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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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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.

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 **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, $W^{\mathrm{p}}(z)$, or dipole moment, $W^{\mathrm{d}}(z)$, 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 $W^{\mathrm{p}}(z)$ 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 $W^{\mathrm{p}}(z)$ 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 $W^{\mathrm{d}}(z)$ 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 ($\varepsilon_i = \mathrm{const}$) [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 $W^{\mathrm{pd}}(z)$ in terms of the substrate dielectric function $\varepsilon(\mathbf{k})$, 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 $W^{\mathrm{p}}(z)$ [22,24,27,32,55]. Analytical and numerical calculations were carried out, and the results for $W^{\mathrm{pd}}(z)$ 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 $\varepsilon(\mathbf{k})$-functions with a proper asymptotics at $|\mathbf{k}| \to \infty$.

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]),

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

Here,

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

$\varepsilon_i\left(|\mathbf{k}| = \sqrt{k_s^2+k_z^2}\right)$ 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 $\varepsilon(\mathbf{k})$ must follow the trend $\varepsilon(\mathbf{k}) \to 1$ at $|\mathbf{k}| \to \infty$ [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

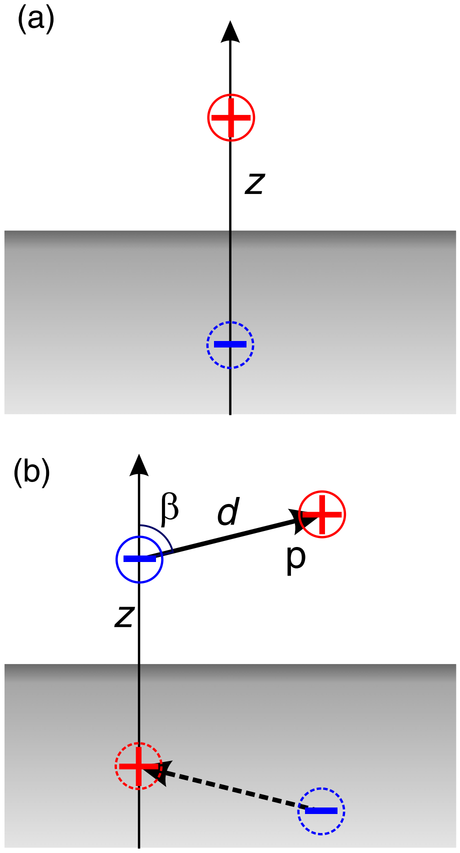

Fig. 1. Charge Ze (a) and dipole moment $p = Zed$ (b) together with their images near the plane interface between dispersionless medium 1 (the upper half-space, $\varepsilon_1 = \mathrm{const}$) and plasma-like medium 2 with the spatial dispersion of its dielectric permittivity (the lower half-space, $\varepsilon_2(\mathbf{k})$). 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.