

## Equation of state for metals based on Thomas–Fermi model

K.V. Khishchenko, O.P. Shemyakin

*Institute for High Energy Densities, Joint Institute for High Temperatures,  
Russian Academy of Sciences, Moscow, Russia*

To analyze the physical processes at high energy densities, an adequate describing the thermodynamic properties of matter over a broad region of states including both the condensed phase under normal conditions and plasma at high pressures and temperatures is required [1].

In the present paper a semiempirical equation-of-state model, which is based on Thomas–Fermi theory [2], is proposed. According to this model, the Helmholtz free energy for matter is considered as a sum of three components,

$$F(V, T) = F_c(V) + F_a(V, T) + F_e(V, T), \quad (1)$$

describing the elastic part of interaction at  $T = 0$  K ( $F_c$ ) and the thermal contributions of atoms ( $F_a$ ) and electrons ( $F_e$ ). The first and second components in Eq. (1) are given by interpolation formulae, the third is calculated within the framework of the Thomas–Fermi model [2].

The volume dependence of the elastic energy under compression  $\sigma_c \geq 1$  (where  $\sigma_c = V_{0c}/V$ ,  $V_{0c}$  is the specific volume at  $P = 0$  and  $T = 0$  K) is given by the relation [3]

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

providing for the normalizing condition

$$F_c(V_{0c}) = 0. \quad (3)$$

As can be readily seen, differentiation of the energy (2) with respect to volume yields an equation for the pressure  $P_c(V)$  which is analogous to the relation proposed previously [4] as an expansion of the Thomas–Fermi model in powers of the atomic cell radius  $r_c \sim (\sigma_c)^{-1/3}$ .

The value of coefficient  $b_2$  in Eq. (2) is determined from the condition of coincidence with the model of degenerate ideal Fermi-gas of nonrelativistic electrons [5] in the range of compressions above  $\sigma_c \sim 10^3$ – $10^4$ ,

$$b_2 = Z^{5/3} \frac{1}{5} (3\pi^2)^{2/3} a_B^2 E_H (Am_u V_{0c})^{-5/3}, \quad (4)$$

where  $E_H$  is the Hartree energy,  $a_B$  is the Bohr atomic radius,  $m_u$  is the atomic mass unit (amu),  $A$  is the atomic mass (in amu) and  $Z$  is the atomic number of an element.

In order to determine the coefficients  $b_1$  and  $a_i$  in Eq. (2), one must solve the problem of minimization of the root-mean-square deviation of pressure at some points  $V_n$ ,  $n = 1, \dots, N$ ,

in the interval  $\sigma_c = 50\text{--}10^3$  from the results of calculation by the Thomas–Fermi model with corrections [6] subject to the conditions for the pressure, bulk modulus and its derivative with respect to pressure at  $\sigma_c = 1$ ,

$$P_c(V_{0c}) = -dF_c/dV = 0, \quad (5)$$

$$B_c(V_{0c}) = -VdP_c/dV = B_{0c}, \quad (6)$$

$$B'_c(V_{0c}) = dB_c/dP_c = B'_{0c}. \quad (7)$$

The problem of conditional minimization is solved with the introduction of Lagrange factors [7]. The values of the parameters  $V_{0c}$ ,  $B_{0c}$  and  $B'_{0c}$  are fitted by iterations so as to satisfy under normal conditions the tabular value of specific volume  $V_0$  and the values of isentropic compression modulus  $B_S = -V(\partial P/\partial V)_S = B_{S0}$  and its pressure derivative  $B'_S = (\partial B_S/\partial P)_S = B'_{S0}$  determined by the data of dynamic measurements.

The energy on the cold curve in the rarefaction region ( $\sigma_c < 1$ ) is given by a polynomial [8]

$$F_c(V) = V_{0c} \left[ a_m \left( \sigma_c^m/m - \sigma_c^l/l \right) + a_n \left( \sigma_c^n/n - \sigma_c^l/l \right) \right] + E_{sub}, \quad (8)$$

which provides for a chosen value of the sublimation energy  $F_c = E_{sub}$  at  $V \rightarrow \infty$  and for Eq. (5). Note that conditions (3), (6) and (7) leave only two free parameters,  $l$  and  $n$ , in Eq. (8).

The component of free energy corresponding to the thermal movement of nuclei is defined as follows,

$$F_a(V, T) = 3RT \ln \left( 1 - \exp \left( -\theta/T - \sqrt{T_a \sigma^{2/3}/T} \right) \right), \quad (9)$$

$$\theta(V) = \theta_0 \sigma^{2/3} \exp \left( \left( \gamma_0 - 2/3 \right) \frac{B^2 + D^2}{B} \operatorname{arctg} \frac{B \ln \sigma}{B^2 + D(\ln \sigma + D)} \right), \quad (10)$$

where  $\sigma = V_0/V$ ,  $\gamma_0$  is the value of Grüneisen coefficient under normal conditions.

The thermal contribution of electrons in equation of state for metals is represented in the following form,

$$F_e(V, T) = E_e(V, T) - TS_e(V, T), \quad (11)$$

$$E_e(V, T) = E_{TF}(V, T) - E_{TF}(V, 0), \quad S_e(V, T) = S_{TF}(V, T), \quad (12)$$

where the internal energy  $E_{TF}$  and entropy  $S_{TF}$  are determined according to the Thomas–Fermi model [2]. To calculate the potential of electrons and nucleus in the electrically neutral spherical atomic cell, we used the shooting method for the classical fourth-order Runge–Kutta formula [6] with initial approximation obtained using sweep method with iterations [9]. For determination of the Fermi–Dirac functions, we used approximation expressions [10].

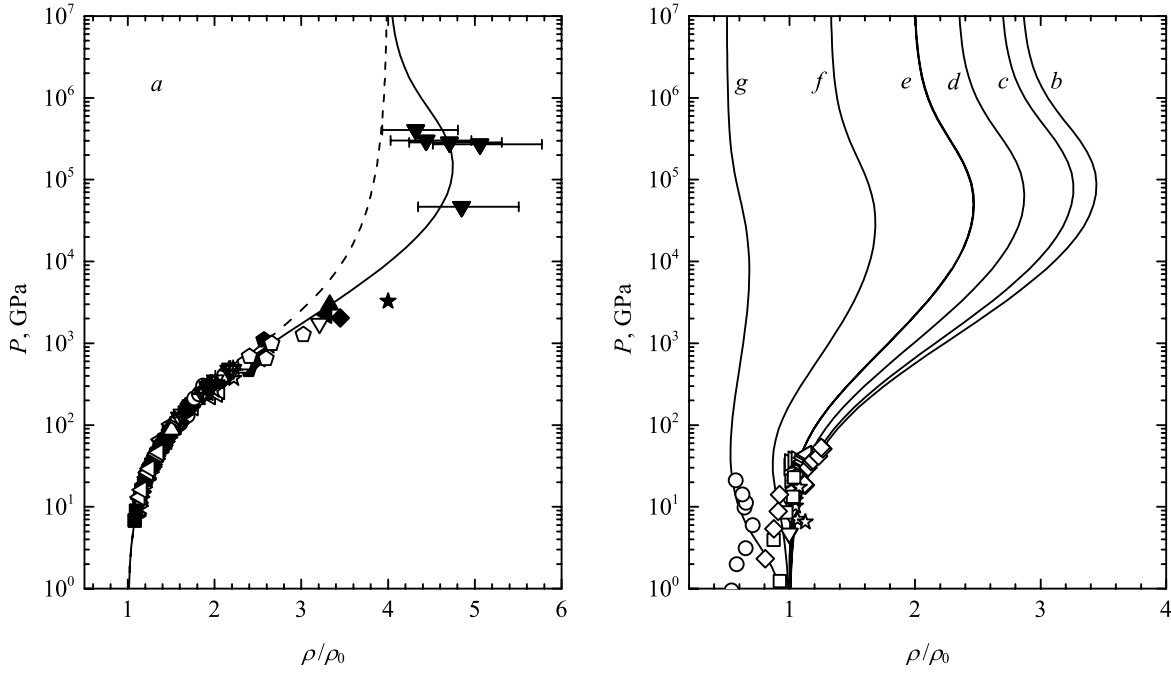


Figure 1: Shock Hugoniots of aluminum samples with initial porosities  $m = \rho_0/\rho_{00} = 1$  (a), 1.408 (b), 1.493 (c), 1.711 (d), 2.012 (e), 3.013 (f) and 9.796 (g),  $\rho_0 = 1/V_0$  is the normal density,  $\rho_{00}$  is the initial density of samples. Lines correspond to results of calculations with taking into account the thermal contribution of electrons (solid lines) and disregarding this contribution (dashed line). Markers denote experimental points from shock-wave database [11]

The coefficients of equation of state that optimally generalize the available thermodynamic information for aluminum within the framework of Eq. (1)–(12) are as follows:  $a_0 = 6923.207$ ,  $a_1 = -4772.762$ ,  $a_2 = 1263.499$ ,  $a_3 = 50.038$ ,  $b_1 = -5061.082$ ,  $b_2 = 1597.1$ ,  $a_m = -332.776$ ,  $a_n = 150.754$ ,  $m = 1.1$ ,  $n = 1.7266$ ,  $l = 1$ ,  $E_{sub} = 12.1$ ,  $T_a = 0.00089443$ ,  $D = 0.35667$ ,  $B = 0.5$ ,  $\gamma_0 = 1.95$ ,  $\theta_0 = 0.2$ ,  $V_0 = 0.3687$ . The units of measurement for the listed coefficients correspond to the original units  $P = 1$  GPa,  $V = 1$  cm<sup>3</sup>/g,  $E = 1$  kJ/g,  $T = 1$  kK.

The calculated shock Hugoniots of aluminum samples of different initial density in comparison with experimental data from [11] are presented in Fig. 1. As one can see in Fig. 1, the equation of state constructed for aluminum adequately describes the experimental data over the entire range of pressures generated in shock waves.

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