Solutions of the Temperature-Perturbed Thomas-Fermi Equation*

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Previous numerical results are extended by using an analytical solution of the temperature-perturbed Thomas-Fermi equation to obtain boundary and initial parameters corresponding to seven neutral-atom zero-temperature solutions given by Slater and Krutter. Fitted functions given previously for the solution parameters in terms of the unperturbed atom radius are revised to include the new data, to obtain a considerable extension in directly-fitted range. Effects of the temperature perturbation on the equation of state, the internal energy, and parameters related to the equation of state are shown graphically for the extended range.

In a previous paper[1] by one of the authors, thermodynamic functions for the Thomas-Fermi atom model at low temperature were obtained by a perturbation method. In a further paper,[2] an analytic solution of the temperature-perturbed Thomas-Fermi equation of general order was given in terms of quadratures on the unperturbed Thomas-Fermi function for zero temperature. This quadrature solution yields the boundary and initial parameters of a solution, which enter the thermodynamic functions, as explicit integrals on the zero-temperature function to which the solution refers.

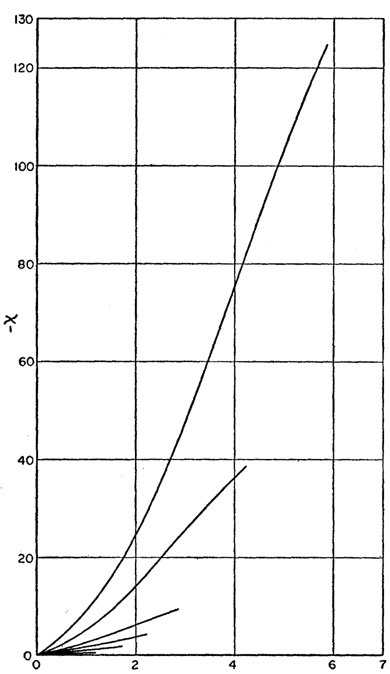

Fig. 1. Solution for the temperature-perturbation function χ as a function of radial distance x in the atom, from data of SK. The solution corresponding to the second parenthetic case in Table I has been omitted.

From these results, accurate values of the boundary and initial parameters of the corresponding first-order temperature-perturbed equation were obtained from six neutral-atom zero-temperature solutions given by FMT.[3] The values of the parameters were fitted semi-empirically by functions of the atom radius having the proper limiting behavior in the cases of an infinitesimal and an infinite atom, to make values of the thermodynamic functions readily accessible without the need for interpolation.

This paper extends the numerical results of II by obtaining the values of the boundary and initial parameters corresponding to seven neutral-atom zero-temperature solutions obtained by SK,[4] as tabulated by Gombas.[5] The solutions of SK refer to considerably smaller atomic volumes than do those of FMT; the smallest volumes approach those corresponding to a degenerate Fermi-Dirac gas. The fitted functions of II have been revised to include the values of the solution parameters derived from the data of both SK and FMT. With this revision, the fitted functions in the tem-

Table I. Boundary and initial parameters from data of SK; zero-temperature case.

$-\phi_i'$ (from SK)	ϕ_b	x_b	x_b (from SK)
1.00	1.447	1.194_2	1.19
1.38	0.946_9	1.696_0	1.69
1.50	0.6650	2.20_4	2.20
1.55	0.477_7	2.80_4	2.80
1.58	0.2556	4.24_4	4.23
1.586	(0.150_2)[a]	(5.86_4)[a]	5.85
1.588	(0.073)[b]	(8.5)[b]	8.59
1.58808	0		∞

[a] The values of SK for ϕ in this case have a discontinuity of jump 0.0037 at the point $x=1.46$. It was concluded that the error probably lay in the region $x<1.46$, since subtraction for $x>1.46$ of the saltus 0.0037 to make ϕ and its derivatives continuous yielded a value of ϕ_b (and of χ_b and χ_i') not smooth with respect to the other values of the table. The tabulated boundary values were derived from unchanged data.

[b] In this case, only two figures are given in the data at the boundary, so that this point is of low weight. The point is bracketed by two points from the data of FMT, which yield by interpolation (for the tabulated x_b) a value of ϕ_b differing by about 4 percent from the tabulated ϕ_b. This case was ignored in obtaining the fitted functions of I for ϕ_b and $\phi_i'-\phi_{i,\infty}'$.

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[1] J. J. Gilvarry, Phys. Rev. **96**, 934 (1954), referred to hereafter as I.

[2] J. J. Gilvarry, Phys. Rev. **96**, 944 (1954), referred to hereafter as II.

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

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

[5] P. Gombas, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949), pp. 53, 357.

TABLE II. Boundary and initial parameters from data of SK, temperature-perturbed case.

x_b	$-\chi_b$	$-\chi_i'$
1.194_2	0.587_5	0.429_5
1.696_0	1.78_5	0.826_6
2.20_4	4.18_7	1.33_2
2.80_4	9.32	2.03_4
4.24_4	38.8_5	4.07_2
5.86_4	$(124._7)$[a]	(6.73_5)[a]
8.5	$(51_1.)$[b]	$(11._4)$[b]

[a] It was found that the values of χ_b and χ_i' depend very little on the values of ϕ to the left of the discontinuity noted in Table I for this case, and hence the saltus in ϕ was removed by fairing the data into the value unity at $x=0$. Different but reasonable fairings yielded changes in χ_b and χ_i' less than their corresponding possible errors. The tabulated values for this case seem smooth with respect to the other values of the table.

[b] The values of χ_b and χ_i' are smooth, within less than 0.5 percent, with respect to the bracketing values from the data of FMT, in spite of the difficulty noted in Table I.

perature-perturbed case cover the same directly fitted range of data as do the fitted functions in the zero-temperature case, as given in I.

The notation used is the same as in papers I and II; the subscript 1 is deleted from the symbols correspond- to the first-order temperature-perturbation function χ and to its boundary value χ_b and initial slope χ_i'.

1. NUMERICAL RESULTS

To obtain accurate values of the integrals entering χ_b and χ_i', the tabulated zero-temperature solutions of SK (given in all but one case to four figures at the atom boundary) were used to obtain improved values of the boundary radius x_b (given to only three figures by SK), and of the boundary value ϕ_b (not given by SK). The computed values of ϕ_b and x_b are tabulated in Table I against the initial slope ϕ_i' to which they correspond, with the values of x_b from SK for comparison. Parenthetic values in the table involve minor discrepancies, as noted. With the exception of the second parenthetic case (in the region of which smoothing was used to give major weight to the data of FMT), the values of ϕ_b given in this table are essentially the ones used to obtain the fitted function[6] of I for ϕ_b. As is evident from the table, the number of significant figures given by SK for the initial slope ϕ_i' (or, more important, for the difference $\phi_i'-\phi_{i,\infty}'$, where $\phi_{i,\infty}'$ is the initial slope corresponding to an atom of infinite radius) is not commensurate in general with the number possible in the other parameters, on the basis of the solutions as tabulated.

TABLE III. Coefficients[a] of fitted functions from data of SK and FMT; temperature-perturbed case.

n	C_n	m	D_m
3	-3.205×10^{-1}	$1-\lambda_2=0.2280$	-5.805×10^{-3}
$n'=4.215$	-2.331×10^{-2}	$m'=0.7400$	-1.925×10^{-1}
5	-2.519×10^{-3}	2	-3.120

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

[6] Boundary and initial parameters, as given by Gombas, corresponding to an eighth solution of SK for large volume, have been ignored in Table I, because of apparent lack of sufficient significant figures in the difference $\phi_i'-\phi_{i,\infty}'$. No solution corresponding to these boundary and initial values is tabulated by Gombas.

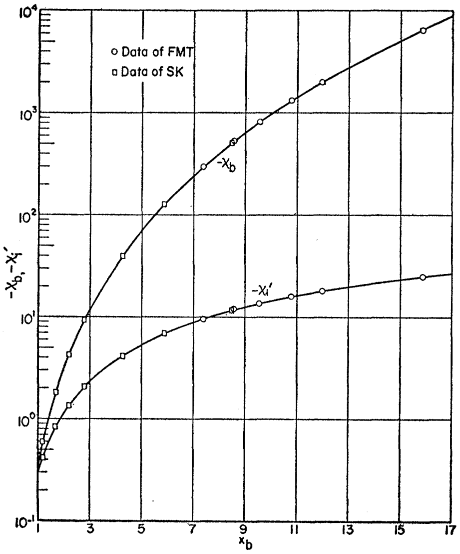

FIG. 2. Fitted functions for χ_b and χ_i' against boundary radius x_b of atom.

With these boundary parameters for the unperturbed case, the values of χ_b and χ_i' corresponding to a temperature perturbation were determined from Eqs. (14) of II by numerical integration on the zero-temperature solutions of SK. The results are tabulated in Table II against the unperturbed radius to which they correspond. The values of χ_i' yield, from Eq. (13) of II, the solutions plotted in Fig. 1 for the temperature-perturbation function χ as a function of radial distance x in the atom. The solutions corresponding to the smaller values of x_b do not differ much from the straight lines

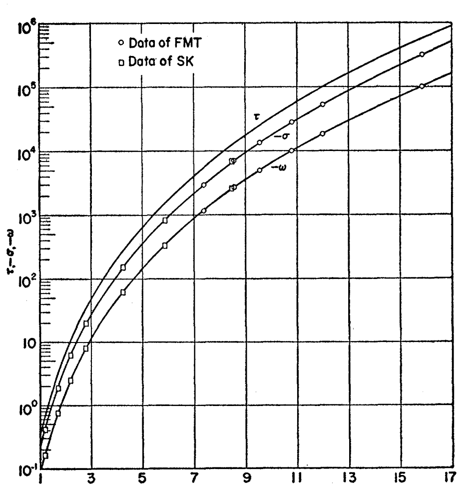

FIG. 3. Perturbation parameters σ, τ, and ω from fitted functions, against boundary radius x_b of atom.

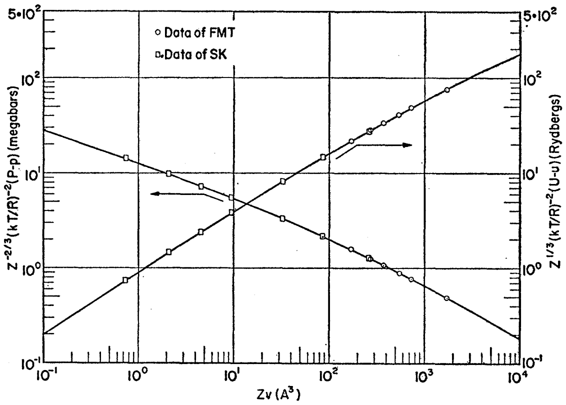

FIG. 4. Scaled pressure and energy perturbations from fitted functions, against scaled volume in cubic angstroms.

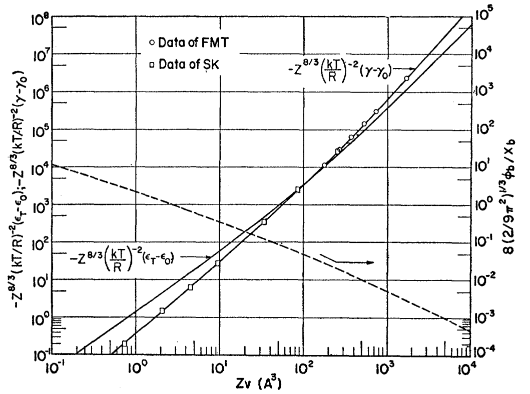

FIG. 5. Scaled perturbations in parameters ϵ_T and γ from fitted functions, against scaled volume in cubic angstroms. The scaled temperature $Z^{-4/3}kT/R$ must be small relative to the quantity shown by the dashed curve.

characteristic (as noted in I) of the Fermi-Dirac limit.

The results of Table II from the data of SK, combined with the results of II from the data of FMT, have been fitted by expressions of the form

$$\chi_b=\sum_n C_n x_b^n, \quad \chi_i'=[\sum_m D_m x_b^{-m}]^{-1}, \tag{1}$$

in which $n=3$, n', 5 and $m=1-\lambda_2$, m', 2, where $\lambda_2=\frac{1}{2}(73^{\frac{1}{2}}-7)$ and n', m' are disposable exponents. As in II, the pair of coefficients C_3, D_2 and the pair C_5, $D_{1-\lambda_2}$ are chosen with their corresponding exponents to yield the proper asymptotic behavior of the fitted functions in the two limits $x_b\rightarrow 0$ and $x_b\rightarrow\infty$, respectively, so that $C_{n'}$ and $D_{m'}$ are the only disposable coefficients. The values of the disposable coefficients and exponents are tabulated in Table III with the values of the others from II. The corresponding fitted functions reproduce the data of Table II, and the data of Table I in II, within 2.3 percent in χ_b and 1.5 percent in χ_i'. The change in the disposable exponent and coefficient in the fitted function for χ_b or χ_i' is relatively small compared to the corresponding value of II. The fitted functions are shown in Fig. 2, with data points from this paper and from II.

Values of the perturbation parameters σ and ω from Eqs. (16) of II, computed by means of these fitted functions and the fitted function for ϕ_b given in I, are shown in Fig. 3 with directly computed values from this paper and from II for comparison. The perturbation parameter τ is shown likewise from results of I. In Fig. 4, the effect of the first-order temperature perturbation on the equation of state is shown graphically by plotting $Z^{-2/3}(kT/R)^{-2}(P-p)$, where R is the Rydberg, against the scaled volume Zv; the ordinate is independent of temperature. The energy perturbation $U-u$ in units of R is shown similarly; the value of $Z^{1/3}(kT/R)^{-1}S$ in $R/°K$, where S is the entropy, differs from the plotted quantity by the numerical factor 1.27×10^{-5}. In Fig. 5, the dimensionless parameters $\epsilon_T-\epsilon_0$ and $\gamma-\gamma_0$ associated with the equation of state are shown in similar manner; data points corresponding to $\epsilon_T-\epsilon_0$ (for which fitted functions must be used to obtain the necessary derivatives) are omitted. The dimensionless quantity $8(2/9\pi^2)^{1/3}\phi_b/x_b$ shown in Fig. 5 represents a limit relative to which the scaled temperature $Z^{-4/3}\,kT/R$ must be small, for validity of the perturbation method.

2. CONCLUSION

The large extension in directly fitted range of the fitted functions, obtained by inclusion of results from the data of SK, is obvious from the figures.

As pointed out by Umeda,[7] and noted in connection with Table I, minor inconsistencies exist between the data of SK and FMT. The discrepancies point to the existence of small systematic errors in one or both sets of data. Extensive numerical solutions of the Thomas-Fermi equation obtained by Dr. R. Latter yield the same conclusion. As a consequence, limits of accuracy quoted for the fitted functions refer only to the data employed; the actual error may be larger.

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[7] K. Umeda, Phys. Rev. 83, 651 (1951).