16 as used in Eq. (13) the agreement between the qualitative result of Inglis and Teller and that of K.B.M. is improved. For most cases of practical interest $\log(\rho_m/\rho_2)\sim 10$ so that the order of magnitude of the agreement is certainly interesting for densities of practical interest.

For velocities less than $v_0/\sqrt{2}$, Inglis and Teller include the electrons with the ions and treat the entire effect according to the statistical theory. K.B.M. deal with *sharp* electron velocities; their formulas will therefore not reduce to those of the statistical theory, which can only result from a distribution of velocities that allows the electrons to be localized.[9] Hence, in this limit the theories cannot be compared.

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[9] L. Spitzer, Jr. Phys. Rev. 55, 699 (1939); H. Margenau and B. Kivel, Phys. Rev. 98, 1822 (1955).

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Temperature Behavior of the Thomas-Fermi Statistical Model for Atoms

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The usual theoretical calculations of equations of state and specific heats, particularly at high temperatures and pressures, are dependent on the Thomas-Fermi statistical model of the atom. The mathematical description of this model involves complicated nonlinear differential equations, for which there have been an inadequate number of solutions available in the past. A number of solutions sufficiently extensive to determine the thermodynamic properties of all elements over an exceedingly wide range of temperatures and densities have been obtained with the aid of an IBM 701 Defense Calculator. The results are presented in graphical form.

In addition, some of the analytic properties of the Thomas-Fermi equations have been investigated and certain approximate analytic solutions have been derived for limiting cases.

I. INTRODUCTION

THEORETICAL calculations with the Thomas-Fermi atomic model are limited by the necessity of solving a difficult nonlinear differential equation. Only rough analytic approximations have been developed in previous investigations and these are primarily asymptotic solutions with a very restricted range of applicability. Principal emphasis in recent years has been toward the numerical treatment of the model. However, the results available at the present time are almost exclusively concerned with the properties of the model at zero temperature. For the temperature behavior of the Thomas-Fermi model the most detailed calculations have been in the limit of small temperatures and small volumes where the problem may be treated as a perturbation from the zero-temperature model. The formulation and solution of the temperature-perturbed model have been given by Bethe and Marshak.[1] Numerical results have been obtained for this theory by Feynman, Metropolis and Teller,[2] and Gilvarry and Peebles.[3] The temperature perturbation theory has the disadvantage, however, that it requires considerable numerical work and, moreover, that it is limited only to the region of large positive work functions. The negative and small positive work functions encompass, on the other hand, an extensive region of interesting atomic states.

The exact treatment of the temperature effects, without the Bethe-Marshak approximation, does not appear to involve appreciably more numerical work than with the approximation, and, of course, it is not restricted to particular physical states. Unfortunately only a few isolated solutions have been obtained, namely by Feynman, Metropolis and Teller,[2] using the exact Thomas-Fermi model. The calculations to be reported here extend these previous solutions so as to provide a detailed and comprehensive description of the thermodynamic behavior of the model. Exchange effects (see Appendix I) were not included. But in determining the electronic specific heat it is known that exchange effects are almost completely cancelled by the effects of correlation at low temperatures[4]; at high temperatures exchange effects become negligible. And therefore the temperature behavior of the atom may be more adequately described by ignoring exchange altogether if the correlation is not included.

II. DESCRIPTION OF THE THOMAS-FERMI MODEL WITH TEMPERATURE

The statistical model of the atom treats the equilibrium properties of Z electrons constrained to lie within a sphere of radius r_0, at the center of which is a fixed positive charge, $+Ze$. The extension of the model to include ions consists in allowing more or fewer electrons within the sphere than positive charges at the center. The present discussion and calculations will be

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[1] H. A. Bethe and R. E. Marshak, Astrophys. J. 91, 239 (1940).
[2] Feynman, Metropolis, and Teller, Phys. Rev. 75, 1561 (1949).
[3] J. J. Gilvarry and G. Peebles, Phys. Rev. 99, 550 (1955).
[4] D. Pines, Phys. Rev. 92, 626 (1953).

limited to the neutral atom; but ions may be treated by only minor changes in the following arguments.

The electrostatic potential is related to the atomic charge distribution through Poisson's equation[5]

$$\nabla^2 V(\mathbf{r}) = 4\pi e\rho(\mathbf{r}). \tag{1}$$

The Thomas-Fermi model provides a simple estimate of the charge density $-e\rho(\mathbf{r})$ in terms of the potential function $V(\mathbf{r})$. The arguments leading to this connection have been given from a number of independent points of view for the case of zero temperature.[6,7] The extension to nonzero temperatures was given by Feynman, Metropolis and Teller.[2] The result of this extension is that

$$\rho(\mathbf{r}) = \frac{8\pi}{h^3}\int_0^\infty p^2 dp \times \frac{1}{\exp\{[-\alpha + p^2/2m - eV(\mathbf{r})]/kT\}+1}. \tag{2}$$

Equations (1) and (2) can be simplified in appearance by making a few notational changes and requiring that the potential and charge distributions be spherically symmetric. Then it is found that

$$\phi''(x) = axI_{\frac{1}{2}}(\phi(x)/x), \tag{3}$$

where

$$\phi(x) = [\alpha + eV(r)]r/kTr_0, \quad x = r/r_0, \quad a = (r_0/c)^2,$$
$$1/c = 4\pi e(2m)^{\frac{3}{4}}(kT)^{\frac{1}{4}}/h^{\frac{3}{2}},$$

and the Fermi-Dirac function is defined for general n by

$$I_n(\eta) = \int_0^\infty dy y^n \frac{1}{\exp(y-\eta)+1}. \tag{4}$$

The zero of the potential function is chosen at $r = r_0$. The differential equation, Eq. (3), must be supplemented with the boundary conditions on the function $\phi(x)$. These conditions state, on the one hand, that the atomic system is neutral so that the potential gradient at the boundary of the atom is zero and, on the other hand, that the potential function has a singularity at the center of the atom corresponding to a charge $+Ze$ at that point. These boundary conditions, when expressed in the present notation, become

$$\phi'(1) = \phi(1), \tag{5}$$

and

$$\phi(0) = Ze^2/kTr_0. \tag{6}$$

All the thermodynamic properties of the atomic system may be related to the solutions of these equations, Eqs. (3), (5), and (6). The quantities of particular interest are the pressure, kinetic and potential energies, and the entropy, since in terms of these quantities all other thermodynamic functions may be derived explicitly.

The pressure is expressed as the rate of transfer of momentum between the electrons and the atomic boundary. Since at the boundary of the atom the electric field is zero, and consequently the potential is a constant, the electrons behave locally as a uniform gas wherein the only interchange of electron momenta is with the boundary. According to Eq. (2) the density of electrons at position r with momenta in the range dp is

$$\rho(r,p) = \frac{8\pi}{h^3}\frac{p^2}{\exp\{[-\alpha + p^2/2m - eV(r)]/kT\}+1}. \tag{7}$$

Since the electrons are moving isotropically, the rate of momentum transfer to the boundary per electron is

$$(2p)(p/3m), \tag{8}$$

and, hence, the pressure is

$$P = \frac{8\pi}{h^3}\int_0^\infty dp \frac{p^2}{\exp[(-\alpha + p^2/2m)/kT]+1} \times (2p)(p/3m), \tag{9}$$

where $V(r_0) = 0$ has been used. With the help of Eq. (4) this expression for the pressure reduces to

$$P = \frac{ZkT}{V}\frac{2}{9}\frac{a}{\phi(0)}I_{\frac{3}{2}}[\phi(1)]. \tag{10}$$

The kinetic energy per electron is $p^2/2m$, which multiplied by the density of electrons from Eq. (7) and integrated over all momenta and the volume of the atom, leads to the total kinetic energy of the atom. Thus

$$E_{\text{kin}} = \frac{32\pi^2}{h^3}\int_0^{r_0} r^2 dr \int_0^\infty dp \times \frac{p^2}{\exp\{[-\alpha + p^2/2m - eV(r)]/kT\}+1}\frac{p^2}{2m} \tag{11}$$

or, in the present notation,

$$E_{\text{kin}} = ZkT\frac{a}{\phi(0)}\int_0^1 dx x^2 I_{\frac{3}{2}}\left[\frac{\phi(x)}{x}\right]. \tag{12}$$

The potential energy of the electrons results from their mutual interaction and their interaction with the nuclear field. This energy may be expressed as

$$E_{\text{pot}} = -\tfrac{1}{2}(4\pi e)\int_0^{r_0} r^2 dr \rho(r) V_e(r) - 4\pi e\int_0^{r_0} r^2 dr \rho(r) V_n(r), \tag{13}$$

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[5] Throughout this discussion e refers to the magnitude of the electronic charge.

[6] E. Fermi, Atti. Accad. Nazl. Lincei Rend. Classe Fis. Matt. E. Nat. **6**, 602 (1927); Z. Physik **48**, 73 (1928).

[7] L. Brillouin, Actualités Sci. et Ind. **160**, 1 (1934).

where $V_e(r)$ is the potential arising from the electrons and $V_n(r)$ the potential from the nuclear field. This may be written

$$E_{\text{pot}}=-\tfrac{1}{2}(4\pi e)\int_0^{r_0} r^2 dr \rho(r)\left[V(r)+\frac{Z}{r}\right]. \tag{14}$$

Using Eq. (2) and re-expressing Eq. (14) in terms of the present notation, it is found that

$$E_{\text{pot}}=-ZkT\frac{a}{2\phi(0)}\int_0^1 dx I_{\frac{1}{2}}\left[\frac{\phi(x)}{x}\right] \times x[\phi(x)-\phi(1)x+\phi(0)]. \tag{15}$$

An important relationship exists between the quantities E_{pot}, E_{kin}, and P, namely,

$$2E_{\text{kin}}+E_{\text{pot}}=3PV. \tag{16}$$

This expression may be derived directly from Eqs. (10), (12), and (15) or from the virial theorem, which states that

$$2E_{\text{kin}}=I. \tag{17}$$

The approach from the virial theorem is simpler and consists in the evaluation of the virial $I=-\langle\sum_i \mathbf{r}_i\cdot\mathbf{F}_i\rangle_{\text{Av}}$. The angular braces indicate a space (or time) average; the subscript i refers to the ith electron, which is subjected to the force $\mathbf{F}_i$ when at position $\mathbf{r}_i$. The force arises from the mutual electronic interaction, from the electron-nuclear interaction and from collisions with the atomic boundary. The virial I may be decomposed into terms arising from the three sources of the force $\mathbf{F}_i$ as follows:

$$I=I_{ee}+I_{en}+I_{eb}. \tag{18}$$

The last term describes the contribution from the atomic boundary and may be evaluated in terms of the applied pressure P. Thus, since the force applied by the boundary is directed toward the center of the sphere and occurs always at the atomic radius r_0,

$$\begin{aligned} I_{eb}&=-\langle\textstyle\sum_i \mathbf{r}_i\cdot\mathbf{F}_{i(\text{boundary})}\rangle_{\text{Av}}\\ &=\langle r_0 \textstyle\sum_i F_{i(\text{boundary})}\rangle_{\text{Av}}.\end{aligned}$$

Now the time-average boundary force is just the pressure P times the area of the atomic surface and thus may be expressed as

$$I_{eb}=4\pi r_0^3 P=3PV, \tag{19}$$

where V is the volume of one atom. The second term in Eq. (18) results from the force exerted by the nucleus on the electrons. This force is directed toward the nucleus and has the magnitude Ze^2/r_i^2, where r_i is the radial distance to the ith electron. Thus

$$I_{en}=\left\langle\sum_i\frac{Ze^2}{r_i}\right\rangle_{\text{Av}},$$

and the space average of this sum is just the negative of the electron-nuclear potential energy, so that

$$I_{en}=-E_{\text{pot}}^{en}. \tag{20}$$

Finally, the term I_{ee} arises from mutual electronic forces. The force on the ith electron due to all other electrons may be written

$$\mathbf{F}_i=e^2\sum_j\frac{(\mathbf{r}_i-\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^3}.$$

Thus

$$\begin{aligned} I_{ee}&=-e^2\left\langle\sum_i\sum_j\frac{\mathbf{r}_i\cdot(\mathbf{r}_i-\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^3}\right\rangle_{\text{Av}}\\ &=-\frac{e^2}{2}\left\langle\sum_i\sum_j\frac{(\mathbf{r}_i-\mathbf{r}_j)\cdot(\mathbf{r}_i-\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^3}\right\rangle_{\text{Av}}\\ &=-\frac{e^2}{2}\sum_i\sum_j\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|},\end{aligned}$$

which is the negative of the mutual electron potential energy. And, hence,

$$I_{ee}=-E_{\text{pot}}^{ee}. \tag{21}$$

Since the total electronic potential energy is

$$E_{\text{pot}}=E_{\text{pot}}^{ee}+E_{\text{pot}}^{en},$$

Eqs. (17)–(21) establish the statement of Eq. (16).

The derivation of the entropy of the Thomas-Fermi model in terms of the solutions of Eq. (3) has been carried out by Brachman[8] and, more simply, by McMillan and Gilvarry.[9] An alternative derivation, presented below, starts from the partition function, which is related to the entropy through the equation

$$S=E/T+k\ln Q, \tag{22}$$

where E is the total internal energy of the atom and Q is the atomic partition function. It has not been possible so far to derive Q rigorously for the Thomas-Fermi model. A form for it which is, however, consistent with the assumptions of the model may be derived heuristically. Thus consider the atom divided into cells small enough so that the potential is essentially constant in each cell but large enough so that any electrons in a given cell occupy a region of phase space large compared to h^3. The Thomas-Fermi assumptions assert that the electrons occupy each cell independently of the occupation of the other cells within the atom and, moreover, obey Fermi-Dirac statistics. If now $n(\mathbf{r}_i,\mathbf{p},\sigma)$ denotes the number of electrons of momentum $\mathbf{p}$ and spin σ in the cell at position $\mathbf{r}_i$ (which number according to the Fermi-Dirac statistics is 0 or 1), then the total energy of the electrons in this cell is

$$\epsilon(\mathbf{r}_i)=\sum_{\mathbf{p},\sigma} n(\mathbf{r}_i,\mathbf{p},\sigma)[p^2/2m-eV(r_i)], \tag{23}$$

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[8] M. Brachman, Phys. Rev. 84, 1263 (1951).

[9] W. G. McMillan and J. J. Gilvarry (unpublished).

where $eV(r_i)$ is the total potential energy of an electron in this cell. The total energy of the atom is not obtained simply by adding together the contributions $\epsilon(\mathbf{r}_i)$ from each cell since the potential energy $E_{\text{pot}}{}^{ee}$ of mutual electronic interaction would be counted twice. Correcting for this duplication, the total energy of the atom becomes

$$E=-E_{\text{pot}}{}^{ee}+\sum\nolimits_i\epsilon(\mathbf{r}_i). \tag{24}$$

The canonical partition function may now be written

$$Q=\sum_{\{n\}=Z}\exp[-[-E_{\text{pot}}{}^{ee}+\sum_i\epsilon(r_i)]/kT], \tag{25}$$

where the first summation is over all values of $n(\mathbf{r}_i,\mathbf{p},\sigma)$ subject to the constraint that there are a total of Z electrons. Several approximations, which appear consistent with the model, must now be made in order to derive the Thomas-Fermi atom. First, $E_{\text{pot}}{}^{ee}$ is treated as independent of the occupation numbers $n(\mathbf{r}_i,\mathbf{p},\sigma)$ and is taken equal to the mean potential energy of mutual interaction. This assumption is consistent with treating the potential function $V(r_j)$ as independent of $n(\mathbf{r}_i,\mathbf{p},\sigma)$ for all i and j. If now $Z\alpha$, where α is the work-function determined so that Z is the total number of electrons, is added and subtracted in the exponent of Q, then Eq. (25) may be written with the aid of Eq. (23) as

$$Q=\sum_{\{n\}=Z}\exp\left\{-\left[-E_{\text{pot}}{}^{ee}+Z\alpha+\sum_{i,\mathbf{p},\sigma}n(\mathbf{r}_i,\mathbf{p},\sigma)\left(\frac{p^2}{2m}-eV(r_i)-\alpha\right)\right]\bigg/kT\right\}, \tag{26}$$

since $\sum_{i,\mathbf{p},\sigma}n(\mathbf{r}_i,\mathbf{p},\sigma)=Z$. The explicit evaluation of Q is very complicated if the constraint $\{n\}=Z$ is retained. However, if the number of electrons is large, this constraint is unimportant and may be removed. The unrestricted sum is easily evaluated due to the separability of the terms $n(\mathbf{r}_i,\mathbf{p},\sigma)$ in the exponent and is

$$Q=\exp\left[\frac{-(-E_{\text{pot}}{}^{ee}+Z\alpha)}{kT}\right]\times\prod_{i,\mathbf{p},\sigma}\left\{1+\exp\left[-\left(\frac{p^2}{2m}-eV(r_i)-\alpha\right)\bigg/kT\right]\right\}^2. \tag{27}$$

Taking the logarithm of both sides of this equation and replacing the summations by integrations lead to

$$\ln Q=-\frac{(-E_{\text{pot}}{}^{ee}+Z\alpha)}{kT}+\frac{32\pi^2}{h^3}\int_0^{r_0}r^2dr\int_0^\infty p^2dp\times\ln\left\{1+\exp\left[-\left(\frac{p^2}{2m}-eV(r_i)-\alpha\right)\bigg/kT\right]\right\}. \tag{28}$$

In terms of the previous notation, this equation becomes

$$\ln Q=\frac{E_{\text{pot}}{}^{ee}}{kT}-Z\phi(1)+\frac{a}{\phi(0)}\int_0^1x^2dx\int_0^\infty q^{\frac{1}{2}}dq\times\ln\left\{1+\exp\left(-q+\frac{\phi(x)}{x}\right)\right\} \tag{29}$$

where $q=p^2/2mkT$. An integration by parts on q, using Eq. (4), gives finally

$$\ln Q=\frac{E_{\text{pot}}{}^{ee}}{kT}-Z\phi(1)+\frac{2}{3}\frac{a}{\phi(0)}\int_0^1x^2dxI_{\frac{3}{2}}\left(\frac{\phi(x)}{x}\right). \tag{30}$$

It is easily shown that a functional differentiation of $\ln Q$ with respect to $\phi(x)/x$ leads to the Thomas-Fermi form for the charge density and hence Eq. (30) is, in this important respect, compatible with the model. Combining Eqs. (12), (30), and (22) yields the expression for the entropy

$$S/Zk=[(5/3)E_{\text{kin}}+2E_{\text{pot}}{}^{ee}+E_{\text{pot}}{}^{en}]/ZkT-\phi(1). \tag{31}$$

III. ANALYTIC PROPERTIES OF THE THOMAS-FERMI EQUATION

Such properties of Eq. (3) as are relevant to the numerical treatment below will now be investigated. For this purpose it is necessary to re-express Eq. (3) as an integral equation, which provides the basis for the numerical procedure to be used. The transformation of Eq. (3) to integral form consists of a straightforward double integration followed by an integration by parts and leads to the result

$$\phi(x)=\phi(1)x+a\int_x^1dy(y-x)yI_{\frac{1}{2}}\left(\frac{\phi(y)}{y}\right), \tag{32}$$

which incorporates implicitly the boundary condition of Eq. (5). It is necessary, however, to impose an important restriction on the class of physically admissible solutions of Eq. (32), namely, that $\phi(x)$ be bounded on the closed interval $0\leq x\leq 1$. This restriction leads in turn to a considerable limitation on the range of admissible values for the parameters a and $\phi(1)$.

An explicit, analytic demarcation of the allowed region for which a and $\phi(1)$ lead to bounded solutions $\phi(x)$ has not been obtained, but the boundary curve has been found numerically in the region of negative $\phi(1)$ and by an approximate analytic solution for positive $\phi(1)$. If the boundary of the admissible region is denoted by the function $\phi(1)=f(a)$, the region is defined by

$$\phi(1)<f(a). \tag{33}$$

To determine the relation $\phi(1)=f(a)$, it is observed first that if

$$1\geq x_1>x_2\geq 0,$$

then Eq. (32), combined with the positivity of $I_{\frac{1}{2}}(\eta)$, asserts that

$$0\leq\phi(x_1)-\phi(1)x_1<\phi(x_2)-\phi(1)x_2.$$

Thus, $\phi(x)-\phi(1)x$ is a positive, monotonic increasing function for decreasing x. If it is assumed that the solutions $\phi(x)$ of Eq. (32) depend continuously upon the parameters a and $\phi(1)$ in the region where $\phi(x)$ is bounded on the interval $1\geq x\geq 0$, it follows that any singularity in the solution of the integral equation must appear first at $x=0$. The nature of the singularity at $x=0$ is easily shown to be

$$\phi(x)\sim\left(\frac{18}{a}\right)^2\frac{1}{x^3}. \tag{34}$$

The solution with this behavior at $x=0$ should then yield the boundary $\phi(1)=f(a)$ of the admissible region. Now defining $\psi(x)$ by

$$\phi(x)=\left(\frac{18}{a}\right)^2\left(\frac{1}{x^3}\right)\psi(x), \tag{35}$$

and substituting this equation into Eq. (32), $\psi(x)$ is seen to satisfy the integral equation

$$\psi(x)=\left(\frac{a}{18}\right)^2\phi(1)x^4+\left(\frac{a}{18}\right)^2 ax^3\int_x^1 dy(y-x)\times yF\left((18/a)^2\frac{\psi(y)}{y^4}\right). \tag{36}$$

This equation has been solved numerically for $\phi(1)\leqq 0$ to obtain the function $\phi(1)=f(a)$, which defines the allowed region. The required solution $\psi(x)$ must be bounded on the interval $0\leq x\leq 1$ and, by virtue of Eqs. (34) and (35), must have the property

$$\psi(0)=1. \tag{37}$$

Figure 1 shows the resultant curve connecting a and $\phi(1)$, which provides the important boundary for delimiting admissible solutions of Eq. (32). The extension to positive values of $\phi(1)$ was obtained by extrapolating the numerical results for $\phi(1)\leq 0$ so as to agree asymptotically with approximate results from Eq. (82). From the latter equation an approximate expression is obtained for the function $\phi(1)=f(a)$ by allowing $\phi(0)$ and, hence, also α (Eq. (72)) to approach infinity. This leads to an explicit relationship between a and $\phi(1)$, where it is necessary in Eq. (82) to make use of the result[10]

$$\psi_0(\alpha)\sim\frac{290}{\alpha^3},$$

which holds approximately for large α.

The physical significance of the boundary curve $\phi(1)=f(a)$ may be seen from the definition of the quantities $\phi(0)$, $\phi(1)$ and a. Since $\phi(0)$ is infinite along this curve, it may be seen from Eq. (6) that either kT or r_0 is zero. As will be shown below a solution $\phi(x)$ is a monotonic increasing function of $\phi(1)$ for fixed x and a, and therefore the admissible region for bounded solutions is defined by $\phi(1)<f(a)$. But by starting at a given point on $\phi(1)=f(a)$ the work function $\phi(1)$ can be made to decrease only by increasing kT or decreasing r_0. Hence, the boundary curve is defined by $kT=0$ and, from the definition of a, by $r_0=\infty$. Physically, the state of the atom is not uniquely defined by the conditions zero temperature and infinite volume. The atomic state under these conditions depends upon the relative rates at which temperature approaches zero and volume approaches infinity. In the present case, this is prescribed by

$$(kT)^{\frac{1}{2}}V^{\frac{2}{3}}\sim\text{constant}.$$

Under this condition, the atom may be shown to approach its ground state as kT approaches zero.

With the assumption that the bounded solutions of Eq. (32) depend sufficiently smoothly on the parameters a and $\phi(1)$ it is possible to demonstrate certain monotonicity properties of the solutions relative to these parameters. These properties are: (i) $\phi(x)$ increases monotonely as a increases provided x and $\phi(1)$ are held fixed, and (ii) $\phi(x)$ increases monotonely as $\phi(1)$ increases provided x and a are held fixed. To prove (i) the derivative of $\phi(x)$ with respect to a can be found from Eq. (32),

$$\frac{\partial\phi(x)}{\partial a}=\int_x^1 dy(y-x)yI_{\frac{1}{2}}\left(\frac{\phi(y)}{y}\right)+a\int_x^1 dy(y-x)I_{\frac{1}{2}}'\left(\frac{\phi(y)}{y}\right)\frac{\partial\phi(y)}{\partial a}. \tag{38}$$

Differentiating with respect to x,

$$\frac{\partial}{\partial x}\frac{\partial\phi(x)}{\partial a}=-\int_x^1 dyyI_{\frac{1}{2}}\left(\frac{\phi(y)}{y}\right)-a\int_x^1 dyI_{\frac{1}{2}}'\left(\frac{\phi(y)}{y}\right)\frac{\partial\phi(y)}{\partial a}, \tag{39}$$

$$\frac{\partial^2}{\partial x^2}\frac{\partial\phi(x)}{\partial a}=xI_{\frac{1}{2}}\left(\frac{\phi(x)}{x}\right)+aI_{\frac{1}{2}}'\left(\frac{\phi(x)}{x}\right)\frac{\partial\phi(x)}{\partial a}. \tag{40}$$

Since

$$\frac{\partial\phi(x)}{\partial a}=\left.\frac{\partial\phi(x)}{\partial a}\right|_{x=1}+\left.\frac{\partial}{\partial x}\frac{\partial\phi(x)}{\partial a}\right|_{x=1}(x-1)+\left.\frac{\partial^2}{\partial x^2}\frac{\partial\phi(x)}{\partial a}\right|_{x=1}\frac{(x-1)^2}{2}+\cdots, \tag{41}$$

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[10] This result was estimated numerically by examining the behavior of the solutions of the Thomas-Fermi equation for zero temperature.

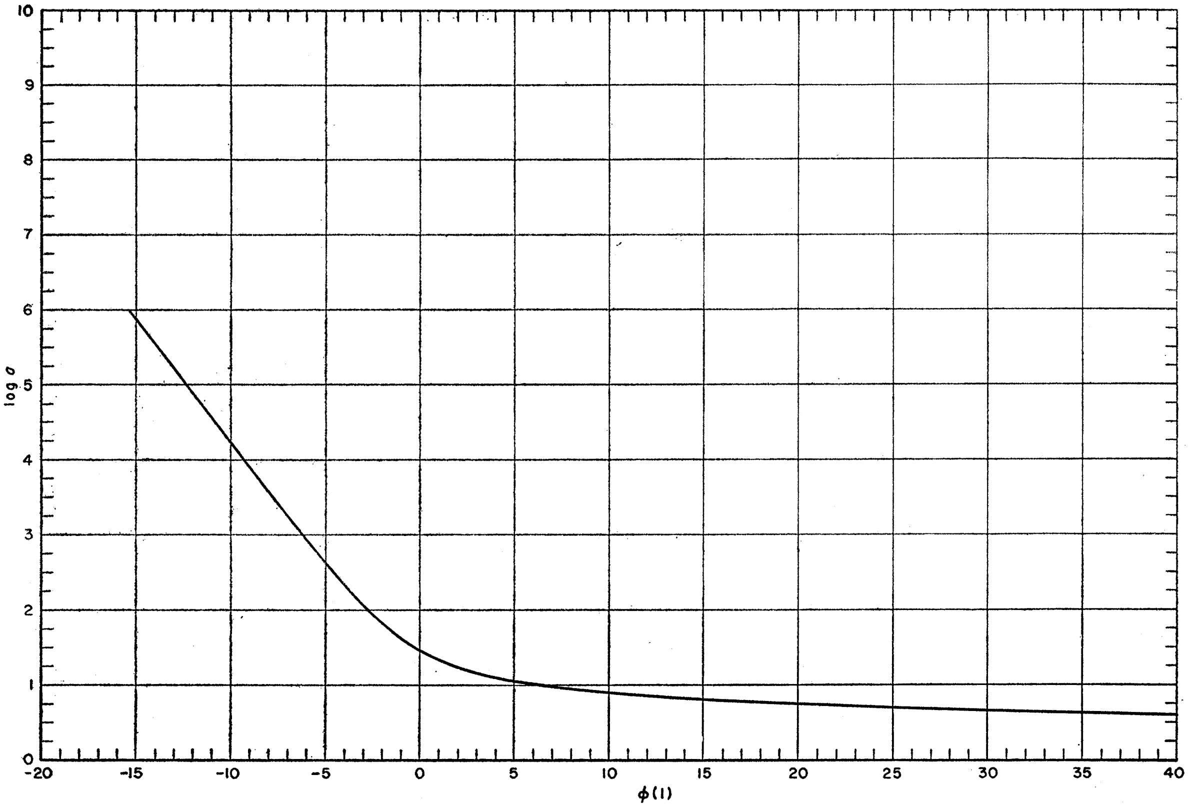

FIG. 1. Boundary curve for the region of admissible solutions of Eq. (32).

it is clear from Eqs. (38), (39), and (40) that

$$\frac{\partial\phi(x)}{\partial a}\sim I_{\frac{1}{2}}(\phi(1))\frac{(x-1)^2}{2}+\cdots. \tag{42}$$

Hence, in a small neighborhood around $x=1$,

$$\frac{\partial\phi(x)}{\partial a}>0. \tag{43}$$

From Eq. (38) it follows that

$$\frac{\partial\phi(x)}{\partial a}>0 \tag{44}$$

everywhere on the interval $0\leq x\leq 1$, since otherwise there would exist a point x_0, $0\leq x_0\leq 1$, for which

$$\frac{\partial\phi(x_0)}{\partial a}=0=\int_{x_0}^{1}dy(y-x_0)yI_{\frac{1}{2}}\left(\frac{\phi(y)}{y}\right) +a\int_{x_0}^{1}dy(y-x_0)I_{\frac{1}{2}}'\left(\frac{\phi(y)}{y}\right)\frac{\partial\phi(y)}{\partial a}. \tag{45}$$

By assumption, however, both integrands in this equation are non-negative on the interval $(x_0,1)$, which denies the existence of the point x_0 and implies that Eq. (44) is true for all x on $(0,1)$. This establishes case (i).

For case (ii), differentiation of Eq. (32) with respect to $\phi(1)$ gives

$$\frac{\partial\phi(x)}{\partial\phi(1)}=x+a\int_{x}^{1}dy(y-x)I_{\frac{1}{2}}'\left(\frac{\phi(y)}{y}\right)\frac{\partial\phi(y)}{\partial\phi(1)}. \tag{46}$$

Since

$$\left.\frac{\partial\phi(x)}{\partial\phi(1)}\right|_{x=1}=1, \tag{47}$$

there exists a neighborhood about $x=1$ for which

$$\partial\phi(x)/\partial\phi(1)>0. \tag{48}$$

The proof that Eq. (48) holds everywhere on the interval $0\leq x\leq 1$ is essentially the same as that given for case (i) and will be omitted.

IV. APPROXIMATE SOLUTIONS OF THE THOMAS-FERMI EQUATION

In this section two approximate solutions for $\phi(x)$ will be developed. They are appropriate to different regions of the $a-\phi(1)$ plane. The first of these concerns the iterates of Eq. (32), given by

$$\phi_{n+1}(x)=\phi(1)x+a\int_{x}^{1}dy(y-x)yI_{\frac{1}{2}}\left(\frac{\phi_n(y)}{y}\right). \tag{49}$$

If

$$\phi_0(x)=\phi(1)x, \tag{50}$$

then

$$\phi_1(x)=\phi(1)x+aI_{\frac{1}{2}}(\phi(1))\left[\frac{(1-x)^2}{2}-\frac{(1-x)^3}{6}\right] \tag{51}$$
$$=\phi(1)x+\tfrac{1}{3}aI_{\frac{1}{2}}(\phi(1))(1-\tfrac{3}{2}x+\tfrac{1}{2}x^3).$$

The next iterate $\phi_2(x)$ involves the integral in Eq. (49) with $n=1$ and does not appear to be analytically evaluable. To estimate the region of applicability of the approximation

$$\phi(x)\approx\phi_1(x), \tag{52}$$

the series expansion of the solution $\phi(x)$ about $x=1$ will be derived. This is useful not only in the present connection but also for the subsequent integration of Eq. (32). The series appears most conveniently obtained indirectly by expanding the function $I_{\frac{1}{2}}(\phi(x)/x)$, defined by Eq. (4), about the point $x=1$. Thus

$$I_{\frac{1}{2}}\left(\frac{\phi(x)}{x}\right)=\sum_{n=0}^{\infty}\frac{A_n}{n!}(1-x)^n, \tag{53}$$

where

$$A_n=\frac{d^n}{dx^n}I_{\frac{1}{2}}\left(\frac{\phi(x)}{x}\right)\Bigg|_{x=1}. \tag{54}$$

With the aid of Eqs. (3) and (5) the expressions for A_n can be evaluated. In particular

$$A_0=I_{\frac{1}{2}}(\phi(1)), \tag{55}$$

$$A_1=0, \tag{56}$$

$$A_2=aI_{\frac{1}{2}}'(\phi(1))\,I_{\frac{1}{2}}(\phi(1)), \tag{57}$$

$$A_3=2aI_{\frac{1}{2}}'(\phi(1))\,I_{\frac{1}{2}}(\phi(1)), \tag{58}$$

$$A_4=3a^2I_{\frac{1}{2}}''(\phi(1))\,I_{\frac{1}{2}}^2(\phi(1))+a^2I_{\frac{1}{2}}'^2(\phi(1))\,I_{\frac{1}{2}}(\phi(1))$$
$$+8aI_{\frac{1}{2}}'(\phi(1))\,I_{\frac{1}{2}}(\phi(1)), \tag{59}$$

$$A_5=20a^2I_{\frac{1}{2}}''(\phi(1))\,I_{\frac{1}{2}}^2(\phi(1))+4a^2I_{\frac{1}{2}}'^2(\phi(1))\,I_{\frac{1}{2}}(\phi(1))$$
$$+40aI_{\frac{1}{2}}'(\phi(1))\,I_{\frac{1}{2}}(\phi(1)), \tag{60}$$

$$A_6=15a^3I_{\frac{1}{2}}'''(\phi(1))\,I_{\frac{1}{2}}^3(\phi(1))+200a^2I_{\frac{1}{2}}''(\phi(1))\,I_{\frac{1}{2}}^2(\phi(1))$$
$$+18a^3I_{\frac{1}{2}}''(\phi(1))\,I_{\frac{1}{2}}'(\phi(1))\,I_{\frac{1}{2}}^2(\phi(1))$$
$$+24a^2I_{\frac{1}{2}}'^2(\phi(1))\,I_{\frac{1}{2}}(\phi(1))+a^3I_{\frac{1}{2}}'^3(\phi(1))\,I_{\frac{1}{2}}(\phi(1))$$
$$+240a^2I_{\frac{1}{2}}'(\phi(1))\,I_{\frac{1}{2}}(\phi(1)). \tag{61}$$

Substitution of Eq. (53) into Eq. (32) leads to

$$\phi(x)=\phi(1)x$$
$$+a\sum_{k=0}^{\infty}\frac{A_k}{k!}\left[\frac{(1-x)^{k+2}}{(k+1)(k+2)}-\frac{(1-x)^{k+3}}{(k+2)(k+3)}\right]. \tag{62}$$

Comparison of this result with Eq. (51) shows that the approximation $\phi_1(x)$ is equivalent to approximating the series by the A_0 term only. Since $A_1=0$, the term A_2 measures the accuracy with which $\phi_1(x)$ represents $\phi(x)$. Thus

$$|\phi(x)-\phi_1(x)|\leq\frac{aA_2}{2}\left[\frac{(1-x)^4}{12}-\frac{(1-x)^5}{20}\right]. \tag{63}$$

It must be understood, however, that Eq. (63) is justified only in case the terms in A_3 and higher are negligible. This point is particularly important in the present case since the series expansion in some regions of the parameters a and $\phi(1)$ is very slowly convergent. This effect becomes quite striking when the term in A_2 is comparable to $\phi_1(x)$. Thus Eq. (63) is valid provided

$$\frac{aA_2}{60}\ll\frac{aA_0}{3}\quad\text{or}\quad\frac{aI_{\frac{1}{2}}'(\phi(1))}{20}\ll 1. \tag{64}$$

Equation (57), combined with Eq. (64), thus defines the region of the parameters a and $\phi(1)$ for which the first iterate $\phi_1(x)$ approximates the solution $\phi(x)$.

The approximation expressed by Eq. (52) has a simple physical interpretation. By comparing the expression for $\phi_1(x)$ from Eq. (51) with the form for $\phi(x)$ derived from assuming a constant electronic charge density, it is observed that $\phi_1(x)$ is the distribution resulting from a central charged nucleus combined with a uniform charge density which has the magnitude given by Eq. (7) with $V(r_0)=0$. Such a constant electron density is reasonable at high temperatures or at low densities where ionization is almost complete. In this limit the thermodynamic functions are easily evaluated from Eqs. (10), (12), (15), and (31). Equations (10) and (31) are unchanged, but Eqs. (12) and (15) simplify to

$$E_{\text{kin}}=\left(\frac{ZkT}{3}\right)\left[\frac{a}{\phi(0)}\right]I_{\frac{3}{2}}(\phi(1)), \tag{12'}$$

and

$$E_{\text{pot}}=-ZkT\left(\frac{11}{20}\right)aI_{\frac{1}{2}}(\phi(1)), \tag{15'}$$

where $\phi(0)=\frac{1}{3}aI_{\frac{1}{2}}(\phi(1))$, as given by Eqs. (51) and (52).

While this approximation gives $\phi(x)$ with reasonable accuracy over a wide range of the parameters a and $\phi(1)$, the energies as specified by Eqs. (12′) and (15′) may be inaccurate. A comparison of this approximation with the numerical results obtained below showed that even if $\phi(1)$ were accurate to one percent, Eq. (12′) was inaccurate by as much as a factor of 1.3 and Eq. (15′) by a factor of 30. However, E_{pot} may be obtained from the virial theorem using the more accurate E_{kin} from Eq. (12′).

Another useful approximation can be obtained if the restriction is made that

$$\phi(1)\geq 0. \tag{65}$$

In this case the function $I_{\frac{1}{2}}(\eta)$ of Eq. (4) is approximated by

$$I_{\frac{1}{2}}(\eta)\sim A+\tfrac{2}{3}\eta^{\frac{3}{2}}. \tag{66}$$

The choice of the constant A is made to depend upon the region of interest for η. From Eq. (32), it is clear that

$$\eta=\phi(y)/y\geq\phi(1). \tag{67}$$

Hence, a reasonable choice[11] appears to be

$$A=I_{\frac{1}{2}}(\phi(1))-\tfrac{2}{3}\phi^{\frac{3}{2}}(1); \tag{68}$$

that is,

$$I_{\frac{1}{2}}(\eta)\sim\{I_{\frac{1}{2}}(\phi(1))-\tfrac{2}{3}\phi^{\frac{3}{2}}(1)\}+\tfrac{2}{3}\eta^{\frac{3}{2}}. \tag{69}$$

The accuracy of this approximation is in general better than 5 percent for $\phi(1)>0$ and increases rapidly with increasing $\phi(1)$. Using Eq. (69) for $I_{\frac{1}{2}}(\eta)$, Eq. (32) becomes

$$\phi(x)=\phi(1)x+\gamma(x)+\frac{2a}{3}\int_x^1 dy(y-x)\frac{\phi^{\frac{3}{2}}(y)}{y^{\frac{1}{2}}} \tag{70}$$

where $\gamma(x)=(aA/3)(1-\frac{3}{2}x+\frac{1}{2}x^3)$ and A is given by Eq. (68). In terms of the quantities

$$\psi(\alpha x)=\phi(x)/\phi(0), \tag{71}$$

$$\alpha=[\tfrac{2}{3}a\phi^{\frac{1}{2}}(0)]^{\frac{2}{3}}, \tag{72}$$

and by changing scale to

$$u=\alpha x,\quad v=\alpha y, \tag{73}$$

Eq. (70) may be expressed as

$$\psi(u)=\psi(\alpha)\frac{u}{\alpha}+\frac{\gamma(u/\alpha)}{\phi(0)}+\int_u^\alpha dv(v-u)\frac{\psi^{\frac{3}{2}}(v)}{v^{\frac{1}{2}}}. \tag{74}$$

Except for the second term on the right-hand side, this equation is identical with the Thomas-Fermi equation for zero temperature, which suggests that a perturbation solution be looked for. Let

$$\psi(u)=\psi_0(u)+\epsilon(u), \tag{75}$$

where

$$\psi_0(u)=\psi_0(\alpha)\frac{u}{\alpha}+\int_u^\alpha dv(v-u)\frac{\psi_0^{\frac{3}{2}}(v)}{v^{\frac{1}{2}}}. \tag{76}$$

If it is assumed that

$$\psi_0(0)=\psi(0)=1, \tag{77}$$

then

$$\epsilon(0)=0,\quad \epsilon'(\alpha)=\epsilon(\alpha)/\alpha, \tag{78}$$

and

$$\epsilon(u)=\epsilon(\alpha)\frac{u}{\alpha}+\frac{\gamma(u/\alpha)}{\phi(0)}+\int_u^\alpha dv(v-u)\frac{\psi^{\frac{3}{2}}(v)-\psi_0^{\frac{3}{2}}(v)}{v^{\frac{1}{2}}}. \tag{79}$$

An approximate solution to this equation is obtained by iteration, assuming, to begin with, that $\epsilon(v)$ in the integrand may be replaced by $\epsilon(\alpha)(v/\alpha)$. Moreover, if $\epsilon(u)\ll\psi_0(u)$,

$$0=\frac{\gamma(0)}{\phi(0)}+\frac{3}{2}\frac{\epsilon(\alpha)}{\alpha}\int_0^\alpha dv v^{\frac{3}{2}}\psi_0^{\frac{1}{2}}(v). \tag{80}$$

Since the integrand in this equation contains the factor $v^{\frac{3}{2}}$, the important contribution arises in the region of the large values of v. But when v is large,

$$\psi_0(v)\sim\psi_0(\alpha)v/\alpha \tag{81}$$

as seen from Eq. (76). Combining Eqs. (80) and (81),

$$\frac{\phi(1)}{\phi(0)}=\psi_0(\alpha)-\tfrac{2}{3}a\frac{I_{\frac{1}{2}}(\phi(1))-\frac{2}{3}\phi^{\frac{3}{2}}(1)}{\phi(0)\alpha^{\frac{3}{2}}\psi_0^{\frac{1}{2}}(\alpha)}, \tag{82}$$

where α is given by Eq. (72). Equation (82) determines $\phi(0)$ implicitly when the basic parameters a and $\phi(1)$ are specified and the solution of Eq. (76) is known. Finally then the approximation for $\phi(x)$ is given by

$$\phi(x)\approx\phi(0)\psi_0(\alpha x)-\tfrac{2}{3}a\frac{I_{\frac{1}{2}}(\phi(1))-\frac{2}{3}\phi^{\frac{3}{2}}(1)}{\alpha^{\frac{3}{2}}\psi_0^{\frac{1}{2}}(\alpha)}x. \tag{83}$$

When $\phi(1)$ is large, only the first term on the right-hand side is important; in this case, solutions of the temperature-dependent problem are found by simply rescaling the zero temperature Thomas-Fermi solutions.

The accuracy of this approximation has been investigated by computing $\phi(1)$ from Eq. (82) for given temperatures and volumes and comparing the results with the results from numerical integrations of the Thomas-Fermi equation. The accuracy of Eq. (82) was found to be better than one percent for $\phi(1)>4$; it was about two percent for $\phi(1)>2$ and better than ten percent for $\phi(1)>1$. For temperatures and volumes corresponding to $\phi(1)=0$, Eq. (82) predicted that $|\phi(1)|<0.3$.

The pressure is calculated in this approximation by a straightforward use of Eqs. (82) and (10). On the other hand, the energies and the entropy require integrations involving the solutions $\psi_0(\alpha x)$ of the zero-temperature Thomas-Fermi equation, which integrations have not been carried out in view of the nonapproximate numerical calculations discussed below.

V. NUMERICAL SOLUTION OF THE THOMAS-FERMI EQUATION

The numerical scheme for treating Eq. (32) consists in replacing the integral in the latter equation by a k-point numerical integration formula. This was taken to be the ordinary Simpson's rule, which is a three-point formula and has the particular advantage that the numerical accuracy is in the fourth power of the interval size.

Before describing further the details of the numerical formulation, it is necessary to make some remarks about the nature of the functions $\phi(x)$ and $I_{\frac{1}{2}}(\eta)$. In the first place, the function $\phi(x)$, which is directly related to the potential distribution within the atom, changes most rapidly in the neighborhood of the origin since, in general, the greatest charge density occurs there. It seemed desirable, therefore, to emphasize the

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[11] This form was suggested by D. Liberman.

neighborhood of $x=0$ by making a change of variable, namely,

$$x=u^2 \quad \text{and} \quad y=v^2. \tag{84}$$

In these variables, Eq. (32) becomes

$$\phi(u)=\phi(1)u^2+2a\int_u^1 dv(v^2-u^2)v^3 I_{\frac{1}{2}}\left(\frac{\phi(v)}{v^2}\right). \tag{85}$$

The division points for the numerical integration are then made on the variable u.

The next point concerns the function $I_{\frac{1}{2}}(\eta)$, which is defined in Eq. (4). Tables of this function for a large range of its argument were obtained by Stoner and McDougall.[12] By numerical fitting of the tables with polynomials and by using asymptotic expansions for $I_{\frac{1}{2}}(\eta)$ outside the range of the tables, a set of simple analytic forms which are conveniently handled numerically were derived. Explicitly, these forms are:

(i) $-\infty<\eta\leq -2.0$,

$$I_{\frac{1}{2}}(\eta)=\frac{\sqrt{\pi}}{2}e^{\eta}\left[1-\frac{e^{\eta}}{2^{\frac{3}{2}}}+\frac{e^{2\eta}}{3^{\frac{3}{2}}}-\frac{e^{3\eta}}{4^{\frac{3}{2}}}+\frac{e^{4\eta}}{5^{\frac{3}{2}}}-\frac{e^{5\eta}}{6^{\frac{3}{2}}}+\frac{e^{6\eta}}{7^{\frac{3}{2}}}\right], \tag{86}$$

(ii) $-2.0\leq\eta\leq 0$,

$$\begin{aligned}I_{\frac{1}{2}}(\eta)=0.678091+0.53619667\eta+0.16909748\eta^2&\\ +0.018780823\eta^3-0.0023575446\eta^4&\\ -0.000639610797\eta^5&,\end{aligned} \tag{87}$$

(iii) $0\leq\eta\leq 3.0$,

$$\begin{aligned}I_{\frac{1}{2}}(\eta)=0.678091+0.53638\eta+0.1668235\eta^2&\\ +0.0206067\eta^3-0.00601491\eta^4+0.000490398\eta^5&,\end{aligned} \tag{88}$$

(iv) $3.0\leq\eta\leq 10.0$,

$$\begin{aligned}I_{\frac{1}{2}}(\eta)=0.757064709+0.3922888\eta+0.2705525\eta^2&\\ -0.01682933\eta^3+0.0008258364\eta^4&\\ -0.00001819771\eta^5&,\end{aligned} \tag{89}$$

(v) $10.0\leq\eta\leq 10^5$,

$$I_{\frac{1}{2}}(\eta)=\tfrac{2}{3}\eta^{\frac{3}{2}}\left[1+\frac{1.2337005}{\eta^2}+\frac{1.0654119}{\eta^4}+\frac{9.7015185}{\eta^6}+\frac{242.71502}{\eta^8}+\frac{12313.691}{\eta^{10}}\right], \tag{90}$$

(vi) $10^5\leq\eta<\infty$,

$$I_{\frac{1}{2}}(\eta)=\tfrac{2}{3}\eta^{\frac{3}{2}}. \tag{91}$$

The fractional error in the fitting of these functions to Eq. (4) was estimated from the tables given by Stoner and McDougall to be at most 6×10^{-5} and, except for a few isolated regions, less than 1×10^{-5}.

Finally, it is necessary to stipulate the accuracy with which $\phi(x)$ must be calculated. Since the Thomas-Fermi model of an atomic system is only a crude approximation to an actual system, it might seem at first that rough accuracy for $\phi(x)$ would be sufficient. A difficulty arises, however, in determining the total energy of the system. An atomic system has, in its ground state, total energies varying from about 10 ev to about 10^6 ev. In estimating the effect of temperature and pressure, it is necessary to evaluate the change in the total energy of the atom in proceeding from one state to a neighboring one. The important physical quantity is this change in the energy, which in cases of interest may be as small as 1 to 10 ev. This implies that for atoms with the largest total binding energies, accuracies of the order of one part in 10^7 to 10^8 are necessary. Moreover, additional figures must be carried in the individual component numbers in order to absorb the inevitable rounding and truncation errors. In the present work, ten figures were employed on all numbers. To insure the desired accuracy of one part in 10^8, the numerical integration of Eq. (85) was repeated, halving each time the interval size in the integration scheme. It is clear, of course, that two such successive integrations need only agree to 2 parts in 10^7 since in using Simpson's rule the error decreases with the fourth power of the interval size; if two integrations agree to 2×10^{-7}, the one with the smaller interval size will have the fractional accuracy of 10^{-8}.

In accordance with the previous remarks, $\phi(x)$ is to be determined from the difference equations corresponding to Eq. (85), replacing the integral by a Simpson's rule sum. In particular if the division points for the integration are denoted by u_n and if the subscript n is used to indicate that a function is evaluated at u_n, then the basic difference equations become

$$\phi_n=\phi(1)u_n^2+2a[Q_n-u_n^2P_n], \tag{92}$$

where

$$Q_n=\frac{\Delta u}{3}[g_n+4g_{n+1}+g_{n+2}]+Q_{n+2}, \tag{93}$$

$$P_n=\frac{\Delta u}{3}[f_n+4f_{n+1}+f_{n+2}]+P_{n+2}, \tag{94}$$

$$g_n=u_n^5 I_{\frac{1}{2}}(\phi_n/u_n^2), \tag{95}$$

$$f_n=u_n^3 I_{\frac{1}{2}}(\phi_n/u_n^2), \tag{96}$$

or

$$\begin{aligned}\phi_n=\phi(1)u_n^2+2a\{\tfrac{1}{3}\Delta u[(4g_{n+1}+g_{n+2})&\\ -u_n^2(4f_{n+1}+f_{n+2})]+Q_{n+2}-u_n^2P_{n+2}\}&,\end{aligned} \tag{97}$$

where $\Delta u=1/N$ and N is the total numbers of integration points. To initiate the solution of Eq. (97), it is necessary to specify $\phi(u)$, $P(u)$ and $Q(u)$ at the first two points of the integration. These can be evaluated from Eq. (62). Namely,

(i) $\phi_N=\phi(1)$,

$Q_N=0$,

$P_N=0$,

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[12] J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. (London) **237**, 67 (1938).

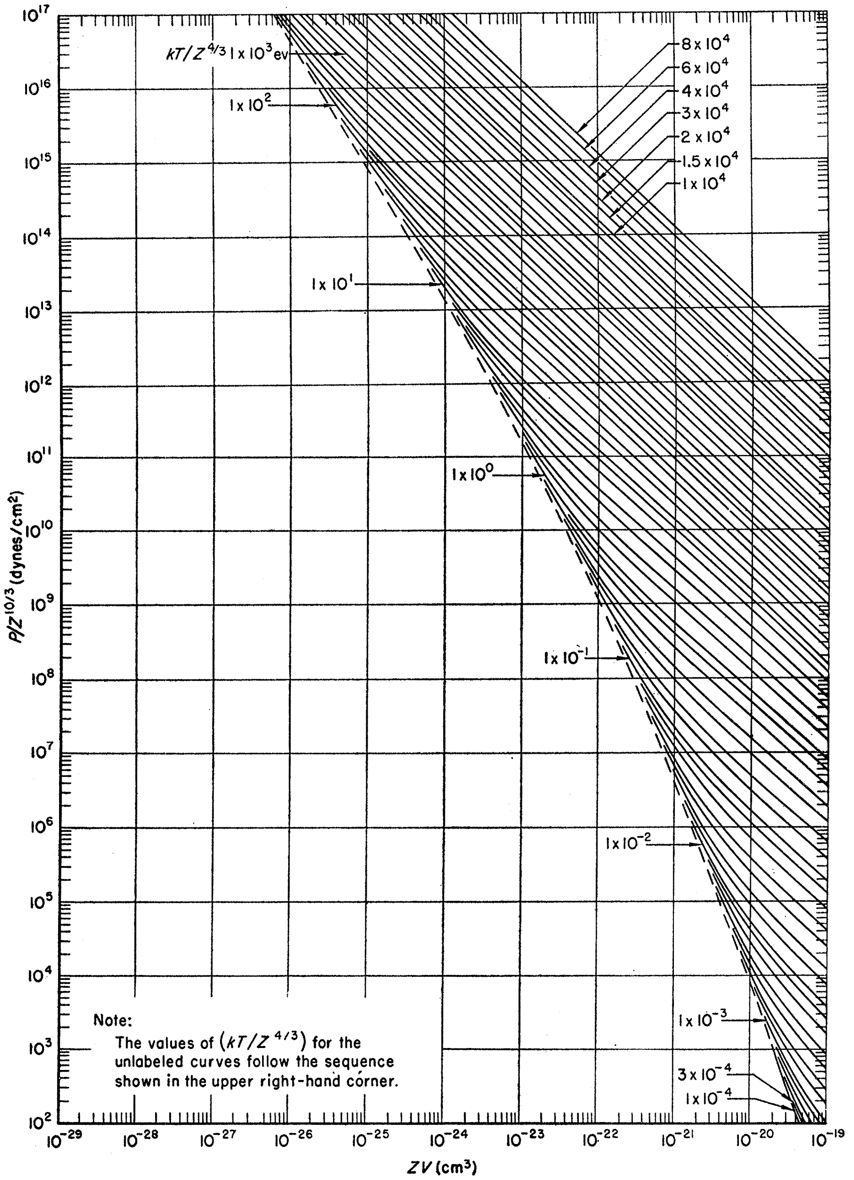

FIG. 2. Pressure *versus* volume for fixed temperature.

(ii)
$$\phi_{N-1}=\phi(1)u_{N-1}{}^2+a\sum_{k=0}^{3}\frac{A_k}{k!}\times\left[\frac{(1-u_{N-1}{}^2)^{k+2}}{(k+1)(k+2)}-\frac{(1-u_{N-1}{}^2)^{k+3}}{(k+2)(k+3)}\right],$$

$$P_{N-1}=\tfrac{1}{2}\sum_{k=0}^{3}\frac{A_k}{k!}\left[\frac{(1-u_{N-1}{}^2)^{k+1}}{k+1}-\frac{(1-u_{N-1}{}^2)^{k+2}}{k+2}\right],$$

$$Q_{N-1}=-\tfrac{1}{2}\sum_{k=0}^{3}\frac{A_k}{k!}\left[\frac{(1-u_{N-1}{}^2)^{k+2}}{k+2}-\frac{(1-u_{N-1}{}^2)^{k+3}}{k+3}\right]+\tfrac{1}{2}\sum_{k=0}^{3}\frac{A_k}{k!}\left[\frac{(1-u_{N-1}{}^2)^{k+1}}{k+1}-\frac{(1-u_{N-1}{}^2)^{k+2}}{k+2}\right],$$

where the coefficients A_k are defined in Eqs. (55)–(58). Terms up to A_3 only are needed to give accuracy consistent with Simpson's rule.

The integration procedure itself is immediately clear from the difference equations. However, it was found convenient to permit changes of interval size in the course of the computation, which necessitates interpolation for intermediate values of $\phi(u)$, $P(u)$, and $Q(u)$. Cubic interpolation had to be used in order that the error be again consistent with the Simpson's formula.

VI. NUMERICAL RESULTS

The calculations, described in the preceding section, were carried out on the IBM 701 Defense Calculator. Solutions to Eq. (85) were obtained for about 1000 sets of values of the parameters a and $\phi(1)$, covering a

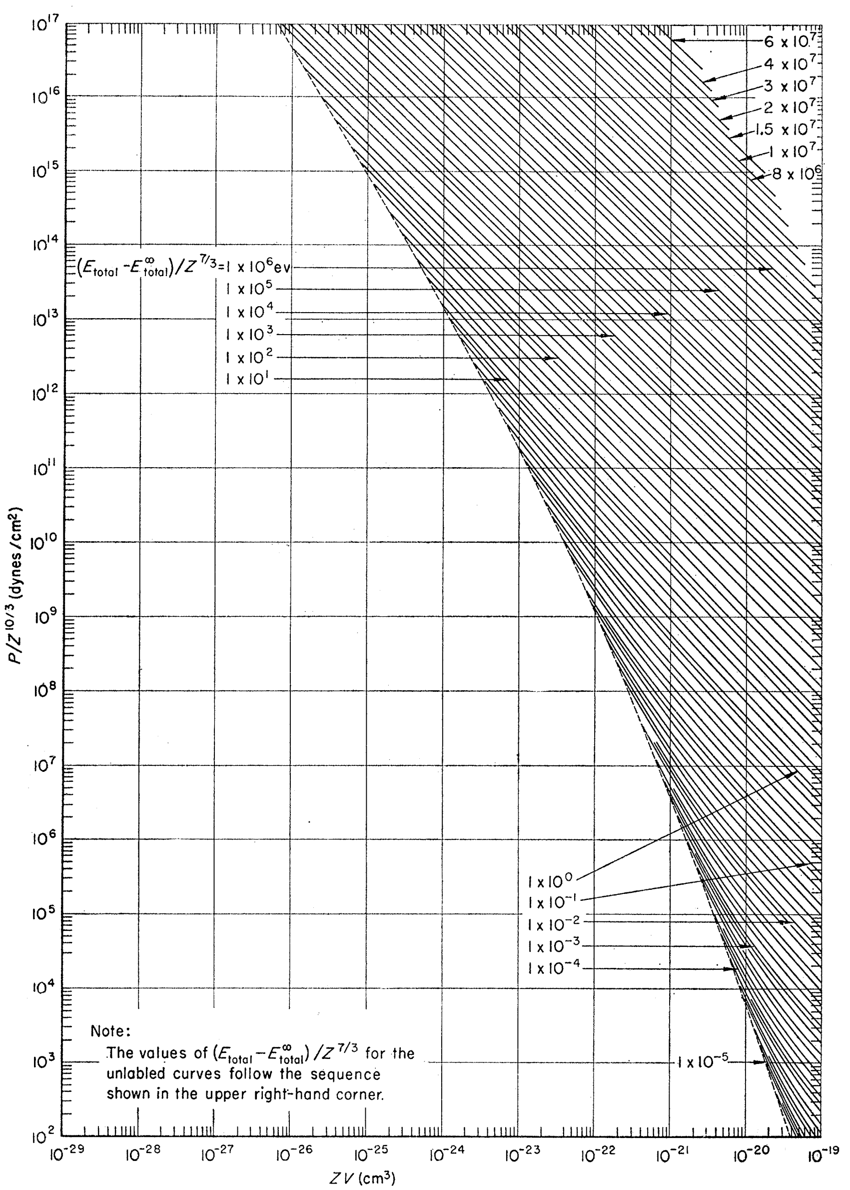

FIG. 3. Pressure *versus* volume for fixed total energy.

range of temperatures from about 10^{-4} ev–10^{5} ev. The particular values of a and $\phi(1)$ were selected to encompass a reasonably complete range of physically interesting atomic states and for ease of interpolation. The resultant physical data[13] are presented in Figs. 2 to 6. A more precise presentation of the data does not appear justified in view of the approximate character of the model.

For clarity in the data, the solutions obtained for particular values of a and $\phi(1)$ were interpolated to intermediate solutions with prescribed values of temperature, energy, or entropy. This procedure involved quadratic interpolation on the basic solutions and consequently introduced a significant depreciation in the accuracy of the data. A check was made on the final accuracy of the data and was found to be in general better than one-tenth percent, with some reservation with respect to the energies and entropy at very low temperatures. The entropy which is graphed in Fig. 4 involves, as can be seen from Eq. (31), the calculation of differences between large numbers, which differences approach zero as the temperature approaches zero. Thus because of the limitation on the number of digits which are carried within the machine, the entropy decreases in numerical accuracy with decreasing temperature. This comment also applies to the quantities $\Delta E_{\rm tot}/Z^{7/3}$ and $\Delta E_{\rm kin}/Z^{7/3}$ which are graphed in Figs. 3,

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[13] The physical parameters employed in these calculations were $m=9.10710\times10^{-28}$ g, $e=4.80217\times10^{-10}$ esu, and $h=6.62363\times10^{-27}$ erg-sec. The conversion factor between electron volts and ergs was taken to be 1.6020×10^{-12}.

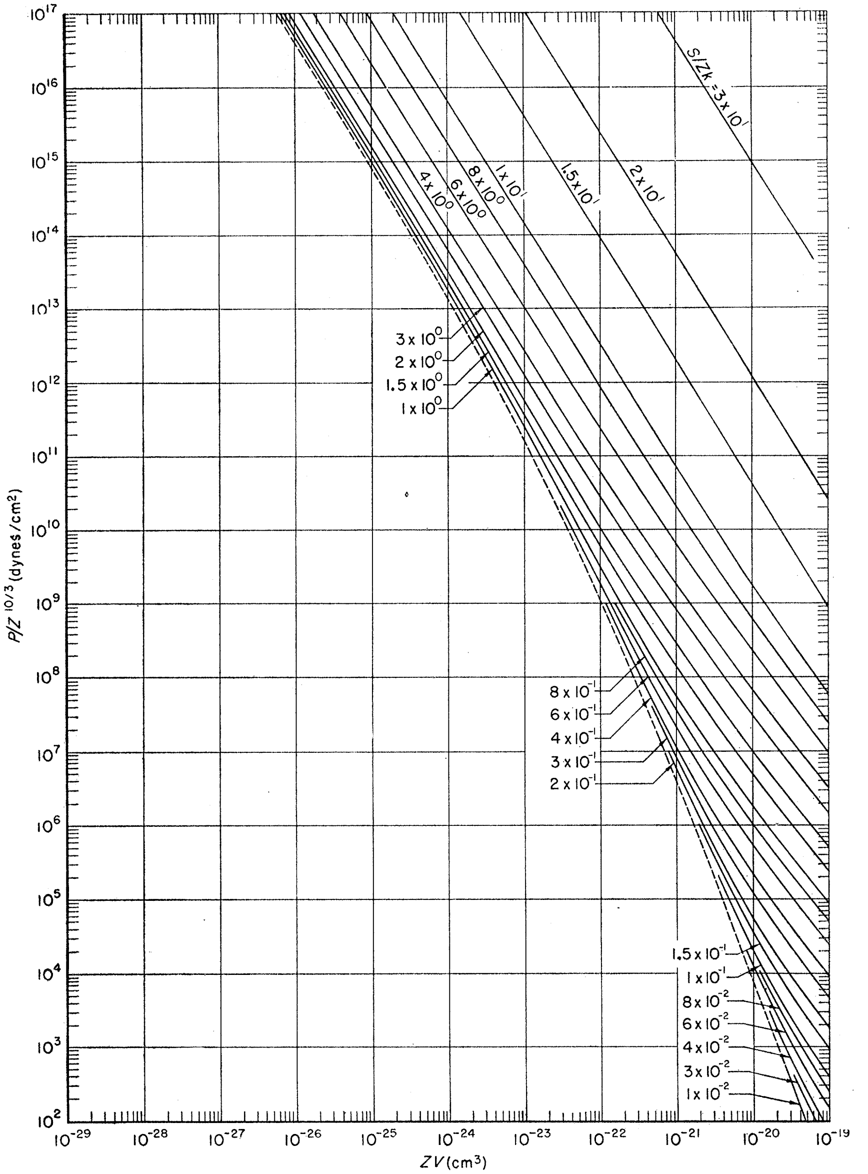

FIG. 4. Pressure *versus* volume for fixed entropy.

5, and 6.[14] These quantities are the differences in the energies of the atom in the prescribed state of temperature and volume and the energies of the atom in its isolated state at zero temperature. $\Delta E_{\text{pot}}/Z^{7/3}$ and the ungraphed region of $\Delta E_{\text{kin}}/Z^{7/3}$ may be obtained approximately from Figs. 2 and 5 by using the virial theorem of Eq. (16). To complete the definition of these energies, it is observed that

$$E^{\infty}{}_{\text{tot}}/Z^{7/3}=-E^{\infty}{}_{\text{kin}}/Z^{7/3}=\tfrac{1}{2}E^{\infty}{}_{\text{pot}}/Z^{7/3}=-20.913065\text{ ev}.$$

The evaluation of these numbers was carried out numerically for the isolated atom at zero temperature. The pressure does not involve differences of large numbers and, consequently, has a uniform accuracy. Similarly, the basic parameter $\phi(0)$, which is shown in Fig. 7, is in general accurate to about one-tenth percent.

There exist some regions of the parameters a and $\phi(1)$ which were not explored, either because they were in physically uninteresting regions or because the states in these regions were negligibly different from the zero temperature states. Also the potential distributions $\phi(x)$, which were determined in the calculations, comprise too large a body of numbers to present conveniently. However, with the aid of the parameter values, a and $\phi(1)$, and $\phi(0)$ of Fig. 7, and the integration formulas, a relatively accurate and simple calculation for $\phi(x)$ may be carried out manually in any specific case.

As a final point, a comparison of the present exact

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[14] The irregularity of Fig. (6) results from the existence of a region of small negative $\Delta E_{\text{kin}}/Z^{7/3}$ which is not conveniently graphed.

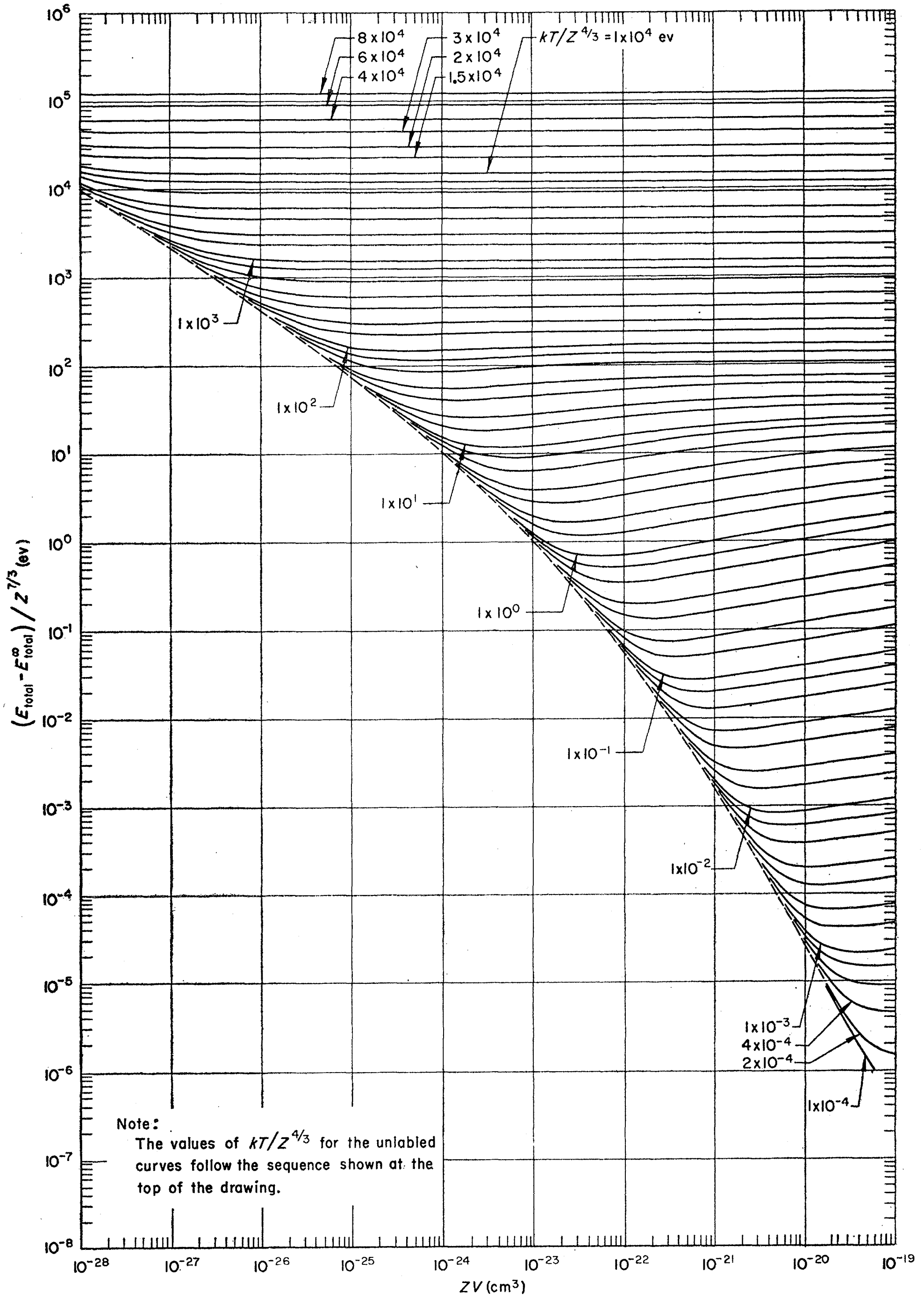
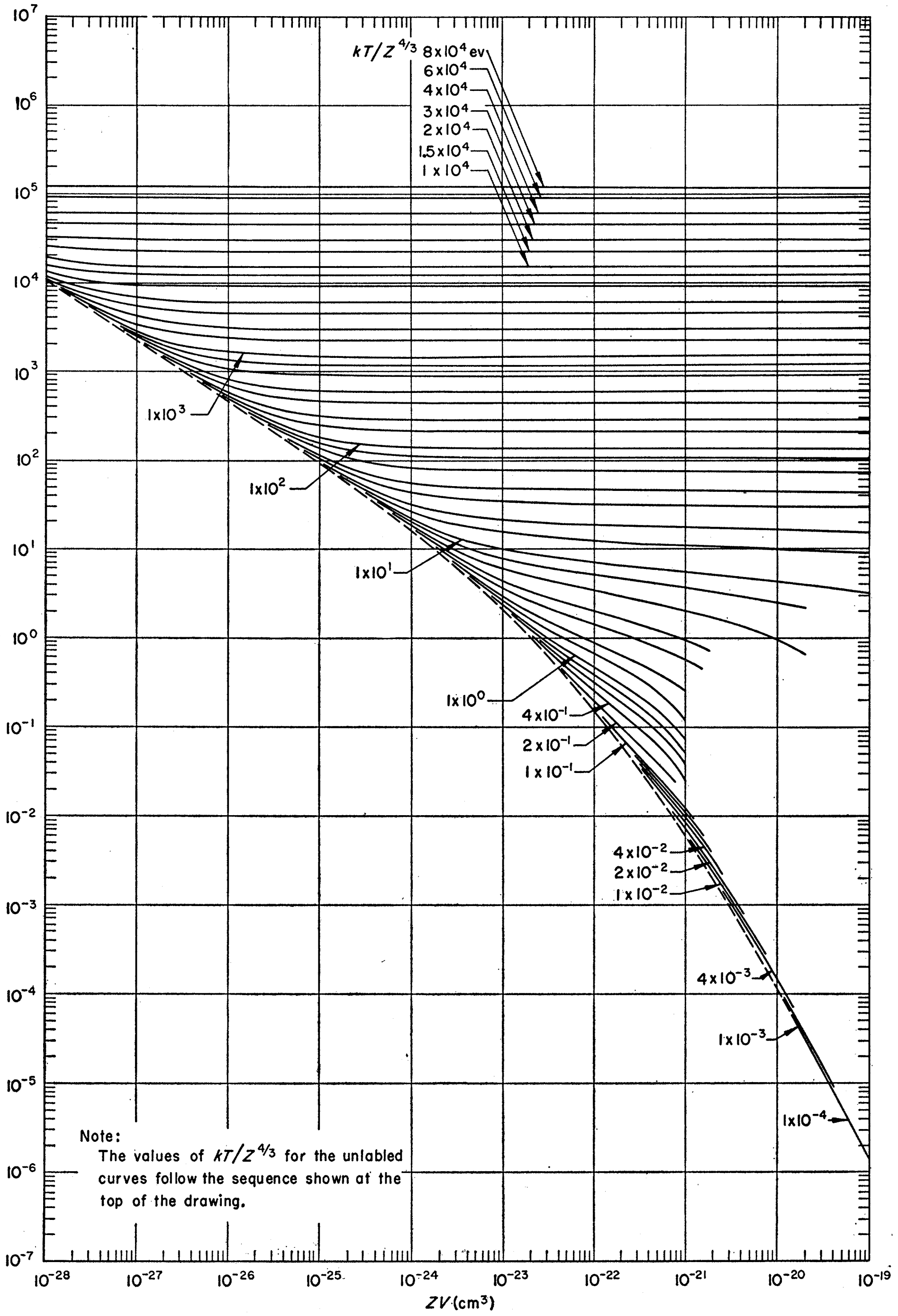


FIG. 5. Total energy *versus* volume for fixed temperature.

results with the results of the temperature-perturbation procedure[3] and with the calculations of Feynman, Metropolis, and Teller[2] has been made. In Figs. 8 and 9, pressures and energies are compared with those derived from the temperature-perturbation procedure, and in Figs. 10 and 11 this same comparison is presented in terms of the scaled variables of that method. The domain of applicability of the perturbation approach is limited to work-functions $\phi(1)$ large compared with unity as a consequence of the asymptotic expansion employed in that method. This region lies below the curves labeled $\phi(1)=1$ in Figs. 8 and 9. It may be observed from Figs. 8 and 9 that the temperature-perturbation method gives satisfactory accuracy in a region which differs by a factor less than about $1\frac{1}{2}$ in pressure and by a factor less than about $1\frac{1}{2}$ to 3 in



Note: The values of $kT/Z^{4/3}$ for the unlabled curves follow the sequence shown at the top of the drawing.

FIG. 6. Kinetic energy *versus* volume for fixed temperature.

energy from the zero-temperature results. When the deviation from the zero-temperature behavior becomes larger, the perturbation results, not unexpectedly, of course, involve sizable errors. Finally, Table I compares the results of Feynman, Metropolis, and Teller (Table XI of reference 2) with the present calculations. This comparison was made by repeating, with the above discussed numerical procedure, the integrations of Feynman, Metropolis, and Teller for the parameter values a and $\phi(1)$ corresponding to their values of $b=a^{\frac{1}{2}}$ and $\beta_b=b\phi(1)$. Since the accuracy of the present calculations is one part in 10^7 to 10^8, the discrepancies in the two sets of data appear to be due to typographical errors or small numerical inaccuracies in the integrations by Feynman, Metropolis, and Teller.

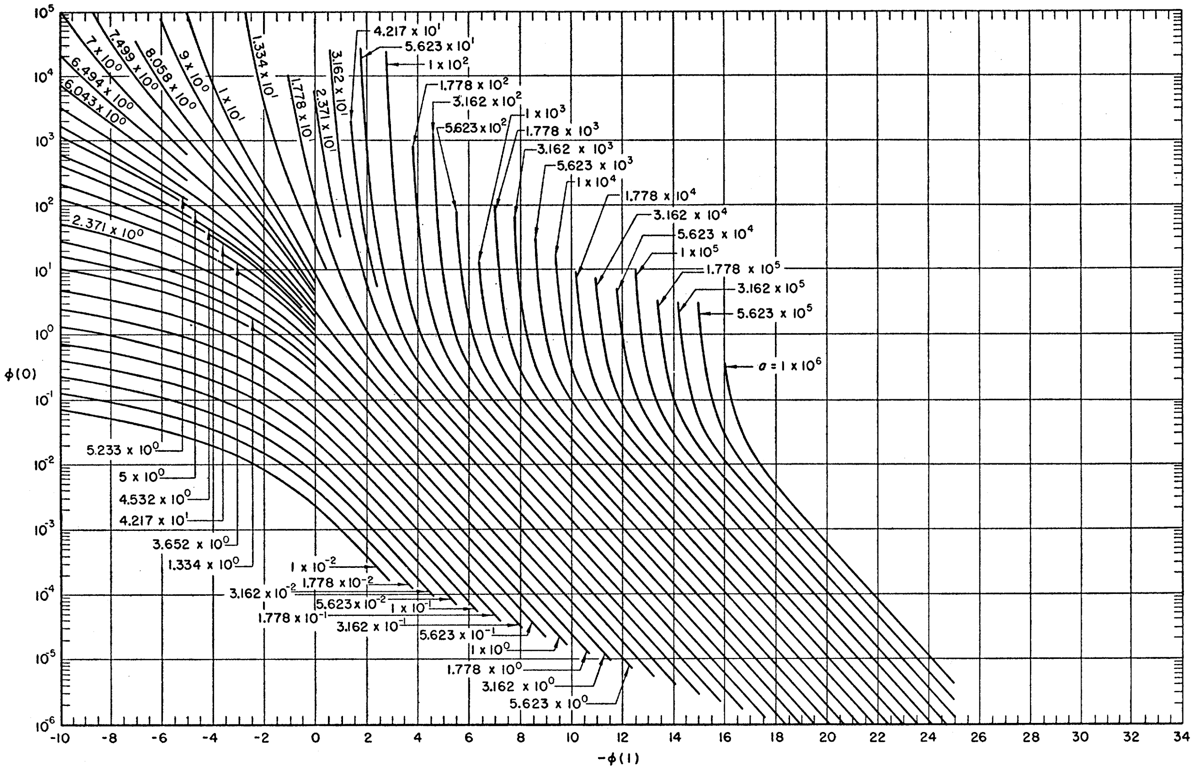


FIG. 7(a). $\phi(0)$ *versus* $\phi(1)$ for fixed a.

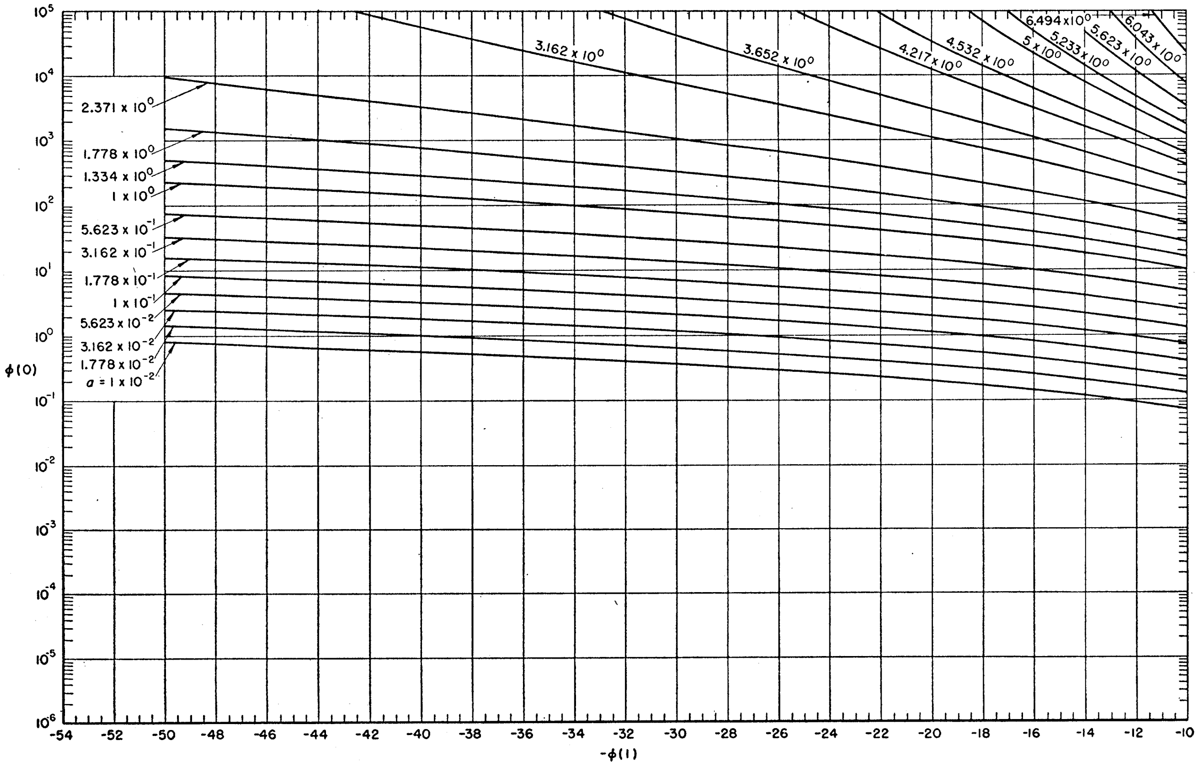


FIG. 7(b). $\phi(0)$ *versus* $\phi(1)$ for fixed a.

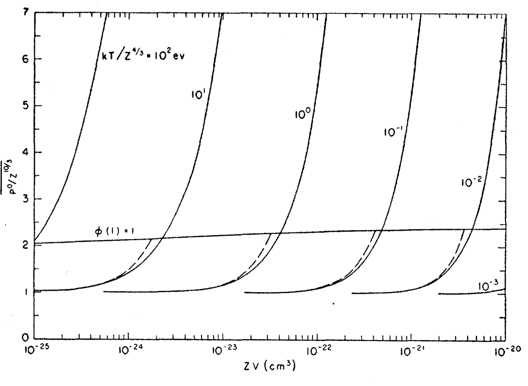


FIG. 8. Comparison of the exact calculations (solid curves) with the results of the temperature-perturbation calculation (dashed curve). P^0 denotes the pressure at zero temperature and at the volume ZV.

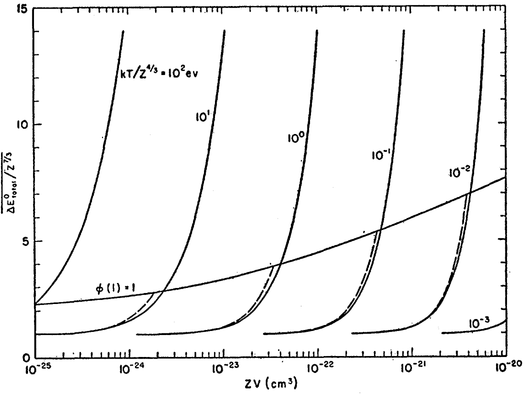


FIG. 9. Comparison of the exact calculations (solid curves) with the results of the temperature-perturbation calculation (dashed curve). $\Delta E_{\text{total}}{}^0$ denotes the difference in total energy between the state of zero temperature and infinite volume and of zero temperature and volume ZV.

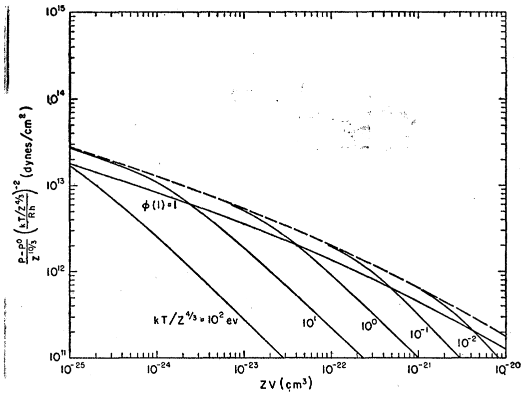


FIG. 10. Comparison of the exact calculations (solid curves) with the results of the temperature-perturbation calculation (dashed curve) in terms of the scaled variables of the temperature-perturbation model. Rh denotes a rydberg; P^0 is defined in Fig. (8).

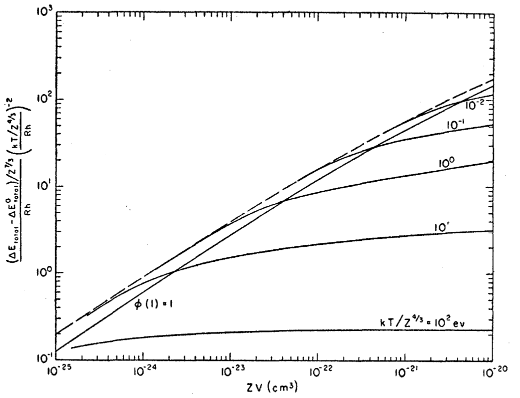


FIG. 11. Comparison of the exact calculations (solid curves) with the results of the temperature-perturbation calculation (dashed curve) in terms of the scaled variables of the temperature-perturbation model. Rh denotes a rydberg; $\Delta E_{\text{total}}{}^0$ is defined in Fig. (9).

TABLE I.[a] Comparison of the calculations of (a) Feynman, Metropolis, and Teller with (b) present calculations.

		a	$\phi(1)$	$\frac{kT}{Z^{4/3}}$(ev)	ZV(cm³)	$\frac{P}{Z^{10/3}}$(dynes/cm²)	$\frac{E_{\text{total}}}{ZkT}$	$-\frac{E_{\text{potential}}}{ZkT}$	$\frac{E_{\text{kinetic}}}{ZkT}$
1	(a)	29.1600	−2.5000	2.896 (0)	2.172 (−22)	1.117 (10)	−6.0035 (0)	1.35750 (1)	7.5715 (0)
	(b)			2.8946 (0)	2.1710(−22)	1.1163(10)	−6.0037 (0)	1.3575 (1)	7.5716 (0)
2	(a)	44.3716	−3.43653	6.395 (0)	2.251 (−22)	3.198 (10)	−1.672 (0)	5.4520 (0)	3.780 (0)
	(b)			6.3726 (0)	2.2546(−22)	3.1742(10)	−1.6841 (0)	5.4713 (0)	3.7872 (0)
3	(a)	132.710	−4.48090	1.916 (0)	2.8740(−21)	5.564 (8)	−9.319 (0)	2.02006 (1)	1.0882 (1)
	(b)			1.9056 (0)	2.8840(−21)	5.4816 (8)	−9.3868 (0)	2.0327 (1)	1.0940 (1)
4	(a)	182.790	−5.10000	3.091 (0)	3.2477(−21)	9.872 (8)	−4.859 (0)	1.16576 (1)	6.799 (0)
	(b)			3.0884 (0)	3.2455(−21)	9.8789 (8)	−4.8592 (0)	1.1663 (1)	6.8033 (0)
5	(a)	245.862	−5.90000	6.877 (0)	2.7789(−21)	3.282 (9)	−8.75 (−1)	4.2351 (0)	3.360 (0)
	(b)			6.8672 (0)	2.7804(−21)	3.2745 (9)	−8.7978(−1)	4.2423 (0)	3.3625 (0)
6	(a)	17.6820	−1.77256	3.072 (0)	9.812 (−23)	2.641 (10)	−5.7104 (0)	1.30006 (1)	7.2902 (0)
	(b)			3.0284 (0)	9.9094(−23)	2.5496(10)	−5.8156 (0)	1.3194 (1)	7.3780 (0)
7	(a)	85.4700	−6.63001	1.9033 (2)	4.722 (−23)	3.188 (12)	7.066 (−1)	6.76 (−2)	7.742 (−1)
	(b)			1.9067 (2)	4.7115(−23)	6.4121(12)	1.4528 (0)	6.1584 (−2)	1.5143 (0)
8	(a)	67.2597	−3.79003	3.795 (0)	6.2122(−22)	6.105 (7)	−3.9075 (0)	9.6867 (0)	5.7792 (0)
	(b)			3.7712 (0)	6.2363(−22)	6.0151 (9)	−3.9462 (0)	9.7552 (0)	5.8090 (0)
9	(a)	313.3325	−6.63002	1.284 (1)	2.504 (−21)	7.536 (9)	5.006 (−1)	1.7505 (0)	2.2511 (0)
	(b)			1.2826 (1)	2.5038(−21)	7.5248 (9)	4.9627(−1)	1.7583 (0)	2.2546 (0)
10	(a)	419.4304	−6.40000	4.435 (0)	8.6070(−21)	6.634 (8)	−2.3425 (0)	7.0961 (0)	4.7536 (0)
	(b)			4.1722 (0)	9.0028(−21)	5.7152 (8)	−2.7103 (0)	7.7300 (0)	5.0197 (0)
11	(a)	89.5143	−3.54002	4.23 (−1)	4.9275(−21)	3.271 (7)	−4.8293 (1)	9.7300 (1)	4.90072 (1)
	(b)			4.1815(−1)	4.9831(−21)	3.1584 (7)	−4.9194 (1)	9.9093 (1)	4.9899 (1)

[a] The numbers in parentheses indicate the powers of ten associated with the entries.

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APPENDIX I

The effect of exchange in the temperature-dependent Thomas-Fermi model has been included and some solutions obtained by Askin[15] and by Cowan.[16] The formulation consists in modifying the density function of Eq. (7) by adding a term to the exponential in that equation which measures the exchange energy per electron at position **r** with momentum **p**, namely

$$\rho(\mathbf{r},\mathbf{p}) = \frac{8\pi}{h^3}\frac{p^2}{\exp(-\alpha+p^2/2m-eV(r)+I(\mathbf{r},\mathbf{p}))/kT+1} \tag{A.1}$$

where $I(\mathbf{r},\mathbf{p})$ is the exchange energy. The quantity $I(\mathbf{r},\mathbf{p})$ may be expressed within the approximation of the Thomas-Fermi model by

$$I(\mathbf{r},\mathbf{p}) = \int d\mathbf{p}' V(\mathbf{p}-\mathbf{p}')\rho(\mathbf{r},\mathbf{p}')/p'^2 \tag{A.2}$$

where the integration extends over all momenta and $V(\mathbf{p}-\mathbf{p}')$ is the exchange potential energy between two plane-wave states of momenta $\mathbf{p}$ and $\mathbf{p}'$. The evaluation of $V(\mathbf{p}-\mathbf{p}')$ is quite straightforward and leads to

$$V(\mathbf{p}-\mathbf{p}') = -4\pi e^2\hbar^2/|\mathbf{p}-\mathbf{p}'|^2. \tag{A.3}$$

Substitution of Eq. (A.3) into Eq. (A.2) and carrying out that part of the integration over the directions of p' gives the result

$$I(\mathbf{r},p) = -\frac{e^2h^2}{4\pi}\frac{1}{p}\int_0^\infty dp'\rho(\mathbf{r},p')\frac{1}{p'}\ln\left|\frac{p+p'}{p-p'}\right|. \tag{A.4}$$

Equations (A.1) and (A.4) define an integral equation for the evaluation of the exchange energy $I(\mathbf{r},p)$. The solution of this integral equation then determines completely the density function of Eq. (A.1), which in turn specifies the thermodynamic properties of the system by a simple modification of the arguments leading to Eqs. (10), (12), (15), and (31).

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[15] J. Askin (unpublished).

[16] R. D. Cowan (unpublished).