THE BINARY DISTRIBUTION FUNCTION FOR A DENSE GAS WITH A COULOMB INTERACTION

G. A. MARTYNOV

Physical Chemistry Institute, Academy of Sciences, U.S.S.R.

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On the basis of the Bogolyubov equations it is shown that the distribution functions $G_{a_1 \dots d_S}$ for a system of charged particles have an essential singularity at the point $\rho = 0$, where ρ is the density. Therefore it is impossible to represent them in the form of a series in positive powers of ρ. A method is proposed of "decoupling" the Bogolyubov equations based on a consistent method of taking into account correlations of higher and higher order. It is shown that already in the first approximation the expression obtained in this manner for the binary distribution function agrees up to $\rho \approx 0.3$ with data obtained by the Monte Carlo method.

1 For systems with a short range potential[1] $\phi_{12}^{(S)}$ the virial expansion of the binary distribution function

$$G_{12} = \sum_{k=0}^{\infty} \rho^k g_{12}^{(k)}$$

in powers of the density ρ is always equivalent to the virial expansion for the free energy

$$F = \sum_{k=0}^{\infty} \rho^k F^{(k)}$$

in the sense that the meaning of each term in the series for F is uniquely determined by the value of the corresponding term of the series for G_{12} (i.e., we always have $F^{(k)} = F^{(k)}(g_{12}^{(n)})$). It might seem that a similar situation should also occur in the case of systems whose particles interact with each other in accordance with the law $\Phi_{ab} = \phi_{ab}^{(S)} + \phi_{ab}^{(el)}$, where $\phi_{ab}^{(el)} = e_a e_b / \epsilon r_{12}$ is the Coulomb component of the pair potential (here e_a is the charge of a particle of type a, ϵ is the dielectric permittivity of the medium, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between particles a_1 and b_2). However, if one utilizes the expansions for the binary distribution function obtained, for example, in [1-3], and compares them with the series of Mayer[4]–Haga[5] for the free energy, then one easily obtains that already the second term of the series $F = \Sigma \delta^k F^{(k)}$ receives contributions from all the terms of the series $G_{ab} = \Sigma \delta^k g_{ab}^k$ (here δ is the plasma parameter). A breakdown of the equivalence in this case is due to the fact that the expansions obtained in [1-3] even though they have the form of virial expansions, are not in fact such expansions, since in obtaining them one has utilized (explicitly or implicitly) different kinds of approximations which cannot be rigorously justified. Moreover, we shall show below that the distribution functions for Coulomb systems cannot generally be represented in the form of a virial series, since at low densities they depend on the expansion parameters in a nonanalytic manner.

This somewhat unexpected result has a very simple physical meaning. As is well known, as the density decreases the Debye radius r_D increases without limit. Therefore in the limit $\delta = 0$ a correlation in the position of all the particles arises in the plasma independently of how large (but finite) are the macroscopic dimensions R of the system. At the same time the position of the particles starts to depend on the shape of the vessel in which the system is placed, on the properties of the vessel walls, etc., which is quite inessential in the case $r_D \ll R$. A qualitative change in the properties of a system of charged particles at very low densities finds its expression in the fact that an essential singularity appears in the binary distribution function at the point $\delta = 0$. At the same time the free energy for a Coulomb gas does not have any singularities at the point $\delta = 0$, since as the density decreases the energy of the electrostatic interaction of the particles with one another tends to zero. Therefore it is quite possible to construct virial expansions for the thermodynamic functions for a system of charged particles.

Since the distribution functions for a Coulomb gas cannot be represented in the form of a power series in δ, then in the initial equations we cannot neglect the corresponding terms on the basis that they are proportional to higher powers of the plasma parameter δ. Therefore there remains only one way out of this difficulty: to carry out simplifications in the initial equations based on different kinds of physical considerations, and to check the correctness of the solutions so obtained a posteriori by comparing them with the virial expansions for the free energy, by estimating the neglected terms with the aid of a successive approximation procedure[2] etc. In such an approach there, of course, arises a certain arbitrariness in the choice of the equation for the first approximation, but as will be shown below, in practice it is not particularly significant.

In the present article we first investigate the problem of the virial expansions basing ourselves on the set of Bogolyubov[7] equations for the distribution functions $G_{a_1 \dots d_n}$, n = 1, 2, ...,

[1] Here and in subsequent discussion the numerical subscripts indicate the numbers, and the letter subscripts the numbers and the kind of particles to which the given function refers.

[2] Bogolyubov[7] was the first to point out the necessity of evaluating the distribution functions for a Coulomb gas by means of the method of successive approximations.

$$\nabla_1\Theta G_{a_1\dots d_n} + G_{a_1\dots d_n}\nabla_1 U_{a_1\dots d_n} + \int_V \sum_{1\leqslant k\leqslant M} \nu_k G_{a_1\dots d_n, k_{n+1}} \nabla_1 \Phi_{a_1, k_{n+1}} d^3 r_{n+1} = 0 \quad (1)$$

(we have here adopted the following notation: $\Theta = kT$ is the temperature, $U_{a_1\dots d_n} = \sum_{1\leq i\leq j\leq n} \Phi a_i b_j$ is the configuration energy of a complex of n particles of the kind a, ..., d, $\nu_a = N/V$ is the number of particles of type a per unit volume, r_i is the position vector of the particle a_i, M is the number of different kinds of particles in the system) and we then consider one of the possible methods of constructing a series of successive approximations for the binary distribution function.

2. From the infinite set of solutions of the Bogolyubov equations (1) only those correspond to a canonical distribution, (and, consequently, have physical meaning) which satisfy the normalization conditions, the symmetry conditions, the condition for reducing the correlations etc. These conditions appear here essentially in the role of ordinary boundary conditions utilized in solving differential equations. It is therefore natural from the outset to attempt to put expression (1) into such a form in which the imposition of supplementary conditions (or, at least, a part of them) would be superfluous. As has been shown in [8], this problem can be solved by going over from the distribution functions $G_{a_1\dots d_n}$ to the correlation functions $g_{a_1\dots d_n}$ by means of the relations of the type[3)]

$$G_{ab} = \gamma_{ab}[1 + g_{ab}], \qquad G_{abc} = \gamma_{ab}\gamma_{ac}\gamma_{bc}[1 + (g_{ab} + g_{ac} + g_{bc}) + g_{abc}] \quad (2)$$

etc., where $\gamma_{ab} = \exp[-\phi_{ab}^{(S)}/\Theta]$. The linear replacement (2) is the most general one in the sense that under appropriate assumptions with respect to the dependence of g_{abc} on g_{ab} it includes also arbitrary nonlinear replacements. Thus, for example, by setting

$$g_{abc} = (g_{ab}g_{ac} + g_{ab}g_{bc} + g_{ac}g_{bc}) + g_{ab}g_{ac}g_{bc} + \overset{*}{g}_{abc},$$
$$C_{ab} = 1 + g_{ab},$$

we obtain for the triple function the multiplicative replacement

$$G_{abc} = \gamma_{ab}\gamma_{ac}\gamma_{bc}(C_{ab}C_{ac}C_{bc} + \overset{*}{g}_{abc}) = G_{ab}G_{ac}G_{bc} + \overset{*}{G}_{abc}$$

Substituting (2) into (1) and going over to the dimensionless coordinates $t_i = r_i/r_0$, where r_0 is the diameter of the particles we obtain

$$\nabla_1 g_{ab} + \lambda_{ab}\chi\nabla_1\left(\frac{1}{t_{12}}\right)[1 + g_{ab}] + \int_V \Big\{ \sum_c n_c[1 + (g_{ab} + g_{ac} + g_{bc}) + g_{abc}]\left[\lambda_{ac}\frac{\varkappa^2}{4\pi}\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{t_{13}}\right) - \frac{\rho}{\pi}\gamma_{23}\nabla_1\gamma_{13}\right]\Big\} d^3t_3 = 0 \quad (3)$$

etc., where

$$\lambda_{ab} = \frac{e_a e_b}{e^2}, \quad n_a = \frac{\nu_a}{\nu}, \quad \nu = \sum_{1\leqslant a\leqslant M}\nu_a, \quad \sum_a n_a = 1,$$
$$\varkappa^2 = \left(\frac{r_0}{r_D}\right)^2 = \frac{4\pi\nu e^2 r_0^2}{\varepsilon\Theta}, \quad \chi = \frac{e^2}{\varepsilon\Theta r_0}, \quad \rho = \pi r_0^3\nu.$$

In (3) we have assumed for the sake of simplicity that $\gamma_{a_i b_j} = \gamma_{ij}$ do not depend on the kind of particles.

[3)] A similar replacement was utilized by Tyablikov and Tolmachev[1] who, however, defined γ_{ab} as $\gamma_{ab} = \exp[-\phi_{ab}^{(S)}/\Theta - \varphi]$, where φ is some component of the potential for the average force.

The condition for reducing the correlations in accordance with which $G_{ab} \to 1$ as $r \to \infty$ can only be satisfied if the system is as a whole neutral[9], i.e., if $\sum_a \nu_a e_a = 0$ or, what is the same thing, if

$$\sum_{1\leqslant a\leqslant M} n_a\lambda_{ab} = 0, \quad (4)$$

while the condition for the finiteness of the density fluctuations from which it follows that $\lim_{r\to\infty} r^3 g_{ab}(r) = 0$ only if the system is locally neutral[9]. The latter statement means that the charge e_a of each ion must be neutralized by the charge of its "atmosphere," i.e.,

$$e_a + 4\pi\int_0^\infty \sum e_b\nu_b G_{ab}(r) r^2\, dr = 0.$$

Substituting into this expression G_{ab} from (2), taking into account the condition of overall neutrality (4), and going over to dimensionless variables we can write the condition for local neutrality in the form

$$\chi + \varkappa^2\int_0^\infty \Big\{\sum_b n_b\lambda_{ab}g_{ab}(t)\Big\}\gamma(t)t^2\, dt = 0. \quad (5)$$

We note, that due to the condition of overall neutrality in (3) the integral satisfies

$$\int_V \sum_c n_c\lambda_{ac}(1 + g_{ab})\frac{\varkappa^2}{4\pi}\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{t_{13}}\right) d^3t_3 = \Big\{\sum_c n_c\lambda_{ac}\Big\}\int_V (\dots) d^3t_3 = 0.$$

Therefore (3) assumes the form

$$\nabla_1 g_{ab} + \lambda_{ab}\chi\nabla_1\left(\frac{1}{t_{12}}\right)[1 + g_{ab}] + \frac{\varkappa^2}{4\pi}\int_V \Big\{\sum_c n_c\lambda_{ac}[(g_{ac} + g_{bc}) + g_{abc}]\Big\}\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{t_{13}}\right) d^3t_3 - \frac{\rho}{\pi}\int_V \Big\{\sum_c n_c[1 + (g_{ab} + g_{ac} + g_{bc}) + g_{abc}]\Big\}\gamma_{23}\nabla_1 f_{13}\, d^3t_3 = 0 \quad (6)$$

etc., where $f_{ik} = \gamma_{ik} - 1$ is the Mayer function. Adding to (6) the boundary conditions at infinity

$$\lim_{ik} g_{a_1\dots d_n} = 0 \quad (7)$$

and the condition for the symmetry of the functions $g_{a_1\dots d_n}$ with respect to the permutation of the coordinates and the charges of the particles a_1, ..., d_n, we obtain a complete system of equations. In this case it turns out to be superfluous to impose normalization conditions, a reduction in the correlations, and a boundary condition at "zero."

3. We investigate first of all the question of the possibility of solving the set of equations (6) by means of virial expansions. It is possible to construct from quantities characterizing the state of a system of charged particles three parameters having the dimensions of length: the diameter of the particles r_0, the Bjerrum radius $r_B = e^2/\epsilon\Theta$, and the Debye radius $r_D = (\epsilon\Theta/4\pi\nu e^2)^{1/2}$. Therefore in (1) one can go over to the dimensionless coordinates in three different ways. If we set $t = r/r_0$ then, as may be seen from (6), three dimensionless parameters appear in the equations $-\chi$, κ and

ρ, in terms of which the expansion must be carried out[4]. Carrying out elementary calculations it can be easily shown that the coefficient in the series of the term of the first degree in χ is equal to λ_{ab}/t. Substitution of this expression into the formulas for the coefficients of higher powers of χ, κ, and ρ leads to the result that the corresponding integrals diverge at infinity. Therefore, it is not possible to perform an expansion in terms of χ, κ, and ρ.

Setting $\tau = \mathbf{r}/r_B$ we obtain instead of (6)

$$\nabla_1 g_{ab} + \lambda_{ab}\nabla_1\left(\frac{1}{\tau_{12}}\right)[1+g_{ab}] + \frac{\rho\chi^3}{\pi}\left\{\int_V (\ldots)\nabla_1\left(\frac{1}{\tau_{13}}\right)d^3\tau_3 - \int_V |(\ldots)\nabla_1 f_{13}\, d^3\tau_3\right\} = 0.$$

This equation depends only on the single parameter $\delta^* = \chi^3\rho$. But it is also not possible to expand in terms of δ^* since the coefficient of the first term in the series $g^0_{ab} = \exp[-\lambda_{ab}/\tau] - 1$ falls off at infinity just as slowly as in the case of expansions in terms of χ, κ, and ρ. Therefore, the only possibility remains to go over to measuring lengths in terms of the Debye radius. In this case (6) assumes the form

$$\nabla_1 g_{ab} + \lambda_{ab}\delta\nabla_1\left(\frac{1}{\tau_{12}}\right)[1+g_{ab}] + \frac{1}{4\pi}\int_V \sum_c n_c\lambda_{ac}[(g_{ac}+g_{bc}) + g_{abc}]\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{\tau_{13}}\right)d^3\tau_3 - \frac{1}{4\pi\delta}\int_V \sum_c n_c[1+(g_{ab}+g_{ac}+g_{bc}) + g_{abc}]\gamma_{23}\nabla_1 f_{13}\, d^3\tau_3 = 0 \quad (8)$$

etc., where $\tau = \mathbf{r}/r_D = \kappa t$ and $\delta = \chi\kappa$ is the plasma parameter.

δ appears in (8) not only explicitly in the form of factors, but also implicitly through $\gamma_{ik} = f_{ik} + 1 = \gamma(t_{ik}) = \gamma(\chi\tau_{ik}/\delta)$. However, one cannot expand γ_{ik} in powers of δ since in this case a pole of order higher than the first[5] appears at the point $\tau = 0$ and all the integrals diverge at the origin. But abandoning the expansion of γ_{ik} is equivalent to the fact that in (8) we retain not only positive, but also negative powers of δ and, consequently, the series for the correlation functions in this case must have the form

$$\sum_{-\infty \leqslant k \leqslant \infty} \delta^k g^{(k)},$$

where $g^{(k)}$ depend on δ through γ_{ik}. Therefore, in specific calculations one can by no means restrict oneself to a finite portion of the series, since, judging by the factors δ^{-k} the neglected terms are certainly greater than the ones that have been retained. However, in fact we can in general say nothing about the magnitude of the remainder of the series since the coefficients of the expansion $g^{(k)} = g^{(k)}(\delta)$ and, consequently, the limit of the product $\delta^k g^{(k)}(\delta)$ is not known a priori for $\delta \to 0$.

Of no lesser significance is the fact that in working with the Bogolyubov equations written in the form (8) it is in general impossible to "uncouple" the whole system, since terms of the same order of smallness in δ appear simultaneously in all the equations of the system (this follows from the fact that there is no factor δ in front of the first (Coulomb) integral in all the equations in (8); cf., note added in proof). Therefore in practice g_{ab} cannot be represented in the form of a series in powers of δ. And since there exist no other dimensionless parameters in addition to those which have been considered above, the latter means that the distribution functions for a Coulomb system cannot in general be expanded in terms of virial series[6].

4. In order to eliminate the difficulties arising in the evaluation of the distribution functions for a Coulomb system one ordinarily utilizes different kinds of approximations which, however, cannot be justified from a formal point of view[7]. But since in the majority of cases these approximations have a clear physical meaning, the results obtained with their aid turn out to be quite sensible. Taking into account what has been said above, we, from the outset, renounce all attempts of justifying the approximation that has been made by estimating the value of the letter factor preceding one or another of the terms, and will proceed only on the basis of physical considerations.

With this aim in view we note that in a sufficiently rarified Coulomb gas the average distances between the particles are large, and, consequently, the average energy of the electrostatic interaction expressed per particle is small in comparison with Θ. Therefore the correlation in the position of individual particles due to this interaction is also small. And this means that in the first approximation it is possible to retain in (6) under the integral only terms with g_{ab} which take into account the linear components of triple correlations, and to neglect terms with g_{abc} which describe the nonlinear components of the correlations. In the second approximation it is possible to neglect the nonlinear components arising in the simultaneous collision of four particles by setting in the equation for g_{abc} the term with $g_{abcd} = 0$, etc. Thus, for the "uncoupling" of the infinite set of equations (6) the use of a series of successive approximations in terms of the order of the correlations naturally suggests itself and we now proceed to investigate it. In doing this we everywhere restrict ourselves to equations of only the first approximation.

5. We begin by considering two limiting cases: a system of uncharged particles and a low density Coulomb gas, and we then go over to a dense Coulomb gas. By setting in (6) $\chi = \kappa = 0$ and $g_{abc} = 0$ we obtain in the first approximation for determining the binary function for a system of particles of one kind the equation

[4] Actually, the expansion must be carried out only in terms of two of them, since only two parameters are independent; the magnitude of the third parameter is determined by the relation $\kappa^2 = 4\chi\rho$. However, in this case this is immaterial.

[5] The presence of such a pole is needed in order that $\Phi_{ab} = \phi_{12}^{(S)} + \phi_{ab}^{(el)}$ should tend to $+\infty$ as $r_{12} \to 0$, which is important in order to guarantee the stability of the system.

[6] Generally speaking an expansion in a series of the type $g_{ab} = \sum_{k=0}^{\infty} \delta^k g_{ab}^{(k)}(\delta)$ is possible (cf., for example, [2]), but in this case the question of the radius of convergence of such a series remains open (since such a series is not a series in powers of a small parameter).

[7] For example, in [1] terms with g_{abc} were omitted in (8), although they are the same order of smallness (with respect to δ), as the terms that have been retained, in [10] terms with $1/\delta$ were omitted, although formally they are larger than the terms that have been retained, in [11] the initial expressions were expanded in terms of different parameters at large and at small distances, etc.

$$\nabla_1 g_{12} = \frac{\rho}{\pi}\int_V [1+(g_{12}+g_{13}+g_{23})]\gamma_{23}\nabla_1 f_{13}\, d^3t_3.$$

Restricting ourselves for the sake of simplicity to a system of hard spheres for which

$$f = \begin{cases} -1, & 0 \leqslant t < 1 \\ 0, & 1 \leqslant t \leqslant \infty \end{cases},$$

we obtain after some elementary transformations

$$g(t) = \rho[1+g(1)]\left(\frac{4}{3} - t + \frac{1}{12}t^3\right) + \rho\left\{\int_t^2 \left(1-\frac{1}{4}\tau^2\right) g(\tau)\, d\tau - \frac{1}{t}\int_1^{t+1} g(\tau)\tau[1-(\tau-t)^2]\, d\tau\right\}, \qquad 1 \leqslant t \leqslant 2;$$

$$g(t) = -\frac{\rho}{t}\int_{t-1}^{t+1} g(\tau)\tau[1-(\tau-t)^2]\, d\tau, \quad 2 \leqslant t \leqslant \infty.$$

We solve this system by the method of iterations. An investigation of the behavior of g(t) at large distances which was carried out in[12], has shown that for $\rho \lesssim 1$ the function g(t) tends very rapidly to zero for $t \to \infty$. Therefore, it is sensible to take for the first approximation

$$g^{(1)}(t) = \begin{cases} \rho[1+g(1)](4/3 - t + 1/12\, t^3), & 1 \leqslant t \leqslant 2 \\ 0, & 2 \leqslant t \leqslant \infty. \end{cases}$$

Substituting this expression into the equations for g we obtain in the second approximation

$$g^{(2)} = g^{(1)}(t) + \rho[1+g(1)]\left\{\frac{9}{70}\frac{1}{t} + \frac{5}{12} - \frac{23}{20}t + \frac{1}{2}t^2 + \frac{1}{9}t^3 - \frac{1}{12}t^4 + \frac{1}{288}t^6\right\}$$

etc. Since the pressure P in a system of hard spheres[12] is determined by the formula

$$p = P/\nu\Theta = 1 + 2/3\rho[1+g(1)],$$

then with the aid of some simple calculations we obtain

$$p = \frac{12 + 3\rho + 0.88214\rho^2 - 0.57222\rho^3 + \ldots}{12 - 5\rho + 0.88214\rho^2 - 0.57222\rho^3 + \ldots}. \tag{9}$$

The results of numerical calculations in accordance with this equation are exhibited below. We also give there for comparison the values of p found with the aid of a 5-term portion of the virial series and of the Percus-Yevick equation[13]. A comparison of these data shows that (9) guarantees quite satisfactory accuracy up to $\rho \approx 1$.

Virial Series (5 terms):	0.238	0.352	0.612	1.069
	1.176	1.273	1.534	2.163
Percus-Yevick equation:				
	1.176	1.273	1.532	2.149
Equation (9):	1.176	1.273	1.535	2.227

6. In the case of a low density Coulomb gas it is possible to neglect in the first approximation not only terms with g_{abc}, but also terms proportional to ρ. As a result of this we obtain

$$\nabla_1 g_{ab} + \lambda_{ab}\chi\nabla_1\left(\frac{1}{t_{12}}\right)[1+g_{ab}] + \frac{\kappa^2}{4\pi}\int_V \left\{\sum_c n_c\lambda_{ac}(g_{ac}+g_{bc})\right\}\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{t_{13}}\right) d^3t_3 = 0. \tag{10}$$

Since the parameters κ, χ and ρ are interrelated by the equation $\rho = \kappa^2/4\chi$, then the condition $\rho \ll 1$ which is needed to make (10) valid assumes that $\kappa^2 \ll 4\chi$.

In what follows we restrict ourselves to a discussion of the binary system of charged hard spheres of diameter r_0 for which

$$\phi^{(s)}(t) = \begin{cases} \infty, & 0 \leqslant t < 1 \\ 0, & 1 \leqslant t \leqslant \infty \end{cases},$$

$$\gamma(t) = \begin{cases} 0, & 0 \leqslant t < 1 \\ 1, & 1 \leqslant t \leqslant \infty \end{cases}, \quad e_+ = -e_- = e, \quad \nu_+ = \nu_- = 1/2\nu. \tag{11}$$

In this case (10) is equivalent to a system of two equations for the two correlation functions $g_{++} = g_{--}$ and $g_{+-} = g_{-+}$, instead of which it is convenient to introduce the functions M(t) and R(t) by means of the relation

$$g_{ab} = 1/2\{g_{ab}(\lambda_{ab}; t) - g_{ab}(-\lambda_{ab}; t)\} + 1/2\{g_{ab}(\lambda_{ab}; t) + g_{ab}(-\lambda_{ab}; t)\} = -\lambda_{ab}M(t) + R(t). \tag{12}$$

Substituting (12) into (10) and combining terms involving λ_{ab} we obtain

$$\nabla_1 M_{12} + \frac{\kappa^2}{4\pi}\int_V{}' M_{23}\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{t_{13}}\right) d^3t_3 = \chi R_{12}\nabla_1\left(\frac{1}{t_{12}}\right), \tag{13}$$

$$\nabla_1 R_{12} = \chi M_{12}\nabla_1\left(\frac{1}{t_{12}}\right) + \frac{\kappa^2}{4\pi}\int_V M_{13}\gamma_{13}\gamma_{23}\nabla_1\left(\frac{1}{t_{13}}\right) d^3t_3, \tag{14}$$

where the prime on the integral in (13) indicates that we have taken into account the condition of local neutrality (5). Replacing in the integrals in (13) and (14) γ_{13} by $\gamma_{13} = 1 + f_{13}$ we reduce each of them to a sum of two integrals one of which is taken over all space with the exclusion of a sphere of unit radius with its center at t_1, and the other over a sphere of unit radius with its center at t_2. The corresponding integrals can be easily evaluated, and as a result of this (13), (14) assume the form

$$M'(t) + \frac{\kappa^2}{t^2}\left\{\int_{t-1}^{\infty}\gamma(\tau)M(\tau)\tau^2\, d\tau + \frac{1}{4}\int_{t-1}^{t+1}\gamma(\tau)M(\tau)\tau[(\tau-1)^2 - t^2]\, d\tau\right\} = -\chi\frac{R(t)}{t^2}, \tag{15}$$

$$R'(t) = -\frac{\chi}{t^2}\left\{M(t) + \frac{1}{2}\rho\int_{t-1}^{t+1}\gamma(\tau)M(\tau) \times\left[2(t^2+1) - \tau^2 - \frac{(t^2-1)^2}{\tau^2}\right] d\tau\right\}. \tag{16}$$

We emphasize that this system is exactly equivalent to the initial equation (10).

Omitting in (16) the term proportional to ρ we obtain

$$G_{ab}(t) = \gamma(t)\left\{1 - \lambda_{ab}M(t) + \chi\int_t^{\infty} M(\tau)\frac{d\tau}{\tau^2}\right\}, \tag{17}$$

since it follows from (16) that

$$R(t) = \chi\int_t^{\infty} M(\tau)\frac{d\tau}{\tau^2}.$$

Finally, substituting the expression for R(t) into (15) and differentiating the resultant equation we transform it to a more convenient form:

$$m''(t) = \chi^2\frac{m(t)}{t^4} + \frac{1}{2}\kappa^2\int_{t-1}^{t+1}\gamma(\tau)m(\tau)\, d\tau, \tag{18}$$

where m = tM. This equation determines the function m(t) up to a factor A which can be obtained from the condition of local neutrality. Substituting into (5) in place of g_{ab} its expression from (12) we obtain

$$\chi + \kappa^2\int_1^{\infty} m(\tau)\tau\, d\tau = 0. \tag{19}$$

The system (18), (19) already completely defines the problem.

7. With the aid of the mean value theorem (18) can be written in the form

$$m''(t) = \chi^2 m(t) / t^4 + \varkappa^2 m(t+\zeta),$$

where $t-1 \leq \zeta \leq t+1$. From here it follows immediately that for $t \gtrsim t_0 = \sqrt{\chi/\kappa}$[8] one can neglect the term involving χ^2 in (18), and after this (18) reduces to

$$m''(t) = \frac{1}{2}\varkappa^2 \int_{t-1}^{t+1} m(\tau)\,d\tau, \quad t_0 \lesssim t \leqslant \infty. \tag{20}$$

The general solution of this equation has the form

$$m(t) = \sum_k A_k \exp[-a_k t], \tag{20'}$$

where

$$a^3 = \varkappa^2 \operatorname{sh} a. \tag{21}$$

In[14] it was shown that equation (21) has two real roots $a_1 = \alpha_1$ and $a_2 = \alpha_2$ and an infinite number of complex conjugate roots $a_k = \alpha_k + i\omega_k$. For $\kappa \to 0$ the quantity $\alpha_1 \to \kappa$, while $\alpha_2, \alpha_3, \ldots \to \infty$, and the inequality $\alpha_1 \leq \alpha_2 < \ldots < \alpha_k < \ldots$ is always satisfied. Because of this one can in (20') to a high degree of accuracy retain only one term setting $m = A\exp(-\alpha_1 t)$.

For $t < t_0$ one can omit in (18) the term with κ^2, and after this it reduces to

$$m''(t) = \chi^2 m(t) / t^4, \quad 1 \leqslant t \lesssim t_0. \tag{22}$$

The general solution of this equation has the form

$$m(t) = At \operatorname{sh}\frac{\chi}{t} + Bt \operatorname{ch}\frac{\chi}{t}. \tag{23}$$

However, here because of the relation (12) the constant B should be set equal to zero.

8. In the case of low concentrations when $\alpha_1 \to \kappa \to 0$, the solution of equation (18) can be easily obtained by the method of iterations. We define the $(n+1)$-st approximation by means of the relation

$$m''_{n+1}(t) = \chi^2 \frac{m_n(t)}{t^4} + \frac{1}{2}\varkappa^2 \int_{t-1}^{t+1} \gamma(\tau) m_n(\tau)\,d\tau, \tag{24}$$

and for m_1 we take $m_1 = A\exp(-\alpha_1 t)$, since in the case of low concentrations the principal contribution to the free energy comes from large distances. Substituting m_1 into the right-hand side of (24), integrating and omitting all terms of the type $\alpha_1^k t^{-p}\exp(-\alpha_1 t)$ for $k \geq 1$ and arbitrary p[9], we obtain the recurrence formula

$$m_{n+1} = m_n + A[\chi^{2n}/(2n+1)!]\cdot \exp(-\alpha_1 t)/t^{2n},$$

whence we have

$$\lim_{n\to\infty} m_n(t) = m(t) = \frac{A}{\chi} t e^{-\alpha_1 t} \operatorname{sh}\frac{\chi}{t}.$$

In determining the constant A from the condition of local neutrality (19) we obtain

$$G_{ab}(t) = \gamma(t)\left\{1 + \frac{\chi}{\varkappa^2 B} \times \exp(-\alpha_1(t-1)) \times\left[\exp\left(-\frac{\lambda_{ab}\chi}{t}\right) - 1\right]\right\}, \tag{25}$$

where

$$B = \int_1^\infty t^2 \exp(-\alpha_1(t-1)) \operatorname{sh}\frac{\chi}{t}\,dt,$$

and for $\alpha_1 \approx \kappa \ll 1$ the quantity B is given by $B \approx \chi(1+\alpha_1)/\kappa^2$. If we now substitute (25) into the formula which relates the internal energy of the system $U = -\frac{1}{2}N\Theta\chi\tilde{U}$ to G_{ab} and if we set $\delta = \chi\kappa$, then we obtain

$$\tilde{U} = \frac{1}{\chi} \times\left\{\delta + \delta^2 \sum_{k=0}^{\infty} \frac{\chi^{2k-1}}{(2k+1)!(2k-1)} + O(\delta^3)\right\}, \tag{26}$$

and this coincides exactly with the first two terms of the series $\tilde{U} = \Sigma_k \delta^k \tilde{u}(k)$ obtained by Mayer[4] and Haga[5] by the method of summing ring diagrams. It can already be seen from here that all the terms of the series $G_{ab} = \Sigma_k \delta^k g_{ab}^{(k)}$ give contributions to the term $\tilde{U}^{(2)}$ in (26), since after going over to the dimensionless coordinates $\tau = \kappa t$ we obtain that in (25)

$$\exp\left(-\frac{\lambda_{ab}\chi}{t}\right) = \exp\left(-\frac{\lambda_{ab}\delta}{\tau}\right) = \sum_{k=0}^{\infty} \frac{(-\lambda_{ab})^k}{k!}\left(\frac{\delta}{t}\right)^k.$$

Table I

ρ	$\varkappa$	α	$\tilde{U}^{(1)}$	$\tilde{U}^{(2)}$	$\tilde{U}^{(3)}$	$\tilde{U}^{(\infty)}$	$\tilde{U}^{(M-C)*}$	$\tilde{U}^{(D-H)}$	$\tilde{U}^{(\alpha)***}$	$\Delta^{(1)}$	$\Delta^{(2)}$	$\Delta^{(D-H)**}$	$\Delta^{(\alpha)***}$
0.0014	0.100	0.100	0.0909	0.0932	0.0934	0.0935	0.935	0.0909	0.0941	0.004	0.002	0.002	—0.027
0.0125	0.298	0.300	0.231	0.238	0.240	0.242	0.242	0.230	0.244	—0.001	0.001	0.010	—0.089
0.0337	0.490	0.500	0.334	0.343	0.345	0.348	0.351	0.329	0.354	—0.013	0.000	0.020	—0.193
0.0635	0.673	0.700	0.412	0.421	0.423	0.426	0.424	0.402	0.437	—0.039	—0.004	0.028	—0.296
0.0996	0.843	0.900	0.474	0.481	0.482	0.485	0.486	0.457	0.500	—0.080	—0.008	0.035	—0.379
0.140	0.998	1.100	0.524	0.528	0.530	0 532	0.543	0.499	0.551	—0.134	—0.015	0.041	—0.437
0.182	1.137	1.300	0.565	0.567	0.568	0.570	0.594	0.532	0.592	—0.202	—0.011	0.046	—0.474
0.223	1.26	1.500	0.600	0.596	0.596	0.596	0.637	0.557	0.626	—0.282	—0.002	0.050	—0.504
0.308	1.48	2.000	0.667	0.650	0.642	0.634	0.678	0.597	0.690	—0.528	0.017	0.058	—0.766
0.373	1.63	2.500	0.715	0.687	0.650	--	0.690	0.620	0.735	—0.823	0.042	0.060	—

*The values of $U^{(M-C)}$ are obtained by means of a graphical interpolation of the table data given in[15].
**The values of $U^{(D-H)}$ and $\Delta^{(D-H)}$ are evaluated on the basis of formula (30).
***The values of $U^{(\alpha)}$ and $\Delta^{(\alpha)}$ are evaluated on the basis of formula (25).

[8] A more exact estimate shows that $t_0 = \sqrt{\chi/\alpha_1}$, where α_1 is the first root of the transcendental equation (21).

[9] One cannot expand the exponentials in terms of α_1 since for $t \to \infty$ the product $\alpha_1 t$ can become arbitrarily large for an arbitrary small but finite value of α_1.

It is essential that in the expansion of the exponential it is not possible to neglect a single term since in the opposite case it is not possible to obtain an exact value for the coefficient of δ^2 in (26).

It can be easily noted that (25) for $t \to 1$ and $t \to \infty$ coincides with the well known formula of Tyablikov-Tolmachev[1]

$$G_{ab}(t) = \gamma(t)\exp\left[-\frac{\lambda_{ab}\chi}{t}e^{-\varkappa t}\right], \qquad (27)$$

while for $\kappa t \approx 1$ an essential difference arises. Remaining within the framework of low densities it is not possible to single out any one of these formulas, since (25) and (27) equally lead to physically sensible results both at large and at small distances (i.e., where they coincide) and equally correctly determine the first two terms of the series (26). However, in all probability formula (25) is nevertheless more accurate, since in extrapolating greater densities it gives considerably better results (cf., Fig. 1 and Table I).

Formula (25) can be easily made more exact. If in the evaluation of the approximations one retains also terms of order $\alpha_1\exp(\alpha_1 t)/t^p$ then in place of (25) we obtain

$$G_{ab}(t) = \gamma(t)\left\{1+\frac{\chi}{\varkappa^2 B}\exp(-\alpha_1(t-1))\left[\exp\left(-\frac{\lambda_{ab}\chi}{t}\right)-1\right]\right.$$
$$\left.\times\left[1+\alpha_1 t\left(1+\frac{\lambda_{ab}\chi}{t}\frac{\exp(-\lambda_{ab}\chi/t)}{\exp(-\lambda_{ab}\chi/t)+1}\right)\right]\right\}, \qquad (28)$$

where the constant B determined by the condition of local neutrality (19) is equal to

$$B = \int_1^\infty (1+\alpha_1 t)t^2\exp(-\alpha_1(t-1))\,\mathrm{sh}\frac{\chi}{t}\,dt$$
$$-\chi\alpha_1\int_1^\infty t^2\exp(-\alpha_1(t-1))\,\mathrm{ch}\frac{\chi}{t}\,dt.$$

One can also group terms of higher order in α_1, but the final expressions in this case turn out to be too awkward.

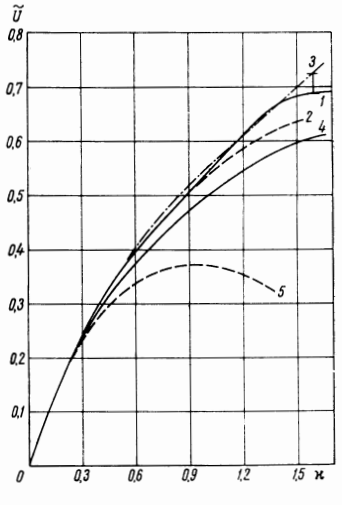

FIG. 1. The internal energy $U = -\frac{1}{2}N\Theta\chi\tilde{U}$ for a system of charged spheres evaluated: 1—by the Monte Carlo method, 2—for $\tilde{U}^{(\infty)}$, 3—by means of formula (25), 4—by means of the Debye-Hückel formula (31), 5—by means of the Tyablikov-Tolmachev formula (27). The notation I indicates the change in the value of $\tilde{U}^{(M-C)}$ with an increase in the number of particles in a cell in the Monte Carlo method.

Table II

$\varkappa$	$\tilde{U}$	χ = 0	1	2	3	4	5
0.490	$\tilde{U}^{(1)}$	0,334	0,334	0,334	0,334	0,334	0,334
	$\tilde{U}^{(2)}$	0,333	0,336	0,345	0,360	0,378	0,398
	$\tilde{U}^{(3)}$	0,333	0,337	0,348	0,368	0,395	0,429
0.922	$\tilde{U}^{(1)}$	0,500	0,500	0,500	0,500	0,500	0,500
	$\tilde{U}^{(2)}$	0,496	0,499	0,508	0,522	0,539	0,557
	$\tilde{U}^{(3)}$	0,495	0,499	0,511	0,531	0,555	0,577
1.26	$\tilde{U}^{(1)}$	0,600	0,600	0,600	0,600	0,600	0,600
	$\tilde{U}^{(2)}$	0,587	0,590	0,598	0,610	0,629	0,639
	$\tilde{U}^{(3)}$	0,585	0,588	0,599	0,618	0,639	0,648
1.48	$\tilde{U}^{(1)}$	0,667	0,667	0,667	0,667	0,667	0,667
	$\tilde{U}^{(2)}$	0,644	0,646	0,652	0,661	0,672	0,684
	$\tilde{U}^{(3)}$	0,637	0,637	0,645	0,663	0,681	0,691

9. From the preceding it can be seen that the series $G_{ab} = \Sigma_n \tilde{g}^{(n)}_{ab}$ based on a consistent taking into account of correlations of higher and higher orders already in the first approximation correctly determines the first two terms of the series $F = \Sigma\delta^n F^{(n)}$ for the free energy. At the same time the series for the binary function is certainly not virial and, consequently, it cannot be a priori asserted that its radius of convergence is restricted by the condition $\delta \lesssim 1$. Moreover, there are definite qualitative considerations which indicate that the domain of convergence of the series with respect to the order of the correlations is restricted by the considerably weaker condition $\rho \lesssim 1$.

Indeed, for $\delta > 1/3$ the screening of the charge of each ion is accomplished by only a single "anti-ion"[10], and this is only possible in the case if both particles appear to unite into a single neutral quasimolecule. At the same time for $\rho \lesssim 1$ the average distance between such quasimolecules is so great that the probability of a simultaneous collision of two or more "molecules" is small. Therefore one can assume that for $\delta > 1$, but $\rho \lesssim 1$, the contribution to the free energy of nonlinear correlations arising due to the simultaneous collision of three or more particles with one another is negligibly small.

In order to check these considerations we obtained a numerical solution of (8) for such values of κ for which it is no longer possible to regard α_1 as small. This solution was also obtained by the method of iterations where for m_1 we have as before taken the solution of (20) $m_1(t) = \exp(-\alpha_1 t)$. From (17) and (19) it follows that in this case in the first approximation the binary distribution function G_{ab} is equal to

$$G^{(1)}_{ab}(t) = \gamma(t)\left\{1-\lambda_{ab}\left(\frac{\alpha_1}{\varkappa}\right)^2\frac{\chi}{1+\alpha_1}\frac{e^{-\alpha_1(t-1)}}{t}\right.$$
$$\left.+\left(\frac{\alpha_1}{\varkappa}\right)^2\frac{\chi^2}{1+\alpha_1}\int_t^\infty\frac{e^{-\alpha_1(\tau-1)}}{\tau^3}\,d\tau\right\}. \qquad (29)$$

Subsequent approximations have been evaluated with the aid of (24), and in each approximation terms of arbitrary order in $\alpha_1^k e^{-\alpha_1 t}/t^p$ were retained. A total of three

[10] It is precisely this that explains the fact that for $\delta \gtrsim 1/3$ the terms of the virial series $F = \Sigma_n \delta^n F^{(n)}$ cease to fall off and the series diverges[9].

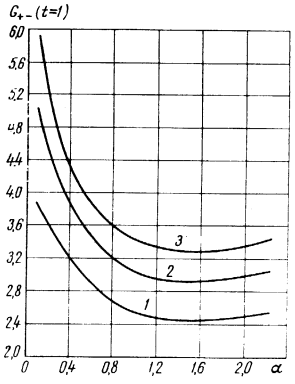

FIG. 2. The dependence of the value of G_{+-} (α_1; t = 1) on the concentration $\alpha_1 = f(\kappa)$ for $\chi = 1.78$: 1—in accordance with formula (29), 2—in accordance with the formula for the second approximation, 3—in accordance with formula (25).

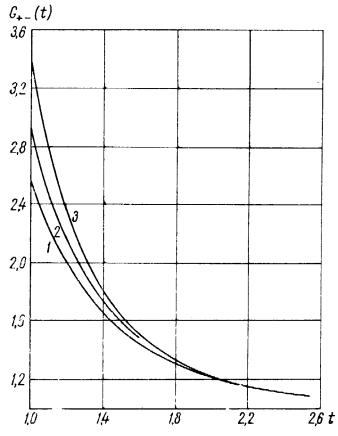

FIG. 3. The dependence of G_{+-} ($\alpha_1 = 1.1$; t) on the distance t for $\chi = 1.78$: 1—in accordance with formula (29), 2—in accordance with the formula for the second approximation and 3—in accordance with formula (25).

approximations was calculated[11] and after this extrapolation to $n \to \infty$ was made. The results of these calculations are shown in the graphs of Figs. 1, 2 and 3, and also in Table I. In all these cases we have taken $\chi = 1.78$, and this enabled us to compare the results obtained for the internal energy with the results of the calculation of the quantity $\tilde{U} = \tilde{U}^{(M-C)}$ by the Monte Carlo method directly from the cannonical distribution[15][12].

From the data of Table I it can be seen that as the ordinal number of the approximation n increases the magnitude of $\tilde{U}^{(n)}$ rapidly tends to its limit, and for $\rho \lesssim 0.1$ (this corresponds to $\kappa \lesssim 0.9$) the difference between $\tilde{U}^{(\infty)}$ and $\tilde{U}^{(M-C)}$ lies within the limits of error of the calculations—it is less than 1%. As ρ increases to ≈ 0.3 (this corresponds to $\kappa \approx 1.5$) the error $\Delta U = (\tilde{U}^{(M-C)} - \tilde{U}^{(\infty)})/\tilde{U}^{(M-C)}$ increases to $\approx 6\%$ [13]. Moreover with the aid of the well known formula connecting the binary distribution function G_{ab} with the pressure P the quantity $P^{(n)}$ was evaluated in different approximations, and then it was checked as to how exactly the thermodynamic identity $(\partial U/\partial V)_\Theta = \Theta(\partial P/\partial\Theta)_V - P$ is satisfied. In Table I we give the corresponding values of the quantity

$$\Delta = \left\{\left[\Theta\left(\frac{\partial P}{\partial \Theta}\right)_V - P\right] - \left(\frac{\partial U}{\partial V}\right)_\Theta\right\} \Big/ \left(\frac{\partial U}{\partial V}\right)_\Theta,$$

from which it can be seen that as the number of the approximation n increases the magnitude of $\Delta^{(n)}$ also rapidly tends to zero.

From all that has been said above it follows that the equation of the first approximation with respect to the correlations (18) in practice exactly defines the free energy of the system up to $\rho \approx 0.3$. If in the initial equations we would have retained terms of order ρ, then quite probably the boundary on the applicability of the equation of the first approximation would have increased to $\rho \approx 1$.

10. The expressions obtained as a result of solving (18) by the method of iterations are not suitable for practical use due to their awkwardness; for this purpose it is necessary to find simpler formulas. In the case $\chi \gg 1$ we can recommend as such a formula either (25) or (28), since evidently in the nearer domain they satisfy sufficiently well (22), while in the further domain they satisfy (20). For $\chi \approx 1$ we can also utilize formula (25) since it determines sufficiently accurately both G_{ab} (cf., Figs. 2, 3), and the value of $\tilde{U}$ (cf., Table I). But the values of the "single-valuedness" parameter $\Delta = \Delta^{(\alpha)}$ evaluated on its basis are quite large (cf., Table I). Therefore it does not guarantee great accuracy in the evaluation of other thermodynamic functions of the system.

More satisfactory for $\chi \approx 1$ is formula (29) for $\kappa = \alpha_1$, when

$$G_{ab}(t) = G_{ab}^{(D\text{-}H)} = \gamma(t)\left\{1 - \lambda_{ab}\frac{\chi}{1+\varkappa}\frac{e^{-\varkappa(t-1)}}{t} + \frac{\chi^2}{1+\varkappa}\int_t^\infty \frac{e^{-\varkappa(\tau-1)}}{\tau^3}d\tau\right\}, \quad (30)$$

which leads to the well known expression for the internal energy:

$$U = -\frac{1}{2}N\Theta\chi\frac{\varkappa}{1+\varkappa}, \quad (31)$$

which was first obtained by Debye and Hückel. Up to those values of κ for which $\alpha_1 \approx \kappa$ (i.e., up to $\kappa \lesssim 1$) it not only gives a sufficiently good description of the binary function (cf., Figs. 2, 3) but it also gives satisfactory values for $\tilde{U}$ and Δ (cf., Table I). It is just this that explains the fact that on the basis of formula (30) it turns out to be possible to develop the thermodynamics of monovalent solutions of strong electrolytes[9][14]

[11] It can be easily shown that with the given choice of m_1 the expression for $m^{(n)}(t)$ has the form $m^{(n)} = m_{00}^{(1)} + \chi^2 m_{20}^{(2)} + \kappa^2 m_{02}^{(2)} + \chi^4 m_{40}^{(3)} + \ldots + \chi^{2k}\kappa^{2l} m_{2k2l}^{(n)}$. We do not quote the corresponding expressions for $m_k^{(n)}$ since they are too awkward.

[12] It would be more consistent to estimate the contribution of g_{abc} obtaining it from the second equation of the Bogolyubov chain. However owing to mathematical difficulties we have not yet succeeded in doing so.

[13] Since $\delta = \delta_0 \approx 1/3$ defines the boundary for the convergence of the virial series for F, Eq. (18) enables one for $\chi = 1.78$ to move through approximately two orders of magnitude into the region of greater concentrations compared with an expansion in terms of the plasma parameter. For $\chi = 10$ this displacement should amount to $\approx 10^4$ since with increasing χ the range of concentrations within which the Mayer-Haga series (26) converges falls off as χ^{-3} (since $\rho_0 = 0.25\delta_0^2/\chi^3$) while the domain of applicability of (18) is as before determined by the condition $\rho \lesssim 1$. For an ordinary plasma for which $\epsilon = 1$ such a displacement with respect to ρ does not have much significance, since the region of convergence of the virial series includes almost all the practically obtainable values of temperatures and densities. But for solutions of electrolytes ($\epsilon = 80$) this is very essential since it enables us to develop a theory of solutions of finite concentration[9].

[14] We recall that for monovalent electrolytes $\chi \approx 2 - 3$.

which gives good agreement with experiment[6]. From the data of Table 2 it can be seen that the value of $\tilde{U}$ right up to $\chi \approx 3-5$ does not depend strongly on the value of the parameter χ[15]. Therefore formula (30) is valid for small values of $\chi \approx 3-5$, but does not hold for large values of $\chi > 5$.

11. As can be seen from the data of Table I for $\kappa \approx 1.5$ the series of successive approximations ceases to converge. The same occurs also in the case of the Monte Carlo method (cf., Fig. 1). All this indicates that somewhere near the point $\kappa = 1.5-1.7$ a singularity arises in the system of charged spheres. And, indeed, an investigation of the transcendental equation (21) shows that when $\kappa = 1.642$ the two real roots α_1 and α_2 merge and two complex conjugate roots $a_{1,2} = \alpha_1 + i\omega_1$ are formed in their place. Correspondingly for $\kappa > 1.642$ the binary distribution function for $t > t_0$ falls off not as $t^{-1}\exp(-\alpha_1 t)$, but as $t^{-1}\exp(-\alpha_1 t)\cos\omega_1 t$. In other words, at the point $\kappa = 1.642$ a change of structure occurs in the system which, possibly, is accompanied by a phase transition.

In the region $\kappa > 1.642$ a system of charged particles acquires all the features characteristic of systems with a short range potential. This manifests itself not only in the appearance of oscillations in G_{ab} which are always observed for uncharged particles with a hard core, but also in the fact that for $\kappa > 1.642$ the correlation radius $R_k = r_0/\alpha_1$ does not fall off with increasing concentration (i.e., with increasing κ), as is characteristic for a dilute plasma, but, on the contrary, increases (the latter can be established by means of investigating the behavior of the roots of the transcendental equation (21)). At the present time there are some indications obtained in the course of an experimental investigation of concentrated solutions of strong electrolytes which confirm this conclusion.

In conclusion the author expresses his deep gratitude to V. I. Kogan for a detailed discussion of the manuscript of the present article.

Note added in proof (December 11, 1967). One can verify that terms of the same order of smallness in δ appear in all the equations of the Bogolyubov chain in the following manner: we replace in (8) all the γ_{ik} by $f_{ik} = \gamma_{ik} - 1$ and we assume that $f_{ik} = \beta\delta f_{ik}$, where β is a parameter which in finite expressions should be set equal to δ^{-1}. If we now substitute

$$g_{a_1,\ldots,d_s} = \sum_{m,n=0}^{\infty} \beta^m \delta^r g^{(m,n)}_{a_1,\ldots,d_s}$$

into (8) and equate terms involving the same powers of β and δ, then it becomes formally possible to uncouple the infinite chain (8), and moreover after a transition to the dimensionless coordinate $t = r/r_0$ we obtain a series in powers of χ,κ and ρ, obtained earlier by Strel'tsova[3]. But the transition to χ,κ and ρ is not justified, since the initial equations cannot be expanded in terms of these parameters. But if we as before measure distances in terms of the Debye radius then it turns out that it is not possible to evaluate the exact value of the coefficient of δ^n since it contains an infinite number of terms (since for $\beta = \delta^{-1}$ all the terms of the type $\beta^k\delta^{n+k}g(k,n+k)$, $k = 0, 1, \ldots$, turn out to be of order δ^n. Since the distribution function of order k $G^{(k)}$ gives a contribution to $g^{(k,n+k)}$, then terms of the same order of smallness appear simultaneously in all the equations of the Bogolyubov chain. This explains the impossibility of obtaining a closed equation for the distribution functions if they are expanded in powers of δ.

[15] This is a consequence of the fact that

$$\tilde{U} = \int_1^\infty m(\chi, t)\,dt \Big/ \int_1^\infty m(\chi, t)\,t\,dt,$$

as a result of which both the numerator and the denominator increase simultaneously with increasing χ.

[1] S. V. Tyablikov and V. V. Tolmachev, Nauchnye doklady vysshei shkoly, seriya fiziko-matematicheskaya, (Scientific Reports of the Higher Schools, physico-mathematical series) No. 1, 101, 1958; Dokl. Akad. Nauk SSSR 114, 1210 (1957) [Sov. Phys.-Dokl. 2, 299 (1958)].

[2] I. R. Yukhnovskiĭ, Ukr. Fiz. Zh. (Ukr. J. Phys.) 4, 169 (1959).

[3] E. A. Strel'tsova, Ukr. Matem. Zh. (Ukr. J. Math.) 18, 69 (1966).

[4] J. E. Mayer, J. Chem. Phys. 18, 1426 (1950).

[5] E. J. Haga, Proc. Phys. Soc. Japan 8, 714 (1953).

[6] G. A. Martynov and Yu. M. Kessler, Élektrokhimiya (Electrochemistry) 3, 76 (1967).

[7] N. N. Bogolyubov, Problemy dinamicheskoĭ teorii v statisticheskoĭ fizike (Problems of Dynamical Theory in Statistical Physics), Gostekhizdat, 1946.

[8] G. A. Martynov, Élektrokhimiya (Electrochemistry) 1, 332 (1965).

[9] G. A. Martynov, Usp. Fiz. Nauk 91, 455 (1967) [Sov. Phys.-Usp. 10, 171 (1967)].

[10] V. I. Tseplyaev, Dokl. Akad. Nauk SSSR 143, 829 (1962) [Sov. Phys.-Dokl. 7, 319 (1962)].

[11] V. S. Markin and Yu. A. Chizmadzhev, Élektrokhimiya (Electrochemistry) 2, 131 (1966).

[12] G. A. Martynov, Zh. Eksp. Teor. Fiz. 45, 656 (1963) [Sov. Phys.-JETP 18, 450 (1963)].

[13] T. Everett, J. Chem. Phys. 9, 474 (1963).

[14] G. A. Martynov, Collection of articles "Issledovaniya v oblasti poverkhnostnykh sil" (Investigations in the Field of Surface Forces) Nauka, 1964, p. 102.

[15] N. N. Vorontsov-Vel'yaminov and A. M. El'yashevich, Élektrokhimiya (Electrochemistry) 4, 1075 (1968).

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