A general theoretical and experimental framework for nanoscale electromagnetism

The macroscopic electromagnetic boundary conditions, which have been established for over a century, are essential for the understanding of photonics at macroscopic length scales. Even state-of-the-art nanoplasmonic studies, exemplars of extremely interface-localized fields, rely on their validity. This classical description, however, neglects the intrinsic electronic length scales (of the order of ångström) associated with interfaces, leading to considerable discrepancies between classical predictions and experimental observations in systems with deeply nanoscale feature sizes, which are typically evident below about 10 to 20 nanometres. The onset of these discrepancies has a mesoscopic character: it lies between the granular microscopic (electron-scale) and continuous macroscopic (wavelength-scale) domains. Existing top-down phenomenological approaches deal only with individual aspects of these omissions, such as nonlocality and local-response spill-out. Alternatively, bottom-up first-principles approaches—for example, time-dependent density functional theory—are severely constrained by computational demands and thus become impractical for multiscale problems. Consequently, a general and unified framework for nanoscale electromagnetism remains absent. Here we introduce and experimentally demonstrate such a framework—amenable to both analytics and numerics, and applicable to multiscale problems—that reintroduces the electronic length scale via surface-response functions known as Feibelman parameters. We establish an experimental procedure to measure these complex dispersive surface-response functions, using quasi-normal-mode perturbation theory and observations of pronounced nonclassical effects. We observe nonclassical spectral shifts in excess of 30 per cent and the breakdown of Kreibig-like broadening in a quintessential multiscale architecture: film-coupled nanoresonators, with feature sizes comparable to both the wavelength and the electronic length scale. Our results provide a general framework for modelling and understanding nanoscale (that is, all relevant length scales above about 1 nanometre) electromagnetic phenomena.
Fig. 1 | Framework, experimental structure and measured nonclassical shifts. a, Classical (a) and mesoscopic (b) electromagnetic boundary conditions. c, Equilibrium and induced densities, \( n(\mathbf{r}) \) and \( \rho(\mathbf{r},\omega) \) (not to scale) at a jellium–vacuum interface (Wigner–Seitz radius, \( r_s = 3.93 \) atomic units; \( \hbar \omega = 1.1 \) eV; \( \hbar \), reduced Planck constant) computed from (time-dependent) density functional theory. \( d_\perp \) is the centroid of the induced charge. d, Nonclassical corrections can be formulated as self-consistent surface polarizations, representing the effective surface dipole density \( \mathbf{m}(\mathbf{r}) \) and the current density \( \mathbf{K}(\mathbf{r}) \). e, Experimental structure: film-coupled Au nanodisks on a Au–Ti–Si substrate, separated by a nanoscale AlO\(_x\) gap (Si and Al nanodisks were also studied). f, Surface dipole density \( \mathbf{m}(\mathbf{r}) \) of the (1,1) gap plasmon of a film-coupled Au nanodisk (\( D = 63 \) nm, \( g = 4 \) nm). g, Observation of large nonclassical corrections (spectral shift \( \approx 400 \) nm) in film-coupled Au nanodisks (\( D = 63 \) nm). Measured frequencies (circles) of the (1,1) resonance blueshift relative to the classical prediction (dashed line), which quantitatively agree with nonclassical calculations (solid line, and the overlain calculated intensity map of the scattering efficiency \( \sigma_{sc}/A \), where \( A = \pi D^2/4 \)).

Experimentally, we establish a systematic approach to measure the \( d \)-parameter dispersion of a general two-material interface and illustrate it using Au–AlO\(_x\) interfaces. Whereas the \( d \) parameters of simple metals can be accurately computed within jellium time-dependent density functional theory\(^{18,24}\), those of noble metals, such as Au, require time-dependent density functional theory beyond the jellium approximation owing to non-negligible screening from lower-lying orbitals\(^{22,26}\). We show that the \( d \) parameters can instead be measured experimentally. By developing and exploiting a quasi-normal-mode (QNM)-based\(^{22,28}\) perturbation expression, we translate these mesoscopic quantities directly into observables—spectral shifting and broadening—and measure them in designed plasmonic systems that exhibit pronounced nonclassical corrections. Our experimental testbed enables a direct procedure to extract the \( d \) parameters from standard dark-field spectroscopic measurements, in a manner analogous to ellipsometric measurements of the local bulk permittivity. Moreover, by investigating a complementary hybrid plasmonic setup, we discover and experimentally demonstrate design principles for structures that are classically robust—that is, they exhibit minimal nonclassical corrections—even under nanoscopic conditions.

The extensive interest in film-coupled nanoantennas\(^{33}\), which combine wavelength-scale resonators with nanometric gaps, is a particularly pertinent example that underscores the need for as a set of mesoscopic boundary conditions (here without external interface currents or charges) for the conventional macroscopic Maxwell equations (also shown in Fig. 1b; see Supplementary Information section S2.B)

\[
[D_\parallel] = -i\omega \nabla V_\perp \cdot \mathbf{K} = d_\perp \nabla_\perp \cdot [D_\parallel] \\
[B_\parallel] = 0 \\
[E_\parallel] = -\varepsilon_0 \nabla \varphi_\perp = -d_\perp \nabla_\perp [E_\parallel] \\
[H_\parallel] = \mathbf{K} \times \mathbf{n} = i\omega d_\perp [D_\parallel] \times \mathbf{n}
\]

These mesoscopic boundary conditions are a twofold generalization from opposite directions. First, they generalize the usual macroscopic electromagnetic boundary conditions \( (D_\parallel) = (B_\parallel) = 0 \) and \( [E_\parallel] = [H_\parallel] = 0 \) to which they reduce in the limit \( d_\perp \rightarrow 0 \). Secondly, they represent a conceptual and practical generalization of the applicability of the Feibelman \( d \) parameters, elevated from their original purview of planar\(^{29}\) and spherical\(^{30}\) interfaces, and beyond recent quasistatic considerations\(^{32}\), to a fully general electrodynamic framework.

Fig. 2 | Measurement setup and sample micrographs. a, Tabletop dark-field scattering setup, where dark-field scattering from nanodisks illuminated by a broadband lamp is collected by a camera and a spectrometer (for details see Methods and Supplementary Information section S10). b, Dark-field optical micrograph of a Au nanodisk array (scale bar, 2 \( \mu \)m). c, Scanning electron microscopy image of a single Au nanodisk (scale bar, 40 nm). d, Cross-sectional transmission electron microscopy image of an AlO\(_x\) gap (scale bar, 10 nm).
multiscale electrodynamic tools that incorporate nonclassical effects. We designed and fabricated film-coupled nanodisks (Figs. 1e, 2b–d) of various materials to verify our framework and directly measure the $d$ parameters. Specifically, an optically thick Au film (atop a Si substrate) was separated from lithographically defined Au, Si or Al nanodisks (of diameter $D$) by a nanoscale AIO spacer, deposited by atomic layer deposition (ALD; see Supplementary Information section S5), demarcating a film–nanodisk gap of thickness $g$. The nanodisks support localized gap–plasmon resonances, which are $(p,q)$ integer-indexable according to their field variations in the azimuthal and radial directions, respectively. The fundamental mode $(1,1)$ is optically accessible in the far field and exhibits highly confined electromagnetic fields within the gap, suggesting potential large nonclassical corrections.

We implemented the mesoscopic boundary conditions (Fig. 1b) in a standard full-wave numerical solver (COMSOL Multiphysics, implementation available at https://github.com/yiyi-mit/nanoEM; see Supplementary Information section S3). With specified $d$ parameters, this permits self-consistent calculations of, for example, the nonclassical surface dipole density $\eta(r)$, as shown in Fig. 1f. If for the $(1,1)$ mode. Similarly, conventional electromagnetic quantities such as the scattering efficiency $\sigma_{\text{sca}}(A = \pi D^2/4)$ can be computed, enabling comparison with experimental results (Fig. 1g). For Au disks, the $(1,1)$ resonance is consistently blueshifted relative to the classical prediction, with shifts exceeding 30% for the smallest considered gaps.

To extract the surface-response functions from observables, we develop a perturbative description of the nonclassical spectral shift using the solver QNMEase of the QNM freeware MAN (Modal Analysis of Nanoresonators), with retardation incorporated explicitly: the true eigenfrequency $\omega = \tilde{\omega}^{(0)} + \tilde{\omega}^{(1)} + \ldots$ (eigenindex implicit) has a first-order nonclassical correction $\tilde{\omega}^{(1)}$ to its classical value $\tilde{\omega}^{(0)}$ (Supplementary Information section S4).

$$\tilde{\omega}^{(1)} = \sum_{\tau} \kappa^{(1)}_{\tau} d^{(1)}_{\tau} + \kappa^{(2)}_{\parallel} d^{(2)}_{\parallel}$$

with mode-, shape- and scale-dependent nonclassical perturbation strengths (units of inverse length)

$$\kappa^{(1)}_{\tau} = -\int_{D_{\parallel}} D^{(0)}_{\parallel} \left| E^{(0)}_{\parallel} \right|^2 d^2 \tau \quad \text{and} \quad \kappa^{(2)}_{\parallel} = \int_{D_{\parallel}} E^{(0)}_{\parallel} \cdot \left| D^{(0)}_{\parallel} \right| d^2 \tau$$

Here, $\tau$ runs over all material interfaces such that $\bigcup_{\tau} \partial D^\tau = \partial D$, that is, $\tau \in \{\text{Au–AlO}, \text{Au–air} \}$ for our setup, and $D^{(0)}_{\parallel}$ and $E^{(0)}_{\parallel}$ denote the $D$ and $E$ fields of the (suitably normalized; see Supplementary Information section S4.) classical QNM under consideration. Conceptually, equation (3) states that the nonclassical perturbation strength is proportional to the difference between the classical surface energy densities evaluated on either side of the interface.

Figure 3a shows the magnitudes of the nonclassical perturbation strengths in a film-coupled Au nanodisk: $\kappa^{(1)}_{\text{Au–AlO}}, \kappa^{(1)}_{\text{Au–air}}, \kappa^{(2)}_{\text{AlO}}, \kappa^{(2)}_{\parallel}$ and $\kappa^{(2)}_{\parallel}$, respectively. Evidently, $\kappa^{(1)}_{\parallel}$ far exceeds $\kappa^{(2)}_{\parallel}$ for all gap sizes of interest, rendering...
Fig. 4 | Robustness to nonclassical corrections. a. The nonclassical perturbation strength is one order of magnitude smaller in the hybrid Si–Au system than in its Au–Au counterpart. b. Observation of robust optical response in a Si–Au setup with the detrimental quantum corrections mitigated. The nonclassical calculation for the Si–Au setup assumes $d_{\text{Au-AlO}}^{\text{Au-Air}} \leq 0.5 \pm 0.3$ nm, a constant extrapolation to higher frequencies from Fig. 3b, c. In d, the measured and calculated spectra are normalized separately. The calculated spectra incorporate inhomogeneous broadening (about 6%) due to disk-size inhomogeneity (Supplementary Information sections S7, S12.B).

![Diagram](image)

the impact of $d_{\text{AlO}}^{\text{Au-Air}}$ negligible. Similarly, the impact of $d_{\text{AlO}}^{\text{Au-Air}}$ is negligible relative to $d_{\text{AlO}}^{\text{Au-AlO}}$, because $\kappa_{\text{AlO}}^{\text{Au-AlO}} \gg \kappa_{\text{AlO}}^{\text{Au-Air}}$ for small $g$, and more generally because $d_{\text{AlO}}^{\text{Au-AlO}} > d_{\text{AlO}}^{\text{Au-Air}}$ owing to screening from AlO (Supplementary Information section S16). Jointly, this justifies the approximation

$$\omega^{(i)} = \omega^{(0)} + d_{\text{AlO}}^{\text{Au-AlO}} d_{\text{AlO}}^{\text{Au-Air}}$$

Inversion of equation (4) enables the direct experimental inference of $d_{\text{AlO}}^{\text{Au-AlO}}$, given the measured $\tilde{\omega}$ and calculated $\omega^{(0)}$ (because, to first order, $\omega^{(i)} \approx \tilde{\omega} - \omega^{(0)}$). We note that $|\text{Re}(\kappa_{\text{AlO}}^{(1)})| \ll |\text{Im}(\kappa_{\text{AlO}}^{(1)})|$ (by 1–2 orders of magnitude) for the considered gap sizes; consequently, $\text{Re}(d_{\text{AlO}}^{(1)})$ contributes to spectral shifting and $\text{Im}(d_{\text{AlO}}^{(1)})$ to broadening.

Ensemble scattering spectra of 15 arrays of Au nanodisks (height, 31 nm) were measured by dark-field scattering microscopy (Fig. 2, Methods), spanning three diameters and six gap sizes (Fig. 3e–j). The associated complex eigenfrequencies $\tilde{\omega}$ were subsequently extracted by Voigt profile deconvolution (Supplementary Information section S12), using the measured particle size distribution (Supplementary Information section S7). For the AlO spacer, we observed ellipsometrically (and include in our calculations) a thickness-dependent refractive index $n_{\text{AlO}}$ (Fig. 3d, Supplementary Information section S9), an effect commonly observed in ultrathin ALD-grown AlO layers and other ALD-grown materials.

Figure 3b shows the complex surface-response function $\tilde{d}_{\text{AlO}}^{\text{Au-AlO}}$, extracted using equation (4). Within the considered spectral range, $\text{Re}(\tilde{d}_{\text{AlO}}^{\text{Au-AlO}})$ (Fig. 3b) reveals a nearly dispersionless surface response of comparatively large magnitude, from $0.5 \text{ nm} \sim 0.4 \text{ nm}$. By contrast, $\text{Im}(\tilde{d}_{\text{AlO}}^{\text{Au-AlO}})$ (Fig. 3c) is strongly dispersive, increasing from $\pm 0.1 \text{ nm}$ in
expectation of monotonically increasing Im(\omega^{(d)}) with decreasing g. Instead, Im(\omega^{(d)}) is minimal there—a consequence of the near-vanishing magnitude of the strongly dispersive Im(\omega_{Au-AlO}^{(d)})(Fig. 3c). This behaviour demonstrates the apparent breakdown of the empirical understanding of nonclassical broadening in nanostructures, known as Kreibig damping, which holds that Im(\omega^{(d)}) is approximately proportional to 1/g.

The observation of large nonclassical corrections in our coupled Au–Au setup frames the question: can nonclassical effects—which are often detrimental—be efficiently mitigated even in nanoscopic settings? To answer by example, we consider a hybrid dielectric–metal design, replacing the Au nanodisks with Si. Such hybrid configurations have been predicted to yield higher radiative efficiency with comparable overall plasmonic response and have two key advantages for mitigating nonclassical effects: first, undoped Si is effectively a purely classical material (that is, \(d_{Au-AlO}^{(d)} = 0\) under the jellium approximation, as it lacks free electrons; second, high-index nanoresonators reduce the field intensity at the metal interface while maintaining confinement in the gap region. This hybridization can be exploited to reduce the nonclassical perturbation strength \(\kappa^{(Au-AlO)}\), by an order of magnitude relative to that in the Au–Au design, as shown in Fig. 4a. Our measurements confirm this prediction: for Si nanodisks with \(D = 104.4\) nm, we observe a high-quality scattering spectrum with a symmetric single-resonance feature for all gap sizes (Fig. 4b). The measured resonance frequencies (Fig. 4c) show only minor deviations from classical predictions, in both real and imaginary parts. Although the inclusion of nonclassical effects improves the experimental agreement, the overall shift remains small and comparable to the uncertainties owing to the intrinsic oxide thickness beneath the Si nanodisk (Supplementary Information section S12.C). By considering a range of nanodisk diameters (Fig. 4d), we reach an identical conclusion, even for the smallest considered gap (about 1.1 nm); classical scattering spectra agree well with measurements, and nonclassical corrections are minor relative to those in the Au–Au system. We found similar robustness across several additional gap sizes and diameters (Supplementary Information section S14).

Equation (2) suggests a complementary strategy for mitigating nonclassical effects: if the sign of Re(\omega^{(d)}) differs at distinct interfaces \(r\), the interface summation Re(\sum \kappa^{(r)}d^{(r)}) will partially cancel. Whereas noble metals are known to spill inwards (Re(\omega^{(d)}) < 0), simple metals (for example, Al) spill outwards (Re(\omega^{(d)}) > 0). We found experimental evidence for such a partial cancellation in a combined noble–simple-metal setup (Al nanodisks on a Au substrate; Supplementary Information section S15).

The mesoscopic framework presented here introduces a general approach for incorporating nonclassical effects in electromagnetic problems by a simple generalization of the associated boundary conditions. Our experiments show how to directly measure the nonclassical surface-response functions—the Feibelman d parameters—in general and technologically relevant plasmonic platforms. Our findings establish the Feibelman d parameters as first-class response functions of general utility. This calls for the compilation of databases of d parameters at interfaces of photonic and plasmonic prominence, analogous and complementary to the existing databases of local bulk permittivities.

Online content

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Methods

Dark-field microscopy
We built a table-top dark-field microscope (Fig. 2a) switchable between imaging and spectroscopy modes and with a 100–700× variable zoom, to measure $\omega$ from the optical response of the samples (Fig. 2b). Optical spectra were recorded at full zoom, capturing the scattered light from an ensemble of $\leq$100 nanodisks (ensemble—rather than single-particle—measurements are necessary owing to the associated low radiative efficiencies; see Supplementary Information section S10). Mutual coupling between nanodisks in the array is negligible, ensured by a lattice periodicity of 2 µm (in-plane filling factor <1%). This allows an isolated-particle treatment.

Structural characterization
The size distribution of the nanodisks was characterized systematically to adjust for the impact of inhomogeneous broadening in the measured scattering spectrum from the ensemble (Fig. 2c, Supplementary Information section S7). We measured the AlO$_x$ gap size $g$ using a variable-angle ultraviolet–visible ellipsometer and confirmed the results through cross-sectional transmission electron microscopy (see Fig. 2d and Supplementary Information section S8), finding good agreement with nominal ALD cycle expectations. A surface roughness of about 0.6 nm (root mean square) was measured for the Au substrate using atomic-force microscopy and was taken as the gap size uncertainty. Owing to the conformal nature of the ALD, such roughness should have negligible influence on the scattering spectra, as we verified by numerical simulations (Supplementary Information section S11). These detailed characterizations eliminate the main sources of geometric uncertainty in the mapping between calculated $\omega^{(0)}$ and measured $\omega$, which is a necessity for an accurate evaluation of the nonclassical shift $\omega - \omega^{(0)}$.

Data availability
The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions
Y.Y. and T.C. conceived the idea. D.Z. fabricated the samples. Y.Y. and D.Z. designed the experiment, built the setup, conducted the scattering measurements and performed the ellipsometry. T.C. derived the mesoscopic boundary conditions. Y.Y., W.Y. and T.C. developed the numerical methods and Y.Y. performed the numerical calculations. W.Y. proposed the auxiliary-potential method, performed density functional theory calculations and implemented the QNM-based perturbation analysis. D.Z. performed the atomic-force microscopy measurement. A.A. and D.Z. performed the transmission electron microscopy measurement. D.Z. and M.Z. characterized nanoparticle size statistics. Y.Y., D.Z., W.Y. and T.C. analysed the data. Y.Y., D.Z. and T.C. drafted the manuscript with extensive input from all authors. J.D.J., P.L., T.C., K.K.B. and M.S. supervised the project.

Competing interests
The authors declare no competing interests.

Additional information
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Correspondence and requests for materials should be addressed to Y.Y., D.Z. or T.C.

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