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Abstract

Full Text

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EQUATIONS FOR THE CORRELATION FUNCTIONS OF AN EQUILIBRIUM SYSTEM OF COULOMB PARTICLES WITH SHORT-RANGE INTERACTION

(Presented by Academician N. N. Bogolyubov, 15 XI 1961)

In this article a method is proposed for taking into account short-range repulsive forces for a classical system of Coulomb particles in thermodynamic equilibrium. Equations are derived for corrections of various orders to the effective interaction energies of two, three, etc., particles. These equations in principle make it possible to calculate, for example, corrections to the Debye potential. At the same time the meaning is clarified of a Kramers-type potential, which is often used in considering systems of Coulomb particles.

Suppose that a system consisting of M species of Coulomb particles is in thermodynamic equilibrium. The charge of a particle belonging to species a_i is equal to z_{a_i} .

At small distances between two particles, let us assume the existence of short-range repulsive forces that do not depend on the particles' belonging to one species or another, i.e., the interaction energy between a pair of particles is

$$U_{a_i a_j} = z_{a_i} z_{a_j} / |\mathbf{r}_i - \mathbf{r}_j| + K(|\mathbf{r}_i - \mathbf{r}_j|). \quad (1)$$

The potential of the short-range forces $K(r)$ may, for example, be chosen in the form u/r^m , with m and u chosen in a corresponding way. In this case there are three independent length parameters: $l_0 = e^2/\theta = e^2/kT$, $l_1 = (u/\theta)^{1/m}$, and $l_2 = n^{-1/3}$, where n is the mean particle density, $e^2 = 4\pi \sum_{a_i} n_{a_i} z_{a_i}^2$, and n_{a_i} is the concentration of particles of species a_i .

In dimensionless form the well-known Bogolyubov chain equations ⁽¹⁾ are written as follows:

$$\begin{aligned} & \frac{\partial F_{a_1 \dots a_s}}{\partial x^\sigma} + F_{a_1 \dots a_s} \left[\alpha \frac{\partial \Phi_{a_1 \dots a_s}}{\partial x_1^\sigma} + \beta \frac{\partial K_{a_1 \dots a_s}}{\partial x_1^\sigma} \right] + \\ & + \gamma \int \sum_{a_{s+1}} n_{a_{s+1}} \left(\alpha \frac{\partial \Phi_{a_1 a_{s+1}}}{\partial x_1^\sigma} + \beta \frac{\partial K_{a_1 a_{s+1}}}{\partial x_1^\sigma} \right) F_{a_1 \dots a_{s+1}} dx_{s+1} = 0, \quad \sigma = 1, 2, 3. \end{aligned} \quad (2)$$

Here

$$\alpha = l_0/r_0, \quad \beta = (l_1/r_0)^m, \quad \gamma = (r_0/l_2)^3, \quad \mathbf{x} = \mathbf{r}/r_0,$$

$$\Phi_{a_1 \dots a_s} = \sum_{1 \leq i < j \leq s} \{z_{a_i} z_{a_j} / e^2 |\mathbf{x}_i - \mathbf{x}_j|\},$$

$$K_{a_1 \dots a_s} = \sum_{1 \leq i < j \leq s} (1/|\mathbf{x}_i - \mathbf{x}_j|)^m,$$

the remaining notation is generally accepted. We determine r_0 from the condition $\alpha\gamma = 1$. In this case $r_0 = r_d = (\theta/n\epsilon^2)^{1/2}$, the Debye screening radius.

Substituting into (2) $F_{a_1 \dots a_s} = f_{a_1 \dots a_s} \exp\{-\beta K_{a_1 \dots a_s}\}$, for $f_{a_1 \dots a_s}$ we obtain the equation

$$\begin{aligned} & \frac{\partial f_{a_1 \dots a_s}}{\partial x_1^\sigma} + \alpha f_{a_1 \dots a_s} \frac{\partial \Phi_{a_1 \dots a_s}}{\partial x_1^\sigma} + \int \sum_{a_{s+1}} n_{a_{s+1}} \frac{\partial \Phi_{a_1 a_{s+1}}}{\partial x_1^\sigma} \times \\ & \times \exp \left\{ -\beta \sum_{1 \leq i \leq s} K_{a_i a_{s+1}} \right\} f_{a_1 \dots a_{s+1}} dx_{s+1} \\ & + \frac{\beta}{\alpha} \int \sum_{a_{s+1}} n_{a_{s+1}} \frac{\partial K_{a_1 a_{s+1}}}{\partial x_1^\sigma} \exp \left\{ -\beta \sum_{1 \leq i \leq s} K_{a_i a_{s+1}} \right\} f_{a_1 \dots a_{s+1}} dx_{s+1} = 0. \quad (3) \end{aligned}$$

Assume that, for the system under consideration, $\beta \ll \alpha \ll 1$. Taking this into account, we shall neglect the last term in equation (3). This means that one considers such a system of particles for which any subsystem is closed with respect to the short-range forces.

We shall seek the solution of equation (3) in the form of an expansion of $\ln f_{a_1 \dots a_s}$ in a series in α :

$$\ln f_{a_1 \dots a_s} = - \sum_n \alpha^n \Psi_{a_1 \dots a_s}^{(n)}, \quad (4)$$

i.e., we shall expand in a series the effective interaction energy $\Psi_{a_1 \dots a_s}$ of the subsystem of s particles, the first of which belongs to species a_1 , the second to a_2 , and so on. The principal contribution to $\Psi_{a_1 \dots a_s}$ is given by one-particle energies; the contribution of first order in α is given by the interactions of all possible pairs, etc.* These energies, in turn, are expanded in a series in α , so that

$$\Psi_{a_1 \dots a_s}^{(n)} = \sum_{1 \leq i \leq s} \varphi_{a_i}^{(n)} + \sum_{1 \leq i < j \leq s} \varphi_{a_i a_j}^{(n-1)} + \dots + \varphi_{a_1 \dots a_s}^{(n-s+1)}; \quad (5)$$

$\varphi_{a_1 \dots a_r}^{(k)}$ is the term of order k in the expansion of the interaction energy of a subsystem of r particles. With this taken into account, the equations for $\Psi_{a_1 \dots a_s}^{(n)}$ take the form

$$\frac{\partial \Psi_{a_1 \dots a_s}^{(0)}}{\partial x_1^\sigma} = \int \sum_{a_{s+1}} n_{a_{s+1}} \frac{\partial \Phi_{a_1 a_{s+1}}}{\partial x_1^\sigma} \exp \left\{ -\beta \sum_{1 \leq i \leq s} K_{a_i a_{s+1}} \right\} [f_{a_{s+1} | a_1 \dots a_s}]^{(0)} dx_{s+1}; \quad (6)$$

$$\begin{aligned} & \frac{\partial \Psi_{a_1 \dots a_s}^{(1)}}{\partial x_1^\sigma} - \frac{\partial \Phi_{a_1 \dots a_s}}{\partial x_1^\sigma} = \\ & = \int \sum_{a_{s+1}} n_{a_{s+1}} \frac{\partial \Phi_{a_1 a_{s+1}}}{\partial x_1^\sigma} \exp \left\{ -\beta \sum_{1 \leq i \leq s} K_{a_i a_{s+1}} \right\} [f_{a_{s+1} | a_1 \dots a_s}]^{(1)} dx_{s+1}; \quad (7) \end{aligned}$$

$$\frac{\partial \Psi_{a_1 \dots a_s}^{(n)}}{\partial x_1^\sigma} = \int \sum_{a_{s+1}} n_{a_{s+1}} \frac{\partial \Phi_{a_1 a_{s+1}}}{\partial x_1^\sigma} \exp \left\{ -\beta \sum_{1 \leq i \leq s} K_{a_i a_{s+1}} \right\} [f_{a_{s+1} | a_1 \dots a_s}]^{(n)} dx_{s+1}. \quad (8)$$

Here $[f_{a_{s+1} | a_1 \dots a_s}]^{(n)}$ is defined as the coefficient of α^n in the expansion of $f_{a_{s+1} | a_1 \dots a_s} = f_{a_1 \dots a_{s+1}} / f_{a_1 \dots a_s}$ in a series in α .

In what follows, in the system (6)–(8) we neglect terms of the form

$$\int y_{a_1 \dots a_{s+1}}(x_1, \dots, x_{i-1}, x_{i+1} \dots, x_{s+1}) \{ \exp(-\beta K_{a_i a_{s+1}}) - 1 \} dx_{s+1},$$

which are of order $\beta^{3/m}$ in comparison with

$$\int y_{a_1 \dots a_{s+1}}(x_1 \dots, x_{i-1}, x_{i+1} \dots, x_{s+1}) dx_{s+1}.$$

* A similar expression for $\Phi_{a_1 \dots a_s}$ was used in Ref. (2).

For one particle in the zeroth approximation, equation (6) is the equation of the self-consistent field:

$$\frac{\partial \varphi_{a_1}^{(0)}}{\partial x_1^\sigma} = \int \sum_{a_2} \frac{\partial \Phi_{a_1 a_2}}{\partial x_1^\sigma} n_{a_2} \exp \{ -\beta K_{a_1 a_2} - \varphi_{a_2}^{(0)} \} dx_2. \quad (9)$$

If the system is homogeneous, then $\varphi_{a_1}^{(0)} = 0$. To calculate the first correction $\varphi_{a_1}^{(1)}$, we have two equations:

$$\frac{\partial \varphi_{a_1}^{(1)}}{\partial x_1^\sigma} + \int \sum_{a_2} n_{a_2} \frac{\partial \Phi_{a_1 a_2}}{\partial x_1^\sigma} \exp\{-\beta K_{a_1 a_2} - \varphi_{a_2}^{(0)}\} (\varphi_{a_2}^{(1)} + \varphi_{a_1 a_2}^{(0)}) dx_2 = 0; \quad (10)$$

$$\frac{\partial \varphi_{a_1 a_2}^{(0)}}{\partial x_1^\sigma} - \frac{\partial \Phi_{a_1 a_2}}{\partial x_1^\sigma} + \int \sum_{a_3} n_{a_3} \frac{\partial \Phi_{a_1 a_3}}{\partial x_1^\sigma} \exp\left\{-\beta \sum_{1 \leq i < 2} K_{a_i a_3} - \varphi_{a_3}^{(0)}\right\} \varphi_{a_2 a_3}^{(0)} dx_3 = 0. \quad (11)$$

For $\beta = 0$, in the case of a homogeneous system, equation (11) is the equation for the Debye potential (see, for example, (1)).

For the next correction we have a system of three equations:

$$\frac{\partial \varphi_{a_1}^{(2)}}{\partial x_1^\sigma} + \int \sum_{a_2} n_{a_2} \frac{\partial \Phi_{a_1 a_2}}{\partial x_1^\sigma} \exp[-\beta K_{a_1 a_2} - \varphi_{a_2}^{(0)}] \left\{ \varphi_{a_2}^{(2)} + \varphi_{a_1 a_2}^{(1)} - \frac{1}{2} [\varphi_{a_1 a_2}^{(0)}]^2 \right\} dx_2 = 0; \quad (12)$$

$$\frac{\partial \varphi_{a_1 a_2}^{(1)}}{\partial x_1^\sigma} + \int \sum_{a_3} n_{a_3} \frac{\partial \Phi_{a_1 a_3}}{\partial x_1^\sigma} \exp\left[-\beta \sum_{1 \leq i < 2} K_{a_i a_3} - \varphi_{a_3}^{(0)}\right] \left\{ \varphi_{a_2 a_3}^{(1)} + \varphi_{a_1 a_2 a_3}^{(0)} - \varphi_{a_1 a_3}^{(0)} \varphi_{a_2 a_3}^{(0)} - \frac{1}{2} [\varphi_{a_2 a_3}^{(0)}]^2 \right\} dx_3 = 0; \quad (13)$$

$$\frac{\partial \varphi_{a_1 a_2 a_3}^{(0)}}{\partial x_1^\sigma} + \int \sum_{a_4} n_{a_4} \frac{\partial \Phi_{a_1 a_4}}{\partial x_1^\sigma} \exp\left[-\beta \sum_{1 \leq i < s} K_{a_i a_4} - \varphi_{a_4}^{(0)}\right] \left\{ \varphi_{a_2 a_3 a_4}^{(0)} - \varphi_{a_2 a_4}^{(0)} \varphi_{a_3 a_4}^{(0)} \right\} dx_4 = 0. \quad (14)$$

Analogously, one can write equations for any correction to the interaction energy of any cluster of particles. The presence in the integral terms of these equations of the factor $\exp\{-\beta \sum_{1 \leq i < s} K_{a_i a_{s+1}}\}$ removes the problem of divergence as $|\mathbf{x}_i - \mathbf{x}_j| \rightarrow 0$.

If $\exp\{-\beta K_{a_1 a_{s+1}}\}$ is approximated by the expression $[1 - \exp\{-b|\mathbf{x}_1 - \mathbf{x}_{s+1}|\}]$, and in the remaining exponentials one sets $\beta = 0$, then this is equivalent to considering a system of particles interacting according to the law

$$U(r) = \{1 - A(r) \exp[-br]\}/r, \quad (15)$$

where $A(r) \rightarrow 1$ as $r \rightarrow 0$.

Further, it can be shown that for a system neutral as a whole, representing a binary mixture of particles such that $z_1 = -z_2$, all $\varphi_{a_1 \dots a_s}^{(n)}$ for which $n+s = 2k+1$ ($k = 0, 1, \dots$) are equal to zero, i.e., in the expansion of $\Psi_{a_1 \dots a_s}$ there are only even powers of α . For any other system, all powers of α will be present in the expansion.

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Note: Figure translations are in progress. See original paper for figures.

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