SOVIET PHYSICS JETP VOLUME 13, NUMBER 4 OCTOBER, 1961

THE EQUATION OF STATE OF PARTIALLY IONIZED HYDROGEN

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Submitted to JETP editor October 29, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) **40**, 1134-1139 (April, 1961)

We propose a method for approximate evaluation of the thermodynamic functions of a partially ionized gas, taking into account deviations from ideality. We obtain an equation of state and an ionization formula which is appreciably different from the Saha formula.

1. A large number of papers have been devoted to a discussion of the equation of state of a totally ionized gas. There is, however, no satisfactory theory to describe the state of a partially ionized gas. We shall consider one possible derivation of an approximate equation of state, using as an example hydrogen at temperatures of the order of several electron volts and pressures of the order of tens of atmospheres.

Let a uniform plasma of temperature T contain within a volume V three components: neutral hydrogen atoms, electrons, and ions. Since the plasma is electrically neutral,

$$n_{i0} = n_{e0}, \qquad (1)$$

where n_{e0} and n_{i0} are the average electron and ion densities, respectively.

The effects of the interaction between particles in the plasma lead to a change in the atomic energy levels and also to the so-called "cut-off" of the atomic partition function, manifest spectroscopically by the vanishing of Fraunhofer lines corresponding to relatively high values of the principal quantum number. The discrete states near the continuum vanish for two reasons. First, because the broadening of the levels caused by the interaction between the atom and the charged component of the plasma or the other atoms may turn out to be comparable with the spacing of the levels, so that levels with relatively high values of the principal quantum number overlap. Second, the action of the quasi-static microfield of the plasma on the atom causes ionization of the upper atomic levels.

Generally, one must take both these effects into account when evaluating the partition function. If, however, the electron density exceeds about 10^{17} cm^{-3}, the second effect is dominant (strong electrical microfield) and one can neglect the first one. Margenau and Lewis[1] have, for instance, studied this problem in detail in their survey article.

We shall consider the influence of the screened electrical charges on the atom. One can describe this influence in the adiabatic approximation by the perturbation of the atom by an electrical field **F**:

$$\mathbf{F} = \sum_i \mathbf{F}_i(\mathbf{r}_i) = e\sum_i \mathbf{r}_i r_i^{-3}(1 + \varkappa r_i)\exp(-\varkappa r_i), \qquad (2)$$

where $\kappa = (r_0^3 kT/3)^{-1/2}$ is the inverse Debye radius (in atomic units) and r_0 the average distance between the ions.

Hoffman and Theimer[2] obtained the statistical distribution of the field. If the ion and electron densities are not too small, one can use for the evaluation of the field distribution the so-called "nearest neighbor" approximation which takes only the influence of the nearest ion on the atom into account. The probability of finding a perturbing ion at a distance r from the atom is then given by an expression of the form

$$dP(r) = 4\pi n \exp\left\{-\frac{U(r)}{kT} - 4\pi n\int_0^r r'^2 \exp\left[-\frac{U(r')}{kT}\right]dr'\right\} r^2 dr, \qquad (3)$$

where U(r) is the potential energy for the interaction between the ion and a hydrogen atom and n the ion density in the plasma.

When the Stark effect in a strong electrical field is evaluated one determines the value of the critical field $F_0^{m_0}$ for which the spectral line corresponding to an initial state of the atomic electron with principal quantum number m_0 vanishes.[3] A classical calculation of the threshold for ionization gives the following value for the critical field $F_0^{m_0}$:

$$F_0^{m_0} = e/16 m_0^4 a_0^2, \qquad (4)$$

where a_0 is the Bohr radius.

A comparison with the quantum-mechanical calculation and with experiment (see reference 3) shows that $F_0^{m_0}$ can be approximated with fair accuracy by an expression of the form

$$F_0^{m_0} = e/8m_0^4a_0^2. \tag{5}$$

If we take the screening of the perturbing ion into account, we get for the field acting upon the atom

$$F(r) = er^{-2}(1+\varkappa r)e^{-\varkappa r}, \tag{6}$$

where r is the distance between the atom and the perturbing proton.

Comparing Eqs. (5) and (6) we get for the quantum number at which the partition function must be cut off:

$$m_0 = 2^{-3/4}(r/a_0)^{1/2}(1+\varkappa r)^{-1/4}e^{\varkappa r/4}. \tag{7}$$

It is necessary to note that the electrical field inside the plasma can be different from the field used in the proposed model. It is thus necessary to compare the theory with an experiment on the vanishing of spectral lines in a plasma, and we shall do this below.

The partition function of the atom as a function of the distance r between the atom and the perturbing ion,

$$Z(r) = 2\sum_{n=1}^{m_0} g_n \exp[-E_n(r)/kT], \tag{8}$$

contains E_n, the energy of the atomic levels in an external electrical field, and g_n, the statistical weight of the corresponding levels. One can show that for electron densities less than 10^{20} cm^{-3} we do not introduce a serious error if we write Z(r) in the form

$$Z(r) = 2\sum_{n=1}^{m_0} n^2 \exp[-I_n(r)/kT], \tag{9}$$

$$I(r) = I_0(1 - 1/m_0^2(r)), \tag{10}$$

where $I_0 = e^2/2a_0 = 13.53$ ev (ionization potential of hydrogen), $I_n = I(r)/n^2$. We have assumed here that the energy levels of the hydrogen atom are unperturbed and that the cut-off occurs at $n = m_0$.

We take the energy of the m_0 level as the zero point of the energy, i.e., we assume that E_{m_0} is the boundary of the discrete and the continuous spectra of the relative motion of the electron and the proton. This corresponds clearly to an effective lowering of the ionization potential [see Eq. (10)]. We assume then that upon going over into the continuous spectrum the electron moves in a potential caused by all the free charged particles in the plasma, i.e., in the Debye potential. We note that this assumption is not an obvious one and needs further justification. A rough estimate shows that this assumption introduces an error of the second order. We shall return in a later paper to a detailed study of this problem.

If we average (9) over the distribution dP(r) given by Eq. (3) we get

$$Z = \int_0^\infty Z(r)\,dP(r). \tag{11}$$

To evaluate the potential energy U(r) of the interaction between an ion and an atom for $r \sim a_0$ (a_0 is the Bohr radius) we use the well-known solution of the Schrödinger equation for the molecular hydrogen ion.[4] We can then neglect the screening of the perturbing ion. However, when $1/\kappa > r \gg a_0$ the potential energy of the interaction between an ion and an atom is evaluated by using the Stark-effect perturbation theory. When $r > 1/\kappa$ the potential U(r) = 0.

2. We write for the free energy of the neutral component in an external field

$$F_a = -N_akT\ln[(MkT/2\pi\hbar^2)^{3/2}eVZ/N_a], \tag{12}$$

where Z is given by Eq. (11), M is the proton mass, N_a is the number of atoms, and V is the volume of the system.

In the Debye approximation we have for the free energy of the charged component

$$F_{\mathrm{ch}} = F_{\mathrm{id}} - \tfrac{2}{3}e^3\sqrt{\pi/kTV}(N_e+N_i)^{3/2}, \tag{13}$$

where F_{id} is the free energy of a perfect gas of electrons and ions and N_e and N_i are, respectively, the numbers of electrons and ions. We have not taken into account in Eq. (13) terms quadratic in the charged component density since the logarithmic term tends to zero for hydrogen (see reference 5), and the other terms give a small contribution.

The condition of chemical equilibrium

$$\mu_a = \mu_i + \mu_e \tag{14}$$

(where μ_a, μ_i, and μ_e are respectively the chemical potentials of the atoms, the ions, and the electrons) leads, if we use (12) and (13), to the following ionization equation:

$$n_{e0}^2/n_a = Z^{-1}g_e^2(mkT/2\pi\hbar^2)^{3/2}\exp\{4e^3(2\pi n_{e0})^{1/2}/(kT)^{3/2}\}, \tag{15}$$

where $g_e^2 = 4$. Equation (15) is the analogue of Saha's ionization formula (see, for instance, reference 6). In the derivation of the Saha formula one does not take into account that the free particles form an imperfect gas and the ionization potential is essentially put equal to the perturbing potential, i.e., one assumes that only the ground state of the atom gives a contribution to the partition function of the neutral component. The ionization potential obtained in the present paper takes into account the deviation of the electron and the proton gas from perfect gases. It is necessary to change the ratio between the neutral and the charged components as compared to the one given by the Saha formula also because of the effective lowering of the ionization potential and because excited states of the hydrogen atom must be taken into account.

The partition function Z is a function of the ion density, i.e., it depends not only on the temperature, but also on the density in the plasma. Conversely, the ion density depends on Z, i.e., it is a self-consistent problem. We obtain the equation of state by differentiating $F = F_a + F_{ch}$ with respect to the volume, keeping T, N_e, and N_a fixed:

$$P = (n_a + 2n_{e0})\,kT - \tfrac{2}{3}e^3\sqrt{2\pi/kT}\,n_{e0}^{3/2} + kTn_a\lambda;$$
$$\lambda = -\,\partial\ln Z/\partial\ln n_{e0}, \qquad 0 < \lambda < 1. \tag{16}$$

Using (15) and (16) we get an ionization formula from which we can calculate the electron density (and the degree of ionization) for a given temperature T and pressure P:

$$n_{e0}^2(1+\lambda) = Z^{-1}g_e^2(mkT/2\pi\hbar^2)^{3/2}\,[P/kT - 2n_{e0}$$
$$+ \tfrac{2}{3}(2\pi)^{1/2}e^3\,(n_{e0}/kT)^{3/2}]\exp\{4e^3(2\pi n_{e0})^{1/2}(kT)^{3/2}\}. \tag{17}$$

For comparison we give here the usual Saha formula for hydrogen:

$$n_{e0}^2 = \tfrac{1}{2}\,g_e^2(mkT/2\pi\hbar^2)^{3/2}\,[P/kT - 2n_{e0}]e^{-I_0/kT}. \tag{18}$$

3. We consider now some effects which may lead to an additional change in the atomic levels and thus to a change in the partition function. If because of the perturbation the electron makes a transition into a state with a sufficiently large principal quantum number (in our conditions ~ 6 to 10), the radius of its Bohr orbit will become appreciable. The electron then moves slowly between the atoms and the position is nearly the same as if a slow free electron moved through the gas. The presence of other atoms will change the energy of the excited state which we are considering on two grounds: firstly, the average potential energy of the field in which the electron moves is changed, and secondly, the bound proton will cause a polarization of the atoms. The result of these two effects is a shift in the level[7]

$$\Delta = a\hbar n_a/2\pi m - 10\varepsilon^2\alpha n_a^4, \tag{19}$$

where a is the magnitude of the effective radius of the elastic scattering of slow electrons by a hydrogen atom and α the polarizability of the atom.

One shows easily that in the range of temperatures and pressures considered both these effects are small, i.e.,

$$|\Delta E/E| \ll 1. \tag{20}$$

Account of the dipole-dipole interactions between the atoms also leads to an insignificantly small correction. To estimate the contribution from this interaction we can use perturbation theory. It turns out that this effect is comparable with the Stark effect only when

$$5\cdot 10^{-18}\,n_a/n_{e0}^{2/3} \sim 1, \tag{21}$$

but this condition is known not to be satisfied under the conditions we consider here.

4. To estimate Z we use a rough model. Let

$$U(r) = \begin{cases} +\infty, & r \leqslant r_1 \\ -U_0, & r_1 < r \leqslant r_2. \\ 0, & r > r_2 \end{cases} \tag{22}$$

From Eq. (3) we then get

$$dP(r) = \begin{cases} 0, & r \leqslant r_1 \\ dP_1(r), & r_1 < r \leqslant r_2, \\ dP_2(r), & r > r_2 \end{cases}$$

$$P_2 = \left(\frac{r}{r_0}\right)^3 \exp\left\{\left[1 - \exp\left(\frac{U_0}{kT}\right)\right]\left(\frac{r_2}{r_0}\right)^3 + \left(\frac{r_1}{r_0}\right)^3\right\}\exp\left[-\left(\frac{r}{r_0}\right)^3\right],$$
$$P_1 = \exp\left(\frac{U_0}{kT}\right)P_2; \tag{23}$$

In (23) r_0 is evaluated from the equation

$$4\pi n r_0^3/3 = 1. \tag{24}$$

However, r_0 is not the quantity that corresponds to the most probable value of the field F. The lower T, the greater the difference between that value and r_0. We estimate

$$Z = \int_0^\infty Z(r)\,dP(r)$$

for $n_i = 10^{17}$ cm^{-3} ($r_0 = 253.7$) and kT = 1.1 ev. Using simple functions for Z(r) we get approximately $Z = 2.25 \times 10^6$.

On the other hand, if we substitute in (9) the value $r_0 = 253.7$ we get $Z = 2.15 \times 10^6$.

From the estimate which we have just given it is clear that we can evaluate Z approximately from the equation

$$Z = Z(r_0) = 2\exp\left\{\frac{I_0}{kT}\left(1 - \frac{1}{m_0^2}\right)\right\}$$
$$= \left[1 + \int_2^{m_0}\exp\left\{-\frac{I_0}{kT}\left(1 - \frac{1}{m_0^2}\right)\left(1 - \frac{1}{x^2}\right)\right\}x^2dx\right], \tag{25}$$

where m_0 is given by Eq. (7).

For actual calculations using Eqs. (16) and (18) one can use the following expressions to work with

$$\tilde{n}_e^2(1+\lambda) = (A_1T^{3/2}/Z)\,[A_2P/T - 2\tilde{n}_e$$
$$+ A_3(\tilde{n}_e/T)^{3/2}]\exp\{A_4^2\,\tilde{n}_e^{1/2}/T^{3/2}\}, \tag{26}$$

$$A_2P/T = \tilde{n}_a(1+\lambda) + 2\tilde{n}_e - A_3(\tilde{n}_e/T)^{3/2}, \tag{27}$$

$$\tilde{n}_a = [A_2P/T - 2\tilde{n}_e + A_3(\tilde{n}_e/T)^{3/2}]\,(1+\lambda)^{-1}, \tag{28}$$

where

P, atm	T, ev	$10^{-18}n_{e0}$(Saha)	10^{-18} n_{e0}	P, atm	T, ev	$10^{-18}n_{e0}$(Saha)	10^{-18} n_{e0}
1	1	$6.21\cdot10^{-2}$	$6,88\cdot10^{-2}$		5	1,22	1,23
	2	0,153	0.154		10	0,612	0.613
	3	0,102	0.103	50	1	0.484	0,662
	5	$6.12\cdot10^{-2}$	$6.13\cdot10^{-2}$		2	5,54	6,19
	10	$3.06\cdot10^{-2}$	$3.06\cdot10^{-2}$		3	5.06	5.00
5	1	0,148	0,176		5	3,06	3.05
	2	0,749	0,752		10	1.53	1,53
	3	0.510	0,513	100	1	0,688	1.021
	5	0.306	0,306		2	11.74	14.83
	10	0.153	0,153		3	10.06	11.69
10	1	0.212	0,259		5	6.12	7,26
	2	1,446	1,595		10	3.06	2.99
	3	1.020	1.029	200	1	0,976	1,57
	5	0,612	0.613		2	20,15	23,02
	10	0.306	0,307		3	19,83	21.99
15	1	0.262	0.322		5	12,23	14.06
	2	2,14	2,29		10	6.12	7,04
	3	1.53	1,59	500	1	1.55	2.89
	5	0,918	0,919		2	38.43	48.30
	10	0.459	0.468		3	47.69	53.46
20	1	0.303	0.378		5	30,52	31,21
	2	2,78	3.18		10	15,31	15,49
	3	2.04	2,09				

$$A_1 = 1{,}1869\cdot10^4, \qquad A_2 = 0{,}6125,$$

$$A_3 = 9{,}1281\cdot10^{-2}, \qquad A_4 = 0{,}2738;$$

$$n_e \equiv n_{e0}\cdot10^{-18}, \qquad \tilde{n}_a \equiv n_a\cdot10^{-18},$$

where we now must express P in atmospheres and T in electron volts.

In the Table we have given values for n_{e0} calculated from Eqs. (26) to (28) for different pressures and temperatures. The calculation was performed on an electronic computer. We also give for comparison the corresponding values for the electron densities in a perfect plasma, calculated with the Saha formula.

We must note that the Debye approximation used here limits the validity of the theory to values of the electron density and the temperature which satisfy the well-known Kirkwood-Onsager inequality

$$e^2 n_{e0}^{1/3}/kT \ll 1. \qquad (29)$$

5. Yamamoto[8] has investigated experimentally the vanishing of spectral lines in a plasma which is caused by interactions in the plasma. The analysis of the experiment given by the author is incorrect and we proceeded therefore as follows to compare the results of the present paper with that experiment. We calculated from Eq. (26) the electron density n_{e0} for the values of P and T corresponding to the experiment and then for that value of the density we used Eq. (7) to find the value of m_0. This calculation gave $m_0 \sim 8$ (P = 1 atm, T $\sim$ 1.5 ev). The experimental value was $m_0 = 7$. We can clearly say that although such a comparison with experiment is an insufficient one, there is no discrepancy between the theory and this particular experiment.

In conclusion I express my gratitude to D. F. Zaretskii for a discussion of the results of this paper.

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Translated by D. ter Haar
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