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Temperature-dependent universal equation of state for solids

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Abstract. On the basis of the universal cohesive energy model of Rose, Smith, Guinea and Ferrante it is shown that the temperature effects can be scaled so that the functional form of the pressure equation at finite temperatures is isomorphic to that of the cohesive pressure. Using the equation of state thus obtained, we calculate Hugoniot curves for some solids and compare the results with experimental data.

1. Introduction

Recently Vinet *et al* [1–3] have proposed a universal equation of state (EOS) for various classes of solids at finite temperatures. This equation has been used successfully to describe the various isotherms up to high pressures (when there are no changes in phase or electronic configurations). The universal form independent of bonding character has been understood [1, 4] based on the nearly universal nature of *ab initio* calculated cohesive energy curves of metals [5, 6] and the closed-shell overlapping interactions [7, 8] dominant in a highly compressed state of solids. The cogency to use the universal EOS at an arbitrary temperature (without changing the functional form) has been supported empirically by thoroughgoing analysis [1, 2] of the experimental pressure–volume data of various solids in a temperature range below room temperature. It has also been demonstrated without theoretical grounds [9] that most isotherms of solids can be fitted to the temperature-dependent Murnaghan equation provided that the volume is rescaled to the equilibrium volume at the temperature under consideration. On the theoretical side, such scaling properties of temperature effects in the EOS problem have been examined [10] using a generic member of the Birch-type isothermal equations. No justification has been given, however, of the universal EOS obtained from the well founded cohesive energy model of Rose, Smith, Guinea and Ferrante (RSGF) [6].

In this work we shall first formulate a rescaling method to support the validity of extending the universal EOS to arbitrary temperatures while keeping its functional form identical with the cohesive pressure by rescaling the volume. Here, the isothermal bulk modulus and its pressure derivatives are necessarily redefined at that temperature. Next we shall restate this isomorphically rescaled temperature-dependent universal EOS in a

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convenient form at a reference temperature and use the equation to evaluate the Hugoniot curves of some solids.

2. Rescaling method

We use the following model of RSGF cohesive energy at 0 K:

$$U_c(x, 0) = -U_0(0) \left(1 + s(0) + \sum_{l=3}^{\infty} a_l(0) s^l(0) \right) \exp[-s(0)]. \tag{1}$$

This leads to the zero-temperature EOS

$$P_c(x, 0) = 3B_0(0)(1 - x)H[x; a(0)] \exp[-s(0)]/x^2$$

$$H[x; a(0)] \equiv 1 - \sum_{l=2}^{\infty} [(l + 1)a_{l+1}(0) - a_l(0)]s^{l-1}(0) \tag{2}$$

where $a_2(0)$ is set to zero, $x \equiv [V/V_0(0)]^{1/3}$ is the linear compression, the subscript zero stands for the zero-pressure condition and the zero in the arguments denotes the zero temperature. Here $s(0) \equiv \eta(0)(x - 1)$ and η is a dimensionless parameter relating the equilibrium isothermal bulk modulus B_0 to the equilibrium cohesive energy U_0 . All $a_l(0)$ can be connected with the successive pressure derivatives of isothermal bulk modulus at equilibrium. RSGF have shown [6] that equation (2) with $a_3(0) = 0.05$ and neglecting higher-order terms can predict accurately the low-temperature isotherm data of various metals up to high pressures.

We may write the pressure at volume V and temperature T , to a good approximation, as the sum of cohesive pressure $P_c(x, 0)$ and thermal contributions $P^*(x, T)$:

$$P(V, T) = P_c(x, 0) + P^*(x, T) \tag{3}$$

where $P^*(x, T)$ is zero at 0 K and assumed infinitely differentiable with respect to x . Now we restate equation (3) in the form

$$P(V, T) = 3B_0(0)\Lambda(x, T) \exp[-s(0)]/x^2 \tag{4}$$

$$\Lambda(x, T) \equiv (1 - x) H[x; a(0)] + x^2 P^*(x, T) \exp[s(0)]/3B_0(0). \tag{5}$$

Let $V_0(T)$ be the equilibrium volume at a finite temperature T ; then obviously $x_0(T) \equiv [V_0(T)/V_0(0)]^{1/3}$ is a non-negative zero of equation (5) for fixed T . We expand $\Lambda(x, T)$ around the new equilibrium point $x = x_0(T)$ and substitute the expression into equation (4). Then the terms can be rearranged so that

$$P(V, T) = 3B_0(T)(1 - z)H[z; a(T)] \exp[-s(T)]/z^2$$

$$= P_c(z, T) \tag{6}$$

after a little algebraic manipulation [11]. Here $z \equiv [V/V_0(T)]^{1/3}$ is the linear compression rescaled at T . Thus the cohesive energy $U_c(x, 0)$ in equation (1) also should be understood in the sense that $U_c(x, 0) = U_c(z, T)|_{T=0}$.

Here the temperature-dependent parameters are defined by

$$B_0(T) = -B_0(0)\Lambda^{(1)} \exp[-s(0)]/x_0(T) \tag{7}$$

$$B_0'(T) = 1 + 2\eta(T)[1 + 3a_3(T)]/3 \tag{8}$$

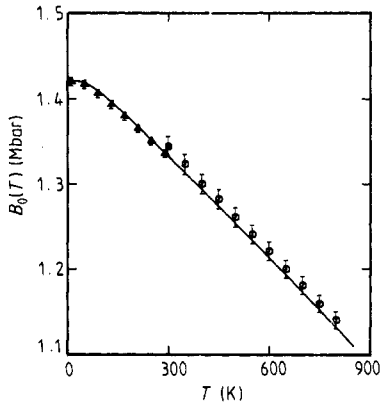


Figure 1. Temperature dependence of the isothermal bulk modulus of copper at equilibrium: —, calculated results of the present model; Δ , ultrasonic data [14]; \odot , ultrasonic data [15].

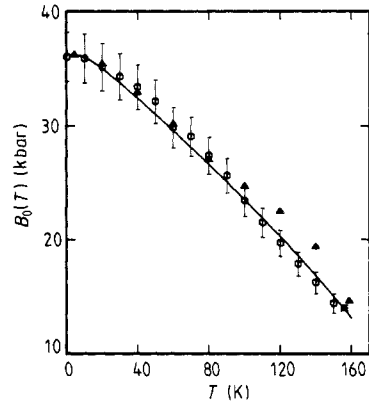


Figure 2. Temperature dependence of the isothermal bulk modulus of solid xenon at equilibrium: —, calculated results of the present model; \odot , ultrasonic measurements [18]; Δ , P - V - T measurements [16]; *, Brillouin scattering data [19].

$$\eta(T) = \eta(0)x_0(T)$$

$$a_{l+1}(T) = [a_l(T) - \Lambda^{(l)}/l!\eta^{l-1}(0)\Lambda^{(l)}]/(l+1)$$

for $l \geq 2$ where $a_2(T) = 0$, the prime indicates the pressure derivative, and the superscript (l) stands for the l th differentiation with respect to x at fixed T where $x = x_0(T)$.

As we hoped, we observe in equations (2) and (6) that the zero- and finite-temperature EOSs are represented by the same functional form. If all $a_l(T)$ ($l \geq 2$) are set to zero, equation (6) simply reduces to the universal EOS [1] proposed by Vinet *et al.* These results justify theoretically to some extent the applications of the universal EOS over a rather wide range of temperatures. It is expected that the series function $H[z; a(T)]$ should converge rapidly, since the universal EOS has already described the energetics of metals well, and the higher-order terms in $s(T)$ should give rise to only small corrections for materials without significant internal degree of freedom.

For practical purposes, we terminate the series in equation (6) at $l = 3$ by setting $a_l(T) = 0$ for all $l \geq 4$ and we present the calculated behaviour of the equilibrium isothermal bulk modulus (equation (7)) for several solids. Thermal pressure contributions will be referred to in the following section. Figures 1 and 2 present, respectively, the results for copper and xenon. For copper the values $B_0 = 1332$ kbar and $B'_0 = 5.615$ were taken from ultrasonic experimental data [12] and other input parameters were from [13]. Our calculated results agree well with available ultrasonic data [14, 15] over the investigated temperature range. In the case of xenon all the input parameters were taken from [16] except B_0 and B'_0 . We used the values $B_0 = 36.26$ kbar and $B'_0 = 7.66$ [17] fitted to the 4 K isotherm [16] using the Birch–Murnaghan EOS. Figure 2 shows good agreement between the calculated results, ultrasonic data [18], P - V - T measurements [17] and Brillouin scattering experiments [19].

3. Shock Hugoniot curves

Since we have shown that the temperature-dependent universal EOS has an identical functional form with the cohesive pressure equation, we can rewrite the pressure at V

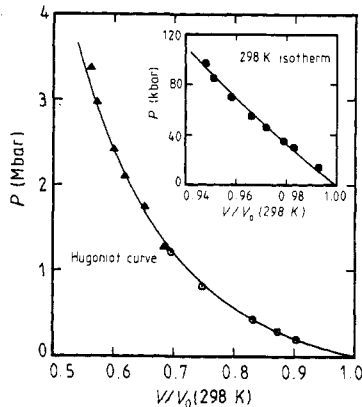


Figure 3. Hugoniot pressure and 298 K isotherm for vanadium: —, calculated results; ●, experimental data [26]; ○, experimental data [24]; ▲, experimental data [25].

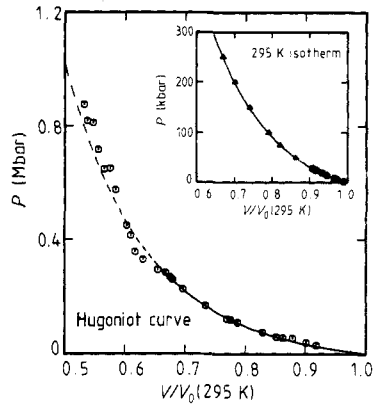


Figure 4. Hugoniot pressure and 295 K isotherm for sodium chloride: —, — —, calculated results; ●, experimental data [28]; ▲, experimental data [29]; ○, experimental data [24].

and T in the following expression rescaled at reference temperature T_0 :

$$P(V, T) = P_c(y, T_0) + \Delta P^* \quad (9)$$

where $y \equiv [V/V_0(T_0)]^{1/3}$ and $\Delta P^* \equiv P^*(y, T) - P^*(y, T_0)$. By making use of equation (9) and the definitions of the free energy and internal energy, we are immediately led to

$$E(V, T) = E_0 + \Delta U_c + \Delta E^* + 3V_0(T_0)T_0 \int_1^y \left(\frac{\partial P^*}{\partial T} \right)_{T_0} y^2 dy \quad (10)$$

where E_0 is the internal energy at the reference equilibrium state, $\Delta U_c \equiv U_c(y, T_0) - U_c(1, T_0)$, $\Delta E^* \equiv E^*(y, T) - E^*(y, T_0)$, and E^* is the thermal energy corresponding to P^* . Equations (9) and (10) help us to avoid the absurd situation of calculating $V_0(T)$ well above the zero-pressure melting temperature of solids in Hugoniot calculations. On the Hugoniot path the pressure and energy are interrelated through the energy conservation equation across the shock front:

$$E(V, T) = E_0 + \frac{1}{2}V_0(T_0)(1 - y^3)P(V, T) \quad (11)$$

where the subscript zero refers to the undisturbed solid in equilibrium at T_0 and zero pressure.

To complete the EOS, we need a definite thermal model. For the thermal free energy, we consider only the sum of the harmonic lattice vibrations approximated by the Debye thermal free energy (see, e.g., [7]) and the electronic excitations $F_e^* = -\frac{1}{2}\beta_0 y^{3/2} T^2$, as proposed in [20]. Here β_0 is the constant to be determined by the electronic specific heat at $y = 1$. The harmonic Grüneisen function is taken as $\gamma_0 y^3$ for simplicity [21, 22] where γ_0 is the thermodynamic Grüneisen parameter at $y = 1$. For the determination of $\eta(T_0)$, we use the information on the heat of sublimation at T_0 .

Using equations (9)–(11) and the truncated three-parameter EOS with the thermal model mentioned above, we calculated the Hugoniot curves of some solids. The input parameters except B_0 and B'_0 were taken from [13] for vanadium, gold and molybdenum, and from [23] for sodium chloride (single crystal).

The calculated Hugoniot pressure curve for vanadium plotted in figure 3 shows good agreement with shock experimental data [24, 25] up to 3 Mbar. Here we used the

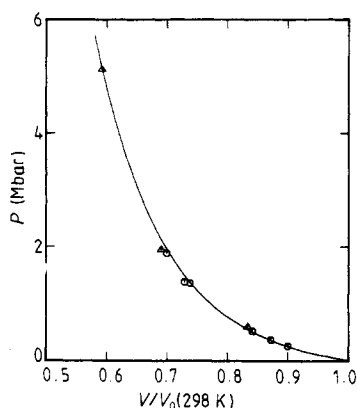


Figure 5. Hugoniot pressure for gold: —, calculated results; ○, experimental data [24]; △, experimental data [32].

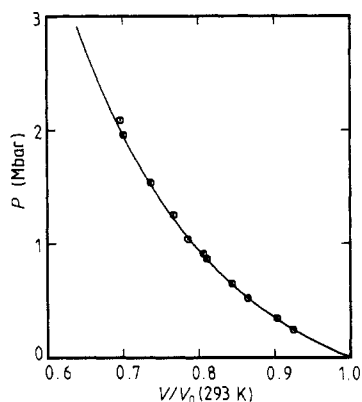


Figure 6. Hugoniot pressure for molybdenum: —, calculated results; ○, experimental data, [24].

ultrasonic values $B_0 = 1556$ kbar and $B'_0 = 4.27$ referred to in [26]. The inset in the figure represents the 298 K isotherm with the measured data of [26]. The results for sodium chloride are depicted in figure 4. The values $B_0 = 233.9$ kbar and $B'_0 = 5.35$ from ultrasonic measurements [27] were used in the calculation. It is shown that our EOS model can predict both the isotherm [28, 29] and the Hugoniot [24] data for NaCl up to 300 kbar. Figure 4 shows, however, a deviation of the predicted Hugoniot curve (broken curve) from the experimental data above about 300 kbar where a phase change occurs [30].

In the case of gold we obtained the values $B_0 = 1667$ kbar and $B'_0 = 5.6$, alternatively, from the fit of the experimental 298 K isotherm data in [31] to the truncated temperature-dependent universal EOS. We can see in figure 5 that the predicted Hugoniot curve agrees well with the shock data [24, 32] up to about 5 Mbar. We also evaluated the shock Hugoniot curves for molybdenum and depict the results in figure 6. The values used are $B_0 = 2670$ kbar and $B'_0 = 4.1$ which have been obtained from the fit of the 293 K isotherm data in [21]. Good agreement between the predicted curve and experiments [24] is found.

4. Conclusion

We have developed a simple method for scaling the temperature effects in the EOS based on the universal cohesive energy model of RSGF so that the finite-temperature pressure equation has an identical functional form with the cohesive pressure. Thus it partly justifies the use of the universal EOS as it stands over a wide range of temperature as proposed by Vinet *et al.* In fact, temperature effects can be scaled in any analytic pressure equation near the equilibrium point through the rescaling procedures that we used.

To illustrate the utility of the equations that we introduced, we have calculated the Hugoniot curves of some solids on the basis of truncated three-parameter EOS and selected thermal model. All the predicted curves are in excellent agreement with the respective experimental shock data as well as isotherms up to high pressures where no phase transition occurs.

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