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LOWERING OF IONIZATION POTENTIALS IN PLASMAS

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ABSTRACT

The average electrostatic potential near a nucleus immersed in a plasma is evaluated using a finite-temperature Thomas-Fermi model. The part of this potential directly attributable to the presence of the plasma is isolated and is used to evaluate the reduction in ionization potential for a wide range of parameters. A simple analytic solution, exhibiting Debye-Hückel and ion-sphere limits, is also obtained and is used as an interpolatory device.

I. INTRODUCTION

In a plasma of finite density the potential distribution in and near a given ion is influenced not only by its own bound electrons but also by free electrons, by neighboring ions, and (slightly) by neutral atoms. These perturbers produce effects of two kinds: their time-averaged effect is to alter the set of energy levels available to the ion in question, and their time-dependent effect is to broaden these levels both by shifting them back and forth adiabatically and by inducing transitions between them. The first effect, besides providing a natural cutoff to the bound-state partition function, effectively lowers all the ionization potentials and shifts the equilibrium occupation numbers in the direction of increased ionization. This effect, which is most important at high densities, is usually called "pressure ionization." The second effect, "pressure broadening," is not considered in this paper.

Pressure ionization has often been treated by assigning to each ion a sphere occupying the ion's share of the total volume and containing the ion and enough free electrons to make the sphere's net charge zero (Mayer 1947; Armstrong, Sokoloff, Nicholls, Holland, and Meyerott 1961). In the simplest form of this "ion-sphere" approach, the free-electron density is assumed spatially uniform. Inside the sphere the potential due to the contents of neighboring spheres is neglected. Thus, close encounters between ions are disregarded, and the picture is basically that of a crystal lattice with strongly correlated ion positions. This strong positional correlation between ions (though not necessarily the uniform free-electron density) may be expected to hold at high densities and at low temperatures. At the opposite extreme is the case of nearly random ion positions; the first-order deviation from randomness leads to the Debye-Hückel potential (Debye and Hückel 1923; Griem 1964), which is valid in the low-density, high-temperature limit. In this paper we develop a theory of pressure ionization which yields the ion-sphere and Debye-Hückel results as approximate limiting cases, and provides results over essentially the entire range of temperatures and densities for which appreciable ionization exists and the free electrons are non-degenerate.

Our starting point is the finite-temperature Thomas-Fermi (TF) model for the electrons, which has previously been employed (Marshak and Bethe 1940; Feynman, Metropolis, and Teller 1949; Latter 1955) to calculate the equation of state of high-temperature, high-density material. In these calculations the entire electron distribution was described as a Fermi gas divided into ion spheres, and the resulting equation of state shows no effects of atomic shell structure. Keller and Meyerott (1952) extended the model to include the ions in the vicinity of a given nucleus, thus relaxing the "frozen" nuclear positions

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of the ion-sphere model; they solved the resulting differential equation for the total potential numerically, subtracted the potential of the nucleus and inner electrons, and interpreted their results in terms of the perturbing potential experienced by bound electrons in various shells, i.e., the lowering of the ionization potential for each shell. Expressing the interactions between bound electrons in terms of screening constants, they then obtained the average occupation number for each shell as a function of temperature and density, using the perturbed binding energies. However, their treatment appears to include *twice* the interaction of a given bound electron with all bound electrons located further from the nucleus: once in the perturbing potential, and once in the screening constants. Consequently they obtained marked differences from shell to shell in the "effect of the surrounding plasma on the ionization potential," since these outer bound electrons were in effect included as part of the "surrounding plasma."

Accordingly, we have reformulated the model so as to isolate the potential due to the *free* electrons and neighboring ions; a free electron is one with sufficient energy to escape to infinity in the plasma. It is this potential which we identify with the "effect of the surrounding plasma," regarding the bound electrons as part of the unperturbed ion; one result is that the perturbing potential is practically the same for all bound electrons except highly excited ones.

An essential physical limitation of the model is its neglect of fluctuations; only time-averaged, spherically symmetric potential and charge distributions are considered. Thus near a given "central" ion the position correlation between each perturber and the central ion is taken into account, as is the correlation between each perturber and the "mean" distribution of the other perturbers, but the correlation between individual perturbers is neglected. This neglect is shown by Keller and Meyerott (1952) to be justified in the case of a multiply charged central ion surrounded by perturbers of smaller charge—e.g., in the astrophysically important case of a stellar mixture consisting mostly of hydrogen and helium in which the ionization potential of a heavy ion is sought. In other circumstances the validity of the model has not been proven, so our results are perhaps provisional; however, because of the relationship of the present model to the simpler treatments mentioned above, we have considered it illuminating to cover a large range of parameters for comparison purposes.

II. FORMULATION

Consider a nucleus Z fixed in a sea of electrons and point ions (we neglect the influence of neutral atoms) at a kinetic temperature T. We wish to find the time-averaged potential distribution around Z, and we assume for the present that only this average is felt by any one particle; that the potential distribution is spherically symmetric around Z; that it is determined by the time-averaged, spherically symmetric charge density; and that it changes only slightly within one particle wavelength. We describe the electrons by non-relativistic Fermi-Dirac statistics and the ions by non-relativistic Maxwell-Boltzmann statistics. These assumptions are those of the finite-temperature TF atomic model, extended to include the neighboring ions. The electrostatic potential $\Phi(r)$ is then determined by the Poisson equation

$$\nabla^2\Phi = \frac{1}{r}\frac{d^2}{dr^2}(r\Phi) = -4\pi e\left(\sum_i z_i n_i - n_e\right),$$

where n_e is the local number density of electrons, n_i is the local number density of ions of charge ez_i, and

$$n_e(r) = n_e(\infty)\frac{F\{[e\Phi(r)/kT] - a\}}{F(-a)}, \qquad n_i(r) = n_i(\infty)\exp\left[-z_i\frac{e\Phi(r)}{kT}\right],$$

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$$F(\eta)=\int_0^{\infty}\frac{t^{1/2}dt}{e^{t-\eta}+1}, \qquad \Phi(\infty)=0, \qquad r\Phi\rightarrow Ze \text{ as } r\rightarrow 0 .$$

The degeneracy parameter α is related to the free-electron density far from the ion $n_e(\infty)$ by

$$n_e(\infty)=\frac{2(2\pi mkT)^{3/2}}{h^3}\frac{2}{\sqrt{\pi}}F(-\alpha) .$$

We consider only applications where α is positive and appreciably larger than unity; i.e., the density is sufficiently low that the free electrons are non-degenerate, and

$$\frac{2}{\sqrt{\pi}}F(-\alpha)\cong e^{-\alpha}\ll 1 .$$

Close to the nucleus, where $e\Phi > \alpha kT$, there is a region of degenerate bound electrons which is, in fact, the ion core. The asymptotic ion densities $n_i(\infty)$ satisfy the condition of electrical neutrality, $\Sigma_i z_i n_i(\infty) = n_e(\infty)$.

Under the substitutions

$$y=\frac{e\Phi}{kT}, \qquad x=\frac{r}{D}, \qquad \frac{1}{D^2}=\frac{4\pi e^2}{kT}\sum_i (z_i^2+z_i)n_i(\infty)$$

(note that D is the Debye length including ions and electrons), the above equations take the non-dimensional form

$$\frac{1}{x}\frac{d^2}{dx^2}(xy)=\frac{1}{z^*+1}\left[\frac{F(y-\alpha)}{F(-\alpha)}-\frac{\langle z\exp(-zy)\rangle}{\langle z\rangle}\right],$$

where $\langle\ \rangle$ denotes an average, weighted with $n_i(\infty)$, over ion species, and $z^* \equiv \langle z^2\rangle/\langle z\rangle$. The second term on the right side may be simplified with small loss of accuracy by noting that it is comparable with the first only for fairly small y; in this region,

$$\frac{\langle z\exp(-zy)\rangle}{\langle z\rangle}\cong\frac{\langle z(1-zy+\ldots)\rangle}{\langle z\rangle}=1-z^*y+\ldots\cong e^{-z^*y},$$

so that to this approximation the assortment of ion species present can be replaced by a single fictitious species with charge z^*; z^* is never less than unity, even when $\langle z\rangle\rightarrow 0$. Our basic equation for the potential distribution is then

$$\frac{1}{x}\frac{d^2}{dx^2}(xy)=\frac{1}{z^*+1}\left[\frac{F(y-\alpha)}{F(-\alpha)}-\exp(-z^*y)\right], \tag{1}$$

with boundary conditions $y(\infty) = 0$ and $xy\rightarrow Ze^2/(DkT) \equiv K_0$ as $x\rightarrow 0$.

Up to this point, our development is essentially the same as that of Keller and Meyerott (1952). Our treatment differs from theirs in the development which follows; we do not consider bound electrons as contributing to the pressure lowering of the ionization potential, since the bound electrons are already present in the isolated ion.

We do not want to treat the ion whose nucleus is Z entirely by the TF model, but we want to isolate and evaluate the effect of the *free* electrons and neighboring ions on the potential distribution. Since the density distribution of these perturbers depends somewhat on the bound-electron distribution, we must assume a bound-electron distribution in order to find the free-electron distribution and the neighboring ion distribution. Having done so by means of the TF model, which approximates the average bound-electron distribution, we may apply this same perturbing potential to better models for the unperturbed bound-electron states, such as those of the isolated ion.

The perturbing potential Φ_f satisfies a Poisson equation in which only the free-electron and ion densities appear, and in dimensionless form this equation is

$$\frac{1}{x}\frac{d^2}{dx^2}(xv)=\frac{1}{z^*+1}\left[\frac{F(y-a,y)}{F(-a)}-e^{-z^*y}\right], \tag{2}$$

where $v = e\Phi_f/kT$ and

$$F(y-a,y)=\int_y^\infty \frac{t^{1/2}dt}{e^{t+a-y}+1}.$$

[Note that $F(y-a,y)/F(y-a)$ is the ratio of free-electron density to total electron density in the TF model; we define a free electron as one whose kinetic energy exceeds $e\Phi$.] Unlike $y(x)$, which contains the nuclear potential, $v(x)$ is finite at the origin, and $v'(0) = 0$. If we choose the zero of potential such that $v(\infty) = 0$, $v(x)$ will be negative; we let $-v(0)$ equal J. Then

$$v(x)=-J+\int_0^x S(t)\,t\,dt-\frac{1}{x}\int_0^x S(t)\,t^2dt, \tag{3}$$

where $S(x)$ is the right-hand side of equation (2), containing the solution $y(x)$ of equation (1). Hence, $J=\int_0^\infty S(x)x\,dx$. We can put equation (3) in a more convenient form:

$$v(x)=-\frac{1}{x}\int_0^\infty S(t)\,t^2dt+\frac{1}{x}\int_x^\infty S(t)\,t^2dt-\int_x^\infty S(t)\,t\,dt, \tag{4}$$

in which the first term, dominant at large x, may be identified as the asymptotic Coulomb potential of the total excess of free electrons over neighboring ions. It will be seen shortly that the total potential $y(x)$ vanishes exponentially at large x. Now the potential due to the nucleus and bound electrons alone, $y(x) - v(x)$, has an asymptotic Coulomb form which depends only on the net ionic charge; this observation permits us to find the net ionic charge in terms of $\int_0^\infty S(t)t^2\,dt$.

In the solution of the foregoing equations, the following expansions (Keller and Fenwick 1953) are useful; they are valid when a is somewhat larger than unity, so that $e^a \gg 1$ and the free electrons are non-degenerate (only this case is treated in what follows):

$$\frac{F(y-a)}{F(-a)}=e^y[1-2^{-3/2}e^{y-a}(1-e^{-y})+\dots] \qquad (y\ll a)$$

$$=\frac{4}{3\sqrt{\pi}}\,e^a(y-a)^{3/2}\left[1+\frac{\pi^2}{8(y-a)^2}+\dots\right] \qquad (y\gg a),$$

$$\frac{F(y-a,y)}{F(-a)}=2\sqrt{\left(\frac{y}{\pi}\right)}+e^y(1-erf\sqrt{y})=2\sqrt{\left(\frac{y}{\pi}\right)}\left[1+\frac{1}{2y}-\frac{1}{4y^2}+\dots\right] \quad (y\gg 1)$$

$$=1+y+\frac{4}{3\sqrt{\pi}}\,y^{3/2}+\tfrac{1}{2}y^2\dots \qquad (y\ll 1).$$

From these and the form of equation (1), we can distinguish four regions of progressively smaller x (larger y).

Region A.—The limiting form of equation (1) for large x, where $y \ll 1/z^*$, is

$$\frac{1}{x}\frac{d^2}{dx^2}(xy)=y,$$

with the solution $y = (C/x)\,e^{-x}$, which is the form of the Debye-Hückel potential. In the region where this holds, the charge densities of ions and electrons nearly cancel, and most of the electrons are free.

Region B.—Proceeding inward, if $z^* \gg 1$, there is a region where $1/z^* \ll y \ll 1$; and the densities of the ions and of the bound electrons are small compared with that of the free electrons, which is approximately constant and equal to its asymptotic value. In this region, equation (1) becomes approximately

$$\frac{1}{x}\frac{d^2}{dx^2}(xy) = \frac{1}{z^* + 1},$$

with the solution

$$y = \frac{A}{x} + B + \frac{x^2}{6(z^* + 1)},$$

in which A and B are arbitrary constants which must be fixed by boundary conditions. The ion-sphere model with uniform free electrons yields a solution of this form.

Region C.—In the next region, $1 \ll y \ll \alpha$, the bound electrons outnumber the free, but the occupation of the bound states is well below their capacity; and the local kinetic-energy distribution is still approximately Maxwellian. The free-electron density is now larger than its asymptotic value. Here,

$$\frac{1}{x}\frac{d^2}{dx^2}(xy) \cong \frac{1}{z^* + 1}\,e^{y}.$$

Region D.—Finally, in the ion core, $y \gg \alpha$ and most of the electrons are in fully occupied states. Equation (1) becomes approximately the zero-temperature TF equation. As the nucleus is approached, the bound-electron density diverges as $x^{-3/2}$ and the free-electron density as $x^{-1/2}$ (fictions peculiar to the TF model); the total potential $y(x)$ approaches $K_0/x +$ const. $+ O(x^{1/2})$, and the perturbing potential $v(x)$ approaches $-J + O(x^{3/2})$.

The procedure for obtaining $v(x)$ should now be clear. There are basically three parameters in the problem: z^*, α, and K_0. More convenient than the last of these, for purposes of inward integration, is C, the normalization constant of the solution in region A. We can choose z^*, α, and C, integrate equation (1) inward to get $y(x)$ and hence $S(x)$, and obtain $v(x)$ from equation (4). The net ionic charge z is given by

$$-\,x\,v \xrightarrow[x\to\infty]{} \frac{ze^2}{DkT} \equiv K = \int_0^\infty S(t)\,t^2 dt,$$

and we recall that the perturbing potential at the origin is found from

$$-\,v(0) \equiv J = \int_0^\infty S(t)\,t\,dt.$$

In application to a specific case, there are four physical parameters: T, z^*, and α for the plasma, and the net charge of the central ion. We take z as the net charge after ionization; e.g., $z = 1$ refers to the process of removing an electron from a neutral atom. Given T, z^*, α, and z, the quantity $-\bar{v}$ measures the lowering of the ionization potential in units of kT, where $-\bar{v}$ is the quantum-mechanical expectation value of $-v$, averaged over the orbital from which the electron is being removed. As we will see from the numerical results, this quantity is closely equal to J for all orbitals except highly excited ones. What is usually needed, then, is J for prescribed T, z^*, α, and z. Our dimensionless formulation replaces T and z by the single parameter K; the numerical results show that J is practically independent of α for fixed z^* and K; and the resulting interpolation prob-

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lem for J as a function of z^* and K can be simplified by means of an approximate but physically suggestive solution, which we discuss in the following section.

III. APPROXIMATE SOLUTION

A very simple approximate solution for equations (1) and (4) is readily obtained by assuming that only regions A and B need be considered, i.e., that an adequate approximation to the perturbing potential is obtained by placing all the bound electrons at the origin and taking the free-electron density to be approximately uniform. Then equation (1) is just

$$\frac{1}{x}\frac{d^2}{dx^2}(xy)=\frac{1}{z^*+1}[1-e^{-(z^*+1)y}].$$

For large z^* we approximate the right-hand side by

$$y \text{ when } (z^*+1)y<1 \text{ (region } A), \qquad \frac{1}{z^*+1} \text{ when } (z^*+1)y>1 \text{ (region } B);$$

and, letting x_1 denote the transition point, we require the potential and its derivative to be continuous at x_1. At small x, $y \rightarrow (K/x) - J + \ldots$, where to this approximation the first term is the Coulomb potential of the central ion and the next is the perturbing potential evaluated at the origin, i.e., the reduction in ionization potential (in units of kT) produced by the free electrons and neighboring ions. Using the solutions in regions A and B, which are, respectively,

$$y=\frac{C}{x}e^{-x} \qquad (x>x_1)$$

$$=\frac{K}{x}-J+\frac{x^2}{6(z^*+1)} \qquad (x<x_1),$$

and the continuity conditions

$$Ce^{-x_1}=K-Jx_1+\frac{x_1^3}{6(z^*+1)}, \qquad Ce^{-x_1}=J-\frac{x_1^2}{2(z^*+1)},$$

we get

$$J=\frac{x_1}{z^*+1}\left(1+\frac{x_1}{2}\right)=\frac{1}{2(z^*+1)}[(x_1+1)^2-1],$$

$$K=\frac{x_1}{z^*+1}\left(1+x_1+\frac{x_1^2}{3}\right)=\frac{1}{3(z^*+1)}[(x_1+1)^3-1]\geq J,$$

or, eliminating x_1,

$$J=\{[3(z^*+1)K+1]^{2/3}-1\}/[2(z^*+1)], \tag{5}$$

which for small $(z^*+1)K$ becomes $J=K$, and for large $(z^*+1)K$ becomes $J=[2(z^*+1)]^{-1}[3(z^*+1)K]^{2/3}$. Defining the ion-sphere radius a for an ion of net charge z by the usual convention $4\pi a^3/3 = z/n_e(\infty)$ and recalling the expression for the Debye length (D),

$$\frac{1}{D^2}=\frac{4\pi e^2}{kT}(z^*+1)n_e(\infty),$$

we see that the parameter $3(z^*+1)K$ is just

$$3(z^*+1)\frac{ze^2}{DkT}=\frac{3z}{4\pi D^3 n_e(\infty)}=\left(\frac{a}{D}\right)^3=\frac{\text{Ion sphere volume}}{\text{Debye sphere volume}}.$$

When this parameter is small,

$$J \to \frac{z e^2}{DkT} = K\,;$$

when it is large,

$$J \to \frac{3}{2}\,\frac{z e^2}{akT}\,.$$

These values of J are, respectively, the results of the Debye-Hückel and ion-sphere models, which result if one retains only region A or only region B a priori. Very roughly, one may say that the model giving the *smaller* depression of the ionization potential is the closer to the truth. (The prescription, which has sometimes been employed, of applying the *sum* of the corrections corresponding to the two models thus can seriously overestimate the depression of the ionization potential.)

Ecker and Kröll (1963) have derived an approximate result resembling our equation (5) in yielding Debye-Hückel and ion-sphere limits, but their ion-sphere radius is independent of z, giving $J \sim z$. Our result, in contrast, gives $J \sim z^{2/3}$ in the ion-sphere limit, corresponding to an ion-sphere radius proportional to $z^{1/3}$—which is consistent with electrical neutrality of the sphere.

IV. NUMERICAL SOLUTIONS

In order to obtain values of J which are more accurate than those provided by equation (5), we have solved equation (1) numerically and evaluated $v(x)$ from equation (4) for a number of values of z^*, α, and C. The calculations were executed on an IBM 7044 digital computer; equation (1) was replaced by a difference equation which was solved inward from large x. Automatic mesh adjustment was employed to handle the steep behavior of $y(x)$ near the origin. The complete Fermi-Dirac function $F(y - \alpha)$ was replaced by Arpigny's (1963) accurate polynomial representation; the incomplete function $F(y - \alpha, y)$ was replaced by the error-function approximation (Keller and Fenwick 1953) noted in § II. The integrals in equation (4) were then evaluated by Simpson's rule. For each z^*, α, and C, the output included the values of K, K_0, and J, and tables of $y(x)$ and $v(x)$. The quantity

$$F = 2(z^* + 1)J\,\{[3(z^* + 1)K + 1]^{2/3} - 1\}^{-1}$$

was also computed (F is the ratio of J to the approximate J given by eq. [5]) in order to facilitate interpolation; K and J range through several orders of magnitude, but F is of the order of unity. The calculations covered the range $1 \leq z^* \leq 100$; $2 < \alpha < 12$; $10^{-4} < K < 3$; this range, we think, covers all possible cases of interest in non-degenerate LTE (local thermodynamic equilibrium) plasmas. Some calculations in this range led to $K_0/K =$ (nuclear charge/net ionic charge) > 103 and were accordingly rejected as unphysical; these occurred for C and α both large. Since large C generally corresponds to high density and large α to low density, it is not surprising that prescribing both quantities can lead to physically unrealizable cases.

We first discuss the behavior of J as a function of z^*, α, and K. In Figure 1 we plot the correction factor F against $(z^* + 1)K$ with z^* as a parameter. The dependence of F on α is all included in the shaded areas and so is generally negligible. (In terms of the qualitative discussion in § II, this means that region D is an insignificant contributor to the perturbing potential; i.e., very few free electrons are found inside the ion core.) The over-all closeness of F to unity shows that the simple equation (5) is usually a fairly good approximation, especially for large z^*; however, better values of J can be obtained from Figure 1.

We consider next the shape of the perturbing potential $v(x)$. If $v(x)$ were independent of x throughout the volume where $y(x) \geq Y$, then all orbitals whose (depressed) ioniza-

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tion potentials exceed YkT would experience essentially the same perturbation of their various ionization potentials, since their classical turning points lie inside the constant-v region and their wave functions are small outside it. Similarly, because $v(x)$ is monotonic in x, the expectation value of $v(x)$ for a given orbital will be (approximately) bounded by the values of $v(x)$ at the outer turning point and at the origin; and at the outer turning point $y(x) \geq I/kT$ with I = perturbed ionization potential. Orbitals for which $v(x) \simeq v(0)$ where $y(x) = I/kT$ accordingly have $-\bar{v}$, the depression of the ionization potential in units of kT, closely equal to J. We therefore ask for the behavior of $v(x)/v(0)$ as a function of $y(x)$. Two specific values of y are of particular interest: $y = \alpha$, which corresponds roughly to the outermost orbital in the ground state of the ion; and the value of y for which $v(x) = 0.9\ v(0)$, which corresponds roughly to the highest excited orbital for which JkT is a close (a few per cent) approximation to the depression of the ionization potential. We find in nearly every case which we have computed that $v(x)$ deviates from $v(0)$ by considerably less than 1 per cent where $y(x) = \alpha$, and that $y(x)$ is considerably less than unity where $v(x) = 0.9\ v(0)$. Therefore, the perturbing potential is indeed nearly constant for any orbital whose depressed ionization potential exceeds kT (and the wave function of such an orbital will be essentially the same as in the isolated ion).

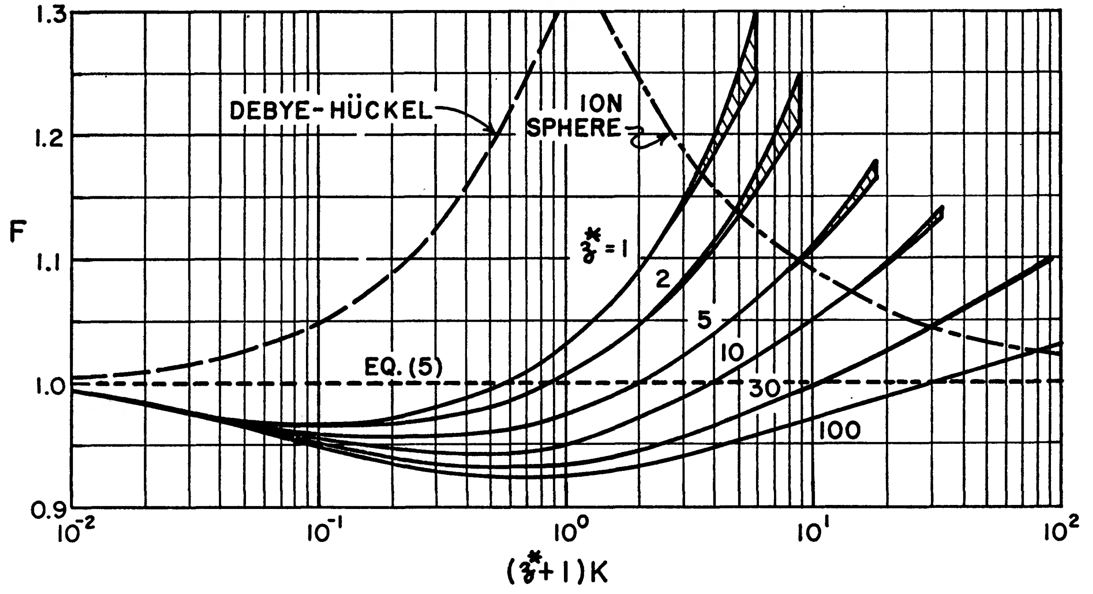

FIG 1.—Depression of the ionization potential, in units of the depression given by eq. (5). *Dotted line:* $F = 1$; *dashed curve:* Debye-Hückel model; *dot-dash curve:* ion-sphere model; *solid curves:* numerical integrations of full Thomas-Fermi model, for various z^*; the shaded areas contain the range of variation of F with α. The abscissa, $(z^* + 1)K$, is $\frac{1}{3}$ of the ratio (ion-sphere volume/Debye-sphere volume); K is also ze^2/DkT, which is the Debye-Hückel depression in units of kT.

The highly excited orbitals with $I \ll kT$ can be neglected in most applications such as calculation of the LTE equation of state of the plasma, since it is easily shown by classical phase-space arguments that their contribution to the total plasma partition function is much less than that of the adjacent continuum of free states. A similar statement holds for their contributions to the opacity (Stewart and Pyatt 1961). Thus, the equation of state can be obtained (starting from α and kT) as follows: Guess z^* in order to get the Debye length; for each z, compute K and (from Fig. 1) J; in each ionic species lower all ionization potentials by JkT and delete all ionic configurations in which the least tightly bound electron is then free; use the Boltzmann-Saha equations to find a revised z^*, and iterate.

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