Electrostatic interaction on a metal-insulator interface

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The distribution of the potential of a static point charge in an insulator is investigated, near a contact with a metal, in a plane passing through the point of localization of the charge and parallel to the interface. Account is taken of the nonlocality of the screening in the metal and in the insulator. The potential is determined by two terms. The first is due to the behavior of the dielectric function of the metal at small wave vectors. It decreases monotonically with the distance R from the charge. The second is connected with the singularities of this function on the real axis and is the surface analog of Friedel oscillations. The amplitude of the latter decreases exponentially with the distance a from the charge to the surface of the metal. In the case of the Kohn singularity for a spherical Fermi surface the oscillations have at $R \gg 2a$ and $R \gg (2k_F)^{-1}$ the asymptotic form $\sim R^{-3} \cos 2k_F R \exp(-4k_F a)$, so that their contribution is negligibly small even at $a \gtrsim 1 Å$. The principal and monotonic term in the region of large R is of the form $2\varepsilon/R^{-3}[L_1 + a/\varepsilon^*(a)]^2$, where L_1 is the characteristic] depth of penetration of the static field in the metal, and $\varepsilon^*(a)$ is determined by the dielectric properties of the medium in contact with the metal, with $1 = \varepsilon^*(0) \leq \varepsilon^*(a) \ll \varepsilon^*(\infty) = \varepsilon$. This expression goes over into the result $2a^2/\varepsilon R^3$ of classical electrostatics only far from the interface, at $L_1 \ll a/\varepsilon^* a)$ and ε $^*\mathrm{P}(a) \approx \varepsilon$. Thus, the penetration of the field into the metal leads to a potential that is much higher than the classical one and to an anomalous dependence of the dielectric constant ε of the medium in contact with the metal.

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1. INTRODUCTION

This paper is devoted to an analysis of the potential of the field produced by a point charge in an insulator near its interface with a metal. Account is taken of both the nonlocality of the screening of the field in the insulator, and of the penetration of the field into the metal. This potential can be used to analyze the Coulomb interaction of charges in a semiconductor at its junction with a metal, of the structure of the adsorption layers of charged adsorbed atoms on a metal—vacuum boundary, of the kinetics of elementary processes on the surface of a metal, of the statistical mechanics of the adsorption of ions on an electrode from an electrolyte solution, and others.

The electrostatic potential produced by a point charge on the surface of a metal bordering on a vacuum was analyzed in a number of papers.[1-5] In the first group of papers[1-3] are used the approximations of the linear response and of the Hartree self-consistent field for the description of the induced space charge in the metal. The papers of the other type[4,5] are based on the model of the specular reflection of the conduction electrons from the surface of the metal[6-8], within the framework of which the electrostatic potential can be expressed in terms of the bulk dielectric function of the metal $\varepsilon_{\alpha\beta}(\mathbf{k})$. Explicit expressions for the potential are obtained by substituting various models for $\varepsilon_{\alpha\beta}(\mathbf{k})$ (for example, approximations corresponding to different shapes of the Fermi surface were used in Ref. 4). An advantage of this procedure is that it makes it possible to obtain in a unified manner the results for different models of the metal. This is precisely the approach that will be used in the present paper.

2. FORMULATION OF PROBLEM AND CALCULATION METHODS

We consider the potential produced by a single point static charge near a plane boundary between two media with spatial dispersion of the dielectric constant. To make the results compact, we confine ourselves to an analysis of the distribution of the potential in a plane passing through the point of localization and parallel to this interface (see Fig. 1).

In the general case the linear response of the contacts, owing to violation of the translational invariance in the z direction, is characterized by a single dielectric function $\varepsilon_{\alpha\beta}(z, z'; \mathbf{R})$:

$$D_\alpha(z, \mathbf{R}) = -\int dz'\, d\mathbf{R}'\, \varepsilon_{\alpha\beta}(z, z'; \mathbf{R}-\mathbf{R}')\, \nabla_\beta \Phi(z', \mathbf{R}'). \tag{2.1}$$

For qualitative investigations, however, one frequently uses assumptions that express $\varepsilon_{\alpha\beta}(z, z'; \mathbf{R})$ in terms of the bulk dielectric functions of the contacting media[6,7,9] $\varepsilon_1(z - z'; \mathbf{R})$ and $\varepsilon_2(z - z'; \mathbf{R})$ (we note that in this case, in particular, the defect properties of the media near the contact are neglected). The most widely used model is that of specular reflection of the polarization waves from the interface[6-8]: at $z, z' > 0$ we have

$$\begin{aligned} \varepsilon_{zz}(z, z'; \mathbf{R}) &= \varepsilon_{zz}^{(2)}(z-z'; \mathbf{R}) - \varepsilon_{zz}^{(2)}(z+z'; \mathbf{R}), \\ \varepsilon_{\alpha\alpha}(z, z'; \mathbf{R}) &= \varepsilon_{\alpha\alpha}^{(2)}(z-z'; \mathbf{R}) + \varepsilon_{\alpha\alpha}^{(2)}(z+z'; \mathbf{R}), \quad \alpha = x, y; \end{aligned} \tag{2.2}$$

at $z, z' < 0$ the analogous relations contain the components $\varepsilon_{\alpha\beta}^{(1)}$, while in all the remaining cases $\varepsilon_{\alpha\beta}(z, z'; \mathbf{R}) = 0$.

We take the cosine Fourier transforms of the func-

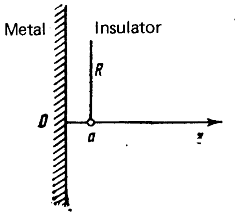

FIG. 1.

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tions $\Phi(z, \mathbf{R}), D_\alpha(z, \mathbf{R}), \alpha = x, y$:

$$\Phi(k_z, \mathbf{K}) = \frac{1}{2\pi}\int dz \cos k_z z \int d\mathbf{R} e^{-i\mathbf{K}\mathbf{R}} \Phi(z, \mathbf{R})$$

and the analogous sine transform for $D_z(z, \mathbf{R})$. At $k_z > 0$ the integration with respect to z is from 0 to ∞, and at $k_z < 0$ from $-\infty$ to 0. As a result, Eq. (2.1) with allowance for (2.2) takes the form

$$D_\alpha(k_z, \mathbf{K}) = -ik_\alpha \varepsilon_{\alpha\alpha}^{(j)}(k_z, \mathbf{K})\Phi(k_z, \mathbf{K}), \quad \alpha = x, y;$$

$$D_z(k_z, \mathbf{K}) = k_z \varepsilon_{zz}^{(j)}(k_z, \mathbf{K})\Phi(k_z, \mathbf{K}), \tag{2.3}$$

where $j = 1$ at $k_z < 0$ and $j = 2$ at $k_z > 0$.

Using (2.3), the Poisson equation

$$\operatorname{div} \mathbf{D} = 4\pi\delta(z-a)\delta(\mathbf{R})$$

and the boundary conditions at $z = 0$, we obtain an expression for the potential

$$\Phi_a(z, R) = \int_0^\infty dK\, K J_0(KR)\Phi_a(z, K), \tag{2.4}$$

$$\Phi_a(z, K) = L(z-a, K) + L(z+a, K) - \frac{2L(z, K)L(a, K)}{L_1(0, K) + L(0, K)}, \tag{2.5a}$$

at $z > 0$ and

$$\Phi_a(z, K) = \frac{2L_1(z, K)L(a, K)}{L_1(0, K) + L(0, K)} \tag{2.5b}$$

at $z < 0$, where

$$L(z, K) = \frac{2}{\pi}\int_0^\infty dk_z \frac{\cos k_z z}{k^2 \varepsilon_2(k)}. \tag{2.6}$$

The integral $L_1(z, K)$ is obtained from (2.6) by the substitution $\varepsilon_2 \to \varepsilon_1$. In these formulas, $k^2 = k_z^2 + K^2$, and the bulk dielectric functions of the media $\varepsilon_i(k)$ are defined by the relations

$$k^2\varepsilon_i(k) = k_z^2 \varepsilon_{zz}^{(i)}(k_z, \mathbf{K}) + \sum_{\alpha = x, y} K_\alpha^2 \varepsilon_{\alpha\alpha}^{(i)}(k_z, \mathbf{K}).$$

In the present paper we use a potential in the form $\Phi_a(a, R) \equiv \Phi_a(R)$ (profile in the plane $z = a$, passing through the inducing charge) as a function of the dielectric properties of the metal $\varepsilon_1(k)$ and of the insulator $\varepsilon_2(k)$. To make the physical picture clear, we consider initially (Sec. 3) in pure form the penetration of the field into the metal. In the next following section (4) we analyze the dependence on the distance a to the surface. This is followed by an analysis (Sec. 5) of the influence of the spatial dispersion of the dielectric $\varepsilon_2(k)$. A number of conclusions are drawn concerning the behavior of the potential without specifying concretely the model of the contacting media (Sec. 5). In Sec. 6 we consider an example of a concrete appproximation for $\varepsilon_2(k)$, demonstrating the model-dependent results.

3. FIELD OF POINT CHARGE AT A JUNCTION OF A METAL (IN THE LINDHARD MODEL) WITH A LOCAL INSULATOR

In Secs. 3 and 4 we describe the metal by using the dielectric function of a degenerate electron gas in the Hartree approximation. For a spherical Fermi surface it is given by the Lindhard formula

$$k^2\varepsilon_1(k) = \frac{\varkappa^2}{2} + k^2 + \varkappa^2 \frac{1 - k^2/4k_F^2}{4k/2k_F} \ln \frac{1 + k/2k_F}{|1 - k/2k_F|}, \tag{3.1}$$

where k_F is the Fermi momentum, $\varkappa^{-1}$ is the Thomas-Fermi screening length. We put in these sections $\varepsilon_2(k) = \varepsilon$.

To analyze the form of $\Phi_0(R)$ (the charge is located on the interface) it is convenient to replace $J_0(KR)$ in (2.4) $\operatorname{Re} H_0^{(1)}(KR)$ and to deform the contour of the integration in the complex K plane. It is shown in the Appendix that at $R \gg (2k_F)^{-1}$ the value of $\Phi_0(R)$ is determined by the contributions from the vicinities of the points $K = 0$ and $K = 2k_F$, so that

$$\Phi_0(R) \approx \Phi^{(1)}(R) + \Phi^{(2)}(R), \tag{3.2}$$

$$\Phi^{(1)}(R) = \begin{cases} 2/\varepsilon R & \text{at} \quad (2k_F)^{-1} \ll R \ll \varepsilon L_1 & (3.3\text{a}) \\ 2\varepsilon L_1^2/R^3 & \text{at} \quad \varepsilon L_1 \ll R & (3.3\text{b}) \end{cases}$$

$$\Phi^{(2)}(R) = \frac{\varkappa^2}{8k_F^4(1 + \varkappa^2/8k_F^2)^2[1 + 2k_F\varepsilon L_1(2k_F)]^2} \frac{\cos 2k_F R}{R^3}. \tag{3.4}$$

Here $L_1 \equiv L_1(0, 0), L_1(2k_F) \equiv L_1(0, 2k_F)$ [see (2.6)].

For a metal-vacuum boundary ($\varepsilon = 1$) the distribution of the potential $\Phi_0(R)$ was analyzed earlier,[4,5] and various asymptotic expressions were obtained for the region $R \gg (2k_F)^{-1}$. It follows from (3.2)–(3.4) that the correct result is that of Kravtsov.[5] At $\varepsilon = 1$ our relations agree with the results of the numerical calculation of Gabovich *et al.*[4] In the Thomas-Fermi approximation there is no oscillating contribution $\Phi^{(2)}$, so that $\Phi_0(R) \approx 2\varepsilon^2/\varkappa^2 R^3$ in agreement with Ref. 10.

According to (3.2), the potential at $R \gg (2k_F)^{-1}$ is equal to the sum of a monotonically decreasing contribution and an oscillating contribution, which are of the same order of magnitude at $\varepsilon = 1$ (typical values are $\varkappa \sim k_F \sim L_1 \gtrsim L_1(2k_F) \sim 0.5$ Å). Replacement of the vacuum by an insulator with $\varepsilon \gg 1$ alters the result drastically: $\Phi^{(2)} \propto 1/\varepsilon^2$, so that at large ε there is essentially no oscillating contribution.

In the region of large R, the monotonic component of the potential has according to (3.3b) an anomalous dependence on the dielectric constant of the medium in contact with the metal, $\Phi^{(1)}(R) \propto \varepsilon$, whereas in the volume of the dielectric the potential is proportional to $1/\varepsilon$. In the intermediate region (3.3a), which exists at $\varepsilon \gg 1$, the potential $\Phi^{(1)}$ is double the potential in the volume of the dielectric.

The unique behavior of the $\Phi^{(1)}(R)$ contribution (which predominates at $\varepsilon \gg 1$) is a direct consequence of the distribution of the induced electron density in the metal. To explain this, we consider the simplest Thomas-Fermi model. The distribution of the electron density differs strongly from the profiles at the junctions of an impermeable metal and an insulator and a metal-vacuum junction: in the former case the dimension of the electron cloud on the surface of the metal is $R_e \propto \varepsilon\varkappa^{-1}$, and for the latter systems $R_e = a = 0$ and $R_e \propto \varkappa^{-1}$. This strong increases of R_e is due to the fact that the role of the perturbing potential, which induces the electron density on the metal, is played by the potential of the point charge located on the vacuum-insulator interface:

$$\Phi = 2/(\varepsilon + 1)R \approx 2/\varepsilon R.$$

This yields for the induced electron density an upper bound estimated at $\varkappa^2\Phi \sim \varkappa^2/\varepsilon R$. Consequently a sphere of radius $\varkappa^{-1}$ contains a charge $(\varkappa^3/\varepsilon)\varkappa^{-3} \sim 1/\varepsilon$, i.e., a small fraction of the summary counter charge (−1), so that we certainly have $R_e \gg \varkappa^{-1}$. To estimate R_e, we take into account the fact that the thickness of the electron cloud in the interior of the metal is equal to $\varkappa^{-1}$, and that the total charge is −1;

$$\int \varkappa^2\Phi\, d\mathbf{R}\, dz \sim \varkappa^2(\varepsilon R_e)^{-1} R_e^2 \varkappa^{-1} \sim 1,$$

i.e., $R_e \sim \varepsilon\varkappa^{-1}$.

Thus, the electron density on the metal takes the form of a flat disk of thickness $\varkappa^{-1}$ and radius $R_e \sim \varepsilon\varkappa^{-1} \gg \varkappa^{-1}$.

The form of the potential in (3.3) is brought about by superposition of the fields of the point charge and of the disk of counter charges. For points inside the disk (at $R \ll R_e$) the field of the latter is homogeneous and has little effect on the potential $\Phi(R)$. Therefore $\Phi(R)$ is identical with the potential of the point-charge on the boundary between the vacuum (in place of the metal) and the insulator, i.e., $\approx 2/\varepsilon R$ [see (3.3a)]. At large $R (\gg R_e)$ the potential is in fact produced by the point charge and by a uniformly charged circle of radius $R_e \sim \varepsilon\varkappa^{-1}$, lying in the vacuum—insulator interface plane. It is easy to show that the potential of the last system is $\Phi(R) \sim \varepsilon\varkappa^{-2}/R^3$, which coincides with (3.3b).

4. INTERACTION OF POINT CHARGES IN A PLANE PARALLEL TO THE SEPARATION BOUNDARY

We analyze now the dependence of the potential $\Phi_a(a, R) \equiv \Phi_a(R)$ on the distance a between the charge and the separation boundary within the framework of the same model of contacting media. The expression for the potential $\Phi_a(R)$ (2.4) – (2.6) can be rewritten in the form

$$\Phi_a(R) = \frac{1}{\varepsilon R} - \frac{1}{\varepsilon(R^2+4a^2)^{1/2}} + \int_0^\infty dK\, K J_0(KR)\, \Phi_0(K)\, e^{-2aK}, \tag{4.1}$$

where $\Phi_0(K) = \Phi(z = 0, K)$. The first two terms correspond here to a potential in a system consisting of an impermeable metal and an insulator. The integral in (4.1) is analyzed in analogy with the data in the Appendix. As a result we have

$$\Phi_a(R) \approx \Phi_a^{(1)}(R) + \Phi_a^{(2)}(R) \tag{4.2}$$

where

$$\Phi_a^{(1)}(R) = \frac{1}{\varepsilon R} + \frac{1}{\varepsilon(R^2+4a^2)^{1/2}}, \quad (2k_F)^{-1} \ll (R^2+4a^2)^{1/2} \ll \varepsilon L_1, \tag{4.3a}$$

$$\Phi_a^{(1)}(R) = \frac{1}{\varepsilon R} - \frac{1}{\varepsilon(R^2+4a^2)^{1/2}} + \frac{4aL_1}{(R^2+4a^2)^{3/2}} + 2\varepsilon L_1 \frac{R^2-8a^2}{(R^2+4a^2)^{5/2}}, \quad \varepsilon L_1 \ll (R^2+4a^2)^{1/2}; \tag{4.3b}$$

$$\Phi_a^{(2)}(R) = \frac{\varkappa^2 \exp(-4k_F a)}{8k_F^4(1+\varkappa^2/8k_F^2)^2[1+2k_F\varepsilon L_1(2k_F)]^2} \tag{4.3}$$

$$\times \frac{\cos(2k_F R - {}^5/_2 \operatorname{arctg}(2a/R))}{R^3(1+4a^2/R^2)^{5/4}}, \tag{4.4}$$

$$(2k_F)^{-1} \ll R.$$

In the region $R \gg 2a$ Eqs. (4.3) and (4.4) take the simpler form

$$\Phi_a^{(1)}(R) \approx 2/\varepsilon R \text{ at } (2k_F)^{-1},\quad 2a \ll R \ll \varepsilon L_1, \tag{4.5a}$$

$$\Phi_a^{(1)}(R) \approx 2(a+\varepsilon L_1)^2/\varepsilon R^3 \text{ at } 2a,\ \varepsilon L_1 \ll R; \tag{4.5b}$$

$$\Phi_a^{(2)}(R) \approx \Phi^{(2)}(R)\exp(-4k_F a).$$

Here $\Phi^{(2)}(R)$ is defined by (3.4). The oscillating term $\Phi_a^{(2)}(R)$ decreases very drastically ($\propto \exp(-4k_F a)$) with increasing distance from the charge to the surface. The quantity $\Phi_a^{(1)}(R)$ depends on a relatively weakly, especially at $\varepsilon \gg 1$. Thus, the oscillating contribution to $\Phi_a(R)$ does not manifest itself in fact at $a \gtrsim k_F^{-1}$ even for a metal-vacuum junction.

At $R \gg 2a \gg \varepsilon L_1$ we obtain for the potential the traditional expression $\Phi_a(R) \approx 2a^2/\varepsilon R^3$, i.e., the potential of a dipole made up by a charge and its image in an ideal metal. However, the effects of penetration of the field into the metal can be neglected only under the condition $a \gg \varepsilon L_1$, which is satisfied in the case of dielectrics with large values of ε only far from the junction.

The factor $\exp(-4k_F a)$ in $\Phi_a^{(2)}(R)$ stems from the Fourier components of the potential with wave vectors $K \approx 2k_F$, which decrease like e^{-2Ka}. The $\Phi_a^{(1)}(R)$ term is due to the contribution at $K \simeq 0$, since no exponential is produced here.

5. CONSEQUENCES OF SPATIAL DISPERSION OF THE DIELECTRIC CONSTANT OF THE MEDIUM IN CONTACT WITH THE METAL

The description used in the preceding section for the medium in contact with the metal, using only the dielectric constant ε, is in the general case insufficient in the analysis of the potential in the considered scales. We present below a generalization of the results in the case when the medium in contact with the metal is characterized by a dielectric function $\varepsilon_2(k)$.[1] This makes it possible, in particular, the limits of applicability of the local-screening approximation $\varepsilon_2(k) = \varepsilon$.

We note beforehand one important result. The interaction of the charges in the interior of an insulator with spatial dispersion of the dielectric constant goes over at sufficiently large distances into the usual Coulomb interaction with the macroscopic $\varepsilon = \varepsilon_2(k = 0)$: $\Phi = 1/\varepsilon R$ [if $\varepsilon_2(k)$ has no singularities on the real k axis]. It will be shown below that the interaction of the charges in such a medium neart he contact with the conductor is determined by the spatial dispersion of $\varepsilon_2(k)$ even at arbitrarily large distances between the charges. Thus, in the general case the local-dielectric approximation is not valid even as $R \to \infty$.

We investigate first this asymptotic form using Eqs. (2.4)–(2.6) for $\Phi_a(R)$. Just as above, the power-law terms of the expansion of $\Phi_a(R)$ are determined as $R \to \infty$ by the behavior of the integrand of (2.5) in the vicinity of $K = 0$, and also of its singularities on the real K axis.

We examine the behavior of the integrals (2.6), as well as of the integral

$$M(a, K) = \frac{4}{\pi}\int_0^\infty dk_z \frac{\sin^2(k_z a/2)}{k^2\varepsilon_2(k)} \tag{5.1}$$

in the vicinity of the point $K=0$. Since there are no mobile carriers in the insulator we have $\varepsilon_2(k)\to\varepsilon_2(0)\equiv\varepsilon, k\to 0$. Therefore $L(0,K)\propto K^{-1}, K\to 0$, whereas $L_1(0,K)$ and $M(a,K)$ are bounded as $K\to 0$:

$$L(0,\ K)\approx 1/K\varepsilon, \tag{5.2}$$

$$L_1(0,K)\approx L_1(0,0)\equiv L_1=\frac{2}{\pi}\int\limits_0^\infty\frac{dk}{k^2\varepsilon_1(k)}; \tag{5.3}$$

$$M(a,\ K)\approx M(a,\ 0)\equiv a/\varepsilon_*(a); \tag{5.4}$$

here

$$\varepsilon_*(a)\equiv\left\{\frac{4}{\pi a}\int\limits_0^\infty dk\frac{\sin^2(ka/2)}{k^2\varepsilon_2(k)}\right\}^{-1}. \tag{5.5}$$

The quantity $\Phi_a(a,K)$ in (2.4), which can be represented with the aid of (5.1) in the form

$$\Phi_a(a,K)=L_1(0,K)+2M(a,K)$$
$$-{}^1\!/_2M(2a,K)-\frac{[L_1(0,K)+M(a,K)]^2}{L_1(0,K)+L(0,K)}, \tag{5.6}$$

tends to a constant value as $K\to 0$. To calculate the integral with respect to K as $R\to\infty$ in (2.4) it is necessary to determine the correction linear in K to $\Phi_a(a,0)$. We assume that the integrals

$$\int\limits_0^\infty\frac{dk}{k}\left[\frac{1}{k^2\varepsilon_1(k)}\right]',\quad\int\limits_0^\infty dk\frac{\sin^2ka}{k}\left[\frac{1}{k^2}\frac{1}{\varepsilon_2(k)}\right]'$$

converge, as is certainly the case for normal metals with spherical Fermi surface and for a large class of insulators. Then as $K\to 0$ the correction terms from $L_1(0,K)$ and $M(a,k)$ do not exceed const$\cdot K^2$. Therefore

$$\Phi_a(a,K)\underset{K\to 0}{\approx}\Phi_a(a,0)-K\varepsilon\left[L_1+\frac{a}{\varepsilon_*(a)}\right]^2+O(K^2). \tag{5.7}$$

Just as in the preceding sections, as $R\to\infty$ it is convenient to replace $J_0(KR)$ by $\operatorname{Re}H_0^{(1)}(KR)$ and deform the contour (Fig. 2). With exponential accuracy we can confine ourselves to contributions from the vicinity of $K=0(\Phi_a^{(2)}(R))$ and from the non-analyticity points $K^*=\{K_1,\ldots,K_j\}$ of the function $\Phi_a(a,K)(\Phi_a^{(2)}(R))$. Then

$$\Phi_a(R)\approx\Phi_a^{(1)}(R)+\Phi_a^{(2)}(R), \tag{5.8}$$

where

$$\Phi_a^{(1)}(R)=-\frac{4}{\pi}\int\limits_0^\infty dt\,tK_0(tR)\operatorname{Im}\Phi_a(a,it), \tag{5.9}$$

$$\Phi_a^{(2)}(R)=2\operatorname{Re}\sum_j\int\limits_{(K_j)}dK\,KH_0^{(1)}(KR)\{\Phi_a(a,K)\}_j; \tag{5.10}$$

$\{F(K)\}_j$ is the difference between the values of the functions on the two functions on the two sides of the cut passing through the point $K=K_j$.

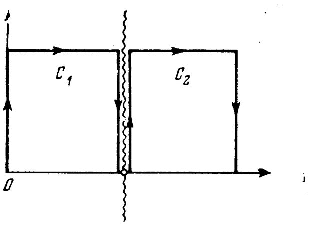

FIG. 2. Deformed integration contour on the complex K plane for the case of one non-analyticity point K^* of the function $\varepsilon_1(k)$. The cut passes through the point $K=K^*$.

The contribution $\Phi_a^{(1)}(R)$ as $R\to\infty$ can be calculated by using (5.7):

$$\Phi_a^{(1)}(R)\approx\frac{2\varepsilon}{R^3}\left[L_1+\frac{a}{\varepsilon_*(a)}\right]^2. \tag{5.11}$$

This result generalizes (3.3b) and (4.5b). The length L_1 characterizes the properties of the electron subsystem in the metal and is determined primarily by the screening length $\varkappa^{-1}$. The dispersion law $\varepsilon_2(k)$ determines the character of the dependence of the "effective dielectric constant" of the insulator $\varepsilon_*(a)$ (5.5). In particular, if a is much less than all the reciprocal characteristic scales of the function $\varepsilon_2(k)$ [the function $\varepsilon_2(k\sim 1/a)\approx 1$], then $\varepsilon_*(a)\approx 1$. At sufficiently large a we have $\varepsilon_2(k\sim 1/a)\approx\varepsilon$ and $\varepsilon_*(a)\approx\varepsilon$. Thus, $\varepsilon_*(a)$ varies from 1 to ε with increasing distance of the charge from the boundary.

We now discuss the contribution $\Phi_a^{(2)}(R)$, connected with the singularities of the functions $\varepsilon_i(k)$ on the real axis at $k\neq 0$. We assume that they are all connected with $\varepsilon_1(k)$. Then

$$\{\Phi_a(a,K)\}_j=-L^2(a,K)\left\{\frac{1}{L_1(0,K)+L(0,K)}\right\}_j, \tag{5.12}$$

and the jump of Φ is due to the jump

$$\{L_1(0,K)\}_j=\left\{\frac{2}{\pi}\int\limits_K^\infty\frac{dk}{k\varepsilon_1(k)(k^2-K^2)^{1/2}}\right\}_j=-\frac{2}{\pi}\int\limits_{K_j}^K\frac{dk}{k(k^2-K^2)^{1/2}}\left\{\frac{1}{\varepsilon_1(k)}\right\}_j. \tag{5.13}$$

Recognizing that as $R\to\infty$ the main contribution to (5.10) is made by $K\approx K_j$, we have

$$\Phi_a^{(2)}(R)\approx-\frac{4}{\pi}\sum_j\frac{L^2(a,K_j)}{K_j\varepsilon_1^2(K_j)[L_1(0,K_j)+L_2(0,K_j)]^2}$$
$$\times\frac{1}{R}\operatorname{Re}\left[e^{iK_jR}\int\limits_0 d\theta e^{-\theta R}\{\varepsilon_1(K_j+i\theta)\}\right], \tag{5.14}$$
$$[R\max\{K_j\}]\to\infty.$$

We consider the particular case when there is only one singularity $\varepsilon_1(k)$ on the real axis at the point $k=k^*$, in the form

$$\varepsilon_1(k)=A(k)+B(k)(k-k^*)\ln|k-k^*|, \tag{5.15}$$

with $A(k)$ and $B(k)$ regular and not equal to zero at $k=k^*$. It follows then from (5.14) that

$$\Phi_a^{(2)}(R)\approx\frac{\cos k^*R}{R^3}\frac{4B(k^*)L^2(a,k^*)}{k^*\varepsilon_1^2(k^*)[L_1(0,k^*)+L(0,k^*)]^2}. \tag{5.16}$$

In the Lindhard model (3.1)

$$k^*=2k_F,\quad B(k^*)=\varkappa^2/16k_F^3,\quad\varepsilon_1(k^*)=1+\varkappa^2/8k_F^2.$$

For the case of a local insulator ($\varepsilon_2(k)=$ const)), Eq. (5.16) goes over into (4.4). Inasmuch as $k^*\sim 4$ Å^{-1}, for a metal, it is obvious that it is impossible to neglect the spatial dispersion of the insulator, i.e., to put $\varepsilon_2(k\sim k^*)=\varepsilon_2(0)\equiv\varepsilon$. For rough estimates at $k^*a\lesssim 1$ we can assume that

$$L(0,\ k^*)\sim[k^*\varepsilon_2(k^*)]^{-1},\quad L(a,\ k^*)\sim[k^*\varepsilon_2(k^*)]^{-1}\exp(-k^*a).$$

Thus, at small distances a from the surface of the metal, allowance for the $\varepsilon_2(k)$ dependence leads to an increase of $\Phi_a^{(2)}(R)$ compared with (4.4).

According to (5.16) and (2.6), the dependence of $\Phi_a^{(2)}(R)$ on a is determined by the analytic properties of $[k^2\varepsilon_2(k)]^{-1}$. In the general case, besides the contribution from the pole $k_\varepsilon = -ik^*(k=0)$, it is necessary to take into account also the singularity $1/\varepsilon_2(k)$. If all lie on the imaginary axis, then they correspond to pure imaginary values of k_ε, with $|k_\varepsilon| > k^*$. In this case, at large a the principal contribution is made by the pole at $k_\varepsilon = -ik^*$ and $L(a, k^*) \approx \exp(-k^*a)/\varepsilon k^*$. If the singularities present are not on the imaginary axis but correspond to the condition $|k| \ll k^*$, then the corresponding values of the variable k_ε lie near k^*, so that we again have $L(a, k^*) \sim \exp(-k^*a)$. If we disregard the exotic case when the dielectric function of the medium in contact with the metal $\varepsilon_2(k)$ has singularities near the real axis (with $\mathrm{Im}\, k < k^*$), then the following important conclusion of Sec. 4 remains in force: at $k^*a > 1$ we have $\Phi_a^{(2)}(R) \sim \exp(-2k^*a)$, i.e., the oscillating term decreases very rapidly with increasing a.

6. EFFECTS OF SPATIAL DISPERSION OF THE MEDIUM AT INTERMEDIATE DISTANCES

EXAMPLE: BEHAVIOR OF THE POTENTIAL FOR THE SINGLE-POLE MODEL

The relations obtained in the preceding section are valid only at sufficiently large R. The behavior of Φ at smaller R depends on the form of $\varepsilon_2(k)$. By way of illustration, we present the results of the calculation of $\Phi(R)$ (case $a=0$) for the "single-pole" model of $\varepsilon_2(k)$ (Ref. 13):

$$\frac{1}{\varepsilon_2(k)} = \frac{1}{\varepsilon_*} - \left(\frac{1}{\varepsilon_*} - \frac{1}{\varepsilon}\right)\frac{1}{1+k^2\Lambda^2}, \quad \varepsilon > \varepsilon_* \geqslant 1 \tag{6.1}$$

which is analogous in form to the known[14] Inkson approximation that describes the smooth transition from $\varepsilon_2(0) = \varepsilon$ to $\varepsilon_2(\infty) = \varepsilon_*$; Λ^{-1} is the characteristic wave vector of the transition. If $\varepsilon_* > 1$, then the spatial dispersion of $\varepsilon_2(k)$ is neglected within the framework of this model at large k, where the transition from ε_* to 1 should take place. For a metal we use again expression (3.1).

We consider first the case of relatively short length Λ: $\Lambda \ll \varepsilon_* L_1$. At sufficiently large $R(\gg \varepsilon L_1)$ we have

$$\Phi^{(1)}(R) \approx 2\varepsilon L_1^2/R^3. \tag{6.2}$$

At smaller values of $R(\varepsilon L_1 \gg R \gg L_1)$,

$$\Phi^{(1)}(R) \approx \frac{2}{\varepsilon R}\left[1 + \left(\frac{\varepsilon}{\varepsilon_*} - 1\right)e^{-R/\Lambda}\right]. \tag{6.3}$$

In particular, at $\varepsilon L_1 \gg R \gg \Lambda \ln(\varepsilon/\varepsilon_*)$ we have

$$\Phi^{(1)}(R) \approx 2/\varepsilon R \tag{6.4}$$

in accordance with (3.3a). At $\varepsilon \gg \varepsilon_*$ and $L_1 \ll R \ll \Lambda$,

$$\Phi^{(1)}(R) \approx 2/\varepsilon_* R, \tag{6.5}$$

and consequently the form of $\Phi^{(1)}(R)$ is different from the result of Sec. 3 only at $R \lesssim \Lambda$, while in the case $R \ll \Lambda$ the insulator can be regarded approximately as local, but with a smaller value of $\varepsilon(\varepsilon_*)$.

In the opposite case, when $\Lambda \gg \varepsilon_* L_1$, expression (6.2) is valid at $R \gg (\varepsilon/\varepsilon_*)\Lambda$. At smaller $R(\varepsilon_* L_1 \ll R \ll (\varepsilon/\varepsilon_*)\Lambda)$ we have

$$\Phi^{(1)}(R) \approx \frac{2\varepsilon_* L_1^2}{R^3}\left[\frac{\varepsilon_*}{\varepsilon}\frac{R^2}{\Lambda^2} + \left(1 + \frac{R}{\Lambda}\right)e^{-R/\Lambda}\right]. \tag{6.6}$$

In particular, at $(\varepsilon/\varepsilon_*)\Lambda \gg R \gg \Lambda \ln(\varepsilon/\varepsilon_*)$

$$\Phi^{(1)}(R) \approx 2\varepsilon_*^2 L_1^2/\varepsilon\Lambda^2 R, \tag{6.7}$$

and at $\Lambda \gg R \gg \varepsilon_* L_1$ we have

$$\Phi^{(1)}(R) \approx 2\varepsilon_* L_1^2/R^3. \tag{6.8}$$

Finally, at still shorter distances $(L \ll R \ll \varepsilon_* L_1)$ we again obtain Eq. (6.5).

The expression for $\Phi^{(2)}(R)$, according to (5.16), retains the form (3.4) with $2\varepsilon k_F L_1(2k_F)$ replaced by $L_1(K=2k_F)/L_2(K=2k_F)$. At $\Lambda \gg k_F^{-1}$ we have $L_2(2k_F) \approx (2k_F\varepsilon_*)^{-1}$. Thus, allowance for the spatial dispersion of $\varepsilon_2(k)$ in the insulator leads to a vanishing of the parameter ε from the expression for the oscillating contribution $\Phi^{(2)}(R)$.

7. CONCLUSION

The general conclusion of this paper is the strong increase of the interaction of the charges near the separation boundary because of the penetration of the field into the metal, and becomes even more substantial when the spatial dispersion of the dielectric constant of the medium in contact with the metal is taken into account. Comparing, for example, the long-distance asymptotic form (5.11) with the classical-electrostatics formula $\Phi_a^{cl}(R) \approx 2a^2/\varepsilon R^3$, we see that

$$\frac{\Phi_a(R)}{\Phi_a^{cl}(R)} \approx \varepsilon^2\left[\frac{L_1}{a} + \frac{1}{\varepsilon_*(a)}\right]^2.$$

Such an appreciable increase of the potential compared with the value predicted by the classical theory is in qualitative agreement with the available data[15,16] on the attraction constants of the adsorption isotherm[17] for alkali and halide ions in solution on the surface of a number of metallic electrodes.

An attempt to satisfy the experimental data on the basis of the formula of classical electrostatics leads to patently overestimated values of the parameter a($\gg$1 Å, even if the macroscopic values of ε for the solvent are not used). When the equations of the present paper are used, the agreement with the experiment is reached at the physically more reasonable values $a \approx 1-2$ Å.

The available data do not lead to a direct correlation between the interaction and the macroscopic dielectric constant of the solvent. This may indicate that it is important to take into account the spatial dispersion of the solvent for the realized ion-ion and ion-boundary distances. For an adequate interpretation of the data that characterize the interaction of the ions adsorbed from solution, it is necessary to take into account also the Debye screening of the potential by the electrolyte plasma.

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APPENDIX

Investigation of the integrand $\Phi_0(K)$ In (2.4) at $a = z = 0$

According to (2.5) and (2.6) we have at $\varepsilon_2(k)=\varepsilon$

$$\begin{gathered} {}^1/_2\Phi_0(K)=\{[L_1(0,K)]^{-1}+K\varepsilon\}^{-1}, \\ L_1(0,K)=\frac{2}{\pi}\int_0^\infty dk_z[k^2\varepsilon_1(k)]^{-1}, \end{gathered} \tag{A.1}$$

where $k^2\varepsilon_1(k)$ is defined in (3.1). The singularities of $\Phi_0(k)$ are determined by the singularities of $\varepsilon_1(k)$, i.e., $K=0$ and $K=2k_F$. As $K\to 0$ we have $L_1(0,K)\to\text{const}$ $\equiv L_1$, so that

$$\Phi_0(K)=\begin{cases} 2L_1-2K\varepsilon L_1^2 & \text{at} \quad K\varepsilon L_1\ll 1 \\ 2/K\varepsilon & \text{at} \quad K\varepsilon L_1\gg 1,\ K\ll k_F \end{cases}. \tag{A.2}$$

At $K\approx 2k_F$ it is convenient to change over in the integral of (A.1) from k_z to $k=(K^2+k_z^2)^{1/2}$ and to integrate by parts twice, after first breaking up the integral into two: $0<k<2k_F$ and $2k_F<k$. Then

$$\frac{1}{K}\frac{d}{dK}\frac{1}{K}\frac{dL_1(0,K)}{dK}=\frac{2}{\pi}\int_K^\infty\frac{dk}{(k^2-K^2)^{1/2}}\left(\frac{1}{k}\left(\frac{1}{k^2\varepsilon_1(k)}\right)'\right)'. \tag{A.3}$$

At $K<2k_F$ the integral is understood here in the sense of the principal value. For the Lindhard model (3.1) at $K<2k_F$ the integrand in (A.3) has a singularity:

$$\begin{gathered} \frac{1}{(k+K)^{1/2}}\left(\frac{1}{k}\left(\frac{1}{k^2\varepsilon_1(k)}\right)'\right)'=\frac{V(K)}{K-2k_F}+W(k,K), \\ V(K)=-\frac{\varkappa^2}{8k_F^2(\varkappa^2/2+4k_F^2)(K+2k_F)^{1/2}}. \end{gathered}$$

The function $W(k,K)$ is integrable at $k=2k_F$. Calculation yields

$$\int_K^\infty\frac{dk}{(k-K)^{1/2}(k-2k_F)}=\begin{cases} 0, & K<2k_F \\ \pi/(K-2k_F)^{1/2}, & K>2k_F \end{cases}.$$

Therefore at $K\approx 2k_F$ we have

$$\begin{gathered} \frac{1}{K}\frac{d}{dK}\frac{1}{K}\frac{dL_1(0,K)}{dK}\approx\text{const}+o(1) \\ +\begin{cases} 0, & K<2k_F \\ 2V(2k_F)/(K-2k_F)^{1/2}, & K>2k_F \end{cases}; \\ L_1(0,K)\approx R(K)+\theta(K-2k_F)(K-2k_F)^{3/2}V(2k_F)\frac{32}{3}k_F^2, \end{gathered}$$

where $R(K)$ is an analytic function at $K\approx 2k_F$.

Thus, the analytic continuation of each of the functions $L_1(0,K)$ and $\Phi_0(K)$ into the complex plane from the segments $0<K<2k_F$ and $2k_F<K$ leads to different analytic functions.

Replacing in the integral (2.4) the function $J_0(KR)$ by $\operatorname{Re}H_0^{(1)}(KR)$ and deforming the integration contour in accordance with Fig. 2, we find that at $R\gg(2k_F)^{-1}$ the main contribution to the potential $\Phi_0(R)(a=z=0)$ is made by the vicinities of the points $K=0$ and $K=2k_F$. Using the relations

$$\begin{gathered} H_0^{(1)}(iy)=\frac{2}{\pi i}K_0(y); \\ H_0^{(1)}(z)\approx\left(\frac{2}{\pi z}\right)^{1/2}e^{iz-i\pi/4},\quad |z|\to\infty,\quad -\pi<\arg z<\pi, \end{gathered}$$

and also the formulas (A.2) obtained for $\Phi_0(K)$ at $K\approx 0$ and

$$\begin{gathered} \Phi_0(K)\approx-\frac{4\varkappa^2[1+2k_F\varepsilon L_1(2k_F)]^{-2}}{3k_F^{1/2}(\varkappa^2/2+4k_F^2)^2}\theta(K-2k_F)(K-2k_F)^{3/2} \\ +\ \textit{regular part},\ \text{at}\quad K\approx 2k_F \end{gathered}$$

we obtain the asymptotic expressions for the potential (3.2)–(3.4).

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1) The function $\varepsilon_2(k)$ can correspond to different models of screening in the medium, which determine the form and the scales of variation of this function. If $\varepsilon_2(k)$ corresponds to the electron polarizability in the crystals, the scale of the spatial dispersion is determined by the characteristic length of the overlap of the Bloch functions in neighboring allowed bands.[11] In a polar liquid, the nonlocality of screening is due primarily to spatail correlation of the orientations of the dipoles, and the scale of the dispersion is determined by the radius of the short-range orientational order of the dipoles.[12]

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