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Image Potential near a Dielectric–Plasma-Like Medium Interface

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The effect of penetration of an electric field into the metal, electrolyte solution, or other plasma-like medium (PLM) on the image-potential energy in a dielectric adjacent to such a PLM is studied. The asymptotics of classical attraction of a test charge to an "impenetrable metal surface" at large distances and of effective interaction with "dielectric–dielectric interface" at small distances are found. The latter results in a repulsion of a charge from the boundary, when the dielectric constant of the background medium, in which plasma particles are dissolved, is smaller than the permittivity of the dielectric. A minimum of the image-potential curve is situated between the "repulsive" and "attractive" limiting branches. Thus an adsorption minimum is predicted within the scope of purely electrostatic considerations, the value of the "desorption energy" being estimated.

Исследован эффект проникновения электрического поля в металл, раствор электролита, или другую плазмоподобную среду на характер сил изображения в диэлектрике, граничащем с такого рода средой. На больших расстояниях от границы полчена асимптотика классического притяжения пробного заряда к ,,непроницаемому'' металлу; асимптотика вблизи границы соответствует эффективно взаимодействию с границей диелектрик–диэлектрик. Последнее приводит к отталкиванию заряда в диэлектрике от границе, в случае, когда диэлектрическая постоянная фона, в котором ,,растворены'' заряды плазмы, меньше диэлектрической постоянной среды, в которой находится пробный заряд. Между предельными ветвями отталкивания и притяжения лежит минимум энергии изображения. Таким образом, своеобразный ,,адсорбционный'' минимум предсказывается в рамках чисто электростатических представлений. Оценивается величина энергии десорбции.

1. Introduction

An external electric field penetrates into both the semi-infinite solid-state plasma and the electrolyte solution over some characteristic distances, due to the finite effective screening length in such media. We are going to show that this fact will produce a striking effect on the character of the image potential in a dielectric near its boundary with a metal or any other system with Debye-like screening. Many works have recently been devoted to the calculation of the field of static external charges near the surface of a semi-infinite solid-state plasma, using different approaches in the description of its dielectric response (see, e.g., [1 to 9]). In all the papers the nonlocal screening effect results in a significant decrease of the image-force potential $W(a)$ (for a point charge located in vacuum at the distance a from the surface) with respect to the classical law, $W(a) = -q^2/4a$. In particular, the value of $\lim\limits_{a\to 0} W(a)$ was found to be finite and negative, in accordance with the simple intuitive estimate [10] $W(a) = -q^2/4(a + \varkappa^{-1})$, where $\varkappa^{-1}$ is the effective screening length. Small corrections in powers of $(\varkappa a)^{-1}$ were obtained at large values of a ($\gg \varkappa^{-1}$). However, an extension of metal–vacuum theories to the case of a bounding medium having a dielectric constant ε leads to a nontrivial new physical result, which is absent for $\varepsilon = 1$.

In electrostatic calculations, the nonlocal screening may be incorporated phenomenologically, starting from the nonlocal constitutive relation between electric field and induction. However, the kernel of this relation is usually unknown for confined systems [11]. Its determination requires assumptions on the properties of the interface. Within simplest models, the permittivity tensor of a semi-infinite plasma-like medium (PLM) is expressed through its bulk dielectric function [12]. However, the limits of applicability of these models to real systems are not well justified. Therefore, in order to clarify the qualitative effect of penetration of the electric field into PLM, we shall use several models of screening near the surface and compare the results. Calculations show that the image-potential energy for a charge in the dielectric (Fig. 1) takes the form

$$\frac{1}{q^2}\,W(a) = -\frac{1}{4\varepsilon a}\{1 - S(a)\} \equiv -\frac{1}{4\varepsilon a} + \int\limits_0^\infty \mathrm{d}K\,[\varepsilon + T(K)]^{-1}\,\mathrm{e}^{-2aK}\,. \tag{1}$$

$S(a) > 0$, $T(K)$ are functions depending upon the model of screening in the PLM half-space. The first term represents the classical attraction of a charge to an impenetrable metal placed at $z = 0$. It is the leading term at large distances, since $S(a)$ decreases with $a \to \infty$. At small distances both terms in (1) are of the same order. In particular, we shall encounter the case when $S(a) > 1$, and $W(a)$, thereby, becomes positive (repulsive).

2. Model Calculations

As a first example, we consider an approach to directly describe the electric field in the half-space occupied by PLM [2, 8, 9]. It reduces to the assumption that the potential in the PLM half-space obeys the equation

$$\triangle\Phi = \varkappa^2\Phi\,. \tag{2}$$

In the theories of electrolytes and the classical plasma, (2) is known as the linearized Poisson-Boltzmann equation, $\varkappa$ being equal to the inverse Debye screening length [14, 15]. In a degenerate solid-state plasma, (2) corresponds to the linearized Thomas-Fermi equation, $\varkappa^{-1}$ playing the role of Thomas-Fermi screening distance [14, 15]. The solution of (2) in the half-space II should be matched with the solution of the Poisson equation $\triangle\Phi = -(4\pi/\varepsilon)\,\delta(\boldsymbol{r} - \boldsymbol{a})$ in the half-space I by means of the boundary conditions

$$\Phi_{\mathrm{I}}(z = +0) = \Phi_{\mathrm{II}}(z = -0)\,, \qquad \varepsilon(\partial\Phi_{\mathrm{I}}/\partial z)_{z=+0} = \varepsilon_0(\partial\Phi_{\mathrm{II}}/\partial z)_{z=-0}\,. \tag{3}$$

Here, ε_0 is the background dielectric constant in the PLM. It is the solvent dielectric constant for the case of an electrolyte solution (which is usually large compared to unity). For metals, a "ionic skeleton" permittivity should be taken for ε_0 (frequently being identified with unity [8]). ε_0 is also incorporated in $\varkappa$: for both the classical Debye and degenerate Thomas-Fermi plasmas, $\varkappa \sim 1/\sqrt{\varepsilon_0}$.[1]) Below, we shall use the

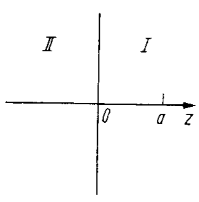

Fig. 1. Point charge near the dielectric–PLM interface. I is the half-space occupied by a local dielectric with dielectric constant ε, II the half-space occupied by a PLM. a indicates the location of the external point charge

[1]) For a Maxwell one-component plasma, $\varkappa = \sqrt{4\pi n_0 e^2/kT\,\varepsilon_0}$; for the degenerate case, $\varkappa = \sqrt{6\pi n_0 e^2/\varepsilon_0 E_{\mathrm{F}}}$, where n_0 is the concentration of charge carriers and E_{F} the Fermi energy [15].

notation $\xi = \varepsilon/\varepsilon_0$. Matching the solutions

$$\Phi_{\rm I} = \frac{q}{\varepsilon}\int\limits_0^\infty {\rm d}K\, {\rm J}_0(K\varrho)\, {\rm e}^{-K|z-a|} + \frac{q}{\varepsilon}\int\limits_0^\infty {\rm d}K\, {\rm J}_0(K\varrho)\, {\rm e}^{-Kz}\, U(K)\,, \tag{4}$$

$$\Phi_{\rm II} = \frac{q}{\varepsilon_0}\int\limits_0^\infty {\rm d}K\, {\rm J}_0(K\varrho)\, {\rm e}^{\sqrt{K^2+\varkappa^2}\,z}\, V(K) \tag{5}$$

one obtains

$$U(K) = \frac{\xi K - \sqrt{K^2+\varkappa^2}}{\xi K + \sqrt{K^2+\varkappa^2}}\,{\rm e}^{-Ka}\,, \qquad V(K) = \frac{2K}{\xi K + \sqrt{K^2+\varkappa^2}}\,{\rm e}^{-Ka}\,. \tag{6}$$

Calculation of the image-potential energy

$$W(a) = \frac{q}{2}\lim_{\substack{z\to a\\ \varrho\to 0}}\left\{\Phi_{\rm I}(\varrho, z) - \frac{q}{\varepsilon}\int\limits_0^\infty {\rm d}K\, {\rm J}_0(\varrho K)\, {\rm e}^{-K|z-a|}\right\} = \frac{q^2}{2\varepsilon}\int\limits_0^\infty {\rm d}K\, {\rm e}^{-Ka}U(K)$$

gives for $S(a)$ (equation (1)) the expression

$$S(a) = 4a\varkappa\xi A(2a\varkappa, \xi)\ ; \qquad A(p, \xi) \equiv \int\limits_0^\infty {\rm d}x\cdot x\,[\sqrt{1+x^2} + \xi x]^{-1}\,{\rm e}^{-px}\,. \tag{7}$$

In the case of $\xi = 1$, this formula reduces to the result obtained by Newns [2] for the PLM–vacuum interface.

Now we turn to the constitutive relation approach. Within the approximation of specular reflection of PLM particles from their surface [12] by an obvious modification of the derivation performed in [8] one obtains

$$S(a) = 4a\varepsilon \int\limits_0^\infty {\rm d}K\, [\varepsilon + \varepsilon_{\rm s}(K)]^{-1}\,{\rm e}^{-2aK}\,, \tag{8}$$

where $\varepsilon_{\rm s}(K)$ is expressed through the wave-number-dependent dielectric function $\varepsilon(k)$ of the infinite PLM,

$$\varepsilon_{\rm s}^{-1}(K) = \frac{K}{\pi}\int\limits_{-\infty}^{+\infty} {\rm d}k_z\, [k^2\varepsilon(k)]^{-1}\,, \qquad k = \sqrt{K^2 + k_z^2}\,. \tag{9}$$

In the diffuse scattering model (dielectric approximation [8]) $T(K)$ can be expressed through ε_0 and the nonlocal part of $\varepsilon(k)$:

$$\varepsilon_0[\delta(z-z') + m(z-z', K)] \equiv \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty} {\rm d}k_z\, \varepsilon(k_z, K)\, {\rm e}^{ik_z(z-z')}\,.$$

With the help of the procedure developed in [13], we obtain

$$T(K) = \varepsilon_0[M(K) + (1 + I(K))\,(1 - N(K))^{-1}]\,, \tag{10}$$

where

$$M(K) = \int\limits_{-\infty}^0 {\rm d}z\, m(-z, K)\, {\rm e}^{Kz}\,, \tag{10a}$$

$$N(K) = \int\limits_{-\infty}^0 {\rm d}z\, n(z, 0, K)\, {\rm e}^{Kz}\,, \tag{10b}$$

$$I(K) = \iint\limits_{-\infty}^0 {\rm d}z\, {\rm d}z'\, m(-z, K)\, n(z', 0, K)\, \times$$
$$\times\, \{\theta(z'-z)\, {\rm e}^{Kz} \sinh Kz' + \theta(z-z')\, {\rm e}^{Kz'} \cosh Kz\} \tag{10c}$$

and $F(\xi = 1) \approx 0.36$. If $\xi \gg 1$, there exists a region of intermediate a, in which an analytic solution is available.

For the model (7) it is given by

$$W(a) = \frac{q^2}{4\varepsilon a}\left[1 - \frac{4\varkappa a}{\xi}\left(\ln\frac{\xi}{2a\varkappa} - C\right) + O\left(\frac{\varkappa^2 a^2}{\xi^2}\ln\frac{\xi}{\varkappa a}, \frac{1}{\varkappa a \xi}\right)\right], \quad 1/2\varkappa \ll a \ll \xi/2\varkappa\,. \tag{20}$$

For the model (13) it takes the form

$$\left.\begin{aligned} W(a) = \frac{q^2}{4\varepsilon a}\left[1 - \pi\sqrt{\frac{3}{2}}\,\frac{a\varkappa}{\sqrt{\xi}} - 3\,\frac{(a\varkappa)^2}{\xi}\left(\ln\frac{a\varkappa}{\sqrt{2\xi/3}} - 1 + C\right) + O\left(\left(\frac{a\varkappa}{\sqrt{\xi}}\right)^3\right)\right], \\ 1/2\varkappa \ll a \ll \sqrt{\xi}/2\varkappa\,, \end{aligned}\right\} \tag{21}$$

C being Euler's constant.

3. Discussion

The first terms both in (16) and (18) are identical with the image-potential energy in a dielectric (ε) near its boundary with another dielectric (ε_0). The second terms represent the interaction of the test charge with the space charge in the PLM. The first term is the leading one, if ξ is not too close to unity. For $\xi < 1$ the charge is attracted to the boundary and the whole curve is monotonic. An effective repulsion of the charge from the surface arises when $\xi > 1$. In this case the $W(a)$ curve has a minimum between the "repulsive" branch at small and the "attractive" branch at large distances. For $\xi \gtrsim 1$, $a_{\min} \sim (2\varkappa)^{-1}$ and $W(a_{\min}) \sim -q^2\varkappa/\varepsilon$. For $\xi \gg 1$, the minimum is situated in the range of $\xi/2\varkappa$ (model (7)) or $\sqrt{\xi}/2\varkappa$ (model (13)). Its depth is of the order of $q^2\varkappa/\varepsilon\xi$ and $q^2\varkappa/\varepsilon\sqrt{\xi}$, respectively. Furthermore, if $\xi \gg 1$, an approximate formula $W(a) \approx q^2/4\varepsilon a$ is valid in the region of $a \ll \xi/2\varkappa$ or $a \ll \sqrt{\xi}/2\varkappa$ for each model, respectively (see (20) and (21)). When $\xi = 1$, the first terms of (16) and (18) are equal to zero, and $W(a)$ at small distances is negative and finite:

$$W(a) \approx -\frac{q^2\varkappa}{\varepsilon}\left(\frac{1}{3} + \frac{1}{4}\,\varkappa a \ln 2\varkappa a\right) \qquad \text{for the model (7)},$$

and

$$W(a) \approx -\frac{q^2\varkappa}{\varepsilon}\left(0.36 + \frac{1}{4}\,\varkappa a \ln 2\varkappa a\right) \qquad \text{for the model (13)}.$$

For ξ close to unity, $W(a)$ at $a \gg a_0 \sim |\xi - 1|/\varkappa$ is monotonic and coincides with the curve for the case $\xi \equiv 1$ [8]. At $a \ll a_0$, $W(a)$ tends to $+\infty$ or $-\infty$, depending on the sign of $\xi - 1$. In the limit $(\xi - 1) \to +0$ the position of the minimum coincides with $a \to +0$ and its depth is equal to $-q^2\varkappa/3$ and $-0.36q^2\varkappa$ for (7) and (13), respectively (cf. [8]). The curves for $W(a)$ in the whole range of a are numerically plotted in Fig. 3a and b.

To elucidate the nature of the obtained results, we consider a system (Fig. 2)[2]) in which the PLM in the half-space II is replaced by a dielectric slab and an impenetrable metal. The image-potential energy in the half-space I has the form of (1) with

$$S(a) = 4\xi\,\frac{a}{d}\,C\left(\frac{2a}{d}, \xi\right); \qquad C(p, \xi) \equiv \int\limits_0^\infty dx\,(\xi + \operatorname{ctgh} x)^{-1}\,e^{-px}\,. \tag{22}$$

[2]) This system was frequently considered in electrochemical literature (see, e.g., [22]).

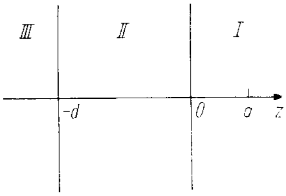

Fig. 2. Auxiliary system, simulating image forces in a dielectric near its boundary to the PLM. I is a semi-infinite local dielectric with dielectric constant ε, II a slab with dielectric constant ε_0, and III a semi-infinite impenetrable metal. $d = \varkappa^{-1}$

Deriving the asymptotic expansions of this integral we have

$$W(a) \approx -\frac{q^2}{4\varepsilon a}\left[1 - \xi\frac{d}{a} + \xi^2\frac{d^2}{a^2} + \mathrm{O}\left(\frac{\xi^3 d^3}{a^3}, \frac{\xi d^3}{a^3}\right)\right], \quad a \gg \xi d/2\,,\ d/2\,, \tag{23}$$

$$W(a) \approx \frac{q^2}{4\varepsilon a}\left[\frac{\xi - 1}{\xi + 1} - \frac{a}{d}\frac{4\xi}{\xi^2 - 1}\ln\frac{\xi + 1}{2} + \frac{a^2}{d^2}\frac{4\xi}{(\xi + 1)^2}\left(1 + \mathrm{O}\left(\frac{a}{d}\right)\right)\right], \quad a \ll \frac{d}{2}, \frac{\xi d}{2}, \tag{24}$$

$$W(a) = \frac{q^2}{4\varepsilon a}\left[1 - \frac{4a}{\xi d}\left(\ln\frac{\xi d}{4a} - 1\right) + \mathrm{O}\left(\frac{a^2}{\xi^2 d^2}\ln\frac{\xi d}{a}, \frac{d}{a\xi}\right)\right], \quad 1 \ll \xi\,, \quad \frac{d}{2} \ll a \ll \frac{\xi d}{2}. \tag{25}$$

Again, we see the attraction to the metal surface at large distances a. The superposition of "effective" interactions with the interface of two semi-infinite dielectrics placed at $z = 0$ and with the metal surface placed at $z = -d$ arises at small distances. If ξ is not too close to unity, the first term in (24) is the leading one. It results in a repulsion from the boundary when $\xi > 1$, and $W(a)$ has a minimum at $a \approx \xi d/2$. For $\xi \gg 1$, an approximate formula, $W(a) \approx q^2/4\varepsilon a$, is valid in the range of $a \ll \xi d/2$. By comparing (14), (15) with (23), and (16), (18) with (24), and also (20), (21) with (25), and looking at Fig. 3a and b, we see that the *system in which the PLM is replaced by an impenetrable metal separated by a dielectric slab from the dielectric, at least qualitatively simulates the image potential in the dielectric. The dielectric constant and the thickness of the slab play the role of a background dielectric constant and an inverse screening length of the PLM, respectively.* In particular $S(a)$ predicted by (7) and (22) are described by the same type of asymptotic expansions with identical main terms.

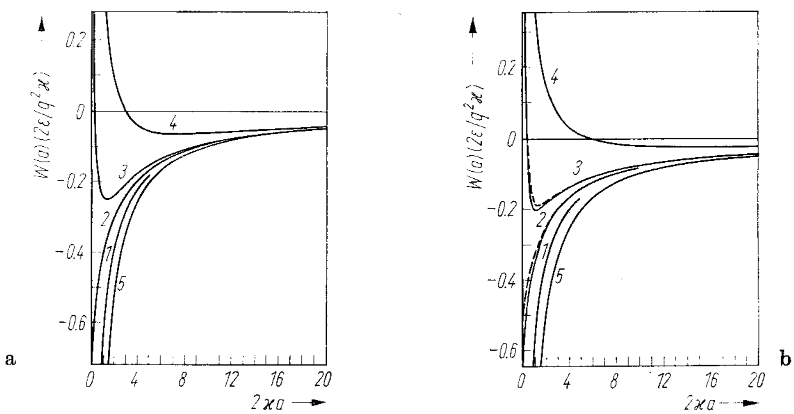

Fig. 3. Image potential energy profile in a dielectric near the boundary of the PLM (Fig. 1). a) Calculated by means of equations (1), (13) and b) calculated by means of equations (1), (7). Dashed lines display the energy profile in a dielectric for a system demonstrated in Fig. 2 (calculated by means of equations (1), (22)). (1) $\xi = 0.5$, (2) 1, (3) 1.5, (4) 10, (5) 0 ($\xi = \varepsilon/\varepsilon_0$)

In the limit $\xi \gg 1$, $W(a)$ is practically the same for (7) and (22) ($A \approx B$, since the denominators in the integrands of (7) and (22) can be approximately replaced by $\xi + 1/x$ and $1 + \xi x$, respectively). However, in the case of large ξ, the model (13) differs from the slab model (22) in the prediction of the position of the minimum.

4. Conclusion

In all the considered models, we obtained the same qualitative profile of the image-potential energy in the dielectric. At large distances the charge is attracted to the surface. When $\varepsilon < \varepsilon_0$, $W(a)$ is monotonic and tends to $(-\infty)$ with $a \to 0$. When $\varepsilon > \varepsilon_0$, $\underset{a \to 0}{W(a)} \to \infty$ and the curve has a minimum. If $\varepsilon \gg \varepsilon_0$, this minimum outstands from the boundary at a distance much larger than the PLM screening length. Usually the adsorption minimum near the dielectric–metal interface is explained by the presence of molecular repulsion forces. We have shown that the adsorption minimum already arises within simple electrostatic considerations (cf. [19]). The value of the "desorption energy", $w = W(a_{\min})$, is estimated as ($w < q^2\varkappa/3\varepsilon$). For a single-charged ion in a dielectric with $\varepsilon \approx 5$, adjacent to a metal with $\varkappa^{-1} \approx 1$ Å and $\varepsilon_0 \approx 1$, we obtain $W \lessapprox 1$ eV. *The decrease of $\varkappa$ in PLM should facilitate the desorption of impurity ions in the dielectric.*

The application of our results to real systems can require in some cases the account of spatial dispersion of the permittivity of the dielectric [16, 17] and of the background dielectric constant ε_0 [18, 15]. These dependences may significantly change the form of the image-potential energy and even lead to new effects. But they evidently would not diminish the possibility to give rise to a repulsive branch and an adsorption