Quantum surface-response of metals revealed by acoustic graphene plasmons

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A quantitative understanding of the electromagnetic response of materials is essential for the precise engineering of maximal, versatile, and controllable light-matter interactions. Material surfaces, in particular, are prominent platforms for enhancing electromagnetic interactions and for tailoring chemical processes. However, at the deep nanoscale, the electromagnetic response of electron systems is significantly impacted by quantum surface-response at material interfaces, which is challenging to probe using standard optical techniques. Here, we show how ultraconfined acoustic graphene plasmons in graphene-dielectric-metal structures can be used to probe the quantum surface-response functions of nearby metals, here encoded through the so-called Feibelman $d$-parameters. Based on our theoretical formalism, we introduce a concrete proposal for experimentally inferring the low-frequency quantum response of metals from quantum shifts of the acoustic graphene plasmons dispersion, and demonstrate that the high field confinement of acoustic graphene plasmons can resolve intrinsically quantum mechanical electronic length-scales with subnanometer resolution. Our findings reveal a promising scheme to probe the quantum response of metals, and further suggest the utilization of acoustic graphene plasmons as plasmon rulers with ångström-scale accuracy.

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light is a prominent tool to probe the properties of materials and their electronic structure, as evidenced by the widespread use of light-based spectroscopies across the physical sciences. Among these tools, far-field optical techniques are particularly prevalent, but are constrained by the diffraction limit and the mismatch between optical and electronic length scales to probe the response of materials only at large length scales (or, equivalently, at small moments). Plasmon polaritons—hybrid excitations of light and free carriers—provide a mean to overcome these constraints through their ability to confine electromagnetic radiation to the nanoscale.

Graphene, in particular, supports gate-tunable plasmons characterized by an unprecedentedly strong confinement of light. When placed near a metal, graphene plasmons (GPs) are strongly screened and acquire a nearly linear (acoustic-like) dispersion (contrasting with the square-root-type dispersion of conventional GPs). Crucially, such acoustic graphene plasmons (AGPs) in graphene–dielectric–metal (GDM) structures have been shown to exhibit even higher field confinement than conventional GPs with the same frequency, effectively squeezing light into the few-nanometer regime. Recently, using scanning near-field optical microscopy, these features were exploited to experimentally measure the conductivity of graphene, \( \sigma(q,\omega) \), across its frequency \( \omega \) and momentum \( q \) dependence simultaneously. The observation of momentum dependence implies a nonlocal response (i.e., response contributions at position \( r \) from perturbations at \( r' \)), whose origin is inherently quantum mechanical. Incidentally, traditional optical spectroscopic tools cannot resolve nonlocal response in extended systems due to the intrinsically small momenta \( k_0 \equiv \omega/c \) carried by far-field photons. Acoustic graphene plasmons, on the other hand, can carry large momenta—up to a significant fraction of the electronic Fermi momentum \( k_F \) and with group velocities asymptotically approaching the electron’s Fermi velocity \( v_F \)—and so can facilitate explorations of nonlocal (i.e., \( q \)-dependent) response not only in graphene itself but also, as we detail in this Article, in nearby materials. So far, however, only aspects related to the quantum response of graphene have been addressed, leaving any quantum nonlocal aspects of the adjacent metal’s response unattended, despite their potentially substantial impact on nanometric graphene–metal separations.

Here, we present a theoretical framework that simultaneously incorporates quantum nonlocal effects in the response of both the graphene and of the metal substrate for AGPs in GDM heterostructures. Further, our approach establishes a concrete proposal for experimentally measuring the low-frequency nonlocal electrodynamic response of metals. Our model treats graphene at the level of the nonlocal random-phase approximation (RPA) and describes the quantum aspects of the metal’s response—including nonlocality, electronic spill-out/spill-in, and surface-enabled Landau damping —using a set of microscopic surface-response functions known as the Feibelman \( d \)-parameters. These parameters, \( d_{\perp} \) and \( d_{\parallel} \), measure the frequency-dependent centroids of the induced charge density and of the normal derivative of the tangential current density, respectively (Supplementary Note 1). Using a combination of numerics and perturbation theory, we show that the AGPs are spectrally shifted by the quantum surface-response of the metal: toward the red for \( \text{Re} d_{\perp} > 0 \) (associated with electronic spill-out of the induced charge density) and toward the blue for \( \text{Re} d_{\parallel} < 0 \) (signaling an inward shift, or “spill-in”). Interestingly, these shifts are not accompanied by a commensurately large quantum broadening nor by a reduction of the AGP’s quality factor, thereby providing the theoretical support explaining recent experimental observations. Finally, we discuss how state-of-the-art measurements of AGPs could be leveraged to map out the low-frequency quantum nonlocal surface response of metals experimentally. Our findings have significant implications for our ability to optimize photonic devices that interface far- and mid-infrared optical excitations—such as AGPs—with metals all the way down to the nanoscale, with pursuant applications in, e.g., ultracompact nanophotonic devices, nanometrology, and in the surface sciences more broadly.

**Results**

**Theory.** We consider a GDM heterostructure (see Fig. 1) composed of a graphene sheet with a surface conductivity \( \sigma \equiv \sigma(q,\omega) \) separated from a metal substrate by a thin dielectric slab of thickness \( t \) and relative permittivity \( \varepsilon_2 \equiv \varepsilon_2(\omega) \); finally, the device is covered by a superstrate of relative permittivity \( \varepsilon_1(\omega) \). While the metal substrate may, in principle, be represented by a nonlocal and spatially non-uniform (near the interface) dielectric function, here we abstract its contributions into two parts: a bulk, local contribution via \( \varepsilon_m \equiv \varepsilon_m(\omega) \equiv \varepsilon_\infty(\omega) - \omega_p^2/(\omega^2 + i\omega\gamma_m) \), and a surface, quantum contribution included through the \( d \)-parameters. These parameters are quantum-mechanical surface-response functions, defined by the first moments of the microscopic induced charge \( (d_{\perp}) \) and of the normal derivative of the tangential current \( (d_{\parallel}) \); see Fig. 1 (Supplementary Note 1 gives a concise introduction). They allow the leading-order corrections to classicality to be conveniently incorporated via a surface dipole density \( (\propto d_{\perp}) \) and a surface current density \( (\propto d_{\parallel}) \), and can be obtained either by first-principles computation, semiclassical models, or experiments.

The electromagnetic excitations of any system can be obtained by analyzing the poles of the (composite) system’s scattering coefficients. For the AGPs of a GDM structure, the relevant coefficient is the \( p \)-polarized reflection (or transmission) coefficient, whose poles are given by \( 1 - r_p^{2\text{ag}} r_p^{2\text{m}} e^{2i\theta_p} = 0 \) (ref. 22). Here, \( r_p^{2\text{ag}} \) and \( r_p^{2\text{m}} \) denote the \( p \)-polarized reflection coefficients for the dielectric–graphene–dielectric and the dielectric–metal interface (detailed in Supplementary Note 2), respectively. Each coefficient yields a material-specific contribution to the overall quantum response:

\[
\begin{align*}
\varepsilon_1 & \equiv \varepsilon_1(q,\omega) \\
\varepsilon_2 & \equiv \varepsilon_2(q,\omega) \\
\varepsilon_m & \equiv \varepsilon_m(q,\omega)
\end{align*}
\]

The complex exponential \( e^{2i\theta_p} \) incorporates graphene’s \( \sigma(q,\omega) \) and \( r_p^{2\text{ag}} \) incorporates graphene’s via \( \sigma(q,\omega) \) and \( r_p^{2\text{m}} \) incorporates the metal’s via the \( d \)-parameters (see Supplementary Note 2). The complex exponential \( e^{2i\theta_p} \) incorporates graphene’s via \( \sigma(q,\omega) \) and \( r_p^{2\text{ag}} \) incorporates graphene’s via \( \sigma(q,\omega) \) and \( r_p^{2\text{m}} \) incorporates the metal’s via the \( d \)-parameters.

**Fig. 1 Schematics of a dielectric-graphene-dielectric-metal (GDM) heterostructure.** The graphene–metal separation, \( t \), is controlled by the thickness of the dielectric \( (\varepsilon_2) \) spacer. The close-up (near the metal–spacer interface) shows a pictorial representation of the surface-response functions \( d_{\perp} \) and \( d_{\parallel} \) along with the related microscopic quantities characterizing the metal surface, namely the equilibrium electronic density, \( n_0(z) \), and the induced charge density, \( \rho_{\text{ind}}(z) \).
factors κ for in-plane AGP wavevector q in the jellium treatment of the metal such that ω ≪ κ (wherein neutrality is assumed). Leaving only the Drude response for the graphene and the metal, respectively [black dashed line]; and (iii) nonlocal RPA and d-parameter-augmented response for the graphene and the metal, respectively [red solid line].

AGPs typically span frequencies across the terahertz (THz) regime, and for encapsulated graphene, i.e., where the carrier density n⊥ is small, graphene’s resonance blueshifts upon inclusion of a metal’s quantum response, followed by a redshift due to the quantum surface-response of the metal (since Re d⊥ > 0 for jellium metals; electronic spill-out)13,15,16,21,27,28. This redshifting due to the metal’s quantum surface-response is opposite to that predicted by the semiclassical hydrodynamic model (HDM) where the result is always a blueshift (corresponding to Re d⊥HDM < 0; electronic “spill-in”) due to the neglect of spill-out effects29. The imaginary part of the AGP’s wavevector (that characterizes the mode’s propagation length) is shown in Fig. 2b: the net effect of the inclusion of d⊥ is a small, albeit consistent, increase of this imaginary component. Notwithstanding this, the modification of Im q is not independent of the shift in Re q: as a result, an increase in Im q does not necessarily imply the presence of a significant quantum decay channel [e.g., an increase of Im q can simply result from increased classical loss (i.e., arising from local response alone) at the newly shifted Re q position]. Because of this, we inspect the quality factor Q = Re q/Im q (or “inverse damping

Quantum corrections in AGPs due to metallic quantum surface-response. The spectrum of AGPs calculated classically and with quantum corrections is shown in Fig. 2. Three models are considered: one, a completely classical, local-response approximation treatment of both the graphene and the metal; and two others, in which graphene’s response is treated by the nonlocal RPA and d-parameter data which assumes a jellium metal with plasma frequency ωp ≈ 9.07 eV (corresponding to τf = 3) where ζ ≈ 0.8 Å and ξ ≈ 0.3 Å24, with Drude-type damping hp = 0.1 eV; for graphene, we take Ef = 0.3 eV and μ = 8 meV; finally, we have assumed εd ≡ ε1 = ε2 = 1 (for consistency with the d-parameter data which assumes a metal–vacuum interface25).

For simplicity and concreteness, we will consider a simple asymptotic relation in Eq. (3) to calculate the dispersion of AGPs with metallic (in addition to graphene’s) quantum response included.
Probing the quantum surface-response of metals with AGPs. The key parameter that regulates the impact of quantum surface corrections stemming from the metal is the graphene–metal separation, \( t \) (analogously to the observations of nonclassical effects in conventional plasmons at narrow metal gaps\cite{13,36,37}); see Fig. 4. For the experimentally representative parameters indicated in Fig. 4, these come into effect for \( t \lesssim 5 \) nm, growing rapidly upon decreasing the graphene–metal separation further. Chiefly, ignoring the nonlocal response of the metal leads to a consistent overestimation (underestimation) of AGP’s wavevector (group velocity) for \( d_⊥ < 0 \), and vice versa for \( d_⊥ > 0 \) (Fig. 4a); this behavior is consistent with the effective renormalization of the graphene–metal separation mentioned earlier (Fig. 4b). Finally, we analyze the interplay of both \( t \) and \( E_F \) and their joint influence on the magnitude of the quantum corrections from the metal (we take \( d_⊥ = -4 \) Å, which is reasonable for the Au substrate used in recent AGP experiments\cite{7,8,11}); in Fig. 4c we show the relative wavevector quantum shift (excited at \( \lambda_0 = 11.28 \) Å\textsuperscript{32}). In the few-nanometer regime, the quantum corrections to the AGP wavevector approach 5%, increasing further as \( t \) decreases—for instance, in the extreme, one-atom-thick limit \( t \approx 0.7 \) nm\textsuperscript{11}, which also approximately coincides with edge of the validity of the \( d \)-parameter framework, i.e., \( t \gtrsim 1 \) nm\textsuperscript{15}) the AGP’s wavevector can change by as much as 10% for moderate graphene doping. The pronounced Fermi level dependence exhibited in Fig. 4c also suggests a complementary approach for measuring the metal’s quantum surface-response even if an experimental parameter is unknown (although, as previously noted, all relevant experimental parameters can in fact be characterized using currently available techniques\cite{8,10,11,15}); such an unknown variable can be fitted at low \( E_F \) using the “classical” theory (i.e., with \( d_⊥ = d_∥ = 0 \)), since the impact of metallic quantum response is negligible in that regime. A parameter-free assessment of the metal’s quantum surface-response can then be carried out subsequently by increasing \( E_F \) (and with it, the metal-induced quantum shift). We emphasize that this can be accomplished in the same device by doping graphene using standard electrostatic gating\textsuperscript{8,10,11}.
denote the AGP wavevector associated with excitation at conditions 15, 16. — e.g., using the framework developed here quantum surface-response needs to be rigorously accounted for separations. Our results also demonstrate that the metal increase of damping, even for atomically thin graphene metallic quantum response but without a clear concomitant the observation of nonclassical spectral shifting of AGPs due to solution of Eq. (1).

Fig. 4 Nonclassical corrections probed by AGPs. a AGP’s wavevector as a function of the graphene–metal separation t, contrasting the metal’s response based on classical (d₀ = 0) and quantum (d₀ = ±4 Å) treatments. Inset: corresponding group velocity v → = dω/[dq]|₀→ω→. b Dependence of the renormalized graphene–metal separation t ≡ t – s versus t. Setup parameters: t₀ = 3, hₓₓ = 0.1 eV, εₓₓ = 4, E₂ = 0.3 eV, and hₓ = 8 meV; we assume an excitation at λ₀ ≡ 11.28 µm (ℏω₀ ≈ 110 meV or f₀ ≈ 26.6 THz)²₅. c Relative quantum shift of the AGP wavevector, Re d/q, with d/q ≡ q₀ – q where q₀ and q denote the AGP wavevector associated with d₀ = 0 and d₀ = –4 Å, respectively. The results presented in both a and c are based on the exact, numerical solution of Eq. (1).

Discussion

In this Article, we have presented a theoretical account that establishes and quantifies the influence of the metal’s quantum response for AGPs in hybrid GDM structures. We have demonstrated that the nanoscale confinement of electromagnetic fields inherent to AGPs can be harnessed to determine the quantum surface-response of metals in the THz and mid-IR spectral ranges (which is typically inaccessible with traditional metal-based plasmonics). Additionally, our findings elucidate and contextualize recent experiments⁶,¹¹ that have reported the observation of nonclassical spectral shifting of AGPs due to metallic quantum response but without a clear concomitant increase of damping, even for atomically thin graphene–metal separations. Our results also demonstrate that the metal’s quantum surface-response needs to be rigorously accounted for — e.g., using the framework developed here—when searching for signatures of many-body effects in the graphene electron liquid imprinted in the spectrum of AGPs in GDM systems⁸, since the metal’s quantum-surface response can lead to qualitatively similar dispersion shifts, as shown here. In passing, we emphasize that our framework can be readily generalized to more complex graphene–metal hybrid structures either by semi-analytical approaches (e.g., the Fourier modal method⁴ for periodically nanopatterned systems) or by direct implementation in commercially available numerical solvers (see refs. ¹⁵,³⁹), simply by adopting d-parameter-corrected boundary conditions¹⁵,¹⁶.

Further, our formalism provides a transparent theoretical foundation for guiding experimental measurements of the quantum surface-response of metals using AGPs. The quantitative knowledge of the metal’s low-frequency, static quantum response is of practical utility in a plethora of scenarios, enabling, for instance, the incorporation of leading-order quantum corrections to the classical electrostatic image theory of particle–surface interaction²⁰ as well as to the van der Waals interaction²¹,²⁵,⁴⁰ affecting atoms or molecules near metal surfaces. Another prospect suggested by our findings is the experimental determination of ζ ≡ d₁(0) through measurements of the AGP’s spectrum. This highlights a new metric for comparing the fidelity of first-principle calculations of different metals (inasmuch as ab initio methods can yield disparate results depending on the chosen scheme or functional)⁴¹,⁴² with explicit measurements.

Our results also highlight that AGPs can be extremely sensitive probes for nanometry as plasmon rulers, while simultaneously underscoring the importance of incorporating quantum response in the characterization of such rulers at (sub)nanometric scales. Finally, the theory introduced here further suggests additional directions for exploiting AGP’s high-sensitivity, e.g., to explore the physics governing the complex electron dynamics at the surfaces of superconductors⁴³ and other strongly correlated systems.

Data availability

The data that underlie the findings of this study are available from the corresponding authors upon reasonable request.
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Author contributions

P.A.D.G., T.C., N.M.R.P., I.E., F.H.L.K., M.S. and N.A.M. conceived the research. P.A.D.G. and N.A.M. supervised the work. All authors provided significant contributions to all aspects of this work and to the writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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