AN EQUATION OF STATE FOR CONDENSED MATTER BEHIND INTENSE SHOCKWAVES

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Abstract. Thermodynamic functions that realistically describe characteristics of substances in various parts of the phase diagram are fundamental characteristics of matter. The necessity in such functions has always been urgent and permanently increases. The advanced equations of state constructed to describe the behavior of metals in a broad range of compression parameters contain tens of free parameters and experimentally found constants (see, for instance, [1, 2]). Such constants were found from shock-wave data, from measured unloading isentropes of porous specimens, and from other experimental thermodynamic data.

In the present paper, we propose new model equations for thermodynamic functions of crystalline and liquid states based on the dependence of the Gruneisen coefficient $\Gamma(V,T)$ on volume and temperature. The difference between the elastic ("cold") components of energy and pressure for a liquid and those for a solid is taken into account. Configurational entropy of a liquid, providing a measure of its disorder and resulting in finite values of the total entropy in the zero-temperature limit, is introduced.

1 Construction of the Gruneisen function

Following [3], we defi ne the Gruneisen coeffi cient $\gamma(V)$ by the formula

$$\gamma(V) = 2/3 - 2/(1 - aV_0/V), \quad a = 1 + 2/(\gamma_s - 2/3) + 2P_{t,0}/K_s, \tag{1}$$

where $\gamma_s = \beta K_s V_0/c_v$, K_s is the adiabatic bulk compression modulus, $c_v = c_{v,l} + c_{v,e}$ is the specifi c heat at constant volume, made by the heat capacities due to the lattice and due to electrons, and $P_{t,0}$ is the thermal pressure under normal conditions. All quantities in (1) are to be calculated at some initial conditions that include specifi c volume V_0, temperature T_0, and pressure P_0.

The equation of state in the Mie-Gruneisen form is

$$E(V,T) = E_x + c_{v,l}T + 0.5c_{v,e0}(V/V_0)^{2/3}T^2, \tag{2}$$

$$P(V,T) = -(dE_x/dV) + \gamma_l c_{v,l}T/V + c_{v,e0}T^2/[3V(V/V_0)^{2/3}], \tag{3}$$

$$F(V,T) = E_x(V) + c_{v,l}T\ln(\Theta(V)/T) - c_{v,e0}(V/V_0)^{2/3}T^2/2. \tag{4}$$

Using the defi nition of the Gruneisen coeffi cient $\gamma = -(d\ln\Theta/d\ln V)\big|_T$ and relation (1), we fi nd the Debye temperature as a function of volume:

$$\Theta(V) = \Theta_0[(a - V/V_0)/(a-1)]^2(V_0/V)^{2/3}, \tag{5}$$

where $\Theta_0 = \Theta(V_0)$ is the Debye temperature under normal conditions.

2 Construction of the energy function on the zero isotherm

To fi nd the Gruneisen coeffi cient $\gamma(V)$ as a function of volume, we use the Landau-Slater theory [4, 5]:

$$\gamma_l(V) = -2/3 - (V/2)(d^2P_x/dV^2)/(dP_x/dV). \tag{6}$$

Solving together (1) at the temperature $T = 0°K$ and (6), we obtain the specifi c energy and pressure on the zero isotherm:

$$E_x(V) = -a_x V_0(C_1H_1(\xi) + C_2\xi) + C_3, P_x(V) = C_1H_2(\xi) + C_2. \tag{7}$$

where C_1,C_2, and C_3 are some unknown functions that depend on characteristics of the particular material, and the H-function is

$$\begin{cases} H_1(\xi) = 9\xi^{-2/3} + 18\xi^{1/3} + 27\xi^{4/3}/2 - 9\xi^{7/3}/7 + 9\xi^{10/3}/70, \\ H_2(\xi) = -3\xi^{-5/3}/5 + 6\xi^{-2/3} + 18\xi^{1/3} - 3\xi^{4/3} + 3\xi^{7/3}/7. \end{cases}$$

A more completed and substantiated method for reconstructing the values of parameters on the zero isotherm can be found elsewhere [6].

The set of semi-empirical relations (1 – 7) describes the behavior of thermodynamic characteristics of a solid. The values of V_0, β, K_t, c_p, Θ_0, and $c_{v,e0}$ are to be taken at some initial conditions and readily available in reference sources on physical and mechanical properties of substances. The quantity a_x is a parameter to be adjusted so that to obtain a best fi t to experimental data.

3 Characteristic Debye temperature

The energy of a system of $3N_A$ independent harmonic oscillators of one and the same frequency is [7]

$$U = 3RT\frac{{}^{h\omega}/_{kT}}{e^{{}^{h\omega}/_{kT}} - 1}$$

where ω is the oscillator frequency, h is the Planck constant, and k is the Boltzmann constant.

Whatever the oscillations that can be executed by the system, the total number of all possible oscillation modes should be equal to the total number of the degrees of freedom of the N particles that compose the system, i.e., to $3N$. Here, according to the quantum theory, the mean energy per one oscillation depends only on the frequency and is given by the formula

$$\bar{\varepsilon} = \frac{h\omega}{e^{{}^{h\omega}/_{kT}} - 1}$$

That is why, to fi nd the energy of a certain volume V of the solid, it is required, fi rst of all, to fi nd the total number of possible oscillation modes in it whose frequencies fall in the interval between ω and $\omega + d\omega$. This interval will be denoted as dN_ω.Then, the energy of the solid can be expressed as a sum over all possible frequencies:

$$U = \int \bar{\varepsilon}_\omega dN_\omega = \int \frac{h\omega dN_\omega}{e^{{}^{h\omega}/_{kT}} - 1}.$$

In determining U, it is possible, following Debye, instead of performing a microscopic consideration of coupled lattice vibrations, to use a phenomenological approach, considering the crystal as an elastic continuum. Thus, instead of the oscillation spectra of individual atoms, we consider the spectrum of elastic vibrations of the crystal as a whole; here we restrict ourselves to low-frequency vibrations whose wavelength is large compared to the interatomic distance (acoustic waves).

Next, we introduce the designation $I = \frac{1}{4\pi}\int\left(\frac{1}{v_0^3} + \frac{1}{v_1^3} + \frac{1}{v_2^3}\right)d\Omega = \sum\limits_{S=0}^{2}\frac{1}{v_S^3}$. For the energy of the solid body of a volume V, we obtain:

$$U = \frac{1}{2\pi^2}VI\int \bar{\varepsilon}\omega^2 d\omega. \tag{8}$$

Here, the integration over frequency is to be performed from zero frequency to some maximum frequency to be determined from the condition that the total number of natural vibrations of the body should be equal to the total number of its degrees of freedom. If N_V is the total number of molecules in the volume V, then the total number of the degrees of freedom is $3N_V$. The latter, however, is only valid in the case in which each of the lattice sites is occupied by a whole molecule of the substance (molecular crystal). Alternatively, as it is the case with an ionic crystal, if individual parts of the molecule

occupy different lattice sites, then the total number of the degrees of freedom increases by the factor that shows how many lattice sites correspond to one molecule. The latter is quite clear since in this case parts of molecules (atomic groups or ions) that occupy different lattice sites can be considered as individual particles. Let s be the number of individual lattice sites that correspond to one molecule. Then, the total number of the degrees of freedom in the volume V is $3sN_V$, and the condition for the maximum frequency is

$$\int dN_k = \frac{1}{2\pi^2} VI \int_0^{\omega_{MAX}} \omega^2 d\omega = 3sN_V, \quad \omega_{MAX} = \left(\frac{18\pi^2 sN_V}{IV} \right)^{1/2}.$$

Thus, expression (8) for the energy of the crystal acquires the form

$$U = \frac{1}{2\pi^2} VI \int_0^{\omega_{MAX}} \frac{h\omega^3 d\omega}{e^{h\omega/kT} - 1}.$$

We introduce the new integration variable $x = \frac{h\omega}{kT}$. Denoting $\theta = \frac{h\omega_{MAX}}{k}$, we obtain

$$U = \frac{1}{2\pi^2} VI \frac{(kT)^4}{h^3} \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1}, \tag{9}$$

The quantity θ is called the *characteristic Debye temperature.*

$$U = 9sN_V kT \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1},$$

The quantity I in (9) equals the sum of all inverted cubes of the phase velocities of elastic waves averaged over all wave-normal directions: $I = \left\langle \frac{1}{v_0^3} + \frac{1}{v_1^3} + \frac{1}{v_2^3} \right\rangle$.

Thus, the theoretical calculation of the characteristic Debye temperature reduces to calculating the quantity I from set elastic constants of the crystal. The simplest method to fi nd the value of I consists in that the crystal of interest is to be replaced by an isotropic medium closest in its properties to the crystal. In isotropic solids, owing to the fact that phase velocities do not depend on wave propagation direction, the averaging becomes unnecessary and can be omitted, and we fi nally obtain:

$$I = \frac{1}{v_l^3} + \frac{2}{v_s^3}.$$

where v_l is the velocity of longitudinal waves and v_s is the velocity of transverse (shear) or twist waves. If the velocities are unknown, we can invoke the theory of elasticity in which the velocities are given by the formula

$$v_l^2 = \frac{K_S + 4/3 G}{\rho_0}, v_S^2 = \frac{K_S}{\rho_0}$$

where G is the shear modulus.

The accuracy of the calculation algorithm depends on material anisotropy, since we use reduction to an isotropic body, and on calculation temperature. The higher the temperature, the more precise the calculation is, since, with increasing temperature, the fraction of excited high-energy (or high-frequency) quantum states increases.

The characteristic Debye temperatures calculated for several crystals for which values of elastic constants are known are listed in the table 1.

The notations in the table are as follows: Θ_0 is the Debye temperature yielded by the above procedure, $\Theta\exp$ is the experimental Debye temperature taken from [9], and $\delta\Theta = \frac{\Theta_{\exp} - \Theta_0}{\Theta_{\exp}}$ is the relative error in predicting the Debye temperature.

The comparison shows good convergence of the values of Θ_0, giving us all grounds to believe that this procedure can be applied to materials with unknown Debye temperatures.

	Al	Cu	Mg	W	Be
Θ_0,K	407.8	323.3	373.3	364.5	1420.1
$\Theta\,\exp$,K	433	347	403	383	1481
$\delta\Theta,\%$	6.1	6.9	7.3	4.9	4.1

Table 1: Debye temperature

4 Equation of state for the liquid phase

As was noted above, the present thermodynamic model describes one phase specifi ed by some initial data. After the shock adiabate crosses the boundary between the phases, the calculations performed according to this model yield, instead of liquid, data for an overheated solid. Hence, it is required to modify the model of the solid so that to take into account the liquid-phase properties and phase-transition phenomena.

It is known that the expression for the free energy $F_L(V,T)$ of a liquid in the "crude" approximation of the model of the classical harmonic oscillator has the form

$$F_L(V,T) = E_{x,L}(V) + c_{v,l}T\ln[\Theta_L(V)/T] - 0.5c_{v,e0}(V/V_0)^{2/3}T^2 + F_c, \tag{10}$$

where $E_{x,L}(V)$ is the cold component of the energy of the liquid, Θ_L is some characteristic temperature, $F_c = -RT/A$ is the contribution due to entropy, and A is the atomic weight. To exert "control" over the value of the confi gurational entropy, we introduce a parameter a_s that has meaning of a residual entropy at the temperature $T = 0°K$. Then, the entropy term in the free energy acquires the form $F_c = -a_sRT/A$.

In its appearance, the expression for the free energy $F_L(V,T)$ of a liquid differs from expression (4) by the additional entropy term. Yet, the difference between the solid and liquid state is also in that these states possess different cold energies and temperatures. These fundamental differences in the description of solid and liquid phases were laid down in [8].

Expression (1) for the Gruneisen coeffi cient was derived without any restrictions on the phase state of the material. We therefore may conclude that these relations have identical meaning and are of identical functional form, and the difference consists in the particular values of parameters, determined by particular initial conditions.

Thus, by analogy with the thermodynamic model for the solid state, one can construct a model for the liquid state. To calculate the parameters of the liquid behind the shock-wave front, in the very like the same manner one can take into account the Rankine-Hugoniot relation, which makes it possible to fi nd the temperature and, afterwards, all thermodynamic parameters along the shock adiabate.

5 Melting under high pressures produced by shock waves

In consideration of particular thermodynamic models, it becomes clear that the ordinary classifi cation of states in the region of high pressures and temperatures often looses its defi niteness and become conventional, and the boundaries between the phases either vanish or become obscure, corresponding, in fact, to a continuous mutual transformation of close states.

As the shock-wave pressure increases, the thermal energy transferred to the substance continuously increases and, from certain pressures on, a transition of the initially solid body into the liquid state should be observed. Further variation of the dependence $T(P)$ along the dynamic adiabate can be fi gured out by invoking analogy with melting under atmospheric pressure, in which situation an increase in the energy transferred to the substance leads to an increase in temperature unless the substance gets completely melted. Further increase is further accompanied by an increase in temperature. A similar pattern is to be expected under shock compression; the difference here consists in the fact that in the region where the two phases co-exist (the segment of the melting curve between the shock adiabates for the liquid and for the solid, i.e., segment 2–3 in Fig. 1) some rise in the temperature should be expected since for the melting curve of most substances, the so-called "normal" ones, $dT/dP > 0$.

The expenditure of energy on melting gives rise to sharp kinks in the shock adiabate in the $T \div P$ plane; for this reason, the neglect of the melting under shock compression of the substance brings about inaccuracies in the determination of temperatures (points 3–4 in Fig. 1). Simultaneously, melting has little effect on kinetic shock-wave parameters and on the behavior of the dynamic adiabate in the $P \div V$ coordinates [10].

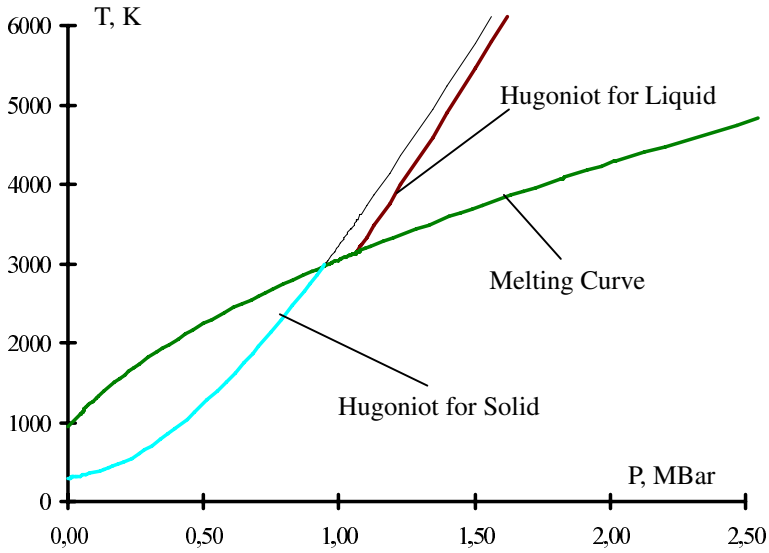

Figure 1: Melting curve and shock adiabate in the solid-phase and liquid-phase regions

To construct the melting curve, we use the condition of phase equilibrium:

$$\begin{cases} P_L = P_S = \bar{P} \\ S_L = S_S + \Delta S_m \\ F_L = F_S + \bar{P}\Delta V_m \end{cases} \tag{11}$$

The third equation in (11) is the condition of equality for the chemical potentials of the two phases per one mole of substance.

6 Results

With gained equations of states for the solid (1-7) and liquid (10) phases and with allowance for the Rankine-Hogoniot relation and phase-equilibrium conditions (11), we calculated dynamic adiabates and melting curves of Al, Cu and Pb crystals. The melting curve of each metal was found as the boundary between the phases with corresponding equations of state. The results are shown in Fig. 2.

Thus, with six constants, V_0, β, K_t, c_p, G, and $c_{v,e0}$ known at some initial point, and also with experimental data on dynamic loading of the solid, one can construct an equation of state of the condensed substance that realistically describes the material behavior in a broad range of pressures and temperatures with allowance for fi rst-kind phase transitions.

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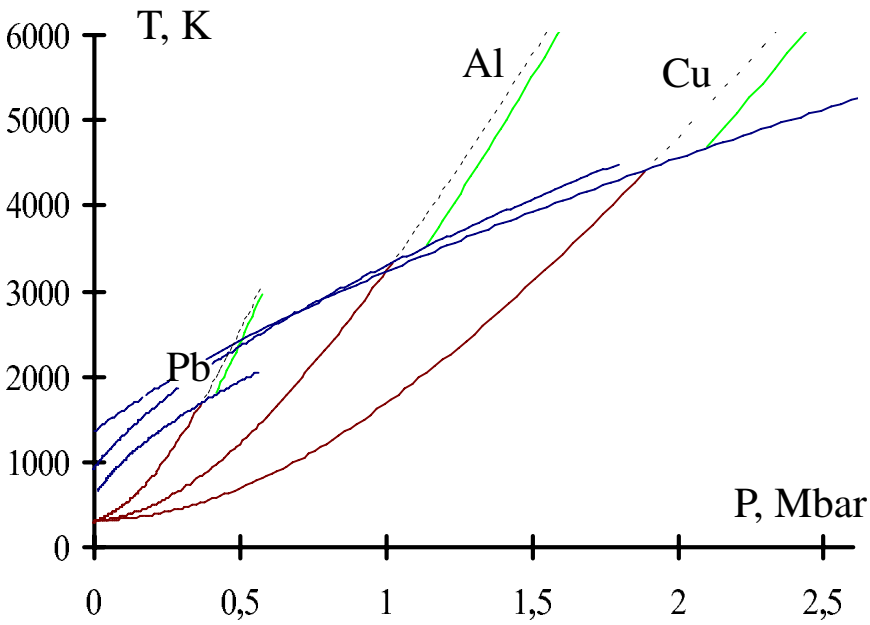

Figure 2: Melting curves and shock adiabates in the solid-phase and liquid-phase regions

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