Introduction

In geophysics and high-pressure research, experimental or theoretical data consisting of pressure, temperature, and volume triplets $PVT$ are parameterized to a functional form for ease of interpolation and extrapolation. These equations of state are then used to compute phase diagrams, or are used in geodynamic or shock compression modeling, etc. A recent book by Anderson (1995) comprehensively reviews equation-of-state formulations, and comprehensive reviews and comparisons of equations of state are given by Hama and Suito (1996), Stacey et al. (1981), and Duffy and Wang (1998). The primary purpose of this paper is to discuss the reasons for the accuracy of the most-used formulation, based on the Birch equation of state (Birch 1978) and compare with the Vinet equation of state (Vinet et al. 1987). Jeanloz (1988) has previously shown that the Birch equation of state and the Vinet equation of state can be similar up to moderate compressions. Here we show that this breaks down at high compressions, and for highly compressible materials the Vinet equation of state is considerably more accurate. A logarithmic equation of state (Poirer and Tarantola 1998) and another exponential equation of state (Holzapfel 1996) are discussed and compared with the Vinet and Birch equations. Finally, we show how subtle transitions can be detected by deviations from an equation of state.

The above equations of state are appropriate for isothermal data. To include thermal expansivity there are three main approaches that have been used. The first is to fit isotherms, and then tabulate or fit the parameters $V_0$, $K_T$, and $K_T'$ as functions of temperature. Since experimental data are not always collected along isotherms, that method is most amenable to analysis of theoretical results. Second, one can assume Debye and Mie-Gruneisen theory, and fit parameters for $\theta_D$, $\gamma$, and $q$ to include thermal effects. Third, one can directly model the thermal pressure. See Anderson (1995), Hama and Suito (1996), and Duffy and Wang (1998) for further discussion of thermal equations of state.

To test equation-of-state formulations, it is important to study large compressions, because most common equations of state will work reasonably over small compression ranges. Thus we choose to study the very compressible materials, hydrogen and neon. We also consider tantalum and platinum, which are useful pressure standards.

Abstract

The accuracy of equation-of-state formulations is compared for theoretical total energies or experimental pressure-volume measurements for $H_2$, Ne, Pt, and Ta. This spans the entire range of compression found for minerals and volatiles in the Earth. The Vinet equation is found to be most accurate. The origin of the behavior of different equation-of-state formulations is discussed. It is shown that subtle phase transitions can be detected by examining the residuals from an equation-of-state fit. A change in the electronic structure of Ta is found at high pressures using this procedure, and a possible new transition in $H_2$. 

Isothermal or Static Equations of State

The Birch equation of state (Birch 1978) is based on a series expansion of pressure

$$P(f) = 3K_0f(1+2f)^{-1/2} \left[ 1 + \frac{3}{2} \left( K'_0 - 4 \right) f + \ldots \right]$$

in terms of the Eulerian strain $f$, where

$$f = \frac{1}{2} \left[ \left( \frac{V}{V_0} \right)^2 - 1 \right].$$

and $V_0$, $K_{T0}$, and $K'_{T0}$ are the zero pressure volume, isothermal bulk modulus, and isothermal bulk modulus pressure derivative. Truncated as written it is called the “third-order” Birch equation. The fourth-order Birch equation, which includes another term in $f^2$ and $K'_{T0}$ is useful for theoretical equations of state, but when applied to experimental data, the added parameter usually induces severe correlations in parameters so that they lose physical significance. The Vinet equation (Vinet et al. 1987) is derived from a scaled approximate form for the energy:

$$E(r) = -\Delta E(1+a^*)\exp[-a^*]; a^* = \frac{r - r_0}{l}$$

where $\Delta E$ is the binding energy, and $r$ is the length per electron. This gives:

$$P(x) = 3K_{T0}(1-x)x^{-2} \exp \left[ \frac{3}{2} \left( K_{T0} - 1 \right) (1-x) \right]$$