three-particle distributions represented by $A(\rho, T)$ and $B(\rho, T)$ which has not been achieved as yet. However, our data should provide a good testing ground in the future both for the Deutch-Oppenheim theory and for our understanding of molecular correlations in dense fluids.

---

*Work performed at the National Bureau of Standards under the sponsorship of the National Aeronautics and Space Administration, Marshall Space Flight Center, Huntsville, Alabama and the U.S. Atomic Energy Commission.

†Now at Engineering Measurements Company, P.O. Box 346, Boulder, Colorado.

‡Now at Belfer Graduate School of Science, Yeshiva University, New York, New York.

[1]M. Bloom, I. Oppenheim, M. Lipsicas, C. G. Wade, and C. F. Yarnell, J. Chem. Phys. 43, 1036, 1965.

[2]J. M. Deutch and I. Oppenheim, J. Chem. Phys. 44, 2843, 1966.

[3]W. P. A. Haas, N. J. Poulis, and W. Borleff, Physica 27, 1037, 1961.

[4]C. E. Miller, T. M. Flynn, T. K. Grady, and J. S. Waugh, Physica 32, 244, 1966.

[5]M. Lipsicas and A. Hartland, J. Chem. Phys. 44, 2839 1966.

[6]Reference (2) p. 2849.

---

# Shell Structure and the Thomas-Fermi Equation of State*

J. W. Zink

*Lawrence Radiation Laboratory, University of California, Livermore, California*

(Received 18 April 1968; revised manuscript received 9 October 1968)

The calculation of the electronic contribution to the equation of state of high-temperature, high-density matter by means of Thomas-Fermi theory is modified to include the effect of shell structure. Shell structure is included by accounting for the discrete nature of the energy levels of the bound states. The free states are treated by means of Thomas-Fermi theory. Comparisons are made between Thomas-Fermi (TF) theory and Thomas-Fermi shell (TFS) theory. The pressure and energy calculated by means of TFS theory vary about those calculated by means of TF theory, and for some temperatures and densities they are substantially different even at pressures far in excess of the 100-Mbar region where TF theory is generally thought to be applicable.

## INTRODUCTION

Thomas-Fermi theory has been used extensively for finding the equation of state of matter at high temperatures and densities.[1,2] TF theory is felt to be particularly applicable to materials of high atomic number and at high pressure. Just where TF theory becomes a poor approximation is not well defined. It is realized that shell structure effects should cause considerable deviations from TF theory, but the nature and size of these deviations have generally been treated only in a qualitative way. The present paper is an attempt to bring out quantitatively the effects of shell structure on the electronic contribution to the pressure and energy of matter at high temperatures and densities.

## THOMAS-FERMI THEORY

The usual Thomas-Fermi theory will be described briefly since it serves as a background for the Thomas-Fermi shell theory. In TF theory an atom is considered to occupy a spherical volume whose size is determined by the atomic weight of the atom and the density of the matter. This volume is given by $v = A_0/\rho_0 N_0$, where $A_0$ is the atomic weight, $\rho_0$ is the density of the matter, and $N_0$ is Avogadro's number. The nucleus of the atom is considered fixed at the center of this volume, and the distribution of electrons is obtained by using TF theory. According to TF theory, the number of states per $cm^3$ available to electrons whose momentum lies between $p$ and $p + dp$ is $8\pi p^2 dp/h^3$. The probability that these states are

full is given by Fermi-Dirac statistics, so that the density of electrons with momentum between $p$ and $p + dp$ is

$$d\rho_{TF} = \frac{8\pi p^2 \, dp/h^3}{\exp(p^2/2mkT - eV_{TF}/kT + \eta) + 1}, \quad (1)$$

where $V_{TF}$ is the Thomas-Fermi central potential, $e$ is the absolute value of the electron's charge, and $\eta$ is the chemical potential. Integrating over all momenta, the density of electrons is given by

$$\rho_{TF} = (4\pi/h^3)(2mkT)^{3/2} I_{1/2}(-eV_{TF}/kT + \eta), \quad (2)$$

where

$$I_n\left(-\left(\frac{eV}{kT} + \eta\right)\right) = \int_0^\infty \frac{y^n dy}{\exp(y - eV_{TF}/kT + \eta) + 1}. \quad (3)$$

Another relation between $\rho_{TF}$ and $V_{TF}$ is obtained from Poisson's equation,

$$\nabla^2 V_{TF} = 4\pi\rho_{TF} e. \quad (4)$$

The integral of $\rho_{TF}$ over the volume of the atom has to be equal to the atomic number $Z$ of the atom. That is,

$$\int_0^R \int_0^\infty \frac{8\pi p^2 dp \, 4\pi r^2 dr/h^3}{\exp(p^2/2mkT - eV_{TF}/kT + \eta) + 1} = Z, \quad (5)$$

where $R$ is the radius of the atom's spherical volume. One way to solve these equations is to guess at a value for $\rho_{TF}$ at the surface of the atom's volume. The quantity $(-eV_{TF}/kT + \eta)$ at the surface of the atom is then known by means of Eq. (2). Equation (4) can then be solved numerically by using the proper boundary conditions and the expression for $\rho_{TF}$ given by Eq. (2). The value of $V_{TF}$ so found is used in Eq. (5). If Eq. (5) cannot be satisfied, the initial guess on $\rho_{TF}$ at the surface of the atom is adjusted, and $V_{TF}$ is recalculated. The process is repeated until Eq. (5) is satisfied.

The Thomas-Fermi pressure is found by evaluating the rate of momentum transfer at the surface of the atom's volume,

$$P = \int_0^\infty \frac{\frac{1}{3}p(p/m)8\pi p^2 \, dp/h^3}{\exp(p^2/2mkT + \eta) + 1}, \quad (6)$$

which can be written

$$P = [\tfrac{2}{3}\rho_s I_{\frac{3}{2}}(\eta)/I_{\frac{1}{2}}(\eta)]kT, \quad (7)$$

where $\rho_s$ is the electron density at the surface of the atom's volume,

$$\rho_s = (4\pi/h^3)(2mkT)^{3/2} I_{\frac{1}{2}}(\eta). \quad (8)$$

The total energy can be expressed in the form[2]

$$E = \tfrac{3}{2}Pv + \tfrac{1}{2}E_{pot}, \quad (9)$$

where $E_{pot}$ is given by

$$E_{pot} = \int_0^R (-Ze^2/r)\rho_{TF} d\tau$$
$$+ \tfrac{1}{2}\int_0^R \left(Ze^2/r - eV_{TF}\right)\rho_{TF} d\tau. \quad (10)$$

The energy of interest in thermodynamic applications is not $E$, but the excess of $E$ at a given temperature and density over $E$ at zero temperature and density. In TF theory, the zero temperature and density energy is given by $E_i = -3.34 \times 10^{-11} Z^{7/3}$ ergs/atom. The excess energy is

$$U = E - E_i. \quad (11)$$

## SHELL STRUCTURE

The effects of shell structure can be taken into account by altering the method in which the total number of electrons within the volume of an atom are counted. The TF method of counting electrons is described by Eq. (5). This method does not allow for the existence of discrete energy levels for the bound electrons, and thereby omits the effects of shell structure. One way to improve the counting of electrons is to use a trial potential function $V$ in Schrödinger's equation, obtain the energy levels that go with $V$, and calculate the number of bound electrons from the relations

$$S_{nl} = \frac{2(2l+1)}{\exp(-E_{nl}/kT + \eta) + 1}, \quad (12)$$

and $N_b = \sum_{nl} S_{nl}$,    (13)

where $n$ and $l$ are the principal and orbital quantum numbers, $S_{nl}$ is the average number of electrons in the subshell $nl$, and $N_b$ is the total number of bound electrons.

Thomas-Fermi theory can be used to count the free electrons. Since the free electrons are contained in a continuum of energy levels, the use of TF theory here seems particularly well justified. In order to count free electrons, Eq. (5) is altered so that the lower limit on the momentum integration is given by

$$p_0^2/2m = eV,$$

or $p_0 = \sqrt{eV2m}$    (14)

The number of free electrons is then given by

$$N_f = \int_0^R \int_{p_0}^\infty \frac{8\pi p^2 dp \, 4\pi r^2 dr/h^3}{\exp(p^2/2mkT - eV/kT + \eta) + 1}. \quad (15)$$

The total number of electrons is given by $N_b + N_f$. If $V$ is equal to $V_{TF}$, the total number of electrons will not, in general, be equal to the correct number of electrons associated with a given atom. If $V_{TF}$ included the effects of shell structure properly, the value of $N_b + N_f$ would equal the correct number of electrons.

## OBTAINING A PROPER POTENTIAL

A potential $V$ which leads to the correct sum for $N_b$ and $N_f$ can be found in the same manner that $V_{TF}$ is found except that in place of Eq. (5) the relation $N_b + N_f = Z$ is used. The electron density at the surface of the atom will thereby be different from a TF calculation and will include the effect of shell structure. Another way to arrive at a potential $V$ which leads to the correct sum of $N_b$ and $N_f$ is to assume for $V$ an analytic form, which is based on physical considerations and contains an adjustable parameter. The parameter can be adjusted so that $N_b + N_f = Z$.

The following model of a partially ionized atom can be used as a basis for finding an analytic form for $V$. The volume of an atom can be divided into two regions: an inner region around the nucleus where the electron density is high and mainly due to bound electrons, and an outer region where the electron density is low and mainly due to free electrons. If it is assumed that all the electrons in the outer region are free and that their distribution is uniform, the potential in this region is

$$V = \frac{Z^*e}{R}\left(\frac{R}{r} + \frac{r^2}{2r^2} - \frac{3}{2}\right), \quad r_1 \le r \le R, \tag{16}$$

where $Z^*$ is the number of free electrons, and $r_1$ is the radius of the inner region. It has been shown[3] that a good approximation to the potential about an isolated, zero-temperature atom is given by the expression $Ze/r(1+Ar)^2$, where $A$ is a constant for a given value of $Z$. It is reasonable to use this same potential for the bound electrons within $r_1$, since the removal of outer electrons by ionization affects very little the distribution of the inner bound electrons. The potential in the inner region, including the effect of bound and free electrons, is then

$$V = \frac{Ze}{r(1+Ar)^2} + \frac{Z^*e}{R}\left(\frac{r^2}{2R^2} - A_1\right), \quad 0 \le r \le r_1, \tag{17}$$

where $A_1$ is chosen to make $V$ continuous at $r = r_1$.

$$A_1 = \frac{ZR}{r_1(1+Ar_1)^2Z^*} - \frac{R}{r_1} + \frac{3}{2}. \tag{18}$$

A relation between $Z^*$ and $r_1$ can be obtained by using Poisson's equation to find the electron density corresponding to $V$, and then setting the integral of this electron density equal to $Z$. The result is

$$Z^* = \frac{2ZAr_1}{(1+Ar_1)^3} + \frac{Z}{(1+Ar_1)^2}. \tag{19}$$

Since TF theory is assumed to apply to the free electrons, Eq. (8) can be used to obtain a relation between the chemical potential and the free electron density at the surface of the atom. For the analytic potential, the electron density $\rho_S$ is given by

$$\rho_S = Z^*/\tfrac{4}{3}\pi R^3. \tag{20}$$

The quantity $Z^*$ occurring in the assumed analytic potential is the parameter to be adjusted so that $V$ will yield a value for $N_b$ and $N_f$ such that $Z = N_b + N_f$.

## A THOMAS-FERMI–LIKE CALCULATION

It is of interest to see what sort of results are obtained for electron pressure and energy when the analytic potential $V$ is used in a Thomas-Fermi–like calculation of these quantities. To make a TF-like calculation, the electrons in the volume of an atom are counted by means of Eq. (5) just as in TF theory, except $V_{TF}$ there is replaced by $V$. The value of $A$ to be used in $V$ is determined by the requirement that the total number of electrons in an isolated, zero-temperature atom be equal to $Z$. That is,

$$\int_0^\infty \rho_i 4\pi r^2 dr = Z, \tag{21}$$

where $\rho_i$ is given by the TF relation,

$$\rho_i = (8\pi/3h^3)(2meV_i)^{3/2},$$

with $V_i = Ze/r(1+Ar)^2$.

The result is that $A = 1.14 \times 10^8 Z^{1/3}$ cm$^{-1}$. The procedure used to find $V$ consists of guessing at a value for $Z^*$ and finding the values of $\eta$, $r_1$, and $A_1$, using Eqs. (8) and (18)–(20). If the value of $V$ so determined does not yield the right value for $Z$ when used in Eq. (5), the guess on $Z^*$ is adjusted and the procedure repeated. Further adjustments are made until some set degree of agreement is attained.

Once agreement has been obtained, the electron pressure can be found from Eq. (7). The electron energy can be found by using Eqs. (9) and (11), where $E_{pot}$ is found with the analytic potential and the electron density given by this potential through Poisson's equation. This electron density is

$$\rho = \frac{Z^*}{\tfrac{4}{3}\pi R^3} + \frac{3ZA^2}{2\pi r(1+Ar)^4}, \quad 0 \le r \le r_1, \tag{22}$$

$$\rho = Z^*/\tfrac{4}{3}\pi R^3, \quad r_1 \le r \le R. \tag{23}$$

The reference energy $E_i$, in ergs/atom, is $E_i = -0.8Z^2e^2A$. This result is obtained when the electron density for an isolated atom at zero temperature is taken to be $\rho_i = 3ZA^2/2\pi r(1+Ar)^4$. This density cannot be used to find $A$ in the manner indicated by Eq. (21) because, for such a density, any value of $A$ will satisfy Eq. (21). The potential $V$ is known only to an arbitrary

constant. It has been assumed here, as in the TF calculations of Refs. 1 and 2, that $V = 0$ at $r = R$.

Figure 1 shows the variation of electron pressure with density for iron at two different temperatures. The dashed lines are the results of calculations made by using the analytic potential in a TF-like calculation. The solid lines are the results of a strictly TF calculation. Figure 2 shows the corresponding curves for the energy $U$. In places where the dashed curve does not appear, it coincides with the TF results. The TF-like results are seen to agree well with the TF results. The largest difference is in the energy at low temperature and density, where the TF-like results are lower than the TF results. As it turns out, the values for $|E_{pot}|$ and $|E_i|$ for the TF-like calculation are as much below reality as the TF results for these quantities are above reality.

## A THOMAS-FERMI SHELL CALCULATION

The Thomas-Fermi-like calculation gives confidence in the appropriateness of the form of the analytic potential for use in a TFS calculation.

The energy levels associated with the analytic potential $V$, were calculated by means of the WKB approximation:

$$\left(n_r + \tfrac{1}{2}\right)\pi = \int_{r_a}^{r_b}\left(\frac{8\pi^2 m}{h^2}\left(-E_{nl} + eV'\right) - \frac{(l + \tfrac{1}{2})^2}{r^2}\right)^{1/2}dr.$$
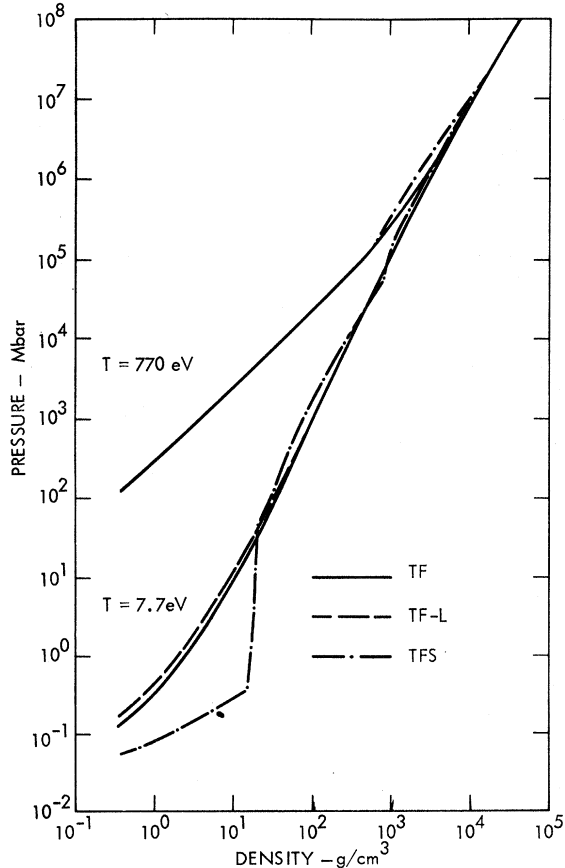
$$(24)$$



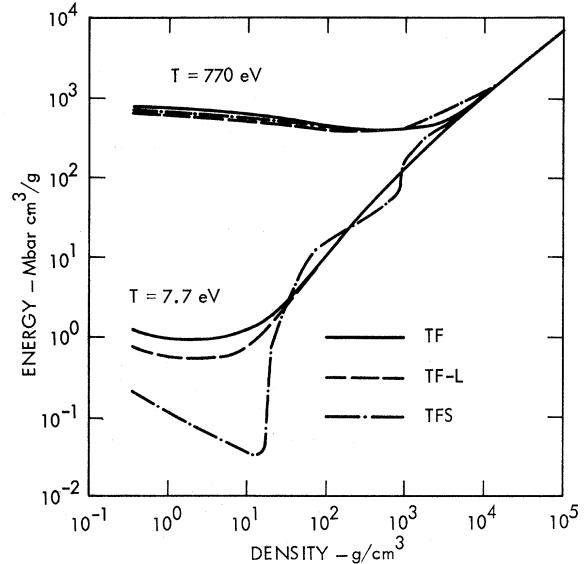FIG. 1. Pressure versus density for iron.



FIG. 2. Energy versus density for iron.

The energy levels found by means of Eq. (24) have been shown to agree closely with those found from Schrödinger's equation when the potential was that of an isolated, zero-temperature TF atom.[4] The potential $V'$, is the analytic potential modified in an approximate way to exclude electron self-interaction.

$$V' = (Z'e/R)(R/r + r^2/2R^2 - \tfrac{3}{2}) + e/r, \quad r_1 \leqslant r \leqslant R, \quad (25)$$

$$V' = (Z - 1)e/r(1 + Ar)^2 + (Z'e/R)(r^2/2R^2 - A_1) + e/r,$$

$$0 \leqslant r \leqslant r_1 \quad (26)$$

$$V = e/r, \quad r \geqslant R, \quad (27)$$

where

$$Z' = Z^*(Z - 1)/Z . \quad (28)$$

The principal quantum number is the sum of the radial quantum number $n_r$ plus the orbital quantum number $l$ plus 1, $n = n_r + l + 1$. The radial and orbital quantum numbers can take on the values zero through $n - 1$. The integrand in Eq. (24) is the radial momentum, and the limits $r_a$ and $r_b$ are the inner and outer turnaround radii. The radii $r_a$ and $r_b$ are the roots of the equation obtained by setting the integrand equal to zero.

The method of determining the parameter $Z^*$ parallels that used in the TF-like calculation. The only difference is in the method of counting the number of electrons within an atom's volume. In the TFS calculation, the quantities $N_b$ and $N_f$ are used to find the correct number of electrons.

One of the effects of a nonzero density for the matter is to limit the number of bound levels that can exist for an atom. For high temperatures, the limitation in the number of bound levels is of no consequence because these levels are empty of electrons anyway. At low temperature and high density, the limitation in the number of

allowable levels can force some electrons to be free that at a lower density would be bound. This phenomenon is termed pressure ionization. This occurs where the momentum of the outer bound electrons is so low that the uncertainty in the electron's position exceeds, roughly, the cube root of the cell volume. A reasonable criterion for finding a minimum momentum is to require that the momentum of an electron be such that the probability of finding the electron within the atom's volume is greater than one-half. Energy levels whose associated momenta are less than this are not considered bound. This criterion can be written

$$\tfrac{4}{3}\pi R^3 \tfrac{4}{3}\pi p_c^{\,3}/h^3 = \tfrac{1}{2} \ . \tag{29}$$

Taking the cutoff energy as $E_c = p_c^{\,2}/2m$, Eq. (29) leads to

$$E_c = (h^2/2m)(3/8\pi)^{2/3}/v^{2/3} \ , \tag{30}$$

or $E_c = 5.9 \times 10^{-27}/v^{2/3}$ ergs. If the ionization potential associated with a subshell is less than $E_c$, the electrons of that subshell are considered to be free. The assumption that $V' = e/r$ for $r \geqslant R$ is more of a convenience than a physical reality. Had $V'$ been taken as zero, for example, when $r \geqslant R$, then there would occur a natural limit to the number of bound levels. However, it turns out to be more convenient, from a computational point of view, to set $V' = e/r$ for $r \geqslant R$ and use $E_c$ to determine the number of bound levels. The results of TFS calculations are not particularly sensitive to variations in the density at which pressure ionization occurs, so the method of determining the number of bound levels is not critical.

The value of the constant $A$ used in the TFS calculation is the same as that used in the TF-like calculation. The energy $U$ for the TFS calculation is found in the same manner as in the TF-like calculation except that in a TFS calculation the radius $r_1$ can be larger than $R$. When this happens, the value of $Z^*$ is obtained by setting $r_1 = R$ and adjusting $A_1$ so that the potential behaves properly at $R$. That is, $A_1$ is obtained by means of Eq. (18) with $r_1$ replaced everywhere by $R$. In finding the pressure, the electron density at the boundary of the atom is taken as $Z^*/\tfrac{4}{3}\pi R^3$. The quantity $\tfrac{3}{2} Pv$ which is involved in the energy uses this pressure. In the other part of the energy, $\tfrac{1}{2}E_{\text{pot}}$, we use $Z^*$ to find a value for $r_1$ by means of Eq. (19), and then set $R$ equal to $r_1$. $A_1$ is then redetermined by Eq. (18) and these new parameters are used to find the analytic potential and electron density appropriate to $Z^*$. This potential and electron density are then used to find $E_{\text{pot}}$. In this way $E_{\text{pot}}$ is determined in a manner consistent with the isolated-atom energy $E_i$. The quantity $\tfrac{3}{2} Pv$ is a measure of the kinetic energy in excess of the amount $|\tfrac{1}{2}E_{\text{pot}}|$.

In obtaining the number of free electrons $N_f$ in a TFS calculation, it should be pointed out that the analytic potential $V$ is used in Eq. (15) and not $V'$. There is some ambiquity here, but $V$ seems more realistic. The use of $V'$ tends to make $Z^*$ too

small so that the pressure and energy results are shifted downward.

In Figs. 1 and 2, the dash-dot curves are the results of TFS calculations. Large differences are seen to occur between TF and TFS results even at pressures well in excess of 100 Mbar. The TFS results approach the TF results in the limit of high density and/or high temperature. The pressure curve for iron at the lower temperature shows a sort of condensation process at low density. Here the pressure increases very little over a large change in density. In the condensation region, as the density increases, the free electrons tend to become bound electrons because there are empty bound states available. When the density becomes sufficiently large, the available bound states become filled and pressure ionization occurs causing a steep rise in the pressure as the density is further increased. Figures 3 and 4 show TF and TFS calculations for lithium. Here the TFS calculation crosses over the TF calculation at a density such that the two $K$-shell electrons are pressure ionized.

## DISCUSSION

In the work described here, a mean atom is used to represent the various ionic species that would actually exist in ionized matter. The effect of
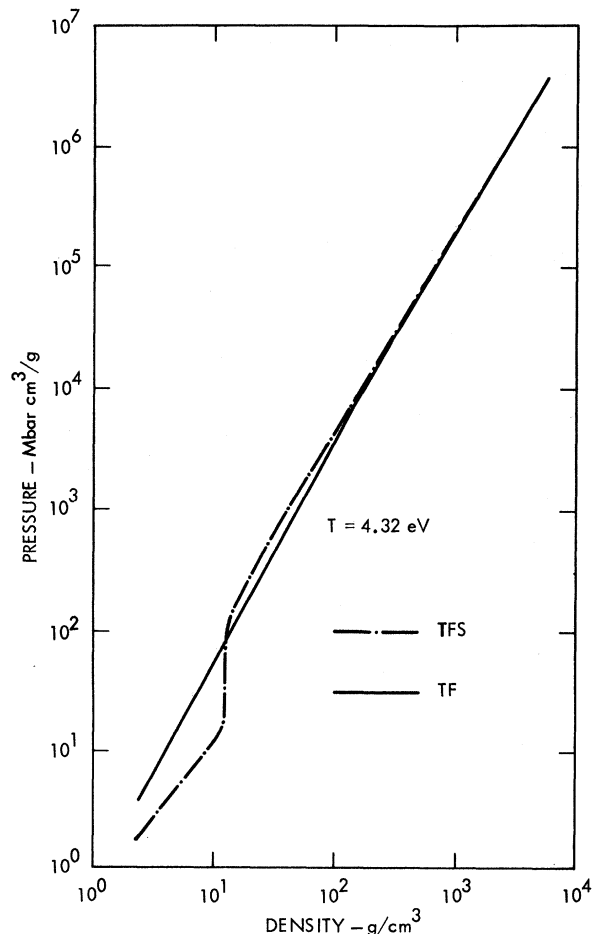


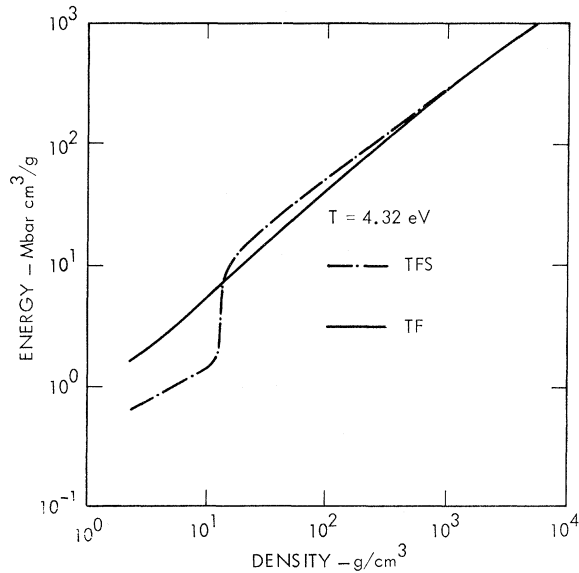FIG. 3. Pressure versus density for lithium.

FIG. 4. Energy versus density for lithium.

this approximation is probably to make the difference between TF and TFS somewhat greater than it should be. However, the mean atom approximation is probably less severe than might at first be thought. When, for example, the first of the two $K$-shell electrons becomes pressure-ionized, the ionization potential of the second electron does not become significantly larger than when the first electron was still bound. This is because the high density inherent in pressure ionization prevents the first electron from leaving the vicinity of the nucleus. The result is that tne screening of the second electron by the first does not change appreciably when the first electron is pressure-ionized. The two electrons, consequently, are pressure-ionized at very nearly the same density. Having the two electrons pressure ionized at exactly the same density is probably a good approximation.

The energy levels obtained using the analytic potential agree well with known values and with values calculated with a TF potential and Schrödinger's equation.

TFS calculations made on heavier elements show more oscillations about TF results, but the oscillations are smaller, for a given shell, the higher the value of $Z$.

It should be noted that other improvements have been made to the TF equation of state, such as the inclusion of exchange and correlation effects. These refinements have been made within the statistical approximation inherent in the TF method. The TFS method is an attempt to do better than the statistical approximation. The TFS method can be considered as an alternative to the quantum corrections of Grover.[6]

The main advantage of including the effects of shell structure on equation-of-state calculations in the manner described here is in the relative simplicity of the calculation. A Hartree-like calculation could be used, but such a calculation would be much more involved and would undoubtedly lead to very much the same sort of results. The whole problem could, of course, be approached more rigorously by including the many-body effects in detail. The object of the present work, however, is to bring out, in a more quantitative way than has been done, the manner in which the often-used TF equation of state is changed when the effect of shell structure is taken into account.

## CONCLUSIONS

The inclusion of shell structure effects in equation-of-state calculations at high pressure indicates that such effects cause significant changes from TF results. The effect of shell structure is to raise or lower the pressure and energy compared to TF theory whenever the temperature and density are such as to allow pressure ionization to be significant.

## ACKNOWLEDGMENTS

*Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] R. P. Feynman, N. Metropolis, and E. Teller, Phys. Rev. 75, 1561 (1949).

[2] R. Latter, Phys. Rev. 99, 1854 (1955), also R. Latter (unpublished).

[3] T. Tietz, Acta Physiol. Acad. Sci. Hung. 9, 73 (1958).

[4] A. Kónya, Acta Physiol. Acad. Sci. Hung. 18, 39 (1964).

[5] N. H. March and J. S. Plaskett, Proc. Roy. Soc. (London) A235, 419 (1956).

[6] R. Grover, J. Math. Phys. 7, 2178 (1966).