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USE OF COLLECTIVE VARIABLES AND TREATMENT OF SHORT-RANGE FORCES IN THE THEORY OF A SYSTEM OF CHARGED PARTICLES

I. R. IUKHNOVSKII

L'vov State University

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The free energy and the distribution functions (binary and ternary) of a system of charged particles are calculated with effects of short-range forces included. Expressions for these quantities are written in terms of series of group integrals (correlations). It is shown that for an electron plasma in a compensating field the Coulomb potential does not give divergences in the expressions for the free energy and the distribution functions. The total free energy of a system of particles with a Coulomb interaction potential is also calculated. The "transition function" for such systems is constructed.

1. STATEMENT OF THE PROBLEM

UNTIL recently the determination of the thermodynamic characteristics of ionic systems has been carried out by the use of partial distribution functions — single-particle and binary functions. The calculations involved cumbersome computations and the solution of complicated systems of

integro-differential equations. In these calculations for systems of charged particles short-range forces could be taken into account only with special forms of force law; for example, with the choice of the mutual potential in the form¹

$$\Phi = (e^2/r) [1 - A(r)e^{-\alpha r}].$$

The construction of the exact binary function of a system by the method of the Bogoliubov equations, independent of the actual form of the short-range part of the total interaction potential, remained an unsolved problem.

Since 1949 there have been appearing papers by Bogoliubov, Zubarev, Bohm, Gross, Pines and others in which a new and original method of collective variables is presented, which makes it possible to find at once the partition functions of systems of interacting particles. In this method the behavior of the system is described from the point of view of the collective vibrations that occur owing to the interaction and motion of the particles. For the appearance of vibrations that include whole groups of particles it is naturally necessary that the sphere of effective action of the field of one particle must extend to many other particles. Langmuir and Tonks have shown² that the wavelength of the oscillations in an ionic system is not smaller than the Debye radius r_d , which is of the order $c^{-1/2} \times 10^{-8}$ cm, where c is the concentration in moles per liter. On the other hand, r_d can be regarded as the radius of the sphere of effective action of the Coulomb forces.

From this it follows that for systems with a Coulomb interaction potential the coordinate space can be replaced by a space of collective variables $\rho_{\mathbf{k}}$, each of which describes a certain monochromatic vibration in the system, with the wave vector \mathbf{k} .

The van der Waals forces and the repulsive forces act at distances considerably smaller than r_d . The action of these forces does not give rise to collective vibrations, and consequently, they cannot be described in the space of the $\rho_{\mathbf{k}}$.

Bogoliubov has suggested the study of the "mixed" problem: the calculation of the integral over states (partition function) of an ionic system, in which the short-range forces are described in the coordinate space and the long-range forces are described by means of collective variables. The present paper is devoted to the solution of this problem.

Let us consider a system in equilibrium, which is neutral as a whole and consists of M kinds of ions, containing N_a particles of type a . The interaction is described by the "exact" potential³

$$U = \frac{1}{2} \sum_{\substack{1 \leq a, b \leq M \\ 1 \leq i \neq j \leq N_a, N_b}} \left(\frac{e_a e_b}{\epsilon r_{ij}} + \frac{A_{ab}}{r_{ij}^6} + b_{ab} e^{-r_{ij}/\rho} \right). \quad (1.0)$$

Let us calculate the free energy of this system

$$F = -kT \ln Z_{id} Z, \quad (1.1)$$

where Z_{id} is the ideal part of the statistical integral (omitted in what follows).

We introduce the collective variable

$$\rho_{\mathbf{k}} = \sum_{a=1}^M \lambda_a N^{-1/2} \sum_{1 \leq i \leq N_a} e^{i\mathbf{k}r_i}$$

which is the Fourier transform of the function

$$f(\mathbf{r}) = \sum_{i,a} \lambda_a N^{-1/2} \delta(\mathbf{r} - \mathbf{r}_i),$$

$$\lambda_a = e_a \left(\sum e_c^2 n_c \right)^{-1/2}, \quad n_c = N_c / N, \quad \mathbf{k} \neq 0.$$

and by its use we write the configuration integral in the form⁴

$$Z = \exp\left(\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k})\right) \int \exp\left(-\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}\right) J(\rho_{\mathbf{k}}) (d\rho_{\mathbf{k}}),$$

$$\alpha(\mathbf{k}) = \sum e_c^2 n_c \nu(\mathbf{k}) / v\Theta, \quad v = \frac{V}{N}, \quad (1.2)$$

where $\nu(\mathbf{k})$ is the Fourier transform of the Coulomb potential. $J(\rho_{\mathbf{k}})$ is the "transition function" providing for the transition from Eq. (1.2) to the usual form

$$Z = \int \exp\{-U(r_1, \dots, r_N) / \Theta\} dq_1 \dots dq_N. \quad (1.3)$$

From $\rho_{\mathbf{k}} \rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^2 + \rho_{\mathbf{k}}^{\mathcal{S}2}$ it follows that the potential energy of the Coulomb interaction of the ions is replaced by the potential energy of a system of harmonic oscillators, over whose amplitudes the integration is to be taken. The sum over \mathbf{k} has an upper limit at some value k_{\max} depending on the concentration, which corresponds to the existence of a value λ_{\min} .

We do not expand the short-range potentials in Fourier series. They remain in the coordinate representation and can enter, for example, into the make-up of the transition function $J(\rho_{\mathbf{k}})$, which is given by

$$J(\rho_{\mathbf{k}}) = \int \exp\left\{-\frac{1}{2\Theta} \sum_{a,b,i,j} \varphi_{ab}(r_{ij})\right\}$$

$$\times \prod_{\mathbf{k} \neq 0} \delta\left(\rho_{\mathbf{k}}^c - \sum_{a,i} \lambda_a N^{-1/2} \cos \mathbf{k}r_i\right) \quad (1.4)$$

$$\times \delta\left(\rho_{\mathbf{k}}^s - \sum_{a,i} \lambda_a N^{-1/2} \sin \mathbf{k}r_i\right) dq_1 \dots dq_N,$$

where

$$\varphi_{ab}(r_{ij}) = A_{ab} / r_{ij} + b_{ab} \exp\{-r_{ij}/\rho\}.$$

Taking $\varphi_{ab}(\mathbf{r}) = 0$, we get the transition function for the Coulomb potential. Since this case is of great importance for the further work, we shall examine it in more detail.

2. THE CONFIGURATION INTEGRAL IN THE CASE OF THE COULOMB INTERACTION POTENTIAL

As in Ref. 4, we substitute into Eq. (1.4) the integral representation of the δ function

$$\delta\left(\rho_{\mathbf{k}} - N^{-1/2} \sum_{a=1}^M \lambda_a \sum_{i=1}^{N_a} e^{i\mathbf{k}r_i}\right) = \int \exp\left\{i\pi\left(\rho_{\mathbf{k}} - \sum_{a,i} \lambda_a N^{-1/2} e^{i\mathbf{k}r_i}\right)\omega_{\mathbf{k}}\right\} d\omega_{\mathbf{k}}.$$

On integrating over the coordinates and over $\omega_{\mathbf{k}}$ we get the transition function in an operator form that is convenient for calculation:

$$J^h(\rho_{\mathbf{k}}) = V^N \exp\left\{\sum_{i \geq 3} (-1)^i D_i\right\} \left\{1 - \sum_a N_a \left(\frac{1}{2 \cdot 3!} \frac{\lambda_a^6}{N^3} \times \sum_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0} \frac{\partial^6}{\partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1} \dots \partial \rho_{-\mathbf{k}_3}} + \dots\right) \times \exp\left\{-\frac{1}{N} \sum_{i \geq 2} (-1)^i D_i^a\right\} - \sum_{a,b} N_a N_b \dots\right\} \exp\left\{-\frac{1}{2} \sum (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln \pi)\right\}, \quad (2.1)$$

where the operators are defined by

$$D_n^a = \frac{\lambda_a^n N^{-(n-2)/2}}{n!} \sum_{\mathbf{k}_1 + \dots + \mathbf{k}_n = 0} \partial^n / \partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_n},$$

$$D_n = \sum_{a=1}^M n_a D_n^a.$$

In the sum $\mathbf{k}_1 + \mathbf{k}_2 + \dots + \mathbf{k}_n = 0$ no sum of order less than n is equal to zero.

We confine ourselves to calculations carried out with only the first two terms in the braces of Eq. (2.1).

We shall show that the first term

$$J_0^h = V^N \exp\left\{\sum_{i \geq 3} (1)^i D_i\right\} \exp\left\{-\frac{1}{2} \sum_{\mathbf{k}} (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln \pi)\right\}, \quad (2.2)$$

gives the main part of the transition function, and the second

$$J_1^h = -V^N \exp\left\{\sum_{i \geq 3} (-1)^i D_i\right\} \sum_a N_a \left(\frac{1}{2 \cdot 3!} \frac{\lambda_a^6}{N^3} \times \sum_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0} \frac{\partial^6}{\partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_3} \partial \rho_{-\mathbf{k}_3}} + \dots\right) + \frac{1}{2 \cdot 4!} \frac{\lambda_a^8}{N^4} \sum_{\mathbf{k}_1 + \dots + \mathbf{k}_4 = 0} \frac{\partial^8}{\partial \rho_{\mathbf{k}_1} \dots \partial \rho_{-\mathbf{k}_4}} + \dots\right) \times \exp\left\{-\frac{1}{N} \sum_{i \geq 2} (-1)^i D_i^a\right\} \exp\left\{-\frac{1}{2} \sum_{\mathbf{k}} (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln \pi)\right\}$$

(and subsequent terms) lead to quantities proportional to $1/V$, which can be neglected. For this purpose we substitute Eq. (2.1) into (1.2) and expand the exponentials of operators in series. Under the integral sign there remains the exponential function

$$\exp\left\{-\frac{1}{2} \sum_{\mathbf{k}} (\alpha(\mathbf{k}) + 1) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}\right\},$$

which is an even function of $\rho_{\mathbf{k}}$. Therefore on integration over the collective variables the expressions different from zero will be those in which the differentiation is an "even" one of the type

$$\partial^{2n} / \partial \rho_{\mathbf{k}_1} \partial \rho_{-\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_n} \partial \rho_{-\mathbf{k}_n}.$$

Let us consider first the main contribution to the statistical integral, in which one takes for the transition function the expression (2.2):

$$Z_0^h = \exp\left(\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k})\right) \int \exp\left(-\frac{1}{2} \sum_{\mathbf{k}} \alpha(\mathbf{k}) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}\right) J_0^h(\rho_{\mathbf{k}}) (d\rho_{\mathbf{k}}). \quad (2.4)$$

The expansions in $J_0^h(\rho_{\mathbf{k}})$ can be written out in the form

$$(1 - D_3 + D_4 - D_5 + \dots + D_3 D_3 - D_3 D_4 + \dots + D_4 D_4 - D_4 D_5 + \dots - D_3 D_3 D_3 + D_3 D_3 D_4 - \dots) \exp\left(-\frac{1}{2} \sum_{\mathbf{k}} (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \ln \pi)\right). \quad (2.5)$$

According to the definition of the $\rho_{\mathbf{k}}$, all $\mathbf{k} \neq 0$; moreover, in the sums $\mathbf{k}_1 + \mathbf{k}_2 + \dots + \mathbf{k}_n = 0$ there is nowhere a \mathbf{k}_i equal to $-\mathbf{k}_j$; therefore the linear terms in Eq. (2.5) (except for the 1) can be dropped, since they give zero when one carries out the integration in Eq. (2.4). The same is true of many of the products of the D_i by twos, threes, and so on.

In the sum in Eq. (2.5) we must consider the terms containing even derivatives. The factors $\rho_{\mathbf{k}} \rho_{-\mathbf{k}}$ obtained after the differentiations in the expression (2.4) for J_0^h can conveniently be replaced by operators $[1 + \partial/\partial \alpha(\mathbf{k})]$, which can be taken outside the sign of integration over $\rho_{\mathbf{k}}$.

Expanding, finally, the combination of operators $[1 + \partial/\partial \alpha(\mathbf{k})]$, we get as the result of the inverse Fourier transformation the main contribution to the configuration integral in the following form:

$$Z_0^h = \prod_{\mathbf{k}} \frac{e^{\alpha(\mathbf{k})}}{\alpha(\mathbf{k}) + 1} \left\{1 + N \left[\frac{N}{V} \sum_{a,b} \frac{n_a n_b}{2!} \int (e^{-g_{ab}} - 1 + g_{ab} - \frac{g_{ab}^2}{2}) dq + \frac{N^2}{V^2} \sum_{a,b,c} \frac{n_a n_b n_c}{3!} \int (e^{-g_{ac}} - 1 + g_{ac}) \times (e^{-g_{cb}} - 1 + g_{cb}) 3g_{ab} dq_1 dq_2 + \int (e^{-g_{ab}} - 1 + g_{ab}) (e^{-g_{ac}} - 1 + g_{ac}) (e^{-g_{cb}} - 1 + g_{cb}) dq_1 dq_2 + \frac{N^3}{V^3} \sum_{a,b,c,d} n_a n_b n_c n_d \dots\right] + \dots\right\}, \quad (2.6)$$

where $\Theta g_{ab}(r)$ is the self-consistent Debye potential*

$$g_{ab}(r) = (e_a e_b / \epsilon \Theta) e^{-\kappa r} / r \text{ for the Coulomb potential} \quad (2.7a)$$

$$g_{ab}(r) = \frac{e_a e_b}{\epsilon \Theta} \frac{1}{V \sqrt{1 - 4\beta^2 \kappa^2}} \frac{e^{-qr} - e^{-pr}}{r},$$

for the potential $\frac{e_a e_b}{\epsilon r} (1 - e^{-\alpha r})$, (2.7b)

$$p = \frac{1}{2} \alpha (\sqrt{1 + 2\beta \kappa} + \sqrt{1 - 2\beta \kappa}),$$

$$q = \frac{1}{2} \alpha (\sqrt{1 + 2\beta \kappa} - \sqrt{1 - 2\beta \kappa}),$$

$$\alpha = 1/\beta \sim 10^8 \text{ cm}^{-1}, \kappa = 1/r_a.$$

For a system of ions of different signs interacting according to the Coulomb law the integral $\int e^{-g_{ab}(r)} dq$ diverges at zero.† Therefore in the case of a system of ions of different signs we shall use a cut off Coulomb potential and substitute the expression (2.7b) for g_{ab} .

In order to get the terms in Eq. (2.6) proportional to $(N/V)^3$ it is necessary to examine products of four operators in Eq. (2.5). For example, the calculation of the operator $D_3 D_3 D_3 D_3$ leads to three integrals

$$N \frac{N^3}{V^3} \int g_{ab} g_{bc} g_{cd} g_{da} g_{ac} g_{bd} dq_1 dq_2 dq_3,$$

$$N \frac{N^3}{V^3} \int \frac{g_{ab}^2}{2} \frac{g_{cd}^2}{2} g_{ac} g_{bd} dq_1 dq_2 dq_3, \quad N^2 \frac{N^2}{2V^2} \left(\int \frac{g_{ab}^3}{3!} dq \right)^2.$$

The first two are the beginning of a series of complicated correlation expressions. The last is the third term of the series expansion of the expression

$$\exp \left(N \frac{N}{V} \int \frac{1}{3!} g_{ab}^3 dq \right).$$

Developing the higher products of operators in Eq. (2.5) we get on one hand, new correlation terms proportional to N , and on the other hand, powers of these terms, corresponding to the expansion of the exponential.

Thus the whole expression for the main part of the statistical integral in an exponential function of the terms proportional to the first power of N . On the other hand, the free energy is the logarithm

*After the inverse Fourier transformation one puts

$$\int \left(g_{ab} - \frac{1}{V} \int g_{ab} dq \right)^i dq \approx \int g_{ab}^i dq, \quad i \geq 3.$$

†For oppositely charged particles $g_{ab}(r) < 0$.

of the statistical integral. The additivity properties require that

$$F = -kT \ln Z = Nf(T, V/N).$$

Therefore in the expansion for $\ln Z$ we must confine ourselves to terms proportional to the first power of N . This combination corresponds to the logarithm of the whole expression for the statistical integral (cf. also Ref. 5, p. 239).

In calculating the expression (2.6) we were examining only the main part of the statistical integral. We shall now show that in the calculation of F the operator J_1^k leads to infinitely small quantities of the order $1/V$ which can be neglected.

To do this we substitute J_1^k into Eq. (2.4) instead of J_0^k and calculate the integral

$$Z_1^k = \exp \left(\frac{1}{2} \sum_k \alpha(k) \right) \int \exp \left(-\frac{1}{2} \sum_k \alpha(k) \rho_k \rho_{-k} \right) J_1^k(\rho_k) (d\rho_k). \quad (2.8)$$

Comparing Eqs. (2.2) and (2.3), we find it useful to write J_1^k in the form

$$J_1^k = - \sum_a N_a \exp \{ -D_2^a / N \} (1 + D_3^a / N - D_4^a / N + \dots) \\ \times \left(\frac{1}{2 \cdot 3!} \frac{\lambda_a^6}{N^3} \sum_{k_1+k_2+k_3=0} \partial^6 / \partial \rho_{k_1} \dots \partial \rho_{-k_3} + \dots \right) J_0^k. \quad (2.3a)$$

After Eq. (2.3a) is substituted into Eq. (2.8), the further calculations are analogous to Eqs. (2.4) – (2.6) and lead to the following result:

$$Z_1^k = -Z_0^k \sum_a \frac{n_a}{2} e^{-g_{aa}(0)} \\ \times \frac{N}{V} \int \left(e^{-g_{aa}(r)} - 1 + g_{aa}(r) - \frac{g_{aa}^2}{2} \right) dq \quad (2.9) \\ \times \left[1 + \frac{N}{3!V} \frac{1}{Z_0^k} \sum_b n_b \int g_{ab}^3 dq + \dots \right] = -Z_0^k \frac{N}{V} \varphi \left(\frac{N}{V} \right),$$

where $\varphi(N/V)$ is a finite function of the concentration.

The general expression for the statistical integral of a system of charged particles (without inclusion of short-range forces) is

$$Z^k = Z_0^k + Z_1^k = Z_0^k (1 + N\varphi/V). \quad (2.10)$$

3. THE FREE ENERGY OF A COULOMB SYSTEM

In the formula

$$F^k = -kT \ln Z^k \quad (3.1)$$

we substitute Z_0^k from Eq. (2.6) and expand the logarithms in powers of N . Taking into account the considerations presented above, we confine ourselves to expressions proportional to the first power of N . Then

$$\begin{aligned}
 F = & -NkT \left\{ \ln V + \frac{1}{N} \sum_k [\alpha(k) - \ln(\alpha(k) + 1)] + \frac{N}{V} \sum_{a,b} \frac{n_a n_b}{2} \int (e^{-g_{ab}} - 1 + g_{ab} - \frac{1}{2} g_{ab}^2) dq \right. \\
 & + \frac{N^2}{V^2} \sum_{a,b,c} \frac{n_a n_b n_c}{3!} \left[\int (e^{-g_{ac}} - 1 + g_{ac})(e^{-g_{cb}} - 1 + g_{cb}) 3 g_{ab} dq_1 dq_2 + \dots \right] \\
 & \left. + \frac{N^3}{V^3} \sum_{a,b,c,d} \dots - \frac{1}{V} \sum_a \frac{n_a}{2} e^{-g_{aa}(0)} \frac{N}{V} \int (e^{-g_{aa}(r)} - 1 + g_{aa}(r) - \frac{1}{2} g_{aa}^2(r)) dq \left[1 + \frac{N}{3!V} \frac{1}{Z_0^k} \sum_b n_b \int g_{ab}^3 dq + \dots \right] \right\},
 \end{aligned} \tag{3.2}$$

where

$$\alpha(k) = \sum (e^2 n_c N / V \Theta) \nu(k), \quad \nu(k) = \int \Phi^h(r) e^{ikr} dq = 4\pi\alpha^2 / k^2 (\alpha^2 + k^2), \quad \Phi^h(r) = (1 - e^{-ar}) / r.$$

The last terms of Eq. (3.2) are smaller than the other terms by a factor 1/V and can be neglected.*

Thus it is established that for the calculation of the free energy of a system of charged particles the transition function is given, apart from terms proportional to 1/V, by the expression

$$J^h = J_0^h = \exp \left(\sum_{i \geq 3} (-1)^i D_i \right) \exp \left(-\frac{1}{2} \sum_k \rho_k \rho_{-k} + \ln \pi \right). \tag{3.3}$$

Terms whose application would result in infinitely small quantities of the order $e^{-g_{aa}(0)}/V$ have been dropped.

We now proceed to substitute into Eq. (3.2) the value of $\alpha(k)$ and to sum over k .

The free energy of a neutral system of ions with (cut off) Coulomb interaction potential is given by the following final formula:

$$\begin{aligned}
 F = & -NkT \left\{ \ln V + \frac{1}{4\pi\beta} \frac{V}{N} \left(\frac{x^2}{2} - \frac{1}{3\beta^2} [1 - (1 - \beta x) \sqrt{1 + 2\beta x}] \right) \right\} + \frac{N}{V} \sum_{a,b} \frac{n_a n_b}{2} \int (e^{-g_{ab}(r)} - 1 + g_{ab} - \frac{1}{2} g_{ab}^2) dq \\
 & + \frac{N^2}{V^2} \sum_{a,b,c} \frac{n_a n_b n_c}{3!} \left\{ \int (e^{-g_{ac}} - 1 + g_{ac})(e^{-g_{cb}} - 1 + g_{cb}) 3 g_{ab} dq_1 dq_2 \right. \\
 & \left. + \int (e^{-g_{ab}} - 1 + g_{ab})(e^{-g_{ac}} - 1 + g_{ac})(e^{-g_{cb}} - 1 + g_{cb}) dq_1 dq_2 \right\} + \frac{N^3}{V^3} \dots
 \end{aligned} \tag{3.4}$$

For small concentrations this goes over into the relation

$$F = -NkT \left[\ln V + \frac{1}{4\pi\beta} \frac{V}{N} \left\{ \frac{x^2}{2} - \frac{1}{3\beta^2} \left(1 - (1 - \beta x) \sqrt{1 + 2\beta x} \right) \right\} \right], \tag{3.5}$$

which can be obtained by means of the zeroth approximation to the binary distribution function.†

It is now easy to go on to treat the problem of constructing the distribution functions and the thermodynamic functions for the case in which one includes in the interaction energy all the central forces, of both long and short ranges. One can also deal with a system of ions in external fields. For the case of an external field potential that possesses a Fourier transform the transition function remains the same as in the absence of the field, and is given by Eq. (3.3).

4. THE DISTRIBUTION FUNCTIONS AND FREE ENERGY OF A SYSTEM OF CHARGED PARTICLES WITH INCLUSION OF EFFECTS OF SHORT-RANGE FORCES

By using the results of Secs. 2 and 3 one can carry out the study of systems of charged particles with the exact interaction law of Eq. (1.0) in two ways, which lead to identical results.

In the first place, one can replace the configuration integral of the system,

$$Z = \int \exp \left\{ - \sum_{a,b,i,j} \frac{1}{\Theta} (\Phi_{ab}^h(r_{ij}) + \varphi_{ab}(r_{ij})) \right\} dq_1 \dots dq_N, \tag{4.1}$$

*In the case of the Coulomb potential $\Phi^k(r) = 1/r$, $g_{aa}(0) = \infty$, and these terms are simply equal to zero.

†In the limit $\beta \rightarrow 0$ Eq. (3.5) goes over into Debye's result, which Zubarev⁴ has obtained by the method of collective variables.

where

$$\Phi_{ab}^k(r_{ij}) = e_a e_b / \varepsilon r_{ij}, \quad \varphi_{ab}(r_{ij}) = A_{ab} / r_{ij}^6 + b_{ab} e^{-r_{ij} \rho}, \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|,$$

by the expression (1.2), in which the Coulomb energy is represented by the energy of the harmonic vibrations, and the short-range part of the force law (1.0) affects the structure of the transition function, given by

$$J(\rho_{\mathbf{k}}) = V^N \left\{ 1 + \sum_{a,b} \frac{N_a N_b}{2V} \int f_{ab}(r) \left(1 - \frac{\lambda_a \lambda_b}{N} \exp \left\{ \sum_{i \geq 2} (-1)^i D_i^{ab} / N \right\} \sum_{\mathbf{k}} \frac{\partial^2}{\partial \rho_{\mathbf{k}} \partial \rho_{-\mathbf{k}}} + \dots \right) dq \right. \\ \left. + \sum_{a,b,c} \frac{N_a N_b N_c}{3! V^2} \int [3f_{ab} f_{bc} + f_{ab} f_{bc} f_{ca}] \left[1 + \frac{1}{N} \exp \left\{ \sum_{i \geq 2} (-1)^i D_i^{abc} / N \right\} \sum_{\mathbf{k}} \frac{\partial^2}{\partial \rho_{\mathbf{k}} \partial \rho_{-\mathbf{k}}} (\lambda_a \lambda_b e^{i\mathbf{k}r_1} + \lambda_a \lambda_c e^{i\mathbf{k}r_2} \right. \right. \\ \left. \left. + \lambda_b \lambda_c e^{i\mathbf{k}(r_1 - r_2)} + \dots \right) dq_1 dq_2 + \sum_{abcd} \dots \right\} J^k(\rho_{\mathbf{k}}), \quad (4.2)$$

Here

$$f_{ab} = e^{-\varphi_{ab} \theta} - 1, \quad D_i^{ab} = \sum_{\mathbf{k}_1 + \dots + \mathbf{k}_i = 0} \frac{\lambda_a^i + \lambda_b^i}{i! N^{(i-2)/2}} \partial^i / \partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_i}, \quad D_i^{abc} = \sum_{\mathbf{k}_1 + \dots + \mathbf{k}_i = 0} \frac{\lambda_a^i + \lambda_b^i + \lambda_c^i}{i! N^{(i-2)/2}} \partial^i / \partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_i};$$

and in the sum $\mathbf{k}_1 + \dots + \mathbf{k}_i$ no sum of order less than i is equal to zero. J^k is the transition function for the Coulomb potential, given by Eq. (3.3). After Eq. (4.2) has been substituted into Eq. (1.2) the further developments are analogous to the treatment for the Coulomb problem. Here one again has to group the operators D_i and to sum complicated series.

This procedure is perhaps the more cumbersome. In this paper the calculation will be carried out by the second method, in which one uses the properties of the free energy as a generating functional.

Let us introduce a functional of the $\psi_{ab}(r_{ij})$, which are an arbitrary system of regular rapidly decreasing radially symmetrical functions:

$$L(\psi) = -\theta \ln Z(\psi) = -\theta \ln \int \exp \left\{ - \sum \frac{1}{\theta} (\Phi_{ab}^k(r_{ij}) + \varphi_{ab}(r_{ij}) + \psi_{ab}(r_{ij})) \right\} dq_1 \dots dq_N. \quad (4.3a)$$

The integrand can be transformed into a sum by the substitution

$$f_{ab}^x(r_{ij}) = \exp \{ - [\varphi_{ab}(r_{ij}) + \psi_{ab}(r_{ij})] / \theta \} - 1.$$

The result is the following way of writing the generating functional $L(\psi)$:

$$L(\psi) = -\theta \ln \int \exp \left(- \frac{1}{\theta} \sum \Phi_{ab}^k(r_{ij}) \right) \left\{ 1 + \sum f_{ab}^x(r_{ij}) + \sum (f_{ab}^x(r_{ij}) f_{bc}^x(r_{jk}) + f_{ab}^x f_{bc}^x f_{ca}^x) + \dots \right\} dq_1 \dots dq_N. \quad (4.3b)$$

Carrying out the integration, we use the sequence of Bogoliubov distribution functions of Coulomb systems

$$Z^{-k} \int \exp \left(- \sum \frac{1}{\theta} \Phi_{ab}^k(r_{ij}) \right) dq_{s+1} \dots dq_N = V^{-s} F_{a_1 \dots a_s}^k(r_1 \dots r_s). \quad (4.4)$$

Then we get from Eqs. (4.3)

$$L(\psi) = -\theta \ln Z^k - \theta \ln \left\{ 1 + \frac{1}{V^2} \sum \int f_{ab}^x(r_{ij}) F_{ab}^k(r_{ij}) dq_i dq_j + \frac{1}{V^3} \sum \int (f_{ab}^x(r_{ij}) f_{bc}^x(r_{jk}) + f_{ab} f_{bc} f_{ca}) \right. \\ \left. \times F_{abc}^k(r_i, r_j, r_k) dq_i dq_j dq_k + \sum_{a,b,c,d} \dots \right\}, \quad (4.5)$$

where Z^k is the statistical integral of the Coulomb system and $F_{ab}^k(r_{12})$ and F_{abc}^k are the binary and ternary distribution functions of the Coulomb system.⁴ The expression (4.5) is the starting point for the solution of the stated problem.

Let us begin with the distribution functions. By the definition of functional differentiation the binary function is given by

$$F_{ab}(r_{12}) = V^2 (\partial L(\psi) / \partial \psi_{ab}(r_{12}))_{\psi=0}$$

or by Eq. (4.5):

$$F_{ab}(r_{12}) = \exp\{-\varphi_{ab}(r_{12})/\Theta\} \left\{ F_{ab}^h(r_{12}) + \sum_c \frac{N_c}{V} \int (f_{ac} + f_{bc} + f_{ac}f_{bc}) F_{abc}^h(r_1 r_2 r_3) dq_3 + \dots \right\}. \quad (4.6)$$

The triple functional derivative leads us to the ternary distribution function

$$F_{abc}(r_1 r_2 r_3) = \exp\left[-\frac{1}{\Theta}(\varphi_{ab} + \varphi_{bc} + \varphi_{ca})\right] \left\{ F_{abc}^h + \sum_x \frac{N_x}{V} \int (f_{ax} + f_{bx} + f_{cx} + f_{ax}f_{bx} + \dots + f_{ax}f_{bx}f_{cx}) F_{abcx}^h dq_x + \dots \right\}. \quad (4.7)$$

Substituting into Eqs. (4.6) and (4.7) the values of F_{ab}^k and F_{abc}^k from Ref. 1,

$$F_{ab}^h(r_{12}) = e^{-g_{ab}(r_{12})} \left\{ 1 + \frac{N}{V} \sum_c n_c \int [(e^{-g_{ac}} - 1)(e^{-g_{cb}} - 1) - g_{ac}g_{cb}] dq_c + \frac{N^2}{V^2} \sum_{cd} n_c n_d \int (e^{-g_{ac}} - 1)(e^{-g_{cd}} - 1 + g_{cd}) \times (e^{-g_{db}} - 1) dq_c dq_d + \frac{N^3}{V^3} \sum_{cde} \dots \right\}; \quad (4.8)$$

$$F_{abc}^h(r_1 r_2 r_3) = F_{ab}^h F_{bc}^h F_{ca}^h + \frac{N}{V} \sum_x n_x \int (e^{-g_{ax}} - 1)(e^{-g_{bx}} - 1)(e^{-g_{cx}} - 1) dq_x + \dots, \quad (4.9)$$

and collecting the terms with equal powers of N/V we get the binary function

$$F_{ab} = \exp\left[-\frac{1}{\Theta}(\varphi_{ab} + g_{ab})\right] \left\{ 1 + \frac{N}{V} \sum_c n_c \left[\int [(e^{-g_{ac}} - 1)(e^{-g_{cb}} - 1) - g_{ac}g_{cb}] dq_c + \int (f_{ac} + f_{bc} + f_{ac}f_{bc}) e^{-(g_{ac} + g_{bc})} dq_c \right] + \frac{N^2}{V^2} \sum_{c,d} \dots \right\}. \quad (4.10)$$

The first term in the expression (4.10) is the product of the Boltzmann and Debye probabilities for the distribution of two particles. The subsequent terms involve group integrals of Coulomb and mixed types. In order to get the free energy of the system, we set $\psi = 0$ in Eq. (4.5). Then

$$F = F^k - \Theta \sum_{a,b} \frac{N_a N_b}{2V} \int f_{ab} F_{ab}^h(r) dq - \Theta \sum_{a,b,c} \frac{N_a N_b N_c}{3!V^2} \int (3f_{ab}f_{bc} + f_{ab}f_{bc}f_{ca}) F_{abc}^h dq_1 dq_2 + \dots, \quad (4.11)$$

where $F^k = -\Theta \ln Z^k$ is the free energy of the Coulomb system, given by Eq. (3.4).

Substituting Eqs. (4.8), (4.9), and (3.4) into Eq. (1.11), we find finally

$$F = -\Theta \left(\ln V + \frac{V}{N} \frac{1}{4\pi\beta} \left(\frac{\kappa^2}{2} - \frac{1}{3\beta^2} (1 - (1 - \beta\kappa) \sqrt{1 + 2\beta\kappa}) \right) + \frac{N}{2V} \sum_{a,b} n_a n_b \left[\int f_{ab} e^{-g_{ab}} dq + \int (e^{-g_{ab}} - 1 + g_{ab} - \frac{1}{2} g_{ab}^2) dq \right] + \frac{N^2}{2V^2} \sum_{a,b,c} n_a n_b n_c \left[\int f_{ab} e^{-g_{ab}} \{ (e^{-g_{ac}} - 1)(e^{-g_{cb}} - 1) - g_{ac}g_{cb} \} dq_1 dq_2 + \int \left\{ f_{ac}f_{cb} + \frac{1}{3} f_{ac}f_{bc}f_{ca} \right\} e^{-(g_{ab} + g_{ac} + g_{bc})} dq_1 dq_2 + \frac{1}{3} \int (e^{-g_{ac}} - 1 + g_{ac})(e^{-g_{cb}} - 1 + g_{cb})(e^{-g_{ab}} - 1 + g_{ab}) dq_1 dq_2 - \int g_{ab}(e^{-g_{cb}} - 1 + g_{cb})(e^{-g_{ac}} - 1 + g_{ac}) dq_1 dq_2 \right] + \frac{N^3}{V^3} \dots \right) \quad (4.12)$$

In Eqs. (4.10) and (4.12) expressions for the binary function and the free energy of a neutral system of ions are written in the form of series of group integrals. The first terms of these series correspond to the self-consistent (Debye) interaction between the ions. The second terms, arising from combinations of pairs of operators D_i , characterize the binary correlation between the particles. After these come triple, quadruple, and still higher correlations.

Each group correlation consists of integrals of Coulomb and mixed types. The integrals corre-

sponding to pure Coulomb (or "cut off" Coulomb) interaction are made up of exponential functions of the type $e^{-g_{ab}} - 1$, where $g_{ab} \cong e^{-r_{ab}/r_d}$ is the self-consistent Debye potential. Thus the integrands go to zero very rapidly with increasing r . Furthermore, the group integrals decrease rapidly with increase of the order of the correlation.

The mixed group correlations involve the usual functions of the van der Waals theory,

$\exp(-\varphi_{ab}/\Theta) - 1$, and functions $e^{-g_{ab}} - 1$. Such group integrals also decrease rapidly with

increasing order of correlation.

The expressions for the free energy and the distribution functions also have the form of power series in N/V . These are not, however, expansions in powers of the concentration. In the first place, such expansions lose their meaning when $N/V > 1$; in the second place, the group integrals depend on N/V .

The expressions for the binary distribution function and the free energy are series expressions in the correlations. Because the Coulomb forces occur in the integrals in the form of the screened self-consistent potential, for which the screening radius (r_d) decreases with increasing concentration, these expansions are obviously valid for high concentrations.

Let us consider further a special case of Eqs. (4.6) and (4.12) — a system of electrons in a compensating external field, for which $\int \Phi^k dq = \nu(0) = 0$. Since in this case $f_{ab}(0) = 0$, the quantities $F_{ab} = F_{ab}^k$ and $F = F^k$ are given by Eqs. (4.8) and (3.4), respectively. The binary and ternary distribution functions do not diverge at zero, and the integrands in the correlation terms of Eqs. (4.8), (4.9), and (3.4) are also free from singularities. This indicates that for electrons in a compensating field there is no need to "cut off" the Coulomb potential.

In a subsequent paper the thermodynamic functions of ionic systems will be calculated and compared with experiment.

In conclusion I express my sincere gratitude to N. N. Bogoliubov for suggesting this problem and to A. E. Glauber for a discussion of the paper.

Note (September 3, 1957). The remark in the recently published paper of Bazarov⁶ about the incorrectness of the formula (2.4) for the free energy in the paper of Glauber and Iukhnovskii⁷ is without foundation. The divergence of F and the departure from the Debye formula for $\beta \rightarrow 0$ are avoided by the choice of the arbitrary constant of integration (to the accuracy with which F is defined), after which Eq. (2.4) takes the form

$$F_e = -\frac{T}{2\epsilon} \sum_a N_a e_a^2 \left\{ \frac{1}{2ac^3} \left[\frac{1}{5} (x-1)^5 - \frac{2}{3} (x-1)^3 + (x-1) + \frac{1}{20} (x-2)^5 - \frac{1}{4} (x-2)^4 x - \frac{8}{15} \right] \right\}.$$

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