Supplementary material for:

An exploration of the electromagnetic boundary conditions for two-dimensional materials with out-of-plane polarization

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1. VACUUM GAP METHOD

In this section, we present a condensed version of the derivation from section 2.3 of reference [1] showing that the total out-of-plane electric field at an interface is proportional to the arithmetic mean of the electric displacement fields in the surrounding dielectrics. In particular, we will consider a simple interface between two non-magnetic, isotropic, lossless dielectrics, with no external charges or currents. We will begin by inserting a small vacuum gap into the interface as shown in Figure S1, and after placing the 2D material in the center of the gap, we will close it, $l \to 0$.

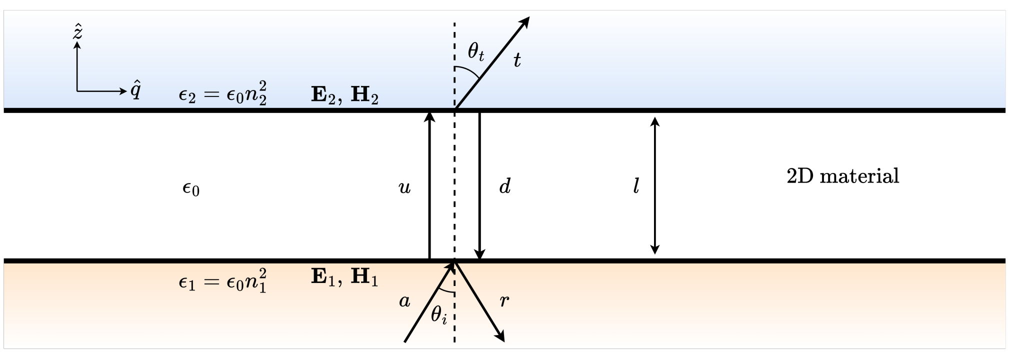

Fig. S1. Diagram of the vacuum gap configuration.

In this configuration, we have two standard dielectric-vacuum interfaces. In the central vacuum region, we can write the total electric field amplitudes as the sum of upward and downward propagating components,

$$\mathbf{E}_T = \begin{bmatrix} -u_p \cos\theta \\ u_s \\ u_p \sin\theta \end{bmatrix} + \begin{bmatrix} d_p \cos\theta \\ d_s \\ d_p \sin\theta \end{bmatrix}. \tag{S1}$$

Now, using the standard electromagnetic boundary conditions on a dielectric interface, we can find the field components in the central region in terms of the fields in region two,

$$u_p = \frac{n_2 \cos\theta + \cos\theta_t}{2\cos\theta} t_p, \quad d_p = \frac{n_2 \cos\theta - \cos\theta_t}{2\cos\theta} t_p, \tag{S2}$$

and in terms of the fields in region one,

$$u_p = \frac{(n_1\cos\theta + \cos\theta_i)a_p + (n_1\cos\theta - \cos\theta_i)r_p}{2\cos\theta}, \quad d_p = \frac{(n_1\cos\theta - \cos\theta_i)a_p + (n_1\cos\theta + \cos\theta_i)r_p}{2\cos\theta}. \tag{S3}$$

With these two definitions, we are able to equivalently define the total field in the central vacuum region in terms of the fields inside either medium 1 or medium 2. For medium 2 we can do so by inserting equation S2, into the z component of the total field in equation S1,

$$E_{Tz}^{(2)} = u_p \sin\theta + d_p \sin\theta = n_2 t_p \sin\theta. \tag{S4}$$

We can then equivalently represent the total field in terms of the fields in medium 1 by instead inserting equation S3 into equation S1,

$$E_{Tz}^{(1)} = u_p \sin\theta + d_p \sin\theta = n_1 a_p \sin\theta + n_1 r_p \sin\theta. \tag{S5}$$

Then, by Snell's law we have $n_1 \sin\theta_i = \sin\theta = n_2 \sin\theta_t$, and so the total fields become

$$E_{Tz}^{(2)} = n_2^2 t_p \sin\theta_t, \tag{S6}$$

and

$$E_{Tz}^{(1)} = n_1^2 a_p \sin\theta_i + n_1^2 r_p \sin\theta_i. \tag{S7}$$

But recalling $E_{Tz}^{(1)} = E_{Tz}^{(2)}$, we can define the total field as the arithmetic mean of the two equivalent representations,

$$E_{Tz} = \frac{1}{2}(E_{Tz}^{(1)} + E_{Tz}^{(2)}), \tag{S8}$$

$$= \frac{1}{2}(n_2^2 t_p \sin\theta_t + n_1^2 a_p \sin\theta_i + n_1^2 r_p \sin\theta_i), \tag{S9}$$

$$= \frac{1}{2\epsilon_0}(D_{2z} + D_{1z}). \tag{S10}$$

We are, of course, justified in using the arithmetic mean in this empty vacuum gap region; however, we remain justified even in the presence of a 2D material, as shown in section 2.3 of reference [1]. As mentioned in the main text, the authors of reference [2] used the arithmetic mean to model the total E_z on graphene and managed to extract quite accurate conductivities through comparison of their resulting Fresnel coefficients to measurements. This is experimental confirmation of the validity of the arithmetic mean model.

2. PLASMON DISPERSION DERIVATION

Here we present a derivation for the plasmon modes of an isotropic 2D material sandwiched between two dielectrics. The pertinent boundary conditions are defined in the main text, but we restate them here for convenience,

$$\left(\mathbf{E}_2(\mathbf{r}_\parallel) - \mathbf{E}_1(\mathbf{r}_\parallel)\right) \cdot \hat{q} = \frac{q}{2\epsilon_0\omega}\tilde{\sigma}_z^e \left(n_1^2 E_{z1} + n_2^2 E_{z2}\right), \tag{S11}$$

$$\left(\mathbf{E}_2(\mathbf{r}_\parallel) - \mathbf{E}_1(\mathbf{r}_\parallel)\right) \cdot \hat{\tau} = 0, \tag{S12}$$

$$\mathbf{H}_2(\mathbf{r}_\parallel) - \mathbf{H}_1(\mathbf{r}_\parallel) = \hat{z} \times \mathbf{J}(\mathbf{r}_\parallel). \tag{S13}$$

Referring to Figure 1 of the main text, we defined here a unit vector $\hat{\tau} = \hat{z} \times \hat{q}$, which points in the in-plane direction that is perpendicular to the wavevector direction $\hat{q}$. We note that application of the Ohm's law in equation 5 of the main text in the right-hand side of S13 involves the in-plane conductivity components along the $\hat{q}$ and $\hat{\tau}$ directions, which are generally different, $\sigma_\tau(q,\omega) \neq \sigma_q(q,\omega)$. While the derivation below holds in that general case, we note that in the local limit of the material response, i.e., when its dependence on the wavenumber q may be discarded, the transverse and longitudinal conductivity components are equal, $\sigma_\tau(\omega) = \sigma_q(\omega)$.

In the absence of an external driving field, the electromagnetic fields surrounding the interface can be defined as

$$\mathbf{E}_1 = \begin{pmatrix} E_q^{(1)} \\ E_\tau^{(1)} \\ E_z^{(1)} \end{pmatrix} e^{i(qx-k_{z1}z-\omega t)}, \quad \mathbf{E}_2 = \begin{pmatrix} E_q^{(2)} \\ E_\tau^{(2)} \\ E_z^{(2)} \end{pmatrix} e^{i(qx+k_{z2}z-\omega t)}, \tag{S14}$$

and

$$\mathbf{H}_1 = \begin{pmatrix} H_q^{(1)} \\ H_\tau^{(1)} \\ H_z^{(1)} \end{pmatrix} e^{i(qx-k_{z1}z-\omega t)}, \quad \mathbf{H}_2 = \begin{pmatrix} H_q^{(2)} \\ H_\tau^{(2)} \\ H_z^{(2)} \end{pmatrix} e^{i(qx+k_{z2}z-\omega t)}. \tag{S15}$$

By choosing this sign convention for the k_z components of the wavevectors, we also assert the condition that the imaginary part must be positive for any solutions to be physical. If this condition is not satisfied, the solutions would be exponentially growing. We can then use Maxwell's equations to derive relationships between the field amplitudes and effectively reduce the free parameters to $E_q^{(1)}$, $E_q^{(2)}$, and $E_\tau^{(1)} = E_\tau^{(2)} = E_\tau$.

The first step in deriving the dispersion relation is to represent the boundary conditions in terms of independent field quantities. The relationships between mutually dependent field quantities can be derived through substitution of equations S14 and S15 into Maxwell's equations. In a region with no external or singular induced charges or currents, the Maxwell-Gauss equation becomes

$$iqE_q^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \pm ik_{zj} E_z^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} = 0, \tag{S16}$$

$$E_z^{(j)} = \mp \frac{q}{k_{zj}} E_q^{(j)}, \tag{S17}$$

and the Maxwell-Faraday equation becomes

$$\begin{pmatrix} \mp ik_{zj} E_\tau^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \\ \pm ik_{zj} E_q^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} - iqE_z^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \\ iqE_\tau^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \end{pmatrix} = i\mu_0\omega \begin{pmatrix} H_q^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \\ H_\tau^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \\ H_z^{(j)} e^{i(qx \pm k_{zj}z-\omega t)} \end{pmatrix}, \tag{S18}$$

$$\begin{pmatrix} H_q^{(j)} \\ H_\tau^{(j)} \\ H_z^{(j)} \end{pmatrix} = \begin{pmatrix} \mp \frac{k_{zj}}{\mu_0\omega} E_\tau^{(j)} \\ -\frac{1}{\mu_0\omega}(\mp k_{zj} E_q^{(j)} + qE_z^{(j)}) \\ \frac{q}{\mu_0\omega} E_\tau^{(j)} \end{pmatrix}, \tag{S19}$$

where k_{zj} is positive in region $j = 1$ and negative in region $j = 2$.

Considering first the simpler case of vacuum surroundings with $n_1 = n_2 = 1$ and $k_{z1} = k_{z2} = k_z$, insertion of equation S17 into equation S11 yields

$$E_q^{(2)} - E_q^{(1)} = -\frac{z_0 q^2 \tilde{\sigma}_z}{2k_0 k_z}(E_q^{(2)} - E_q^{(1)}), \tag{S20}$$

$$\left(1 + \frac{q^2\tilde{\sigma}_z}{2k_0k_z}\right) E_q^{(2)} - \left(1 + \frac{q^2\tilde{\sigma}_z}{2k_0k_z}\right) E_q^{(1)} = 0, \tag{S21}$$

where the substitution $\omega\epsilon_0 = k_0/z_0$ was used, and $\tilde{\sigma}_z = z_0\sigma_z$. Next, equation S12 gives

$$E_\tau^{(2)} = E_\tau^{(1)}. \tag{S22}$$

The continuity of the $\hat{\tau}$ component of the electric field can be used to simplify the magnetic field condition S13. Applying equation S19 to the $\hat{\tau}$ component of equation S12 yields

$$-\frac{k_z}{k_0}(E_\tau^{(2)} + E_\tau^{(1)}) = \frac{1}{2}\tilde{\sigma}_\tau(E_\tau^{(2)} + E_\tau^{(1)}), \tag{S23}$$

where the substitutions $\mu_0 = z_0/c$ and $k_0 = \omega/c$ were applied. Application of equation S22 yields

$$-\frac{k_z}{k_0}E_\tau^{(1)} = \frac{1}{2}\tilde{\sigma}_\tau E_\tau^{(1)}, \tag{S24}$$

$$-\left(\tilde{\sigma}_\tau + \frac{2k_z}{k_0}\right)E_\tau^{(1)} = 0. \tag{S25}$$

Then, applying equations S17 and S19 to the $\hat{q}$ component of equation S13,

$$\frac{k_0}{k_z}(E_q^{(2)} + E_q^{(1)}) = -\frac{\tilde{\sigma}_q}{2}(E_q^{(2)} + E_q^{(1)}), \tag{S26}$$

$$\left(\frac{k_0}{k_z} + \frac{\tilde{\sigma}_q}{2}\right)E_q^{(2)} + \left(\frac{k_0}{k_z} + \frac{\tilde{\sigma}_q}{2}\right)E_q^{(1)} = 0, \tag{S27}$$

where the substitutions $\mu_0 = z_0/c$, $k_0 = \omega/c$, and $q^2 + k_z^2 = k_0^2$ were applied. Between equations S21, S25, and S27, we have a homogeneous system of three equations and three unknowns in the field amplitudes. A system of this kind can be represented as a matrix,

$$\begin{bmatrix} 0 & 0 & -\frac{2k_z}{k_0} - \tilde{\sigma}_\tau \\ \frac{k_0}{k_z} + \frac{\tilde{\sigma}_q}{2} & \frac{k_0}{k_z} + \frac{\tilde{\sigma}_q}{2} & 0 \\ -1 - \frac{q^2\tilde{\sigma}_z}{2k_0k_z} & 1 + \frac{q^2\tilde{\sigma}_z}{2k_0k_z} & 0 \end{bmatrix} \begin{pmatrix} E_q^{(1)} \\ E_q^{(2)} \\ E_\tau^{(1)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{S28}$$

For physically meaningful solutions, the field amplitudes need to be non-zero. The condition for non-trivial solutions on a system of homogeneous equations such as this is that the determinant of the coefficient matrix be zero. This is equivalent to the statement that the system is linearly dependent. Linear dependency means the system has infinitely many solutions with non-zero field amplitudes.

The determinant of the coefficient matrix S28 is,

$$\det\begin{bmatrix} 0 & 0 & -\frac{2k_z}{k_0} - \tilde{\sigma}_\tau \\ \frac{k_0}{k_z} + \frac{\tilde{\sigma}_q}{2} & \frac{k_0}{k_z} + \frac{\tilde{\sigma}_q}{2} & 0 \\ -1 - \frac{q^2\tilde{\sigma}_z}{2k_0k_z} & 1 + \frac{q^2\tilde{\sigma}_z}{2k_0k_z} & 0 \end{bmatrix} = -\frac{(\tilde{\sigma}_q k_z + 2k_0)(\tilde{\sigma}_\tau k_0 + 2k_z)(q^2\tilde{\sigma}_z + 2k_0k_z)}{2k_z^2k_0^2}. \tag{S29}$$

So, the condition on non-trivial solutions is,

$$(\tilde{\sigma}_q k_z + 2k_0)(\tilde{\sigma}_\tau k_0 + 2k_z)(q^2\tilde{\sigma}_z + 2k_0k_z) = 0. \tag{S30}$$

Eliminating k_z by substituting in $k_z = \sqrt{k_0^2 - q^2}$, and then solving for q yields

$$q = \pm k_0\frac{\sqrt{\tilde{\sigma}_q^2 - 4}}{\tilde{\sigma}_q},\ \pm\frac{k_0}{2}\sqrt{4 - \tilde{\sigma}_\tau^2},\ \pm k_0\frac{\sqrt{2}\sqrt{-1 \pm \sqrt{\tilde{\sigma}_z^2 + 1}}}{\tilde{\sigma}_z} \tag{S31}$$

for the in-plane longitudinal, in-plane transverse, and the OOP modes, respectively.

With vacuum surroundings, the plasmon modes remain decoupled despite the inclusion of OOP response. The in-plane longitudinal mode $(\tilde{\sigma}_q k_z + 2k_0)$ can be recognized as the standard result which, for a Drude conductivity model for doped graphene in the non-retarded limit, will yield the square-root dispersion relation, $\omega = \sqrt{2v_B\omega_F}\sqrt{q}$, where $\omega_F = E_F/\hbar$ and v_B is the Bohr speed. In the non-retarded limit, the OOP dispersion relation becomes

$$2i\omega\epsilon_0 + q\sigma_z = 0. \tag{S32}$$

Unlike the Drude model for in-plane conductivity, there are no well-accepted simple models for the OOP conductivity. However, we can make a reasonable guess with a Lorentzian, which takes into account that the OOP polarization is governed by high-energy inter-band electronic transitions in graphene,

$$\sigma_z = \frac{i}{\pi}\frac{\omega S_b}{\omega^2 - \omega_b^2 + i\omega\tau_f^{-1}}. \tag{S33}$$

We consider the limit that the frequency is small and define the lossless conductivity as,

$$\sigma_z = -\frac{i}{\pi}\frac{\omega S_b}{\omega_b^2}. \tag{S34}$$

This result is corroborated by *ab initio* calculations of the OOP conductivity [3] which show low frequency linear behaviour. Then, substituting this conductivity into equation S32 gives

$$q = \frac{2\pi\epsilon_0\omega_b^2}{S_b}. \tag{S35}$$

The factor of ω cancels, and so there is no longer a continuum of states, meaning there is no out-of-plane plasmon mode when one assumes a Lorentzian line shape.

This same process for finding the interface modes can be applied to the case with material surroundings. When a 2D material is surrounded by non-magnetic, isotropic, lossless dielectrics, the system of equations describing interface states is given by

$$\begin{bmatrix} 0 & 0 & -\frac{k_{z2}}{n_2 k_0} - \frac{k_{z1}}{n_1 k_0} - \tilde{\sigma}_\tau \\ \frac{n_1 k_0}{k_{z1}} + \frac{\tilde{\sigma}_q}{2} & \frac{n_2 k_0}{k_{z2}} + \frac{\tilde{\sigma}_q}{2} & 0 \\ -1 - \frac{n_1^2 q^2 \tilde{\sigma}_z^e}{2k_0 k_{z1}} & 1 + \frac{n_2^2 q^2 \tilde{\sigma}_z^e}{2k_0 k_{z2}} & 0 \end{bmatrix} \begin{pmatrix} E_q^{(1)} \\ E_q^{(2)} \\ E_\tau^{(1)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \tag{S36}$$

The determinant in this case is far more complex, though it can be collected into two primary factors,

$$\det \begin{bmatrix} 0 & 0 & -\frac{k_{z2}}{n_2 k_0} - \frac{k_{z1}}{n_1 k_0} - \tilde{\sigma}_\tau \\ \frac{n_1 k_0}{k_{z1}} + \frac{\tilde{\sigma}_q}{2} & \frac{n_2 k_0}{k_{z2}} + \frac{\tilde{\sigma}_q}{2} & 0 \\ -1 - \frac{n_1^2 q^2 \tilde{\sigma}_z^e}{2k_0 k_{z1}} & 1 + \frac{n_2^2 q^2 \tilde{\sigma}_z^e}{2k_0 k_{z2}} & 0 \end{bmatrix} = -\frac{AB}{4k_0^2 k_{z1} k_{z2}}, \tag{S37}$$

where

$$A = k_0\tilde{\sigma}_\tau + k_{z1} + k_{z2}, \tag{S38}$$

and

$$B = q^2\tilde{\sigma}_q\tilde{\sigma}_z^e(n_2^2 k_{z1} + n_1^2 k_{z2}) + 4k_0(n_1^2 n_2^2 q^2 \tilde{\sigma}_z^e + k_{z1}k_{z2}\tilde{\sigma}_q) + 4k_0^2(n_2^2 k_{z1} + n_1^2 k_{z2}). \tag{S39}$$

Setting $AB = 0$ then gives a dispersion relation, which shows that the transverse in-plane mode, defined by $A = 0$, is decoupled from the in-plane longitudinal mode and the OOP mode, which have become coupled via the condition $B = 0$ in the presence od different refractive constants, $n_1 \neq n_2$, as discussed in equation 19 of the main text.

3. ELLIPSOMETRIC AMPLITUDE

In addition to the ellipsometric phase parameters considered in the main text, we also compared the amplitude parameters from the three data sets. This comparison is given in Figure S2 for the same sets of parameters as those used in Figure 2 of the main text. The ellipsometric amplitude Ψ is largely insensitive to the out-of-plane response, except for small variance at higher frequencies.

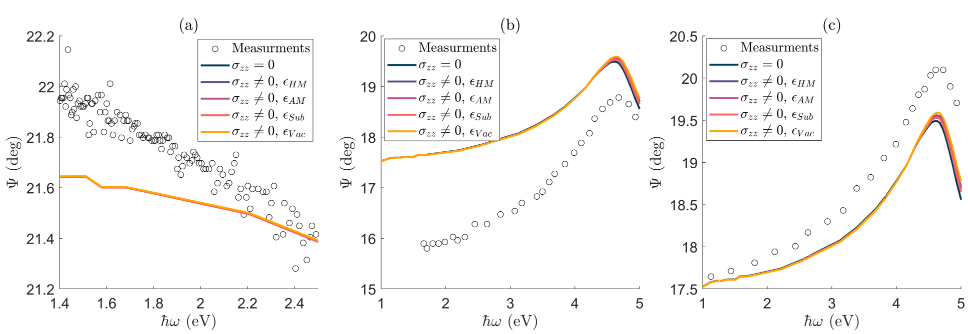

Fig. S2. Ellipsometric amplitude parameter of graphene with (a) PDMS substrate, $\theta_i = 70°$ [2], (b) fused quartz substrate, $\theta_i = 45°$ [4], (c) glass substrate, $\theta_i = 45°$ [5].

4. DIELECTRIC SCREENING IN THE PLASMONIC REGIME

The OOP modified plasmon dispersion relation shown in equation 23 of the main text exhibits a non-monotonic arch shape regardless of the choice of screening model. A comparison between the dispersion curves with various screening models from equation 17 of the main text for doped graphene with Fermi energy $E_F = 0.5$ eV is shown in Figure S3. Note that the range of confidence in that figure is limited to the wavenumbers $q \ll k_F \approx 0.76\,\mathrm{nm}^{-1}$ because of our use of the Drude model for $\sigma_q(\omega)$.

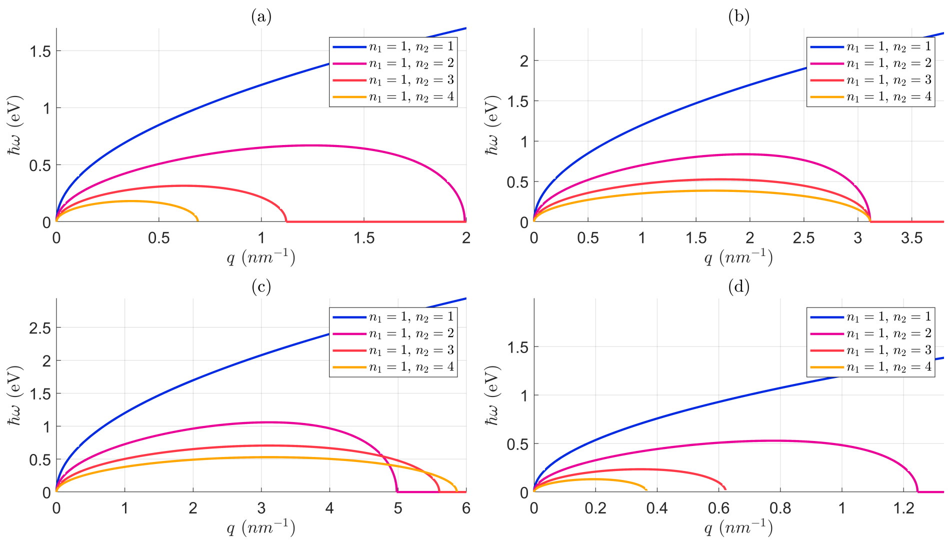

Fig. S3. Comparison between the choice of screening model on the OOP modified plasmon dispersion shown in equation 22 of the main text for (a) harmonic mean, (b) the arithmetic mean, (c) the substrate, and (d) unscreened.

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