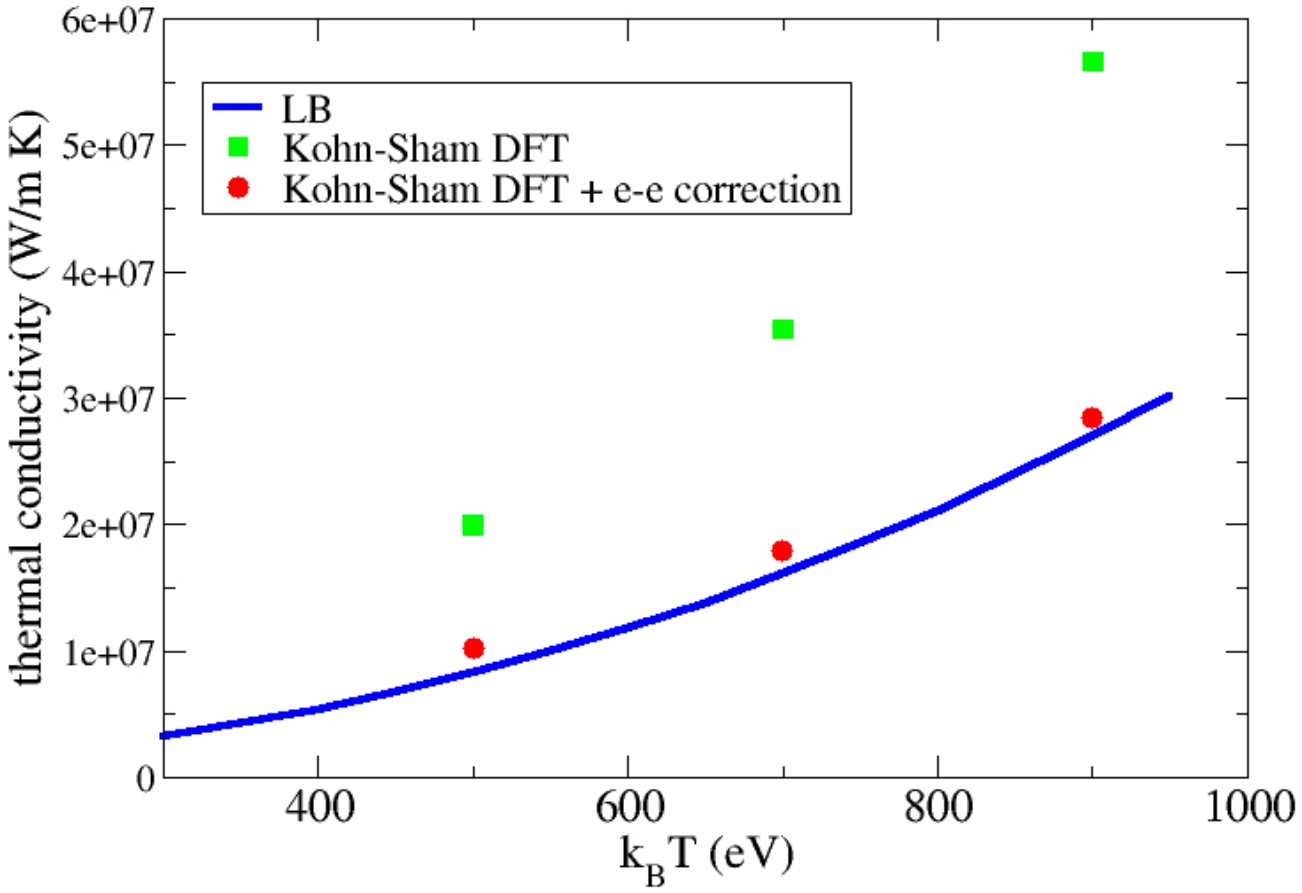
$$\frac{1}{K} = \frac{1}{S_\sigma K_{ei}} + \frac{1}{K_{ee}}$$

Assume $S_K = S_\sigma$

For the 3 cases considered with DFT, the latter equation is satisfied at the 99% level within the Zubarev/T-matrix framework

We argue that $S_\sigma K_{ei} = K_{DFT}$

The thermal conductivities from the Kubo-Greenwood calculations with an e-e correction (•) agree with our quantum Lenard-Balescu results



The red points show the agreement when an explicit e-e scattering correction, calculated in the Zubarev formalism (T-matrix, Boltzmann collision operator) is added to the thermal.

Small differences due to the treatment of degeneracy remain

Summary

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- Thermal and electrical conductivity calculations have been performed for 40 g/cc hydrogen from 1 eV to 900 eV (> 10 million Kelvin).
- Convergence of the thermal conductivity is very slow. Earlier published results (my work, and others) are under-converged in the high T limit.
- An approach for extrapolation to infinite bands is proposed.
- The conclusion is that the distribution reshaping aspect of e-e collisions is included within DFT, for both the electrical and thermal conductivities.
- The electrical conductivities within DFT require no e-e correction (for plasmas).
- An explicit e-e scattering contribution K_{ee} should be added to the thermal.