A note on the thermal component of the equation of state of solids

(Letter to the Editor)

Vladan Celebonovic
Institute of Physics, Pregrevica 118, 11080 Zemun-Beograd, Yugoslavia

(received: 15 November, 1990)

reference: Earth, Moon and Planets, 54, pp. 145-149 (1991).

Abstract: A simple method for determining the thermal component of the EOS of solids under high pressure is proposed. Applications to the interior of the Earth gives results in agreement with recent geophysical data.

1. Introduction

Imagine a specimen of any chemical substance. In the case of a thermo-mechanical system, its equation of state (EOS) will have the general form $f(p, V, T) = 0$, where $p, V, T$ denote, respectively the pressure to which the system is subjected, its volume and temperature.

Proposing a realistic EOS for a given class of physical systems is, generally speaking a highly non-trivial problem (see, for instance, Eliezer et al., 1986; Schatzman and Praderie, 1990 for details). One usually starts from an assumed interparticle potential, determines the form of the Hamiltonian, and from it the thermodynamical functions and the EOS. In order to render the calculations more tractable, the EOS is usually determined in form of isoterms in the $p − V$ plane. The thermal component is often introduced at a later stage (for example, Holian, 1986; Eliezer et al., 1986).
In laboratory studies, EOS of various systems can be determined experimentally (examples of recent reviews concerning the subject are Jayaraman, 1986; Jeanloz, 1989; Drickamer, 1990). The situation is much more complicated in astrophysics, because planetary and stellar structure is inaccessible to direct experiments. What is observable, however, are the consequences on the surfaces and in the vicinity of these objects of the processes occurring in their interiors. Progress in the understanding of the Earth’s interior has, for example, been provoked by a combination of observation in geophysics and seismology, with laboratory studies of the relevant materials performed under high pressure and high temperature (Jeanloz, 1990a).

The purpose of this letter is to propose a simple method for the determination of the thermal component of the EOS of solids subdued to high pressure. Details of the calculations, and application to the interior of the Earth are presented in the following section, while the third part contains a discussion of various factors influencing our results, as well as the possibilities of their improvement. Physically, our calculations are based on combination known results of solid-state physics with a particular semiclassical theory of dense matter proposed by Savic and Kasanin (1962/65; for a recent application, see Celebonovic, 1990b, and references given there). Compared with recent work on the subject (such as Renero et al., 1990; Kumari and Dass, 1990a, b), the approach proposed in this letter has the advantage of physical and mathematical simplicity, but a disadvantage of being applicable only to solids.

2. Calculations

One of the general characteristics of solid bodies is that the atoms (or ions) in them, perform small vibrations about their equilibrium positions. Let \( N \) be the number of molecules in the body, and denote by \( \nu \) the number of atoms per molecule. The total number of atoms in the system is \( N \nu \) and the number of vibrational degrees of freedom is \( 3N\nu \) (speaking exactly, it is \( 3N\nu - 6 \), but \( 3N\nu \gg 6 \)).
A system of $3N\nu$ mutually independent vibrational degrees of freedom is equivalent to an ensemble of independent oscillators. The free energy of such an ensemble can be expressed as

$$ F = N\epsilon_0 + k_B T \sum_\alpha \ln(1 - \exp(-\beta \hbar \omega_\alpha)) \tag{1} $$

where the first term on the right side represents the interaction energy of all the atoms in the system in the equilibrium state, and the summation is carried over all the normal vibrations, indexed by $\alpha$.

At low temperatures, only low frequency terms (i.e., sound waves) with $k_B T \approx \hbar \omega_\alpha$ have an important contribution to eq. (1). It can be shown (for example Landau and Lifchitz, 1959) that the number of vibrations $dN$ per interval of frequency $d\omega$ is

$$ \frac{dN}{d\omega} = \frac{3V\omega^2}{2\pi^2\bar{u}^3} \tag{2} $$

The volume of the system is denoted by $V$, and $\bar{u}$ is the mean velocity of sound. Changing from summation to integration in eq. (1), one finally obtains

$$ F = N\epsilon_0 + \frac{3k_B TV}{2\pi^2\bar{u}^3} \int_0^\infty \ln(1 - \exp(-\hbar \omega_\alpha/k_B T)) d\omega \tag{3} $$

If we apply the standard thermodynamic identity $E = F - T \frac{\partial F}{\partial T}$ it follows from eq. (3) that the energy of the system is

$$ E = N\epsilon_0 + V\pi^2 (k_B T)^4/10(\hbar \bar{u}^3) \tag{4} $$

The mean velocity of sound can be approximated by the Bohm-Staver formula

$$ \bar{u}^2 = (1/3) \left( Zm/Mv_F^2 \right) \tag{5} $$

(Bohm and Staver, 1951; Ashcroft and Mermin, 1976), where $m$ and $M$ denote, respectively, the masses of electrons and ions in the solid, $v_F$ is the Fermi velocity and $Z$ is the charge of ions.
A detailed discussion of the basic ideas of the theory of Savic and Kasanin (the SK theory for short) has recently been published (Celebonovic, 1989d). Within the framework of this theory, the energy per unit volume of a solid is given by

\[ E = 2e^2 Z (N_A \rho / A)^{4/3} \]  

where \( A \) is the mass number and \( N_A \) denotes Avogadro’s constant.

Using equations (4)-(6), after some algebra one obtains the following expression for the temperature of a solid as a function of its density \( \rho \)

\[ T = 1.4217 \times 10^5 (\rho / A)^{7/12} (m/M)^{3/8} Z^{7/8} \]  

The thermal component of the EOS of a solid can be obtained by multiplying this result by the density (expressed in suitable units).

As an astrophysical test, eq. (7) was applied to the model of the Earth discussed previously within the SK theory (Savic, 1981 and earlier work). The following results were obtained

| TABLE I         |         |         |         |         |
|-----------------|---------|---------|---------|---------|
| Depth (km)      | 0-39    | 39-2900 | 2900-4980 | 4980-6371 |
| \( \rho_{\text{max}} \) (g cm\(^{-3}\)) | 3.0     | 6.0     | 12.0     | 19.74    |
| \( Z \)         | 2       | 3       | 3        | 4        |
| \( T_{\text{max}} \) (K) | 1300    | 2700    | 4100     | 7000     |

where the values of the temperatures have been rounded to the nearest \( \pm 100K \).
3. Discussion

The distribution of temperature with depth within the Earth, or any other celestial body, is not directly measurable. In order to draw conclusions about the thermodynamics of our planet’s interior, geophysicists are bound to combine examination of rock samples from the outer ~ 200 km of the Earth, with high pressure-high temperature experiments (Jeanloz, 1990a,b). It has thus been shown that, for example, \( T = (4500 \pm 500) K \) at the base of the mantle, and that \( T = (6900 \pm 1000) K \) in the center (Jeanloz, 1990a).

These experiments were performed on materials known to exist in a thin layer beneath the Earth’s surface, and assumed to represent its composition in bulk. One could conjecture that, such an assumption not being directly verifiable by experiments, it has strong influence on the results. Some influence it certainly has, but it can not be extremely important. Namely, it is possible within the SK theory, to determine the bulk chemical composition of an astronomical object (i.e., the mean value of the mass number of the mixture of materials that it is made of); the only input data needed for such a calculation are the mass and radius of the object. It turns out that the value of \( A \) obtained in this way corresponds closely to the value of \( A \) for the materials used in experiments.

The calculations discussed in this letter are strongly influenced by a combination of several factors from the domain of solid state physics.

The upper limit of integration in eq. (3) is infinite, which simplifies mathematics, but renders physics unrealistic - there are no infinite frequencies. The difficulty could be, at first sight, circumvented by introducing a suitable cut-off frequency, in the spirit of Debye’s model. However, one would then encounter the following obstacle, which would be the density dependence of the cut-off frequency (and the corresponding cut-off temperature). Solving this problem demands a knowledge of the elastic constants and inter-particle potentials of the material (a solution for some types of crystal lattices within Debye’s model is given in de Launay, 1953, 1954).
It is clear that attempting to perform such a calculation for the case of the interior of the Earth would quickly render the results questionable, due to the accumulation of various approximations. Another “solid-state” factor influencing our results is the method of calculation of the speed of sound. The use of the Bohm-Staver formula amounts to taking into account only the main term in the calculation of the band-structure energy of a solid (see Harrison, 1989 for details), which is, in turn, used in determining the value of the velocity of sound. The formula is known to give qualitatively correct results when applied to materials under standard conditions, but its applicability can be expected to increase for materials subjected to high pressure.

Finally, a few words about one more “influential” factor. It could be questioned whether it is correct to compare equations which do not contain parameters of the same physical nature: equation (4) contains the temperature, while eq. (6) does not. It is true that the SK theory has been developed for the case \( T=0 \, \text{K} \). However, this should be understood just as a simplifying assumption, whose physical meaning is that this theory is applicable to materials at small temperatures and subjected to high pressure, for which \( \epsilon_F/k_B T \gg 1 \) (see Eliezer et al., 1986 for details).

4. Conclusions

In this letter we have discussed a simple method for determining the thermal component of the EOS of solids under high pressure, thus correcting a small error made in a similar discussion (Cebonovic, 1982). Application to the interior of the Earth gives results in good agreement with geophysical data. Possible influence of several factors on the values obtained has been described in some detail. Using this method in laboratory high pressure work would necessitate an improvement in the calculation of the velocity of sound, and the introduction of a suitable density-dependent cut-off frequency in equation (3).
References

Ashcroft,N.W.,and Mermin,D.N.: 1976,Solid State Physics,Holt,Rinehart and Winston,London.

Bohm,D. and Staver,T.:1951,Phys.Rev.,84,836.

Celebonovic,V.:1982,in W.Fricke and G.Teleki (eds.),Sun and Planetary System,D.Reidel Publ.Comp., Dordrecht,Holland.

Celebonovic,V.:1989d,Earth,Moon and Planets,45,291.

Celebonovic,V.:1990b,High Pressure Research,5,693.

de Launay,J.:1953,J.Chem.Phys.,21,1975.

de Launay,J.:1954,J.Chem.Phys.,22,1676.

Drickamer,H.G.:1990,Ann.Rev.Mater.Sci.,20,1.

Eliezer,S.,Ghatak,A.and Hora,H.:1986,An Introduction to Equations of State:Theory and Applications,Cambridge University Press,Cambridge,UK.

Harrison,W.A.:1989,Electronic Structure and the Properties of Solids,Dover Publications Inc.,New York.

Holian,K.S.: 1986,J.Appl.Phys.,59,149.

Jayaraman,A.:1986,Rev.Sci.Instr.,57,1013.

Jeanloz,R.:1989,Ann.Rev.Phys.Chem.,40,237.

Jeanloz,R.:1990a,Ann.Rev.Earth Planet.Sci.,18,357.

Jeanloz,R.:1990b,preprint,to appear in Gibbs symposium Proceedings.

Kumari,M.and Dass,N.:1990a,J.Phys.:Condens.Matt.,2,3219.

Kumari,M.and Dass,N.:1990b,ibid,7891.

Landau,L.and Lifchitz,E.:1959,Statistical Physics, Pergamon Press,Oxford.

Renero,C.,Prieto,F.E.and de Icaza,M.:1990,J.Phys.: Condens.Matt., 2,295.

Savic,P.and Kasanin,R.:1962/65,The Behaviour of Materials Under High Pressure I-IV,Ed.SANU,Beograd.

Savic,P.:1981,Adv.Space Res.,1,131.

Schatzman,E.and Praderie,F.:1990,Astrophysique:Les Etoiles, InterEditions/Editions du CNRS,Paris.