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SEMI-EMPIRICAL EQUATION OF STATE OF NON-IDEAL PLASMA

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Calculations of the equation of the state for a fully ionized nondegenerate plasma, based on the application of a radial distribution function are obtained by combining the approximations of pair collisions and the polarization approximation. Plasma polarization is introduced in a semi-empirical way via an effective interaction distance differing from the Debye screening radius. In addition to numerical calculations an analytic formula is derived and compared with experimental data of other authors.

ПОЛУЭМПИРИЧЕСКОЕ УРАВНЕНИЕ СОСТОЯНИЯ НЕИДЕАЛЬНОЙ ПЛАЗМЫ

На основе сочетания приближения парных столкновения и поляризованного определено уравнение состояния полностью ионизированной невырожденной плазмы. Поляризация плазмы вводится полуэмпирическим путем при помощи эффективной длины взаимодействия, отличающейся от радиуса дебаевской экранировки. В дополнении к численным вычислениям выведена аналитическая формула и проведено ее сравнение с экспериментальными данными авторов.

I. INTRODUCTION

Plasma with a low number of particles in the Debye sphere ($N_D \lesssim 1$) is called Coulomb non-ideal. It is obtained at high concentrations of charged particles and comparatively low temperatures. This plasma can be well characterized by the ratio of the mean potential and mean kinetic energy of particles — the coefficient of nonideality γ, or the plasma parameter μ having in the nondegenerate case following form:

$$\gamma = \frac{|\bar{\varepsilon}_{pot}|}{\bar{\varepsilon}_{kin}} = \frac{e^2 \bar{Z}}{4\pi\varepsilon_0 kT\bar{r}}\,; \qquad \mu = \gamma\,\frac{\bar{r}}{r_D} \tag{1}$$

where e is the elementary charge, $\bar{Z}$ the mean charge number of ions, ε_0 vacuum permittivity, k the Boltzmann constant, T temperature, $\bar{r}$ the mean distance of charged particles, r_D the Debye screening radius.

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In the case of plasma with one-time ionized atoms

$$r_D = \left(\frac{\varepsilon_0 kT}{2ne^2}\right)^{1/2}, \quad \bar{r} = (2n)^{-1/3}, \quad \gamma \doteq 0.21\, N_D^{-2/3}, \quad \mu \doteq 3.54\, \gamma^{3/2},$$

where the concentrations of electrons and ions are equal; $n_e = n_i = n$.

Recently, on investigating mainly the stability [1—4] and phase changes [5—7] in non-ideal plasma, there has been an increasing interest in the equation of state in the Coulomb nonideal medium besides degeneration. The experiments in electric conductivity and other parameters in non-ideal plasma [8—11] cannot be interpreted precisely without the knowledge of the equation of state or other equations of equilibrium. B. L. Timan [12], Š. Veis [13], W. Ebeling et al. [7] have been studying the modification of the Saha equation for the ionization equilibrium for a non-ideal medium.

P. Debye and E. Hückel have already considered the fundamental thermodynamics of the ideal plasma. Their theory, however, cannot be directly generalized for the calculation of further approximations via concentration. N. N. Bogolyubov has elaborated an exacting method of correlation functions that elmininates this imperfection. Through the approximation of pair correlations this method leads to the same results as the Debye—Hückel method [14]. Higher approximations become mathematically very complicated. The pressure of the approximation of triple correlations was derived in [15, 16] but within the polarization approximation ($\gamma \ll 1$). Thus, the equation of state is expressed there more precisely only for the ideal plasma (the second approximation via the plasma parameter μ, which itself remains small). The calculation of T. O'Neil, N. Roztoker [17] is also unsatisfactory with regard to the experiment [5].

In our considerations we use only pair correlation functions. Instead of the pair distribution function polarization approximation for the ideal plasma we apply a more real one obtained by combining approximations of pair collisions and a polarization collision (suggested already by Yu. L. Klimontovich [18]). In addition, using the experimental notion [8, 19] that the effective interaction radius r_{Int} in plasma does not fall below the mean particle distance $\bar{r}$ with increasing non-ideality, we modify the pair distribution function for higher γ and so express the equation of state of nondegenerate fully ionized plasma.

II. METHODS

T. L. Hill derived [20] a direct connection among the pressure p, the radial distribution $f(r)$ and the potential energy of the interaction $\varphi(r)$:

$$p = p_{id} - \frac{2}{3}\pi \sum_{a,b} n_a n_b \int_0^\infty r \frac{d\varphi_{a,b}(r)}{dr} f_{a,b}(r) \cdot r^2\, dr\,, \tag{2}$$

$$\varphi_{a,b}(r) = Z_a Z_b e^2 / 4\pi\varepsilon_0 r\,, \tag{3}$$

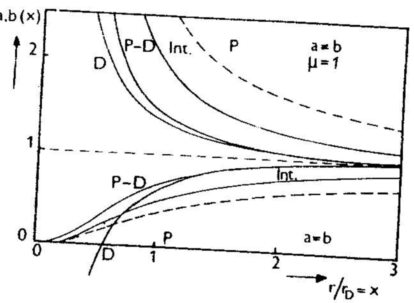


Fig. 1. Radial distribution function $f_{a,b}$: in the Debye—Hückel approximation (D), in the approximation of pair collisions (P), combined ($P-D$), modified $r_D \to r_{Int} = r(Int)$; for $\mu = 1$.

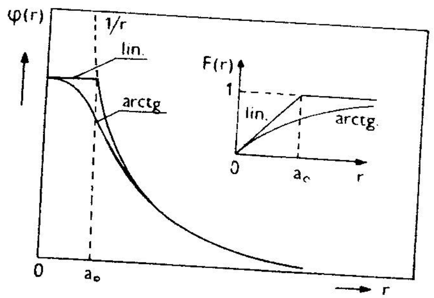


Fig. 2. Illustration of the limitation of the Coulomb potential by the correction function $F(r)$ according to (6a, b); lin ... (6a), arc tg ... (6b).

where $a, b = e, i$ (electrons, ions in plasma with one-time ionized atoms), and r is the distance. In his considerations in [18] Yu. L. Klimontovich suggested to combine in the non-ideal plasma two antagonistic (complementary) approximations: the aproximation of pair collisions and the polarization one (suitable for ideal plasma). This procedure appeared to be from the point of view of the radial distribution function much more effective than that via the complicated kinetic equation of Balescu—Lenard in the polarization approximation. The combination was solved by introducing an average dynamic polarization into the Boltzmann kinetic equation for the non-ideal plasma in the approximation of pair collisions. Then $f_{a,b}$ has the form (Fig. 1)

$$f_{a,b}^{P-D}(r) = \exp\left[-\frac{Z_a Z_b e^2}{4\pi\varepsilon_0 kT}\frac{1}{r}\exp(-r/r_D)\right], \tag{4}$$

consistent with the Boltzmann distribution law with a pseudopotential equal to the Debye screened potential φ^D, ($f^{P-D} = \exp(-Z_a e\varphi^D/kT)$). The pressure in the Debye approximation (when $n_e = n_i = n$) is obtained by linearizing f^{P-D} and substitution into equation (2):

$$p^D = 2nkT\left(1 - \frac{\mu}{6}\right). \tag{5}$$

Substituting the complete radial function $f_{a,b}^{P-D}$ into the expression (2) we state that the integrals corresponding to the atractive forces ($a \neq b$) are divergent for $r \to 0$, where the character of $f_{a,b}^{P-D}$ is determined by the unscreened Coulomb potential. Thus, the form of $f_{a,b}$ given by Klimontovich is suitable for the repulsive action but less so for the attractive one. From this aspect $f_{a,b}^{P-D}$ will be modified in two ways:

i) The expression (4) for the case $a \neq b$ will be linearized: $f_{a,b}^{P-D} \to f_{a,b}^{D} = 1 -$

$- Z_a Z_b a_c \frac{1}{r} e^{-r/r_D}$, where $a_c = e^2/4\pi\varepsilon_0 kT$ is the known Coulomb scattering parameter. (The linearization is consistent with the polarization or the Debye approximation). In the case of a repulsive action, $a = b$, the radial function retains the form $f_{a,b}^{P-D}$. Such a combined procedure is suitable for an analytic calculation.

ii) The Coulomb potential will be naturally limited in the region $r \to 0$: $e^2/r \to e^2/r \,.\, F(r)$. The correction function $F(r)$ is chosen in two ways:

$$\text{a)}\quad F(r) = r/a_0 \quad \text{for} \quad 0 \leq r \leq a_0$$
$$F(r) = 1 \qquad r > a_0 \tag{6a}$$

$$\text{b)}\quad F(r) = \frac{2}{\pi} \operatorname{arc\,tg} \frac{\pi}{2a_0} r \,, \text{(Fig. 2)}. \tag{6b}$$

$f_{a,b}^{P-D}$ in this case shifts to the form:

$$f_{a,b}^{F} = \exp\left[- Z_a Z_n a_c \frac{1}{r} F(r)\, e^{-r/r_D} \right]. \tag{7}$$

For convergence of the expression (2) it is sufficient to substitute $f_{a,b}^F$ into integrals corresponding to attractive forces, but it is natural to introduce the limitation of the Coulomb potential into the repulsive action, too. In additon the limitation can be introduced also into the potential appearing in the derivative included in integral (2):

$$\frac{d\varphi}{dr} \to \frac{d\varphi^F}{dr}, \qquad \varphi^F = \frac{Z_a Z_b e^2}{4\pi\varepsilon_0} \frac{1}{r} F(r)\,. \tag{8}$$

The process ii) is suitable for a numerical solution of the problem. The constant a_0 (6) is determined so that the calculated pressure for low values of the coefficient of non-ideality γ must be consistent with the pressure p^D (5) for the ideal plasma.

The forms of $f_{a,b}^{P-D}$ have been treated only for the purpose of the qualitative convergence of pressure in the region $r \to 0$. But in the quantitative expression of pressure it is just the region of high r (integration via r^2/dr) that plays an important role. Here we meet with the problem of the effective screening distance r_{int}, which in non-ideal plasma is not equal to r_D. With $\gamma = 0.08$ we have $r_D = \bar{r}$ and for higher γ we have $r_D < \bar{r}$ (possibly $r_D \ll \bar{r}$). From this it follows that r_D cannot play the role of r_{int} in non-ideal plasma which we assume intuitively not to decrease below $\bar{r}$ even for high γ. Several authors tried to corraborate this hypothesis (experimentally [8, 21], theoretically [19, 22]). From Monte-Carlo calculations of the authors of [22] the effective radius of interaction can also be determined within the kinetic model of one-component plasma with a homogeneous neutralization background. The ratio $r_{int}/\bar{r}$ is illustrated for all the mentioned cases in Fig. 3. We estimated the

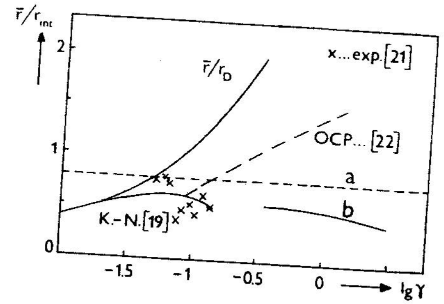


Fig. 3. Correlation between the mean distance of charged particles $\bar{r}$ and the effective interaction distance r_{int} in dependence on the coefficient of non-ideality of plasma according to various approximations and authors. a ... $r_{int} = n^{-1/3}$ — used in analytic calculations; b ... "Debye" gas with triple collisions — our approximation (9).

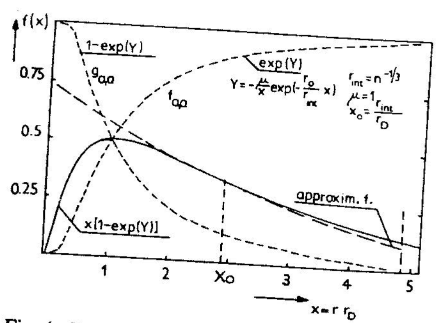


Fig. 4. Demonstration of approximation of the integral used in correlation (11). The integral of the dashed line from 0 to $2x_0$ is substituted for the integral of the solid line $x[1-\exp Y]$ from 0 to ∞. In addition the radial function $f_{a,a}(x)$ and the absolute value of the pair correlation function $g_{a,a}(x)$ are illustrated.

magnitude of r_{int} with the aid of a model of plasma as a nonideal gas with triple collisions with an interaction potential in the form:

$$\Phi_{ij}(r) \sim \frac{1}{r_{ij}} \exp\left(-r_{ij}/r_{int}\right). \tag{9}$$

From the Boltzmann kinetic equation for gas with triple collisions it follows:

$$f_{12}(r) = 1 + n \int_{(r_3)} [e^{-e\Phi_{13}/kT} - 1][e^{-e\Phi_{23}/kT} - 1]\, d^3 r_3\,.$$

This integral was solved by the Monte-Carlo method. The magnitude of r_{int} in (9) was treated so that the calculated f_{12} might correspond to the results of [22]. In this way we obtained the value of $r_{int} \sim 2\bar{r}$ (for $\gamma \sim 1$) — line b in Fig. 3.

The previous considerations have led us to modify the expressions for the radial distribution function (4) and (7) by substituting $r_D \to r_{int}$ with the retained form of $f_{a,b}$ (Fig. 1). We obtain expression (7) in the form:

$$f_{a,b}^{F,int} = \exp\left[- Z_a Z_b a_c \frac{1}{r} F(r) \exp\left(-r/r_{int}\right) \right]. \tag{10}$$

Analytic solution (i)

Let there be $f_{a,b} = f_{a,b}^{D,int}$ for the attractive action ($a \neq b$, $a, b = e, i$) and $f_{a,b} = f_{a,a}^{P-D,int}$ for the repulsive action ($a = b$). The index *int* symbolizes the substitution $r_D \to r_{int}$. From equation (2), after substituting $x = r/r_D$ it follows that the pressure is:

$$p = 2nkT - \frac{1}{6} nkT \left\{ \mu \frac{r_{int}}{r_D} + \int_0^\infty \left[1 - \exp\left(-\frac{\mu}{x} \exp\left(-x \frac{r_D}{r_{int}} \right) \right) \right] x \, dx \right\} . \quad (11)$$

For the ideal plasma, when $r_{int} = r_D$, the pressure shifts to the equation:

$$p^{P-D} = 2nkT \left\{ 1 - \frac{\mu}{12} - \frac{1}{12} \int_0^\infty \left[1 - \exp\left(-\frac{\mu}{x} e^{-x} \right) \right] x \, dx \right\} . \quad (12)$$

With a very low plasma parameter μ the exponential expression in (12) can be linearized, the entire integral obtains the value of μ and the pressure p^{P-D} shifts into p^D (5). Therefore, the expression p^{P-D} presents a higher approximation for the pressure of the ideal plasma ($\mu \ll 1$) than that of Debye—Hückel.

The integral $I(\mu, r_{int})$ in the expression (11) can be solved approximatly. The sub-integral expression developes according to the Taylor series in the neighbourhood of the point $x_0 = r_{int}/r_D$, Fig. 4. (Round the point $x_0 = 0$ the function cannot be developed as all derivatives are zero except the first one). The comparison of the obtained analytic expressions for $I(\mu, r_{int} = n^{-1/3})$ and $I(\mu, r_{int} = r_D)$ with accurate numerical calculations of the integrals (for μ, selected from the interval $\langle 0.08; 3.42 \rangle$, interesting for us) shows that already on using the second order of the Taylor expansion there is a deviation in the determination of the integrals less than 5 % (in the determination of pressure ~1 %). Let us presume that r_{int} remains at the level of the mean distance of particles, as it has been discussed. More precisely, let $r_{int} \equiv n^{-1/3} = \bar{r}_{ee}$ (the mean distance of particles of the same kind), line „a" in Fig. 3. Then we obtain, within the second order approximation of the Taylor expansion from expression (11), for the pressure:

$$p = 2nkT \left[1 - \frac{\mu^{4/3}}{4.1} - \frac{0.21\mu^{4/3} - 0.004\mu^2}{1 + 0.13\mu^{2/3} + 0.008\mu^{4/3}} \right] . \quad (13)$$

It represents the solid line (analytic) in Fig. 5. On extrapolating the Debye screening distance into non-ideal plasma $r_{int} = r_D$) for the pressure p^{P-D} (12) in the same approximation we obtain:

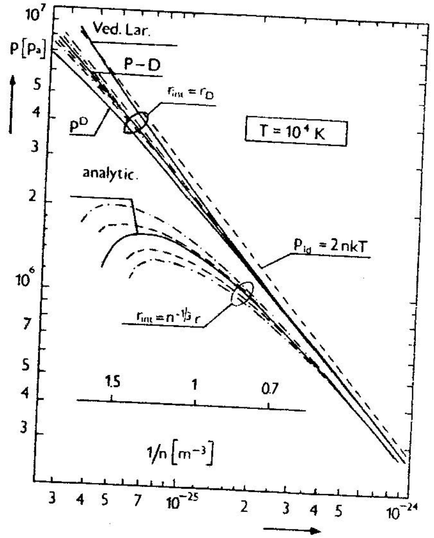
$$p = 2nkT \left[1 - \frac{\mu}{12} - \frac{\mu}{12} \frac{1 - 0.05\mu}{1 + 0.37\mu + 0.07\mu^2} \right] . \quad (14)$$

Numerical solution (ii)

By substitution of (10) into the equation (2) we obtain:

$$p = p_{id} - \frac{1}{3} nkT \int_0^\infty x \sinh \left[\frac{\mu}{x} F(x) \exp(-x r_D / r_{int}) \right] dx , \quad (15)$$

Fig. 5. Pressure dependence on one-particle volume (p—V diagram) for various approximations of non-ideal fully ionized plasma at the temperature of 10 000 K.



where $x = r/r_D$. When the correction function is introduced also into the potential (8), then

$$p = p_{id} - \frac{1}{3} nkT \int_0^\infty x[F(x) - xF'(x)] \sinh \left[\frac{\mu}{x} F(x) \exp(-x r_D / r_{int}) \right] dx . \quad (16)$$

Both equations (15, 16) were numerically solved for $r_{int} = \bar{r}_{ee}$, resp. r_D, for two different forms of the correction function (6a, b). The parameter a_0 was determined by comparing the calculated pressure with p^D for low μ ($\mu \leq 0.04$ where $r_D \geqq n^{-1/3}$ ... shift to the ideal plasma).

From the form $F(r)$ it follows clearly that a_0 should be a physical constant characterizing the "electrostatic dimension" of the ion. On substituting $x = r/r_D$:

$$r/a_0 = x r_D / a_0 = \frac{1}{a_0} \frac{e^2}{4\pi\varepsilon_0 kT} \frac{x}{\mu} = \frac{b}{\mu} x . \quad (17)$$

Comparing the pressure obtained numerically from (15) with the pressure p^D for low μ we determined first the value b, already independent of μ. $b = 1.6$ and 3.8 for the forms of the correction function (6a), resp. (6b). When the correction function is also included into the potential, correlation (16), the values of b differ from the previous ones only a little: 1.8 and 4.0 for the forms (6a) and (6b), resp. From the equation (17) it follows:

$$a_0 = \frac{1}{b} \frac{e^2}{4\pi\varepsilon_0 kT} = \frac{1}{b} a_c .$$

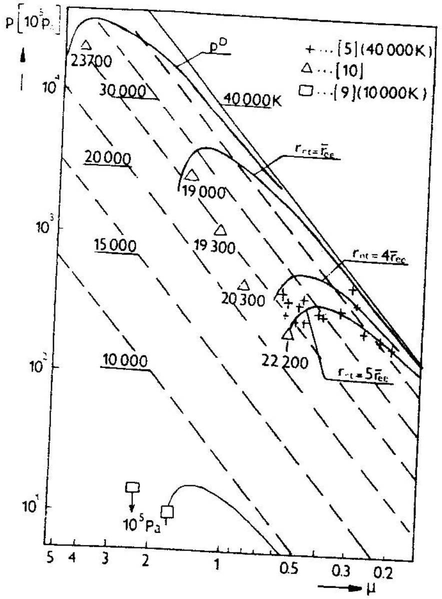


Fig. 6. Pressure dependence of plasma without a neutral component on the plasma parameter μ for various temperatures (from 10 to 40 000 K) calculated according to a semi-empirical formula (13) for $r_{int} = \bar{r}_{ee}, 4\bar{r}_{ee}, 5\bar{r}_{ee}$. In addition experimental points of erosive plasma in capillary (temperature of experiment 40 000 K) [5] and others are illustrated.

With regard to the values of b, a_0 appears to be comparable with a Coulomb scattering parameter a_c. The values of pressures calculated for two different forms of $F(r)$ differ only very little in spite of a_0 varying greatly for the individual forms. The diversity of a_0 reflects only the dissimilarity of the forms of the correction function.

III. RESULTS AND DISCUSSION

Fig. 5 shows the dependence of pressure on the specific volume for non-ideal, resp. ideal plasma in all the mentioned approximations at the temperature of $T = 10^4$ K. The analytic solutions are marked by a solid line, the numerical ones — according to (6a) by a dashed line, according to (6b) by a dot — and — dashed line. The higher and lower curves are calculated according to (16) and (15), resp. Every isotherm occurring between the pressure of the ideal gas p_{id} and the pressure p^D is numbered pressuming $r_{int} = r_D$, suitable for $\mu \lesssim 0.04$ and $\mu < 0.7$ practically merges with p^D. Hence, their extrapolation into the region $\mu > 0.1$ ($\mu \sim 1$) is forced and does not accord with the reality. This holds also for the pressure calculated in [16, 17] within the higher approximation via concentration (n^2, $n^2 \ln(n)$). The calculation carried out in [16] is illustrated by the curve "Ved.—Lar.".

When we modified in our case Klimontovich's expression for the radial distribution function f^{P-D} only in the region of a low r (for the sake of the divergence of p^{P-D}), the pressure never decreased below p^D. Much larger changes in the pressure occur for a high r even with a small modification of $f_{a,b}(r)$. Thus, the estimation of r_{int} and the form of $f_{a,b}(r)$ for $r \gtrsim r_{int}$ are determining for the pressure. On giving up the polarization approximation ($r_{int} = r_D$) and introducing $r_{int} = n^{-1/3}$, a substantial deviation from p^D towards lower pressures appeared (Fig. 5). It led to an instability of plasma for comparatively low $\mu \sim 1$. (Instability in the meaning of $\partial p/\partial V > 0$; possibility of phase transition). Deviation of a similar character for p^D occurs beyond the point $\mu \sim 5$ (Fig. 6).

The differences between the pressure calculated according to the various forms of $F(r)$ and equations (15, 16), resp., and analytically, vary only with a high μ. They are well represented by the analytic semi-emipirical formula (13).

According to the experimental data of N. N. Ogurtsova et al. [5], dealing with the equation of state of the erosive plasma of capillary discharge, a marked deviation of pressure from that of the ideal plasma p^D (phase transition) occurs even in the regions of lower $\mu \sim 0.4$ (Fig. 6) than our, differing from what our formula (13) predicts at $r_{int} = \bar{r}_{ee}$. To obtain an approximate consistency with the results of [5] r_{int} is to be substituted by $5\bar{r}_{ee}$. This indicates that the effective interaction radius in non-ideal plasma not only remains at the level of the mean distance of the charged particles but even represents low multiple (compare with Fig. 3). The magnitude of the multiple is, however, distorted by the presence of twice ionized atoms (cca 30 % C^{2+} and Cl^{2+}) at the temperature of 40 000 K.

There are very few experimental data responsibly comparable with the expressions given, as it is necessary to measure independently not only n_e, T, but also the concentration of the neutral particles n_a, mainly in high-pressure experiments. Fig. 6 shows two points from the experiments [1, 7] of the explosion of Cs cord at high pressure of the inert atmosphere. The illustrated points correspond to the explosion at 10^5 and 10^6 Pa of argon, when the ionized atoms still prevail over neutral ones. The other results (at higher pressures up to 5×10^7 Pa) are inapplicable, due to either space inhomogeneity or non-isothermicity ($T_a \neq T_e$). After a subtraction of pressure of the neutral component (the degree of ionization is lower than 30 %) it shows negative pressures. Conversely, in the experiments [14, 15] the pressure is higher than p_{id}.

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