Solution of the Temperature-Perturbed Thomas-Fermi Equation

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An analytic solution of the temperature-perturbed Thomas-Fermi equation of nth order is given in terms of quadratures on the unperturbed solution corresponding to zero temperature. The boundary and initial parameters corresponding to a solution, necessary for the thermodynamics, are given as explicit integrals in terms of the unperturbed solution, on the basis of a boundary condition for fixed atomic volume. Thus, every thermodynamic function at low temperature can be written as an asymptotic series, either in the even or the odd powers of the temperature, with coefficients which can be expressed in terms of quadratures on the zero-temperature solution. In particular, the coefficients of the asymptotic series corresponding to the basic thermodynamic functions (pressure, energy, entropy, enthalpy, Helmholts and Gibbs functions) can be expressed algebraically in terms of such quadratures. These results extend and generalize a similar result obtained by M. G. Mayer, restricted to the first-order temperature-perturbed case. The theory is applied in detail to the first-order case. From six neutral-atom zero-temperature solutions due to Feynman, Metropolis, and Teller, accurate values of the corresponding boundary and initial parameters of the first-order temperature-perturbed equation are obtained for the case of fixed atomic volume under the temperature perturbation.

In a previous paper[1] by this author, a general perturbation procedure of obtaining thermodynamic functions at low temperature for the temperature-perturbed Thomas-Fermi atom was outlined. The method was applied in detail to obtain the thermodynamic functions corresponding to a first-order temperature perturbation. The numerical results were based on three numerical solutions of the first-order perturbation equation due to FMT.[2]

This paper gives an analytic solution of the temperature-perturbed Thomas-Fermi equation of nth order in terms of quadratures on the unperturbed solution corresponding to zero temperature. Further, the boundary and initial parameters corresponding to a solution, necessary for the thermodynamics, can be written as explicit integrals on the basis of a boundary condition for fixed volume. Hence, one can show that all the basic thermodynamic functions (pressure, energy, entropy, enthalpy, Helmholtz and Gibbs functions) can be expressed as asymptotic series, either in the even or the odd powers of the temperature, with coefficients which can be written algebraically in terms of quadratures on the zero-temperature Thomas-Fermi function. A result similar to the last has been given by Mayer[3] for the first-order case, but with the salient difference that the pressure cannot be obtained except by a numerical differentiation with respect to volume.

This quadrature solution has been applied to six zero-temperature solutions of FMT to obtain accurate values of the boundary and initial parameters for the corresponding first-order temperature-perturbed cases, on the basis of a fixed atom volume. The temperature-perturbation solutions of FMT correspond to an atomic volume which is a function of temperature; the process in I of transforming (for convenience in the thermodynamics) the pertinent parameters derived from these solutions into parameters corresponding to a fixed volume degraded the accuracy to a few percent. This loss of accuracy is avoided in the direct solutions for fixed volume given here.

1. INTRODUCTION

The Thomas-Fermi function Φ is connected with the electrostatic potential V at a point r in an atom of atomic number Z by

$$Ze^2\Phi/\mu x = eV + kT\eta, \tag{1}$$

where e is the electronic charge, k is Boltzmann's constant, T is the temperature, $kT\eta$ is the chemical potential, and x is defined by $r=\mu x$, where $\mu = a_0(9\pi^2/128Z)^{\frac{1}{3}}$ in terms of the radius a_0 of the first Bohr orbit for hydrogen. The asymptotic form for low temperature of the generalized Thomas-Fermi equation which Φ satisfies is

$$d^2\Phi/dx^2 = (\Phi^{\frac{3}{2}}/x^{\frac{1}{2}})[1+\textstyle\sum_n \zeta_n (kTx/\Phi)^{2n}], \tag{2}$$

in which $n \geq 1$,

$$\zeta_n = (\mu/Ze^2)^{2n} a_n, \tag{3}$$

and the coefficients a_n are defined and tabulated by McDougall and Stoner.[4]

The function Φ can be expanded as an asymptotic series,

$$\Phi = \phi + \textstyle\sum_n \chi_n \zeta_n (kT)^{2n}, \tag{4}$$

where ϕ is the Thomas-Fermi function corresponding to $T=0$, and the perturbation χ_n of order n is a function of x. The function ϕ satisfies the differential equation

$$d^2\phi/dx^2 = \phi^{\frac{3}{2}}/x^{\frac{1}{2}}, \tag{5}$$

[1] J. J. Gilvarry, preceding paper [Phys. Rev. 96, 944 (1954)], referred to hereafter as I.
[2] Feynman, Metropolis, and Teller, Phys. Rev. 75, 1561 (1949), referred to hereafter as FMT.
[3] M. G. Mayer (private communication).
[4] J. McDougall and E. C. Stoner, Trans. Roy. Soc. (London) A237, 67 (1939).

and each perturbation χ_n satisfies an inhomogeneous linear differential equation of the form

$$d^2\chi_n/dx^2=\tfrac{3}{2}(\phi/x)^{\frac{1}{2}}\chi_n+f_n, \tag{6}$$

where f_n is a function of x, ϕ and the perturbations χ_1, χ_2, $\cdots$, χ_{n-1}. The form of f_n can be found by substituting the series (4) into the differential equation (2). The initial and boundary conditions on $\chi_n(x)$ are

$$\chi_n(0)=0, \tag{7a}$$

$$\chi_{n,b}=x_b[d\chi_n/dx]_{x=x_b}, \tag{7b}$$

where $\chi_{n,b}$ is the boundary value of χ_n at the boundary x_b of the unperturbed atom. The atomic volume corresponding to the boundary condition (7b) is $v=(4\pi/3)(\mu x_b)^3$; thus, the volume is unperturbed.

Fermi[5] has shown that one solution of the homogeneous equation corresponding to Eq. (6) is $\xi_1=\phi+\frac{1}{3}xd\phi/dx$ if ϕ satisfies Eq. (5). It follows that a second solution of the homogeneous equation is $\xi_2=\xi_1\int\xi_1^{-2}dx$. By the method of variation of parameters, one can then obtain the general solution of Eq. (6) in terms of integrals on ϕ and f_n. It is convenient to define four integrals, of which the first,

$$J_1(x)=\int_0^x[\phi+\tfrac{1}{3}x'd\phi/dx']^{-2}dx', \tag{8}$$

is a function only of x, and the three,

$$J_2(f,x)=\int_0^x f(x')[\phi+\tfrac{1}{3}x'd\phi/dx']dx', \tag{9a}$$

$$J_{12}(f,x)=\int_0^x J_1(x')f(x')[\phi+\tfrac{1}{3}x'd\phi/dx']dx', \tag{9b}$$

$$J_{21}(f,x)=\int_0^x J_2(f,x')[\phi+\tfrac{1}{3}x'd\phi/dx']^{-2}dx', \tag{9c}$$

are functionals of a function f of x. These four integrals satisfy the identity

$$J_{12}(f,x)+J_{21}(f,x)=J_1(x)J_2(f,x). \tag{10}$$

The general solution of Eq. (6) is then

$$\chi_n=[c_1+c_2J_1(x)+J_{21}(f_n,x)][\phi+\tfrac{1}{3}xd\phi/dx], \tag{11}$$

where c_1 and c_2 are constants.

2. FIRST-ORDER TEMPERATURE PERTURBATION

a. Quadrature Solution

The first-order differential perturbation equation corresponds to Eq. (6) with

$$f_1=x^{\frac{3}{2}}/\phi^{\frac{1}{2}}. \tag{12}$$

[5] E. Fermi, Mem. reale accad. Italia Classe sci. fis. mat. e nat. **1**, 1 (1930).

The solution satisfying the initial condition $\chi_1(0)=0$ is, from Eq. (11),

$$\chi_1=[\chi_{1,i}'J_1(x)+J_{21}(f_1,x)][\phi+\tfrac{1}{3}xd\phi/dx], \tag{13}$$

where $\chi_{1,i}'$ is the initial slope of the solution. Substitution of $x=x_b$ in this solution yields one equation connecting the boundary value $\chi_{1,b}$ with the initial slope $\chi_{1,i}'$, and the boundary condition (7b) provides another. The solution of these two equations yields, with use of the identity (10),

$$\chi_{1,b}=-12\phi_bJ_{12}(f_1,x_b)[9+4x_b^{\frac{1}{2}}\phi_b^{5/2}J_1(x_b)]^{-1}, \tag{14a}$$

$$\chi_{1,i}'=-\frac{9J_2(f_1,x_b)+4x_b^{\frac{1}{2}}\phi_b^{5/2}J_{21}(f_1,x_b)}{9+4x_b^{\frac{1}{2}}\phi_b^{5/2}J_1(x_b)}, \tag{14b}$$

where ϕ_b is the boundary value of ϕ. The boundary and initial parameters ($\chi_{1,b}$ and $\chi_{1,i}'$, respectively) of the solution, necessary for the thermodynamics, are thus obtained directly in terms of quadratures on ϕ.

In I, thermodynamic functions for the first-order temperature-perturbed case were given in a form in which the coefficient of T^2 or T was expressed in terms of the parameters σ, τ, and ω, of which

$$\tau=(x_b/\phi_b)^2 \tag{15}$$

depends on the solution of the zero-temperature equation, and

$$\sigma=\chi_{1,b}/\phi_b,\quad \omega=\chi_{1,i}'/(x_b^{\frac{1}{2}}\phi_b^{5/2}), \tag{16}$$

depend on the solution of the corresponding differential perturbation equation. Thus, the pressure P from I is

$$P=p[1+(5/2)(\sigma+2\tau)\zeta_1(kT)^2], \tag{17}$$

where p is the pressure

$$p=(Z^2e^2/10\pi\mu^4)(\phi_b/x_b)^{5/2}, \tag{18}$$

corresponding to the unperturbed atom of the same volume. By means of Eqs. (14), the parameters σ and ω can be written directly in terms of quadratures on ϕ. Hence, one obtains Mayer's result[3,6]: the coefficient of T^2 or T in the first-order perturbation of every thermodynamic function can be expressed in terms of quadratures on ϕ. This statement does not imply that the coefficient of T^2 or T may not contain a derivative with respect to x_b (or volume), as is necessarily the case, for example, in the differential parameter ϵ_T defined by

$$\epsilon_T=-(\partial\ln P/\partial\ln v)_T, \tag{19}$$

[6] M. G. Mayer derived this result independently of (and prior to) the considerations of this paper. It follows directly from the quadrature expression (22) for the entropy, since every thermodynamic function can be derived from the entropy. There is a slight difference between the result obtained by the method of Mayer and the result by the method of this paper: in the former case, thermodynamic functions are expressed in terms of quadratures on ϕ, while the method of this paper expresses them in terms of quadratures on ϕ and $d\phi/dx$ (since ϕ is given in tabular form for a solution, $d\phi/dx$ is also directly available). The pressure obtained by Mayer's method contains an integral on the function $\partial\phi/\partial x_b$, which is not obtained usually in a solution.

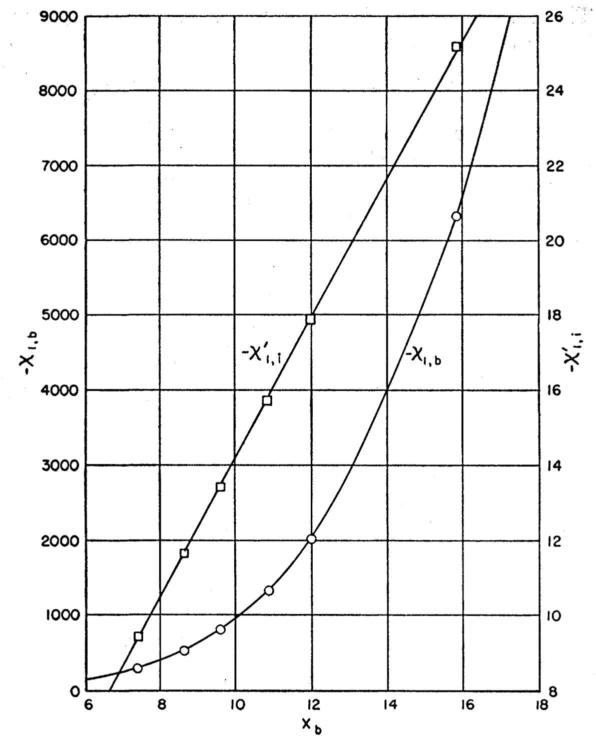

FIG. 1. Fitted functions for $\chi_{1,b}$ and $\chi_{1,i}'$ against boundary radius; first-order temperature-perturbed case.

and evaluated in I as

$$\epsilon_T=\epsilon_0-[(5/6)d\sigma/d\ln x_b+4\epsilon_0\tau]\zeta_1(kT)^2, \qquad (20)$$

where $\epsilon_0=(5/6)(1-d\ln\phi_b/d\ln x_b)$ corresponds to zero temperature.

The basic thermodynamic functions do not involve σ, τ, or ω differentially. In such a case, the coefficient of T^2 or T in the first-order perturbation can be evaluated algebraically in terms of quadratures on ϕ. Thus, the pressure P from Eq. (17) becomes

$$P=p\left\{1+5\left[\frac{x_b^2}{\phi_b^2}-\frac{6J_{12}(f_1,x_b)}{9+4x_b^{\frac{1}{2}}\phi_b^{5/2}J_1(x_b)}\right]\zeta_1(kT)^2\right\}. \qquad (21)$$

Computation of the entropy S in this manner yields the result of Mayer[3]

$$S=4(Z^2e^2/\mu)\zeta_1k^2T\int_0^{x_b}x^{\frac{3}{2}}\phi^{\frac{1}{2}}dx, \qquad (22)$$

where the special result

$$J_2(f_1,x)=\frac{2}{3}\left[x^{5/2}\phi^{\frac{1}{2}}-\int_0^{x}x^{\frac{3}{2}}\phi^{\frac{1}{2}}dx\right] \qquad (23)$$

for a first-order perturbation has been used. The energy U is

$$U=u+2(Z^2e^2/\mu)\zeta_1(kT)^2\int_0^{x_b}x^{\frac{3}{2}}\phi^{\frac{1}{2}}dx, \qquad (24)$$

where u is the energy at zero temperature corresponding to the unperturbed atom of the same volume, given by

$$u=(Z^2e^2/\mu)[(3/7)(\phi_i'-\phi_{i,\infty}')+(2/35)x_b^{\frac{1}{2}}\phi_b^{5/2}], \qquad (25)$$

in terms of the initial slope ϕ_i' and boundary value ϕ_b of ϕ ($\phi_{i,\infty}'$ is the initial slope corresponding to an infinite atom). The quadrature expressions of the enthalpy, and of the Helmholtz and Gibbs functions follow directly. The method of Mayer[3,6] does not yield the pressure, enthalpy, or Gibbs function in the form of an algebraic function of quadratures on ϕ, since the pressure must be determined from Eq. (22) by means of the relation $(\partial P/\partial T)_v=(\partial S/\partial v)_T$.

The statement made without proof in I that $\chi_{1,b}$ and $\chi_{1,i}'$ are monotonic functions of the radius x_b follows directly from Eqs. (14).

b. Numerical Results

The quadrature expressions (14) have been applied to the six neutral-atom zero-temperature solutions available from the work of FMT to obtain accurate values by numerical integration of the corresponding parameters $\chi_{1,b}$ and $\chi_{1,i}'$. The results are tabulated in Table I against the radius of the unperturbed atom to which they correspond, with those of I for comparison. The tabulated results have been fitted by expressions of the form

$$\chi_{1,b}=\sum_n C_n x_b^n, \quad \chi_{1,i}'=[\sum_m D_m x_b^{-m}]^{-1}, \qquad (26)$$

in which $n=3$, n', 5, and $m=1-\lambda_2$, m', 2, where $\lambda_2=[(73)^{\frac{1}{2}}-7]/2$ and n', m' are disposable exponents. The pair of coefficients C_3, D_2 and the pair C_5, $D_{1-\lambda_2}$ are chosen (with the corresponding exponents) to yield the proper asymptotic behavior of the fitted functions in the two limits $x_b\rightarrow 0$ and $x\rightarrow\infty$, respectively; thus $C_{n'}$ and $D_{m'}$ are the only disposable coefficients. The values of $C_{n'}$ and $D_{m'}$ (and their corresponding exponents) are tabulated in Table II, in conjunction with the values of the other coefficients from I. The tabulated coefficients yield fitted functions which reproduce the data of Table I within less than 0.4 percent in the cases of both $\chi_{1,b}$ and $\chi_{1,i}'$. The fitted functions and the data points are shown in Fig. 1.

Values of the parameters σ and ω computed from these fitted functions and from the fitted function for ϕ_b given in I are shown in Fig. 2 with the directly com-

TABLE I. Boundary and initial parameters, first-order temperature perturbation.

x_b	$-\chi_{1,b}$	$-\chi_{1,i}'$	$-\chi_{1,b}$ (from I)	$-\chi_{1,i}'$ (from I)
7.3851	$297._9$	9.41_5		
8.5880	$532._7$	11.6_2		
9.5651	$810._6$	13.4_2	$81_2.$	$13._4$
10.8038	$131_7.$	15.7_4	$13_{20}.$	$15._7$
11.9634	$198_5.$	17.9_1		
15.8698	$634_7.$	25.1_5	$64_{20}.$	$24._8$

puted values for comparison (the parameter τ from results of I is shown likewise). In Fig. 3, the effect of the first-order temperature perturbation on the equation of state is shown graphically by plotting $Z^{-\frac{2}{3}}(kT/R)^{-2}\times(P-p)$, which is independent of T, as a function of Zv (R is the Rydberg); the energy perturbation $U-u$ in units of R is shown similarly. The value of $Z^{\frac{1}{3}}(kT/R)^{-1}S$ in $R/°\mathrm{K}$ differs from $Z^{\frac{1}{3}}(kT/R)^{-2}(U-u)$, as plotted, by the numerical factor 1.27×10^{-5}. The dimensionless parameters ϵ_T and γ, defined by Eq. (19) and by $U=Pv/(\gamma-1)$, respectively, are shown in similar fashion in Fig. 4 (γ_0 corresponds to zero temperature).

3. GENERAL TEMPERATURE PERTURBATION

The functions f_n of Eq. (6) are

$$f_2=(x\phi)^{-\frac{1}{2}}\left\{\frac{x^4}{\phi^2}-\frac{a_1^2}{a_2}\left[\frac{1}{2}\frac{x^2}{\phi}\chi_1-\frac{3}{8}\chi_1^2\right]\right\}, \tag{27a}$$

$$f_3=(x\phi)^{-\frac{1}{2}}\left\{\frac{x^6}{\phi^4}+\frac{a_1^3}{a_3}\left[\frac{3}{8}\frac{x^2}{\phi^2}\chi_1^2-\frac{1}{16\phi}\chi_1^3\right]\right.$$
$$\left.-\frac{a_1a_2}{a_3}\left[\frac{5}{2}\frac{x^4}{\phi^3}\chi_1+\frac{1}{2}\frac{x^2}{\phi}\chi_2-\frac{3}{4}\chi_1\chi_2\right]\right\}, \tag{27b}$$

for $n=2, 3$. A general (but rather complex) formula can be given for arbitrary n. The general solution of the differential perturbation equation of nth order is, from Eq. (11),

$$\chi_n=[\chi_{n,i}'J_1(x)+J_{21}(f_n,x)][\phi+(1/3)xd\phi/dx], \tag{28}$$

where $\chi_{n,i}'$ is the initial slope of the solution. It has been shown in the preceding that χ_1 can be expressed in terms of quadratures on ϕ. It follows by induction that f_n (which in the first instance is a function of x, ϕ and $\chi_1, \chi_2, \cdots, \chi_{n-1}$) and thus χ_n can be so expressed. The boundary value $\chi_{n,b}$ and initial slope $\chi_{n,i}'$ of χ_n are then obtainable from the equations derived by replacing f_1 with f_n in Eqs. (14a) and (14b), respectively. Thus the solution of the perturbation equation of nth order and the associated boundary and initial parameters can all be expressed in terms of quadratures on ϕ.

The thermodynamic functions that are available directly from a solution of the Thomas-Fermi equation are essentially the pressure and the volume. The

TABLE II. Coefficients[a] of fitted functions, first-order temperature perturbation.

n	C_n	m	D_m
3	-3.205×10^{-1}	$1-\lambda_2=0.2280$	-5.805×10^{-3}
$n'=4.059$	-3.424×10^{-2}	$m'=0.8159$	-2.325×10^{-1}
5	-2.519×10^{-3}	2	-3.120

[a] The coefficients are given to four figures to minimize round-off error.

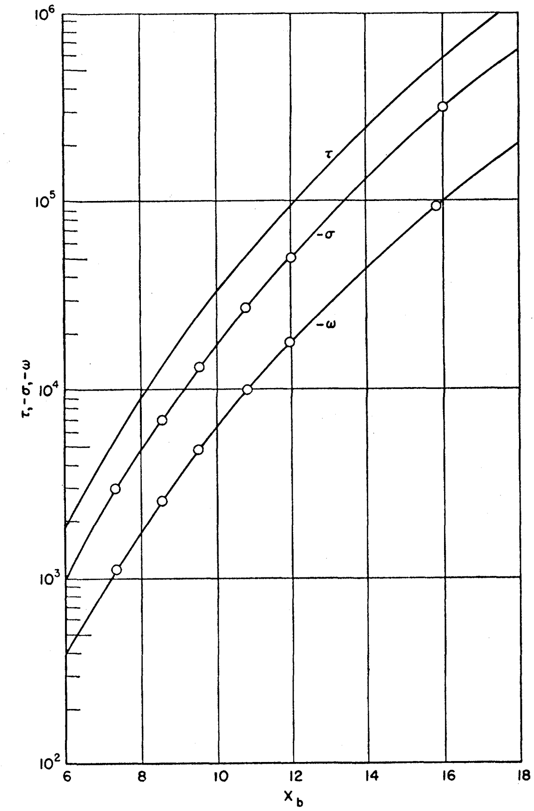

FIG. 2. Perturbation parameters σ, τ, and ω from fitted functions for $\chi_{1,b}$, $\chi_{1,i}'$, and ϕ_b, against boundary radius; first-order temperature-perturbed case.

pressure P is given by the asymptotic series,

$$P=\frac{Z^2e^2}{10\pi\mu^4}\left(\frac{\Phi_b}{x_b}\right)^{5/2}\left[1+\sum_n\frac{5\zeta_n}{5-4n}\left(\frac{kTx_b}{\Phi_b}\right)^{2n}\right], \tag{29}$$

where Φ_b, given by

$$\Phi_b=\phi_b+\sum_n\chi_{n,b}\zeta_n(kT)^{2n}, \tag{30}$$

is the boundary value of Φ. Thus, the pressure can be expressed as an asymptotic series in T^2, with coefficients which can be evaluated in terms of quadratures on ϕ. From I, the energy[7] E is given by

$$E=\tfrac{3}{4}T^{7/4}\int_0^T T^{-\frac{3}{4}}(\partial/\partial T)_v$$
$$\times\{T^{-1}[Pv+(Z^2e^2/\mu)\Phi_i']\}dT, \tag{31}$$

where the integration is carried out at constant volume, and Φ_i', defined by

$$\Phi_i'=\phi_i'+\sum_n\chi_{n,i}'\zeta_n(kT)^{2n}, \tag{32}$$

is the initial slope of Φ. If this series for Φ_i' and the series (29) for P are substituted into Eq. (31), E can

[7] The energy E differs from U introduced previously by the energy corresponding to a standard state (an infinite atom at zero temperature).

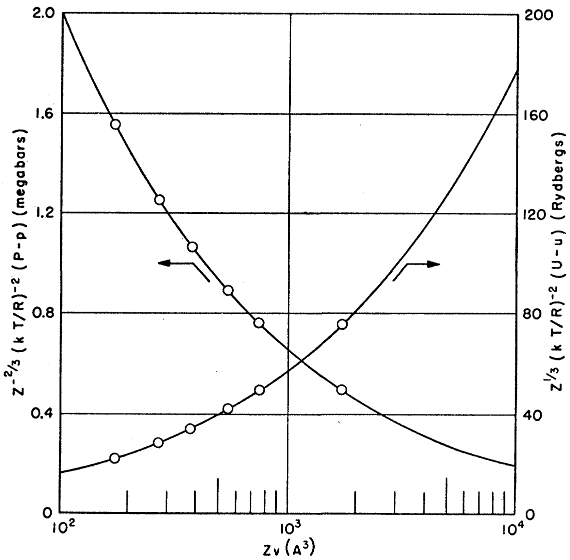

FIG. 3. Scaled pressure perturbation and energy perturbation from fitted functions for $\chi_{1,b}$, $\chi_{1,i}'$, and ϕ_b, against scaled volume in cubic angstroms; first-order temperature-perturbed case.

be expressed as an asymptotic series in T^2,

$$E=E_0+\sum_n E_n\zeta_n(kT)^{2n}, \tag{33}$$

where the term E_0 corresponds to zero temperature, and the temperature-independent coefficients E_n are functions in the first instance of x_b, ϕ_b; $\chi_{1,b}$, $\cdots$, $\chi_{n,b}$; $\chi_{1,i}'$, $\cdots$, $\chi_{n,i}'$. Thus, the energy likewise can be expressed as an asymptotic series in T^2, with coefficients in terms of quadratures on ϕ. This expansion is analogous to the corresponding result[8] in the case of a degenerate Fermi-Dirac gas. From the energy, one can obtain every thermodynamic function by algebraic, differential, or integral processes. Hence the result follows: every thermodynamic function at low temperature can be written as an asymptotic series, either in the even or the odd powers of the temperature, with coefficients in terms of quadratures on ϕ. This statement is the generalization to a perturbation of nth order of Mayer's result for the case $n=1$ cited previously.

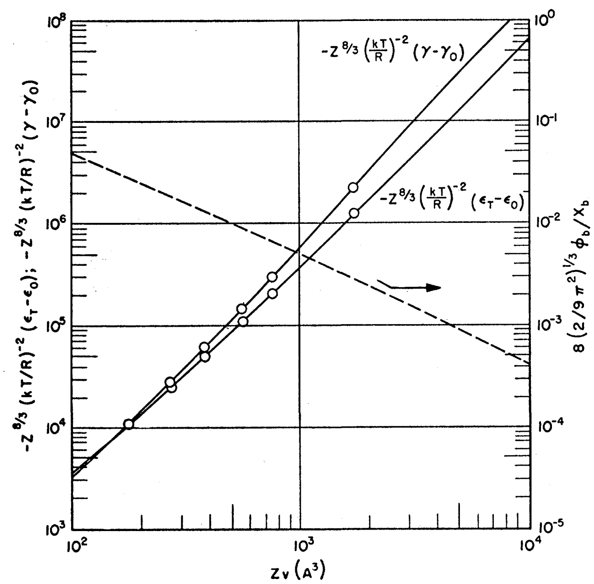

FIG. 4. Scaled perturbations in parameters γ and ϵ_T from fitted functions, against scaled volume in cubic angstroms; first-order temperature-perturbed case. The scaled temperature $Z^{-4/3}kT/R$ must be small relative to the quantity shown by the dashed curve.

The coefficients of the asymptotic series corresponding to the basic thermodynamic functions can be written in algebraic form in terms of quadratures on ϕ. This statement is obvious in the case of the pressure and the energy, from which it follows for the enthalpy. The entropy S, from Eq. (33) and the relation $T(\partial S/\partial T)_v=(\partial E/\partial T)_v$, is

$$S=\sum_n[2n/(2n-1)]E_n\zeta_n k^{2n}T^{2n-1}, \tag{34}$$

from which the statement follows for the corresponding coefficients. The result for the Helmholtz and Gibbs functions then follows directly.

The method of this paper of solving the temperature-perturbed Thomas-Fermi equation can be used likewise to obtain a solution of the Thomas-Fermi-Dirac[2] equation in powers of the parameter $\epsilon=(3/32\pi^2)^{\frac{1}{3}}Z^{-\frac{2}{3}}$. The corresponding approximation improves for higher Z and for higher compressions. To a degree depending on the powers of ϵ retained, it should be valid except at the immediate boundary of the limiting atom (atom of largest radius); the type of difficulty that enters at this boundary is the same as appears in Sommerfeld's perturbation treatment of the positive ion.[9] This approximation yields a method of determining the exchange correction to the binding energy of an atom, alternative to that of Scott[10] or March.[11] Difficulties associated with the boundary of the atom should be unimportant in this application, since the boundary region of the limiting atom contributes little to the energy.

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