IONIC INTERACTIONS IN POLAR LIQUIDS

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The pair interaction energy of ions dissolved in a medium is very important in the thermodynamics of electrolyte solutions and in several kinetic problems. For sufficiently large interionic distances this quantity is usually described by a Coulomb law, with account of the dielectric constant of the solvent. It is shown below that the Coulomb model becomes incorrect for interionic distances of the order of the polarization fluctuation correlation length in the medium.

Using the results of a recent paper [1], where a phenomenological theory of polar systems with spatial dispersion was developed, we consider the interaction of charges located on two impurity sites. We limit the discussion to the case where frequencies of motion of the particles are lower than all optic frequencies of the solvent. The purpose of this paper is to find the field of such ions. According to [1] the free energy of the system consisting of the medium plus the external electric field $(\mathfrak{G}(\mathbf{r}))$ is, within the linear theory, $F = F_0 + \Delta F$, where F_0 is the free energy of the medium in the absence of fields,

$$\Delta F = \frac{1}{8\pi}\sum_{\alpha\beta}\int d\mathbf{r}\, d\mathbf{r}'\, \varepsilon^{-1}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathfrak{G}^{\alpha}(\mathbf{r})\, \mathfrak{G}^{\beta}(\mathbf{r}'), \tag{1}$$

where $\varepsilon^{-1}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is the reciprocal static dielectric constant tensor of the medium. The field gives rise to two sources inside the medium, but their sizes and charges are such that effects of dielectric saturation can be neglected. The free energy of such a system is $F \equiv F_{12} = F_0 + \Delta F_{12}$, where F_0 is the free energy of the inhomogeneous medium (due to the finite size of the sources) in the "absence" of the charge fields, and ΔF_{12} is determined from (1) with $\mathfrak{G} = \mathfrak{G}_1 + \mathfrak{G}_2$ and with the dielectric constant of the medium and the impurities. Removing conceptually the charge with the first particle, we have $F \equiv F_2 = F_0 + \Delta F_2$, and repeating the same procedure with the second, we have $F \equiv F_1 = F_0 + \Delta F_1$, where ΔF_1 and ΔF_2 are determined by (1) with $\mathfrak{G} = \mathfrak{G}_1$ and $\mathfrak{G} = \mathfrak{G}_2$, respectively. Obviously, the electric interaction energy of the particles in the medium is

$$F(1, 2) = \Delta F_{12} - \Delta F_1 - \Delta F_2 = \frac{1}{4\pi}\sum_{\alpha\beta}\int d\mathbf{r}\, d\mathbf{r}' \varepsilon^{-1}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \mathfrak{G}^{\alpha}_1(\mathbf{r})\, \mathfrak{G}^{\beta}_2(\mathbf{r}'). \tag{2}$$

For ions 1, 2 in a polar liquid we use the Born model of metallic spheres [2]

$$\mathfrak{G}_{1,2}(\mathbf{r}) = z_{1,2}\, e\, \frac{(\mathbf{r} - \mathbf{R}_{1,2})}{|\mathbf{r} - \mathbf{R}_{1,2}|^3}\, \theta(|\mathbf{r} - \mathbf{R}_{1,2}| - r_{1,2}) \tag{3}$$

(r_1, r_2 and $\mathbf{R}_1$, $\mathbf{R}_2$ are the radii and center coordinates of the spheres, and $\theta(x)$ is the Heaviside function) and the "cut-out" sphere approximation

$$\begin{aligned}\varepsilon^{-1}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \varepsilon^{-1}_{\alpha\beta}(\mathbf{r} - \mathbf{r}')\, \theta(|\mathbf{r} - \mathbf{R}_1| - r_1)\, \theta(|\mathbf{r}' - \mathbf{R}_1| - r_1)\, \theta(|\mathbf{r} - \mathbf{R}_2| - r_2) \\ \times \theta(|\mathbf{r}' - \mathbf{R}_2| - r_2) + \delta_{\alpha\beta}\delta(\mathbf{r} - \mathbf{r}')\, \theta(r_1 - |\mathbf{r} - \mathbf{R}_1|)\, \theta(r_2 - |\mathbf{r} - \mathbf{R}_2|)\end{aligned} \tag{4}$$

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where $(\varepsilon_{\alpha\beta}(\mathbf{r}-\mathbf{r}')$ is the solvent dielectric constant. We have

$$F(1,2)=\frac{z_1z_2e^2}{2\pi^2}\sum_{\alpha\beta}\int d\mathbf{k}\varepsilon^{-1}_{\alpha\beta}(\mathbf{k})\exp\{-i\mathbf{kR}\}$$

$$\times\left\{\frac{k_\alpha}{k^2}\frac{\sin kr_1}{kr_1}+i\exp\{i\mathbf{kR}\}I^\alpha(\mathbf{k},r_2,\mathbf{R})\right\}\left\{\frac{k_\beta}{k^2}\frac{\sin kr_2}{kr_2}-i\exp\{i\mathbf{kR}\}\right.$$

$$\left.\times I^\beta(-\mathbf{k},r_1,-\mathbf{R})\right\}, \tag{5a}$$

$$I(\mathbf{k},r,\mathbf{R})=\int d\mathbf{x}\exp\{i\mathbf{kx}\}(\mathbf{x}+\mathbf{R})^\alpha|\mathbf{x}+\mathbf{R}|^{-3}\theta(r-x), \tag{5b}$$

where $\mathbf{R}=\mathbf{R}_2-\mathbf{R}_1$. Since $r_1+r_2<R$ we can expand (5b) in Legendre polynomials in $r_1/R, r_2/R$. Since both initial approximations are valid only when $r_2\sim r_1\ll R$, we will consider distant ions and will neglect all terms except the dominant one. Taking into account the liquid isotropy $\left(\varepsilon^{-1}_{\alpha\beta}(\mathbf{k})=\frac{k_\alpha k_\beta}{k^2}\frac{1}{\varepsilon_\parallel(k)}+\left(\delta_{\alpha\beta}-\frac{k_\alpha k_\beta}{k^2}\right)\frac{1}{\varepsilon_\perp(k)}\right)$, we have as a result

$$F(1,2)\simeq F^{(0)}(1,2)=z_1z_2e^2\frac{2}{\pi}\int_0^\infty\frac{dk}{\varepsilon_\parallel(k)}\frac{\sin kR}{kR}\frac{\sin kr_1}{kr_1}\frac{\sin kr_2}{kr_2}, \tag{6}$$

and the contribution of the discarded terms is $F(1,2)/F^{(0)}(1,2)-1\lesssim(r_1^2+r_2^2)/R^2$.

A number of general statements can be made concerning the spatial dispersion spectrum of the static dielectric constant if the absorption zones of the system are sufficiently far from the wide transparency zones [1]. In this case the polarization vector of the medium can be represented as a superposition of polarizations of different, practically uncorrelated subsystems. We enumerate the absorption zones from left to right (by increasing frequency) in such a manner that the transparency zone n_* (of characteristic frequency ω_{n_*}) separates the absorption zones n and n−1; also $\omega_{n=0}=0$. At the same time the transparency zone n_* separates the quantum (q) and classical (c) degrees of freedom of the solvent ($\omega_n=2T$). We then have [1]

$$\frac{1}{\varepsilon_{\parallel n+1}(k)}-\frac{1}{\varepsilon_{\parallel n}(k)}=D_nF_n(k\lambda_n), \tag{7}$$

where $\varepsilon_n(k)=\varepsilon(\omega_n,k)$; $D_n=(1/\varepsilon_{n+1})-(1/\varepsilon_n)$; $\varepsilon_n\equiv\varepsilon_n(0)$; $F_n(0)=1$, $F_n(\infty)=0$, $F_n(x)$ is damped at $x=1$ and λ_n is the characteristic correlation length of the polarization fluctuations, brought about by excited degrees of freedom of subsystem n (with characteristic frequencies $\omega_n<\omega<\omega_{n+1}$). The function $F_n(x)$ was investigated for $n<n_*$ [1]. Thus

$$\varepsilon_\parallel(k)=\left\{1-\sum_n D_nF_n(k\lambda_n)\right\}^{-1}. \tag{8}$$

Substituting (8) into (6), we have

$$F(1,2)=\frac{z_1z_2e^2}{R}\left\{1-\sum_n D_n\frac{2(\lambda_n)^2}{\pi r_1r_2}\int_0^\infty dx\frac{F_n(x)}{x^3}\sin\frac{R}{\lambda_n}x\cdot\sin\frac{r_1}{\lambda_n}x\cdot\sin\frac{r_2}{\lambda_n}x\right\}. \tag{9}$$

We consider the important limiting case, when all n can be divided into two classes $-\{n\}=\{n_1,n_2\}$, so that $\lambda_{n_2}\ll R\ll\lambda_{n_1}$. Retaining only the asymptotic terms in (9), we have

$$F(1,2)=\frac{z_1z_2e^2}{R}\left\{1-\sum_{n_1}D_n\frac{R}{\lambda_n}-\sum_{n_2}D_n\right\}, \tag{10}$$

where $\tilde{\lambda}_n = \lambda_n / \int_0^\infty F_n(x)\,dx$. In particular, when $R \gg \lambda_n$, we have for all n, $F(1, 2) = z_1 z_2 e^2 / R \cdot \{1 - \sum_n D_n\} =$ $z_1 z_2 e^2 / R\,\varepsilon_0$. If $n_2 > n_1$ and if for all subsystems of the class $\{n_1\}$ $\tilde{\lambda}_{n_1}$ are roughly identical ($\tilde{\lambda}_{n_1} \equiv \lambda$), we obtain

$$F(1, 2) = z_1 z_2 e^2 \left\{ \frac{1}{\varepsilon_{\lim} R} - \left(\frac{1}{\varepsilon_{\lim}} - \frac{1}{\varepsilon_0} \right) \frac{1}{\lambda} \right\}, \text{ here } \varepsilon_{\lim} = \varepsilon_n = \min\{n_2\}.$$

Thus, the interaction of the charged particles at a distance R much larger than their sizes is described by:

1) The "ordinary" Coulomb law, if R exceeds significantly the maximum correlation length of polarization fluctuations in the medium.

2) A modified Coulomb law $F(1, 2) = z_1 z_2 e^2 / \varepsilon_n R$, if the correlation lengths of degrees of freedom with frequencies right of the transparency zone n are small compared with R, but the others are large.

3) *A generalized Coulomb law $F(1, 2) = z_1 z_2 e^2 / DR$, if no correlation length in the medium is of the order of R, and the dependence of the correlation lengths on the subsystem index is not monotonic. Here $D = \{1 - \sum_{n_2} D_n\}^{-1}$, where the summation is over the subsystem indices with correlation lengths small compared to R.

4) Equation (6), if there exist correlation lengths of the order of R.

It is physycally obvious that in quantum subsystems of polar liquids correlations occur at distances of the order of the molecular size. Therefore, considering $R \gg r_{1,2}$, it is reasonable to assume that $R \gg \lambda_n^{(q)}$. To obtain analytic results for arbitrary $\lambda_n^{(c)}$ we use the approximation $F_{n<n_*}(x) = (1+x^2)^{-2}$, justified in [1] for "strongly nonmagnetic" liquids, and assume, as above, $\lambda_n^{(c)} \equiv \lambda_{n<n_*} = \Lambda$. We then have

$$F(1, 2) = \frac{z_1 z_2 e^2}{R} \left\{ \frac{1}{\varepsilon_*} - \left(\frac{1}{\varepsilon_*} - \frac{1}{\varepsilon_0} \right) \left[1 + \frac{1}{2} \exp\{-R/\Lambda\} \right.\right.$$
$$\left.\left. \times \left(\frac{\Lambda}{r_1} \operatorname{sh} \frac{r_1}{\Lambda} \operatorname{ch} \frac{r_1}{\Lambda} + \frac{\Lambda}{r_2} \operatorname{sh} \frac{r_2}{\Lambda} \operatorname{ch} \frac{r_2}{\Lambda} - \frac{R\Lambda + 4\Lambda^2}{r_1 r_2} \operatorname{sh} \frac{r_1}{\Lambda} \operatorname{sh} \frac{r_2}{\Lambda} \right) \right] \right\}, \tag{11}$$

where $\varepsilon_* = \varepsilon_{n_*}$. When $\Lambda \gg r_1 \sim r_2$

$$F(1, 2) = \frac{z_1 z_2 e^2}{R} \left\{ \frac{1}{\varepsilon_*} + \left(\frac{1}{\varepsilon_*} - \frac{1}{\varepsilon_0} \right) \left[\left(1 + \frac{R}{2\Lambda} \right) \exp\left\{ -\frac{R}{\Lambda} \right\} - 1 \right] \right\}. \tag{12}$$

As the estimates show, for water in normal conditions this value is approximately 10 times larger than that of the "ordinary" Coulomb law for $R \approx \Lambda$.

LITERATURE CITED

1. R. R. Dogonadze and A. A. Kornyshev, Phys. Stat. Sol. (b), 53, 439 (1972).
2. M. Born, Z. Phys., 1, 45 (1920).

*Cases 1 and 2 are special cases of 3.