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WORKING PARTY
ON
"PHYSICS OF CONDENSED MATTER AT PLANETARY PRESSURES"
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THE EQUATION OF STATE IN SOLID PLANET INTERIORS

O.L. ANDERSON
Department of Earth and Space Sciences
University of California
Los Angeles, California 90024
U.S.A.

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1
O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 1
(July 16, 1984)

The Equation of State in Solid Planet Interiors

I. Introduction.

In describing properties of planet interiors, one often needs to know the formal relationship between pressure, volume and temperature. Such an equation is called an Equation of State (EOS).

The EOS we seek is

$$P = P(V, T) \quad (1)$$

In general, pressure is related to the free energy

$$P = - (\partial F / \partial V)_T \quad (2)$$

The contributions of deformation of all kinds to the free energy F , comes through internal energy U , where

$$U = F - TS, \quad (3)$$

and S is the entropy.

Now in specifying (1) as the EOS and (2) as its relationship to F , we are ignoring the contribution of shear deformations to U . This is justified in deep planetary interiors because the pressure P is large compared to the shear stresses. Similarly the time variation of deformation is not significant in our EOS, although it may be important in tectonic processes near the Earth's surface where the stress deviatorial stresses are no longer small compared to pressure.

In this course we are interested in planet interiors where shear stresses are small compared to P .

Now in applying (2) to fundamental formulations of F , we arrive at the following general equation for pressure

$$P(V, T) = P(T=0)(V) + P_{TH}(V, T) \quad (4)$$

The first term on the right is the so called isothermal EOS, being the relationship between P and V at absolute zero. The second term on the right is the thermal pressure of the solid. We shall be concerned with the magnitude of thermal pressure of the minerals compressing the Earth, but first a description of the thermal pressure may be useful.

A useful analogy exists between the thermal pressure of a solid and the kinetic energy of a gas. The perfect gas law is an EOS for an ensemble of ideal gas particles

2
O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 2
(July 16, 1984)

$$PV = 3NkT \quad (5)$$

where N is Avogadro's number, k is the Boltzman constant, and 3 accounts for three degrees of freedom of an individual particle. This equation, one of the introductory concepts of kinetic theory, is found by equating the mean kinetic energy of a particle to momentum transfer in a unit time over a unit area. The kinetic energy is $E_K = 3NkT$, and the kinetic energy density is identical to the kinetic pressure. Thus (5) can be written

$$P_K = E_K/V \quad (6)$$

An analog exists to (6) in solids which relates P_{TH} to E_{TH} (the thermal energy), but it requires the introduction of a very important parameter, called the Grüneisen parameter. We shall call this parameter here γ_M , the subscript being necessary because γ can and is defined in a variety of ways which are close but not always equal. We have

$$P_{TH} = (\gamma_M/V)E_{TH} \quad (7)$$

In solids, the kinetic energy E_{TH} arises from the motion of the atoms as they vibrate back and forth, each constrained to oscillate around a particular lattice point. There are significant differences between (6) and (7). First, while $P_K = P$ for a gas, P_{TH} is only a component and often a small one of P for a solid. Second, the Grüneisen parameter, so important for solids, is absent in the EOS of a gas. No such parameter arises because in ideal gases $F = F_K = E_K - TS$, and $(\partial E_K / \partial V)_T = 0$.

At temperatures high enough that the equipartition of energy assumption is appropriate but sufficiently low that anharmonic terms are unimportant (a classical solid), we have

$$E_{TH} = 3pRT$$

While γ_M is sometimes independent of T , or nearly so, it is quite crude to take γ_M to be independent of V . We know that γ diminishes with V .

II. The Grüneisen Parameter.

The value of the Grüneisen parameter often depends upon the definitions involved and thus, there are several forms, each having a definite physical meaning.

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 3
(July 16, 1984)

1. From (7), we have the Mie-Grüneisen definition for gamma; simply the ratio of the thermal pressure to the thermal energy density (Grüneisen, 1924).

$$\gamma_M = P_{TH}/(E_{TH}/V) \quad (8)$$

2. A more general definition of γ is as a dimensionless parameter with the value near unity, much like the dimensionless constants of hydrodynamics (Reynolds no, Nusselt no, etc.) (Grüneisen, 1924).

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \left\{ -V \left(\frac{\partial P}{\partial V} \right)_T \right\}}{\left(\frac{\partial E}{\partial T} \right)_V} V \quad (9)$$

This ratio of parameters is called the Grüneisen ratio. Although each of these quantities varies with T, this ratio is often independent of T or nearly so. K_T is the isothermal bulk modulus, C_V is the specific heat at constant volume, and α is the volume coefficient of thermal expansion.

3. The gamma of (9) is also the adiabatic lapse rate in a solid (similar to that in a gas) (Grüneisen, 1924).

$$\gamma = \frac{K_S}{T} \left(\frac{\partial T}{\partial P} \right)_S \quad (10)$$

A change in P results in a given change in T according to the above if no heat flows in or out of the solid, and γ is a measure of the effect.

4. Another form of the (10) is

$$\gamma = (\partial \ln T / \partial \ln p)_S \quad (11)$$

Equation (9) is useful for measuring γ at high temperature, but at zero pressure. It involves three separate experiments. Equation (10) is useful for measuring γ as a function of pressure and temperature, using adiabatic decompression (Boehler, et al., 1977; Ramakrishnan, et al., 1978). Equation (11) is useful for estimating the adiabatic temperature change arising from a density change, provided $\gamma(T, \rho)$ are known.

Values of γ have been measured using (9) and (10), as shown in Table 1.

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 4
(July 16, 1984)

Table 1

Values of the measured Grüneisen ratio. Data for parameters taken from tables assembled by Sumino and Anderson (1980)^a, Chung (1976)^b Boehler and Ramakrishnan, (1980)^c, Guinan and Beshers (1968)^d and Anderson (1979)^e.

Compound	Measured Gamma	
	γ by (10) $K_S/T (\partial T/\partial P)_S$	γ by (9) $\alpha K_T V/C_V$
Corrundum ^a	---	1.32
Periclase ^a	1.39 ^c	1.54
Kcl ^a	1.47 ^c	1.37
LiF ^{1a}	---	---
KBr ^a	1.43 ^c	1.66
NaCl ^a	1.62 ^c	1.58
Spinel ^a	---	1.13
Garnet ^a	---	1.21
Hematite ^a	---	1.91
Forsterite ^a	1.15 ^c	1.15
Olivine ^a	---	1.21
Rutile ^a	---	1.28
α -quartz ^a	0.57 ^c	0.67
α -iron ^d	---	1.81
Eclogite ^b	---	---
Peridotite ^b	---	---
Orthopyroxene ^a	---	1.56
Trevoite ^b	---	1.24
Earth's lower mantle (uncompressed)	(1.50)	---

Boehler and his coworkers (Boehler and Ramakrishnan, 1980; Boehler, 1981; Boehler, 1982) were able to estimate γ as a function of V/V_0 , by using Eq. (10). They measured $(\partial T/\partial P)_S$ as a function of P, and then used other data for K_S as a function of P to complete the data for (10). The data allowed γ to be reinterpreted as a function of V along an isotherm. In general they found that

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 5
(July 16, 1984)

$$\gamma/\gamma_0 = (\rho/\rho_0)^q \quad (12)$$

where q is a number near 1, for the oxides and silicates. The value of q is higher than 1 for the alkali metals (Boehler, 1983). The results are shown in Table 1.

Careful measurements of Boehler on the alkali metals taken out to very large compressions indicate that q does not remain independent of density at the largest compressions (Boehler, 1983). But for compressions out to, say, $V/V_0 \approx 0.75$, $d\gamma/d\rho$ is reasonably independent of ρ . Thus, Eq. (12) would appear to be reliable for pressures in the terrestrial planets, even though it may not be reliable for the deep interiors of the outer planets.

Table 2

The variation of γ with V according to V/V_0 (after Boehler and Ramakrishnan (1980) and Boehler (1982))

Metals	γ_0	q	Alkali Halides	γ_0	q
Al	2.14	1.0	NaCl	1.62	1.3
Cu	2.01	1.3	KBr	1.43	1.2
In	2.42	1.5	KCl	1.47	1.7
Fe	1.66	0.6	<u>Minerals</u>		
Pb	2.63	1.2	MgO	1.39	~1.0
Na	1.2	0.91	Mg ₂ SiO ₄	1.15	~1.0
K	1.19	1.7	Quartz	0.57	1.0
Si	1.0	1.4	Fluorite	1.95	4.6

The variation of γ vs T has been measured by O. L. Anderson and his colleagues, using Eq. (9) (for example, Anderson and Suzuki, 1983). Their measurements are in the high T region, which is of prime concern to geophysical problems.

Eq. (9) refers to measurements made at constant P (isobars). Using the following equation $(\partial\gamma/\partial T)_V$ can be determined, (isochores), from $(\partial\gamma/\partial T)_P$.

$$\left(\frac{\partial\gamma}{\partial T}\right)_V = \left(\frac{\partial\gamma}{\partial T}\right)_P + \left(\frac{\partial\gamma}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 6
(July 16, 1984)

The following graph, Figure 1, shows that γ is not independent of T at high T for the three minerals examined, either at constant V or constant P .

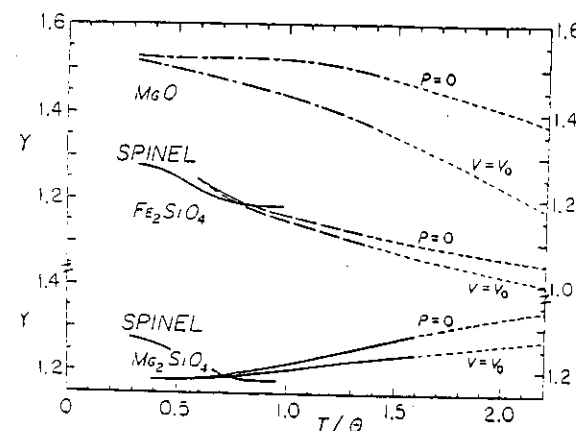


Figure 1. Measured values of γ vs T at constant P and constant volume for four minerals at high temperature (modified from Anderson and Sumino (1983)).

Now it is clear from Figure 1 that $(\partial\gamma/\partial T)_V$ is probably not zero at planetary temperatures ($T/\theta \sim 2$ for the Earth's mantle). This has important consequences.

The value of γ_M used in (8) is not measured, but γ in (9) is measured. The condition that γ can be used for γ_M has been derived by Mulargia (1977). One form of his equation is

$$\gamma - \gamma_M = \frac{E_{TH}}{C_V} \left(\frac{\partial\gamma}{\partial T} \right)_V \quad (13)$$

Since high temperature measurements on minerals indicate that $(\partial\gamma/\partial T)_V$ is not zero, it follows that γ_M , given by (7), must be largely empirical for the Earth's mantle calculations. That is, the measurements such as shown in Table 2, cannot be applied to (7) without corrections.

The abscissa of Figure 1 is the dimensionless T/θ , where θ is the Debye temperature. θ helps define the limit where a solid enters the high temperature regime. At $T > \theta$, the solid is said to be at high temperature, but the value of θ varies from solid to solid.

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 7
(July 18, 1984)

III. The Debye Temperature.

In the classical theory of a thermal solid, Debye approximated the phonon spectrum by assuming all the phonons are acoustic and that the frequency of the phonons was controlled by the sound velocities of an isotropic body, v_p and v_s . The result of this theory lead to good approximations of specific heat and entropy vs T, by using the so called Debye function. In the course of this derivation Debye defined the relationship between the Debye frequency (maximum frequency) and the mean velocity of sound, v_m

$$\omega_m = \left(\frac{3pN}{4\pi V} \right)^{1/3} v_m \quad (14)$$

where the mean velocity is given by

$$v_m = v_s \left[\frac{3}{2 + (v_s/v_p)^2} \right]^{1/3} \quad (15)$$

and where p is the number of atoms per molecule, N is Avogadro's number and V is the molecular volume. Now since the average atomic mass is equal to $M/p = Nm/p$

$$N/V = \frac{p}{M/p}$$

Further, ω_m can be converted to a temperature (the Debye temperature) by $\omega_m = (k/h)\theta$.

Thus the Debye temperature is

$$\theta = \frac{k}{h} \left(\frac{3n}{4\pi} \right)^{1/3} \left[\frac{p}{M/p} \right]^{1/3} v_m = 251.2 \left(\frac{p}{M/p} \right)^{1/3} v_m \cdot K \quad (16)$$

where m/p is the mean atomic mass, ρ is in gm/cc and v_m is in km/sec.

Using (16), the Debye temperature can be estimated for any solid (including zones of the Earth) from data on sound velocities.

Since the sound velocity varies very little between absolute zero and room temperature, the room temperature values of v_p , v_s and ρ are used in (16). Estimated values of θ are given in the following table.

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 8
(July 16, 1984)

Table 3

Compound	Measured v_p (km/sec)	v_s	M/p Mean Atom. Weight	ρ Density (g/cm ³)	(16) θ
MgO	9.5	5.99	20.16	3.583	931
Al ₂ O ₃	10.9	6.45	20.35	3.99	1042
Mg ₂ SiO ₄	8.65	5.07	20.10	3.22	767
Topaz	9.59	5.75	20.45	3.52	889
BeO	12.3	7.3	12.5	3.01	1265
Al	6.4	3.11	26.98	2.70	407
Fe	5.9	3.25	55.85	7.37	473
W	5.2	2.86	183.9	19.92	383
Earth's lower mantle (uncompressed)					~ 960

IV. Thermal Energy and Vibrational Energy at High Temperature.

In the following, we shall be concerned about the thermal pressure, especially at high T, but a distinction needs to be made between the thermal energy and the vibrational energy.

The internal energy of an insulating solid arises from two major sources. One term is due to the potential of the static lattice at absolute zero, E_{AZ} , and the other is due to the dynamical motion of the atoms as they vibrate around the lattice points, E_{VIB} .

Thus, in an insulator where the energy of electrons can be neglected

$$U = E_{AZ} + E_{VIB} \quad (17)$$

Now, E_{VIB} is a function of temperature, but it also contains a term which is independent of T, called the zero-point vibrational energy, or

$$E_{VIB} = E_{ZV} + E_{TH} \quad (18)$$

The thermal energy, being dependent only on T, is the vibrational energy less the zero point energy, and

$$U = E_0 + E_{TH} \quad (19)$$

where E_0 is the sum of the static lattice energy at

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 9
(July 16, 1984)

absolute zero, plus the zero point vibrational energy. They are both functions of V only.

Now in simple systems where anharmonicity is small, the vibrational energy can be approximated by $3pN$ independent harmonic oscillations. In such a system, the free energy ($F = U - TS$) is the following (Girifalco, 1973).

$$F = E_{AZ} + E_{ZP} + F_{TH} \quad (20)$$

$$E_{ZV} = \frac{1}{2} \sum_{j=1}^{3pN} h\nu_j \quad (21)$$

$$F_{TH} = kT \sum_{j=1}^{3pN} \ln \left(1 - e^{-h\nu_j/kT} \right) \quad (22)$$

Huang (1951) described the ambiguity associated with E_{VIB} and E_{TH} . They approach the same high-temperature limit, but the rate of convergence to this limit is quite different. Fumi and Tosi (1962) showed that E_{VIB} converges to E_∞ at $T \propto 2/(3\theta)$, while E_{TH} converges to E_∞ at $T \propto \theta$, where θ is the Debye temperature.

V. The Thermal Pressure in the h.T. Approximation.

The description of the quantum harmonic crystal reduces to simple terms at high temperatures, which are very useful to guide experiments. At high temperatures (22) becomes an integral part of F , and cannot be ignored. At sufficiently high T , (22) can be simplified due to the convergence of certain series expansions. The argument in (22) becomes small since $h\nu_j \ll kT$. Thus,

$$\begin{aligned} \ln(1 - e^{-x_j}) &= \ln \left\{ x_j - \frac{x_j^2}{2} + \dots \right\} \\ &\approx \ln x_j + \ln \left(1 - \frac{x_j}{2} \right) \end{aligned} \quad (23)$$

Expanding the last logarithmic term above,

$$\ln(1 - e^{-x_j}) \approx \ln \left(x_j - \frac{x_j^2}{2} \right) \quad (24)$$

O. L. Anderson
August 21-24, 1984

10

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 10
(July 16, 1984)

$$F = E_{AZ} + E_{ZP} + kT \sum \ln \frac{h\nu_j}{kT} - \frac{1}{2} \sum h\nu_j \quad (25)$$

From (11) we see that the last term above just cancels E_{ZP} . Thus,

$$F = E_{AZ} + kT \sum (\ln h\nu_j - \ln kT) \quad (26)$$

An equivalent derivation is found in Zharkov and Kalinin (1971), but they deal with a Debye function in the high temperature limit.

Equation (26) is the important result. Its validity depends upon the condition that the anharmonicity is small. If anharmonicity is significant, then this simplified derivation is not valid as a description of the free energy of an insulator. The theory including anharmonicity effects has been presented by Mulargia and Boschi, (1978). The test of anharmonicity rests with experiments. In the next lecture, we shall review the experimental evidence in support of the conclusion that anharmonicity is not significant in minerals at high pressure, at Earth temperatures, and thus (26) stands as a useful approximation for our purposes.

The high-temperature pressure is found from (2):

$$P = P_0(V) + \frac{1}{V} \left\{ \frac{1}{3pN} \sum_{j=1}^{3pN} \left(\frac{\partial \ln \nu_j}{\partial \ln V} \right) \right\} 3pN kT \quad (27)$$

Now, since $3pNkT$ is the harmonic high temperature value of the energy, we have

$$P = P_0(V) + \frac{3pNkT}{V} \frac{\sum \frac{\partial \ln \nu_j}{\partial \ln V}}{(3pN)} \quad (28)$$

The average mode gamma at high temperature is given by

$$\gamma_j = \frac{\partial \ln \nu_j}{\partial \ln V} \quad (29)$$

called the high temperature γ_{∞} .

The numerous derivatives of frequencies, ν_j , with respect to V , are called mode gammas

$$\gamma_{\infty} = \frac{1}{3pN} \sum_{j=1}^{3pN} \gamma_j \quad (30)$$

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 11
(July 16, 1984)

Eq. (30) is the arithmetic average of all normal modes in a solid. Now there are many different kinds of modes in a solid, but they can be lumped into two classes: acoustical and optical. There is little possibility of measuring the optical modes of vibration of the Earth's interior. However, the low frequency acoustic modes can be measured because the acoustic vibrations are measured (the seismic velocities, v_s and v_p).

We have the same recourse that Debye did when he derived his famous theory of specific heats. Debye assumed that all vibrations of a solid could be represented as either longitudinal acoustic vibrations or transverse acoustic vibrations, and that these vibrations could be measured by velocities of sound. The Debye model neglects all optical vibrations and all high frequency acoustic vibrations. Even with these drastic assumptions, the Debye theory of specific heat has often been successful, even at high temperature.

Following Debye's reasoning, then the sum of the $3pN$ modes in (30) is replaced by only three modes, one longitudinal and 2 equal shear acoustic modes. That is to say, the average gamma of all the modes is close to average of the three acoustic modes.

$$\gamma_{ac} = \frac{1}{3} \left[\frac{\partial \ln v_p}{\partial \ln V} + 2 \frac{\partial \ln v_s}{\partial \ln V} \right] \quad (31)$$

where γ_{ac} (for acoustic) replaces γ_{∞}

Now the relationship between frequency and velocity of acoustic modes involves the wave length, $v = \lambda / v$

$$\left(\frac{\partial \ln v}{\partial \ln V} \right)_{IT} = \left(\frac{\partial \ln \lambda}{\partial \ln V} \right)_{IT} - \left(\frac{\partial \ln v}{\partial \ln V} \right) \quad (32)$$

The first term on the right is $1/3$ because λ is proportional to $V^{1/3}$ if the number of modes remains fixed as the volume changes.

Using Eq. (32), Eq. (31) is replaced by

$$\gamma_{ac} = \frac{1}{3} \left[\gamma_p + 2 \gamma_s \right] \quad (33)$$

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 12
(July 16, 1984)

where
$$\gamma_p = \frac{1}{3} + \left(\frac{\partial \ln v_p}{\partial \ln V} \right)_T \quad (34)$$

$$\gamma_s = \frac{1}{3} + \left(\frac{\partial \ln v_s}{\partial \ln V} \right)_T \quad (35)$$

VI. The Acoustic Grüneisen Parameter.

We may evaluate γ_{ac} for the Earth's mantle using the appropriate seismic data. Using the data from the PREM model (Dziewonski and Anderson, 1982), γ_{ac} can be found vs depth.

From the PREM data γ_{ac} decreases from 1.29 at 770 km to 0.98 at 2700 km. The plot of $\log \gamma_{ac}$ vs $\log \rho$ is shown in Figure 2. A straight line confirms (11), where q is independent of ρ .

It is found that the slope yields $q = 1.3$, and the intercept yields $\gamma_0 = 1.5$, where $\rho_0 = 4.00$ gm/cm³.

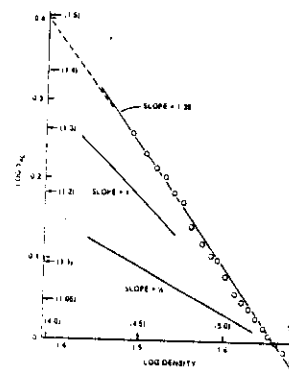


Figure 2. The determination of $q = - (\partial \ln \gamma_{ac} / \partial \ln \rho)$ for the lower mantle using the PREM data (Dziewonski, et al., 1975). These data indicate that $q = 1.35$ over the whole of the lower mantle (Anderson, 1979).

The comparison of γ_{ac} with γ for minerals is shown in Table 4. Sometimes the agreement between γ_{ac} and γ is good, but often it is not, as has been noted by Mulargia and Boschi (1980). For those minerals which have a tightly packed structure [the corundum, the perovskite, hexagonal close packed in Table 4], the value of γ_{ac} is close to that of γ . The error in γ itself can be estimated by comparing values of γ from Eq. (9)

August 21-24, 1984

with those from Eq. (10). For the fcc structure, the agreement is good when the size of cation is close to that of the anion (NaCl, CaO) and becomes worse as the cation/anion size ratio departs from unity (KBr and BaO). For minerals with open structures such as TiO_2 , the agreement is not good, but for the same atoms in a close packed structure, Ti_2O_3 , the agreement is satisfactory. The worst agreement between γ_{ac} and γ is for silica glass, but the coordination number of silica glass is 2 and 4, which permits a very loose structure.

Now these correlations are similar to those found for the low temperature expansivity in certain solids (Barron, et al., 1980). For open structures, especially those with tetrahedral coordination, the value of thermal expansivity is negative at low temperature, and therefore γ is negative; while the thermal expansivity found at high temperature on the same materials is normal. As an example, γ_{ac} is negative for ZnO (Soga and Anderson, 1967) (see Table 4), and also the expansivity is negative at low T for ZnO, see Yates, et al., (1971).

On the other hand, for densely packed compounds, such anomalies in γ_{ac} and thermal expansivity are absent. Barron, et al., (1980) concluded that open structures allow the excitation of certain shear vibrations, which tend to contract the lattice as the temperature rises, but in close packed structures, such vibrations cannot occur.

We may conclude, therefore, that since compounds in planet interiors always have dense packing--having been brought into such a state by pressure induced phase transitions--that the approximation $\gamma_{ac} = \gamma$ is reasonably good for the geophysical problems discussed in this course. We may conclude that (31) is satisfactory for thermal calculations of the Earth's and the Moon's interiors, where V_s and V_p are measured.

August 21-24, 1984

Table 4

Values of γ_{ac} estimated from sound velocities (at room temperature) compared with γ found from Eq. (9) and (10).
Data taken from tables by Sumino and Anderson (1984)^a,
Boehler and Ramakrishnan (1980)^b, Guinan and Beshers (1966)^c,
Anderson (1978)^d, and Soga and Anderson 1967^e.

Material	γ_{ac}	γ	γ	Material	γ_{ac}	γ
		(9)	(10)			(9)
Al_2O_3^a	1.31	1.32	--	KMgF_2^a	1.50	1.60
				(Petrovskite)		
MgO^a	1.50	1.54	1.39	CsCl^a	2.21	2.30
CaF_2^a	1.89	1.20	--	Ti_2O_3^a	1.140	1.13
Forscrite^a	1.47	1.15	1.15	$\alpha\text{-iron}^c$	1.01	1.61 ^a
Olivine^a	1.33	1.21	--			
Spinel^a	0.8	1.13	--	BaO^a	1.05	1.13
				CaO^a	1.57	1.72
NaCl^a	1.36	1.58	1.62	BaO^a	1.23	1.03
KCl^a	1.50	1.54	1.39	ZnO^e	-0.44	0.814
KBr^a	1.17	1.66	1.43	AgBr^a	2.15	2.55
				AgCl^a	1.69	2.31
Fe_2O_3^a	0.94	1.91	--	UO_2^a	1.71	1.55
TiO_2^a	1.07	1.28	--	SnO_2^a	.85	.75
				GeO_2^a	1.13	1.17
SiO_2^a (quartz)	0.46	0.67	0.57			
SiO_2^a (glass)	-2.46	0.036	--			
CaCO_3^a	-1.004	0.507	--			

Note: Earth's lower mantle, uncompressed $\gamma = 1.50$

Earth's inner core, compressed $\gamma = 1.5$

VII. Evaluating the Thermal Pressure.

Eq. (31) now becomes

$$P = P_0 + \frac{3\rho N R T \gamma_{ac}}{V} \quad (36)$$

Replacing

$$\frac{P}{V} = \frac{\rho}{(M/\rho)} \quad (37)$$

where M/ρ is the average mass, and recalling that $R = 3pNk$, we have

$$P = P_0 + \frac{\gamma_{ac} \rho}{(M/\rho)} 3RT \quad (38)$$

We note that according to (38) the thermal pressure is proportional to T . For $q = 1$ (Table 2) the thermal pressure would be independent of ρ . For some solids where q is different from 1, P_{TH} would depend slightly on ρ . Eq. (38) is valid only insofar as the anharmonicity effects in pressure are shown to be negligible (as will be demonstrated in the next lecture).

Thus, to the extent that (22) describes the free energy of an insulator, the thermal pressure is linear with T and slightly dependent upon density, (or volume), or perhaps not dependent upon volume at all.

Let us evaluate the thermal energy, P_{TH} , in the lower mantle of the Earth according to the formula found in (38)

$$P_{TH} = \frac{3\gamma_{ac} \rho}{(M/\rho)} RT \quad (39)$$

Take the average atomic mass M/ρ as 21 gm/mole (Watt, et al., 1975) throughout the lower mantle, and the dimensions of ρ as gm/cm³. Recalling that $R = 8.314 \times 10^7$ erg/deg⁻¹ mole⁻¹, and noting the dimensions of P , one GPa = 10^{-10} dyne/cm² and one erg equals one dyne cm, then for the lower mantle, (39) is found to be

$$P_{TH} = 11.88 \times 10^{-4} \rho \gamma_{ac} T \text{ GPa} \quad (40)$$

Computing P_{TH} using the Brown and Shankland thermal model for γ_{ac} and T , (Brown and Shankland, 1981) and

ρ and P from the PREM model (Dziewonski and Anderson, 1982), we have:

Depth km	Density gm/cc	γ_{ac}	T °K	P_{TH}	P	P_{TH}/P
771	4.437	1.291	1907	12.90	28.30	0.46
971	4.553	1.251	1972	13.34	37.3	0.36
1171	4.688	1.229	2034	13.92	46.5	0.30
1371	4.779	1.193	2092	14.17	55.9	0.25
1571	4.889	1.166	2147	14.54	65.5	0.22
1771	4.996	1.133	2199	14.79	75.3	0.20
1971	5.101	1.095	2246	14.89	85.4	0.17
2171	5.203	1.056	2295	14.98	95.7	0.16
2371	5.303	1.022	2341	15.06	106.4	0.14
2571	5.401	0.987	2384	15.09	117.7	0.13
2771	5.496	0.943	2425	14.94	128.7	0.12
(PREM)		(B & S)	(B & S)	(40)	(PREM)	

When the thermal pressure is subtracted from the total seismically determined pressure, we have the isothermal pressure. The plot of the total pressure and the isothermal pressure for the Earth's lower mantle is plotted in Figure 3. The pressure curves look parallel to the unaided eye, but they are not. The difference between Curves A and B is nearly 4 GPa greater at 2771 km than it is at 771 km.

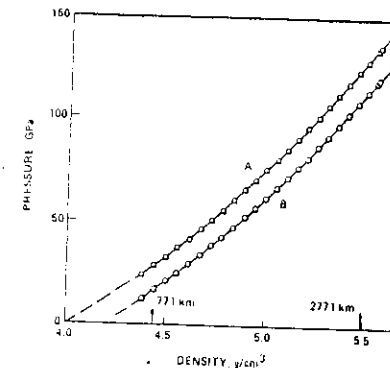


Figure 3. The variation of pressure with density. Curve A is the total pressure P , with density obtained from seismology; PREM (Dziewonski and Anderson, 1982). Curve B is the isothermal pressure P_{1S0} , obtained by subtracting the thermal pressure, P_{TH} .

For iron, where $m = 55.83$ gm/mol, we find

$$P = 4.46 \times 10^{-4} \rho \gamma_{ac} T \text{ GPa} \quad (41)$$

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 17
(July 18, 1984)

VIII. Choosing the Isothermal Equation of State.

Great progress has been made in the last few years in theory where the $P(\rho)$ (at $T = 0$) equations have been derived using fundamental methods. An example of this approach is shown by Bukowski (1977), who started only from Schroedinger's equation and found the EOS of iron (FCC). Remarkable progress has been made by Marvin Cohen and his colleagues (for example, Yin and Cohen, 1982), who have theoretically determined the 0° K EOS properties of Be, Si, Ge, and diamond, starting with Schroedinger's equation. The derivation of the EOS and the melting of aluminum (Moriarty, et al., 1984) is another example of recent progress. The work of Young and Ross (1982) on the EOS at high T , including melting, shows that theoretical methods have great promise for elements and perhaps the simplest compounds.

However, for the more complicated minerals, of which the mantles of the terrestrial planets are constructed, it will be many years before the fundamental approaches of physics are worked out. We shall present a brief discussion of the empirical equations appropriate for the silicate mantle. For the near future, empirical EOS equations have to suffice for the rocky mantles of planet interiors.

We now concentrate on the first term on the right of Eq. (4), $P_0(V)$. The subscript zero stands for the isotherm at absolute zero.

There are a large number of equations in the literature which are suitable for expressing the isothermal pressure-volume relationship. It is now becoming recognized that all such equations are essentially empirical.

The empirical variety of EOS can be lumped into three classes: (1) those based upon finite strain; (2) those based upon interatomic potentials, and (3) those based upon assumed relationships between the variables K_0 , γ , and γ . (K_0 is the bulk modulus and K_0' its pressure derivative at zero pressure.)

To proceed with the derivation of $P_0(V)$, we use (1) and (2), and in addition, the following

$$P = -\left(\frac{\partial E}{\partial V}\right)_{T=0} = \left(\frac{\partial E_{st}}{\partial V}\right)_T = V_0 \left(\frac{\partial E_{st}}{\partial \chi}\right)_T \quad (42)$$

$$K = -\frac{1}{V} \left(\frac{\partial P}{\partial V}\right)_T = -\frac{V_0}{V} \left(\frac{\partial^2 E_{st}}{\partial \chi^2}\right)_T \quad (43)$$

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 18
(July 18, 1984)

$$K' = \left(\frac{\partial K}{\partial P}\right)_T = -\frac{V}{K} \left(\frac{\partial K}{\partial V}\right)_T = -\frac{V}{K} \left(\frac{\partial K}{\partial \chi}\right)_T \quad (44)$$

$$K_0 = K \text{ as } P \rightarrow 0$$

$$K'_0 = K' \text{ as } P \rightarrow 0$$

IX. The Third Order Isothermal EOS.

Because K_0 , K'_0 , and ρ_0 can be precisely measured in the laboratory, these are available to define the isothermal EOS. Thus, any isothermal EOS with only three arbitrary constants can be defined in terms of the parameters ρ_0 , K_0 , K'_0 . Since the pressure function, P , vanishes at $\rho = \rho_0$, these three parameters define four related functions of the EOS: $E - E_0$, P , K_T , and K'_T at all pressures. Higher order derivatives of K_0 beyond K'_0 have not been measured in the laboratory to uniform satisfaction, so a fourth order equation of state (four arbitrary constants) usually involves some assumption about K_0 .

A three-parameter EOS arises from three parameters in the potential. The potential could include three terms in a polynomial expansion in strain, for example:

$$E = E_{st} - E_0 = a\epsilon + b\epsilon^2 + c\epsilon^3 \quad (45)$$

where $\epsilon = f(\chi)$ and $\chi = V/V_0 = \rho_0/\rho$.

Now the isothermal equation of state means setting all the functions to absolute zero in temperature so that strain energy dominates the internal energy, or $U(V, T) = E_{st}(V, 0)$. Changing to the reduced variable $\chi = V/V_0$, our known quantities are $P(1, 0) = 0$, K_0 , K'_0 , ρ_0 , all at $T = 0$. Using (8), the three parameter isothermal EOS is now completely defined as a set of the four equations:

$$E - E_0 = f_1(\chi, K_0, K'_0)$$

$$P(\chi, 0) = f_2(\chi, K_0, K'_0)$$

$$K(\chi, 0) = f_3(\chi, K_0, K'_0)$$

$$K'(\chi, 0) = f_4(\chi, K_0, K'_0)$$

Our focus will be upon $P(\chi, 0)$. P has the same dimensions as K_0 , and K'_0 is dimensionless, as is

χ . Therefore, the pressure function will be given in its general form by

$$P(\chi, 0) = K_0 g_2(\chi, K_0'). \quad (46)$$

where $g_2(\chi, K_0')$ is dimensionless. The function $g_2(\chi, 5.4)$ is illustrated in Figure 5, with data from four alkali halides.

X. Parameters in the Isothermal EOS.

The isothermal EOS, $P(\chi, 0)$, is strictly applicable only at absolute zero. It is, however, often used to describe the EOS of geophysical materials at room temperature or to duplicate the experimental data of materials taken at the room temperature isotherm. The justification of this rests upon the similarity of the values of the bulk modulus of geophysical materials at room temperature and at absolute zero. That is, for $\chi = 1$,

$$K(1, 273^\circ) \approx K(1, 0) \quad (47)$$

Such a statement cannot be made for soft solids like Rb; however, for the hard minerals of geophysics, room temperature is well below the Debye temperature, and K_T changes little between 0°K and 273°K. See Figure 4.

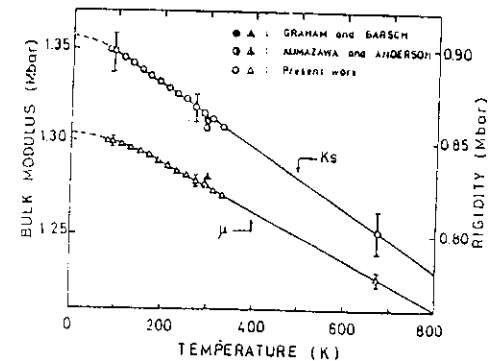
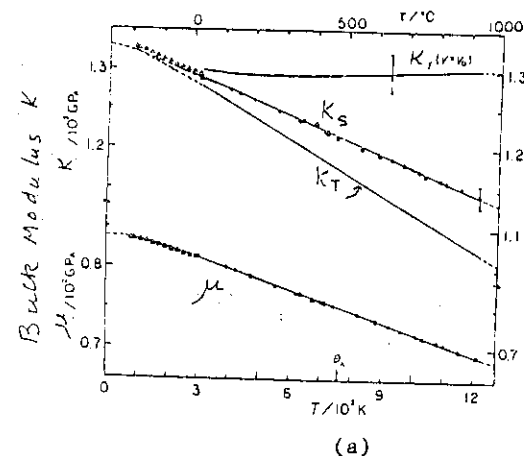
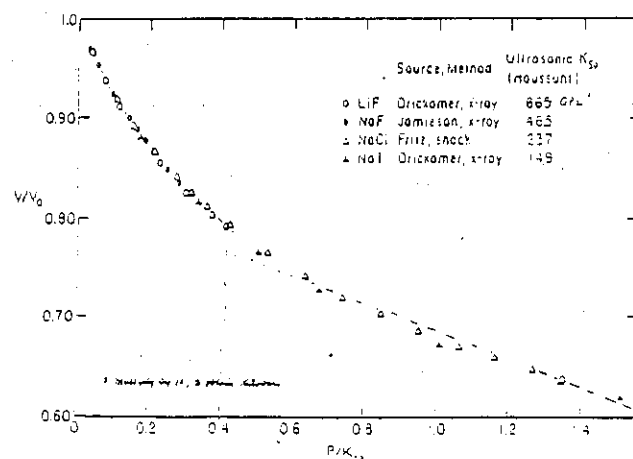


Figure 4.(a) The temperature dependence of the measured adiabatic bulk modulus, K_S , and μ , the rigidity modulus for forsterite vs T . The calculated isothermal bulk modulus, K_T at $P = 0$ is shown as a lower light line. The calculated isothermal K_T with constant volume is shown as the upper line (Sumino and Anderson, 1983). The triangles are by Sumino et al. (1977), which is given in more detail at the right. (b) The Debye temperature θ_A is 760°K.

There is little point in insisting that only the zero-degree bulk modulus data be used for the EOS, because the variation of the measured value of $K(1,273)$ from author to author is as large as the difference between $K(1,273)$ and $K(1,0)$ reported by the same one author.

The experimental dimensionless EOS plot -- $P(\chi)/K_0$ versus χ -- does not change significantly from solid to solid. Here $K = K_0$ as $\chi \rightarrow 1$, where K_0 is not an adjustable parameter, but is measured. Dimensionless plots of EOS data tend to overlap each other at low pressure because they have a common slope, -1. At higher compressions, they diverge, but the divergence is not marked whenever the values of K_0 are close for solids.

The experimental data of four halides (LiF, NaF, NaCl, and NaI) are shown in Figure 5, which shows the remarkable overlap of the data on some reduced EOS curve $P(\chi)/K_0$ versus χ . The values of K_0 are 5.4 ± 0.15 for the four compounds. Solids of interest to geophysics also have values of K_0 reasonably close to each other, although the spread is greater than shown for the four alkali halides.



* Figure 5. The dimensionless experimental EOS of LiF, NaF, NaCl, and NaI at room temperature (after Smith & McLean, 1973).

Table 5

Representative values of $K'_0 = K'_{20}$ for minerals related to geophysical problems (source: Sumino and Anderson, 1984). Measured by ultrasonics, compression, or shock waves.

Compound	K'_0	Compound	K'_0
FeO	4.0	Fayalite, Fe_2SiO_4	6.0
Al_2O_3	4.0	Diopside, $\text{CaMgSi}_2\text{O}_6$	6.2
Fe_2O_3	4.5	Garnet, $(\text{Py}_{23}\text{Al}_{16})$	5.5
MgO	4.5	Spinel, MgAl_2O_4	4.3
CaO	5.3	Spinel, $\text{Mg}(2.6)\text{Al}_2\text{O}_4$	4.2
SiO	6.1	Spinel, NiFe_2O_4	4.4
BeO	5.5	Forsterite, Mg_2SiO_4	5.0
ZnO	4.8	Olivine $(\text{Fe}_{93}\text{Fa}_7)$	5.1
SiO_2 (aQ)	6.7		
GeO_2	6.2		
TiO_2	5.7		
Lower Mantle			3.3

Figure 5 shows that a simple theoretical EOS ought to be attainable to match the data. A theoretical isothermal EOS of the third order, Eq. (45), may be suitable to match the experimental data of minerals at comparable compressions. The question is, what theoretical isothermal EOS is best? Unfortunately, an arbitrary assumption about the interatomic potential, ϕ , or equivalently an arbitrary assumption about the strain energy function $\epsilon(\chi)$, is behind the specification of E_{st} . Thus the theoretical isothermal EOS often rests upon arbitrary grounds. We now discuss the strain energy formulation of the EOS.

XI. Finite Strain Formulation of the EOS.

The finite strain representations of EOS are based upon the generalized elasticity theory going back to Love (1927), but most literature refers to the expressions given for geophysical problems due to Birch (1938, 1952).

The basic foundation of finite strain theory is the inclusion of the square of the ratio of displacement with regard to coordinate displacement (see Stacey, et al.,

O. L. Anderson

August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 23
(July 16, 1984)

1981). One form taken for the relationship between compression and strain is

$$V/V_0 = x = (1 + 2\epsilon)^{3/2} \quad (48)$$

The energy, $E(\epsilon)$, will be some assumed function of ϵ , usually expressed as a polynomial in ϵ , and the pressure is $P = x(\partial E/\partial x)_T$. Thus, there are a large variety of paths in obtaining the desired EOS, $P(x)$.

The relationship between x and strain is not unique. An equally plausible alternate to (48) is

$$x = (1 - 2\epsilon)^{-3/2} \quad (49)$$

The difference between (48) and (49) arises from different reference states; the former is the Lagrangian formulation while the latter is the Eulerian formulation. Other formulations are possible including a linear combination of (48) or (49). Thus, the possible constructions of EOS are endless (Knopoff, 1963).

The basic foundation of the EOS based upon atomic theories is the adoption of interatomic potential. Some interatomic potentials are clearly identified with particular solids. For example, ionic bonding potentials are appropriate for alkali-halide solids. Other interatomic potentials are appropriate for metals. It is not yet clear what interatomic potential functions are best for representing the EOS of minerals.

We shall begin by writing out the so-called Birch-Murnaghan isothermal EOS, because it is the EOS most favored in the literature of geophysics.

$$P = \frac{3}{2} K_0 \left[\left(\rho/\rho_0 \right)^{2/3} - \left(\rho/\rho_0 \right)^{1/3} \right] \left\{ 1 + \frac{3}{4} [K_0' - 4] \left[\left(\rho/\rho_0 \right)^{2/3} - 1 \right] \right\} \quad (50)$$

Note that P is proportional to K_0 , and the remaining factor is dimensionless, a form of (46). Note that there are three parameters ρ_0 , K_0 , and K_0' , which are the measured boundary conditions. They are all measurable constants. This is a third order equation, because it is derived from a strain energy polynomial expansion with three terms; see Eq. (45).

Also note that in the case $K_0' = 4$, the second term in the braces drops out. However, when $K_0' \neq 4$, we see that the second term in the braces is of the order of unity. Looking at data in Table 5, we see that often $K_0' > 4$, so that the second term in the braces should be retained. This point is emphasized, because in

O. L. Anderson

August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 24
(July 16, 1984)

the older geophysical literature, we often see the following equation referred to as the Burch-Murnaghan EOS.

$$P = \frac{3}{2} K_0 \left[\left(\rho/\rho_0 \right)^{2/3} - \left(\rho/\rho_0 \right)^{1/3} \right] \quad (51)$$

Thus, we see that Eq. (51) would not be sufficient for the lower mantle, where $K_0 = 3.19$, nor for many materials when $K_0 > 4$.

We shall proceed with a general series expansion in place of Eq. (45). Since the product $K_0 V_0$ has the dimensions of energy, the strain energy will be proportional to $K_0 V_0$ times a dimensionless polynomial series.

$$E_{st} = E - E_0 = K_0 V_0 \sum_{n=2}^{\infty} \frac{C_n}{n!} \epsilon^n \quad (52)$$

The $n = 1$ term is missing to satisfy the condition that $P(1) = 0$ (when $\epsilon = 0$). The factor n denotes a power, not a derivative. The primes shall denote derivatives, $\epsilon' = d\epsilon/dV$, $\epsilon'' = d^2\epsilon/d^2V$.

Inverting Eqs. (42), (43) and (44)

$$E' = -P \quad (53)$$

$$E'' = K/V \quad (54)$$

$$E''' = -(K/V^2)(K' + 1) \quad (55)$$

Now, operating to find E' , E'' , and E''' in terms of ϵ^n , we find E and P in terms of ϵ^n and the coefficients C_n . The boundary conditions specify that $C_1 = 0$, and $C_2 = 1$. From this we have

$$E - E_0 = \frac{1}{2} K_0 \left(\epsilon^2/\epsilon_0^2 \right) \left[1 + \frac{C_3}{3} \epsilon \right] \quad (56)$$

where

$$P = -K_0 \left(\epsilon'/\epsilon_0^2 \right) \epsilon \left[1 + \frac{C_3}{2} \epsilon \right] \quad (57)$$

$$C_3 = - \left[K_0' + 1 + 3 \frac{\epsilon_0'}{\epsilon_0^2} \right] \quad (58)$$

We now have our equation of state in terms of the strain parameters ϵ and its derivatives. We prefer to have the primary variable as V , rather than ϵ . To do

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 25
(July 16, 1984)

that, we must specify $\epsilon = \epsilon(V)$. At this point various derivations diverge. As a first case, let us take the Eulerian strain given by solving (48) for $\epsilon(\chi)$. At this point, the derivation is called the Birch-Murnaghan EOS.

$$\epsilon = 3/2 (1 - \chi^{-2/3}) = 3/2 \left[1 - \left(\frac{V_0}{V} \right)^{2/3} \right] \quad (59)$$

We run out the various derivatives of ϵ , ϵ' , etc. for (57) and find

$$\epsilon' = (1/V_0)(1 - 2/3 \epsilon)^{5/2}; \epsilon'' = -(5/3 V_0^2)(1 - 2/3 \epsilon)^4; \epsilon_0''/(\epsilon_0')^2 = -5/3; \epsilon''' = (40/9 V_0^2)(1 - 2/3 \epsilon)^{1/2}; \epsilon_0'''/(\epsilon_0')^3 = 40/9. \chi = (1 - 3/2 \epsilon)^{-3/2}.$$

Putting ϵ_0'' and $(\epsilon_0')^2$ into (29), we find C_3 .

$$C_3 = -[K_0' - 4] \quad (60)$$

thus, the energy and the pressure, in terms of ϵ , from (56) and (57) are:

$$E - E_0 = K_0 V_0 \epsilon^2/2 \left(1 - \frac{[K_0' - 4]}{3} \epsilon \right) \quad (61)$$

$$P = -K_0 (1 - 2/3 \epsilon)^{5/2} \epsilon (1 - \frac{1}{2} (K_0' - 4) \epsilon) \quad (62)$$

Eqs. (61) and (62) represent the Birch-Murnaghan EOS to the third degree. To obtain the EOS in the more common form, (50), place (48) in (62).

There is no analytical obstacle to finding formulae for C_4 , C_5 , etc. However, C_4 requires knowledge of K_0 in addition to K_0 and K_0' . K_0'' , the second derivative of K with respect to P , is not well known experimentally, so C_4 is mostly of interest in terms of convergent problems in the series expansion of $E - E_0$. However, information about K_0 is not completely lacking, and we may use C_4 to constrain an EOS at very high pressure to satisfy certain limits. The formula for C_4 is

$$C_4 = \left[(K_0' + 1) \left(K_0' + 2 + 2 \frac{\epsilon_0'''}{(\epsilon_0')^2} \right) + K_0 K_0'' \right] + 15 \left[\frac{\epsilon_0'''}{(\epsilon_0')^2} \right]^2 - 4 \left[\frac{\epsilon_0'''}{(\epsilon_0')^2} \right] \quad (63)$$

$$= (3 - K_0') (4 - K_0') + 33/9 + K_0 K_0' \quad (64)$$

26

O. L. Anderson
August 21-24, 1984

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 26
(July 16, 1984)

To fourth order in the Eulerian strain, the Birch-Murnaghan EOS is (Stacey, et al., 1981)

$$P = \frac{3}{2} K_0 \left((\rho/\rho_0)^{1/3} - (\rho/\rho_0)^{1/3} \right) \left\{ 1 + \frac{3}{4} [K_0' - 4] \left((\rho/\rho_0)^{1/3} - 1 \right) + \frac{3}{8} (K_0 K_0'' + K_0' [K_0' - 4] + \frac{35}{9}) \left((\rho/\rho_0)^{1/3} - 1 \right)^2 + \dots \right\} \quad (65)$$

$$K = K_0 (\rho/\rho_0)^{2/3} \left\{ 1 + \left(\frac{3}{2} K_0' - \frac{5}{2} \right) \left((\rho/\rho_0)^{1/3} - 1 \right) + \frac{2}{3} (K_0 K_0'' + K_0' [K_0' - 4] + \frac{35}{9}) \left((\rho/\rho_0)^{1/3} - 1 \right)^2 + \dots \right\} \quad (66)$$

$$K' = K_0' + \frac{3}{2} K_0 K_0'' \left((\rho/\rho_0)^{1/3} - 1 \right) + \dots \quad (67)$$

We see the inclusion of the dimensionless term $K_0 K_0''$ in P and K .

Now if (49) is placed in (48) to find $\epsilon(V)$, then the various derivatives ϵ_0 , ϵ_0' , etc. will be different than above. When these are placed in (57), we have the Lagrangian EOS.

Thus, to the fourth order, the Lagrangian EOS is (Stacey, et al., 1981).

$$P = \frac{3}{2} K_0 (\rho/\rho_0)^{1/3} \left\{ 1 - (\rho/\rho_0)^{-2/3} \right\} \left\{ 1 + (3/4) K_0' [1 - (\rho/\rho_0)^{-2/3}] + \frac{3}{8} (K_0 K_0'' + K_0' + K_0'^2 - \frac{1}{9}) [1 - (\rho/\rho_0)^{-2/3}]^2 + \dots \right\} \quad (68)$$

$$K = K_0 (\rho/\rho_0)^{1/3} \left\{ 1 + \frac{1}{2} (3K_0' - 1) [1 - (\rho/\rho_0)^{-2/3}] \right\} \quad (69)$$

$$+ \frac{1}{8} (9 K_0 K_0'' + 9 K_0'^2 - 1) [1 - (\rho/\rho_0)^{-2/3}]^2 + \dots \quad (70)$$

$$K' = K_0' + (3/2) K_0 K_0'' [1 - (\rho/\rho_0)^{-2/3}].$$

There are problems of convergence which will not be discussed here. For compressions such as in the Earth, convergence problems are not serious. They would probably be serious, if these equations were applied to the rocky cores of the major planets.

There are many other applications of finite strain theory, which will not be discussed here.

Now as χ approaches 1, all of these finite strain formulations yield in the limit of lower pressure

$$K = K_0 + K_0' P \quad (71)$$

O. L. Anderson

August 21-24, 1984

27

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 27
(July 16, 1984)

Therefore, at low compressions there will be little distinction between one formulation of the strain energy EOS and another. They begin to diverge from each other when P/K_0 approaches 0.3.

The integration of (71) gives the Murnaghan EOS (Murnaghan, 1937, 1944).

$$P = \frac{K_0}{K'_0} \left[\left(\frac{P}{P_0} \right)^{K'_0} - 1 \right] \quad (72)$$

which is adequate for density-pressure calculations at modest pressure along an isotherm.

Equation (72) often adequately follows the pressure density changes along an adiabat at quite high pressure. For example, Eq. (71) accounts quite well for the pressure-density data derived for the Earth's lower mantle from seismic models (Bullen, 1968; Anderson and Sumino, 1980). But, when (71) or (72) is used for the P-V relation along an adiabat, it is not a very helpful EOS, because the temperature profile can neither be injected into nor derived from the P-V calculation.

There are many equations based upon using the pair-potential of atoms in a lattice as the energy, E, in place of (45). A number of these have proved quite useful, (Morse, 1929; Zharkov, et al, 1972; Brennan and Stacey, 1979; Anderson, 1970). The reader is referred to the excellent review article on this subject by Stacey, et al., (1979). We shall use some of these EOS based on pair-potentials for calculations later described in Lecture 3.

O. L. Anderson

August 21-24, 1984

28

ICTP: "Physics of Condensed Matter"
Trieste, Italy
Lecture 1, Page 28
(July 20, 1984)

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O. L. Anderson
August 21-24, 1984
ICTP: "Physics of Condensed Matter"
Trieste, Italy
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