Thermoelectric transport properties of warm dense molybdenum from first-principles simulations

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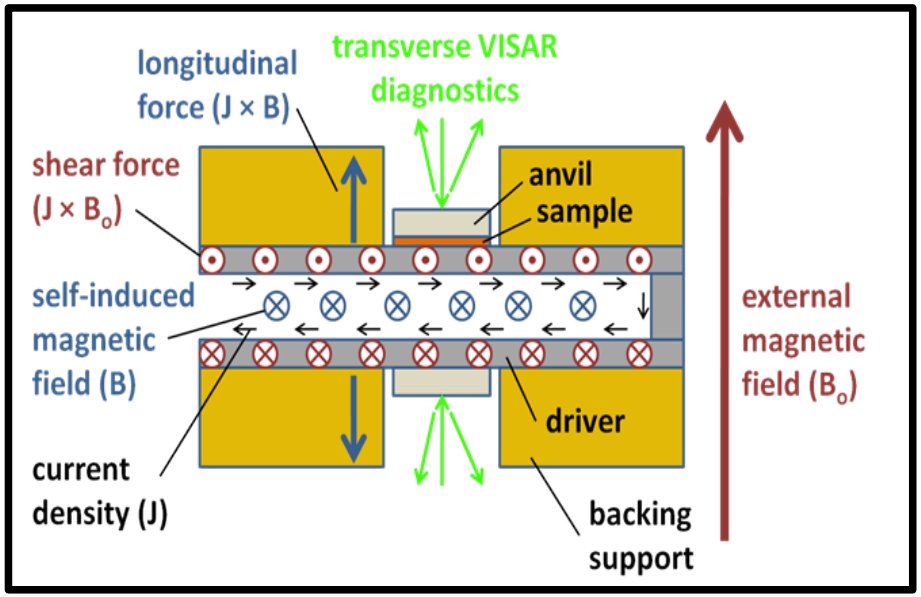
Motivation to examine electronic transport properties of warm dense molybdenum

- Fundamental science study of the influence of density and temperature on the transport coefficients of a refractory metal with strongly correlated electrons.

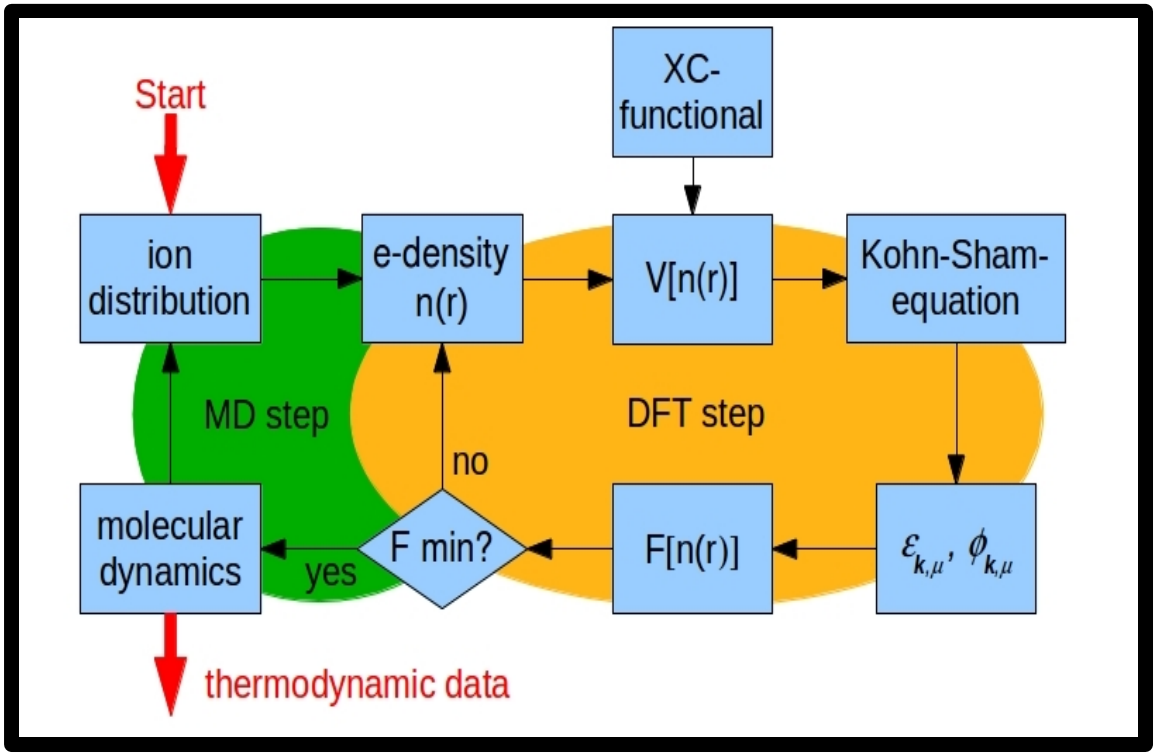
- Mo is used as a driver material in Z experiments that measure the yield strength of materials under shear stress (MAPS) [1].



- Density functional theory (DFT) is the method of choice to calculate such data with high accuracy.

[1] C. S. Alexander, J. R. Asay, T. A. Haill, *J. Appl. Phys.* **108**, 126101 (2010)

Flowchart of DFT-MD simulations: VASP [1]



- Exchange-correlation functional: AM05 [2].
- Careful optimization of simulation parameters (particle number, cutoff energy, k points,...) with several convergence tests.

[1] G. Kresse & J. Hafner, *Phys. Rev. B* **47**, 558 (1993)
J. Hafner, *J. Comput. Chem.* **29**, 2044 (2008)
[2] R. Armiento & A. E. Mattsson, *Phys. Rev. B* **72**, 085108 (2005)

Thermoelectric transport properties from DFT [1]

The ***electronic*** transport properties can be obtained within DFT by calculating the following frequency-dependent Onsager coefficients:

$$L_{mn}(\omega)=\frac{2\pi(-e)^{4-m-n}}{3V\omega}\sum_{\vec{k},\mu,\nu}\left|\langle\phi_{\vec{k},\nu}|\vec{v}|\phi_{\vec{k},\mu}\rangle\right|^2\left(f_{\vec{k},\nu}-f_{\vec{k},\mu}\right)\left(\frac{\varepsilon_{\vec{k},\mu}+\varepsilon_{\vec{k},\nu}}{2}-h_e\right)^{m+n-2}$$
$$\times\delta\left(\varepsilon_{\vec{k},\mu}-\varepsilon_{\vec{k},\nu}-\hbar\omega\right)$$

With the calculated L_{mn} the desired transport coefficients follow as:

- electrical conductivity: $\sigma=\lim_{\omega\to 0} L_{11}$ (Kubo-Greenwood-formula)

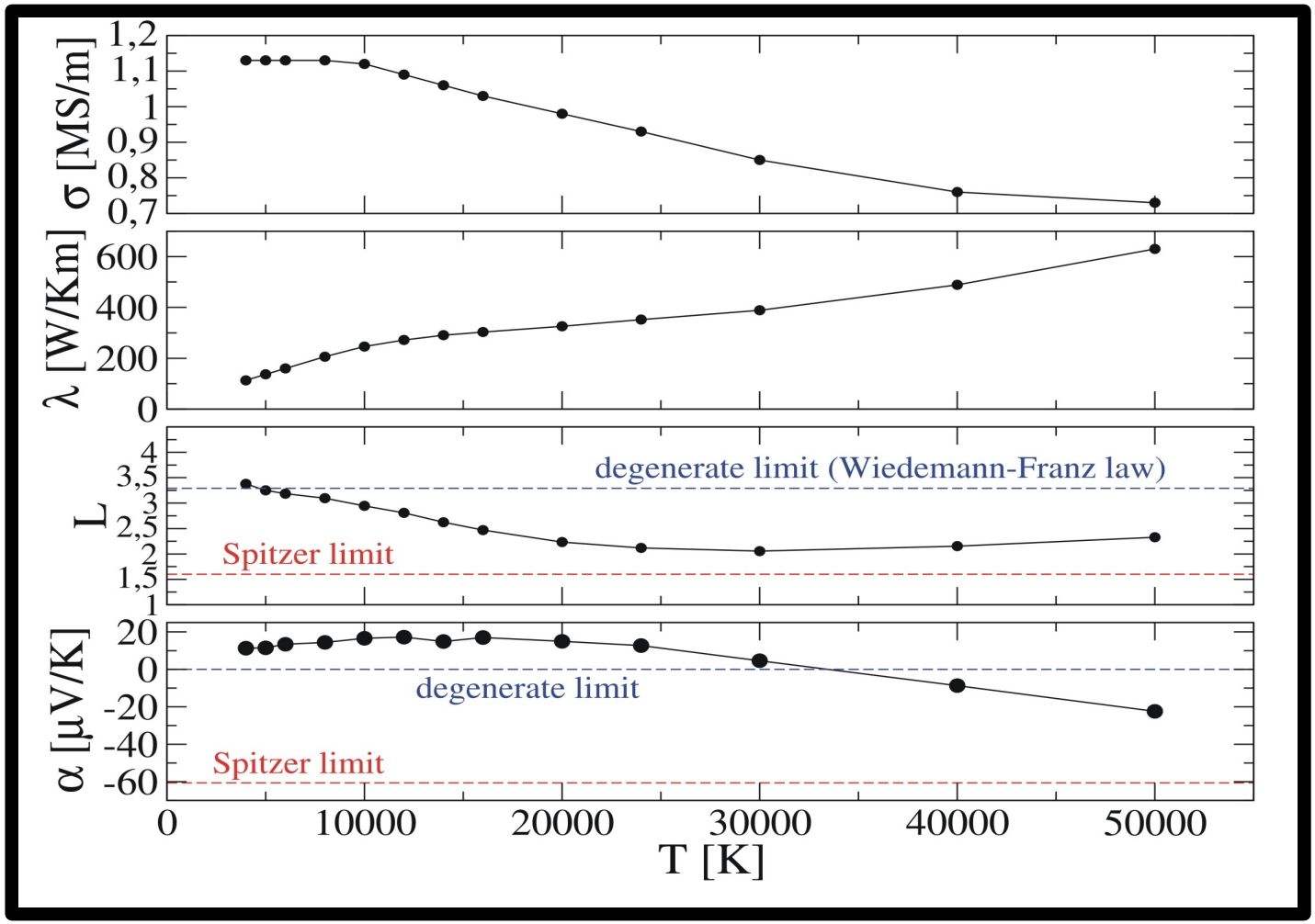
- thermal conductivity: $\lambda=\lim_{\omega\to 0}\frac{1}{T}\left(L_{22}-\frac{L_{12}^2}{L_{11}}\right)$

- thermopower: $\alpha=\lim_{\omega\to 0}\frac{L_{12}}{T L_{11}}$ and Lorenz number: $L=\lim_{\omega\to 0}\frac{e^2\lambda}{k_B^2 T\sigma}$

These expressions are evaluated for ensembles of 25-100 ionic configurations from each DFT-MD simulation.

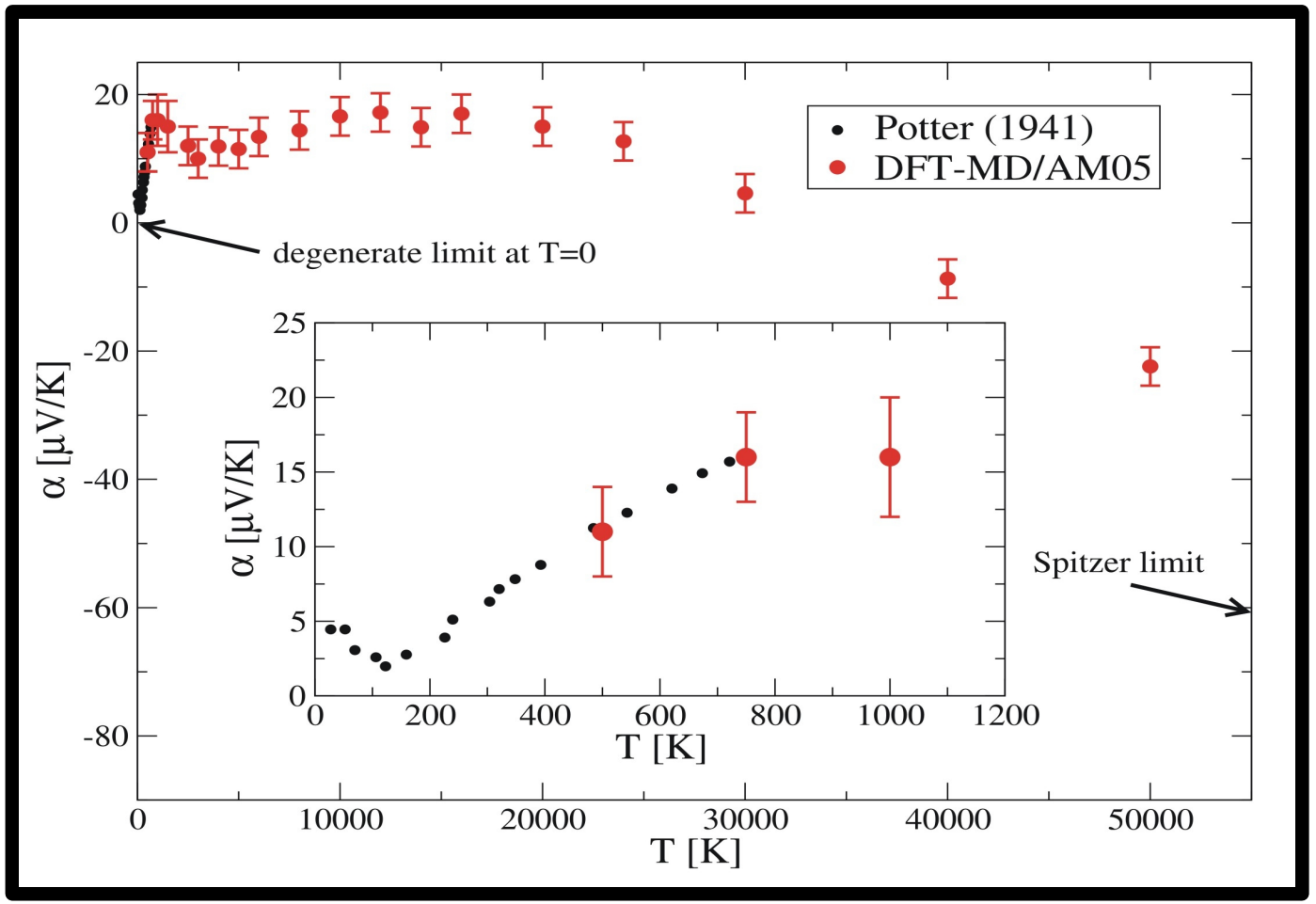
[1] B. Holst, M. French, R. Redmer, *Phys. Rev. B* **83**, 235120 (2011)

Transport properties at the 10 g/cm³ isochor



- Typical effects of ionization can be seen in the electrical and thermal conductivity above 20 000 K.
- **Positive** sign in thermopower up to 30 000 K.

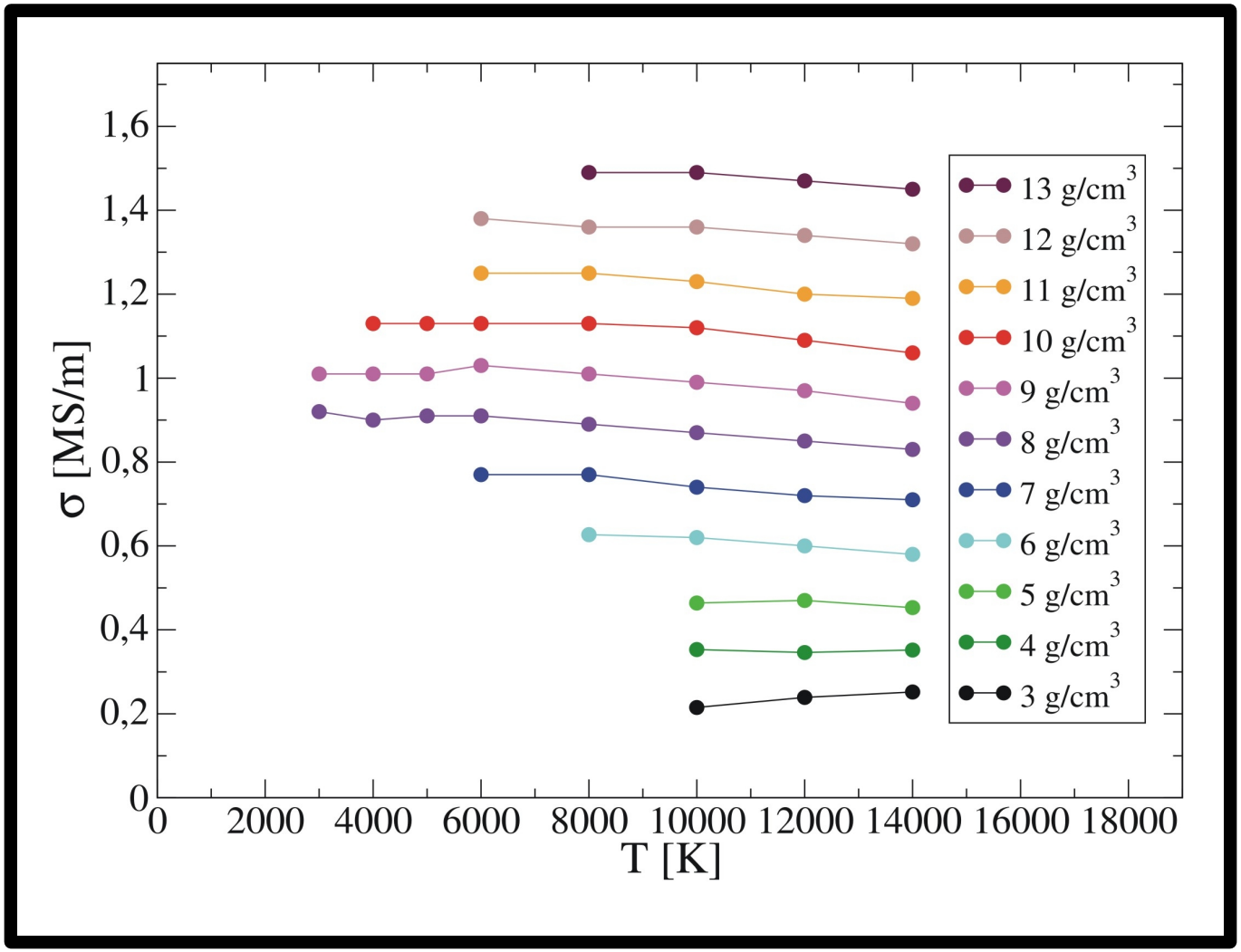
Experimental thermopower of solid Mo



A **positive**, thermopower is known from experiments in the solid. The experimental data is reproduced very well by DFT (with AM05).

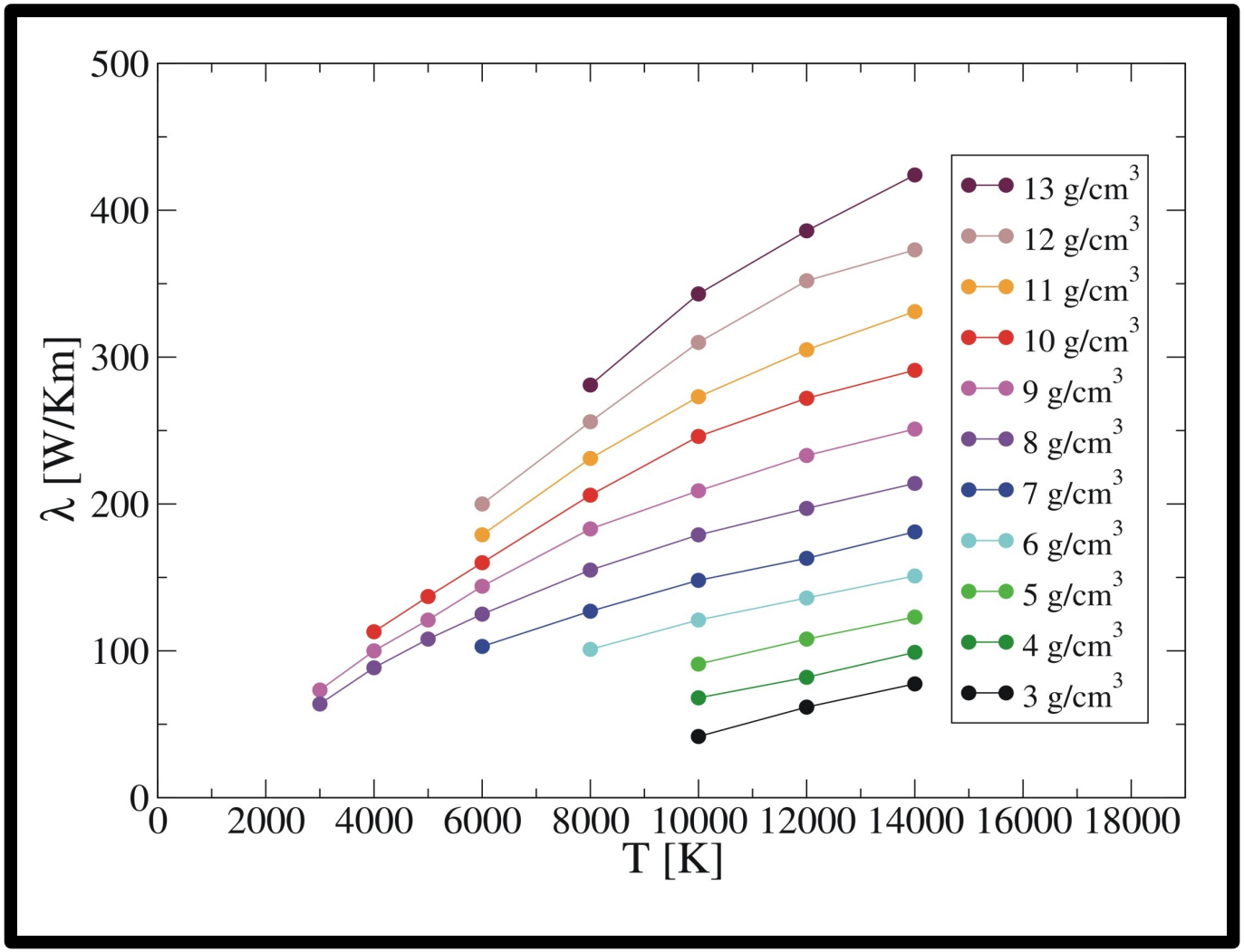
H. H. Potter, *Proc. Phys. Soc.* **53**, 695 (1941)

Building a conductivity data set for liquid Mo I



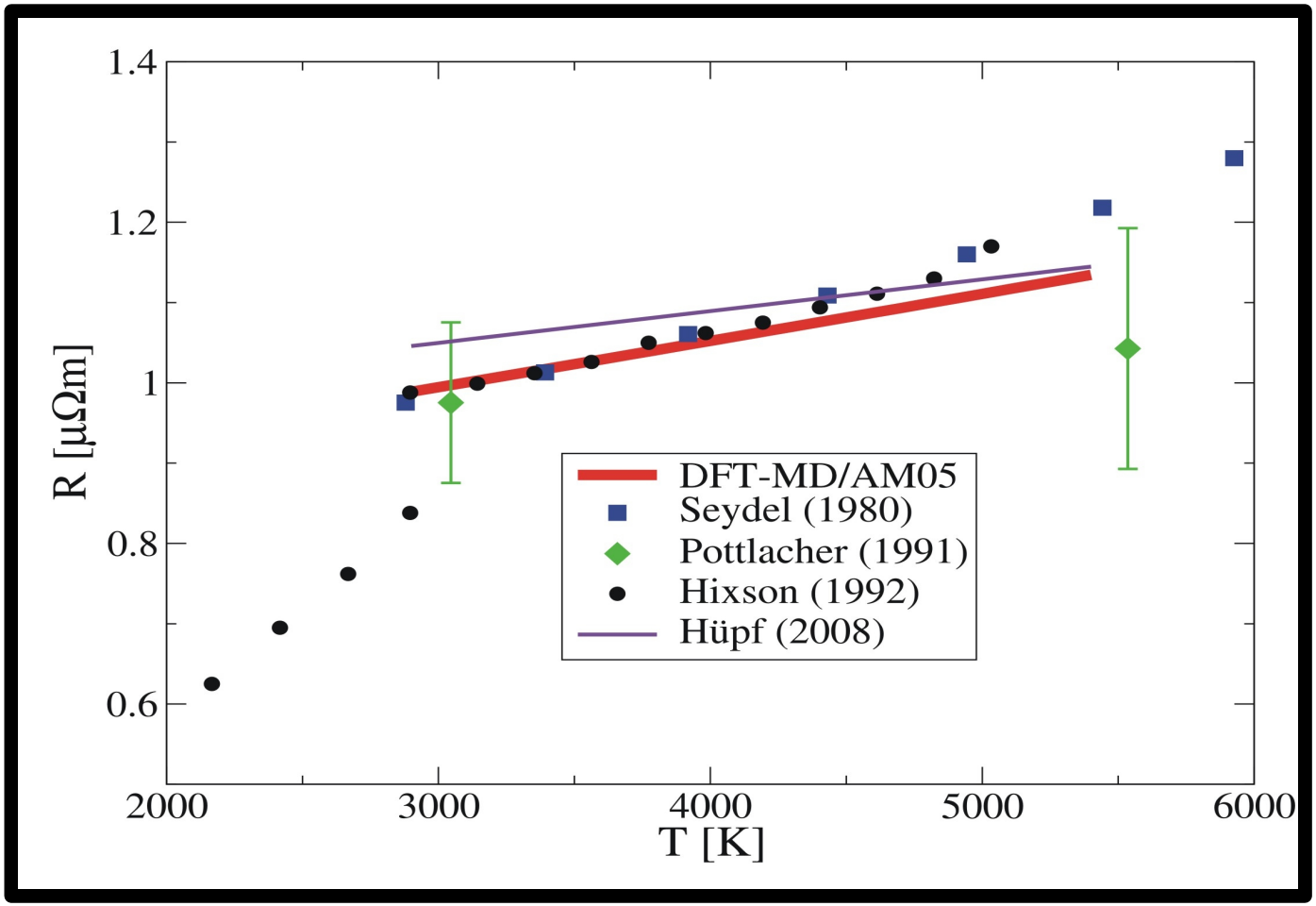
The electrical conductivity is almost independent from the temperature, $\sigma = A + B\varrho$ for T<8000 K.

Building a conductivity data set for liquid Mo II



Nonlinear behavior in the thermal conductivity with density and temperature.

Comparison with exploding wire experiments



Very good agreement with various experimental data.

T. Hüpf, C. Cagran, G. Lohöfer, G. Pottlacher, *J. Phys: Conf. Ser.* **98**, 062002 (2008)
R. S. Hixson, M. A. Winkler, *Int. J. Thermophys.* **13**, 477 (1992)
G. Pottlacher, E. Kaschnitz, H. Jäger, *J. Phys.: Condens. Matter* **3**, 5783 (1991)
U. Seydel, W. Fucke, H. Wadle (Mannhold, Düsseldorf, 1980)

Conclusions and acknowledgements

- The full set of thermoelectric transport properties of of liquid Mo was calculated with DFT-MD.

- Very good agreement with experiments shows that DFT is able to predict these transport coefficients with high fidelity.

Things to do:

- Calculate conductivities also for solid Mo.

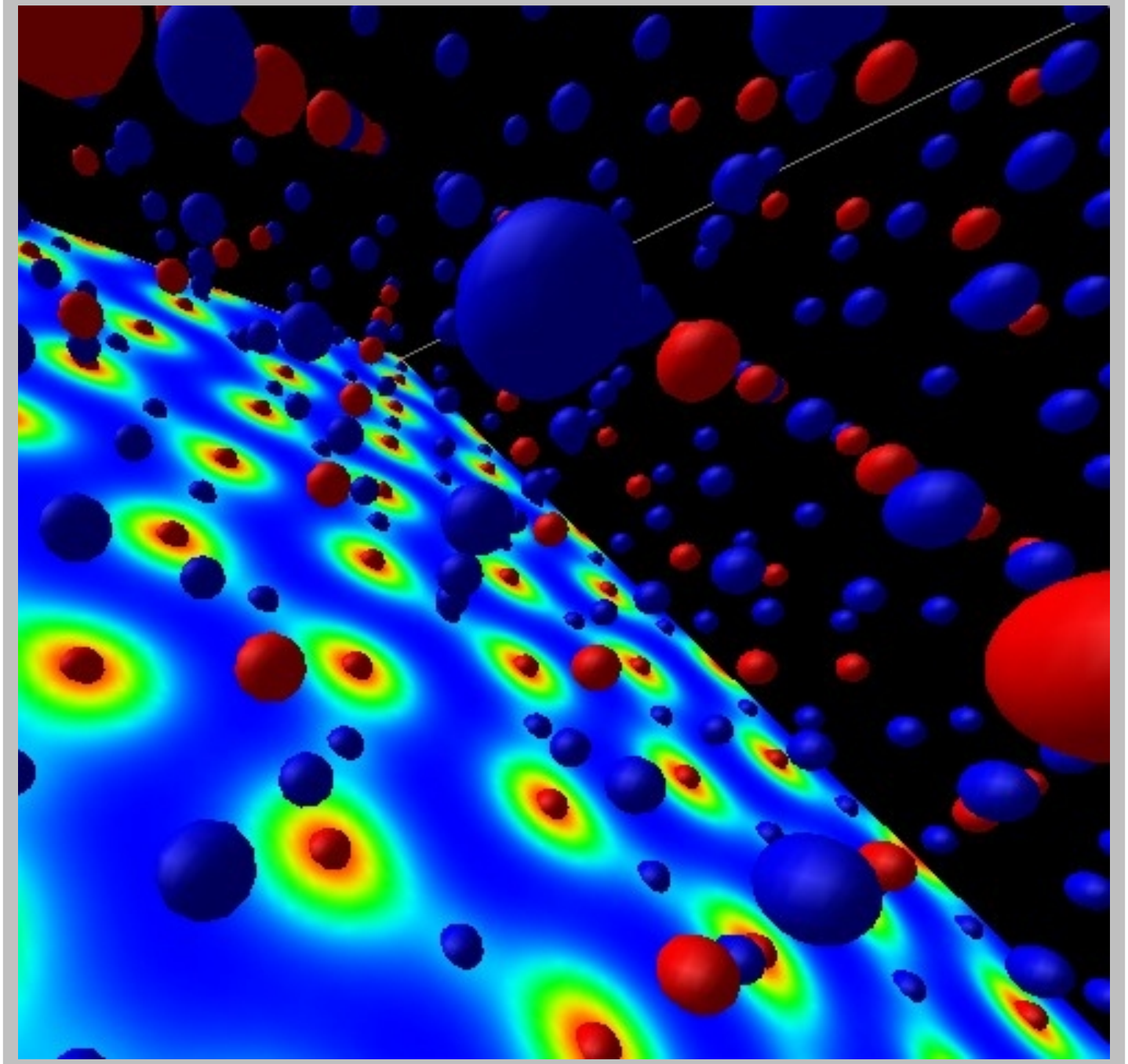
- Find appropriate fit formulae.

- Apply the data to MAPS simulations.

Acknowledgements:

- Kyle Cochrane, Luke Shulenburger

- E-Bird (Sandia), Stampede (TACC) via XSEDE



THANK YOU

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Calculation Details

General:
- AM05 [1] exchange-correlation functional
- PAW pseudopotentials with 14 electrons per atom
- 54 or 24 atoms in the fluid, 250 atoms in the solid

MD simulations (for EOS and snapshots):
- Baldereschi point, 800 eV plane-wave cutoff
- 5000-10000 time steps of length 2-4 fs

Calculation of the Onsager coefficients:
- 4 k points, 300 eV plane-wave cutoff
- 25-100 ionic configurations

All checked with several convergene tests.

[1] R. Armiento & A. E. Mattsson, *Phys. Rev. B* **72**, 085108 (2005)

Pressure and internal energy of liquid Mo