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Abstract

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ON THE CLASSICAL THEORY OF STRONG ELECTROLYTES

(Presented by Academician N. N. Bogolyubov, 19 VIII 1957)

The principal problem in the theory of strong electrolytes is the calculation of the correction ΔF to the free energy arising from the interaction of ions with one another. A substantial advance in this field was made by Debye, who correctly treated the electrostatic interaction of ions and obtained for ΔF the expression

$$\Delta F = -\frac{N\theta}{12\pi}\frac{v}{r_d^3}, \tag{1}$$

where N is the number of ions; $\theta = kT$; v is the volume per ion; r_d is the Debye radius:

$$r_d^2 = D\theta v\left(4\pi\sum_{(a)} n_a e_a^2\right)^{-1}; \qquad n_a = \frac{N_a}{N}, \tag{2}$$

where N_a and e_a are the number of ions and the charge of each of them for species a; D is the dielectric constant of the solvent.

Debye and Hückel [1] obtained a correction to (1) for the finite radius of the ions r_0:

$$\Delta F = -\frac{N\theta}{12\pi r_d^3}\, v\left(1 - \frac{3}{4}\frac{r_0}{r_d} + \cdots\right). \tag{3}$$

By comparing (3) with experimental data, values of r_0 were obtained that agree well with other estimates of r_0 in the case of large ionic radii. In the case of small ionic radii, this agreement is violated.

Bjerrum [2] found another correction to (1), which, for small concentrations of pairs of ions of opposite signs situated close to one another, has the form:

$$\Delta F = -\frac{1}{2}N\theta\alpha - \frac{N\theta}{12\pi r_d^3}\, v(1-\alpha)^{3/2}, \tag{4}$$

where $N\alpha/2$ is the number of pairs of ions of opposite signs situated at distances from one another smaller than $q = e^2/D\theta$;

$$\alpha = \frac{1}{2v}\int_{r_0}^{q} e^{e^2/D\theta r}\, 4\pi r^2\, dr. \tag{5}$$

The essence of this correction is that, in Bjerrum' s opinion, Debye' s theory may be applied only to those ions that are sufficiently far apart from one another. Pairs of ions of opposite signs should rather be considered similarly to neutral molecules than treated by Debye's theory. We note that in Bjerrum's expression for ΔF there are correction terms of the Debye–Hückel type, which are omitted in (4).

In the present note we investigate the question of the statistical justification of the Debye—Hückel and Bjerrum corrections by N. N. Bogoliubov' s method of correlation functions ([3])*.

The chain of equations for the correlation functions has the form: ([3])

$$\frac{\partial F_{a_1\ldots a_s}}{\partial q_1^\alpha} + \frac{F_{a_1\ldots a_s}}{\theta}\frac{\partial U_{a_1,\ldots,a_s}}{\partial q_1^\alpha} +$$

$$+\frac{1}{\theta v}\int \sum_{(1\le a_{s+1}\le M)} F_{a_1\ldots a_{s+1}} n_{a_{s+1}} \frac{\partial \Phi_{a_1 a_{s+1}}(|q_1 - q_{s+1}|)}{\partial q_1^\alpha}\, dq_{s+1} = 0 \tag{6}$$

$$U_{a_1\ldots a_s} = \sum_{(1\le i<j\le s)} \Phi_{a_i a_j}(|q_i - q_j|). \tag{7}$$

As in ([3]), we shall assume that

$$\sum_{(1\le a\le M)} e_a n_a = 0,$$

and moreover

$$\sum_{(1\le a\le M)} n_a = 1.$$

Following the basic idea of ([4]), we seek the solution of (6) in the form

$$F_{a_1\dots a_s} = C_{a_1\dots a_s} \exp\left\{-\frac{1}{\theta}\,\overline{U}_{a_1\dots a_s}\right\}, \tag{8}$$

$$\overline{U}_{a_1\dots a_s} = \sum_{(1\le i<j\le s)} \overline{\Phi}_{a_i a_j}(|q_i - q_j|). \tag{9}$$

Instead of $C_{a_1\dots a_s}$, introduce new correlation functions $g_{a_1\dots a_s}$:

$$C_{a_1} = g_{a_1}, \tag{10}$$

$$C_{a_1 a_2} = g_{a_1} g_{a_2} + v g_{a_1 a_2},$$

$$C_{a_1 a_2 a_3} = g_{a_1} g_{a_2} g_{a_3} + v\left(g_{a_1} g_{a_2 a_3} + g_{a_2} g_{a_1 a_3} + g_{a_3} g_{a_1 a_2}\right) + v^2 g_{a_1 a_2 a_3},$$

and make the substitution:

$$\frac{1}{\theta}\Phi = v\psi; \qquad \frac{1}{\theta}\overline{\Phi} = v\overline{\psi}.$$

Then, seeking $g_{a_1\dots a_s}$ in the form of a series in powers of v,

$$g_{a_1\dots a_s} = g^0_{a_1\dots a_s} + v g^1_{a_1\dots a_s} + \cdots, \tag{11}$$

we obtain for g^0_{ab} the following equation:

$$g^0_{ab}(|q|) + \psi_{ab}(|q|) - \overline{\psi}_{ab}(|q|) +$$

$$+ \sum_{(1\le c\le M)} n_c \int \psi_{ac}(|q - q'|)\{g^0_{bc}(|q'|) - \overline{\psi}_{bc}(|q'|)\}\, dq' = 0 \tag{12}$$

(by virtue of the spatial homogeneity of the problem, $g_{a_1} = 1$).

From the requirement that g^0_{ab} vanish, equation (12) can be used to find $\overline{\psi}_{ab}(|q|)$ from the known $\psi_{ab}(|q|)$. In the case where the ions are assigned one and the same radius r_0, we obtain for the binary correlation function:

$$F_{ab}(|q|) \simeq \begin{cases} \exp\left\{-\dfrac{e_a e_b}{\theta}\dfrac{1}{|q|} e^{-|q|/r_d}\right\}, & |q| > r_0, \\ 0, & |q| \le r_0 \end{cases} \tag{13}$$

(with accuracy up to and including terms of first order in the plasma parameter). Such a form for F_{ab} was natural to expect in advance.

* On the question of the statistical justification of the results of Debye' s theory, see also works ([7,8]).

For the part of the free energy ΔF arising from the interaction of ions, we use the general formula (5)

$$\Delta F = \frac{N}{2v} \sum_{(1 \le a,b \le M)} n_a n_b \int_V \int_0^1 \Phi_{ab}(|q|)\, F_{ab}(|q|; \tau\Phi)\, dq\, d\tau. \tag{14}$$

Substituting (13) into (14), we shall have:

$$\Delta F = N\,\frac{2\pi}{vD} \sum_{(1 \le a,b \le M)} n_a n_b e_a e_b \int_{r_0}^{\infty} \int_0^1 \left(\exp\left\{ -\frac{\tau e_a e_b}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}} \right\} - 1 \right) r\, dr\, d\tau. \tag{15}$$

In the case where the ionic radii are sufficiently large, i.e.

$$r_0 \gg \max_{(a,b)} \left| \frac{e_a e_b}{D\theta} \right| = q, \tag{16}$$

the exponential in the integrand of (15) may be expanded in a series. In this way we arrive at the results of the Debye–Hückel theory (3).

We shall now show that expression (15) contains, at least for small concentrations of pairs of ions of opposite signs that are close to one another, Bjerrum' s correction. For simplicity, let us consider the special case of an electrolyte consisting of two kinds of ions with charges equal in absolute value. In this case formula (15) assumes the simpler form:

$$\begin{aligned}
\Delta F = {} & N\,\frac{e^2}{D}\,\frac{\pi}{v} \int_{r_0}^{q} \int_0^1 \exp\left\{ -\tau \frac{e^2}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}} \right\} r\, dr\, d\tau \\
& - N\,\frac{e^2}{D}\,\frac{\pi}{v} \int_{r_0}^{q} \int_0^1 \exp\left\{ \tau \frac{e^2}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}} \right\} r\, dr\, d\tau \\
& + N\,\frac{e^2}{D}\,\frac{\pi}{v} \int_{q}^{\infty} \int_0^1 \left(\exp\left\{ -\tau \frac{e^2}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}} \right\} - 1 \right) r\, dr\, d\tau \\
& - N\,\frac{e^2}{D}\,\frac{\pi}{v} \int_{q}^{\infty} \int_0^1 \left(\exp\left\{ \tau \frac{e^2}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}} \right\} - 1 \right) r\, dr\, d\tau,
\end{aligned} \tag{17}$$

where, for convenience of consideration, the integral with respect to r has been divided into two parts: from r_0 to q and from q to ∞.

Replacing the exponential by unity in the first term of (17), one can verify that it will be smaller than $N\theta$ multiplied by the square of the plasma parameter v/r_d^3. In the second term we expand the exponential factor standing in the exponent of the integrand; then:

$$\int_{r_0}^{q}\int_0^1 \exp\left\{\frac{\tau e^2}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}}\right\} r\,dr\,d\tau = \int_{r_0}^{q}\int_0^1 \exp\left\{\frac{\tau e^2}{D\theta r}\right\} r\,dr\,d\tau -$$

$$-\frac{e^2}{D\theta r_d}\int_{r_0}^{q}\int_0^1 \exp\left\{\frac{\tau e^2}{D\theta r}\right\}\tau^{3/2} r\,dr\,d\tau + \cdots .$$

In the case of electrolytes, the quantity $e/D\theta r_0$ cannot be regarded as small in comparison with unity; therefore the principal contribution to the integrals with respect to r is given by the regions where $r \sim r_0$. Consequently, from the integrals with respect to τ only their asymptotic behavior for $r \sim r_0$ is required, which is easily found, in view of

that

$$\int_0^1 e^{\tau\beta}\,d\tau \simeq \frac{e^\beta}{\beta}; \qquad \int_0^1 e^{\tau\beta\tau^{3/2}}\,d\tau \simeq \frac{e^\beta}{\beta} \quad (\beta \gg 1).$$

Thus,

$$-N\frac{e^2}{D}\frac{\pi}{v}\int_{r_0}^{a}\int_0^1 \exp\left\{\frac{\tau e^2}{D\theta r}\, e^{-\frac{r}{r_d}\sqrt{\tau}}\right\} r\,dr\,d\tau = -\frac{1}{2}N\theta\alpha +$$

$$+\frac{1}{8\pi}N\theta\alpha\,\frac{v}{r_d^3} + N\theta\alpha\, O\left(\left[\frac{v}{r_d^3}\right]^2\right),$$

where α is determined by formula (5).

The third and fourth terms in (17) are readily estimated by expanding the exponential in the integrand, which gives

$$-\frac{1}{12\pi}N\theta\,\frac{v}{r_d^3}\left(1 - \frac{3}{4}\frac{q}{r_d} + \cdots\right).$$

Neglecting terms of the order of the square of the plasma parameter, we finally obtain:

$$\Delta F = -\frac{1}{2} N\theta\alpha - \frac{1}{12\pi} N\theta \frac{v}{r_d^3} + \frac{1}{8\pi} N\theta\alpha \frac{v}{r_d^3}, \tag{18}$$

which, for small α, agrees exactly with expression (4) of Bjerrum' s theory.

A more detailed comparison of expression (17) with the corresponding expression of Bjerrum' s theory can be carried out only after numerical calculation of the integrals.

Doubts have repeatedly been expressed regarding the justification of Bjerrum' s theory (see, for example, the discussion of this question in [6]). It seems to us that our results clarify to a sufficient extent the basic points of Bjerrum' s theory.

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