DIPOLE-DIPOLE INTERACTION NEAR THE SURFACE OF A MEDIUM WITH THE SPATIAL DISPERSION OF ITS DIELECTRIC PERMITTIVITY

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EXPERIMENT: METALLIC STRUCTURES ON METAL OR SEMICONDUCTOR SUBSTRATES FORMED BY *DIRECT COULOMB* AND *INDIRECT* INTERACTIONS

**Fig. 3.** Linear structures on the furrowed surfaces. Two characteristic structures of the layers at $\theta = 0.5$ are presented on the bottom.

**Fig. 8.** STM images of Cs chains on the GaAs(110) surface at $\theta = 0.03$. Left: General view (1370 x 1370 Å). Right: a single Cs zigzag chain (70 x 70 Å). Adapted from Ref. 12 with permission.

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Atomic Wires on Furrowed Transition Metal Surfaces

FIG. 7. (Color online) Surface structure of H-passivated SiNWs. (a) Cross-sectional view of 3 nm SiNWs grown along three different directions (100), (110), and (111). (b) Side view of three different surface structures; in the last configuration the surface first reconstructs and then is passivated. From Vo et al., 2006.
COMPONENTS OF ATOM (MOLECULE) – SUBSTRATE INTERACTION (IMAGE FORCES)

1. Electrostatic polarization (image) force
2. Fluctuation-driven van der Waals force
3. Pauli repulsion at small distances
4. Covalent bonding at small distances

Classical polarization (image) forces are universal. Image forces must be calculated in the non-classical approximation taking into account specific properties of the substrate material.
NON-LOCAL ELECTROSTATIC APPROACH

\[ W^p(z) = -(Ze) \int_{0}^{\infty} k_z dk_z \left\{ \frac{a_1^2(k_z, z)}{[a_1(k_z, 0) + a_2(k_z, 0)]} - \frac{1}{2} a_1(k_z, 2z) \right\}. \]  \hspace{1cm} (1)

Here,

\[ a_i(k_z, z) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{dk_z \exp(ik_z z)}{(k_z^2 + k_s^2)\varepsilon_i(\sqrt{k_s^2 + k_z^2})}, \]  \hspace{1cm} (2)

\[ \varepsilon_i(|\mathbf{k}| = \sqrt{k_s^2 + k_z^2}) \] 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

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Screening of charges and Friedel oscillations of the electron density in metals having differently shaped Fermi surfaces
IMAGE FORCES. CONCLUSIONS

1. Quantum mechanical treatment of the substrate and the account of the dielectric function spatial dispersion are necessary to adequately calculate the adsorption energies.

2. Classical treatment of the dipole image forces is inadequate.

3. Specific inclusion of dipole image forces is necessary to make allowance for orientation dependence of the adsorption energies.

4. Quantum chemical and non-local electrostatic approaches are mutually complementary.
Here direct and indirect interactions act together!
EXAMPLE: THOMAS-FERMI APPROXIMATION FOR THE SUBSTRATE DIELECTRIC FUNCTION $\varepsilon(k)$

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

The integrals are calculated numerically. However, the long-range asymptotics behavior can be found analytically!

In both limiting cases the charge-charge interaction is a dipole-dipole one rather than the Coulomb (in the classical bulk medium) or the exponential (in the Thomas-Fermi bulk medium) one.
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,

$$W_{PP'} = \sum_{q=Q,-Q} W_{qq'}.$$  \hspace{1cm} (26)

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).
The solution of the divergence problem is the same as in the case of image forces: a quantum-mechanical dielectric function should be used.
DIPOLE-DIPOLE INTERACTION NEAR INTERFACES
(PLANAR DIPOLES, GENERAL CASE)

\[ W_{\text{planar,gen}}^{PP'}(L,z) = W_{\text{planar,gen}}^{PP',0}(L,z) + W_{\text{planar,gen}}^{PP',1}(L,z), \]  

(36)

where

\[ W_{\text{planar,gen}}^{PP',0}(L,z) = \frac{PP'}{\varepsilon_0 L^3} \times \]

\[ \times \left\{ -\frac{3}{2} \cos(\alpha + \alpha') - \frac{1}{2} \cos(\alpha - \alpha') + \cos(\alpha - \alpha') \right\} \frac{L^3}{s^3 (L, 2z)} - \]

\[ -\frac{3}{2} \left[ \cos(\alpha + \alpha') + \cos(\alpha - \alpha') \right] \frac{L^5}{s^5 (L, 2z)} \} \right. \]  

(37)

\[ W_{\text{planar,gen}}^{PP',1}(L,z) = -\frac{2PP'}{\varepsilon_0} \int_0^\infty dq \frac{q}{1 + \varepsilon_0 qa(q)} e^{-2qz} \times \]

\[ \times \left\{ \frac{1}{L} J_0(Lq) \left[ \cos(\alpha + \alpha') + \cos(\alpha - \alpha') \right] - \right. \]

\[ -\frac{1}{L} J_1(Lq) \cos(\alpha + \alpha') \right\}. \]  

(38)

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

CLASSICAL ELECTROSTATICS
The $L^{-3}$-asymptotics survives!

NON-LOCAL ELECTROSTATICS (THOMAS-FERMI)

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:

$$W_{PP'}^{\text{planar, TF, asymp}}(z) \approx -\frac{3PP'}{\varepsilon_0\varepsilon_m^2\kappa^2 L^5} W_{PP'}^{\text{planar, TF, asymp}}(z),$$  \hspace{1cm} (39)

where

$$W_{PP'}^{\text{planar, TF, asymp}}(z) = \left(\varepsilon_0 + \kappa\varepsilon_m\right)^2 \times$$

$$\times \left[5\cos(\alpha + \alpha') + 3\cos(\alpha - \alpha')\right].$$  \hspace{1cm} (40)

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.
Conclusions:

1. **Direct** and **indirect** electrostatic interactions cannot be separated.

2. Quantum mechanical treatment of the substrate and the account of the dielectric function spatial dispersion are necessary to avoid divergences of the interaction energy at small dipole-dipole distances.

3. *Classical* treatment of the dipole-dipole interaction energy is unsatisfactory.

4. For planar dipoles, the asymptotic distance dependence of the interaction energy at large dipole-dipole distances is *substantially modified* by the metallic substrate influence.