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1990 J. Phys.: Condens. Matter 2 295

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Comparison of two universal equations of state for solids

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Received 14 March 1989

Abstract. A comparison between two of the so-called universal equations of state for solids is made. It is shown that although the Vinet equation and the Prieto–Renero equation are obtained on very different bases, their general form is very similar. Furthermore, the coefficients of the temperature dependent terms in the two equations are identical. This leads to a new relationship between the isothermal bulk modulus and other measurable parameters of the material. Numerical results obtained using both equations are shown to be in good agreement with some reported experimental data for gold, and for sodium chloride. The meaning of universality is different from one equation to the other; however, both of these meanings have been already accepted and used in relation to the scope of validity of equations of state. It is concluded that the use of one or the other equation depends more on the availability of the physical parameters needed than on the reliability of the equation itself.

1. Introduction

Some years ago, the present authors reported a universal equation of state for solids [1], later extended to liquids and gases [2]. More recently Vinet *et al* [3, 4] have also established a universal equation of state for solids. Although the titles and the intention of these papers are rather similar, the equations themselves are quite different. A comparison between these two equations is reported in this paper. The comparison is made considering the following aspects: basic assumptions, information needed to use the equations, general form of both equations, numerical results obtained for some materials, comparison with the corresponding experimental data for these materials, and meaning given to the concept of universality.

2. The Vinet *et al* equation

From their studies of solid state energetics Rose *et al* suggested, some years ago, the existence of a universal relationship between metallic binding energies and lattice parameters [5]. Then, through a series of papers [6–8] they derived a universal form of the relation between pressure and volume for metals on the cold isotherm, which was generalised, in collaboration with Vinet, to obtain the analytical form for an equation of state of solids [3, 4]. It is to be noted that although their universal forms for binding or total energies were expressed in terms of microscopic quantities and scaled parameters, the final form of their P – V – T equation of state contains only the usual

thermodynamical quantities and no scaled variables; it is obtained through the use of the thermodynamical relation

$$P(T, V) = -\left(\frac{\partial F(T, V)}{\partial V}\right)_T = -\frac{dE(V)}{dV} + P^*(T, V) \quad (1)$$

where $F(T, V)$ is the Helmholtz free energy and $P^*(T, V)$ is the thermal pressure. They then justify the assumption that $P^*(T, V)$ is independent of volume and linearly dependent on temperature for temperatures larger than the Debye temperature θ_D . This assumption leads to a universal form of an equation of state

$$P(T, V) = P(T_R, V) + \alpha_0(T_R)B_0(T_R)(T - T_R) \quad (2)$$

and its analytic approximation, the Vinet *et al* equation

$$P(T, X) = (3B_0(T_R)/X^2)(1 - X) \exp[\eta_0(T_R)(1 - X)] \\ + \alpha_0(T_R)B_0(T_R)(T - T_R) \quad (3)$$

where $\alpha_0(T_R)$ and $B_0(T_R)$ are the values at a reference temperature T_R of the thermal expansion coefficient, and the isothermal bulk modulus at zero pressure, respectively. The functions X and η_0 are defined by

$$X = (V/V_0(T))^{1/3} \quad \eta_0(T) = \frac{3}{2}((\partial B/\partial P)_0(T) - 1). \quad (4)$$

For temperatures larger than θ_D , and in the absence of phase transitions, equation (2) is a universal equation of state for solids. Here universality is to be understood in the same way as when the equation $PV = nRT$ is referred to as the universal equation of state for gases. That is, for each solid there is an equation of the form of equation (2), with different values of the coefficients for each material, but the equation being always of the same form.

3. The Prieto–Renero equation

Based on a different meaning of universality, the equation of state we have proposed [1] is system-independent, and so, expressed in dimensionless variables. A law of corresponding states [9] enables one to obtain scaling factors for pressure, volume and temperature. The corresponding reduced variables are defined by

$$p = P/P_c \quad x = b(1 - V/V_0) \quad t = \alpha b T \quad (5)$$

where $P_c = \rho_0 a^2/b$, a and b being the coefficients of the linear relationship between the shock (U_s), and particle (U_p) velocities, $U_s = a + bU_p$, and ρ_0 is the initial density.

The semi-empirical equation of state is obtained from the combination of the Rankine–Hugoniot energy conservation equation and the first of the $T dS$ equation and the linear relationship. In order to simplify the notation, let

$$r = (\partial p / \partial t)_x \quad m = r / C_{Vr} \tag{6}$$

C_{Vr} being the reduced specific heat at constant volume defined as $C_{Vr} = C_V b / \alpha a^2$. The equation of state is then expressed as [1]

$$p(x, t) = F(m, x) + G(m, x) + r(t - t_0 e^{mx}) \tag{7}$$

where the auxiliary volume dependent functions F and G are defined by

$$F(m, x) = \frac{2 - m}{2(1 - x)^2} - \frac{2 + m(m - 4)}{2(1 - x)} - \frac{m}{2}(3 - m)e^{mx} \tag{8}$$

$$G(m, x) = \frac{m}{2}(4m - m^2 - 2)e^{-m(1-x)} \overline{\text{Ei}}(m, x) \tag{9}$$

with

$$\overline{\text{Ei}}(m, x) = \overline{\text{Ei}}(m) - \overline{\text{Ei}}[m(1 - x)] \tag{10}$$

the function $\overline{\text{Ei}}(y)$ being the exponential integral of negative argument [10].

This universal equation is dimensionless and system-independent, the characteristics of each material being introduced through the scaling factors. The universality is to be understood here in the same way as it is, for instance, in the case of the Van der Waals equation when expressed in reduced variables; that is, a unique equation is valid for all materials. A final comment on equation (7) is perhaps worthwhile. The initial temperature t_0 is usually the laboratory temperature at which the shock compression experiments to determine the parameters a and b are performed. It plays, to a certain extent, a role similar to the reference temperature of equation (3).

4. Comparison between the two equations

Looking at the two equations of state under consideration, it can be seen that they are of the same general form, in the sense that both have a volume dependent part, $P(T_R, V)$ of equation (2), and $F(m, x) + G(m, x)$ of equation (7), and they have also an explicitly temperature dependent term, $\alpha_0(T_R)B_0(T_R)(T - T_R)$ of equation (2), and $r(t - t_0 e^{mx})$ of equation (7). To go on with the comparison, it is convenient to express both equations in the same language. We will then reduce equation (2) using the scaling factors defined by equation (5), to obtain a dimensionless Vinet *et al* equation in the form

$$P = P_R + (B_{0R}/b)(t - t_R) \tag{11}$$

where B_{0R} stands for the reduced isothermal bulk modulus, always at the reference temperature defined by Vinet *et al*. Now, the initial reduced temperature t_0 of equation (7) can be considered as playing the same role as the reference temperature t_R of equation

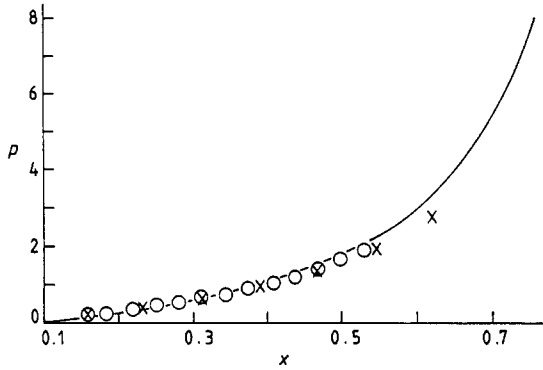


Figure 1. Plot of the universal 1000 K isotherm from (7) (full curve) together with points predicted by (3) for gold (\times) and experimental points reported by Heinz and Jeanloz (\circ) [14].

(11); then, we can identify the coefficients of both temperature dependent terms in equations (7) and (11), so

$$B_{0R}/b = r \quad (12)$$

and consequently

$$B_0 = \rho_0 a^2 r. \quad (13)$$

Upon substitution in this equation of the thermodynamical definition of the coefficient of thermal expansion α , and of the parameter r , we get

$$B_0 = \frac{\rho_0 a^2}{P_c \alpha b} \left(\frac{\partial P}{\partial T} \right)_V = -V_0 \left(\frac{\partial P}{\partial V} \right)_T \quad (14)$$

which means that equation (13) is in fact a thermodynamical identity. It represents then a different way of expressing the isothermal bulk modulus, or alternatively, another definition of the parameter r .

We have already pointed out that the value of the parameter r should be very near unity [1]. The same result can be obtained as a consequence of equation (13) recalling that the adiabatic bulk modulus B_S can be expressed as $B_S = \rho_0 c^2$ in terms of the sound velocity c in the material. Since $B_T/B_S \approx 1$ within 1% [11], and $a/c \approx 1$ [12], it follows that $r \approx 1$.

So, the two equations have then not only the same general form, but the same coefficient of the temperature dependent pressure term.

Let us now compare the equations from the point of view of the numerical results predicted. Since the comparison of the Prieto–Renero equation against experimental results, for many different solids, has already been made [13], we shall limit our attention to the same solids used by Vinet *et al*. These solids fulfil the conditions of validity of the Vinet *et al* equation, and the given numerical values of constants at the reference temperature are already given.

Figure 1 shows a plot of points predicted by equation (3) for the 1000 K isotherm of gold, together with the universal 1000 K isotherm calculated using equation (9), as well

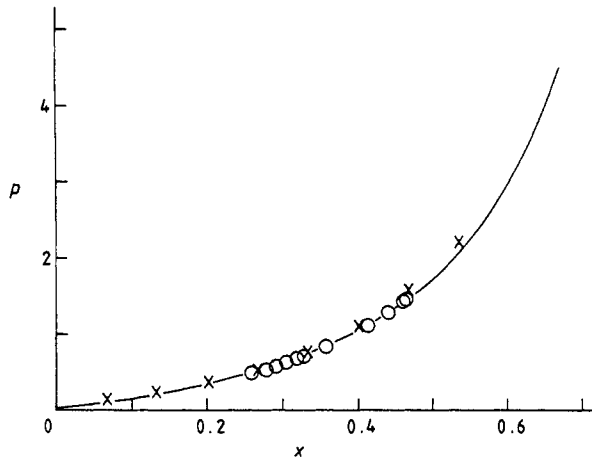


Figure 2. Plot of the 773 K universal isotherm of (7) (full curve) and the values for sodium chloride (\times) calculated from (3), together with experimental data reported by Decker (\circ) [15].

as the experimental points reported by Heinz and Jeanloz [14]. Figure 2 shows the 773 K universal isotherm of equation (9), the corresponding values computed using equation (3) for sodium chloride, and the experimental values reported by Decker [15]. In order to compare with the universal isotherms, all data have been reduced using the scaling factors defined by equations (5). In both cases, gold and sodium chloride, the agreement with the experimental data is good, being perhaps slightly better in the case of the universal isotherm of equation (9), in particular at high compressions. This is not surprising because this equation has been established for shock compressed materials.

5. Conclusions

It is interesting to remark that although the two equations were obtained in very different ways, they both have the same general form, a combination of a volume dependent term and a temperature dependent term; that is, the so-called elastic component of pressure, independent of temperature, and the thermal component. Numerical results obtained with both equations are in good agreement with the experimental data and so they are both reliable in predicting the thermodynamical behaviour of solids. The meaning of universality is different from one equation to the other, but the two different meanings given to the term universality have been already used and accepted in characterising the scope of application of a given equation of state. It is then clear that the choice of one or the other equation must rely on other kind of criteria, for example, the availability of the physical parameters involved, or the kind of information one is looking for, either specific for one material, or general for many materials.

References

- [1] Prieto F E and Renero C 1976 *J. Phys. Chem. Solids* **37** 151

- [2] Prieto F E and Renero C 1979 *High Pressure Science and Technology* vol 1, ed K Timmerhaus and M S Barber (New York: Plenum) p 50
- [3] Vinet P, Ferrante J, Smith J R and Rose J H 1986 *J. Phys. C: Solid State Phys.* **19** L467-73
- [4] Vinet P, Smith J R, Ferrante J and Rose J H 1987 *Phys. Rev. B* **35** 1945
- [5] Rose J H, Ferrante J and Smith J R 1981 *Phys. Rev. Lett.* **47** 675
- [6] Ferrante J, Smith J R and Rose J H 1983 *Phys. Rev. Lett.* **50** 1385
- [7] Rose J H, Smith J R, Guinea F and Ferrante J 1984 *Phys. Rev. B* **29** 2963
- [8] Guinea F, Rose J H, Smith J R and Ferrante J 1984 *Appl. Phys. Lett.* **44** 53
- [9] Prieto F E 1974 *J. Phys. Chem. Solids* **35** 279
- [10] Jahnke E and Emde F (ed.) 1945 *Tables of Functions* (New York: Dover)
- [11] Gschneidner K A Jr 1964 *Solid State Physics* vol 16, ed F Seitz and D Turnbull (New York: Academic)
- [12] Pastine D J and Piacesi D 1966 *J. Phys. Chem. Solids* **27** 1782
- [13] Prieto F E and Renero C 1982 *J. Phys. Chem. Solids* **43** 147
- [14] Heinz D L and Jeanloz R 1984 *J. Appl. Phys.* **55** 885
- [15] Decker D L 1971 *J. Appl. Phys.* **42** 3239