

CONCERNING THE THERMODYNAMICS OF A DENSE PLASMA

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The thermodynamic properties of a dense low-temperature plasma are considered on the basis of a method in which the Bloch equation and a diagram technique are employed to extend Mayer's group-integral theory to a quantum system of interacting particles. Divergences inherent in the Coulomb interaction are removed by rearranging the terms of the perturbation theory series. The first stage of the rearrangement corresponds to the Gell-Mann-Brueckner procedure, and the second to summation of ladder diagrams containing the effective interaction potential. From the physical point of view this approximation corresponds to simultaneously taking into account collective and individual effects in the plasma. The Gibbs free energy of the plasma is calculated by the proposed method for Boltzmann statistics.

1. INTRODUCTION

A dense plasma is usually defined as a strongly ionized gas in which the density of the charged particles is sufficiently high, so that the average energy of the interaction between the charged particles is comparable with the thermal energy. Unlike ordinary gases, in a plasma the forces of interaction between the particles are long-range, so that the effects connected with the interaction can be appreciable at low temperatures (10^4 °K) already at charged-particle densities $n \sim 10^{18} \text{ cm}^{-3}$. In addition, quantum-mechanical effects appear in a dense plasma: first, degeneracy effects can occur, and second, when the Coulomb-interacting particles are not very far from each other, their relative motion must be described quantum-mechanically, and not with the aid of the laws of classical mechanics. Up to densities $\sim 10^{20} \text{ cm}^{-3}$ and temperatures $\sim 10^4$ °K and higher, the average electronic de Broglie wavelength ($\lambda_e = \hbar/(2m_e T)^{1/2}$) remains smaller than the average distance between the particles is proportional to $n^{-1/3}$, so that the known degeneracy parameter $n\lambda_e^3$ is much smaller than unity, and consequently degeneracy effects can be neglected. A characteristic parameter of the Coulomb interaction between the particles is the ratio of the de Broglie wavelength of the particle to the average amplitude of the Coulomb scattering $f = e^2/T$ (e —electron charge). When $\lambda/f \ll 1$, the motion of the charged particle is quasiclassical and to calculate the corrections to the thermodynamic functions it is possible to replace the statistical sum over the states of the continuous spectrum by an integral, using for this purpose the quasiclassical expression for the energy level density. In this case an appreciable contribution to the thermodynamic functions can be made by the bound states. In the opposite limiting case $\lambda/f \gg 1$, the interaction between the charged particles can be treated by perturbation theory. Both these cases were considered by Vedenov and Larkin^[1,2].

We consider below the thermodynamic properties of a plasma with charged-particle density up to 10^{20} cm^{-3} at relatively low temperatures $\sim 10^4$ — 10^5 °K. We neglect here the effects of degeneracy, but take into account the interactions between the particles, and at

small distances we take into account the quantum-mechanical character of these interactions. The thermodynamic quantities are calculated on the basis of the Bloch equation. The latter are investigated with the aid of the approach proposed by Montroll and Ward^[3].

2. FUNDAMENTAL EQUATIONS

Let us consider a system of particles interacting in accordance with the Coulomb law and situated in a volume V in a state of thermodynamic equilibrium at a temperature $T = 1/\beta$. This system is described with the aid of a propagation function (Green's function) $G_N(\mathbf{q}^N\beta; \mathbf{q}'^N\beta')$, which depends on two systems of Cartesian coordinates $\mathbf{q}^N = \mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N$; $\mathbf{q}'^N = \mathbf{q}'_1, \mathbf{q}'_2, \dots, \mathbf{q}'_N$ ($\mathbf{q} = \{x, y, z\}$) and the two reciprocal temperatures $\beta = 1/T$ and $\beta' = 1/T'$ (N —number of particles in the system). The function $G_N(\mathbf{q}^N\beta; \mathbf{q}'^N\beta')$ satisfies the Bloch equation, whose integral form is

$$G_N(\mathbf{q}^N\beta; \mathbf{q}'^N\beta') = G_N^0(\mathbf{q}^N\beta; \mathbf{q}'^N\beta') - \int_V \int_{\beta'}^{\beta} G_N^0(\mathbf{q}^N\beta; \mathbf{x}^N\beta'') U(\mathbf{x}^N) \times G_N(\mathbf{x}^N\beta''; \mathbf{q}'^N\beta') d\mathbf{x}^N d\beta'', \tag{1}$$

where $G_N^0(\mathbf{q}^N\beta; \mathbf{q}'^N\beta)$ corresponds to the system of non-interacting particles and $U(\mathbf{q}^N)$ is the interaction potential.

If we put $\mathbf{q}'^N = \mathbf{q}^N$ and $\beta = 0$, that the function $G_N(\mathbf{q}^N\beta; \mathbf{q}^N0)$ can be interpreted as the amplitude of the probability that a system of many particles situated at the points \mathbf{q}^N at infinite temperature will return to the same points after slow cooling of the system to a temperature $T = 1/\beta$. The partition function represents in this case the mean value of the probability amplitude of such a process taken over all the possible initial points:

$$Z_N = \int_V G_N(\mathbf{q}^N\beta; \mathbf{q}^N0) d\mathbf{q}^N, \tag{2}$$

where

$$d\mathbf{q}^N = dq_1 dq_2 \dots dq_N \quad (d\mathbf{q} = \{dx dy dz\}).$$

In the case of a system of interacting particles, the solution of (1) can be obtained in principle with the aid of iterations. Such a solution is in fact an expansion of the propagation function in a perturbation-theory series. However, the integrals that enter in this expansion diverge, owing to the long-range character of the Coulomb potential. Nonetheless, it is possible to separate from the sequence of the expansion terms definite classes of integrals, the sum of which is finite. It will be shown later that these integrals play the principal role in the theory of systems of charged particles.

To interpret the different terms of the perturbation-theory series, it is convenient to use a diagram technique. From the very outset, we shall confine ourselves to Boltzmann statistics and represent the well known single-particle propagation function of the *i*-th free particle

$$G^0(q_i \beta; q_i' \beta') = \left[\frac{m_i}{2\pi(\beta - \beta')\hbar^2} \right]^{1/2} \exp \left\{ -\frac{m_i(q_i - q_i')^2}{2\hbar^2(\beta - \beta')} \right\} \quad (3)$$

graphically in the form of the vertical line going from the point $q_i' \beta'$ to the point $q_i \beta$ (diagram a of Fig. 1). Then the first term of the perturbation-theory series can be represented graphically in the form of *N* such lines.

Assuming that the interaction potential is the sum of partial potentials, we can describe with the aid of relatively simple types of diagrams also the succeeding terms of the perturbation-theory series. For example, the second term of this series, besides the indicated diagram, will contain diagram b of Fig. 1. On this diagram, the segments of the vertical lines between the points $(q_i' \beta'; x_i \beta'')$, $(x_i \beta''; q_i \beta)$, $(q_j' \beta'; x_j \beta'')$, and $(x_j \beta''; q_j \beta)$ correspond to the single-particle Green's functions (3), and the wavy line corresponds to the interaction potential $\Phi(|x_i - x_j|)$. In order to write down with the aid of this diagram an expression for the quantity $G^{(1)}(q_i q_j \beta; q_i' q_j' \beta')$ it is necessary to multiply the indicated Green's function by the potential, and integrate over the nodes of the diagram with coordinates x_i and x_j and the reciprocal temperature β'' within the volume of the system *V* and the reciprocal-temperature interval (β', β) . The quantity $G^{(1)}(q_i q_j \beta; q_i' q_j' \beta')$ can be interpreted as the Green's function of two particles situated initially at the points $(q_i' \beta'; q_j' \beta')$, and then interacting with each other at the points $(x_i \beta''; x_j \beta'')$ and ending up at the points $(q_i \beta; q_j \beta)$.

When considering the higher orders of perturbation theory, other more complicated types of interactions arise, which can also be set in correspondence with definite diagrams. The general rule for the construc-

tion of such diagrams for *n*-th order perturbation theory is to take into account all the possible arrangements of the interaction lines (there will be *n* such lines for the *n*-th term) between the *N* vertical lines. In analogy with the classical Mayer groups, the entire manifold of the diagrams can be classified in accordance with the sums of the group diagrams.

By way of an example, Fig. 2 shows the diagrams for groups of one, two, and three particles. With the aid of the group sums it is possible to write the propagation function in the form

$$G_N(q^N \beta; q'^N \beta') = \sum_l \prod_i S_l(q^l \beta; q'^l \beta'), \quad (4)$$

where the summation should be extended over all distributions of *N* particles in *m*₁ groups of one, *m*₂ groups of two, . . . , *m*_{*l*} groups of *l* particles, with allowance for the condition $\sum l m_l = N$. When (4) is substituted in (2), we get

$$Z_N = \sum_{m_l} \prod_{l=1}^N \frac{(V b_l)^{m_l}}{m_l!}, \quad \sum l m_l = N.$$

This expression coincides formally with the Z_N representation in the Mayer theory. The only difference is that the group integrals

$$b_l = \frac{1}{V l!} \int S_l(q^l \beta; q^0) d q^l \quad (5)$$

are calculated with the aid of the quantum-mechanical group sums $S_l(q^l \beta; q'^l \beta')$. With the aid of the group integrals *b_l* (*l* = 1, 2, . . .) it is possible to write down an expression for any thermodynamic quantity. In particular, for the thermodynamic potential Ω in a grand canonical ensemble we obtain

$$-\beta \Omega = p V \beta = \sum_{l=1}^N z^l V b_l \quad (6)$$

where *z* is the activity.

$$S_l(q_i \beta; q_i' \beta') = G^l(q_i \beta; q_i' \beta')$$

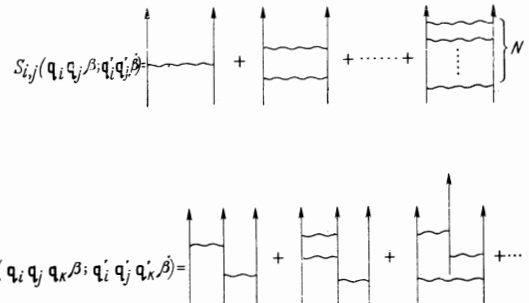


FIG. 2.

3. SUMMATION OF DIAGRAMS

Individual group integrals for a system of charged particles diverge as a result of the long-range character Coulomb interaction. It is possible, however, to

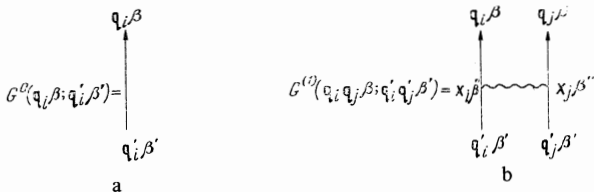


FIG. 1.

separate from each group integral definite particular integrals whose infinite sum is finite and can be calculated to conclusion. The following consideration is used here: Since the general perturbation-theory series is an expansion in powers of the coupling constant, which is proportional to the square of the electron charge e^2 , it follows that the terms of each of the particular series separated from the general series should be arranged in increasing powers of e^2 , and the largest contribution to b_l will be made by those particular series whose terms contain the lowest powers of e^2 . This procedure for constructing such series becomes much simpler when diagrams are used. We separate from each group sum a diagram with the smallest number of interaction lines and sum all such diagrams. Thus, the unit diagram in the unit group (Fig. 2) makes a contribution to the thermodynamic potential of an ideal gas: the first diagram for the group of two particles determines in the group integral b_2 the linear term in the coupling parameter e^2 , which drops out as a result of the electroneutrality condition, so that the second diagram must be taken into consideration. Owing to the foregoing condition, any more complicated diagram containing a single node (i.e., one of the vertical lines crosses only one interaction line) will likewise make no contribution to the thermodynamic quantities. For this reason the only lowest-order diagram which makes a nonzero contribution to b_3 in the group sum $S_{i,j,k}$ is the third diagram.

Such a procedure of separating the lowest-order diagram from all the succeeding group sums leads ultimately to a sum of the so called "ring diagrams" (Fig. 3). Ring diagrams are all of the same type: each vertical line is connected with the neighboring one by a single interaction line. The integrals (5) corresponding to such diagrams are multiplicative integrals of the convolution type and are calculated with the aid of Fourier transforms. As a result, formula (6) determines the contribution made to the thermodynamic potential by the sum of the diagrams indicated above

$$-\frac{\beta \Delta \Omega'}{V} = \frac{1}{2(2\pi\hbar)^3} \sum_{k=-\infty}^{\infty} \int [\Pi_p^{(k)} - \ln(1 + \Pi_p^{(k)})] dp, \quad (7)$$

where

$$\Pi_p^{(k)} = \sum_{1 \leq a \leq M} \frac{4\pi\hbar^2 e_a^2 z_a \lambda_a^{(k)}}{p^2},$$

$$\lambda_a^{(k)} = \left(\frac{m_a}{2\pi\beta\hbar^2}\right)^{3/2} \int_0^{\beta} \exp\left\{-\frac{(\beta-\beta')\beta'}{2m_a\beta} p^2\right\} \exp\left(\frac{2\pi i k \beta'}{\beta}\right) d\beta'.$$

The index a denotes the type of particle, M is the number of different types of particle, $p = \{p_x, p_y, p_z\}$ is the particle momentum, and $dp = dp_x dp_y dp_z$. Such an expression was obtained for an electron gas by Montroll and Ward^[3].

To determine the next order of the contribution to the group integrals b_l ($l = 1, 2, \dots$) it is necessary to separate from the perturbation-theory series a par-

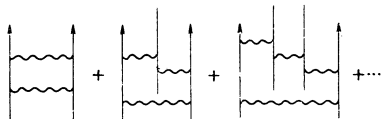


FIG. 3.

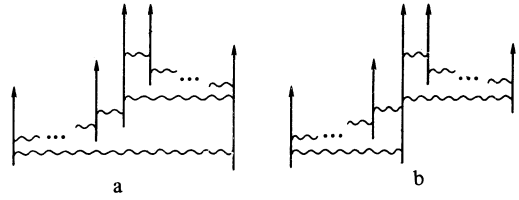


FIG. 4.

ticular series whose terms can contain the coupling constant e^2 raised to a power larger by unity compared with the terms of the series described by the ring diagrams. The terms of this series correspond to diagrams which contain one more interaction line each than the ring diagrams. From the group sum for the two particles (Fig. 2) we separate the diagrams with three interaction lines; for the group sum for four particles, the diagrams with four interaction lines, etc. In the final analysis we get the sums for the two classes of diagrams shown in Fig. 4.

With the aid of the indicated diagrams we can write down the corresponding expressions for the group integrals and calculate the contribution to the thermodynamic potential. As a result we obtain for the sum of diagrams of type a in Fig. 4

$$\begin{aligned} -\frac{\beta \Delta \Omega''}{V} &= \frac{1}{4(2\pi\hbar)^6} \sum_{k_1, k_2=-\infty}^{\infty} \int \xi^2 d\xi \\ &\times \int \frac{A_{p_1, p_2}^{(k_1, k_2)}}{(1 + \xi \Pi_p^{(k_1)}) (1 + \xi \Pi_p^{(k_2)})} dp_1 dp_2, \\ A_{p_1, p_2}^{(k_1, k_2)} &= \sum_{1 \leq a, b \leq M} A_{ab}^{(k_1, k_2)} \frac{(4\pi\hbar^2)^2 e_a^2 e_b^2 z_a z_b}{p_1^2 p_2^2 |p_1 - p_2|^2}, \\ A_{ab}^{(k_1, k_2)} &= \beta \int_0^{\beta} \dots \int_0^{\beta} W_a(p_1, p_2; \beta_1, \beta_2) W_b(p_1, p_2; \beta_2, \beta_3) \\ &\times \varphi_{k_1}(\beta_1) \varphi_{k_1}^*(\beta_2) \varphi_{k_2}(\beta_3) \varphi_{k_2}^*(\beta_4) d\beta^4, \\ \varphi_k(\beta_i) &= \exp(2\pi i k \beta_i / \beta), \quad d\beta^4 = d\beta_1 d\beta_2 d\beta_3 d\beta_4, \\ W_a(p_1, p_2; \beta_1, \beta_2) &= \left(\frac{m_a}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left\{\frac{p_1 p_2}{\beta m_a} \beta_1 \beta_2 \right. \\ &\left. - \frac{p_1^2}{2\beta m_a} \beta_1(\beta - \beta_1) - \frac{p_2^2}{2\beta m_a} \beta_2(\beta - \beta_2)\right\}. \end{aligned} \quad (8)$$

For the sum of diagrams of type b in Fig. 4 we obtain

$$\begin{aligned} -\frac{\beta \Delta \Omega'''}{V} &= \frac{1}{4(2\pi\hbar)^6} \sum_{k_1, k_2=-\infty}^{\infty} \int \xi^2 d\xi \\ &\times \int \frac{B_{p_1, p_2}^{(k_1, k_2)} \Pi_{p_1}^{(k_1)} \Pi_{p_2}^{(k_2)}}{(1 + \xi \Pi_p^{(k_1)}) (1 + \xi \Pi_p^{(k_2)})} dp_1 dp_2, \\ B_{p_1, p_2}^{(k_1, k_2)} &= \sum_{1 \leq a \leq M} \frac{(4\pi\hbar^2)^2 e_a^4 B_a^{(k_1, k_2)} z_a}{p_1^2 p_2^2}, \\ B_a^{(k_1, k_2)} &= \beta \int_0^{\beta} \int_0^{\beta} W_a(p_1, p_2; \beta_1, \beta_2) \varphi_{k_1}(\beta_1) \varphi_{k_2}(\beta_2) d\beta^2. \end{aligned} \quad (9)$$

The main contributions to the integrals (7)–(9) are made by small momenta, and therefore the integrands $\lambda_a^{(k)}(p)$, $A_{ab}^{(k_1, k_2)}(p_1, p_2)$, and $B_a^{(k_1, k_2)}(p_1, p_2)$ can be replaced by their values at $p_1, p_2 = 0$ and then we can calculate the sums and the integrals. As a result, expression (7) reduces to the usual Debye formula

$$-\frac{\beta\Delta\Omega'}{V} = \frac{\kappa^3}{12\pi}, \quad \kappa^2 = \sum_{1 \leq a \leq M} 4\pi e_a^2 \beta n_a, \quad n_a = z_a / \lambda_a^3. \quad (10)$$

For expressions (8) and (9) we obtain respectively

$$-\frac{\beta\Delta\Omega''}{V} = -\pi\beta \sum_{1 \leq a, b \leq M} e_a^3 e_b^3 n_a n_b \beta^2 \int_0^1 \xi^2 d\xi \int_0^\infty \frac{dr}{r} \exp(-2r\sqrt{\xi}\kappa), \quad (11)$$

$$-\frac{\beta\Delta\Omega'''}{V} = \frac{\kappa^2}{8} \sum_{1 \leq a \leq M} e_a^4 n_a \beta. \quad (12)$$

We see that the integral with respect to r , which is contained in (11), diverges logarithmically at small distances. This is due to the fact that the considered classes of diagrams take into account primarily collective effects connected with small momentum transfers, while the contribution from the individual behavior of the particles is described incorrectly. The simplest way of taking into account pair collisions is to cut off the obtained integral at small distances on the order of the Coulomb scattering amplitude $f_{ab} = \beta e_a e_b$. We then obtain the well known logarithmic correction to the thermodynamic potential

$$-\frac{\beta\Delta\Omega'''}{V} = \frac{\pi}{3} \sum_{1 \leq a, b \leq M} e_a^3 e_b^3 n_a n_b \beta^3 \ln \kappa f_{ab}. \quad (13)$$

It is possible to obtain more accurate results for the quantities (7)–(9) in the form of an expansion in the small parameter $\lambda_e \kappa$. However, under the conditions noted in the introduction, this parameter remains small, so that all the corrections to the main terms of (10), (12), and (13) due to this parameter are small and can be disregarded. It should be noted that when such expansions are used the main terms of (10), (12), and (13) are contained in expressions (7)–(9) only in the terms of the sums with $k = 0$, $k_1 = 0$, and $k_2 = 0$. All the remaining terms of these sums ($k \neq 0$, $k_1 \neq 0$, $k_2 \neq 0$) contain powers of the parameter $\lambda_e \kappa$.

4. MODIFIED LADDER APPROXIMATION

In calculating the contribution made to the thermodynamic potential by the sum of diagrams of type a in Fig. 4, difficulties were encountered in connection with the divergence of the integrals in (11) at short distances. Taking into account the logarithmic character of the divergence, we got around these difficulties by cutting off the integrals at the lower limit. On the other hand, when attempts are made to consider sums of similar diagrams of higher order (with a larger number of interaction lines), stronger divergences appear, and this method is not suitable for their elimination. It turns out, however, that a finite expression is obtained for the thermodynamic potential when such diagrams are summed. The following circumstances are important for the summation. The contribution made to the thermodynamic potential (7) by the sum of the ring diagrams (3) at $k = 0$ it is described exactly by a single two-particle diagram (the first diagram of Fig. 5), where the wavy line corresponds as before to the Coulomb potential and the dashed line corresponds to the effective potential

$$\tilde{\Phi}_{ab}(r) = \frac{2\xi}{\pi} \frac{e_a e_b}{r} \int_0^\infty \frac{p \sin(pr/\hbar)}{p^2(1 + \xi\Pi_p^{(0)})} dp. \quad (14)$$

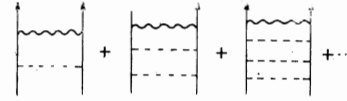


FIG. 5.

The contribution made to the thermodynamic potential (8) by the sum of diagrams of type a in Fig. 4 at $k_1 = k_2 = 0$ is described exactly by a two-particle diagram (second diagram of Fig. 5) with a single Coulomb line and two lines corresponding to the potential (14). The contribution to the thermodynamic potential from the sum of diagrams of type a with an added interaction line is described by a two-particle diagram with one Coulomb and three effective-interaction lines, etc. As a result we obtain a sum of ladder diagrams where one “rung” differs from all others (Fig. 5).

The contribution made to the thermodynamic potential in this case is

$$-\frac{\beta\Delta\Omega}{V} = -\frac{1}{2} \sum_{1 \leq a, b \leq M} n_a n_b \lambda_{ab}^3 \beta \int_0^1 d\xi \int \Phi_{ab}(\mathbf{q}) \times \left\{ \sum_{(n)} \tilde{\psi}_n^*(\mathbf{q}) e^{-\beta\tilde{E}_n} \tilde{\psi}_n(\mathbf{q}) - \sum_{(n)} \psi_n^*(\mathbf{q}) e^{-\beta E_n} \psi_n(\mathbf{q}) \right\} d\mathbf{q}, \quad (15)$$

where $\Phi_{\alpha\beta}(\mathbf{q})$ is the Coulomb potential, $\psi_n(\mathbf{q})$ and \tilde{E}_n are respectively the eigenfunctions and eigenvalues of the three-dimensional Schrödinger equation with potential (14), and $\psi_n^0(\mathbf{q})$ and E_n are the eigenfunctions and the eigenvalues of the Schrödinger equation for the free motion. The summation is over all the sets of quantum numbers $\{n\} = n_1, n_2, \dots$

In expression (15) it is possible to separate the discrete spectrum of the negative-energy values \tilde{E}_n from the continuous spectrum of the positive values \tilde{E}_k . The contribution made by the latter to the thermodynamic potential can be calculated in the quasiclassical approximation. For identically charged particles, which have only a positive energy spectrum we obtain in this case the expression

$$-\frac{\beta\Delta\Omega_{ii}^{ab}}{V} = 2\pi\beta n_a n_b \int_0^1 d\xi \int_0^\infty \Phi_{ab}(r) r^2 dr \{1 - \exp[-\beta\tilde{\Phi}_{ab}(r)]\}. \quad (16)$$

Formula (16) coincides with the well known classical result, if it is assumed that the effective potential $\tilde{\Phi}_{ab}(r)$ is a Debye potential. It can be shown that expression (14) coincides, accurate to terms $(\lambda_e \kappa)^2$, with the Debye expression. In this case the integrand in (16) will contain the classical correlation function

$$F_{ab}(r) = \exp\left\{-\frac{\beta e_a e_b}{r} e^{-\kappa r}\right\}. \quad (17)$$

For differently charged particles, the contribution to the thermodynamic potential of the continuous spectrum of positive energies is in this case equal to

$$-\frac{\beta\Delta\Omega_{ii}^{ae}}{V} = -2\pi\beta n_a n_e \int_0^1 d\xi \int_0^\infty \Phi_{ae}(r) r^2 dr \times \left\{ \frac{2}{\sqrt{\pi}} \exp[-\beta\tilde{\Phi}_{ae}(r)] \Gamma\left(\frac{3}{2}; -\beta\tilde{\Phi}_{ae}\right) - 1 \right\}, \quad (18)$$

where $\Gamma(3/2; -\beta\tilde{\Phi}_{ae})$ is the incomplete gamma function. Under the integral side we have here, in place of the usual classical expression (17) (which causes a

strong exponential divergence of the integral at the lower limit when $r \rightarrow 0$), the quantity

$$F_{ae}(r) = \exp\left\{\frac{\beta e_a e}{r} e^{-\kappa r}\right\} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}; \frac{\beta e_a e}{r} e^{-\kappa r}\right), \quad (19)$$

which tends to infinity as $r \rightarrow 0$, but like $2\sqrt{\beta e_a e}/\pi r$. This singularity is integrable, and the expression (18) is finite. By analogy with (17), the quantity (19) can be identified with the correlation function for differently charged particles.

The negative eigenvalues \tilde{E}_n and the eigenfunctions $\tilde{\psi}_n(\mathbf{q})$, which are necessary for the determination of the contribution made to the thermodynamic potential by the discrete spectrum, can be found by numerically solving the Schrödinger equation with potential (14). For a Debye potential, the \tilde{E}_n were calculated by Bonch-Bruevich and Glasko [5]. The contribution made to the thermodynamic potential by the upper levels can be taken into account with the aid of the quasiclassical approximation. It is necessary in this case to choose the principal quantum number n_0 in the sum over $\{n\}$ in (15) such as to make $\beta \tilde{E}_{n_0} \ll 1$, and then, by virtue of the quasiclassical nature of the states with large quantum numbers, the spectrum of the negative energies $\tilde{E}_{n_0} \leq \tilde{E}_n \leq 0$ will be sufficiently dense and the corresponding part of the sum over $\{n\}$ can be replaced by an integral, using quasiclassical expressions for the level density and for the wave functions. This integral is calculated simultaneously with the integral of the spectrum of the positive energies. The result is the expression

$$\begin{aligned} -\frac{\beta \Delta \Omega_n^{ae}}{V} &= -2\pi \beta n_a n_e \int_0^1 d\xi \left\{ \int_0^{r_0} r^2 \Phi_{ae}(r) dr \right. \\ &\times \left[\frac{2}{\sqrt{\pi}} \exp(-\beta \tilde{\Phi}_{ae}) \Gamma\left(\frac{3}{2}; -\beta \tilde{\Phi}_{ae} + \beta \tilde{E}_{n_0}\right) - 1 \right] \\ &\left. + \int_{r_0}^{\infty} r^2 \Phi_{ae}(r) dr [\exp(-\beta \tilde{\Phi}_{ae}) - 1] \right\}, \quad (20) \end{aligned}$$

where r_0 is the root of the equation

$$E_{n_0} - \tilde{\Phi}_{ae}(r_0) = 0.$$

When $2m_e e^2/\hbar^2 \kappa \gg 1$ and $n < n_0$, the shift of the levels \tilde{E}_n can be neglected and the remaining part of the sum

over $\{n\}$ in (15) can be calculated by assuming the quantities \tilde{E}_n and $\tilde{\psi}_n(\mathbf{q})$ to be Coulomb quantities. Then

$$-\frac{\beta \Delta \Omega_n^{ae}}{V} = n_a n_e \lambda_{ae}^3 \sum_{n=1}^{n_0} n^2 (e^{|\beta E_n|} - 1). \quad (21)$$

Strictly speaking, formula (21) describes the contribution to the thermodynamic potential from the bound states in a hydrogen plasma. However, it can be used to a certain degree of approximation also to calculate a non-hydrogen plasma. In this case, if the ion is not a nucleus, then it is necessary to take experimental or approximately-calculated values for the level energy, E_n . If the parameter $\gamma_{ae} = \beta e_a e \kappa$ is small, then the integrand in (20) can be expanded in a series in this parameter. If we retain at the same time the terms of order $\gamma_{ae} \ln \gamma_{ae}$ inclusive, and let $n_0 \rightarrow \infty$ in formulas (20) and (21), then we obtain the expression

$$\begin{aligned} -\frac{\beta \Delta \Omega^{ae}}{V} &= -\frac{\beta \Delta \Omega_n^{ae}}{V} - \frac{\beta \Delta \Omega_n^{ae}}{V} \\ &= n_a n_e \lambda_{ae}^3 \sum_{n=1}^{\infty} n^2 (e^{|\beta E_n|} - |\beta E_n| - 1) \\ &+ \frac{4}{3\kappa} \pi \beta^2 e_a^2 e^2 n_a n_e - \frac{2\pi}{3} n_a n_e e_a^3 e^3 \beta^3 \ln \gamma_{ae}, \end{aligned}$$

which coincides with the result of Larkin's paper [2].

¹A. A. Vedenov and A. I. Larkin, Zh. Eksp. Teor. Fiz. 36, 1133 (1959) [Sov. Phys.-JETP 9, 806 (1959)].

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