Supplementary Material for: Surface-response functions obtained from equilibrium electron-density profiles

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☞ Throughout this Supplementary Material, the superscript "cl" (classical) has the same meaning as the the superscript/subscript "PCA" (piecewise-constant approximation) used in the main manuscript.

S1. FEIBELMAN *d*-PARAMETERS: CHARACTERIZING THE DIFFERENCE BETWEEN THE MICROSCOPIC AND FRESNEL FIELDS

Since we are considering a planar system, we may make use of translational symmetry to write the fields—for p-polarized waves—as

$$\mathbf{F}(\mathbf{r}) = \mathbf{F}(z)\, \mathrm{e}^{\mathrm{i}qx}\, \mathrm{e}^{-\mathrm{i}\omega t}, \tag{S1}$$

without loss of generality. Exploiting this, the classical, "Fresnel" fields (i.e., the reference/asymptotic fields which are only *strictly* valid for $|z| \gg |z_{1,2}|$; see Fig. 1) take the form (ω-dependence implicit):

$$\mathbf{E}^{\mathrm{cl}}(z) = \mathbf{E}^{-}(z)\Theta(-z) + \mathbf{E}^{+}(z)\Theta(z), \tag{S2a}$$

$$\mathbf{D}^{\mathrm{cl}}(z) = \epsilon_0\left[\epsilon_{\mathrm{m}}\mathbf{E}^{-}(z)\Theta(-z) + \epsilon_{\mathrm{d}}\mathbf{E}^{+}(z)\Theta(z)\right], \tag{S2b}$$

$$\mathbf{H}^{\mathrm{cl}}(z) = \mathbf{H}^{-}(z)\Theta(-z) + \mathbf{H}^{+}(z)\Theta(z), \tag{S2c}$$

where

$$\mathbf{H}^{+}(z) = \left[\mathrm{e}^{-\mathrm{i}k_{z,\mathrm{d}}z} + r_p\, \mathrm{e}^{\mathrm{i}k_{z,\mathrm{d}}z}\right]\hat{\mathbf{y}} \equiv H_y^{+}(z)\,\hat{\mathbf{y}}, \tag{S3a}$$

$$\mathbf{H}^{-}(z) = t_p\, \mathrm{e}^{-\mathrm{i}k_{z,\mathrm{m}}z}\hat{\mathbf{y}} \equiv H_y^{-}(z)\,\hat{\mathbf{y}}, \tag{S3b}$$

$$\mathbf{E}^{+}(z) = \underbrace{\frac{k_{z,\mathrm{d}}}{\omega\epsilon_0\epsilon_{\mathrm{d}}}\left[-\mathrm{e}^{-\mathrm{i}k_{z,\mathrm{d}}z} + r_p\, \mathrm{e}^{\mathrm{i}k_{z,\mathrm{d}}z}\right]}_{E_x^{+}(z)}\hat{\mathbf{x}} + \underbrace{\frac{q}{\omega\epsilon_0\epsilon_{\mathrm{d}}}\left[-\mathrm{e}^{-\mathrm{i}k_{z,\mathrm{d}}z} - r_p\, \mathrm{e}^{\mathrm{i}k_{z,\mathrm{d}}z}\right]}_{E_z^{+}(z)}\hat{\mathbf{z}}, \tag{S3c}$$

$$\mathbf{E}^{-}(z) = \underbrace{-\frac{k_{z,\mathrm{m}}}{\omega\epsilon_0\epsilon_{\mathrm{m}}} t_p\, \mathrm{e}^{-\mathrm{i}k_{z,\mathrm{m}}z}}_{E_x^{-}(z)}\hat{\mathbf{x}} + \underbrace{\frac{-q}{\omega\epsilon_0\epsilon_{\mathrm{m}}} t_p\, \mathrm{e}^{-\mathrm{i}k_{z,\mathrm{m}}z}}_{E_z^{-}(z)}\hat{\mathbf{z}}. \tag{S3d}$$

In the absence of external charges, we have [1]

$$\boldsymbol{\nabla}\cdot\mathbf{D} = 0 \qquad \longrightarrow \qquad \mathrm{i}qD_x(z) + \partial_z D_z(z) = 0, \tag{S4}$$

for the microscopic displacement field. Naturally, the same holds for its classical counterpart, that is,

$$\boldsymbol{\nabla}\cdot\mathbf{D}^{\mathrm{cl}} = 0 \qquad \longrightarrow \qquad \mathrm{i}qD_x^{\mathrm{cl}}(z) + \partial_z D_z^{\mathrm{cl}}(z) = 0, \tag{S5}$$

Combining Eqs. (S4)–(S5) and integrating over the surface region $z \in [z_1, z_2]$, we find

$$D_z^{+}(0^{+}) - D_z^{-}(0^{-}) = -\mathrm{i}q\int_{z_1}^{z_2} \mathrm{d}z\left[D_x(z) - D_x^{\mathrm{cl}}(z)\right], \tag{S6}$$

where we have used the fact that, by definition of $z_{1,2}$, $D_z(z_1) = D_z^-(z_1)$ and $D_z(z_2) = D_z^+(z_2)$. Notice that, for an infinitesimally thin surface region (or, in other words, for an abrupt dielectric–metal interface), the classical Maxwell's boundary condition $\hat{\mathbf{z}} \cdot (\mathbf{D}^+ - \mathbf{D}^-)|_{z=0} = 0$ is recovered. Alternatively, the same is true in the $q = 0$ case.

Next, proceeding in a similar fashion, but now considering Maxwell's curl equation $\boldsymbol{\nabla} \times \mathbf{E} = \mathrm{i}\omega\mu_0\mathbf{H}$ instead, one obtains

$$E_x^+(0^+) - E_x^-(0^-) = \mathrm{i}q \int_{z_1}^{z_2} \mathrm{d}z \left[E_z(z) - E_z^{\mathrm{cl}}(z)\right] , \tag{S7}$$

up to first-order in $q|z_2 - z_1|$ and ignoring other "second-order small" terms (e.g., second-order in $\frac{\omega}{c}|z_2 - z_1|$). Similarly to Eq. (S6), the previous equation amount to a "generalized boundary condition" which expresses the discontinuity of the tangential component of the electric field across the interface, with such discontinuity being proportional to the "surface integral" in the right-hand side of Eq. (S7).

Following Refs. [2, 3], we introduce the quantities

$$\Delta\bar{D}_x(z) \equiv \int_{z_1}^{z_2} \mathrm{d}z \frac{D_x(z) - D_x^{\mathrm{cl}}(z)}{E_x^-(0^-)}, \tag{S8a}$$

$$\Delta\bar{E}_z(z) \equiv \int_{z_1}^{z_2} \mathrm{d}z \frac{E_z(z) - E_z^{\mathrm{cl}}(z)}{E_z^-(0^-)}, \tag{S8b}$$

and thus write Eqs. (S6)–(S7) as

$$D_z^+(0^+) - D_z^-(0^-) = -\mathrm{i}q\, E_x^-(0^-)\, \Delta\bar{D}_x(z), \tag{S9a}$$

$$E_x^+(0^+) - E_x^-(0^-) = \mathrm{i}q\, E_z^-(0^-)\, \Delta\bar{E}_z(z). \tag{S9b}$$

Then, substituting the fields (S2)–(S3) into Eqs. (S9), we arrive to

$$1 + r_p - t_p \left[1 - \mathrm{i}\frac{k_{z,\mathrm{m}}}{\epsilon_0\epsilon_\mathrm{m}} \Delta\bar{D}_x(z)\right] = 0, \tag{S10a}$$

$$\frac{k_{z,\mathrm{d}}}{\epsilon_\mathrm{d}} \left[1 - r_p\right] - t_p \left[\frac{k_{z,\mathrm{m}}}{\epsilon_\mathrm{m}} + \mathrm{i}\frac{q^2}{\epsilon_\mathrm{m}} \Delta\bar{E}_z(z)\right] = 0. \tag{S10b}$$

From Eqs. (S10), it then follows that the "generalized" reflection and transmission coefficients for a dielectric–metal interface are given by

$$r_p = \frac{\epsilon_\mathrm{m} k_{z,\mathrm{d}} - \epsilon_\mathrm{d} k_{z,\mathrm{m}} + \left[-\mathrm{i}q^2\epsilon_\mathrm{d}\Delta\bar{E}_z(z) - \mathrm{i}k_{z,\mathrm{d}}k_{z,\mathrm{m}}\epsilon_0^{-1}\Delta\bar{D}_x(z)\right]}{\epsilon_\mathrm{m} k_{z,\mathrm{d}} + \epsilon_\mathrm{d} k_{z,\mathrm{m}} - \left[-\mathrm{i}q^2\epsilon_\mathrm{d}\Delta\bar{E}_z(z) + \mathrm{i}k_{z,\mathrm{d}}k_{z,\mathrm{m}}\epsilon_0^{-1}\Delta\bar{D}_x(z)\right]}, \tag{S11a}$$

$$t_p = \frac{2\epsilon_\mathrm{m} k_{z,\mathrm{d}}}{\epsilon_\mathrm{m} k_{z,\mathrm{d}} + \epsilon_\mathrm{d} k_{z,\mathrm{m}} - \left[-\mathrm{i}q^2\epsilon_\mathrm{d}\Delta\bar{E}_z(z) + \mathrm{i}k_{z,\mathrm{d}}k_{z,\mathrm{m}}\epsilon_0^{-1}\Delta\bar{D}_x(z)\right]}, \tag{S11b}$$

from which we recognize (e.g., by comparing Eqs. (S11) with the d-parameter-corrected reflection and transmission coefficients [4–6]) the Feibelman d-parameters as[1] [2]

$$d_\perp = -\frac{\epsilon_\mathrm{d}}{\epsilon_\mathrm{m} - \epsilon_\mathrm{d}} \int_{-\infty}^{\infty} \mathrm{d}z\, \frac{E_z(z) - E_z^{\mathrm{cl}}(z)}{E_z^-(0^-)}, \tag{S12a}$$

$$d_\parallel = \frac{\epsilon_0^{-1}}{\epsilon_\mathrm{m} - \epsilon_\mathrm{d}} \int_{-\infty}^{\infty} \mathrm{d}z\, \frac{D_x(z) - D_x^{\mathrm{cl}}(z)}{E_x^-(0^-)}, \tag{S12b}$$

where we have changed the limits of integration from $[z_1, z_2]$ to $]-\infty, \infty[$, as this leaves the d-parameters unchanged (since, by definition of $z_{1,2}$, the microscopic fields are equal to the classical fields for $|z| \geq |z_{1,2}|$).

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[1] Recall that, here, the superscripts "cl" correspond to the "PCA" ones used in the main manuscript.

S2. d-PARAMETERS ASSOCIATED WITH A METAL SURFACE DESCRIBED BY A CONTINUOUS DIELECTRIC FUNCTION

We consider a planar dielectric–metal interface described by a spatially varying dielectric function $\epsilon(z)$, treated in the local-response approximation (LRA), that characterizes a metal surface where the electron density varies smoothly between a constant value deep inside the metal's bulk and the dielectric's permittivity far away from the said surface. Below, we present (following Refs. [2, 7–12]) a concise derivation of the main steps leading to the expressions for the d-parameters taking $\epsilon(z)$ as input [i.e., instead of the fields as in Eqs. (S12)].

$d_\perp$-parameter. In the long-wavelength limit (frequency-dependence implicit throughout),

$$D_z(z) = \epsilon_0 \int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{zz}(q \to 0; z, z') E_z(z') \simeq \text{const.} \equiv \epsilon_0 \epsilon_\mathrm{m} E_z^-(0^-). \tag{S13}$$

Introducing the inverse dielectric function, $\epsilon_{zz}^{-1}(q \to 0; z, z')$, satisfying (dropping the $q \to 0$ in the argument, which is implicitly assumed hereafter)

$$\int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{zz}(z, z') \epsilon_{zz}^{-1}(z', z'') = \delta(z' - z''),$$

we may write

$$\begin{aligned} E_z(z) &= \epsilon_\mathrm{m} E_z^-(0^-) \int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{zz}^{-1}(z, z') \\ &\equiv \epsilon_\mathrm{m} E_z^-(0^-) \langle \epsilon_{zz}^{-1}(z) \rangle, \end{aligned} \tag{S14}$$

where we have defined

$$\langle \epsilon_{zz}^{-1}(z) \rangle \equiv \int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{zz}^{-1}(z, z'), \tag{S15}$$

and thus Eq. (S12a) becomes

$$d_\perp = -\frac{\epsilon_\mathrm{d}}{\epsilon_\mathrm{m} - \epsilon_\mathrm{d}} \int_{z_1}^{z_2} \mathrm{d}z \Big[\epsilon_\mathrm{m} \langle \epsilon_{zz}^{-1}(z) \rangle - \underbrace{\frac{E_z^-(z)}{E_z^-(0^-)}}_{\approx 1} \Theta(-z) - \underbrace{\frac{E_z^+(z)}{E_z^-(0^-)}}_{\approx \frac{E_z^+(0^+)}{E_z^-(0^-)} = \frac{\epsilon_\mathrm{m}}{\epsilon_\mathrm{d}}} \Theta(z) \Big], \tag{S16}$$

where the approximations are valid in the long-wavelength limit. Hence, we find

$$\boxed{d_\perp = \frac{1}{\epsilon_\mathrm{m}^{-1} - \epsilon_\mathrm{d}^{-1}} \int_{z_1}^{z_2} \mathrm{d}z \left[\langle \epsilon_{zz}^{-1}(z) \rangle - \frac{1}{\epsilon^\mathrm{cl}(z)} \right]}, \tag{S17a}$$

where

$$\frac{1}{\epsilon^\mathrm{cl}(z)} \equiv \frac{1}{\epsilon^\mathrm{PCA}(z)} = \frac{1}{\epsilon_\mathrm{m}} \Theta(-z) + \frac{1}{\epsilon_\mathrm{d}} \Theta(z). \tag{S17b}$$

$d_\parallel$-parameter. Similarly, one may write

$$D_x(z) = \epsilon_0 \int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{xx}(q \to 0; z, z') E_x(z') \approx \epsilon_0 E_x(0) \int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{xx}(z, z') \tag{S18}$$

since $E_x(z)$ is slowly varying/approximately continuous in the long-wavelength regime. Therefore, adopting a similar approach as before [see Eq. (S15)], namely, defining $\langle \epsilon_{xx}(z) \rangle \equiv \int_{-\infty}^{\infty} \mathrm{d}z'\, \epsilon_{xx}(z, z')$, leads to

$$D_x(z) = \epsilon_0 E_x^-(0^-) \langle \epsilon_{xx}(z) \rangle, \tag{S19}$$

so that $d_\parallel$ takes the form

$$d_\parallel = \frac{1}{\epsilon_\mathrm{m} - \epsilon_\mathrm{d}} \int_{z_1}^{z_2} \mathrm{d}z \Big[\langle \epsilon_{xx}(z)\rangle - \epsilon_\mathrm{m} \underbrace{\frac{E_x^-(z)}{E_x^-(0^-)}}_{\approx \frac{E_x^-(0^-)}{E_x^-(0^-)} = 1} \Theta(-z) - \epsilon_\mathrm{d} \underbrace{\frac{E_x^+(z)}{E_x^-(0^-)}}_{\approx \frac{E_x^+(0^+)}{E_x^-(0^-)} = 1} \Theta(z)\Big], \tag{S20}$$

that is

$$\boxed{d_\parallel = \frac{1}{\epsilon_\mathrm{m} - \epsilon_\mathrm{d}} \int_{z_1}^{z_2} \mathrm{d}z \Big[\langle \epsilon_{xx}(z)\rangle - \epsilon^\mathrm{cl}(z)\Big]}, \tag{S21a}$$

where

$$\epsilon^\mathrm{cl}(z) \equiv \epsilon^\mathrm{PCA}(z) = \epsilon_\mathrm{m}\Theta(-z) + \epsilon_\mathrm{d}\Theta(z). \tag{S21b}$$

Summary. Finally, assuming a isotropic metal and adopting the local-response approximation[2], the d-parameters given by Eqs. (S17a) and (S21a) can now be (re)written as

$$\boxed{d_\perp = \frac{1}{\epsilon_\mathrm{m}^{-1} - \epsilon_\mathrm{d}^{-1}} \int_{-\infty}^{\infty} \mathrm{d}z \left[\epsilon^{-1}(z) - \epsilon_\mathrm{m}^{-1}\Theta(-z) - \epsilon_\mathrm{d}^{-1}\Theta(z)\right]}, \tag{S22a}$$

and

$$\boxed{d_\parallel = \frac{1}{\epsilon_\mathrm{m} - \epsilon_\mathrm{d}} \int_{-\infty}^{\infty} \mathrm{d}z \, [\epsilon(z) - \epsilon_\mathrm{m}\Theta(-z) - \epsilon_\mathrm{d}\Theta(z)]}. \tag{S22b}$$

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[2] That is, $\epsilon_{xx}(z,z') \to \epsilon(z)\delta(z-z')$ and $\epsilon_{zz}^{-1}(z,z') \to \epsilon^{-1}(z)\delta(z-z')$ so that $\langle\epsilon_{xx}(z)\rangle \to \epsilon(z)$ and $\langle\epsilon_{zz}^{-1}(z)\rangle \to \epsilon^{-1}(z)$, respectively.