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EQUATION OF STATE OF A PLASMA

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The free energy F of a completely ionized gas is given in terms of an expansion in the density n:

$$F = F_{\text{ideal}} + An^{3/2} + Bn^2 \ln n + Cn^2.$$

The term $An^{3/2}$ is identical with the familiar Debye-Hückel term. Expressions for B and C have been obtained. A diagram technique has been used to carry out the calculations.

THE equation of state of a system of particles which interact via Coulomb forces has been considered in a great number of papers. The usual formulas for the virial coefficients do not apply in this case. Because the Coulomb forces are long-range, even in the first term of an expansion of the thermodynamic quantities in powers of the gas density it is impossible to consider pair interactions alone. Debye and Hückel[1] have used a self-consistent field method for finding the first term in the expansion of the free energy in the density of the interacting particles n; this term was found to be proportional to $n^{3/2}$ (per unit volume). In the work of Glauberman and Yuchnovskiĭ at attempt was made to compute the following terms in the expansion, but the methods used in this work do not appear to be valid and lead to erroneous results.

In the present work, the first terms in the density expansion have been determined using a graphical method similar to the Feynman method in quantum electrodynamics.

1. DIAGRAM TECHNIQUE. GAS APPROXIMATION.

We consider a system of interacting particles in a volume V in a state of thermodynamic equilibrium at a temperature $T = 1/\beta$. The Hamiltonian for the system is $H = H_0 + H'$ where

$$H_0 = \sum_p \varepsilon_p a_p^+ a_p,$$

$$H' = \frac{1}{2V} \sum_{p_1 p_2 q} V_q a_{p_1}^+ a_{p_2}^+ a_{p_2+q} a_{p_1-q}, \qquad \varepsilon_p = p^2/2m.$$

Here a_p and a_p^+ are the particle annihilation and creation operators; $V_q = \int e^{i-qx} V(\mathbf{x})\, d\mathbf{x}$ where $V(\mathbf{x})$ is the potential for the pair interaction. In the case of a Coulomb interaction $V_q = 4\pi e^2/q^2$.

The partition function for a gas of interacting particles is given by the expression

$$Z = \operatorname{Sp} \exp\left\{-\beta H + \beta\mu \sum_p a_p^+ a_p\right\},$$

where μ is the chemical potential.

Matsubara has shown[3] that the ratio Z/Z_0 (where $Z_0 = \operatorname{Sp} \exp\{-\beta H_0 + \beta\mu \sum a_p^+ a_p\}$) can be computed conveniently by a method similar to that used in quantum electrodynamics for finding the S matrix. The quantity Z/Z_0 is given as the sum of all graphs which in electrodynamics serve for computation of the vacuum expectation value of the S matrix. The solid line corresponds to the zeroth Green's function

$$G_0(p, t_1 - t_2) = \frac{\operatorname{Sp} T \exp\{-\beta H_0 + \beta\mu \sum a_p^+ a_p\}\, a_p(t_1) a_p^+(t_2)}{\operatorname{Sp} \exp\{-\beta H_0 + \beta\mu \sum a_p^+ a_p\}} = \begin{cases} (1 \mp n_p)\, e^{-(\varepsilon_p - \mu)\tau} & \tau > 0 \\ \mp n_p e^{-(\varepsilon_p - \mu)\tau} & \tau < 0 \end{cases}. \tag{1}$$

Here the upper and lower signs refer respectively to Fermi and Bose particles, and T is an ordering operator which operates on the argument t,

$$\tau = t_1 - t_2; \quad a_p(t) = a_p e^{-(\varepsilon_p - \mu)t};$$

$$a_p^+(t) = a_p^+ e^{(\varepsilon_p - \mu)t}, \quad n_p = [e^{(\varepsilon_p - \mu)\beta} \pm 1]^{-1}.$$

The dashed line corresponds to $V_q \delta(\tau)$. Time increases going upward in the figure. Then all the dashed lines are horizontal. The solid line which goes upwards then corresponds to the factor $\mp n_p e^{-(\epsilon_p - \mu)\tau}$, the line which goes downward corresponds to the factor $(1 \mp n_p)\, e^{-(\epsilon_p - \mu)\tau}$.

As in quantum electrodynamics, the sum of graphs which give Z/Z_0, may be given in the form e^{-L}. The quantity L is the sum of all connected closed graphs and all the graphs considered below appear in the sum with the factor $(-1)^{r+1+k}/2k$ where k is the number of dashed lines in a given graph and r is the number of closed loops. All

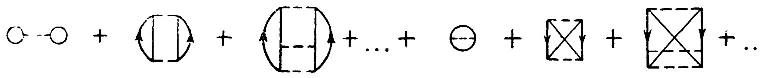

FIG. 1

the graphs being considered are closed; hence the factor $e^{\mu\tau}$ in Eq. (1) can be neglected.

The thermodynamic potential $\Omega = -T \ln Z$ is

$$\Omega = \Omega_0 + \Delta\Omega = \Omega_0 + TL, \qquad \Omega_0 = -T \ln Z_0.$$

In what follows we will assume that the gas is nondegenerate (so that departures from the Boltzmann distribution are small); we introduce the quantity n which is related to the chemical potential by the expression

$$n = e^{\beta\mu}(m/2\pi\hbar^2\beta)^{3/2}. \tag{2}$$

We first consider short-range forces. We will assume that the particles have no spin. In order to find the second virial coefficient it is necessary to sum all graphs which contain two solid lines which go in the upward direction and whose remaining lines go downward (Fig. 1). In these graphs we neglect n_p as compared with unity.

To the k-th order perturbation approximation there are k identical graphs which differ only in the way in which the pair of solid lines go upwards. Hence in each order we need consider only one graph and can neglect the factor 1/k. Then

$$-\beta\Delta\Omega = {}^1/_2 \int_0^\beta dt_2 \int_0^{t_2} dt_1\, G_{p_1}(t_1 - t_2)\, G_{p_2}(t_1 - t_2)$$
$$[\Gamma(p_1p_2p_1p_2\, t_2t_1) + \Gamma(p_1p_2p_2p_1\, t_2t_1)]\, d^3p_1\, d^3p_2. \tag{3}$$

The factor $\Gamma(p_1p_2p_3p_4t_1t_2)$ is the sum of graphs of the "ladder" type (Fig. 2) and satisfies the equation

$$\Gamma_g(pp'\, t_1t_2) = V_{p-p'}\, \delta(t_1 - t_2)$$
$$-\int_{t_2}^{t_1} dt'\, d^3p_1\, V_{p-p_1}\, G_{g/2+p_1}(t_1t')\, G_{g/2-p_1}(t_1t')\, \Gamma_g(p_1p't't_2).$$

Here

$$d^3p = dp_x\, dp_y\, dp_z/(2\pi)^3,$$

$$\Gamma_g(pp') = \Gamma(g/2 + p, g/2 - p, g/2 + p', g/2 - p')$$

Introducing the variables $\tau = t_1 - t_2$, $\tau' = t' - t_2$ and making the substitution $G(p\tau) = e^{-\epsilon_p\tau}$ $(\tau > 0)$, we have

$$\Gamma_g(pp'\tau) = V_{p-p'}\, \delta(\tau)$$
$$-\int_0^\tau d\tau'\, d^3p_1\, V_{p-p_1} \exp\left\{-\frac{1}{m}\left(p_1^2 + \frac{g^2}{4}\right)(\tau - \tau')\right\}\Gamma_g(p_1p'\tau')$$

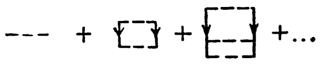

FIG. 2

or, in the Laplace transform representation

$$\Gamma_\omega = \int_0^\infty e^{-\omega\tau}\, \Gamma(\tau)\, d\tau$$

$$\Gamma_g(pp'\omega) = V_{p-p'} - \int d^3p_1\, V_{p-p_1} \frac{\Gamma_g(p_1p'\omega)}{(p_1^2 + g^2/4)/m + \omega}.$$

The equation for

$$\chi_g(pp'\omega) = \Gamma_g(pp'\omega) \Big/ \left[\frac{1}{m}\left(p^2 + \frac{g^2}{4}\right) + \omega\right]$$

is in the form of an inhomogeneous Schrödinger equation with potential V_q:

$$\left(\frac{p^2 + g^2/4}{m} + \omega\right)\chi(p) + \int V_{p-p_1}\, \chi(p_1)\, d^3p_1 = V_{p-p'}.$$

Hence its solution is expressed in terms of the wave functions for the relative motion of the particles

$$\chi_g(pp'\omega) = \int V_{p-p_1} \sum_k \frac{\psi_k(p_1)\, \psi_k^*(p')}{E_k + g^2/4m + \omega}\, d^3p_1$$
$$= -\sum_k \psi_k(p)\, \psi_k^*(p')\, \frac{E_k - p^2/m}{E_k + g^2/4m + \omega}. \tag{4}$$

Substituting in Eq. (3)

$$G(p, \tau) = \exp[\mu\beta - (\beta + \tau)\varepsilon_p], \quad \tau < 0,$$

we find the Laplace transform of the function $\varphi(\beta) = -\beta\Delta\Omega e^{-2\mu\beta}$:

$$\varphi(\omega) = \int_0^\infty e^{-\beta\omega}\, \varphi(\beta)\, d\beta$$

$$= \int d^3p d^3g \frac{1}{(p^2/m + g^2/4m + \omega)^2}[\Gamma_g(p, p, \omega) + \Gamma_g(p, -p, \omega)].$$

Using Eq. (4) we have

$$\varphi(\omega) = -\int d^3p d^3g \frac{1}{p^2/m + g^2/4m + \omega}$$
$$\times \sum_k \psi_k(p)\, [\psi_k^*(p) + \psi_k^*(-p)]\, \frac{E_k - p^2/m}{E_k + g^2/4m + \omega}.$$

Inasmuch as $\psi_k(-p) = \pm\psi_k(p)$, corresponding to the states with positive and negative parity, this expression can be written in the form

$$\varphi(\omega) = -2\int d^3p d^3g \frac{1}{p^2/m + g^2/4m + \omega}$$
$$\times {\sum}' \psi_k(p)\, \psi_k^*(p)\, \frac{E_k - p^2/m}{E_k + g^2/4m + \omega},$$

where $\sum'$ is taken over even states. Returning to $\varphi(\beta)$, for the correction to $\Delta\Omega$ we obtain the expression

$$-\beta\Delta\Omega = \tfrac{1}{2}e^{2\mu\beta}\int 2\sum_k{}'\left(e^{-\beta E_k} - e^{-\beta p^2/m}\right)\psi_k(p)\psi_k^*(p)\,d^3p$$

$$\times\int e^{-\beta g^2/4m}\,d^3g$$

$$= \tfrac{1}{2}e^{2\mu\beta}\left(\frac{m}{\pi\hbar^2\beta}\right)^{3/2}\left\{\sum_k{}' e^{-\beta E_k} - \int e^{-\beta p^2/m}\,d^3p\right\}, \qquad (5)$$

which coincides with that found in reference 4. For Fermi particles with spin $1/2$ we obtain a similar expression which differs only in that in place of the sum over even states $\sum'$ we have $1/4\sum' + 3/4\sum''$, where $\sum''$ is the sum over odd states.

In the quasi-classical case the summation in Eq. (5) can be replaced by the integral

$$2\sum_k{}' e^{-\beta E_k} = \int e^{-\beta E}\frac{dn}{dE}\,dE,$$

where

$$n(E) = \frac{2}{\pi}\int_0^\infty dr\int_0^{r\sqrt{E-U}} 2l\,dl\sqrt{m(E - l^2/mr^2 - U)}.$$

Substituting in Eq. (5) we have

$$-\beta\Delta\Omega = \frac{1}{2}n^2\int_0^\infty\left(e^{-\beta U} - 1\right)4\pi r^2\,dr, \qquad (5a)$$

where n is defined by Eq. (2), coinciding with the correction to $\Delta\Omega$ due to the second virial coefficient in the classical case.

2. SUMMATION OF GRAPHS IN THE CASE OF A COULOMB INTERACTION

It is shown in the Appendix that in order to find the thermodynamic potentials of the plasma it is sufficient to know Ω for $V_{q=0} \equiv V_0 = 0$: $\Omega_{V_0=0} = \Omega$. Hence it is possible to neglect the graphs with V_0 (for example the graph of Fig. 3a). Divergences arise in the first-order graphs (Fig. 3, b and c).

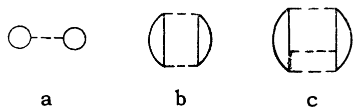

FIG. 3

Figure 3b gives a contribution equal to

$$-\frac{1}{4}\int d^3\mathbf{q}\int_0^\beta dt_1\int_0^\beta dt_2\,V_{\mathbf{q}}^2\Pi_{\mathbf{q}}^2(t_1t_2), \qquad (6)$$

where

$$\Pi_{\mathbf{q}}(t_1t_2) = \int G_{\mathbf{p}-\mathbf{q}/2}(t_1t_2)\,G_{\mathbf{p}+\mathbf{q}/2}(t_2t_1)\,d^3p.$$

The integral in Eq. (6) diverges linearly in the region of small $\mathbf{q}$. Hence it is convenient to give $\Pi_{\mathbf{q}}^2$ in the form of a sum

$$\Pi_0^2 + \{2(\Pi_{\mathbf{q}} - \Pi_0)\Pi_0 + (\Pi_{\mathbf{q}} - \Pi_0)^2\},$$

where Π_0 is the value of $\Pi_{\mathbf{q}}$ at the point $q = 0$: $\Pi_0 \equiv \Pi_{\mathbf{q}=0} = -n$.

If this expression is substituted in Eq. (6) the integral containing the brackets has no singularities and becomes

$$1/4\,\pi^{3/2}\,n^2e^4\beta^{5/2}\,\hbar\,m^{-1/2}. \qquad (7)$$

The divergence in the integral which contains Π_0 is due to the fact that it is not valid to neglect certain higher-order terms in the density. For example, when the contribution of the graphs of Fig. 4 is taken into account the integrand in the region of small $\mathbf{q}$ becomes larger than the corresponding expression for the graph in Fig. 3b.

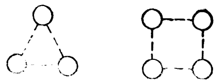

FIG. 4

Hence, in carrying out the integration over $\mathbf{q}$ it is necessary to sum the integrands in all the graphs in which each $V_{\mathbf{q}}$ has the same vector $\mathbf{q}$. Since $\Pi_0 = -n$ is independent of t, the summation is carried out easily:

$$\frac{1}{4}(\beta\Pi_0V_{\mathbf{q}})^2 + \frac{1}{6}(\beta\Pi_0V_{\mathbf{q}})^3\ldots$$

$$= \frac{1}{2}\int_0^1\frac{d\lambda}{\lambda}\left[(\beta\Pi_0V_{\mathbf{q}}\lambda)^2 + (\beta\Pi_0V_{\mathbf{q}}\lambda)^3 + \ldots\right]$$

$$= \frac{1}{2}\int_0^1\frac{d\lambda}{\lambda}\,\frac{\beta^2\Pi_0^2V_{\mathbf{q}}^2\lambda^2}{1 - \beta\Pi_0V_q\lambda}.$$

The integration over q and λ then gives

$$\Delta\widetilde{\Omega} = -2/3\sqrt{\pi\beta}\,e^3(-\Pi_0)^{3/2}. \qquad (8)$$

The contribution from the graph of Fig. 3c gives an integral which diverges logarithmically in the region in which all the q are small:

$$\frac{1}{2}\int d\mathbf{q}_1\,d\mathbf{q}_2\,V_{\mathbf{q}_1}V_{\mathbf{q}_2}V_{\mathbf{q}_1+\mathbf{q}_2}I_{\mathbf{q}_1\mathbf{q}_2};$$

$$I_{\mathbf{q}_1\mathbf{q}_2} = \int_0^\beta dt_3\int_0^{t_3}dt_2\int_0^{t_2}dt_1\,G_{\mathbf{p}_1}(t_1t_3)G_{\mathbf{p}_2}(t_1t_3)$$

$$G_{\mathbf{p}_1+\mathbf{q}_1}(t_3t_2)\,G_{\mathbf{p}_2-\mathbf{q}}(t_3t_2)G_{\mathbf{p}_1-\mathbf{q}_2}(t_2t_1)G_{\mathbf{p}_2+\mathbf{q}_2}(t_2t_1).$$

In carrying out the calculation it is convenient to give I in the form

$$I_{q_1q_2} = \{I_{q_1q_2} - \beta^3n^2/6\,(1 + \lambda\mathbf{q}_1^2)(1 + \lambda\mathbf{q}_2^2)(1 + \lambda(\mathbf{q}_1 + \mathbf{q}_2)^2)\}$$

$$+ \beta^3n/6\,(1 + \lambda\mathbf{q}_1^2)(1 + \lambda\mathbf{q}_2^2)(1 + \lambda(\mathbf{q}_1 + \mathbf{q}_2)^2) \qquad (9)$$

(where $\lambda = \beta\hbar^2/m$). The integral which contains the brackets has no singularities and is

$$\tfrac{1}{3}\pi a n^2 (\beta e^2)^3, \tag{10}$$

where a is a numberical coefficient of order unity. We shall not make an exact computation of this coefficient for the following reasons. In the case of low or high temperatures (where we use correspondingly the quasi-classical or Born approximations for the electrons) the coefficient in front of the term of order n^2 in the expansion of Ω in the density turns out to be of order $(\hbar^2\beta/m)^{3/2}$, i.e., considerably larger than the quantity $(\beta e^2)^3$ which appears in Eq. (10). On the other hand, since the term of order n^2 is the smallest of those given in the present work, small corrections of order $(\beta e^2)^3$ to the coefficient for this term can be neglected.

In the remaining second term in $I_{q_1q_2}$ in carrying out the integration over $q_{1,2}$ we sum the contribution of those graphs of higher order in the density in which all the momenta $\mathbf{q}$ along the dashed lines correspond to one of the momenta, $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_1+\mathbf{q}_2$. This summation means that we replace V_q by

$$V_{\mathbf{q}}/(1-\beta\Pi_0 V_{\mathbf{q}}) = 4\pi e^2/(\mathbf{q}^2+\varkappa^2), \quad \varkappa^2 = -4\pi e^2\beta\Pi_0.$$

Under these conditions the integral of the second term in I converges. In order to compute this integral it is convenient to introduce the Fourier transform for q:

$$\frac{4\pi}{q^2+\varkappa^2}\frac{1}{1+\lambda q^2} = \int e^{i\mathbf{q}\mathbf{r}}\,\frac{e^{-\varkappa r}-e^{-r/\sqrt{\lambda}}}{r}\,\frac{1}{1-\lambda\varkappa^2}\,d\mathbf{r},$$

after which the integral assumes the form

$$\frac{1}{2}e^6\frac{\beta^3 n^2}{6}4\pi\int\frac{dr}{r}\left(e^{-\varkappa r}-e^{-r/\sqrt{\lambda}}\right)^3(1-\lambda\varkappa^2)^{-3}. \tag{10a}$$

Computing this integral to accuracy of order $n^{5/2}$ in the density and neglecting the correction $(\beta e^2)^3$ in the quadratic term we have

$$(\pi/3)\,n^2(e^2\beta)^3\ln(\sqrt{\lambda}\varkappa). \tag{10b}$$

Thus, to obtain the correct virial correction to $\Delta\Omega$ of this system with a Coulomb interaction it is necessary to correct the contributions from the lower-order graphs. The first terms in the expansion in powers of the interaction in (5) are replaced by the corrected expressions obtained by the methods indicated above.

In the quasi-classical case $e^2/\hbar v \gg 1$; thus, replacing the first terms of the expansion in e^2 in Eq. (52) by the corrected terms (8), (9), and (10a) we have:

$$-\beta\Delta\widetilde{\Omega} = \frac{n^2}{2}\int\limits_0^\infty\left[\left(e^{-\beta e^2/r}-1+\frac{\beta e^2}{r}-\frac{(\beta e^2/r)^2}{2}+\frac{(\beta e^2/r)^3}{6}\right)-\frac{(\beta e^2)^3}{6}\frac{e^{-3\varkappa r}}{r^3}\right]4\pi r^2\,dr+\frac{2}{3}\sqrt{\pi\beta^3}e^3 n^{3/2}. \tag{11}$$

Here we have not taken account of the quantum corrections since the contribution in (7) is neglected and we have assumed $\lambda = 0$. Limiting ourselves to the principal values of the expansion in n and computing the integral we have

$$-\beta\Delta\widetilde{\Omega} = \frac{2}{3}\sqrt{\pi\beta^3}\,e^3 n^{3/2} + \frac{\pi}{3}n^2(\beta e^2)^3\ln\frac{1}{\beta e^2\varkappa}. \tag{12}$$

3. EQUATION OF STATE OF THE PLASMA

We consider a system consisting of ions of charge z and electrons. We consider only classical ion motion.

It is necessary to make the following changes in Eqs. (8) to (10a) above: the quantity Π_0, which represents the contribution from the electron and ion loop, becomes

$$\Pi_0 = -(z^2 n_i + n_e), \qquad n_{i,e} = e^{\beta\mu_{i,e}}(m_{i,e}/2\pi\hbar\beta)^{3/2}. \tag{13}$$

Consequently, the quantity $\kappa^2 = -4\pi\beta e^2\Pi_0$ becomes $4\pi\beta e^2(z^2 n_i + n_e)$.

We consider two limiting cases.

a) $T \ll me^4/\hbar^2$

In this case the motion of both the ions and electrons is quasi-classical. The Debye term in $\Delta\Omega$ (proportional to $n^{3/2}$) is obtained from Eq. (8) by substituting Eq. (13) in place of Π_0. The next term in the expansion of Ω in powers of the density, which is proportional to $n^2 \ln n$, is obtained from the graphs of Fig. 3c in which the solid lines may be considered electron and ion Green's functions. The contributions from the graphs containing two electron or two ion loops are obtained from the second term of Eq. (12) by replacing n^2e^6 by $n_e^2e^6$ and $z^6n_i^2e^6$ respectively. In computing the contribution from the graph with one electron and one ion loop from Eq. (11) we would obtain an integral which diverges exponentially at small values of r, since in this case the quantity e^2 in Eq. (11) is replaced by $-z^2e^2$. This results from the inapplicability of the classical expression (11) at small distances. Nonetheless in obtaining the term $n^2 \ln n$ it is possible to use Eq. (11), limiting ourselves in the integration to the region in which (11) applies. We obtain (neglecting terms n_en_i):

$$-\frac{\pi}{3}(ze^2\beta)^3 n_i n_e \ln\frac{1}{\beta e^2\varkappa}. \tag{14}$$

In computing the term of order n_in_e in Eq. (5) we keep only the first term in the sum; this term corresponds to the ground state of the electron in the field of an ion of charge z:

$$n_i n_e \exp\{\beta z^2 m e^4/2\hbar^2\}.$$

We note that the error in the calculation of Eq. (14) is exponentially small as compared with this term; the other terms in Eq. (5) are also exponentially small.

Thus, in the quasi-classical case the expression for the potential Ω is of the form:

$$\beta\widetilde{\Omega} = \beta\Omega_0 - \frac{2}{3}\sqrt{\pi\beta^3}\, e^3 (z^2 n_i + n_e)^{3/2} + \frac{\pi}{3}(\beta e^2)^3 (z^2 n_i - n_e)^2 \ln\frac{1}{\beta e^2 \varkappa} + \left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2} n_i n_e \exp\left\{\frac{\beta z^2 m e^4}{2\hbar^2}\right\}. \qquad (15)$$

We may note that this expression applies when $T \ll z^2 me^4/\hbar^2$.

b) $T \gg z^2 me^4/\hbar^2$

In this case the electron-electron and electron-ion interactions considered in accordance with perturbation theory. The term proportional to $n^{3/2}$ remains unchanged. The ion-ion interaction leads to a correction in Ω which arises from the second term in Eq. (12) when n^2e^6 is replaced by $n_i^2 z^6 e^6$.

The "non-exchange" terms of the electron-electron interaction of second and third order in e^2 give the expressions in (7) and (10b) respectively, in which n must be replaced by n_e. The corresponding terms of the electron-ion interactions are obtained by the following substitution: in second-order it is necessary to replace n^2e^4 by $z^2 n_i n_e e^4$ and to add the factor $1/\sqrt{2}$ which arises because the reduced mass is increased by a factor of 2; in the third-order graph it is necessary to replace n^2e^6 by $-z^3 n_i n_e e^6$. The "exchange" terms arising in the electron-electron interaction (corresponding to the graphs in Fig. 5)

FIG. 5

lead to the following contribution in the correction term to $\beta\Delta\Omega$: the first-order exchange term (Fig. 5a) is:

$$\frac{\beta}{2}\int V_q n_{p+q/2} n_{p-q/2} d^3p d^3q = \pi n^2 \beta^2 e^2 \frac{\hbar^2}{m},$$

the second-order term (Fig. 5b) is:

$$\frac{1}{2}\int_0^\beta dt_2 \int_0^{t_2} dt_1 \int G_{p+q/2+q_1/2}(t_1t_2)\, G_{p-q/2+q_1/2}(t_2t_1)\, G_{p-q/2-q_1/2}(t_1t_2) \times G_{p+q/2-q_1/2}(t_2t_1)\, V_q V_{q_1} d^3p\, d^3q d^3q_1;$$

replacing G by (1), we have

$$\pi^{3/2} \ln 2 \cdot n^2 e^4 \beta^{5/2} \hbar/\sqrt{m}.$$

Thus, in the case $T \gg z^2me^4/\hbar^2$ the expansion of the thermodynamic potential $\widetilde{\Omega}$ in terms of the density is

$$\beta\widetilde{\Omega} = \beta\Omega_0 - {}^2/_3\sqrt{\pi\beta^3} e^3 (z^2 n_i + n_e)^{3/2} + (\pi/3)(\beta e^2)^3 [z^6 n_i^2 \ln(1/z^2\beta e^2\varkappa) + n_e^2 \ln(m^{1/2}/\hbar\beta^{1/2}\varkappa) - 2z^3 n_i n_e \ln(m^{1/2}/\hbar\beta^{1/2}\varkappa)] + {}^1/_4\pi^{3/2} n_e^2 \hbar^3 \beta^{3/2} m^{-3/2} + n_e^2\{-\pi e^2\hbar^2\beta^2 m^{-1} + \pi^{3/2}(\ln 2 + {}^1/_4)\, e^4\hbar\beta^{5/2} m^{-1/2}\} + n_i n_e \{2^{-1/2}\pi^{3/2} z^2 e^4 \hbar\beta^{5/2} m^{-1/2}\}. \qquad (16)$$

The terms $\frac{1}{4} n_e^2 \hbar^3 (\pi\beta/m)^{3/2}$ in this expression is independent of the interaction and is due to the departure of the electron momentum distribution function from a Maxwellian distribution (due to the identity of the electrons).

Using the equations

$$\partial\widetilde{\Omega}/\partial\mu_i = -N, \quad \partial\widetilde{\Omega}/\partial\mu_e = -zN$$

we express μ_i and μ_e in terms of the atomic density $N/V \equiv n$; substituting in the formula

$$F = \Omega + \mu_i N + \mu_e z N,$$

we find the free energy per unit volume:

$$\beta F = \beta F_0 - \frac{2}{3}\sqrt{\pi\beta^3} e^3 [z(z+1)]^{3/2} n^{3/2} + \frac{\pi}{3}(\beta e^2)^3 z^2 (z^2-1)^2 n^2 \ln\frac{m^{1/2}}{\beta^{1/2}\hbar\varkappa} + n^2 \left\{\frac{\pi^{3/2}}{4} z^2 \frac{\hbar^3\beta^{3/2}}{m^{3/2}} - \pi z^2 e^2 \frac{\beta^2\hbar^2}{m} + \left(\ln 2 + \frac{1}{4} + \frac{z}{\sqrt{2}}\right)\pi^{3/2} z^2 e^4 \frac{\hbar\beta^{5/2}}{m^{1/2}}\right\}. \qquad (17)$$

4. CONCLUSIONS

Equation (17) represents an expansion of the free energy in terms of the density. The coefficient of the quadratic density term is a function of the parameter $ze^2\sqrt{\beta m}/\hbar$. The three first terms of the expansion involve this parameter. In the case in which $ze^2\sqrt{\beta m}/\hbar \sim 1$ the function is expressed in terms of the phase in the Coulomb field and can be computed. The term of the expansion of F in the density proportional to $n^{5/2}$ may also be expressed in terms of the phase; however, in order to find the higher order terms in the expansion in density it is necessary to know the wave functions of s system of three interacting Coulomb particles.

In conclusion the authors wish to thank L. D. Landau and V. M. Galitskiĭ for valuable comments.

APPENDIX

We find Ω for $V_0 \to \infty$, knowing the quantity $\widetilde{\Omega} = \Omega_{V_0=0}$ computed in the text.

The interaction Hamiltonian is of the form

$$H' = \frac{1}{2V}\sum_q V_q \sum_{pp'} (a_p^+ a_{p'}^+ a_{p'-q} a_{p+q}$$

$$+ z^2 \alpha_p^+ \alpha_{p'}^+ \alpha_{p'-q} \alpha_{p+q} - 2z a_p^+ \alpha_{p_1}^+ \alpha_{p_1-q} a_{p+q}),$$

where a_p and α_p are the annihilation operators for electrons and ions respectively. The quantity Ω is given as a function of μ_e, μ_i and V_0 by (per unit volume)

$$\beta\Omega = -\frac{1}{V}\ln \operatorname{Sp}\exp\Big\{-\beta\Big(H_0 + H'$$

$$-\mu_e \sum_p a_p^+ a_p - \mu_i \sum_p \alpha_p^+ \alpha_p\Big)\Big\}.$$

Differentiating this expression with respect to V_0, μ_e and μ_i it is easy to find the relation (to terms which approach zero as $V \rightarrow \infty$):

$$\partial\Omega / \partial V_0 = -{}^1\!/\!_2\,(z\partial\Omega / \partial\mu_i - \partial\Omega / \partial\mu_e)^2.$$

We introduce the variables

$$M = z\mu_e + \mu_i, \quad \mu = (z\mu_e - \mu_i) / 2z,$$

whence the equation assumes the form

$$\partial\Omega / \partial V_0 = -{}^1\!/\!_2\,(\partial\Omega / \partial\mu)^2. \tag{I}$$

It is required to find the solution of this equation for the initial condition $\Omega(\mu, 0) = \widetilde{\Omega}(\mu)$. The general integral is of the form

$$\Omega = -\frac{a^2}{2}V_0 + a\mu + b(a), \tag{II}$$

where a is a function of μ and V_0 defined by the equation

$$-aV_0 + \mu + b'(a) = 0. \tag{III}$$

The function $b(a)$ is expressed so as to satisfy the initial condition

$$a(\mu, 0)\mu + b[a(\mu, 0)] = \widetilde{\Omega}(\mu). \tag{IV}$$

It is apparent from Eq. (III) that as $V_0 \rightarrow \infty$ the quantity $a(\mu, V_0)$ approaches zero as $(\mu + b'(0))/V_0$; hence $\Omega(\mu, \infty) = b(0)$ and is independent of the variable μ.

In order to find $b(0)$ we differentiate (IV) with respect to μ; then, using (III), we have $a(\mu, 0) = d\widetilde{\Omega}/d\mu$.

We define μ_0 by the equation

$$(d\widetilde{\Omega} / d\mu)_{\mu=\mu_0} = 0. \tag{V}$$

Substituting in Eq. (IV) $\mu = \mu_0$, we find $b(0) = \widetilde{\Omega}(\mu_0)$.

Thus,

$$\Omega(\mu, \infty) = \widetilde{\Omega}(\mu_0, 0), \tag{VI}$$

where μ_0 is defined by Eq. (V).

The free energy of the system if $F = \Omega + MN$ where M is found from the condition $\partial\Omega/\partial M = -N$. Returning to the variables μ_e and μ_i, taking account of Eqs. (V) and (VI) we have

$$F = \widetilde{\Omega} + z\mu_e N + \mu_i N,$$

where μ_i and μ_e are defined by the relations

$$\partial\widetilde{\Omega} / \partial\mu_i = -N, \quad \partial\widetilde{\Omega} / \partial\mu_e = -zN.$$

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