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Ab-initio Calculations in Physics of Extreme States of Matter

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Seminar for young scientists “Physics of High Energy Density in Matter”
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Outline

- Extreme States of Matter
- Ab-initio calculations
- Quantum-statistical models
- Density functional theory
- Quantum molecular dynamics
- Quantum Monte Carlo
- Conclusions

Ab-initio calculations

- Thermodynamic, transport and optical properties
- Use the following information:
  - fundamental physical constants
  - charge and mass of nucleus
  - thermodynamic state

Extreme States of Matter

- Kirzhnits D.A., Phys. Usp., 1971
- Atomic system of units:
  - $m_e = \hbar = a_0 = 1$
- Extreme States of Matter (Kalitkin N.N.)
  - $P = e^2/a_0^4 = 294.2\ \text{Mbar}$
  - $E = e^2/a_0 = 27.2\ \text{eV}$
  - $V = a_0^3 = 0.1482\ \text{A}$
- Hypervelocity impact, laser, electronic, ionic beams, powerful electric current etc.

EOS: Traditional Form

Adiabatic (Born-Oppenheimer) approximation ($m_e << m_i$)

$$F(V,T) = F_e\left(V,T,\left\{R_t^0\right\}\right) + F_n\left(V,T,\left\{R_t^0\right\}\right)$$

Free energy of electrons in the field of fixed ions

Free energy of ions interacting with potential depending on V and T

Traditional form of two-temperature EOS. Free energy

$$F(V,T) = F_c(V) + F_i(V,T) + F_e(V,T)$$

Cold curve

Thermal contribution of atoms and ions

Thermal contribution of electrons

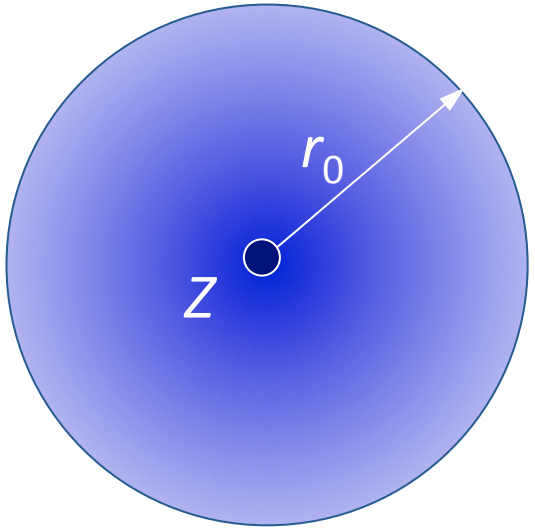
Semiempirical expressions

DFT, mean atom models

Mean atom models or DFT calculations might help to decrease the number of fitting parameters

Electronic Contribution to Thermodynamic Functions

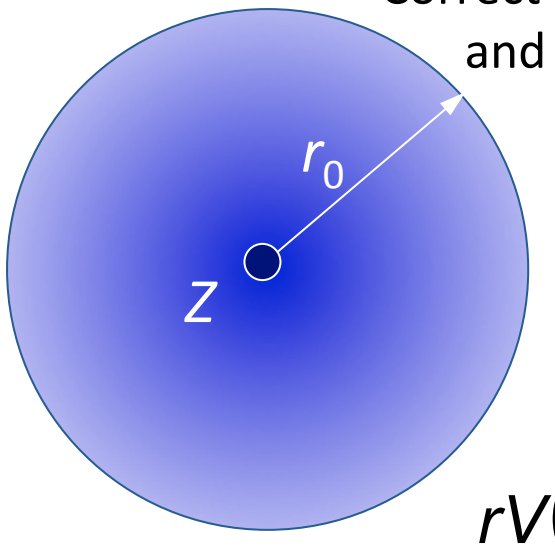
- Exact solution of the 3D multi-particle Schrödinger equation
- Atom in spherical cell
- Hartree-Fock method (1-electron wave functions)
- Hartree-Fock-Slater method
- Hartree method (no exchange)
- Thomas-Fermi method
- Ideal Fermi-gas



$$\frac{4}{3}\pi r_0^3 = \frac{1}{n}$$

Finite-Temperature Thomas-Fermi Model

- The simplest mean atom model
- The simplest (and fully-determined) DFT model
- Correct asymptotic behavior at low *T* and *V* (ideal Fermi-gas) and at high *T* and *V* (ideal Boltzmann gas)



Poisson equation

$$\Delta V = -4\pi Z\delta(r) + \frac{2}{\pi}(2\theta)^{3/2} I_{1/2}\left(\frac{V(r)+\mu}{\theta}\right)$$

$$(0 \le r < r_0)$$

$$rV(r)\big|_{r=0} = Z \qquad V(r_0) = 0 \qquad \frac{dV(r)}{dr}\bigg|_{r=r_0} = 0$$

Is the TF model reliable at low *T* and relatively high *V*?

For $F(T, V)$ - No

For $F(T, V) - F(0, V)$ - ?

Feynman R., Metropolis N., Teller E. // Phys. Rev. 1949. V.75. P.1561.

Thermodynamic Functions of Thomas-Fermi Model

Free energy:

$$F(V,T) = \frac{2\sqrt{2}\upsilon_a T^{5/2}}{\pi^2}\left[I_{3/2}\left(\frac{\mu}{T}\right) - 8\int_0^1 u^5 I_{3/2}(\phi)du + 3\int_0^1 u^5\phi I_{1/2}(\phi)du\right]$$

φ - dimensionless atomic potential, $\phi = \varphi / (u^2 T)$, υ_a – cell volume, $u = (r / r_0)^{1/2}$

Expressions for 1st derivatives of F (P and S) are known.

Second derivatives of free energy

$$P_V' = -F_{VV}'' = \frac{(2\theta)^{3/2}}{2\pi^2} I_{1/2}\left(\frac{\mu}{T}\right)\left(\mu_V'\right)_{N,T}$$

$$P_T' = -F_{VT}'' = \frac{(2\theta)^{3/2}}{2\pi^2}\left[I_{1/2}\left(\frac{\mu}{T}\right)\left(\mu_T'\right)_{N,V} + \frac{5}{3}I_{3/2}\left(\frac{\mu}{T}\right) - \frac{\mu}{T}I_{1/2}\left(\frac{\mu}{T}\right)\right]$$

$$S_T' = -F_{TT}'' = \frac{3\sqrt{2}\upsilon_a}{\pi^2 T^{3/2}}\int_0^1\left[5T^2u^5 I_{3/2}(\phi) + 3u^3\left(\varphi_T' T^2 - 2\varphi T\right)I_{1/2}(\phi) - u\varphi\left(\varphi_T' T - \varphi\right)I_{-1/2}(\phi)\right]du$$

Shemyakin O.P. et al., JPA **43,** 335003 (2010)

Second Derivatives of the Thomas-Fermi Model

The number of particles and potential are the functions of the grand canonical ensemble variables, which are in turn depend on the variables of the canonical ensemble:

$$N = N\left[\mu(N,V,T),\upsilon(N,V,T),T(N,V,T)\right]$$

$$\varphi = \varphi\left[\mu(N,V,T),\upsilon(N,V,T),T(N,V,T)\right]$$

From the expressions for $(N'_T)_{N,\upsilon}$, $(\varphi'_T)_{N,\upsilon}$ и $(N'_\upsilon)_{T,N}$ one can obtain:

$$\left(\frac{\partial\mu}{\partial T}\right)_{V,N} = -\frac{(\partial N/\partial T)_{\upsilon,\mu}}{(\partial N/\partial\mu)_{\upsilon,T}}$$

$$\left(\frac{\partial\mu}{\partial V}\right)_{N,T} = -\frac{(\partial N/\partial \upsilon)_{\mu,T}}{(\partial N/\partial\mu)_{\upsilon,T}}$$

$$\left(\frac{\partial\varphi}{\partial T}\right)_{N,\upsilon} = \left(\frac{\partial\varphi}{\partial T}\right)_{\mu,\upsilon} - \frac{(\partial N/\partial T)_{\mu,\upsilon}}{(\partial N/\partial\mu)_{\upsilon,T}}\left(\frac{\partial\varphi}{\partial\mu}\right)_{\upsilon,T}$$

We need
6 derivatives in the grand canonical ensemble

$$\left(\varphi'_\upsilon\right)_{\mu,T} \qquad \left(\varphi'_T\right)_{\mu,\upsilon} \qquad \left(\varphi'_\mu\right)_{T,\upsilon}$$

$$\left(N'_T\right)_{\upsilon,\mu} \qquad \left(N'_\mu\right)_{T,\upsilon} \qquad \left(N'_\upsilon\right)_{T,\mu}$$

Shemyakin O.P. et al., JPA **43,** 335003 (2010)

TF Potential and its Derivatives on μ, υ and T

Poisson equation

$$\begin{cases} W = \varphi - u^2\mu; \\ W_u^{'} = 2uV; \\ V_u^{'} = 2au^3T^{3/2}I_{1/2}\left(\dfrac{W+u^2\mu}{Tu^2}\right); \\ W\big|_{u=0} = Z/r_0\,, W\big|_{u=1} = W_u^{'}\big|_{u=1} = 0. \end{cases}$$

$\Downarrow$

φ

Derivative of the Poisson equation on υ:

$$\begin{cases} L = \left(\varphi_\upsilon^{'}\right)_{\mu,T}; \\ L_u^{'} = 2uM; \\ M_u^{'} = \dfrac{4au^3T^{3/2}}{3\upsilon}I_{1/2}(\phi) + auT^{1/2}I_{-1/2}(\phi)L; \\ L\big|_{u=1} = L_u^{'}\big|_{u=1} = 0. \end{cases}$$

$\Downarrow$

$\left(N_\upsilon^{'}\right)_{\mu,T}$

Derivative on μ:

$$\begin{cases} \Phi = \left(\varphi_\mu^{'}\right)_{\upsilon,T} - u^2; \\ \Phi_u^{'} = auT^{1/2}\left(\Phi + u^2\right)I_{-1/2}(\phi); \\ \Psi_u^{'} = auT^{1/2}\left(\Phi + u^2\right)I_{-1/2}(\phi); \\ \Phi\big|_{u=1} = F_u^{'}\big|_{u=1} = 0. \end{cases}$$

$\Downarrow$

$\left(N_\mu^{'}\right)_{\upsilon,T}$

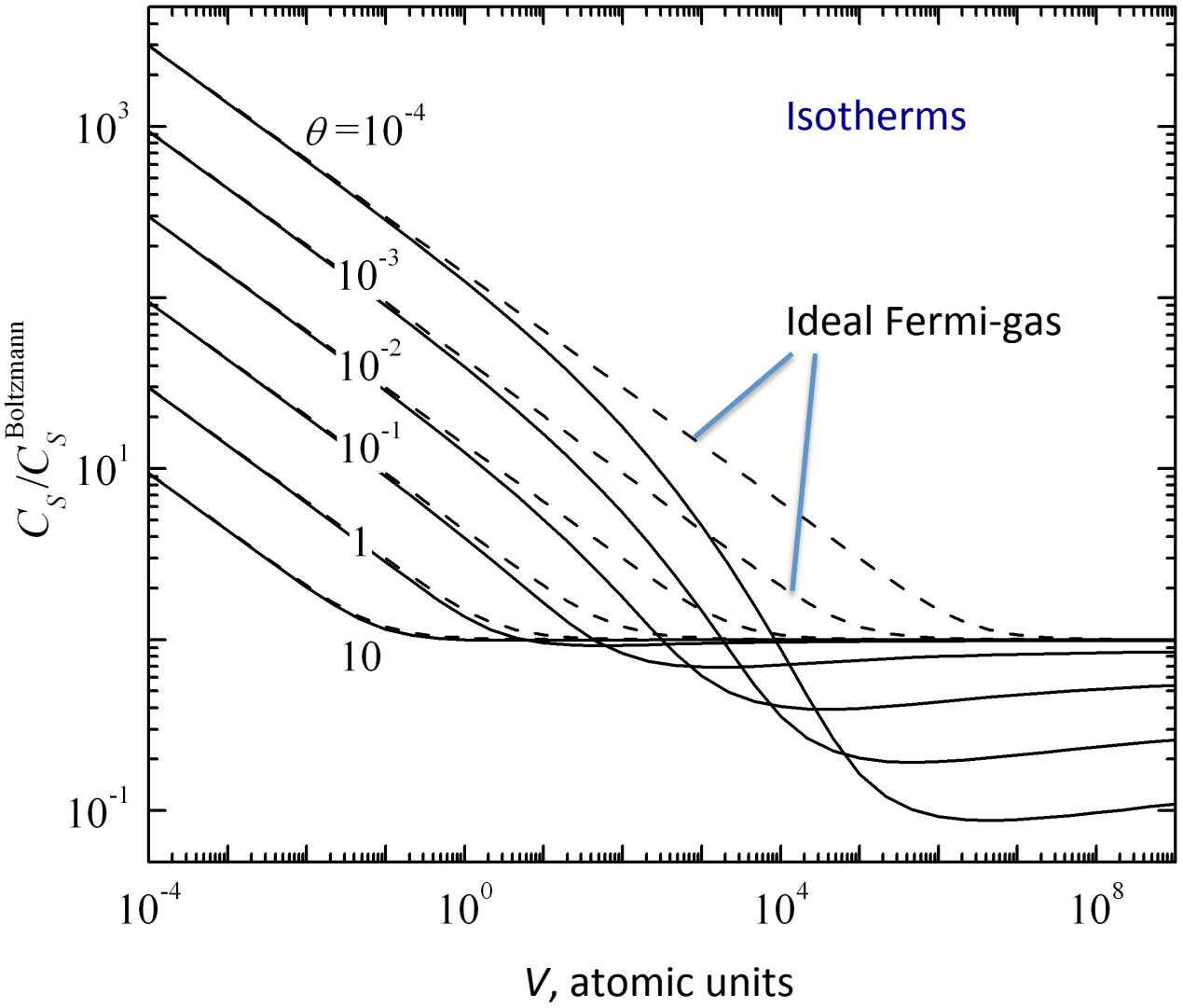
Derivative on T:

$$\begin{cases} Q = \left(\varphi_T^{'}\right)_{\mu,\upsilon}; \\ Q_u^{'} = 2uR; \\ R_u^{'} = au^3T^{1/2}\left[3I_{1/2}(\phi) - \phi I_{-1/2}(\phi)\right] + auT^{1/2}QI_{-1/2}(\phi); \\ Q\big|_{u=1} = Q_u^{'}\big|_{u=1} = 0. \end{cases}$$

$\Downarrow$

$\left(N_T^{'}\right)_{\mu,\upsilon}$

Adiabatic Sound Velocity by Thomas-Fermi Model



PROBLEMS OF TF MODEL

- Thomas-Fermi method is quasiclassical; if one calculates energy levels in $V_{TF}(r)$ using the Shrödinger equation and then electron density $\rho_{quant}(r)$, it will differ from the original TF electron density $\rho(r)$
- Mean ion charge is roughly determined
- The solution is to make $\rho(r)$ self-consistent and use the corrected potential and electron density

HARTREE-FOCK-SLATER MODEL

Nikiforov A.F., Novikov V.G., Uvarov V.B. Quantum-statistical models of high-temperature plasma. M.: Fizmatlit, 2000.

Atom with mean populations

$$N_{nl} = \frac{2(2l+1)}{1+\exp(\varepsilon_{nl} - \mu/\theta)}$$

ε_{nl} – energy levels in $V(r)$

From the Schrödinger equation

Potential:

$$V(r) = V_c(r) + V_{ex}(r)$$

Poisson equation solution:

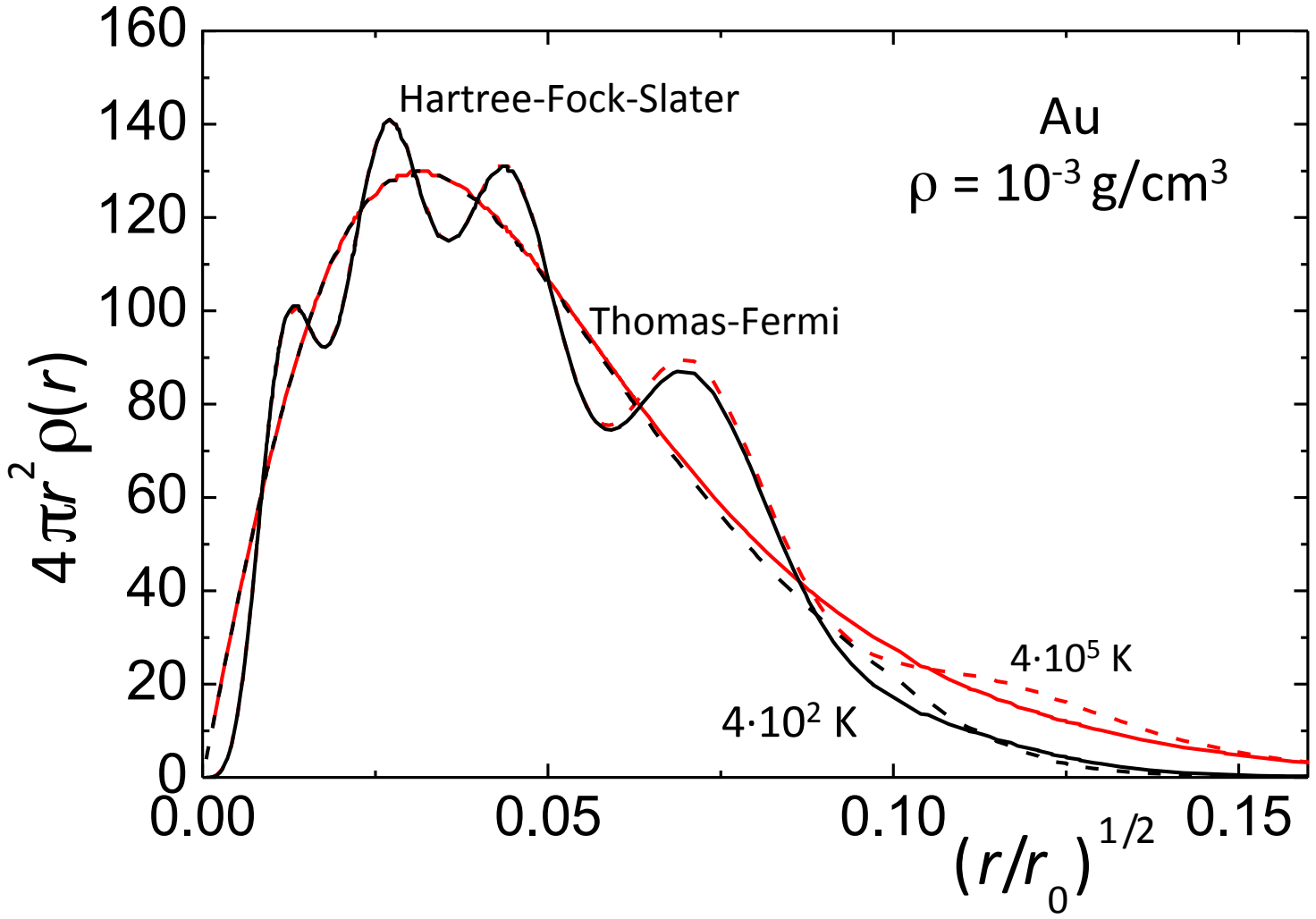
$$V_c(r) = \frac{Z}{r} - 4\pi\left[\frac{1}{r}\int_0^r r'^2\,\rho(r')dr' + \int_r^{r_0} r'\rho(r')dr'\right]$$

Exchange potential:

$$V_{ex}(r) = \frac{\pi r(r)}{\theta}\left[1 + 5.7\frac{\rho(r)}{\theta^{3/2}} + \frac{\pi^4}{3}\frac{\rho^2(r)}{\theta^3}\right]^{-1/3}$$

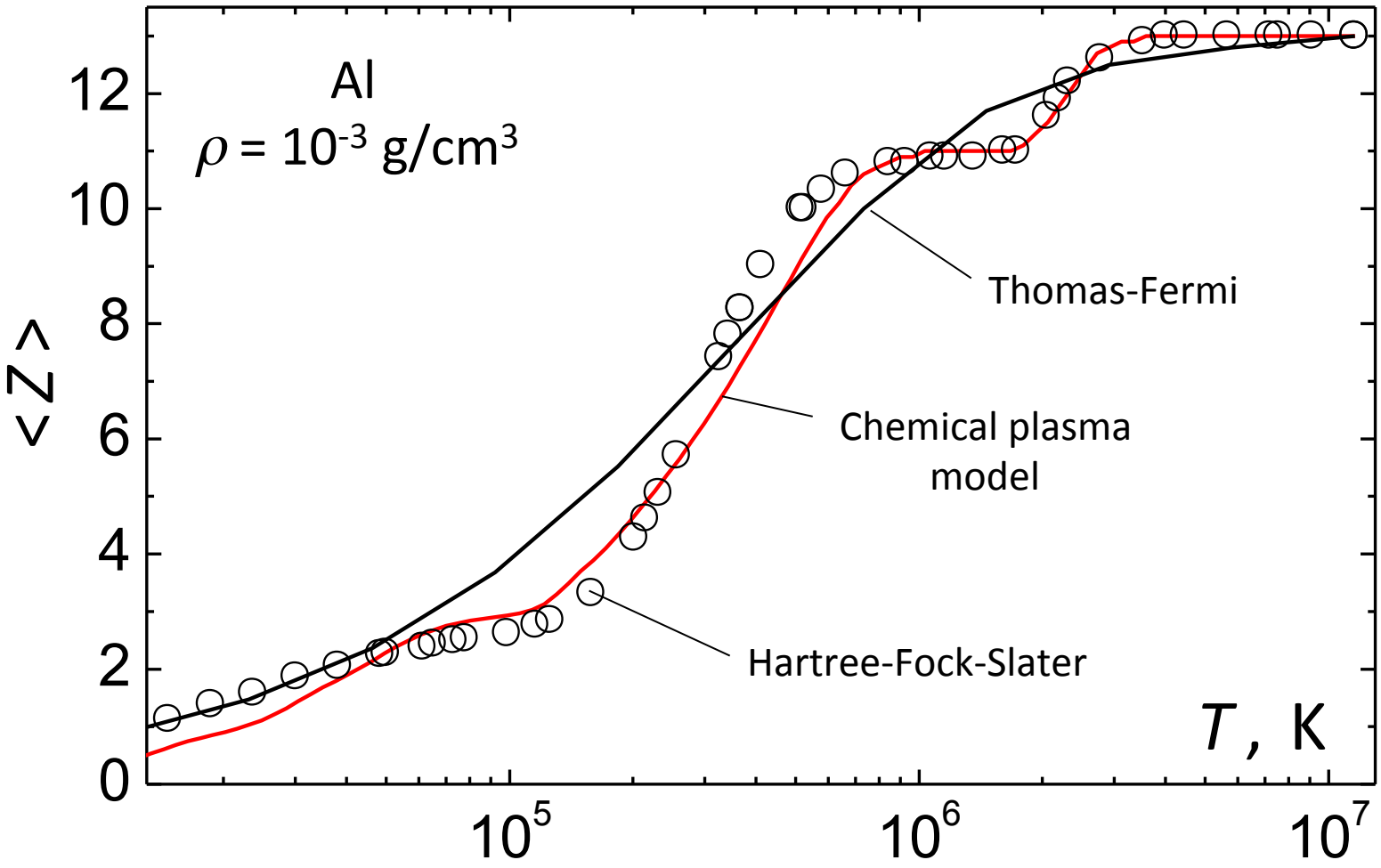
Iterative procedure for determination of $\rho(r)$, ε_{nl} and $V(r)$

RADIAL ELECTRON DENSITY $r^2\rho(r)$ BY HARTREE-FOCK-SLATER MODEL



MEAN ION CHARGE (HFS)

ρ = const



Density Functional Theory

- Thomas-Fermi theory is the density functional theory:

kinetic energy

external potential

$$E_{TF}[n] = C_1 \int d^3 r n(\mathbf{r})^{5/3} + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) +$$

$$C_2 \int d^3 r n(\mathbf{r})^{4/3} + \frac{1}{2} d^3 r d^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

exchange energy

Hartree energy

- Is it a general property?

Density Functional Theory

For systems with Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

the following theorems are valid:

Theorem 1. For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$ the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.
Therefore, all properties are completely determined given only the ground state density $n_0(\mathbf{r})$.

Theorem 2. A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. For any particular $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

Hohenberg, Kohn, 1964

Kohn-Sham Functional

The system of interacting particles is replaced by the system of non-interacting particles:

$$E_{KS}[n] = T_s[n] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{XC}[n]$$

kinetic energy

ion-ion interaction

exchange-correlation functional

All many-body effects of exchange and correlation are included into $E_{XC}[n]$

$$E_{XC}[n] = \left\langle \hat{T} \right\rangle - T_s[n] + \left\langle \hat{V}_{\text{int}} \right\rangle - E_{Hartree}[n]$$

true system

non-interacting system

Kohn, Sham, 1965

Minimization in HFS and DFT

- In Hartree-Fock(-Slater) method we find

$$\min_{\Psi_i(\mathbf{r})} \Omega\left[\Psi_i(\mathbf{r})\right]$$

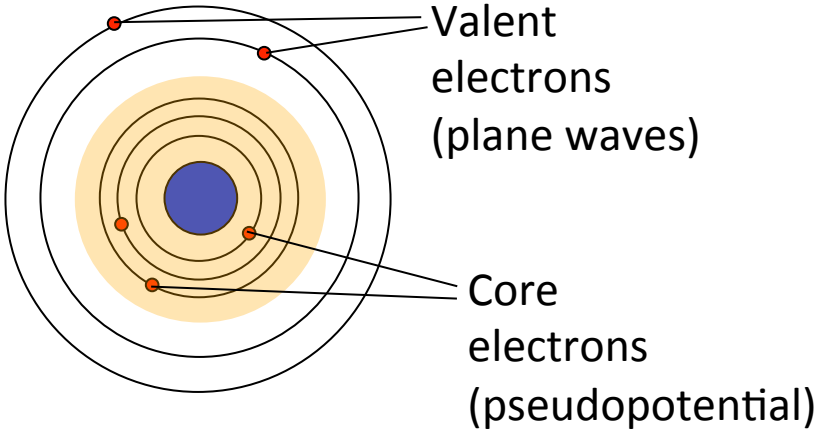
- In DFT we find

$$\min_{n(\mathbf{r})} \Omega\left[n(\mathbf{r})\right]$$

PSEUDOPOTENTIALS IN DFT

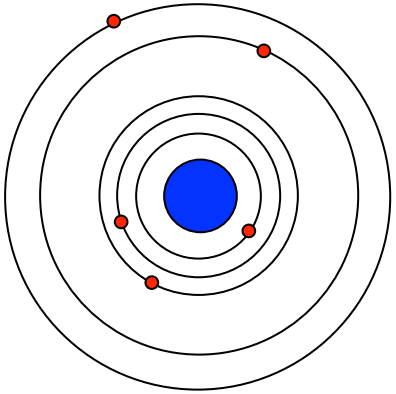
- Diminish the number of plane waves necessary for the good representation of inner electrons wave functions
- Part of electrons are considered as a core, part as valent
- Pseudopotential is constructed at $T = 0$ and doesn't depend on pressure and temperature

Pseudopotential approach



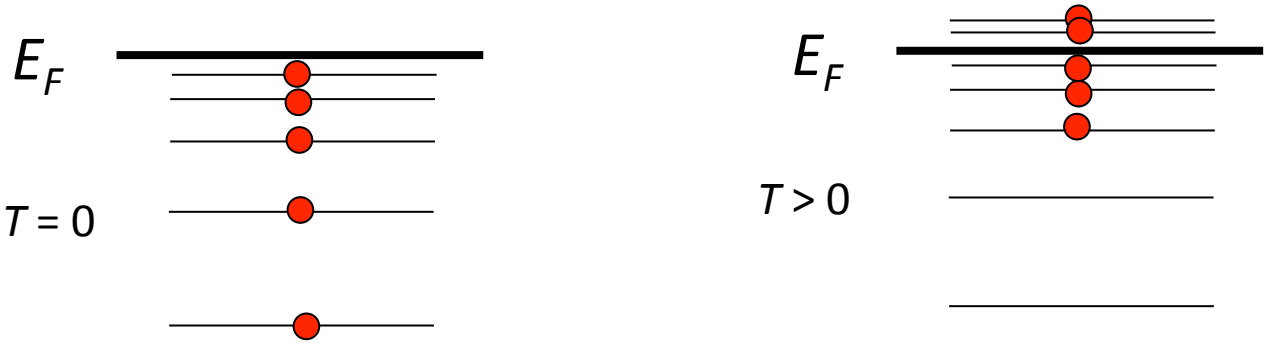
Full-potential approach

muffin-tin orbitals
for all electrons



APPROXIMATIONS IN PSEUDOPOTENTIAL APPROACH

Pseudopotential describes electrons with energies less than the Fermi energy – errors at relatively high temperatures



Spatial distribution of core electrons in a pseudopotential is unchanged – errors at relatively high pressures

Density Functional Theory: All-Electron and Pseudopotential Approaches

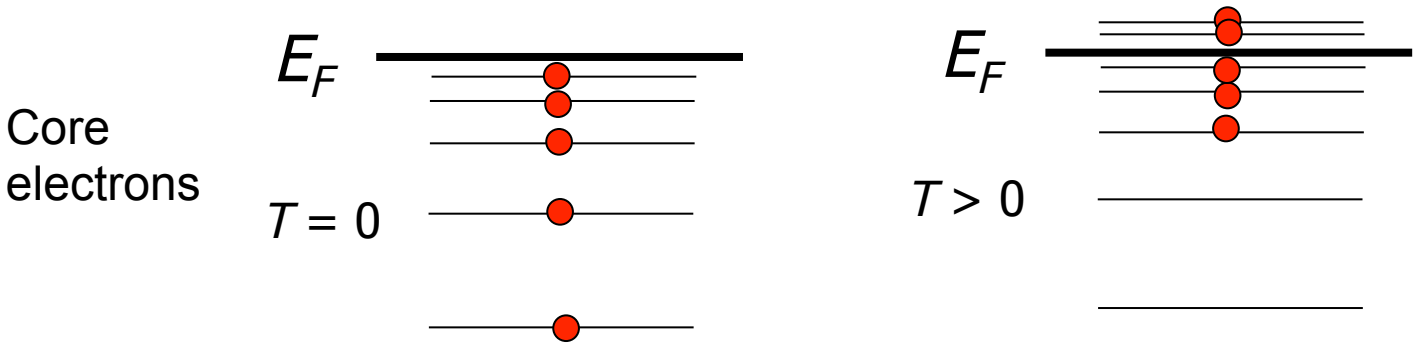
Full-potential approach: all electrons are taken into account (FP-LMTO)

(S. Yu. Savrasov, PRB **54** 16470 (1996),
G. V. Sin'ko, N. A. Smirnov, PRB **74** 134113 (2006)

At $T > 0$: occupancies are $f(\varepsilon, \rho, T) = 1 / \left\{1 + \exp\left[(\varepsilon - \mu(\rho, T)) / T\right]\right\}$

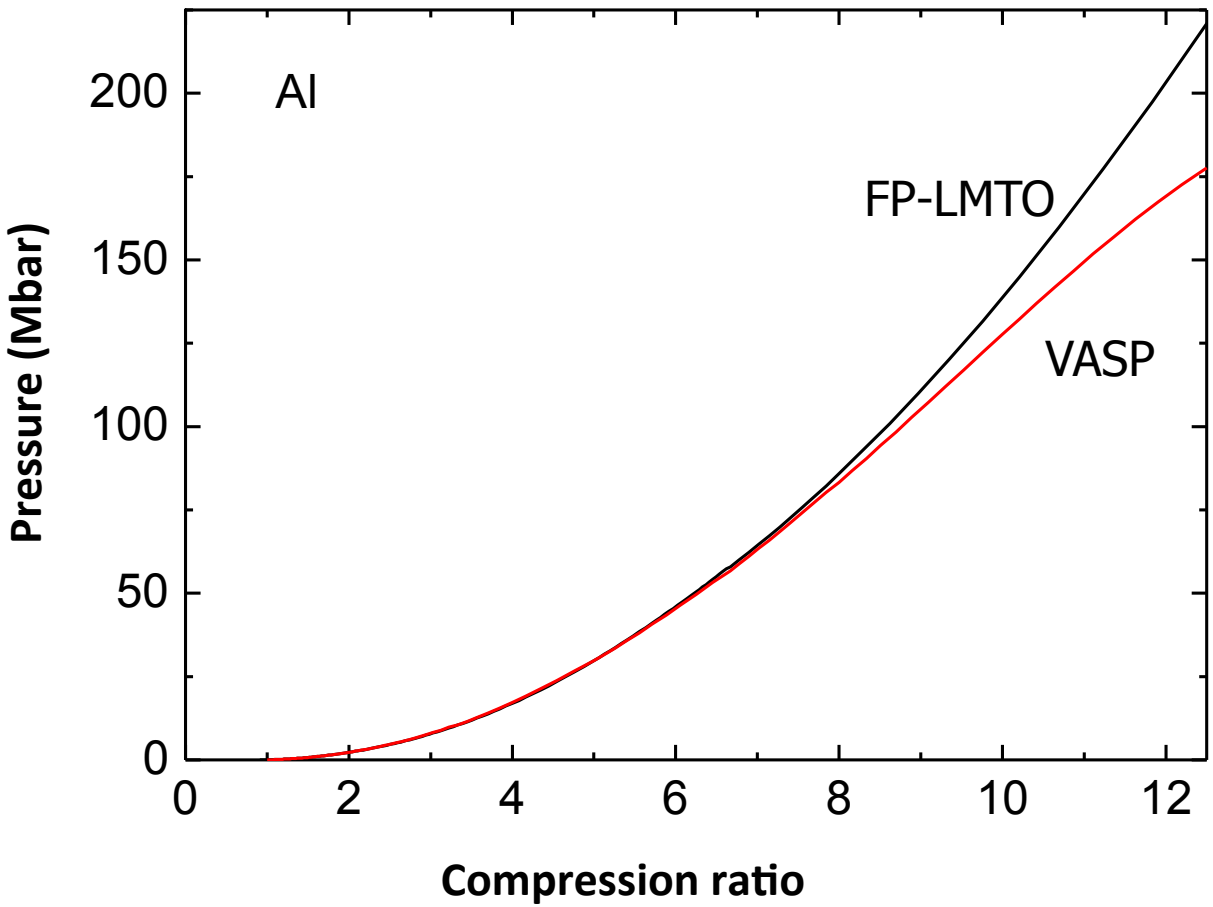
Pseudopotential approach: the core is replaced by a pseudopotential, the Kohn-Sham equations are solved only for valent electrons (VASP)

G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14251 (1994).
G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).



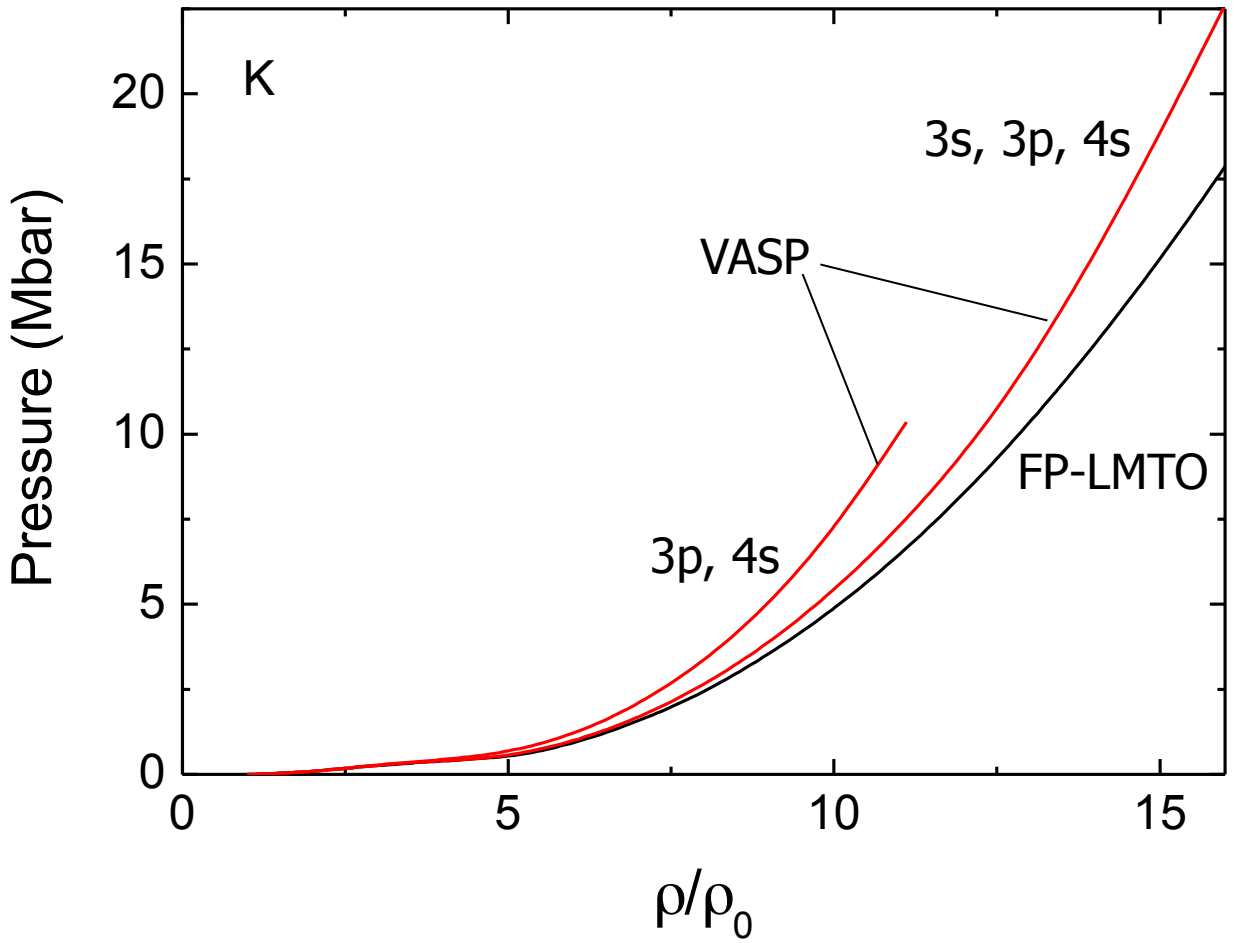
Calculations were made in the unit cell at fixed ions and heated electrons

Aluminum. Cold Curve



Al is more compressible in VASP calculations than in FP-LMTO

Potassium. Cold Curve

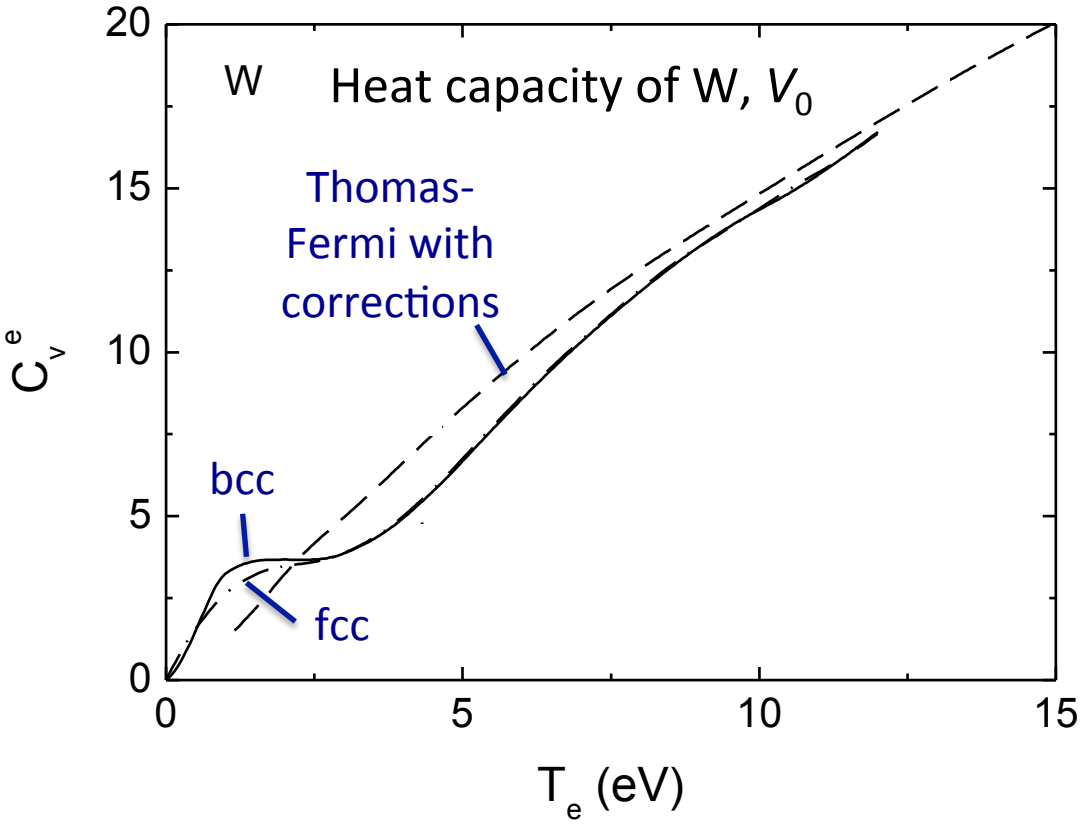


K is less compressible in VASP calculations than in FP-LMTO

Less number of valent electrons leads to bigger disagreement with FP-LMTO

DFT-calculations of $F_e(T_e, V)$

Why can we use DFT for thermodynamic properties of electrons?



$$P_T^e = -\rho^2 \left.\frac{\partial F_T^e(\rho, T_e)}{\partial \rho}\right|_{T_e} - P_c$$

$$C_V^e = \left[\frac{\partial E_T^e(\rho, T_e)}{\partial T_e}\right]_V$$

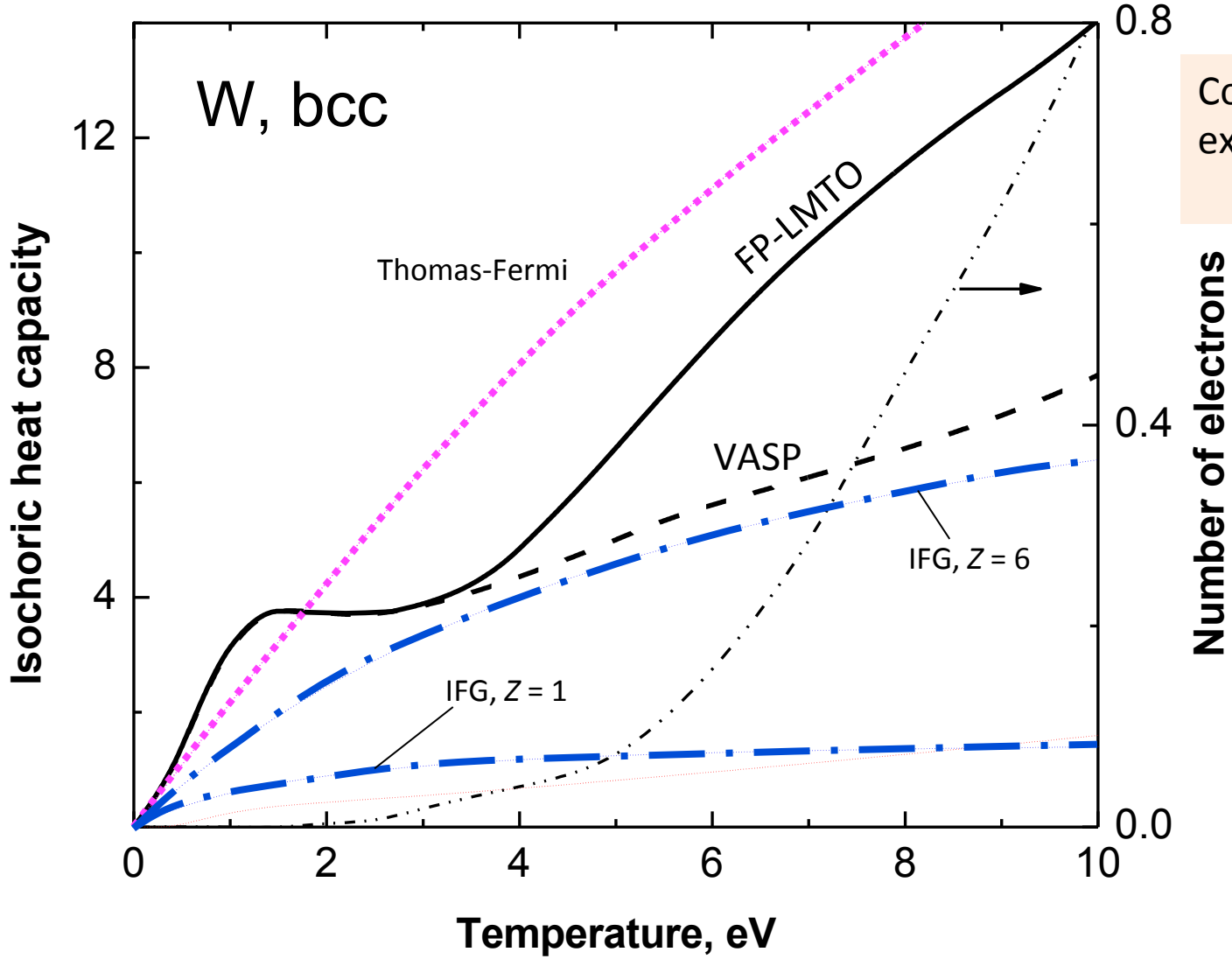
24x24x24 mesh of k-points

N_{bands} = 94

E_{cut} = 1020 eV

- Cold ions, hot electrons
- Heat capacity is very close for fcc and bcc structures of W
- It should be close to unordered phase at the same density

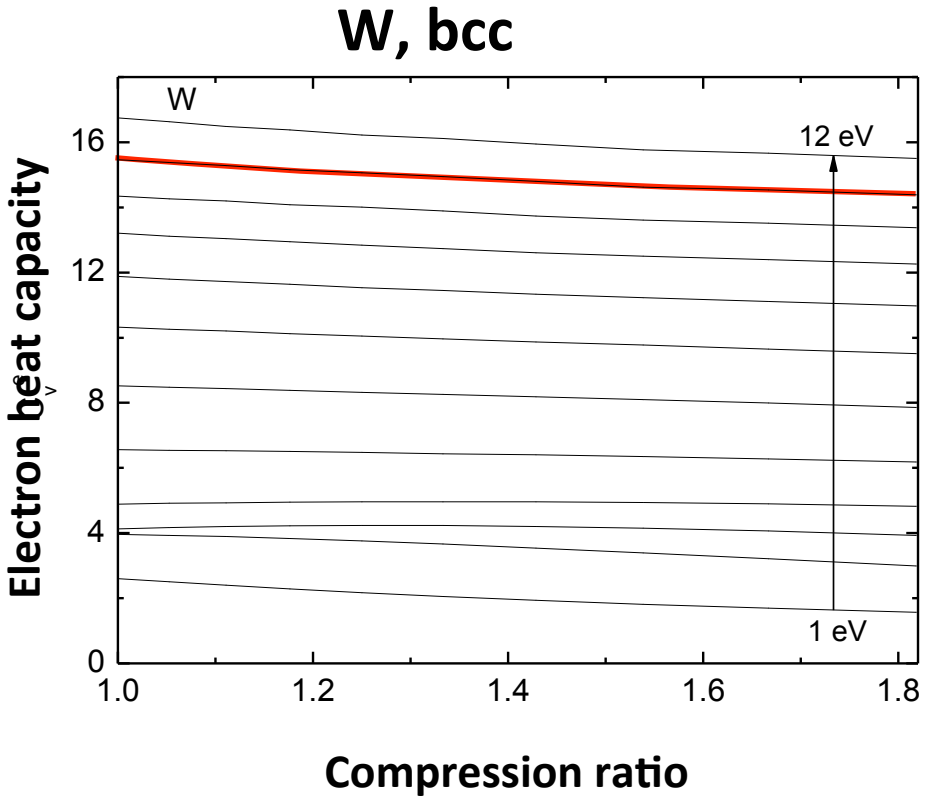
Tungsten, $T_i = 0$, $V = V_0$. Electron Heat Capacity

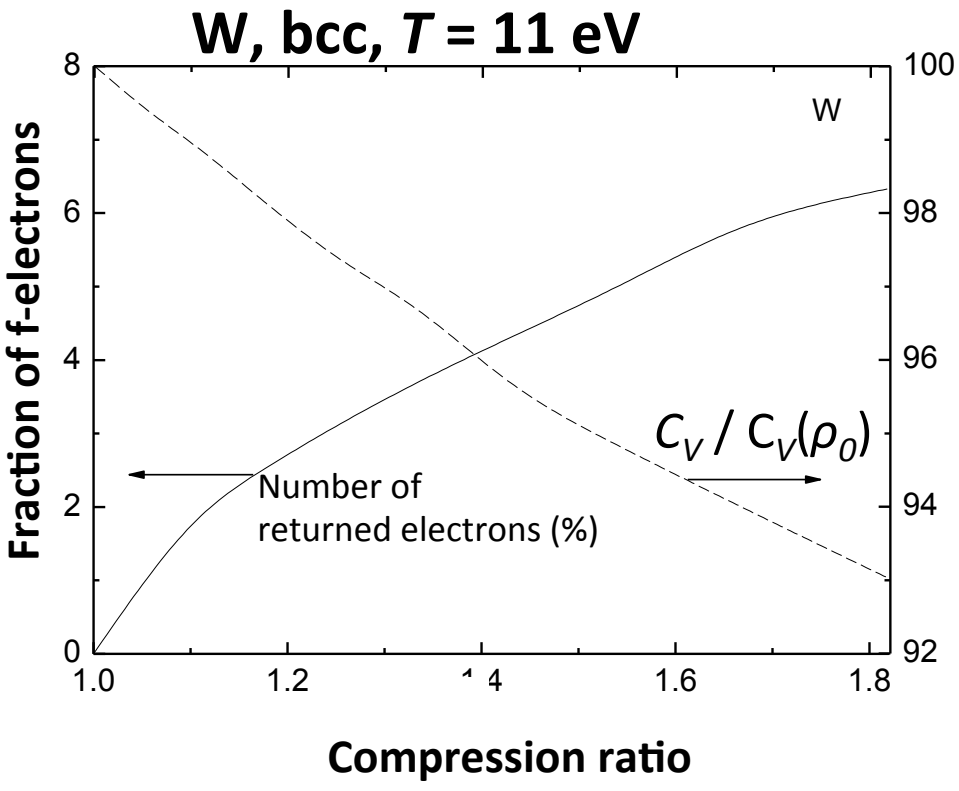


Core electrons become excited at ~3 eV

Levashov P.R. et al., JPCM **22** (2010) 505501

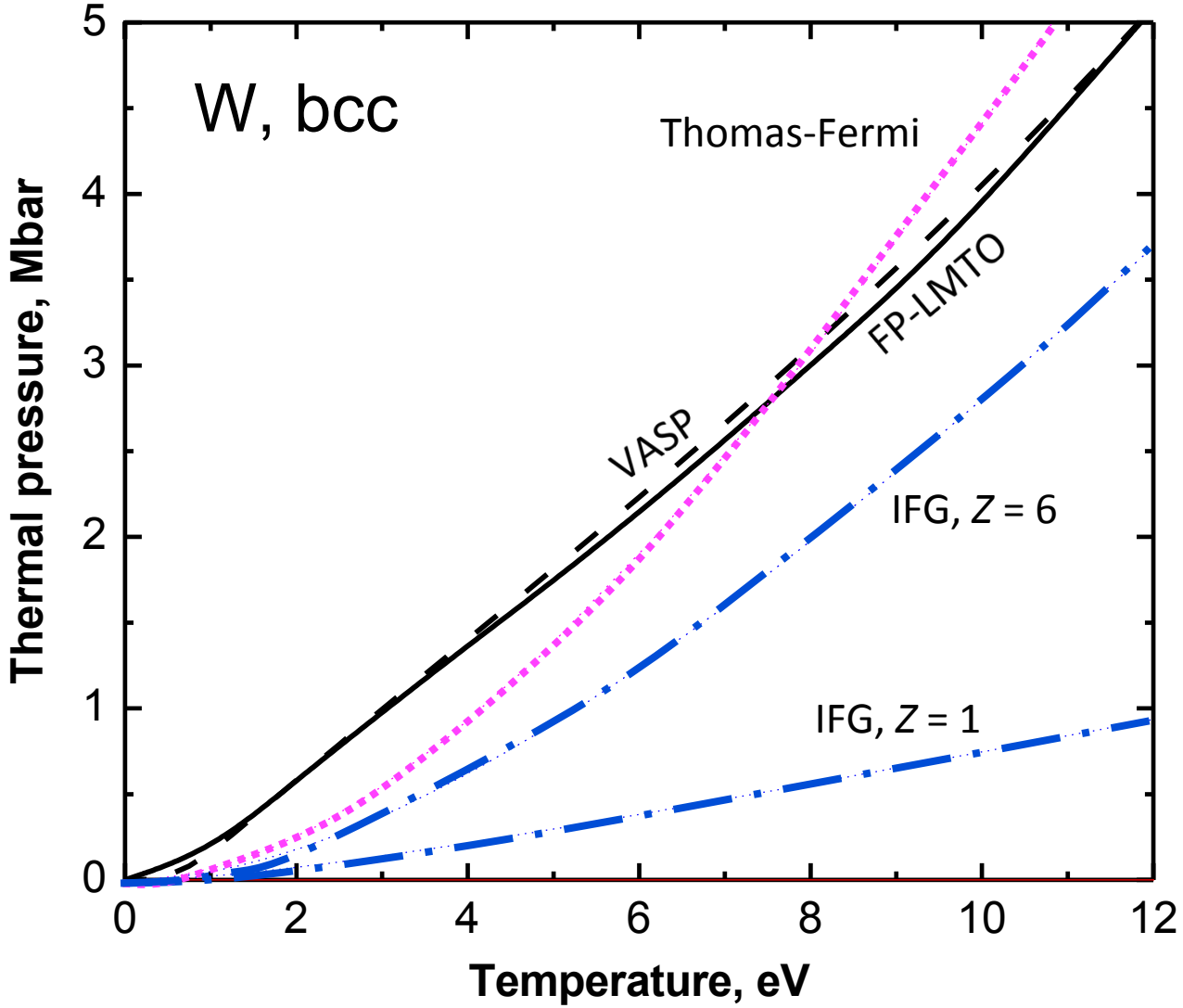
Electron Heat Capacity for W at T = 11eV. Return of Free Electrons into 4*f*-state under Compression





Electrons return to 4f state under compression

Tungsten, $T_i = 0$, $V = V_0$. Thermal Pressure



- Pressure is determined by free electrons only
- Interaction of electrons should be taken into account

Levashov P.R. et al., JPCM **22** (2010) 505501

Thermal contribution of ions

Ab-initio molecular dynamics (AIMD) simulations

$$F(V,T) = F_c(V) + F_i(V,T) + F_e(V,T)$$

$$F_{AIMD}(V,T) - F_e(V,T) - F_c(V) + F_{ions,kin}(V,T)$$

From AIMD — From AIMD — From DFT — Analytic expression

But it's better to use AIMD to calibrate the EOS by changing fitting parameters

Desjarlais M., Mattson T.R., Bonev S.A., Galli G., Militzer B., Holst B., Redmer R., Renaudin P., Clerouin J. and many others use AIMD to compute EOS for many substances

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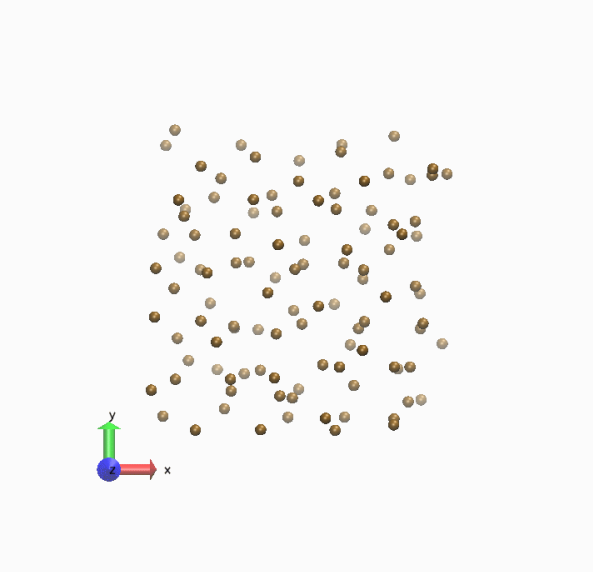
Details of the AIMD simulations

- We use **VASP** (Vienna Ab Initio Simulation Package) - package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudopotentials and a plane wave basis set.
- Generalized Gradient Approximation (**GGA**) for Exchange and Correlation functional
- Ultrasoft Vanderbilt pseudopotentials (**US-PP**)
- One point (**Γ-point**) in the Brillouin zone
- The QMD simulations were performed for **108 atoms** of Al
- The dynamics of Al atoms was simulated within **1 ps** with **2 fs time step**
- The electron temperature was equal to the temperature of ions through the **Fermi–Dirac** distribution
- $0.1 < \rho / \rho_0 < 3$, $T < 75000$ K



G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14251 (1994).
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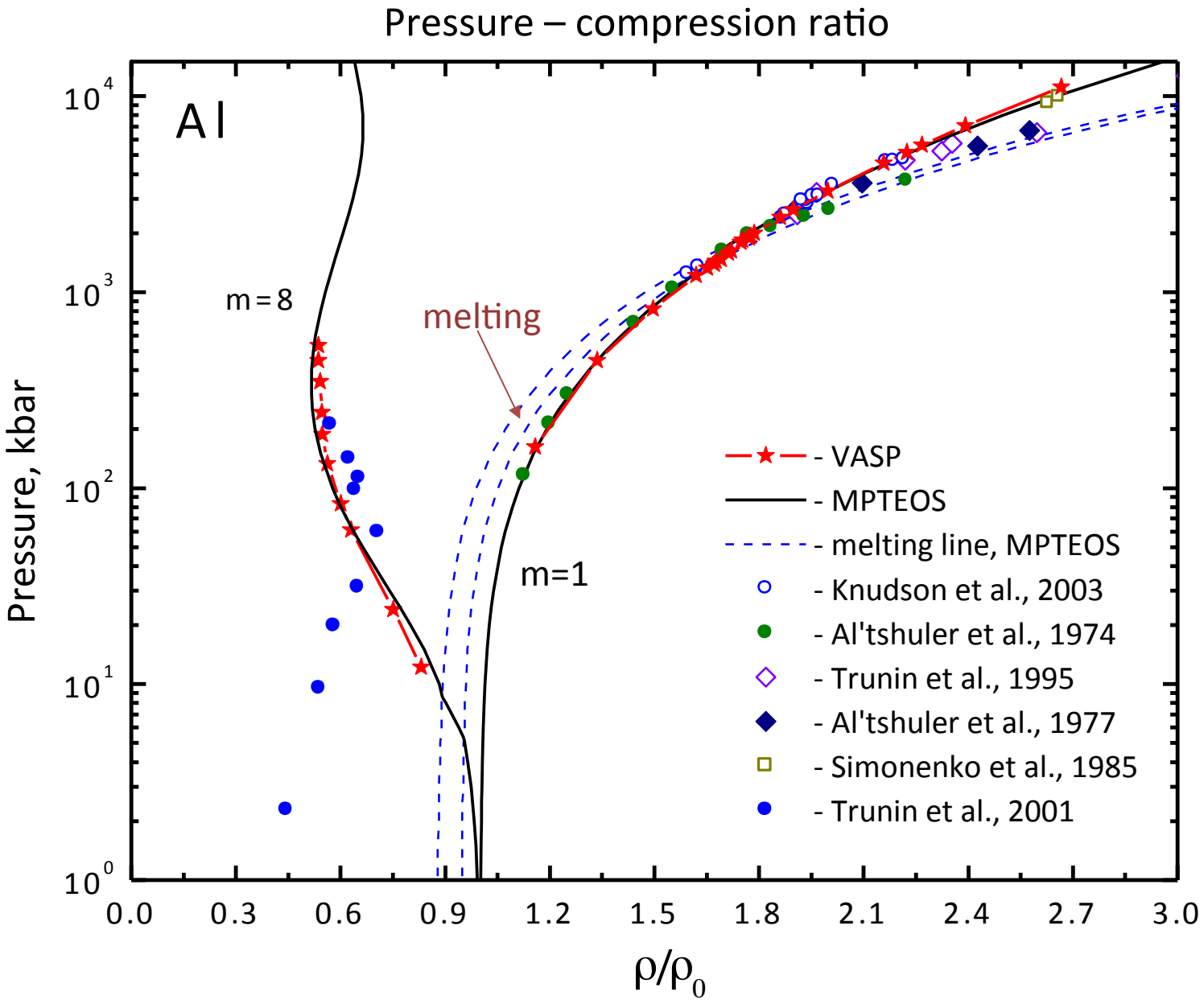
Shock Hugoniots of Al



Release isentropes of Al: reconstruction

- Zel'dovich method (Zel'dovich, 1957):

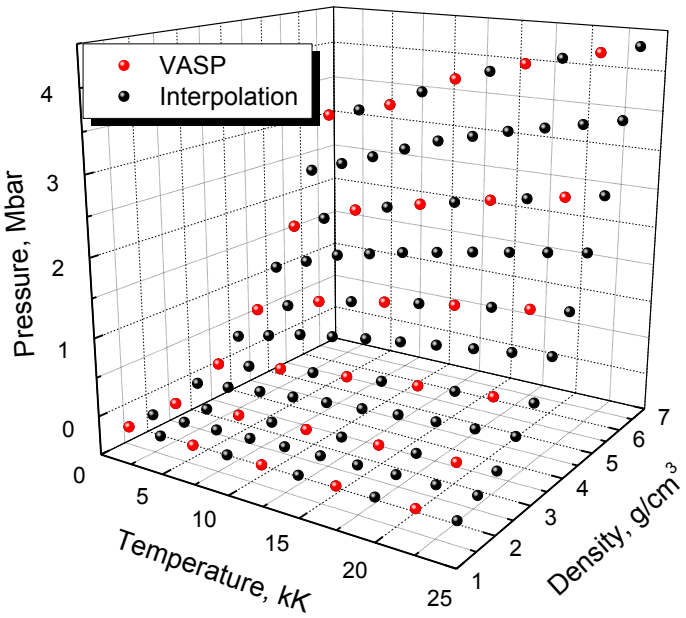
$$\frac{dT}{dV} = -\frac{T}{\left(\partial E/\partial P\right)_V}$$

- **Global isentrope reconstruction:** interpolate $P(T, V)$ and $E(T, V)$ on the mesh of isotherms and isochors

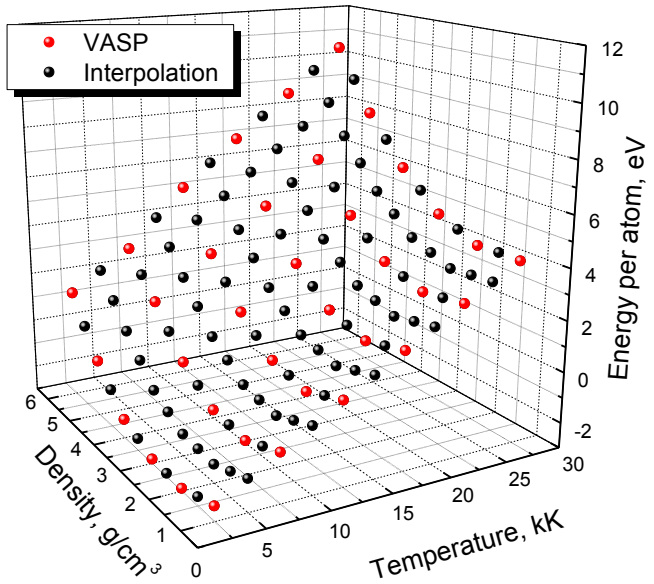
$$\left(\frac{\partial E}{\partial P}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \Big/ \left(\frac{\partial P}{\partial T}\right)_V$$

  - Integration with any step on V
  - Isentrope can be improved by mesh refinement

Pressure

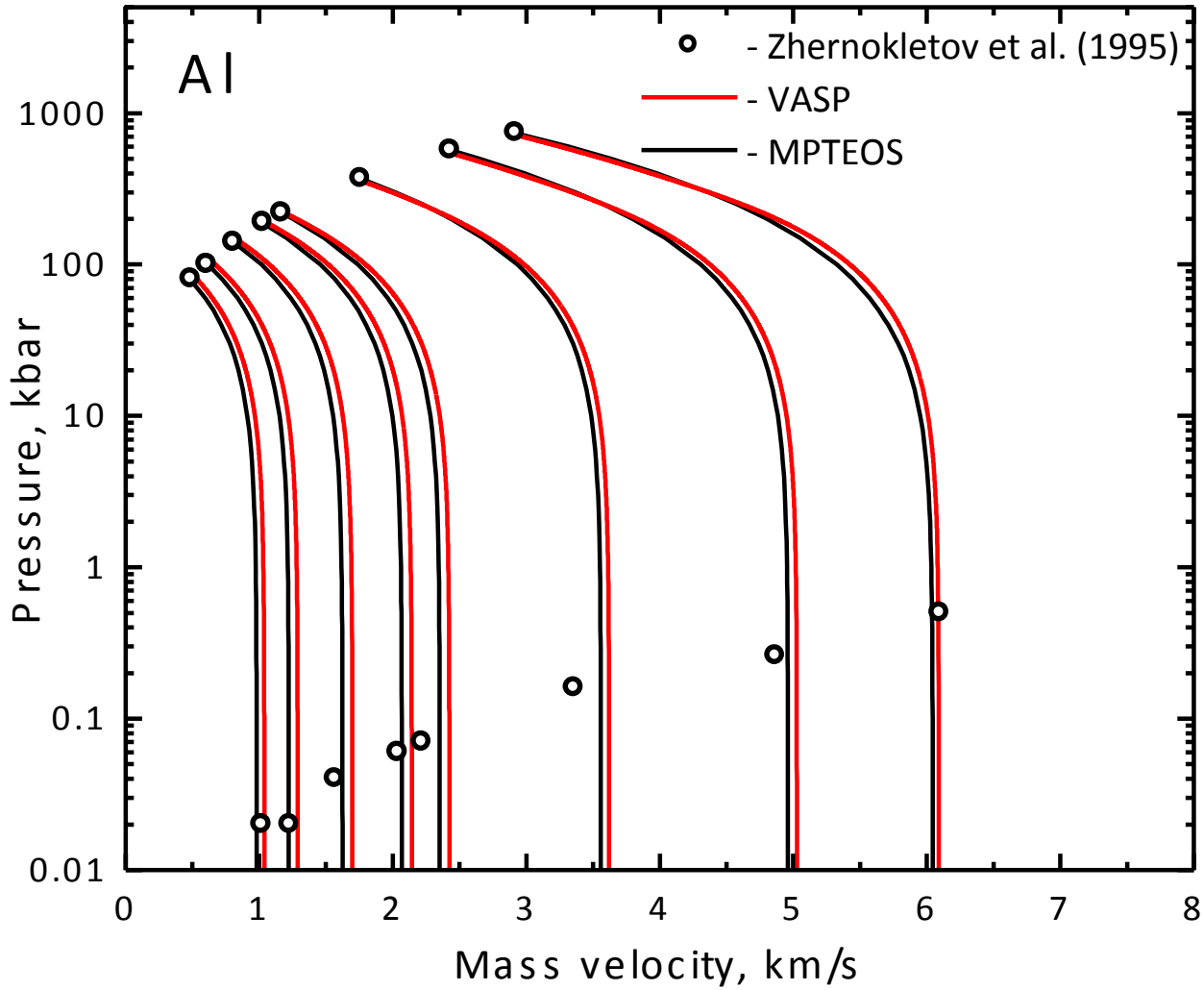


Energy



Release Isentropes of Al

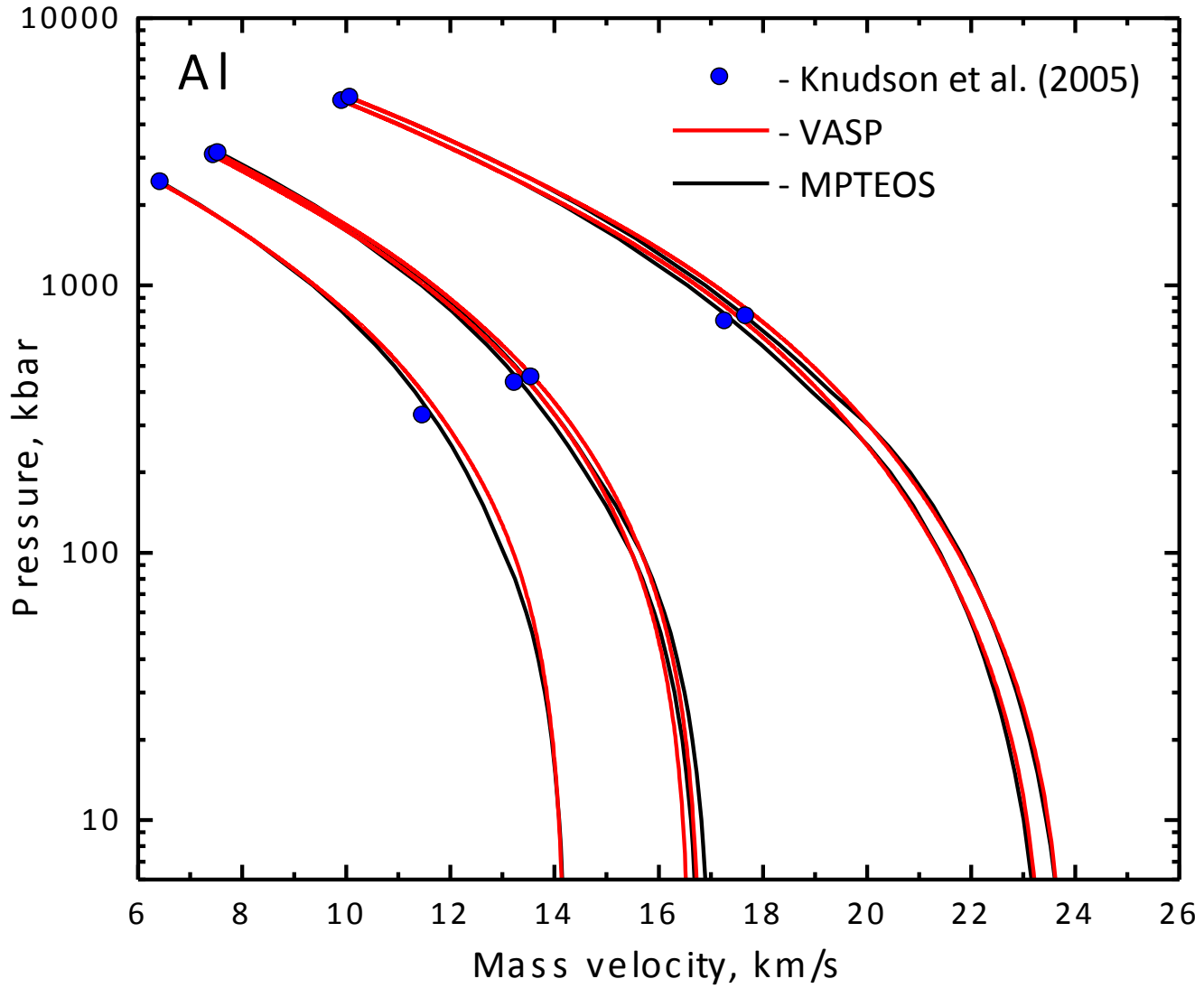
correspond to the experiments from
M. V. Zhernokletov et al. // Teplofiz. Vys. Temp. 33(1), 40-43 (1995) [in Russian]



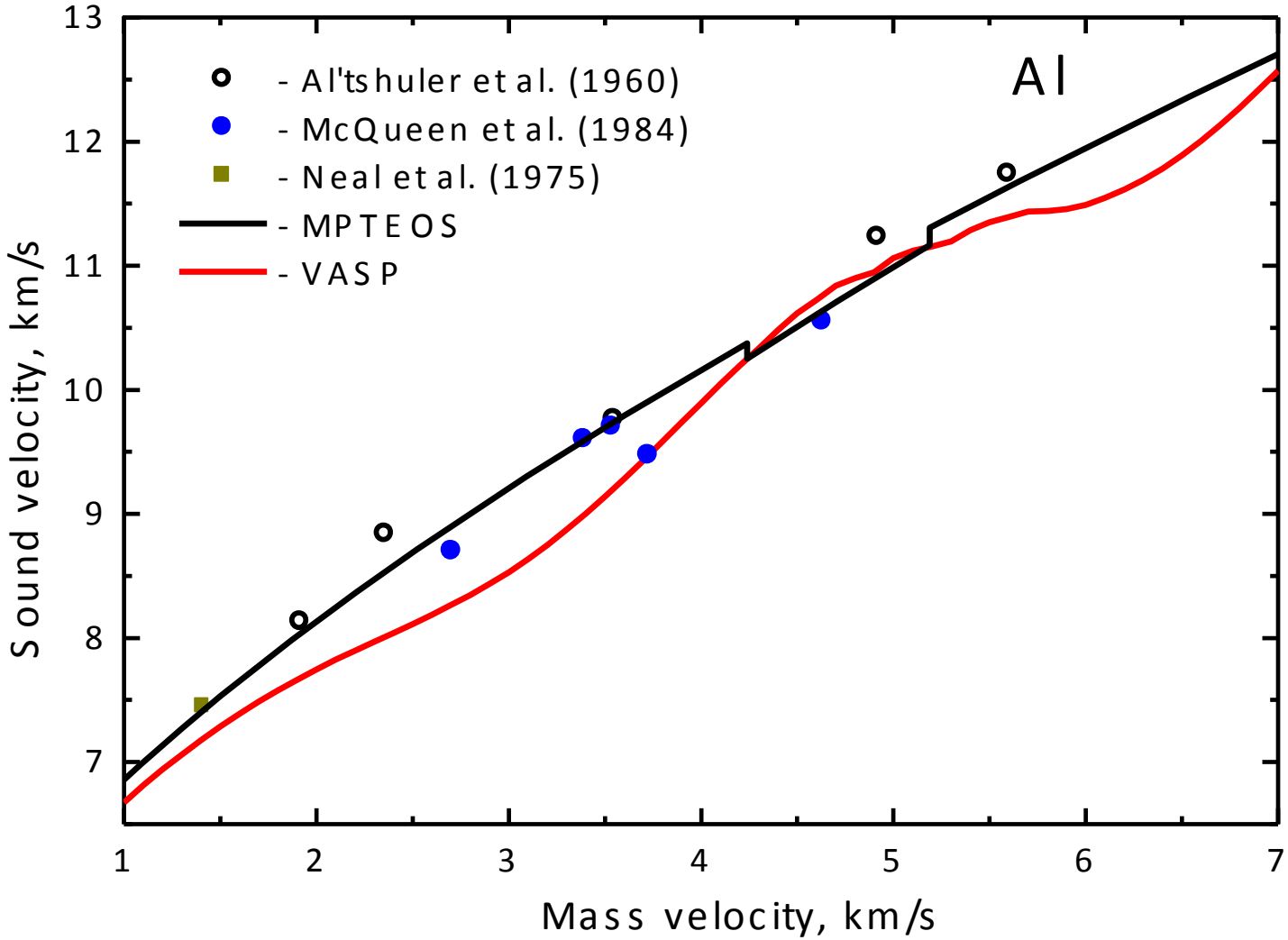
Release Isentropes of Al

correspond to the experiments from

Knudson M.D., Asay J.R., Deeney C. // J. Appl. Phys. V. 97. P. 073514. (2005)

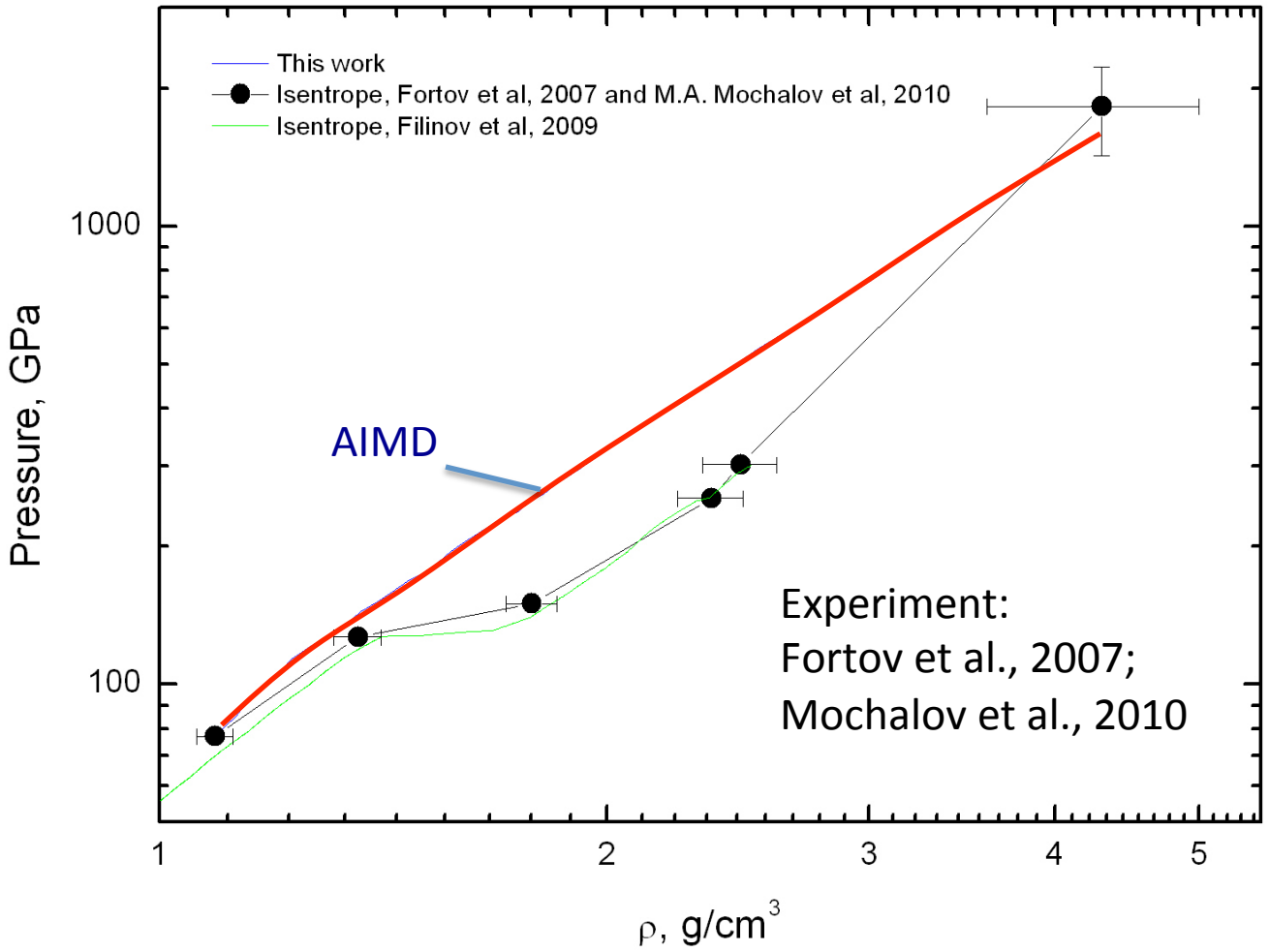


Sound Velocity in Shocked Al



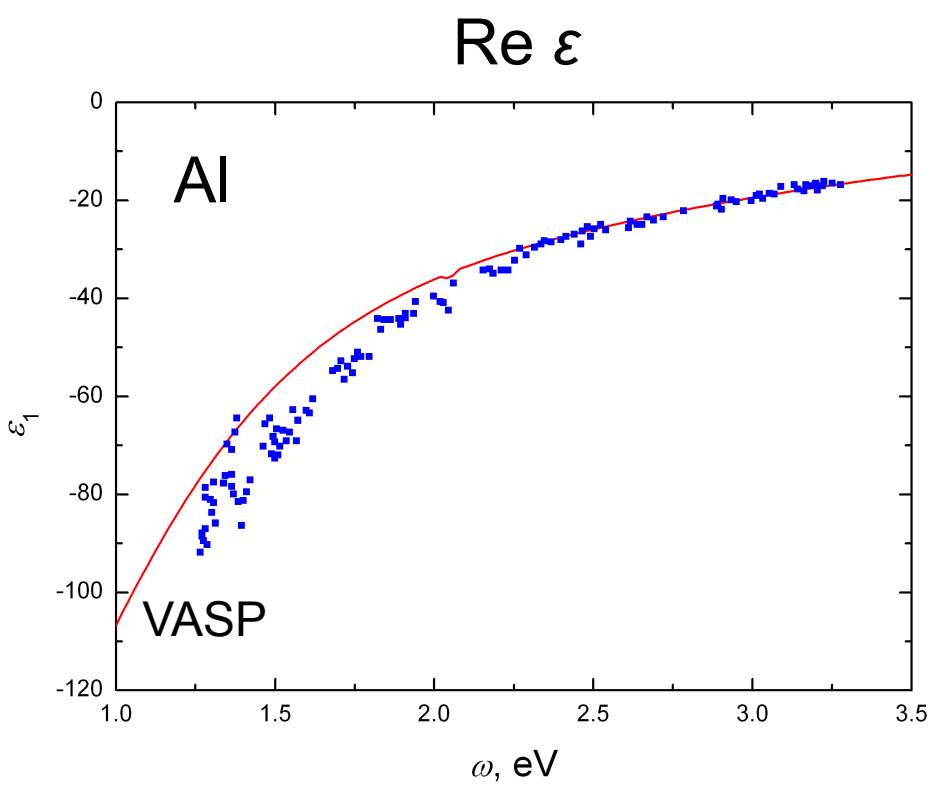
Oscillations are caused by errors of interpolation

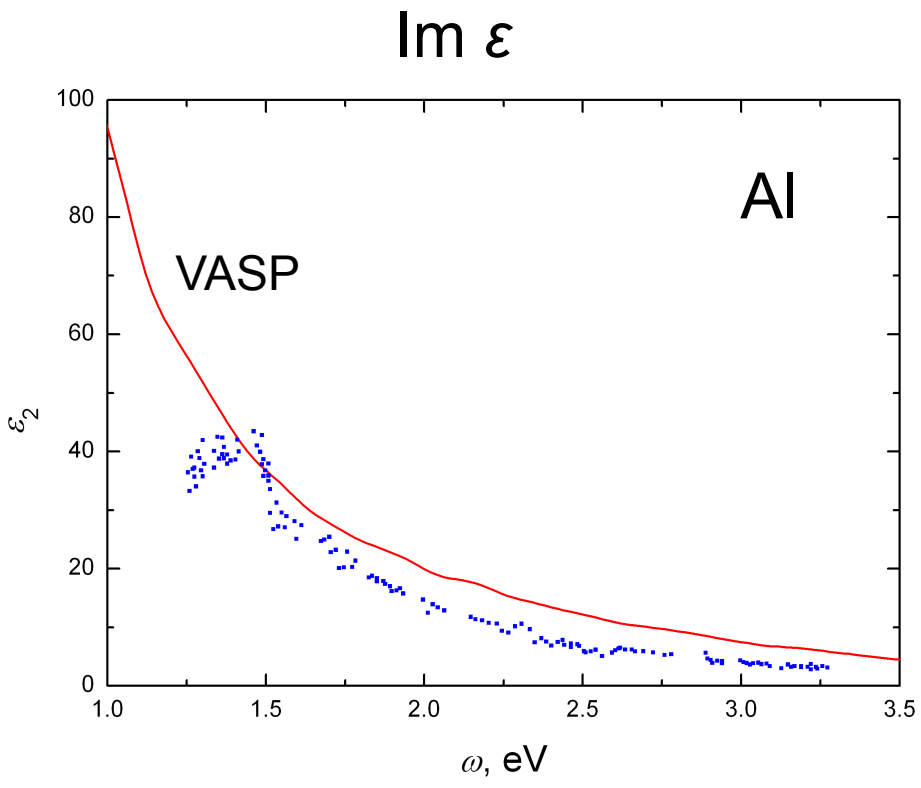
Quasi-Isentropic Compression of Deuterium by AIMD



Quantum vibrations of atoms in D_2 molecules should be taken into account

Complex dielectric function of liquid Al, T = 1550 K, ρ = 2.231 g/cm^3





108 atoms; US pseudopotential; 9x9x9 k-points in the Brillouin zone; cut-off energy 100 eV; δ-function broadening 0.1 eV

Drude-like dependencies of dielectric function

Experiment: Krishnan S. and Nordine P.C. PRB 47, 11780 (1993)

Beyond DFT and Mean Atom: Path Integral Monte Carlo

PATH INTEGRAL MONTE-CARLO METHOD

for degenerate hydrogen plasma

(V. M. Zamalin, G. E. Norman, V. S. Filinov, 1973-1977)

- Binary mixture of N_e quantum electrons,
  N_i classical protons

- Partition function:

$$Z(N_e,N_i,V,\beta)=Q(N_e,N_i,\beta)/N_e!N_i!$$

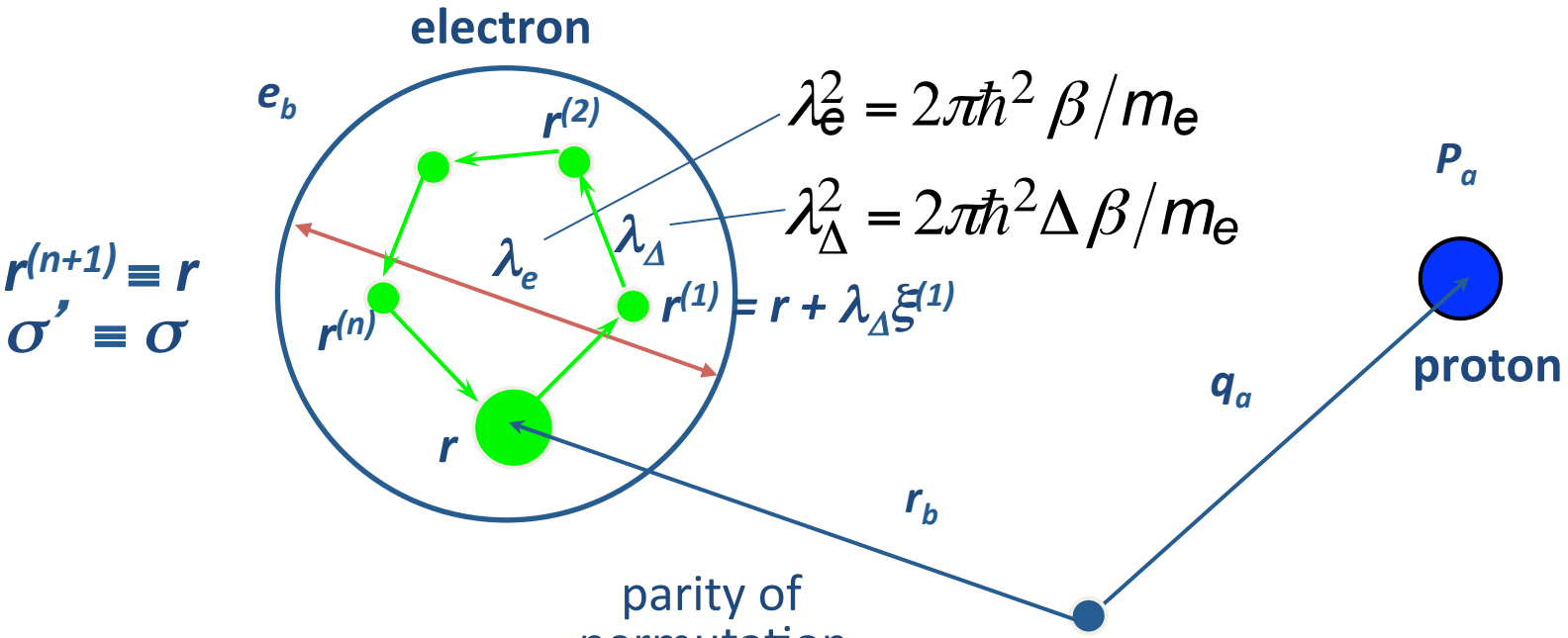
$$Q(N_e,N_i,\beta)=\sum_{\sigma}\int_{V}dqdr\,\rho(q,r,\sigma;\beta)\Big/N_e!N_i!$$

- Density matrix:

$$\rho=\exp\left(-\beta H\right)=\underbrace{\exp\left(-\Delta\beta H\right)\times\ldots\times\exp\left(-\Delta\beta H\right)}_{n+1}$$

$$\beta=1/kT \qquad \Delta\beta=\beta/(n+1)$$

PATH INTEGRAL MONTE-CARLO METHOD



parity of permutation

$$\rho(q,r,\sigma;\beta) = \frac{1}{\lambda_i^{3N_i}\lambda_\Delta^{3N_e}} \sum_P (-1)^{\kappa_P} \int_V dr^{(1)} \ldots dr^{(n)} \times$$

$$\rho\left(q,r,r^{(1)};\Delta\beta\right)\ldots\rho\left(q,r^{(n)},Pr^{(n+1)};\Delta\beta\right)S\left(\sigma,P\sigma'\right),$$

thermal wavelengths of electron and ion

permutation operator

spin matrix

PATH INTEGRAL MONTE-CARLO METHOD

Path integral representation of density matrix:

$$\rho(q,r,\sigma;\beta)=\int_V dR^{(1)}\ldots dR^{(n)}\,\rho^{(1)}\ldots\rho^{(n)}\sum_P(-1)^{k_P}\,S\left(\sigma,\hat{P}\sigma'\right)\hat{P}\,\rho^{(n+1)}$$

$$R^{(i)}=\left(q^{(i)},r^{(i)}\right)$$

$$\rho^{(i)}=\left\langle R^{(i-1)}\left|e^{-\Delta\beta\hat{H}}\right|R^{(i)}\right\rangle$$

spin matrix

permutation operator

$$\hat{H}=\hat{K}+\hat{U}_c,\quad \hat{U}_c=\hat{U}_c^p+\hat{U}_c^e+\hat{U}_c^{ep}$$

$$\sum_\sigma\rho(q,r,\sigma;\beta)=\left(\prod_{l=1}^{n}e^{-\Delta\beta U_l(\Delta\beta)}\prod_{p=1}^{N_e}\phi_{pp}^{l}\right)\sum_{s=0}^{N_e}C_{N_e}^{s}\,\det\left\|\psi_{ab}^{n,1}\right\|_s$$

$$U_l^p(\Delta\beta)+U_l^e(\Delta\beta)+U_l^{ep}(\Delta\beta)$$

kinetic part of density matrix

exchange effects

KELBG PSEUDOPOTENTIAL

First order perturbation theory solution of two-particle Bloch equation for density matrix in the limit of weak coupling

$$\Phi^{ab}\left(\mathbf{r}_{ab},\mathbf{r}'_{ab},\Delta\beta\right)=e_a e_b\int_0^1\frac{d\alpha}{d_{ab}(\alpha)}\operatorname{erf}\left(\frac{d_{ab}(\alpha)}{2\lambda_{ab}\sqrt{\alpha(1-\alpha)}}\right)$$

$$d_{ab}(\alpha)=\left|\alpha\mathbf{r}_{ab}+(1-\alpha)\mathbf{r}'_{ab}\right|$$

$$\lambda_{ab}=\hbar^2\beta/2\mu_{ab}$$

$$\mu_{ab}^{-1}=m_a^{-1}+m_b^{-1}$$

Diagonal Kelbg potential:

$$\Phi^{ab}\left(\mathbf{r}_{ab},\Delta\beta\right)=\frac{e_a e_b}{\lambda_{ab}x_{ab}}\left\{1-e^{-x_{ab}^2}+\sqrt{\pi}x_{ab}\left[1-\operatorname{erf}(x_{ab})\right]\right\}$$

$$x_{ab}=\left|\mathbf{r}_{ab}\right|/\lambda_{ab}$$

$$\left|\mathbf{r}_{ab}\right|\to 0:\quad\frac{\sqrt{\pi}e_a e_b}{\lambda_{ab}}$$

$$\left|\mathbf{r}_{ab}\right|>>\lambda_{ab}:\quad\frac{e_a e_b}{\left|r_{ab}\right|}$$

Ebeling et al., Contr. Plasma Phys., 1967

ACCURACY OF DIRECT PIMC

$$\hat{\rho} = e^{-\beta \hat{H}} = \underbrace{e^{-\Delta\beta\hat{H}} \times \ldots \times e^{-\Delta\beta\hat{H}}}_{n+1}$$

$\beta = 1/k_B T$

$\hat{H} = \hat{K} + \hat{U}$

$\Delta\beta = \beta/(n+1)$

$$\hat{\rho}_{\Delta\beta} = e^{-\Delta\beta\hat{H}} = e^{-\Delta\beta\hat{K}} e^{-\Delta\beta\hat{U}} e^{-\frac{(\Delta\beta)^2}{2}\left[\hat{K},\hat{U}\right]}$$

1 at $n \to \infty$

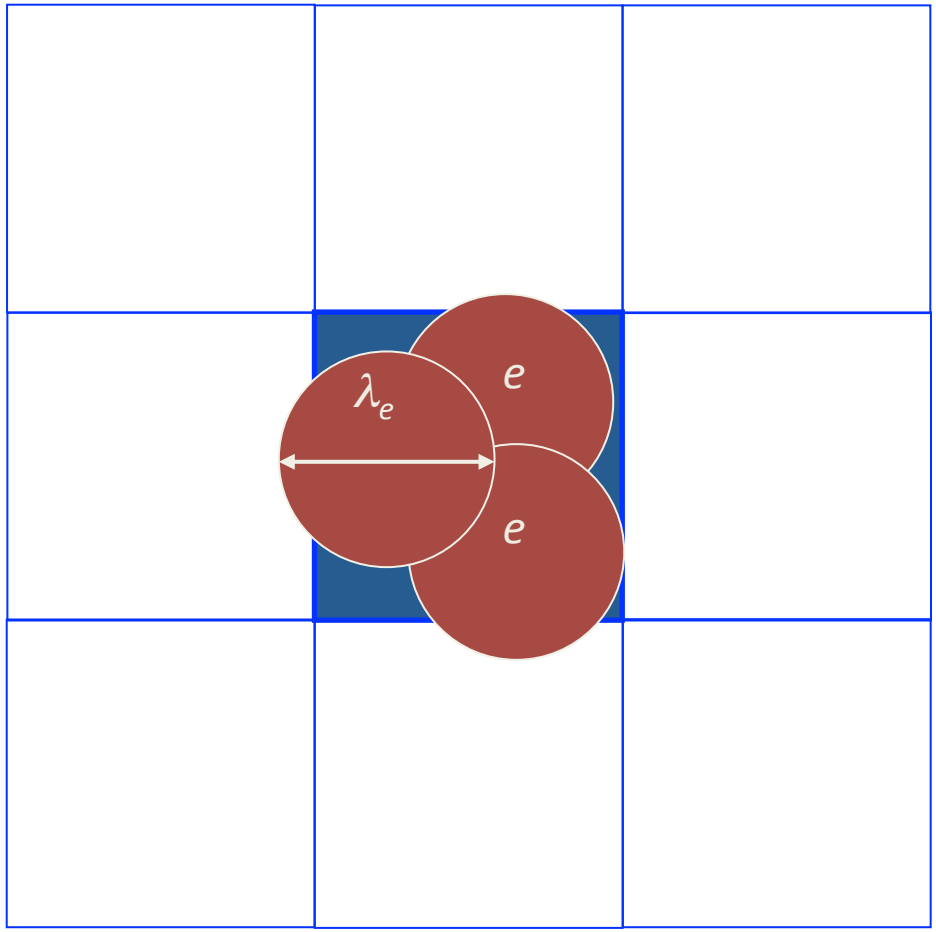
Error ~ $(\beta / n)^2$ for every multiplier

Total error $\Delta\rho \sim \beta^2 / n \to 0$ at $n \to \infty$

$$\rho_{\Delta\beta} = \rho_{free}\rho_{pot}(\Delta\beta)$$

High-temperature pseudopotential

TREATMENT OF EXCHANGE EFFECTS



Inside main cell –
exchange matrix

Outside main cell –
by perturbation theory

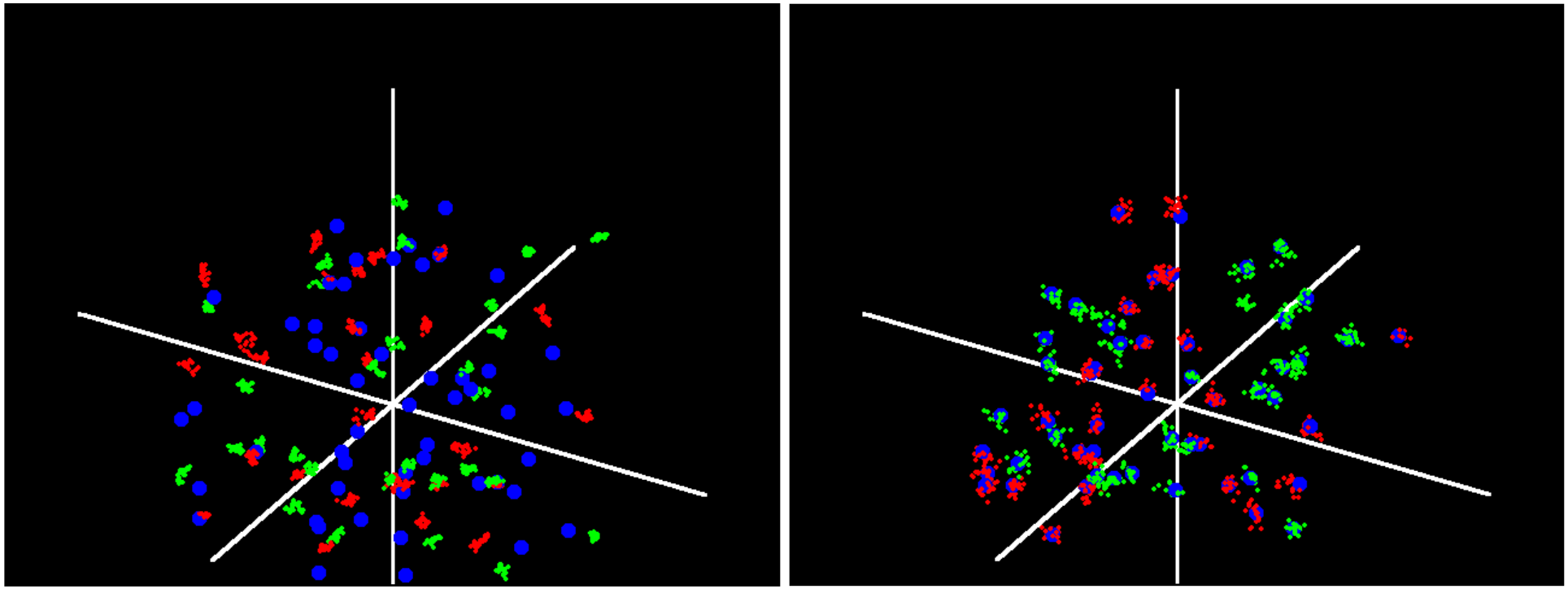
Accuracy control –
comparison with ideal
degenerate gas

$$n_e \lambda_e^3 \sim 300$$

Filinov V.S. // J. Phys. A: Math. Gen. ***34****, 1665 (2001)*
Filinov V.S. et al. // J. Phys. A: Math. Gen. ***36****, 6069 (2003)*

HYDROGEN, PIMC-SIMULATION, $n = 10^{21}$ cm^{-3}

$N_e = N_i = 56$, $n = 20$



T = 50 kK

$\rho = 1.67 \cdot 10^{-3}$ g/cm^3

$\Gamma = 0.54$

$n\lambda^3 = 3.7 \cdot 10^{-2}$

T = 10 kK

$\Gamma = 2.7$

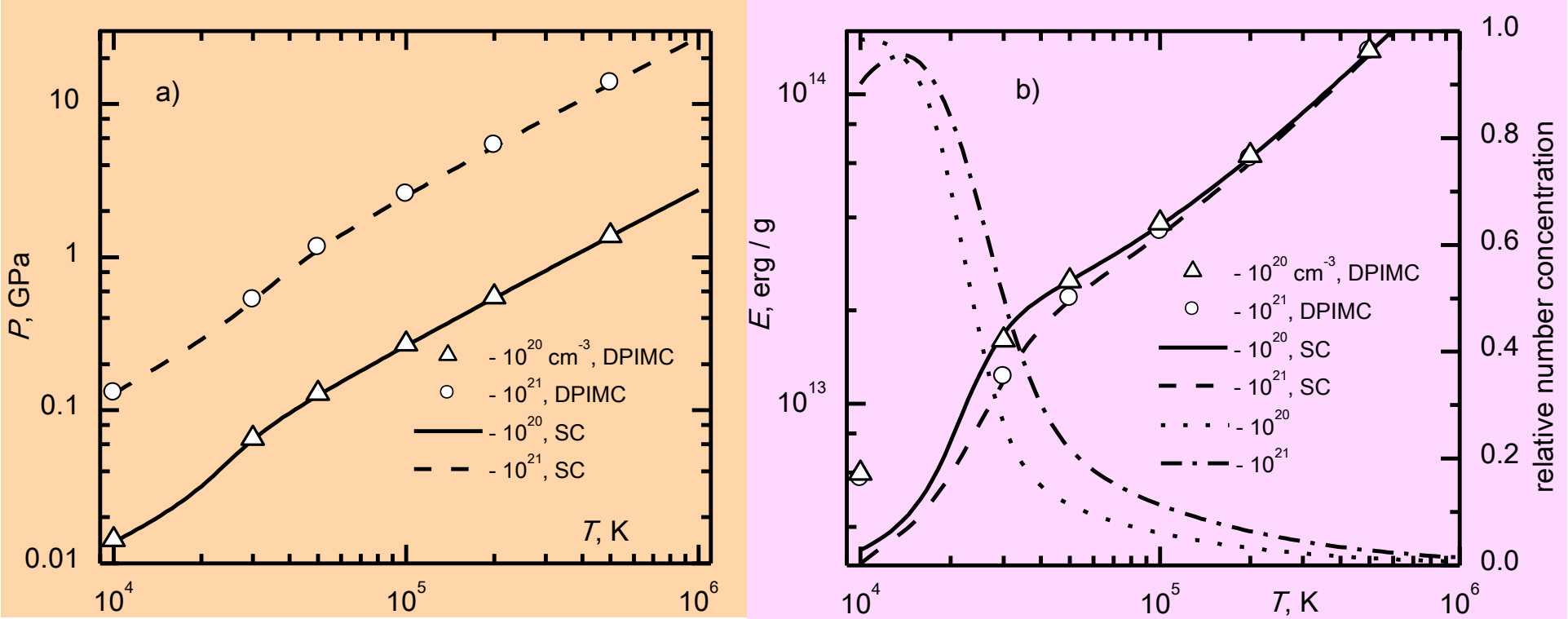
$n\lambda^3 = 0.41$

- proton
- electron
- electron

HYDROGEN, PIMC-SIMULATION AND CHEMICAL PICTURE, $n_e = 10^{20}, 10^{21}$ cm^{-3}

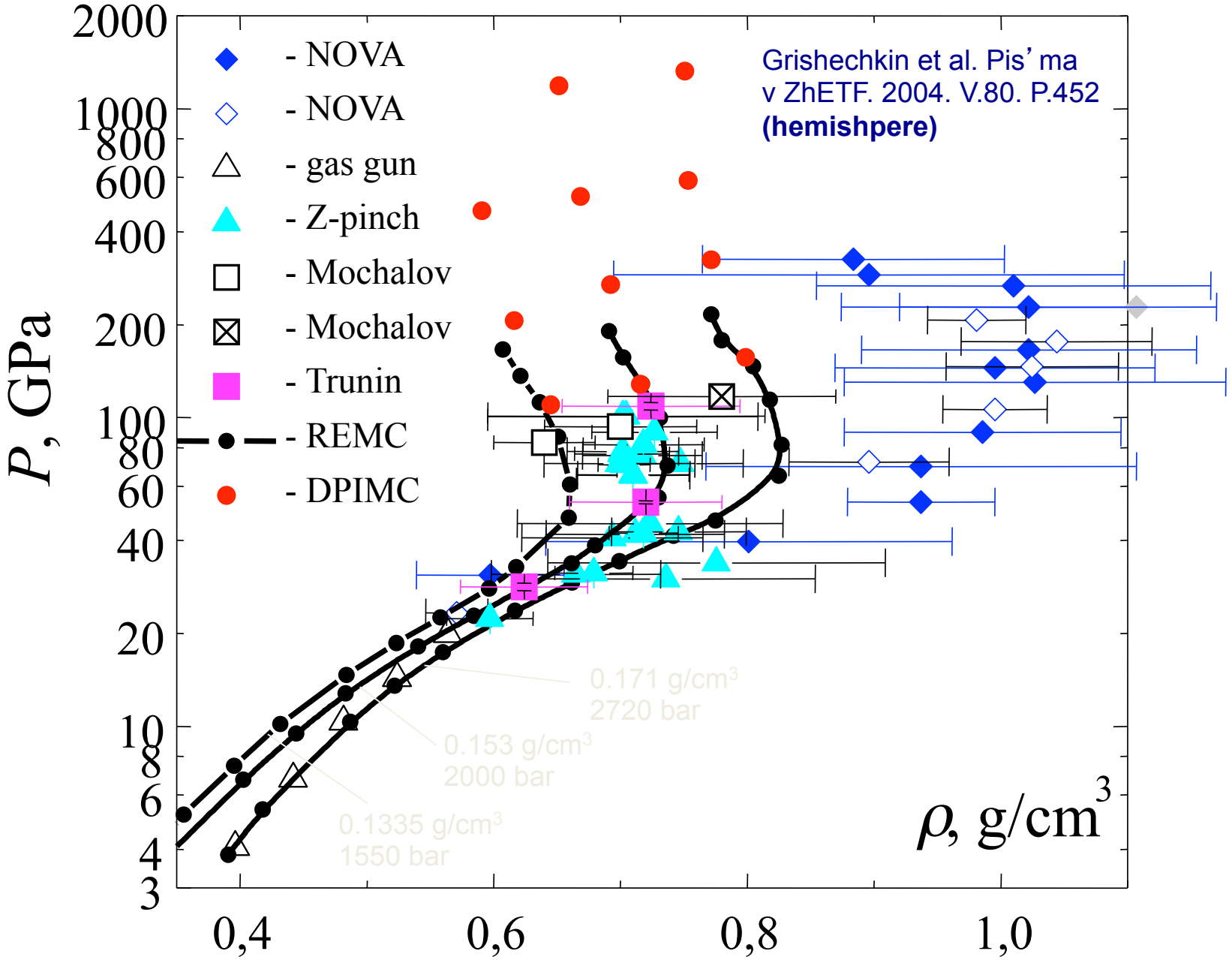
Pressure

Energy



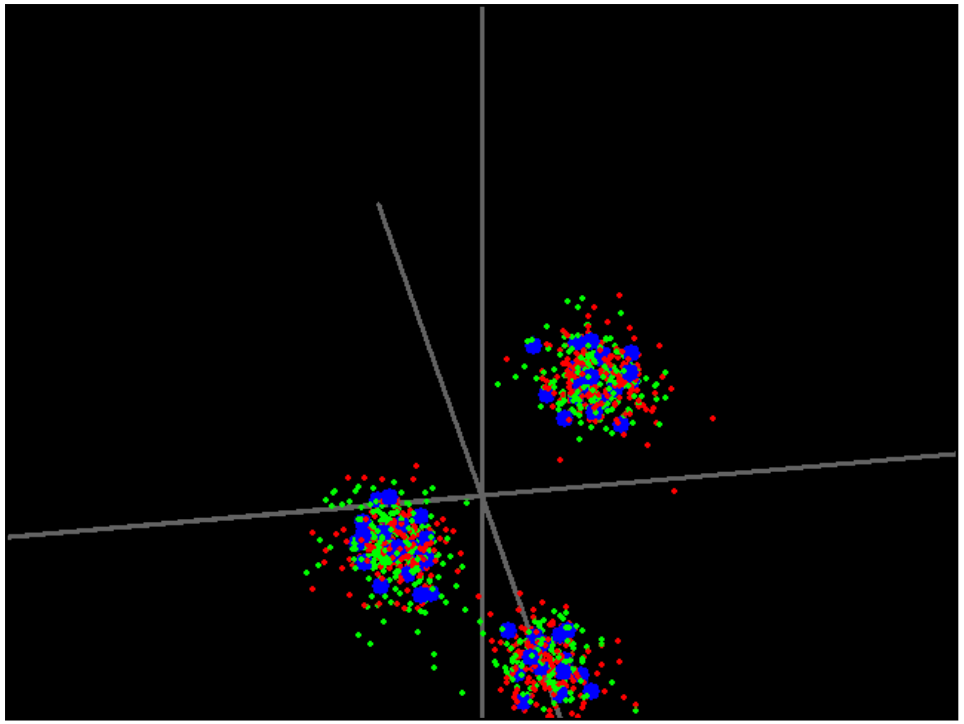
D. Saumon, G. Chabrier, H.M. Van Horn, Astrophys. J. Suppl.Ser. 1995. V.99. P.713

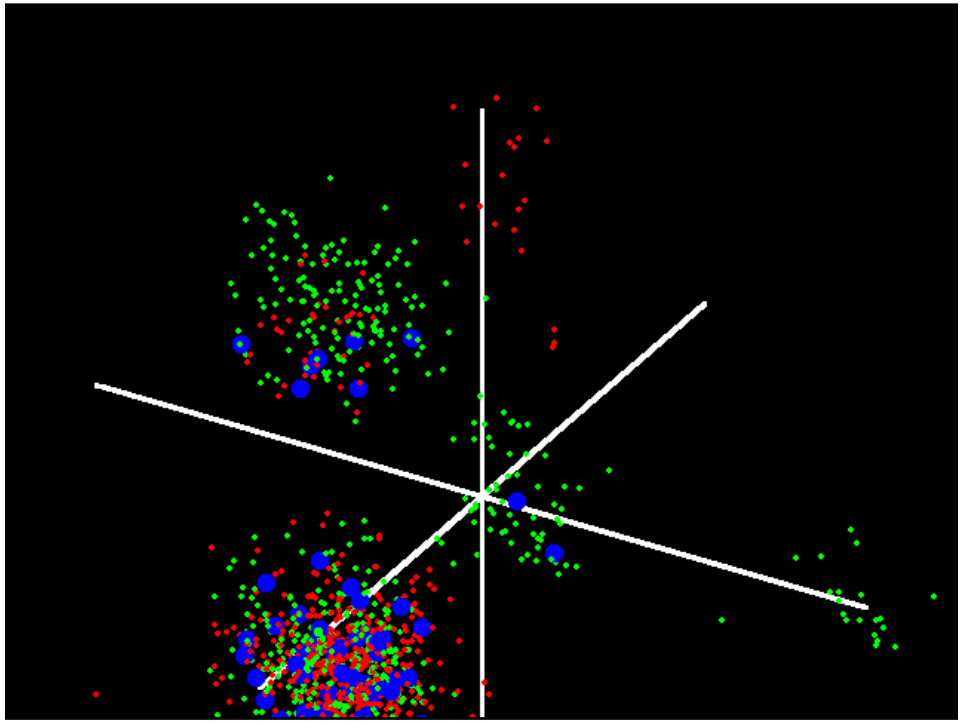
DEUTERIUM SHOCK HUGONIOTS



HYDROGEN, PIMC-SIMULATION, T = 10000 K

$N_e = N_i = 56$, $n = 20$





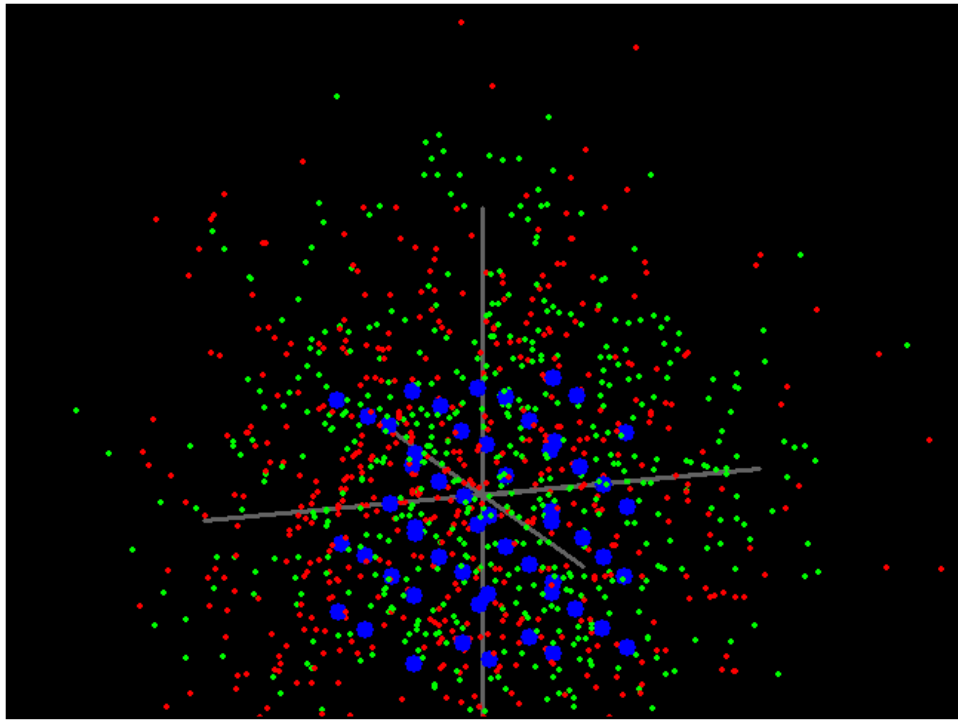
$n = 3 \cdot 10^{22}$ cm^{-3}
$\rho = 0.05$ g/cm^3
$\Gamma = 8.4$
$n\lambda^3 = 12.4$

$n = 10^{23}$ cm^{-3}
$\rho = 0.167$ g/cm^3
$\Gamma = 12.5$
$n\lambda^3 = 41$

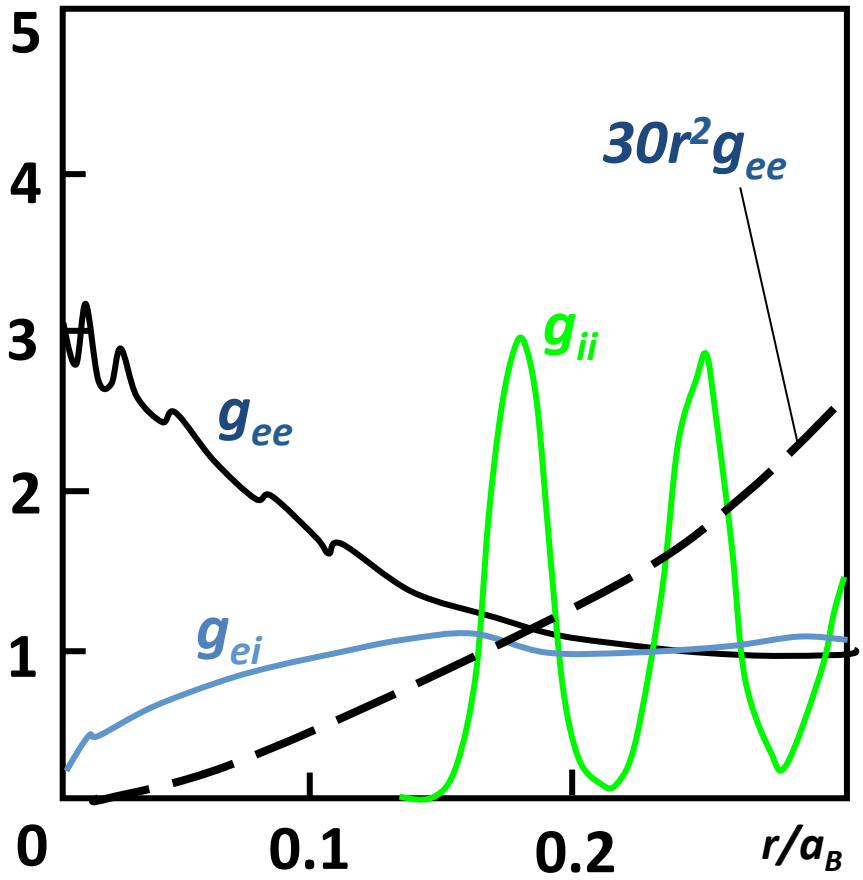
- proton
- electron
- electron

PIMC SIMULATION

$N_e = N_i = 56$, $n = 20$
protons ordering



- proton
- electron
- electron



$T = 10000$ K,
$n = 3 \cdot 10^{25}$ cm^{-3},
$\rho = 50.2$ g/cm^3
$\Gamma = 84$
$n\lambda^3 = 12400$

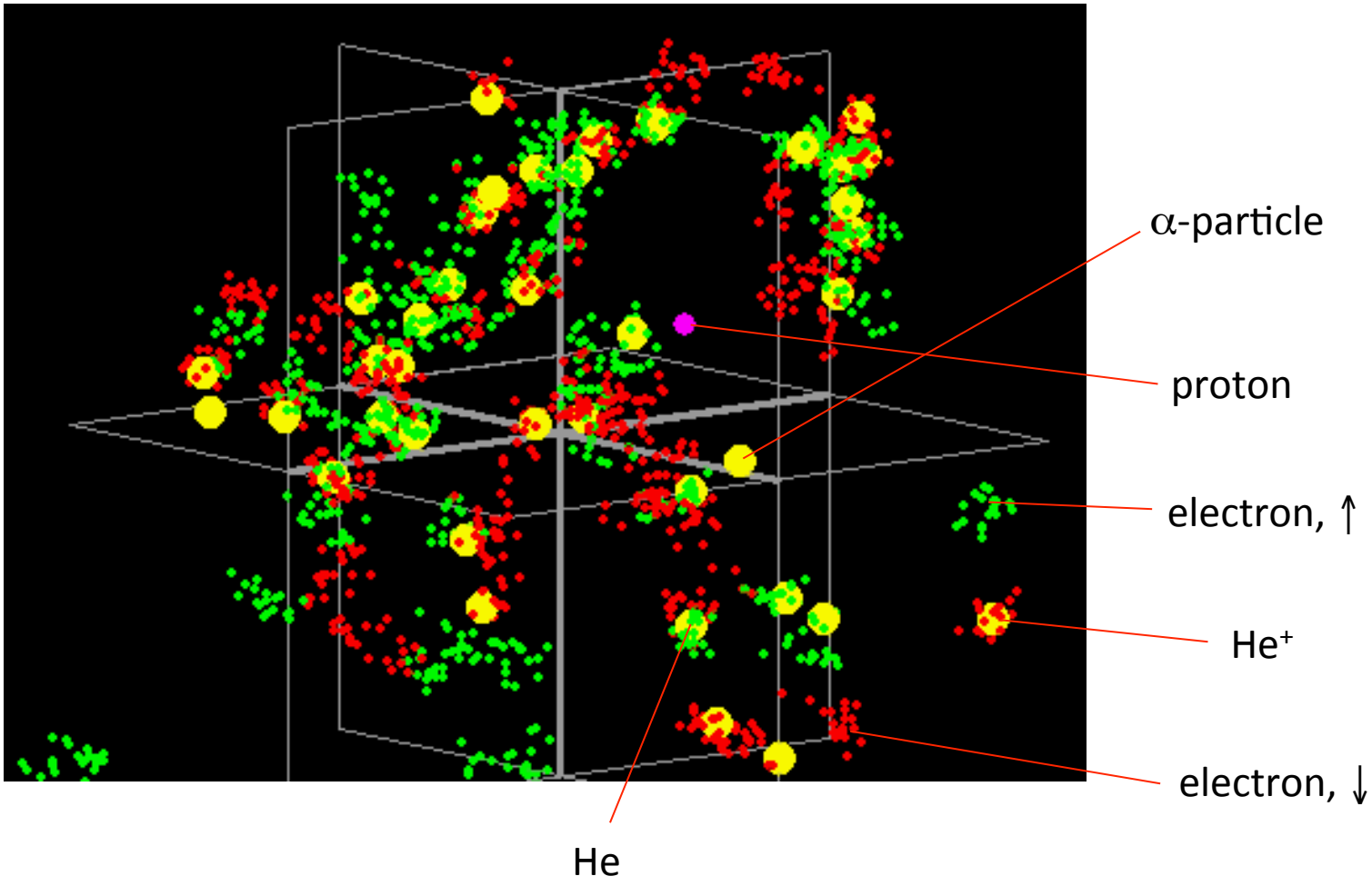
JETP Letters **72**, 245 (2000)

TYPICAL CONFIGURATION OF PARTICLES

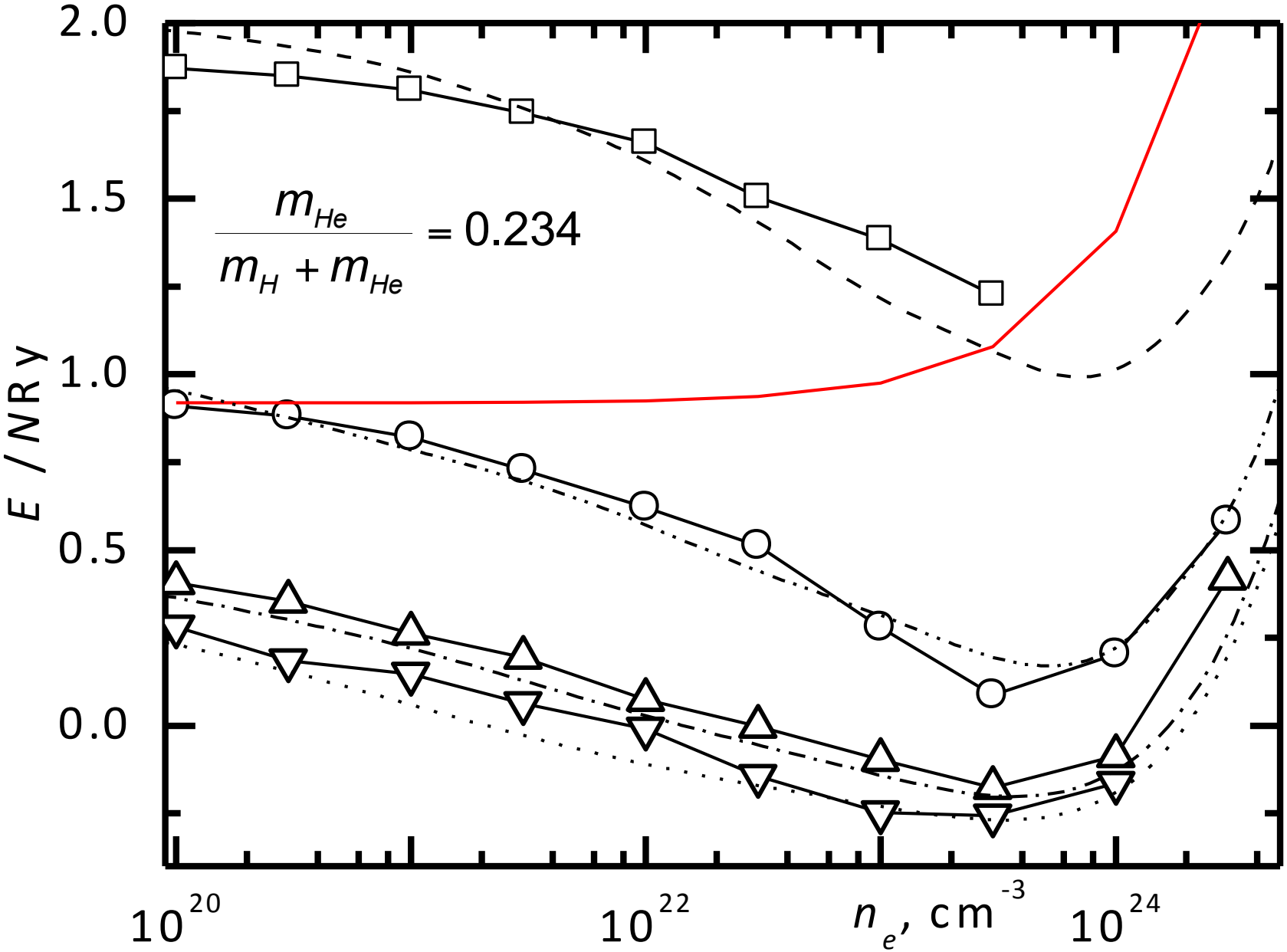
H + He mixture, $T = 10^5$ K, $n_e = 10^{23}$ cm^{-3}

$$m_{\mathrm{He}} / \left(m_{\mathrm{He}} + m_{\mathrm{H}} \right) = 0.988$$

40 α-particles, 2 protons, 82 electrons



ENERGY IN H + He MIXTURE ON ISOTHERMS



D. Saumon, G. Chabrier, H.M. Van Horn, Astrophys. J. Suppl.Ser. 1995. V.99. P.713

ELECTRON-HOLE PLASMA. PIMC SNAPSHOT

crystal, m_h(eff) = 800, m_e(eff) = 1

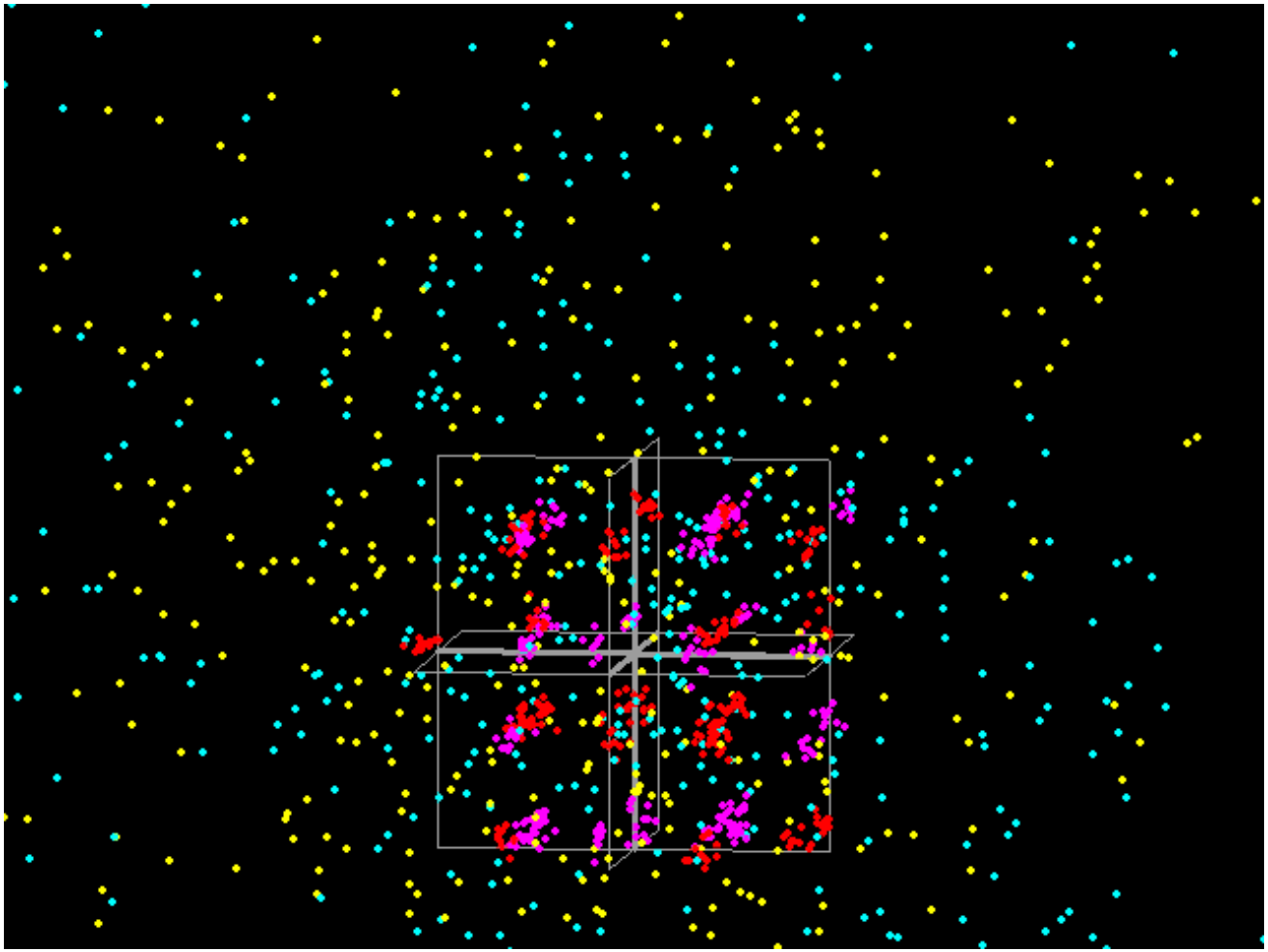
$\langle r \rangle / a_B = 0.63$

$T = 0.064 E_b$

- hole
- hole
- electron
- electron

ELECTRON-HOLE PLASMA. PIMC SNAPSHOT

still crystal, m_h(eff) = 100, m_e(eff) = 1



$\langle r \rangle / a_B = 0.63$

$T = 0.064 E_b$

- hole
- hole
- electron
- electron

ELECTRON-HOLE PLASMA. PIMC SNAPSHOT

liquid, m_h(eff) = 25, m_e(eff) = 1

$\langle r \rangle / a_B = 0.63$

$T = 0.064 E_b$

- hole

- hole

- electron

- electron

ELECTRON-HOLE PLASMA. PIMC SNAPSHOT

unordered plasma, m_h(eff) = 1, m_e(eff) = 1

$\langle r \rangle / a_B = 0.63$

$T = 0.064 E_b$

- hole

- hole

- electron

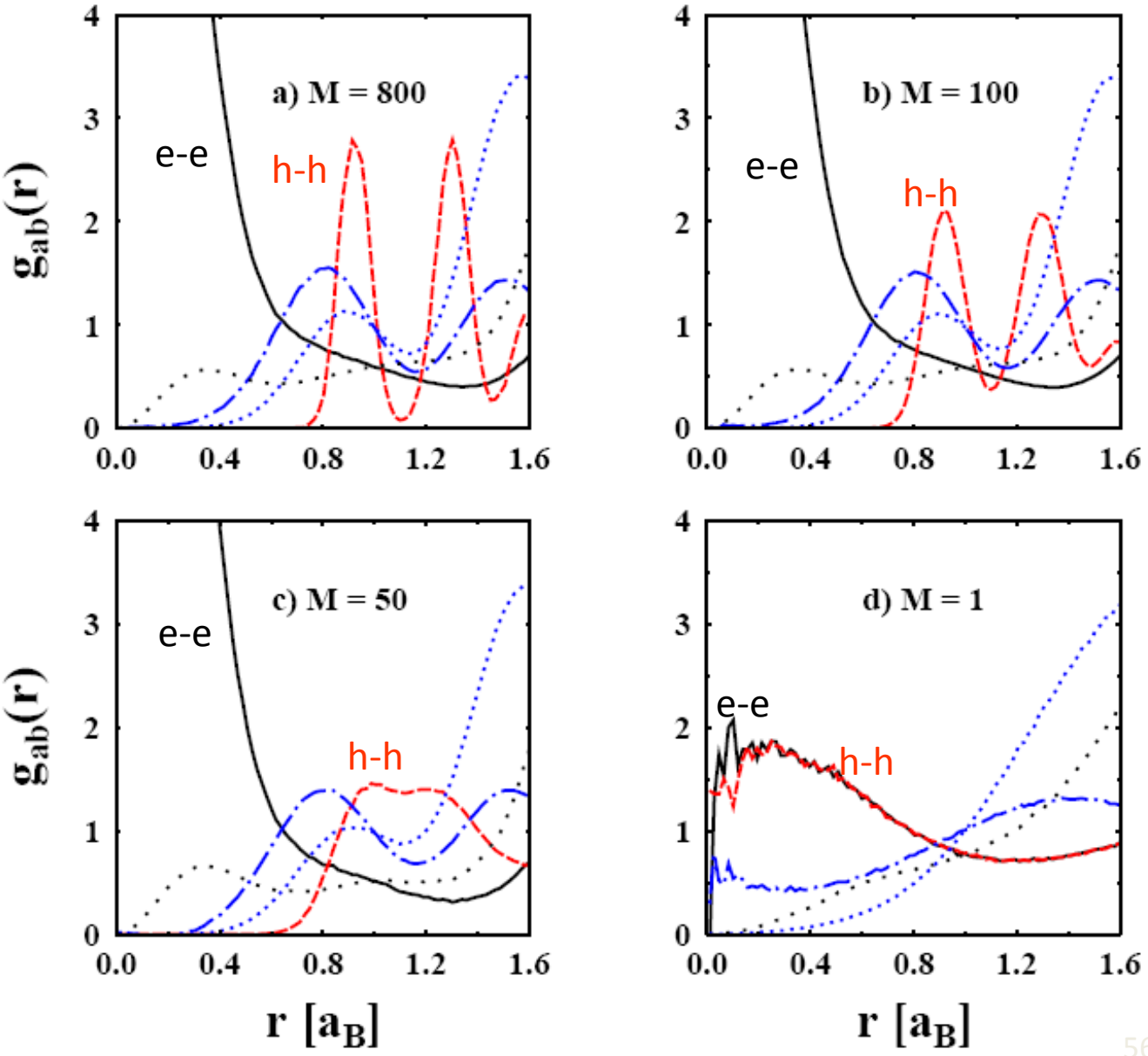
- electron

PAIR DISTRIBUTION FUNCTIONS. QUANTUM MELTING

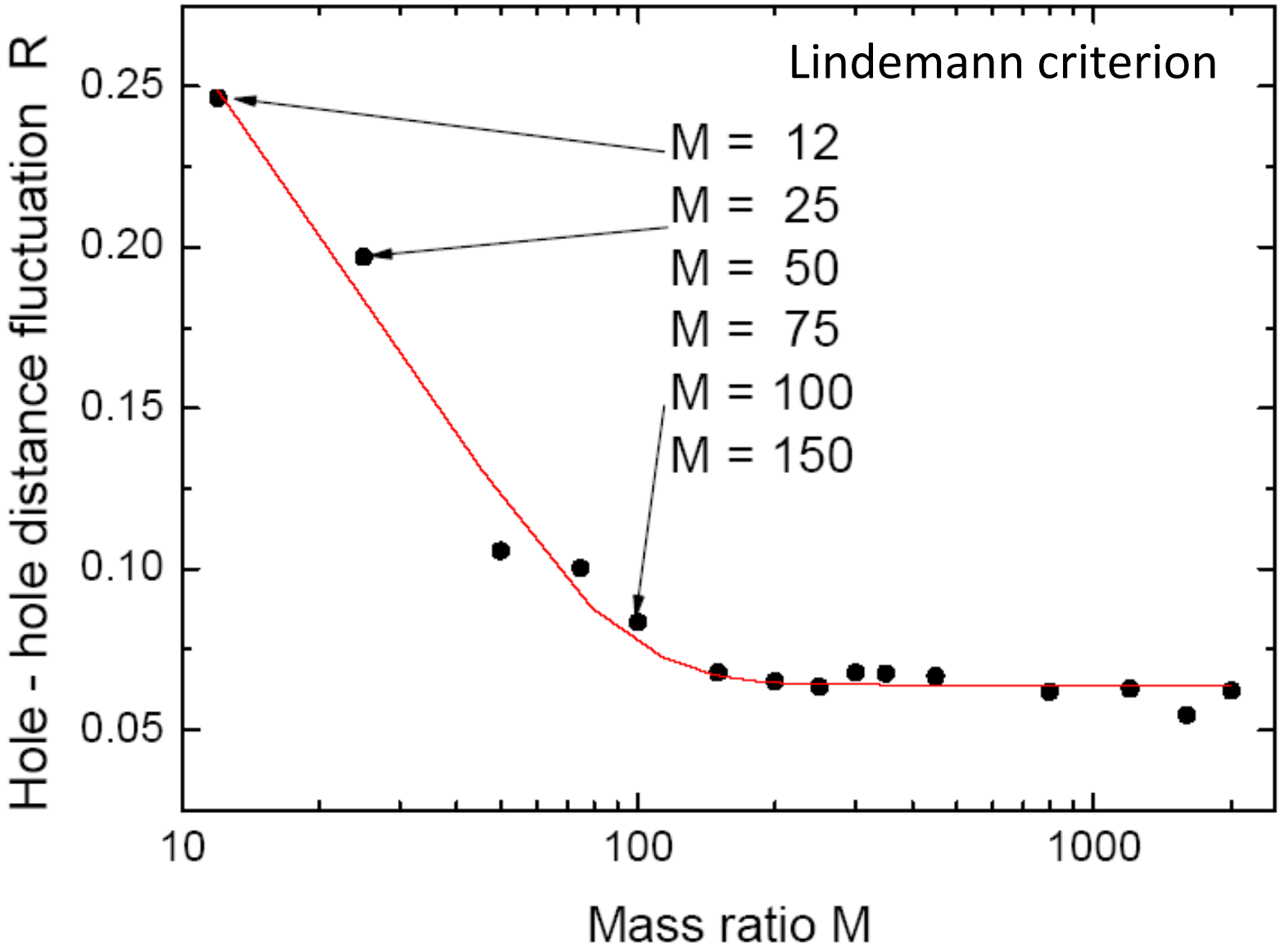
$\langle r \rangle / a_B = 0.63$

$T = 0.064 E_b$

$M = m_h / m_e$



HOLE-HOLE DISTANCE FLUCTUATIONS



ELECTRON DENSITY DISTRIBUTION

IN COULOMB CRYSTAL

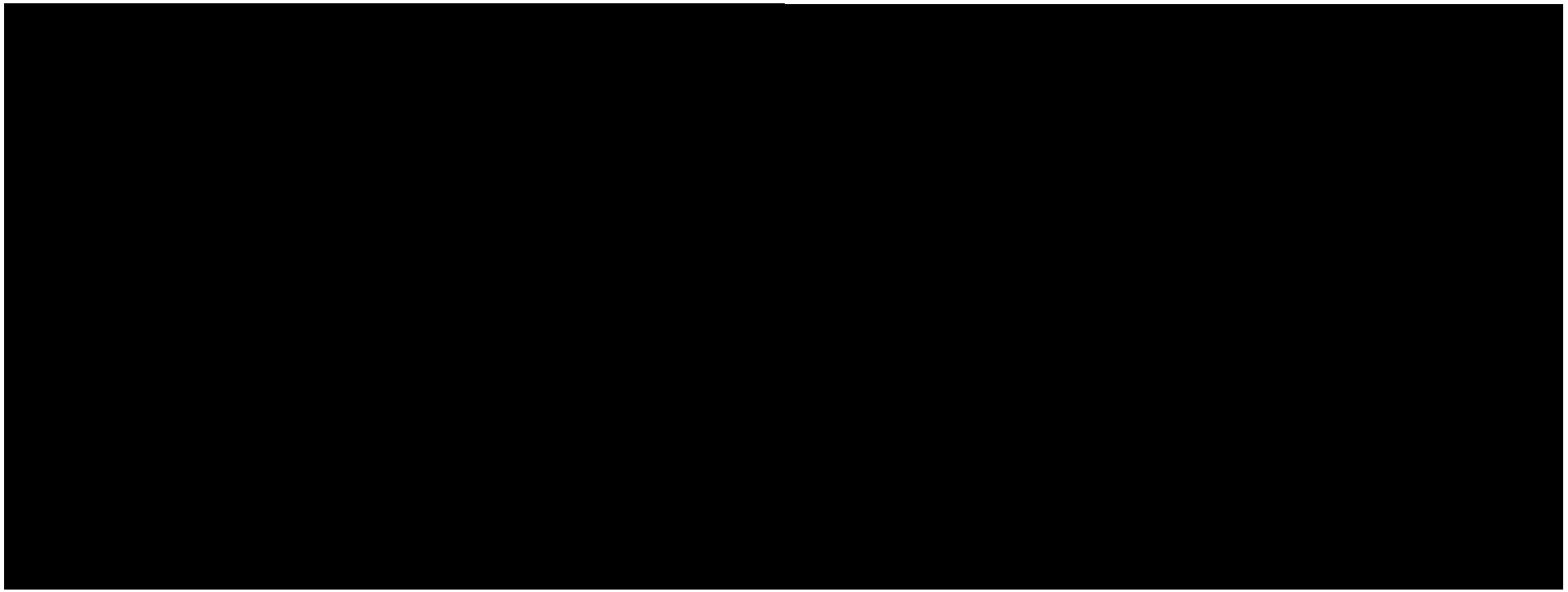
$m_h = 800$
$m_e = 2.1$
$\langle r \rangle / a_B = 3$

$\varepsilon = 25$
$T / E_b = 0.002$

- hole
- hole
- electron
- electron

top view

side view



Conclusions

- Ab initio methods are useful for calculation of different properties of matter at high energy density
- The main goal of ab initio methods is to replace experiment; in some cases it's already possible
- Currently, however, semiempirical approaches are main workhorses; ab initio methods are used for calibration of such models