

## Theoretical High-Pressure Equations of State including Correlation Energy\*

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The correlation energy of the electron gas is treated as a perturbation on the total free energy computed for the zero-temperature Thomas-Fermi-Dirac (TFD) model of a solid. The contribution to the free energy is computed on the basis of two extreme assumptions: (i) The correlation energy is considered to be a local function of position inside the Wigner-Seitz sphere; and (ii) correlation forces are sufficiently long range so that the correlation part of the free energy is determined only by the average electron density. It is argued that (ii) is the more valid approach in the region of normal metallic densities. In terms of the parameter  $sa_0$ , the radius of a sphere occupied by a single electron, an interpolation formula is developed for the correlation energy in the intermediate region between  $s \ll 1$  (degenerate electron gas) and  $s \sim 60$  (electron lattice-fluid phase transition). At extremely high densities, a series expansion in  $s$  is used to obtain an analytic expression for the electron pressure up to terms of order  $s^3$ . For these high densities, prescriptions (i) and (ii) are equivalent. At lower densities, numerical results are presented for an assortment of elements for the TFD model, and TFD with correlations based on (i) and (ii). These are compared with shock-wave and seismic data, and the average correlation contribution computed from (ii) is found to be in better agreement than the other two procedures. A semiempirical formula is presented, which fits the numerical data to better than 0.5% for all pressures and atomic numbers, and reduces to the correct expression in the high-density limit. From this semiempirical formula, pressure-density curves are obtained for a variety of elements and minerals which have been considered as likely constituents of the core and mantle of the earth. A table of effective atomic numbers, to be used in the semiempirical formula, is given for the minerals.

### I. INTRODUCTION

NUMEROUS authors<sup>1</sup> have used the Thomas-Fermi model of a solid to derive the equation of state for degenerate matter at extremely high pressures and densities. Since this model takes into account only first-order Coulomb interactions between the electrons and the nuclei, and neglects exchange and higher-order correlation effects, it does not yield a minimum value in the free energy of the solid as a function of the lattice constant. Hence it cannot account for the binding of a solid at zero pressure. Dirac,<sup>2</sup> and Slater and Krutter<sup>3</sup> have prescribed a method for including exchange forces in the Thomas-Fermi model, and the resulting Thomas-Fermi-Dirac (TFD) equation has been solved numerically by Feynman, Metropolis, and Teller.<sup>4</sup> Although these solutions display a minimum in the free energy curve, the resultant zero-pressure densities are smaller than the empirical ones by a factor of three for the

heavy elements,<sup>5</sup> where one expects this description of the condensation process to be most valid. It has long been conjectured that if one includes in the total free energy the "correlation energy" due to long-range interactions between electrons in the Fermi sea, the resulting theoretical equation of state will be in much better agreement with experimental data.

In order to make such a calculation, one needs a theory of correlation interactions at degenerate-electron-gas densities, and a prescription for interpolating the correlation energy from the high-density regime to connect with the expression first derived by Wigner<sup>6,7</sup> for the low-density electron gas (the electron lattice). The correlation energy for an extremely high-density electron gas was evaluated by Brueckner and Gell-Mann,<sup>8,9</sup> and, using an especially simple interpolation formula, Lewis<sup>10</sup> has written an equation of the TFD-type which includes both the exchange and correlation energy contributions. The resultant equation of state includes the first two terms of the equation derived from the TFD model,<sup>3,4</sup> and an additional negative

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<sup>1</sup> An excellent survey of this work is contained in N. H. March, *Advan. Phys.* **6**, 1 (1957).

<sup>2</sup> P. A. M. Dirac, *Proc. Cambridge Phil. Soc.* **26**, 376 (1930).

<sup>3</sup> J. C. Slater and H. M. Krutter, *Phys. Rev.* **47**, 559 (1935).

<sup>4</sup> R. P. Feynman, N. Metropolis, and E. Teller, *Phys. Rev.* **75**, 1561 (1949).

<sup>5</sup> W. M. Elsasser, *Science* **113**, 105 (1951).

<sup>6</sup> E. Wigner, *Phys. Rev.* **46**, 1002 (1934).

<sup>7</sup> E. Wigner, *Trans. Faraday Soc. (London)* **34**, 678 (1938).

<sup>8</sup> M. Gell-Mann and K. Brueckner, *Phys. Rev.* **106**, 364 (1957).

<sup>9</sup> M. Gell-Mann, *Phys. Rev.* **106**, 369 (1957).

<sup>10</sup> H. Lewis, *Phys. Rev.* **111**, 1554 (1958).

term which is a function only of the Fermi momentum,  $p_F(R)$ , at the edge of the atom. Unfortunately, this elegant and simple theory does not surmount the difficulties normally associated with the TFD description of matter; the differential equation which must be solved to obtain  $p_F(r)$  is nonlinear, and a series expansion is good only near the atomic nucleus. Numerical integration must be employed to continue the integration out to the edge of the atom.

In this paper, we take a somewhat different approach to the problem. Ultimately, we wish to write an equation of state which can conveniently (if not trivially) be used in numerical integrations of zero temperature stellar and planetary models. Such an equation, including the correlation energy, has been derived for the extreme high density regime by Salpeter,<sup>11</sup> and has been applied by Hamada and Salpeter<sup>12</sup> in zero temperature stellar model integrations to determine the corrections to the Chandrasekhar limiting mass.<sup>13,14</sup> In Ref. 12, the problem of the maximum radius for a cold object was also discussed, but because of the breakdown of the high-density equation of state near the relevant densities, no very reliable conclusions could be drawn.

The purpose of this paper is to present a semiempirical equation of state which reduces in the limit to the analytic expressions which can be derived for the high-density electron gas, and fits the numerical solutions of the TFD equation with correlation corrections to better than 1% at low densities. We find it most convenient to carry out this program by treating the correlation energy as a small perturbation on the TFD solutions.

In Sec. II, we begin by reviewing the TFD model. Two procedures are defined for including the correlation energy as a perturbation in this model. In the first of these, we imagine the correlation energy to be due to "local" forces which are of short range compared to the size of the atom, while the second procedure treats these forces as long range, and correlation energy is then determined by a single parameter, the mean density of electrons in the atom.

In Sec. III we discuss the correlation energy in the low-density regime (the electron fluid) and we write an interpolation formula to connect this regime with the high density one. We also discuss the relative merits of including the correlation energy as a local or an average contribution, and, although it is clear that the correct prescription involves some compromise between these extreme assumptions, we conclude that the average correlation energy should yield more accurate results in the case of normal metallic densities.

In Sec. IV we examine the high-density limit, and we

obtain an analytic equation of state from a series solution of the TFD equation.

In Sec. V, we summarize the results obtained from numerical solutions of the TFD equation, including both the local and the average correlation corrections. We present a semiempirical equation of state which agrees with the numerical data for the average correlation corrections to better than 0.5% for a large range of pressures and atomic numbers. This semiempirical formula is then used to compute the equation of state of an assortment of elements and compounds, and the results are compared with experimental data obtained from shock-wave measurements, and seismic soundings from the core and mantle of the earth. For convenience in geophysical calculations, we also present a table of effective atomic numbers (as a function of pressure) for a group of suggested core and mantle minerals.

## II. THE GENERALIZED THOMAS-FERMI-DIRAC METHOD

### (a) The Free Electron Gas

Consider first the hypothetical case of an electron gas at zero temperature with  $n$  particles per  $\text{cm}^3$  in a neutralizing background of continuous and uniform positive charge. Instead of  $n$ , we shall use a dimensionless density parameter,  $s$

$$n^{-1} = (4\pi/3)(sa_0)^3, \quad a_0 = (\hbar^2/mc^2) = 5.29 \times 10^{-9} \text{ cm}. \quad (1)$$

The average energy per electron,  $\bar{E}_k(s)$  can be written as the sum of three terms,

$$\bar{E}_k(s) = \bar{E}_f(s) + \bar{E}_x(s) + \bar{E}_c(s), \quad (2)$$

where

$$\bar{E}_f(s) = \frac{3}{5} \frac{p_f^2}{2m} = \frac{2.21}{s^2} \text{ Ry}, \quad p_f = \left(\frac{9\pi}{4}\right)^{1/3} \frac{\hbar}{sa_0}, \quad (3)$$

$$\text{Ry} = m_e^4 / 2\hbar^2.$$

$\bar{E}_f(s)$  is the average zero-point kinetic energy, while  $p_f$  and  $E_f \equiv (5/3)\bar{E}_f$  are the Fermi momentum and Fermi energy, respectively.  $\bar{E}_x$  is the well-known expression for the "exchange energy" obtained from the first-order Coulomb matrix elements for electron-electron interactions in the Fermi sea<sup>15</sup>

$$\bar{E}_x(s) = -\frac{3}{4} \left(\frac{9}{4\pi^2}\right)^{1/3} \frac{e^2}{sa_0} = -\frac{0.916}{s} \text{ Ry} \quad (4)$$

while all higher order terms are lumped into the "correlation energy" part,  $\bar{E}_c(s)$ . An explicit analytical approximation for  $\bar{E}_c(s)$  is presented in Sec. III. The total energy,  $E_k(s)$ , of an electron at the top of the Fermi sea is given by the energy increment due to the addition

<sup>11</sup> E. E. Salpeter, *Astrophys. J.* **134**, 669 (1961).  
<sup>12</sup> T. Hamada and E. E. Salpeter, *Astrophys. J.* **134**, 683 (1961).  
<sup>13</sup> S. Chandrasekhar, *Monthly Notices Roy. Astron. Soc.* **95**, 207 (1935).  
<sup>14</sup> S. Chandrasekhar, *Introduction to the Study of Stellar Structure* (Dover Publications, Inc., New York, 1957).

<sup>15</sup> See, for example, K. A. Brueckner, in *The Many Body Problem*, edited by C. De Witt and P. Nozières (John Wiley & Sons, Inc., New York, 1959).

of a single electron to the sea<sup>2</sup>:

$$E_k(s) = \left(1 + n \frac{\partial}{\partial n}\right) \bar{E}_k(s) = \left(1 - \frac{s}{3} \frac{\partial}{\partial s}\right) \bar{E}_k(s) \quad (5)$$

and the electron pressure,  $P(s)$  is given by

$$P(s) = n^2 \frac{\partial \bar{E}_k}{\partial n} = -\frac{ns}{3} \frac{\partial \bar{E}_k(s)}{\partial s}. \quad (6)$$

### (b) The Differential Equation

We now return to the actual problem of a solid at zero temperature, with mass density  $\rho$ , nuclei of atomic mass  $A$  (in physical atomic mass units), and atomic charge  $Z$ . Let  $n$  be the average number density of electrons and  $r_e$  a dimensionless density parameter defined analogously to  $s$  above:

$$\bar{n}^{-1} = (4\pi/3)(r_e a_0)^3 \quad (7a)$$

so that

$$\rho = (A/Zr_e^3) \times 2.679 (\text{g/cm}^3). \quad (7b)$$

If the electronic charge,  $e$ , were zero, the electron density would be uniform,  $\bar{E}_e$  and  $\bar{E}_k$  in Eq. (2) would be zero, and Eq. (6) would give for the pressure,

$$P_0(r_e) = 51.6 r_e^{-5} \text{ Mbar} \quad (8)$$

where  $1 \text{ Mbar} = 10^{12} \text{ dyn/cm} = 1.053 \times 10^6 \text{ atm}$ . Equation (8) is just the Chandrasekhar equation of state<sup>14</sup> for a nonrelativistic, zero-temperature Fermi gas, written in terms of a different variable than is customary.

At pressures of about 1-10 Mbar and larger, the stable lattice phase of a simple solid is usually a close packed structure with one nucleus at the center of a lattice cell in the form of a regular polyhedron. It is then a reasonably good approximation to replace the lattice cell by a "Wigner-Seitz sphere" of radius

$$R_0 a_0 \equiv Z^{1/3} r_e a_0. \quad (9)$$

We shall also neglect the zero-point motion of the nuclei. In this approximation, the electrostatic potential,  $V(r)$ , is spherically symmetric and (since the sphere contains  $Z$  electrons in addition to the nucleus) is taken to be zero on the surface of the sphere, as is the electric field (which follows more generally from symmetry arguments). In the spirit of the Thomas-Fermi method, we pretend that  $Z \gg 1$  and that we can speak of a local number density,  $n(r)$  [and corresponding density parameter,  $s(r)$ ] with  $V(r)$  satisfying Poisson's equation:

$$(1/r^2)(d/dr)(r^2(dV/dr)) = 4\pi en(r) = (3e/s^3(r)a_0^3) \quad (10)$$

and boundary conditions

$$\lim_{r \rightarrow 0} erV(r) = -Ze^2, \quad (11)$$

$$V = (dV/dr) = 0 \quad \text{at} \quad r = R_0 a_0,$$

For the moment, let us assume further that  $s(r)$  varies slowly enough so that the electron energy,  $\bar{E}_k$ , can also be considered as localized and, in the neighborhood of point  $r$ , can be replaced by  $\bar{E}_k(s(r))$  according to Eq. (2). The requirement of a constant thermodynamic potential throughout the Wigner-Seitz sphere then leads to

$$eV(r) + E_k(s(r)) = E, \quad (12)$$

where  $E_k$  is the explicit function of  $s$  defined by Eq. (5). Equations (10) and (12) can be combined to give a single differential equation for  $s(r)$  with  $E$  as an eigenvalue. For given values of  $Z$  and radius,  $R_0 a_0$ , the solution of this equation gives  $E$ ,  $s(r)$ ,  $V(r)$  and also

$$s_0 \equiv s(R_0 a_0), \quad \lambda \equiv (r_e/s_0) \quad (13)$$

which we shall need for determining the pressure.

In the unmodified Thomas-Fermi-Dirac procedure one simply omits the correlation energy,  $\bar{E}_e$  from the expression for  $\bar{E}_k$  and Eq. (12) can then be written as

$$\left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{s} = \left\{ \frac{1}{\pi^2} + \frac{2ma_0^2}{\hbar^2} [E - eV(r)] \right\}^{1/2}. \quad (14)$$

Changing variables to

$$x \equiv \left(\frac{128}{9\pi^2}\right)^{1/3} Z^{1/3} \frac{r}{a_0}, \quad x_0 \equiv \frac{R_0 a_0}{r} x$$

$$\psi \equiv \frac{r}{2a_0 Z} \left\{ \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{s} - \frac{1}{\pi} \right\}^2 \quad (15)$$

one can rewrite Eq. (10) as<sup>3</sup>

$$\frac{d^2\psi}{dx^2} = x \left\{ \epsilon + \left[ \frac{\psi(x)}{x} \right]^{1/2} \right\}^3, \quad \epsilon \equiv \left( \frac{3}{32\pi^2 Z^2} \right)^{1/3} \quad (16)$$

with the boundary conditions

$$\psi(0) = 1, \quad (d\psi/dx)_{x_0} = (\psi(x_0)/x_0) \quad (17)$$

and with  $(d\psi/dx)$  at  $x=0$  as an eigenvalue. For given values of  $\epsilon$  and  $x_0$ , numerical integration gives  $\psi(x)$  and hence  $E$ ,  $s(r)$ ,  $s_0$ , and  $\lambda$ .

Since the electric field vanishes at the boundary of the Wigner-Seitz sphere, and since we are assuming the electron energy is a local quantity, the pressure in the solid equals that of a free electron gas at the density of the sphere boundary. The pressure is then given by Eq. (6) with  $s_0$  substituted for  $s$ .<sup>4</sup> Thus, using Eqs. (3) and (4), the TFD pressure formula is

$$\frac{P}{P_0} = \lambda^5 \left\{ 1 - \frac{5}{4\pi} \left(\frac{4}{9\pi}\right)^{1/3} s_0 \right\}, \quad (18)$$

where  $P_0$  is the Chandrasekhar expression given in Eq. (8) and  $\lambda^3$  is the ratio of the TFD density at the sphere boundary to the mean-electron density. Numer-

ical solutions of Eq. (16) and tables of the corresponding pressures have been given by Feynman, Metropolis, and Teller.<sup>4</sup> Provided  $\epsilon$  is not zero, there is always some finite value of  $x_0$  for which  $\psi(x_0)=0$ . Equation (18) gives a negative pressure for this value of  $x_0$  when we use the corresponding value of  $s_0$  determined from Eq. (15). At a somewhat lower value of  $x_0$ , the pressure goes to zero, and the TFD model always leads to this condensation at a nonzero density.

For a solid consisting of a pure element,  $r_e$  and  $R_0$  are given directly in terms of the mass density,  $\rho$ , by Eqs. (7) and (9). Equation (18) can be inverted to give the function  $R_0(P, Z)$ . For a solid consisting of a compound or alloy, the Thomas-Fermi philosophy ascribes a separate Wigner-Seitz sphere to each nucleus with the constraint that the pressure at the surface of each of the constituent spheres be the same. Knowing  $R_0(P, Z)$ , and the number of nuclei of each species, one simply adds the volumes of the separate spheres to obtain the average density of the compound as a function of  $P$ .

### (c) Correlation Corrections

In Sec. V, we present numerical results obtained from three alternative prescriptions. One is the unmodified TFD procedure, described above, where the correlation energy,  $\bar{E}_c$  is simply omitted from Eq. (2) wherever  $\bar{E}_k$  occurs.

In the second procedure for computing the pressure, we include the correlation energy,  $\bar{E}_c(s)$ , and consider this as a localized quantity. Here, in contrast to the TFD method,  $\bar{E}_c(s)$  is a transcendental function of  $s$ , and Eq. (12) cannot be inverted analytically to give  $s(V(r), E)$ . This means that Eq. (10) must be written explicitly in terms of the parameter  $s$ , rather than the variable  $\psi$  which is linear in  $V(r)$ . Lewis<sup>10</sup> has followed this procedure, and obtained an equation involving transcendental terms in the independent variable. Instead of attempting to numerically integrate such an equation, we shall make a further approximation, as follows. For  $Z \gg 1$  one can show that  $\bar{E}_c \ll \bar{E}_f + \bar{E}_x$  everywhere except possibly very close to the boundary,  $x_0$ . (For  $r_e \ll 1$ , this is true regardless of the magnitude of  $Z$ .) We then treat the change in the energy eigenvalue due to the inclusion of  $\bar{E}_c$ ,  $\Delta E \equiv E' - E$ , as a small perturbation. We denote by  $s'$  the parameter analogous to  $s$  which we would obtain by actually inverting the transcendental equation

$$eV(r) + E_f(s') + E_x(s') + E_c(s') = E' = E + \Delta E \quad (19)$$

and we now write

$$E_c(s') \simeq E_c(s), \quad (20)$$

where we take  $s$  as the TFD value given in Eq. (15).

We then find

$$\frac{1}{s'} \simeq \frac{1}{s} \left\{ 1 + \left[ 1 - \frac{1}{\pi} \left( \frac{4}{9\pi} \right)^{1/3} s \right] \times \left[ \frac{\pi^2 m a_0^2 \delta}{\hbar^2 + 2\pi^2 m a_0^2 (E - eV(r))} \right] \right\}, \quad (21)$$

where

$$\delta \equiv \Delta E - \bar{E}_c(s).$$

The new density distribution,  $n'(r)$ , thus induced inside the Wigner-Seitz sphere,

$$n'(r) = \frac{3}{4\pi} \frac{1}{a_0^3 s'^3} \quad (22a)$$

must satisfy the consistency requirement

$$\int_0^{R_0 a_0} r^2 n'(r) dr = \int_0^{R_0 a_0} r^2 n(r) dr \quad (22b)$$

to insure that we still have  $Z$  electrons contained in the sphere. Equations (21) and (22) lead to

$$\Delta E = \frac{\int_0^{x_0} f(x) E_c(x) dx}{\int_0^{x_0} f(x) dx} \quad (23)$$

with

$$f(x) = \frac{1}{\psi(x) \left[ \frac{r_e x}{s(x)} \right]^3} \left[ 1 - \frac{\epsilon}{\epsilon + (\psi/x)^{1/2}} \right],$$

where  $s(x)$  and  $\psi(x)$  are taken from the TFD solution. One could continue to iterate with this procedure, but we have stopped after a single iteration in our numerical calculations. We then insert our new eigenvalue,  $E' = E + \Delta E$ , into Eq. (19), with  $V(r) = 0$  at the Wigner-Seitz boundary, and solve the resulting transcendental equation numerically for the new parameters  $\lambda'$  and  $s_0'$ . The pressure of the free electron gas at the boundary is now given by

$$\frac{P_{100}}{P_0} = \lambda'^5 \left\{ 1 - \frac{5}{4\pi} \left( \frac{4}{9\pi} \right)^{1/3} s_0' - \frac{5}{6} \left( \frac{4}{9\pi} \right)^{2/3} s_0'^3 \left[ \frac{d}{ds} \bar{E}_c(s) \right]_{s=s_0'} \right\}. \quad (24)$$

Our third prescription for computing the pressure is based on the assumption that the correlation energy is not a localized quantity, but, on the contrary, averages over distances of the order of the sphere radius,  $R_0 a_0$ . In this case, we simply add the TFD pressure in Eq. (18) to the correlation pressure of a uniform electron gas at

the average electron density,  $\bar{n}$ , to get

$$\frac{P_{av}}{P_0} = \lambda^5 \left[ 1 - \frac{5}{4\pi} \left( \frac{4}{9\pi} \right)^{1/3} s_0 \right] - \frac{5}{6} \left( \frac{4}{9\pi} \right)^{2/3} r_e^3 \left[ \frac{d}{ds} \bar{E}_c(s) \right]_{s=r_e}. \quad (25)$$

### III. THE CORRELATION ENERGY FOR AN ELECTRON FLUID

We return to the hypothetical problem of electrons at zero temperature immersed in a homogeneous background of positive-continuum charge density (giving over-all neutrality) with density parameter  $s$  according to Eq. (1). At high densities,  $s \ll 1$ , the electrons approximate a degenerate Fermi gas and in Eqs. (2)–(4) we have  $\bar{E}_f \gg \bar{E}_x \gg \bar{E}_c$ . Gell-Mann and Brueckner,<sup>8,9</sup> have obtained

$$\bar{E}_c(s) = -0.0622 \ln(4.69s^{-1}) \text{Ry} \quad (26)$$

with an error proportional only to the first or higher powers of  $s$ .

On the other hand, at a sufficiently low density, say  $s > 100$ , the electrons form an almost perfect lattice. Carr *et al.*<sup>16,17</sup> have obtained for the average total energy per electron

$$\bar{E}_k(s) = \{-1.792s^{-1} + 2.66s^{-3/2}(1 - 0.27s^{-1/2})\} \text{Ry} \quad (27)$$

with an error of order  $s^{-5/2}$  or higher. The first term in this expression is the Madelung or classical Coulomb energy, the second term is the lowest order expression for the zero-point energy of the lattice vibrations, and the third term is the first anharmonic correction to the zero-point energy. The numerical coefficient, 1.792, in the Madelung energy applies to within one part in five thousand for the body-centered and face-centered cubic lattices and for the hexagonal lattice. This coefficient has a remarkably weak dependence on the lattice type; for the simple cubic lattice, for instance, it is only replaced by 1.760 and in the Wigner-Seitz spherical approximation (with no long-range order at all) by 1.800.

At low densities where Eq. (27) applies, the lattice has perfect long-range order, whereas the almost perfect Fermi gas at high densities has no long-range order at all. It is likely that the change from the lattice phase with long-range order to the "fluid" phase without such order is a sharp first order transition, even at absolute zero temperature.<sup>18</sup> For the fluid phase, but near the transition density (parameter  $s_{\text{crit}}$ ) we assume the absence of long-range order but still some short-

range order. For the energy we adopt

$$\bar{E}_k(s) = [-(1.792 - a)s^{-1} + 2.66(1 - b)s^{-3/2} \times (1 - 0.27s^{-1/2})] \text{Ry}. \quad (28)$$

The factor  $(1 - b)$  takes account of the fact that transverse vibrational modes of long wavelength are missing in the fluid phase and do not contribute to the zero-point energy, whereas the longitudinal compression modes and transverse modes with short wavelength are present in the fluid with  $s$  near  $s_{\text{crit}}$ , and are similar to those in the solid. The term involving  $a$  in Eq. (28) accounts for the fact that we are not dealing with perfect lattice cells to optimize the Madelung energy. The value of  $a$  for the fluid is presumably slightly larger than the value of 0.032 one would get for a simple cubic lattice. Comparing Eqs. (27) and (28) for the two phases gives roughly

$$s_{\text{crit}} \simeq 7.1(b/a)^2. \quad (29)$$

We can get another very rough estimate for  $s_{\text{crit}}$  by arguing, as did Nozières and Pines,<sup>19</sup> that Lindemann's law for melting points also holds for the electron fluid-lattice phase transition. Let  $(\Delta r^2)^{1/2}$  be the root-mean-square amplitude of lattice vibrations for one particle. Lindemann's rule states that the lattice will "melt" when  $(\Delta r^2)^{1/2}$  is about one-quarter to one-third the lattice spacing, or about  $0.5 s_{\text{crit}} a_0$ . At zero temperature one can derive from the virial theorem the relation

$$\langle \Delta r^2 \rangle_{av} = (3\hbar/2m) \langle \omega_j^{-1} \rangle_{av},$$

where  $\omega_j$  is the frequency of the  $j$ th mode of lattice vibrations. A rough numerical calculation of the average over Carr's frequency spectrum<sup>16</sup> gives  $1.3 s^{3/2}$  atomic units for  $\langle \omega_j^{-1} \rangle_{av}$ . Lindemann's rule then gives  $s_{\text{crit}} \simeq 60$ , which is in agreement with de Wette's recent calculation<sup>20</sup>; and Eq. (29) gives  $b \simeq 3a$ . With  $\bar{E}_c$  defined by Eq. (2), we then have for the fluid with  $s$  near  $s_{\text{crit}}$ ,

$$\bar{E}_c(s) = [-0.826s^{-1} + 2.26s^{-3/2} - 2.83s^{-2}] \text{Ry}. \quad (30)$$

For use in our TFD calculations we need expressions for  $\bar{E}_c(s)$  for high and intermediate electron densities, but never for very low densities, since even at zero pressure  $s \leq 4.8$  according to Eq. (18). In this range we are dealing with the continuous transition from the low-density fluid to the high-density gas, and we expect  $\bar{E}_c(s)$  and its derivative to be smoothly varying functions of  $s$ . We simply adopt the analytical interpolation formula

$$\bar{E}_c(s) = -0.0622 \ln \left[ 1 + \frac{4.69(1 + 0.676s^{1/2})}{s(1 + 0.236s^{1/2})} \right] \text{Ry}. \quad (31)$$

For  $s > 20$  this expression can be expanded in powers of  $s^{-1/2}$  and the first two nonzero terms (but not the third) agree with those in Eq. (30). The expression in Eq. (31)

<sup>16</sup> W. J. Carr, Jr., Phys. Rev. **122**, 1437 (1961).

<sup>17</sup> W. J. Carr, Jr., Rosemary A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961).

<sup>18</sup> N. F. Mott, Phil. Mag. **6**, 287 (1961).

<sup>19</sup> P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

<sup>20</sup> F. W. de Wette, Phys. Rev. **135**, A287 (1964).

agrees to within 0.01 Ry with the interpolations of Hubbard,<sup>21</sup> Nozières and Pines,<sup>19</sup> and Carr *et al.*<sup>17</sup> for the range of metallic densities,  $1 \leq s \leq 5$ , falling roughly between the two extremes of these previous results. For  $s \ll 1$ , (31) reduces to the high-density expression, Eq. (26), and it should be in error by less than  $\pm 0.02$  Ry in the whole intermediate range.

We now turn to the question of the localization of  $\bar{E}_c(r)$  as a function of  $s(r)$  in the Wigner-Seitz sphere in an actual solid [ $s(r)$  increases monotonically from zero at the origin to  $s_0$  somewhat larger than  $r_e$  at the surface]. For the exchange energy,  $E_x$ , the situation is clearcut since the "range" for exchange forces is of order  $sa_0$ , so that the averaging volume contains about one electron, and for  $Z$  appreciably larger than unity, i.e.,

$$r_e = (R_0/Z^{1/3}) \ll R_0$$

the localized approximation is a good one at all densities.

For the correlation energy, Dubois and Kivelson<sup>22</sup> have used field-theoretic arguments to show formally that Lewis's localization procedure<sup>10</sup> would become valid in the limit of  $Z \rightarrow \infty$  at constant density. However, in practical cases where we require nonnegative pressures, the minimum density increases with  $Z$  and the situation is as follows. It is highly plausible<sup>23</sup> that the "averaging length,"  $l_c a_0$ , for the correlation energy, is of order  $s^{1/2}(r)a_0$ . At low pressures, near the boundary of the Wigner-Seitz sphere,  $R_0$  and  $l_c$  are both of order unity, even for  $Z \gg 1$ . At low or medium pressures for distances near  $r_{TF}$ , inside which about half the electrons are contained,  $r_{TF}$  and  $l_c$  are both of order  $Z^{-1/3}$ . Finally, for  $r \ll r_{TF}$  and any  $Z$ , we have  $l_c/r \simeq (r_{TF}/r)^{3/4} \gg 1$ . Thus, the extreme localization procedure is never valid and the opposite approximation of a fully averaged correlation energy is valid only for  $r \ll r_{TF}$ . We have carried out calculations on each of these extreme assumptions (see Sec. II) and expect the correct correlation energy to lie in between but closer to the fully averaged value.

#### IV. THE HIGH-DENSITY LIMIT

At sufficiently high average density the actual electron density varies little from the mean value except near the origin of the Wigner-Seitz sphere, and expansion methods can be used. The criterion for high density in this case is not simply  $r_e \ll 1$ , but that  $x_0 \simeq Z^{2/3} r_e \ll 1$ . The problem is to solve Eq. (15), which, in terms of a new dimensionless parameter,

$$y \equiv (x/x_0)$$

can be written

$$(d^2\psi/dy^2) = x_0^{3/2} y \{ \epsilon x_0^{1/2} + (\psi/y)^{1/2} \}^3 \quad (32)$$

<sup>21</sup> J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1957).

<sup>22</sup> D. F. Dubois and M. G. Kivelson, Phys. Rev. **127**, 1182 (1962).

<sup>23</sup> See, for example, A. J. Glick, Phys. Rev. **129**, 1399 (1963).

with the boundary conditions

$$\psi(0) = 1, \quad \psi'(1) = \psi(1). \quad (33)$$

We expand the solution in the form

$$x_0\psi = A_0 + A_1x_0 + A_2x_0^2 + \dots + x_0[f_0(y) + x_0f_1(y) + x_0^2f_2(y) + \dots], \quad (34)$$

where  $A_0, A_1, A_2, \dots$  are constants and

$$\begin{aligned} f_0(0) &= 1; & f_0'(1) &= f_0(1) = 0, \\ f_1(0) &= f_1(1) = f_1'(1) = 0, \\ f_2(0) &= f_2(1) = f_2'(1) = 0, \quad \text{etc.} \end{aligned} \quad (35)$$

Inserting this expression in Eq. (32) and equating coefficients of powers of  $x_0$ , we obtain after some algebra,  $A_0, A_1, A_2, f_0, f_1, f_2$ , and, to this order, the quantity  $\lambda$  defined in Eq. (13), is

$$\lambda^3 = 1 - \frac{3^{4/3}}{20}x_0 + \left( \frac{3^{5/3}}{400} + \frac{3}{20}\epsilon \right)x_0^2 + \dots \quad (36)$$

The expansion technique breaks down for the next order (in  $x_0^3$ ) since  $f_3(y) \propto \ln y$  as  $y \rightarrow 0$  and the boundary conditions of Eq. (35) cannot be satisfied. It will suffice for our argument, however, to retain only terms up to  $O(x_0^2)$ . Equation (18) for the pressure then gives

$$\frac{P}{P_0} = 1 - \left[ \frac{3}{2} \left( \frac{4}{9\pi} \right)^{2/3} Z^{2/3} + \frac{5}{4\pi} \left( \frac{4}{9\pi} \right)^{1/3} \right] r_e + O(Z^2 r_e^3). \quad (37)$$

One of us<sup>11</sup> has derived the first three terms of this formula previously by a different method. The first term is simply the Chandrasekhar pressure for a uniform density, perfectly degenerate Fermi gas; the second term comes from the Coulomb energy of a uniform distribution of  $Z$  electrons in the Wigner-Seitz sphere; the third term gives the pressure due to "exchange" forces. We note that there is no term of order  $r_e^2$  in the formula. It has been shown<sup>11</sup> that this is also the case for the ordinary Thomas-Fermi atom, and the physical interpretation is that the first-order distortion of the electronic charge distribution away from uniformity (due to the point charge at the center of the Wigner-Seitz sphere) vanishes in the high-density limit. It is now also clear that the effect of exchange forces in inducing a nonuniform charge distribution also vanishes in lowest order. The corresponding term in the total energy per lattice cell is independent of  $r_e$ . Although the TFD model is based on the assumption that  $Z \gg 1$ , the expansion in Eq. (36) is exact up to order  $r_e^3$  even for small  $Z$ . For  $r_e \leq Z^{2/3} r_e \ll 1$ , the correlation energy to lowest order in  $r_e$  is given by

$$\bar{E}_c(s(r)) = -0.0622 \ln(4.69 r_e^{-1}) \text{Ry} \quad (38)$$

and  $\Delta E$  in Eq. (29) has the same value. Hence the quantity  $\delta$  defined in Eq. (21) vanishes in this order, and the effect of a localized correlation energy correction

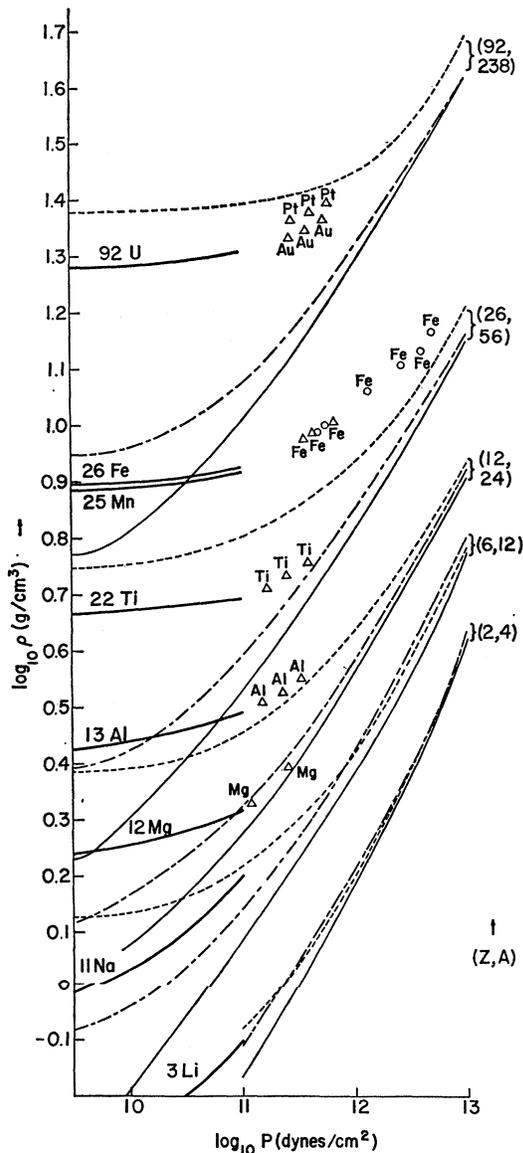


FIG. 1. Density versus pressure for an assortment of elements. The heavy solid curves on the left summarize Bridgman's data (Ref. 5), triangular and circular points are the shock wave data of Rice, McQueen, Walsh (Ref. 24) and Altschuler *et al.* (Ref. 25), respectively. The solid curves on the right are obtained from the TFD equation of state, the dashed curves include "local" correlation corrections, and the dotted curves show the effect of "average" correlation corrections.

on  $\lambda$  is then found to be only of order  $x_0^3$ . Like exchange and Coulomb forces, correlation forces at high densities do not induce nonuniformities in the electronic charge distribution in lowest order. To order  $x_0^2$  we then get the *same* (nonlocal) correlation contribution to the pressure from Eqs. (24) and (25), namely

$$(\Delta P_c/P_0) = -\frac{5}{6} \times 0.0622 (4/9\pi)^{2/3} r_e^2 \quad (39)$$

to be added to Eq. (37).

## V. NUMERICAL RESULTS AND A SEMI-EMPIRICAL EQUATION OF STATE

We have used an IBM7090 computer to numerically integrate the TFD equation, and to evaluate pressure as a function of density on the three assumptions of (a) negligible correlation corrections [Eq. (18)], (b) local correlation corrections [Eq. (24)], and (c) average correlation corrections [Eq. (25)]. These computations have been done for seven elements with  $Z$  ranging from 1–92 and  $A$  from 1–238. The results for five representative elements are plotted in Fig. 1. The solid curves on the left, labeled by element and atomic number represent a survey of Bridgman's data on a sample of elements, as plotted by Elsasser.<sup>5</sup> The triangular points are data obtained by Rice, McQueen, and Walsh<sup>24</sup> from shock-wave measurements, and the circular points are some of the shock-wave data of Altschuler, *et al.*<sup>25</sup> The five sets of three curves coming from the upper right and labeled by  $A$  and  $Z$  summarize our numerical calculations. In each set, the solid curve is the TFD result without correlation effects, the dashed curve is the theoretical equation of state with local correlations, and the dotted curve gives the average correlations. Below a pressure of one megabar it is clear that the TFD model with correlations is an oversimplification of the problem, and individual differences in crystal structure must be invoked to explain the large discrepancies in density, say, between Na, Mg, and Al which differ from each other only by two atomic mass units. At larger pressures, however, one begins to get good agreement with the TFD results. In all cases, the method of average correlations yields a larger density at "zero" pressure, than the local correlations, and, as expected, the inclusion of correlation effects by either method increases the zero pressure density rather noticeably over the straightforward TFD value. The average correlation curves show the most drastic deviation at low pressures, and, at least for  $25 \leq Z \leq 100$ , show the best agreement with the data at these pressures. Since the local approximation becomes more accurate with increasing  $Z$ , we argue on the basis of the experimental data that, for all practical values of  $Z$ , the average correlation correction is more realistic of the two. We have used the results of our calculations to derive a semiempirical formula for density as a function of pressure based on the average correlation correction. From Eqs. (25), (37), and (39), it is easy to obtain an approximate analytic expression in the high pressure limit. Recalling that the Chandrasekhar pressure can be written

$$P_c = (\kappa/x_0^5),$$

<sup>24</sup> M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Phys.* **6**, 1 (1957).

<sup>25</sup> L. V. Altschuler, K. K. Krupnikov, and M. I. Brazhnik, *Zh. Eksperim. i Teor. Fiz.* **34**, 886 (1958) [English transl.: *Soviet Phys.—JETP* **7**, 614 (1958)].

TABLE I. Value of  $\gamma_{in}$  in Eq. (45d).

$n$	$\gamma_{0n}$	$\gamma_{1n}$	$\gamma_{2n}$	$\gamma_{3n}$	$\gamma_{4n}$
2	$1.512 \times 10^{-2}$	$8.955 \times 10^{-2}$	$1.090 \times 10^{-1}$	5.089	-5.980
3	$2.181 \times 10^{-3}$	$-4.015 \times 10^{-1}$	1.698	-9.566	9.873
4	$-3.328 \times 10^{-4}$	$5.167 \times 10^{-1}$	-2.369	$1.349 \times 10$	$-1.427 \times 10$
5	$-1.384 \times 10^{-2}$	$-6.520 \times 10^{-1}$	3.529	$-2.095 \times 10$	$2.264 \times 10$

where

$$\kappa = \frac{3}{20\pi} \left(\frac{9\pi}{4}\right)^{2/3} \left(\frac{e^2}{\hbar c}\right)^5 \left(\frac{mc}{h}\right)^3 mc^2 \left(\frac{1}{2\pi^2 \epsilon^2 Z^{2/3}}\right)^5$$

$$= 9.524 \times 10^{13} \frac{\text{dyn}}{\text{cm}^2} \times Z^{-10/3} \quad (40)$$

and defining

$$\zeta \equiv (P/\kappa)^{1/5}, \quad (41)$$

we find,

$$x_0(\zeta) \sim \left(\frac{1}{\zeta + \phi}\right), \quad \zeta \gg 1 \quad (42)$$

with

$$\phi = \frac{3^{1/3}}{20} + \frac{\epsilon}{4.3^{1/3}}, \quad \epsilon = \left(\frac{3}{32\pi^2 Z^2}\right)^{1/3}.$$

For low densities, we have obtained an empirical fit to the numerical data for the zero-pressure TFD radius,  $x_0(0)$ . To an accuracy of better than 0.2%, for the seven cases which were computed, we get

$$x_0(0) = [8.884 \times 10^{-3} + \epsilon^{1/2} \times 4.988 \times 10^{-1} + \epsilon \times 5.2604 \times 10^{-1}]^{-1}. \quad (43)$$

In fact, the numerical results approach the asymptotic form of Eq. (42) extremely rapidly. The empirical criterion turns out to be not  $\zeta \gg 1$ , but rather  $\zeta \gg \phi$ . In practice, this means that even for the least favorable case,  $Z=1$  ( $\phi=0.109$ ), one finds agreement between Eq. (42) and the exact numerical calculations to within several percent for  $\zeta > 0.5$ . We have succeeded in reproducing this behavior with a formula of the following form:

$$(\zeta + \phi)x_0(\zeta) = 1 + e^{-\alpha\zeta} \{\beta_0 + \beta_1\zeta + \beta_2\zeta^2 + \beta_3\zeta^3 + \beta_4\zeta^4 + \beta_5\zeta^5\}. \quad (44)$$

To obtain the correct zero pressure result, we must have

$$\beta_0 = x_0(0)\phi - 1. \quad (45a)$$

Since the sound velocity,  $(dP/d\rho)^{1/2}$ , is always finite and nonzero in a solid at zero pressure, and our formulas above give  $(d\rho/dP) \propto (1/\zeta^4)(dx_0/d\zeta)$  for  $\zeta \ll 1$ , we should, ideally, use a polynomial in Eq. (44) which has no terms of order less than  $\zeta^5$  for  $\zeta \ll 1$ . We have found that this procedure does not give a good fit to the numerical data at high pressures, however, and the best we have been able to do is eliminate the linear term in  $x_0(\zeta)$

for  $\zeta \ll 1$ . Thus, we set

$$\beta_1 = \beta_0\alpha + [(1 + \beta_0)/\phi]. \quad (45b)$$

With the above values of  $\beta_0$  and  $\beta_1$ , we find a fit with the computer data to better than 0.5% for  $1 \leq Z \leq 92$ , and all pressures. We take

$$(1/\alpha) = 1.941 \times 10^{-2} - \epsilon^{1/2} \times 6.277 \times 10^{-2} + \epsilon \times 1.076 \quad (45c)$$

and

$$(1/\beta_n) = \{\gamma_{0n} + \gamma_{1n}\epsilon^{1/2} + \gamma_{2n}\epsilon + \gamma_{3n}\epsilon^{3/2} + \gamma_{4n}\epsilon^2\}^n$$

$$n = 2, 3, 4, 5. \quad (45d)$$

The values of  $\gamma_{in}$  are displayed in Table I. Considered as functions evaluated at all real values of  $\epsilon$ , Eq. (45d) and the coefficients of Table I yield poles in  $\beta_n$ , but these are well outside the range of "physical" values of  $\epsilon$ , defined by  $0.212 \leq \epsilon \leq 0.0104$  for  $1 \leq Z \leq 92$ . In this range, the functions  $\beta_n(\epsilon)$  are smoothly varying.

Recalling that the radius,  $R$ , of the TFD atom is given by

$$R = (9\pi^2/128)^{1/3} Z^{-1/3} x_0(\zeta) a_0 \quad (46a)$$

we get, finally,

$$\rho(\zeta) = (3AM_\mu/4\pi R^3) = 3.886(AZ/x_0^3)g/\text{cm}^3,$$

$$\zeta = \left[\frac{P(\text{dyn}/\text{cm}^2)}{9.524 \times 10^{13}}\right]^{1/5} Z^{-2/3}, \quad (46b)$$

with  $x_0$  given by (44). For a compound or an alloy, the total volume occupied by a single molecule is simply the sum of the individual atomic volumes, and we have

$$\rho(\zeta) = \frac{\sum n_i A_i}{\sum [n_i x_{0i}^3(\zeta)/Z_i]} \times 3.886 \frac{\text{g}}{\text{cm}^3}, \quad (49)$$

where  $n_i$  is the relative abundance by number of the  $i$ th element.

We have used the above formulas to compute the equation of state and sound velocity as a function of pressure for a large assortment of elements and compounds. In Fig. 2, we plot the theoretical equation of state for six selected elements. These appear as dashed curves. The solid curves show the shock-wave data<sup>24,25</sup> as reduced by Knopoff and MacDonald<sup>26</sup> for the same six elements. With the exception of Fe and Sn, all of these elements have a face-centered cubic lattice structure at zero pressure. Fe is body-centered cubic

<sup>26</sup> L. Knopoff and J. F. MacDonald, Geophys. J. 3, 68 (1960).

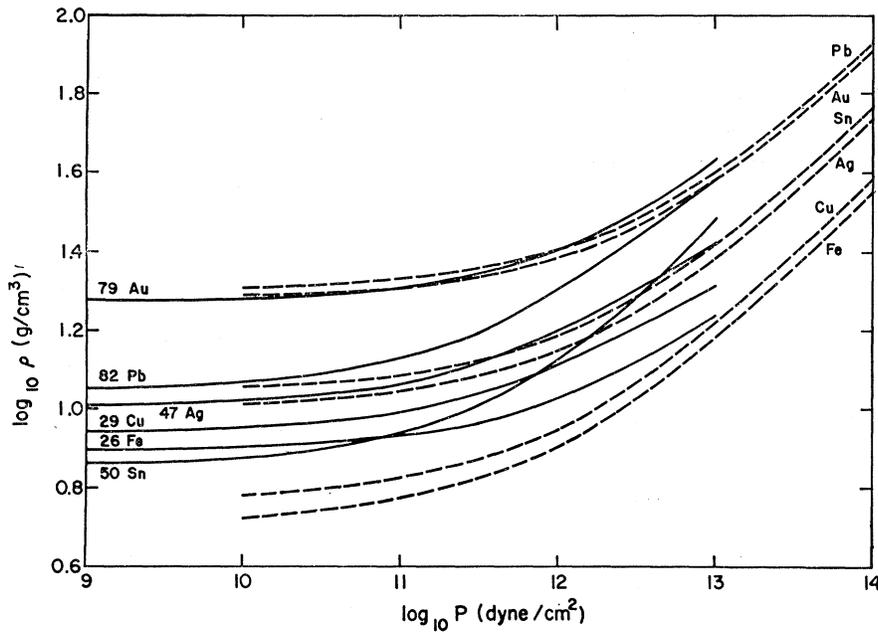


FIG. 2. Density versus pressure for six selected elements. The solid curves summarize the reduced shock wave data (Refs. 24-26) and the dashed curves show the average correlation corrections.

and Sn has a diamond lattice, which would tend to give it a far more open structure at low pressures than the simple TFD spherical model. Three other elements plotted in Ref. 4, Cd and Zn, and Bi have been omitted from Fig. 2 to avoid cluttering the graph. Cd and Zn both have hexagonal close packed structures at zero pressure, and compared with our equation of state, the former has an "anomalously" low density and latter an "anomalously" high density at low pressures. Bi is rhombohedral, and its measured density at zero pressure is a factor of 2 lower than the value given by our equation of state. There is a clear qualitative agreement

between theory and experiment for elements with cubic structures at all pressures, and this agreement becomes quantitative at pressures near 10 Mbar.

In Fig. 3, we plot the theoretical values for sound velocity,  $v_s$ , (dashed curves) and compare them with the reduced data of Ref. 26 for the same six elements. There is a negligible difference in  $(dP/d\rho)$  as determined from our empirical formula for elements with neighboring atomic numbers, so we have plotted the mean theoretical curves for the three pairs indicated. Because the semiempirical formula gives zero  $v_s$  at zero pressure, it should not be compared with the experimental data

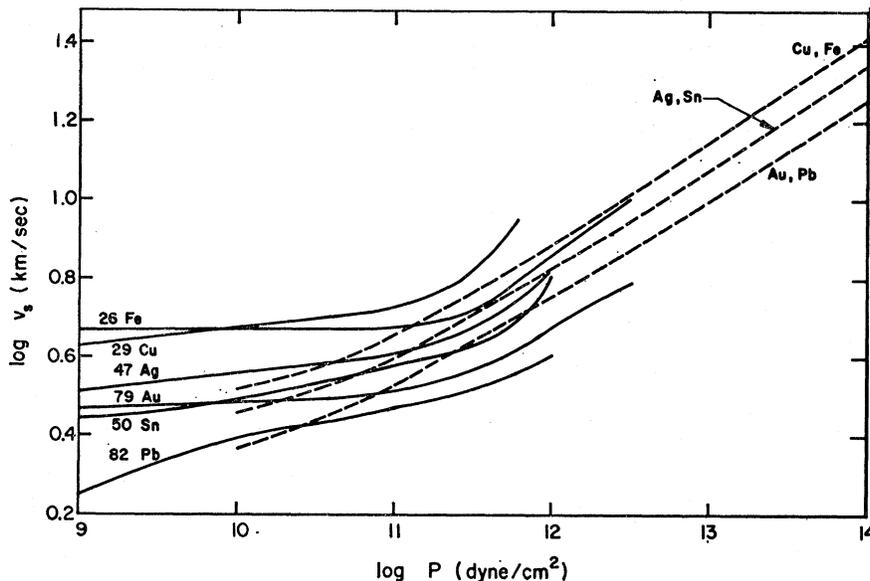


FIG. 3. Sound velocity versus pressure for six selected elements. The solid curves summarize the reduced shock-wave data (Refs. 24-26) and the dashed curves show the average correlation corrections.

at pressures below, say, 0.1 Mbar. Here, also, one begins to see quantitative agreement between theory and experiments at 10 Mbar.

Since 10 Mbar is not much larger than the run of pressures in the core and lower mantle of the earth, one can attempt a comparison of state equations obtained from seismic measurements for the core with our semi-empirical equation for various compounds which have been suggested in the literature as good candidates for core material.

In Fig. 4, we plot Birch's solution I<sup>27</sup> for the run of density and pressure in the lower mantle and upper core of the earth. The seismic discontinuity at a depth of approximately 2900 km, which is reflected as a discontinuity in density at a pressure of 1.35 Mbar in Fig. 4, has been interpreted by Ramsey<sup>28</sup> and others as due to a phase change (silicate compounds going into their metallic phase, for example), and by MacDonald and Knopoff<sup>29</sup> as caused by an abrupt change in chemical composition. The latter authors<sup>26</sup> and Knopoff and Uffen<sup>30</sup> have computed state equations from numerical solutions of the TFD equation without correlation corrections, and have compared them with seismic models such as Birch's in order to determine the chemical composition on both sides of the discontinuity. When correlation effects are taken into account, the numerical results are altered quite drastically in the range of pressures near the discontinuity. In Fig. 4 we plot as dashed lines the results of our equation of state for a selection of compounds discussed in Refs. 26, 29, and 30. At a pressure of 0.1 Mbar, the correlation effects increase the density by approximately a factor of 2 over the TFD densities for the assortment of compounds and minerals considered.

No very serious comparison of the numerical values of our purely theoretical densities with the seismic data for the core and mantle should be made at these still relatively low pressures. It is clear, for example, that pure iron should be at least as dense as the core at the pressures which prevail in that region. Ultimately, the problem of the core's composition will probably be solved by a combination of theoretical and experimental arguments. Such an attack has been made by MacDonald and Knopoff.<sup>29</sup> They have normalized the theoretical TFD equation of state so that it agrees with experimental data at low pressures, and on the basis of this procedure, they conclude that the core composition lies somewhere between the iron-silicon mixtures,  $\text{Fe}_{2.1}\text{Si}$  and  $\text{Fe}_{1.6}\text{Si}$ . Two definite conclusions can be made from our theoretical results: (1) Correlation corrections to the TFD equation of state very definitely go in the right direction to give agreement with the

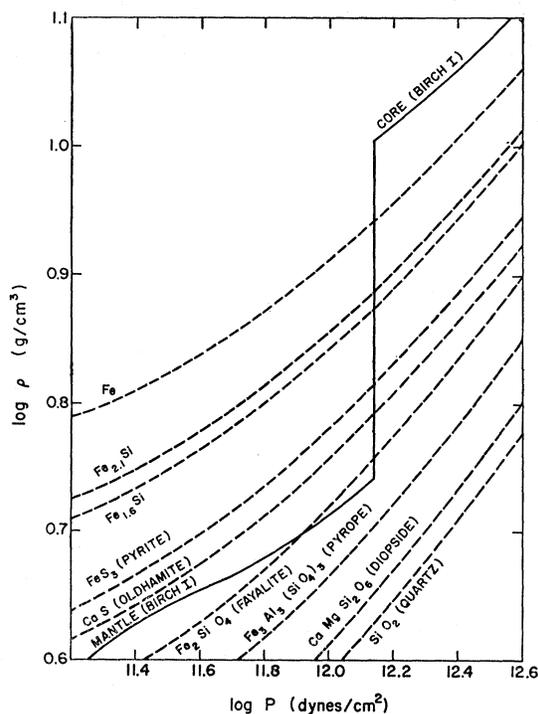


FIG. 4. Theoretical density-pressure curves (TFD plus average correlation corrections) for an assortment of minerals. The solid curve with the step discontinuity is Birch's solution I (Ref. 27) for the actual run of pressures and densities in the lower mantle and upper core of the earth.

empirical data; and (2) even in their metallic phase (which is the only phase we can hope to even approximately describe with a TFD model), the silicate compounds will not have sufficiently large densities at core pressures to fit the seismic data. This latter point is one more supporting argument for the interpretation of the core-mantle discontinuity as a composition discontinuity, rather than a phase transition.

It has been customary in the literature to summarize the data for a given compound or mixture by computing an effective  $Z$ ,  $\bar{Z}$ , which when inserted into the TFD equation of state for a single element, yields the pressure-density values for the compound. In general,  $\bar{Z}$  is a very slowly varying function of the pressure, and its precise numerical value depends on how one defines the average mass,  $\bar{A}$ , for the compound. In Ref. 29, the ratio of neutrons to protons is held fixed to its actual physical value, while, in Ref. 30, this ratio is defined to be unity. We have found it more convenient to fix  $\bar{A}$  as the average value for the compound,  $\bar{A} = \sum n_i A_i$  and vary  $\bar{Z}$  such that, when inserted in Eqs. (44)–(46), it gives agreement with the numerical results for the compound. In Table II, we summarize the results obtained for a large assortment of minerals, pure elements, and mixtures at pressures of 0.1, 1.0, and 10 M bar. At extremely high pressures, all Thomas-Fermi type equations of state give densities proportional

<sup>27</sup> F. Birch, *J. Geophys. Res.* **69**, 4377 (1964).

<sup>28</sup> W. H. Ramsey, *Monthly Notices Roy. Astron. Soc. Geophys. Suppl.* **5**, 409 (1949).

<sup>29</sup> G. J. F. MacDonald and L. Knopoff, *Geophys. J.* **1**, 284 (1958).

<sup>30</sup> L. Knopoff and R. J. Uffen, *J. Geophys. Res.* **59**, 471 (1954).

TABLE II.  $\bar{Z}$  and  $\rho$  are tabulated at pressures of 0.1, 1.0, and 10 Mbar for an assortment of pure elements and minerals. The quantity  $\bar{Z}$ , when used in Eqs. (44)–(46), gives the same density for mineral at a given pressure as Eq. (49).  $\bar{A}$  and  $\bar{Z}_0$  are the mean atomic weight and atomic number, respectively;  $\bar{A} = \sum m_i A_i$ ,  $\bar{Z}_0 = \sum m_i Z_i$ .

Mineral or element	$\bar{A}$	$\bar{Z}_0$	$P=0.1$ Mbar		$P=1.0$ Mbar		$P=10$ Mbar	
			$\bar{Z}$	$\rho$	$\bar{Z}$	$\rho$	$\bar{Z}$	$\rho$
Bi	209	83		21.8		26.2		41.0
Pb	207	82		21.6		26.0		40.7
Au	197	79		20.5		24.8		39.2
Galena-PbS	119.5	49.0	20.73	12.8	29.23	17.0	35.86	29.6
Sn	119	50		12.3		15.6		26.6
Cd	112	48		11.6		14.7		25.4
Ag	108	47		11.1		14.3		24.6
Zn	65	30		6.78		9.20		17.0
Cu	64	29		6.71		9.11		17.0
Ni	59	28		6.18		8.45		15.9
Fe	56	26		5.90		8.13		15.4
Sphalerite-ZnS	48.50	23.00	20.61	5.22	21.47	7.37	21.95	14.2
Fe <sub>2.1</sub> Si	46.98	22.14	20.26	5.06	20.98	7.17	21.36	13.9
Fe <sub>1.6</sub> Si	45.22	21.38	19.46	4.89	20.16	6.98	20.55	13.6
Troilite-FeS	44.00	21.00	19.77	4.76	20.19	6.78	20.45	13.3
Pyrite-FeS <sub>2</sub>	38.00	16.50	17.73	4.17	17.95	6.04	18.10	12.0
Wustite-FeO	36.00	17.00	12.58	4.15	13.84	6.17	14.74	12.4
Oldhamite-CaS	36.00	18.00	17.88	3.94	17.89	5.72	17.92	11.5
Magnetite-Fe <sub>3</sub> O <sub>4</sub>	33.12	15.70	11.70	3.88	12.77	5.83	13.55	11.9
Hematite-Fe <sub>2</sub> O <sub>3</sub>	32.00	15.20	11.38	3.76	12.38	5.68	13.12	11.7
Fayalite-Fe <sub>2</sub> SiO <sub>4</sub>	29.16	14.01	11.08	3.44	11.83	5.25	12.38	10.9
Rutile-TiO <sub>2</sub>	26.66	12.66	10.43	3.19	11.00	4.92	11.42	10.4
Andradite-Ca <sub>3</sub> Fe <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	25.40	12.50	10.56	3.04	11.06	4.70	11.42	9.88
Pyrope-Fe <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	25.01	12.15	10.42	3.00	10.64	4.65	11.16	9.83
Grossularite-Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	22.50	11.20	10.12	2.71	10.41	4.24	10.61	9.06
Diopside-CaMgSi <sub>2</sub> O <sub>6</sub>	21.60	10.80	9.94	2.62	10.16	4.11	10.32	8.82
Anorthite-CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	21.39	10.62	9.84	2.60	10.04	4.09	10.19	8.80
Orthoclase-KAlSi <sub>3</sub> O <sub>8</sub>	21.39	10.62	9.86	2.60	10.06	4.09	10.20	9.78
Corundum-Al <sub>2</sub> O <sub>3</sub>	2.040	10.00	9.60	2.49	9.71	3.95	9.78	8.56
Spinel-MgAl <sub>2</sub> O <sub>4</sub>	20.29	10.00	9.63	2.47	9.73	3.92	9.80	8.50
Jadeite-NaAlSi <sub>3</sub> O <sub>6</sub>	20.20	10.00	9.57	2.46	9.69	3.91	9.77	8.48
Albite-NaAlSi <sub>3</sub> O <sub>8</sub>	20.16	10.00	9.55	2.46	9.67	3.90	9.76	8.46
Quartz-SiO <sub>2</sub>	20.00	10.00	9.49	2.44	9.63	3.88	9.72	8.40
Forsterite-Mg <sub>2</sub> SiO <sub>4</sub>	20.00	10.00	9.62	2.44	9.72	3.87	9.80	8.39
Enstatite-MgSiO <sub>3</sub>	20.00	10.00	9.58	2.44	9.69	3.87	9.77	8.39
Periclase-MgO	20.00	10.00	9.72	2.44	9.80	3.86	9.85	8.37
Spodumene-LiAlSi <sub>2</sub> O <sub>6</sub>	18.60	9.20	8.28	2.35	8.56	3.78	8.73	8.27
Beryl-Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub>	18.52	9.17	8.46	2.33	8.66	3.74	8.79	8.20

to  $(A/Z)^{3/5}$  at a fixed pressure. At the pressures given in Table II, however, the densities are still far more strongly correlated with the atomic mass numbers,  $\bar{A}$ , although occasional exceptions to this rule can be found in the table. For instance, the mineral Wustite, with  $\bar{A}=36.00$ , is more dense than Pyrite which has  $\bar{A}=38.00$  at a pressure of 1.0 Mbar. The former has a ratio  $(\bar{A}/\bar{Z})=2.599$  at this pressure, while for the latter,  $(\bar{A}/\bar{Z})=2.117$ .

In a future publication, we will consider the application of our equation of state to computations of models for the Jovian planets.

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