

Image forces for a point-like dipole near a plane metal surface: An account of the spatial dispersion of dielectric permittivity

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ARTICLE INFO

Article history:

Received 8 July 2011

Accepted 15 November 2011

Available online 26 November 2011

Keywords:

Electrostatics

Image forces

Point dipole

Dielectric permittivity

Spatial dispersion

Quantum–mechanical effects

ABSTRACT

Image-force energy profiles were calculated for a constant point-like dipole located in a dispersionless semi-infinite medium adjacent to a medium with the spatial dispersion of its dielectric permittivity. Three models for the substrate were considered: classical (dispersionless), Thomas–Fermi (classical, but taking non-local screening effects into account), and Schulze–Unger (the approximation to the quantum–mechanical non-local Lindhard dependence, reproducing short-range spatial asymptotics correctly). The results obtained taking into account the non-local character of charge-carrier screening differ drastically from those obtained in the classical limit. Hence, classical electrostatics is inadequate, when being applied to analyze the dipole energy at the interface between two polarizable media. In particular, non-local screening results in finite values of the dipole image force energies at the interfaces.

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1. Introduction

Atoms and molecules can be adsorbed at condensed matter substrates under the influence of various factors [1–4]. When the adsorption is a physical one, the potential well for adsorbed entities, e.g., molecules, is formed by relatively weak van der Waals interaction, which can be considered as a consequence of emerging fluctuating dipoles [5,6]. Sometimes, the term “van der Waals forces” is applied to other interactions of the electrostatic nature occurring in surface science [7]. In the general case, the molecule–substrate interaction is a complex one, named chemisorption [4, 8–12], which includes Pauli repulsion and covalent bonding near the interface and electrostatic interactions at larger distances. The later interaction is a polarization one, similar to its van der Waals counterpart, and is most often treated in the framework of classical electrostatics [13], if the adsorbed object has a fixed charge Ze or a permanent dipole moment \mathbf{p} . Here, $e > 0$ is the elementary charge, and Z is the ionization degree, which can be of either sign.

Of course, any separation of the actual molecule–surface bonding into components is approximate. However, even modern sophisticated methods [9, 14–16] for calculating electronic structures of surfaces covered with adsorbates, using, in particular, the density-functional approach, are also approximate bearing in mind, for instance, our incomplete knowledge of many-body electron correlations. Anyway, the interaction between a (classical) dipole and its image in the substrate

(the latter is mostly adopted as a metal, although a generalization to the semiconductor case is straightforward from the theoretical point of view) is usually considered to be valid only at distances of more than 3 a.u. from the surface [17–19]. This conclusion is heavily based on classical electrostatics, whereas in the vicinity of a condensed matter half-space or a film, non-local electrostatics adapted for layered structures should be applied [20–33], taking into account the spatial dispersion of the medium dielectric functions. As is shown below, the non-local treatment of electrostatic problems leads to more involved conclusions. Namely, the approach that takes into account quantum mechanics and non-locality brings about dipole image forces that do not diverge in the surface region and do not coincide with the classical ones even far away from the substrate. It should also be noted that even the classical description of molecules as point dipoles interacting with one another and with the classical perfect-metal substrate mimics the density-functional quantum–mechanical picture successfully enough at large distances, being at the same time much simpler and easily tractable [19,34,35].

The reason of the necessity to modernize the model of electrostatic interaction between a charge or a dipole and a near-by surface in the classic scenario is as follows. Any probe charge always polarizes its environment. But the proximity of another medium with different polarization properties modifies the overall polarization response of the system; in particular, the energy of the charge (the dipole) changes. The difference between those two charge/dipole states (in an infinite uniform medium and in the vicinity of the interface between two different uniform media) is associated with the action of the image forces. The latter, in their turn, act on atoms and molecules that which generate them. The dipole moments of polarizable adsorbed entities depend, in

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principle, on the total electrostatic field, including the image-force one, which requires that the problem should be solved self-consistently in this case [8, 19,34,36–38]. We note that it is impossible to express all information concerning the interaction between a molecule and a substrate in terms of the molecular dipole moment and the dielectric function of the substrate (see a significant example of water molecules on 4d-metal surfaces [39]). The chemical constituent is always present, being dominant close to the surface, whereas the dipole image force becomes crucial at larger distances [17,35]. In any case, the latter contribution should be calculated properly in the whole range of molecule–surface separations.

Anyway, to study all kinds of adsorption phenomena including the interaction between adsorbed species [19, 24, 40–47], it is necessary to know the energy profile of electrostatic image forces for a single constant point charge, $W^p(z)$, or dipole moment, $W^d(z)$, where z is the distance reckoned from the charge (the dipole) to the interface between a condensed-matter substrate and vacuum or gas phase, in which the adsorbate concerned is positioned. Knowledge of the indicated energies is interesting per se. Moreover, these quantities can serve the role of input parameters, when calculating van der Waals forces [48], surface electron states [49–51], and statistical charge distributions near various interfaces [1,2,4].

The quantity $W^p(z)$ has been studied rather well especially in the approximation of the infinitely sharp smooth plane interface [22, 24–28, 31–33, 52–55]. In the particular case of the quasiclassical Thomas–Fermi approximation for the substrate dielectric function, which is explicitly studied below, one can obtain simple instructive analytical results (for the point-charge case, see, e.g., Refs. [56–59]). Note that the details of atomic substrate structures [8] and interfacial regions [60] should not be crucial for the energy $W^p(z)$ calculated, when the center-of-charge location is well away from the image plane at the atomic scale.

To our knowledge, contrary to the charged-particle case, no general theoretical expressions for the energy $W^d(z)$ have been obtained so far, although the importance of the problem was recognized long ago [36,61–64]. Some unsystematic results were obtained only for special cases of media described by constant dielectric permittivities ($\epsilon_i = \text{const}$) [65–68] or in the Thomas–Fermi (TF) approximation for the dielectric function [36,61]. It might happen that the reason of this lacuna in the surface-science literature is connected with a widely spread opinion that the classical description is valid beyond a close vicinity of the surface, whereas dipole image forces are all the same negligible at short distances in comparison with quantum–mechanical chemical bonding [17–19]. Our results presented below do not confirm this extreme viewpoint, although the traditional Langmuir–Gurney idea that adsorption is a result of an interplay between two factors, namely, dipole-surface attraction and Pauli electron repulsion, still remains quite reasonable [69]. In this paper, we filled the gap in this field and found, for the first time, the point-dipole image force energy $W^{pd}(z)$ in terms of the substrate dielectric function $\epsilon(\mathbf{k})$, depending on the wave number \mathbf{k} , i.e. making allowance for the spatial dispersion of this function, which describes the screening ability of the corresponding medium. The calculations were based on our preceding works dealing with $W^p(z)$ [22,24,27,32,55]. Analytical and numerical calculations were carried out, and the results for $W^{pd}(z)$ were found to be substantially different from those based on classical electrostatics. Hence, any analysis of the adsorbate static or dynamic properties using classical estimations (see, e.g., Refs. [19,46,70]) is at least incomplete, sometimes being even *qualitatively* wrong. We emphasize that the applied non-local electrostatic method allows the quantum–mechanical short-range (large $|\mathbf{k}|$) peculiarities of the substrate-material screening to be taken into account by incorporating adequate $\epsilon(\mathbf{k})$ -functions with a proper asymptotics at $|\mathbf{k}| \rightarrow \infty$.

2. Theory

We proceed from the expression obtained for the image-force energy in the specular-reflection approximation, written for a point

charge Ze located in medium 1 near (above) a plane interface with medium 2 (see Fig. 1(a)) [22,24,27,29,32,55] (see also related works by other groups [21,25,28,31,54,71]),

$$W^p(z) = -(Ze) \int_0^\infty k_s dk_s \left\{ \frac{a_1^2(k_s, z)}{[a_1(k_s, 0) + a_2(k_s, 0)]} - \frac{1}{2} a_1(k_s, 2z) \right\}. \quad (1)$$

Here,

$$a_i(k_s, z) = \frac{1}{\pi} \int_{-\infty}^\infty \frac{dk_z \exp(ik_z z)}{(k_s^2 + k_z^2) \epsilon_i(\sqrt{k_s^2 + k_z^2})}, \quad (2)$$

$\epsilon_i(\sqrt{k_s^2 + k_z^2})$ is the bulk dielectric permittivity of the i -th medium with allowance for its spatial dispersion (the wave-number dependence), and k_s and k_z are the components of the wave vector \mathbf{k} along and normally to the surface. It should be noted that, at short distances (i.e. at large $|\mathbf{k}|$'s), bound charges in any medium cannot be distinguished from their free counterparts, so that the corresponding plausible *total* static dielectric function $\epsilon(\mathbf{k})$ must follow the trend $\epsilon(\mathbf{k}) \rightarrow 1$ at $|\mathbf{k}| \rightarrow \infty$ [72]. However, if the charge is located in the vacuum, a gas phase or a wide-gap semiconductor [73,74], i.e. in a medium where the non-locality of Coulomb screening can be neglected, non-local effects originate only from the adjacent medium (medium 2) with a high density of free or quasi-free charge carriers, e.g., a (semi)metal, an electrolyte melt

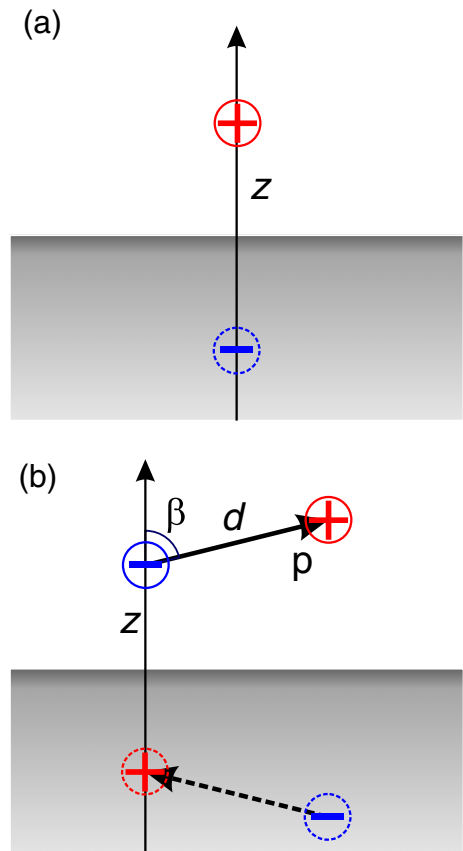


Fig. 1. Charge Ze (a) and dipole moment $p = Zed$ (b) together with their images near the plane interface between dispersionless medium 1 (the upper half-space, $\epsilon_1 = \text{const}$) and plasma-like medium 2 with the spatial dispersion of its dielectric permittivity (the lower half-space, $\epsilon_2(\mathbf{k})$). Here, \mathbf{k} is the wave vector, and $e > 0$ is the elementary charge. In panel (a), z is the distance of the charge from the interface. In panel (b), z is the distance of the dipole negative charge from the interface, d is the dipole arm, and β is the dipole orientation angle.

or solution, or a narrow-band-gap semiconductor. Then, the dielectric function of medium 1 can be regarded as a dispersionless constant ε_1 , and Eq. (1) can be substantially simplified,

$$W^p(z) = -\frac{(Ze)^2}{2\varepsilon_1} \int_0^\infty dk_s \exp(-2k_s z) \frac{\varepsilon_{s2}(k_s) - \varepsilon_1}{\varepsilon_{s2}(k_s) + \varepsilon_1}. \quad (3)$$

Here, a so-called surface dielectric function [54]

$$\varepsilon_{s2}(k_s) = [k_s a_2(k_s, 0)]^{-1} = \left\{ \frac{k_s}{\pi} \int_{-\infty}^{\infty} \frac{dk_z}{(k_s^2 + k_z^2) \varepsilon_2(\sqrt{k_s^2 + k_z^2})} \right\}^{-1} \quad (4)$$

for medium 2 (in our case, a substrate) was introduced.

For the sake of generality and comparison with the results of classical electrostatics [75], where every insulator is described by a specific screening constant $\varepsilon > 1$ and the ideal conductor (the “metal”) corresponds to the limiting case $\varepsilon \rightarrow \infty$, we should adopt $\varepsilon_1 \neq 1$ in Eq. (3). Then, if $\varepsilon_2(|\mathbf{k}| \rightarrow \infty) < \varepsilon_1$ and $\varepsilon_2(|\mathbf{k}| \rightarrow 0) > \varepsilon_1$, certain interesting phenomena can arise at the interface insulator–non-local metal. For instance, image force energies become non-monotonic in the insulator near the plasma-like medium (e.g., metal) surface, exhibiting adsorbing potential wells for charged particles [29,32,56,57], whereas charge–charge [26,25] and dipole–dipole [44] interactions reveal new features. Such a non-monotonicity can also be observed in the general case, when both media are assumed to be non-local electrostatically. In essence, the very existence of those phenomena depends on the difference between the behaviors of $\varepsilon_1(|\mathbf{k}| \rightarrow \infty)$ - and $\varepsilon_2(|\mathbf{k}| \rightarrow \infty)$ -values. In principle, the image-force potential profile can be rather involved, especially for complex structured solvents [72,76,77]. Hence, the Coulomb adsorption minima can survive even in the case when both $\varepsilon_1(|\mathbf{k}| \rightarrow \infty)$ and $\varepsilon_2(|\mathbf{k}| \rightarrow \infty)$ tend to unity. Nevertheless, in this article dealing with a particular case of *dispersionless* medium 1—namely, a gas or the vacuum, so that we may put $\varepsilon_1(\mathbf{k}) = 1$ —and *non-local metallic* substrate 2, those effects will not influence the monotonic character of the dipole–surface attraction, so that we can consider the background bound–electron dielectric constant in the metal $\varepsilon_2 = 1$ without any loss of generality. Note that reasonable estimations of this parameter for metals give $\varepsilon_2 \leq 2$ [64,78].

The dipole configuration together with its image in the substrate is shown in Fig. 1b. We assume that the presence of external charges does not affect the polarization properties of the substrate, so that the problem can be examined in the linear approximation. In particular, the total polarization energy in this case is a sum of four terms,

$$W^d = W_{11'} + W_{22'} + W_{12'} + W_{21'}. \quad (5)$$

The first two terms are the interaction energies of negative charge 1 and positive charge 2 with their own image charges (1' and 2', respectively), both terms being attractive,

$$W_{11'} = W^p(z), \quad W_{22'} = W^p(z + d \cos \beta). \quad (6)$$

Hereafter, z is the distance between negative charge 1 and the interface, d is the dipole arm, and β is the angle between the normal z axis and the dipole arm, as is defined in Fig. 1b. The last two terms in Eq. (5) correspond to the interaction of either charge (1 or 2) with the image of its partner charge (2' and 1', respectively). Both terms are repulsive and equal to each other,

$$W_{12'} = W_{21'} = +\frac{(Ze)^2}{2\varepsilon_1} \int_0^\infty dk_s J_0(k_s d \sin \beta) \frac{\varepsilon_{s2}(k_s) - \varepsilon_1}{\varepsilon_{s2}(k_s) + \varepsilon_1} \times \exp(-k_s(2z + d \cos \beta)), \quad (7)$$

where $J_0(x)$ is the Bessel function of the first kind. Then, the expression for the image force energy of the dipole reads

$$W^d(z, \beta) = -\frac{(Ze)^2}{2\varepsilon_1} \int_0^\infty dk_s \frac{\varepsilon_{s2}(k_s) - \varepsilon_1}{\varepsilon_{s2}(k_s) + \varepsilon_1} \times \{ \exp(-2k_s z) + \exp[-2k_s(z + d \cos \beta)] - 2J_0(k_s d \sin \beta) \exp(-k_s(2z + d \cos \beta)) \}. \quad (8)$$

One should pay attention that the orientational (β) dependence in Eq. (8) for the extended dipole is rather involved. In the classical case, i.e. at $\varepsilon_{s2}(k_s) = \varepsilon_2 = \text{const}$, all integrals in Eq. (8) become elementary ones, so that

$$W_{cl}^d(z, \beta) = -\frac{(Ze)^2}{2\varepsilon_1} \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right) \times \left[\frac{1}{2z} + \frac{1}{2(z + d \cos \beta)} - 2 \frac{1}{\sqrt{(2z + d \cos \beta)^2 + (d \sin \beta)^2}} \right]. \quad (9)$$

In the particular case of the dipole oriented perpendicularly to the surface ($\beta = 0$), Eq. (8) can also be substantially simplified,

$$W^d(z, 0) = -\frac{2(Ze)^2}{\varepsilon_1} \int_0^\infty dk_s \frac{\varepsilon_{s2}(k_s) - \varepsilon_1}{\varepsilon_{s2}(k_s) + \varepsilon_1} \times \exp(-2k_s z) \exp(-k_s d) \sinh^2\left(\frac{k_s d}{2}\right). \quad (10)$$

In this paper, we would like to examine the point-dipole limit of Eq. (8), which is valid for small enough molecules located not too close to the interface. In the spirit of classical approach [75] and Thomas–Fermi approximation (which is mathematically identical to the Debye one used in the classical plasma theory) for the substrate dielectric function [36], we make an expansion in the small parameter $d/z \ll 1$ to obtain

$$W^{pd}(z, \beta) = -\frac{p^2(1 + \cos^2 \beta)}{4\varepsilon_1} \times \int_0^\infty k_s^2 \exp(-2k_s z) \frac{\varepsilon_{s2}(k_s) - \varepsilon_1}{\varepsilon_{s2}(k_s) + \varepsilon_1} dk_s \equiv W_{coord}^{pd}(z)(1 + \cos^2 \beta). \quad (11)$$

Here, we introduced the point dipole moment $p = Zed$. It is remarkable that, in the point-dipole limit, a rather complicated angular dependence in $W^d(z, \beta)$ (see formula (8)) degenerates into a multiplier.

There is a difference between simple initial Eq. (3) and its consequence, Eq. (11). Namely, as is well known [22,27,33], Eq. (3) does not diverge at the interface, if one chooses the Debye or the quasi-classical (Thomas–Fermi, Inkson) $\varepsilon(\mathbf{k})$ -function (see the discussion above). The expression $W^{pd}(z)$ also diverges or not at $z \rightarrow 0$, depending on the screening properties of the media. However, its tendency to diverge near the interface is stronger because of the additional factor k_s^2 in the integrand of Eq. (11). Physically, it is a consequence of the passing to the limits $Z \rightarrow \infty$ and $d \rightarrow 0$ keeping $p = Zed = \text{const}$. Hence, as we shall see below, only the correct quantum–mechanical behavior of $\varepsilon(|\mathbf{k}| \rightarrow \infty)$ ensures finite values for $W^{pd}(z)$ and image forces themselves, $dW^{pd}(z)/dz$. It justifies the usage of the point-dipole approximation even in the nearest vicinity of the interface, the more so because average equilibrium positions of adsorbed molecules lie well apart from the substrate [8]. On the other hand, the classical electrostatic theory, exhibiting a too strong universal z^{-3} singularity at $z \rightarrow 0$, fails altogether.

Formula (11) includes the classical case as a special one, when $\varepsilon_{s2}(k_s) = \varepsilon_2 = \text{const}$. Indeed, in this limit, one can easily arrive at

$$W_{\text{cl}}^{\text{pd}}(z, \beta) = -\frac{p^2(\varepsilon_2 - \varepsilon_1)(1 + \cos^2\beta)}{16\varepsilon_1(\varepsilon_2 + \varepsilon_1)z^3}. \tag{12}$$

Of course, Eq. (12) follows from Eq. (9) at $d/z \rightarrow 0$. On the other hand, when the charged pair comes closer to the interface, i.e. $z/d \rightarrow 0$, the dipole approximation fails and one obtains the energy of classical *charge image forces*.

Let us turn back to the general formulation for point dipoles. Our task is to elucidate what are the consequences of the non-classical character of dipole screening by the neighbor substrate. To this end, we shall use two approximations for $\varepsilon_2(\mathbf{k})$, which reflect the main features associated with the metal free-electron-gas component. Note that strong correlations between interacting charge carriers [79–82] are not crucial for the calculations presented below (see the corresponding analysis for $W^{\text{p}}(z)$ in Ref. [29]). At the same time, the anisotropy and connectivity of the Fermi surface may become very important for long-range ordering in solids governed by Friedel oscillations [83]—in particular, for adsorbate properties [20,24,40,81,82,84–87].

We emphasize once more that below we suppose both background (short-wave, $|\mathbf{k}| \rightarrow \infty$) dielectric constants ε_i ($i = 1, 2$) equal to unity in order to avoid unphysical singularities of $W^{\text{pd}}(z)$ at the interface. Besides, according to Eq. (11), the angular dependence of $W^{\text{pd}}(z, \beta)$ is universal for all $\varepsilon_2(\mathbf{k})$ functions. Therefore, we shall consider only the coordinate term $W_{\text{coord}}^{\text{pd}}(z)$ and use the notation $W^{\text{pd}}(z)$ for it.

The simplest possible screening function for a metal, which makes allowance for screening non-locality, is the quasi-classical Thomas–Fermi one [80]

$$\varepsilon_{\text{TF}}(k) = 1 + \frac{\kappa^2}{k^2}, \tag{13}$$

where

$$\kappa = \left(\frac{6\pi n e^2}{E_F} \right)^{1/2} \tag{14}$$

is the Thomas–Fermi screening wave number, n and E_F are the charge carrier concentration and the Fermi energy, respectively. In this case, the quantity κ^{-1} is the only characteristic length of the substrate and the whole problem, so that all distances should be measured in terms of this unit. Using Eqs. (4), (11), and (13), one obtains

$$W_{\text{TF}}^{\text{pd}}(z) = -\frac{p^2}{4} \int_0^\infty k_s^2 dk_s \exp(-2k_s z) \frac{(\kappa^2 + k_s^2)^{1/2} - k_s}{(\kappa^2 + k_s^2)^{1/2} + k_s}. \tag{15}$$

The right-hand-side of Eq. (15) can be expressed analytically via the special functions, similarly to what was done for $W^{\text{p}}(z)$ in work [53],

$$W_{\text{TF}}^{\text{pd}}(z) = -\frac{\kappa^3 p^2}{4} \left\{ \frac{1}{\kappa^2 z^2} \left(2 - \frac{1}{4\kappa z} - \frac{3}{2\kappa^3 z^3} \right) + \frac{1}{2\kappa z} U_0(2\kappa z) \left(1 - \frac{3}{\kappa^2 z^2} \right) - \frac{\pi}{2\kappa^2 z^2} \left(\frac{5}{2} - \frac{3}{\kappa^2 z^2} \right) U_1(2\kappa z) \right\}, \tag{16}$$

where $U_n(x) \equiv \mathbf{H}_n(x) - N_n(x)$ is the difference between the Struve and Neumann functions [88]. Note that the pioneer of the topic, Antoniewicz, obtained similar formulas for a number of quantities related to the image

point-dipole energy [36]. The asymptotic expansions near the interface and far from it can be easily obtained from Eq. (16)

$$W_{\text{TF}}^{\text{pd}}(z) = -\frac{p^2}{16z^3} \left(1 - \frac{3}{\kappa z} + \dots \right), \kappa z \ll 1, \tag{17}$$

$$W_{\text{TF}}^{\text{pd}}(z) = -p^2 \kappa^3 \left(\frac{1}{32\kappa z} - \frac{1}{15} + \dots \right), \kappa z \gg 1. \tag{18}$$

As is easily seen from Eq. (17), classical behavior (Eq. (12)) is restored at distances larger in comparison with the Thomas–Fermi screening length $\lambda_{\text{TF}} = \kappa^{-1}$. Bear in mind that the first dominant classical term in Eq. (17) corresponds to the case $\varepsilon_1 = 1$ and $\varepsilon_2 \rightarrow \infty$. The second correction term is material-specific, i.e. κ -dependent.

On the other hand, in the vicinity of the Thomas–Fermi metal, $W_{\text{TF}}^{\text{pd}}(z)$ diverges as z^{-1} , which is a much weaker singularity than the universal (distance-independent) classical one, $\sim z^{-3}$. The screening ability of the metal governs the depth of the potential well near its surface. Note that the dipole image-force energy $W_{\text{TF}}^{\text{pd}}(z)$ is negative at any z , which can be seen already from initial Eq. (15) or, more evidently, its asymptotics Eq. (18). Therefore, there is no overscreening in this basic model (such a phenomenon is possible, in principle, for polar substances [89–94], when $\varepsilon(k)$ becomes negative for certain k 's), so that the metal attracts a permanent point dipole irrespective of its orientation.

Nevertheless, the near-surface behavior of the quasi-classical function $W_{\text{TF}}^{\text{pd}}(z)$ cannot be accepted as a true one even in the framework of the adopted simple infinite-barrier model [22,24,27,28,31–33,36,55]. Indeed, as we showed long ago [27], correct short- z asymptotics for the *charge image-force* energy can be obtained, if one takes into account true quantum–mechanical effects of the electron-gas screening at short distances from the test charge (large transferred momenta $\hbar k$, where \hbar is Planck's constant). The idea originating from the Schulze–Unger considerations [95] was applied to the bulk screening properties of semiconductors. Namely, to study the electrostatic behavior in a dispersionless medium at short distances, the famous quantum–mechanical Lindhard dielectric function [96], which corresponds to the random-phase approximation [97] and has a logarithmic singularity at $k = 2k_F$ (it is responsible for the Friedel oscillations of the electron density [83,98,99]), may be substituted by its simple model approximation exact at $k \rightarrow \infty$ but free of this singularity. Here, k_F is the Fermi wave number. In the metal case, which is studied here, one should take

$$\varepsilon_{\text{SU}}(k) = 1 + \frac{\kappa^2}{k^2} \frac{1}{\left(1 + \frac{3k^2}{4k_F^2} \right)}. \tag{19}$$

Thus, the dimensionless metal-specific electron-gas density parameter $\alpha = \kappa^2/4k_F^2$ enters the problem concerned. This function wipes out any traces of classical divergence not only in the image force energy $W^{\text{p}}(z)$ but also in its spatial derivative (image forces per se) [27]. In our case, the same formula Eq. (19) should be substituted into Eqs. (4) and (11) to obtain $W_{\text{SU}}^{\text{pd}}(z)$. A substantial weakening of the dipole image attraction in comparison to $W_{\text{TF}}^{\text{pd}}(z)$ is inherent to $W_{\text{SU}}^{\text{pd}}(z)$ (see below).

3. Results and discussion

According to Eq. (17), the difference between the coordinate part of asymptotic classical expression (12) for the dipole-surface energy $W^{\text{pd}}(z)$ and that derived making allowance for the spatial dispersion of the dielectric permittivity decreases slowly with z at large κz , which is demonstrated in Fig. 2. Indeed, the calculated difference remains conspicuous even at $\kappa z > 20$. The same is true for the Schulze–Unger approximation. From Fig. 2, one can see that the Thomas–Fermi and Schulze–Unger models give almost identical results at large distances.

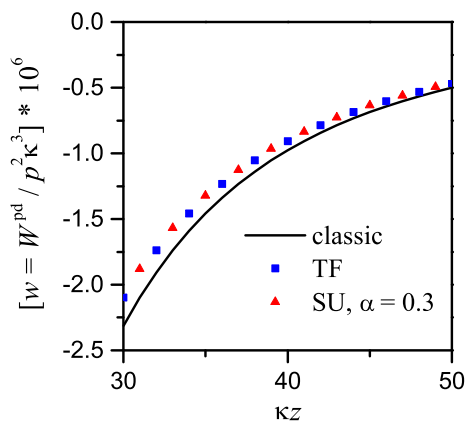


Fig. 2. Long-range asymptotics of the dimensionless dipole image-force energy w in the classical (solid curve), Thomas–Fermi (TF, squares), and Schulze–Unger (SU, triangles) approximations. κ is the inverse TF screening length. The electron gas parameter $\alpha = 0.3$.

At shorter distances, both models making allowance for the dielectric function spatial dispersion give different results, as can be seen from Fig. 3. It is natural that $W_{\text{SU}}^{\text{pd}}(z)$ deviates from $W_{\text{TF}}^{\text{pd}}(z)$ more than $W_{\text{TF}}^{\text{pd}}(z)$ does, because the Schulze–Unger model makes allowance for quantum–mechanical effects, whereas the Thomas–Fermi approach takes into account only quantum statistics of degenerate fermions. Image force energies for quantum–mechanical model (4) depend on the material-specific parameter α , while the Thomas–Fermi curve is universal for distances scaled with $\lambda_{\text{TF}} = \kappa^{-1}$.

As is evident from Eq. (18), the classical picture [13,65,66,75,100–102] becomes totally unreliable at short distances from the interface. Moreover, the quasi-classical Thomas–Fermi model is only qualitatively valid (see the speculations above). The corresponding dimensionless profiles of $W^{\text{pd}}(z)$ calculated numerically and depicted in Fig. 4 confirm these conclusions. The necessity of quantum–mechanical treatment is clearly demonstrated, since the Schulze–Unger dipole image-force energy is finite at $z \rightarrow 0$. Besides, the Schulze–Unger model is α -dependent, whereas its Thomas–Fermi counterpart is universal and unphysically diverges as z^{-1} (see Eq. (18)). Therefore, the dipole–surface electrostatic interaction in the region $\kappa z \leq 1$ must be considered quantum–mechanically in order to study a true dipole (molecular) behavior as well as dipole–dipole correlations [44,45,100,102,103]. The finiteness of $W_{\text{SU}}^{\text{pd}}(z)$ is due to the stronger decrease of $\varepsilon_{\text{SU}}(\mathbf{k})$ at large $|\mathbf{k}|$ than that of $\varepsilon_{\text{TF}}(\mathbf{k})$.

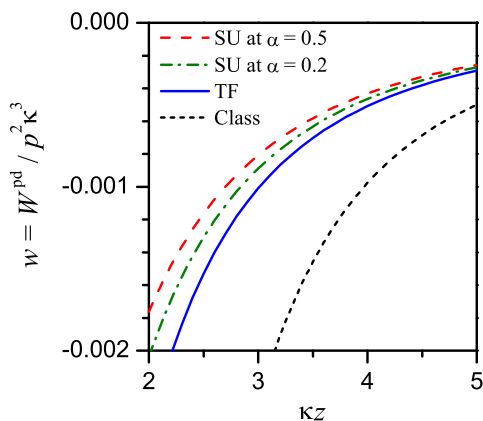


Fig. 3. The same as in Fig. 2 but in the intermediate range of dipole–surface distances. Classical and Thomas–Fermi approximations are represented by short-dashed and solid curves, respectively. The Schulze–Unger curves are shown for $\alpha = 0.5$ and 0.2 (dashed and dashed–dotted curves, respectively).

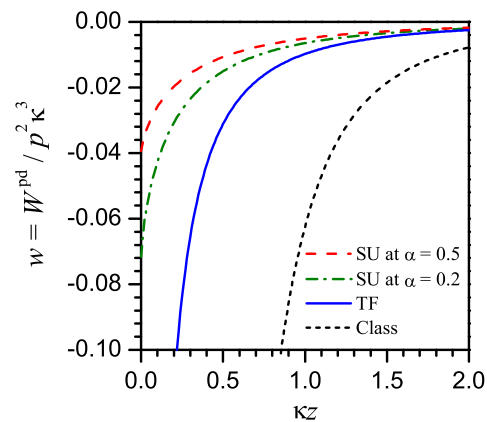


Fig. 4. The same as in Fig. 3 but in the close vicinity of the interface.

The behavior shown in Fig. 4 testifies that, near the surface, where the molecular adsorption is realized [4,6,8,68], the corresponding electrostatic dipole contribution is a *non-classical* one. A proper account of the spatial dispersion of the dielectric function leads to the saturation of $W^{\text{pd}}(z)$ at $z \rightarrow 0$ in contrast to the classical picture. This effect should be important, e.g., for liquid–crystal director orientation studies near the metal electrodes of the liquid–crystal cells, if the molecular dipole moment is large enough [4], or for thermally stimulated depolarization current measurements of the dipolar orientation relaxation [104].

The dipole–image dipole attraction studied here should always give way to repulsion, stemming from the Pauli principle, when a molecule approaches the surface. This part of the total molecule–surface interaction has to be included, if one wants to properly describe the overall adsorbate behavior [35,19]. Nevertheless, the attractive branch of the total energy profile for the adsorbed molecule near the surface, in its turn, has to be not overlooked and must be correctly calculated making allowance for the quantum–mechanical nature of screening by the substrate electron gas. This was precisely the purpose of our study presented here, where it was found that dipole image forces dig potential–energy wells, which are much shallower than is predicted by classical electrostatics.

To summarize, when studying dipole adsorption and dipole–dipole interaction or ordering on a surface, it is very important to go beyond the framework of classical approach. It is so because of drastic changes to the dipole image forces induced by the effects of non-local electrostatic screening (the spatial dispersion of the dielectric function). It is especially valid and important for huge biological macromolecules [105,103]. The results of the paper make it evident that interaction of dipoles on the surface [19,46] will also be substantially modified, if the non-locality of the substrate screening properties is taken into account. In this paper we restricted ourselves to a simple (but important and instructive) particular case of point dipoles. A more general case of extended dipoles is more cumbersome and will be treated in subsequent publications.

Acknowledgments

AIV is grateful to Kasa im. Józefa Mianowskiego, Fundacja na Rzecz Nauki Polskiej, and Fundacja Zygmunta Zaleskiego for the financial support of his visits to Warsaw. MSL is grateful to the Ministry of Science and Informatics of Poland (grant No. 202–204–234). AMG highly appreciates the 2010 Visitors Program of the Max Planck Institute for the Physics of Complex Systems (Dresden, Germany). The work was partially supported by the Project N 23 of the 2009–2011 Scientific Cooperation Agreement between Poland and Ukraine. AMG is very much indebted to Anton Kokalj (Ljubljana, Slovenia) and Vladimir Gun'ko (Kiev, Ukraine) for useful discussions. The authors thank the Referee for his/her valuable remarks.

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