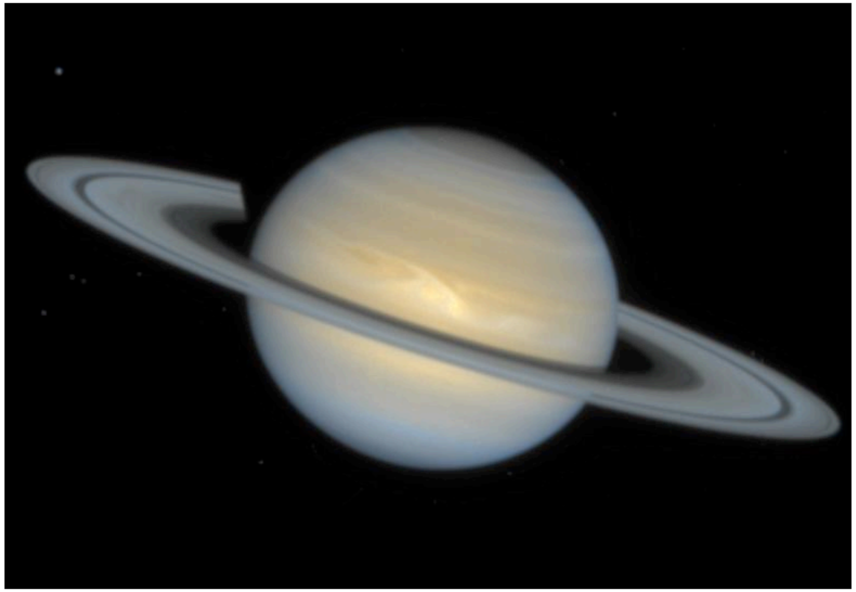
Helmholtz International Summer School on Dense Matter, Dubna/Russia, Aug 21 – Sep 1, 2006

Physics of warm dense matter



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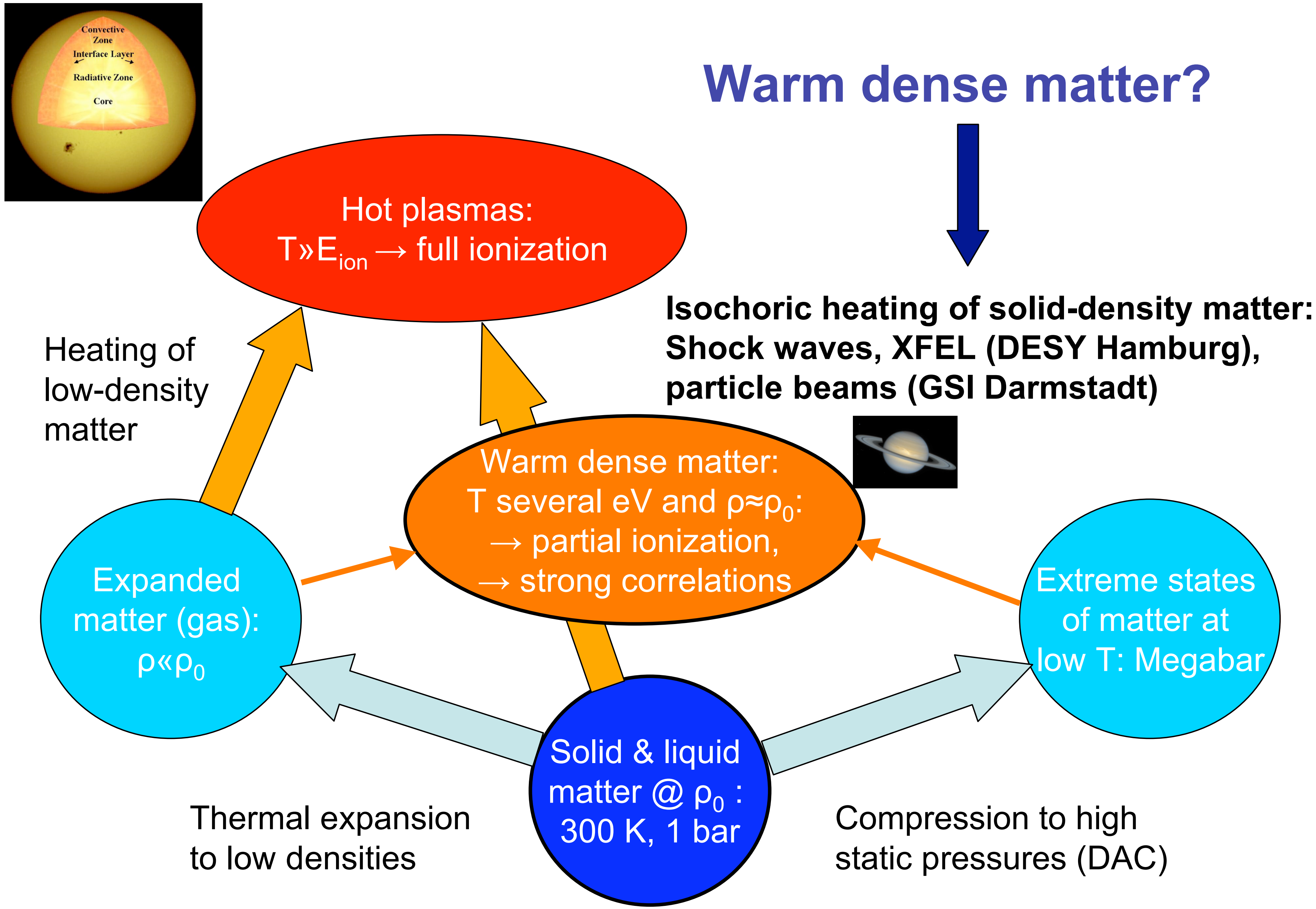
Contents

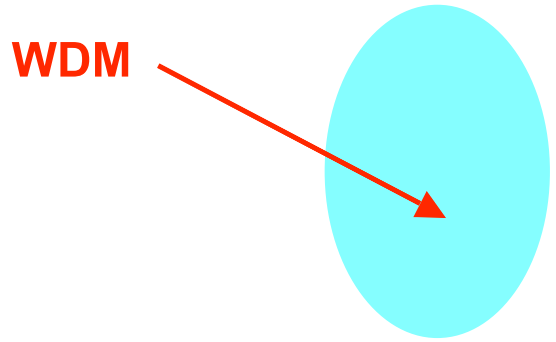
- What is „warm dense matter“ (WDM)?
- Shock-wave experiments generate WDM
- Pump-probe experiments for WDM
- Chemical picture and WDM
- Quantum Molecular Dynamics (QMD)
- Outlook



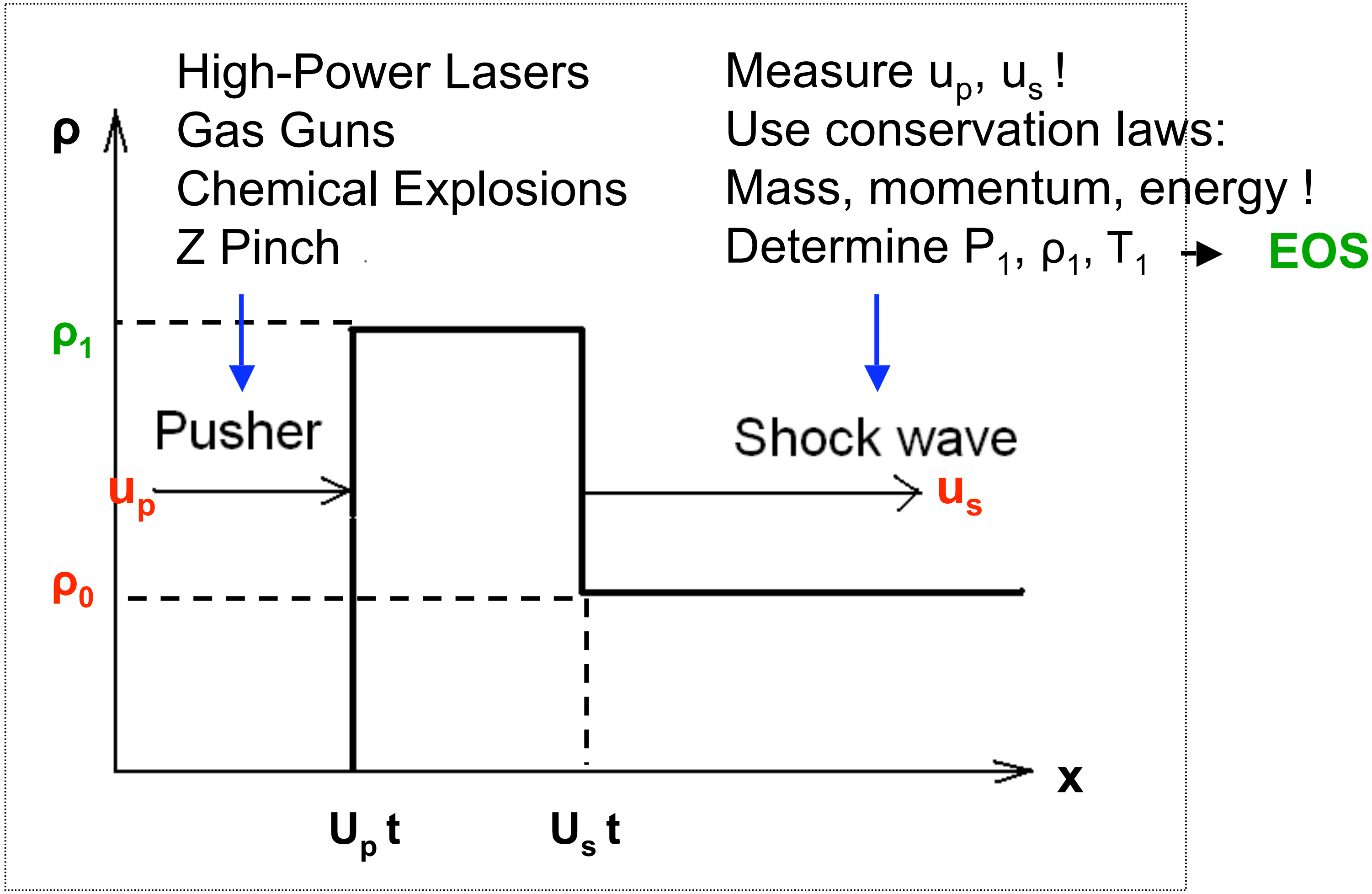
Convective Zone
Interface Layer
Radiative Zone
Core
Warm dense matter?
Hot plasmas:
T»E_{ion} → full ionization
Isochoric heating of solid-density matter:
Shock waves, XFEL (DESY Hamburg), particle beams (GSI Darmstadt)
Heating of low-density matter
Warm dense matter:
T several eV and $\rho \approx \rho_0$:
→ partial ionization,
→ strong correlations
Expanded matter (gas):
$\rho \ll \rho_0$
Extreme states of matter at low T: Megabar
Solid & liquid matter @ ρ_0 :
300 K, 1 bar
Thermal expansion to low densities
Compression to high static pressures (DAC)

Density-temperature plane

Coupling $\Gamma = \ell / d$, Degeneracy $\Theta = k_B T / E_F$



Shock wave techniques: Compression of materials to high pressure



Ya. B. Zeldovich, Yu. B. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (Dover, New York, 2002)

Hugoniot relations

- Compression ratio: $$\frac{1}{\eta} = \frac{\rho_0}{\rho_1} = 1 - \frac{u_p}{u_s}$$
- Final pressure: $$P_1 - P_0 = \rho_0 u_s u_p$$
- Hugoniot relation: $$\varepsilon_1 - \varepsilon_0 = \frac{1}{2}\left(P_1 + P_0\right)\left(\frac{1}{\rho_0} - \frac{1}{\rho_1}\right)$$
- Ideal atomic gas: η_{max}=4, ideal molecular gas: η_{max}=8
- Check EOS of materials at ultra-high pressures

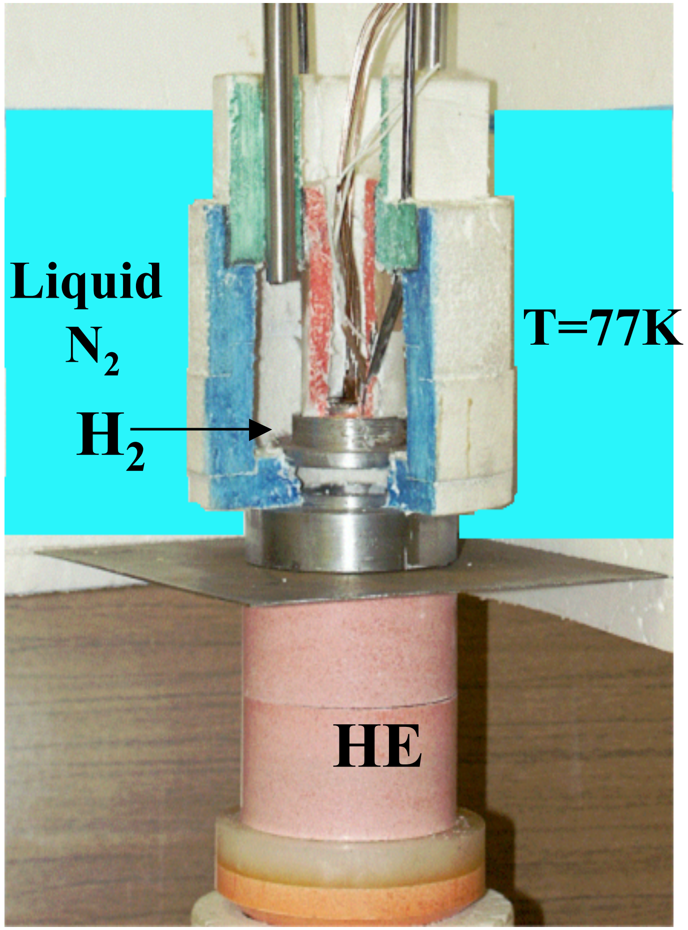
Typical pressures

(1 bar$=10^5$ Pa, 1 Mbar=100 GPa)

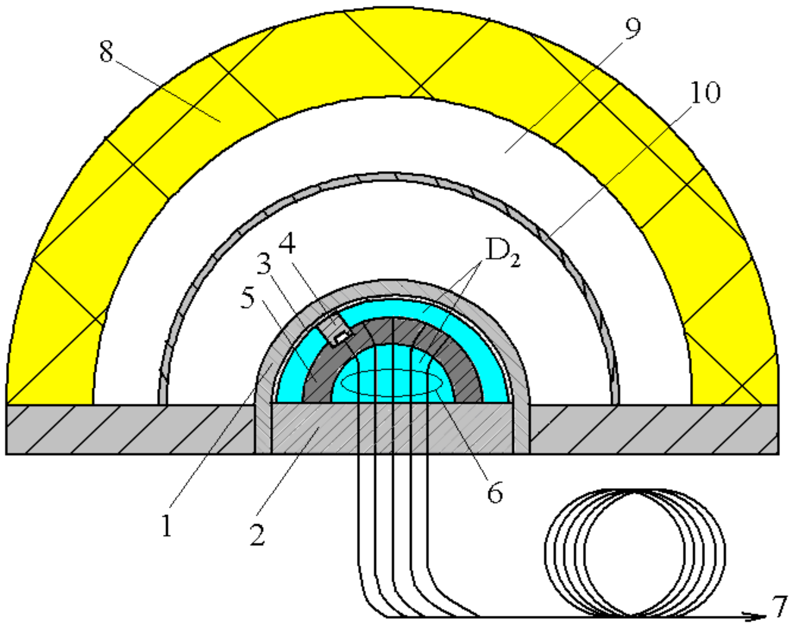
Cosmic background radiation	10^{-20} bar
UHV in laboratory	10^{-16} bar
Atmosphere at sea level	1 bar
Moon center	50 kbar
Earth center	3,6 Mbar
Jupiter center	50 Mbar
Sun center	100 Gbar
Red Giants	10^{15} bar
White Dwarfs	10^{18} bar
Neutron stars	10^{29} bar

Chemical explosions

- Institute of High Temperatures, Moscow, RAS
- Institute of Problems of Chemical Physics, Chernogolovka, RAS
- Russian Federal Nuclear Center, Sarov

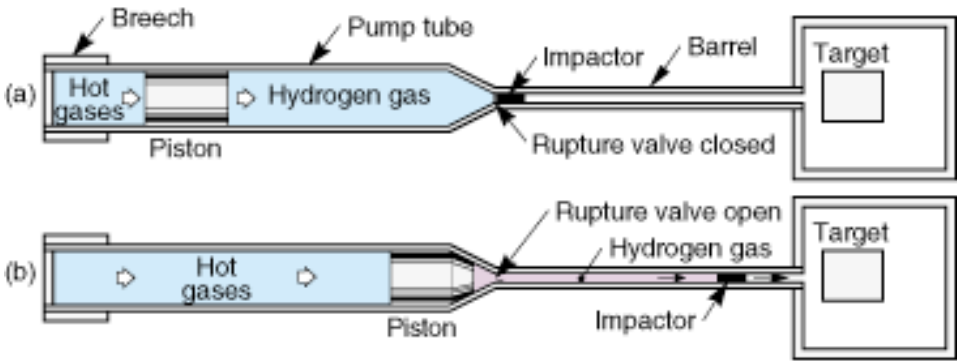


Multiple shock compression
Spherical cumulation

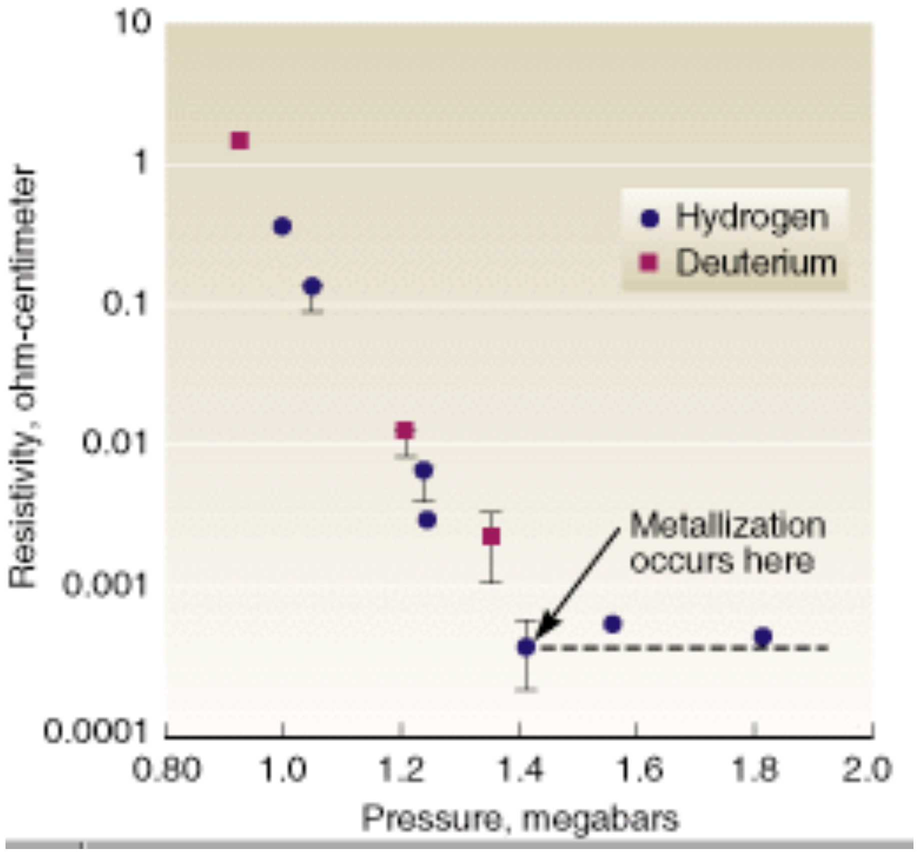


V.E. Fortov et al., JETF **97**, 259 (2003)

Two-stage light gas gun



(a) In the first stage of the gas gun (blue shading), hot-burning gases from gunpowder drive a piston, which in turn compresses hydrogen gas. (b) In the second stage (pink shading), the high-pressure gas eventually ruptures a second-stage valve, accelerating the impactor down the barrel toward its target.



Multiple shock waves in sandwich target

Isentropic process ⟶ low temperatures

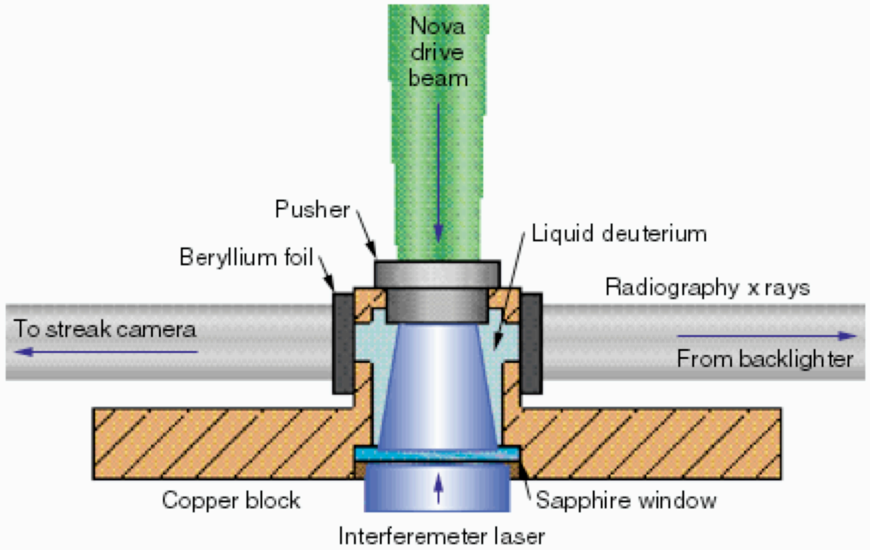
Metallic conductivity at 2500 K, 1.4 Mbar

(proposed by Wigner & Huntington 1936)

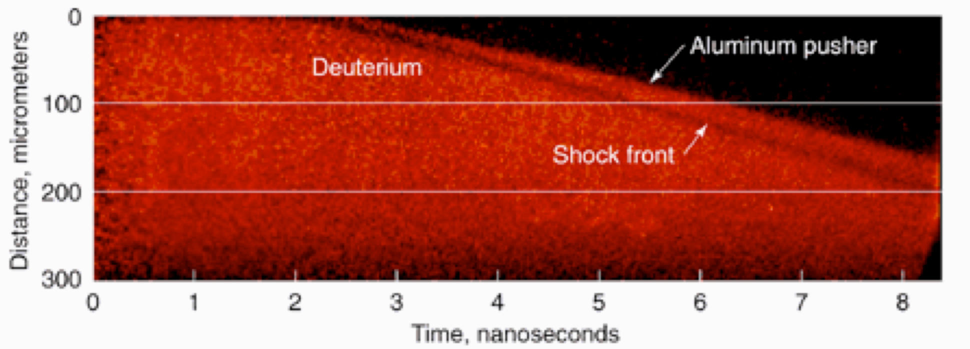
W.J. Nellis et al., PRL **68**, 2937 (1992)

S.T. Weir et al., PRL **76**, 1860 (1996)

High-power lasers

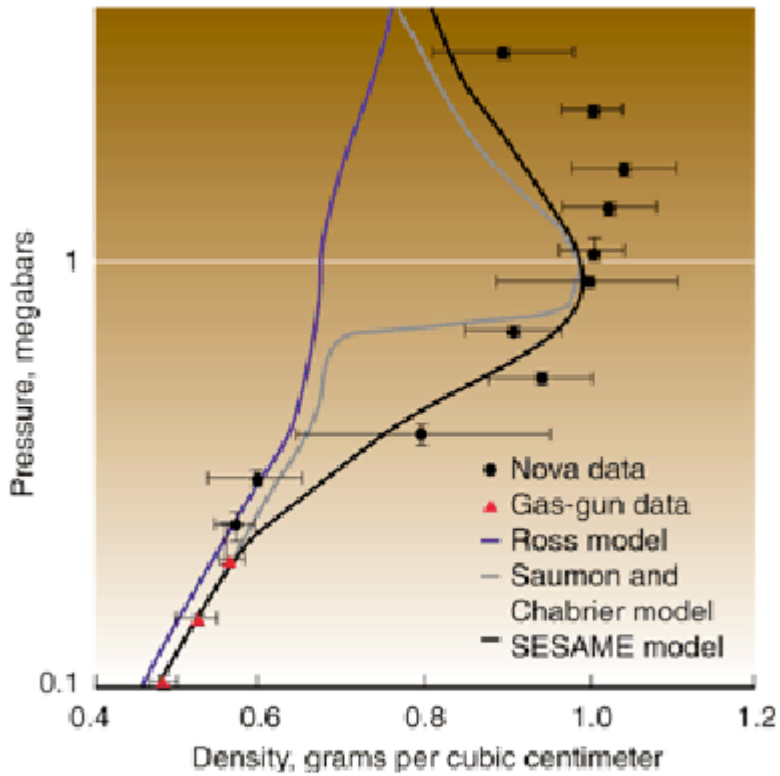


Schematic of the Nova laser shocking a target cell filled with liquid deuterium and machined into a copper block. One end of the cell is capped by an aluminum pusher, the other by a sapphire window used for rearview diagnostics. X-ray transmitting windows made of beryllium foil are located on each side of the cell.



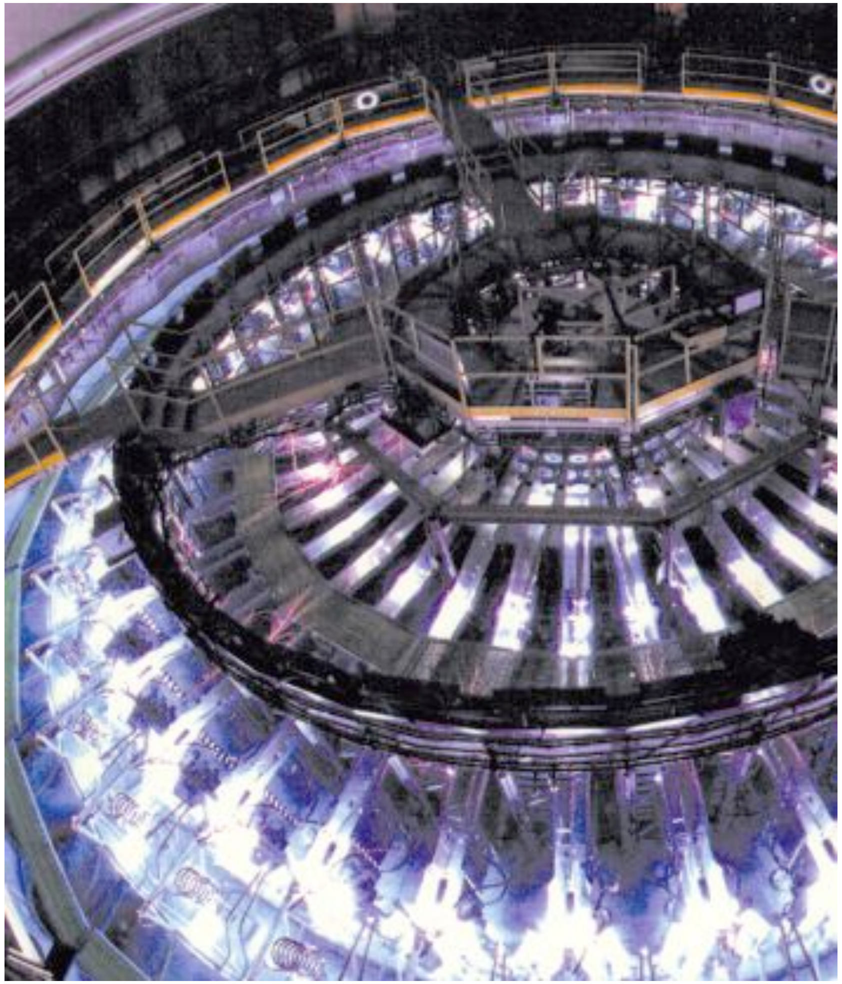
The image of the deuterium is moved across the film over time, producing a streak radiograph. In the figure, the pusher is above the deuterium, so the shock travels from top to bottom.

Nova @ LLNL
Omega @ Rochester
Vulcan @ RAL
Gekko in Japan
NIF @ LLNL
LMJ in France



L.B. DaSilva et al., PRL **78**, 483 (1997)

Z pinch at Sandia National Laboratory



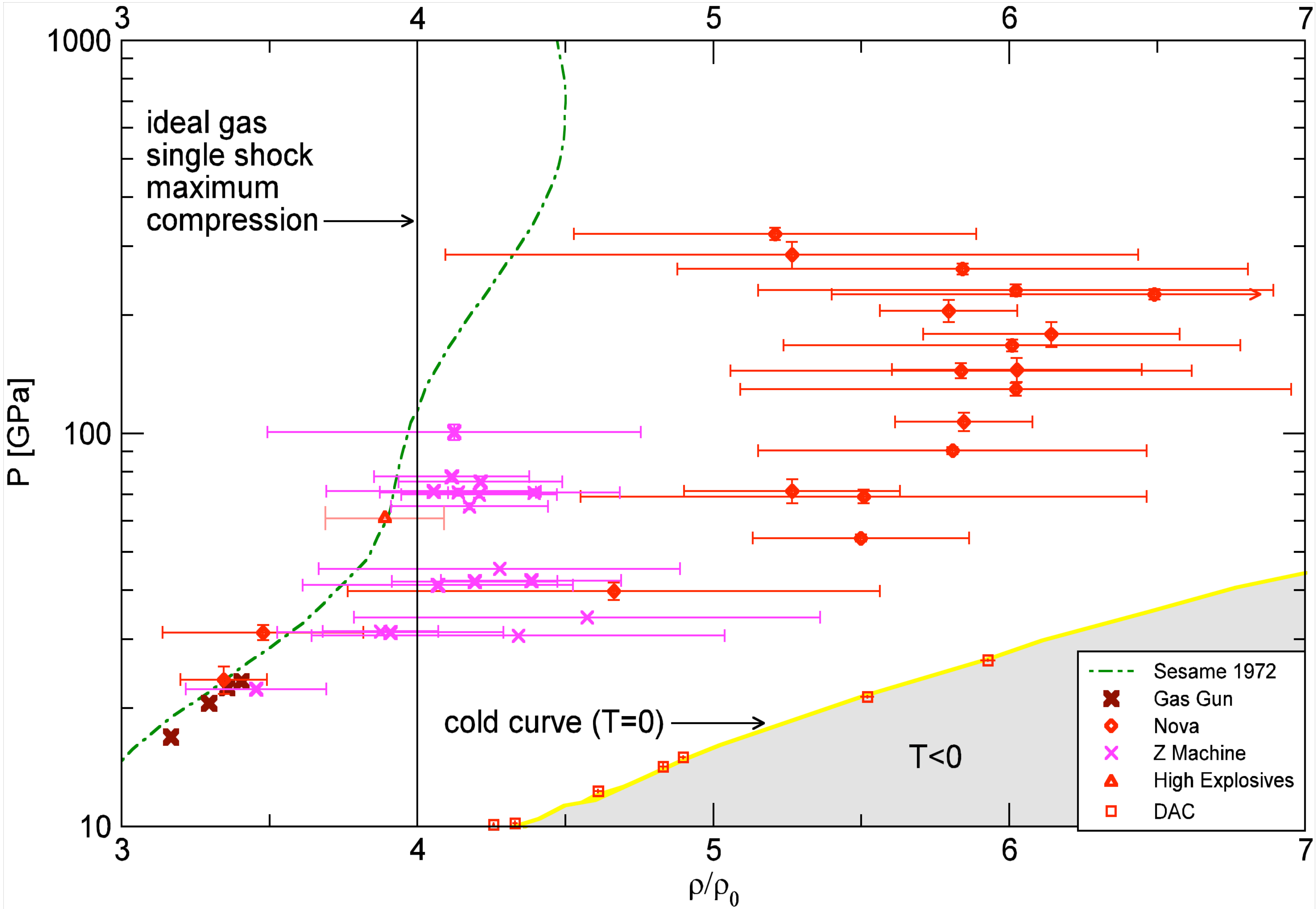
- 20 MA current in 100 ns
- through 240 thin W wires
- 200 TW x-ray power
- 2 MJ energy output

- Short-circuit load: magnetically launched flyer plates generate shock waves in fluid D_2

- u_p ~ 10-22 km/s
- Principal Hugoniot up to 4 Mbar
- η_{max}=4.3 ⟶ stiff EOS

M.D. Knusdon et al., PRL **87**, 225501 (2001), PRB **69**, 144209 (2004)

Experimental Hugoniot points for D_2



Problems

- Shock wave experiments have relatively large error bars
- u_s-u_p relation provides EOS:

► Behavior at megabar pressure?

► Maximum compression?

► Phase diagram and phase transitions?

- Path in the n-T plane restricted to:

► Hugoniot curve (single shocks) determined by ρ_0, P_0, T_0

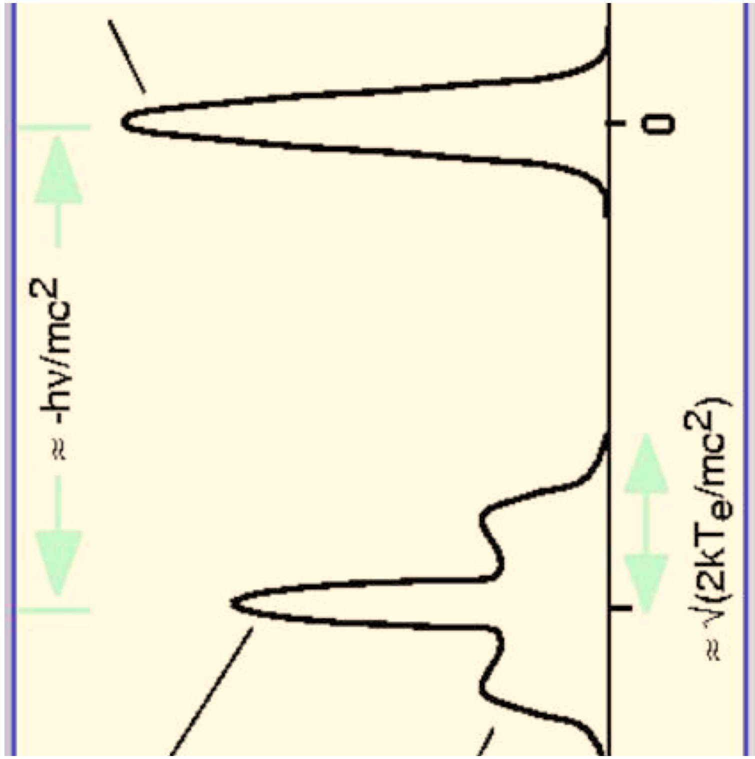
► Isentrope (multiple shocks) $\rightarrow$ low temperatures

► Use precompressed targets, pulse shaping

Alternative: Apply X-rays or particle beams
to isochorically heat solid/liquid targets
and to probe WDM by scattering experiments

Pump-probe experiments in WDM

O.L. Landen et al., JQSRT **71**, 465 (2001)

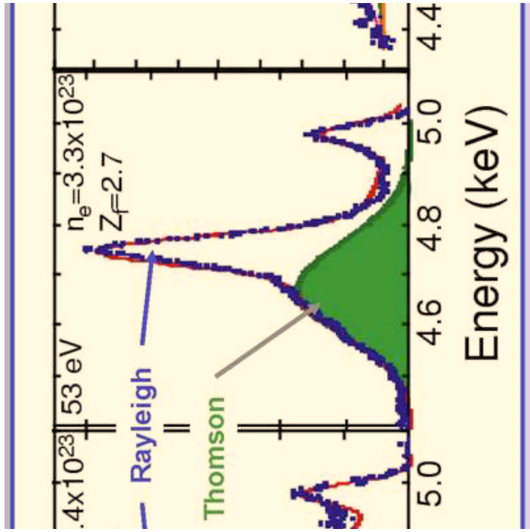


Isochoric heating of solid density materials by intense x-rays (PUMP)

Perform x-ray scattering in the cold, warm, or hot material (PROBE)

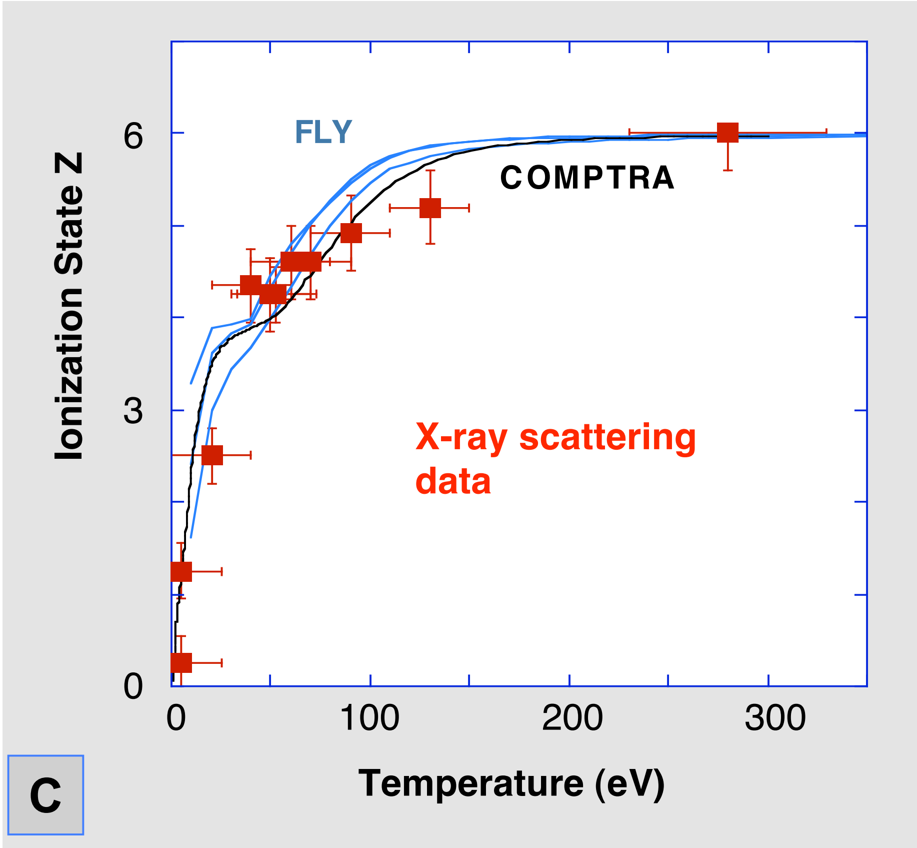
Study of strongly coupled matter: T_e, T_i, n_e, Z_{eff}

G. Gregori et al.,
PRE **67**, 026412 (2003)



Efficient tool for plasma diagnostics: Determine T_e and Z_{eff}

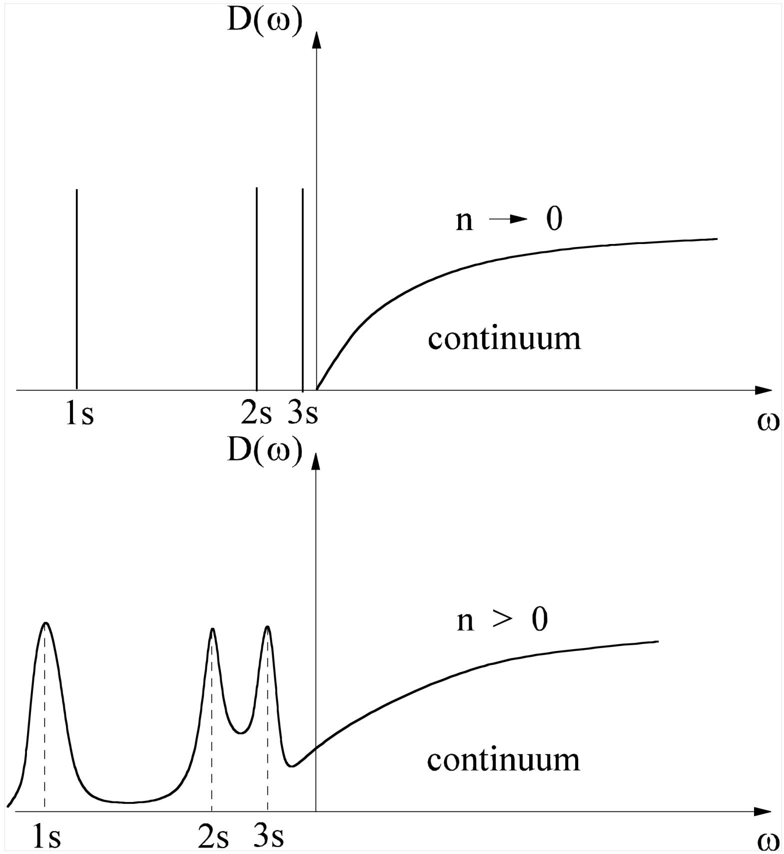
Requires sophisticated many-particle theory for S(q,ω) and ε(q,ω)



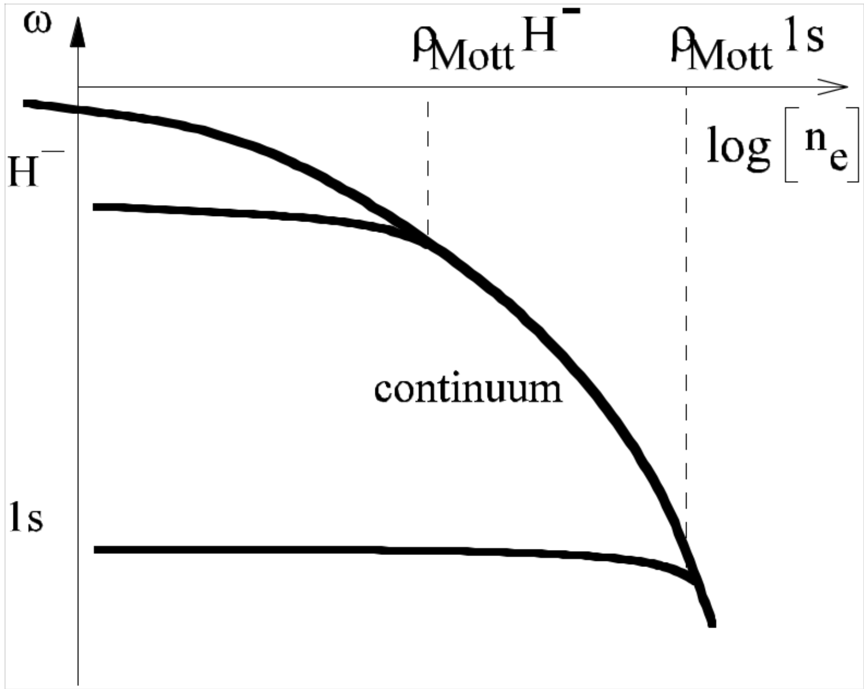
G. Gregori et al.,
JQSRT **99**, 225 (2006)

Dense matter: Strong correlation effects

Case study hydrogen: Bound and free electron states → chemical picture at low ρ
Shift and damping of one- and two-particle states with increasing ρ → Mott effect
Derive and solve Bethe-Salpeter equations accounting for in-medium effects
(dynamical screening, self-energy, Pauli blocking, degeneracy)



DOS in hydrogen (schematic)



Mott effect in hydrogen (schematic)

Chemical picture and WDM: Dense hydrogen

Free energy model: $F(T,V,\{N_c\}) = F_0 + F_{\pm} + F_{pol}$

- neutral fluid: H, H_2 - Fluid Variational Theory (FVT)
- plasma component: e, p, H^-, H_2^+ - quantum virial expansion
- polarization term: e-H, e-H_2 – 2nd virial coefficient
- multicomponent system: c = e, p, H, H_2
- hydogen-helium mixtures: He^+, He^{2+} in addition
- chemical reactions: $H_2 \leftrightarrow 2H$, $H \leftrightarrow e+p$, …
- chemical equilibrium: $\mu_{H_2} = 2\mu_H$, $\mu_H = \mu_e + \mu_p$, …

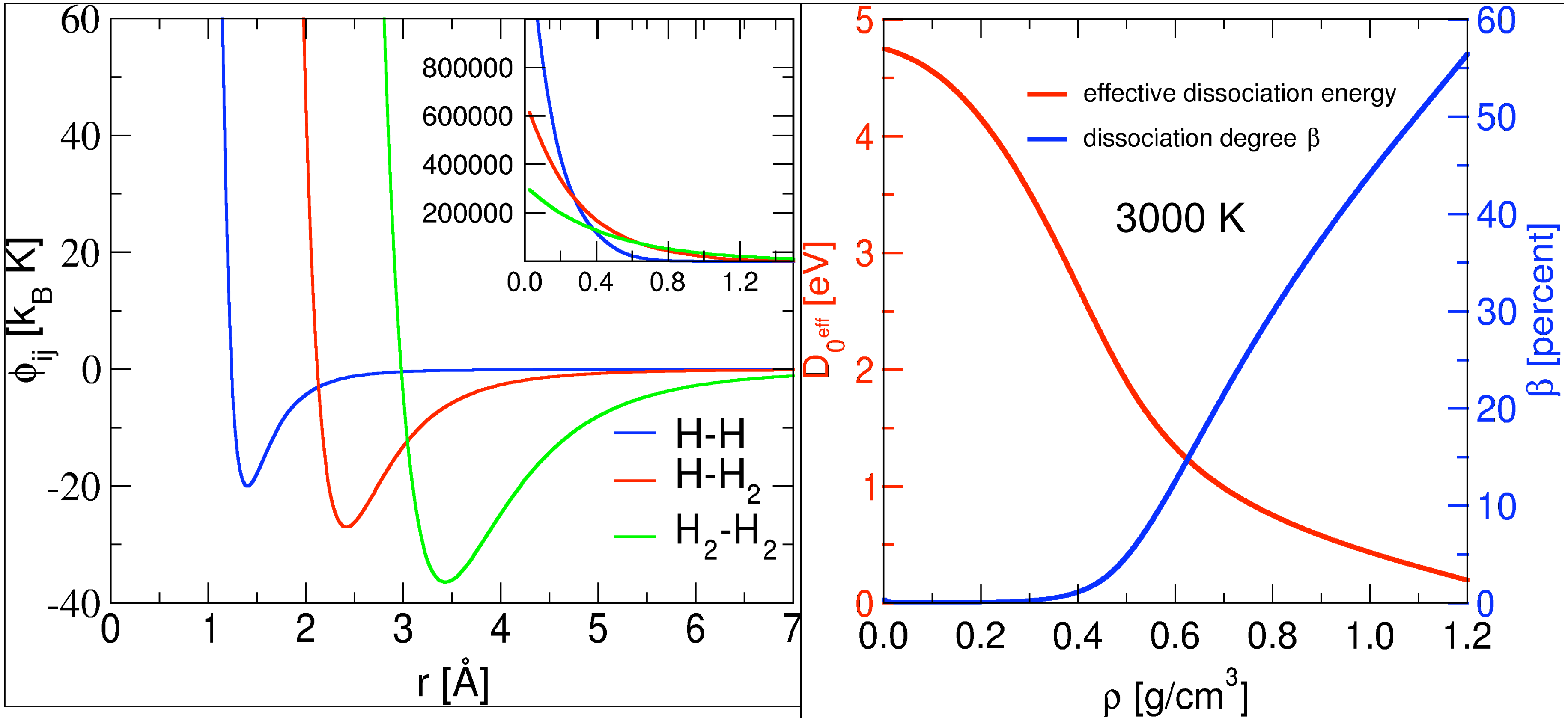
Equation of state: $F = U - TS$

$$p=-(dF/dV)_{T,N} \,,\; \mu_c = (dF/dN_c)_{T,V} \,,\; S=-(dF/dT)_{V,N}$$

D. Beule et al., PRB **59**, 14177 (1999), PRE **63**, 060202 (2001); H. Juranek et al., JCP **112**, 3780 (2000), **117**, 1768 (2002)

Effective potentials of exp-6 type
for neutral particle interactions

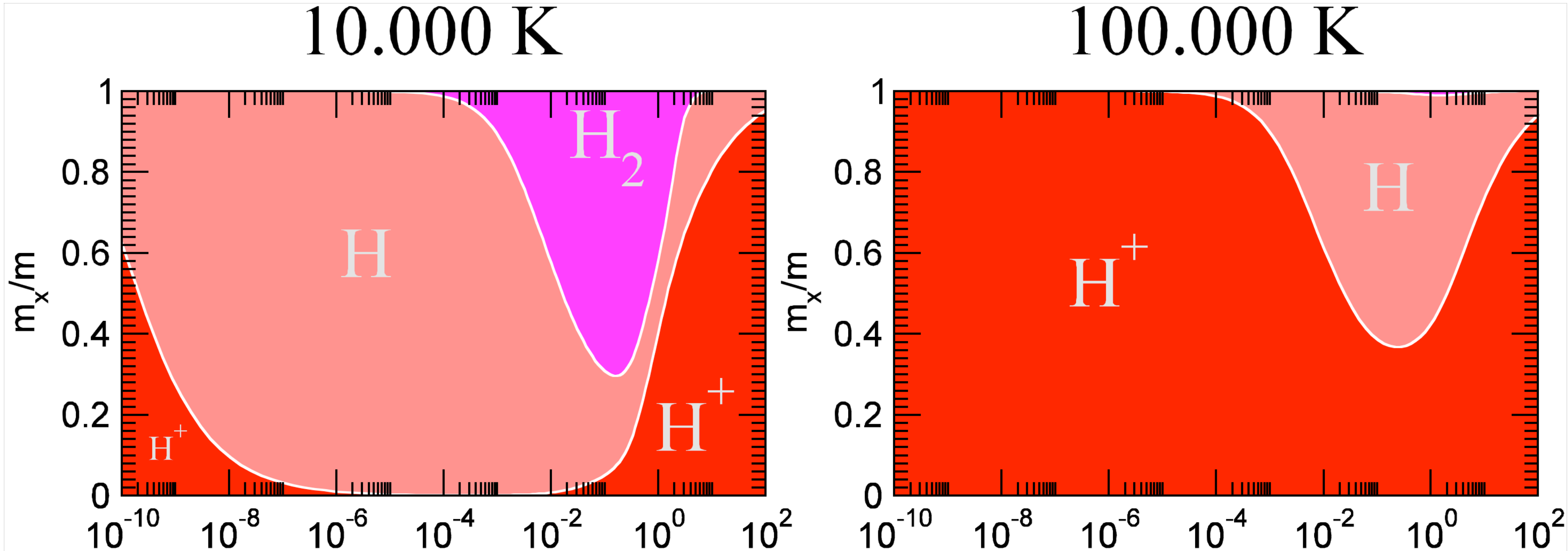
Self-consistent fluid variational theory for hydrogen



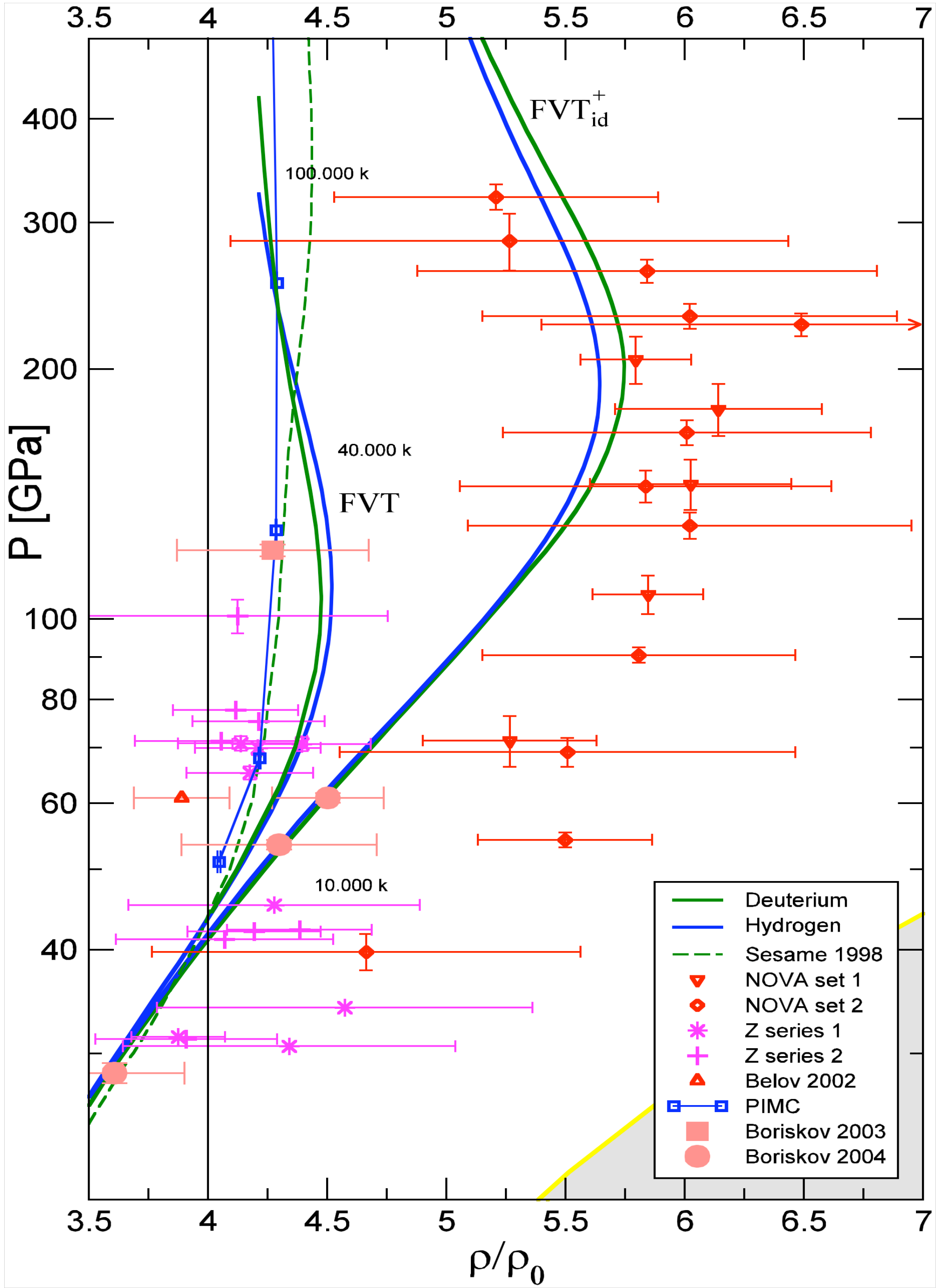
H. Juranek, R. Redmer, Y. Rosenfeld, J. Chem. Phys. **117**, 1768 (2002)

V. Schwarz, H. Juranek, R. Redmer, Phys. Chem. Chem. Phys. **7**, 1990 (2005)

Include ionization equilibrium (plasma): Partial dissociation and ionization



H. Juranek et al., Contrib. Plasma Phys. **45**, 432 (2005)



Hugoniot curves

FVT: pure fluid hydrogen H, H_2
FVT$_{id}^{+}$: ideal plasma contribution included

All shock-wave experiments except Nova, PIMC and QMD simulations:

maximum compression < 4.5

Nova data probably incorrect!
Include nonideality corrections!
B. Holst (Diploma 2006)

H. Juranek et al., Contrib. Plasma Phys. **45**, 432 (2005)

Alternative theoretical methods

- Chemical picture is based on the definition of bound states (atoms, molecules) as new species
- Employs effective two-particle potentials and cross sections

- Virial, fugacity, activity expansions (Rogers, Ebeling …)
- Integral equation methods: HNC, MHNC, VHNC … (Ichimaru, Rosenfeld …)
- Combine DFT and HNC: QHNC (Chihara, Perrot, Dharma-wardana …)
- Quantum simulations: Path-Integral Monte Carlo (PIMC) and Quantum Molecular Dynamics (QMD)

Quantum Molecular Dynamics (QMD)

- combination of DFT and MD is possible in Born-Oppenheimer approximation:
  - Electrons are treated quantum mechanically on the level of the Schrödinger equation (KS equations):

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{KS}(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

  - Ions are handled classically (Newton's equation of motion):

$$m_\alpha \ddot{\vec{r}}_\alpha = \vec{F}_\alpha$$

  - Forces on the ions are calculated by using the "Hellmann-Feynman theorem":

$$\vec{F}_\alpha(\vec{r}) = -\nabla_\alpha E[n(\vec{r})]$$

Basics of DFT

- Theorems of Hohenberg and Kohn:
  1. The energy can be described by a functional of the electron density: E=E[n(r)]
  2. The functional E[n(r)] is unique for the ground state.

$$E[n] = T_s[n] + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})\, d^3r + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d^3r d^3r' + E_{\text{xc}}[n]$$

- Kohn-Sham equations (KS)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

- Kohn-Sham potentials

$$v_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d^3r' + v_{\text{xc}}(\mathbf{r})$$

- LDA, GGA, exact exchange (EXX) and hybrid schemas

Accessible quantities in QMD: Electronic properties, structure, EOS

- Each time step: $\vec{r}_i, \vec{v}_i, \vec{F}_i, \Psi_i$
- Full DFT calculation ➔ Band structure, DOS
- Finite temperatures: $n(r)=\Sigma_i f(\varepsilon_i)\, |\Psi_i(r)|^2$ (Mermin)
- Calculation of T and p ➔ EOS
- Average over hundreds of time steps: g(r) ➔ S(k)
- Autocorrelation function: self-diffusion coefficient via Einstein's relation:

$$D_S = \frac{1}{6t}\left\langle \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle$$

$$D_S = \frac{1}{3}\int_0^\infty dt \left\langle \vec{v}_i(t) \cdot \vec{v}_i(0) \right\rangle$$

Dynamic (optical) conductivity via QMD

- Interpretation of the wave function: dynamic conductivity

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$$

- Kubo-Greenwood formula $\sigma_1(\omega) = \frac{2\pi}{\Omega} \sum_{ij} F_{ij} \left| D_{ij} \right|^2 \delta(\varepsilon_i - \varepsilon_j - \omega)$

$$F_{ij} = \left[f(\varepsilon_i) - f(\varepsilon_j) \right] / \omega \quad , \quad \left| D_{ij} \right|^2 = \frac{1}{3} \sum_{\alpha} \left| \left\langle \Psi_i \middle| \nabla_\alpha \middle| \Psi_j \right\rangle \right|^2$$

- Dielectric function: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = 1 - \frac{4\pi}{\omega} \sigma_2(\omega) + i \frac{4\pi}{\omega} \sigma_1(\omega)$

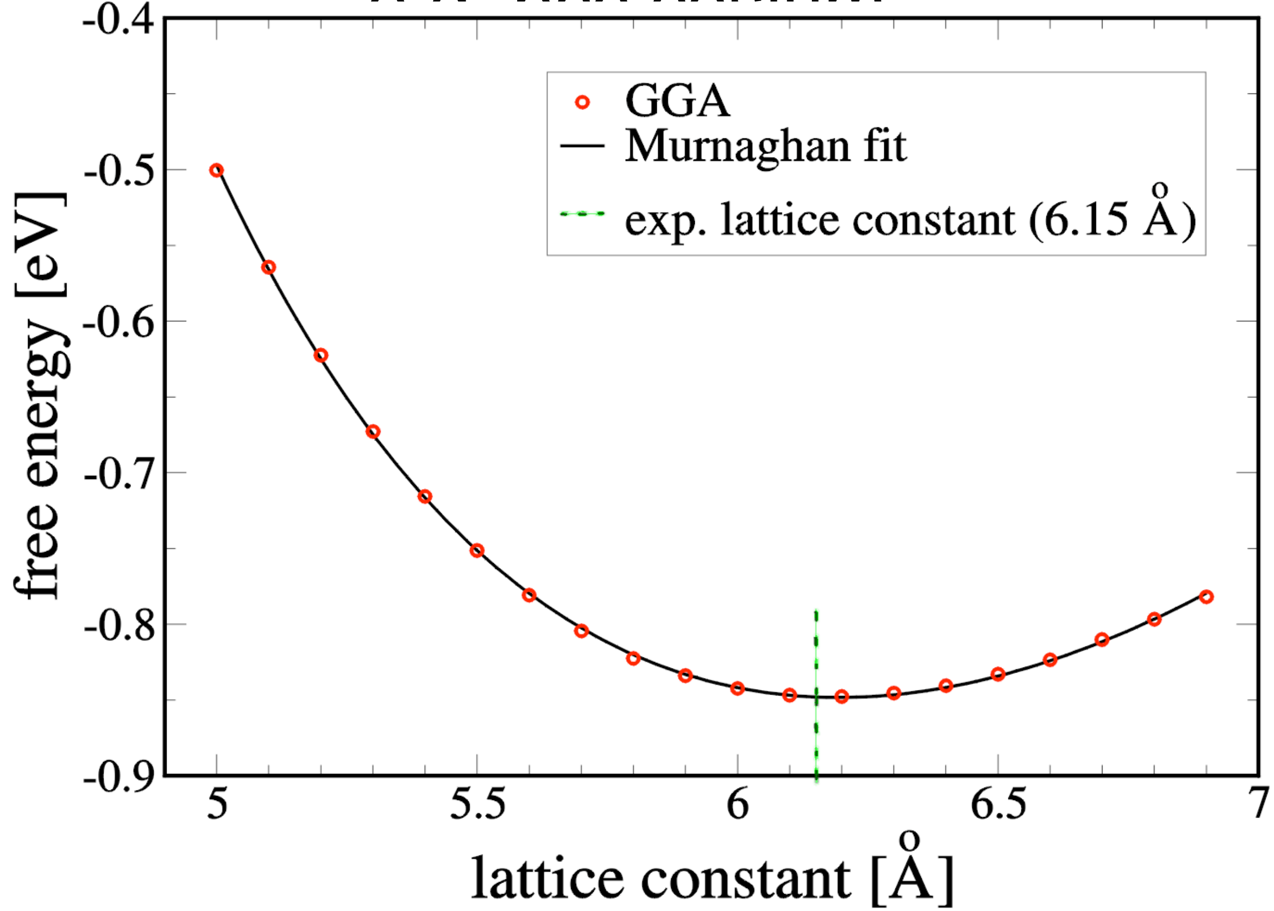
- Kramers-Kronig relation: $\sigma_2(\omega) = \frac{2}{\pi} P \int \frac{\sigma_1(\nu)\omega}{\left(\nu^2 - \omega^2\right)} d\nu$

- Index of refraction: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \left[n(\omega) + ik(\omega) \right]^2$

- Reflectivity **r(ω)** and absorption coefficient **α(ω)** via standard relations
- Dynamic structure factor **S(q,ω)** via fluctuation-dissipation theorem

Ground state properties using DFT

Optimization of the lattice constant of solids:



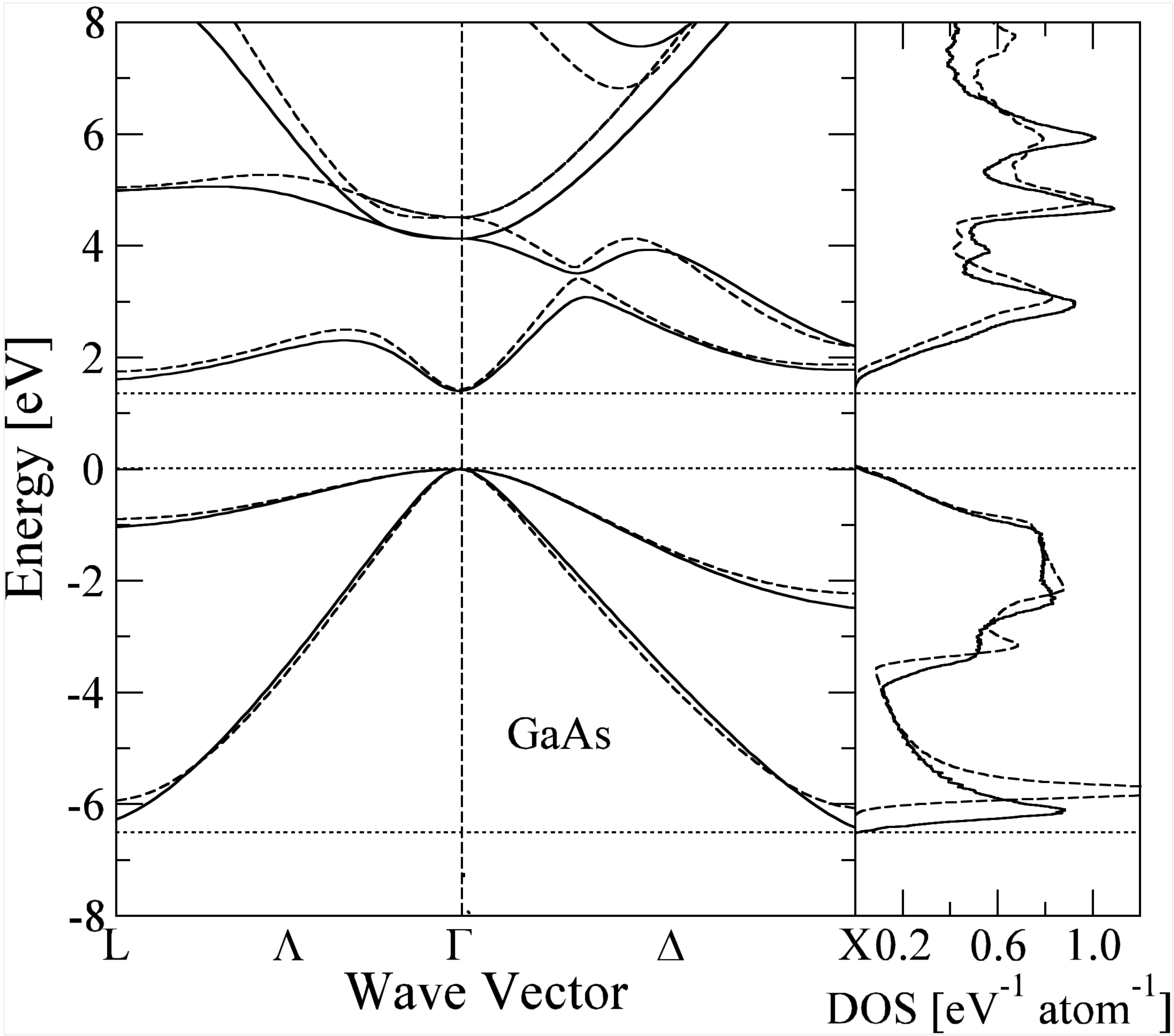
Band structure of semiconductors: GaAs

Solid lines:

EXX-LDA

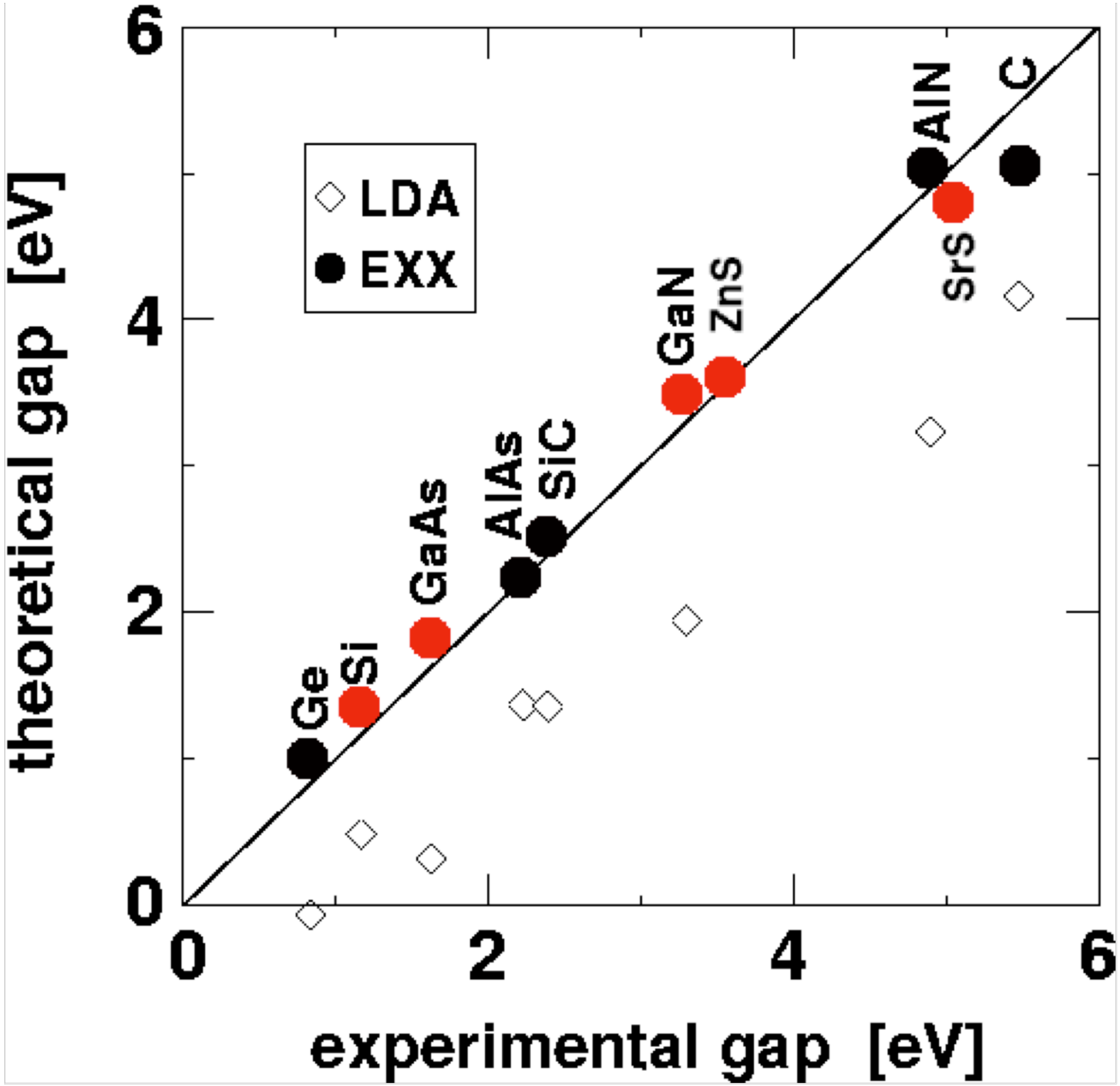
Broken lines:

EPM



A. Kuligk et al.; PRB **71**, 085201 (2005)

Band gap problem of DFT



N. Fitzer, PhD Thesis (Rostock, 2002)

QMD simulations for expanded and compressed fluids (WDM)

Thermal expansion of fluid metals (Hg, alkali metals) from the melting point to the critical point:

Metal-to-nonmetal transition (localization of electrons)

Compression of molecular fluids (H_2, N_2, O_2, H_2O, CO_2) and noble gases (He, Ar, Xe) to high pressure:

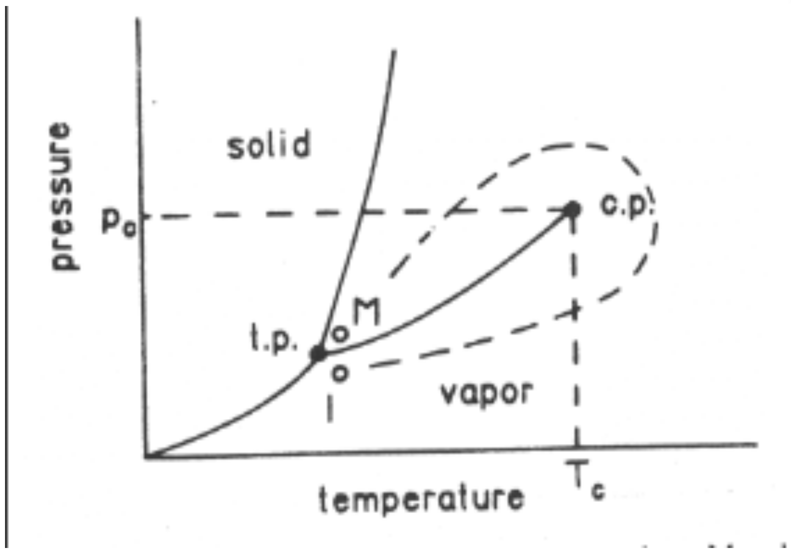
Nonmetal-to-metal transition (delocalization of electrons, band gap closure → band gap problem!)

Test of the QMD method:

Comparison with accurate static high-pressure experiments and dynamic shock wave experiments

Structure of expanded liquid metals

- Continuous phase transition by expanding the liquid thermally to the vapor phase around the critical point
- Pair correlation function determines the number of next neighbors, the next neighbor distance and the phase state



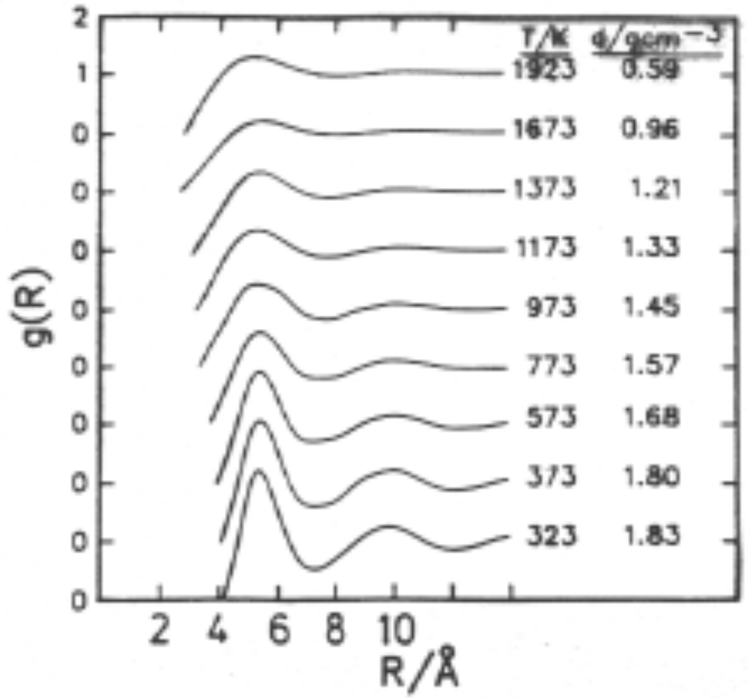
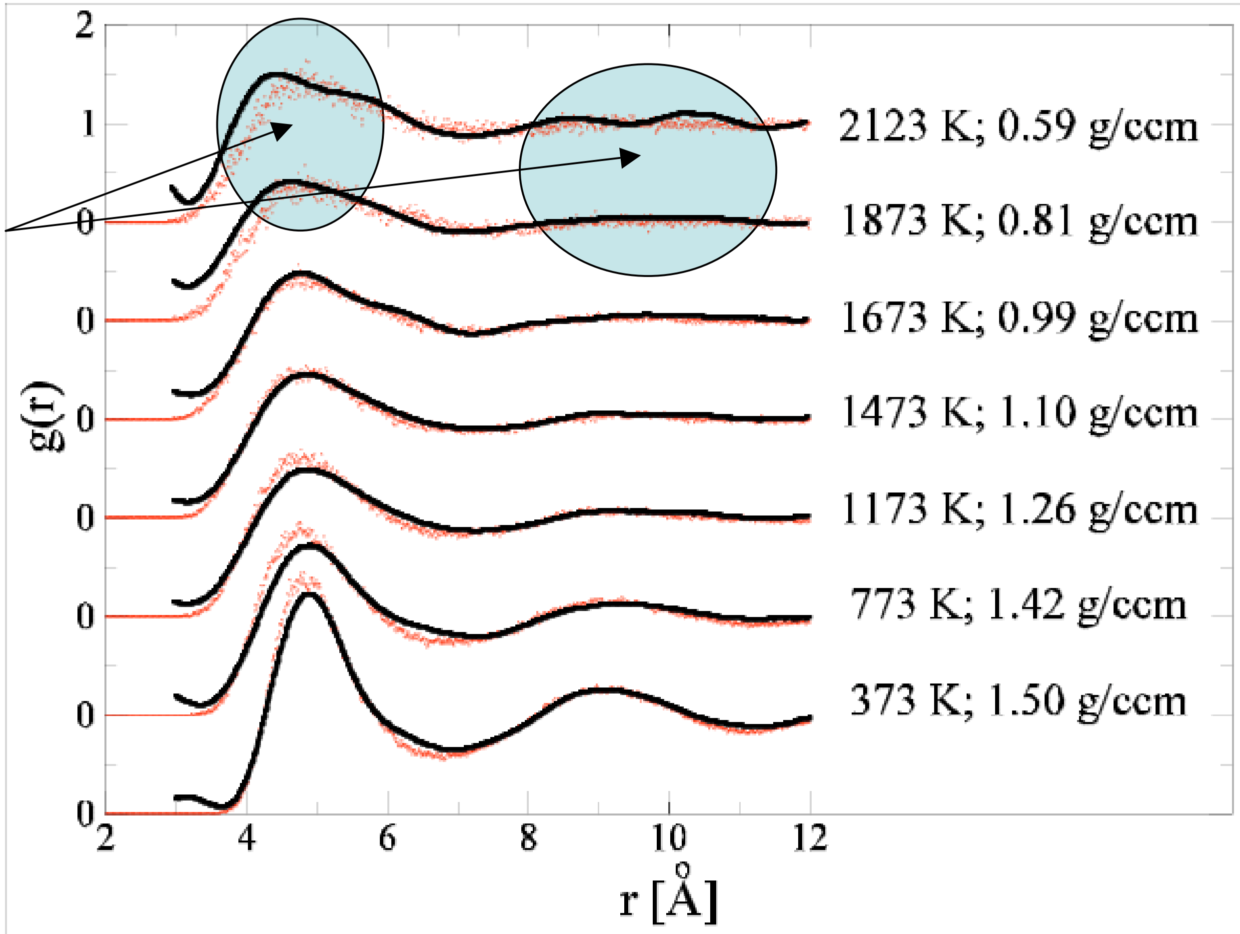


Fig. 1 Pair correlation function g(R) of expanded liquid Cs.

F. Hensel, W.W. Warren: Fluid Metals (Princeton Univ. Press, Princeton, 1999)

Pair correlation function of Rb

Slight change of the shape at the first and second peak can be interpreted as the occurrence of dimers and trimers (Rb_2, Rb_3) in liquid Rb at lower densities.

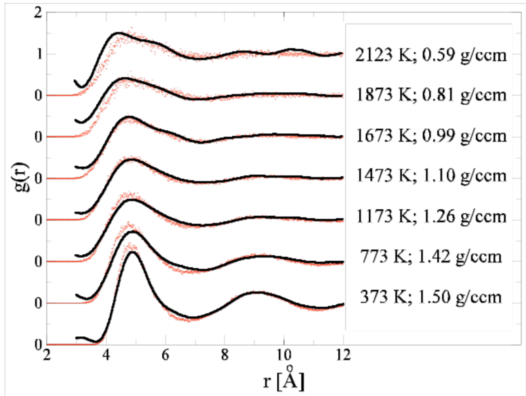


Red circles: QMD data

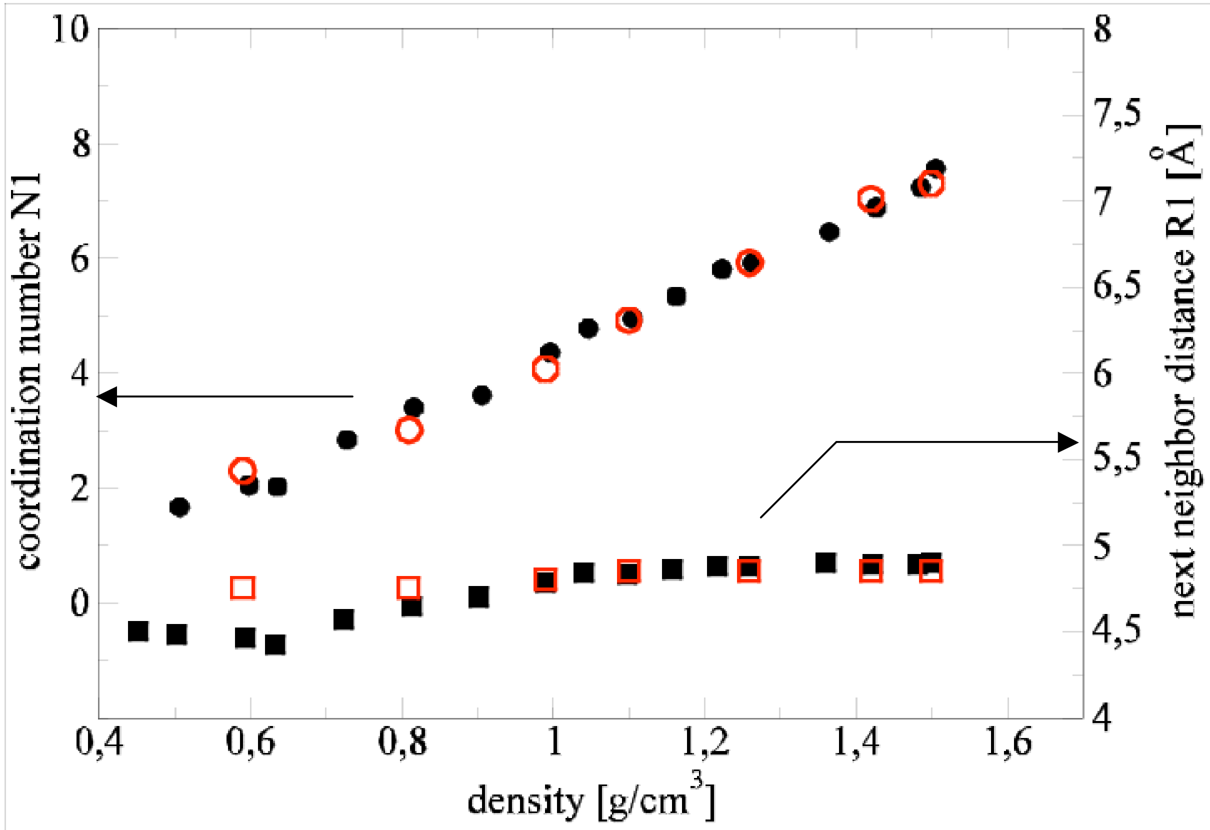
Black line: Experimental data (Matsuda et al., 2006)

QMD with VASP:
32 to 64 atoms with 7 electrons per atom, canonical ensemble (Nosé-thermostat), 500-1000 time steps per run with 5-20 fs time step, 2.5-20 ps simulation time

Coordination number N_1
Next neighbor distance R_1



Rb

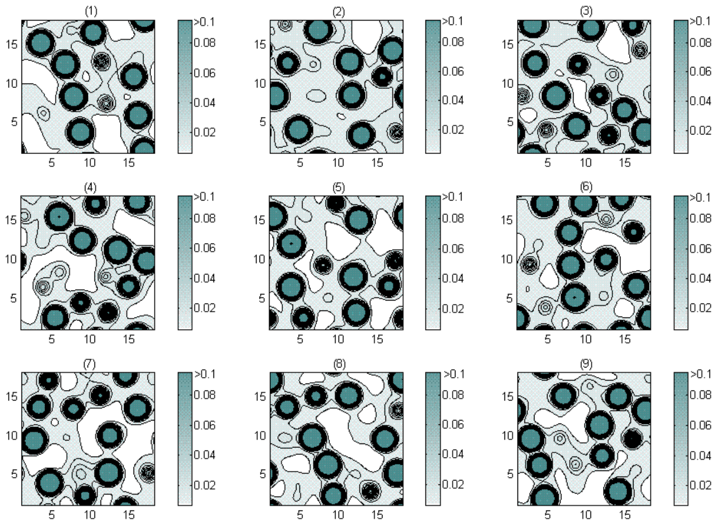


Open red symbols: QMD-data

Closed black symbols: Experimental data

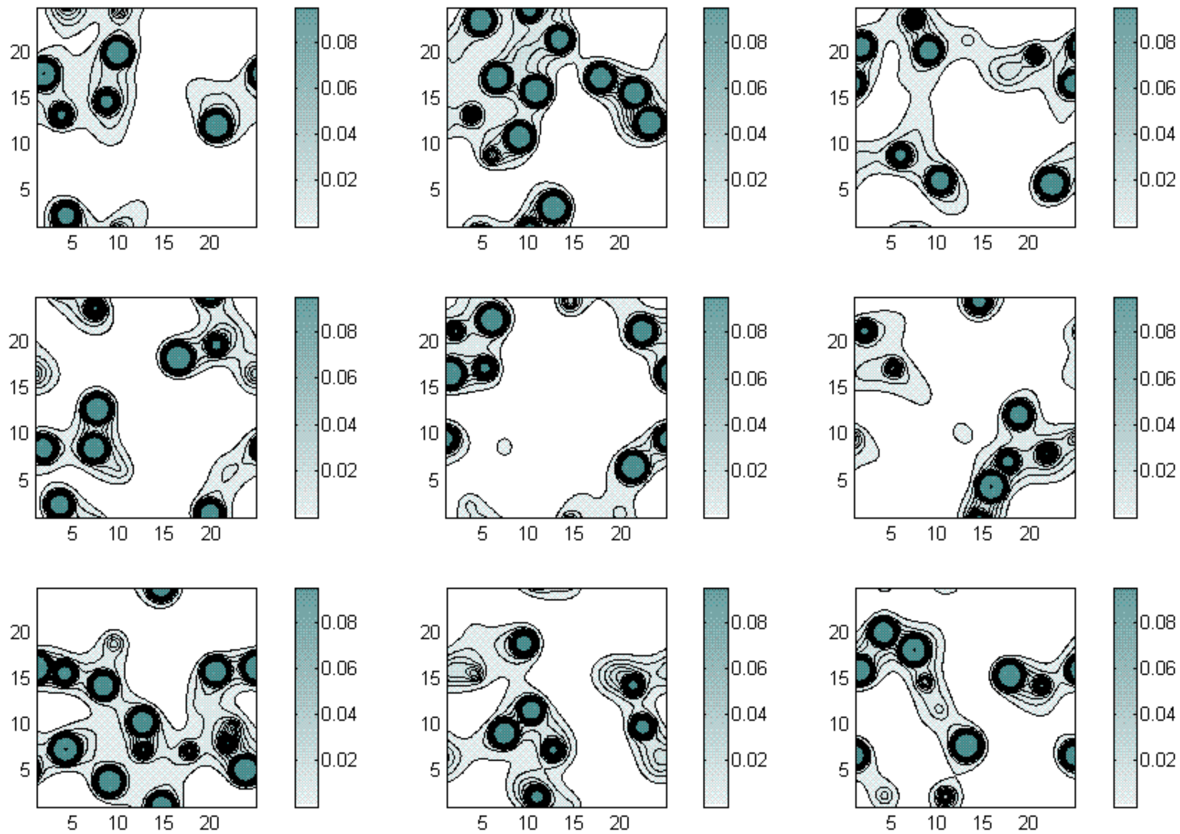
A. Kietzmann, R. Redmer, F. Hensel, M.P. Desjarlais, T.R. Mattsson,
J. Phys.: Condensed Matter **18**, 5597 (2006)

Charge density of Rb: Contour plots



373 K and 1.5 g/cm^3 near the melting point

2123 K and 0.59 g/cm^3
near the critical point

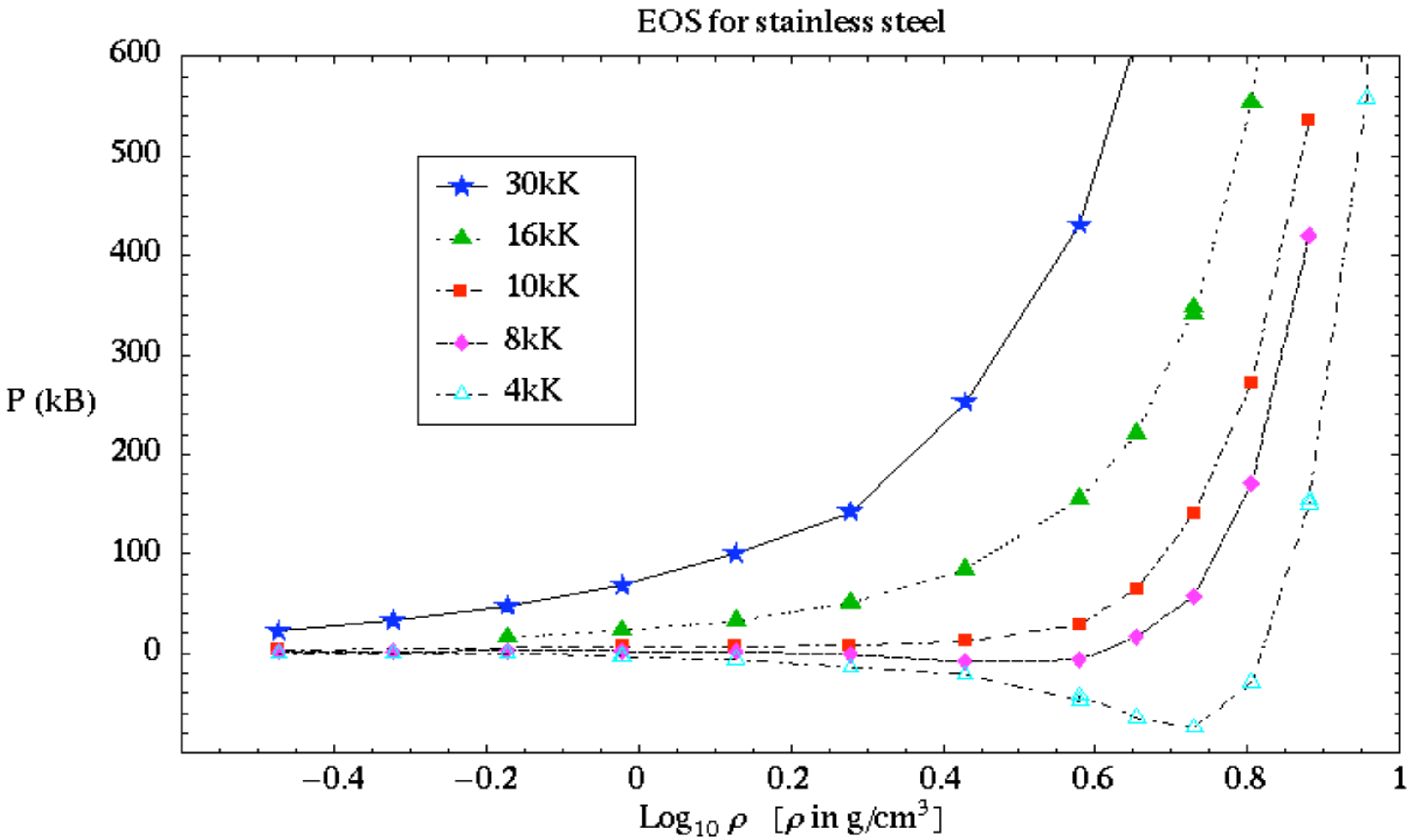


- Clustering: Rb_2, Rb_3
- Large voids
- Metal-nonmetal transition

A. Kietzmann, R. Redmer, F. Hensel, M.P. Desjarlais, T.R. Mattsson,
J. Phys.: Condensed Matter **18**, 5597 (2006)

Equation of state for steel:
Location of the critical point

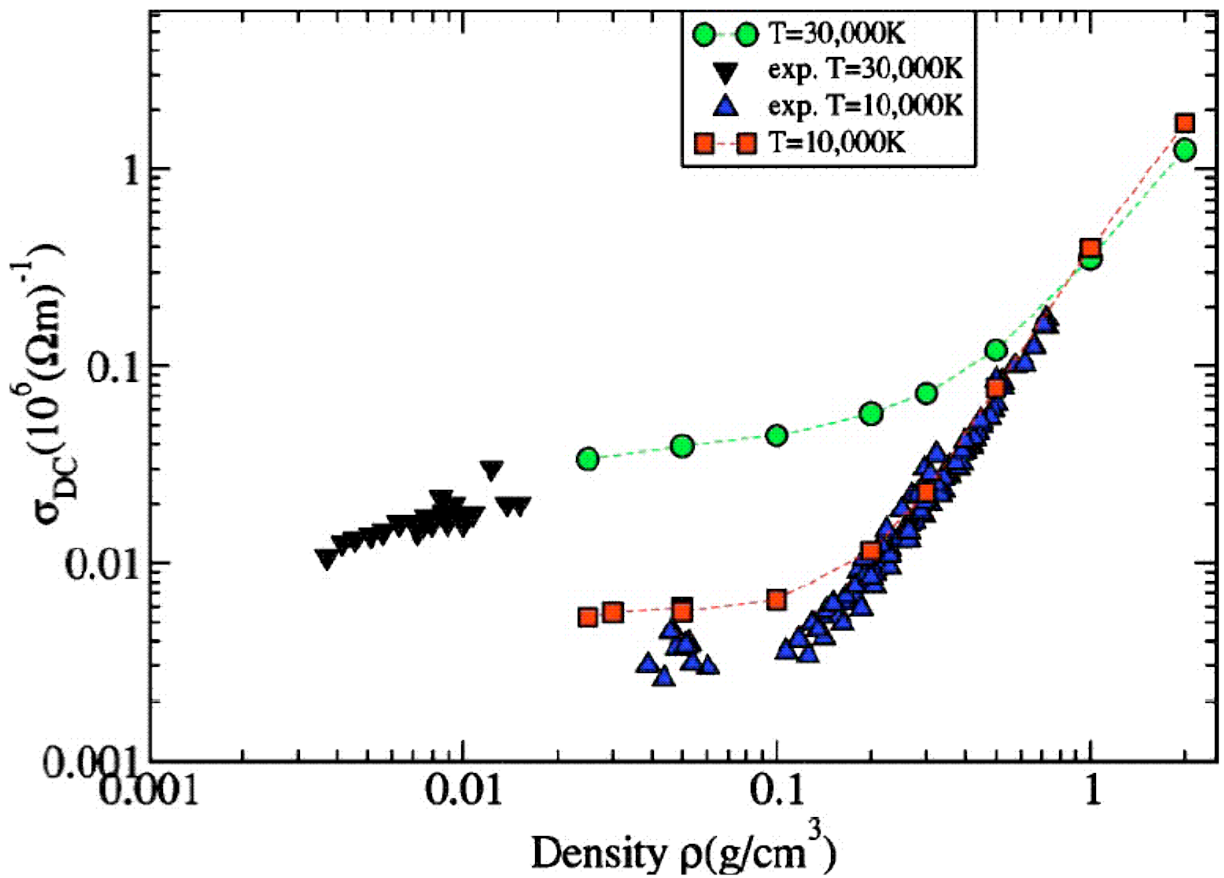
M.P. Desjarlais, T.R. Mattsson (Sandia Natl. Lab.)



CP: QMD simulation yields 10 000 K, 1 g/cm^3, 6 kbar
SESAME tables give 8800 K, 2.2 g/cm^3, 1.5 kbar

QMD simulation for the dc conductivity in Al:

Evaluating the Kubo-Greenwood formula



M.P. Desjarlais et al., PRE **71**, 016409 (2005)

Summary and outlook

- WDM as perfect case study for strongly coupled systems
- Shock-wave and pump-probe experiments access WDM
- Codes for EOS and transport coefficients within the efficient chemical picture: FVT, FVT^+, COMPTRA04
- Physical picture: (M,V,Q)HNC, PIMC …
- QMD simulations for liquid H_2, He, H_2O …: EOS data, Hugoniot curves, to be used in planetary physics
- QMD simulations for expanded and compressed metallic liquids:

► structural changes

► EOS data and location of the CP

► melting line at high pressures

► dynamic conductivity and reflectivity

► metal-nonmetal transition

THANKS TO

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F. Hensel, T.R. Mattsson, H. Reinholz, G. Röpke
for discussions and cooperation!

SUPPORTED BY

SFB 652 „Strong Correlations and Collective Phenomena in Radiation Fields: Coulomb Systems, Clusters, and Particles“

GRK 567 „Strongly Correlated Many-Particle Systems“

Virtual Institute of the Helmholtz Gemeinschaft
VH-VI-104 „Plasma Physics Research Using FEL Radiation“