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STATISTICAL THEORY OF A DENSE PLASMA

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A strongly non-ideal nondegenerate plasma is considered. The partition function is reduced to the form of a classical configuration integral in which the interaction energy for each pair of particles is expressed by means of a pseudopotential determined from the quantum mechanical analysis of a two-particle system. This enables one to take into account quantum effects in the dense plasma and at the same time to utilize for the calculation of thermodynamic quantities the Monte Carlo method developed in the theory of strongly imperfect classical fluids. In carrying out the calculations the electrons and the ions are not segregated into free and bound ones. The form of the pseudopotential is discussed. Calculations are performed for a hydrogen plasma at T equal to 10,000 and 30,000°K. The results for a plasma close to an ideal one are in satisfactory agreement with the results of other calculations. The degrees of ionization in a dense plasma are found and its equation state is discussed. The limits of applicability of the method proposed for the investigation of a dense plasma due to extreme concentrations of atoms and electrons, to the effect of microfields and to the possibility of molecule formation are discussed.

CONSIDERABLE attention has been devoted to the equation of state of a real plasma.[1-9] The principal results for a weakly imperfect (Debye) plasma were obtained by Vedenov and Larkin.[1] In a number of subsequent papers (cf., for example, [2-4] and the references contained therein) the results of [1] were made somewhat more precise.

Deviation from ideal behavior is characterized by the parameter $\gamma = \beta e^2 n^{1/3}$, where $\beta = (kT)^{-1}$, T is the temperature, $n = n_e + n_i$, n_e and n_i are the densities of the free electrons and of the ions (for the sake of simplicity we restrict ourselves to singly charged ions, $n_e = n_i$). The results of [1-4] are valid for $\gamma \ll 1$.[1)] In [5,6] an attempt is made to consider a strongly non-ideal (dense) plasma, i.e., the case $\gamma \gtrsim 1$, but in [7] it was shown that the equations of state obtained in [5,6] do not satisfy the conditions of thermodynamic stability.[2)]

The discussion in [5,6] was very approximate. Of greater interest are [8-10], but only models of Coulomb systems were investigated in those references: charges of one sign on a neutralizing background[8] and charged hard spheres.[9,10] Therefore the possibility of applying the results of these references to a dense plasma is doubtful. All the more so since in [8-10], and also in [5,6], the discussion is carried out only within the framework of classical statistics, while, as shown in [7], in determining the interaction energy in a dense plasma (even a nondegenerate one) it is necessary to take quantum effects into account. The quantum effects in a dense plasma play a role significant in principle: thermodynamic stability is guaranteed by them; but this does not exclude the possibility of the breaking up of a dense plasma into two phases.[7]

In this paper we investigate a dense nondegenerate plasma (as we shall see, such a plasma exists at $T \cong 10^5$ °K and below). In the absence of degeneracy configurations in which three or more particles are situated within the limits of a single de Broglie electron wavelength λ are less probable than two-particle configurations. In this case in taking quantum effects into account it is possible to restrict oneself to the pair approximation. Then the partition function of the system reduces to the configuration integral in which the interaction between the particles is described by an effective potential—a pseudopotential.[11,2,3] At distances $r \gg \lambda$ the pseudopotential coincides with the Coulomb potential, while at smaller distances it is determined from the quantum-mechanical consideration of a system of two particles.

The pseudopotential introduced in this manner takes quantum effects into account and formally allows us to reduce the determination of the different thermodynamical quantities to the evaluation of the classical configuration integral. The methods of calculation[11,3,12] developed for a weakly imperfect plasma become invalid for a dense plasma in view of the absence of a small parameter in terms of which one can carry out an expansion. Therefore we have utilized the Monte Carlo method which is not associated with an expansion in terms of a small parameter. The Monte Carlo method in classical statistical physics has been developed for one-component systems[13-15,8] and for electrolytes[10] and can be extended to our problem. Since one cannot exclude the appearance of phase transitions in a dense one should utilize the Monte Carlo method for a grand canonical ensemble (MCMGCA)[15] which anticipates the possibility of investigating them.

In this paper we consider the principal relations for the pseudopotential, we present the required modification of the MCMGCA, we discuss the results of calculations for weakly and strongly non-ideal hydrogen

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[1)] Krasnikov [4], by summing certain classes of diagrams, obtained an expression in a rather complex integral form for the thermodynamic potential. It is shown only that in limiting cases it yields previously known results. The question of the limits of applicability of this expression is not discussed.

[2)] The possibility of thermodynamic instability of a dense plasma has already been indicated in [6], but excessively weak conditions of stability were utilized in that reference.

plasma, and we consider the limits of applicability of the method proposed for the investigation of a dense plasma.

THE PSEUDOPOTENTIAL

General relations. The pseudopotential $\Phi_{ab}(r, \beta)$ is determined from the expression in which the quantity $S_{ab}(r)$—the quantum statistical probability density for finding two particles (of a and b kinds) at a distance r —is formally represented in the form of the classical probability density for the same event:

$$S_{ab}(r) = 8\pi^{3/2}\lambda_{ab}^3 \sum_{\alpha} |\psi_\alpha(r)|^2 \exp(-\beta E_\alpha) \equiv \exp[-\beta\Phi_{ab}(r, \beta)], \quad (1)$$

where E_α and $\psi_\alpha(r)$ are the relative energy and the wave function for two particles in the state α, $\lambda_{ab} = \hbar\sqrt{\beta/2m_{ab}}$, $m_{ab} = m_a m_b/m_a + m_b)$, m_a and m_b are the masses of the particles. In this paper we consider only two kinds of particles: electrons (e) and single charged ions (i).

Expression (1) is written for a system consisting of two particles. We utilize the pseudopotential defined in this manner for writing down the partition function (the configuration integral Z) for N_e electrons and N_i ions ($N_e = N_i = N/2$) situated in a volume V:

$$Z = \int_V \ldots \int \exp[-\beta U(N, \beta)]\, dq_1 \ldots dq_N, \quad U(N, \beta) = \sum_{a,\, b;\; i<j}^{N} \Phi_{ab}(r_{ij}, \beta), \quad (2)$$

where $q_1, \ldots, q_N$ are the coordinates of the particles; $r_{ij} = |q_i - q_j|$. We emphasize that in evaluating Z, and also the thermodynamic quantities discussed below we do not segregate the particles into free and bound ones. The number N includes all the electrons and ions situated in the volume V: both those which have united into atoms, and the free ones. Consequently, $U(N, \beta)$ includes within it the following interactions: those of the free charges among themselves, of the electrons and the ions inside atoms, of free charges with atoms and of atoms among themselves.[3]

Expression (2) differs from the classical configuration integral by the fact that the pseudopotential Φ_{ab} depends on the temperature. Therefore, the thermodynamic quantities should be calculated in accordance with the general rules of thermodynamics, starting directly with (2). The expressions so obtained can be represented in the form

$$\bar{F} = Z^{-1} \int_V \ldots \int F(q_1, \ldots, q_N, \beta) \exp[-\beta U(N, \beta)]\, dq_1 \ldots dq_N. \quad (3)$$

The form of the functions $F(q_1, \ldots, q_N, \beta)$ can differ from the corresponding classical expressions. Thus, for the energy (F = E) we have

$$E(q_1, \ldots, q_N, \beta) = {}^3/_2 kTN + \sum_{a,\, b;\; i<j}^{N} [\Phi_{ab}(r_{ij}, \beta) + \beta\partial\Phi_{ab}(r_{ij}, \beta)/\partial\beta].$$

Determination of the pseudopotential. The summation in (1) is carried out over all the possible states of two interacting particles. Therefore, in the calculation of Φ_{ei}, Φ_{ee} and Φ_{ii} we must carry out the integration over all the states of the continuous spectrum, while in the evaluation of Φ_{ei} we must also carry out the summation over all the discrete states. Even for the case of an electron and a proton when the functions $\psi_\alpha(r)$ are known exactly, the expressions for $S_{ab}(r)$ cannot be represented in a form useful for practical utilization.[12] Therefore, for our purposes it is necessary to obtain for $S_{ab}(r)$ simple approximate expressions. In this paper we shall restrict ourselves to electrons and protons.

At large distances the quantum effects in the Coulomb interaction are not essential and expression (1) must coincide with the classical one:

$$S_{ab}(r) = \exp(-\beta e_a e_b / r) = \exp(-\xi_{ab} / x),$$

$$\xi_{ab} = \beta e_a e_b / \lambda_{ab} = c_{ab} e^2 \hbar^{-1} \sqrt{2\beta m_{ab}} = 2c_{ab}\sqrt{\beta I m_{ab} / m_e}, \quad (4)$$

where e_a and e_b are the charges of the particles, $x = r/\lambda_{ab}$, $c_{ab} = e_a e_b/e^2$, $I = \mathrm{Ry}$.

We consider another limiting case—that of very small r, when $\psi_\alpha(r) = \psi_\alpha(0) + \psi'_\alpha(0)r + {}^1/_2\psi''_\alpha(0)r^2$. Then[12][4]

$$S_{ab}(r) = S_{ab}(0, \xi_{ab})(1 + \xi_{ab}x + {}^1/_2\xi_{ab}x^2 + \ldots) \cong S_{ab}(0, \xi_{ab}) \exp(\xi_{ab}x), \quad (5)$$

$$S_{ab}(0, \xi_{ab}) = (1 - \delta_{ab}) S_d(0, \xi_{ab}) + S_c(0, \xi_{ab})[1 + \delta_{ab}(-1)^{2s}(2s + 1)^{-1}], \quad (6)$$

$$S_d(0, \xi_{ei}) = \pi^{1/2} |\xi_{ei}|^3 \sum_{n=1}^{\infty} n^{-3} \exp(\beta I/n^2), \quad (7)$$

$$S_c(0, \xi_{ab}) = -4\pi^{1/2}\xi_{ab} \int_0^\infty x \exp(-x^2)[1 - \exp(\pi\xi_{ab}/x)]^{-1}\, dx, \quad (8)$$

where s is the particle spin, $S_d(0, \xi_{ei})$ is the contribution of the bound states, n is the principal quantum number, $S_c(0, \xi_{ab})$ is the contribution of the states of the continuous spectrum. Numerical values of $S_d(0, \xi_{ei})$ and of $S_c(0, \xi_{ab})$ are given in [12]. We emphasize that expression (5) is obtained from exact wave functions for the two-particle problem taking both free and bound states and also exchange effects into account.

For the region of interest to us $\xi_{ab} > 1$ and expressions (7) and (8) can be simplified:

$$S_d(0, \xi_{ei}) \cong \pi^{1/2} |\xi_{ei}|^3 \exp(\beta I),$$

$$S_c(0, \xi_{ab}) \cong \begin{cases} -2\pi^{1/2}\xi_{ei} \text{ for particles of opposite sign,} \\ (4\pi / 3^{1/2})\xi_{aa}(\pi\xi_{aa} / 2)^{1/3} \exp[-3(\pi\xi_{aa} / 2)^{2/3}] \end{cases}$$

for particles of the same sign.

In the temperature range under investigation we have $S_d \gg S_c$, and the form of Φ_{ei} in the neighborhood of r = 0 is practically determined by the contribution of the ground state. In contrast to the Coulomb expression the pseudopotential has a finite value at r = 0, the value of which depends on β and on the kind of particles, for example

$$\Phi_{ei}(0, \beta) = -\beta^{-1}[\ln(\pi^{1/2}|\xi_{ei}|^3) + \beta I].$$

One can say that the quantum mechanical effects lead to an effective repulsion of an electron and an ion at small distances.

In order to determine the form of $\Phi_{ei}(r, \beta)$ for arbi-

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[3] We note that in the theory of dense (non-ionized) gases difficulties arise frequently due to insufficient information concerning the law of interaction between atoms. The evaluation of pseudopotentials is associated with considerably smaller difficulties than the determination of the atom-atom interaction. Therefore it is possible that the expression (2) will turn out to be useful not only in plasma theory, but also in the theory of dense gases and liquids.

[4] The next terms in the expansion in terms of r have also been obtained in [12].

trary values of r we segregate in the sum in (1) the first few terms ($E_\alpha < E'$) and evaluate them exactly in terms of the known $\psi_\alpha(r)$, while the remaining terms ($E' < E_\alpha < \infty$) are taken into account in the classical approximation.[12] We then have

$$S_{ei}(x, E > E') = \begin{cases} \exp(-\xi_{ei}x^{-1}), & \text{if } \beta|E'|x \geqslant |\xi_{ei}| \\ [1 - y(\sqrt{\beta E' - \xi_{ei}x^{-1}})]\exp(-\xi_{ei}x^{-1}) + \\ + 2\pi^{-1/2}(\beta E' - \xi_{ei}x^{-1})^{1/2}\exp(-\beta E'), & \text{if } \beta|E'|x \leqslant |\xi_{ei}|. \end{cases} \tag{9}$$

where

$$y(z) = 2\pi^{-1/2}\int_0^z \exp(-t^2)\,dt.$$

The curve 5 in Fig. 1 is calculated by separating out the first three states (with the principal quantum numbers n = 1, 2, 3). The result practically changes very little if we separate out only the ground state (curve 6). In order to illustrate the role played by the individual terms in the sum (1) we have constructed curves 1–4. Curve 1 is obtained if we restrict ourselves in (1) only to the first term, 2 if we restrict ourselves to the first two terms, 3 if we restrict ourselves to the first three terms, 4 if we restrict ourselves to the discrete states with $n \geq 4$ and to the continuous spectrum (curve 4 is constructed in accordance with formula (9)). We note that the contribution of the ground state (line 1) coincides with formula (5). The excited states begin to give a contribution to $S_{ei}(r)$ for $x \gtrsim 2.5$ leading to the transition from curve 1 to the Coulomb dependence-curve 7. Approximately one can consider that the pseudopotential differs from the Coulomb potential for $x \lesssim x_0$, where x_0 corresponds to the point of intersection of the lines 1 and 7 (this intersection occurs for $T \lesssim \beta I/2$, then $x_0 \cong (\beta I)^{1/2}/2$.

In Fig. 2 we have given examples of the pseudopotential $\Phi_{ee}(r)$. In this case the transition from (5) to (4) occurs at $x \cong 1$.

In the case $\beta I \ll 1$ in order to determine the boundaries of the quantum region we use the expansion of the thermodynamic quantities in powers of $\hbar$:[16]

$$S_{ab}(r) = \exp(-e_a e_b \beta / r)\,[1 + \hbar^2\beta^3 e^4 / 24mr^4 - \hbar^2\beta^2 e^2 / 6mr^3]. \tag{10}$$

The terms quadratic in $\hbar$ become essential at $x \cong (\beta I/3)^{1/4}$ or $x \cong (4\beta I/9)^{1/6}$, i.e., for $x \cong 1$.

Knowing the limiting expressions for $S_{ab}(r)$ and the limits for their applicability, one can construct for concrete calculations interpolation formulas valid for all r.

THE MONTE CARLO METHOD FOR THE GRAND CANONICAL ENSEMBLE

The MCMGCA for a cone-component system has been considered in [15]. We dwell on the special features associated with our problem. Expressions (2) and (3) have been written down for a canonical ensemble. In a grand canonical ensemble for a two-component system we have

$$\bar{F} = Q^{-1}\sum_{N=0}^{\infty} N_{i0}^{N_i} N_{e0}^{N_e} (N_l!N_i!)^{-1} V^{-N} \int_V \ldots \int F(q_1, \ldots, q_N, \beta) \times \exp[-\beta U(N, \beta)]\,dq_1 \ldots dq_N, \tag{11}$$

where $N_{s_0} = V\lambda_s^{-3}\exp(\beta\mu_s)$, $s = e, i$; μ_s is the chemical potential; $\lambda_s = (2\pi\hbar^2\beta/m_s)^{1/2}$, Q is a normalizing factor. Breaking up the volume V into a large number $B = V(\Delta q)^{-3}$ of elementary cells of equal size $(\Delta q)^3$ and replacing the configuration integrals by sums we obtain

$$\bar{F} = Q^{-1}\sum_{A_j} F(A_j)\,u_j, \tag{12}$$

where $F(A_j) \equiv F(q_1, \ldots, q_N, \beta)$, A_j is the state of the system in which it has N particles with these particles being distributed in a definite manner among the elementary cells,

$$u_j = Q^{-1}N_{i0}{}^{N_i}N_{e0}{}^{N_e}(N_i!N_e!)^{-1}B^{-N}\exp[-\beta U(A_j)]. \tag{13}$$

We consider in a set of events A_j a Markov chain (MC) with a limiting distribution of probabilities u_j. Then the average over the MC of $F(A_j)$ is the desired $\bar{F}$

$$\bar{F} = M^{-1}\sum_{j=1}^{M} F(A_j). \tag{14}$$

The single-step probabilities p_{kj} of the required MC can be obtained from the known u_j by using the usual system of equations:[14]

$$\sum_j p_{kj} = 1, \qquad u_k p_{kj} = u_j p_{jk}. \tag{15}$$

Specifying the values of T, V, $\mu_e + \mu_i$ and the pseudopotentials Φ_{ab} it is possible to obtain the p_{kj}, to construct the MC and to determine with the aid of (14)[5] the densities $n_i = n_e = N_e/V$, the pressure P and other quantities, and also the correlation functions. Periodic boundary conditions are introduced in the usual manner so that the volume V is interpreted as being the volume of a Monte-Carlo cell.

In the system (15) the number of unknowns exceeds the number of equations. Therefore, for a specific choice of p_{kj} one can take into account the requirements of the reduction of the nonequilibrium portion

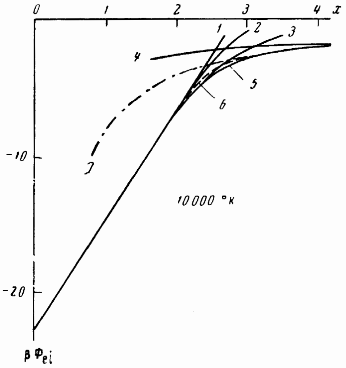

FIG. 1

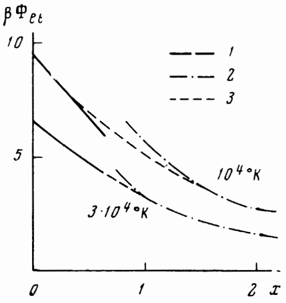

FIG. 2

FIG. 1. The pseudopotential for the interaction between an electron and a proton for T = 10,000°K.

FIG. 2. The pseudopotential for the electron-electron interaction for T equal to 10,000 and 30,000°K. 1 – according to formula (5), 2 – according to formula (4), 3-intermediate segment.

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[5] In the case of practical calculations it is more convenient to utilize a different form of writing down the expression

$$\bar{F} = F(A_M) - M^{-1}\sum_{j=1}^{M-1} j\,[F(A_{j+1}) - F(A_j)],$$

by carrying out calculations not of the quantities $F(A_j)$, but of changes in these quantities.

of the MC, of the possibility of determining $\bar{F}$ in terms of a minimum number of steps M etc.[13-15]

In our MC two types of steps have been realized: 1) steps characterized by a change in the position of a single randomly selected particle, with the total number of particles in the volume V being conserved, and 2) steps characterized by a change in the number of particles in the volume V by two (one electron and one ion—in order to preserve electric neutrality) for a fixed position of all the remaining particles. The realization of steps of the first type was a standard one (the maximum displacement was determined by λ_{ei}). We now explain the realization of steps of the second kind. Let the state A_j have two particles more than A_k, i.e., $(N_e)_j = (N_e)_k + 1$, $(N_i)_j = (N_i)_k + 1$. The single-step probabilities were taken in the form

$$p_{kj} = \alpha_+ \tilde{u}_j / B^2[(N_i)_k + 1][(N_e)_k + 1](\tilde{u}_k + \tilde{u}_j),$$
$$p_{jk} = \alpha_- \tilde{u}_k / (N_i)_j (N_e)_j (\tilde{u}_k + \tilde{u}_j),$$

which is a natural generalization of the expressions for p_{kj} considered in [15]; $\alpha_+ (\alpha_-)$ are the probabilities of steps with an increase (decrease) of the number of particles $\tilde{u}_j = B^N u_j$. We denote by α_0 the probability of a step without a change in the number of particles, and we obtain from the condition of normalization that $\alpha_0 + \alpha_+ + \alpha_- = 1$.

The concrete construction of the steps consists of the following. After a random choice of the nature of the step in the case when the number of particles increases, a new electron and a new ion were placed in two randomly selected points, while in the case of a decrease in the number of particles a randomly selected electron and ion were removed from a Monte Carlo cell. In conclusion a random selection is made of the probability $\tilde{u}_j/(\tilde{u}_k + \tilde{u}_j)$ or $\tilde{u}_k/(\tilde{u}_k + \tilde{u}_j)$.

The quantities α_+, α_- and α_0 were varied within wide limits. For the calculation of the state of a gas close to an ideal gas the values $\alpha_\pm = 0$ turn out to be optional, and, thus, the calculation was carried out in a canonical ensemble. In the calculation of a strongly imperfect plasma α_0 was varied from $1/3$ to $7/8$. At first a MC was constructed which is optimal for finding the densities for a given μ, and then, a MC which is optimal for finding other thermodynamic quantities, with the average density here now remaining practically constant.

In order to have the possibility of carrying out calculations for values of N contained within the specified limits the possibility was anticipated in the MCMGCA algorithm of having discontinuous changes in the volume V of the Monte Carlo cell when the MC tends to equilibrium.[15]

The energy of the system was calculated by the method of the nearest image,[13,8] since it was shown in [8] that this method gives reliable results for values of γ considered in this paper.

INVESTIGATION OF THE HYDROGEN PLASMA

Plasma close to ideal. The temperature T = 10,000°K was selected and two cases were considered in which the combined density of the heavy particles $n_i + n_a$ was equal to 10^{13} and 10^{19} cm^{-3}. Calculation by means of the Saha formula shows that in the former case complete ionization occurs and the plasma is a mixture of ideal electron and ion gases; the pressure of such a plasma is $P = 2n_i kT$, while the energy of interaction U_0 evaluated per single heavy particle is much smaller than kT.[6] In the case when $n_i + n_a = 10^{19}$ the degree of ionization turns out to be small and we are dealing with an ideal gas of hydrogen atoms; the pressure of such a gas is $n_a kT$, while the energy U_0 is equal to the ionization potential of the hydrogen atom. Below we give the results of our calculations according to MCMGCA for hydrogen at 10,000°K while in parenthesis are given numbers corresponding to the estimates quoted above.

$n_i + n_a$, cm^{-3}	$P/(n_a + n_i)kT$	U_0/kT
10^{13}	2.0 (2)	0.01 (< 1)
10^{19}	1.3 (1)	16 (15.8)

It should be explained that the initial density in the MC in both cases was given arbitrarily. When the MC approaches equilibrium in the former case the distribution of the electrons and of the ions over the volume turns out to be uniform on the average. But in the latter case when the MC approaches equilibrium the electrons and the ions approach each other pairwise, forming atoms. This is supported both by the results quoted above and by a direct analysis of the coordinates of the particles in equilibrium configurations.

In the present paper we have considered relatively short MC (10^4 steps) and the number of particles in a Monte Carlo cell amounted to only $N_i + N_e = 30$–40. Taking this into account one should acknowledge that the results obtained are satisfactory and give a correct idea of the state of the plasma under investigation.[7]

Strongly non-ideal plasma. Calculations have been carried out of several states of plasma in the region $\gamma \gtrsim 1$ for T = 30,000°K. Such a choice of the temperature is explained by the fact that the conditions corresponding to $\gamma \gtrsim 1$ are attained for T = 30,000°K for a minimum value of $n_i + n_a$ and, thus, the errors associated with taking quantum effects into account pairwise turned out to be least. For T < 25,000–30,000°K there is a sharp increase in the density of atoms corresponding to the value of n_i which guarantees $\gamma \cong 1$, while for greater values of T the values of n_i increase ($n_i \sim \gamma^3 T^3$).

The correlation functions obtained with the aid of the MCMGCA enable us to analyze the microstructure of the plasma. Figure 3 shows graphs of the quantity $\Delta N(r)$ which characterizes the relative situation of opposite charges (for the sake of definiteness we shall speak of the distribution of the electrons around the ions) and which is defined in the following manner. For each ion the space around this ion is divided into spherical layers of thickness Δr and the number of electrons in each layer is calculated. The values obtained for all the ions

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[6] We cannot make an estimate of this energy in the Debye approximation since the interaction energy also contains the energy of the non-ionized atoms, and in spite of the smallness of the density of the latter the value of this energy turns out to be much larger than the Debye value. We point out that the calculation according to the MCMGCA carried out in [15] in which in evaluating the energy only the free charges were taken into account gave good agreement for the energy obtained with the value obtained according to the Debye-Hückel formula.

[7] We intend to consider longer MC, to determine the dependence of the results on the number of particles and on the degree of exactness of the approximation to the pseudopotential.

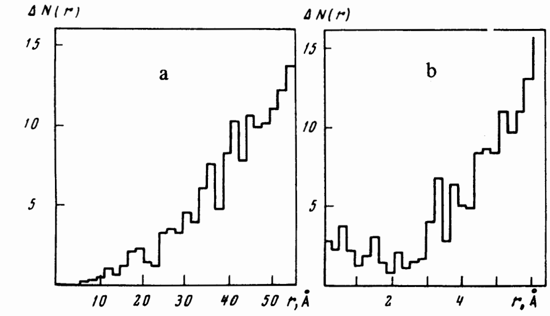

FIG. 3. The functions ΔN(r) in the cases: a – T = 10,000°K, $n_i \cong n_i + n_a = 10^{13}$ cm^{-3}; b – T = 30,000°K, $n_i + n_a = 6 \times 10^{21}$ cm^{-3}.

of a given configuration in a Monte Carlo cell are added, and the value so obtained is averaged over all the configurations of the stationary segment of the MC; the result of this is ΔN(r). Since Δr is a finite quantity, it is convenient to represent ΔN(r) by a stepped graph with a step of magnitude Δr.

The relative variation of ΔN(r) in the immediate neighborhood of the ion reproduces the distribution of the charge in a hydrogen atom. As can be seen from Fig. 3b the shape of ΔN(r) for small r is close to the charge distribution in the ground state of the hydrogen atom, in which the maximum of the distribution is situated at $r \cong 0.5$ Å. But for large r we have $\Delta N(r) \simeq r^2$.

The radius of the electron cloud in the ground state of the hydrogen atom amounts to $\sim 2.5a_0$.[7] Therefore, if we take the sum of the values of ΔN(r) for $r < 2.5a_0$, then in the case of total ionization we shall obtain zero, while in the case of the absence of ionization we obtain a number which is equal to the average number of electrons in a Monte Carlo cell which in this case coincides with the number of atoms. These results were obtained in the two examples for T = 10,000°K. We shall utilize this method of evaluating the number of bound electrons, i.e., of the number of atoms $\overline{N}_a$, in a Monte-Carlo cell also in the arbitrary case

$$\overline{N}_a = \sum_{r<2,5a_0} \Delta N(r), \qquad n_a = \overline{N}_a/V.$$

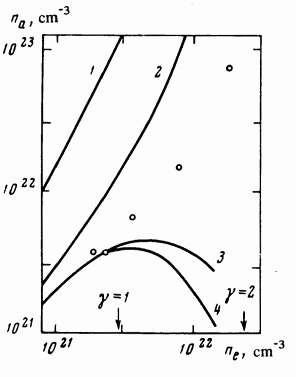

FIG. 4

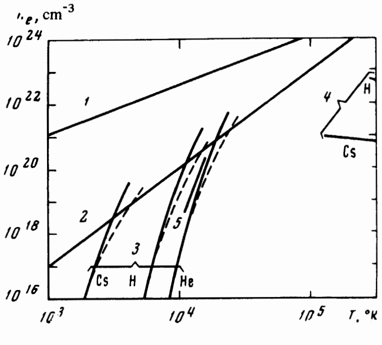

FIG. 5

FIG. 4. The relation $n_a = n_a(n_e)$ for hydrogen for T = 30,000°K. Circles are our calculations according to MCMGCA. The curves are constructed according to several formulas obtained utilizing different approximations for ΔF: 1 – it is equal to zero (Saha formula); 2 – according to [1,2]; 3 – according to [18]; 4 – according to Debye-Hückel. Arrows indicate values of n_e for which γ is equal to 1 and 2.

FIG. 5. Diagram elucidating the region of the values of the electron density and of the temperature where the approximation is applicable which is considered in the present paper. The lines correspond to: 1 – $n_e\lambda_{ee}^3 = 1$; 2 – γ = 1; 3 – $n_a = d^{-3}$ (the dotted line is constructed in accordance with the Saha formula, i.e., for ideal gases; the solid line takes imperfection into account; three atoms are considered); 4 – $E_H = E_0$; 5 – see the text.

The quantity $\overline{N}_e - \overline{N}_a$ gives the number of free electrons, $n_e = (\overline{N}_e - \overline{N}_a)/V$. Such a "spatial" division of the charges into bound and free charges is to a large extent arbitrary, but it enables us to make an estimate of the microstructure of the plasma in usual terms.

In Fig. 4 results are presented obtained by us for $n_a(n_e)$ in a dense plasma with the aid of the MCMGCA. We have also plotted there: a line constructed according to the Saha formula, and three curves obtained on the assumption that the atoms are an ideal gas, and utilizing different approximations for ΔF—the change in the free energy due to the interaction of free charges. Curves 2 and 4 are sensible approximations only for $\gamma \ll 1$ and their extrapolation into the region $\gamma \gtrsim 1$ has *no theoretical foundation whatsoever*. Curve 3 corresponds to papers[5,6] devoted in particular to the case $\gamma > 1$.[8] But when $\gamma \gtrsim 1$ curve 3 has $(\partial n_a/\partial n_e)_T < 0$. In [7] it is shown that this is evidence of thermodynamic instability of the corresponding equation of state.

Thermodynamic stability of a dense plasma is guaranteed by quantum effects in the interaction between charged particles. The method of calculation proposed in the present paper takes these effects into account, and the results of the MCMGCA give values of $n_a(n_e)$ which lie on a curve for which everywhere $(\partial n_a/\partial n_e)_T > 0$. We note that ΔF[1,2] differs from the Debye-Hückel expression just by taking into account the quantum effects in a rarified plasma and correspondingly curve 2 has a positive derivative everywhere, while curve 4 differs little from curve 3. We note that the expression ΔF[1,2] has been obtained for a high-temperature plasma ($T \gg 160{,}000$°K) and its utilization for T = 30,000° (and also for $\gamma \gtrsim 1$) is, generally speaking, completely unjustified. However, as can be seen from Fig. 4, curve 2 has turned out to be the nearest to MCMGCA even though the existing difference is still significant.

As can be seen from Fig. 4, the degree of ionization in a strongly imperfect plasma is relatively low (0.4 for γ = 1 and less than 0.2 for γ = 2). This leads to the fact that under the conditions being considered the principal contribution to the pressure is made by atoms which under our conditions do not yet differ appreciably from a perfect gas. This has been confirmed in the case of pressure also by the results of the MCMGCA. Unfortunately, the insufficient accuracy of the results obtained does not allow us to determine confidently the difference between the equation of state obtained above and the ideal one.

As we can see, the densities n_a and n_e introduced in

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[8] The formulas in [5] and [6] differ numerically somewhat from each other, but this difference, as has been pointed out in [7], is not essential and the resultant relations for n_a (n_e) are very similar. Of these formulas that one is the more convenient in which ΔF is taken in the form obtained in [18] since in such a case a smooth transition to the Debye-Hückel expression is guaranteed for $\gamma \gtrsim 1$.

the discussion of the microstructure of a dense plasma have also turned out to be useful for the interpretation of results obtained for the equation of state. The concepts n_a and n_e in the statistical theory of a dense plasma are auxiliary ones, and their introduction is not at all obligatory, since in calculating thermodynamic quantities by the MCMGCA method it is not necessary to segregate the charges in any manner into bound and free ones.

LIMITS OF APPLICABILITY

In view of the absence of degeneracy electrons which are not bound inside atoms are situated on the average at distances greater than a de Broglie wavelength:

$$n_e < \lambda_{ee}^{-3}. \qquad (16)$$

This condition can also be written in the form $\gamma < \gamma_{\max} \cong 2\sqrt{\beta I}$.

The atoms can be satisfactorily described with the aid of a pseudopotential if the volume calculated per single atom is greater than the proper volume of the atom d^3:

$$n_a < d^{-3}. \qquad (17)$$

For hydrogen $d^{-3} = 10^{24}$ cm^{-3}, while for atoms with the greatest and the least ionization potentials (He and Cs) d^{-3} is equal to 10^{25} and 10^{22} cm^{-3} 9)

In the n_e-T diagram (Fig. 5) we draw lines along which n_a which corresponds to the given n_e and T is equal to d^{-3}. Such lines can be easily drawn in the region where the Saha formula is valid, and they can be tentatively extrapolated into the strongly imperfect region by utilizing the results of the present paper. Since the magnitudes of n_a and n_e in a dense plasma are not known in advance, then in doubtful cases the fact that (16) and (17) are satisfied should be checked after the calculations have been carried out. Moreover, the free charges must not perturb the atoms too strongly. The reduction of the barrier in an atom under the action of a homogeneous field E is equal to $2e\sqrt{eE}$. We make an estimate of the destructive microfield E_0 by setting $2e\sqrt{eE_0} = I_0$, where I_0 is the ionization potential of an isolated atom. Utilizing the relation between the most probable intensity of the microfield E_H, n_e and T which is known for $\gamma < 0.2$,[19] we plot in Fig. 5 the lines $E_H = E_0$. One could expect that the corresponding values of $n_e(T)$ will increase even more strongly with a decrease in T when we go over into the strongly imperfect domain.10)

In dense media molecules, molecular ions and other complexes can be formed the validity of describing which with the aid of a pair pseudopotential is doubtful. In addition to (16) and (17) we write

$$n_M < n_a, \quad n_+ < n_i, \quad n_- < n_e, \qquad (18)$$

where n_M, n_+ and n_- are the densities of molecules, of positive molecular ions and of negative ions. For example, in a hydrogen plasma the formation of H_2, H_2^+, and H^- is possible.11) Curve 5 in Fig. 5 bounds the region where at least one of the conditions (18) is violated. This line is constructed on the assumption that the reactions proceed as in an ideal gas. Under this assumption for T ≲ 7,000°K the most restrictive is the condition for H_2, for 7,000 ≲ T ≲ 30,000°K the most restrictive is the condition for H^-, and for T ≳ 30,000°K the most restrictive is the condition for H_2^+. If we construct an analogous line for Cs, it will lie considerably closer to curve 3. Taking the deviation from ideal behavior into account in determining chemical equilibrium can significantly reduce the fraction of molecular components. Thus, negative ions with a low energy of affinity are in general not formed in a dense plasma.[20]

All the effects considered above are partially taken into account also within the framework of the pair approximation. Therefore, the method for investigating a dense plasma developed in the present paper possibly yields fairly good results also in certain cases when the restrictions introduced above are violated.

In this paper calculations have been carried out for a hydrogen plasma. By altering the form of the pseudopotential one can carry out an investigation of a plasma of different chemical composition.

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9) This size is in fact determined by the ground state. The excited atoms give no appreciable contribution to the partition function even of a weakly imperfect plasma [3,12].

10) The distribution of the microfields in a dense plasma, which is independently of interest, can be investigated by the methods of the present paper.

11) Generally speaking, one cannot exclude the possibility of appearance of even more complicated complexes.

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