

Thermodynamics of the Thomas-Fermi Atom at Low Temperature

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It is shown that an expression for the Helmholtz function on the Thomas-Fermi atom model permits one, in the limit of low temperature T , to expand the total energy as an asymptotic series in T^2 . The leading term of the expansion is a known analytic expression for the energy at $T=0$, from which one can calculate the pertinent thermodynamic functions for this case in their dependence on the atom radius and on the boundary and initial parameters associated with a solution of the zero-temperature Thomas-Fermi equation. Published values of these parameters are fitted by functions of the atom radius having the correct asymptotic behavior in the two limiting cases of an infinitesimal and an infinite atom. This procedure makes thermodynamic functions in this case directly available. Thermodynamic functions for the case of a first-order temperature perturbation are derived from the corresponding term in the asymptotic expansion of the energy. They depend (in addition to dependence on parameters of the unperturbed atom) on two parameters derived from solution of the differential perturbation equation. These parameters differ according as the differential perturbation equation is solved under a condition of fixed atomic volume or of zero initial slope (which is computationally more convenient and corresponds to published solutions). The asymptotic forms of the parameters in the first case are determined for the two limits of an infinitesimal and an infinite atom. The boundary and initial parameters corresponding to fixed atomic volume are expressed in terms of the parameters corresponding to a solution under zero initial slope, and are evaluated in three cases from published solutions. These values are fitted by functions of the atom radius which have the proper limiting behavior for an infinitesimal and an infinite atom. Thus, approximate values of the first-order temperature perturbations of thermodynamic functions become directly available.

THE statistical theory of Thomas¹ and Fermi,² generalized to arbitrary temperature, contains implicitly a complete thermodynamic specification of the atom model. Brachman³ has derived expressions on this model for the Helmholtz function, the entropy, and the heat capacity at constant volume. This paper shows that Brachman's results permit one to expand the energy as an asymptotic series in powers of the temperature. With this expansion available, it is possible to exhibit explicitly the thermodynamics of the Thomas-Fermi atom model for the case of a first-order temperature perturbation. The thermodynamic functions for the case of zero temperature can be obtained directly from an analytic expression due to Milne⁴ for the energy. In this case, the thermodynamic functions can be made directly accessible by fitting semi-empirically as a function of atom radius the pertinent parameters derived from solution⁵⁻⁷ of the Thomas-Fermi equation. A corresponding procedure can be carried out in the temperature-perturbed case.⁵ The effect of exchange⁸ will be neglected throughout, which makes the results valid only in the limit of high atomic number at sufficiently high compression.

1. INTRODUCTION

By the generalized Thomas-Fermi equation shall be meant Poisson's equation $\nabla^2 V = 4\pi e\rho$ for the potential $V(r)$, at a point r in a spherically symmetric atom and due to electrons of charge $-e$ and a number density $\rho(r)$ which is a function of the temperature T :

$$\rho = (4\pi/h^3)(2m)^{3/2}(kT)^{3/2}I_3(eV/kT + \eta). \quad (1)$$

Here m is the electron mass, $kT\eta$ is the chemical potential, h and k are the Planck and Boltzmann constants, respectively. The function $I_4(\lambda)$ is defined by

$$I_k(\lambda) = \int_0^\infty y^k [\exp(y - \lambda) + 1]^{-1} dy. \quad (2)$$

The kinetic energy E_{kin} on this model corresponds to a kinetic energy density $\epsilon_{\text{kin}}(r)$ given by

$$\epsilon_{\text{kin}} = (4\pi/h^3)(2m)^{3/2}(kT)^{5/2}I_3(eV/kT + \eta). \quad (3)$$

The potential energy E_{pot} consists of two terms, E_{ee} and E_{en} , where E_{ee} corresponding to the electron-electron interaction equals the integral $-(e/2)\int_\nu \rho V_e d\tau$ over the volume ν of the atom ($d\tau = 4\pi r^2 dr$), and $E_{en} = -e\int_\nu \rho V_n d\tau$ corresponding to the electron-nucleus interaction is

$$E_{en} = ZeV_e(0) = Ze[d(Vr)/dr]_{r=0}, \quad (4)$$

if $V_e(r)$ and $V_n(r) = Ze/r$ are the potentials due to the electrons and the nucleus, respectively. If one of the energies $E_{\text{kin}} = \int_\nu \epsilon_{\text{kin}} d\tau$, E_{pot} or the total energy $E = E_{\text{kin}} + E_{\text{pot}}$ is known, the other two energies can be determined directly from the virial theorem,

$$E = \frac{3}{2}P\nu + \frac{1}{2}E_{\text{pot}}, \quad (5)$$

¹ L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

² E. Fermi, Z. Physik **48**, 73 (1928).

³ M. K. Brachman, Phys. Rev. **84**, 1263 (1951).

⁴ E. A. Milne, Proc. Cambridge Phil. Soc. **23**, 794 (1927).

⁵ Feynman, Metropolis, and Teller, Phys. Rev. **75**, 1561 (1949) (referred to hereafter as FMT).

⁶ J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935) (referred to hereafter as SK).

⁷ P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer Verlag, Vienna, 1949), pp. 53, 357.

⁸ P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

where P is the pressure given by

$$P = \frac{2}{3} \epsilon_{\text{kin}}(a), \quad (6)$$

in which a is the atom radius.

Brachman³ has shown by an explicit temperature integration of the Gibbs-Helmholtz equation, that the Helmholtz function F on the Thomas-Fermi model is given by

$$F = -\frac{2}{3} E_{\text{kin}} - E_{ee} + ZkT\eta, \quad (7)$$

from which the entropy S and heat capacity C_v at constant volume follow directly. His expression for the heat capacity C_v can be written

$$TC_v = (7/4)E + \frac{3}{4}T^2(\partial/\partial T)_v[(Pv + E_{ee} + ZkT\eta)/T], \quad (8)$$

by means of Eqs. (4) and the virial theorem (5).

2. GENERAL PERTURBATION METHOD

Brachman's Eq. (8) for C_v will be made the basis in this section of a perturbation calculation of the total energy E . All the thermodynamic functions can be obtained once the energy is available.

It is convenient to define a Φ (generalizing in the manner of MB⁹ the usual Thomas-Fermi function ϕ corresponding to zero temperature) by

$$Ze^2\Phi/\mu x = eV + kT\eta, \quad (9)$$

where x is defined by $r = \mu x$, and μ equals $a_0(9\pi^2/128Z)^{1/3}$ in terms of the radius a_0 of the first Bohr orbit for hydrogen. By means of an asymptotic expansion¹⁰ for $I_{3/2}(\lambda)$ applied to ρ of Eq. (1), which is valid for $\lambda = Ze^2\Phi/\mu x kT \gg 1$, the asymptotic form of the generalized Thomas-Fermi equation for low temperatures becomes

$$\partial^2\Phi/\partial x^2 = (\Phi^{1/3}/x^3) \left[1 + \sum_{n=1}^N \zeta_n (kTx/\Phi)^{2n} \right], \quad (10)$$

in which $n \geq 1$,

$$\zeta_n = (\mu/Ze^2)^{2n} a_n, \quad (11)$$

and the coefficients a_n are defined and tabulated by McDougall and Stoner.¹⁰ Equation (10) reduces to the usual Thomas-Fermi equation for $T=0$ (where $kT\eta$ approaches a constant η'). The function Φ is subject to a boundary condition at the radius x_b of the atom which makes it a function $\Phi(x, x_b)$ of the two variables x and x_b . The initial and boundary conditions on $\Phi(x, x_b)$ are, respectively,

$$\Phi(0, x_b) = 1, \quad (12a)$$

$$\Phi_b = x_b \left[\frac{\partial\Phi(x, x_b)}{\partial x} \right]_{x=x_b}, \quad (12b)$$

⁹ R. E. Marshak and H. A. Bethe, *Astrophys. J.* **91**, 239 (1940) (referred to hereafter as MB).

¹⁰ J. McDougall and E. C. Stoner, *Trans. Roy. Soc. (London)* **A237**, 67 (1938).

where $\Phi_b = \Phi(x_b, x_b)$ is the boundary value of Φ . The distinction implied by the partial derivative notation in Eqs. (10) and (12b) will be germane later. It is possible to show¹¹ that Φ/x is a monotone-decreasing function of x for any neutral atom solution of the generalized Thomas-Fermi equation; hence the domain of validity $\lambda \gg 1$ of Eq. (10) becomes

$$kT \ll (Ze^2/\mu)\Phi_b/x_b. \quad (13)$$

The asymptotic series on which Eq. (10) is based is divergent for N sufficiently large, so that an optimum N exists for a given accuracy when the inequality (13) is fulfilled for a given λ .

For this same domain of validity, the corresponding asymptotic expansion of $I_{3/2}(\lambda)$ yields for the pressure P from Eq. (6),

$$P = \frac{Z^2 e^2}{10\pi\mu^4} \left(\frac{\Phi_b}{x_b} \right)^{5/2} \left[1 + \sum_{n=1}^N \frac{5\zeta_n}{5-4n} \left(\frac{kTx_b}{\Phi_b} \right)^{2n} \right], \quad (14)$$

where the chemical potential $kT\eta$ has been evaluated from Eq. (9) as

$$kT\eta = (Ze^2/\mu)\Phi_b/x_b \quad (15)$$

(since $V=0$ at the atom boundary). From Eqs. (4) and (9), the energy E_{ee} can be evaluated as

$$E_{ee} = (Z^2 e^2/\mu)(\Phi'_i - \Phi_b/x_b), \quad (16)$$

where Φ'_i is the initial slope $[\partial\Phi/\partial x]_{x=0}$. The volume v of the atom is determined by the boundary condition (12b) as $v = (4\pi/3)\mu^3 x_b^3$. These thermodynamic functions are the ones given directly by solution of the differential Eq. (10).

With use of Eqs. (15) and (16), Brachman's Eq. (8) for C_v yields

$$T \left(\frac{\partial E}{\partial T} \right)_v - \frac{7}{4} E = \frac{3}{4} T^2 \left(\frac{\partial}{\partial T} \right)_v \left\{ T^{-1} \left[Pv + \frac{Z^2 e^2}{\mu} \Phi'_i \right] \right\}, \quad (17)$$

where the right-hand side contains no terms depending on integrals over the volume. This equation is a first-order partial differential equation in T for the total energy E . Its solution is

$$E = \frac{3}{4} T^{7/4} \int_0^T T^{-1/4} (\partial/\partial T)_v \times \{ T^{-1} [Pv + (Z^2 e^2/\mu)\Phi'_i] \} dT, \quad (18)$$

where the integration is carried out at constant volume. For $T=0$, in which case the integrand appearing is singular, this equation gives correctly the result of Milne⁴ for the energy.

Since P is expressed by Eq. (14) as an asymptotic series in T^2 whose coefficients depend on Φ only through boundary values, the integral on the temperature in

¹¹ This result has been shown by Dr. R. Latter by means of an integral equation formulation of the generalized Thomas-Fermi equation.

Eq. (18) can be evaluated if Φ_i' can be obtained as a function of T^2 . This can be done by expanding Φ as an asymptotic series

$$\Phi = \phi + \sum_{n=1}^N \zeta_n \chi_n (kT)^{2n}, \quad (19)$$

in T^2 , where ϕ is the Thomas-Fermi function corresponding to $T=0$, and the coefficients χ_n are functions only of x and x_b , determined by solution of the asymptotic Thomas-Fermi Eq. (10). Determination of the χ_n requires the solution of N separate differential equations, whose analytical form can be found by substituting Eq. (19) into Eq. (10). The differential equation for χ_n is an inhomogeneous linear equation involving ϕ and all perturbations of lower order. With the functions χ_n available, Φ_i' becomes

$$\Phi_i' = \phi_i' + \sum_{n=1}^N \zeta_n \chi_{n,i}' (kT)^{2n}, \quad (20)$$

where ϕ_i' and $\chi_{n,i}'$ are the initial slopes corresponding to ϕ and χ_n , respectively. Since the integrand in Eq. (18) then depends on Φ only through boundary and initial parameters, the equation yields an asymptotic series for the energy E in powers of T^2 through T^{2N} , which is analogous to the corresponding expansion in the case of a degenerate Fermi-Dirac gas.¹²

In the literature, two methods of solving the differential perturbation equations (for the case $N=1$) have been used. In the method of MB, the radius of the atom is kept at its unperturbed value x_b , and the boundary condition (12b) is met by requiring

$$\chi_{n,b} = x_b \left[\frac{\partial \chi_n(x, x_b)}{\partial x} \right]_{x=x_b}, \quad (21)$$

where $\chi_{n,b}$ is the boundary value of χ_n at the atom boundary x_b . In this case, the initial slope of the perturbation must be selected (by trial) so that Eq. (21) is met at the boundary. In the method of FMT, the initial slope is set equal to zero, and a perturbed radius x_b^* of the atom is determined at which the boundary condition (12b) is met. The method of FMT is computationally far more convenient, but the method of MB avoids the complication of introducing a perturbation in the volume. In any event, solutions of the differential perturbation equation of any order by the two methods can differ only by a solution of the corresponding homogeneous equation. Thus it is possible to express the pertinent parameters on the method of MB in terms of corresponding parameters derived by the computationally more convenient method of FMT; in Sec. 4b, this process is carried out explicitly for the case $N=1$.

For the subsequent development of the thermodynamics, it is convenient to modify the total energy E

by subtraction of the energy of a standard state to obtain a total energy U which is always positive. The standard state is taken as a neutral atom of infinite radius at zero temperature, for which the energy is $(3/7)(Z^2 e^2/\mu)\phi_{i,\infty}'$, where $\phi_{i,\infty}'$ is the corresponding initial slope of ϕ . Accordingly, one has

$$U = E - (3/7)(Z^2 e^2/\mu)\phi_{i,\infty}'. \quad (22)$$

In terms of U , a parameter γ can be defined at this point by

$$U = P\nu/(\gamma - 1). \quad (23)$$

Further, it is convenient to introduce two differential parameters:

$$\epsilon_S = -(\partial \ln P / \partial \ln \nu)_S, \quad \epsilon_T = -(\partial \ln P / \partial \ln \nu)_T, \quad (24)$$

which are the (negative) slopes of the pressure-volume curves in log-log coordinates for constant entropy and for constant temperature respectively. These parameters are connected by the relation¹³

$$\epsilon_S / \epsilon_T = C_P / C_V, \quad (25)$$

where C_P is the heat capacity at constant pressure. The energy equation of thermodynamics¹³ provides a connection

$$\epsilon_S = \gamma - [\partial \ln(\gamma - 1) / \partial \ln \nu]_S \quad (26)$$

between ϵ_S and γ . An integral relation between ϵ_S and γ can be derived directly from the first law of thermodynamics; it is¹⁴

$$\gamma = U^{-1} \int_0^U \epsilon_S dU = \langle \epsilon_S \rangle_U, \quad (27)$$

which one can show by direct mathematical processes to be an integral of Eq. (26). An integration by parts on the integral in Eq. (27) shows that $\gamma \geq \epsilon_S$.

3. CASE OF ZERO TEMPERATURE

In this section, the thermodynamic functions corresponding to the case $T=0$ will be developed. For reasons that will become clear in the next section, thermodynamic variables corresponding to this case will be distinguished by a special notation.

For the case $T=0$, the Thomas-Fermi Eq. (10) becomes

$$\partial^2 \phi / \partial x^2 = \phi^{3/2} / x^{3/2}. \quad (28)$$

The initial value $\phi(0, x_b)$ of ϕ is unity, and the boundary value ϕ_b satisfies the condition (12b) at the atom radius x_b . Since the entropy is zero, the isothermal and isentropic equations of state are identical in this case; the common value of ϵ_S and ϵ_T will be denoted by ϵ_0 , and the value of γ by γ_0 . For the other thermodynamic

¹³ M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1937), first edition, pp. 222, 225, 227.

¹⁴ This result for zero temperature was derived by the author; the generalization to nonzero temperature, by Dr. W. G. McMillan.

¹² J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), p. 374.

functions, the values corresponding to the case $T=0$ will be distinguished by use of lower case letters.

The basic thermodynamic function is the total energy u [corresponding to U of Eq. (22)], evaluated by Milne⁴ and SK as

$$u = (Z^2 e^2 / \mu) [(3/7)(\phi_i' - \phi_{i,\infty}') + (2/35)x_b^3 \phi_b^{5/2}]. \quad (29)$$

The pressure p is

$$p = (Z^2 e^2 / 10\pi\mu^4) (\phi_b / x_b)^{5/2}, \quad (30)$$

from Eq. (14). The enthalpy h is accordingly

$$h = (Z^2 e^2 / \mu) [(3/7)(\phi_i' - \phi_{i,\infty}') + (4/21)x_b^3 \phi_b^{5/2}]. \quad (31)$$

The Helmholtz function is identical, of course, with the total energy, and the Gibbs function is identical with the enthalpy. The connection between the three variables x_b , ϕ_b and ϕ_i' which enter the functions is provided by $p = -du/dv$, which yields the differential relation

$$x_b^3 d\phi_i' / dx_b = -\phi_b^{5/2} - \frac{1}{3} x_b \phi_b^3 d\phi_b / dx_b. \quad (32)$$

The parameter ϵ_0 can be evaluated directly from Eq. (30) as

$$\epsilon_0 = (5/6) [1 - d \ln \phi_b / d \ln x_b], \quad (33)$$

and the parameter γ_0 can be evaluated from Eqs. (29) and (30) as

$$(\gamma_0 - 1)^{-1} = (3/7) [1 + (15/2)(\phi_i' - \phi_{i,\infty}') / (x_b^3 \phi_b^{5/2})]. \quad (34)$$

For the case $T=0$, the partial derivative in Eq. (26) becomes a total derivative, so that ϵ_0 and γ_0 are equal whenever either is constant. A lower bound on γ_0 can be written immediately from the virial theorem in the form (5); since E_{pot} is necessarily negative, it follows that¹⁵ $\gamma_0 \geq 5/3$ at $T=0$.

The limiting values of the thermodynamic functions for high and low pressures can be evaluated if the corresponding asymptotic forms of ϕ_b and ϕ_i' as a function of x_b can be determined for $x_b \rightarrow 0$ and $x_b \rightarrow \infty$. For sufficiently high pressures, the Thomas-Fermi atomic model must pass over into the degenerate Fermi-Dirac gas, since the kinetic energy (varying as $1/r^2$ in the limit of small volume) dominates the potential energy (varying as $1/r$). Accordingly, the potential inside the atom for this limiting case is

$$V = (Ze/\mu) [x^{-1} + \frac{1}{2} x_b^{-3} x^2 - \frac{3}{2} x_b^{-1}], \quad (35)$$

which corresponds to the sum of the nuclear potential and the potential due to a uniform distribution of Z electrons within the atomic volume. The corresponding value of ϕ is thus

$$\phi = 1 + \frac{1}{2} (x/x_b)^3 - \frac{3}{2} (x/x_b) + 3\frac{1}{2} x/x_b^2, \quad (36)$$

where the last term arises by evaluating the chemical potential $\eta' = \lim_{T \rightarrow 0} kT\eta$ for the Thomas-Fermi atom

¹⁵ This result was derived by Dr. W. G. McMillan. The lower limit in question does not hold for temperatures other than zero, because of the presence in the definition of U by Eq. (22) of the energy of a standard state corresponding to $T=0$.

from the expression¹² $\eta' = (h^2/8m)(3Z/\pi v)^{2/3}$ for the chemical potential of a Fermi-Dirac gas of Z electrons in the atomic volume v , as

$$\eta' = 3^{2/3} Z e^2 / \mu x_b^2 \quad (37)$$

in terms of x_b . Since the last term of Eq. (36) dominates in ϕ for x_b small, one obtains

$$\phi_b = 3^{2/3} / x_b, \quad \phi_i' = 3^{2/3} / x_b^2, \quad (38)$$

in the limit $x_b \rightarrow 0$. With these asymptotic forms for x_b small, all the thermodynamic functions derived reduce to the corresponding functions for a Fermi-Dirac gas,¹² as one can verify. The common limiting value of ϵ_0 and γ_0 in this case is $5/3$.

The corresponding forms for the limit of low pressure (infinite atom) can be obtained from an asymptotic formula due to Sauvenier¹⁶ (derived from a result of Sommerfeld,¹⁷), which represents an approximate solution of the Thomas-Fermi Eq. (28) which is perturbed slightly from the solution for an infinite atom. The solution is

$$\phi = (1+z)^{-\lambda_1/2} \left[1 + \frac{4z_b+1}{(\lambda_1-4)z_b+1} \left(\frac{1+z}{1+z_b} \right)^{\lambda_1/\lambda_2} \right], \quad (39)$$

where

$$z = (x/12^3)^{\lambda_2}, \quad z_b = (x_b/12^3)^{\lambda_2}, \quad (40)$$

and

$$\lambda_1 = \frac{1}{2} [73^{1/2} + 7], \quad \lambda_2 = \frac{1}{2} [73^{1/2} - 7]. \quad (41)$$

This expression yields¹⁶

$$\phi_b = 16(3+2\lambda_1)x_b^{-3} [1 - (3+8\lambda_1)12^{3\lambda_2}/18x_b^{\lambda_2}] \quad (42)$$

as the asymptotic form of ϕ_b for $x_b \rightarrow \infty$. The corresponding asymptotic form of ϕ_i' follows from Sauvenier's result, by means of Eq. (32), as

$$\phi_i' = \phi_{i,\infty}' + (256/9)(2+3\lambda_2)(3+2\lambda_1)^{5/2} 12^{3\lambda_2} x_b^{-\lambda_1}, \quad (43)$$

and is determined only by the second term of Eq. (42). The common limiting value of ϵ_0 and γ_0 is $10/3$ from these asymptotic forms. It is possible to show¹¹ that ϕ_b and $d\phi_b/dx_b$ are monotonic functions of x_b , which shows that ϵ_0 and γ_0 between the limits $5/3$ and $10/3$ are monotonic functions of x_b .

To determine thermodynamic functions for a given volume v , one needs values of ϕ_b and ϕ_i' (and their derivatives) corresponding to $x_b = (3v/4\pi)^{1/3}/\mu$. Fourteen values of ϕ_b and $\phi_i' - \phi_{i,\infty}'$ corresponding to values of x_b are available from numerical results¹⁸ of FMT and

¹⁶ H. Sauvenier, Bull. Soc. Roy. Sci. Liege 8, 313 (1939).

¹⁷ A. Sommerfeld, Z. Physik 78, 19 (1932).

¹⁸ The data consists of results from six solutions of FMT (Table III of their paper), and from eight solutions of SK, as tabulated in Table V of Gombas (see reference 7). The value of $\phi_{i,\infty}'$ (-1.58875) given by FMT was associated with their data, and the value (-1.58808) given by SK was associated with theirs, in obtaining the difference $\phi_i' - \phi_{i,\infty}'$. In the region of x_b , where they overlap, the results of FMT and SK are discrepant; the discrepancy is more significant in $\phi_i' - \phi_{i,\infty}'$ than in ϕ_b . The data was smoothed in this region with major weight given to the data of FMT. For this reason, and because insufficient significant figures apparently appear in the difference $\phi_i' - \phi_{i,\infty}'$, results of a seventh and eighth solution of SK corresponding to the largest volumes, as given by Gombas, have been ignored in showing data points in Figs. 1, 2, and 3. The discrepancy in question has been noted by K. Umeda [Phys. Rev. 83, 651 (1951)].

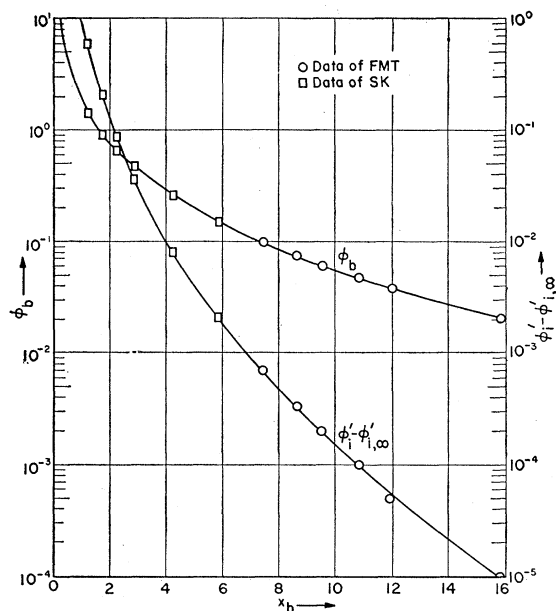


FIG. 1. Fitted functions for ϕ_b and $\phi'_i - \phi_{i,\infty}'$ against boundary radius in zero-temperature case.

SK. To reduce the labor of interpolation, and in the interest of direct accessibility of the data, it is convenient to fit these results by empirical formulae chosen to have the correct asymptotic forms in the two limits $x_b \rightarrow 0$ and $x_b \rightarrow \infty$. A fitting function for ϕ_b yielding the correct asymptotic forms can be written as

$$\phi_b = [\sum A_n x_b^{n/2}]^{-1}, \quad (44)$$

if n ranges over the sequence $n=2, 3, \dots, 6$ and if the coefficients A_2 and A_6 are chosen to agree with the corresponding coefficients in the asymptotic forms (38) and (42), respectively. It has been found possible to choose the intermediate coefficients A_n to represent the smoothed data¹⁸ of FMT and SK within about 1.5 percent. The coefficients A_n are tabulated in Table I; since they are all positive, the fitted function is monotone, as is¹¹ ϕ_b . The fitted function ϕ_b is shown in Fig. 1 for comparison with the data points.

The corresponding fitted function for $\phi'_i - \phi_{i,\infty}'$ could be determined, in principle, from Eq. (32), but it is simpler to fit the data for $\phi'_i = \phi_{i,\infty}'$ directly. A reasonable fitting function is

$$\phi'_i - \phi_{i,\infty}' = [\sum B_n x_b^n]^{-1}, \quad (45)$$

in which n ranges over the sequence $n=2, 3, \dots, 7, \lambda_1$, and the coefficients B_2 and B_{λ_1} are chosen to agree with the corresponding coefficients in the asymptotic forms (38) and (43), respectively. The smoothed data¹⁸ of FMT and SK for the difference $\phi'_i - \phi_{i,\infty}'$ can be reproduced within about 1.5 percent by means of the coefficients B_n tabulated in Table I. It is possible to show¹¹ that ϕ'_i is a monotonic function of x_b ; the fitted

function has this property likewise.¹⁹ The fitted function and the data points are shown in Fig. 1.

With these fitted functions for ϕ_b and ϕ'_i , all the thermodynamic functions discussed previously can be determined by direct algebraic or differential processes. In the range covered by the data of FMT and SK, thermodynamic functions can be obtained with an accuracy of the order of a few percent, on the basis of the data¹⁸ employed. Outside this range the fitted functions yield results which are correct in both asymptotic limits, and their monotonic character gives some assurance of approximate validity, at least, outside of the regions fitted directly. The fitted function for ϕ_b yields the equation of state

$$p^{2/5} \sum_{n=2}^6 A_n (3v/4\pi\mu^3)^{(n+2)/6} = (Z^2 e^2 / 10\pi\mu^4)^{2/5}. \quad (46)$$

Pressures from this equation are shown in Fig. 2 for comparison with the corresponding quantities as calculated directly from the data of FMT and SK. The energy u from Eq. (29) is shown likewise; the unit of energy is the Rydberg, $R = e^2/2a_0$. A similar comparison with directly calculated values is shown in Fig. 3 for γ_0 (directly calculated values are not given for ϵ_0 since it is a differential parameter). Note that pressure and energy scale as $Z^{10/3}$ and $Z^{7/3}$, respectively, while the volume scales as Z^{-1} .

4. FIRST-ORDER TEMPERATURE PERTURBATION

In this section, the thermodynamic functions derived for the case $T=0$ will be generalized to include terms in T^2 . The procedure corresponds to retaining terms through T^2 in the expansion of the right-hand side of the asymptotic Thomas-Fermi Eq. (10). Setting $\chi_1 = \chi$ and $\zeta_1 = \zeta$ in Eq. (19), one can write

$$\Phi = \phi + \chi \zeta (kT)^2 \quad (47)$$

as a solution of the resulting equation, where ϕ is an unperturbed solution corresponding to $T=0$, and the perturbation χ satisfies

$$\partial^2 \chi / \partial x^2 = \frac{3}{2} (\phi/x)^{1/2} \chi + x^{1/2} / \phi^{1/2} \quad (48)$$

TABLE I. Coefficients^a of fitted functions, zero-temperature case.

n	A_n	B_n
2	4.8075×10^{-1}	4.8075×10^{-1}
3	7.009×10^{-3}	4.3462×10^{-1}
4	7.003×10^{-2}	6.9203×10^{-2}
5	8.901×10^{-3}	5.9472×10^{-2}
6	3.3704×10^{-3}	-4.9688×10^{-3}
7		4.3386×10^{-4}
$\lambda_1 = 7.77200$		1.5311×10^{-6}

^a The coefficients are given to four or five figures to minimize round-off error and to yield smoothness in computational work.

¹⁹ The coefficient B_6 is negative, but one can show that ϕ'_i and $d\phi'_i/dx_b$ from the tabulated coefficients have no zeros for x_b positive.

under the initial condition $\chi(0, x_b) = 0$. The coefficient ζ can be evaluated (with $a_1 = \pi^2/8$) as $\pi^2 \mu^2 / 8 Z^2 e^4$, or as $(2.034 Z^{4/3} R)^{-2}$ in terms of the Rydberg. The limitation (13) on the temperature can be written

$$Z^{-4/3} kT / R \ll 8(2/9\pi^2)^{1/2} \phi_b / x_b. \quad (49)$$

A particular perturbation χ always corresponds to a definite $\phi(x, x_b)$; the atom corresponding to this ϕ will be referred to as the unperturbed atom to which the perturbation χ corresponds.

In Sec. 4a following, the thermodynamic functions will be developed in terms of parameters corresponding to the method of MB. In Sec. 4b following, these parameters will be expressed in terms of parameters on the method of FMT, in order to yield the thermodynamic functions in that case. In a final section, numerical results will be presented.

a. Method of MB

In this case, the perturbation leaves the volume v unchanged. The boundary value $\chi_b = \chi_{1,b}$ satisfies the boundary condition (21) at the radius x_b of the unperturbed atom. The initial slope $\chi'_i = \chi_{1,i}'$ must be selected by trial so that this condition is met.

It is convenient to introduce two parameters,

$$\sigma = \chi_b / \phi_b, \quad \omega = \chi'_i / (x_b^{1/2} \phi_b^{5/2}), \quad (50)$$

in terms of which the boundary value Φ_b and initial slope Φ'_i of Φ can be written

$$\Phi_b = \phi_b [1 + \sigma \zeta(kT)^2], \quad (51a)$$

$$\Phi'_i = \phi'_i + x_b^{1/2} \phi_b^{5/2} \omega \zeta(kT)^2, \quad (51b)$$

respectively. With use of Eq. (51a), the pressure P of the perturbed atom follows directly from Eq. (14), by retention only of terms through T^2 , as

$$P = p [1 + (5/2)(\sigma + 2\tau) \zeta(kT)^2], \quad (52)$$

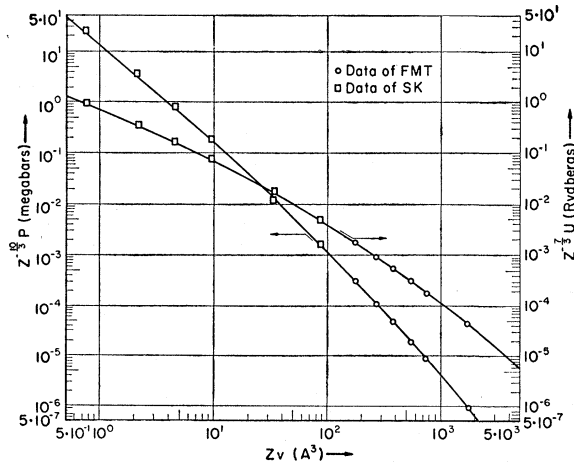


FIG. 2. Scaled pressure and energy from fitted functions for ϕ_b and $\phi'_i - \phi_{i,\infty}'$, against scaled volume in cubic angstroms; zero-temperature case.

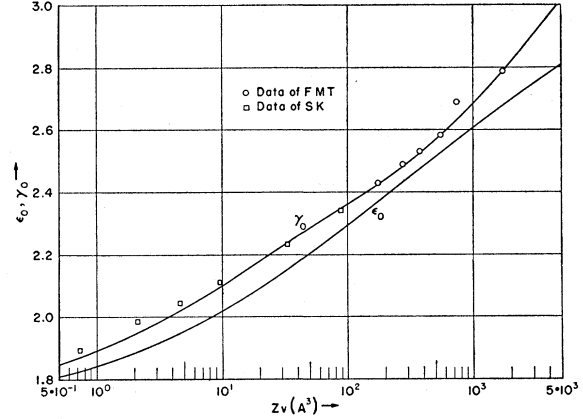


FIG. 3. Parameters γ_0 and ϵ_0 from fitted functions for ϕ_b and $\phi'_i - \phi_{i,\infty}'$, against scaled volume in cubic angstroms; zero-temperature case.

where p is the pressure of Eq. (30) corresponding to the unperturbed atom, and

$$\tau = (x_b / \phi_b)^2. \quad (53)$$

The parameters σ , τ , and ω are functions of x_b , and thus of v .

Equations (52) and (51b) provide expansions through terms in T^2 of P and Φ'_i , respectively, so that the total energy can be evaluated from Eq. (18). The energy U is

$$U = u + (15/2) p v (\sigma + 2\tau + 3\omega) \zeta(kT)^2, \quad (54)$$

where u is the energy of the unperturbed atom, given by Eq. (29). The entropy S is

$$S = 15 p v (\sigma + 2\tau + 3\omega) \zeta(kT)^2, \quad (55)$$

from the relation $T(\partial S / \partial T)_v = (\partial E / \partial T)_v$. The enthalpy H is

$$H = h + (5/2) p v (4\sigma + 8\tau + 9\omega) \zeta(kT)^2, \quad (56)$$

where h is the enthalpy of the unperturbed atom. The Helmholtz function F is

$$F = u - (15/2) (\sigma + 2\tau + 3\omega) \zeta(kT)^2, \quad (57)$$

and the Gibbs function G is

$$G = h - (5/2) (2\sigma + 4\tau + 9\omega) \zeta(kT)^2. \quad (58)$$

One can verify (with the aid of the virial theorem) that F satisfies the Brachman relation (7).

The parameter γ is determined by

$$\gamma = \gamma_0 - (5/2) (\gamma_0 - 1) \times [(3\gamma_0 - 4)(\sigma + 2\tau) + 9(\gamma_0 - 1)\omega] \zeta(kT)^2, \quad (59)$$

where γ_0 corresponds to the unperturbed atom. The differential parameter ϵ_T can be obtained from the definition as

$$\epsilon_T = \epsilon_0 - [(5/6) d\sigma/d \ln x_b + 4\epsilon_0 \tau] \zeta(kT)^2, \quad (60)$$

where use has been made of the relation

$$d\tau/d \ln x_b = (12/5) \epsilon_0 \tau, \quad (61)$$

and ϵ_0 corresponds to the unperturbed atom. To obtain ϵ_S , note that the heat capacity C_v is equal to S in this approximation, and that the heat capacity C_P is given in general by¹³

$$C_P = C_v + (\epsilon_T/v)(\partial v/\partial T)_P PT. \quad (62)$$

From this equation, one can show that

$$C_P = C_v = S \quad (63)$$

in this approximation, and one obtains

$$\epsilon_S = \epsilon_T \quad (64)$$

from Eq. (25).

The parameters σ , τ , and ω are subject to an equation of connection fixed by the identity $(\partial P/\partial T)_v = (\partial S/\partial v)_T$, which yields the differential relation

$$d(\sigma + 3\omega)/d \ln x_b = (3\epsilon_0 - 2)\sigma + [(6/5)\epsilon_0 - 4]\tau + 9(\epsilon_0 - 1)\omega. \quad (65)$$

As one can verify, this relation is necessary and sufficient for the differentials of U , H , F and G , as derived above, to be exact differentials of their arguments, and for the Maxwell relations to be satisfied. Equation (65) implies a differential relation between χ_b , χ'_b and ϕ_b which is the analog of Eq. (32) in the zero-temperature case.

In the limit $x_b \rightarrow 0$ of vanishing atomic volume, the thermodynamic functions derived must reduce to the corresponding functions for a degenerate Fermi-Dirac gas through terms of order T^2 . Substitution in the differential equation (48) for χ of the dominant terms of Eq. (36) for ϕ in the Fermi-Dirac limit, solution of the resulting equation, and imposition of the boundary condition (21) yields

$$\chi'_b = -(2/3^{5/3})x_b^2 \quad (66)$$

for the initial slope. The corresponding solution for χ in the Fermi-Dirac limit is

$$\chi = -(2/3^{5/3})x_b^2 x, \quad (67)$$

which is a straight line in x . The boundary value of χ is thus

$$\chi_b = -(2/3^{5/3})x_b^3 \quad (68)$$

and the parameters σ and ω become

$$\sigma = -(2/3^{7/3})x_b^4, \quad \omega = -(2/3^{10/3})x_b^4, \quad (69)$$

with use of the first of Eqs. (38). The parameter τ is

$$\tau = (1/3^{4/3})x_b^4. \quad (70)$$

One can verify that, with these asymptotic forms, all the thermodynamic functions derived reduce to the corresponding functions for a degenerate Fermi-Dirac gas through terms of order T^2 . The inequality (49) in this case requires that $Z^{-4/3}kT/R$ be less than a quantity proportional to x_b^{-2} , so that large temperatures are permitted.

In the opposite limit of an infinite atom, for $x_b \rightarrow \infty$,

the corresponding asymptotic forms can be obtained from the differential equation (48) by substitution of the approximation for ϕ in this case,

$$\phi = (144/x^3)(1 - \lambda_1 12^{3/2}/2x^{\lambda_2}), \quad (71)$$

which corresponds, in Eq. (39), to replacing the square bracket by unity and expanding the factor $(1+z)^{-\lambda_1/2}$. The solution for χ in this limit is

$$\chi = Ax^{\lambda_1-3} \left[1 + \frac{3\lambda_1 12^{3/2}}{4x^{\lambda_2}} \right] + \frac{x^5}{24} \left[1 + \frac{(4+5\lambda_1)12^{3/2}}{6x^{\lambda_2}} \right], \quad (72)$$

where the constant A is fixed by the boundary condition (21) as

$$A = -[(\lambda_1 - 3)/108]x_b^{8-\lambda_1} [1 + (\lambda_1 - 1)12^{3/2}/6x_b^{\lambda_2}]. \quad (73)$$

This solution yields

$$\chi_b = -[(2\lambda_2 - 1)/216]x_b^5 [1 + \lambda_1 12^{3/2}/2x_b^{\lambda_2}] \quad (74)$$

for the boundary value of χ . The value of σ follows as

$$\sigma = -[(4\lambda_2 - 3)/2^7 3^4] \times x_b^8 [1 + (3 + 17\lambda_1)12^{3/2}/6x_b^{\lambda_2}], \quad (75)$$

with use of Eq. (42), and the value of τ is

$$\tau = [(33 - 40\lambda_2)/2^8 3^6]x_b^8. \quad (76)$$

The parameter ω is determined by the differential identity (65), and is independent of the first-order terms of σ and τ in x_b^8 . With inclusion of a second-order term in ϵ_0 by

$$\epsilon_0 = (10/3)[1 - (\lambda_1 + 9)12^{3/2}/24x_b^{\lambda_2}], \quad (77)$$

integration of Eq. (65) yields

$$\omega = -[(30 + 7\lambda_2)/2^9 3^7]12^{3/2}x_b^{8-\lambda_2}. \quad (78)$$

The corresponding value of the initial slope χ'_b is

$$\chi'_b = -(2/3^7)(30 + 7\lambda_2)(3 + 2\lambda_1)^{5/2}12^{3/2}x_b^{1-\lambda_2}. \quad (79)$$

The inequality (49) limiting the temperature requires that $Z^{-4/3}kT/R$ be much less than a quantity proportional to x_b^{-4} in this case, and thus demands temperatures approaching zero as $x_b \rightarrow \infty$.

b. Method of FMT

In this case, the perturbed volume of the atom is allowed to differ from the unperturbed volume. The perturbation function χ^* satisfies Eq. (48), with an initial slope equal to zero. The radius of the atom boundary is fixed by the condition (12b).

For a definite zero-temperature solution ϕ and corresponding perturbation χ^* , the radius x_b^* can be determined approximately from the boundary condition in terms of the radius x_b corresponding to the unperturbed atom, if ϕ , χ^* and their derivatives are expanded in Taylor series about the point $x = x_b$. Making use of the differential Eqs. (28) and (48) and the boundary con-

dition on ϕ , one obtains in first order

$$x_b^* = x_b[1 + \nu\zeta(kT)^2], \quad (80)$$

where the parameter ν is defined by

$$\nu = (\chi_b^* - x_b\chi_b^{*'})/(x_b\phi_b)^{1/2}, \quad (81)$$

in which ϕ_b is the value of ϕ at the boundary $x = x_b$ of the unperturbed atom, and χ_b^* and $\chi_b^{*'}$ are the values of χ^* and $\partial\chi^*/\partial x$, respectively, evaluated at the same point $x = x_b$. The volume v^* of the perturbed atom is accordingly

$$v^* = v[1 + 3\nu\zeta(kT)^2], \quad (82)$$

in terms of the volume v of the corresponding unperturbed atom.

To relate χ^* with χ for the same volume v^* , where χ is the perturbation function computed by the method of MB, one notes that χ must satisfy Eq. (48) with a $\phi = \phi^*$ chosen to correspond to the perturbed atom radius x_b^* . The value of ϕ^* is, accordingly,

$$\phi^* = \phi(x, x_b) + [\partial\phi(x, x_b)/\partial x_b](x_b^* - x_b), \quad (83)$$

where $\phi(x, x_b)$ is the unperturbed solution to which χ^* corresponds. Substitution of ϕ^* into the perturbation Eq. (48) to obtain the differential equation for χ , and comparison of the result with the differential equation for χ^* , yields

$$\chi^* = \chi + \nu x_b \partial\phi/\partial x_b \quad (84)$$

with use of Eq. (80).

The function $\partial\phi/\partial x_b$ is a solution of the homogeneous equation,

$$\partial^2(\partial\phi/\partial x_b)/\partial x^2 = \frac{3}{2}(\phi/x)^{1/2}\partial\phi/\partial x, \quad (85)$$

corresponding to the inhomogeneous perturbation equation, as one can verify by differentiating the zero-temperature Eq. (28) with respect to x_b . At the origin, the function vanishes and its slope satisfies the initial condition,

$$[\partial(\partial\phi/\partial x_b)/\partial x]_{x=0} = d\phi_i'/dx_b, \quad (86)$$

where ϕ_i' is the initial slope of the zero-temperature solution $\phi(x, x_b)$. The function ϕ^* then satisfies the boundary condition (12b) at x_b^* automatically.

Evaluation at $x = x_b$ of Eq. (84) for χ^* , with use of

$$d\phi_b/dx_b = \phi_b/x_b + [\partial\phi(x, x_b)/\partial x_b]_{x=x_b}, \quad (87)$$

yields the relation

$$\chi_b = \chi_b^* + (6/5)\epsilon_0\nu\phi_b \quad (88)$$

between boundary values computed under the two methods. Differentiation of the same equation with respect to x and evaluation at $x=0$ yields the further relation

$$x_b^{1/2}\phi_b^{1/2}\chi_b + 3\chi_i' = x_b^{1/2}\phi_b^{1/2}\chi_b^* + 4\nu x_b^{1/2}\phi_b^{5/2}, \quad (89)$$

when Eqs. (86) and (32) are employed. The last two equations give

$$\chi_i' = [4/3 - (2/5)\epsilon_0]\nu x_b^{1/2}\phi_b^{5/2}. \quad (90)$$

TABLE II. Boundary and initial parameters, temperature-perturbed case.

x_b	χ_b^*	$\chi_b^{*'}$	χ_b	χ_i'
9.5651	1747.3	834.82	-812	-13.4
10.8038	3068.2	1315.7	-1320	-15.7
15.8698	18731.	5689.1	-6420	-24.8

Equations (88) and (90) fix completely the significant parameters χ_b and χ_i' on the method of MB in terms of quantities computed by the method of FMT. In terms of the parameters σ and ω , one obtains, from Eq. (88),

$$\sigma = \sigma^* + (6/5)\epsilon_0\nu, \quad (91)$$

where $\sigma^* = \chi_b^*/\phi_b$, and one obtains

$$\omega = [4/3 - (2/5)\epsilon_0]\nu, \quad (92)$$

from Eq. (90).

Thermodynamic functions for the volume v are available from preceding results in terms of the parameters σ and ω corresponding to the method of MB. To determine a thermodynamic function for the volume v^* in terms of the parameters σ^* and ν corresponding to the method of FMT, it is necessary merely to take account of the perturbation in the temperature-independent term due to the volume change, $v^* - v$, and to transform σ and ω into σ^* and ν by the preceding equations. Thus, if P^* is the pressure corresponding to the volume v^* , one has

$$P^* = P + (dp/dv)(v^* - v), \quad (93)$$

if P corresponds to v . With use of Eq. (82) for $v^* - v$ and the defining equation for ϵ_0 , one obtains

$$P^* = p[1 + (5/2)(\sigma^* + 2\tau)\zeta(kT)^2]. \quad (94)$$

In a similar manner, it can be shown that the energy U^* corresponding to v^* is

$$U^* = u + \frac{3}{2}pv(5\sigma^* + 10\tau + 18\nu)\zeta(kT)^2, \quad (95)$$

and that the entropy S^* is

$$S^* = 15pv(\sigma^* + 2\tau + 4\nu)\zeta k^2T. \quad (96)$$

It is clear that these results are easily modified to take account of the use of an arbitrary initial slope (rather than zero) in the method of FMT.

c. Numerical Results

Three solutions by their method of the first-order temperature-perturbation equation have been tabu-

TABLE III. Coefficients* of fitted functions, temperature-perturbed case.

n	C_n	n	D_n
3	-3.205×10^{-1}	$1 - \lambda_2 = 0.22800$	-5.805×10^{-3}
4	-4.021×10^{-2}	1	-3.755×10^{-1}
5	-2.519×10^{-3}	2	-3.120

* The coefficients are given to four figures to minimize round-off error and to yield smoothness in computational work.

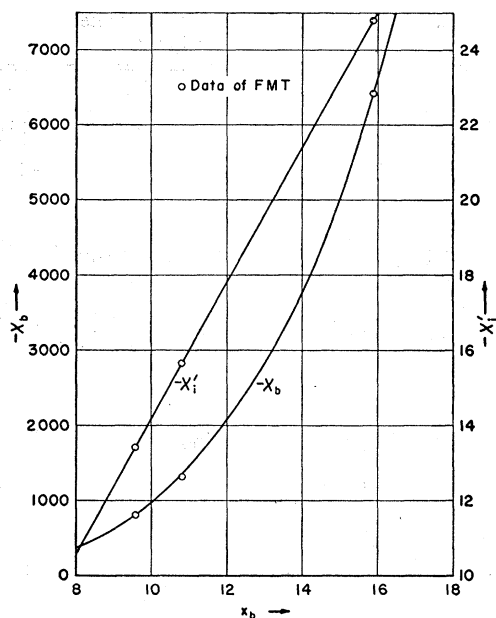


FIG. 4. Fitted functions for χ_b and χ'_b against boundary radius in temperature-perturbed case.

lated by FMT. The corresponding values of χ_b^* and $\chi_b^{*'}$ have been determined by quartic interpolation from their data and are tabulated in Table II against the unperturbed radius x_b to which they correspond. The corresponding values of χ_b and χ'_b on the method of MB have been determined by use of Eqs. (88) and (90) respectively and tabulated likewise. Since these equa-

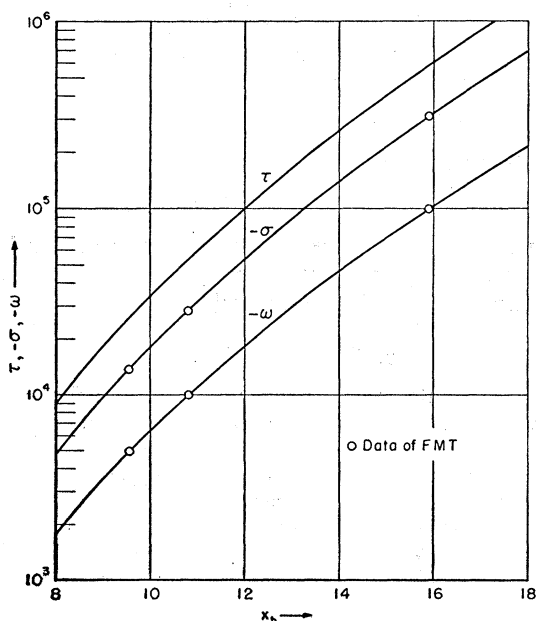


FIG. 5. Perturbation parameters σ , τ , and ω from fitted functions for χ_b , χ'_b and ϕ_b , against boundary radius in temperature-perturbed case.

tions involve the differential parameter ϵ_0 , which has been determined from the fitted function (44) for ϕ_b , the accuracy of χ_b and χ'_b cannot be guaranteed as better than a few percent.

As in the zero-temperature case, it is desirable to represent the pertinent quantities, which the differential equation yields, by fitted functions having the proper asymptotic behavior in the two limits $x_b \rightarrow 0$ and $x_b \rightarrow \infty$. It is convenient to use parameters corresponding to the method of MB, in order to avoid the complication of a perturbation in the volume. The quantity χ_b can be represented by

$$\chi_b = \sum C_n x_b^n, \quad (97)$$

if $n=3, 4, 5$, and the coefficients C_3 and C_5 are chosen to agree with the corresponding coefficients in the asymptotic forms (68) and (74), respectively. Similarly χ'_b can be represented by

$$\chi'_b = [\sum D_n x_b^{-n}]^{-1}, \quad (98)$$

if n ranges over the sequence $1-\lambda_2, 1, 2$ and the coefficients D_2 and $D_{1-\lambda_2}$ are fixed by Eqs. (66) and (79), respectively. The coefficients C_n and D_n tabulated in Table III reproduce²⁰ the values of Table II within about 1 percent in the case of χ_b and within about 3 percent in the case of χ'_b . It can be shown that χ_b and χ'_b are monotonic functions of x_b , as are the fitted functions. The fitted functions and the data points are

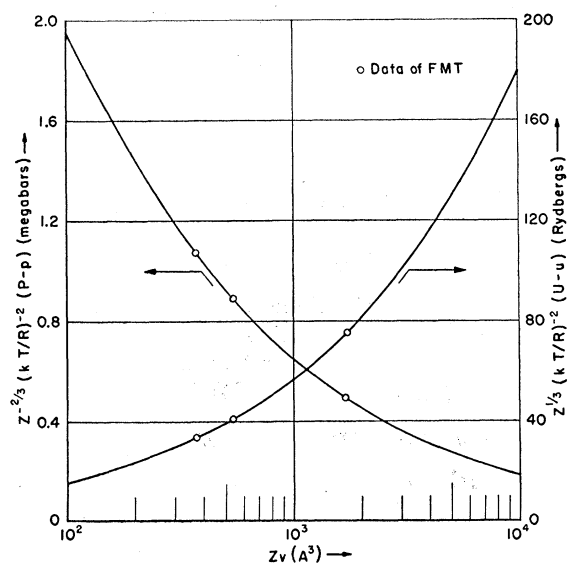


FIG. 6. Scaled pressure perturbation and energy perturbation from fitted functions for χ_b , χ'_b and ϕ_b , against scaled volume in cubic angstroms; temperature-perturbed case.

²⁰ By adjusting the exponent as well as the coefficient of the middle term in Eqs. (97) and (98), one can obtain a much closer fit. The accuracy obtained is considered sufficient, however, since χ_b and χ'_b are perturbation parameters. Note further that τ (known only to a few percent from the fitted function for ϕ_b) exceeds $-\sigma$ by a factor of about two and $-\omega$ by a factor of five or six, over the range of x_b corresponding to the data (Fig. 5).

shown in Fig. 4. Values of the parameters σ and ω computed from the fitted functions, as well as values of τ , are shown in Fig. 5 with directly computed values (omitted in the case of τ).

In Fig. 6, the effect of the first-order temperature perturbation on the equation of state is shown graphically by plotting $Z^{-1/3}(kT/R)^{-2}(P-p)$, which is independent of T , as a function of Zv . The energy perturbation $U-u$ in units of the Rydberg is shown similarly. The entropy S is not shown, since the value of $Z^{1/3}(kT/R)^{-1}S$ in $R/^\circ\text{K}$ differs from $Z^{1/3}(kT/R)^{-2}(U-u)$, as plotted, by the numerical factor 1.27×10^{-5} . The parameters ϵ_T and γ are shown in similar fashion in Fig. 7. The quantity $8(2/9\pi^2)^{1/3}\phi_b/x_b$, relative to which $Z^{-4/3}kT/R$ must be small, is shown by the dashed curve in Fig. 7. Note that the perturbation in a thermodynamic function scales with Z differently than does the unperturbed function (for fixed temperature).

5. CONCLUSION

As mentioned in the Introduction, neglect of exchange makes the results obtained valid only in the limit of high Z and high compression. It is hoped to extend this work by including exchange to remove this limitation. Since initiation of this work, extensive numerical results obtained by Dr. R. Latter indicate some systematic errors in the published data used; it is planned in the future to give fitted functions for the solution parameters which are based on more accurate data.

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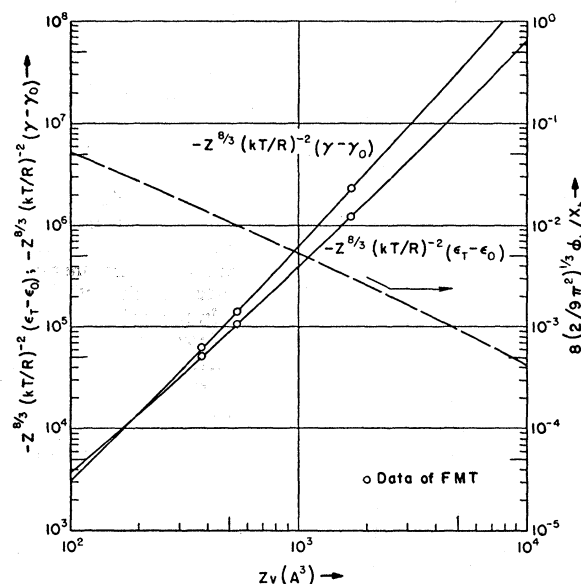


FIG. 7. Scaled perturbations in parameters γ and ϵ_T from fitted functions, against scaled volume in cubic angstroms; temperature perturbed case. The scaled temperature $Z^{-4/3}kT/R$ must be small relative to the quantity shown by the dashed curve.

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