

Universal equation of state for compressed solids

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We derive a universal equation of state for compressed solids, based on thermodynamic arguments applied to virial expansions of $E(\rho, T)$ and $p(\rho, T)$, of the form $p(v/v_0)^2 = A_0 + A_1(\rho/\rho_0) + A_2(\rho/\rho_0)^2$. The thermal pressure is included from the beginning, and the only essential approximation is the truncation of expansions, which is justified by molecular arguments. Agreement with experiment is very good for a wide range of materials, including quantum solids, noble-gas and polar-gas solids, metals, ionic compounds, and hydrocarbons. A separate assumption gives the temperature dependence of the parameters as $A_i(T) = A_i + b_i T - c_i T \ln T$, for $T > \theta_D$. The usual behavior of the Grüneisen number as a function of temperature and density is accounted for in a simple way by these results.

I. INTRODUCTION

The equation of state of compressed solids (p - v - T relation) plays an important role in many fields, such as condensed-matter physics and geophysics. Perhaps the best-known equation of state (EOS) for solids is credited to Murnaghan,¹ and is based on the empirical observation that the isothermal bulk modulus (reciprocal compressibility) is a linear function of pressure. The origin of this relation actually goes back to the work of Tait on liquids, published in 1888.² A modification and improvement of the Murnaghan EOS by Birch^{3,4} has been widely used in geophysics.

In an extensive review in 1969, Macdonald⁵ stated, "It is extremely unlikely that there exists a 'universal' equation of state, of useful degree of simplicity, best for all condensed materials." Despite this rather gloomy prediction, a universal EOS for solids was proposed in 1986 by Vinet and co-workers,^{6,7} valid for ionic, metallic, covalent, and noble-gas solids, which was found to be more accurate than both the Murnaghan and Birch equations, especially at large compressions. No extra adjustable constants were required. The basis of this universal EOS was a universal relation between the binding energy of the solid and intermolecular distance, from which the EOS could be calculated via the thermodynamic relation

$$p = T \left[\frac{\partial p}{\partial T} \right]_v - \left[\frac{\partial E}{\partial v} \right]_T, \quad (1)$$

where p is the pressure, T is the temperature, v is the molar volume, and E is the internal energy (per mole). Vinet and co-workers neglected the term $T(\partial p/\partial T)_v$, the so-called thermal pressure, and used the volume derivative of the binding energy to approximate the term $(\partial E/\partial v)_T$, the so-called internal pressure. The resulting EOS contained only three parameters: the zero-pressure values of the molar volume, of the isothermal bulk modulus, $B = -v(\partial p/\partial v)_T$, and of the pressure derivative of the bulk modulus, $B' = (\partial B/\partial p)_T$.

Strictly speaking, the approximations made the universal EOS valid only at $T=0$ K, but, in fact, it was accu-

rate at least up to ordinary temperatures, with different parameters v_0 , B_0 , and B'_0 for each p - v isotherm. The authors later extended the results to include high-temperature behavior⁸ by introducing as a parameter the zero-pressure value of the thermal expansion coefficient, $\alpha = v^{-1}(\partial v/\partial T)_p$.

Another universal relation for the compressibility of solids was independently proposed in 1987 by Dodson,⁹ using the same input data of v_0 , B_0 , and B'_0 for each isotherm. The accuracy of the Dodson EOS is similar to that of the EOS of Vinet and co-workers, even though the explicit formulas differ. The Dodson EOS does not include temperature dependence.

The purpose of this paper is to present an improved universal EOS for compressed solids. The development uses some of the ideas of Vinet and co-workers,⁶⁻⁸ but the results are both simpler and somewhat more accurate for a wide variety of substances, including those with phase transitions. The simplification follows from the restriction to solids in compression, so that we need to fit only the rather featureless repulsive branch of the binding-energy curve rather than the entire curve. This simple fit of the repulsive branch also allows us to include the thermal pressure from the beginning, instead of grafting on temperature effects at the end. The final result is that pv^2 is a quadratic in the density. This EOS contains three parameters, which can be determined by fitting high-pressure measurements, or can be taken as v_0 , B_0 , and B'_0 in the absence of phase transitions, as in the EOS of Vinet and co-workers and of Dodson.

We first show how the repulsive branch of binding-energy curves can be represented by a simple function of density, and then use this result to obtain the EOS. This EOS is compared with measured p - v isotherms for a large number of different types of solids. The temperature dependences of the parameters are also considered. The method of Vinet *et al.*⁸ predicts at most a linear temperature dependence for the present EOS parameters, which is found to be satisfactory for some substances, but not for all. We introduce a more accurate procedure. Finally, we examine the predicted behavior of the Grüneisen

number, and find it to be only a weak function of temperature at constant density, but a stronger function of density at constant temperature.

II. BINDING ENERGY

To show how the repulsive branch of the binding energy curve can be represented in a simple way, we first consider the two-body interatomic potentials $u(r)$ of the noble gases, which are accurately known. In Fig. 1 we show the result for argon,¹⁰ plotted in dimensionless form as $u^* = u/\epsilon$ vs $(r_e/r)^3$, where ϵ is the potential well depth and r_e is the position of the potential minimum. The reason for this representation is that $(r_e/r)^3$ is proportional to the density in a solid. If the potential energy is pairwise additive, this is virtually the same as the zero-temperature binding energy of the solid as a function of density (except for scale factors). The repulsive branch ($r < r_e$) can be fitted very accurately by a simple polynomial, of order 3 in this case. Such a representation of the attractive branch ($r > r_e$) is of course completely erroneous, but this is of no importance for compressed solids.

The universal binding-energy function of Vinet and co-workers^{6,7} can also be represented in a similar fashion for $r < r_e$. This function is⁷

$$U = -\Delta U(1+a^*)e^{-a^*}, \quad (2)$$

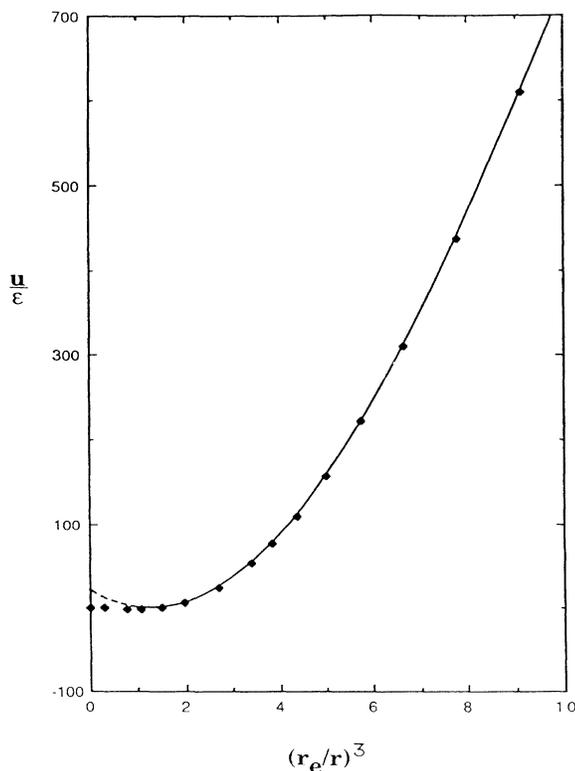


FIG. 1. Argon pair potential. The points are calculated from the potential of Aziz and Slaman, and the curve is a third-degree polynomial fitted to the repulsive wall.

where ΔU is the equilibrium binding energy at $a^* = 0$, and

$$a^* = (r - r_e)/l, \quad (3)$$

in which l is a scaling length that is treated as an adjustable parameter. This can be written for our purposes as

$$U(r) = \Delta U[\eta - 1 - \eta(r/r_e)]e^{\eta(1-r/r_e)}, \quad (4)$$

where $\eta = r_e/l$ is a dimensionless "shape" parameter whose values lie between about 3 and 8.¹¹ In Fig. 2 we show $U^* = U(r)/\Delta U$ as a function of $(r_e/r)^3$ for $\eta = 6$ and 8; results for other values of η are similar. Again the repulsive branches are accurately fitted by third-degree polynomials.

It should be mentioned that we have used the symbol U rather than E for the binding-energy function of Vinet and co-workers, in order to indicate that it is a configurational potential energy and not the thermodynamic internal energy. The latter must depend on temperature in order to have a nonzero specific heat.

On the basis of the above results, we conclude that the binding energy in the repulsive region can generally be represented by a cubic expression in the density, $\rho = 1/v$,

$$U = u_0 + u_1\rho + u_2\rho^2 + u_3\rho^3, \quad (5)$$

where u_0, u_1, \dots are constants characteristic of the particular substance. This result can be extended to the

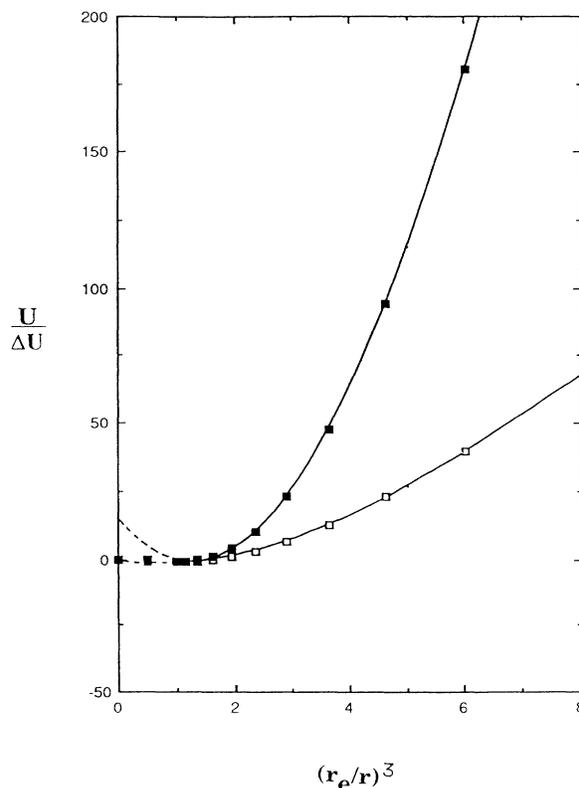


FIG. 2. Universal binding-energy function of Vinet and co-workers for $r_e/l = 6$ (\square) and 8 (\blacksquare). The points are calculated from Eq. (4), and the curves are third-order polynomials fitted to the repulsive walls.

thermodynamic internal energy E by allowing the coefficients to depend on temperature,

$$E = e_0(T) + e_1(T)\rho + e_2(T)\rho^2 + e_3(T)\rho^3. \quad (6)$$

This is just a virial expansion and involves no approximation other than the truncation of the series after the cubic term, which is suggested by the results illustrated in Figs. 1 and 2.

III. UNIVERSAL EQUATION OF STATE

The calculation of the EOS (i.e., of the pressure) is based on the exact thermodynamic relation of Eq. (1). The universal EOS of Vinet and co-workers is obtained by neglecting the thermal pressure and approximating $(\partial E/\partial v)_T$ by $(\partial U/\partial v)_T$ from Eq. (4). Their result is

$$p = 3B_0 \left[\frac{1-X}{X^2} \right] e^{\eta(1-X)}, \quad (7)$$

$$X \equiv (v/v_0)^{1/3}, \quad (8)$$

from which the shape parameter $\eta = r_e/l$ can be found in terms of $B'_0 = (\partial B/\partial p)_{p=0}$ to be $\eta = 3(B'_0 - 1)/2$. This expresses each p - v isotherm in terms of the parameters v_0 , B_0 , and B'_0 , which can, in principle, be found experimentally. The approximation of $p \approx -(\partial U/\partial v)_T$ should make this result valid only at low temperatures, but Vinet and co-workers⁶⁻⁸ have shown that room temperature is "low" for many substances. Notice that this EOS requires that $v = v_0$ when $p = 0$, which rules out phases that are stable only for $p > 0$, unless v_0 , B_0 , and η are considered to be arbitrary constants.

For comparison, the empirical EOS of Dodson has the form

$$p = \frac{3}{2} \frac{B_0}{(1-\beta)^2} \left[\frac{1}{X^2} - \frac{4\beta}{X} - 2\beta^2 \ln X + 4\beta - 1 \right], \quad (9)$$

where $\beta = 1 - (2/3B'_0)$.

Our result is obtained by substitution of Eq. (6) for E into Eq. (1) for p , which yields without approximation the following differential equation for the EOS:

$$T^2 \left[\frac{\partial(p/T)}{\partial T} \right]_{\rho} = -\rho^2(e_1 + 2e_2\rho + 3e_3\rho^2). \quad (10)$$

Integration of Eq. (10) at constant density gives

$$\begin{aligned} \frac{p}{T} = C(\rho) - \rho^2 \int \frac{e_1(T)}{T^2} dT - 2\rho^3 \int \frac{e_2(T)}{T^2} dT \\ - 3\rho^4 \int \frac{e_3(T)}{T^2} dT, \end{aligned} \quad (11)$$

where the "constant" of integration, $C(\rho)$, is a function of density only. If $C(\rho)$ is expanded in general as a power series, all power of ρ should appear, but a simplification is possible if we need to represent $C(\rho)$ only for $\rho \geq \rho_{\text{ref}}$, where ρ_{ref} is some nonzero reference density (not necessarily that corresponding to $p = 0$). Since the range $0 < \rho < \rho_{\text{ref}}$ is then irrelevant, a reasonable representation of $C(\rho)$ can be taken to be

$$C(\rho) \approx C_2\rho^2 + C_3\rho^3 + C_4\rho^4, \quad (12)$$

in which the constants C_2 , C_3 , and C_4 can be imagined to be determined, for example, by matching $C(\rho)$ and its first two derivatives at $\rho = \rho_{\text{ref}}$.

Combining the foregoing results, we can write our final EOS in reduced form as follows:

$$p(v/v_0)^2 = A_0 + A_1(\rho/\rho_0) + A_2(\rho/\rho_0)^2, \quad (13)$$

where $v_0 = 1/\rho_0$ is some standard volume, which is often taken to be the (molar) volume at $p = 0$, but which can be quite arbitrary. The coefficients A_i are functions of temperature, given by

$$\begin{aligned} A_0(T) &= T \left[C_2 - \int \frac{e_1(T)}{T^2} dT \right] \rho_0^2, \\ A_1(T) &= T \left[C_3 - 2 \int \frac{e_2(T)}{T^2} dT \right] \rho_0^3, \\ A_2(T) &= T \left[C_4 - 3 \int \frac{e_3(T)}{T^2} dT \right] \rho_0^4. \end{aligned} \quad (14)$$

Notice that the coefficients $A_i(T)$ are linear in T if the coefficients $e_i(T)$ are constants. Such a result, however, implies zero specific heat, since $C_v = (\partial E/\partial T)_v$.

If v_0 is taken to be the zero-pressure volume, then the A_i can be expressed in terms of B_0 and B'_0 , and the EOS (13) can be written in terms of the three parameters v_0 , B_0 , and B'_0 , just as the EOS (7) of Vinet and co-workers was. The result is

$$\begin{aligned} p(v/v_0)^2 = \frac{1}{2} B_0 [(B'_0 - 7) - 2(B'_0 - 6)(\rho/\rho_0) \\ + (B'_0 - 5)(\rho/\rho_0)^2]. \end{aligned} \quad (15)$$

In practice, we have determined the A_i by fitting p - v isotherms over the whole pressure range, rather than from the limiting behavior of the isotherms at $p = 0$. This procedure allows us to keep v_0 as arbitrary, and hence to handle systems with phase transitions, in which one or more phases exist only at higher pressures.

The important features of the present universal EOS (13), irrespective of its particular mathematical form, are that it involves no assumptions that limit its applicability to low temperatures, and that it can be applied to systems with phase transitions.

IV. CORRESPONDING STATES AND THE REPRESENTATION OF DATA

An important feature of any universal EOS should be its ability to be put in a convenient reduced form that provides a principle of corresponding states and that suggests a convenient way of analyzing experimental data. Vinet and co-workers^{6,7} did this by writing their EOS in the following form:

$$\ln \left[\frac{pX^2}{3(1-X)} \right] = \ln B_0 + \eta(1-X), \quad (16)$$

so that a plot of the experimental quantities given by the

left-hand side vs $(1-X)$ should give a straight line whose intercept is $\ln B_0$ and whose slope gives η and hence B'_0 . They showed that compression data on many substances gave good straight lines when plotted in this way, and that the derived values of B_0 and B'_0 were in agreement with literature values.

The present EOS (13) can be treated similarly in the absence of phase transitions. After invoking the condition that $v = v_0$ at $p = 0$, which requires that $A_0 + A_1 + A_2 = 0$, and performing some algebra, we obtain the linear relation

$$\frac{p(v/v_0)^2}{(\rho/\rho_0)-1} = I + S \left[\frac{\rho}{\rho_0} \right], \tag{17}$$

where the (extrapolated) intercept is $I = -A_0$, and the slope is $-S = A_0 + A_1$. The quantities B_0 and B'_0 are then readily found to be

$$B_0 = I + S, \quad B'_0 = (5I + 7S)/(I + S). \tag{18}$$

Plotting data according to Eq. (17) gives straight lines over a large density range. This method of plotting amplifies small irregularities in the data at low pressures, which is sometimes useful. As an example, we show in Fig. 3 the data for copper at pressures up to 4.5 Mbar at 25°C, taken from the compilation of Kennedy and Keeler.¹²

It should be emphasized that both Eqs. (16) and (17) require that $v = v_0$ at $p = 0$. This is not an inherent limitation of either equation, however. The present EOS can still be used in the form of Eq. (13) without the condition $A_0 + A_1 + A_2 = 0$, and the EOS of Vinet and co-workers can be used with arbitrary v_0 (as long as $v/v_0 < 1$) provided that B_0 and η are considered to be only adjustable constants.

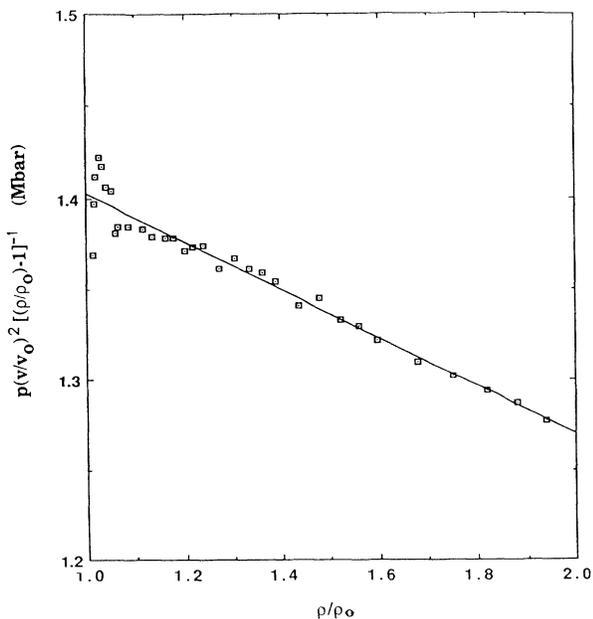


FIG. 3. Linearized plot of the 25°C p - v isotherm of Cu according to Eq. (17). The points are from the AIP compilation (Ref. 12).

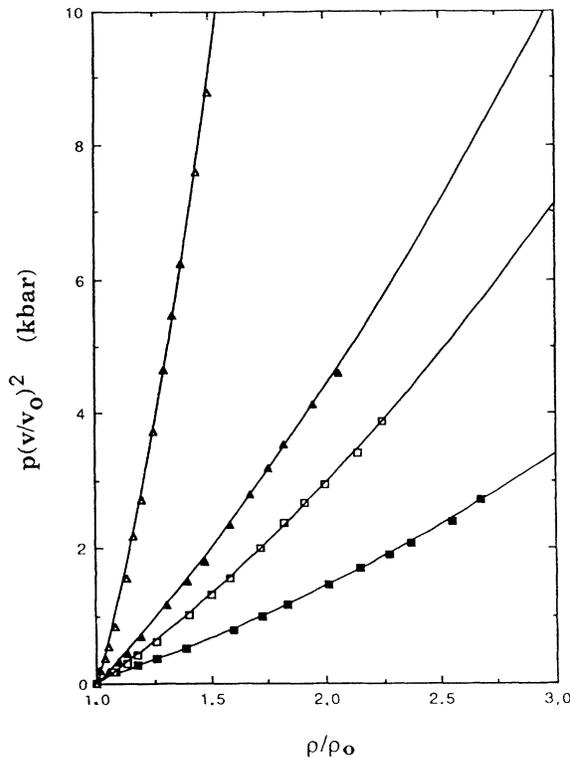


FIG. 4. Test of Eq. (13) for the 4 K isotherms of the quantum solids He (■), H₂ (□), D₂ (▲), and Ne (△).

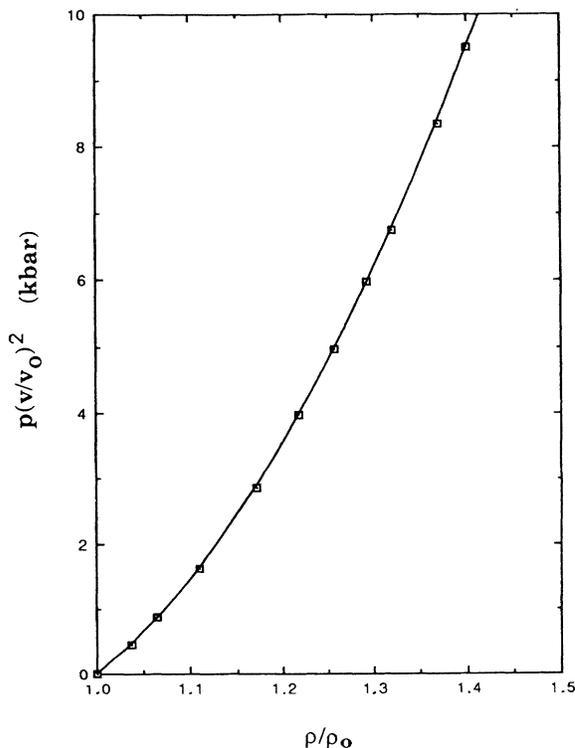


FIG. 5. Test of Eq. (13) for the 77 K isotherm of Ar.

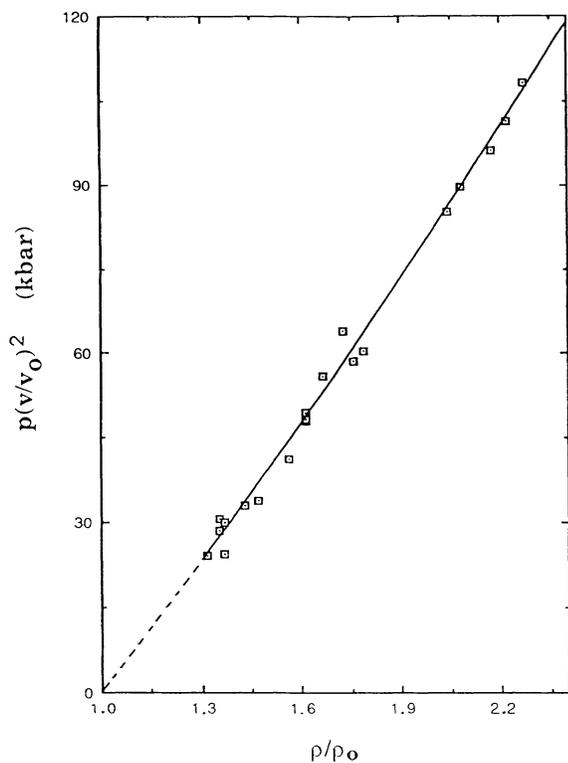


FIG. 6. Test of Eq. (13) for the room-temperature isotherm of NH_3 .

V. COMPARISON WITH EXPERIMENT

We begin with the quantum solids He, H_2 , D_2 , and Ne, which are very compressible because of their zero-point

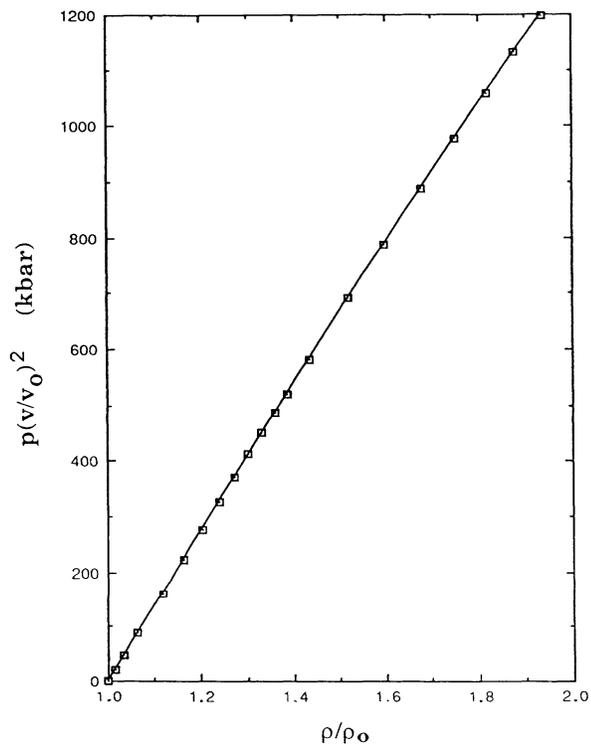


FIG. 7. Test of Eq. (13) for the 25°C isotherm of Cu; same data as in Fig. 3.

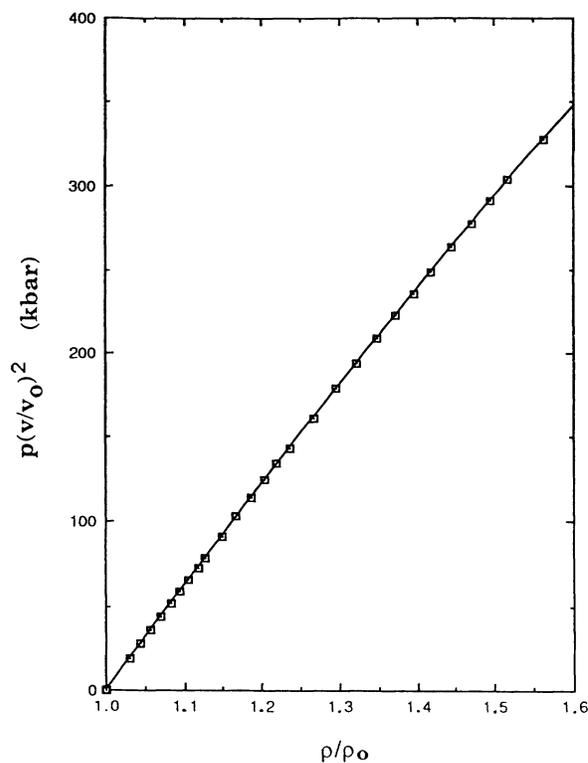


FIG. 8. Test of Eq. (13) for the 25°C isotherm of LiF.

energy. There is nothing in the derivation of Eq. (13) that limits it to classical solids. The measurements of Stewart¹³ at 4 K are shown in Fig. 4 as $p(v/v_0)^2$ vs ρ/ρ_0 , and can be seen to be fitted very well by quadratic functions, shown as the curves. The curves have not been

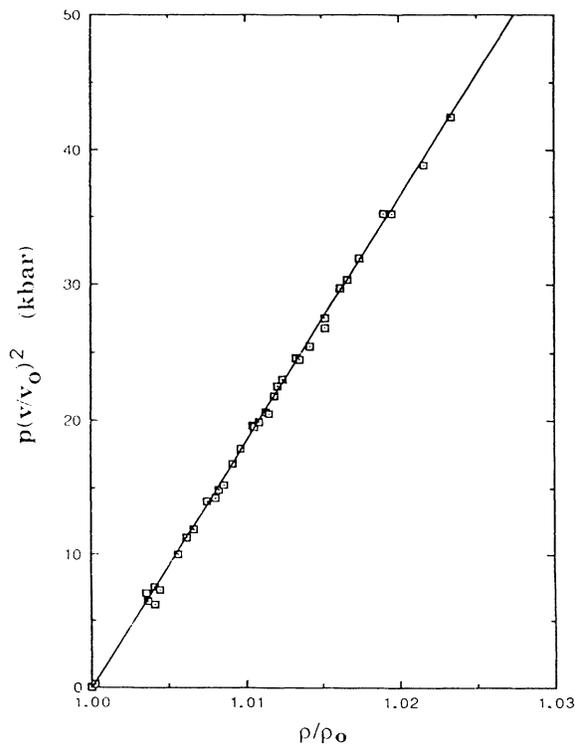


FIG. 9. Test of Eq. (13) for the room-temperature isotherm of magnetite (Fe_3O_4).

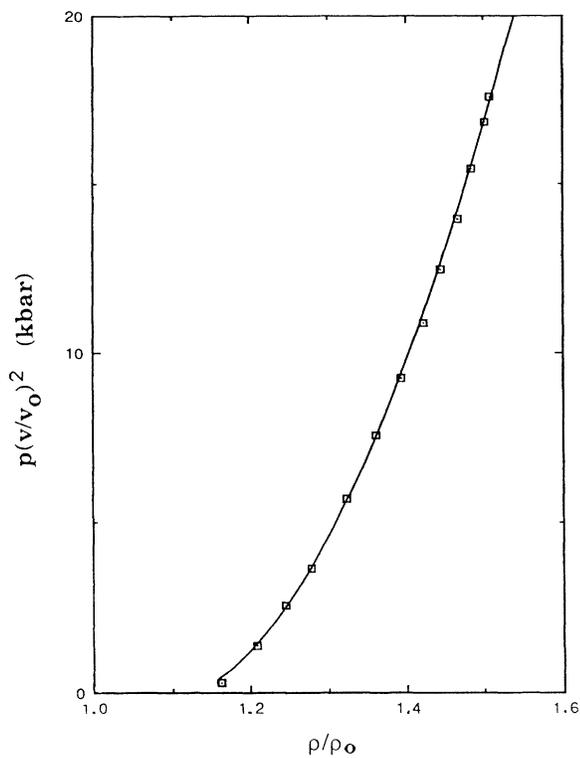


FIG. 10. Test of Eq. (13) for the 25°C isotherm of *n*-hexadecane ($n\text{-C}_{16}\text{H}_{34}$).

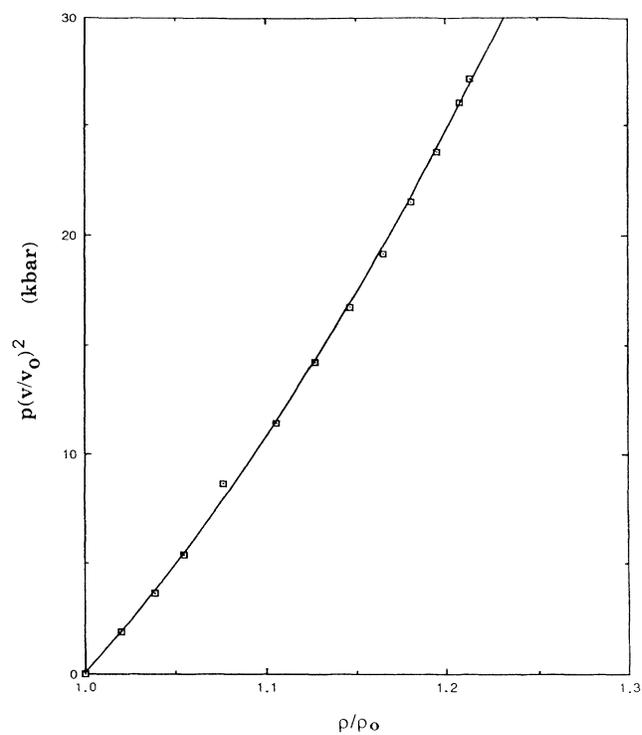


FIG. 12. Test of Eq. (13) for the 25°C isotherm of Melmac 404, a melamine-formaldehyde polymer.

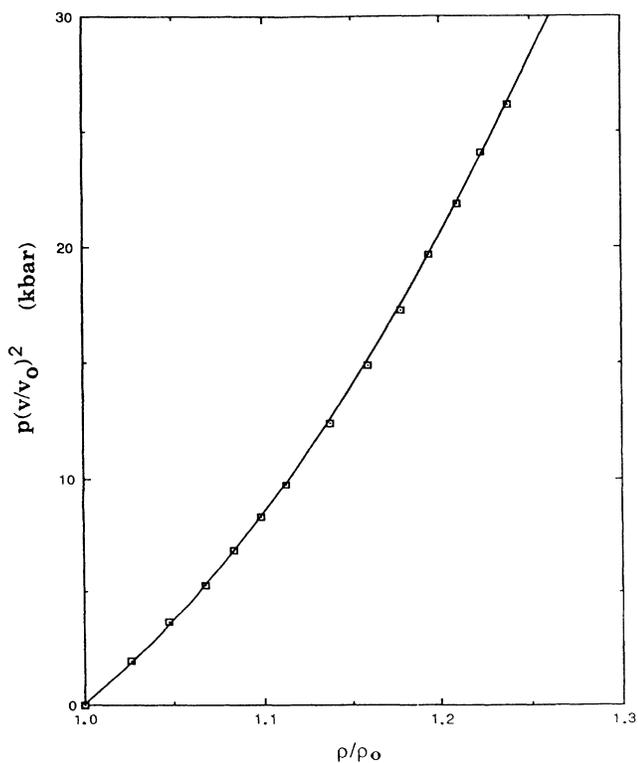


FIG. 11. Test of Eq. (13) for the 25°C isotherm of acenaphthene ($\text{C}_{12}\text{H}_{10}$).

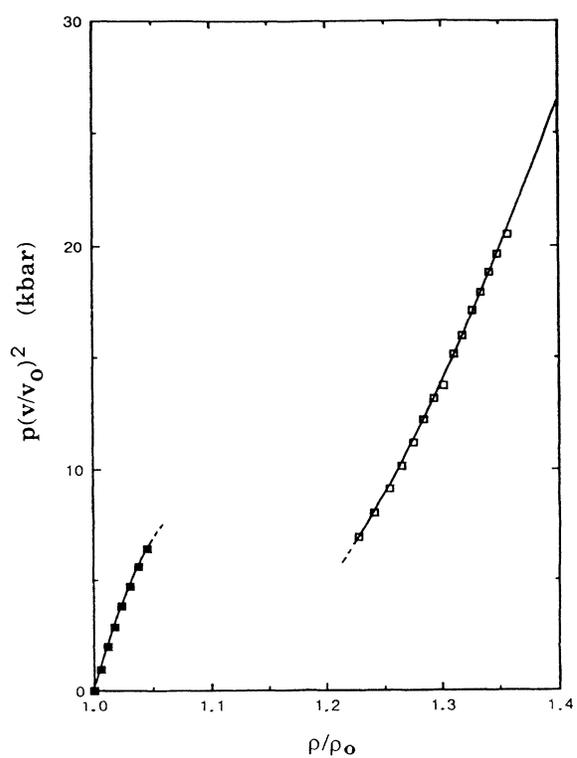


FIG. 13. Test of Eq. (13) for the two-phase system of α and γ cerium.

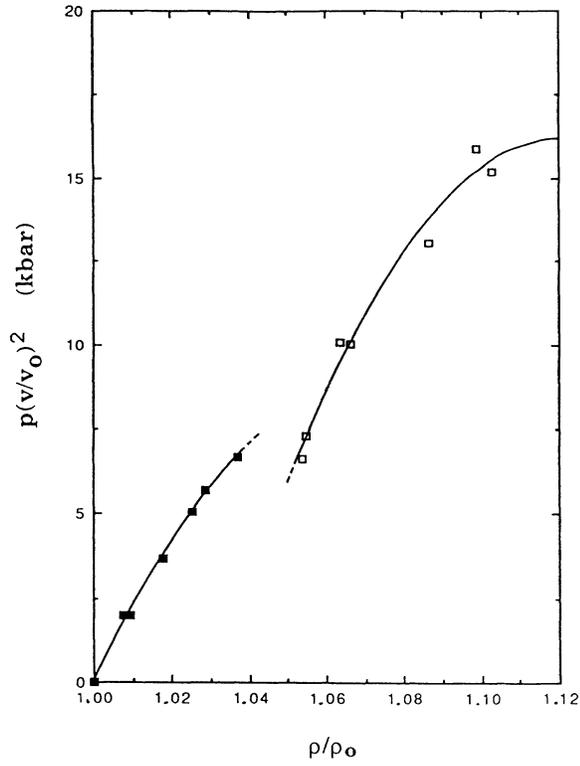


FIG. 14. Test of Eq. (13) for the two-phase system MnSnO_3 .

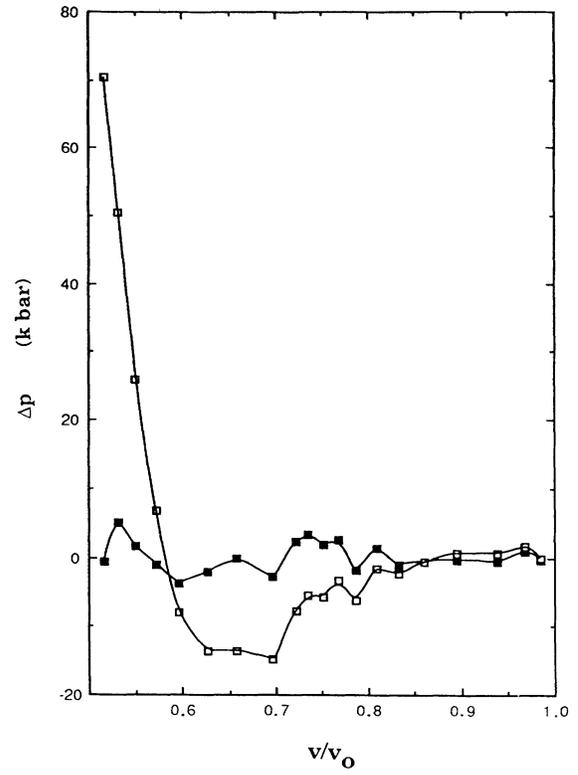


FIG. 16. Deviation plots for Eqs. (7) (\square) and (13) (\blacksquare) for the 25°C isotherm of Cu.

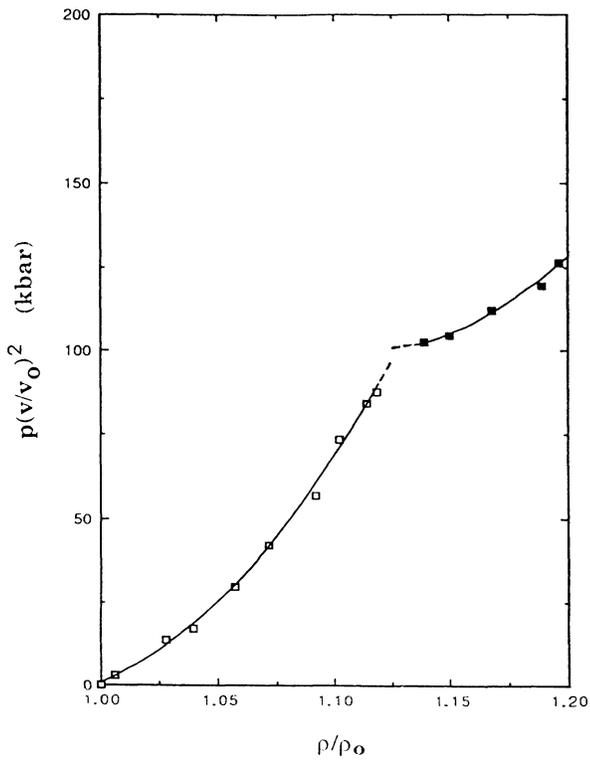


FIG. 15. Test of Eq. (13) for the two-phase system AgReO_4 .

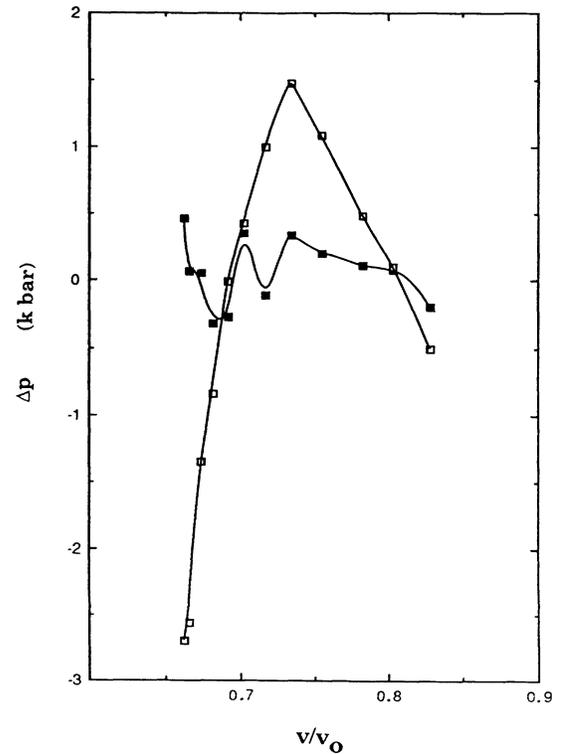


FIG. 17. Deviation plots for Eqs. (7) (\square) and (13) (\blacksquare) for the 25°C isotherm of *n*-hexadecane.

constrained to give $\rho/\rho_0=1$ at $p=0$, but those for H_2 , D_2 , and Ne very nearly meet this requirement. The curve for He clearly does not, nor should it, since He melts at about 130 bar at 4 K.

A similar plot is shown in Fig. 5 for the 77 K isotherm of Ar.¹³ Again a quadratic fit is very good.

Results are shown in Fig. 6 for the polar material NH_3 at room temperature,¹⁴ like the above systems a gas under ordinary conditions. The data are for the hexagonal close-packed phase that forms at 42.1 kbar, and v_0 is the (extrapolated) molar volume at 1 atom. A quadratic gives a very good fit, although, because of the scatter, a straight line would probably fit about as well in the experimental range.

Data for Cu are shown in Fig. 7. These are the same results as shown plotted differently in Fig. 3. Small irregularities in the low-pressure data do not show up in this type of plot. Notice that the pressure range is very much greater than for the previous systems, although the volume change is comparable.

Results for the ionic compound LiF are shown in Fig. 8, taken from the AIP compilation.¹² The quadratic fit is excellent.

Room-temperature results¹⁵ on the mineral magnetite (Fe_3O_4) are shown in Fig. 9. The quadratic fit is once more very good.

Equation (13) also works very well for organic compounds, as illustrated in Fig. 10 for *n*-hexadecane and

TABLE I. Fitted parameters for the EOS (13); Δp gives the pressure range of the data fitted.

Solid	<i>T</i> (K)	<i>A</i> ₀ (kbar)	<i>A</i> ₁ (kbar)	<i>A</i> ₂ (kbar)	Δp (kbar)
He ^a	4	-0.7466	0.5013	0.2930	0-20
Ne ^a	4	1.73	-15.21	13.40	0-20
Ar ^a	65	14.80	-46.72	31.92	0-19
	77	-19.34	-50.06	30.72	0-19
N ₂ ^a	65	-1.55	-9.35	10.93	0-10
<i>n</i> -H ₂ ^b	4.2	-1.505	0.739	0.724	0-25
<i>n</i> -D ₂ ^b	4.2	-2.585	1.291	1.247	0-25
NH ₃ ^c	298	-67.7	60.7	7.0	42-559
Cu ^d	298	-1535	1668	-133	20-4500
Au ^e	298	-1613	1584	41	44-701
α -Mn ^f	298	-471.5	-392.1	862.9	13-420
γ -Ce ^g	298	-1194	2202	-1008	1-7
LiF ^d	298	-710.6	792.1	-81.6	15-800
NaCl ^h	298	-254.4	267.1	-12.8	1-31
CsI ⁱ	298	-74.30	26.89	47.24	0-508
MgO ^j	298	-6349	9071	-2936	437-941
CaO(<i>B</i> 1) ^k	298	-1477	1837	-358	0-641
MnO ^l	298	-1622	1633	-10	30-605
SiO ₂ ^m	298	-10.15 × 10 ³	17.29 × 10 ³	-7.13 × 10 ³	7-111
TiO ₂ ^m	298	3357	-8591	5234	6-60
Fe ₃ O ₄ ⁿ	298	-3010	4168	-1158	0-44
MgSiO ₃ ^o	298	-12.13 × 10 ³	22.46 × 10 ³	-10.34 × 10 ³	20-62
Mg ₂ SiO ₄ ^o	298	-778	361	417	18-99
MnSnO ₃ ^p	298	-17.80 × 10 ³	33.23 × 10 ³	-15.43 × 10 ³	0-72
MnSnO ₃ ^p	298	-25.62 × 10 ³	46.01 × 10 ³	-20.52 × 10 ³	74-192
γ -Fe ₂ SiO ₄ ^m	298	-6.12 × 10 ³	10.15 × 10 ³	-4.03 × 10 ³	8-78
γ -Co ₂ SiO ₄ ^m	298	2.1	-1960	1959	6-71
γ -Ni ₂ SiO ₄ ^m	298	2548	-7219	4671	7-74
AgReO ₄ ^q	298	3453	-7208	3755	0-110
<i>n</i> -C ₈ H ₁₈ ^d	298	143.2	-220.9	87.0	0-40
<i>n</i> -C ₁₆ H ₃₄ ^d	298	114.8	-211.3	97.2	0-40
acenaphthene ^d	298	138.0	-337.8	199.9	0-40
Melmac 404 ^d	298	90.3	-267.4	177.2	0-40

^aReference 13.

^bReference 16.

^cReference 14.

^dReference 12.

^eReference 17.

^fReference 18.

^gReference 19.

^hReference 20.

ⁱReference 21.

^jReference 22.

^kReference 23.

^lReference 24.

^mReference 25.

ⁿReference 15.

^oReference 26.

^pReference 27.

^qReference 28.

TABLE II. Comparison of values of B_0 and B'_0 from the present EOS (13) and from the literature.

Solid	B_0 (kbar)		B'_0	
	Eq. (13)	Lit.	Eq. (13)	Lit.
$n\text{-H}_2$	2.10	1.74 ^a	5.85	5.4 ^a
$n\text{-D}_2$	3.69	3.37 ^a	5.75	5.4 ^a
NH_3	74.9	75.6 ^b	5.18	5.29 ^b
Au	1691	1666 ^c	5.01	5.5 ^c
$\alpha\text{-Mn}$	1332	1310 ^d	6.30	6.6 ^d
$\gamma\text{-Ce}$	186	191 ^e	-5.84	-10 ^e
NaCl	241	240 ^f	4.90	5.01 ^f
CsI	121	119 ^g	5.79	5.93 ^g
CaO($B1$)	1127	1147 ^h	4.35	4.10 ^h
MnO	1617	1620 ⁱ	4.98	4.8 ⁱ
SiO_2	3023	2980 ^j	0.23	0.7 ^j
TiO_2	1877	1880 ^j	10.6	10.6 ^j
Fe_3O_4	1852	1810 ^k	3.75	5.5 ^k
Mg_2SiO_4	1196	1200 ^l	5.70	5.6 ^l
$\gamma\text{-Fe}_2\text{SiO}_4$	2078	2020 ^j	1.12	2.2 ^j
$\gamma\text{-Co}_2\text{SiO}_4$	1960	2030 ^j	7.00	5.0 ^j
$\gamma\text{-Ni}_2\text{SiO}_4$	2123	2030 ^j	9.40	12.1 ^j
AgReO_4	302	309 ^m	29.9	30.9 ^m

^aReferences 16 and 29.

^bReference 14.

^cReference 17.

^dReference 18.

^eReference 19.

^fReference 20.

^gReference 21.

^hReference 23.

ⁱReference 24.

^jReference 25.

^kReference 15.

^lReference 26.

^mReference 28.

Fig. 11 for acenaphthene ($\text{C}_{12}\text{H}_{10}$, a derivative of naphthalene), with data taken from the AIP compilation.¹² The alkane is liquid at 25°C, and v_0 refers to the liquid volume; freezing occurs at 0.4 kbar. Figure 12 shows results¹² for a melamine-formaldehyde polymer, Melmac 404.

We have carried out similar comparison with experiment for a number of other systems; the main results are summarized in Table I.¹²⁻²⁸ In all cases the data were fitted very well by quadratics.

For systems with phase transitions, each phase can be fitted separately by Eq. (13). Examples for Ce,¹⁹ MnSnO_3 ,²⁷ and AgReO_4 (Ref. 28) are shown in Figs. 13-15.

The bulk modulus and its pressure derivative at any density and temperature are easily calculated from Eq. (13). The zero-pressure values of these quantities, B_0 and B'_0 , are often reported in the literature. They determine the linear dependence of B upon p that is specified by the Tait-Murnaghan relation. Comparisons of some values of B_0 and B'_0 for Eq. (13) and from the literature are given in Table II. The agreement is generally satisfactory, and most the variation arises from different methods of fitting p - v - T data, with the exception of the ultrasonic

measurements²⁹ on $n\text{-H}_2$ and $n\text{-D}_2$.

In order to illustrate the pressure range over which the present EOS holds, we have examined a deviation plot for Cu, for which data exist up to 4.5 Mbar.¹² The results are shown in Fig. 16, where they are compared with those for the EOS of Vinet and co-workers. The deviations for both equations are very small at low pressures. However, the deviations from Eq. (13) do not exceed a few kilobars over the whole pressure range, whereas the deviations from Eq. (7) rise to some tens of kilobars at the highest pressures. Even so, the percentage deviations are small.

The present EOS is accurate for organic solids as well, as shown in Figs. 10-12. However, we have noticed that the semilog plots of Eq. (16) of Vinet and co-workers deviate significantly from linearity for organic solids. The difference is shown in a deviation plot for n -hexadecane in Fig. 17. Since the highest pressure reported is only 40 kbar,¹² even the percentage deviations are appreciable for Eq. (16).

VI. TEMPERATURE DEPENDENCE OF PARAMETERS

Knowledge of the temperature dependence of the parameters of an EOS greatly increases the power of prediction from minimal input data. This is especially important in geophysical applications, for example, where knowledge of high-temperature behavior is often needed.

To predict high-temperature behavior, Vinet *et al.*⁸ assumed that the thermal pressure is (i) linear with respect to T and (ii) independent of density, when $T > \theta_D$, where θ_D is the Debye temperature. With these assumptions they showed that

$$p(v, T) = p(v, T_R) + \alpha_0(T_R)B_0(T_R)(T - T_R), \quad (19)$$

where T_R is a reference temperature and α_0 is the thermal expansion coefficient at $p=0$. Using Eq. (7) for the reference isotherm $p(v, T_R)$, they tested Eq. (19) with data on Au, NaCl, and Xe and obtained good agreement with experiment. The important feature of Eq. (19) plus Eq. (7) is that only four constants— $v_0(T_R)$, $B_0(T_R)$, $B'_0(T_R)$, and $\alpha_0(T_R)$ —are needed to predict all the p - v isotherms at temperatures above θ_D .

The essential final feature of Eq. (19) is that

$$\left[\frac{\partial p}{\partial T} \right]_v = \alpha_0(T_R)B_0(T_R) = \text{const.} \quad (20)$$

Indeed, Eq. (19) is obviously just the integrated form of $(\partial p / \partial T)_v = \text{const.}$ Examination of the p - v - T data for Au,¹⁷ NaCl,²⁰ and Xe (Ref. 30) shows that $\Delta p / \Delta T$ at constant volume is only a weak function of T and v , and Eq. (19) is quite successful for these systems.⁸ However, many substances do not meet the criterion of constant $(\partial p / \partial T)_v$ and so would not be accurately described by Eq. (19); for example, $\Delta p / \Delta T$ for CsI varies by an order of magnitude over the experimental range.²¹ We therefore attempt a more accurate description of the temperature dependence of the EOS parameters.

Regarding the present Eq. (13), the condition of con-

stant $(\partial p/\partial T)_v$ leads to the conclusion that A_0 , A_1 , and A_2 are all independent of T , which is generally contrary to experiment. However, if we use just the first assumption of Vinet *et al.* and define the thermal pressure to be $p - p(T=0)$, we obtain the more reasonable conclusion that all the A_i are linear in T . As already mentioned, this conclusion has the annoying side effect that the coefficients $e_i(T)$ in Eq. (14) are constants, and hence that the internal energy E is independent of temperature and $C_v=0$. However, this side effect has no direct influence on the EOS (only on its present derivation), and it is therefore worth examining the linearity of the $A_i(T)$.

For this purpose we use the experimental p - v - T data on Au,¹⁷ NaCl²⁰ and CsI,²¹ with the results shown in Figs. 18–20. It is clear that the linearity is good for Au, only fair for NaCl, and rather poor for CsI.

In order to obtain a more accurate description of the temperature dependence of the $A_i(T)$, we assume that the $e_i(T)$ are linear in T rather than constants. This assumption makes C_v a function only of density, not of temperature, and restricts the results to $T > \theta_D(\rho)$. Integration of Eq. (14) then yields the following form for the temperature dependence of the $A_i(T)$:

$$A_i(T) = a_i + b_i T - c_i T \ln T, \quad (21)$$

where a_i , b_i , and c_i are constants (independent of both T and ρ). The curves in Figs. 18–20 are the least-square fits of Eq. (21) to the experimental results.

In other words, if $(\partial p/\partial T)_v$ is not constant, the EOS for $T > \theta_D$ requires not the four constants of Vinet *et al.*,

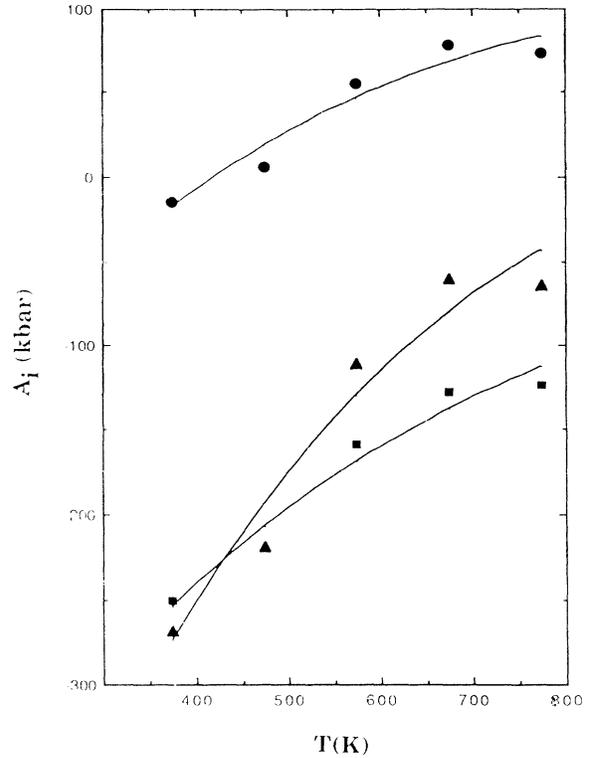


FIG. 19. Same as Fig. 18, for NaCl.

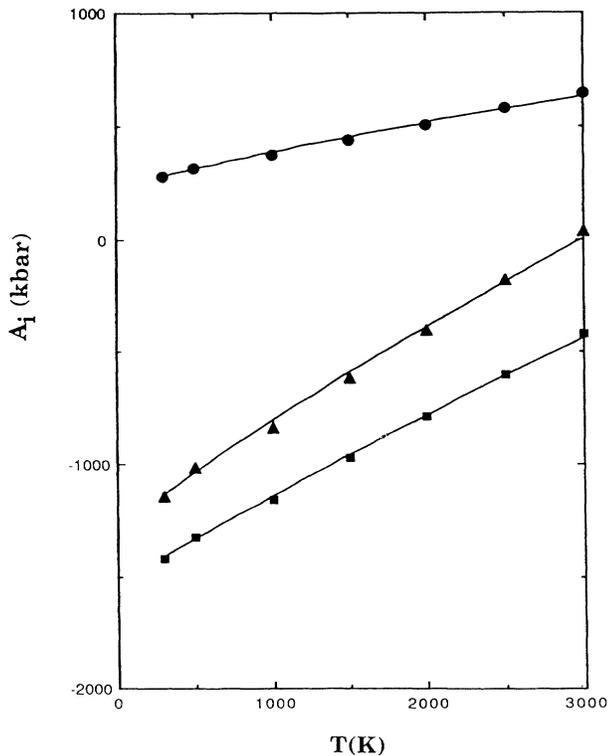


FIG. 18. Temperature dependence of the EOS parameters for Au: A_0 (■), $-A_1$ (▲), and A_2 (●). The curves are least-square fits of Eq. (21) to the points.

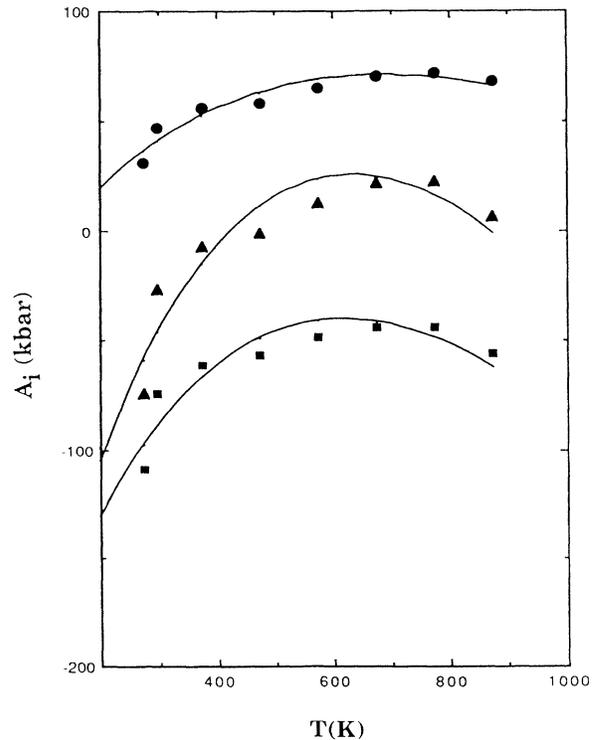


FIG. 20. Same as Fig. 18, for CsI.

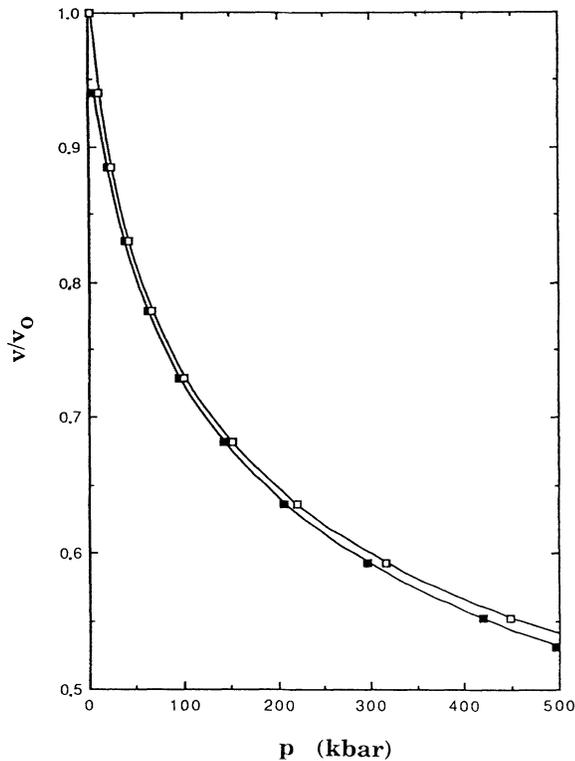


FIG. 21. Predicted (curves) and experimental (points) volumes as a function of pressure for CsI at 0°C (■) and 200°C (□).

but rather nine constants—three for each of the three $A_i(T)$. That is, measurements of three p - v isotherms are required to predict the entire p - v - T surface. Any reduction in the number of constants needed would seem to require a more detailed microscopic theory of the solid state than we have used.

Since the fit of Eq. (21) to the experimental results is only approximate, especially for CsI (Fig. 20), we have carried out a sensitivity test to see how the fit of Eq. (21) affects the p - v isotherms. We have used the experimental data²¹ on CsI at 25, 300, and 600°C, which give the points in Fig. 20 that are not well fitted by the curves, to calculate the nine constants, and then used these constants to predict the p - v isotherms at 0 and 200°C. The results are shown in Fig. 21; the agreement is quite good, which suggests that there is some compensation of errors in the determination of the three $A_i(T)$.

VII. GRÜNEISEN NUMBER

An important parameter related to the EOS of solids is the Grüneisen number γ , given in terms of experimental quantities as

$$\gamma = \frac{v\alpha B}{C_v} = \frac{v}{C_v} \left[\frac{\partial p}{\partial T} \right]_v, \quad (22)$$

where $\alpha = v^{-1}(\partial v / \partial T)_p$ is the coefficient of thermal expansion. Grüneisen³¹ noted empirically in 1908 that the ratio α/C_v is almost independent of temperature for a

number of metals, and γ now appears in many discussions of compressed solids. In particular, it is used to reduce shock-compression data to p - v isotherms,¹² on the assumption that γ depends on density alone. It is therefore of interest to see what the EOS predicts about the behavior of γ .

If C_v is known as a function of temperature at $p=0$, then γ can be determined from the EOS because the density dependence of C_v is given by

$$C_v(T, \rho) = C_{v0}(T) + T \int_{v_0}^v \left[\frac{\partial^2 p}{\partial T^2} \right]_v dv, \quad (23)$$

in which the integral is evaluated at constant T . For the EOS of Vinet *et al.*,⁸ $C_v = C_{v0}$ because $(\partial^2 p / \partial T^2)_v = 0$; γ , therefore, should vary directly as v at constant T . Direct measurements on NaCl show this behavior.³² The temperature dependence of γ at constant ρ thus is determined by $C_{v0}(T)$, which depends only weakly on temperature for $T > \theta_D$.

However, for a substance such as CsI, $(\partial p / \partial T)_v$ increases very rapidly with increasing pressure²¹ and consequently so does γ . The temperature dependence of $(\partial p / \partial T)_v$ for CsI is weak, however, and in fact changes sign as the pressure is increased. The net result is that γ is a strong function of density but only a weak function of temperature.

The general behavior of γ is easily assessed for the present EOS. For $T > \theta_D$ the dominant explicit temperature dependence of γ arises from $(\partial p / \partial T)_v$ and $(\partial^2 p / \partial T^2)_v$, and hence from the temperature dependence of the $A_i(T)$. From Eq. (21) we find

$$\frac{dA_i}{dT} = (b_i - c_i) - c_i \ln T, \quad (24)$$

$$T \frac{d^2 A_i}{dT^2} = -c_i, \quad (25)$$

from which we can see that γ has only a weak logarithmic temperature dependence at constant ρ . The density dependence of γ at constant T can be quite strong, however, depending on the signs and magnitudes of the $A_i(T)$. This is in general accord with available experimental information.^{12,21,32}

VIII. DISCUSSION

Although we have used several microscopic arguments in a heuristic way in obtaining the universal EOS (13), its actual basis amounts only to the use of virial expansions for $E(\rho, T)$ and $p(\rho, T)$, and truncation of these expansions is the only approximation. As justification for the accuracy of the truncation, other than good agreement with experimental data, we note that the energy $E(\rho, T)$ has to account only for the repulsive energy in a compressed solid, and that $p(\rho, T)$ has to cover a density range of only about a factor of 2 or less. However, there is no direct indication of any upper density limit on the EOS.

These latter two facts probably also account for the fact that many of the EOS proposed for solids can

represent experimental data with similar accuracy over a reasonable range of compression, despite the fact that the equations often have quite different mathematical forms. Schlosser and Ferrante³³ have compared a number of popular EOS. By expanding in powers of the compression they showed that all the EOS agreed at small compressions, but differed at high compressions. They concluded that the EOS of Vinet and co-workers gave the best fit of experimental data over the full range of compressions experimentally available. This justifies the restriction of our detailed comparisons to just the EOS of Vinet and co-workers.

Compared with the universal EOS (7) of Vinet and co-workers, the present Eq. (13) gives p - v isotherms that are somewhat more accurate and that apply to a wider range of materials, especially hydrocarbons. Both universal equations can be put into forms that show how to plot experimental data to give straight lines, a convenient feature for the analysis of data. However, the present results do not give any *a priori* way of finding cohesive energies, as does the universal binding-energy function (2) of Vinet and co-workers. The best that can be done is to calculate the binding energy at higher densities from a known binding energy at lower density, by integration of the thermodynamic relation

$$\left[\frac{\partial E}{\partial v} \right]_T = T \left[\frac{\partial p}{\partial T} \right]_v - p.$$

Although the thermal pressure is included from the beginning in the derivation of Eq. (13), no explicit information is forthcoming on the temperature dependence of the parameters $A_i(T)$. The method used by Vinet and co-workers to include temperature effects is equivalent to taking $(\partial p / \partial T)_v = \text{const}$, which is too restrictive a result. The simplest assumption leading to satisfactory results for Eq. (13) is that $E(\rho, T)$ is linear in T , which leads to Eq. (21) for the $A_i(T)$. This gives useful predictions for $T > \theta_D$, but the price is that nine constants must be determined experimentally, rather than four constants if $(\partial p / \partial T)_v$ is assumed to be constant. The appearance of undetermined constants is one of the limitations of an essentially thermodynamic approach.

Finally, Eqs. (13) and (21) account in a direct and simple way for the behavior of the Grüneisen number with temperature and density.

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