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Equation of State of Liquid Iron at the Earth's Core Conditions

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Abstract. The Earth's outer core is generally believed to be a mixture of iron and one or more lighter constituents. This assumption is based on shock-compression data. Here it is shown that at high pressures the current interpretation of these data is highly questionable. An equation of state, derived following selfconsistent quantum mechanics, is proposed. This equation is of general validity and can be applied to any state of matter in any thermodynamical condition. However the lack of precision in the parameters involved in this equation, when applied to iron makes still impossible a rigorous solution of the problem of the Earth's core composition.

Key words: Earth's core – Shock waves – Grüneisen's parameter – Liquid iron – Equation of state.

Introduction

The purpose of this paper is to derive and discuss an equation of state for liquid iron at conditions of the Earth's outer core, based on a self-consistent quantum-mechanical approach. The Earth's outer core is defined, from seismological data, as a region with very small rigidity and a density ranging from 9.91 to 12.14 g/cm^3 (Dziewonski et al., 1975), and calculations under the assumption of hydrostatic equilibrium give corresponding pressures ranging from 1.37 to 3.14 Mbars (Bullen, 1975). The shear wave opacity suggests immediately the presence of a liquid phase, while the pressure-density curve and considerations about the distribution of elements in meteorites give iron as the most probable component. A more detailed analysis is necessary to reach a precise conclusion about the chemical composition. The generally accepted method in solving this problem mainly consists in 3 steps:

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(i) determination of an equation of state for the Earth's core;

(ii) determination of equations of state of materials at conditions of the Earth's core;

(iii) comparison between the 2 sets of Equations (i) and (ii) in order to find an identity. The material satisfying such an identity may be present in the Earth's core.

Concerning (i), recent seismic data inversion models give reliable density-radius relations, and the assumption of hydrostatic equilibrium leads to the dependence of pressure on radius. In this way it is possible to obtain an accurate equation of state for the Earth's core. By contrast, the currently accepted solution to the problem (ii) is highly questionable. The thermodynamical conditions of the Earth's core can be reproduced only by shock-wave experiments. Unfortunately, the data obtained in this way, in spite of the large number of studies about their interpretation, are not reliable just in the pressure range we are interested in, as will shown below.

The Inversion of Shock-Wave Data

The fundamental assumption behind any reduction of shock-waves data is the validity of the Hugoniot equations

$$V_0/V_1 = D/(D-A_1) \tag{1}$$

$$P_1 = A_1 D/V_0 \tag{2}$$

$$E(P_1, V_1) = \tfrac{1}{2} P_1 (V_0 - V_1) \tag{3}$$

where V_0 is the initial specific volume, V_1 the specific volume behind the shock front, D the shock-wave velocity, A_1 the particle velocity of the material, P_1 the shock-wave pressure, and E the internal energy. These equations are valid if the shock front is thin, i.e. if immediately behind the shock front the sample is in thermodynamic equilibrium (Courant and Friedrichs, 1948). In fact shock-wave experiments for pressures larger than 3 Mbars involve so high temperatures that melting occurs in all substances and therefore this condition is surely violated for the whole pressure range (see e.g., Benedek, 1959). These basic considerations reduce the range of rigorous applicability of shock experiments to rather low pressures, comparable with those achieved by modern static anvil devices, and make very doubtful the results relative to core pressures, because it is not possible to evaluate the phenomena related to shock melting. Apart from this fundamental point, which implies a source of systematic errors practically impossible to correct, the equation of state used by the totality of the authors (Walsh et al., 1957; Altshuler et al., 1958; Takeuchi and Kanamori, 1966) is greatly questionable for many reasons. In fact, all the above authors use the classical Mie-Grüneisen equation

$$P = -dU/dV + \gamma(E_{VIB}/V) \tag{4}$$

where P is the total pressure, V is the volume, U the static lattice potential, γ the Grüneisen's parameter, and E_{VIB} the vibrational part of the internal energy.

E_{VIB} is given by

$$E_{VIB} = E - U(V) \tag{5}$$

Equation (4) is generally solved simultaneously for dU/dV, γ, and E_{VIB} under the following two assumptions:

(a) E_{VIB} is harmonic, i.e. the anharmonic terms of the free energy, which are of main importance at the high temperatures of shock experiments, are systematically disregarded;

(b) γ is assumed constant (Altshuler et al., 1958), or as a Dugdale-MacDonald function of the volume (Dugdale and MacDonald, 1953).

Regarding assumption (a), the account of anharmonic terms at the temperatures involved in shock experiments is vital (Leibfried and Ludwig, 1961). Furthermore, iron is a metal and therefore, at shock-wave temperatures, also electronic contributions become relevant (Kittel, 1963; Mulargia and Boschi, 1976). With respect to assumption (b), we must remember that the original definition of γ

$$\gamma = \gamma_i = \frac{\partial \ln v_i}{\partial \ln V} \tag{6}$$

where v_i is the normal mode of i, is valid only in the case of a harmonic solid with a flat frequency spectrum. This model is a poor approximation of a perfect solid at 0° K, and it loses any meaning with increasing temperatures. Nevertheless, Altshuler et al. (1958) use it for inverting shock data for temperatures of the order of 20,000° K. Takeuchi and Kanamori (1966) use a Dugdale-MacDonald expression for γ. It is well-known (see e.g., Irvine and Stacey, 1976) that this formulation is wrong, but we wish also to point out that a quantity defined by (6), as the Dugdale-MacDonald γ, has sense in an equation of state such as (4) only in the harmonic case, as we will show in the next section.

The Equation of State

From the above discussion it emerges that at present we still have too poor a knowledge of the mechanical properties of materials at core conditions to risk any assertion. To say something certain, we need mainly two things:

(1) a reliable theoretical equation of state;

(2) a rigorous check of the equation of state by high precision high pressure data.

The equation of state we propose is valid irrespectively of thermodynamical conditions and for any kind of matter in any kind of state. Practically it is a generalization of the Mie-Grüneisen equation. By writing the Helmoltz free energy F as

$$F = E - TS \tag{7}$$

and

$$F = U(V) + \mathrm{F}_{VIB} \tag{8}$$

where S is the entropy, T the temperature, and F_{VIB} the vibrational free energy. A differentiation of (8) gives

$$P = -(\partial F/\partial V)_T = -dU/dV - (\partial F_{VIB}/\partial V)_T \tag{9}$$

which can always be written as

$$P = -dU/dV + \varphi E_{VIB}/V \tag{10}$$

where φ, according to Equations (5) and (9), is a function of T and V defined by

$$\varphi = -V[(\partial F_{VIB}/\partial V)_T/E_{VIB}] \tag{11}$$

Equation (10) represents a form of equation of state of general validity since it has been derived without any restrictive assumption. The function φ coincides with the original definition of Grüneisen's parameter (6) and therefore with the Dugdale-MacDonald one, which in turn is based on (6), if F_{VIB} and E_{VIB} are considered in the harmonic approximation. In this case Equation (11) goes back to the classical Mie-Grüneisen equation.

In general the function φ has nothing to do with the thermodynamical Grüneisen's gamma, γ_{th}, defined by

$$\gamma_{th} = V\alpha K/C_V \tag{12}$$

where α is the thermal expansion coefficient, K the bulk-modulus C_V is the specific heat at constant V. α K stands for $(\partial S/\partial V)_T$. However it can be shown (Mulargia and Boschi, 1976) that in the harmonic approximation definitions (6), (11), and (12) coincide, while it is well-known that the harmonic approximation is valid for temperatures in the range of a few times the Debye temperature.

Evaluation of the Quantities in the Equation of State

In order to show the applicability of our equation of state, we consider in detail the problem of liquid iron at conditions of the Earth's outer core. The evaluation of the quantities in Equation (11) is performed starting from the identity

$$F_{VIB} = E_{VIB} - TS \tag{13}$$

which gives

$$\varphi = -V[(\partial E_{VIB}/\partial V)_T - T\alpha K]\, E_{VIB}^{-1} \tag{14}$$

Instead of extrapolating, with dubious rigour, values relative to solid crystals, we apply our theory to the liquid state. By liquid state we intend a lattice with a simple cubic structure in which transverse waves have a trasmission coefficient irrelevant in comparison with the longitudinal transmission coefficient. This liquid model arises from experimental diffraction data on liquid metals (see e.g., Maddin et al., 1957), which show a nearest-neighbour pattern similar to that for solids and the next-nearest neighbour pattern much more randomly located than for solids. This gives the reasons to support, for liquids,

Table 1. The harmonic Grüneisen's function γ_{th}^{H}, the anharmonic leading term coefficient A_2 and the 0° K static pressure as functions of the compression $\Delta V/V_0$

$\Delta V/V_0$	γ_{Th}^{H}	A_2 $\left(\frac{\text{erg}}{{}^{\circ}K^2}\right)$	$-\frac{dU}{dV}$ (Mbars)
0.00	1.90	1.8×10^3	0.0
0.02	1.85	1.7×10^3	0.004
0.10	1.68	1.7×10^3	0.13
0.20	1.50	1.6×10^3	0.41
0.30	1.36	1.4×10^3	1.0
0.40	1.22	1.1×10^3	2.0
0.50	1.10	1×10^3	4.3

a lower coordination number than for solids, and a very low transverse force constant in order to allow nearly free shear movements in the lattice. On this basis, we can, under hydrostatic pressure conditions, write $V\alpha K$ as (Wallace, 1972)

$$V\alpha K = 3Nk\gamma_{th}^{H} + [Vd(\Gamma - 2A_2)/dV]\,T \tag{15}$$

where k is the Boltzmann constant, N is the Avogadro number, A_2 is the anharmonic leading term of the free energy (Leibfried and Ludwig, 1961), Γ is the electronic specific heat coefficient (Kittel, 1963), and γ_{th}^{H} is the thermodynamical gamma. γ_{th}^{H}, according to definition (12), can be easily written as (Born and Huang, 1954)

$$\gamma_{th}^{H} = \left(\frac{\partial E_{VIB}^{H}}{\partial V}\right) \frac{V}{T\left(\frac{\partial E_{VIB}^{H}}{\partial T}\right)_V - E_{VIB}^{H}} \tag{16}$$

while the harmonic internal vibrational energy E_{VIB}^{H} is defined by (see e.g., Wallace, 1972)

$$E_{VIB} = E_{VIB}^{H} - (A_2 - \tfrac{1}{2}\Gamma)\,T^2 \tag{17}$$

We have now all the quantities of (11) written as functions of E_{VIB}, Γ, A_2, T, V. E_{VIB}^{H} can be evaluated without finding the explicit eigenvalues of the dynamical matrices by using a Thirring's series expansion (Thirring, 1913), namely

$$E_{VIB}^{H} = 5NkT\left\{1 - \sum_{1}^{\infty}{}_{n}(-1)^n \frac{B_{2n}}{(2n)!}\,\mu_{2n}\left(\frac{\hbar}{kT}\right)^{2n}\right\} \tag{18}$$

where $\hbar$ is the Planck constant, B_{2n} are Bernouilli numbers, and μ_{2n} are the statistical moments of the frequency distribution function of the eigenvibrations of the medium. In our case, Equation (17) is evaluated using the values of μ_{2n} computed on the basis of a Rydberg type intermolecular potential given by

$$U = -D[1 + b(r_{ij} - r_e)]\exp[-b(r_{ij} - r_e)] \tag{19}$$

Table 2. The values of φ as function of temperature and compression. The vibrational internal energy E_{VIB} is given for different temperatures at normal pressure. These values are obtained by using the Shimizu-Terao electronic term coefficient (Shimizu and Terao, 1967)

$T, {}^0K$ / $\Delta V/V_0$	2000	2500	3000	3500	4000	4500	5000	5500	6000	6500
0.00	1.81	1.83	1.78	1.75	1.74	1.73	1.72	1.71	1.70	1.69
0.02	1.76	1.74	1.71	1.70	1.68	1.67	1.66	1.65	1.64	1.62
0.10	1.60	1.57	1.54	1.52	1.51	1.50	1.50	1.49	1.48	1.47
0.20	1.43	1.41	1.37	1.36	1.35	1.34	1.33	1.32	1.31	1.31
0.30	1.30	1.28	1.25	1.24	1.22	1.21	1.20	1.19	1.18	1.17
0.40	1.16	1.14	1.12	1.10	1.08	1.06	1.04	1.03	1.02	1.01
0.50	1.06	1.04	1.02	1.00	1.00	0.99	0.96	0.97	0.96	0.95
E_{VIB} at $\Delta V/V_0=0.00$; ergs	5.03×10^{11}	6.29×10^{11}	7.57×10^{11}	8.83×10^{11}	1.02×10^{11}	1.14×10^{12}	1.27×10^{12}	1.4×10^{12}	1.53×10^{12}	1.66×10^{12}

Table 3. The same as Table 2, but using the Wood electronic term coefficient (Wood, 1962)

$T, {}^0K$ / $\Delta V/V_0$	2000	2500	3000	3500	4000	4500	5000	5500	6000	6500
0.00	1.64	1.60	1.54	1.48	1.43	1.38	1.34	1.31	1.29	1.27
0.02	1.60	1.55	1.49	1.44	1.39	1.34	1.30	1.27	1.25	1.23
0.10	1.45	1.40	1.34	1.30	1.26	1.22	1.18	1.15	1.13	1.11
0.20	1.29	1.25	1.19	1.15	1.11	1.08	1.04	1.02	1.0	0.98
0.30	1.18	1.14	1.09	1.05	1.01	0.98	0.94	0.92	0.90	0.88
0.40	1.05	1.01	0.97	0.93	0.89	0.86	0.83	0.80	0.78	0.76
0.50	0.96	0.93	0.89	0.85	0.83	0.80	0.77	0.75	0.73	0.71
E_{VIB} at $\Delta V/V_0=0.00$; ergs	5.56×10^{11}	7.12×10^{11}	8.76×10^{11}	1.05×10^{12}	1.22×10^{12}	1.41×10^{12}	1.61×10^{12}	1.8×10^{12}	2.01×10^{12}	2.22×10^{12}

where r_e is the distance of approach of the molecules, r_{ij} is the instantaneous distance, and D, b are constants. This potential leads to the best agreement in the description of the thermodynamical properties of iron (Varshni and Bloore, 1963). A_2 is computed according to Wallace (1965) while Γ is taken from extrapolated experimental values (Shimizu and Terao, 1967; Wood, 1962). Γ is assumed constant in T because we are far from the Fermi temperature, and in V because extremely high pressure computations (Henry, 1962) show a very low pressure gradient. The quantities of Equation (11) are computed for the density range up to $V/V_0=2.0$ and for temperatures up to 6,500° K. The results are shown in Tables 1, 2, 3.

Discussion

As it appears from the tables the uncertainty in Γ alone is capable of a noticeable shift in the results. Furthermore, also A_2 and mainly the intermolecular potential parameters are not completely sure because the Varshni-Bloore potential was derived from shock compression data of Walsh et al. (1957), data which can be criticized as already pointed out above.

In conclusion the problem of the composition of the Earth's core is still open. We have pointed out that current theories based on shock-wave inversion are misleading. We derived a general equation of state and checked its parameters with the most reliable data available for iron. Unfortunately the precision of these experimental quantities is up to now insufficient to give an answer to our problem. However we think that the development of static high precision high pressure equipment will make possible the solution of this question in the next future.

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