

## THERMODYNAMIC PROPERTIES OF SOLIDS AT HIGH PRESSURES AND TEMPERATURES FROM SHOCK-WAVE EXPERIMENTS. THE COMPLETE EQUATION OF STATE

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**Keywords:** complete equation of state, shock Hugoniot, Debye solid.

**Abstract:** This paper deals with the analytic derivation of thermodynamic properties of solids from shock-wave experiments in the range of pressures and temperatures, attained by detonation of chemical explosives. First, we derive the complete equation of state (EOS). In principle, all the thermodynamic properties of a system can be predicted once precise knowledge of the complete EOS becomes known. But the single Hugoniot curve determined from shock-wave experiments does not provide enough thermodynamic information to specify an EOS. The assumptions which, along with shock-wave data, are used in this work to determine a complete EOS are the Grüneisen assumption (1), the volume dependence of the Grüneisen parameter (2), and the Debye model for the specific heats (3). Consequently, the thermodynamic functions of the system under consideration are expressed as a superposition of a cold (0 K) term corresponding to the cold compressed state, and a second one, corresponding to the thermal vibrations of atoms in the crystal lattice about their mean positions. The cold isotherm was derived in a previous paper, also presented here. In the present work we focus on the Debye model of a solid and the insertion of pressure dependence of the thermodynamic properties into it using Grüneisen's assumption. The results are combined to obtain a complete EOS for a solid. The thermal and the caloric EOS are also derived.

### I. Introduction

#### I. 1. Context

Equations of state (EOS) of matter, obtained both theoretically and experimentally are of immense current importance in the basic and the applied sciences. In principle, all the thermodynamic properties of a system may be predicted, once precise knowledge of the complete EOS becomes known. Unfortunately, this is very rarely the case. On surveying the literature we find that a plethora of expressions are being used to represent pressure-volume data of solids and liquids. Further, pressure-volume-temperature ( $P-V-T$ ) data for these substances are also represented through the temperature dependence of the parameters involved in representing  $P-V$  data. Although some of the equations have only a partial theoretical basis even then such empirical relations are of much value for smoothing, interpolation, and extrapolation of pressure-volume data and also in determining the values of isothermal bulk modulus or isothermal compressibility and their first or higher derivatives with respect to pressure for the solid or liquid concerned.

With the advancement of high pressure physics extensive experimental results on pressure-volume data have been obtained. Shock-wave experiments, aimed at EOS investigations, render it possible to extend the range of pressure-volume data beyond the region that can be reached with conventional static pressure experiments and to use much bigger specimens of the investigated material. All this brings to the forefront the problem of the complete EOS of matter at high pressures and temperatures.

#### I. 2. Objectives

The range of pressures and temperatures, considered in the present work is the one attained by detonation of chemical explosives in contact with the specimen or by explosively accelerated flyer plate methods. It does not extend beyond  $10^4 K$  and  $10^2 GPa$  [1]. The behavior of a solid within this range of pressures and temperatures is determined by the thermal lattice vibrations. That is why it is often called *the phonon region*. In addition to being easily accessible experimentally, it covers a wide variety of processes and phenomena of interest to science and technology. Therefore, we shall aim our considerations at the phonon region and seek an EOS valid in it.

A systematic theoretical calculation of an EOS in the phonon region on the basis of quantum mechanics of many-particle systems is very difficult because of the difficulties in incorporating correctly the strong collective interparticle interaction. Therefore, for the description of thermal properties of matter in this

range of thermodynamic parameters, one could apply phenomenological models in which experimental data are used to determine the coefficients in general functional dependencies derived from theoretical considerations. The purpose of the present paper is to derive such an EOS from shock-wave data.

### I. 3. Approximations

This work is based mainly on classical thermodynamics. To make the analysis of problems with shock-wave propagation in solids tractable within the framework of thermodynamics we need to make some approximations:

- First, since shock pressures are several hundred times the yield points of the materials involved, rigidity effects are neglected and an ordinary *fluid* type equation of state is assumed to be an adequate representation of the material. This implies that nevertheless the shock wave is usually one-dimensional its action is considered equivalent to that of hydrostatic pressure with the same magnitude.

- Second, thermodynamic equilibrium is assumed for the calculation of states behind the shock front.

- A third, basic for shock physics assumption concerns the form of the relation between shock velocity  $u_s$  and the velocity of the material flow behind the shock front -- the particle velocity  $u_p$ . The relation  $u_s(u_p)$  is the shock Hugoniot in kinematic form and it is assumed to be linear in a range of particle velocities where no phase changes or chemical reactions occur [2,3]. It has the form

$$(1) \quad u_s = c_0 + su_p$$

The intercept corresponds to the velocity of an infinitesimal pressure pulse, or the bulk sound speed,  $c_0 = [(\partial P/\partial \rho)_s]^{1/2}$  at  $P = 0$ . Since the slope is linearly related to the pressure derivative of the adiabatic bulk modulus,  $(\partial B_s/\partial P)_s$ , a linear  $u_s - u_p$  Hugoniot then reflects a nearly linear dependence of  $B_s$  on pressure.

We shall also employ:

- the Debye model for the specific heats [4]
- the Mie-Grüneisen equation which connects two points lying on an equilibrium thermodynamic surface described by an equation of state [3]
- Grüneisen's hypothesis that the thermodynamic functions of a solid may be expressed as a superposition of terms appropriate to various physical interactions [5]:

$$(2) \quad F = F_c(V) + F_{vib}(V, T), P = P_c(V) + P_{vib}(V, T), E = E_c(V) + E_{vib}(V, T),$$

where we have restricted our considerations to the contribution of the cold components and the lattice vibrations [6,7].

Using the definition of the Grüneisen parameter  $\gamma \equiv V(\partial P/\partial E)_V$  we assume that the parameter-to-volume ratio is constant and temperature independent:  $\gamma/V = \gamma_0/V_0 = const$ . Experimental work on a number of materials, as well as theoretical considerations, indicate this to be an adequate approximation [8,9]. The specific heat at constant volume  $C_v$  which also appears in the model is taken constant. This holds for most of the solids above the Debye temperature.

The approximations, stated above, are universally accepted and widely used in solid state physics and in shock physics. No *ad hoc* assumptions are made in this paper.

Therefore the objective of the work presented herein is to obtain a complete EOS for solids from shock-wave data using the Debye -- Mie-Grüneisen model and the shock Hugoniot as a reference curve, and to establish the thermodynamic properties of a system with such an EOS.

### II. General formulation

A thermodynamically complete EOS is defined by one of the thermodynamic potentials expressed as a function of its characteristic variables. In the case of the Helmholtz free energy  $F$  we have

$$(3) \quad F = F(V, T).$$

It is clear that  $F$  depends on the microscopic structure of the solid under consideration, which would vary as a function of volume and temperature. At different temperatures and densities, the corresponding region of matter will be dominated by different interactions. In view of the above, we may write the free energy as a superposition of terms appropriate to various physical interactions (Grüneisen's assumption [5])

$$(4) \quad F(V, T) = F_c(V) + F_{vib}(V, T) + F_e(V, T).$$

Here  $F_c$  is the configurational free energy at 0 K.  $F_{vib}$  corresponds to the contribution of the zero and thermal vibrations of the ions of the crystal lattice.  $F_e$  is the conduction electrons thermal excitations contribution. It manifests itself at temperatures  $\geq 10^4$  K and pressures  $\geq 10^2$  GPa [1]. At lower temperatures and pressures it may be neglected and Eq.(4) takes the form

$$(5) \quad F(V, T) = F_c(V) + F_0(V) + F_{IT}(V, T),$$

where  $F_0$  is the quantum zero-degree contribution. It is a function of volume only like the configurational term.  $F_{IT}$  is the thermal lattice contribution.

From the relation  $F = E - TS$  and the fundamental thermodynamic identity  $dE = -PdV + TdS$  it follows that at  $T = 0K$

$$(6) \quad F_c = E_c \quad \text{and} \quad P_c = -dF_c/dV = -dE_c/dV.$$

The specific form of the second of Eqs.(6) is derived from the Mie--Grüneisen equation using the shock Hugoniot as a reference curve in a paper which is also presented at this conference.

The calculation of Helmholtz free energy components  $F_0(V)$  and  $F_{IT}(V, T)$  will be performed within the framework of the Debye model for the specific heats.

### III. Contribution of the quantum zero Kelvin and lattice thermal vibrations to the EOS

In accordance with the quasiharmonic approximation the vibrational energy levels of a crystal lattice with  $N$  atoms may be treated as the energy levels of a system of  $3N$  independent linear harmonic oscillators. For the logarithm of the partition function of such a system we can write

$$(7) \quad \ln Z = \sum_{i=1}^{3N} \ln z_i = \sum_{i=1}^{3N} \ln \frac{\exp(-h\nu_i/2kT)}{1 - \exp(-h\nu_i/kT)},$$

where  $z_i$  is the partition function of the  $i$ -th oscillator.

In the Debye model [4] the crystal lattice is replaced by an isotropic elastic medium with a continuous dispersion law function. Further it is assumed that the magnitude of frequency in such a system does not exceed a certain boundary value, the Debye frequency  $\nu_D$ , chosen so that the number of the independent lattice oscillations is equal to the total number  $3N$  of the lattice degrees of freedom. It follows from this approximation that we can replace the summation in Eq.(7) by integration. Let us omit the index  $i$  of the oscillations. Then

$$\ln \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)}$$

is  $\ln z$  for all oscillators in the frequency range between  $\nu$  and  $\nu + d\nu$ . The number of these oscillators is equal to  $g(\nu)d\nu$ , where

$$(8) \quad g(\nu) = 9N\nu^2/\nu_D^3$$

is the density of distribution of oscillators among frequencies [4]. We introduce the Debye temperature  $\theta_D = h\nu_D/k$ , which depends on volume and is specific for each substance, and the new integration variable  $x = h\nu/kT$ . Then Eq.(7) takes the form

$$(9) \quad \ln Z = -\frac{9}{8}N(\theta_D/T) - 9N \frac{1}{(\theta_D/T)^3} \int_0^{\theta_D/T} x^2 \ln[1 - \exp(-x)] dx.$$

Integration by parts of Eq.(9) gives

$$\ln Z = -\frac{9}{8}N(\theta_D/T) - 3N \ln[1 - \exp(-\theta_D/T)] + 3N \frac{1}{(\theta_D/T)^3} \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1}.$$

The last equation can be written in a more compact form if we introduce the function

$$D(z) = \frac{3}{z^3} \int_0^z \frac{x^3 dx}{e^x - 1},$$

which is known as the Debye function and  $z = \theta_D/T$ . Then the logarithm of the partition function takes the form

$$(10) \quad \ln Z = -\frac{9}{8} N(\theta_D/T) - 3N \ln[1 - \exp(-\theta_D/T)] + ND(\theta_D/T).$$

From Eq.(10) and the thermodynamic identities

$$F = -kT \ln Z, \quad E = F - T(\partial F/\partial T)_V,$$

$$P = -(\partial F/\partial V)_T, \quad C_V = (\partial E/\partial T)_V$$

we can derive expressions for the specific free and internal energy, the pressure and the specific heat:

$$F_{vib}(T, V) = \frac{9}{8} Nk\theta_D + NkT \{3 \ln[1 - \exp(-\theta_D/T)] - D(\theta_D/T)\},$$

$$E_{vib}(T, V) = \frac{9}{8} Nk\theta_D + 3NkTD(\theta_D/T),$$

$$C_V = 3Nk [D(\theta_D/T) - (\theta_D/T) D'(\theta_D/T)],$$

where  $(9/8) Nk\theta_D$  is the contribution of the *quantum zero oscillations* in terms of the Debye model, and  $D'$  is the derivative of  $D$  with respect to  $\theta_D/T$ .

In order to derive  $P_{vib}$  it is necessary to compute the volume derivative of  $\ln Z$ . The partition function does not depend explicitly on volume but through the dependence of the energy levels on it. It is not possible to obtain this relation from first principles. This imposes the use of various approximations. In the case of a solid the volume dependence of the energy levels is reduced to volume dependence of the lattice frequencies. This relation cannot be obtained from first principles as well. According to Grüneisen

$$(11) \quad d \ln \nu_j / d \ln V = -\gamma \quad (j = 1, 2, \dots, 3N),$$

where  $\nu_j$  ( $V$ ) are lattice frequencies, and  $\gamma$  is a positive quantity, one and the same for all the  $3N$  normal modes of the crystal lattice. It is assumed that these frequencies, and hence,  $\gamma$ , do not depend on temperature, but on volume only. This is sometimes referred to as the *quasiharmonic approximation*.

Equation (11) is the statistical definition of the Grüneisen parameter. It holds for any frequency, hence it may be written for the Debye frequency  $\nu_D$

$$d \ln \nu_D / d \ln V = -\gamma$$

and since  $\nu_D$  and  $\theta_D$  are proportional, it follows

$$d \ln \theta_D / d \ln V = -\gamma \quad \text{or} \quad d \ln \theta_D / dV = -\gamma/V.$$

Accordingly, we obtain for  $P_{vib}$

$$P_{vib} = \frac{9}{8} [\gamma(V)/V] Nk\theta_D + 3[\gamma(V)/V] NkTD(\theta_D/T)$$

or

$$P_{vib} = [\gamma(V)/V] E_{vib},$$

which in terms of the assumed approximation  $\gamma/V = \gamma_0/V_0 = \text{const.}$  takes the form

$$P_{vib} = (\gamma_0/V_0) E_{vib}.$$

Now, using Eq. (5) and its dependencies we can assemble the complete equation of state. It has the form

$$\begin{aligned}
(12) \quad F(\varepsilon, T) &= c_0^2 \left(1 - \frac{\gamma_0}{2}\right) \frac{\frac{1}{s}(1-s\varepsilon) \left(1 - \frac{\gamma_0}{s}\right) \left[ \text{Ei}\left(\frac{\gamma_0}{s}\right) - \text{Ei}\left(\frac{\gamma_0}{s}(1-s\varepsilon)\right) \right] e^{-\frac{\gamma_0}{s}(1-s\varepsilon)}}{s(1-s\varepsilon)} \\
&+ \frac{9}{8} Nk\theta_D + NkT \{3 \ln[1 - \exp(-\theta_D/T)] - D(\theta_D/T)\} \\
&+ E_{c_0} e^{\gamma_0 \varepsilon}.
\end{aligned}$$

For the internal energy we can write

$$\begin{aligned}
E(\varepsilon, T) &= c_0^2 \left(1 - \frac{\gamma_0}{2}\right) \frac{\frac{1}{s}(1-s\varepsilon) \left(1 - \frac{\gamma_0}{s}\right) \left[ \text{Ei}\left(\frac{\gamma_0}{s}\right) - \text{Ei}\left(\frac{\gamma_0}{s}(1-s\varepsilon)\right) \right] e^{-\frac{\gamma_0}{s}(1-s\varepsilon)}}{s(1-s\varepsilon)} \\
&+ \frac{9}{8} Nk\theta_D + 3NkTD(\theta_D/T) \\
&+ E_{c_0} e^{\gamma_0 \varepsilon}.
\end{aligned}$$

This equation is often called the caloric EOS.

Once we know Eq.(12) we can derive all the thermodynamic properties of the system under consideration.

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