Theoretical Equations of State for Metals at High Energy Densities

- EOS definition & motivation
- Phase diagram:
  - theories of solid, liquid, plasmas
  - experiments: static & dynamic
- Wide-range multi-phase EOS for metals
  - semi-empirics origin – quasiharmonic model
  - EOS model, construction of EOS for U
- EOS accuracy
- High pressure, high temperature melting & evaporating
- Regularities: IEX vs. shockwave data & Birch law
- EOS applications
  - expert calculations
  - melting & evaporating in shock-wave processes
  - isochoric heating – high-entropy states
  - shock wave stability

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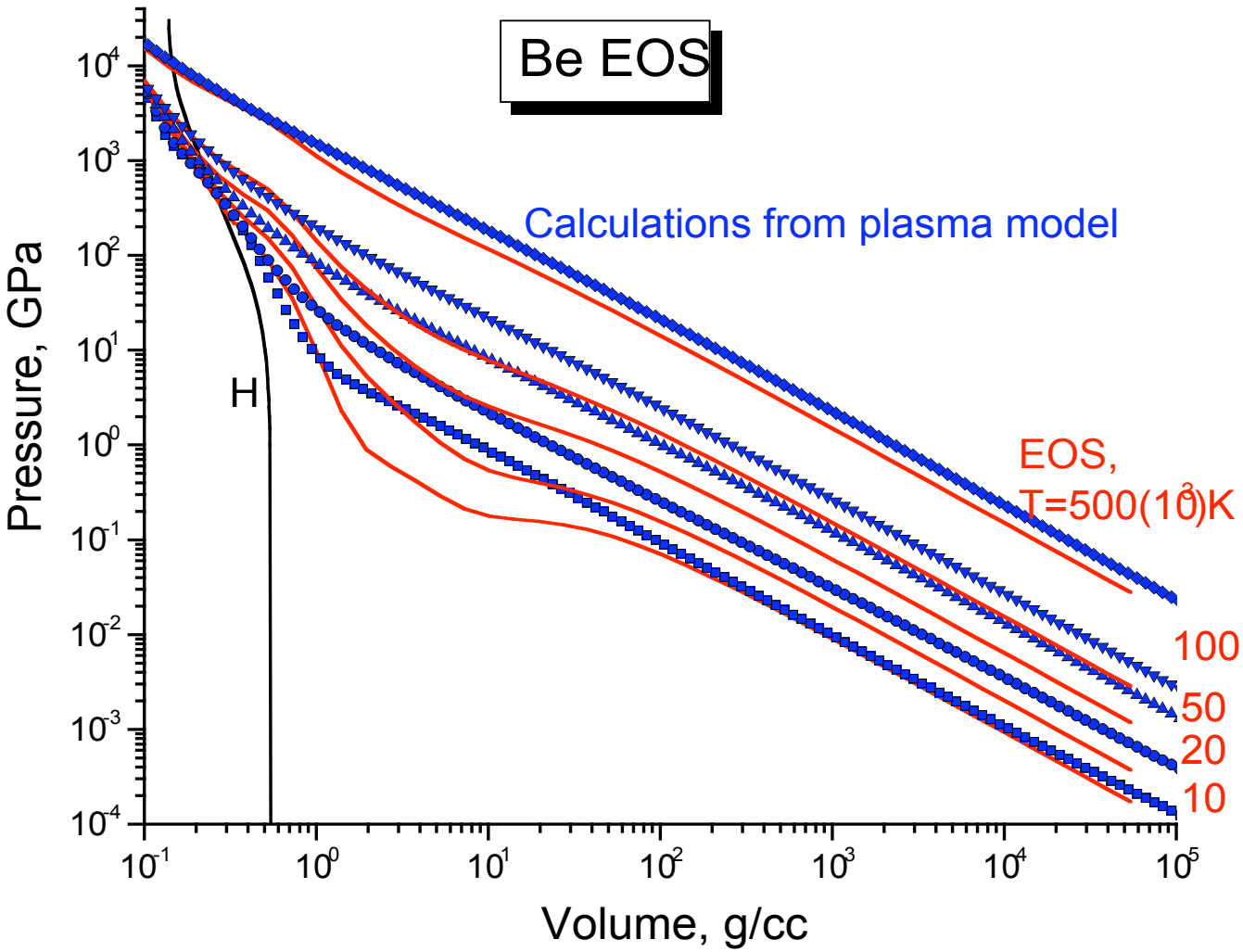
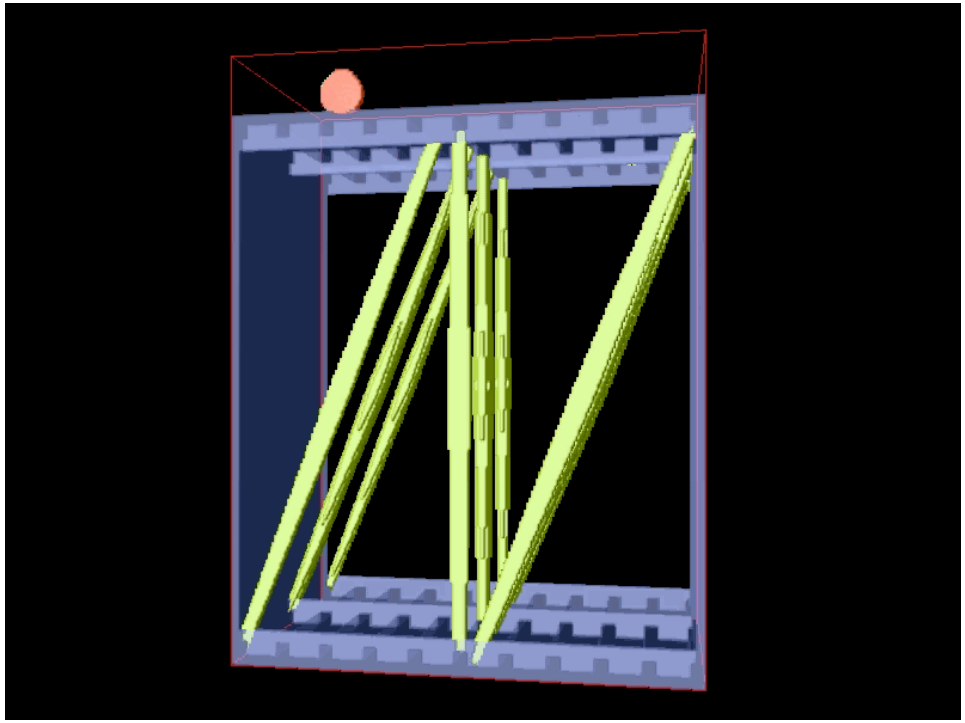
EOS - fundamental property of matter, defining its thermodynamic, mechanic,… as functional form *f(x,y,z)*=0 (V,T,P,…) or tables or graphs.



Motivation

- Fundamental properties
- R&D at high pressure
- Geophysics, planets
- Numerical modeling:

  ICF, hypervelocity impacts, …



EOS information: summary

Theory:

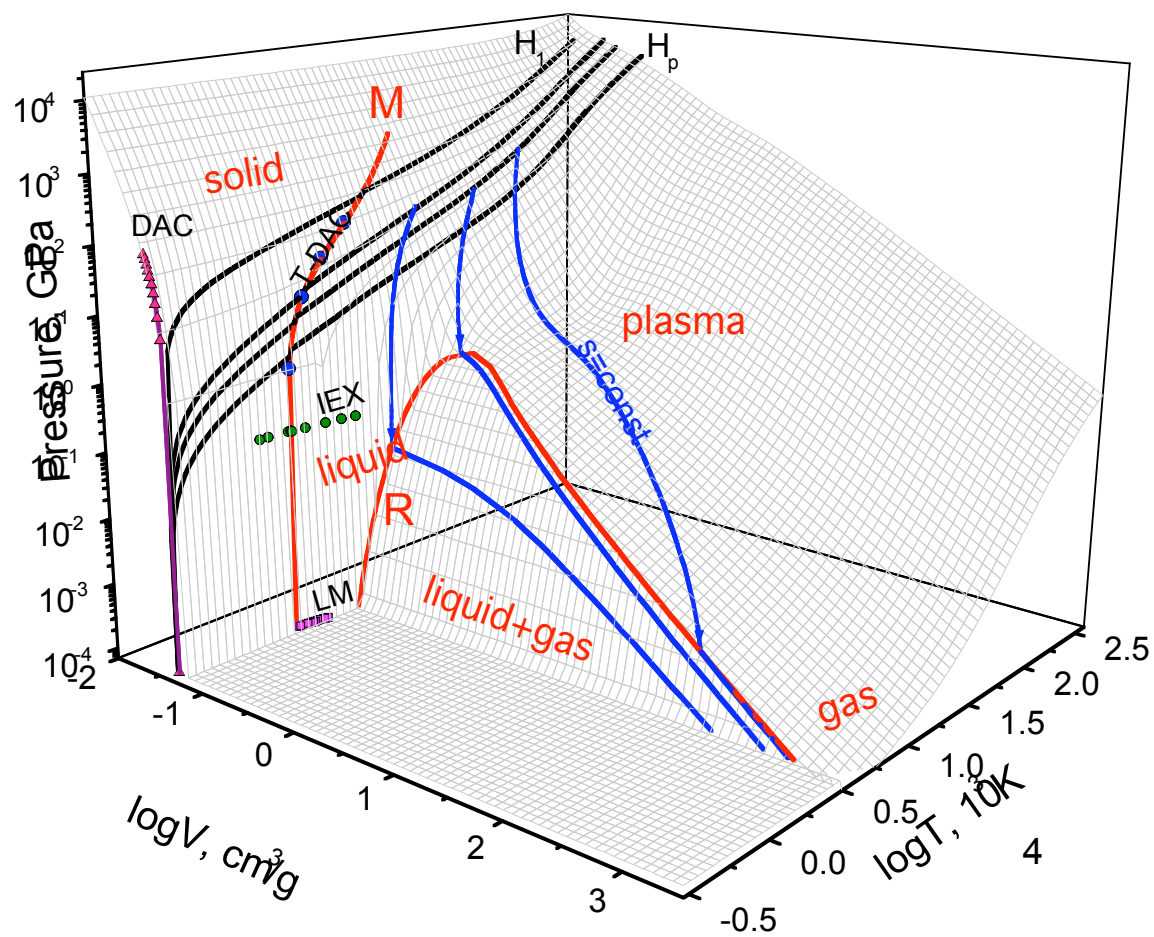
solid (T=0 K) band structure
liquid
plasmas

Experiment:

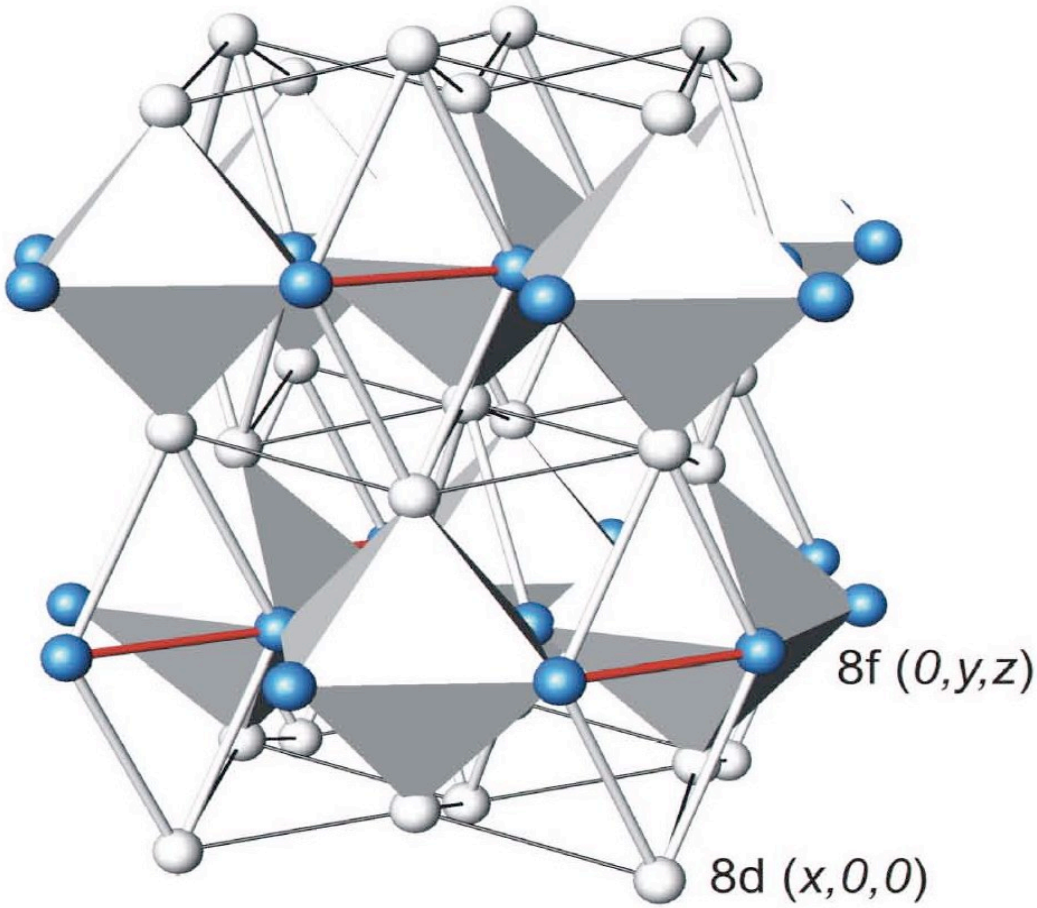
DAC, T-DAC P(V,T=const)
LM - ρ(T,P=1 bar)
IEX - H, E, Cs, T, V (P=const)
H_1 - P,V, E, T
s=const - P, U, T

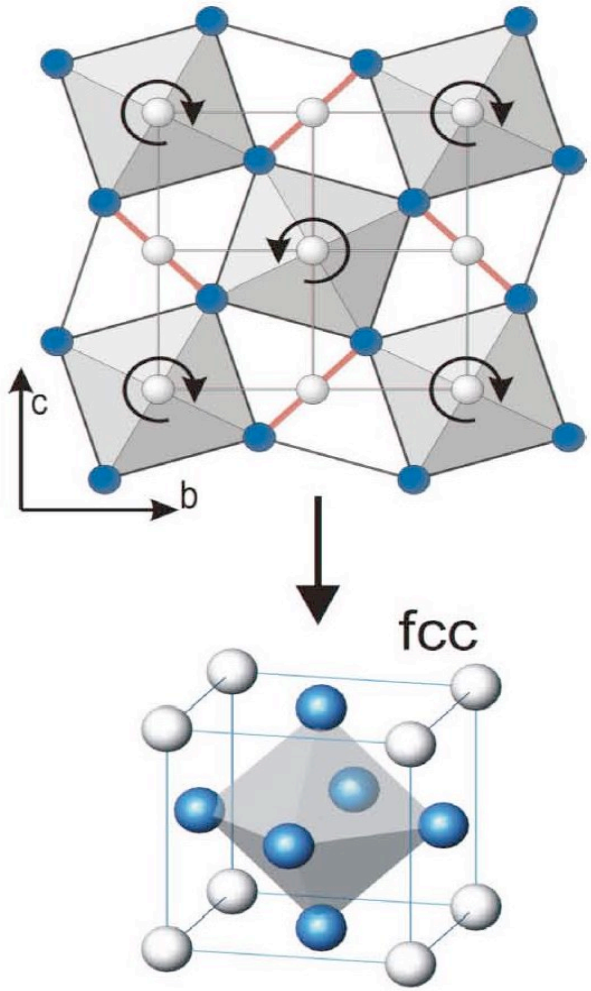
H_1, H_p - P,V, E (Cs)
s=const - P,U

P(V,T) - Uranium

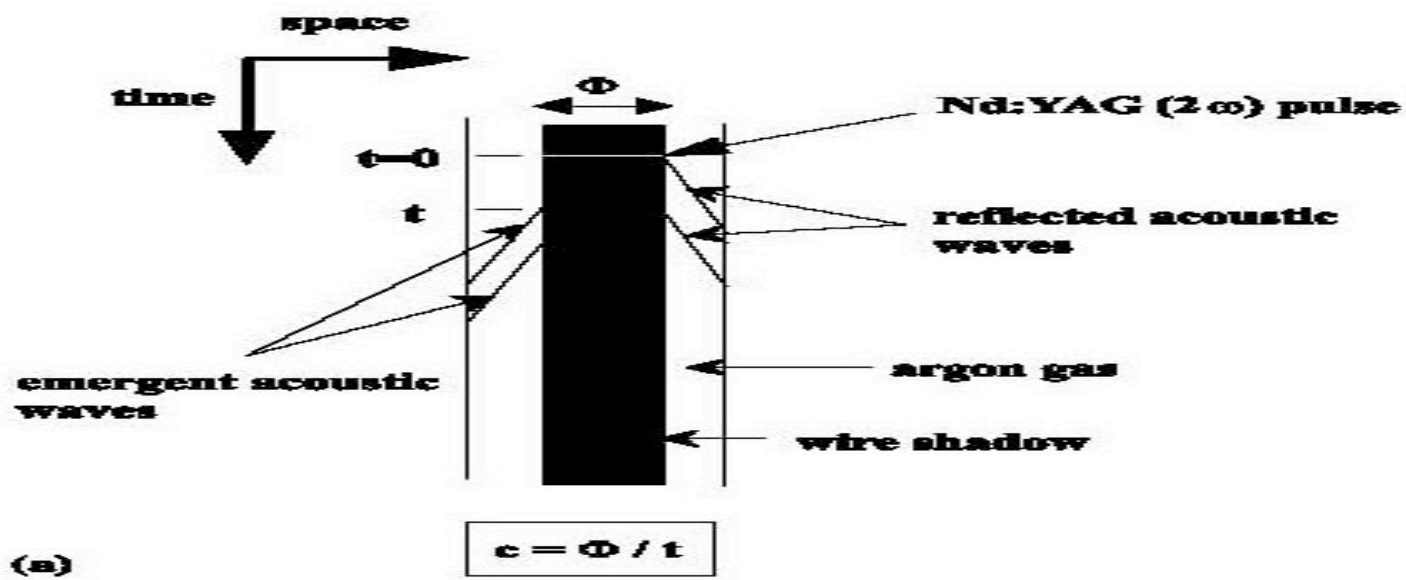


Experiment: static

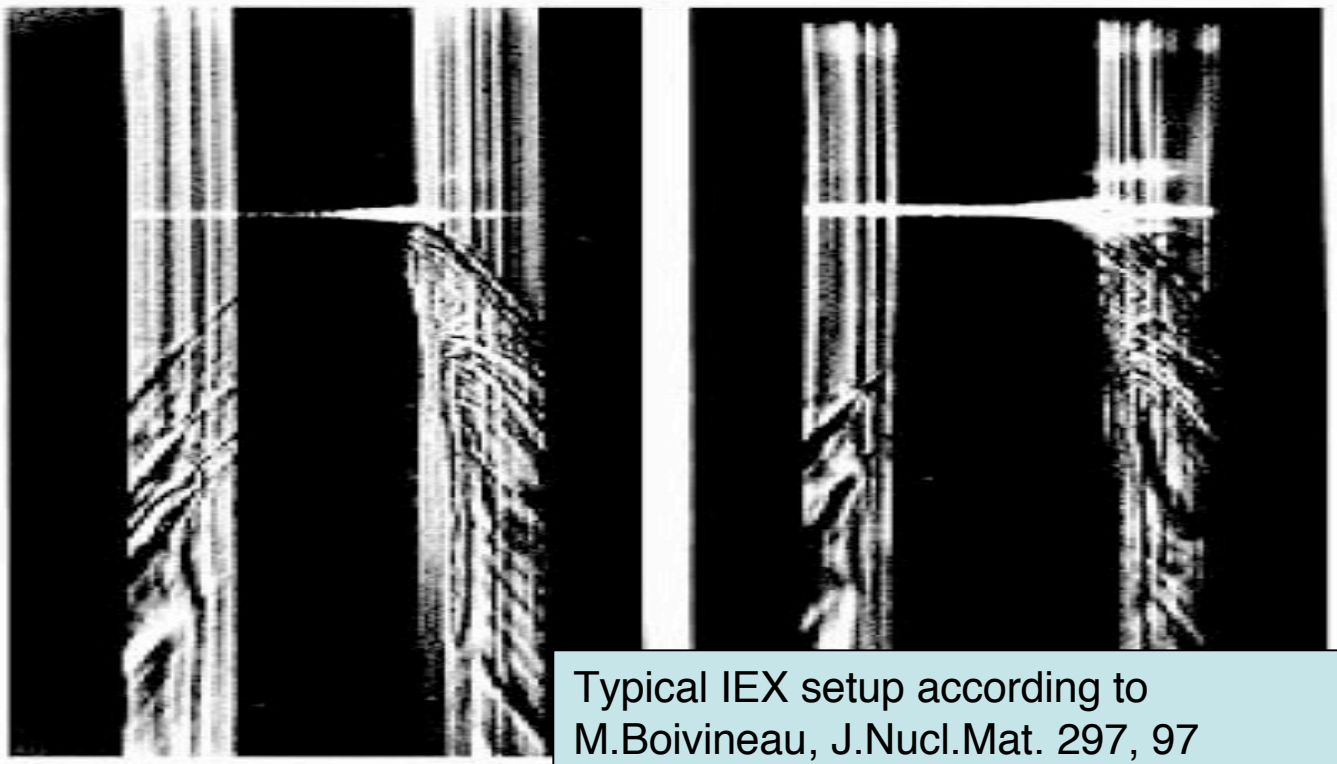




Angle dispersion and structure of Cs-V according to K.Syassen, Proceed. Enrico Fermi School - 2003

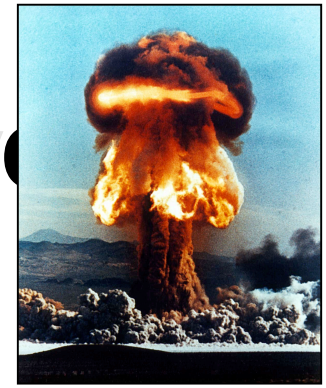


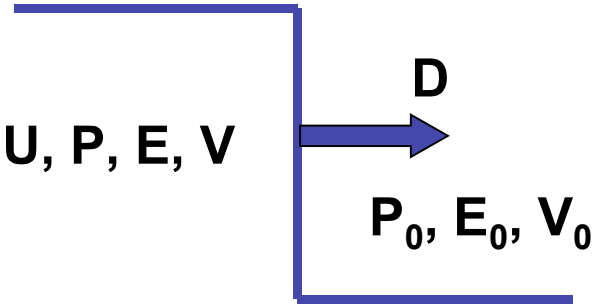
(a)



Typical IEX setup according to M.Boivineau, J.Nucl.Mat. 297, 97 (2001)

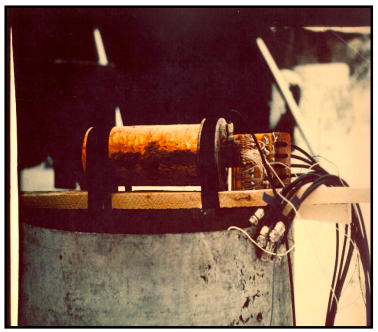
Experiment: shock wave





shock compression

Lasers



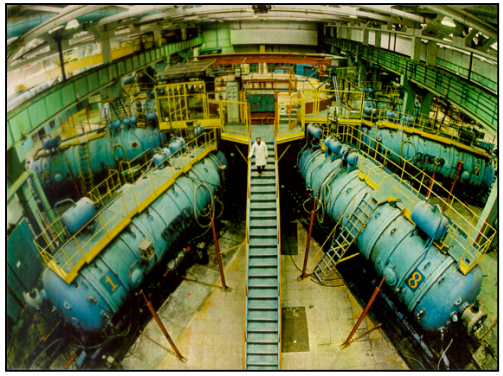
HE gun

Hugoniot relations:

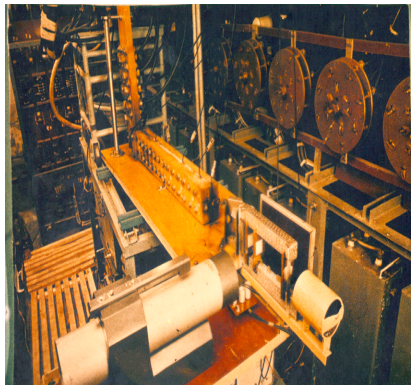
$$V_0/V = D/(D-U)$$

$$P = P_0 + DU/V_0$$

$$E = E_0 + 1/2(V_0 - V)(P_0 + P)$$

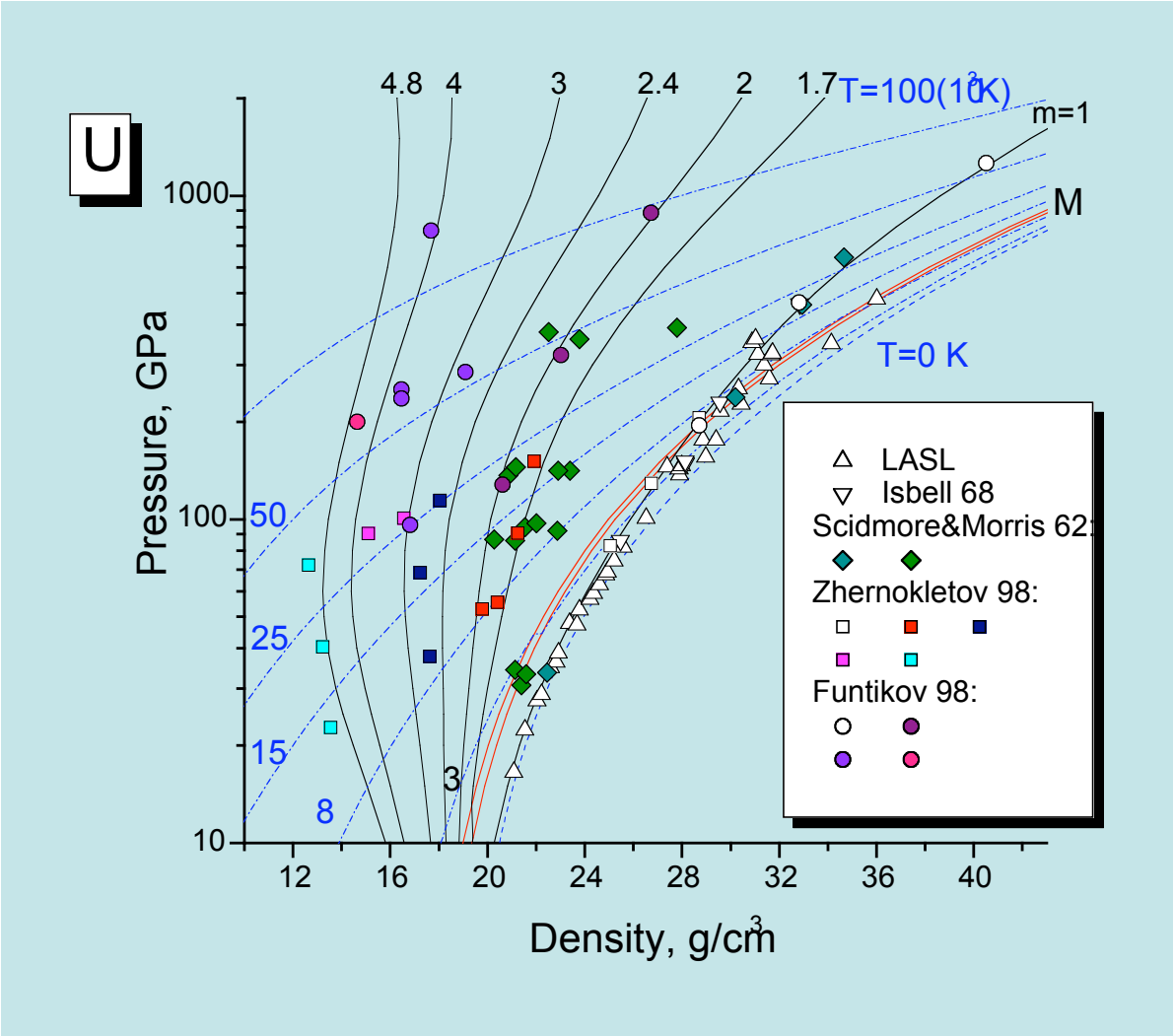


Z-pinch

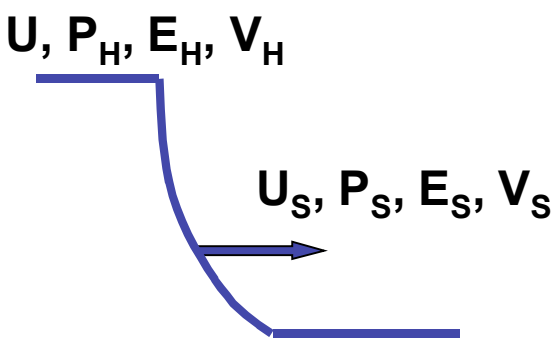


Railgun

Experiment: shock waves



Experiment: shock waves

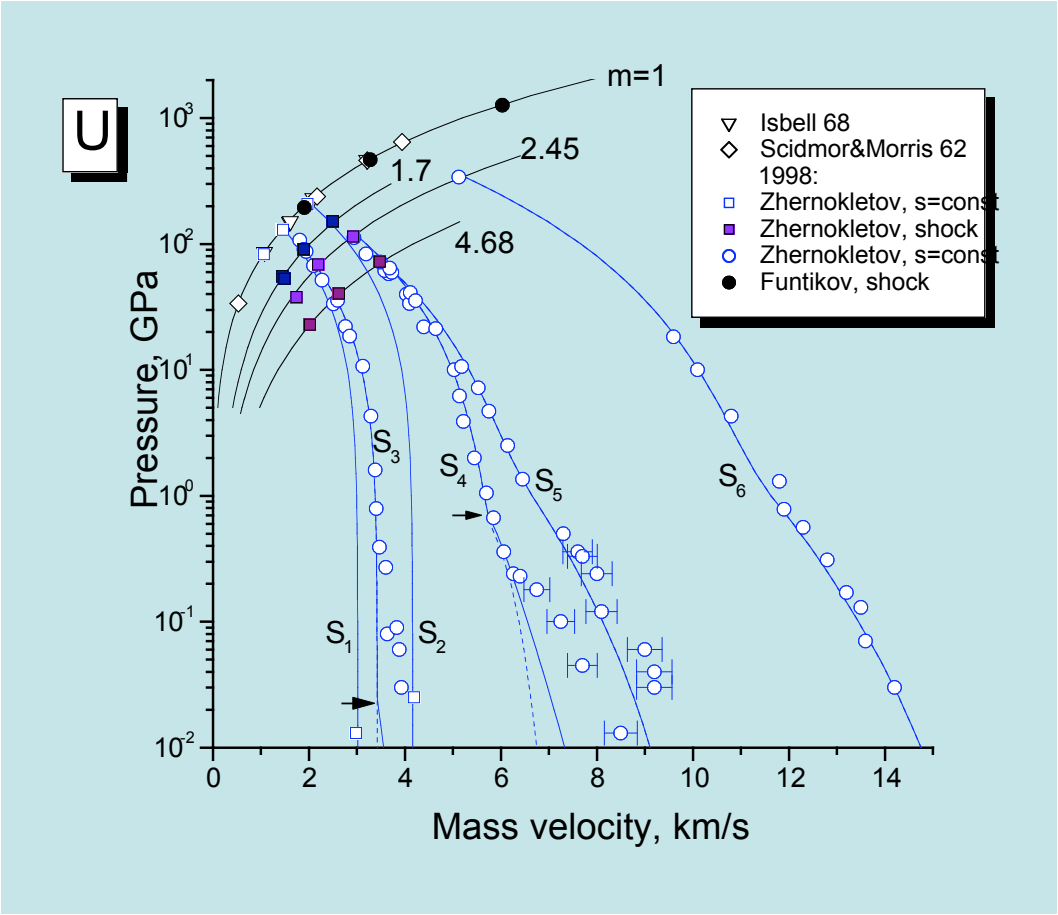


adiabatic expansion

Riemann invariants:

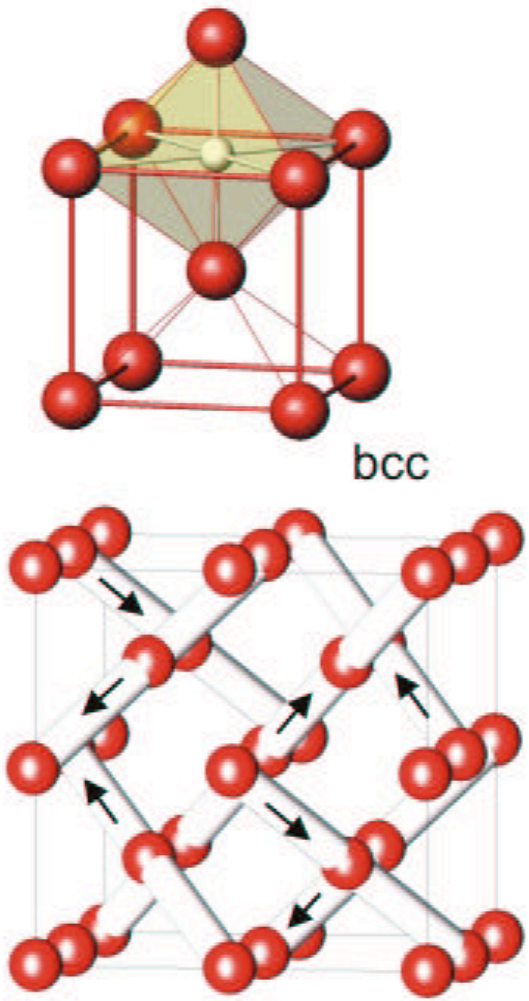
$$V_s = V_H + \int_{P_S}^{P_H} (dU/dP)^2 \, dP$$

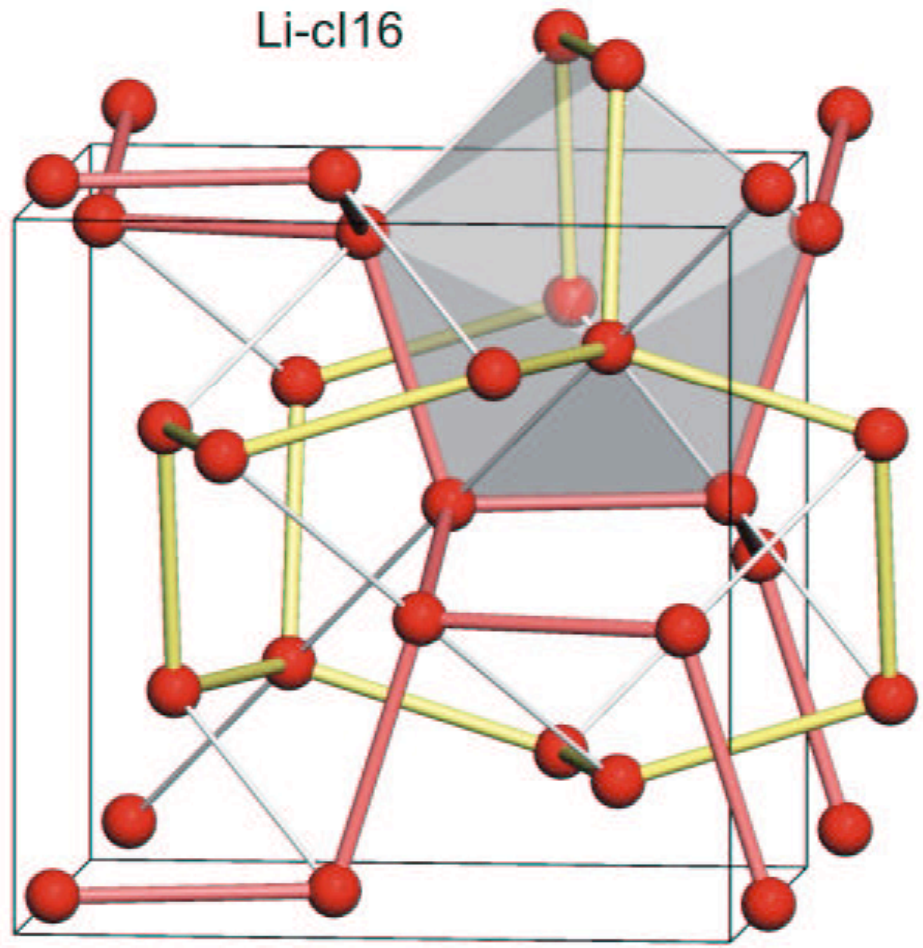
$$E_s = E_H - \int_{P_S}^{P_H} P (dU/dP)^2 \, dP$$



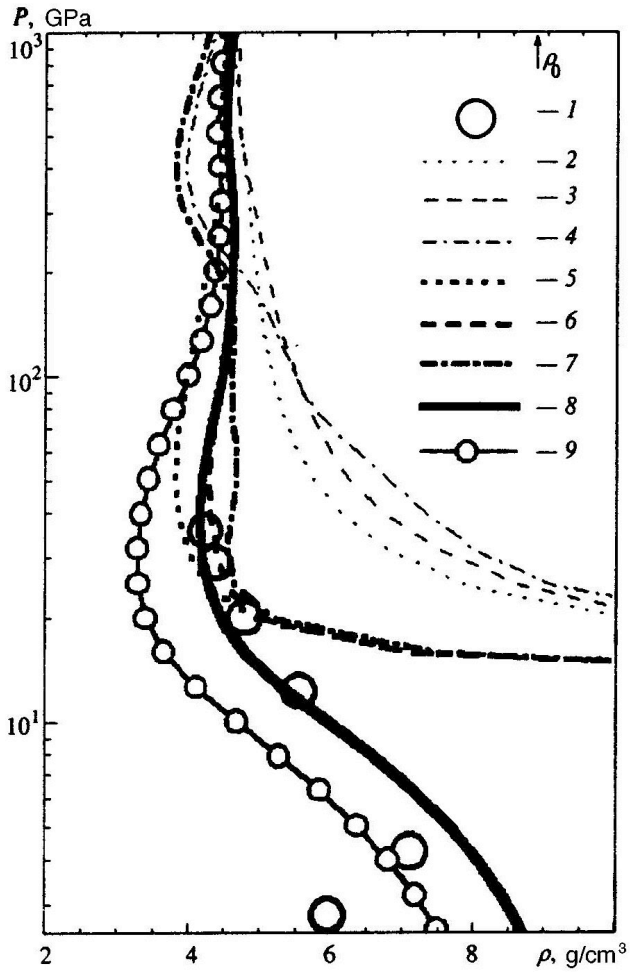
Theory: solid st

Li structures according to M. Hanfland, K. Syassen, N. E. Christensen, D. L. Novikov, Nature 408, 174 (2000)





Theory: liquid & plasmas



s.

"Chemical"model of plasmas

$$\sum \mu_j = 0$$

$$\left(\partial F(V,T,\{N_j\}/\partial N_k\right)_{V,T} = 0$$

$$F(V,T,\{N_j\}) = F_k + F_d + F_c + F_l$$

Calculated shock adiabat of porous Ni by Fortov et al.

JETP, 87, 678 (1998)

EOS information: summary

	Physical properties	Limitations
Theory: solid (T=0 K, final T), liquid, plasmas	structure, thermodynamics	different approaches local applicability
Experiment: DAC, T-DAC LM IEX $H_1 - H_p$ (Hugoniot) s =const	 structure, P(V,T=const) ρ(T,P=1 bar) H, E, Cs, T, V (P=const) P,V, E, Cs, T P, U, T	 thermal-strength, P<3 Mbar --- * ---, T<3500 K --- * ---, P<4 kbar, T<8000 K final density (physics)

EOS problems

Insufficient theoretical basis:

- best integral equation in plasma&liquid (hypernetted, BGY, PY,…)?
- critical point's evaluations
- pair (triple) potential in plasma&liquid?
- quantum many-bodies problem

Lack of experimental data:

- H_1 for most metals E(P,V)
- ρ(T) at 1 bar
- s=const - P(U) - E(P,V)
- IEX - H,E,Cs,T(P=const)

Semiempirical EOS

Quasi-harmonical model:

3N harmonic oscillators - ω_i(V), thermal energy and pressure

$$E_a(V,T)=\sum_{i=1}^{3N}\frac{\hbar\omega_i(V)}{\exp\left(\hbar\omega_i(V)/kT\right)-1}$$

$$p_a(V,T)=\sum_{i=1}^{3N}\frac{\gamma_i}{V}\frac{\hbar\omega_i(V)}{\exp\left(\hbar\omega_i(V)/kT\right)-1}$$

$$\gamma_i=-\frac{d\ln\omega_i}{d\ln V}$$

$$p_a(V,T)=kT\sum_{i=1}^{3N}\ln\left[1-\exp\left(-\hbar\omega_i/kT\right)\right]$$

$$F_a(V,T)=kT\int Z(\omega)\ln\left[1-\exp\left(-\hbar\omega_i/kT\right)\right]d\omega$$

$$Z(\omega)=\begin{cases}\frac{\omega^2}{2\pi}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right), & \omega\le\omega_D\\ 0, & \omega>\omega_D\end{cases}$$

$$\omega_D=V\int_0^{\omega_D}Z(\omega)d\omega$$

$$F_a(V,T)=RT\left\{3\ln\left(1-\exp\left(-\theta_D/T\right)\right)-D(\theta_D/T)\right\}$$

$$p_a(V,T)=\frac{\gamma(V)}{V}3RTD(\theta_D/T),$$

$$E_a(V,T)=3RTD(\theta_D/T),\qquad \theta_D=\hbar\omega_D/k$$

$$D(x)=\frac{3}{x^2}\int_0^x\frac{t^3}{e^t-1}dt\qquad \gamma=-\frac{d\ln\theta_D}{d\ln V}$$

$$\theta_D\approx 100\div 300K$$

$$F_a(V,T)=3RT\ln(\theta_D/T)$$

$$p_a(V,T)=\frac{\gamma(V)}{V}3RT$$

$$E_a(V,T)=3RT$$

Mie-Gruneisen EOS

$$p(V,E) = p_c(V) + \frac{\gamma(V)}{V}\left[E - E_c(V)\right]$$

EOS

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

Gruneisen gamma

$$\gamma \times \rho = cons$$

$$\gamma(V) = \frac{t-2}{3} - \frac{V}{2}\frac{\left(p_c V^{2t/3}\right)_{VV}}{\left(p_c V^{2t/3}\right)_V}$$

$$t = \begin{cases} 0, & \text{Slater–Landau} \\ 1, & \text{Dugdal–McDonald} \\ 2, & \text{Vashenko–Zubarev} \end{cases}$$

T=0K potentials

$$p_c^B(V) = B\left(\sigma_c^{7/3} - \sigma_c^{5/3}\right)\left[1 - \beta\left(\sigma_c^{2/3} - 1\right)\right] \quad \text{Birch}$$

$$p_c^M(V) = A\sigma_c^{2/3}\left[\exp\left\{2\alpha\left(1-\sigma_c^{-1/3}\right)\right\} - \exp\left\{\alpha\left(1-\sigma_c^{-1/3}\right)\right\}\right] \quad \text{Morse}$$

$$p_c^{BM}(V) = Q\left[\sigma_c^{2/3}\exp\left\{q\left(1-\sigma_c^{-1/3}\right)\right\} - \sigma_c^{4/3}\right] \quad \text{Born-Mayer}$$

Anharmonic atoms

$$\Delta F_a(V,T) = \frac{3RT}{2}\ln(1+z) \quad z = \frac{lRT}{c_c^2}$$

$$F_a(V,T) = \begin{cases} 3RT\ln\dfrac{\theta_D(V)}{T}, & z \approx 0 \quad cr. \\ \dfrac{3RT}{2}\ln\dfrac{\sigma^{2/3}}{T}, & z \to \infty \quad i.g. \end{cases}$$

Melting (Grover)

$$C_{VL} = C_{VS} - 1.5R\frac{\alpha\tau}{\alpha+\tau}$$

$$E_l(V,T) = E_s(V,T) + RT_m$$

$$\left\{\frac{\Delta S_m}{R} - \frac{3\alpha}{4} + 1.5\tau\left[\frac{\ln(1+\alpha\tau)}{\alpha\tau} - 1\right]\right\}$$

Thermal electrons

$$E_e(V,T) = \frac{\pi^2}{6}(kT)^2\nu(\varepsilon_F)$$

$$E_e(V,T) = (b^2/\beta)\ln ch(\beta T/b)$$

$$E_e(V,T) = \frac{\beta T^2}{2}\frac{T_F}{T_F + T\sigma^{-\gamma_e}}$$

$$F_e(V,T) = -\frac{\beta T^2}{2}\sigma^{-\gamma_e}$$

Multi-phase EOS

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

Solid

$$F_c^{(s)}(V) = 3V_{0c}\sum_{i=1,5}\frac{a_i}{i}\left(\sigma_c^{i/3}-1\right) \quad \sigma_c = V_{0c}/V$$

$$\sum_{i=1,5} a_i = 0 \quad \sum_{i=1,5} a_i\, i/3 = B_{0c} \quad \sum_{i=1,5} a_i (i/3)^2 = B'_{0c}$$

$$\sigma = 25 \div 500$$

$$\Re(x) = \sum_{n=1,N} g_n\left[1-\frac{P_c(a_i,\sigma_n)}{P_c^{TFC}(\sigma_n)}\right]^2 + \lambda\sum_{i=1,5} a_i +$$

$$+\mu\left(\sum_{i=1,5} a_i\, i/3 - B_{0c}\right) + \nu\left(\sum_{i=1,5} a_i (i/3)^2 - B'_{0c}\right)$$

$$F_a^{(s)}(V,T) = 3RT\ln\frac{\theta_c^{(s)}(V)}{T}$$

$$\theta_c^{(s)}(V) = \theta_{0s}\sigma^{2/3} *$$

$$\exp\left\{\frac{(\gamma_{0s}-2/3)(B_s^2+D_s^2)}{B_s}\, arctg\left[\frac{xB_s}{B_s^2+D_s(x+D_s)}\right]\right\}$$

$$x = \ln\sigma$$

Liquid

$$F_c^{(l)}(V) = 3V_{0c}\sum_{i=1,5}\frac{a_i}{i}\left(\sigma_c^{i/3}-1\right) \qquad \sigma_c \geq 1$$

$$F_c^{(l)}(V) = V_{0c}\left[A_c\frac{\sigma_c^m}{m} + B_c\frac{\sigma_c^n}{n} + C_c\frac{\sigma_c^l}{l}\right] + E_{sub} \qquad \sigma_c < 1$$

$$F_a^{(l)}(V,T) = F_t(V,T) + F_m(V,T)$$

$$F_t^{(l)}(V,T) = c_a(V,T)T\ln\frac{\theta^{(l)}(V,T)}{T}$$

$$c_a(V,T) = \frac{3R}{2}\left[1+\frac{\sigma T_a}{(\sigma+\sigma_a)(T+T_a)}\right] \quad \theta^{(l)}(V,T) = T_{sa}\frac{\left(T_{ca}\theta_c^{(l)}+T\right)\sigma_c^{2/3}}{T_{ca}+T}$$

$$\theta_c^{(l)}(V) = \theta_0^l \exp\left\{\frac{(\gamma_{0l}-2/3)(B_l^2+D_l^2)}{B_l}\, arctg\left[\frac{xB_l}{B_l^2+D_l(x+D_l)}\right]\right\}$$

$$F_m(V,T) = 3R\left\{\frac{2\sigma_m^2 T_{m0}}{1+\sigma_m^3}\left[C_m + \frac{2A_m}{5}\left(\sigma_m^{5/3}-1\right)\right] + (B_m - C_m)T\right\}$$

Thermal electrons

$$F_e(V,T) = -c_e(V,T)T \times \ln\left[1 + \frac{B_e(T)T}{2c_{ei}}\sigma^{-\gamma_e(V,T)}\right]$$

$$B_e(T) = \frac{2}{T^2}\int\left(\int_0^T \beta(\tau)d\tau\right)dT \qquad c_{ei} = \frac{3RZ}{2}$$

$$c_e(V,T) = \frac{3R}{2}\left[Z + \frac{\sigma_z T_z^2(1-Z)}{(\sigma+\sigma_z)(T^2+T_z^2)}\right]\exp\left[-\frac{\tau_i}{T}\right] \qquad \tau_i = T_i \exp(-\sigma_i/\sigma)$$

$$\beta(T) = \beta_i + \left(\beta_0 - \beta_i + \beta_m \frac{T}{T_b}\right)\exp\left[-\frac{T}{T_b}\right]$$

$$\gamma_e(V,T) = \gamma_{ei} + \left(\gamma_{e0} - \gamma_{ei} + \gamma_m \frac{T}{T_g}\right)\exp\left[-\frac{T}{T_g} - \frac{(\sigma-\sigma_e)^2}{\sigma\sigma_d}\right]$$

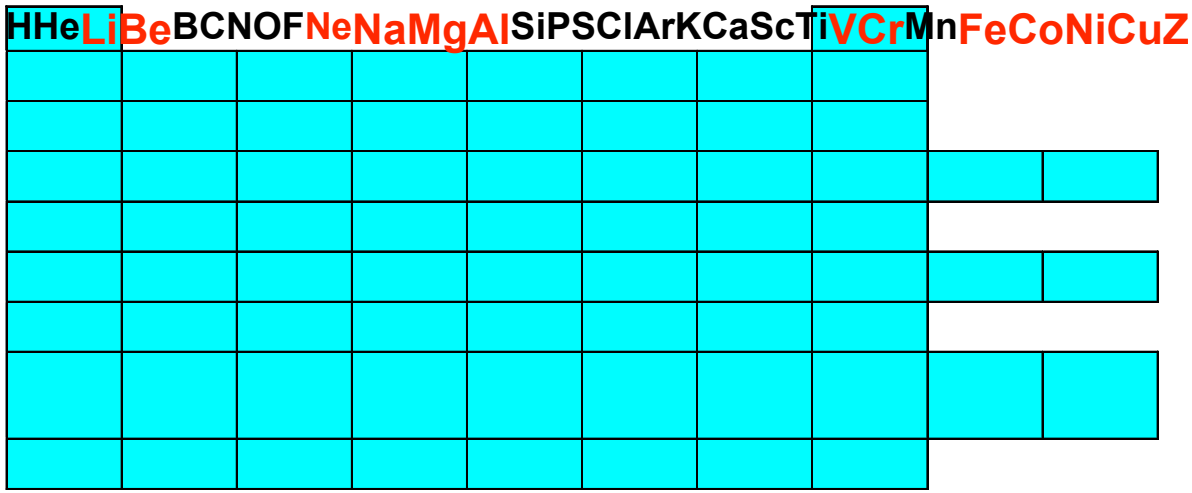
Asymptotes:

$$T << T_{Fermi} \quad F_e(V,T) = -\frac{\beta_0 T^2}{2}\sigma^{-\gamma_0} \qquad T \to \infty \quad F_e(V,T) = \frac{3RZ}{2}\ln\left(\sigma^{2/3} const' T\right)$$

MULTI-PHASE EOS

Free energy potential

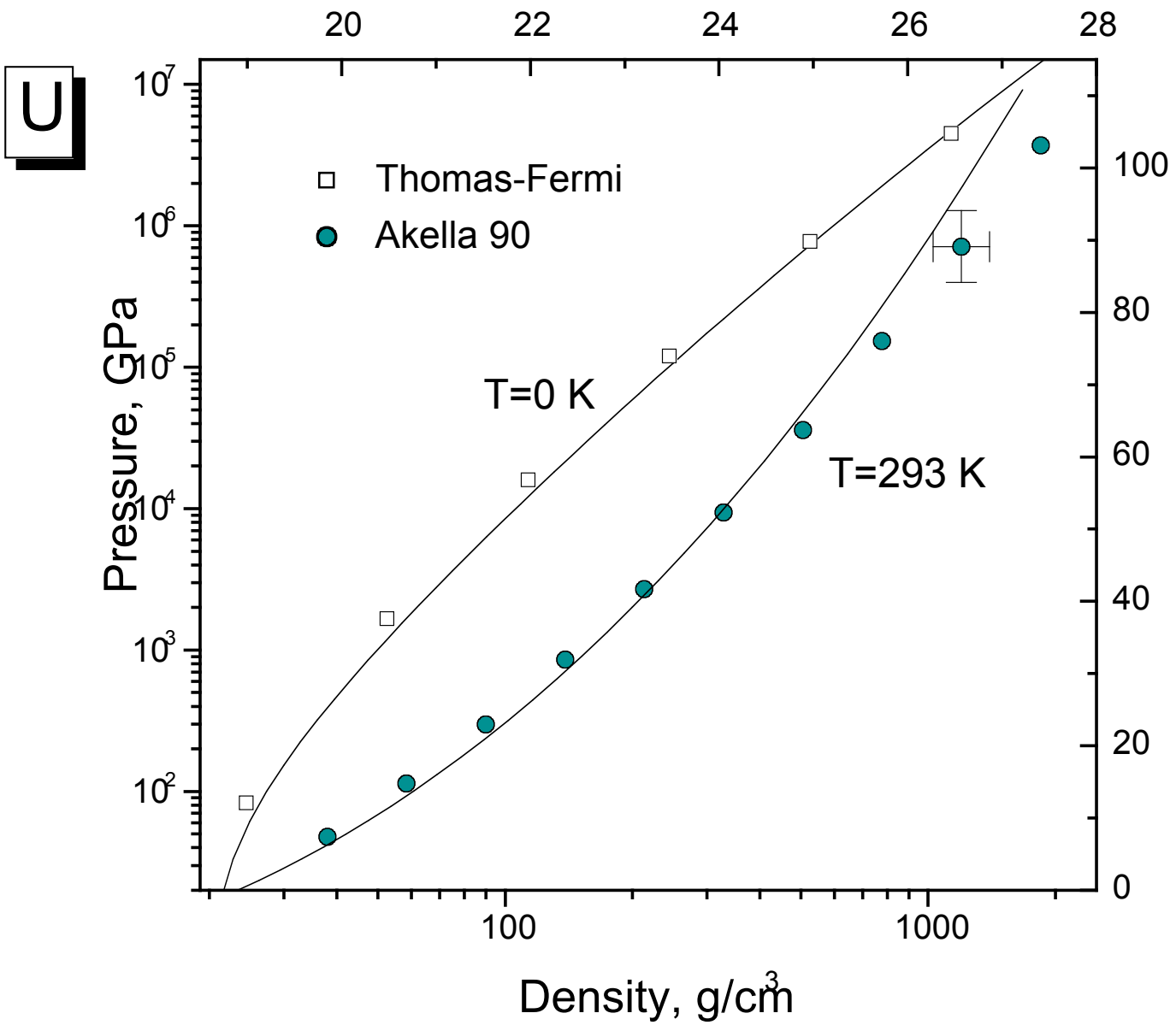
- Thomas-Fermi
- Debay model
- anharmonicity
- melting
- liquid phase Cv - MC
- ionization
- metal-insulator



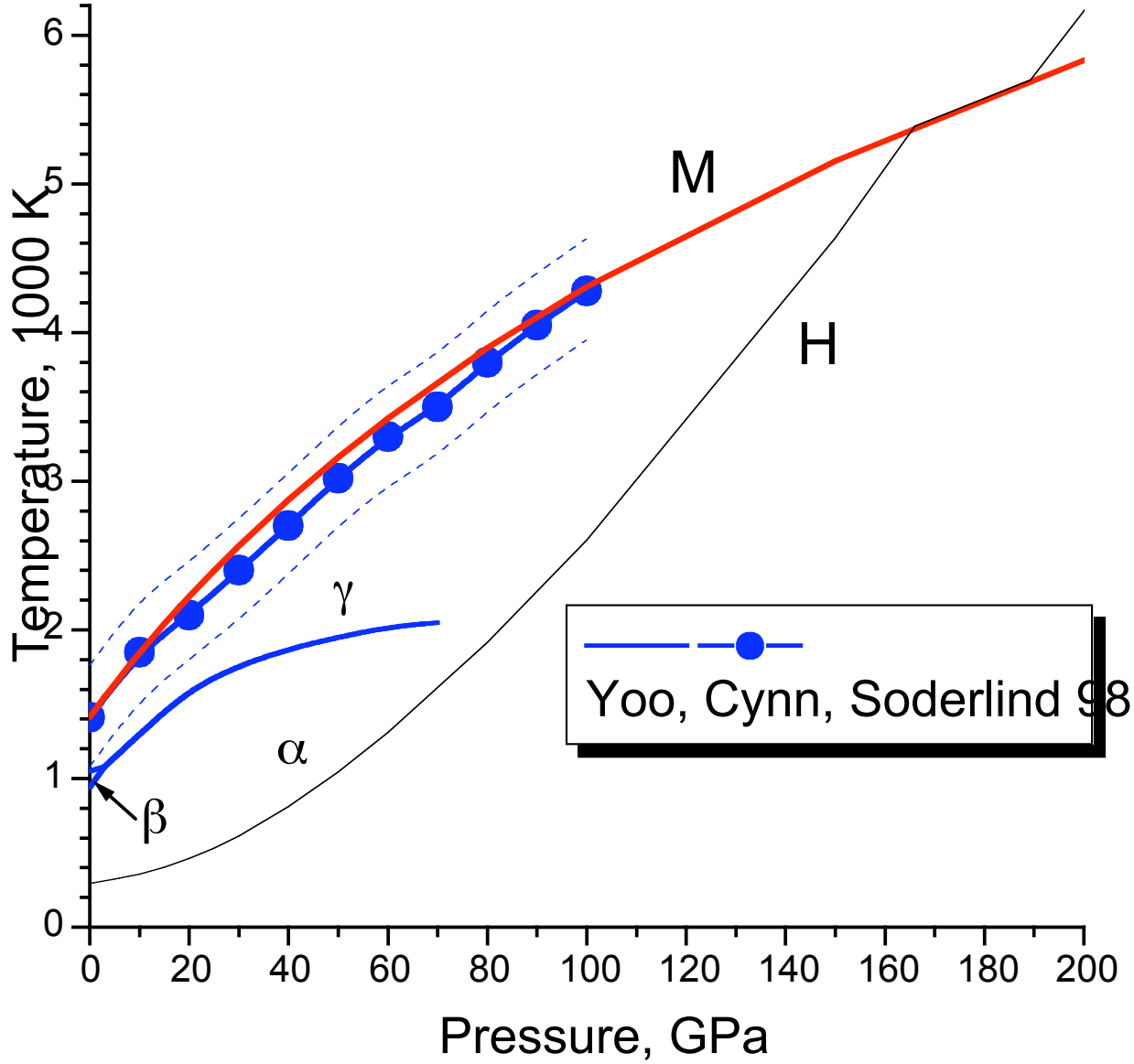
Solid, liquid, gas, plasma

- phase boundaries - melting, evaporation

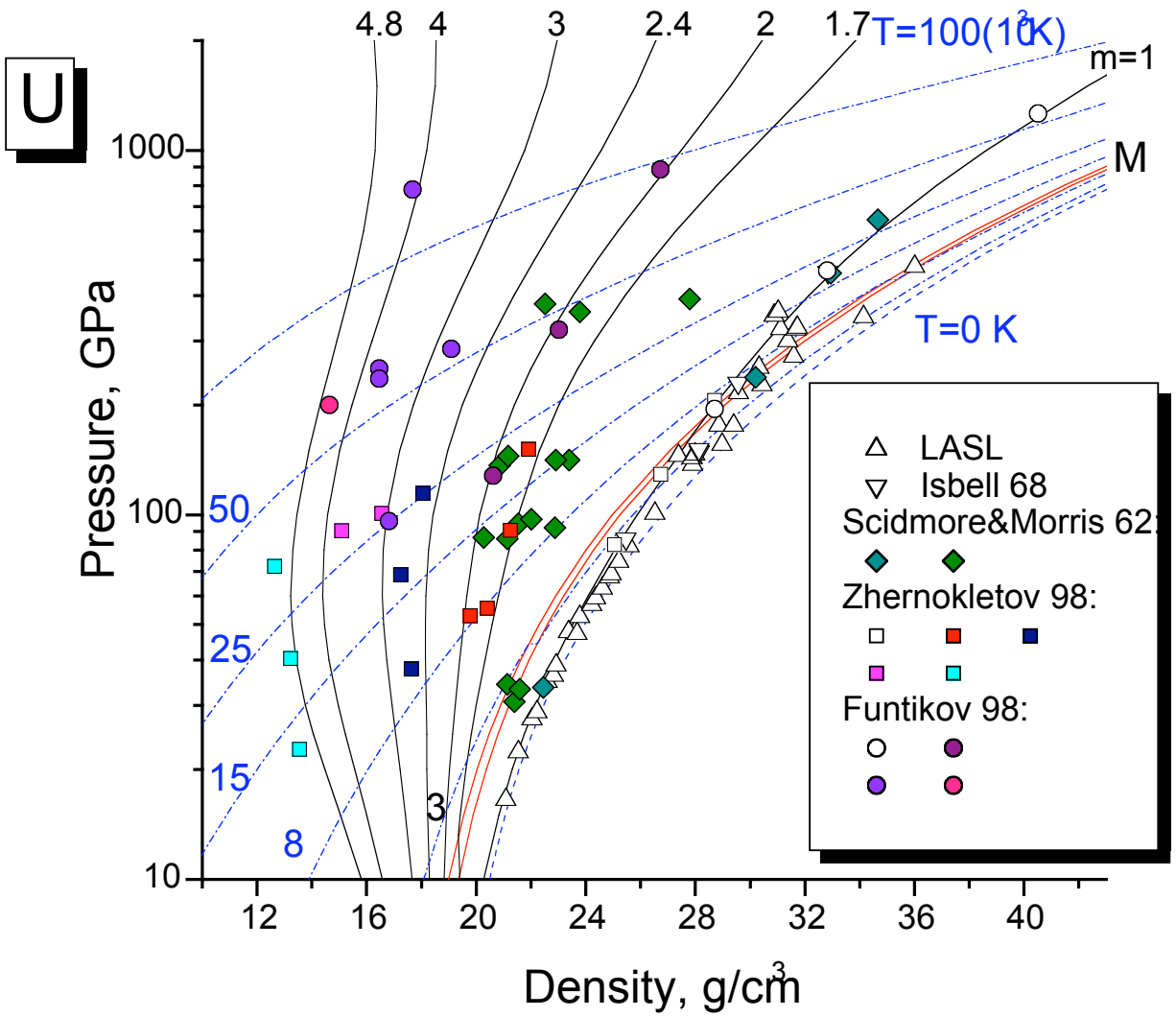
U AT T=0&293K


U
Thomas-Fermi
Akella 90
T=0 K
T=293 K
Pressure, GPa
Density, g/cm3
20
22
24
26
28
100
1000
0
20
40
60
80
100

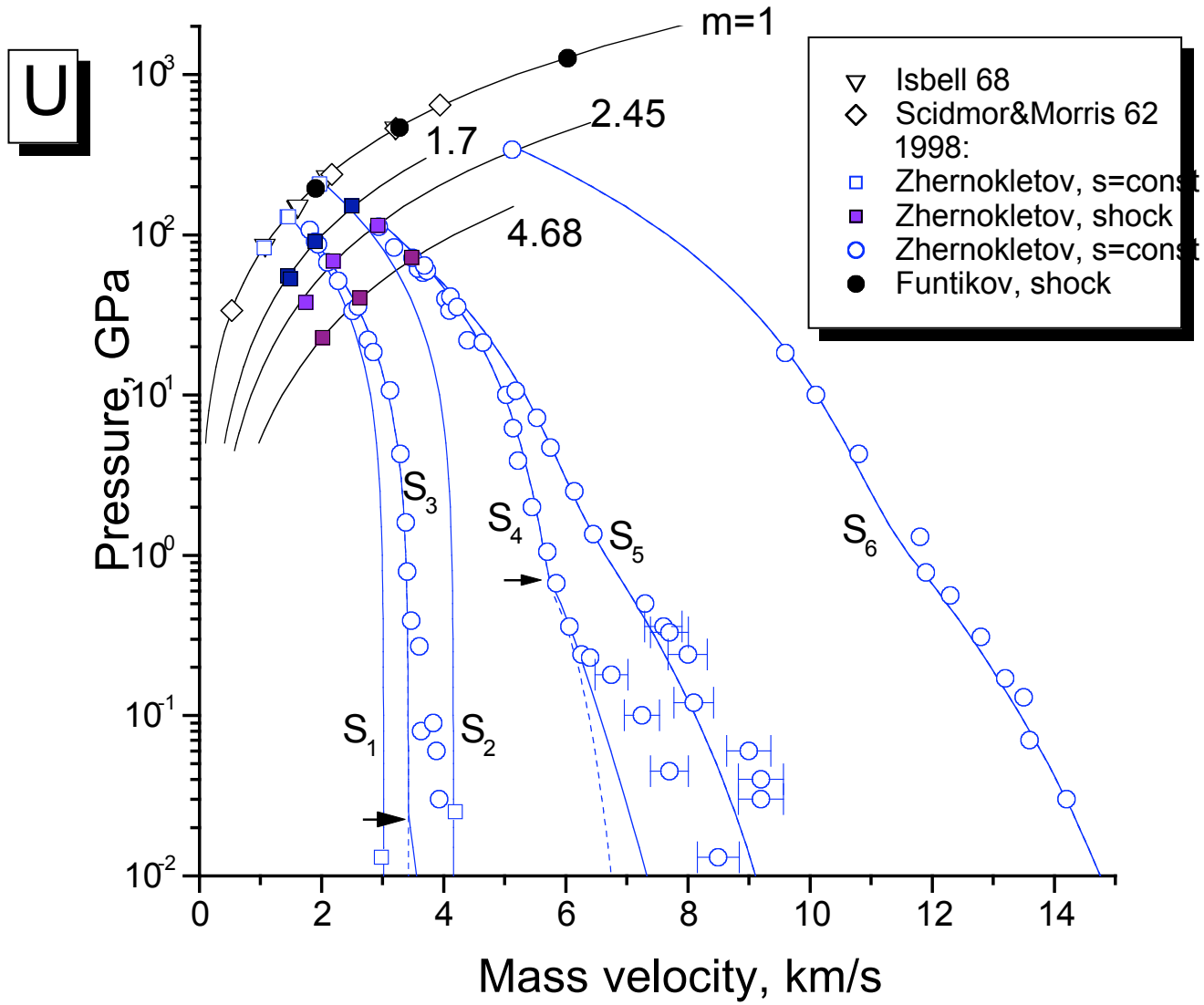
U P-T AT HIGH PRESSURE



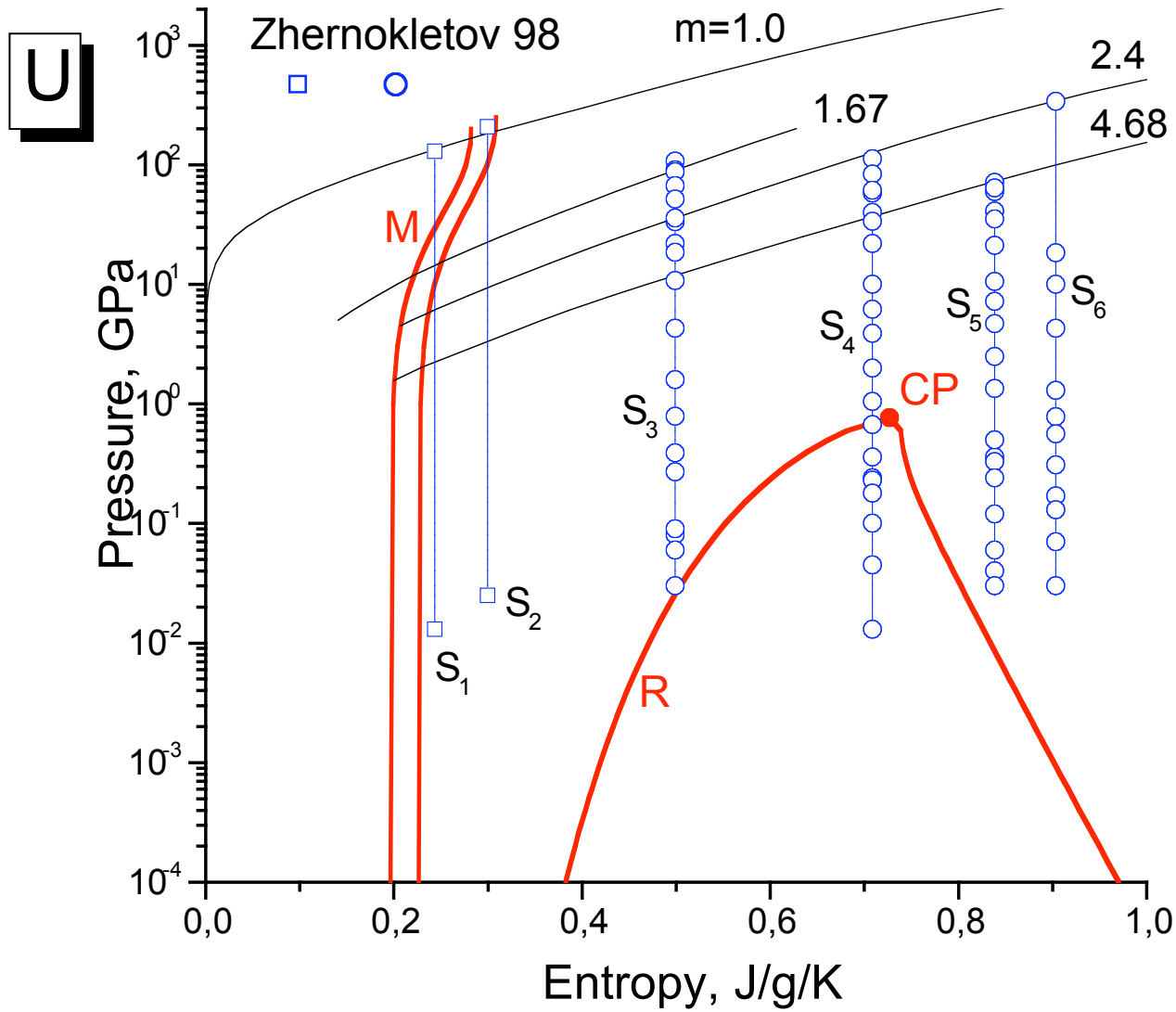
U AT HIGH PRESSURE



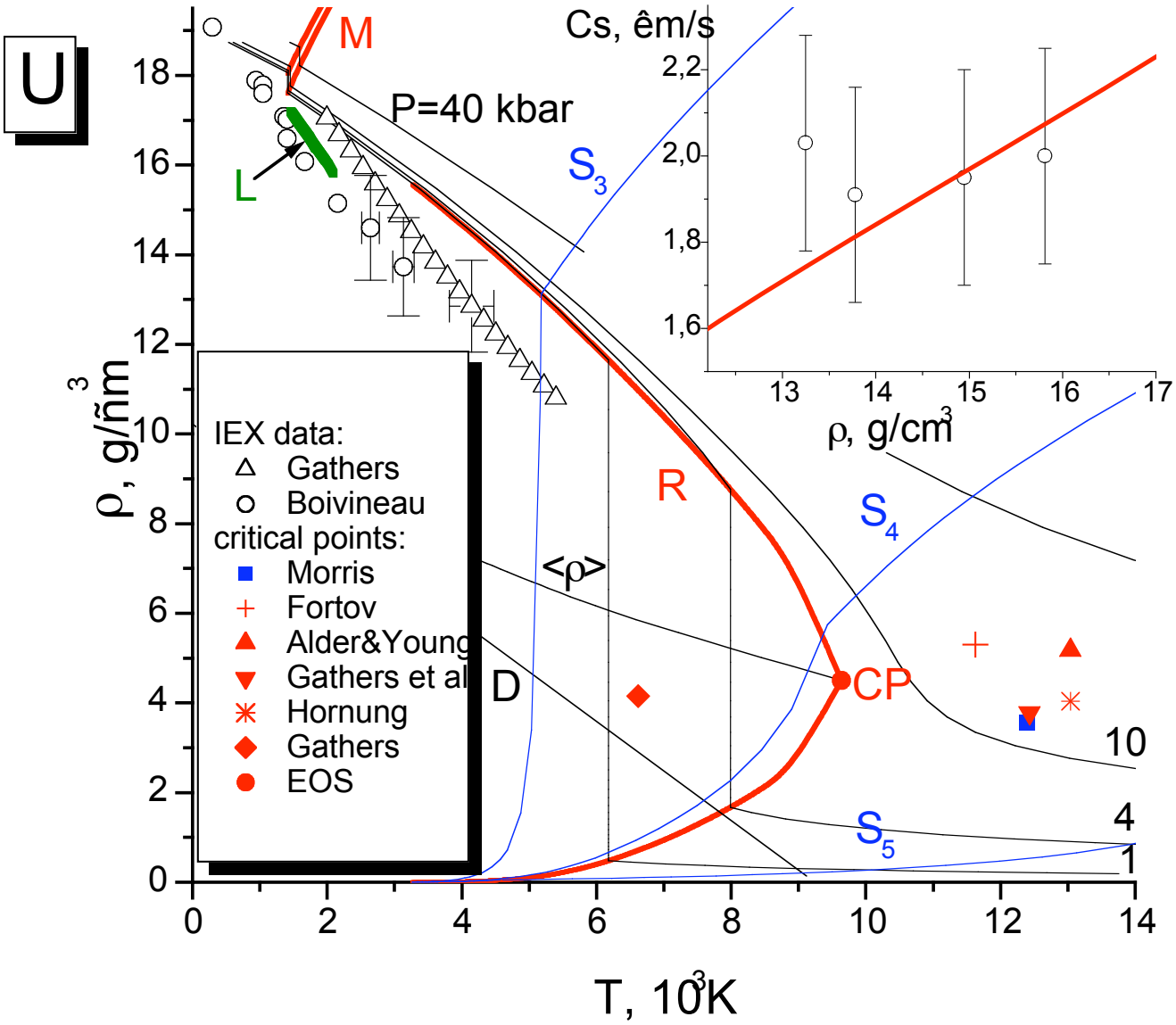
U EVAPORATION



U EVAPORATION



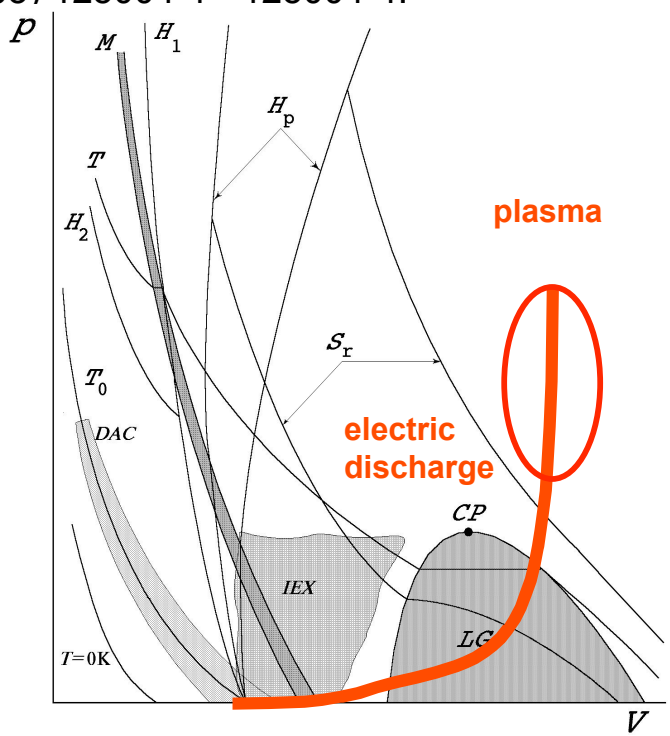
U AT LOWER DENSITIES



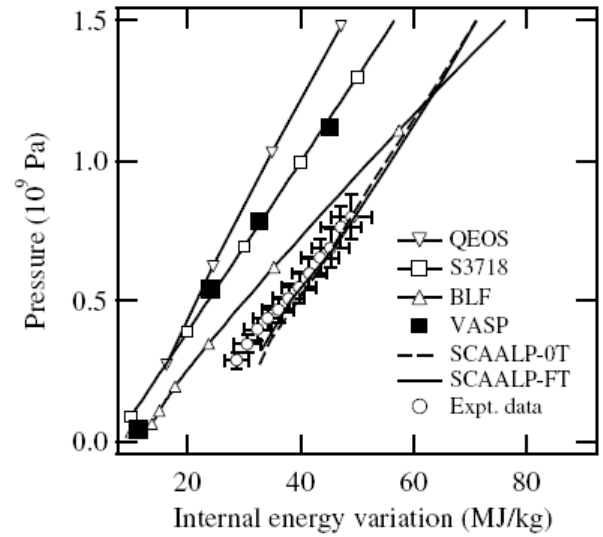
EOS accuracy

DAC, shock-wave data < 3%
IEX < 6-8%
Novel data?

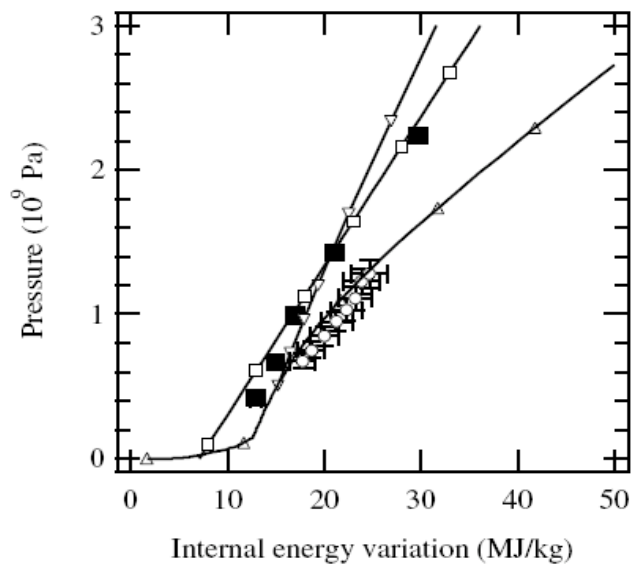
Isochoric plasma closed vessel:
P. Renaudin, C. Blancard, J. Cle´rouin, G. Faussurier, P. Noiret, and V. Recoules, “Aluminum Equation-of-State Data in the Warm Dense Matter Regime”, *Phys. Rev. Lett.,* 91 (2003) 125004-1 - 125004-4.



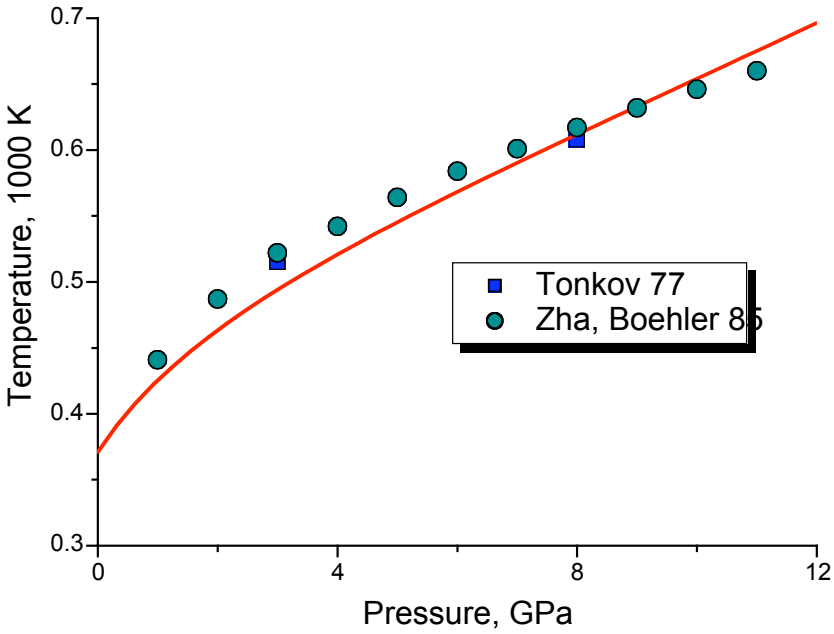
Al 0.3 g/cc

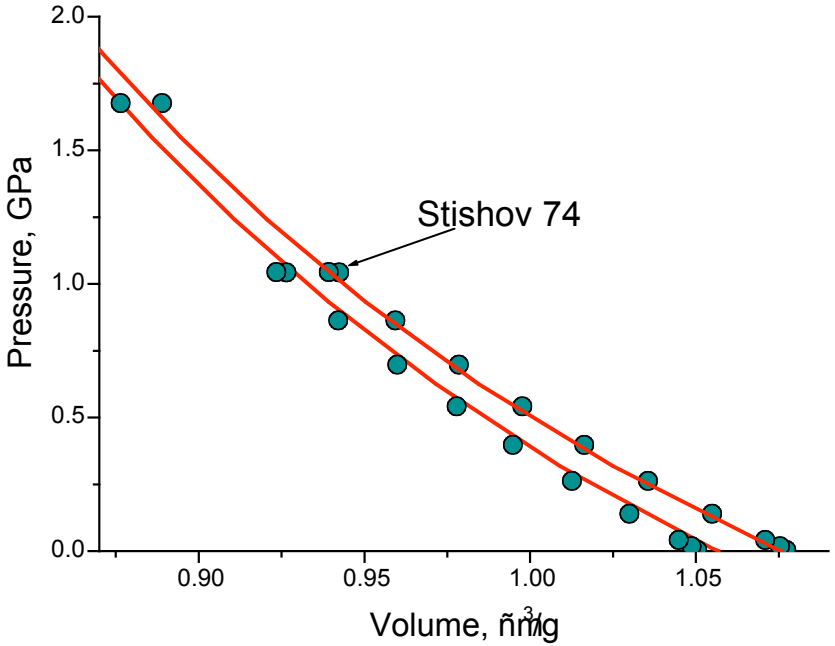


Al 0.1 g/cc

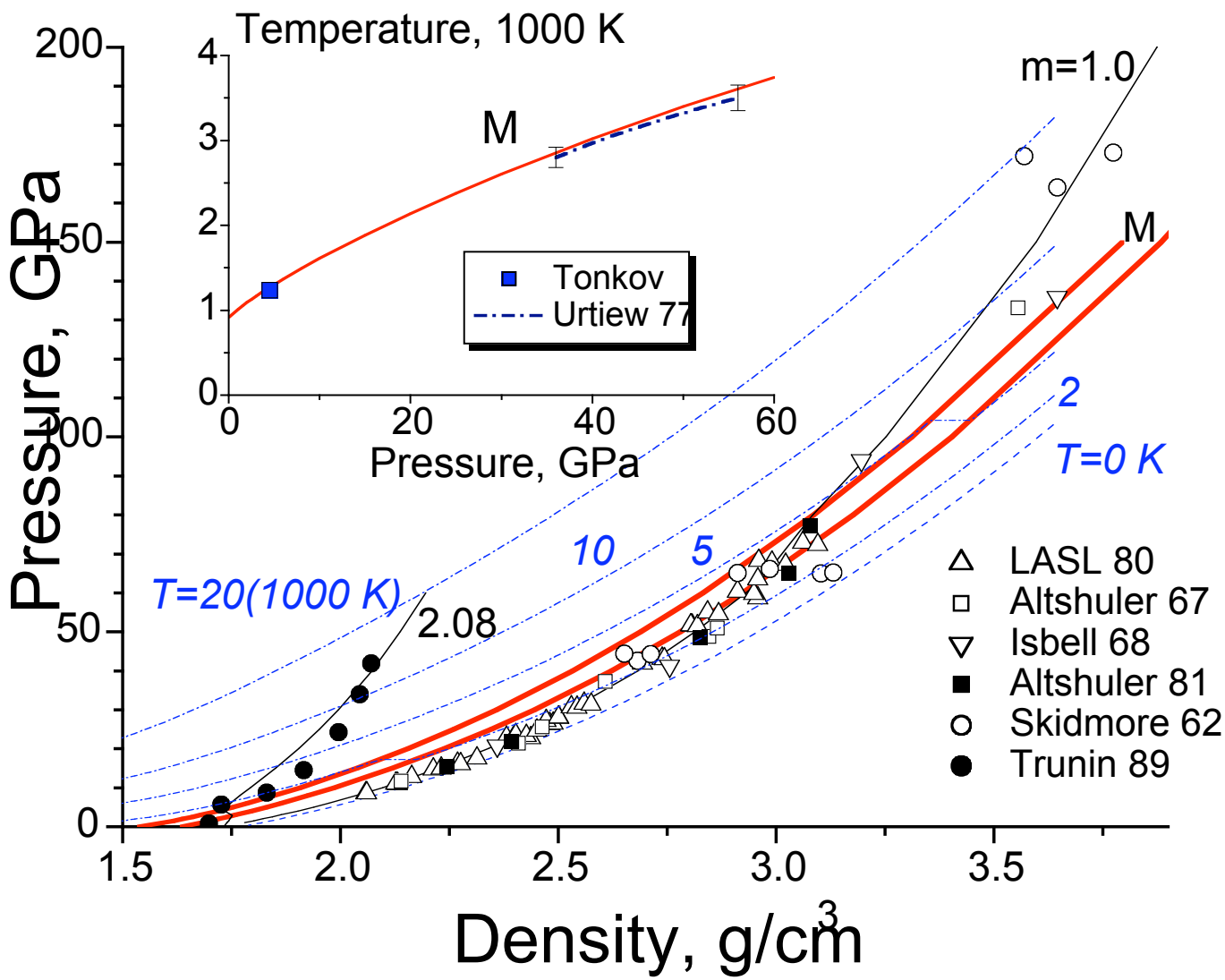


Na MELTING

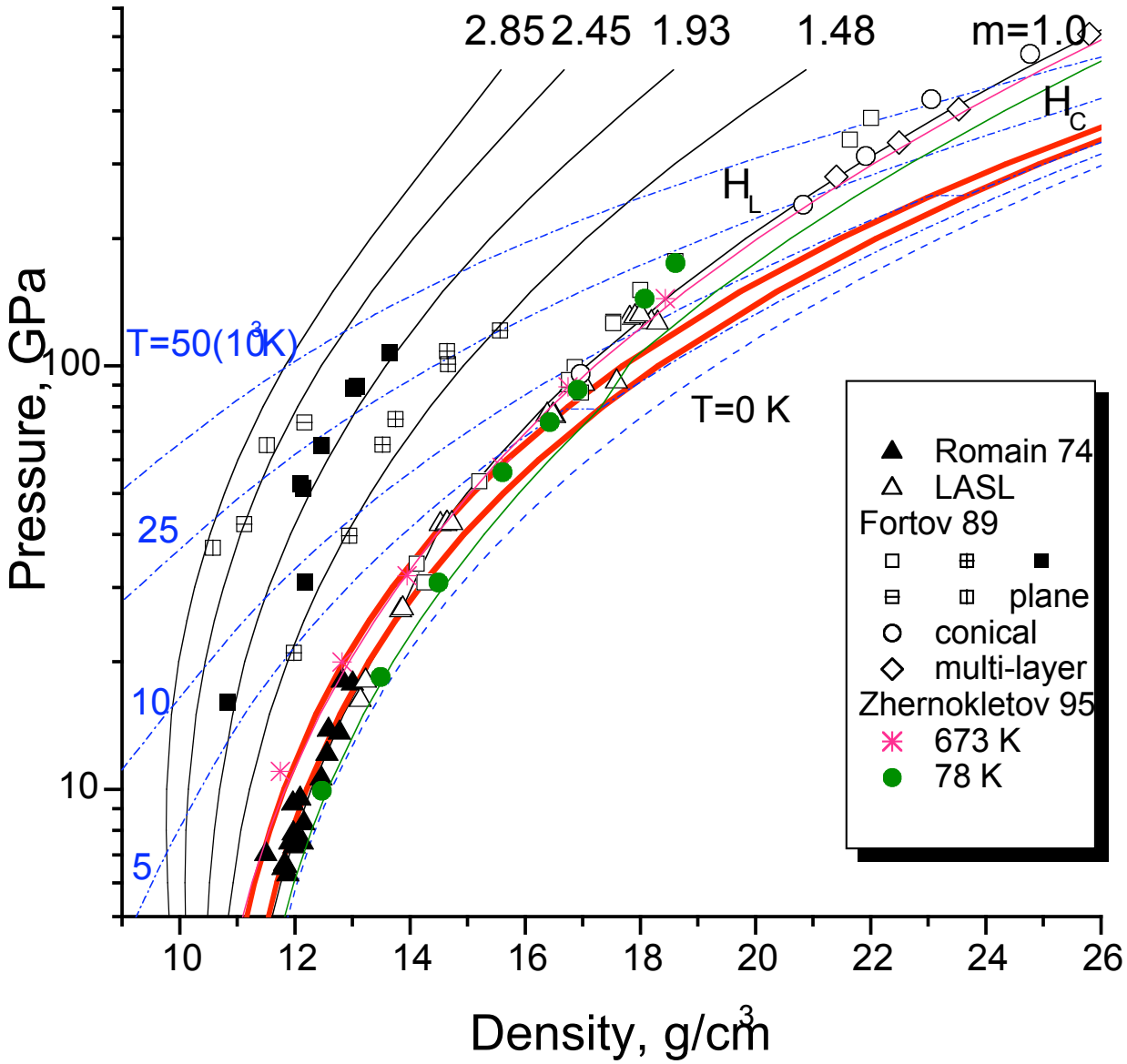

Temperature, 1000 K
0.7
0.6
0.5
0.4
0.3
0
4
8
12
Pressure, GPa
Tonkov 77
Zha, Boehler 85


Pressure, GPa
2.0
1.5
1.0
0.5
0.0
0.90
0.95
1.00
1.05
Volume, ñm3/g
Stishov 74

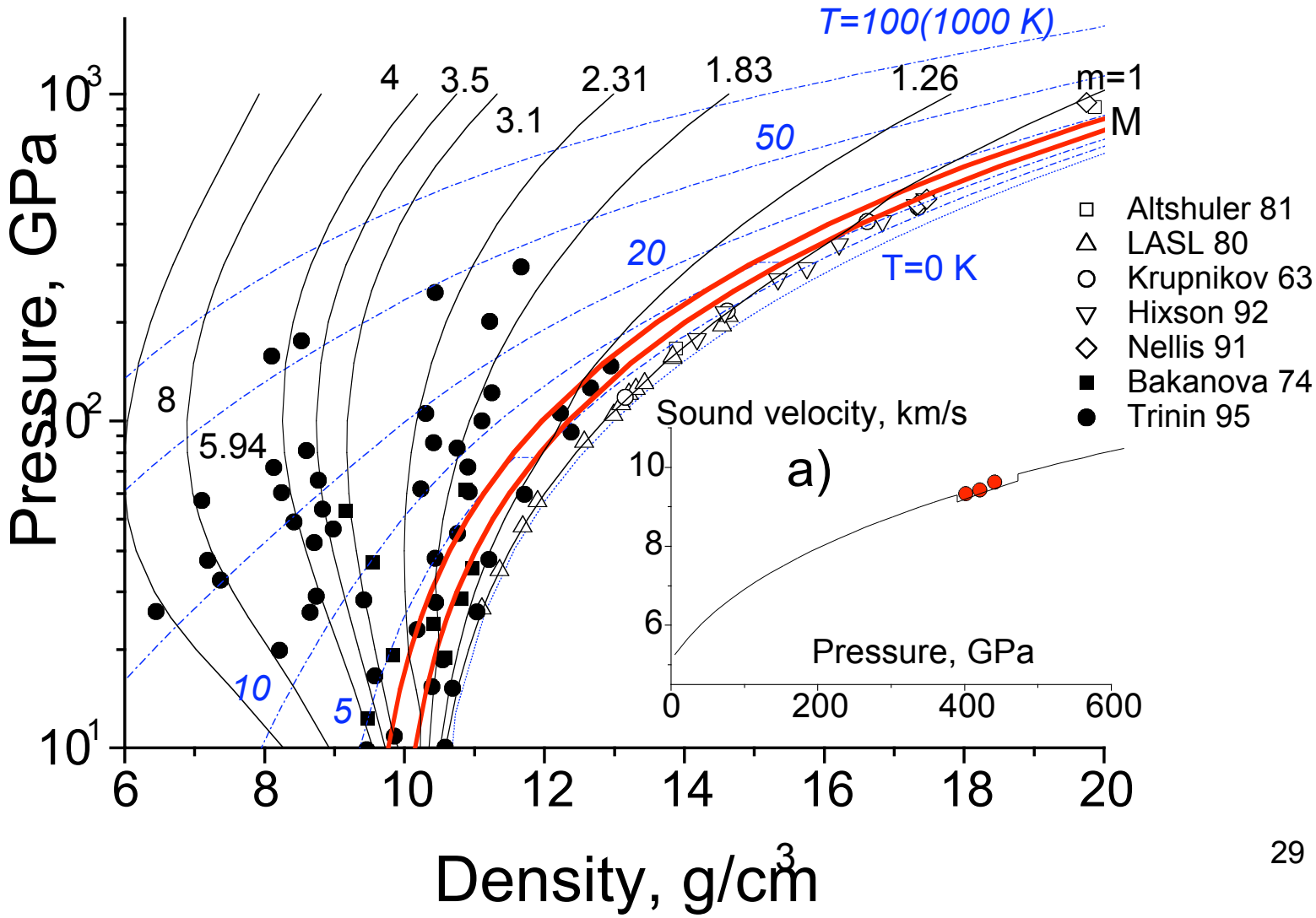
Mg AT HIGH PRESSURE



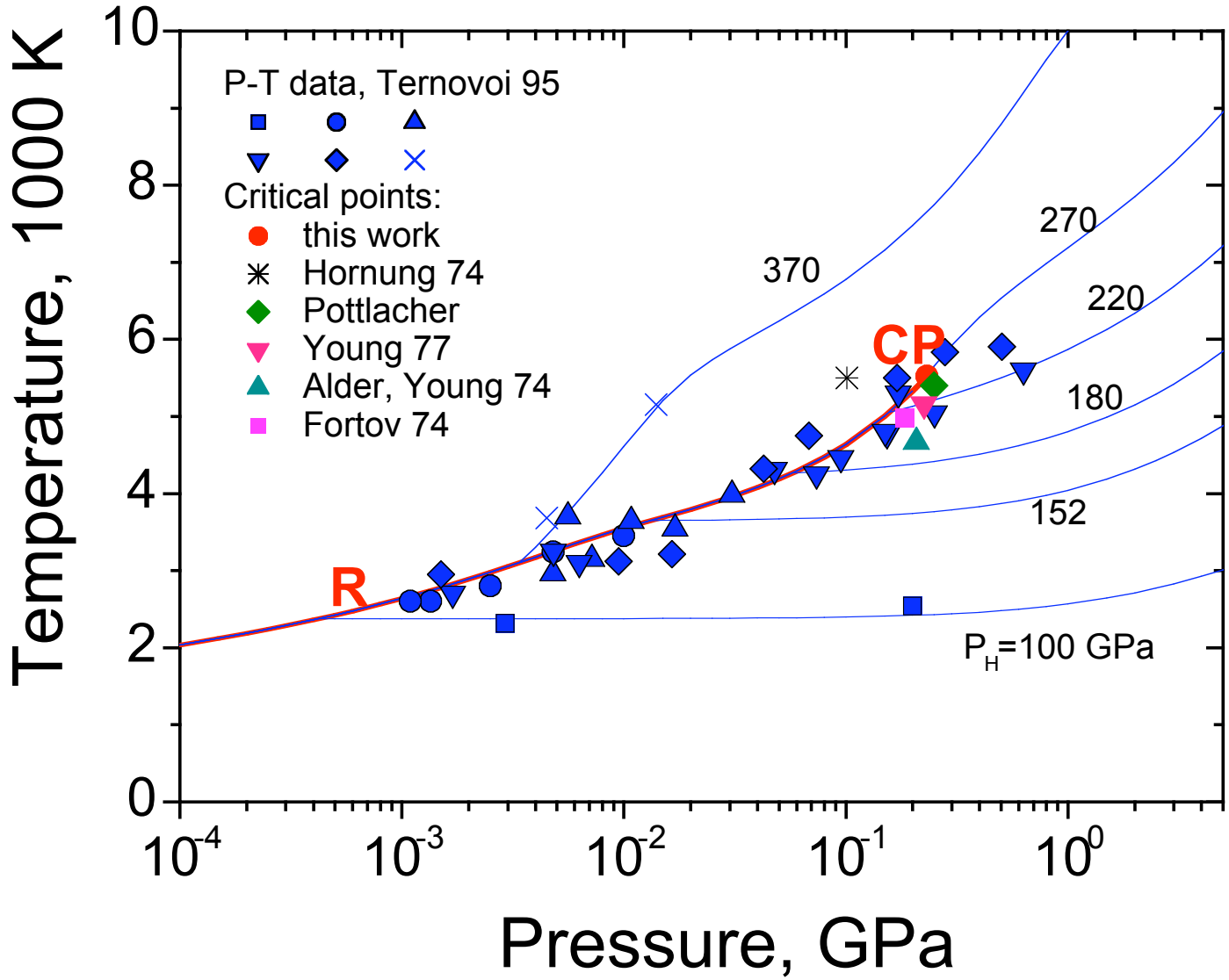
Bi AT HIGH PRESSURE



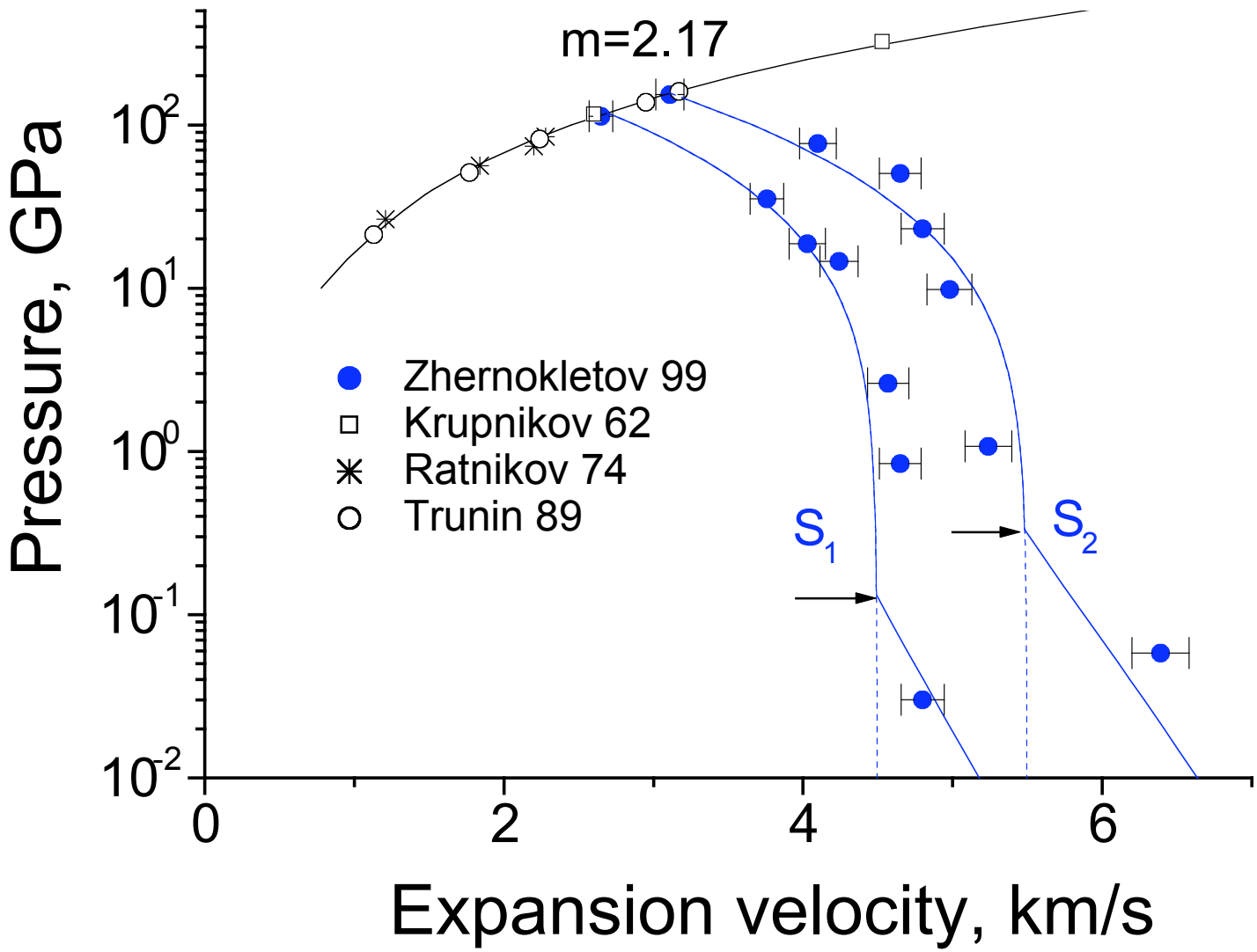
Mo at high pressure



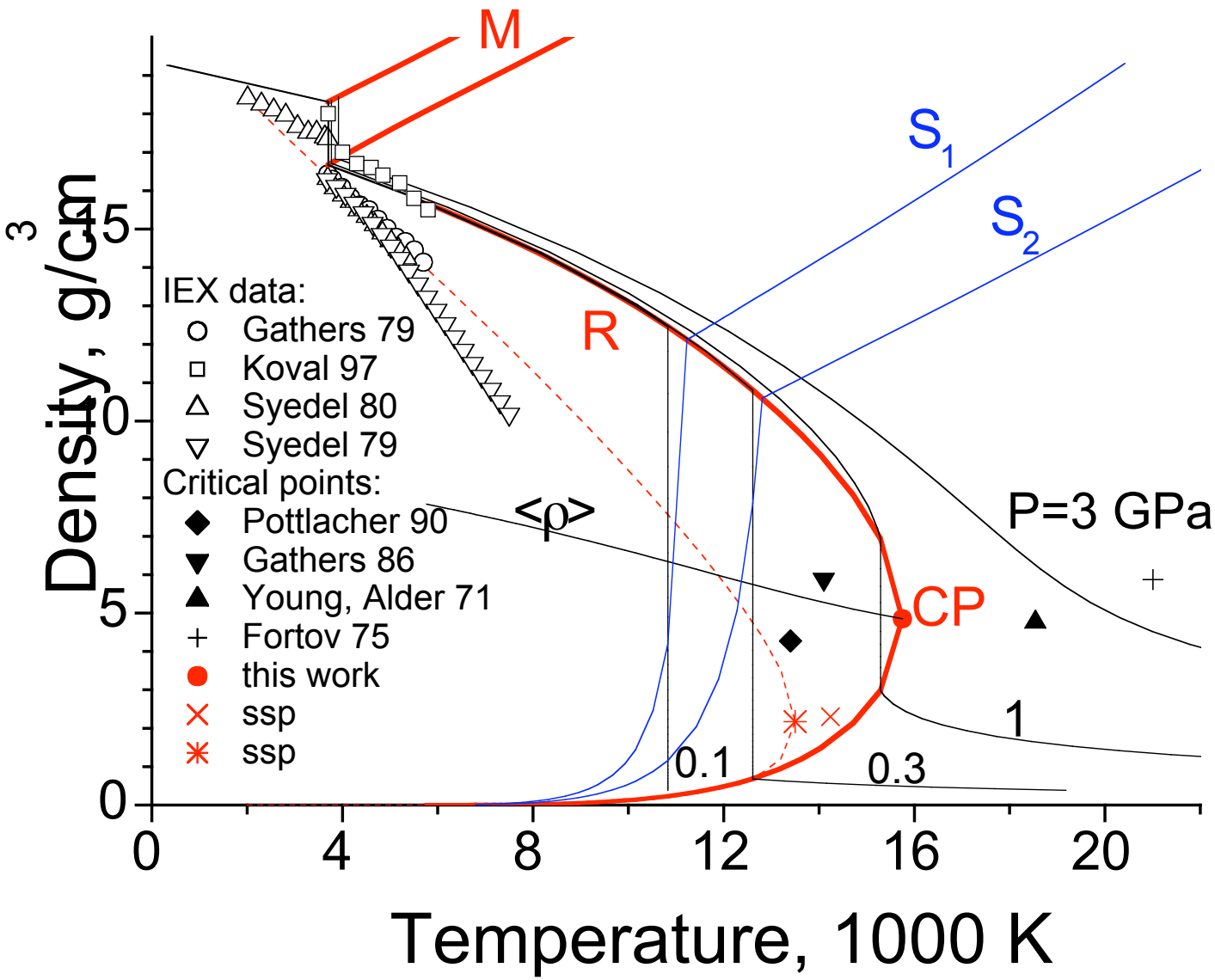
Pb EVAPORATION



W EVAPORATION



W AT LOWER DENSITY



GENERAL REGULARITIES

Melting

P – *T*-diagrams to 10 GPa

ρ(T, P):

Na

T-DAC:

U, Fe

Cs in shocked:

Ta, Mo, Fe

shocked liquid:

Zn, Cd, Sn, Bi

T shock:

Fe

porous Hugoniots:

Mg, Cr, Co, Fe, Ni, Mo, Ta, W, Zn, U

Evaporation

T evaporation (p=1 bar) = experiment

ρ(T, P=1 bar):

Na, Fe, Co, Ni, Zn, Ag, Cd, Sn, U

IEX:

Be, V, Nb, Fe, Ta, W, Ni, Re, Pt, U

T for S=const:

Ni, Pb (Sn)

S=const:

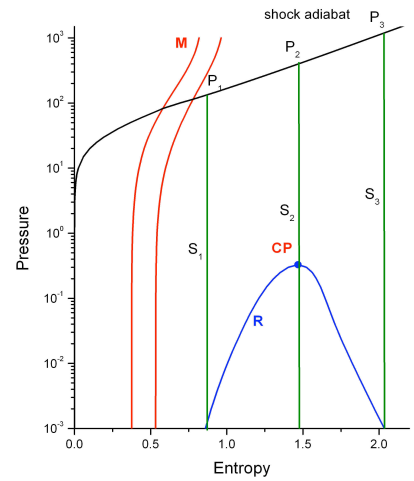
Mg, Mo, W, Zn, Cd, Sn, Bi, U

S=const – entrance into liquid-gas region:

Mo, U

CP: soft spheres ***– EOS - Fortov***

MELTING & EVAPORATION



Hugoniot melting pressure

PressurePm, GPaPressurePc,

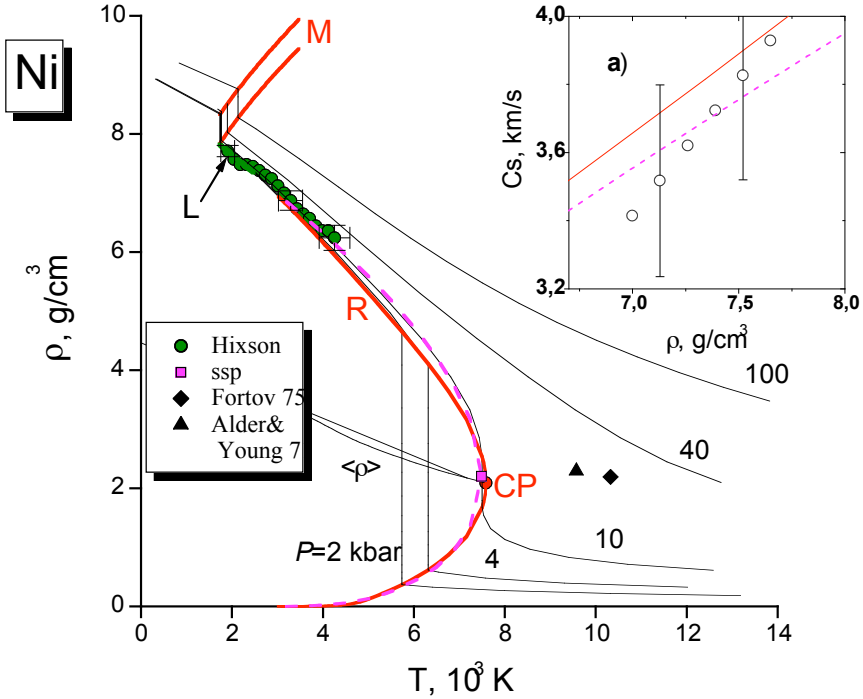
Critical points of metals

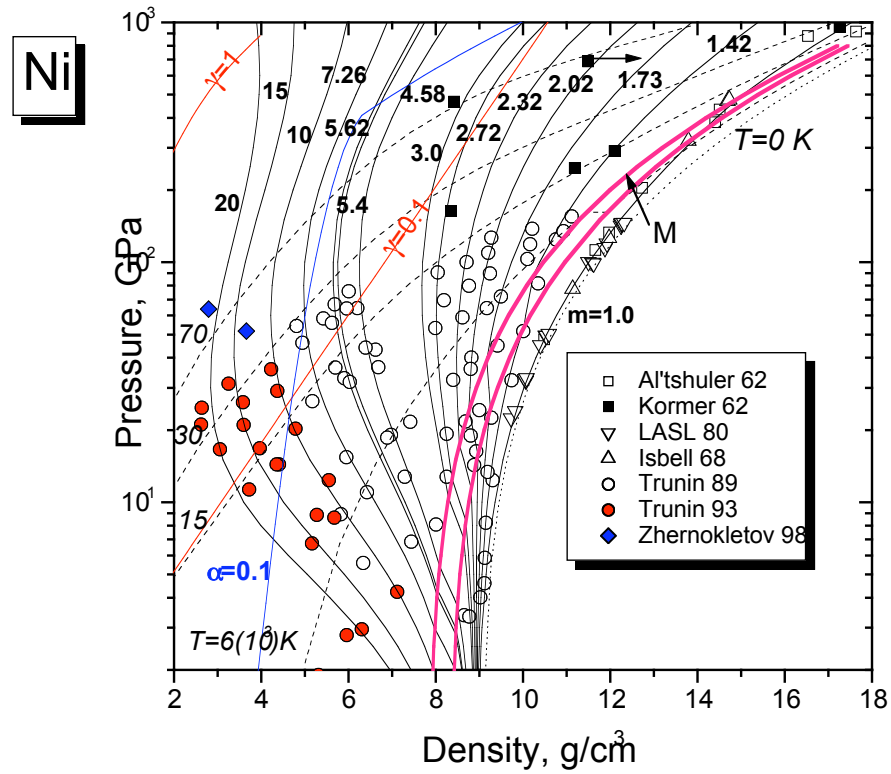
eTc, KDensityc, g/ñ m³EntropySc, J/g/KBe402-462Be2.8788770.39813.18M ρ

Metal	P_1, GPa	P_2, GPa	P_3, GPa
Li	36.9	125	808
Be	374	1720	9260
Na	17.3	57.2	413
Mg	67.9	205	964
Al	211	546	2360
K	8.9	28.9	86.9
V	322	1070	4270
Cr	347	1140	5580
Fe	354	1500	5550
Co	486	2120	7140
Ni	489	1880	5880
Cu	317	966	3230
Zn	111	397	1850
Zr	188	744	1800
Nb	408	2140	4000
Mo	476	1510	5250
Ag	246	902	2750
Cd	76	329	1280
Sn	138	512	1280
Hf	255	990	2110
Ta	452	1690	3780
W	627	2150	10280
Re	658	2030	4680
Ir	597	1950	4440
Pt	546	1680	4240
Au	316	815	2520
Pb	87.3	262	569
Bi	47.7	189	610

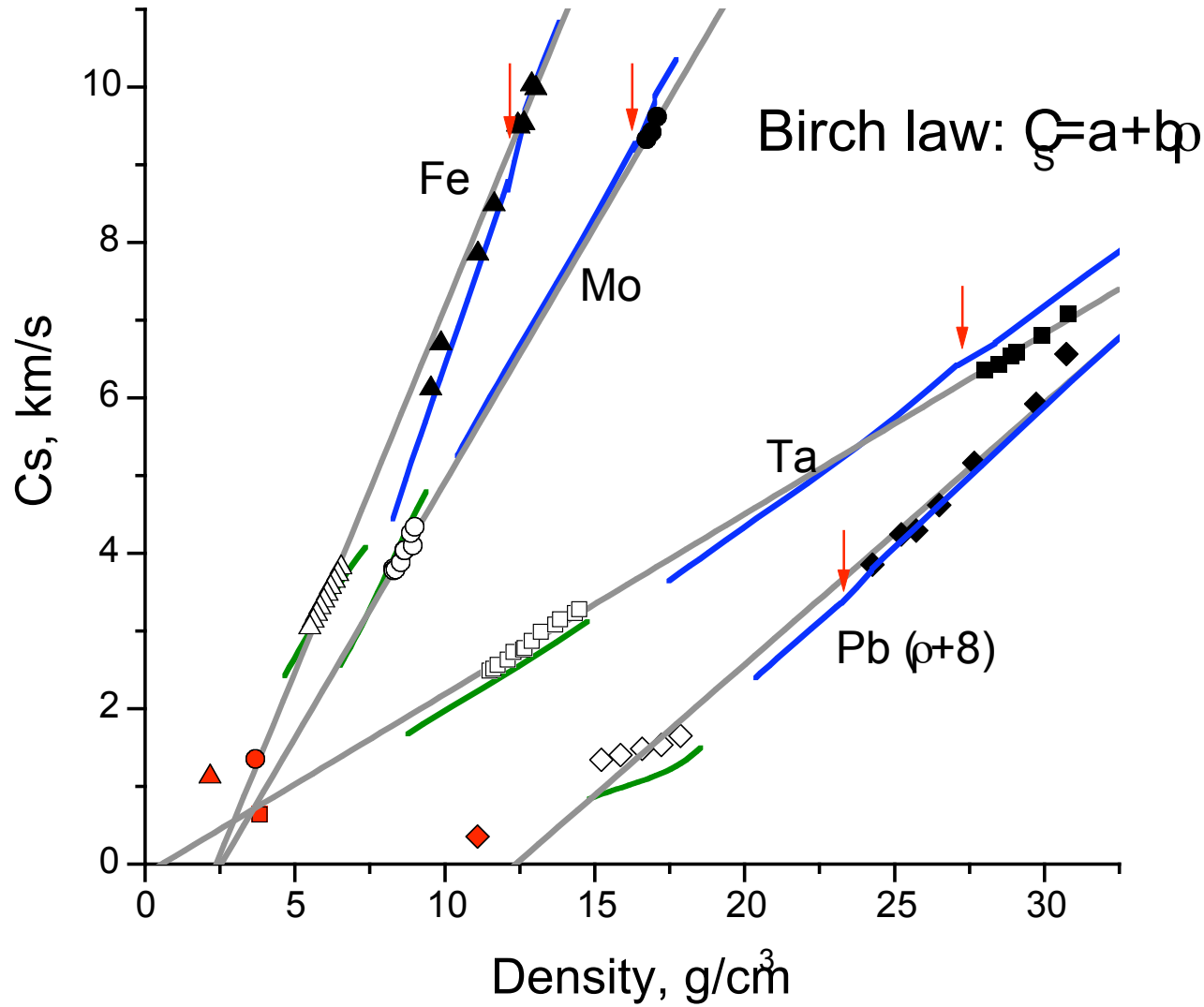
Liquid metals: general reqularities

IEX ⟷ SW data

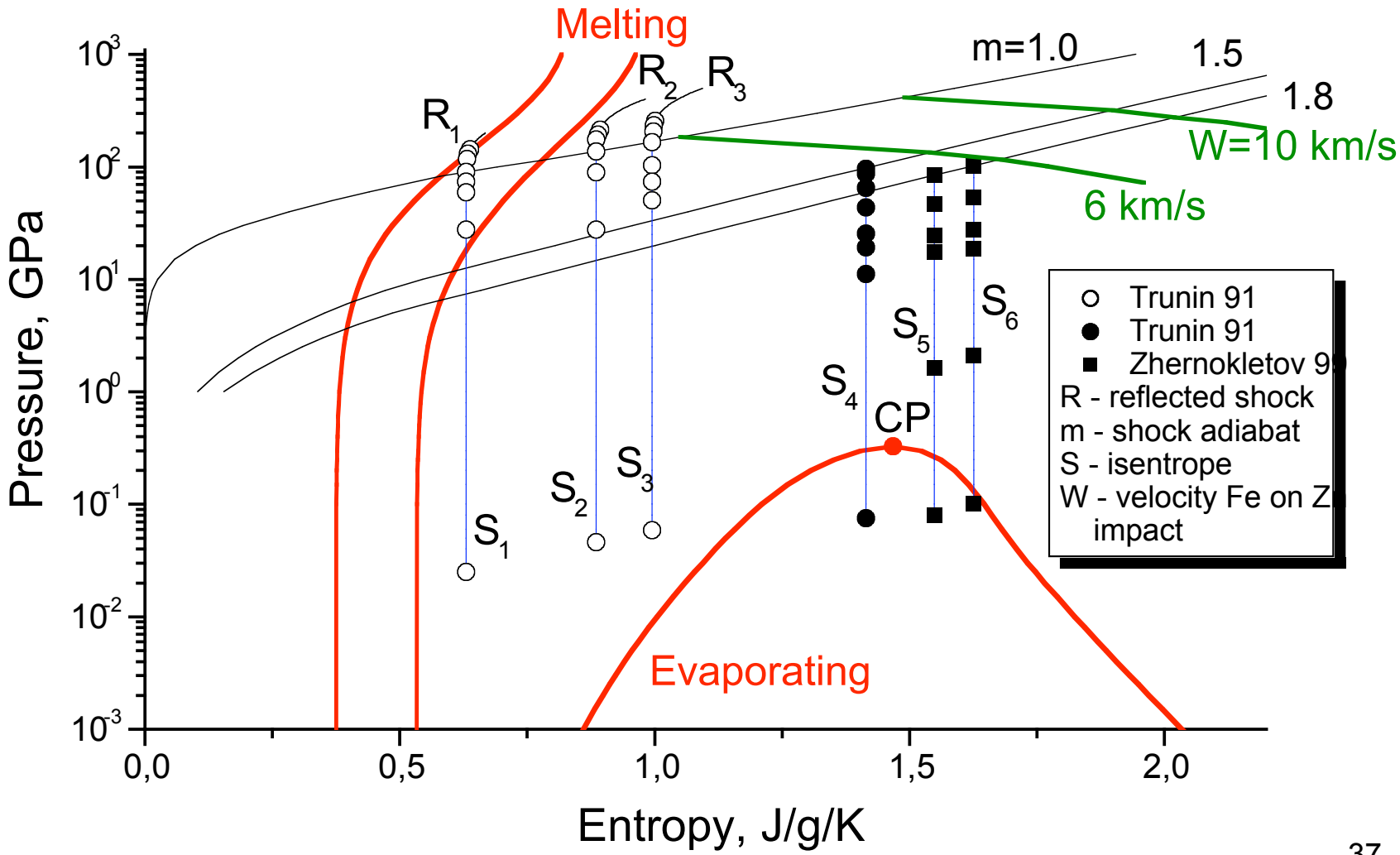




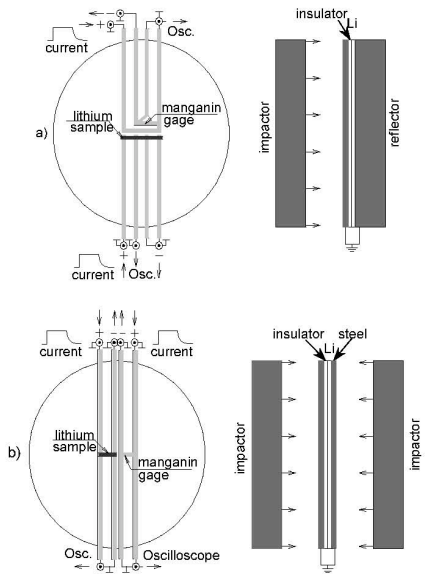
Liquid metals: general reqularities

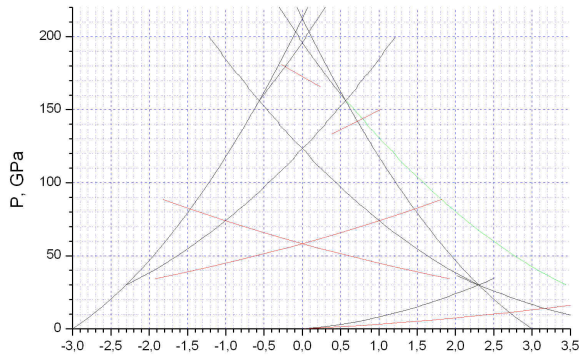


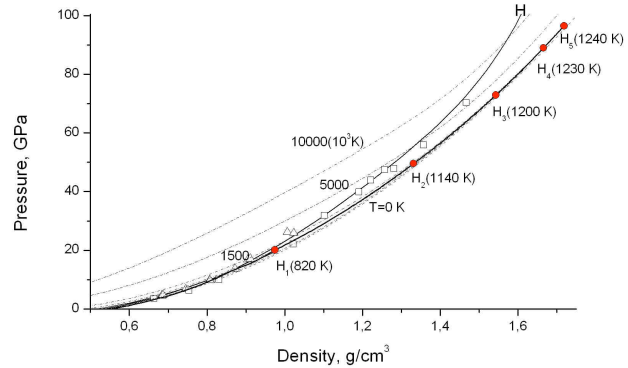
Expert calcualtions: Fe strikes Zn

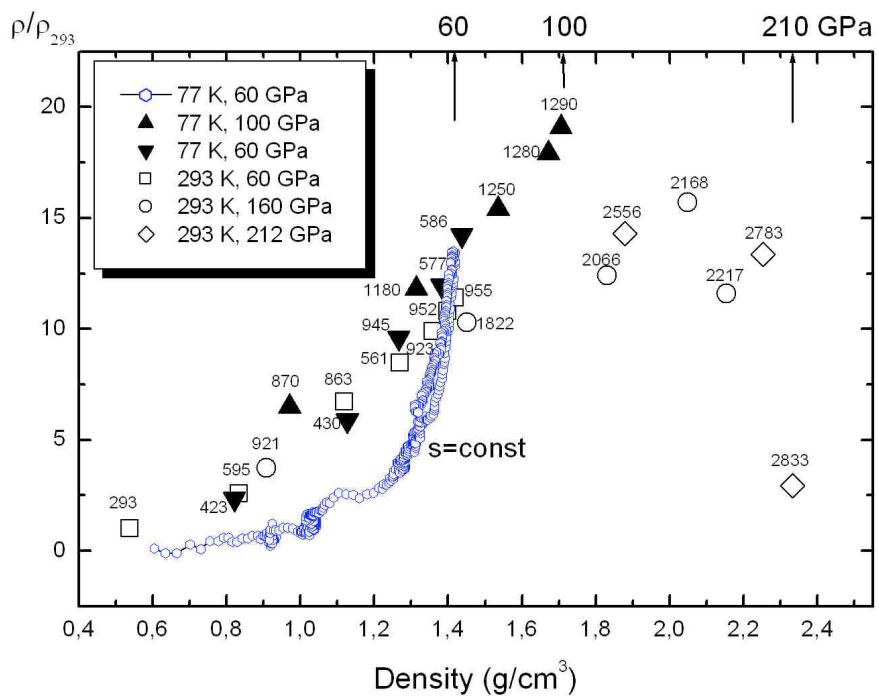


Expert calcualtions: resistivity of Li



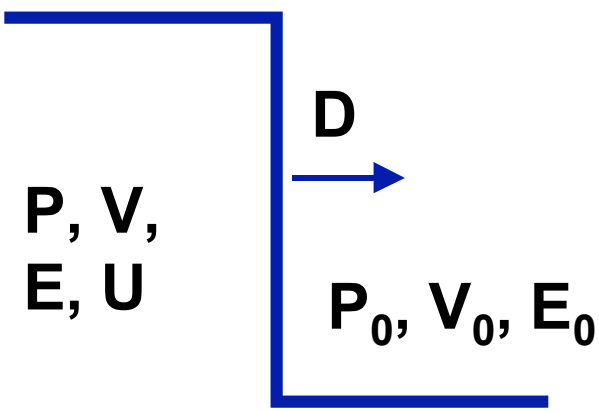






Shock-wave stability

Shock wave – unique tool in physics of high pressures, producing homogeneous distribution of P, E, V, T in short time



shock compression

Hugoniot relations:

$$V_0/V=D/(D-U)$$

$$P=P_0 + DU/V_0$$

$$E=E_0 + 1/2(P_0 + P)(V_0 - V)$$

Criteria of shock wave stability

- linearized gas dynamic equations: D'yakov 1954, Kontorovich 1957
- general theory of decay and branching of arbitrary discontinuity: Kuznetsov 1985

Absolute instability:

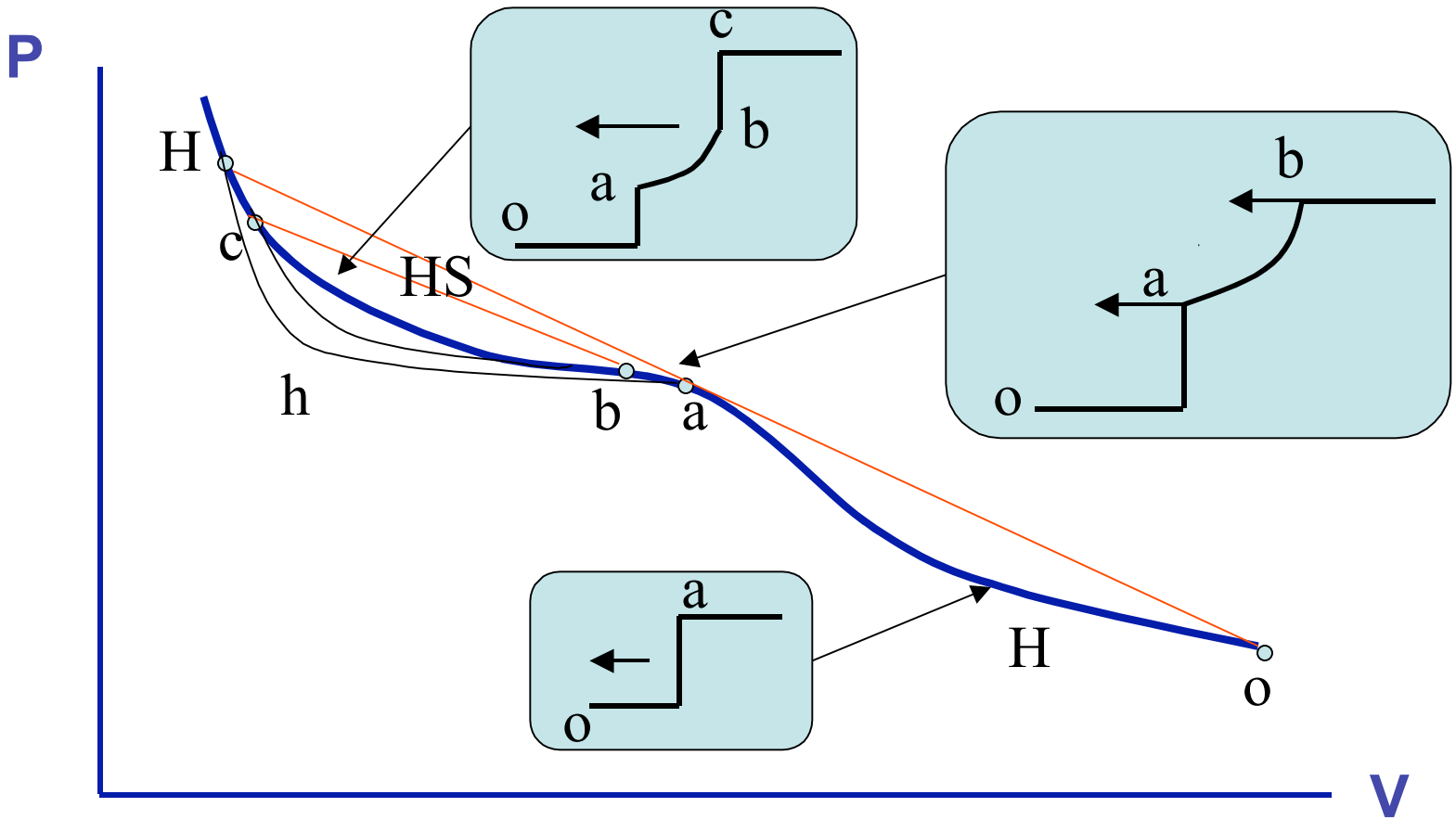
$$(\partial V/\partial P)_H < \frac{V - V_0}{P - P_0}$$

$$(\partial V/\partial P)_H > \frac{V_0 - V}{P - P_0}\,(1 + 2\sigma^{-1}(D/C_S))$$

Sound («D'yakov») instability:

$$\frac{V_0 - V}{P - P_0} \times \frac{1 - \sigma^{-2}(D/C_S)^2 - \sigma^{-1}(D/C_S)^2}{1 - \sigma^{-2}(D/C_S)^2 + \sigma^{-1}(D/C_S)^2} < \left(\frac{\partial V}{\partial P}\right)_H < \frac{V_0 - V}{P - P_0}\left(1 + 2\sigma^{-1}\frac{D}{C_S}\right)$$

Shock wave in media with $0>(d^2P/dV^2)_S<0$

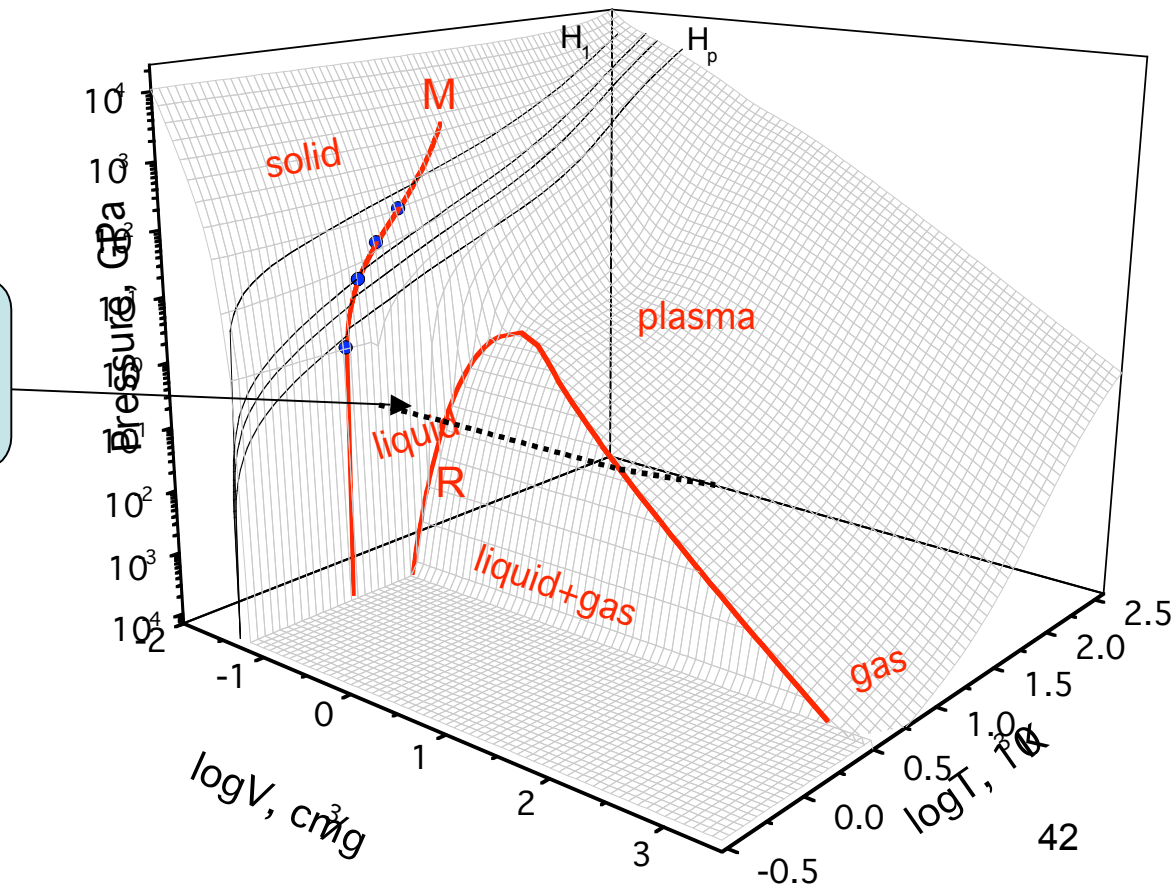


Methodology

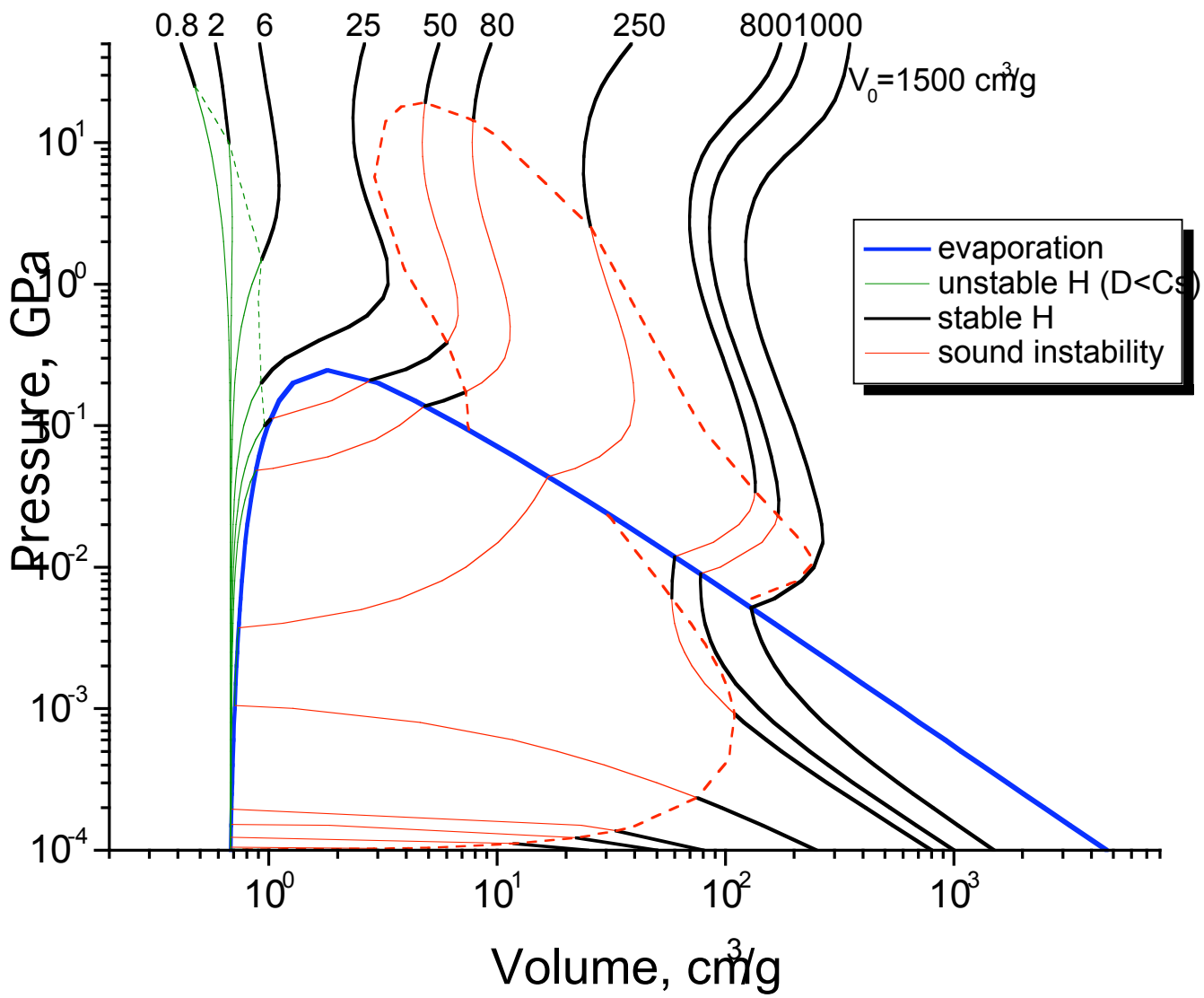
Multi-phase EOS for 30 metals

Shock adiabats start at different P_0, V_0

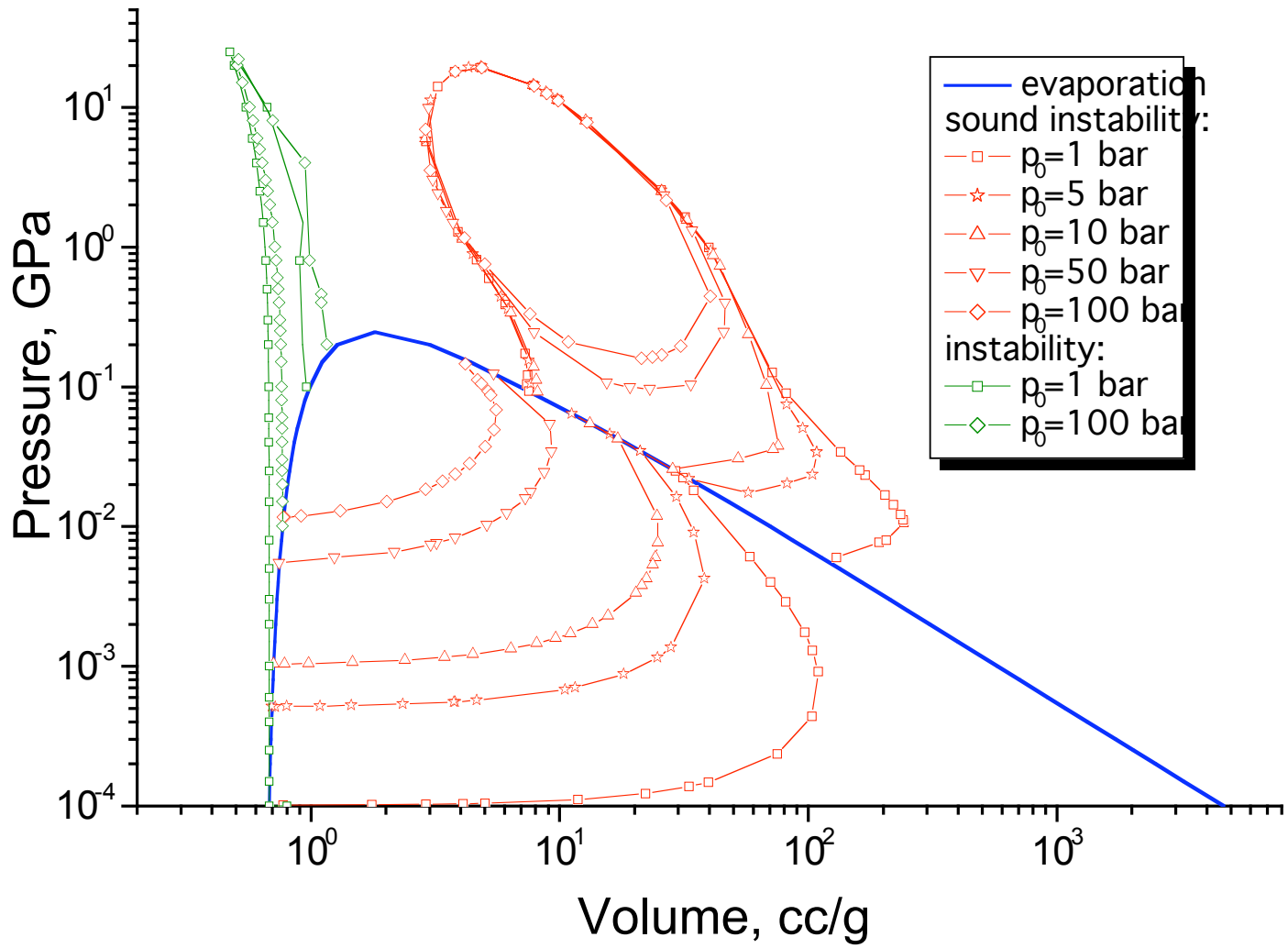
Analysis of stability with criteria



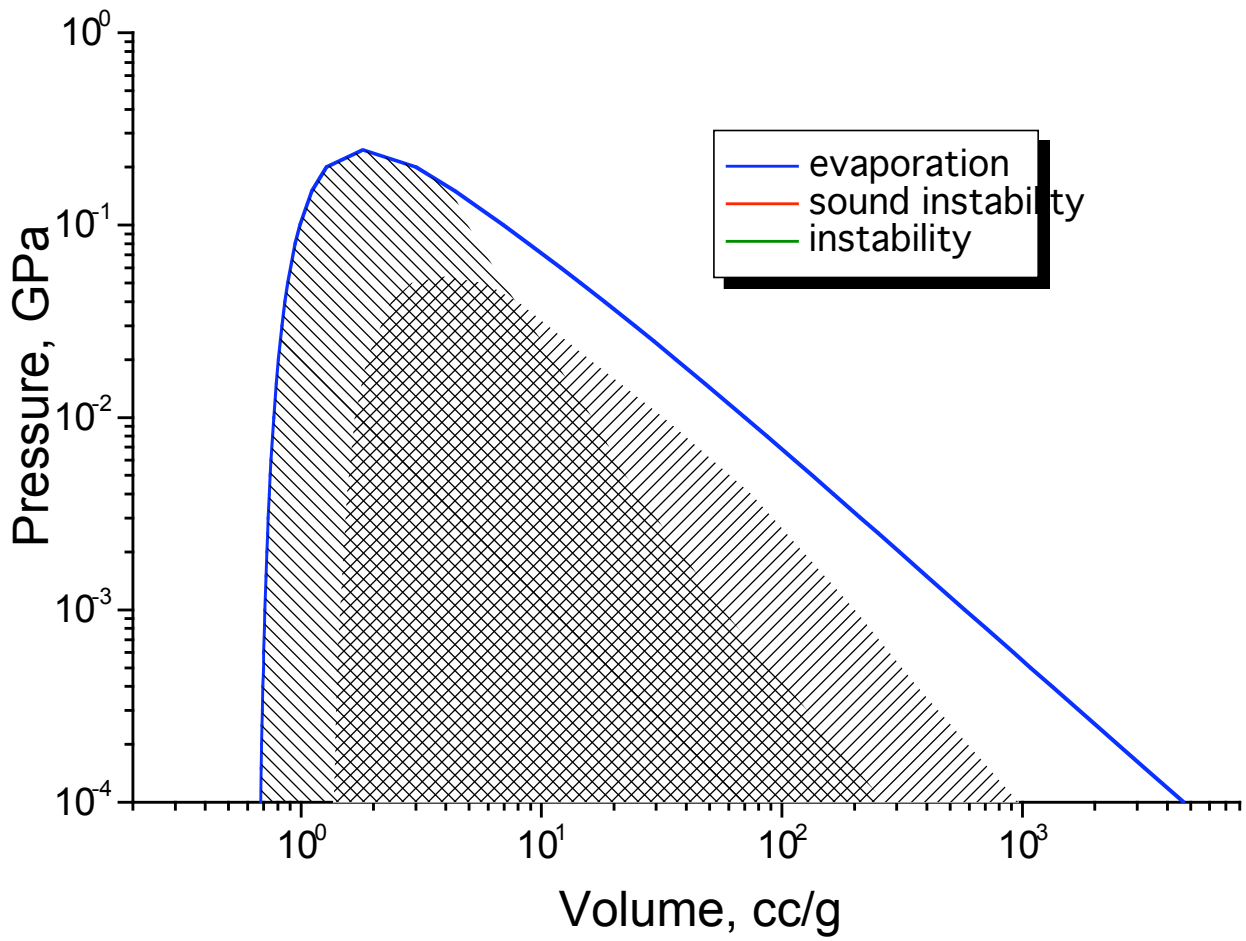
Shock wave stability in Mg at P_0=1 bar



Shock wave stability in Mg at different P_0



Instabilities in Mg at different P_0 & V_0



Conclusions

- ❖ EOS for 30 metals
- ❖ Agreement with experiment & theory
- ❖ Phase boundaries of melting & evaporation
- ❖ EOS applications for high-energy-density physics
- ❖ Successful implementation in 2D,3D codes

Thank You. Questions?