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Equations with Variational Derivatives in Statistical Equilibrium Theory

I. P. BAZAROV
Moscow State University

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Equations with variational derivatives for correlation functions have been derived. A method is developed for solving these for various systems in statistical equilibrium. A "superposition" theorem is derived for obtaining the correlation functions when the interaction between the particles of the system can be described as the sum of long and short range forces.

THE BEHAVIOR OF A statistical system of interacting particles is determined by the corresponding distribution functions of these particles $F_s(x_1, x_2, \ldots, x_s)$ $(s = 1, 2, 3, \ldots)$. Bogoliubov[1] has shown that the functions F_s can be represented by variational derivatives of the functional introduced by him, and the series of equations for the determination of these distribution functions were first obtained by him. As Bogoliubov also pointed out[2], his functional does not have a direct physical interpretation; he therefore pointed out a method in Ref. 2 for the construction of other functionals, based on the idea of the inclusion of the external field, in a manner similar to that employed in the Schwinger theory of the Green function.

In the present work, starting out from a functional for the free energy of a system of M types of particles in an external field $\varphi(x)$, closed equations are found with variational derivatives for the unitary distribution function for different forms of the functional argument; with the help of these derivatives, a method of determining the correlation functions has been deduced for systems of particles with different interactions: Coulombic $\Phi_0(r)$, an interaction decreasing rapidly with distance, $\Phi_1(r)$, and an interaction of the form $\Phi(r) = \Phi_0(r) + \Phi_1(r)$.

1. FREE ENERGY AS A FUNCTIONAL. DISTRIBUTION FUNCTIONS. EQUATIONS WITH VARIATIONAL DERIVATIVES

Let us consider a system of M types N_a molecules of the ath type. Let this system be located in an external field $\varphi(\mathbf{r})$. The probability density function of the position of the molecules is determined by the Gibbs function:

$$D = \frac{1}{Q}\exp\left\{-\frac{1}{\Theta}\left(U_N + \sum_{a,i}\varphi_a(\mathbf{r}_i)\right)\right\},$$
$$Q = \int \exp\left\{-\frac{1}{\Theta}\left(U_N + \sum_{a,i}\varphi_a(\mathbf{r}_i)\right)\right\}d\tau, \qquad (1)$$
$$U_N = \sum \Phi_{ab}(|\mathbf{r}_{ai} - \mathbf{r}_{bj}|),$$

where U_N is the potential energy of interaction of the particles with each other; $\mathbf{r}_{ai}$ determines the position of the ith molecule of the ath type, while the summation is taken over all different pairs of molecules; Q is the configuration integral of the system; the mutual potentials Φ_{ab} are assumed to be symmetric functions relative to a, b; $\Theta = kT$.

The free energy of such a system,

$$F = -\Theta \ln Q = -\Theta \ln \int \exp\left\{-\frac{1}{\Theta}\left(U_N + \sum_{a,i} \varphi_a(\mathbf{r}_i)\right)\right\} d\tau \qquad (2)$$

is a functional of the external field $\varphi(\mathbf{r})$. The distribution functions of complex particles $F_{a_1,\ldots,a_s}(\mathbf{r}_1, \ldots, \mathbf{r}_s)$ which are so normalized that $V^{-s} F_{a_1,\ldots,a_s} d\mathbf{r}_1 \ldots d\mathbf{r}_s$ defines the probability that s particular molecules of types $a_1, \ldots, a_s$ having specified coordinates in the volume V, can be expressed by variational derivatives of the functional (2).

Actually, we have from (2) (we shall denote the $\mathbf{r}_i$ as $x, y, \ldots$):

$$\delta F / \delta\varphi_a(x) = N_a\, E_a(x \mid \varphi) / Q, \qquad (3)$$

$$F_a(x \mid \varphi) = (V / N_a)\, \delta F / \delta\varphi_a(x), \qquad (4)$$

where

$$E_a(x \mid \varphi) = \overline{\exp\left\{-\frac{1}{\Theta}\left(U_N + \sum_{a,i} \varphi_a(x_i)\right)\right\}}^{\,x_{a_1} = x},$$

$$F_a(x \mid \varphi) = \overline{VD} = V \frac{E_a(x \mid \varphi)}{Q},$$

F_a is the distribution function of a single particle (the number density of particles of the ath type) in the presence of the external field $\varphi(x)$. (Here the bar over quantities denotes integration over all variables $\{x_{a,i}\}$ except $x_{a_1} = x$.) It is easy to find the distribution function of a pair of particles $F_{ab}(x, y \mid \varphi)$ by taking the functional derivative of (3). We then get:

$$\frac{\delta^2 F}{\delta\varphi_a(x)\, \delta\varphi_b(y)} = \frac{N_a}{\Theta}\left\{-(N_b - \delta_{ab}) \frac{E_{ab}(x, y \mid \varphi)}{Q} - \frac{E_a(x \mid \varphi)}{Q} + N_b \frac{E_a(x \mid \varphi)}{Q} \frac{E_b(y \mid \varphi)}{Q}\right\} \qquad (5)$$

or

$$\frac{\delta^2 F}{\delta\varphi_a(x)\, \delta\varphi_b(y)} = -\frac{N_a (N_b - \delta_{ab})}{\Theta V^2} F_{ab}(x, y \mid \varphi) - \frac{N_a}{\Theta V} F_a(x \mid \varphi)\, \delta(x - y) + \frac{N_a N_b}{\Theta V^2} F_a(x \mid \varphi) F_b(y \mid \varphi), \qquad (6)$$

where

$$E_{ab}(x, y \mid \varphi) = \overline{\exp\left\{-\frac{1}{\Theta}\left(U_N + \sum_{a,i} \varphi_a(x_i)\right)\right\}}^{\,x_{a_1} = x,\; x_{b_2} = y},$$

and δ_{ab} is the Kronecker delta. From (6) we obtain

$$F_{ab}(x, y \mid \varphi) = \frac{N_b}{N_b - \delta_{ab}} F_a(x \mid \varphi) F_b(y \mid \varphi) - \frac{V}{N_b - \delta_{ab}} F_a(x \mid \varphi)\, \delta(x - y) - \frac{\Theta V^2}{N_a (N_b - \delta_{ab})} \frac{\delta^2 F}{\delta\varphi_a(x)\, \delta\varphi_b(y)} \qquad (7)$$

or

$$F_{ab}(x, y \mid \varphi) = \frac{N_b}{N_b - \delta_{ab}} F_a(x \mid \varphi) F_b(y \mid \varphi) - \frac{V}{N_b - \delta_{ab}} F_a(x \mid \varphi)\, \delta(x - y) - \frac{\Theta V}{N_b - \delta_{ab}} \frac{\delta F_a(x \mid \varphi)}{\delta\varphi_b(y)}. \qquad (8)$$

It is then obvious that the pair correlation function is entirely expressed in terms of unitary functions with the help of variational derivatives.

If, just as we did with Eq. (3), we continue to take functional derivatives of Eq. (5), then we find the value of the third functional derivative and the four-particle distribution function $F_{abc}(x,y,y \mid \varphi)$ which, similar to $F_{ab}(x, y \mid \varphi)$ is also entirely expressed in terms of unitary distribution functions with variational derivatives.

Thus, finding the correlation functions $F_s(x_1, x_2, \ldots, x_s)$ ($s = 2, 3, \ldots$) reduces to the determination of the unitary distribution function and the corresponding variational derivatives.

Beginning with the determination of the unitary distribution function

$$F_a(x \mid \varphi) = \overline{VD}^{\,x_{a_1} = x}, \qquad (9)$$

it is easy to find a closed differential equation with variational derivatives. Actually, differentiating the Gibbs distribution with respect to $x_{a_1}^{\alpha}$, we get

$$\frac{\partial D}{\partial x_{a_1}^{\alpha}} + \frac{1}{\Theta}\frac{\partial \varphi_{\alpha}(x)}{\partial x_{a_1}^{\alpha}} D + \frac{1}{\Theta}\frac{\partial U_N}{\partial x_{a_1}^{\alpha}} D = 0 \quad (\alpha = 1, 2, 3).$$

Multiplying by V and integrating, we have

$$\frac{\partial F_a(x\,|\,\varphi)}{\partial x^{\alpha}} + \frac{1}{\Theta}\frac{\partial \varphi_a(x)}{\partial x^{\alpha}} F_a(x\,|\,\varphi) + \frac{1}{\Theta V}\sum_{b=1}^{M}(N_b - \delta_{ab}) \times \int \frac{\partial \Phi_{ab}(|x-y|)}{\partial x^{\alpha}} F_{ab}(x, y\,|\,\varphi)\,dy = 0.$$

Substituting (7), and carrying out the transition to the limit $N \to \infty$, $V \to \infty$ for the finite ratios $V/N = v$, $N_a/N = n_a$ $(a = 1, 2, \ldots, M)$ we obtain a closed equation for $F_a(x|\varphi)$ with variational derivatives:

$$\frac{\partial F_a(x\,|\,\varphi)}{\partial x^{\alpha}} + \frac{1}{\Theta}\frac{\partial \psi_a(x)}{\partial x^{\alpha}} F_a(x/\varphi) = 0, \tag{10}$$

$$\psi_a(x) = \varphi_a(x) + \sum_{b=1}^{M}\int \Phi_{ab}(|x-y|)\left\{\frac{n_b}{v}F_b(y\,|\,\varphi) - \delta(x-y) - \Theta\frac{\delta}{\delta\varphi_b(y)}\right\}dy \tag{11}$$

or an equation in variational derivatives of the functional $F(\varphi)$:

$$\frac{\partial}{\partial x^{\alpha}}\frac{\delta F}{\delta \varphi_a(x)} + \frac{1}{\Theta}\frac{\partial \varphi_a(x)}{\partial x^{\alpha}}\frac{\delta F}{\delta\varphi_a(x)} + \frac{1}{-}\sum_{b=1}^{M}\int\frac{\partial \Phi_{ab}(|x-y|)}{\partial x^{\alpha}} \times\left\{\frac{\delta F}{\delta\varphi_a(x)\,\delta\varphi_b(y)} - \frac{\delta F}{\delta\varphi_a(x)}\delta(x-y) - \Theta\frac{\delta^2 F}{\delta\varphi_a(x)\,\delta\varphi_b(y)}\right\}dy = 0. \tag{12}$$

It is evident from (10) that the equation for the distribution function $F_a(x|\varphi)$ is the same form of an equation as in the case of the motion of two particles of an ideal gas in a given external field $\psi_a(x)$. A real interaction between the particles is expressed by the fact that $\psi_a(x)$ is not the usual field but an operator one.

Let us now analyze the method of finding the correlation functions, starting out from Eq. (10), with variational derivatives of the unitary distribution function, for the case of a different sort of system.

2. SYSTEM WITH COULOMBIC INTERACTION BETWEEN THE PARTICLES

We consider a system of electrically charged particles interacting according to Coulomb's law. The operator field in which the particles of the system are placed has the form (11). If the second and third terms in the integral of this operator field are small in comparison with the first term, we then have the ordinary field

$$\psi_a(x) = \varphi_a(x) + \sum_{b=1}^{M}\int \Phi_{ab}(|x-y|)\frac{n_b}{v}F_b(y\,|\,\varphi)\,dy. \tag{13}$$

Neglect of these terms corresponds to ignoring the short-range interaction forces between the particles.

Equation (10) for the distribution function $F_a(x|\varphi)$ of a system of particles between which only long-range forces act (for example, Coulomb forces) will then be

$$\frac{\partial F_a(x\,|\,\varphi)}{\partial x^{\alpha}} + \frac{1}{\Theta}\frac{\partial \varphi_{\alpha}(x)}{\partial x^{\alpha}}F_a(x\,|\,\varphi) + \frac{1}{\Theta}F_a(x\,|\,\varphi)\sum_{b=1}^{M}\int\frac{\partial\Phi_{ab}(|x-y|)}{\partial x^{\alpha}}\frac{n_b}{v}F_b(y|\varphi)\,dy = 0. \tag{14}$$

Let the total charge of the system be zero and let the different particles differ only in charge. We denote the charge of the particles of type a by the symbol e_a; there are M types. Then

$$\sum_{a=1}^{M} n_a = 1, \quad \sum_{a=1}^{M} n_a e_a = 0. \tag{15}$$

For Coulombic interaction $\Phi_{ab} = e_a e_b/\varepsilon r$, where ε is the dielectric constant of the medium. In our case, this includes electrolytes phenomenologically.

In looking for a quantity which serves as the small parameter in powers of which we shall expand $F_a(x|\varphi)$, we can, following Bogoliubov[1], transform to dimensionless quantities, taking the Debye radius r_d as the unit of length:

$$r_d^2 = \Theta\varepsilon v / 4\pi \sum_{a=1}^{M} n_a e_a^2. \tag{16}$$

Then for the case of the Debye theory of electrolytes at low concentration, when the interaction energy at distances of the order of r_d is much smaller than the thermal energy ($e_a e_b / \varepsilon r_d \ll \Theta$), the volume per particle in dimensionless units is our small parameter:

$$v^* = v / r_d^3 = \mu = 4\pi \sum_a n_a e_a^2 / \Theta \varepsilon r_d \ll 1.$$

In this case, introducing variables of the order of unity

$$\lambda_a = e_a \Big/ \sqrt{4\pi \sum_a n_a e_a^2},$$

we note that $\Phi_{ab}(r)/\Theta = \mu \lambda_a \lambda_b / r^*$. Keeping this in mind, we shall not transform to dimensionless units but immediately expand $F_a(x|\varphi)$ in powers of v, remembering that $\Phi_{ab}(r)/\Theta$ is proportional to v:

$$\Phi_{ab}(r) / \Theta = v\psi_{ab}(r), \qquad \psi_{ab}(r) = \lambda_a \lambda_b / r_d^2 r. \quad (17)$$

Thus, we shall solve Eq. (14) with the help of the expansion

$$F_a(x|\varphi) = F_a^0(x|\varphi) + vF_a^1(x|\varphi) + v^2 F_a^2(x|\varphi) + \dots \quad (18)$$

with the normalization condition

$$\lim_{V \to \infty} \frac{1}{V} \int F_a(x|\varphi)\, dx = 1,$$

i.e.,

$$\lim_{V \to \infty} \frac{1}{V} \int F_a^0(x|\varphi)\, dx = 1, \qquad \lim_{V \to \infty} \frac{1}{V} \int F_a^1(x|\varphi)\, dx = 0. \quad (19)$$

Substituting (18) in (14) and setting the sum of terms of a given power of v equal to zero, we obtain the equations for the approximation:

$$\frac{\partial F_a^0(x|\varphi)}{\partial x^\alpha} + \frac{1}{\Theta} \frac{\partial \varphi_a(x)}{\partial x^\alpha} F_a^0(x|\varphi) + F_a^0(x|\varphi) \sum_{b=1}^{M} \int \frac{\partial \psi_{ab}(|x-y|)}{\partial x^\alpha} n_b F_b^0(y|\varphi)\, dy = 0, \quad (20)$$

$$\frac{\partial F_a^1(x|\varphi)}{\partial x^\alpha} + \frac{1}{\Theta} \frac{\partial \varphi_a(x)}{\partial x^\alpha} F_a^1(x|\varphi) + F_a^0(x|\varphi) \sum_{b=1}^{M} \int \frac{\partial \psi_{ab}(|x-y|)}{\partial x^\alpha} n_b F_b^1(y|\varphi)\, dx + F_a^{1'}(x|\varphi) \sum_{b=1}^{M} \int \frac{\partial \psi_{ab}(|x-y|)}{\partial x^\alpha} n_b F_b^0(y|\varphi)\, dy = 0. \quad (21)$$

Setting the external field $\varphi_a(x) = 0$, we get equations for the approximation in the absence of such a field. We note that, according to (15), the following condition holds:

$$\sum_{b=1}^{M} \psi_{ab}(r)\, n_b = (e_a / \Theta \varepsilon v r) \sum_{b=1}^{M} n_b e_b = 0. \quad (22)$$

By virtue of the normalization condition, Eq. (20) has, at $\varphi_a(x) = 0$, the obvious solution

$$F_a^0(x) = 1. \quad (23)$$

From Eq. (21) [at $\varphi_a(x) = 0$], we get $F_a^1(x) = 0$ by taking (22), (23), and (29) into account. Solution of the equation for subsequent approximations similar to the solution of Eq. (21), gives [for $\varphi_a(x) = 0$]: $F_a^i(x) = 0$, $i = 1, 2, \dots$. Thus, in the absence of an external field, in a system of charged particles in the approximation in which the second and third terms in the operator field (11) are small in comparison with the first term, the distribution function for a single particle $F_a(x)$ has a value exactly equal to unity:

$$F_a(x) = F_a^0(x) = 1, \quad (24)$$

which corresponds to a spatially homogeneous distribution of the particles.

The correlation pair function in the absence of field will be, by Eq. (8):

$$F_{ab}(x, y) = F_a(x) F_b(y) - (v / n_b) F_a(x) \delta(x-y) - (v\Theta / n_b) (\delta F_a(x|\varphi) / \delta\varphi_b(y))_{\varphi=0}$$

or

$$F_{ab}(x, y) = 1 - (v / n_b) \delta(x-y) - (v\Theta / n_b) (\delta F_a(x|\varphi) / \delta\varphi_b(y))_{\varphi=0}.$$

In the first approximation,

$$F_{ab}(x, y) = 1 - (v/n_b)\,\delta(x-y) - (v\Theta/n_b)\,(\delta F_a^0(x\,|\,\varphi)/\delta\varphi_b(y))_0. \qquad (25)$$

We find the variational derivative here by taking the functional derivative of Eq. (20) with respect to $\varphi_b(y)$ and assuming $\varphi(x) = 0$, taking Eqs. (22) and (24) into account. We then obtain

$$\left(\frac{\delta F_a^0(x\,|\,\varphi)}{\delta\varphi_b(y)}\right)_0 + \frac{1}{\Theta}\,\delta(x-y) + \sum_{c=1}^{M}\int \psi_{ac}(|x-z|)\,n_c\left(\frac{\delta F_c^0(z\,|\,\varphi)}{\delta\varphi_b(y)}\right)_0 dz = 0,$$

or, on the basis of Eq. (25):

$$1 - F_{ab}(x, y) + \sum_{c=1}^{M}\int \psi_{ac}(|x-z|)\,n_c\Big((1 - F_{bc}(y, z) - \frac{v}{n_b}\,\delta(y-z)\Big)dz = 0,$$

$$1 - F_{ab}(x, y) - v\psi_{ab}(|x-y|) + \sum_{c=1}^{M}\int \psi_{ac}(|x-z|)\,n_c\,(1 - F_{bc}(y, z))\,dz = 0$$

Writing $(F_{ab}(x, y) - 1)/v = g_{ab}(x, y)$, we get the equation

$$g_{ab}(x, y) + \sum_{c=1}^{M}\int \psi_{ac}(|x-z|)\,n_c g_{cb}(z, y)\,dz = -\psi_{ab}(|x-y|), \qquad (26)$$

the solution of which is well known[1]:

$$g_{ab}(x, y) = g_{ab}(|x-y|) = g_{ab}(r) = -\lambda_a\lambda_b r_d^{-2}\exp(-r/r_d)/r$$

and, consequently,

$$F_{ab}(r) = 1 - v\lambda_a\lambda_b r_d^{-2}\exp(-r/r_d)/r. \qquad (27)$$

The variational derivatives of F_a^1, F_a^2, *etc.*, are equal to zero, as is not difficult to show by taking functional derivatives of Eq. (21). So also is the equation for the other approximations.

Thus the solution of Eq. (10) with variational derivative reduces in our approximation (for Coulomb forces) to the value of the binary distribution function $F_{ab}(x, y)$, which coincides with the first approximation for this function, which was first found by Bogoliubov[1] and which is well known in the Debye theory of electrolytes.

Determination of the pair distribution function by starting out from the exact Eq. (10) for Coulomb forces, reduces to finding the variational derivatives $(\delta F_a^0(x\,|\,\varphi)/(\delta\varphi_b(y))_0$, $(\delta F_a^1(x\,|\,\varphi)/\delta\varphi_b(y))_0$, *etc.*, from the corresponding equations for the aproximation in the expansion of the unitary distribution functions in powers of v. This is the procedure that we have already carried out. In Sec. 3, we shall consider the details of finding these derivatives for systems of particles with short-range interaction forces.

3. SYSTEM OF PARTICLES WITH SHORT-RANGE INTERACTION FORCES

Suppose that we have a molecular system (of weak concentration) of identical particles whose mutual interaction falls off rapidly with distance, so that r_0^3/v is a small parameter (r_0 = effective action radius of the molecule). We can find the correlation function of such a system by starting from Eq. (10) with variational differentiation with the aid of an expansion in powers of the density $n = 1/v$. In order to determine the coefficients of this expansion for the correlation function, it is advantageous to replace the functional argument $\varphi(x)$ by $u(x)$ in Eq. (12) for one type of particle ($M = 1$), using the formula

$$\varphi(x) = -\Theta\ln(1 + vu(x)) \qquad (28)$$

and then represent the correlation functions by the variational derivatives of the new functional with another argument. In such a substitution of the functional argument, we have:

$$\frac{\partial \varphi (x)}{\partial x^\alpha} = - \frac{v\Theta}{1 + vu(x)} \frac{\partial u(x)}{\partial x^\alpha},$$

$$\frac{\delta F}{\delta \varphi (x)} = \int \frac{\delta F}{\delta u(y)} \frac{\delta u(y)}{\delta \varphi (x)} dy = - \int \frac{\delta F}{\delta u(y)} \frac{1 + vu(y)}{v\Theta} \delta (x - y)\, dy = - \frac{1 + vu(x)}{v\Theta} \frac{\delta F}{\delta u(x)}, \tag{29}$$

$$\frac{\delta^2 F}{\delta \varphi (x)\, \delta \varphi (y)} = \frac{(1 + vu(y))(1 + vu(x))}{v^2 \Theta^2} \frac{\delta^2 F}{\delta u(x)\, \delta u(y)} + \frac{1}{v\Theta^2} \delta (x - y) \frac{\delta F}{\delta u(x)} (1 + vu(x)).$$

Substituting (29) in (12) (for $M = 1$), we find that the new functional $F(u)$ satisfies the following equation in variational derivatives:

$$- \frac{\partial}{\partial x^\alpha} \frac{\delta F}{\partial u_x} + \frac{1}{\Theta^2} \int \frac{\partial \Phi (|x - y|)}{\partial x^\alpha} (n + u_y) \left(\frac{\delta F}{\delta u_x} \frac{\delta F}{\delta u_y} - \Theta \frac{\delta^2 F}{\delta u_x \delta u_y} \right) dy = 0 \tag{30}$$

[here we write $u(x) = u_x$ for brevity].

We introduce the functions

$$g_s (x_1, x_2, \ldots, x_s) = \delta^s F / \delta u_{x_1} \ldots \delta u_{x_s}, \tag{31}$$

which are connected with the distribution functions in the following way:

$$F_1(x_1/\varphi) = \frac{V}{N} \frac{\delta F}{\delta \varphi_{x_1}} = - \frac{1 + vu_{x_1}}{\Theta} \frac{\delta F}{\delta u_{x_1}}, \qquad F_1(x_1) = - \frac{1}{\Theta} \left(\frac{\delta F}{\delta u_{x_1}} \right)_{u=0} = - \frac{1}{\Theta} g_1(x_1) \tag{32}$$

and on the basis of Eqs. (7) and (29):

$$\begin{aligned} F_2 (x_1, x_2 | \varphi) &= \frac{N}{N-1} F_1 (x_1 | \varphi) F_1 (x_2 | \varphi) - \frac{V}{N-1} \delta (x_1 - x_2) F_1 (x_1 | \varphi) \\ - \frac{V\Theta}{N-1} \frac{\delta F_1 (x_1 | \varphi)}{\delta \varphi_{x_2}} &= \frac{V^2}{N(N-1)} \left\{ \frac{\delta F}{\delta \varphi_{x_1}} \frac{\delta F}{\delta \varphi_{x_2}} - \delta (x_1 - x_2) \frac{\delta F}{\delta \varphi_{x_1}} - \Theta \frac{\delta^2 F}{\delta \varphi_{x_1} \delta \varphi_{x_2}} \right\} \\ &= \frac{V^2}{N(N-1)} \frac{(1 + vu_x)(1 + vu_y)}{v^2 \Theta^2} \left\{ \frac{\delta F}{\delta u_{x_1}} \frac{\delta F}{\delta u_{x_2}} - \Theta \frac{\delta^2 F}{\delta u_{x_1} \delta u_{x_2}} \right\}, \end{aligned}$$

and in the limiting case ($V, N \to \infty$, $N/V = n$) and for $u = 0$, we get

$$F_2 (x_1, x_2) = \Theta^{-2} \{ g_1 (x_1) g_1 (x_2) - \Theta \delta g_1 (x_1) / \delta u_{x_2} \}. \tag{33}$$

Similarly we can represent the other F_s in terms of g_s. Using Eq. (31), we can put Eq. (30) in the form

$$- \frac{\partial g_1 (x | u)}{\partial x^\alpha} + \frac{1}{\Theta^2} \int \frac{\partial \Phi (|x - y|)}{\partial x^\alpha} (n + u_y) \left\{ g_1 (x | u) g_1 (y | u) - \Theta \frac{\delta g_1 (x | u)}{\delta y_y} \right\} dy. \tag{34}$$

We expand $g_1(x | u)$ in a power series in the density $n = 1/v$:

$$g_1 (x | u) = g_1^0 (x | u) + n g_1^1 (x | u) + n^2 g_1^2 (x | u) + \cdots, \tag{35}$$

Substituting this expression in Eq. (34), we get equations with variational derivatives for determining the expansion coefficients

$$-\frac{\partial g_1^0(x\mid u)}{\partial x^\alpha}+\frac{1}{\Theta^2}\int\frac{\partial\Phi(|x-y|)}{\partial x^\alpha}u_y\left\{g_1^0(x\mid u)\,g_1^0(y\mid u)-\Theta\frac{\delta g_1^0(x\mid u)}{\delta u_y}\right\}dy=0, \tag{36}$$

$$-\frac{\partial g_1^1(x\mid u)}{\partial x^\alpha}+\frac{1}{\Theta^2}\int\frac{\partial\Phi(|x-y|)}{\partial x^\alpha}\left\{g_1^0(x\mid u)\,g_1^0(y\mid u)-\Theta\frac{\delta g_1^0(x\mid u)}{\delta u_y}\right.$$
$$\left.+u_y\left(g_1^0(x\mid u)\,g_1^1(y\mid u)+g_1^0(y\mid u)\,g_1^1(x\mid u)\right)-\Theta\frac{\delta g_1^1(x\mid u)}{\delta u_y}\right\}dy=0. \tag{37}$$

Setting $u=0$, we get from Eq. (36): $\partial g_1^0(x)/\partial x^\alpha=0$, whence $g_1^0(x)=\text{const}$, since g_1^0 is symmetric relative to x, y, z.

We have from Eqs. (32) and (19):

$$g_1^0(x)=-\Theta \tag{38}$$

and consequently,

$$F_1^0(x)=-g_1^0(x)/\Theta=1. \tag{39}$$

We find the following approximation for $F_1(x)$. By substitution of $u=0$ in Eq. (37), we determine $F_1^1(x)=-g_1^1(x)/\Theta$:

$$-\frac{\partial g_1^1(x)}{\partial x^\alpha}+\int\frac{\partial\Phi(|x-y|)}{\partial x^\alpha}\left(1-\frac{1}{\Theta}\frac{\delta g_1^0(x)}{\delta u_y}\right)dy=0. \tag{40}$$

The expressions under the integral in this equation can be found by functional differentiation of (36) with respect to u_{x_2} and subsequent equating of u to zero:

$$-\frac{\partial}{\partial x^\alpha}\frac{\delta g_1^0(x)}{\delta u_{x_2}}+\frac{1}{\Theta^2}\frac{\partial\Phi(|x-x_2|)}{\partial x^\alpha}\left(g_1^0(x)\,g_1^0(x_2)-\Theta\frac{\delta g_1^0(x)}{\delta u_{x_2}}\right)$$
$$+\frac{1}{\Theta^2}\int\frac{\partial\Phi(|x-y|)}{\partial x^\alpha}u_y\left(g_1^0(x)\frac{\delta g_1^0(y)}{\delta u_{x_2}}+g_1^0(y)\frac{\delta g_1^0(x)}{\delta u_{x_2}}-\Theta\frac{\delta^2 g_1(x)}{\delta u_y\delta u_{x_2}}\right)dy=0. \tag{41}$$

Employing (38) and setting $u=0$, we get, upon integration

$$\delta g_1^0(x)/\delta u_y=\Theta\left(1-c_1\exp\left\{-\frac{1}{\Theta}\Phi(|x-y|)\right\}\right). \tag{42}$$

Substituting (41) in (40), and making use of (19), we find

$$g_1^1(x)=0 \tag{43}$$

and, consequently, $F_1^1(x)=0$. Similarly, the following approximations are determined:

$$F_1^2(x)=F_1^3(x)=\cdots=0.$$

Thus

$$F_1(x) = 1, \tag{44}$$

which corresponds to a uniform spatial distribution of particles with short-range interaction forces in statistical equilibrium.

We now determine the pair distribution function. If we substitute the expansion (35) for $g_1(x)$ in Eq. (39), we obtain an expansion of the function $F_2(x_1, x_2)$ in powers of the density of the form:

$$F_2(x, y) = F_2^0(x, y) + nF_2^1(x, y) + n^2F_2^2(x, y) + \cdots,$$

where

$$F_2^0(x_1, x_2) = \frac{1}{\Theta^2}\left\{g_1^0(x_1)\, g_1^0(x_2) - \Theta\, \frac{\delta g_1^0(x_1)}{\delta u_{x_2}}\right\} = 1 - \frac{1}{\Theta}\, \frac{\delta g_1^0(x_1)}{\delta u_{x_2}} = c_1 \exp\left\{-\frac{1}{\Theta}\Phi(|x_1 - x_2|)\right\},$$

or

$$F_2^0(x_1, x_2) = \exp\left\{-\frac{1}{\Theta}\Phi(|x_1 - x_2|)\right\}, \tag{45}$$

since, from the boundary condition:

$$F_2^0(x_1, x_2) \to F_1(x_1)\, F_1(x_2) = 1 \quad \text{at} \quad |x_1 - x_2| \to \infty$$

it follows that the constant $c_1 = 1$;

$$F_2^1(x_1, x_2) = \Theta^{-2}\{g_1^0(x_1)\, g_1^1(x_2) + g_1^1(x_1)\, g_1^0(x_2) - \Theta\delta g_1^1(x_1)/\delta u_{x_2}\} = -\Theta^{-1}\delta g_1^1(x_1)/\delta u_{x_2}, \tag{46}$$

$$F_2^2(x_1, x_2) = -\Theta^{-1}\delta g_1^2(x_1)/\delta u_{x_2}, \ldots \tag{47}$$

As is evident from (46), $F_2^1(x_1, x_2)$ is proportional to the variational derivative $\delta g_1^1(x_1)/\delta u_{x_2}$. We can find this derivative by functional differentiation of Eq. (37) with respect to u_{x_2} and setting $u = 0$. We then get, taking Eqs. (38), (42) and (43) into account:

$$\begin{aligned} -\frac{\partial}{\partial x_1^\alpha}\, \frac{\delta g_1^1(x_1)}{\delta u_{x_2}} + \int \frac{\partial \Phi(|x_1 - y|)}{\partial x_1^\alpha}\Big\{\exp\Big[-\frac{1}{\Theta}(\Phi(|x_1 - x_2|) + \Phi(|x_2 - y|))\Big] \\ - 2 - \frac{1}{\Theta}\, \frac{\delta^2 g_1^0(x_1)}{\delta u_y \delta u_{x_2}}\Big\}\, dy - \frac{1}{\Theta}\, \frac{\partial \Phi(|x_1 - x_2|)}{\partial x_1^\alpha}\, \frac{\delta g_1^1(x_1)}{\delta u_{x_2}} = 0. \end{aligned} \tag{48}$$

We find the derivative of g_1^0 here from Eq. (41) by functional differentiation with respect to u_y and substitution of $u = 0$, and also, making use of Eqs. (38) and (42). We then get:

$$\begin{aligned} \delta^2 g_1^0(x_1)/\delta u_y \delta u_{x_2} = \Theta\Big\{\exp\Big[-\frac{1}{\Theta}(|x_2 - y|)\Big] + \exp\Big[-\frac{1}{\Theta}\Phi(|x_1 - x_2|)\Big] \\ + \exp\Big[-\frac{1}{\Theta}\Phi(|x_1 - y|)\Big] - 2\Big\} \\ + c_2 \exp\Big\{-\frac{1}{\Theta}\Big[\Phi(|x_1 - x_2|) + \Phi(|x_1 - y|) + \Phi(|x_2 - y|)\Big]\Big\}. \end{aligned} \tag{49}$$

The constant c_2 is determined similarly to c_1, and is equal to unity.

Substituting Eq. (49) in (48) for $c_2 = 1$, we get the equation

$$\frac{\partial}{\partial x^{\alpha}}\frac{\delta g_1^1(x_1)}{\delta u_{x_2}} + \frac{1}{\Theta}\frac{\partial\Phi(|x_1-y|)}{\partial x_1^{\alpha}}\frac{\delta g_1^1(x_1)}{\delta u_{x_2}} = \exp\left\{-\frac{1}{\Theta}\Phi(|x_1-x_2|)\right\}\int\frac{\partial\Phi(|x_1-y|)}{\partial x_1^{\alpha}} \times \exp\left\{-\frac{1}{\Theta}[\Phi(|x_1-y|)+\Phi(|x_2-y|)]\right\}dy. \quad (50)$$

Moreover, since

$$\frac{\partial\Phi(|x_1-y|)}{\partial x_1^{\alpha}}\exp\left\{-\frac{1}{\Theta}[\Phi(|x_1-y|)+\Phi(|x_2-y|)]\right\} = -\Theta\frac{\partial}{\partial x^{\alpha}}\{(1+f(|x_1-y|))(1+f(|x_2-y|))\},$$

where

$$f(r) = \exp\{-\Phi(r)/\Theta\} - 1,$$

then, taking (46) into consideration, we get the following equation for $F_2^1(x_1, x_2)$:

$$\frac{\partial F_2^1}{\partial x_1^{\alpha}} + \frac{1}{\Theta}\frac{\partial\Phi(|x_1-x_2|)}{\partial x_1^{\alpha}}F_2^1 = \exp\left\{-\frac{1}{\Theta}\Phi(|x_1-x_2|)\right\}\frac{\partial}{\partial x_1^{\alpha}}\int f(|x_1-y|)f(|x_2-y|)\,dy. \quad (51)$$

Looking for a solution of this equation in the form

$$F_2^1(x_1, x_2) = \psi(|x_1-x_2|)\exp\left\{-\frac{1}{\Theta}\Phi(|x_1-x_2|)\right\},$$

we get (after substitution):

$$F_2^1(|x_1-x_2|) = F_2^1(|x|) = \exp\left\{-\frac{1}{\Theta}\Phi(|x|)\right\}\int f(|x-x'|)f(|x'|)\,dx'. \quad (52)$$

Similarly, we can find the other terms of the expansion of F_2^2, F_2^3, etc.

Thus the pair distribution function of a system of particles with short-range interaction is equal, with accuracy up to terms of second order, to

$$F_2(x_1, x_2) = F_2(|x|) = \exp\left\{-\frac{1}{\Theta}\Phi(|x|)\right\}\left(1 + n\int f(|x-x'|)f(|x'|)\,dx'\right). \quad (53)$$

Other correlation functions are found by the method of variational derivatives in the same way as the pair functions.

4. SUPERPOSITION THEOREM

In Secs. 2 and 3 we developed a method for finding the correlation functions for systems of particles corresponding to the Coulomb interaction potential $\Phi_0(r)$, and to a potential $\Phi_1(r)$ which falls off rapidly with distance. In the first case, these functions are found by an expansion in powers of v; in the second case, by an expansion in powers of $n = 1/v$. Here, the first approximation for the pair distribution function (27) loses its applicability for small r, and finding higher approximations would be senseless since they diverge even more strongly for small r.[1]

Real interaction between charged particles consists of Coulomb forces ($r > r_0$) and short-range forces, such that the potential of this interaction has the form $\Phi_0(r) + \Phi_1(r)$. However, as Bogoliubov pointed out in Ref. 1, the problem is open at the present time of the construction of expansions by which we could find the correlation functions for systems with interaction including both Coulomb and short-range forces; such a construction would make it possible to obtain asymptotic formulas for any approximation.

In the present Section, making use of variational derivatives, we establish a "superposition theorem", *i.e.*, we set forth a method of investigation of a system with interaction of the form

$$\Phi(r) = \Phi_0(r) + \Phi_1(r). \tag{54}$$

Let the total energy of interaction of a system of N particles in the potential (54) be equal to

$$U = U_0 + \sum_{1\leqslant i<j\leqslant N} \Phi_1(|x_i - x_j|),$$

where U_0 is the part of the interaction energy of the system of particles which corresponds to the potential $\Phi_0(r)$. Moreover, if our system is located in an external field $\varphi(x)$, then the configurational integral of the system is

$$\begin{aligned} Q &= \int \exp\Big\{-\frac{1}{\Theta}U - \frac{1}{\Theta}\sum_{1\leqslant i\leqslant N}\varphi(x_i)\Big\}dx_1\ldots dx_N \\ &= \int \exp\Big\{-\frac{1}{\Theta}U_0 - \frac{1}{\Theta}\sum_{1\leqslant i\leqslant N}\varphi(x_i)\Big\}\prod_{1\leqslant i<j\leqslant N}(1+f(x_i, x_j))\,dx_1\ldots dx_N, \end{aligned} \tag{55}$$

where

$$f(x_i, x_j) = \exp\{-\Phi_1(|x_i - x_j|)/\Theta\} - 1.$$

The free energy of the system is equal to $F = -\Theta \ln Q$. Both the configurational integral (55) and the free energy are themselves functionals of the external field $\varphi(x)$ and the interaction energy $f(x_i, x_j)$. The correlation functions of the system $F_1(x_1 \mid \varphi \mid f)$, $F_2(x_1, x_2 \mid \varphi \mid f)$, etc., are expressed in terms of the variational derivatives of the functional F with respect to $\varphi(x)$ according to Eqs. (4) and (7).

In Secs. 2 and 4, we found $F_1(x_1 \mid \varphi)$ from the corresponding equations with variational derivatives with the help of well known expansions. We now proceed otherwise. We shall show that the functional $F(\varphi \mid f)$ can be expressed by the correlation functions of the system for a potential $\Phi_0(r)$, so that, for finding the variational derivatives of $F(\varphi \mid f)$ with respect to $\varphi(x)$ and, consequently, the correlation functions $F_s(x_1, \ldots, x_s \mid \varphi \mid f)$, it is not necessary to construct and solve the differential equations for these functions; it is necessary to know them only for the potential $\Phi_0(r)$, the determination of which was carried out in Sec. 2.

With this end in view, we expand the function $F(\varphi \mid f)$ in a series

$$F(\varphi \mid f) = F_{f=0} + \int f(x, y)\Big(\frac{\delta F}{\delta f_{x,y}}\Big)_{f=0} dx\,dy + \frac{1}{2}\int f(x, y) f(x', y')\Big(\frac{\delta^2 F}{\delta f_{x,y}\delta f_{x',y'}}\Big)_{f=0} dx\,dy\,dx'\,dy' + \ldots \tag{56}$$

and find expressions for the variational derivatives therein: On the one hand, we have from (55):

$$\begin{aligned} \delta Q &= \int \exp\Big\{-\frac{1}{\Theta}U_0 - \frac{1}{\Theta}\sum_{1\leqslant j\leqslant N}\varphi(x_j)\Big\}\sum_{1\leqslant r<j\leqslant N}\delta f(x_i, x_j) \\ &\quad\times\Big[\prod_{1\leqslant r<s\leqslant N}(1+f(x_r, x_s))/(1+f(x_i, x_j))\Big]dx_1\ldots dx_N, \\ (1+f(x, y))\frac{\delta Q}{\delta f_{x,y}} &= \frac{N(N-1)}{2}\int \exp\Big\{-\frac{1}{\Theta}U_0 - \frac{1}{\Theta}\sum_j \varphi(x_j)\Big\} \\ &\quad\times\prod_{1\leqslant r<s\leqslant N}(1+f(x_r, x_s))\,dx_3\ldots dx_N \end{aligned} \tag{57}$$

(here we have set $x_1 = x$, and $x_2 = y$), and on the other hand:

$$\frac{\delta Q}{\delta\varphi_x} = -\frac{N}{\Theta}\int \exp\left\{-\frac{1}{\Theta}U_0 - \frac{1}{\Theta}\sum_j \varphi(x_j)\right\}\prod_{1\leqslant r<s\leqslant N}(1+f_{r,\,s})\,dx_2\ldots dx_N, \tag{58}$$

$$\frac{\delta^2 Q}{\delta\varphi_x\delta\varphi_y} = \frac{N(N-1)}{\Theta^2}\int \exp\left\{-\frac{1}{\Theta}U_0 - \frac{1}{\Theta}\sum_j \varphi(x_j)\right\}\prod_{1\leqslant r<s\leqslant N}(1+f_{r,\,s})\,dx_3\ldots dx_N$$
$$+\frac{N}{\Theta^2}\delta(x-y)\int \exp\left\{-\frac{1}{\Theta}U_0 - \frac{1}{\Theta}\sum_j \varphi(x_j)\right\}\prod_{1\leqslant r<s\leqslant N}(1+f_{r,\,s})\,dx_2\ldots dx_N. \tag{59}$$

Comparing (57) with (58) and (59), we find

$$(1+f_{x,\,y})\frac{\delta Q}{\delta f_{x,\,y}} = \frac{\Theta^2}{2}\left\{\frac{\delta^2 Q}{\delta\varphi_x\delta\varphi_y} - \frac{\delta(x-y)}{\Theta}\frac{\delta Q}{\delta\varphi_x}\right\}, \tag{60}$$

and since $Q = e^{-F/\Theta}$, then, substituting the values of the corresponding variational derivatives in Eq. (60), we get

$$(1+f_{x,\,y})\frac{\delta F}{\delta f_{xy}} = \frac{\Theta^2}{2}\left\{\frac{\delta^2 F}{\delta\varphi_x\delta\varphi_y} - \frac{1}{\Theta}\frac{\delta F}{\delta\varphi_x}\frac{\delta F}{\delta\varphi_y} + \frac{\delta(x-y)}{\Theta}\frac{\delta F}{\delta\varphi_x}\right\}. \tag{61}$$

Again taking functional derivatives of this equation with respect to $f_{x'y'}$, we find an expression for the second derivative. The right side of (61), in accord with Eqs. (8) and (4), is equal to

$$-\tfrac{1}{2}\Theta N(N-1)V^{-2}F_2(x,\,y\,|\,\varphi\,|\,f),$$

therefore

$$(1+f_{xy})\,\delta F/\delta f_{xy} = -\tfrac{1}{2}n^2\Theta F_2(x,\,y\,|\,\varphi\,|\,f). \tag{62}$$

Setting $f_{xy} = 0$, we get

$$(\delta F/\delta f_{xy})_{f=0} = -\tfrac{1}{2}n^2\Theta F_2(x,\,y\,|\,\varphi\,|\,0),$$

i.e., this variational derivative is expressed by the pair distribution function for the potential $\Phi_0(r)$. Therefore, in first approximation, and in accord with (56), the free energy of the system for the potential (54) is equal to

$$F(\varphi\,|\,f) = F_{f=0} - n^2\frac{\Theta}{2}\int f(x,\,y)\,F_2(x,\,y\,|\,\varphi)\,dx\,dy. \tag{63}$$

Knowing $F_2(x,\,y\,|\,\varphi)$, taking the functional derivative of (63) with respect to $\varphi(x)$, we can find the correlation functions $F_1(x\,|\,\varphi\,|\,f)$, $F_2(x,\,y\,|\,\varphi\,|\,f)$ *etc.*, and then setting $\varphi = 0$, we find $F_1(x\,|\,f)$, $F_2(x,\,y\,|\,f)$ etc. for our system.

A calculation carried out by the method of correlation functions of a system for the concrete case $\Phi_0(r)$ and $\Phi_1(r)$ will form the subject of another paper.

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[1] N. N. Bogoliubov, *Problems of Dynamical Theory in Statistical Physics*, Gostekhizdat, 1946.

[2] N. N. Bogoliubov, Vestnik, Moscow State Univ. Nos. 4–5, 115 (1955).

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