THERMODYNAMIC PROPERTIES OF SOLIDS AT HIGH PRESSURES AND TEMPERATURES FROM SHOCK-WAVE EXPERIMENTS. THE ZERO TEMPERATURE ISOTHERM

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Keywords: cold isotherm, shock Hugoniot, Debye solid.

Abstract. In modeling the equation of state of solids in the cases where the region of interest is several orders of magnitude of pressure and temperature, it is standard to divide the problem into three contributions: the zero temperature (cold) isotherm, the contribution of thermal vibrations of ions, and the conduction electron thermal excitation contribution. In this paper we consider only the first one. We derive a differential equation for the cold isotherm and solve it in quadratures. It is based on the Mie-Grüneisen equation and uses the shock Hugoniot as a reference curve. The quantum zero vibrations of the crystal lattice are obtained within the framework of the Debye model. The solution is expressed in terms of the integral exponential function.

I. Introduction

The study of shock-wave propagation in solids has added significantly to our understanding of physical processes which take place at high pressures, high temperatures and very short times. One particular aspect of these studies is to determine the equations of state (EOS) for different materials from shock-wave data. 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.

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In this paper we consider only the first one. We derive a differential equation for the cold isotherm and solve it in quadratures. It is based on the Mie-Grüneisen equation and uses the shock Hugoniot as a reference curve. The solution is expressed in terms of the integral exponential function. The quantum zero vibrations of the crystal lattice are obtained within the framework of the Debye model.

II. Semi-empirical calculations of the zero temperature isotherm

Analytic semi-empirical expressions for the computation of the cold compression curve have been mainly employed in earlier years to extend experimental EOS data to regimes not accessible to experimentation. The basic ingredient of these representations has been volume-dependent pair potential with terms representing repulsive and attractive atomic interactions. The parameters in these were fitted either to some experimental data or some theory. For the ionic, rare gas and molecular materials, the two-body Lennard-Jones or Born-Mayer forms of the potential energy curve has often been employed. A good example of such an approach is that of Ross [1] for \( \text{Ar} \), through the use of exponential-six potential with constants reproducing the results of molecular beam experiments. For alkali halides Boyer [2] used exponential pair potential with constants for kinetic, exchange and correlation contributions determined from fits to Hartree-Fock calculations and predicted with good accuracy a host of properies (lattice dynamics, \( P-V \) curves, thermal expansion and the overall stability of the lattice as a function of temperature and pressure).

For metallic solids, as no agreed theoretical analytical form for the potential energy has been known, there has been a plethora of expressions. The most popular expression is the second order Birch-Murnaghan equation [3]:

\[ \frac{1}{k} = \frac{k_0}{k_0 + k_1 (1 - \epsilon)} \]

where \( k_0 \) and \( k_1 \) are constants, and \( \epsilon \) is the volume fraction.
where $K'_{T_0}$ is the initial bulk modulus, $K'_T = dK_T/d\rho$ and $\eta = \rho_0/\rho$. The validity of this equation for extrapolation purposes has been examined by Jamieson [4]. Fisher et al. [5] have used this equation to fit 0 $K$ isotherms derived from shock data and the $K'_T$ values so derived agree quite with those from ultrasonic data.

In the present work a potential-free method is elaborated to obtain the zero temperature isotherm from shock-wave experiments. It is applicable to materials with all types of chemical bond. The detailed derivation is given in the next section.

III. Calculation of the zero-degree Kelvin isotherm

III. 1. 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 we have

\begin{equation}
F = F(V, T).
\end{equation}

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 [6])

\begin{equation}
F(V, T) = F_c(V) + F_{vib}(V, T) + F_e(V, T).
\end{equation}

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 electron thermal excitations contribution. $F_c$ may be neglected in the phonon region and Eq.(3) takes the form

\begin{equation}
F(V, T) = F_c(V) + F_0(V) + F_{IT}(V, T),
\end{equation}

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 $T = 0K$

\begin{equation}
F_c = E_c \quad \text{and} \quad P_c = -dF_c/dV = -dE_c/dV.
\end{equation}

The specific form of the second of Eqs.(5) will be derived from the Mie—Grüneisen equation using the shock Hugoniot as a reference curve. Actually it is a first-order ordinary differential equation (ODE) for $E_c$ (e.g for $F_c$).

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. 2. Deriving the zero-degree Kelvin isotherm from shock-wave data

The shock-wave methods for deriving the cold isotherm are based on the measurement of the Hugoniot curve. The quantities directly measured are the kinematic parameters of the shock wave—the shock front velocity $u_s$ and the particle velocity in the compressed region $u_p$. The relation $u_s(u_p)$ is the shock Hugoniot. Most substances in the absence of phase transitions have a linear shock Hugoniot [7]
\( \text{(6) } u_s = c_0 + su_p \)

in a wide range of particle velocities. The Hugoniot intercept, \( c_0 \), and the slope, \( s \), are determined from the data by the method of least squares. If rigidity effects and possible low pressure phase changes are neglected, the intercept should correspond to the velocity of an infinitesimal pressure pulse, or the bulk sound speed,

\[ c_0 = \left[ \frac{(\partial P/\partial \rho)_s}{\rho} \right]^{1/2} \]  

(at \( P = 0 \)). Since the slope is linearly related to the pressure derivative of the adiabatic bulk modulus, \((\partial B/\partial P)_s\), a linear \( u_s - u_p \) Hugoniot then reflects a nearly linear dependence of \( B \) on the pressure.

The transition from kinematic \( (u_s, u_p) \) to thermodynamic \( (P, V, E) \) variables is done using the laws of conservation of mass, momentum and energy across the shock front [8]

\( \text{(7) } \rho_0 u_s = \rho(u_s - u_p), \)

\( \text{(8) } P - P_0 = \rho_0 u_s u_p, \)

\( \text{(9) } \left[ (E - E_0) - \frac{u^2}{2} \right] \rho_0 u_s = P_0 u_p. \)

Here \( E, P \) and \( \rho \) are the specific internal energy, the pressure and the density behind the shock front, and \( E_0, P_0, \rho_0 \) are the values of these quantities ahead of the shock front. From Eqs.(7) and (8) we obtain

\( \text{(10) } u_s = V_0 \left[ (P - P_0)/(V_0 - V) \right]^{1/2}, \)

\( \text{(11) } u_p = \left[ (P - P_0)(V_0 - V) \right]^{1/2}. \)

Solving Eqs.(10) and (11) for \( P \) gives

\( \text{(12) } P = P_0 \left[ 1 + \frac{1}{V_0} u_s u_p \right], V = V_0 \left( \frac{u_s - u_p}{u_s} \right). \)

Equations (12) give the relationship between the kinematic variables \( u_s, u_p \) and the thermodynamic variables \( P \) and \( V \).

Substituting with the right-hand sides of Eqs.(10)-(11) in Eq.(9) gives the Hugoniot equation of energy

\( \text{(13) } E - E_0 = \left( P + P_0 \right)(V_0 - V)/2. \)

that defines all states on the \( (E-P-V) \) surface that can be reached from an initial state \( (E_0, P_0, V_0) \) by a single shock.

If the linear \( u_s - u_p \) relation holds, the Rankin-Hugoniot equations ((12)) and ((13)) can be used to express pressure and energy as functions of volume along the Hugoniot by the following convenient analytic expressions (with \( P_0 \) and \( E_0 \) taken to be zero at ambient conditions)

\( \text{(14) } P_{H} = \frac{\rho_0 c_0^2 \epsilon}{(1 - \epsilon \delta)^2}, \)

\( \text{(15) } E_{H} = \frac{c_0^2 \epsilon^2}{2(1 - \epsilon \delta)^2}, \)

\( \text{(16) } \epsilon = 1 - V/V_0 = 1 - \rho_0/\rho. \)

Equations (14)-(15) and the values of \( c_0 \) and \( s \) summarize all the experimental thermodynamic information which is available from shock-wave measurements.
To compute the cold compression curve we shall employ the Mie-Grüneisen equation [7] in the form

\( P(V, T) - P(V, 0) = \frac{\gamma(V)}{V} \left[ E(V, T) - E(V, 0) \right] \)

where \( \gamma(V) \) is the Grüneisen parameter. Equations (14), (15) give the pressure \( P_H \) and the specific internal energy \( E_H \) on the shock Hugoniot. Since it connects equilibrium thermodynamic states we can write

\( P_H(V) - P(V, 0) = \frac{\gamma(V)}{V} \left[ E_H(V) - E(V, 0) \right] \)

We shall assume that \( \gamma \) is a function only of volume and, specifically, that the product \( \rho \gamma \) is constant. Experimental work on a number of materials [9], as well as theoretical considerations [10], indicate this to be an adequate approximation. With this assumption, \( \gamma \) is given by

\( E(V, 0) = 0 \) is the thermodynamic value at ambient conditions given by ,

\( \gamma = \frac{c_s}{c_p} \alpha \) is the thermal expansion coefficient, \( c_s \) --- the sound speed, and \( c_p \) --- the specific heat at constant pressure.

\( T = 0 \) is defined in the domains

\( \frac{1}{s} < \varepsilon \leq \infty \)

Let us limit our considerations to the first domain. Instead of the indefinite integral we may use a definite integral that is a function of its upper limit. Then the expression for \( E, (\varepsilon) \) becomes

\( E, (\varepsilon) = c_0 \left( 1 - \gamma_0 \right) + \int_{0}^{\varepsilon} e^{-\gamma_0 e} \left( s - \gamma_0 \right) (s \varepsilon - 1) \frac{e^{-\gamma_0 e}}{s \varepsilon - 1} \, d\varepsilon - 1 

\)

Equation (24) is the general solution to the ODE for \( E, (\varepsilon) \). The integral in it is defined in the domains

\( 0 \leq \varepsilon < 1/s \) and \( 1/s < \varepsilon < +\infty \). Let us limit our considerations to the first domain. Instead of the indefinite integral we may use a definite integral that is a function of its upper limit. Then the expression for \( E, (\varepsilon) \) becomes

\( E, (\varepsilon) = c_0 \left( 1 - \gamma_0 \right) + \int_{0}^{\varepsilon} e^{-\gamma_0 e} \left( s - \gamma_0 \right) (s \varepsilon - 1) \frac{e^{-\gamma_0 e}}{s \varepsilon - 1} \, d\varepsilon - 1 + E, 0 

\)
Let us change the variable in the integral from the last equation. We shall assume \( \xi = 1 - sx \). Then
\[
x = \frac{1}{s} (1 - \xi), \quad dx = -\frac{1}{s} d\xi, \quad \xi = 1 \text{ when } x = 0 \text{, and } \xi = 1 - s\varepsilon \text{ when } x = \varepsilon.
\]
Now, we may write the integral in the form
\[
\int_{\xi}^{\infty} e^{-\gamma_0 x} dx = -\frac{e^{-\gamma_0 \varepsilon}}{s} \int_{1-\varepsilon}^{\infty} \frac{e^{s\xi}}{\xi} d\xi.
\]
The last integral cannot be presented by combinations of elementary functions. It can be expressed, however, in terms of the integral exponential function
\[
\text{Ei}(bx) = \int_{0}^{\infty} \frac{e^{bx}}{x} dx,
\]
that arises in a variety of applications. Substituting with it in Eq.(25) we get
\[
E_\varepsilon(\varepsilon) = c_0^2 \left( 1 - \frac{\gamma_0}{2} \right) \frac{s}{s(1 - s\varepsilon)} \left[ -\text{Ei} \left( \frac{\gamma_0}{s} \right) - \text{Ei} \left( \frac{\gamma_0}{s} (1 - s\varepsilon) \right) \right] + E_{00} e^{\gamma_0 \varepsilon}.
\]
This is the final form of the configurational internal energy as obtained from shock-wave experiments. At \( T = 0 \) it coincides with the configurational free energy. Since the contribution of the zero quantum vibrations is small it is often neglected and Eq.(26) is called the zero Kelvin (cold) isotherm. Its derivation was the purpose of the present work.

The zero quantum vibrations and the thermal vibrations of the crystal lattice are derived within the framework of the Debye model in another paper, which is a continuation of this one and will be also presented at this conference.

References:

5. Fisher E.S., Ibid.