

Electrostatic charge-charge and dipole-dipole interactions near the surface of a medium with screening non-locality

(Review Article)

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Interaction energy between two point charges, W_{QQ} , or two point dipoles, W_{PP} , located in a medium with a constant dielectric permittivity near the plane surface of a metallic or semiconducting substrate with the spatial dispersion of its dielectric function has been revisited. The calculations were made on the basis of the Green's function method for layered systems. Long-range lateral asymptotics were found. The non-local character of screening in the substrates was shown to substantially modify the dependences of W_{QQ} and W_{PP} on the distance between the objects concerned. Thus, the purported conventional electrostatic interactions between adsorbed atoms and molecules (modeled by point charges and point dipoles) should be reconsidered making allowance for the substrate polarization. In particular, this factor may significantly influence the structure of electrostatic dipole lattices arising near the surfaces of solids, as well as the kinetics of charge or dipole motion over the surface.

PACS: **73.20.-r** Electron states at surfaces and interfaces;
68.43.Fg Adsorbate structure (binding sites, geometry);
71.10.Ca Electron gas, Fermi gas.

Keywords: charge-charge interaction, dipole-dipole interaction, spatial dispersion of the dielectric permittivity, non-local electrostatics, Thomas–Fermi approximation.

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1. Introduction

It is well known that adsorption on the solid surface is driven by several interaction mechanisms and, as a result, the adsorbed atoms or molecules look like “dressed” by the substrate [1–5]. When this is the so-called physical adsorption, the potential well, which determines the mean equilibrium distance between the adsorbates and the substrate, is formed by the charge-fluctuation-induced Van der Waals attraction [6–8] and the Pauli repulsion between the electron shells of adsorbates and substrate atoms [5]. The term “Van der Waals forces” is also used to label other electrostatic contributions to adsorbate energies [9]. The most

often, the interaction between the adsorbates and the substrate is stronger and is called chemisorption [4,10–14]. The consideration of this phenomenon is based on the account of the Pauli repulsion and the covalent electron bonding near the substrate, as well as the purely electrostatic attraction at larger distances. The latter contribution is a result of the substrate polarization and can be approximately treated in the framework of classical electrostatics [15,16] if the adsorbed object is a fixed charge Q or a permanent dipole \mathbf{P} .

However, in the vicinity of a metal or semiconductor surface, classical electrostatics fails, and non-local electro-

statics elaborated for layered structures has to be applied [17–33]. In other words, the spatial dispersion of the substrate dielectric functions (i.e., the non-local character of charge and dipole screening in the medium) should be taken into account. In particular, the indicated approach leads to the charge and dipole image forces that are finite near the interface. It is remarkable that even the crude description of molecules in the framework of classical electrostatics as interacting point dipoles mirrored in the classical perfect-metal substrate mimics the complicated density-functional quantum-mechanical picture successfully enough at large distances between them [34–36]. One should note that the non-local electrostatics turned out to be useful for bulk-condensed-matter problems as well [37,38].

Thus, the analysis of many-body image forces testifies that, for many purposes, adsorbed atoms and molecules can be represented to a high degree of accuracy as either constant charges or constant dipoles. Hence, it is also quite natural to consider their interactions as electrostatic charge-charge [17,21,22,39,40] or dipole-dipole ones [34,41–43]. Similarly to the case of polarization (image) forces, the proper electrostatics must be non-local and should take into account the quantum-mechanical nature of charge carriers. Of course, it cannot be the whole truth, and one should make allowance for other relevant interactions mediated through the solid-state substrate [44]. Various types of such interactions can be called “indirect” in the sense that they include a mediator [40,45–51].

We note that it is impossible to clearly separate Coulomb (electrostatic) contributions and more complex quantum-mechanical ones in the overall adsorbate-adsorbate interactions, since the electromagnetic forces dominate in the condensed matter and determine both apparently classical and quantum-mechanical phenomena [52,53], with the nuclear interaction being responsible only for definitely important but subtle effects [54,55]. Nevertheless, if the atomic or molecular objects concerned have no permanent charge or dipole, all fluctuation-induced van der Waals-like interactions are definitely of quantum-mechanical origin, and the resulting dipole-dipole attraction is rather weak [6–8]. The famous Casimir interaction between mesoscopic and macroscopic bodies has a similar nature [56,57].

In this work, we restrict the consideration to a specific case, when the charges or dipole moments of adsorbed atoms (or molecules) can be considered as permanent, and neglect all fluctuation-induced phenomena, which are subdominant against the electrostatic background. We briefly review the previous results obtained in the infinite-barrier interface model [17,18,21,22,58–61] with the specular reflection of the medium charge carriers for the interaction energy $W_{QQ'}(\mathbf{r})$ between two point charges located near the condensed-matter substrate and separated by the vector \mathbf{r} when the substrate is characterized by the spatial dispersion of its dielectric function $\epsilon(\mathbf{k})$; \mathbf{k} is the wave vector [17,21,39]. On this basis, we obtain general expressions for

the electrostatic energy $W_{pp'}(r)$ between two point dipoles (unfortunately, previous essential results concerning dipole-dipole correlations near condensed-matter substrates are incomplete [41,42,62]). The substrate dielectric function $\epsilon(\mathbf{k})$ can describe either itinerant or bound electrons and may reflect the quantum-mechanical peculiarities of the Coulomb-field screening. Specific calculations were carried out in the point-dipole approximation for classical electrostatics (dielectric constants instead of dielectric functions, which is a natural reference model [15,16]) and the simplest model for the metal substrate, namely, the quasi-classical Thomas–Fermi dielectric permittivity [63].

We show that while studying the interaction between electric charges and dipoles near the interfaces, one must take into account (i) the influence of the substrate, whatever its screening properties, and (ii) the finite radius of screening, i.e. the spatial dispersion of the substrate dielectric permittivity, $\epsilon(\mathbf{k})$. This is a first step in the consideration of the substrate influence on the adsorption processes and the kinetics of adsorbate arrangement on the surface. Anyway, the dipole-dipole interaction is a main input to be used in the problems of surface dipole-lattice structures, which serve as models of adsorbate patterns on various substrates [34,43,64–72].

2. Electrostatic interaction of point charges near the interface

The geometry of the problem is shown in Fig. 1. Namely, two point charges Q and Q' are located in a dispersionless medium with the dielectric constant $\epsilon_0 = \text{const}$ at the distances z and z' , respectively, from the neutral substrate. They perturb the electron subsystem of the substrate ($z < 0$) and induce a non-uniform charge redistribution in it. In the classical electrostatics, the induced (polarization) charge is smeared over the surface and its point-like equivalent is called the image charge. In the non-local approach, when the substrate is characterized by the dielectric function $\epsilon(\mathbf{k}, \omega)$, where ω is the transferred frequency, it has a qualitatively different spatial distribu-

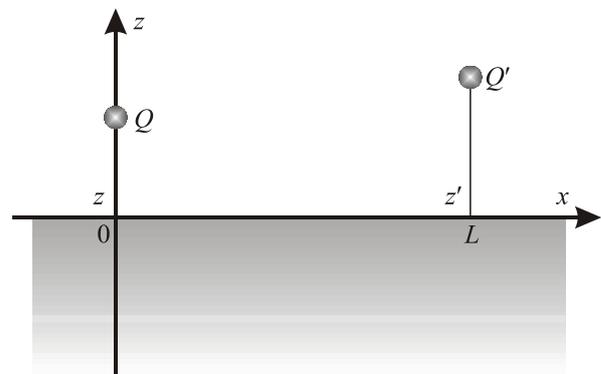


Fig. 1. Layout of interacting charges Q and Q' located in the insulator above the metallic (semiconducting) substrate (shaded) at the distances z and z' , respectively.

tion character — three-dimensional rather than two-dimensional — depending on the nature of the substrate, as well as on its ability to respond to external charges (to screen them). But the essence of the phenomenon remains the same [17–23,25–33]. Since we examine the interaction between two charges, all interactions of each charge with its partner and the partner's image charge have to be taken into consideration. On the contrary, the interaction of any charge with its own image has not to be taken into account, when calculating the interaction energy between the charges, $W_{QQ'}(\mathbf{r})$, because it makes a contribution to another quantity, the polarization energy W_{image} . The latter, as was explained above, substantially contributes to the interaction of the species concerned with the substrate, but not with each other.

In the approximation of charge-carrier specular reflection from the plane interface between two plasma-like media, i.e. making allowance for screening effects, the electrostatic interaction energy between two charges Q and Q' located at the points \mathbf{R} and \mathbf{R}' , respectively, near the interface is determined by the formula [17,21]:

$$W_{QQ'} = -4\pi QQ' D(\mathbf{R}, \mathbf{R}'), \quad (1)$$

where $D(\mathbf{R}, \mathbf{R}')$ is a function, the form of which depends on the geometry of the problem. After required substitutions, this equation can be rewritten in the form

$$W_{QQ'}(z, z', \boldsymbol{\rho}, \boldsymbol{\rho}') = -4\pi QQ' \int \frac{d^2 q}{(2\pi)^2} D(q, z, z') \exp[iq(\boldsymbol{\rho} - \boldsymbol{\rho}')], \quad (2)$$

where $\boldsymbol{\rho}, \boldsymbol{\rho}'$ are the horizontal (in the geometry of the problem) components of charge radius vectors. After the angular variable separation, it looks like

$$W_{QQ'}(z, z', L) = -4\pi QQ' \frac{1}{4\pi^2} \int_0^\infty q dq D(q, z, z') \int_0^{2\pi} d\varphi \exp(iqL \cos \varphi). \quad (3)$$

Here, the notation

$$L = |\boldsymbol{\rho} - \boldsymbol{\rho}'|, \quad (4)$$

for the distance between the charges measured along the interface was introduced.

In our particular case (see Fig. 1), when the charges are in the dispersionless medium with the dielectric constant $\varepsilon_0(\omega)$, ω is the transferred frequency, and $z, z' \geq 0$, the Romanov Green's function takes the form

$$D(q, \omega, z, z') = \frac{1}{2k_{\parallel} \varepsilon_0} \times \left\{ \exp(-q|z+z'|) \frac{1-\varepsilon_0 q a(q)}{1+\varepsilon_0 q a(q)} - \exp(-q|z-z'|) \right\}. \quad (5)$$

On the other side of the interface, i.e., at $z < 0$, there is a metallic or semiconducting half-space with the dielectric permittivity $\varepsilon(\mathbf{k}, \omega) = \varepsilon(\mathbf{q}, k_{\perp}, \omega)$, $\mathbf{k} = \mathbf{q} + \mathbf{k}_{\perp}$. The wave vector $\mathbf{q} = (k_x, k_y, 0)$ is the longitudinal (along the surface) component of the wave vector \mathbf{k} , whereas \mathbf{k}_{\perp} is its component directed along the z -axis. All subsequent calculations are valid if the frequency dependence is retained in both Eq. (4) and the dependence $\varepsilon_0(\omega)$. Nevertheless, we omit the argument ω below, $D(q, \omega, z, z') \rightarrow D(q, \omega=0, z, z') = D(q, z, z')$, because the temporal dispersion is not relevant in the static case considered here. If the substrate is a thin film, the generalized Green's function can also be found [17,19,21,73]. But this situation goes beyond the scope of this article and will be treated elsewhere.

We emphasize that the overall interaction energy (1) between two charges makes allowance for the image-force component automatically if one starts from the Coulomb Green's function (4) first obtained by Romanov [73] and applied later to a number of surface science problems [17,19,21,30] or any equivalent scheme [18,22,26,29,59,60,74]. Hence, $W_{QQ'}(\mathbf{R})$ is the expression that needs no other electrostatic addenda. Other indirect terms of a different nature, which can contribute to the overall interaction between the two charges, are not taken into consideration by function (5).

On the basis of the Jacoby–Anger formula [75]

$$\begin{aligned} \exp(iz \cos \varphi) &= \sum_{n=-\infty}^{n=+\infty} i^n \exp(in\varphi) J_n(z) = \\ &= J_0(z) + 2 \sum_{n=1}^{n=+\infty} i^n \cos(n\varphi) J_n(z), \end{aligned}$$

where $J_n(z)$ is the Bessel function of the first kind of the n th order, Eq. (2) is transformed as follows:

$$\begin{aligned} W_{QQ'}(z, z', L) &= -2QQ' \int_0^\infty q dq D(q, z, z') J_0(qL) = \\ &= \frac{QQ'}{\varepsilon_0} \int_0^\infty dq J_0(qL) \times \\ &\times \left\{ \exp(-q|z-z'|) - \exp[-q(z+z')] \frac{1-\varepsilon_0 q a(q)}{1+\varepsilon_0 q a(q)} \right\}. \quad (6) \end{aligned}$$

The first integral is tabular [76], and one has

$$\begin{aligned} W_{QQ'}(z, z', L) &= \frac{QQ'}{\varepsilon_0} \times \left\{ \frac{1}{s(L, z-z')} - \right. \\ &\left. - \int_0^\infty dq J_0(qL) \exp[-q(z+z')] \frac{1-\varepsilon_0 q a(q)}{1+\varepsilon_0 q a(q)} \right\}, \quad (7) \end{aligned}$$

where the notation $s(x, y) = \sqrt{x^2 + y^2}$ was introduced. Hence, the overall interaction is a sum of a trivial direct

Coulomb term and an additional interaction between the charges Q and Q' induced by the substrate polarization.

The substrate screening properties enter Eqs. (5) and (7) through the function $a(q)$, which is given by the formula

$$a(q) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{dk_{\perp}}{(k_{\perp}^2 + q^2) \varepsilon(\mathbf{q}, k_{\perp})}. \quad (8)$$

The combination $[qa(q)]^{-1}$ is usually called the surface dielectric function [59].

To obtain an insight, let us consider the simplest local electrostatic case, according to which $\varepsilon(\mathbf{k}) = \varepsilon_m = \text{const}$, so that $a(q) = 1/(q\varepsilon_m)$. Then

$$W_{QQ'}(z, z', L) = \frac{QQ'}{\varepsilon_0} \times \left\{ \frac{1}{s(L, z - z')} + \left(\frac{\varepsilon_0 - \varepsilon_m}{\varepsilon_0 + \varepsilon_m} \right) \frac{1}{s(L, z + z')} \right\}. \quad (9)$$

The second term reflects the appearance of the “image charges” at the interface and their interaction with real two charges. If both charges are located at the interface (in the adopted approach, this is an infinitely thin plane), so that $z = z' = 0$, Eq. (9) gives

$$W_{QQ'}(0, 0, L) = \frac{2QQ'}{(\varepsilon_0 + \varepsilon_m)L}. \quad (10)$$

We see that expression (10) contains both dielectric constants on equal footing, which is correct of course, since now neither medium is preferential. When the distinction between the media disappears altogether ($\varepsilon_0 = \varepsilon_m = \varepsilon$), we obtain the conventionally screened Coulomb interaction in the bulk

$$W_{QQ'}(L) = \frac{QQ'}{\varepsilon L}. \quad (11)$$

Surely, the classical electrostatics is a crude approximation for substrates with itinerant electrons (metals or degenerate semiconductors). In this case, its predictions become wrong due to the strong screening ability of mobile charge carriers. One can try to avoid the failure by going to the perfect conductor with $\varepsilon_m \rightarrow \infty$. Then Eq. (9) leads to

$$W_{QQ'}(z, z', L) = \frac{QQ'}{\varepsilon_0} \left\{ \frac{1}{s(L, z - z')} - \frac{1}{s(L, z + z')} \right\}. \quad (12)$$

In the practically important limiting case, when the both charges are arranged rather close to the interface in comparison with the distance between them ($z, z' \ll L$), one obtains

$$W_{QQ'}(z, z', L) = \frac{2QQ'zz'}{L^3 \varepsilon_0}, \quad (13)$$

i.e., the lateral interaction between the charges are dipole-like rather than Coulomb. This is due to the partial charge neutralization by their images (polarization distributions at the perfect conductor surface). Hence, the effective-dipole arms are $2z$ and $2z'$, so that the numerator in Eq. (13) for real dipoles would have included the product $4zz'$, although the image charges in the substrate, being the constituents of both dipoles, are actually only the descriptive interpretation of the interfacial charges induced by their real counterparts [16,31]. Nevertheless, the result is twice smaller. It can be explained as follows. The electric field value of the first dipole at the point (\mathbf{L}', z') located far enough does indeed include factor 2

$$E = \frac{2Qz}{L^3 \varepsilon_0}. \quad (14)$$

However, its electrostatic potential Φ should be E multiplied by z' without such a factor, because the potential is reckoned from the perfect conductor surface. Therefore, the energy of the second charge Q' is given by Eq. (13). Similar considerations were first applied to the dipoles adsorbed on the metal surface [41]. The energy (13) becomes zero when both charges are located on the substrate, $z = z' = 0$, in accordance with Eq. (10). It means that the screening by the perfect conductor is complete at its surface.

The classical approach does not make allowance for the finite screening length inherent even to the best conductors. The proper account of the effect needs the knowledge of the spatial dispersion of the bulk dielectric permittivity $\varepsilon(\mathbf{k})$. Several adequate models have been proposed not only for plasma-like media (metals, doped semiconductors, electrolyte solutions) [29,37,53,77–79] but also for media with bound electrons (insulators, intrinsic semiconductors) [80–83]. The quantum-mechanical character of $\varepsilon(\mathbf{k})$ [84,85] was shown to be important in surface problems [25,27,32,33,86]. However, the main features of the non-local electrostatics can be understood on the basis of the simple quasi-classical models based on the Pauli principle and applied to metals [78,87] or semiconductors [80,81]. Therefore, we will illustrate the role of $\varepsilon(\mathbf{k})$ -dispersion using the conventional Thomas–Fermi model for metals [88]. The corresponding expression, with an accuracy of notations, coincides with the Debye–Hückel formula for electrolyte solutions [89–91].

Namely, in the Thomas–Fermi approximation,

$$\varepsilon_{TF}(\mathbf{k}) = \varepsilon_m \left(1 + \frac{\kappa^2}{k^2} \right), \quad (15)$$

so that

$$a_{TF}(q) = \frac{1}{\varepsilon_m \sqrt{q^2 + \kappa^2}}. \quad (16)$$

Strictly speaking, the constant ε_m actually depends on q as well and tends to 1 for $q \rightarrow \infty$, i.e., at small distances from the screened charge ($r \rightarrow 0$), being the source of the Coulomb field. This limit must be achieved for the total dielectric permittivity describing any material [37]. However, in the q -range, important for applications, the phenomenological constant ε_m in metals may be identified with the dielectric constant $\varepsilon_\infty = \varepsilon(\omega \rightarrow \infty)$ in the metal electrodynamics [52,53], which is about or less than 2 [92,93].

Substituting Eq. (16) into Eq. (7), we obtain

$$W_{QQ'}(z, z', L) = \frac{QQ'}{\varepsilon_0} \times \left\{ \frac{1}{s(L, z-z')} - \int_0^\infty dq J_0(qL) \exp[-q(z+z')] \frac{\varepsilon_m \sqrt{q^2 + \kappa^2} - \varepsilon_0 q}{\varepsilon_m \sqrt{q^2 + \kappa^2} + \varepsilon_0 q} \right\}. \quad (17)$$

This expression is rather cumbersome and cannot be treated analytically for arbitrary values of system parameters. In Appendix, we develop a regular method for calculating such expressions numerically and obtaining their asymptotics of any order. But it is instructive here to consider another method for the simplest particular case of lateral interaction between the charges located at the interface ($z = z' = 0$):

$$W_{QQ'}(0, 0, L) = \frac{2QQ'}{(\varepsilon_0 + \varepsilon_m)} \times \left\{ \frac{1}{L} - \varepsilon_m \int_0^\infty dq J_0(qL) \frac{\sqrt{q^2 + \kappa^2} - q}{\varepsilon_m \sqrt{q^2 + \kappa^2} + \varepsilon_0 q} \right\} \equiv \frac{2QQ'}{(\varepsilon_0 + \varepsilon_m)L} - I(L, \kappa, \varepsilon_0, \varepsilon_m). \quad (18)$$

When the distance between the charges is short ($\kappa L \ll 1$), the Thomas–Fermi screening in the substrate constitutes only a small correction to the direct Coulomb interaction

$$W_{QQ'}(0, 0, L) = \frac{2QQ'}{L(\varepsilon_0 + \varepsilon_m)} \left\{ 1 + \frac{\kappa L \varepsilon_m}{(\varepsilon_0 - \varepsilon_m)} \times \left[1 + \frac{\varepsilon_0}{2\sqrt{\varepsilon_0^2 - \varepsilon_m^2}} \ln \left| \frac{\sqrt{\varepsilon_0^2 - \varepsilon_m^2} - \varepsilon_0}{\sqrt{\varepsilon_0^2 - \varepsilon_m^2} + \varepsilon_0} \right| \right] \right\}. \quad (19)$$

If the “pure” Thomas–Fermi model of the metal ($\varepsilon_m = 1$) is applied and the upper medium is the vacuum ($\varepsilon_0 = 1$), Equation (19) is simplified

$$W_{QQ'}(0, 0, L) = \frac{QQ'}{L} \left(1 - \frac{2}{3} \kappa L \right). \quad (20)$$

One sees that in this case the substrate polarization reduces the direct interaction insignificantly, as it should be for short distances between the charges.

Before calculating the integral $I(L, \kappa, \varepsilon_0, \varepsilon_m)$ in Eq. (18) in the opposite case $\kappa L \gg 1$, we emphasize that the first term in the I -expansion in $(\kappa L)^{-1}$ does not depend on κ and equals $-L^{-1}$. Hence, $W_{12}(0, 0, L) \approx 0$, which means that the interaction between the charges is completely screened at large enough distances. The next approximation should give the law of the $W_{12}(0, 0, L)$ decrease with L . To the second order in $(\kappa L)^{-1}$, we obtain

$$I = \frac{\varepsilon_m}{\varepsilon_0} \left[\frac{1}{L} - \int_0^\infty dq J_0(qL) \frac{\frac{\varepsilon_m \kappa}{\varepsilon_0} + \kappa}{\frac{\varepsilon_m \kappa}{\varepsilon_0} + q} \right] = \frac{\varepsilon_m}{\varepsilon_0 L} - \frac{2e^2 \varepsilon_m \kappa}{\varepsilon_0^2} \frac{\pi}{2} \left[\mathbf{H}_0 \left(\frac{\varepsilon_m \kappa L}{\varepsilon_0} \right) - N_0 \left(\frac{\varepsilon_m \kappa L}{\varepsilon_0} \right) \right]. \quad (21)$$

Here, $\mathbf{H}_0(x)$ and $N_0(x)$ are the Struve and Neumann functions, respectively [75]. For large arguments, $x \gg 1$, the difference in brackets has the following asymptotics:

$$[\mathbf{H}_0(x) - N_0(x)]_{x \gg 1} \rightarrow \frac{2}{x \sqrt{\pi} \Gamma \left(\frac{1}{2} \right)} \left(1 - \frac{1}{x^2} \right).$$

Therefore, substituting Eq. (21) into Eq. (18), we arrive at the final result

$$W_{QQ'}(\kappa L \gg 1) \approx \frac{2QQ' \varepsilon_0}{\varepsilon_m^2 \kappa^2 L^3}. \quad (22)$$

Thus, we obtained the dipole-dipole residual interaction instead of the parent Coulomb one. It is easy to verify that the method expounded in Appendix brings about the same result in this (κL) -expansion order. It is of no wonder, because the incomplete screening by the itinerant electrons in the substrate produces dipoles composed of the external charges and their images, although the charges are located at the interface ($z = z' = 0$). Indeed, the effective dipole arms are of the order of κ^{-1} . The dielectric constant ε_0 of the upper half-space increases the magnitude of the dipole-dipole interaction (repulsion for like adsorbates), which is appropriate only to the asymptotic region [see Eq. (10) for comparison]. One should also mention that result (22) resembles the Thomas–Fermi screening behavior in two-dimensional sheets, i.e., the screening becomes weaker there than in the bulk. Namely, the power-law spatial decrease rather than the exponential decay must be observed in thin films, because there are not enough mobile charge carriers to completely screen the applied electric field [94].

At the same time, we should emphasize that the method applied above for obtaining large- (κL) asymptotics allows the correct expansions with an accuracy not higher than to the $(\kappa L)^{-5}$ -order to be obtained. It is so because the approximation used for the integrand in Eq. (18) is correct

only to the $(\kappa L)^{-3}$ -order. For the majority of calculations, this order is enough to obtain required asymptotics. Otherwise, the regular expansion method (see Appendix) should be applied.

In the case of $z \neq z' \neq 0$ and the Thomas–Fermi dielectric function (15), the analysis of Eq. (17) demonstrates that the answer depends on the ratio between $\sqrt{zz'}$ and $\varepsilon_0/\kappa\varepsilon_m$:

$$W_{QQ'}(\kappa L \gg 1) = \frac{2QQ'}{\varepsilon_0 L^3} \times \begin{cases} \frac{\varepsilon_0^2}{\kappa^2 \varepsilon_m^2} & \text{if } L \gg \frac{\varepsilon_0}{\kappa \varepsilon_m} \gg \sqrt{zz'} \\ zz' & \text{if } L \gg \sqrt{zz'} \gg \frac{\varepsilon_0}{\kappa \varepsilon_m} \end{cases}. \quad (23)$$

Expectedly, the result described by the first row coincides with Eq. (22), whereas the second row is nothing else but the classical dipole-dipole interaction (13), which replaces the Coulomb interaction due to the substrate polarization.

If one turns from the quasi-classical [88] to the quantum-mechanical [84,85] dielectric permittivity with spatial dispersion, the existence of a steep Fermi surface and its specific form [95,96] become crucial for the surface electrostatics [17,21,39]. In particular, in isotropic conductors, the weak $\varepsilon(\mathbf{k})$ Lindhard–Kohn anomaly at $k = 2k_F$, where k_F is the Fermi wave vector, leads to the Friedel oscillations of the charge-charge interaction energy along the metallic substrate surface, [22,97,98]

$$W_{QQ'}(L) \sim \frac{\cos(2k_F L)}{L^3}, \quad (24)$$

which have the same form as their conventional bulk counterparts [99]. On the other hand, for quasi-two- and quasi-one-dimensional metals, the $\varepsilon(\mathbf{k})$ -anomalies are much stronger [100]. Therefore, the $W_{12}(L)$ oscillations become long-range ones [17,21,39]:

$$W_{QQ'}^{2D}(L) \sim \frac{\cos(2k_F L)}{L^2}, \quad W_{QQ'}^{1D}(x) \sim \frac{\cos(2k_F x)}{x}, \quad (25)$$

where the coordinate x is reckoned perpendicularly to the Fermi surface sheets. This long-range behavior may be especially important for adsorbates on the surfaces of superconductors with the nested sections on their Fermi surfaces [101,102], because possible regular surface structures of adsorbed atoms may melt below the superconducting critical temperature [103]. This phenomenon is driven by the disappearance of the sharp Fermi surface edge in the superconducting state due to the development of the energy gap Δ [104,105]. Hence, Friedel oscillations decay in the real space as $\sim \exp(-2\Delta R/\hbar v_F)$ [104]. Here, \hbar is the Planck constant, and v_F the Fermi velocity of the electron gas.

As was emphasized above, the spatial dispersion of dielectric permittivity in a semiconducting substrate influences the charge-charge interaction in the adjacent medium [22,23], although not so severely, because the screening by bound electrons is more gentle [19,25,37, 80–83,106]. The more general case of the charge-charge (ion–ion, in this case) interaction in the electrolyte solution near the metallic electrode [22,23] is also of importance, although it is more difficult to be measured directly in experiments. The Romanov method or its equivalent versions may be applied to such a situation as well [22,107,108], but the physical problems of adsorption treated here can be solved without the corresponding generalization.

3. Electrostatic interaction of dipoles near the interface

Dipoles with the permanent dipole moment are a good model for a lot of kinds of adsorbed molecules [109–112]. In order to describe the electrostatic interaction between them, it is reasonable to start from the consideration of two pairs of opposite charges, i.e., from two extended dipoles. For large distances between those dipoles, the latter can be regarded as point ones. The planar and perpendicular arrangements of dipoles near the surface are the most natural and experimentally observable ones, although tilted configurations can also be possible [34]. Therefore, only those two configurations will be considered in this work (see Fig. 2).

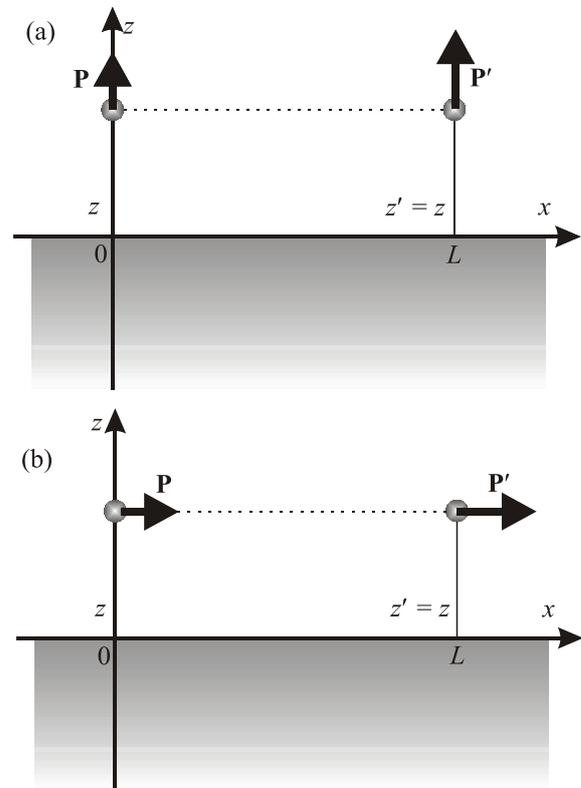


Fig. 2. Layout of interacting dipoles \mathbf{P} and \mathbf{P}' located in the insulator above the metallic (semiconducting) substrate (shaded) at the distance $z = z'$. The dipoles are perpendicular (a) and parallel to the interface (b).

Let the dipole \mathbf{P} be composed of two point charges, Q and $-Q$, separated by the distance d (the dipole arm), and the dipole \mathbf{P}' by two point charges, Q' and $-Q'$, separated by the distance d' . Following the discussion presented at the beginning of section 2, the expression for the Coulomb interaction energy of two dipole should include only the cross terms (1) between the charges belonging to different dipoles,

$$W_{PP'} = \sum_{\substack{q=Q, -Q \\ q'=Q', -Q'}} W_{qq'}. \quad (26)$$

All other possible qq' -combinations give us the interaction energy between the constituents within the same dipoles, as well as the dipole image force energies, which was considered earlier [32,33,113].

Each term in Eq. (26) is given by Eq. (6), in which the specific parameters L , z , and z' correspond to the specific charge pair (q, q'). For simplicity, let us further assume that the adsorbed dipoles are located at the same distance from the substrate, so that $z = z'$ (Fig. 2). In the case of planar orientation (Fig. 2(b)), the both dipole vectors can be rotated by the corresponding angle (α for \mathbf{P} and α' for \mathbf{P}') in the plane perpendicular to the OZ axis. Since we are interested in the spatial asymptotics of the dipole-dipole interaction energy, all results will be formulated for point dipoles only ($d \ll z, L$). In this case, four parameters (Q, d, Q', d') are reduced to only two (P, P').

First, let us look at the pair of vertical dipoles. Similarly to what was done for two charges in the previous Section, we will begin with the classical electrostatics, e.g., examine two media with the dielectric constants ϵ_0 and ϵ_m . Then all components from Eq. (26) have the form of Eq. (9). The sum of all four terms in the point-dipole limit gives the following result [42]

$$W_{PP'}^{\text{vert,class}}(L, z) = \frac{PP'}{\epsilon_0} \left[\frac{1}{L^3} + \frac{(\epsilon_0 - \epsilon_m)}{(\epsilon_0 + \epsilon_m)s^3(L, 2z)} \left(1 - \frac{12z^2}{s^2(L, 2z)} \right) \right]. \quad (27)$$

The second term in Eq. (27) describes the influence of substrate polarization. The classical repulsion of identical parallel dipoles can be reduced or increased by the dipole images, depending on the sign of the difference ($\epsilon_0 - \epsilon_m$). If the distance of the molecule (dipole) from the substrate z is much smaller than the distance L between the molecules, one obtains from Eq. (27) that

$$W_{PP'}^{\text{vert,class}}(L, z) = \frac{2PP'\epsilon_m}{\epsilon_0 L^3 (\epsilon_0 + \epsilon_m)} \left[1 + \frac{9(\epsilon_0 - \epsilon_m)z^2}{L^2} \right]. \quad (28)$$

If the second term in Eq. (28) is neglected as a small correction, we obtain the dipole repulsion at the interface screened by both media on the same footing. Furthermore, if both media are identical, the classical interaction energy

[16] of parallel dipoles in the insulator with the permittivity $\epsilon = \epsilon_0 = \epsilon_m$ is recovered.

In the general case, it is possible to unite all terms in Eq. (26) using the following approximation in the integrand

$$1 - e^{-dq} - e^{-d'q} + e^{-(d+d')q} \approx dd'q^2. \quad (29)$$

Then, isolating the classical term (27), we arrive at the general expression for the interaction energy of two point dipoles, which is formally valid for any dielectric function of the substrate,

$$V_{PP'}^{\text{vert,gen}}(L, z) = \frac{PP'}{\epsilon_0 L^3} \left[1 + \frac{2}{s^3(L, 2z)} - 24 \frac{z^2}{s^5(L, 2z)} \right] + 2PP' \int_0^\infty dq J_0(qL) e^{-2qz} \frac{q^3 a(q)}{1 + \epsilon_0 q a(q)}. \quad (30)$$

The exponential factor e^{-2qz} in Eq. (30) ensures the integral convergence. However, when the molecule is located at the interface ($z=0$), the convergence at the upper limit becomes dependent on the behavior of the dielectric function $\epsilon(\mathbf{k})$ and, consequently, on the function $a(q)$. Such models as the Thomas–Fermi one (or its Inkson analog for bound electrons [80,106]) lead to the dependence $\epsilon(\mathbf{k}) \approx 1 + (\bar{\kappa}^2/k^2)$ for $k \rightarrow \infty$ (here, $\bar{\kappa}$ is a certain momentum inherent to the specific model), so that $a(q) \sim q^{-1}$ at $q \rightarrow \infty$ (the limit is important to identify $W_{PP'}^{\text{vert,gen}}(L, z)$ at small distances L). This power exponent is not enough to compensate the factor q^3 in the integrand of Eq. (30), making the whole formula useless in the case $z=0$.

However, the apparent divergence is not an indispensable property of the dipole-dipole interaction energy. Indeed, the true quantum-mechanical dielectric permittivity of non-interacting three-dimensional electron gas described by the Lindhard formula [84] gives the following asymptotics at $k \rightarrow \infty$:

$$\epsilon(\mathbf{k}) \rightarrow 1 + \frac{4k_F^2 \kappa^2}{3k^4}. \quad (31)$$

The same behavior preserves for the dielectric function $\epsilon(\mathbf{k})$ of the electron liquid, when many-body correlations are taken into account [114]. Moreover, a similar behavior should be appropriate for bound electrons [81], because the screening response of the bound electrons at small enough distances from the perturbing charge tends to that of their itinerant counterparts. That is why, strictly speaking, any dielectric constant ϵ in the non-local electrostatics is somewhat artificial. Actually, it is a function of k and should tend to unity at $k \rightarrow \infty$ [27,29,37]. The raised issue of convergence due to the quantum-mechanical nature of screening is similar to that concerning the dipole image force energy saturation at the interface, which was considered earlier [32,33].

Thus, the problems of the integral convergence at large q 's is extremely significant for the screening behavior at short distances from the Coulomb field source. The proper choice for the dielectric function in Eq. (30) will remove any divergences in $W_{PP'}^{\text{vert,gen}}(L, z)$ in the whole range of L and z . However, this can be done at the expense of making the treatment numerical. On the other hand, if one wants to gain an insight into the essence of the problem and obtain an analytical asymptotics for large L , which is the only needed information in the majority of cases, we can restrict ourselves to simple model dielectric functions $\varepsilon(\mathbf{k})$ and calculate the sought asymptotics using our simple method outlined in Appendix. We emphasize that the quantum-mechanical Lindhard function tends to the Thomas–Fermi quasi-classical limit (15) for small k (of course, the background constant ε_m must be equal to 1 for the electron gas). Therefore, the large- L Thomas–Fermi asymptotics tends to that for the “true” quantum-mechanical one, so that it will give a good solution to the problem if we are limited to the monotonic part of the dependence $W_{PP'}^{\text{vert,gen}}(L, z)$. Of course, to uncover the long-range Friedel oscillations like Eqs. (24) and (25), which are a consequence of the sharp Fermi-surface, the form of the metal dielectric function $\varepsilon(\mathbf{k})$ with an exact singularity at $k = 2k_F$ should be preserved. In this case, another kind of asymptotics extraction should be used, e.g., which is based on the Lighthill analysis [115]. Hereafter, the Friedel oscillations are totally ignored.

Returning to our specific problem, which consists in the determination of the spatial characteristics of the dipole-dipole interaction near the substrate surface, we apply the approach described in Appendix, obtain the proper asymptotics of all terms from Eq. (26) in the Thomas–Fermi approximation, and sum them up. The transition to the point-dipole limit, when $d, d' \rightarrow 0$, is made after all asymptotic terms are combined. In the case of the normal dipole orientation with respect to the substrate (Fig. 2(a)), the asymptotic result for $L \gg \kappa^{-1}$, z is as follows:

$$W_{PP'}^{\text{vert,TF,asympt}}(L, z) \approx \frac{2PP'}{\varepsilon_0 L^3} - \frac{18PP'}{\varepsilon_0 \varepsilon_m^2 \kappa^2 L^5} (\varepsilon_0 + \kappa z \varepsilon_m)^2. \quad (32)$$

The main L^{-3} -term in this expression coincides with that in Eq. (28) only in the limit $\varepsilon_m \gg \varepsilon_0$, i.e., for the extremely strong screening in the substrate (the perfect-conductor model). Since, actually, the screening ability of the Thomas–Fermi metal is weaker than that of the perfect conductor, a correction term with the opposite sign appears in asymptotics (32). We emphasize that in the general case of arbitrary constants ε_m and ε_0 , the dipole-dipole interaction substantially differs from the classical case. However, the qualitative spatial behavior of $W_{PP'}^{\text{vert,class,asympt}}$ and $W_{PP'}^{\text{vert,TF,asympt}}$ is similar, contrary to the case of the charge-to-charge interaction [Eq. (22)]. When the mole-

cules are located at the interface ($z = 0$), the asymptotics becomes

$$W_{PP'}^{\text{vert,TF,asympt}}(L, z = 0) \approx \frac{2PP'}{\varepsilon_0 L^3} - \frac{18PP' \varepsilon_0}{\varepsilon_m^2 \kappa^2 L^5}. \quad (33)$$

Another important pattern is a pair of planar dipoles located above the substrate surface (Fig. 2(b)). The angles between the vectors \mathbf{P} and \mathbf{P}' , on the one hand, and the x -axis, on the other hand, will be denoted as α and α' , respectively. The classical electrostatics leads to the following result for the lateral dipole-dipole interaction

$$W_{PP'}^{\text{planar,class}}(L, z) = -\frac{PP'}{\varepsilon_0 L^3} \times \left\{ \frac{1}{2} [3 \cos(\alpha + \alpha') + \cos(\alpha - \alpha')] + \frac{(\varepsilon_m - \varepsilon_0)}{(\varepsilon_0 + \varepsilon_m)} \frac{L^5}{s^5(L, 2z)} \times \left[\frac{4z^2}{L^2} \cos(\alpha - \alpha') - \frac{3}{2} \cos(\alpha + \alpha') - \frac{1}{2} \cos(\alpha - \alpha') \right] \right\}. \quad (34)$$

For the small ratio z^2/L^2 , Eq. (34) can be simplified

$$W_{PP'}^{\text{planar,class}}(L, z) \approx -\frac{PP'}{L^3 (\varepsilon_0 + \varepsilon_m)} \times \left\{ \cos(\alpha - \alpha') + 3 \cos(\alpha + \alpha') + \frac{3z^2 (\varepsilon_0 - \varepsilon_m)}{\varepsilon_0 L^2} [3 \cos(\alpha - \alpha') + 5 \cos(\alpha + \alpha')] \right\}. \quad (35)$$

One sees that, if the dipoles are arranged head-to-tail along the x -axis ($\alpha = \alpha' = 0$), they attract each other. On the other hand, if they are oriented head-to-head ($\alpha = 0, \alpha' = \pi$), the attraction is transformed into repulsion, which is also qualitatively understood.

Starting from Eq. (26) and expanding it in qd and qd' , it is easy to obtain a general formula for the lateral dipole-dipole interaction energy in the framework of the non-local electrostatics for planar dipoles:

$$W_{PP'}^{\text{planar,gen}}(L, z) = W_{PP',0}^{\text{planar,gen}}(L, z) + W_{PP',1}^{\text{planar,gen}}(L, z), \quad (36)$$

where

$$W_{PP',0}^{\text{planar,gen}}(L, z) = \frac{PP'}{\varepsilon_0 L^3} \times \left\{ -\frac{3}{2} \cos(\alpha + \alpha') - \frac{1}{2} \cos(\alpha - \alpha') + \cos(\alpha - \alpha') \frac{L^3}{s^3(L, 2z)} - \frac{3}{2} [\cos(\alpha + \alpha') + \cos(\alpha - \alpha')] \frac{L^5}{s^5(L, 2z)} \right\}, \quad (37)$$

$$\begin{aligned}
 W_{PP',1}^{\text{planar,gen}}(L,z) = & -\frac{2PP'}{\varepsilon_0} \int_0^\infty dq \frac{q}{1+\varepsilon_0 qa(q)} e^{-2qz} \times \\
 & \times \left\{ \frac{1}{2} q J_0(Lq) [\cos(\alpha+\alpha') + \cos(\alpha-\alpha')] - \right. \\
 & \left. - \frac{1}{L} J_1(Lq) \cos(\alpha+\alpha') \right\}. \quad (38)
 \end{aligned}$$

Expression (36) for $W_{PP',1}^{\text{planar,gen}}(L,z)$ converges with any proper quantum-mechanical dielectric function $\varepsilon(\mathbf{k})$ used to calculate $a(q)$ in Eq. (38) due to the same reasons as those indicated above while analyzing the validity of Eq. (30).

The large- L asymptotics of Eqs. (36)–(38) was calculated for the Thomas–Fermi model of the metal substrate dielectric function using the expansion method described in Appendix:

$$\begin{aligned}
 W_{PP'}^{\text{planar,TF,asympt}}(z) & \approx \\
 & \approx -\frac{3PP'}{\varepsilon_0 \varepsilon_m^2 \kappa^2 L^5} w_{PP'}^{\text{planar,TF,asympt}}(z), \quad (39)
 \end{aligned}$$

where

$$\begin{aligned}
 w_{PP'}^{\text{planar,TF,asympt}}(z) = & (\varepsilon_0 + \kappa z \varepsilon_m)^2 \times \\
 & \times [5 \cos(\alpha + \alpha') + 3 \cos(\alpha - \alpha')]. \quad (40)
 \end{aligned}$$

One sees that, in the general case of planar dipoles, the classical L^{-3} -asymptotics is transformed into a more severely decreasing one (L^{-5}) under the influence of the adjacent metal substrate with its strong (although not perfect!) screening, contrary to the situation for the dipoles perpendicular to the interface (cf. Eq. (32)), when the classical dipole-dipole interaction survived the metallic substrate impact.

It is remarkable that the angular dependence of the asymptotics (39) does not depend on the dipole-substrate distance z . This is not the case in the classical model, as can be seen from Eqs. (34) and (36). On the other hand, the classical angular dependence for negligibly small ratios z/L is different from the universal one in Eq. (39). Hence, an analysis of the planar dipole-lattice configurations (see, e.g. the article [34]) can reveal the substrate effect.

The weakening of the dipole-dipole interaction by the extra L^{-2} factor in Eq. (39) as compared to the charge-charge counterpart, Eq. (22), can be qualitatively understood as a consequence of the extra q^2 -factor in Eqs. (29) and (38). We note that the obtained power-law asymptotics of the charge-charge and dipole-dipole interactions near the metal surface differs much from the exponential screening in the bulk of the Thomas–Fermi metal: $\exp(-\kappa L)$ [88]. The strong modification of conventional electrostatic results by non-local effects is analogous to that found for the interaction of helical molecules in biological systems [116–118].

4. Conclusions

In this work, we presented an analysis of non-local electrostatic effects revealed by charge-charge and dipole-dipole interactions in a dispersionless medium (the vacuum or a vapour phase) near the surface of a metallic or semi-conducting substrates with the spatial dispersion of its dielectric permittivity $\varepsilon(\mathbf{k})$. It was shown that the electrostatic component of the interaction between the permanent charges or dipoles, which are often considered as adequate models for adsorbed atoms and molecules, may drastically differ from the classical Coulomb or dipole-dipole interactions in the bulk medium, both with the dispersion and dispersionless. In particular, the charge-charge interaction is no longer the Coulomb one, which is inherent to classical insulators. On the other hand, it does not demonstrate the exponential dependence typical of the screening by itinerant electrons in the bulk. Instead, the asymptotic lateral dependence of the interaction becomes a dipole-dipole one determined by the Thomas–Fermi screening radius. At the same time, the dipole-dipole interaction between planar dipoles near the interface is weakened and becomes proportional to L^{-5} .

The pairwise interaction considered here can serve as an input in the calculations of possible electric-dipole lattice structures [34,43,66,68,71,72]. Therefore, the whole procedure of such calculations should take into account the substrate-induced distortion of lateral interactions. Although this viewpoint is not new [39], the substrate electrostatic effects are mostly overlooked in the existing treatments, perhaps due to the cumbersome mathematics. Nevertheless, as we have showed here, the interaction asymptotics are very simple to handle, so that in many important cases, when the dipole lattices are rather loose, those asymptotics can be easily incorporated into consideration. Of course, such a generalization should substantially improve the applicability of calculation results to real adsorbate systems.

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Appendix A:

In the considered model, the problem of calculating the electrostatic interaction between two charges Q and Q' located in a dispersionless medium near the interface with a medium, where the dispersion of its dielectric permittivity has to be taken into account, and, in particular, evaluating its asymptotics at large distances between those charges, is reduced to the calculation of the integral

$$W_2 = \int_0^\infty J_0(Lq) \exp(-Zq) F(q) dq, \quad (A.1)$$

where the constants $L > 0$ and $Z \geq 0$, and $F(q)$ is a finite smooth function. If $F(q) = \text{const}$, the integral is easily calculated using the tabular expression [76]:

$$I(L, Z) = \int_0^\infty J_0(Lq) \exp(-Zq) dq = \frac{1}{\sqrt{L^2 + Z^2}}. \quad (A.2)$$

However, if $F(q) \neq \text{const}$, the evaluation of this integral faces difficulties. In particular, we cannot expand the function $F(q)$ in a power series of q , because the integral

$$I_n = \int_0^\infty J_0(Lq) \exp(-Zq) q^n dq \quad (A.3)$$

diverges at $n \geq 2$, and even at $n = 1$ if $Z \rightarrow 0$. At the same time, unlike the power function q^n , the functions $F(q)$ that are dealt with in our case are finite in the whole integration interval $q \in (0, \infty)$. In particular, they have the finite limiting values $F(q=0) = F_0$ and $F(q \rightarrow \infty) = F_\infty < F_0$.

Without loss of generality, let us introduce a new variable

$$x = \exp\left(-\frac{q}{K}\right), \quad (A.4)$$

which is confined to the finite interval $x \in (0, 1]$. In principle, the positive parameter K can be taken arbitrary, but in our specific case of a medium with the spatial dispersion of the dielectric permittivity, it is associated with the inverse screening length. Using the new variable, let us introduce the function $f(x)$ by the formula

$$F(q) = F_\infty + f(x), \quad (A.5)$$

where x and q are related by Eq. (A.4). It is easy to verify that $f(x=0) = 0$ and $f(x=1) = F_0 - F_\infty$. Let us expand $f(x)$ in a power series in the vicinity of the point $x = 1$:

$$f(x) = \sum_{k=0}^\infty \frac{1}{k!} \left[f_x^{(k)}(x) \right]_{x=1} (x-1)^k. \quad (A.6)$$

Substituting this formula into expression (A.5), using the binomial expansion for $(x-1)^k$, we obtain

$$f(x) = \sum_{k=0}^\infty \frac{1}{k!} \left[f_x^{(k)}(x) \right]_{x=1} \sum_{i=0}^k \frac{k!}{i!(k-i)!} x^i (-1)^{k-i}. \quad (A.7)$$

In essence, this is a series expansion of the function $f(x)$ near the point $x=0$, but with the expansion coefficients calculated at the point $x=1$. A significant advantage of expansion (A.7) is the fact that all its terms of the order $k > 0$ equal zero at $x=0$. Substituting this formula into Eq. (A.5) and using relation (A.4), we obtain

$$F(q) = F_\infty + \sum_{k=0}^\infty \left[f_x^{(k)}(x) \right]_{x=1} \sum_{i=0}^k \frac{(-1)^{k-i}}{i!(k-i)!} \exp\left(-\frac{iq}{K}\right). \quad (A.8)$$

Now it becomes evident that the procedure described above is no more than the expansion of the function $F(q)$ in a series of exponential functions. This expansion allows integral (A.1) to be represented as a series of tabular ones [76], each of which giving a simple inverse square root of type (A.2). Really, substituting Eq. (A.8) into expression (A.1) and applying relation (A.2), we obtain

$$W_2 = \frac{F_\infty}{\sqrt{L^2 + Z^2}} + \sum_{k=0}^\infty C_k \left[f_x^{(k)}(x) \right]_{x=1}, \quad (A.9)$$

where

$$C_k = \frac{1}{L} \sum_{i=0}^k \frac{(-1)^{k-i}}{i!(k-i)!} \frac{1}{\sqrt{1 + \frac{1}{L^2} \left(Z + \frac{i}{K} \right)^2}}. \quad (A.10)$$

In this formula, the behavior of the function $F(q)$, which contains the specific features of charge screening in the substrate, are hidden in the derivatives $\left[f_x^{(k)}(x) \right]_{x=1}$ and the constant F_∞ , whereas the ‘‘coefficients’’ C_k are universal and depend only on the geometrical parameters of the problem (we recall that K can be selected arbitrarily, without any relationship to the substrate parameters). The iterative calculation of the derivative $f_x^{(k)}(x)$ in Eq. (A.9) is simple, but cumbersome:

$$\begin{aligned} \frac{\partial^k}{\partial x^k} f(x) &= \frac{\partial}{\partial x} \left(\frac{\partial^{k-1}}{\partial x^{k-1}} f(x) \right) = \left(\frac{\partial x}{\partial q} \right)^{-1} \frac{\partial}{\partial q} \left(\frac{\partial^{k-1}}{\partial x^{k-1}} f(x) \right) = \\ &= -K \exp\left(\frac{q}{K}\right) \frac{\partial}{\partial q} \left(\frac{\partial^{k-1}}{\partial x^{k-1}} f(x) \right), \end{aligned} \quad (A.11)$$

so that

$$\left[f_x^{(k)}(x) \right]_{x=1} = \left[\left(-K \exp\left(\frac{q}{K}\right) \frac{\partial}{\partial q} \right)^k f(x) \right]_{q=0}, \quad (A.12)$$

where (see Eq. (A.5))

$$f(x) = F(q) - F_\infty. \quad (A.13)$$

Series (A.9) converges rather rapidly, being much more convenient for calculations than the initial integral (A.1) of an oscillating function over the semi-infinite interval $q \in (0, \infty)$.

If we are interested in the long-range ($L \rightarrow \infty$) asymptotic of W_2 , expression (A.9) can be strongly simplified. Using the formula

$$(1+x)^{-1/2} = \sum_{j=0}^\infty (-1)^j \frac{(2j)!}{(2^j j!)^2} x^j, \quad (A.14)$$

we obtain

$$C_k = \frac{1}{L} \sum_{i=0}^k \frac{(-1)^{k-i}}{i!(k-i)!} \times \sum_{j=0}^{\infty} (-1)^j \frac{(2j)!}{(2^j j!)^2} \left(\frac{1}{L} \left(Z + \frac{i}{K} \right) \right)^{2j}. \quad (\text{A.15})$$

Now, applying the binomial formula to the multiplier $\left(\frac{1}{L} \left(Z + \frac{i}{K} \right) \right)^{2j}$, we have

$$C_k = \frac{1}{L} \sum_{i=0}^k \frac{(-1)^{k-i}}{i!(k-i)!} \sum_{j=0}^{\infty} (-1)^j \frac{(2j)!}{(2^j j!)^2} \frac{1}{L^{2j}} \times \sum_{m=0}^{2j} \frac{(2j)!}{m!(2j-m)!} Z^m \left(\frac{i}{K} \right)^{2j-m}. \quad (\text{A.16})$$

Changing the summation order, this formula reads

$$C_k = \frac{1}{L} \sum_{j=0}^{\infty} (-1)^j \frac{(2j)!}{(2^j j!)^2} \frac{1}{L^{2j}} \times \sum_{m=0}^{2j} \frac{(2j)!}{m!(2j-m)!} \frac{Z^m}{K^{2j-m}} \sum_{i=0}^k \frac{(-1)^{k-i}}{i!(k-i)!} i^{2j-m}. \quad (\text{A.17})$$

The most important feature of the last sum in Eq. (A.17), which can be rewritten in the form

$$s(k, n) = (-1)^k \sum_{i=0}^k \frac{(-1)^i}{i!(k-i)!} i^n, \quad (\text{A.18})$$

is that [76]

$$s(k, n) = \begin{cases} 0 & \text{if } n < k \neq 0 \\ 0 & \text{if } n \neq 0, k = 0 \\ 1 & \text{if } n = 0, k = 0 \end{cases} \quad (\text{A.19})$$

Therefore, in Eq. (A.17), all sums over i with $m > 2j - k$ equal zero, and the summation over m can be truncated to $\sum_{m=0}^{2j-k} \dots$. However, in the new sum, for at least the first ($m=0$) summand to exist, there must be $2j > k$. In expression (A.17) for the coefficient C_k , the summation over j begins from the summand of the $[k/2]$ -th order, where the notation [...] means the integer part of the bracketed number. As a result, the principal term in this expansion is $O(L^{-(k+1)})$. It means that, if we are interested in the asymptotics of the $O(L^{-N})$ -order for W_2 , we may break off the summation in Eq. (A.9) after the ($k=N$)-summand.

In order to obtain the final asymptotic formula for W_2 , we should make some additional transformations. First, let us extract the zero-order term from the sum in Eq. (A.9). Together with the first summand in the right hand side of

this formula, it gives $F_0/\sqrt{L^2 + Z^2}$ (see Eq. (A.13)), which has to be expanded in a series up to the $O(L^{-N})$ -term (see below). Then, in the second summand, we may sum up over i in formula (A.17) from $i=1$ (rather than 0) to k . Omitting the $o(L^{-N})$ -terms in the both summands, we obtain

$$W_2 \approx \frac{1}{\epsilon_0 L} (W_{20} + W_{21}) + o(L^{-N}), \quad (\text{A.20})$$

where

$$W_{20} = F_0 \sum_{k=0}^{\lfloor \frac{N-1}{2} \rfloor} (-1)^k \frac{(2k)!}{(2^k k!)^2} \left(\frac{Z}{L} \right)^{2k}, \quad (\text{A.21})$$

$$W_{21} = \sum_{k=1}^{\lfloor \frac{N-1}{2} \rfloor} C'_k \left[f_x^{(k)}(x) \right]_{x=1}, \quad (\text{A.22})$$

$$C'_k = \sum_{j=\lfloor \frac{k}{2} \rfloor}^{\lfloor \frac{N-1}{2} \rfloor} (-1)^j \frac{((2j)!)^2}{(2^j j!)^2} \frac{1}{(KL)^{2j}} \times$$

$$\sum_{m=0}^{2j-k} \frac{(LK)^m}{m!(2j-m)!} \left(\frac{Z}{L} \right)^m \sum_{i=1}^k \frac{(-1)^{k-i}}{i!(k-i)!} i^{2j-m}, \quad (\text{A.23})$$

with making allowance for Eq. (A.12).

Thus, expressions presented above comprise a solution of the long-range asymptotics problem. It depends on two intrinsic small dimensionless parameters: KL and Z/L . From the basic solid-state physics, it is known that, for typical metals, the screening parameter K is about 1 \AA^{-1} [63]. Hence, the smallness of the former parameter is ensured at $L \gg 1 \text{ \AA}$. It is appropriate for loose adsorbate structures [17,21,22,34,39–43]. At the same time, the parameter Z is the sum of the charges' distances from the substrate, $z+z'$ (see Eq. (5)). The spacing z from the substrate to the adsorbed charge (molecule) is determined by the covalent-bond length and is also equal to about 1 \AA [5]. Therefore, the latter parameter can be regarded small at $L \gg 2 \text{ \AA}$. One can see that the both estimates are practically equivalent.

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