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A multiphase equation of state for lead

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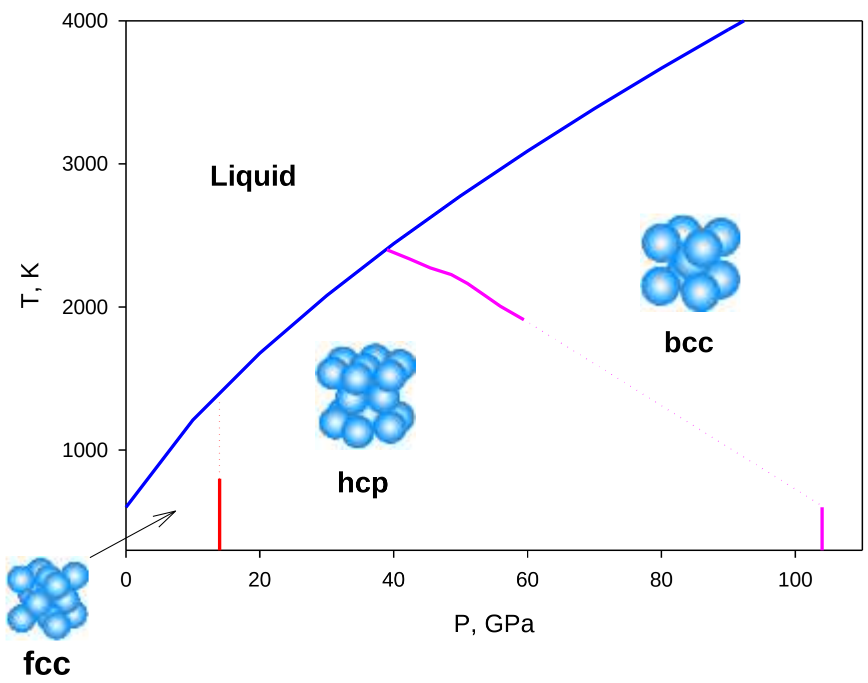
Zababakhin Scientific Talks
international conference
March 18-22, 2019

Introduction

- It is impossible to simulate the behavior of structures under intense energy flows without an equation of state (EOS) which would adequately describe material properties in a wide range of temperatures and pressures, including solid, liquid and gaseous states.

- The restless desire for more and accurate calculations requires the more and more realistic material models which allow, in particular, for polymorphic transformations in the solid state and thus dramatic changes in material density, compressibility and other thermodynamic characteristics.



EOS expressions

The free Helmholtz energy reads as

1 $$F(V,T)=F_C(V)+F_A(V,T)+F_E(V,T)-S_{Tr}T,$$

where V is molar volume, $F_C=E_C$ is cold energy at $T=0K$, F_A и F_E are thermal contributions from atoms and thermally excited electrons, and $S_{Tr}T$-provides the experimental value for the entropy jump during melting.

The cold energy is written as follows

In the compression at x<1:

2 $$E_C(V)=E_{0K}-\int_{V_{0K}}^{V}P_C(V)dV$$

$$P_C(y)=3B_{0K}\frac{1-y}{y^5}\exp\left[C_0(1-y)\right]\left\{1+C_1y(1-y)+C_2y(1-y)^2+C_3y(1-y)^3\right\}$$

In the tensile range at x>1:

3 $$E_C(x)=V_{0K}\left[\frac{A}{m}\left(x^{-m}-1\right)+\frac{B}{n}\left(x^{-n}-1\right)+\frac{C}{k}\left(x^{-k}-1\right)\right]+E_{0K}$$

$$P_C(x)=Ax^{-(1+m)}+Bx^{-(1+n)}+Cx^{-(1+k)}$$

where $x=V/V_{0K}$, $y=x^{1/3}$, V_{0K} and B_{0K} are molar volume and bulk modulus at $x=1$

EOS expressions

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The thermal component F_A is written as

4
$$F_A(V,T) = 3RTf(\tau) - A_{Ah}RT\left(e^{\tau} - 1\right)^{-1}$$

$$f(\tau) = \frac{3}{8}\tau + \ln(1 - e^{-\tau}) - \frac{1}{3}D(\tau), \qquad \tau = \frac{\theta(V)}{T}, \qquad D(\tau) = \frac{3}{\tau^3}\int_0^{\tau}\frac{x^3dx}{e^x - 1}, \qquad \theta(V) - Debye\ temperature$$

The Gruneisen function is taken in the form of the empirical expression

5
$$\Gamma(V) = \frac{2}{3} + \frac{\left(\Gamma_0 - \frac{2}{3}\right)\left(B^2 + D^2\right)}{B^2 + \left(D - \ln x\right)^2}$$

The Debye temperature is determined from the integration of $\Gamma(V) = -\frac{\partial \ln \theta(V)}{\partial \ln V}$

6
$$\theta(V) = \theta_0 \exp\left\{-\int_{V_{OK}}^{V}\frac{\Gamma(V)}{V}dV\right\} = \theta_0 x^{-\frac{2}{3}} \exp\left\{\frac{\left(\Gamma_0 - \frac{2}{3}\right)\left(B^2 + D^2\right)}{B^2}\left[arctg\frac{D - \ln x}{B} - arctg\frac{D}{B}\right]\right\}$$

In the liquid region the thermal component is written as

7
$$F_A(V,T) = \frac{3RT}{2}\left[1 + \frac{x_a}{x + x_a}\cdot\frac{T_a}{T + T_a}\right]\ln\left[\frac{T_{as}\left(\theta(V) + Tx^{-2/3}\right)}{T\left(T + T_{ac}\right)}\right]$$

EOS expressions

The electron component F_E is written as[1)]:

8
$$F_E(V,T) = -C_E(V,T)T\ln\left[1+\frac{B_E(T)T}{2C_{Ei}}x^{\Gamma_E(V,T)}\right]$$

$$B_E(T) = \frac{2}{T^2}\int\left[\int_0^T \beta(\tau)d\tau\right]dT, \qquad C_{Ei} = \frac{3RZ}{2},$$

$$C_E(V,T) = \frac{3R}{2}\left[Z+(1-Z)q\frac{x^{N_Z}}{(x^{N_Z}+x_Z^{N_Z})}\frac{T_Z^{M_Z}}{(T^{M_Z}x^{S_e}+T_Z^{M_Z})}\right]\exp\left(-\frac{\tau_i}{T}\right)$$

$$\tau_i = T_i\exp\left(-\frac{x}{x_i}\right)$$

$$\Gamma_E(V,T) = \Gamma_{Ei} + \left(\Gamma_{E0}-\Gamma_{Ei}+\gamma_m\frac{T}{T_g}\right)\exp\left(-\frac{T}{T_g}\right)$$

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

As $T\to\infty$ free energy (8) tends to the expression for the ideal gas of fully ionized electrons

1) L.V.Altshuler, A.V.Bushman, M.V.Zhernokletov, V.N.Zubarev, A.A.Leontiev, V.E.Fortov // J. Exp. and Theor. Phys, Is.2, p.741-760 (1980)

Calculations

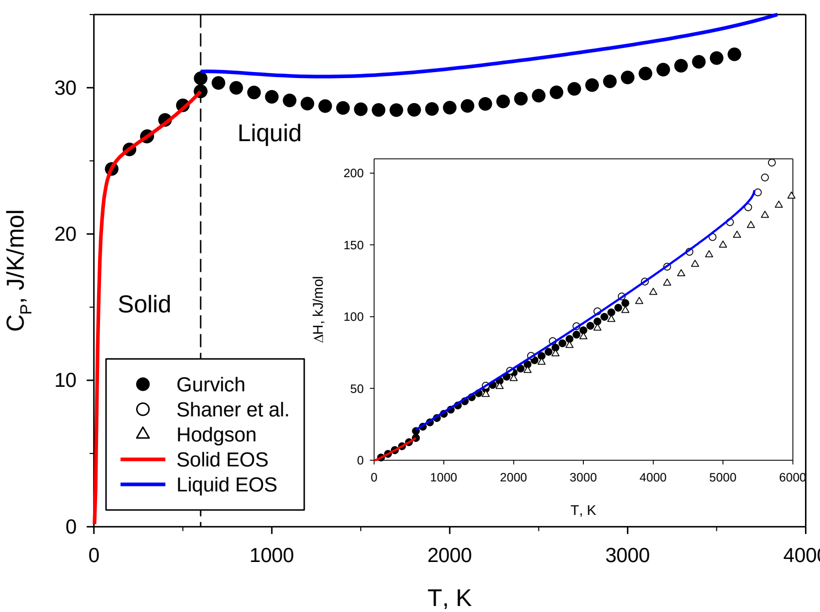

Fig.1. Heat capacity versus temperature for solid and liquid lead. Difference of enthalpy versus temperature on insertion.

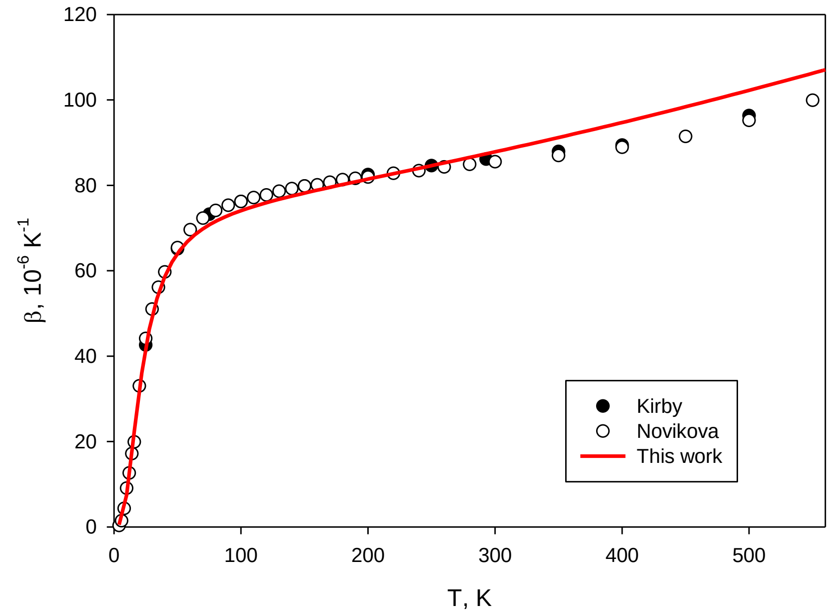

Fig. 2. Volume heat expansion coefficient versus temperature for solid lead.

Calculations

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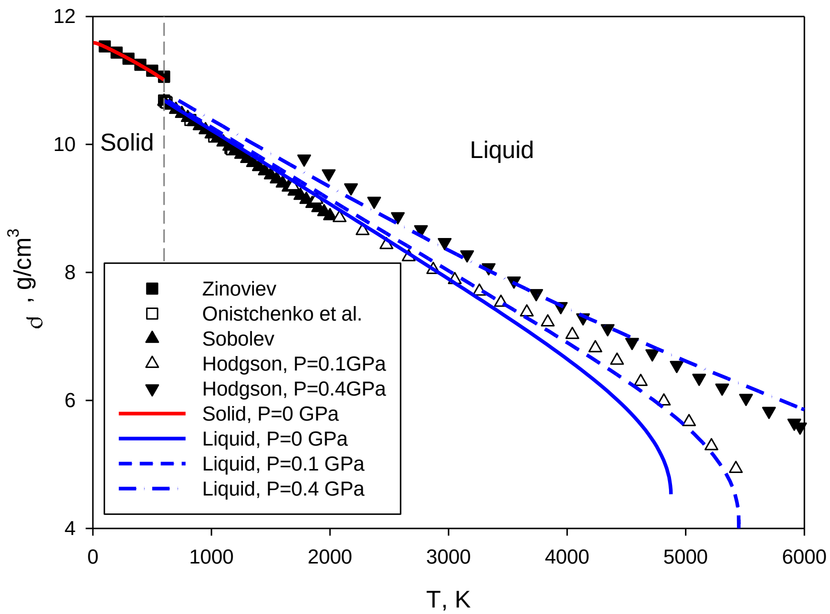

Fig. 3. Density versus temperature at various pressure.

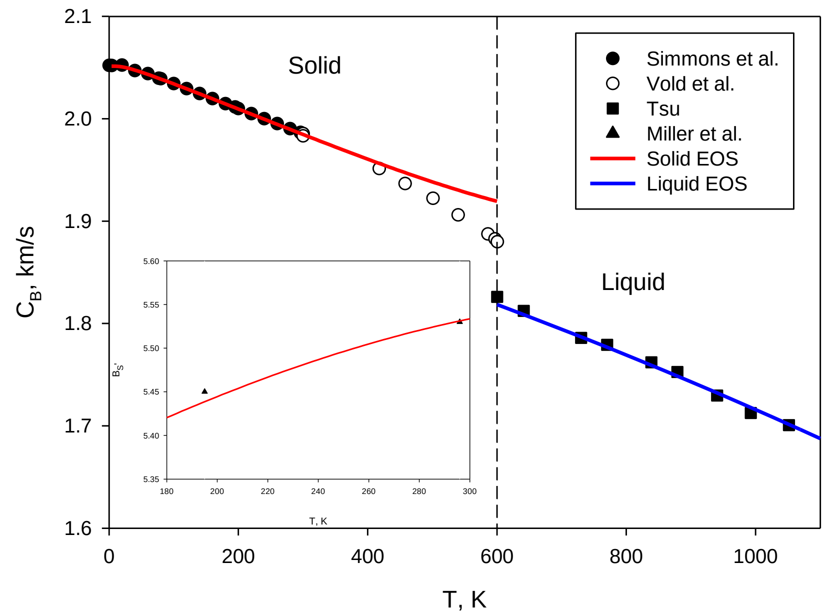

Fig.4. Bulk velocity and derivative of isothermal bulk modulus versus temperature (insertion)

Calculations

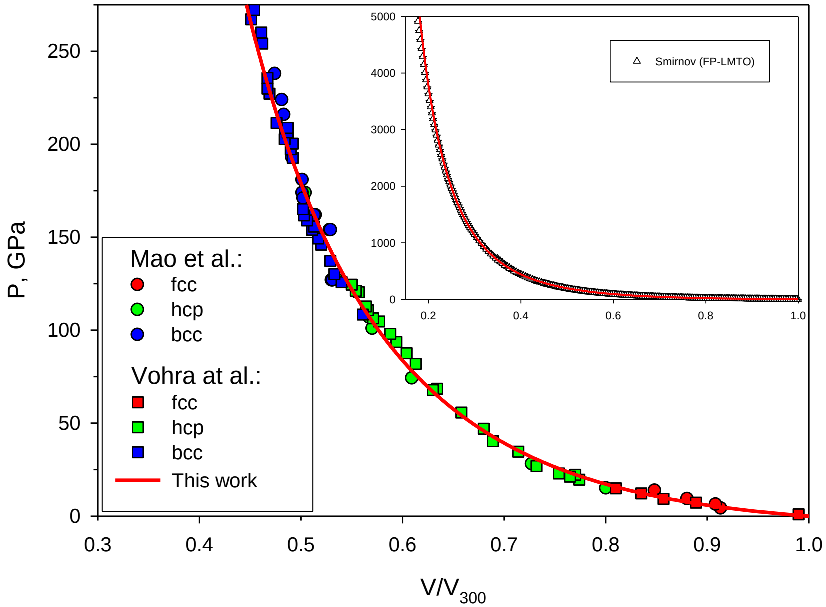

Fig. 5. Solid lead compression isotherm at T=300K under experimental pressures and under ultrahigh pressures (insertion, T=0K)

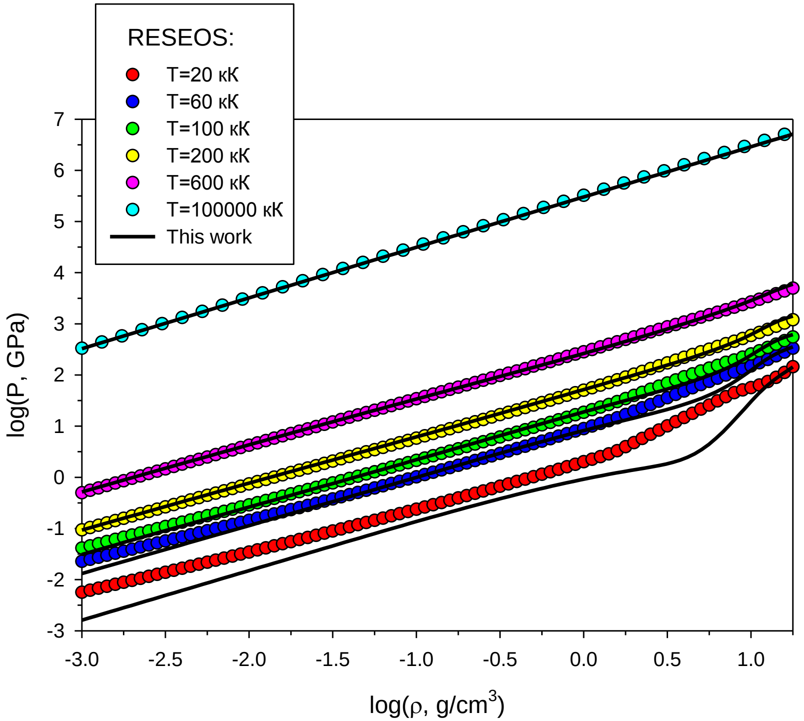

Fig. 6. Liquid lead extension isotherms versus Liberman's model (RESEOS)

Calculations

	Density, g/cm³	Pressure, GPa	Temperature, K
Start of melting	16.628	52.55	3004.12
End of melting	17.399	70.82	3556.4

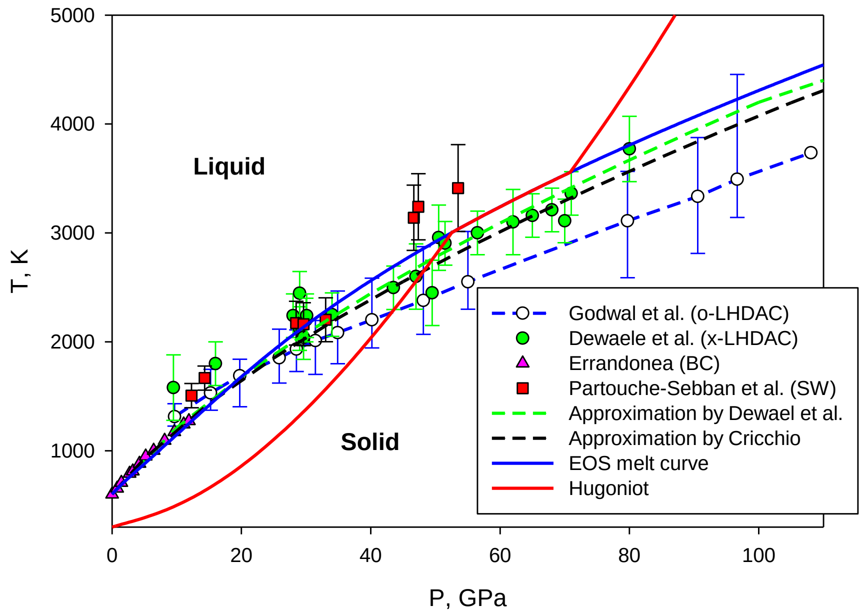

Fig 7. Temperature on the Hugoniot and phase diagram for lead

Temperature, K	Pressure, GPa	Density, g/cm³	Source
4980	0.184	3.25	Corresponding states
5158	0.225	3.06	Soft sphere
4663	0.208	3.1	Hard sphere
5300	0.17	2.31	Shock wave
5300-6000	0.2-0.3	3.06-3.15	Exp. data (Hodgson)
5996	0.17	3.29	This work

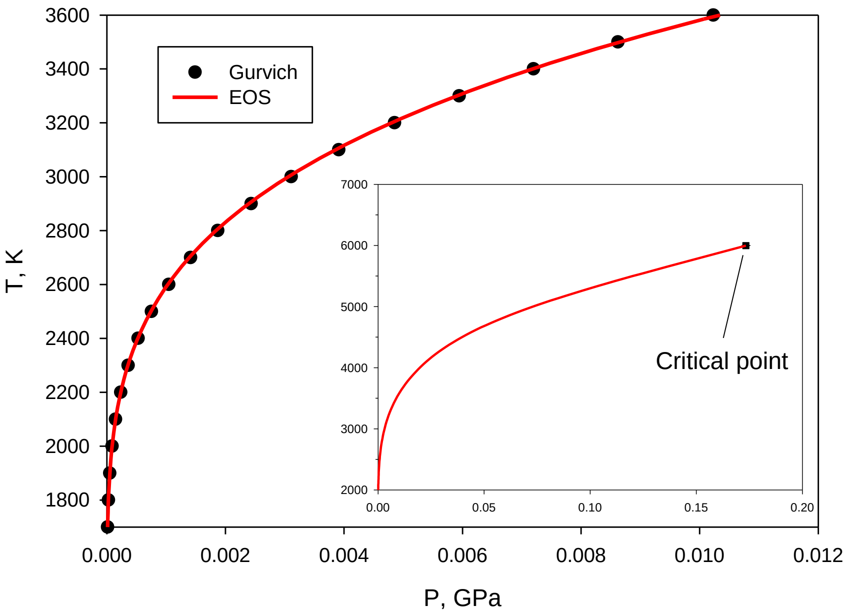

Fig. 8. Liquid-vapor curve and critical point (insertion) for lead.

Calculations

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	Density, g/cm³	Pressure, GPa	Temperature, K
Start of melting	16.628	52.55	3004.12
End of melting	17.399	70.82	3556.4

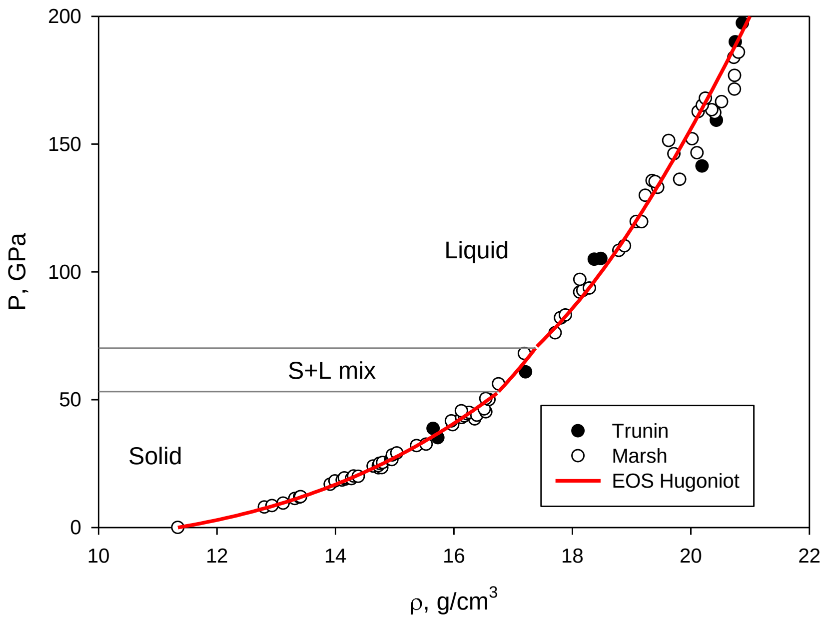

Fig. 9. Shock Hugoniot of lead up to 200GPa

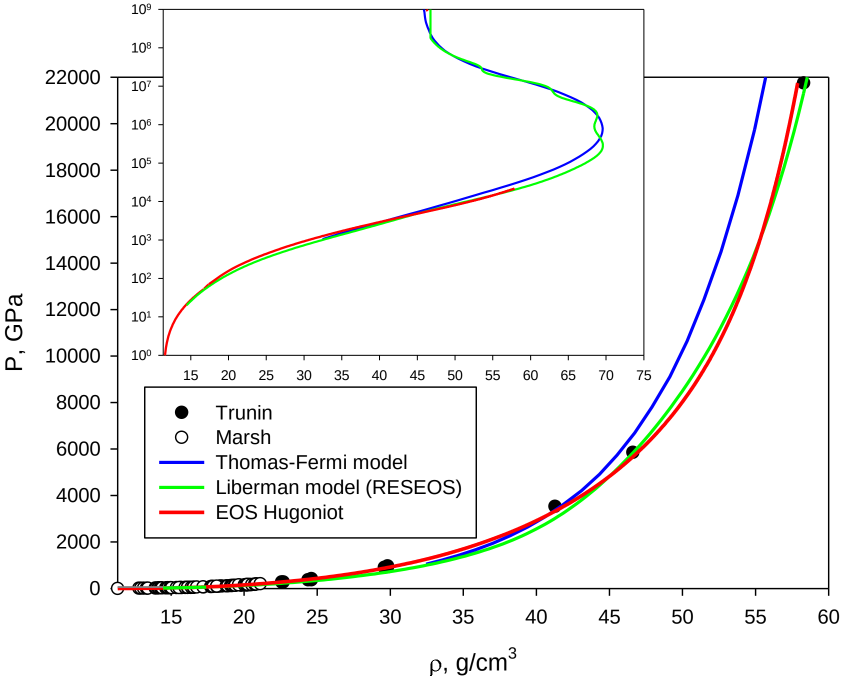

Fig. 10. Shock Hugoniot in the experimentally studied range of pressures.

Calculations

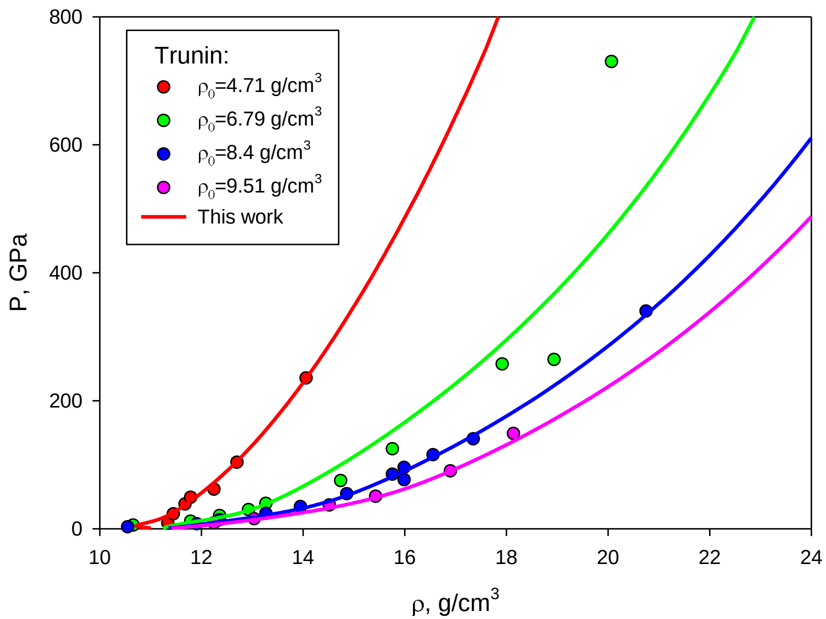

Fig. 11. Shock Hugoniots of porous lead.

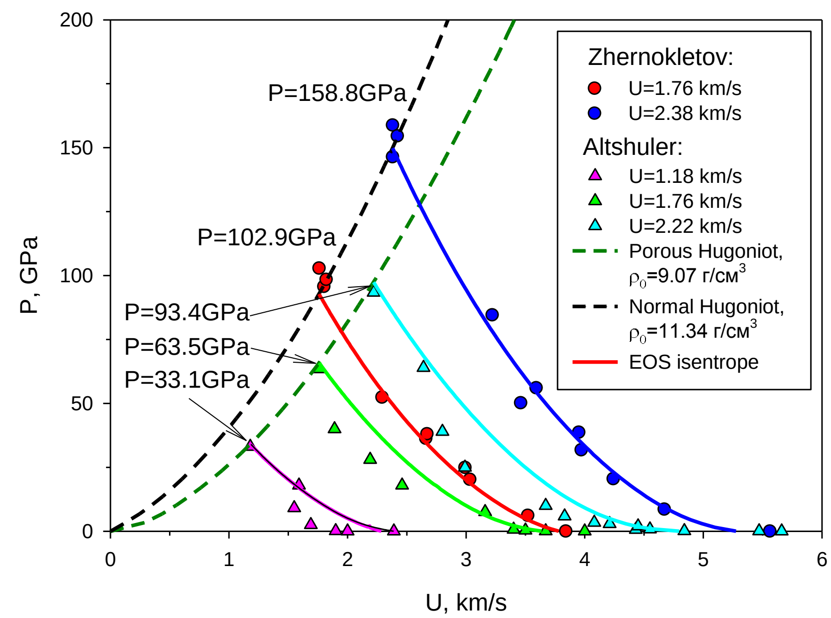

Fig. 12. Isentropes of unloading for solid and porous lead

Conclusion

We have constructed a two-phase equation of state for lead with evaporation. It is fit to available data from static and dynamic experiments in the region of moderate temperatures and pressures where solid phases exist, and in the high-pressure region of shock compression to 22 TPa. Also, in the high-pressure region the equation is adjusted against calculations by the Kopyshev-corrected Thomas-Fermi and Liberman models.

The presence of gas asymptotic in the equation of state for liquid helped us describe the liquid-vapor equilibrium curve and calculate coordinates of the critical point in agreement with literature data.