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Abstract

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ON INTERPOLATION EQUATIONS OF STATE OF METALS FOR THE REGION OF ULTRAHIGH PRESSURES

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The extensive experimental material published in recent years on shock compression of metals by pressures of hundreds of thousands and millions of atmospheres ([1,2]) makes it possible to reveal the character of the interaction of atoms in the region of relatively large compressions, where repulsive forces predominate. Using the expression for the Grüneisen coefficient ([3,4]), in ([1,7]) the curves of cold compressibility $P_x(\rho)$ at $T = 0°\text{K}$ were found. In the present communication a method is considered for finding the indicated dependence without using experimental data on shock compression of metals.

Gombás ([6]) succeeded in describing quite satisfactorily Bridgman' s data on the compressibility of alkali and alkaline-earth metals up to pressures of 40000 atm, proceeding from quantum-mechanical concepts of interatomic interaction, according to which the expression for the elastic pressure is written in the form of a power series in δ ($\delta = \rho/\rho_k$ is the relative density, ρ_k is the density of the substance at $P = 0$ and $T = 0$). At pressures of the order of 10^9 atm, the elastic curve is described with sufficient accuracy by the Thomas-Fermi-Dirac (TFD) model.

To describe the experimental data on shock compression, which lie in the intermediate region, we shall require that the sought dependence $P_x(\rho)$ satisfactorily describe both the parameters of the substance under normal conditions and its behavior in the region where the TFD model is valid.

We shall seek the elastic curve in the form

$$P_x = \sum_{i=1}^{n} a_i \delta^{i/3+1}. \tag{1}$$

At the density ρ_k, when $\delta = 1$, $P_x = 0$. Hence it follows that

$$\sum_{i=1}^{n} a_i = 0. \tag{2}$$

The region with $\delta < 1$ is determined by the binding energy

$$\Lambda = \int_{\rho_k}^{0} \frac{P_x \, d\rho}{\rho^2} = -\frac{3}{\rho_k} \sum_{i=1}^{n} \frac{a_i}{i},$$

whence

$$\sum_{i=1}^{n} \frac{a_i}{i} = -\frac{\Lambda \rho_k}{3}. \tag{3}$$

The bulk modulus of compression at $T = 0^{\circ}\mathrm{K}$

$$K_x = \delta \frac{dP_x}{d\delta} = \frac{1}{3} \sum_{i=1}^{n} (i+3) a_i \delta^{i/3+1}. \tag{4}$$

For $\delta = 1$, from $(4')$ and (2) we obtain*

$$\sum_{i=1}^{n} i a_i = 3K \ . \tag{4}$$

Let us further assume that, in the region of interest to us, the theory of small oscillations ([8,4]) is valid, which relates the Grüneisen coefficient to the first and second derivatives of the cold curve:

$$\gamma = \frac{1}{3} + \frac{\delta}{2} \frac{d^2 P_{\mathrm{x}}/d\delta^2}{dP_{\mathrm{x}}/d\delta}. \tag{5'}$$

For $\delta = 1$, $(5')$ becomes

$$\gamma_{\mathrm{k}} = \frac{1}{6} \left[\sum_{i=1}^{n} (i-1)(i+6) a_i \right] \Big/ \left[\sum_{i=1}^{n} (i-1) a_i \right]. \tag{5}$$

Finally, the requirement of agreement with the TFD theory at large δ gives two more equations

$$\sum_{i=1}^{n} a_i \delta_1^{i/3+1} = P_{\mathrm{x}1}; \tag{6}$$

$$\frac{1}{3\delta_1} \sum_{i=1}^{n} (i+3) a_i \delta_1^{i/3+1} = \left(\frac{dP_{\mathrm{x}}}{d\delta} \right)_1, \tag{7}$$

where the index 1 denotes a state on the TFD curve $P_{\text{x}}(\rho)$.

Equations (2)–(7) make it possible to find the 6 coefficients a_i in (1). A series of check calculations showed that an attempt to reduce the number of parameters being described by discarding one or another condition leads to the discarded condition not being satisfied. The exception is (3), whose omission, or the choice of a sufficiently arbitrary value of Λ, does not affect the course of the curve $P_{\text{x}}(\rho)$ for $\delta > 1$. This condition, however, is introduced in order to describe more physically correctly the course of the elastic curve for $\delta < 1$.

The density of the substance ρ_{k} at $T = 0^{\circ}\text{K}$ and $P = 0$ was found from the relation $\rho_{\text{k}} = \rho_0(1 + \alpha_0 E_0/c_{v0})$, obtained by integrating the expression for the volumetric coefficient of thermal expansion $\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$, under the Grüneisen assumption $\alpha/c_v = \text{const}$ in the temperature interval from $T = 0$ to $T = T_0$. Here $E_0 = \int_0^{T_0} C_v dT$ is the internal energy. The subscript zero denotes the state under normal conditions: $T_0 = 300^{\circ}\text{K}$, $P = 0$.

K and γ_{k} were found by the method of successive approximations. K was found from the relation

$$K = K_{\text{k}} - P\left[1 + (d\ln\gamma/d\ln\rho)_{\rho=\rho_{\text{k}}}\right], \tag{8}$$

obtained by differentiating the expression for the isotherm $P = P_{\text{x}} + E_0\gamma\rho$ at the point $P_{\text{k}}, \rho_{\text{k}}$. In (8), $K_{\text{k}} = \rho_0/\rho_{\text{k}}(a - 2bP_{\text{k}})$, where a and b are the coefficients in Bridgman' s equation; K_{k} and P_{k} are the bulk compression modulus and the pressure on Bridgman' s isotherm at $\rho = \rho_{\text{k}}$,

$$3\left(\frac{d\ln\gamma}{d\ln\delta}\right)_{\delta=1} = \sum_{i=1}^{n}(i-1)(i+2)(i+3)a_i \Big/ \sum_{i=1}^{n}(i-1)(i+6)a_i - \sum_{i=1}^{n}(i-1)(i+3)a_i \Big/ \sum_{i=1}^{n}(i-1)a_i.$$

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* Bardin ([10]) used equations analogous to (2)–(4) to find three unknown parameters in a relation similar to (1). In this way he succeeded in satisfactorily describing Bridgman' s data on the compression of alkali metals up to pressures of 40000 atm.

Table 1

Parameter	Al	Ni	Cu	Zn	Ag	Sn	Au	Pb	Mg	Cr	Zr	Ta	Pt
ρ_0, g/cm^3	2.71	8.90	8.93	7.14	10.49	7.28	19.3	11.34	1.735	7.13	6.49	16.46	21.37
$c_0 \cdot 10^{-5}$, erg/g-deg	67.77	40.32	48.98	41.8	56.1	60.5	42.2	84.5	75	25.0	27.7	14.82	26.5

Parameter	Al	Ni	Cu	Zn	Ag	Sn	Au	Pb	Mg	Cr	Zr	Ta	Pt
$C_c \cdot 10^{-10}$, erg/g*	8.589	4.353	3.716	5.228	2.249	2.185	1.69	1.215	8.791	4.385	15.335	1.493	1.299
$E_0 \cdot 10^{-10}$, erg/g*	0.1702	0.0789	0.0787	0.0830	0.0525	0.0450	0.0304	0.0323	0.2417	0.0863	0.0573	0.0302	0.0287
$A \cdot 10^{-10}$, erg/g	1.636	7.71	5.71	1.77	2.022	2.339	1.095	0.866	6.60	6.86	5.736	4.222	2.207
$\alpha \cdot 10^{-5}$, deg^{-1}	11.268	0.535	0.929	1.693	1.002	1.88	0.5775	0.445	2.778	0.525	7.115	0.498	0.637
$b \cdot 10^{2}$, cm^4/dyn^2	5.060	1.4	1.56	9.35	3.8	11	0.83	16.3	0.7	0.65	6.1	0.2	0.25
δ_1	60	5.53	6.0	9.04	10.74	11.63	8.58	4.67	7.45	0.1	26.6	0.59	8.8
ρ_t	24.6	225.3	244.0	290.0	680.4	836.2	902.5	659.1	25.5	186.5	380.4	693.6	865.0
$P_{\text{TFD}} \cdot 10^{-12}$, dyn/cm^2	11.3	104.4	105.0	92.5	160.8	118.4	213.4	114.8	7.7	76.4	78.4	163.9	230.6
$P_{\text{TF}} \cdot 10^{-12}$, dyn/cm^2	518	1240	108.8	100	57.1	141	37.6	144	551	306	333	326	342
β_0, erg/g-deg^2	2.745	8.966	9.025	7.337	10.627	7.368	19.51	11.59	1.764	7.164	6.509	16.525	21.496
P_x, g/cm^3	2.060	1.952	2.043	2.667	2.334	1.978	3.064	2.446	1.629	1.506	0.723	1.590	2.663
γ_k	0.768	1.188	1.427	0.711	1.00	0.670	2.31	0.699	0.360	1.933	0.923	2.008	2.855
$K_x \cdot 10^{-12}$, dyn/cm^2	22	92	1291.4[illegible]	[illegible]8.47	6.99	38.84	731.96	−49.8[illegible]	[illegible]4.15	1628.3[illegible]	[illegible]53.83	1184.3[illegible]	[illegible]520.08
$a_1 \cdot 10^{-10}$	−192.6[illegible]	[illegible]705.6	10971.6[illegible]	[illegible]799.0[illegible]	[illegible].18	−143.34	[illegible]540.2[illegible]	[illegible]80.13	−442.31	[illegible]12688.6[illegible]	[illegible]19.7[illegible]	[illegible]974.30[illegible]	[illegible]074.75
$a_2 \cdot 10^{-10}$	1823.0[illegible]	[illegible]1634[illegible]	[illegible]	[illegible]	[illegible]	[illegible]9.88	10170.5[illegible]	[illegible]	[illegible]6.95	−2630[illegible]	[illegible]49.7[illegible]	[illegible]2037[illegible]	[illegible]31.73
$a_3 \cdot 10^{-10}$	−4521[illegible]	[illegible]	[illegible]1202.7[illegible]	[illegible]738.1[illegible]	[illegible]70.6[illegible]	[illegible].93	7629.5[illegible]	[illegible]28.67	−348.9[illegible]	[illegible]30764.1[illegible]	[illegible]	[illegible]	[illegible].38
$a_4 \cdot 10^{-10}$	5347.0[illegible]	[illegible]4044[illegible]	[illegible]	[illegible]	[illegible]1.3	49.97	−1662.[illegible]	[illegible]45.1[illegible]	[illegible]2.47	[illegible]14698.[illegible]	[illegible]57.0[illegible]	[illegible]450.4[illegible]	[illegible]25.64
$a_5 \cdot 10^{-10}$	−2472[illegible]	[illegible]	[illegible]069.4[illegible]	[illegible]325.3[illegible]	[illegible]36.6	−1.48	62.44	14.25	−11.49	−2674.9[illegible]	[illegible]25.88	[illegible]576.4[illegible]	[illegible]15.86

$a_6 \cdot 10^{-10}$	422.93	3942.32	297.54	41.12

* According to Debye theory.

The values P_{x1} and δ_1 were chosen where $(P_{\text{TF}} - P_{\text{TFD}})/P_{\text{TF}} < 0.2$, since in this region it may be assumed [8] that the TFD model gives correct results. The values $P_{x1} = f(\delta_1)$ themselves are taken from (9). For metals not listed in (9), the values $P_{x1} = f(\delta_1)$ were found by interpolation in the coordinates $\lg(P_x/Z^{10/3}) - \rho/ZA$, where metals close in atomic number are described by similar curves. All initial data and the obtained parameters a_i for Al, Ni, Cu, Zn, Ag, Sn, Au, Pb are given in Table 1.

For comparison with experiment, the Hugoniot adiabats were calculated from the found $P_x(\rho)$. In doing so, the equation of state and the expression for the internal energy were written in the same form as in (7):

$$P = P_x(\rho) + \gamma(\rho) c_v \rho \left(T - T_0 + \frac{E_0}{c_v} \right) + \frac{1}{4} \beta_0 \rho_0 \left(\frac{\rho}{\rho_0} \right)^{1/2} T^2; \tag{9}$$

$$E = E_x(\rho) + c_v \left(T - T_0 + \frac{E_0}{c_v} \right) + \frac{1}{2} \beta_0 \left(\frac{\rho}{\rho_0} \right)^{-1/2} T^2, \tag{10}$$

where β_0 is the coefficient of the electronic heat capacity, whose value was taken equal to that found at very low temperatures [7], and the dependence $\gamma = f(P_x)$ was taken in the Slater–Landau form (5)*.

* Calculations showed that using the relation $\gamma = f(P_x)$ in the Dugdale–MacDonald form (5) leads to a somewhat worse description of the experimental data.

Comparison of the calculated dynamic adiabats with the experimental ones ([1,2,7]) showed that for Al, Ni, Cu, Pb, and Sn the agreement is quite satisfactory

Fig. 1

Figure 1: Fig. 1

(the discrepancy does not exceed 5-8% over the entire range of experimentally investigated pressures). For Ag the discrepancy is $\approx 15\%$, and for Zn $\approx 25\%$. Finally, for Au it is $\approx 25\%$ at $P \approx 2$ million atm. and $\approx 5\%$ at $P = 5$ million atm.

In addition to those considered, the authors calculated adiabats for a number of other metals not yet investigated experimentally at $P > 0.5$ million atm. Table 1 gives the initial parameters and the found values of the coefficients a_i for some of them (Mg, Cr, Zr, Ta, Pt), and Fig. 1 shows the calculated Hugoniot adiabats.

Fig. 1

The sufficiently satisfactory agreement obtained between the calculated dynamic adiabats and the experimental ones shows that the analytical form of the elastic curve as a series in δ, with the free parameters found by the method described above, basically correctly describes the interatomic potential for a number of metals over a wide pressure range, from the Bridgman region to several million atmospheres. This, on the one hand, makes it possible, without carrying out a dynamic experiment, to obtain an idea of the behavior of substances at ultra-high pressures, and, on the other hand, to process experimental data on shock compression of substances by a method different from ([1,7]). The latter has the advantage that, unlike ([1,7]), it makes it possible to determine $P_x(\rho)$ and $\gamma(\rho)$ from one or two experimental points without using the slope of the dynamic adiabat, which is not very reliable experimentally.

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Note: Figure translations are in progress. See original paper for figures.