

Here $h = -b_0(c_1^2 + c_2^2)$. In particular, when condition (2.7) is satisfied, we have

$$c_2 = \pm ic_1, \Phi = ce^{i\sigma} + c^*e^{i\sigma} \quad (2.26)$$

which gives the solution to the ordinary Dirac equation.

It is also of interest to investigate the nonlinear generalization of the Duffin-Kemmer equation

$$(\beta_\mu \partial / \partial x_\mu - c(\bar{\varphi}, \varphi))\varphi = 0, \quad (2.27)$$

where the β_μ are Kemmer-Duffin matrices, and $c(\bar{\varphi}, \varphi)$ is an arbitrary scalar function.

I consider it my duty to express my deep gratitude to Professor D. D. Ivanenko for constant attention to the work and to Professor Kh. Ia. Khristov for valuable comments.

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Translated by E. J. Saletan
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Statistical Theory of Systems of Charged Particles With Account of Short Range Forces of Repulsion

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(Submitted to JETP editor July 5, 1956)

J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 1163-1170 (May, 1957)

The free energy of an electrically neutral system of charged particles (ions) has been found by taking into account the repulsive forces between them. The general expression obtained for the free energy of such systems is applied to its calculation for a concrete form of "long-range" and "short-range" forces.

THE EQUILIBRIUM STATE of each statistical system of N particles is entirely determined by a knowledge of the Gibbs distribution function D or the equivalent aggregate distribution function $F_s(x_1, x_2, \dots, x_s)$ ($s = 1, 2, \dots$)¹. For example, the pair distribution function $F_s(x_1, x_2)$ permits us to find the thermodynamic potential of the system, knowing which we can solve any problem pertaining to the state of thermodynamic equilibrium.

Ways of finding the correlation functions of systems of particles both with Coulomb (slowly decreasing with distance) potential of interaction $\Phi^0(r)$, and with molecular (rapidly decreasing with distance) interaction $\Phi^1(r)$, were first developed by Bogoliubov¹. However, the problem of the con-

struction of an expansion by which we could find the correlation functions in the case of a system with an interaction containing both Coulomb and short-range forces, remained unsolved.

Making use of an equation with variational derivatives, we² succeeded in outlining a method of finding the correlation functions both for systems with interaction $\Phi^0(r)$ or $\Phi^1(r)$, and for the "additive" interaction $\Phi(r) = \Phi^0(r) + \Phi^1(r)$ which contains, in the terminology of Vlasov³, both "short-range" and "long-range" forces. In this paper, following Ref. 2, we define as the thermodynamic potential the free energy $F(\Phi)$ of a system of charged particles with explicit account of the short-range repulsive forces between them, which enables us to de-

velop the entire thermodynamics of such a type of system.

1. FREE ENERGY OF A SYSTEM OF CHARGED PARTICLES

Let us consider a system of M types of different charged particles (for example, a solution of strong electrolytes) with numbers N_a and charges e_a ($a = 1, 2, \dots, N$) of particles of each type, and with interaction potentials

$$\Phi_{ab}(r) = \Phi_{ab}^0(r) + \Phi_{ab}^1(r), \quad (1)$$

where $r = r_{ab}$ = distance between particular particles of types a and b . Let the system as a whole

be electrically neutral and the various particles differ only in charge; then

$$\sum_a N_a e_a = 0 \quad \text{or} \quad \sum_a n_a e_a = 0, \quad (2)$$

where $n_a = N_a/N$ = concentration of particles of the a th type and $N = N_a$ is the total number of particles in a system of volume V . If this system is found in an external field $\varphi(\mathbf{r})$, then the configuration integral of such a system is equal to*

$$Q = \int \exp \left\{ -\frac{1}{\theta} U - \frac{1}{\theta} \sum_{i,a} \varphi_a(\mathbf{r}_i) \right\} d\tau, \quad (3)$$

where

$$\begin{aligned} U &= \sum_{\substack{a < b \\ i, j}} \Phi_{ab}(|\mathbf{r}_{a,i} - \mathbf{r}_{b,j}|) = \sum \Phi_{ab}^0(|\mathbf{r}_{a,i} - \mathbf{r}_{b,j}|) + \sum \Phi_{ab}^1(|\mathbf{r}_{a,i} - \mathbf{r}_{b,j}|) \\ &= U^0 + \sum \Phi_{ab}^1(|\mathbf{r}_{a,i} - \mathbf{r}_{b,j}|) \end{aligned}$$

is the potential energy of interaction of the particles with one another, $\mathbf{r}_{a,i}$ defines the position of the i th molecule of the a th type (below, we shall call \mathbf{r}_i , or any set r_{ix}, r_{iy}, r_{iz} , by the letter x_i), $d\tau$ is the element of phase volume of the system and $\theta = kT$.

We can also put the configuration integral in the form

$$Q = \int \exp \left\{ -\frac{1}{\theta} U^0 - \frac{1}{\theta} \sum_{a,i} \varphi_a(x_i) \right\} \prod_{\substack{a < b \\ i, j}} (1 + f_{ab}(x_i, x_j)) d\tau, \quad (4)$$

$$f_{ab}(x_i, x_j) = \exp \left\{ -\frac{1}{\theta} \Phi_{ab}^1(|x_i - x_j|) \right\}. \quad (5)$$

The free energy of our system, $F(\varphi | \Phi) = F(\varphi | \Phi^0 + \Phi^1)$, is a functional of the external field and the interaction potential between the particles and is equal to

$$F(\varphi | \Phi) = -\theta \ln Q(\varphi | \Phi). \quad (6)$$

As for an arbitrary functional,

$$\begin{aligned} F(\varphi | \Phi^0 | f) &= F(\varphi | \Phi^0) + \sum_{a,b} \int f_{ab}(x, y) \left(\frac{\delta F}{\delta f_{ab}(x, y)} \right)_{f=0} dx dy + \\ &+ \frac{1}{2} \sum_{a,b} \sum_{a',b'} \int f_{ab}(x, y) f_{a'b'}(x', y') \left(\frac{\delta^2 F}{\delta f_{ab}(x, y) \delta f_{a'b'}(x', y')} \right)_{f=0} dx dy dx' dy' + \dots \end{aligned} \quad (7)$$

Determining the different variational derivatives of F from Eq. (6), and comparing them, we find

$$\begin{aligned} (1 + f_{ab}(x, y)) \frac{\delta F}{\delta f_{ab}(x, y)} &= \frac{\theta^2}{2} \left\{ \frac{\delta F}{\delta \varphi_a(x) \delta \varphi_b(y)} - \frac{1}{\theta} \frac{\delta F}{\delta \varphi_a(x)} \frac{\delta F}{\delta \varphi_b(y)} \right. \\ &\left. - \frac{\delta(x-y)}{\theta} \frac{\delta F}{\delta \varphi_a(x)} \right\} = -\frac{\theta}{2} \frac{N_a(N_b - \delta_{ab})}{V^2} F_{ab}(x, y | \Phi^0 + \Phi^1), \end{aligned} \quad (8)$$

*Sums of products over a, b, c, \dots run everywhere from 1 to M . The sums over i and j run, respectively, from 1 to N_a and from 1 to N_b (if not stated otherwise).

whence

$$\left(\frac{\delta F}{\delta f_{ab}(x, y)}\right)_{f=0} = -\frac{\theta}{2} \frac{N_a(N_b - \delta_{ab})}{V^2} F_{ab}(x, y | \Phi^0), \quad (9)$$

where $F_{ab}(x, y | \Phi^0)$ is the pair distribution function of the system for the potential $\Phi^0(r)$, and δ_{ab} is the Kronecker symbol. If we set the external field $\varphi(x)$ in Eq. (7) equal to zero, then we can find the value of the free energy of the system of charged particles for the potential $\Phi(r) = \Phi^0(r) + \Phi^1(r)$. For the free energy of such a system, we get, with accuracy up to the second term in the expansions of (7) and (9):

$$F(\Phi) = F(\Phi^0) - \frac{\theta}{2} \sum_{a,b} \frac{N_a(N_b - \delta_{ab})}{V^2} \int f_{ab}(x, y) F_{ab}(x, y | \Phi^0) dx dy. \quad (10)$$

We can represent the free energy $F(\Phi^0)$ of a system of particles with an interaction potential $\Phi^0(r)$ by a pair distribution function $F_{ab}(x, y | \Phi^0)$ for this system.

Thus Eq. (10) gives the possibility of calculating the free energy of a system of charged particles with consideration of short-range repulsive forces between them if the pair distribution function $F_{ab}(x, y | \Phi^0)$ is known for the $\Phi^0(r)$ potential of "long-range" forces.

2. PAIR DISTRIBUTION FUNCTIONS AND THE FREE ENERGY OF A SYSTEM OF PARTICLES FOR THE POTENTIAL

The first approximation for the pair distribution function for a Coulomb interaction potential between ions:

$$\Phi_{ab}^0(r) = e_a e_b / \varepsilon r, \quad (11)$$

was first found by Bogoliubov¹ by the method of equations with variational derivatives²; it corresponds to the well-known⁴ Debye-Hückel self-consistent potential

$$V(r) = (e_a / \varepsilon) e^{-\kappa r} / r \quad (12)$$

and is equal to

$$F_{ab}^1(r) = - (e_a e_b / \varepsilon \theta v) e^{-\kappa r} / r, \quad (13)$$

where ε is the dielectric constant of the solution, and the quantity

$$\frac{1}{\kappa} = r_d = \left(\frac{\varepsilon \theta v}{4\pi \sum_a n_a e_a^2} \right)^{1/2} = \left(\frac{\varepsilon \theta}{4\pi n \sum_a n_a e_a^2} \right)^{1/2} \quad (14)$$

determines the mean radius of the ionic cloud which surrounds the given ion (and is known as the Debye radius), $v = V/N$ is the volume per particle, and $n = N/V$ is the concentration of the solution.

The pair function $F_{ab}(x, y | \Phi^0)$ for the potential (11) is, in first approximation (*i.e.*, with accuracy to quantities of second order of smallness):

$$F_{ab}(r) = 1 + v F_{ab}^1(r) = 1 - (e_a e_b / \varepsilon \theta) e^{-\kappa r} / r. \quad (15)$$

As is evident from (13) and (15), the first approximation of the pair distribution function for the potential (11) diverges when $r \rightarrow 0$, which demonstrates the invalidity of the extrapolation of the Coulomb potential to a distance of the order of the particle radius, and the necessity of considering short-range repulsive forces. The second approximation for $F_{ab}(x, y | \Phi^0)$ in the case of a system with Coulomb interaction was found in Ref. 5, where, as was also pointed out in Ref. 1, this approximation becomes even more divergent for small r .

This difficulty with the divergence (at zero) of the pair distribution function in the use of the Coulomb potential of interaction between particles can be avoided as Kramers^{6,4} bypassed the difficulty in the case of a purely statistical derivation of the free energy of an electrolyte, in which, in place of the energy of a solution with Coulomb interaction between the particles

$$U = \sum_{1 \leq i < j \leq N} \frac{e_i e_j}{\varepsilon r_{ij}}$$

he used an expression of the form

$$U_1 = \sum_{1 \leq i < j \leq N} \frac{e_i e_j}{\varepsilon r_{ij}} G_{ij},$$

where

$$G_{ij} = \frac{1}{r_{ij}} (1 - e^{-\lambda h_{ij}}), \quad h_{ij} \rightarrow r_{ij},$$

λ is a constant quantity. From the physical point of view, the introduction of the functions G_{ij} denotes implicit account of the short-range forces of repulsion between the ions. A qualitative account of repulsive forces of such a nature, which reduces to relieving the divergence (at zero) of the pair distribution function $F_{ab}(x, y | \Phi^0)$, was carried out in Refs. 7-9, in which, in place of the Coulomb potential (11), the interaction between the particles is determined by the potential

$$\Phi_{ab}^0(r) = (e_a e_b / \epsilon r) (1 - e^{-\lambda r}). \quad (16)$$

In accord with Ref. 9, the pair distribution function for the potential $\Phi^0(r)$ with accuracy up to quantities of third order of smallness, is equal to

$$\begin{aligned} F_{ab}(r) &= 1 + v F_{ab}^1(r) + v^2 \frac{1}{2} \{F_{ab}^2(r) \\ &+ \sum n_c \int [F_{ac}^1(r_1) F_{cb}^1(r_2) + F_{ac}^1(r_1) F_{cb}^1(r_2)] dx_c \\ &+ \sum_c \sum_d n_c n_d \int F_{ac}^1(r_1) F_{cd}^1(r_3) F_{db}^1(r_4) dx_c dx_d, \end{aligned} \quad (17)$$

where $F_{ab}^1(r)$ is the first approximation of the pair distribution function determined in Ref. 9 for the potential (16). In the present research we shall find the free energy (10) of a system of charged particles with explicit account of the short-range forces of repulsion, taking for the potentials $\Phi^0(r)$ and $\Phi^1(r)$ functions of the form

$$\Phi^0(r) = \begin{cases} 0 & \text{for } r < \sigma \\ \frac{e_a e_b}{\epsilon r} & \text{for } r > \sigma, \end{cases} \quad (18)$$

$$\Phi^1(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 1 & \text{for } r > \sigma, \end{cases} \quad (19)$$

where σ is the diameter of the particle (for an ion, $\sigma \sim 10^{-8}$ cm). We find the first approximation of the pair distribution function $F_{ab}(x, y | \Phi^0)$ for a potential (18) from the Bogoliubov equation for the first approximation¹:

$$\begin{aligned} F_{ab}^1(x, x') + \sum_c n_c \int \psi_{ac}(|x - x''|) F_{cb}^1(x'' x') dx'' \\ = -\psi_{ab}(|x - x'|), \end{aligned} \quad (20)$$

where

$$\psi_{ab}(r) = \frac{1}{\theta v} \Phi_{ab}^0(r) = \begin{cases} 0 & \text{for } r < \sigma, \\ e_a e_b / \epsilon \theta v r & \text{for } r > \sigma. \end{cases} \quad (21)$$

Substituting the Fourier transform into Eq. (20):

$$F_{ab}^1(x, x') = \int L_{ab}(v, x) \exp \{i(\mathbf{v} \mathbf{x}')\} d\mathbf{v}, \quad (22)$$

$$\begin{aligned} \psi_{ab}(|x - x'|) &= \frac{1}{4\pi} \int Y_{ab}(|v|) \exp \{i(\mathbf{v}, \mathbf{x} - \mathbf{x}')\} d\mathbf{v} \\ &= \frac{1}{r} \int_0^\infty v \sin vr Y_{ab}(|v|) dv, \end{aligned} \quad (23)$$

we get a system of linear algebraic equations

$$\begin{aligned} L_{ab}(v, x') + 2\pi^2 \sum_c n_c Y_{ac}(|v|) L_{cb}(v, x') \\ = -\frac{1}{4\pi} Y_{ab}(|v|) \exp \{-i(\mathbf{v}, \mathbf{x}')\}. \end{aligned} \quad (24)$$

Setting

$$L_{ab}(v, x') = K_{ab} \exp \{-i(\mathbf{v} \mathbf{x}')\} \quad (25)$$

we get

$$K_{ab} + 2\pi^2 \sum_c n_c Y_{ac}(|v|) K_{cb} = -\frac{1}{4\pi} Y_{cb}(|v|). \quad (26)$$

Since, from (21) and (23),

$$Y_{ab}(|v|) = \frac{1}{2\pi^2} \int \psi_{ab}(|x - x'|) \exp \{-i(\mathbf{v}, \mathbf{x} - \mathbf{x}')\} d\mathbf{x}' = \frac{2}{\pi v^2} \frac{e_a e_b}{\epsilon \theta v} \cos \sigma v, \quad (27)$$

then the solution of the system (26) can be written in the form

$$K_{ab} = -\frac{\lambda_a \lambda_b}{2\pi^2} \frac{\cos \sigma v}{v^2 r_d^2 + \cos \sigma v},$$

$$\lambda_a = e_a \left(4\pi \sum_a n_a e_a^2 \right)^{-1/2}.$$

We see from (22) and (25) that $F_{ab}^1(|x - x'|)$ is a radially symmetric function and is equal, according to the inversion formula of the Fourier integral, to

$$\begin{aligned} F_{ab}^1(r | \Phi^0) \\ = \frac{4\pi}{r} \int_0^\infty v K_{ab}(|v|) \sin rv dv = -\frac{2e_a e_b}{\pi r \epsilon \theta v} r_d^2 I, \end{aligned} \quad (28)$$

where

$$I = \int_0^\infty \frac{v \cos \sigma v \sin rv}{v^2 r_d^2 + \cos \sigma v} dv. \quad (29)$$

It is not difficult to see that at $\sigma = 0$ we get the expression (13) for $F_{ab}^1(r | \Phi^0)$.

In accord with (17), the second approximation of the function $F_{ab}(x_1, x_2 | \Phi^0)$ consists of three components, of which the latter two determine the effect of all the remaining particles of the system on the probability of finding two particular particles a and b at the points x_1 and x_2 . Therefore, for small concentrations, in which the collective interaction between the particles is small, both these components are small (the third is smaller than the second) and the principal term is the first component $\frac{1}{2}F_{ab}^1(r)$; in case of symmetric solutions, the second approximation is exactly equal to this first term, since the two remaining terms are identically equal to zero, because of the neutrality of the system.

Thus, with account only of the principal term of the second approximation, the pair distribution function $F_{ab}(r | \Phi^0)$ is, in the second approximation for the potential (18), equal to

$$\begin{aligned} F_{ab}(r | \Phi^0) &= 1 + vF_{ab}^1(r) + v^2 \frac{1}{2} F_{ab}^2(r) \\ &= 1 - \frac{2e_a e_b}{\pi r \varepsilon \theta} r_d^2 I + 2 \left(\frac{e_a e_b r_d^2}{\pi r \varepsilon \theta} \right)^2 I^2. \end{aligned} \quad (30)$$

Knowing $F_{ab}(r | \Phi^0)$, it is easy to calculate the free energy $F(\Phi^0)$ for the potential $\Phi^0(r)$ by the Gibbs-Helmholtz equation, and then, in accord with Eq. (10), we also calculate the free energy of the system of charged particles with consideration of short-range forces of repulsion. Actually, integrating the Gibbs-Helmholtz equation $F = E + T(dF/dT)_v$, we get for the free energy corresponding to the interaction of particles with the potential $\Phi^0(r)$ the expression

$$F(\Phi^0) = -T \int T^{-2} E(\Phi^0) dT. \quad (31)$$

The average energy of interaction of the particles $E(\Phi^0)$ for the potential $\Phi^0(r)$ is equal to

$$\begin{aligned} E(\Phi^0) &= \int U^0 Dd\tau \\ &= \int \sum_{\substack{a < b \\ i, j}} \Phi_{ab}^0(|x_{ai} - x_{bj}|) \cdot Ddx_1 \dots dx_N \\ &= \sum_{a < b} N_a N_b \int \Phi_{ab}^0(|x_1 - x_2|) dx_1 dx_2 \int Ddx_3 \dots dx_N \end{aligned}$$

or

$$E(\Phi^0) = \frac{2\pi}{V} \sum_{a, b} N_a N_b \int \Phi_{ab}^0(r) F_{ab}(r | \Phi^0) r^2 dr. \quad (32)$$

Substituting (18) and (30), and taking into account the neutrality condition (2), we get

$$\begin{aligned} E(\Phi^0) &= -\frac{4}{V} \sum_{a, b} N_a N_b \\ &\times \int_{\sigma}^{\infty} \frac{e_a e_b}{\varepsilon r} \left(\frac{e_a e_b r_d^2}{\varepsilon \theta r} I - \frac{e_a^2 e_b^2 r_d^4}{\pi \varepsilon^2 \theta^2 r^2} I^2 \right) r^2 dr. \end{aligned} \quad (33)$$

For symmetric solutions, $\sum_a N_a e_a^3 = 0$; therefore, the integral of the second term in (33) is equal to zero* and $E(\Phi^0)$ for such solutions will be

$$E(\Phi^0) = -\frac{\sum_a N_a e_a^2}{\pi \varepsilon} \int_0^{\infty} \frac{\cos^2 \sigma v}{v^2 r_d^2 + \cos \sigma v} dv. \quad (34)$$

The integral here does not reduce to finite form; limiting ourselves to the first term of the asymptotic expression of this integral, we get

$$E(\Phi^0) = -\left(\sum_a N_a e_a^2 / 2\varepsilon \right) \cdot \kappa / \sqrt{1 - 1/2 \sigma^2 \kappa^2}, \quad (35)$$

or

$$\begin{aligned} E(\Phi^0) &= -\frac{\sum_a N_a e_a^2}{2\varepsilon} \kappa \left(1 + \frac{1}{4} \sigma^2 \kappa^2 + \frac{3}{32} \sigma^4 \kappa^4 + \dots \right). \end{aligned} \quad (36)$$

In the case of vanishingly small concentrations, where

$$\sigma \kappa \ll 1, \quad (37)$$

Equation (36) gives the Debye value for the energy of solution of a strong electrolyte⁴:

$$E = -(\kappa / 2\varepsilon) \sum_a N_a e_a^2.$$

Equation (35) for the energy of solution, being a function of the variables T , V , N_a , is not a thermodynamic potential, and consequently does not permit us to develop the thermodynamics of strong electrolytes. Therefore, we must calculate the free energy, which is precisely the potential in these variables. For this purpose, we substitute (36) in (31). After integration we obtain the free energy of the system of charged particles for an interaction potential in the form of (18):

* In the case of non-symmetric solutions, the second term in (33) is not equal to zero, as a consequence of which, $E(\Phi^0)$ diverges logarithmically for $\sigma \rightarrow 0$.

$$F(\Phi^0) = -\frac{\kappa}{3\epsilon} \sum_a N_a e_a^2 \left(1 + \frac{3}{20} \sigma^2 \kappa^2 + \frac{9}{224} \sigma^4 \kappa^4 + \dots \right) \quad (38)$$

For very small concentrations, in which the condition (37) of the applicability of the Debye theory is satisfied, we get from (38) the value given by this theory for the free energy of a strong electrolyte*:

$$F = -\frac{\kappa}{3\epsilon} \sum_a N_a e_a^2.$$

$$F(\Phi) = F(\Phi^0) - \frac{\theta}{2V} \sum_{a,b} N_a (N_b - \delta_{ab}) \int_0^\infty \left[\exp \left\{ -\frac{1}{\theta} \Phi_{ab}^1(r) \right\} - 1 \right] \times F_{ab}(r | \Phi^0) 4\pi r^2 dr.$$

For the potential of "short-range" forces in the form (19) and for the value of $F(\Phi^0)$ determined by (38), the free energy of a system of charged particles [keeping only the first approximation in $F_{ab}(r | \Phi^0)$] will be:

$$F(\Phi) = -\frac{\kappa}{3\epsilon} \sum_a N_a e_a^2 \left(1 + \frac{3}{20} \sigma^2 \kappa^2 + \dots \right) + \frac{2\pi\sigma^3\theta}{3V} \sum_{a,b} N_a (N_b - \delta_{ab}). \quad (39)$$

The expression obtained for the free energy is the thermodynamic potential and therefore permits the determination of both the thermal and the caloric properties of the system: the osmotic pressure (more precisely, the change in the osmotic pressure relative to the pressure in ideal solutions), the activity coefficients f_a of ions of the a th type, etc. We shall not determine these quantities, inasmuch as their computation reduces merely to differentiation of (39) with respect to V , T and N_a .

The free energy (39), and also Eqs. (35) and (38), were obtained for symmetric solutions with the exact value of the second approximation of the pair distribution function. In the case of asymmetric solutions, the expression for the pair distribution function (30) takes account only of the principal term of the second approximation of this function, which applies to solutions of low concentration. Upon increase in the concentration, the collective

* The expression found in Ref. 8 for the first approximation of the free energy of a symmetric solution for the potential (16) [Eq. (2.4) of Ref. 8], diverges for $\sigma \rightarrow 0$, but does not go over into the Debye form, which points out the error of this expression. The correct value of the free energy of a symmetric solution, for the potential (16), is

$$F = -\frac{1}{12 \epsilon \kappa^2 \sigma^3} \left(\sqrt{1+2\kappa\sigma} - 1 \right)^3 \left(\sqrt{1+2\kappa\sigma} + 3 \right).$$

3. FINAL RESULTS. FURTHER IMPROVEMENT IN ACCURACY

Knowing the free energy $F(\Phi^0)$ of a system of particles for the potential $\Phi^0(r)$ of "long-range" forces, we can calculate the free energy $F(\Phi)$ of a system of charged particles with account of short-range forces of repulsion.

According to Eq. (10), $F(\Phi^0)$ is equal to

interactions between particles increase, and the value of the second and third terms in the expression of the second approximation of the pair distribution function (17) increase. Inasmuch as both these terms are expressed by the function $F_{ab}^1(r | \Phi^0)$, the value of which is given by Eq. (8), then even in this case we can compute the free energy of the system of charged particles with account of repulsive forces, similarly to what was done above.

In conclusion, I express my deep gratitude to Academician N. N. Bogoliubov for discussions on the results and for valued advice.

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SOVIET PHYSICS JETP

VOLUME 5, NUMBER 5

DECEMBER, 1957

Relation Between Scattering and Multiple Particle Production

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(Submitted to JETP editor July 5, 1956)

J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 1171-1175 (May 1957)

According to Fermi's theory, the multiple production of particles in high-energy collisions should be determined by the statistical weight of the respective states. In the present investigation, the statistical weight is calculated while taking into account the mutual interaction of pairs of particles, and it is shown that in this case the phase shift of the interacting particles is involved as a characteristic of the interaction. In resonance scattering, the effect of the scattering reduces to the appearance of an intermediate "isobaric" state which should be included in the statistical theory.

THE STATISTICAL THEORY of multiple production as originally suggested by Fermi¹ is well known to be in disagreement with experiments. In neutron-proton collisions, at energies around 2 Bev, the production of two mesons is considerably more probable than predicted by the theory².

Theoretical and experimental results disagree by a factor of 20. It was suggested by Nikishov and the author³ to modify Fermi's theory according to the following considerations. The cross section of the scattering of π -mesons against nucleons has a strong maximum at a center-of-mass energy of about 160 Mev. This maximum corresponds to a *P*-state and isotopic spin $\frac{3}{2}$. These experiments indicate the presence of a strong interaction between π -mesons and nucleons in these circumstances. Such an interaction must also manifest itself in multiple particle production. It is evidently not taken into account in the original form of Fermi's theory.

A strong interaction between mesons and nucleons may be described qualitatively through the presence of an intermediate, rapidly decaying state of the meson-nucleon system with spin $\frac{3}{2}$ and isotopic spin $\frac{3}{2}$.

This concept of a so-called "isobaric" state was used in a number of articles^{5,6}, including also the work of Tamm and his collaborators⁷. We have suggested (see Ref. 3) that this isobaric state should

be included in the statistical theory of multiple production, thus effectively allowing for the strong interaction between the particles. It was suggested that in a collision between two nucleons or a nucleon and a meson, there may appear "quasi-particles" (isobaric states of the system) of mass $1.32 M_0$, where M_0 is the nucleon mass, having isotopic spin $\frac{3}{2}$ and ordinary spin $\frac{3}{2}$, and rapidly decaying into a nucleon and a meson. It was also suggested that the probability for the production of such "particles" may be determined from their statistical weight. A comparison was made between the modified Fermi theory and experimental results on the multiple production of mesons in nucleon-meson and meson-nucleon collisions in the energy range of 1.4 to 5 Bev (see Refs. 3 and 8). Comparison shows that the theory agrees with experiments regarding the probability of various multiple production processes, and also regarding the energy distribution of secondary particles.

In the present article we want to bring up certain theoretical considerations regarding the relation between resonance scattering and multiple particle production.

First we shall introduce the following example suggested by Landau. We shall consider the statistical sum of the states of a non-ideal gas. In the first approximation we shall assume an ideal gas,