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Abstract

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On Correlation Functions for a System of Identical Charged Particles

(Presented by Academician N. N. Bogolyubov on 18 VII 1958)

The basic problem of the theory of statistical equilibrium of a system of particles, consisting in the determination of the distribution functions $f_s(q_1, q_2, \dots, q_s)$ for subsystems of any number s of particles, was reduced by N. N. Bogolyubov (^{1}) to the integration of the chain of equations

$$\frac{\partial f_s(q_1,\dots,q_s)}{\partial q_i} + \frac{f_s(q_1,\dots,q_s)}{\theta}\frac{\partial}{\partial q_i}\sum_{\substack{1\le k\le s\\ k\ne i}}\Phi(q_i - q_k) + \frac{n_0}{\theta}\int\frac{\partial \Phi_s(q_i - q_{s+1})}{\partial q_i} f_{s+1}(q_1,\dots,q_{s+1})\,dq_{s+1} = 0 \tag{1}$$

$$i = 1, 2, \dots, s,$$

with the boundary conditions and normalization relations

$$f_s(q_1,\dots,q_s) \to \prod_{1\le i\le s} f_1(q_i), \qquad |q_i - q_k| \to \infty; \qquad \lim_{V\to\infty} V^{-1}\int_V f_1(q)\,dq = 1, \tag{2}$$

where $\Phi(q_i - q_k)$ is the potential energy of interaction of two particles, θ is the temperature, and n_0 is the density.

For charged particles, approximate expressions for the correlation functions were found by N. N. Bogolyubov (^{1}): for small mutual distances—by expansion in n_0, and for large distances—by expansion in $4\pi a = 1/n_0 r_d^3$, where r_d is the Debye radius. In both cases the determination of subsequent approximations proved impossible because of the appearance of integrals diverging at either large or small distances.

The results of N. N. Bogolyubov were refined by S. V. Tyablikov and V. V. Tolmachev (^{2}), who constructed, for the spatially homogeneous case, approximate expressions for the correlation functions suitable for all distances. However, the method they used for finding the first correction (V_2) is not directly applicable to finding subsequent corrections, since, owing to the expansion of $\exp\left(-\frac{a}{r/r_d}e^{-r/r_d}\right)$ in a series in a, divergent integrals arise in the next approximation.

In the present work, the correlation functions for charged particles in the inhomogeneous case are constructed by means of an iteration method*, which makes it possible to find corrections of any approximation, and the physical essence of this method is clarified.

* The assumption that it is expedient to apply the iteration method in the case of Coulomb interaction was expressed by N. N. Bogolyubov (^{1}).

Let us single out in equation (1) the potential energy of a particle in the self-consistent field
$U(q) = n_0 \int \Phi(q-q_1) f_1(q_1)\, dq_1$* and divide (1) by f_s; for $s = 1, 2$ we obtain

$$\frac{\partial}{\partial q_1}\{\ln f_1(q_1) + U(q_1)\} = \frac{n_0}{\theta}\int \frac{\partial \Phi(q_1-q_2)}{\partial q_1}\left\{f_1(q_2) - \frac{f_2(q_1,q_2)}{f_1(q_1)}\right\} dq_2, \quad (3)$$

$$\frac{\partial}{\partial q_1}\left\{\ln f_2(q_1,q_2) + \frac{1}{\theta}[U(q_1) + \Phi(q_1-q_2)]\right\} = \\ = \frac{n_0}{\theta}\int \frac{\partial \Phi(q_1-q_3)}{\partial q_1}\left\{f_1(q_3) - \frac{f_3(q_1,q_2,q_3)}{f_2(q_1,q_2)}\right\} dq_3. \quad (4)$$

The main difficulty in solving the chain of equations (1), connected with the fact that f_2 is determined through f_3, etc., can be overcome on the basis of the following considerations. Consider the interaction of a pair of charged particles situated in a "medium" of the same particles. At small mutual distances this interaction obeys Coulomb' s law, while at large distances the direct Coulomb interaction is screened by the "medium," and the interaction is effected through the self-consistent field. The right-hand sides of equations (3) and (4) express the force acting on the first particle and caused by fluctuations of the density of the "medium," i.e., by the deviation of the correlation density $n_0\frac{f_{s+1}(q_1,\dots,q_{s+1})}{f_s(q_1,\dots,q_s)}$ of the "medium" from the mean density $n(q_{s+1}) = n_0 f_1(q_{s+1})$.

In calculating the force acting on the first particle, one must take into account that the contribution to this force from density fluctuations of the medium around the first particle is equal to zero (for a spherically symmetric potential) in the spatially homogeneous case and is small in the inhomogeneous case. The contribution to this force from density fluctuations of the medium around the second particle, however, is substantial and at large distances can noticeably weaken the direct Coulomb interaction. Therefore, in the first approximation one may neglect the correlations of the medium with the first particle, replacing in (4) the ternary correlation density of the medium

$n_0 \dfrac{f_3(q_1, q_2, q_3)}{f_2(q_1, q_2)}$ by the binary one $n_0 \dfrac{f_2(q_2, q_3)}{f_1(q_2)}$; for this purpose we rewrite (4) in the form

$$\begin{aligned} &\frac{\partial}{\partial q_1} \left\{ \ln f_2(q_1, q_2) + \frac{1}{\theta}[U(q_1) + \Phi(q_1 - q_2)] \right\} = \\ &\qquad = \frac{n_0}{\theta} \int \Phi(q_1 - q_3) \left[f_1(q_3) - \frac{f_2(q_2, q_3)}{f_1(q_2)} \right] dq_3 = \\ &\qquad = \frac{n_0}{\theta} \int \frac{\partial \Phi(q_1 - q_3)}{\partial q_1} \left[\frac{f_2(q_2, q_3)}{f_1(q_2)} - \frac{f_3(q_1, q_2, q_3)}{f_2(q_1, q_2)} \right] dq_1 \end{aligned} \tag{5}$$

and solve (3) and (5), discarding the right-hand sides.

From (3) we obtain the Boltzmann distribution in the self-consistent field: $f_1(q) = C \exp[-U(q)/\theta]$, where C is determined from (2).

Representing f_2 in the form

$$f_2(q_1, q_2) = f_1(q_1) f_1(q_2) \chi_2(q_1, q_2),$$

$$\chi_2(q_1, q_2) = e^{-\varphi(q_1, q_2)/\theta}, \qquad \varphi(q_1, q_2) \to 0, \quad |q_1 - q_2| \to \infty,$$

we obtain from (5) the equation for φ:

$$\varphi(q_1, q_2) + \int n(q_3) \Phi(q_1 - q_3) \left[1 - \exp\left(-\frac{\varphi(q_2, q_3)}{\theta} \right) \right] dq_3 = \Phi(q_1 + q_2) \tag{6}$$

or the equivalent differential equation

$$\Delta_{q_1} \varphi(q_1, q_2) - 4\pi e^2 n(q_1) \left[1 - \exp\left(-\frac{\varphi(q_1, q_2)}{\theta} \right) \right] = -4\pi e^2 \delta(q_1 - q).$$

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* Strictly speaking, the limiting transition to an infinite volume in the problem of the equilibrium of a system of like charges requires the introduction of an external field replacing the real boundary conditions. It is easy to see that the introduction of such a field changes only the form of the function $U(q)$, but not the correlation functions.

If the variation of the density $n(q_1)$ over distances of order r_d is neglected, then φ will depend only on the distance $r = |q_1 - q_2|$ between the particles, and in the approximation linear in φ/θ we obtain the Debye potential (3)

$$\varphi(r) = \frac{e^2}{r} e^{-r/r_d}, \qquad \chi_2(r) = \exp\left(-\alpha \frac{r_d}{r} e^{-r/r_d}\right), \qquad r_d = \left(\frac{\theta}{4\pi e^2 n(q)}\right)^{1/2}. \tag{7}$$

It should be emphasized that, owing to the presence of a pole in φ at $r = 0$, the expansion of (6) in powers of α leads to divergent integrals. Therefore a formal expansion is unsuitable, and we shall use the method of iterations.

In an analogous way we find the functions f_s in the zeroth approximation

$$f_s(q_1, \dots, q_s) = \prod_{1 \le i \le s} f_1(q_i) \prod_{1 \le k < l \le s} \chi_\lambda(q_k - q_l). \tag{8}$$

Formulas (7) and (8) have been obtained for the spatially homogeneous case in (2).

We shall find corrections to the distribution functions for the spatially homogeneous case. Introduce dimensionless variables

$$x = \frac{q}{r_d}, \qquad \alpha\Phi(x) \equiv \frac{\alpha}{|x|} = \frac{\Phi(q)}{\theta}, \qquad f_s(q_1, \dots, q_s) = \exp[-\alpha\Psi_s(x_1, \dots, x_s)]$$

and obtain from (1) the equation for Ψ_s

$$\frac{\partial}{\partial x_1}\left[\Psi_s(x_1, \dots, x_s) - \sum_{2 \le i \le s} \Phi(x_1 - x_i)\right] =$$

$$= \frac{1}{4\pi\alpha} \int \frac{\partial\Phi(x_1 - x_{s+1})}{\partial x_1} \left\{\exp\left[\alpha\{\Psi_s(q_1, \dots, q_s) - \Psi_{s+1}(q_1, \dots, q_{s+1})\}\right] - 1\right\} dx_{s+1}. \tag{9}$$

We shall seek Ψ_s in the form of a sum of binary, ternary, ..., s-particle potentials and denote by φ_k^m the m-th correction to the k-particle potential. Then in the first approximation (with accuracy up to quantities of order α^2)

$$\Psi_s(x_1, \dots, x_s) = \sum_{1 \le i < k \le s} [\varphi_2^0(x_i - x_k) + \varphi_2^1(x_i, x_k)] + \sum_{1 \le i < k < l \le s} \varphi_3^0(x_i, x_k, x_l),$$

where $\varphi_2^0(x) = \exp(-|x|)/|x|$, while φ_2^1 and φ_3^0 satisfy the nonlinear equations*

$$\frac{\partial}{\partial x_1}\left[\varphi_2^1(x_1, x_2) + \frac{1}{4\pi\alpha}\int \Phi(x_1 - x_3)\mu_2^1(x_2, x_3)\,dx_3\right] =$$

$$= \frac{1}{4\pi\alpha}\int \frac{\partial \Phi(x_1 - x_3)}{\partial x_1}\left[\mu_2^0(x_1, x_3)\mu_2^0(x_2, x_3) - \mu_3^0(x_1, x_2, x_3)\right] dx_3,$$

$$\frac{\partial}{\partial x_1}\left[\varphi_3^0(x_1, x_2, x_3) + \frac{1}{4\pi\alpha}\int \Phi(x_1 - x_4)\mu_3^0(x_2, x_3, x_4)\,dx_4\right] =$$

$$= \frac{1}{4\pi\alpha}\frac{\partial}{\partial x_1}\int \Phi(x_1 - x_4)\mu_2^0(x_2, x_4)\mu_2^0(x_3, x_4)\,dx_4,$$

$$\mu_k^m = 1 - \exp(-\alpha\varphi_k^m),$$

from which it is not difficult to obtain, for example, an expression for φ_3^0* accurate up to quantities of order α^2:

$$\varphi_3^0(x_1, x_2, x_3) = \frac{1}{4\pi}\int \mu_2^0(x_1, x_4)\mu_2^0(x_2, x_4)\mu_2^0(x_3, x_4)\,dx_4. \tag{10}$$

With the aid of the method applied above one can find all k-particle potentials with any desired accuracy. However, their actual determination is connected with cumbersome calculations and is not of interest from the physical point of view.

Thus, the potential energy of interaction of a subsystem of s charged particles has (in the inhomogeneous case) the form

$$\alpha\Psi_s(x_1, \dots, x_s) = \sum_{1 \le i \le s} U(x_i) + \alpha \sum_{1 \le i < k \le s} \varphi_2(x_i, x_k) +$$

$$+\alpha \sum_{1 \le i < k < l \le s} \varphi_3(x_i, x_k, x_l) + \dots + \alpha\varphi_s(x_1, \dots, x_s), \tag{11}$$

i.e., it is the sum of the interaction energies of each particle with the "medium," the energies of the screened interaction of all pairs, all triples, ⋯, all s particles. The principal role is played by the interaction with the self-consistent field (of zeroth order in α) and the pair Debye interaction (of order α); the remaining

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* The expression for the first correction to the binary potential found in (2) is inaccurate, since it does not ta

terms in (11) are of higher order of smallness: $\alpha\varphi_k = O(\alpha^{k-1})$. The Debye potential describes the continuous transition from the pair Coulomb interaction of two charges at small distances ($r \ll r_d$) to the collective interaction through the self-consistent field at large distances ($r \gg r_d$).

Thus, for charged particles effective short-range forces can be introduced, described by the Debye potential.

The expressions obtained for the correlation functions in the inhomogeneous case are applicable to systems occupying a finite volume; they are valid throughout the volume, except for a boundary layer of thickness of order r_d. Therefore, with their aid the equation of state for a gas of identical charged particles can be established$^{(1)}$:

$$pV = N\theta + \eta_1 \frac{e^2 N^2}{V^{1/3}} - \eta_2 \frac{|e|^3 N^{3/2}}{\theta^{1/2} V^{1/2}}, \tag{12}$$

where

$$\eta_1 = \frac{1}{6V^2} \iint_{VV} \frac{f_1(q_1) f_1(q_2)}{|q_1 - q_2|}\, dq_1 dq_2, \qquad \eta_2 = \frac{\sqrt{\pi}}{3V} \int_V f_1^2(q)\, dq$$

are coefficients of order unity, depending on the shape of the volume V (the influence of the shape is connected with the long-range character of the Coulomb forces). The term with η_1 expresses the mean energy of Coulomb interaction, and that with η_2 the correction to it due to density fluctuations (it coincides with the corresponding expression for a plasma$^{(4)}$).

The method set forth above for determining the correlation functions for charged particles can apparently be applied to systems with charges of different signs, and also in the kinetic theory of charged particles.

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* Let us note that φ_3^0 decreases exponentially at large distances and remains finite when particles approach one another.

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

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