

# ACCOUNTING FOR THE INFLUENCE OF A SHORT-RANGE POTENTIAL IN THE THEORY OF ELECTROLYTES

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## Abstract

## Full Text

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MATHEMATICAL PHYSICS

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# ACCOUNTING FOR THE INFLUENCE OF A SHORT-RANGE POTENTIAL IN THE THEORY OF ELECTROLYTES

(Presented by Academician N. N. Bogolyubov on 25 XII 1965)

As is known, the classical theory of electrolytes <sup>(1)</sup> does not take into account the potential of short-range repulsive forces, which cause the mutual impenetrability of particles; at the same time, the theory of real gases <sup>(2)</sup>, studying the action of a potential of this kind, does not consider systems with charged particles. A method for studying systems of particles with both kinds of interaction was first proposed by N. N. Bogolyubov <sup>(3)</sup> and developed in works <sup>(4-17)</sup>, in which a number of particular results were obtained. The aim of the present work is to create a general method of asymptotic expansions in the statistical mechanics of classical systems, allowing simultaneous account of both the Coulomb and the short-range potential.

We consider a system of  $N$  particles of  $m \geq 2$  species, enclosed in a macroscopic volume  $V$  and interacting by means of the binary potential

$$U_N = \sum \Phi_{ab}(|q_{a_i} - q_{b_j}|) + \Psi_{ab}(|q_{a_i} - q_{b_j}|), \quad (1)$$

(the summation is over all distinct pairs of particles). The number of particles of species  $a$  is denoted by  $N_a$ ; the charge of the electron by  $e$ ;  $Z_a$  is the valence of an ion of species  $a$ ;  $q_{a_i} = \{q_{a_i}^\sigma\}$ ,  $\sigma = 1, 2, 3$ , is the Cartesian coordinate of particle  $i$  of the  $a$ -th species.

The first term in (1) is a potential of Coulomb type

$$\Phi_{ab} = -\frac{e^2 Z_a Z_b}{B\theta |q_{a_i} - q_{b_j}|} \exp\{-\alpha |q_{a_i} - q_{b_j}|\}, \quad (2)$$

smoothed by the presence of an exponential factor, differing from the Debye damping factor in that in the exponent, instead of the quantity  $\chi$ , the reciprocal Debye radius, there stands a factor  $\alpha > 0$  (a potential of this type was considered in work <sup>(18)</sup>). The presence of this exponential factor guarantees the convergence

of the integrals considered below. The quantity  $\alpha$  does not enter the final results, disappearing after the limiting transition as  $\alpha \rightarrow 0$ . The second term is the potential of short-range forces. In the present work, for simplicity of exposition, we shall consider the case of elastic spheres and set

$$\Psi_{ab}(|q_{a_i} - q_{b_j}|) = \begin{cases} 0, & \text{if } |q_{a_i} - q_{b_j}| > d_0, \\ \infty, & \text{if } |q_{a_i} - q_{b_j}| < d_0, \end{cases} \quad (3)$$

where  $d_0$  is the maximum collision diameter of the particles.

For the potential (1), the Gibbs distribution function can be represented in the form

$$D_N = Q_N^{-1} \prod_{a \neq b} (1 + P_{ab})(1 + \varepsilon f_{ab}),$$

where it is denoted:  $Q_N$  is the configurational integral,  $\lambda = 4\pi e^2/B\theta$ ;  $\theta = kT$ ,  $P_{ab} = \exp\{-\lambda\Phi_{ab}\} - 1$ ,  $\varepsilon f_{ab} = \exp\{-\Psi_{ab}/\theta\} - 1$ ,

$$\Phi_{ab} = \frac{Z_a Z_b}{4\pi|q_{a_i} - q_{b_j}|} \exp\{-\alpha|q_{a_i} - q_{b_j}|\}, \quad (4)$$

$\varepsilon$  is a formal parameter.

Following N. N. Bogolyubov<sup>(3)</sup>, we introduce into consideration the set of distribution functions  $F_{a_1 \dots a_s}(q_1 \dots q_s)$  and, using the method of variational differentiation of the generating functional, derive integral equations for the distribution function which, after the change of variables

$$F_{a_1 \dots a_s} = g_{a_1 \dots a_s} \prod_{1 \leq i \neq j \leq s} (1 + \varepsilon f_{a_i a_j})$$

will have the form

$$\begin{aligned}
& g_{a_1 \dots a_s} \left\{ 1 + \frac{1}{v} \int \sum_{b'} \frac{N_{b'}}{N} [P_{a_1 b'} + \varepsilon f_{a_1 b'} (1 + P_{a_1 b'})] dq' + \right. \\
& + \frac{1}{2v^2} \iint \sum_{b' b''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} [P_{a_1 b'} + \varepsilon f_{a_1 b'} (1 + P_{a_1 b'})] [P_{a_1 b''} + \varepsilon f_{a_1 b''} (1 + P_{a_1 b''})] (1 + \\
& + \varepsilon f_{b' b''}) g_{b' b''} dq' dq'' + \frac{1}{6v^3} \iiint \sum_{b' b'' b'''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} \frac{N_{b'''}}{N} [P_{a_1 b'} + \varepsilon f_{a_1 b'} (1 + P_{a_1 b'})] \times \\
& \times [P_{a_1 b''} + \varepsilon f_{a_1 b''} (1 + P_{a_1 b''})] [P_{a_1 b'''} + \varepsilon f_{a_1 b'''} (1 + P_{a_1 b'''})] \times \\
& \left. \times (1 + \varepsilon f_{b' b''}) (1 + \varepsilon f_{b' b'''}) (1 + \varepsilon f_{b'' b'''}) g_{b' b'' b'''} dq' dq'' dq''' \right\} = \\
& = \prod_{2 \leq j \leq s} (1 + P_{a_1 a_j}) \left\{ g_{a_2 \dots a_s} + \frac{1}{v} \int \sum_{b'} \frac{N_{b'}}{N} [P_{a_1 b'} + \varepsilon f_{a_1 b'} (1 + P_{a_1 b'})] \times \right. \\
& \times \prod_{2 \leq j \leq s} (1 + \varepsilon f_{b' a_j}) g_{b' a_2 \dots a_s} dq' + \frac{1}{2v^2} \iint \sum_{b' b''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} [P_{a_1 b'} + \\
& + \varepsilon f_{a_1 b'} (1 + P_{a_1 b'})] [P_{a_1 b''} + \varepsilon f_{a_1 b''} (1 + P_{a_1 b''})] \times \\
& \times \prod_{2 \leq j \leq s} (1 + \varepsilon f_{b' a_j}) (1 + \varepsilon f_{b'' a_j}) g_{b' b'' a_2 \dots a_s} dq' dq'' + \\
& + \frac{1}{6v^3} \iiint \sum_{b' b'' b'''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} \frac{N_{b'''} }{N} [P_{a_1 b'} + \varepsilon f_{a_1 b'} (1 + P_{a_1 b'})] [P_{a_1 b''} + \\
& + \varepsilon f_{a_1 b''} (1 + P_{a_1 b''})] [P_{a_1 b'''} + \varepsilon f_{a_1 b'''} (1 + P_{a_1 b'''})] \times \\
& \times (1 + \varepsilon f_{b' b''}) (1 + \varepsilon f_{b' b'''}) (1 + \varepsilon f_{b'' b'''}) \prod_{2 \leq j \leq s} (1 + \varepsilon f_{b' a_j}) (1 + \varepsilon f_{b'' a_j}) \times \\
& \left. \times (1 + \varepsilon f_{b'' a_j}) g_{b' b'' b'''} a_2 \dots a_s dq' dq'' dq''' \right\}. \tag{5}
\end{aligned}$$

Two length-dimensional parameters are associated with the Coulomb field:  $l^2/\theta$ , which is approximately the distance at which the absolute value of the Coulomb potential becomes equal to the thermal energy, and  $1/\chi$ , the distance at which the effective potential is cut off owing to Debye screening. At sufficiently low concentrations the first should be much smaller than the mean distance between ions, and the second much larger.

One more characteristic length is associated with the short-range potential field—the collision diameter  $d_0$ . At low concentrations the ratio  $d_0^3/v$ , where  $v = V/N$ , must be a small quantity. Under these conditions

quantities, the quantity  $\lambda$ , proportional to the first parameter and further reduced by the introduction of the dielectric constant of the solution  $B$ , the density  $1/v$ , and  $\chi_0^2 = \lambda/v = 4\pi l^2 N/B\Theta V$ , may be regarded as small parameters.

We shall solve equations (5) by successive expansions in powers of three parameters: the  $\lambda$  and  $1/v$  considered above, and also the formal parameter  $\varepsilon$ , indicating the degree to which the short-range interaction enters. This last parameter, after the completion of the calculations, may simply be omitted. The quantity  $\chi_0^2$  will be introduced later as an auxiliary summation parameter.

Restricting ourselves to finding the binary distribution function, we expand the desired function in powers of the indicated three parameters:

$$g_{a_1 a_2} = \sum_p \varepsilon^p g_{a_1 a_2}^{(p)} = \sum_p \varepsilon^p \sum_l \left(\frac{1}{v}\right)^l g_{a_1 a_2}^{(p,l)} = \sum_p \varepsilon^p \sum_l \left(\frac{1}{v}\right)^l \sum_m \lambda^m g_{a_1 a_2}^{(p,l,m)}. \quad (6)$$

Let us first note that, putting  $\lambda = 0$ , we exclude the action of Coulomb forces, and, since in this case  $\rho_{ab} = 0$ , equation (5) yields the equation for pure short-range interaction. Expanding in it  $g_{a_1 a_2}$  in powers of  $\varepsilon$ , we obtain a solution which, after the inverse change of variables, coincides with the known result of the theory of real gases of Ursell-Mayer <sup>(2)</sup>.

If we now substitute into equation (5) the expansion of the function  $g_{a_1 a_2} = \sum_p \varepsilon^p g_{a_1 a_2}^{(p)}$  and collect in it the terms of zero order with respect to  $\varepsilon$ , we obtain an equation for systems with purely Coulomb interaction. Solving it by expansion in the remaining two parameters and then carrying out the summation over the auxiliary parameter  $\chi_0^2$ , we arrive at the known result of Debye's theory <sup>(1)</sup> and at the result of work <sup>(4)</sup>.

To determine the contribution to the distribution function due to the presence of both the Coulomb and the short-range potential, we obtain from (5) the equations of first and second approximation in  $\varepsilon$ . Then solving these equations by the same method and carrying out the corresponding summations over the auxiliary parameter, we obtain the following results:

$$\begin{aligned} G_{a_1 a_2}^{1,1} &= \int \sum_{b'} \frac{N_{b'}}{N} (G_{a_1 b'}^{0,1} f_{b' a_2} + f_{a_1 b'} G_{b' a_2}^{0,1}) dq' + \\ &+ \chi_0^2 \iint \sum_{b' b''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} G_{a_1 b'}^{0,1} f_{b' b''} G_{b'' a_2}^{0,1} dq' dq'', \\ G_{a_1 a_2}^{2,0} &= g_{a_1 a_2}^{(2,1,0)} + \chi_0^2 \left\{ \iint \sum_{b'} \frac{N_{b'}}{N} (G_{a_1 b'}^{0,1} g_{b' a_2}^{(2,1,0)} + g_{a_1 b'}^{(2,1,0)} G_{b' a_2}^{0,1}) dq' + \right. \\ &\left. + \iint \sum_{b' b''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} f_{a_1 b'} G_{a_1 b''}^{0,1} f_{b'' a_2} dq' dq'' \right\} + \end{aligned}$$

$$\begin{aligned}
 & +(\chi_0^2)^2 \left\{ \iint \sum_{b'b''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} G_{a_1 b'}^{0,1} g_{b' b''}^{(2,1,0)} G_{b'' a_2}^{0,1} dq' dq'' + \right. \\
 & \left. + \iiint \sum_{b'b''b'''} (f_{a_1 b'} G_{b' b''}^{0,1} f_{b'' b'''} G_{b''' a_2}^{0,1} + G_{a_1 b'}^{0,1} f_{b' b''} G_{b'' b'''}^{0,1} f_{b''' a_2}) dq' dq'' dq''' \right\}. \quad (7)
 \end{aligned}$$

If we now make the inverse change of variables, then, taking into account the known results for purely Coulomb forces and for pure short-range interaction,

$$\begin{aligned}
 G_{a_1 a_2}^{0,1} &= -\frac{Z_{a_1} Z_{a_2}}{4\pi|q_1 - q_2|} \exp\{-\chi|q_1 - q_2|\}, \\
 G_{a_1 a_2}^{0,2} &= -\frac{1}{2} \left\{ [G_{a_1 a_2}^{0,1}]^2 + \chi_0^2 \int \sum_{b'} \frac{N_{b'}}{N} \left( G_{a_1 b'}^{0,1} [G_{b' a_2}^{0,1}]^2 + [G_{a_1 b'}^{0,1}]^2 G_{b' a_2}^{0,1} \right) dq' + \right. \\
 & \left. + (\chi_0^2)^2 \iint \sum_{b'b''} \frac{N_{b'}}{N} \frac{N_{b''}}{N} G_{a_1 b'}^{0,1} [G_{b' b''}^{0,1}]^2 G_{b'' a_2}^{0,1} dq' dq'' \right\}, \\
 g_{a_1 a_2}^{(2,1,0)} &= \int \sum_{b'} \frac{N_{b'}}{N} f_{a_1 b'} f'_{b' a_2} dq',
 \end{aligned}$$

and, omitting the formal parameter  $\varepsilon$ , one can write the expansion of the binary distribution function

$$F_{a_1 a_2} = (1 + f_{a_1 a_2}) \left\{ 1 + \lambda G_{a_1 a_2}^{0,1} + \lambda^2 G_{a_1 a_2}^{0,2} + \frac{1}{\nu} (G_{a_1 a_2}^{2,0} + \lambda G_{a_1 a_2}^{1,1}) \right\},$$

in which both purely Coulomb terms and terms containing the short-range potential up to and including second order have been taken into account.

Questions of the mathematical justification of the method considered have been left aside because of their complexity and are the subject of a separate investigation.

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

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