Thermodynamic and transport properties of metals based on density functional theory for laser-matter interaction problems

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GOAL:

Using DFT calculations as reference data construct semiempirical models of thermodynamic and transport properties

For EOS:

- exclude fitting parameters from the contribution of electrons

For thermal conductivity and dielectric function:

- *f*it coefficients in the semiempirical expressions for the models to be consistent with DFT results

Traditional Form of a Semiempirical Equation of State

Adiabatic approximation ($m_e << m_i$)

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

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 semiempirical EOS. Free energy

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

Cold curve

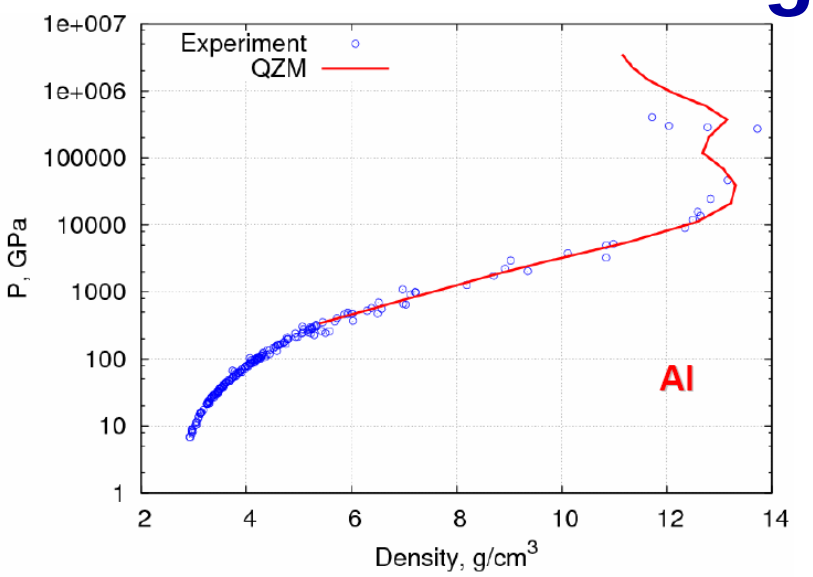
Thermal contribution of atoms and ions

Thermal contribution of electrons

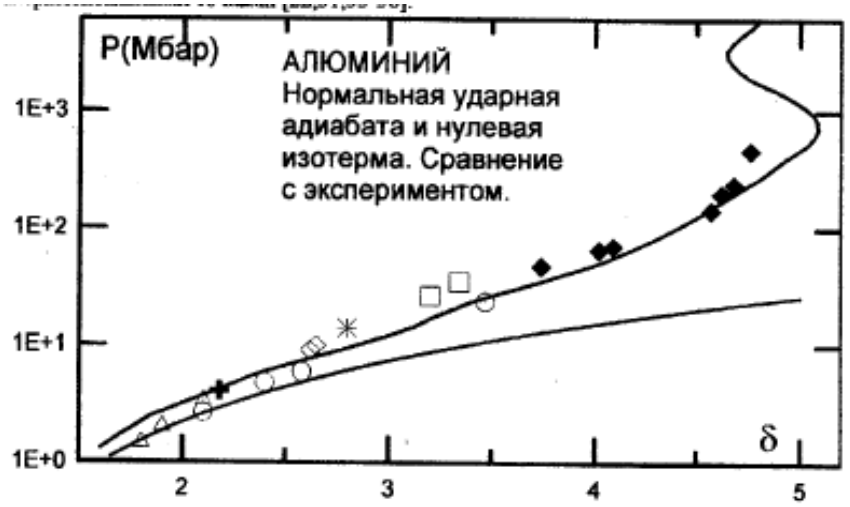
Semiempirical expressions

Mean atom model

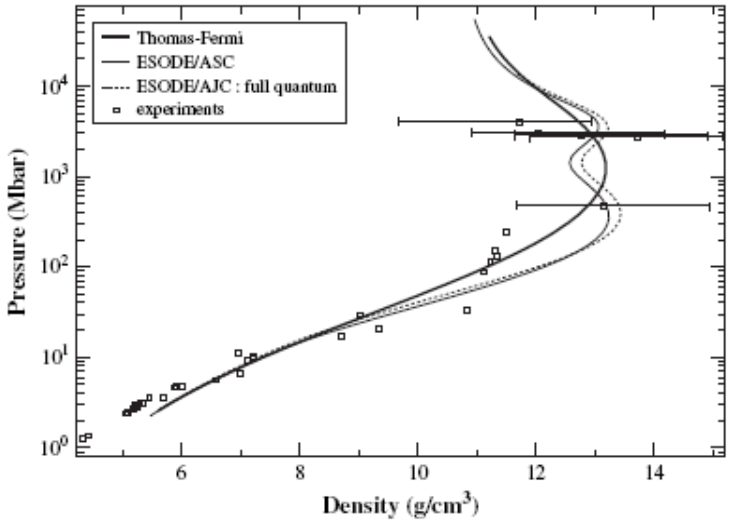
Shock Hugoniot of Al



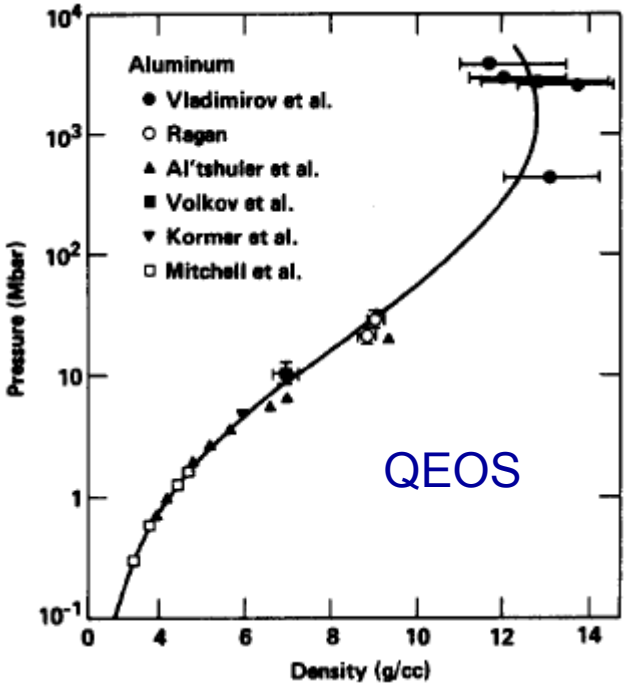
Grushin A.S., Novikov V.G.



Kirzhnits D.A., Shpatakovskaya G.V.
Preprint 33. M,. 1998



Pain J.C. // High Energy Density Physics.
2007. V. 3. P. 204-210



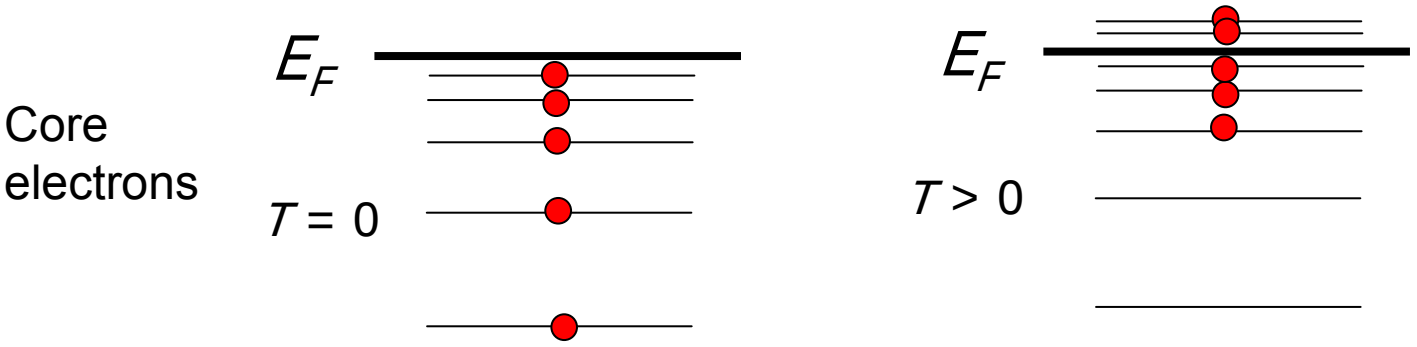
Density functional theory: full-potential and pseudopotential approaches

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)

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

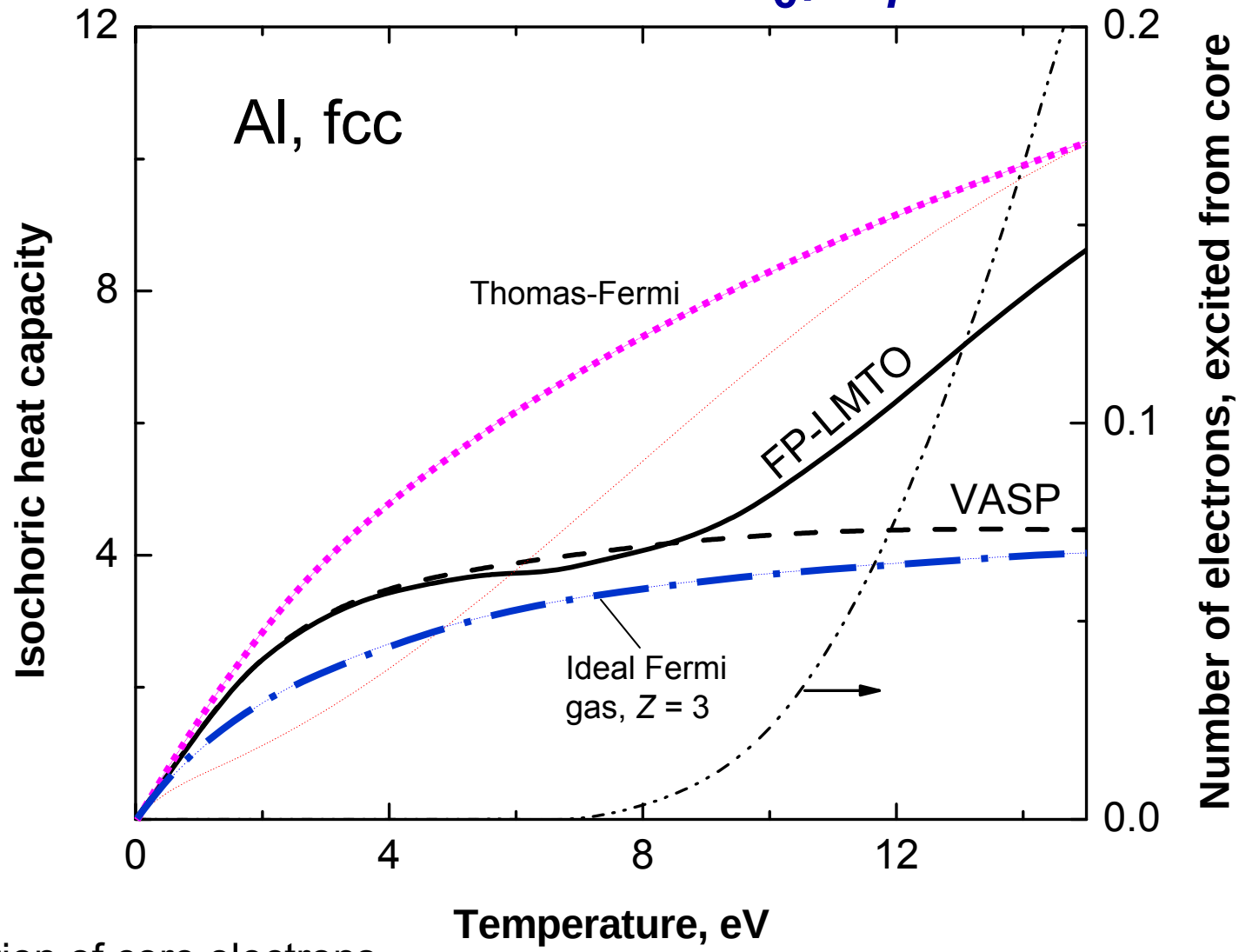
G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14251 (1994).
G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).



Calculations were made for the fcc unit cell for Al at cold ions. In VASP calculations the number of valent electrons were taken $Z = 3$ for Al

For dielectric function: 108 particles of Al in a cubic supercell, DFT-MD, 15 configurations

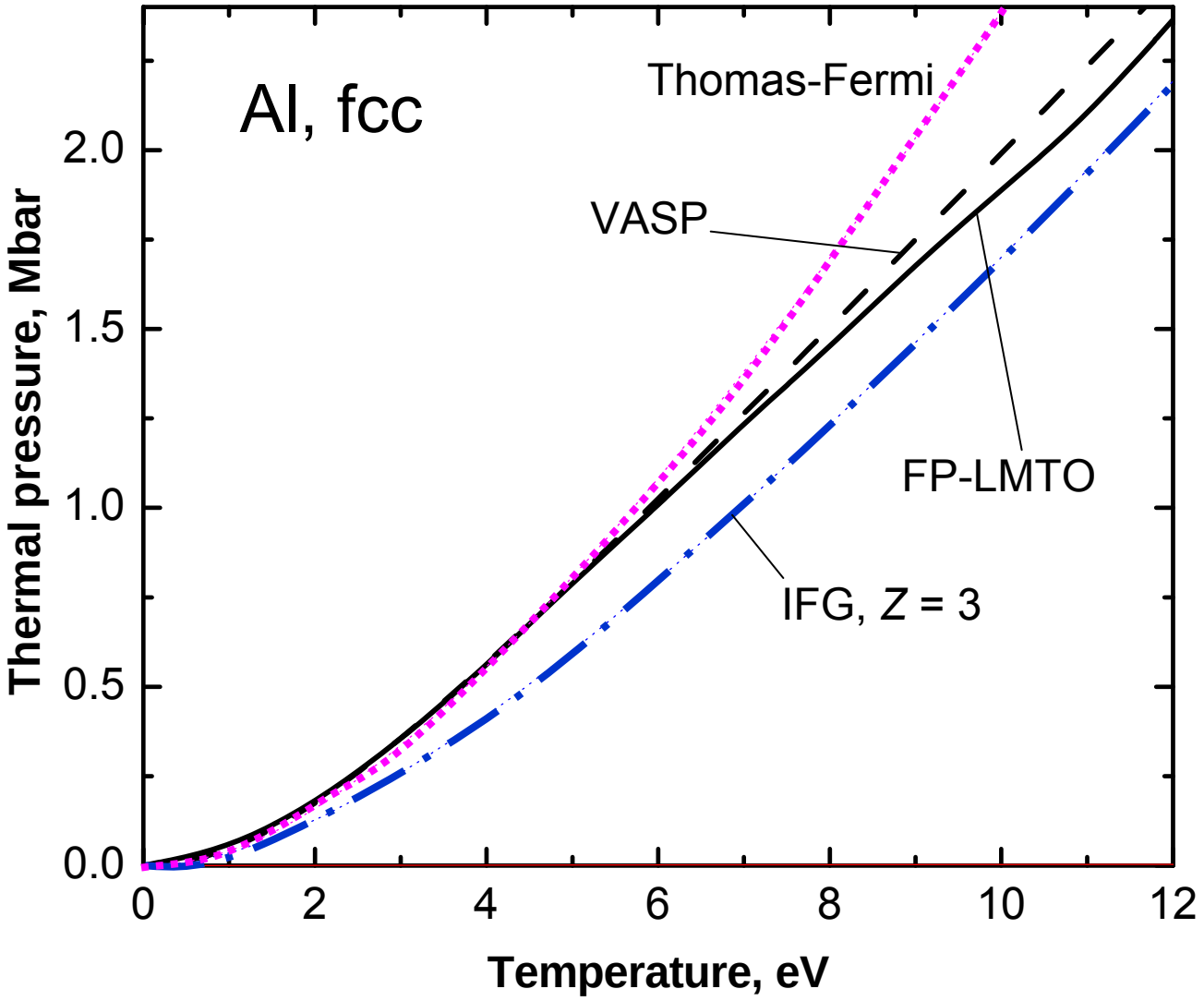
Electron heat capacity of Al, isochore $V = V_0$, $T_i = 0$



Excitation of core electrons increases heat capacity

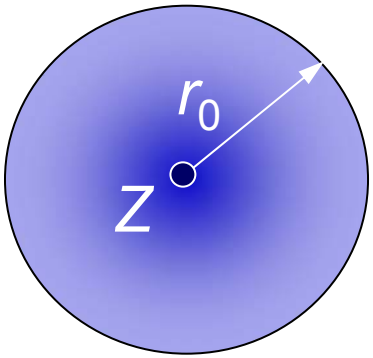
Levashov P.R. et al., JPCM **22,** 505501 (2010)

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



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

Thermal contribution of electrons in average atom models (Thomas-Fermi)



- Calculation of first and second derivatives of free energy

  Using grand canonical ensemble derivatives at high T

  Asymptotic expressions at low T

- Calculation of thermal contribution

$$F_T(V,T) = F(V,T) - F(V,0)$$ at high temperatures

Asymptotic expressions at low temperatures

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

Cold Curve and Thermal Contribution of Atoms and Ions

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

Cold curve

$$F_c(V) = a_0 V_{0c} \ln\sigma_c - 3V_{0c}\sum_{i=1}^{3}\frac{a_i}{i}\left(\sigma_c^{-i/3} - 1\right) + 3V_{0c}\sum_{i=1}^{2}\frac{b_i}{i}\left(\sigma_c^{i/3} - 1\right), \quad \sigma_c \geq 1$$

$$F_c(V) = V_{0c}\left[A\sigma_c^m/m + B\sigma_c^n/n + C\sigma_c^l/l\right] + E_{sub}, \qquad \sigma_c < 1$$

$$\sigma_c = V_{0c}/V$$

Thermal contribution of atoms and ions (quasiharmonic model)

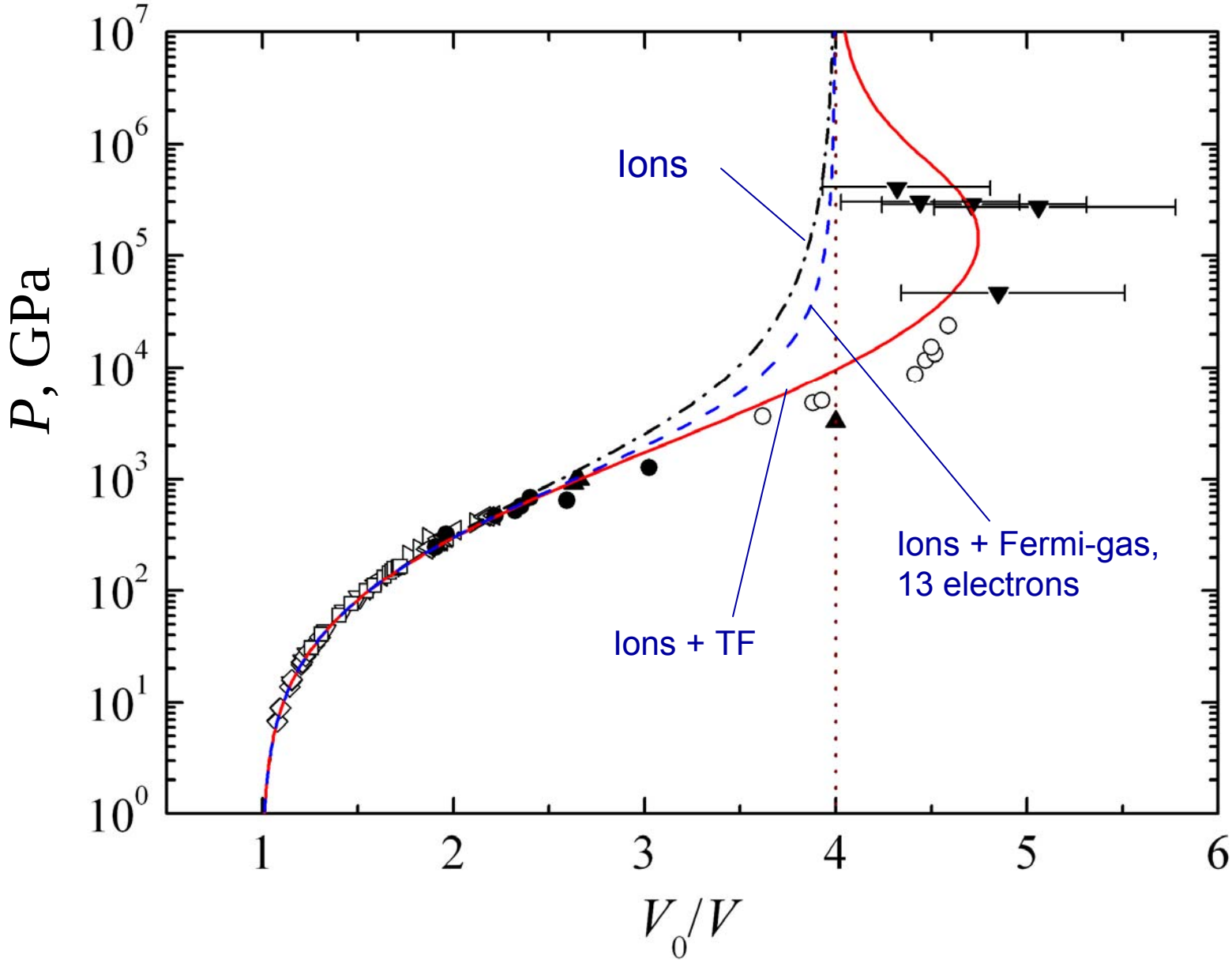
$$F_a(V,T) = 3RT\ln\left(1 - \exp\left(-\theta(V)/T - \sqrt{T_a\sigma^{2/3}/T}\right)\right)$$

$$\theta(V) = \theta_0\sigma^{2/3}\exp\left[\left(\gamma_0 - 2/3\right)\frac{B^2 + D^2}{B}\operatorname{arctg}\frac{B\ln\sigma}{B^2 + D\left(\ln\sigma + D\right)}\right]$$

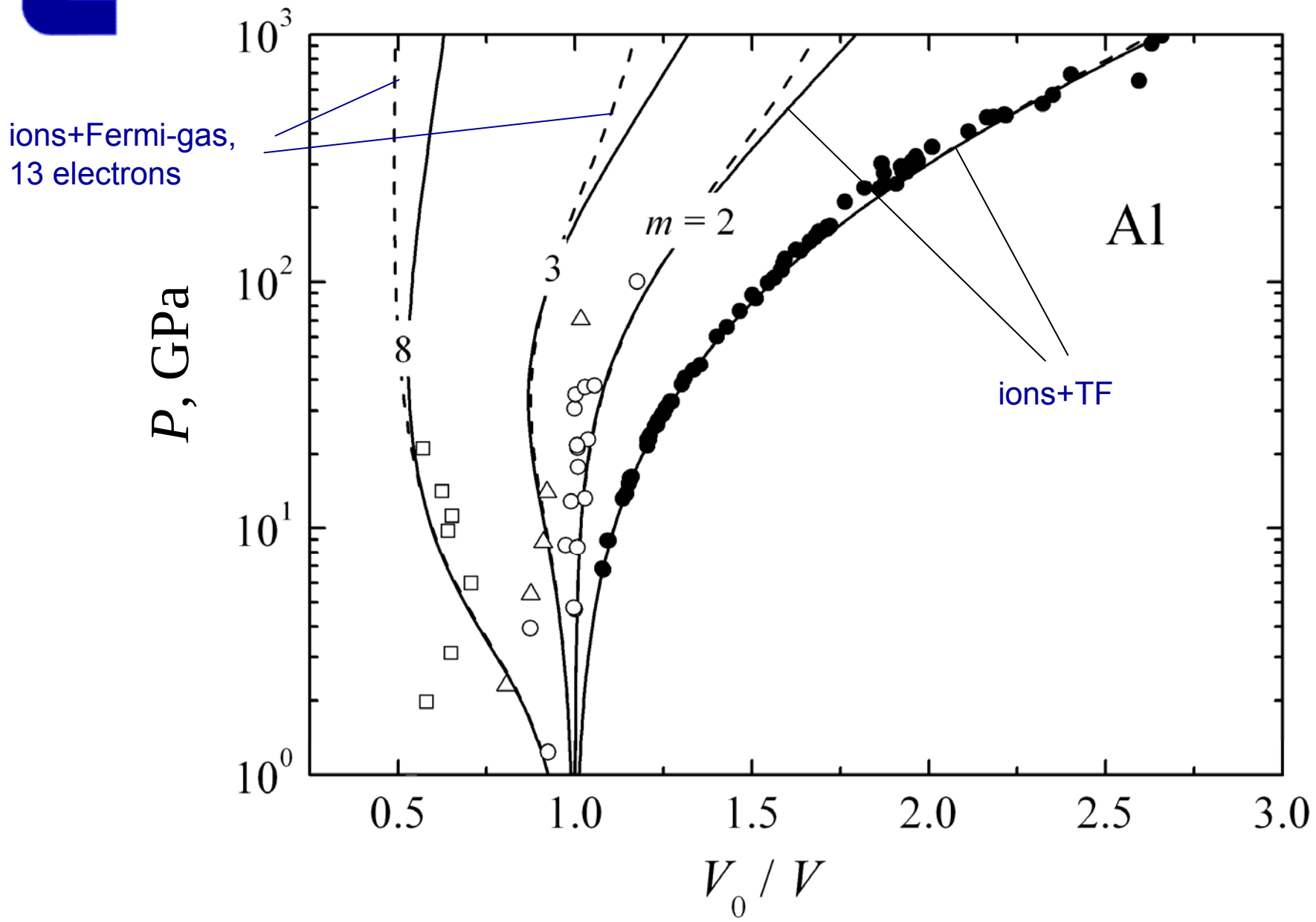
(Bushman, Fortov, Lomonosov, Khishchenko)

Unknown parameters a_0, a_1, a_2, a_3, b_1, b_2, A, B, C, m, n, l, T_a, D, B, θ_0, V_{0c} are determined from the comparison with experimental and theoretical data

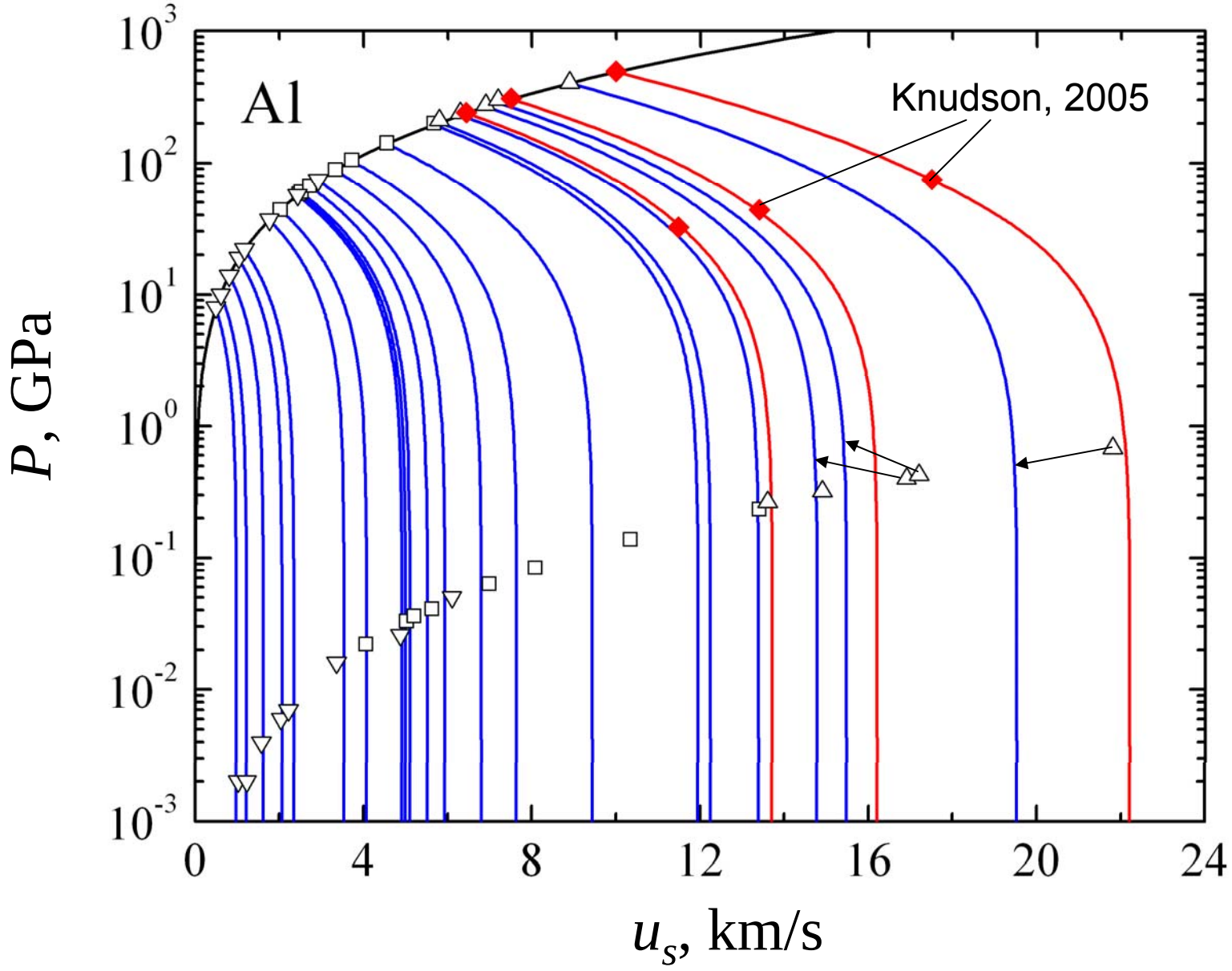
Shock Hugoniot of Al



Porous Shock Hugoniots of Al



Release Isentropes of Al



Complex dielectric function

$$\varepsilon_{\mathrm{met}}(\omega_L, \rho, T_i, T_e) = \varepsilon_{bb} + 1 - \frac{n_e}{n_{\mathrm{cr}}(1 + i\nu_{\mathrm{eff}}/\omega_L)}$$

Interband transitions

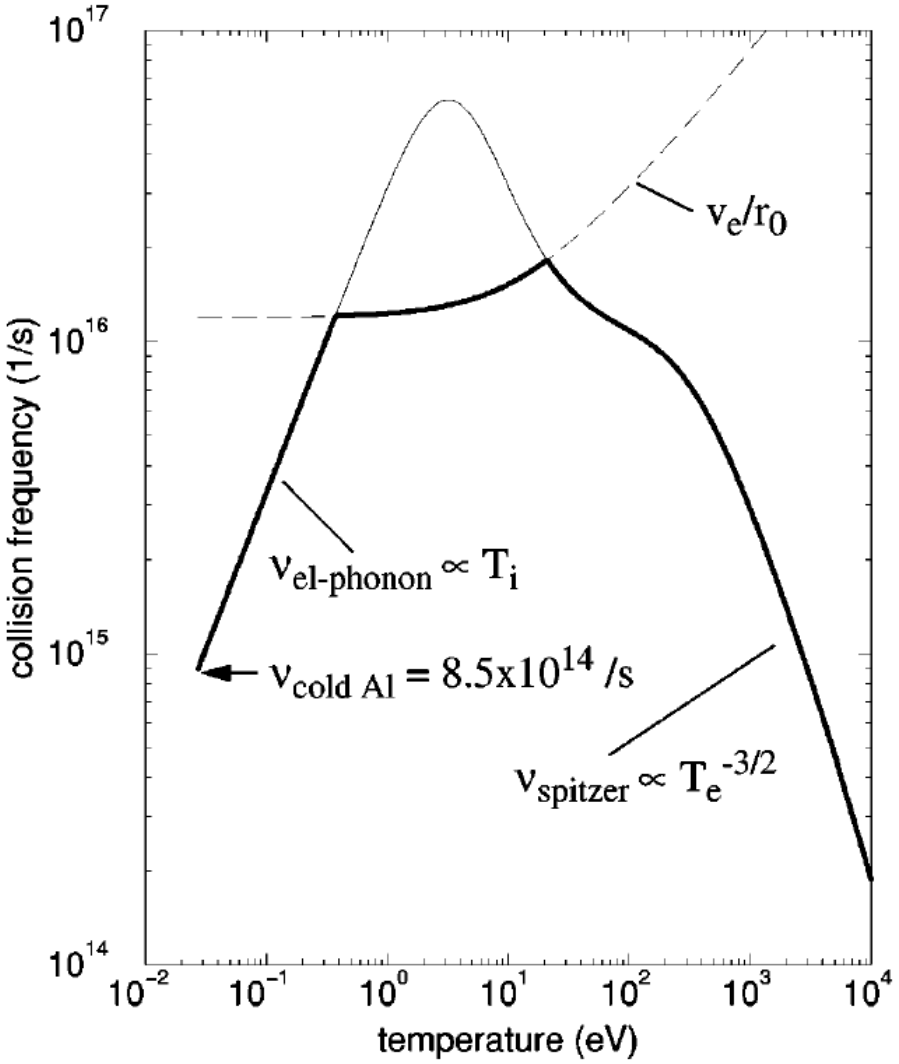
$$\varepsilon_{\mathrm{pl}}(\omega_L, \rho, T_e) = 1 - \frac{n_e}{n_{\mathrm{cr}}}\left[K_1(\xi) - i(\nu_{\mathrm{eff}}/\omega_L)K_2(\xi)\right]$$

Approximation:

$$\varepsilon = \frac{1}{2}(\varepsilon_{\mathrm{met}} + \varepsilon_{\mathrm{pl}}) + \frac{1}{2}(\varepsilon_{\mathrm{pl}} - \varepsilon_{\mathrm{met}}) \tanh\left(2\frac{2T_e - T_2 - T_1}{T_2 - T_1}\right)$$

Agranat M.B. et al., JETP Lett. **85**, 271 (2007)

Electron-ion collision frequency



Eidmann et al. PRE 62 (2000)

Pump-probe for ν_{cold}

[30] Elsayed et al. PRL 58, 1212 (1987)

[31] Groeneveld et al. PRL 64, 784 (1990)

[32] Schoenlein et al. PRL 58, 1680 (1987)

Complex electrical conductivity from first-principle calculations

Real part: from Kubo-Greenwood formula:

$$\sigma_1(\mathbf{k},\omega) = \frac{2\pi}{3\omega\Omega}\sum_{j=1}^{n_b}\sum_{i=1}^{n_b}\sum_{\alpha=1}^{3}\left[F(\epsilon_{i,\mathbf{k}}) - F(\epsilon_{j,\mathbf{k}})\right]$$

Fermi-Dirac functions

$$\times \langle\Psi_{j,\mathbf{k}}|\nabla_\alpha|\Psi_{i,\mathbf{k}}\rangle^2 \delta(\epsilon_{j,\mathbf{k}} - \epsilon_{i,\mathbf{k}} - \omega).$$

broadening

Imaginary part: from Kramers-Kronig relation:

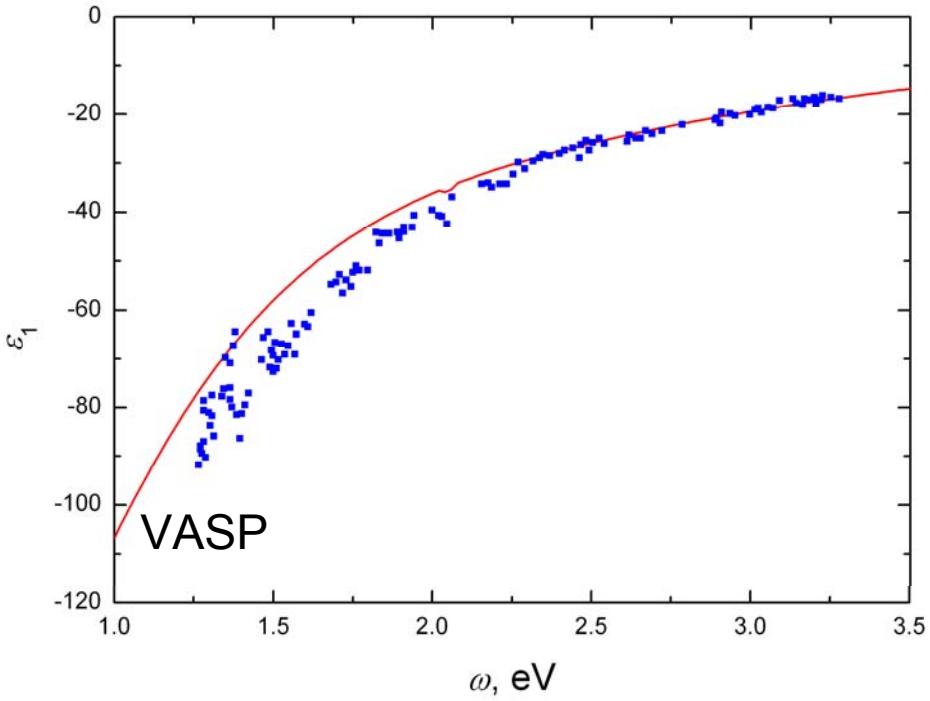
$$\sigma_2(\omega) = -\frac{2}{\pi}\mathrm{P}\int \frac{\sigma_1(\nu)\omega}{(\nu^2-\omega^2)}d\nu.$$

- DFT-MD calculations with 108 Al particles
- Thermal equilibrium ~100 MD steps
- 2000 time steps (15 configuration for averaging)

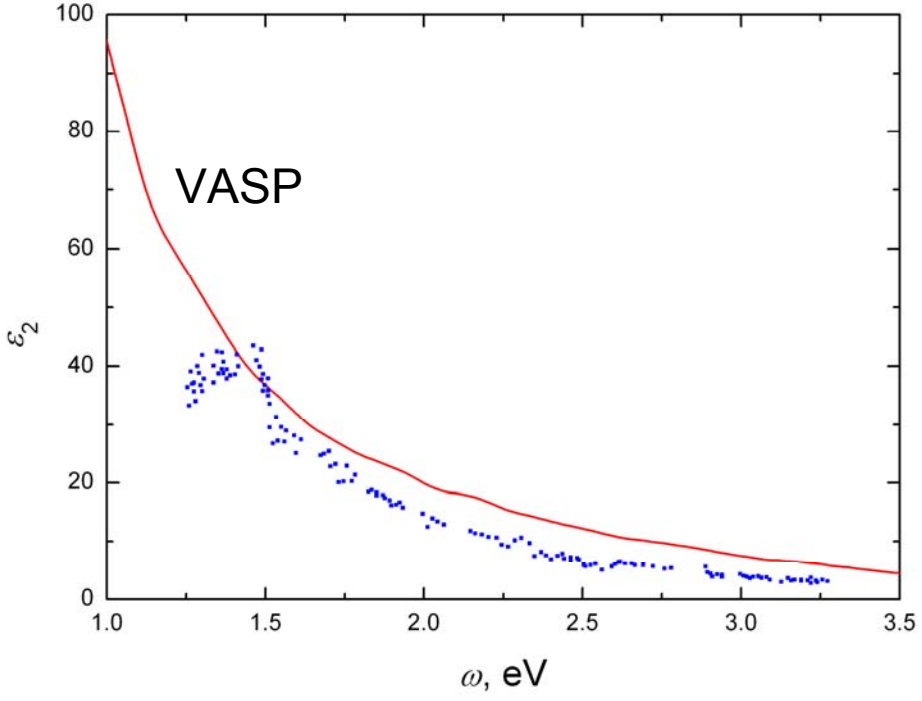
Desjarlais M.P. et al., PRE **66**, 025401(R) (2002)
Mazevet et al., PRE **71**, 016409 (2005)

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

Re ε



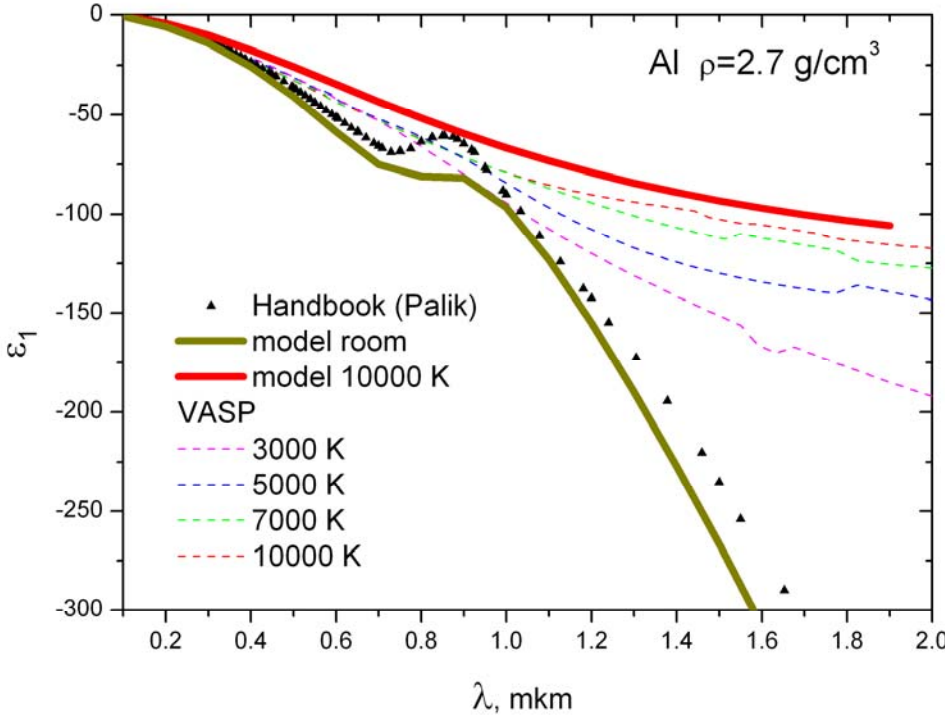
Im ε



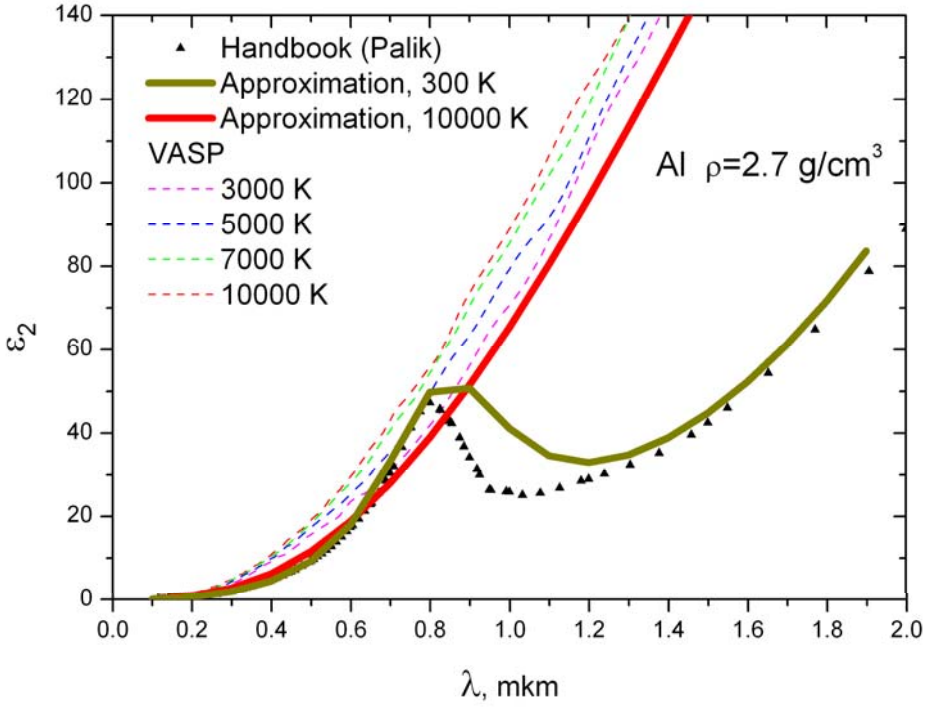
Experiment: Krishnan S. and Nordine P.C. PRB 47, 11780 (1993)

Complex dielectric function of Al at normal density

Re ε



Im ε



Electon-phonon contribution to dielectric function should be reduced after melting

Application to Laser-Matter Interaction: Influence of EOS

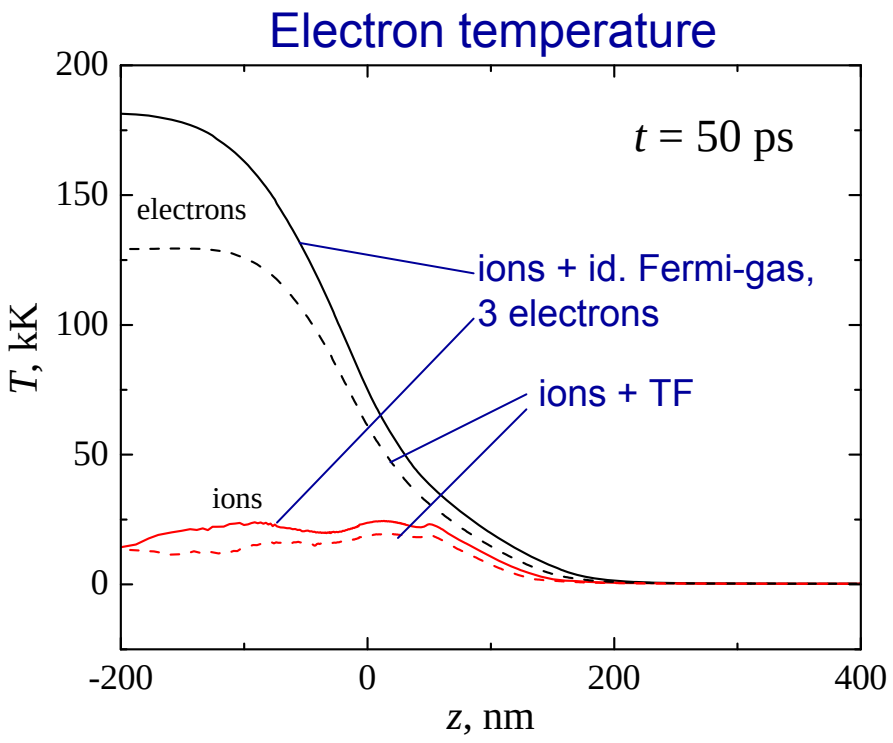
Al, $I = 10^{12}$ W/cm^2, τ = 10 ps, λ = 800 nm

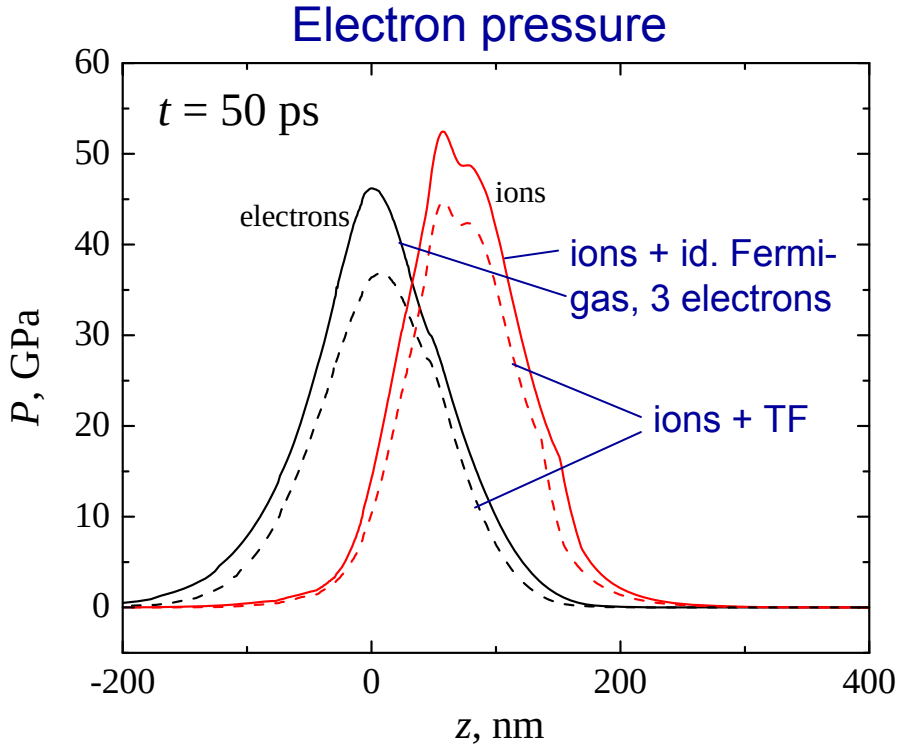
1D 2T one-velocity hydrodynamic model

Povarnitsyn et al., PRB 75, 235414 (2007)
Povarnitsyn et al., PRL 103, 195002 (2009)

EOS1: ions + ideal Fermi-gas (3 electrons)

EOS2: ions + Thomas-Fermi





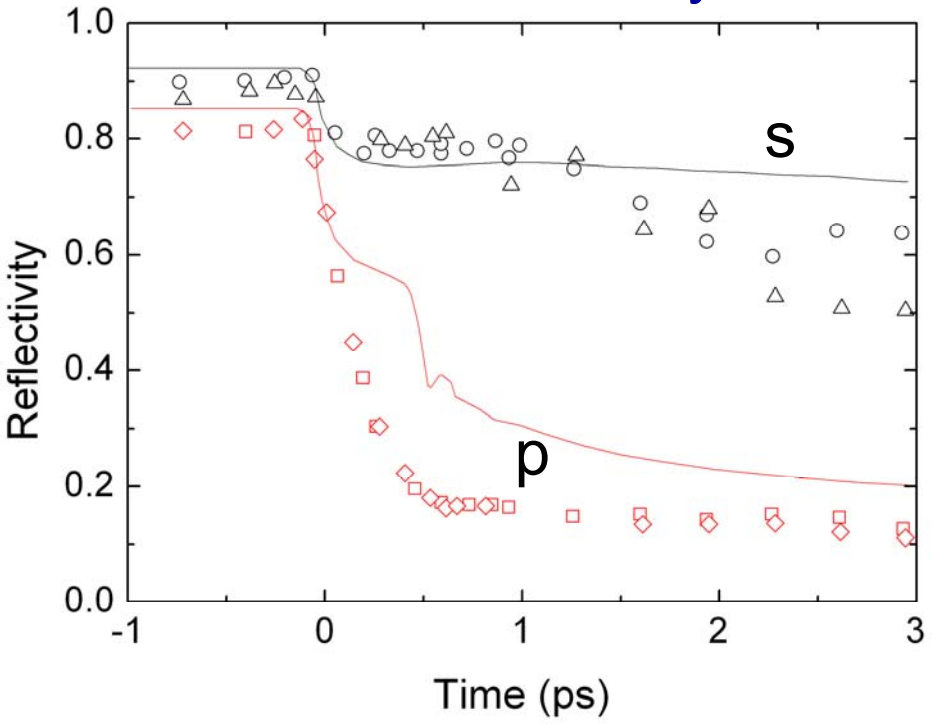
Application to Laser-Matter Interaction

Pump pulse: Al, $I = 10^{14}$ W/cm^2, τ = 120 fs, λ = 400 nm

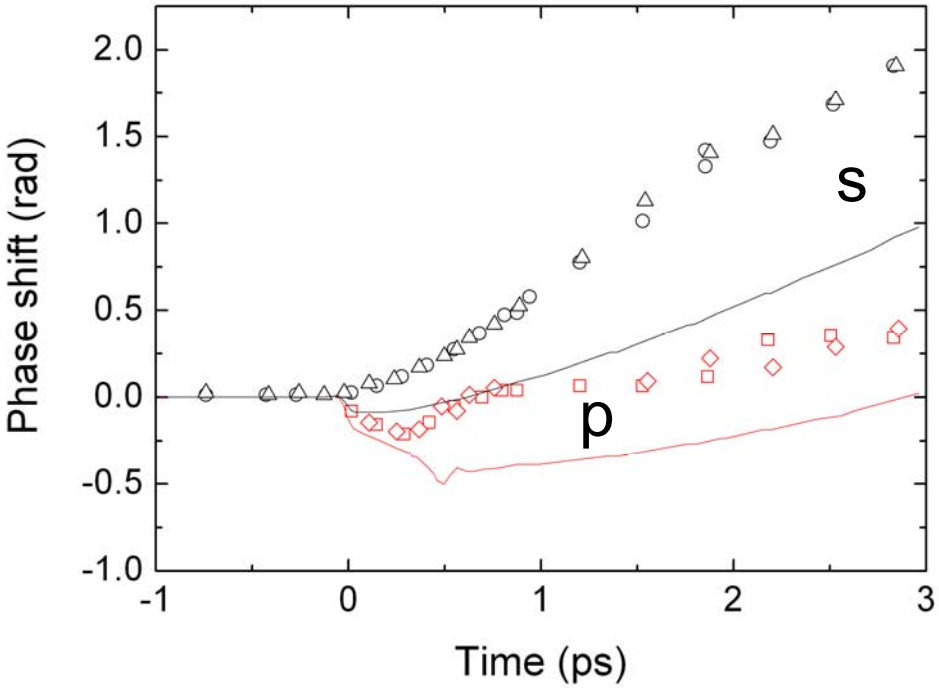
Probe pulse: τ = 110 fs, λ = 800 nm, θ = 45°

Experiment: Widmann et al. Phys. Plasmas **8**, 3869 (2001)

Reflectivity



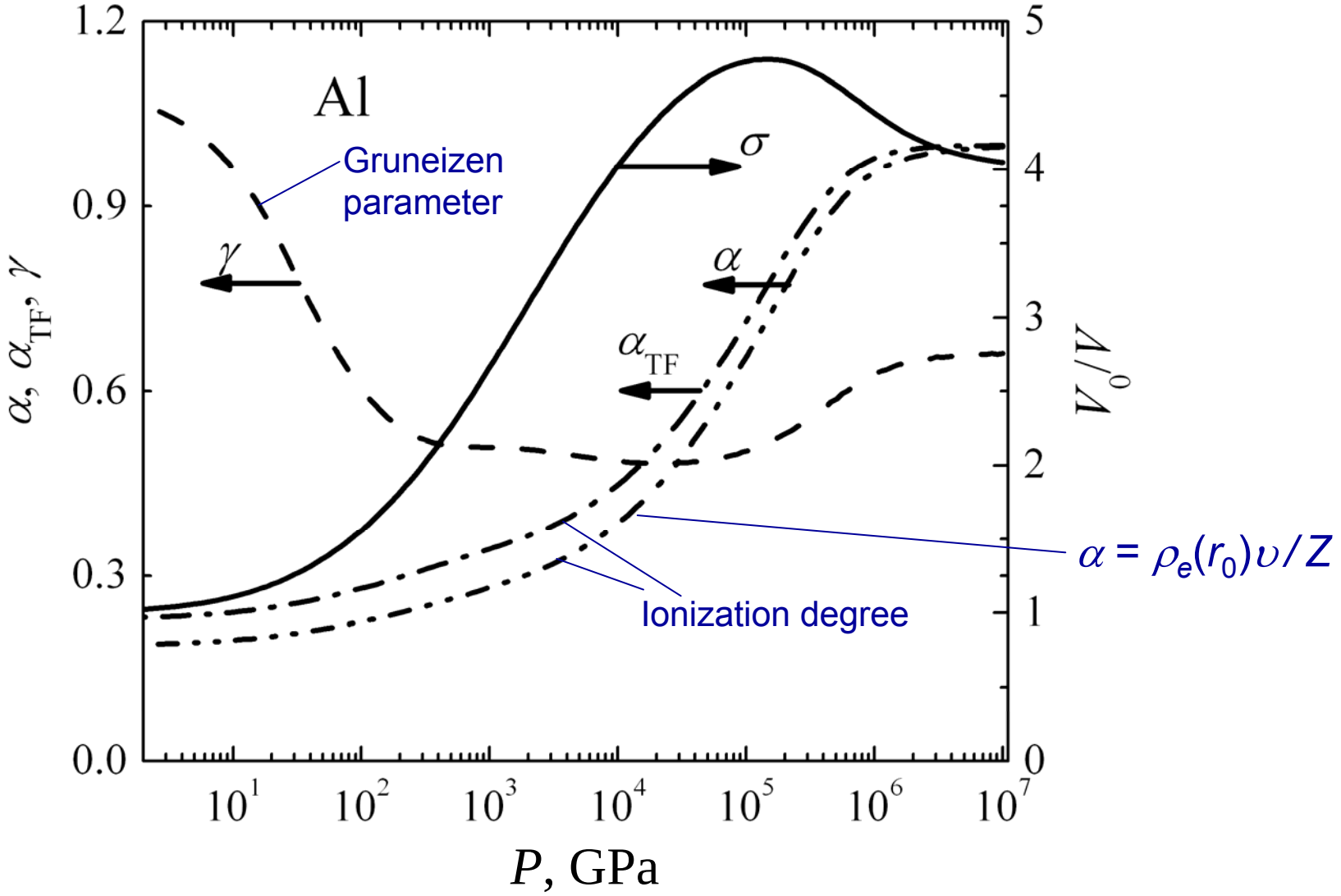
Phase shift



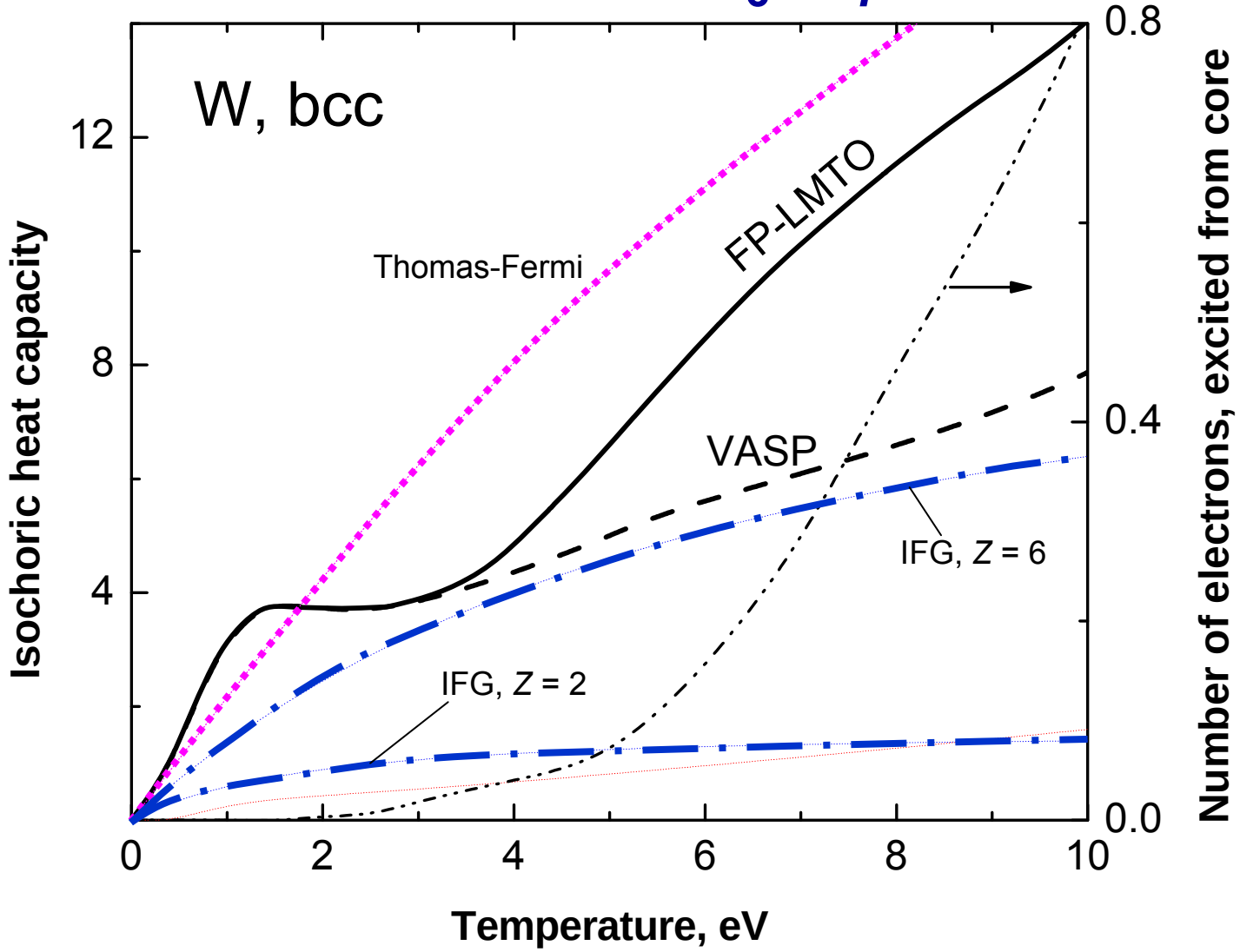
Conclusions

- DFT is a useful tool for t calculations of thermodynamic and transport properties of metals
- Thermal contribution of electrons to semiempirical EOSs can be replaced by expressions from average atom models (without fitting parameters)
- DFT gives reliable results for dielectric function in liquid and dense plasma at low temperatures; higher temperatures require huge computational efforts
- Other values (thermal conductivity, electron-ion exchange) should be investigated with DFT

Compression Ratio, Gruneizen Parameter and Mean Degree of Ionization on the Shock Hugoniot of Al

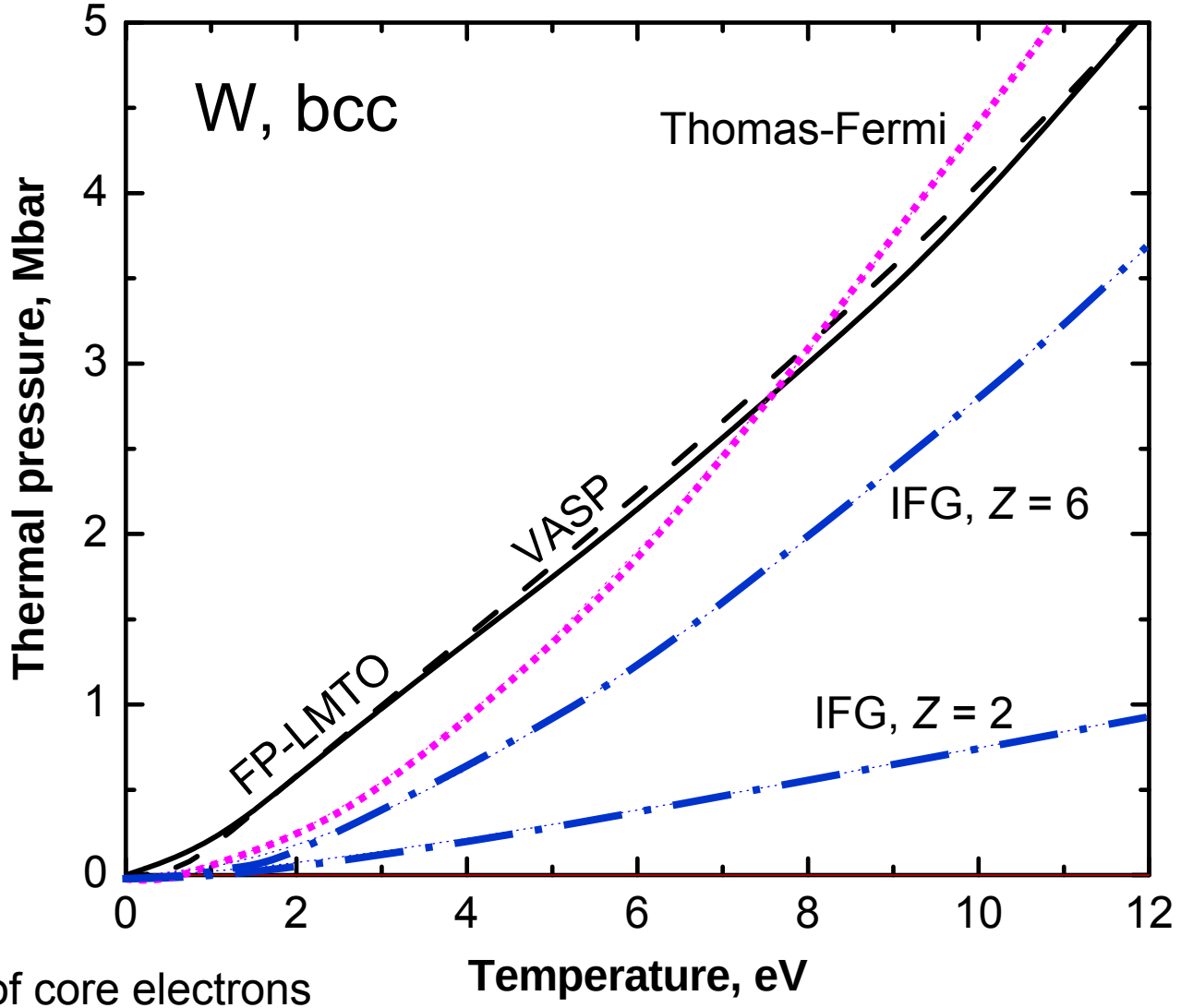


Electron heat capacity of W, isochore $V = V_0$, $T_i = 0$



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

Electron thermal pressure of W, isochore $V = V_0$, $T_i = 0$

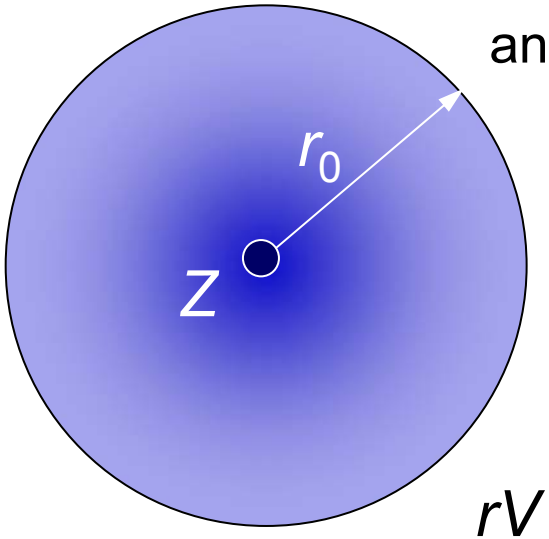


Excitation of core electrons has weak influence on pressure

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

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:

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

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

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

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

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

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TF Potential and its Derivatives on μ, υ and T

Poisson equation

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

Derivative of the Poisson equation on υ:

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

Derivative on μ:

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

Derivative on T:

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

Thermal Contribution of Electrons into TF

At $\mu / T \le 1$:

$$F_T(V,T) = F(V,T) - F(V,0)$$

At $\mu / T >> 1$:

For $(F_T)'_T$, $(F_T)'_{TV}$, $(F_T)'_{TT}$ Poisson equations are solved at low T for the TF potential and its derivatives

<u>For other derivatives asymptotic expressions are used</u>

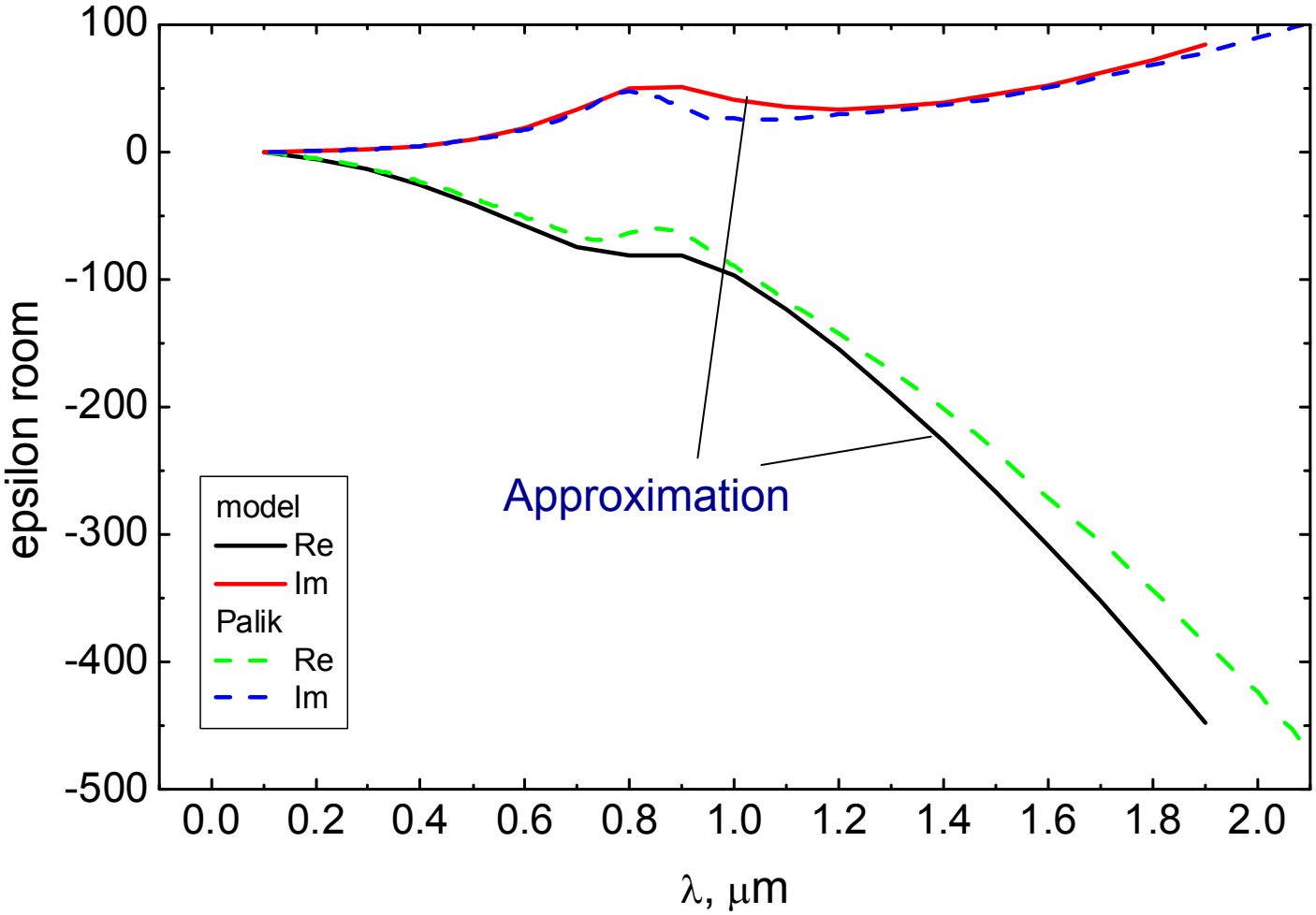
$$\begin{cases} F_T = F_T^* \left(T/T^*\right)^2 \\ E_T = E_T^* \left(T/T^*\right)^2 \\ (F_T)'_V = (F_T^*)' \left(T/T^*\right)^2 \\ (F_T)''_{VV} = (F_T^*)''_{VV} \left(T/T^*\right)^2 \end{cases}$$

Values with * are taken at $\mu^* / T^* = 1000$

<u>For the energy</u> we use the expression

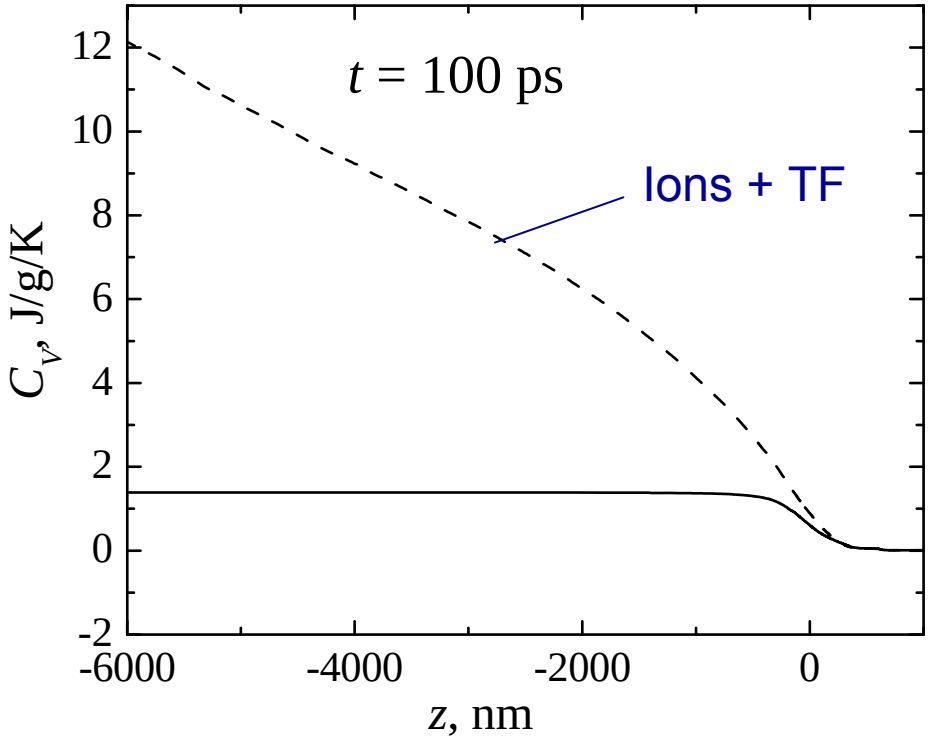
$$E_T = E(V,T) - E(V,0) = \int_0^T T_1 S'_T(V,T_1)\, dT_1$$

Permittivity of Al at normal conditions

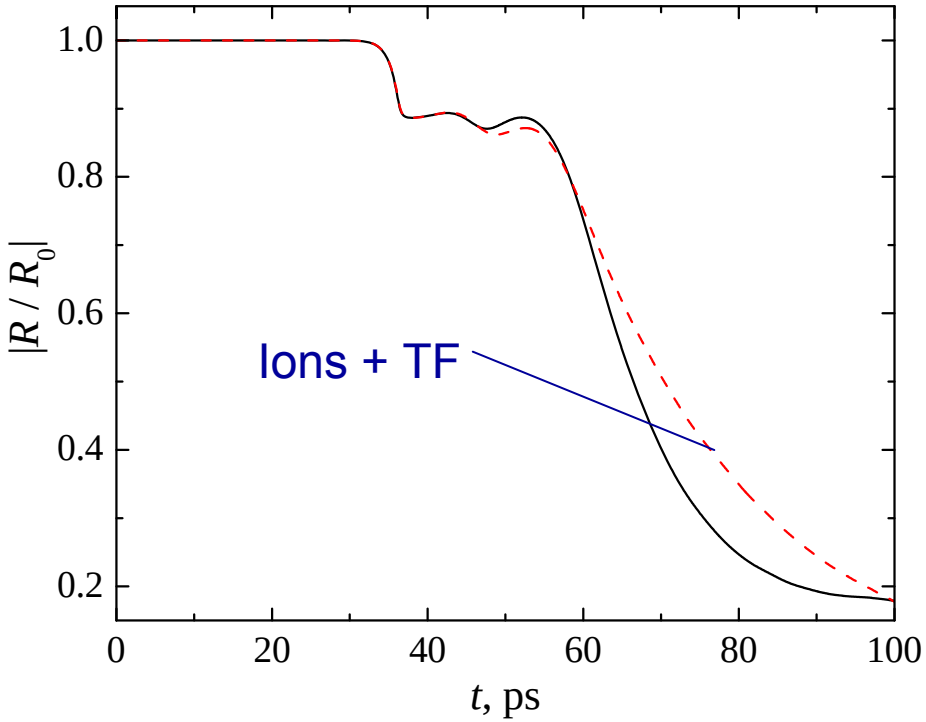


Influence of EOS

Electronic heat capacity



Reflection coefficient



Difference in electronic heat capacity leads to up to 30% difference in reflection coefficient