

Limits to the Optical Response of Graphene and Two-Dimensional Materials

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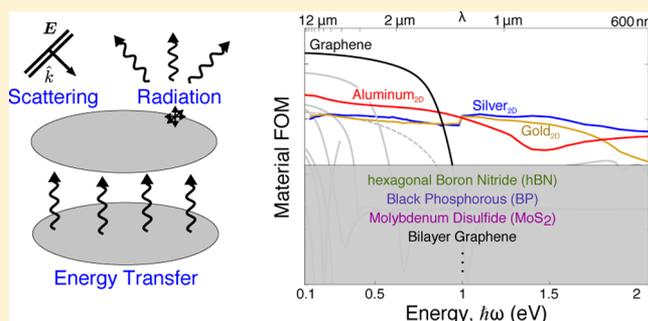
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S Supporting Information

ABSTRACT: Two-dimensional (2D) materials provide a platform for strong light–matter interactions, creating wide-ranging design opportunities via new-material discoveries and new methods for geometrical structuring. We derive general upper bounds to the strength of such light–matter interactions, given only the optical conductivity of the material, including spatial nonlocality, and otherwise independent of shape and configuration. Our material figure-of-merit shows that highly doped graphene is an optimal material at infrared frequencies, whereas single-atomic-layer silver is optimal in the visible. For quantities ranging from absorption and scattering to near-field spontaneous-emission enhancements and radiative heat transfer, we consider canonical geometrical structures and show that in certain cases the bounds can be approached, while in others there may be significant opportunity for design improvement. The bounds can encourage systematic improvements in the design of ultrathin broadband absorbers, 2D antennas, and near-field energy harvesters.

KEYWORDS: 2D materials, graphene, upper bounds, near-field optics, nonlocality



Two-dimensional (2D) materials^{1,2} and emerging methods^{3–8} for patterning 2D layers and their surroundings are opening an expansive design space, exhibiting significantly different optical^{9–11} (and electronic) properties from their 3D counterparts. In this Letter, we identify energy constraints embedded within Maxwell’s equations that impose theoretical bounds on the largest optical response that can be generated in any 2D material, in the near or far field. The bounds account for material loss as encoded in the real part of a material’s conductivity (in the case of a spatially local conductivity tensor σ , they are proportional to $\|\sigma^{\dagger}(\text{Re } \sigma)^{-1}\sigma\|$ and are otherwise independent of shape and configuration. We derive the bounds through convex constraints imposed by the optical theorem^{12–14} and its near-field analogue, leveraging a recent approach we developed for spatially local 3D materials.¹⁵ In addition to accommodating nonlocal models, this work demonstrates starkly different near-field dependencies of 2D and 3D materials. For graphene, the 2D material of foremost interest to date, the bounds bifurcate into distinctive low- and high-energy regimes: the low-energy bounds are proportional to the Fermi level, whereas the high-energy bounds are proportional to the fine-structure constant, α , for any geometrical configuration. We find that far-field bounds on the extinction cross-section can be approached by elliptical

graphene disks, whereas the near-field bounds on the local density of states^{16–20} and radiative heat transfer rate^{21–26} cannot be approached in prototypical flat-sheet configurations. The bounds presented here provide a simple material figure-of-merit (FOM) to evaluate the emerging zoo of 2D materials and offer the prospect of greater optical response via computational design. The material figure-of-merit can guide ongoing efforts in 2D-material discovery, while the general bounds can shape and drive efforts toward new levels of performance and better optical components.

Plasmonics in 2D materials opens the possibility for stronger light–matter interactions, which may be useful for technological applications, including single-molecule imaging^{27–30} and photovoltaics,^{31,32} as well as for basic-science discoveries, such as revealing forbidden transitions,³³ and achieving unity optical absorption in graphene through optical impedance matching.^{5,34–36} Theoretical work toward understanding optical response in 2D materials has focused on analytical expressions using specific geometrical^{5,9,37} or metamaterial-based³⁸ models but from a design perspective such assumptions are restrictive.

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Quasistatic sum rules can yield upper limits on the cross-section,^{39,40} but have been restricted to far-field quantities and isotropic and spatially local materials. A well-known microwave-engineering bound, known as Rozanov's theorem,⁴¹ offers a bandwidth limit as a function of material thickness, but its contour-integral approach requires perfectly conducting boundaries that are not applicable for 2D materials at optical frequencies. Here, we find constraints that do yield 2D-material optical-response bounds given only the material properties. We provide a general framework to derive limits to any optical-response quantity (including cross sections, spontaneous-emission enhancements, and radiative-heat exchange), and we present computational results suggesting pathways to approach the new bounds. For a broad class of hydrodynamic nonlocal-conductivity models,^{42,43} which capture several important nonclassical features at length scales approaching the quantum regime, we derive general bounds in terms of a constitutive-relation operator. We show that the nonlocal response is necessarily bounded above by the local-response bounds; further, by exploiting the quasistatic nature of interactions at nonlocal length scales, we show that the maximum response must be reduced in proportion to a ratio of the scatterer size to the effective "diffusion" length.

To derive general scattering bounds, consider a 2D scatterer embedded in a possibly heterogeneous background. Passivity, which implies the absence of gain and that polarization currents do no work,⁴⁴ requires that the powers absorbed (P_{abs}) and scattered (P_{scat}) by the target body are non-negative.¹⁵ These almost tautological conditions in fact dictate bounds on the largest currents that can be excited at the surface of any 2D structure. The key is that their sum, extinction ($P_{\text{ext}} = P_{\text{abs}} + P_{\text{scat}}$), is given by the imaginary part of a forward-scattering amplitude, which is a well-known consequence of the optical theorem.^{12–14} For an arbitrarily shaped 2D scatterer with area A that supports electric surface currents \mathbf{K} (a magnetic-current generalization is given in the Supporting Information), the absorbed and extinguished powers are given by^{13,45}

$$P_{\text{abs}} = \frac{1}{2} \text{Re} \int_A \mathbf{E}^* \cdot \mathbf{K} \, dA \quad (1a)$$

$$P_{\text{ext}} = \frac{1}{2} \text{Re} \int_A \mathbf{E}_{\text{inc}}^* \cdot \mathbf{K} \, dA \quad (1b)$$

where, in the latter expression, $\int_A \mathbf{E}_{\text{inc}}^* \cdot \mathbf{K} \, dA$ is a forward-scattering amplitude. A key feature of the optical theorem is that the extinction is the real part of an *amplitude*, which is linear in the induced currents. By contrast, absorption is a *quadratic* function of the currents/fields. Yet extinction must be greater than absorption (due to the $P_{\text{scat}} \geq 0$ condition noted above), requiring the linear functional to be greater than the quadratic one, a condition that cannot be satisfied for large enough currents. The inequality $P_{\text{abs}} \leq P_{\text{ext}}$ thereby provides a convex constraint for any optical-response function. Any optical-response maximization can thus be formulated as an optimization problem subject to this convex passivity constraint.¹⁵ For a generic figure-of-merit $f(\mathbf{E})$ of the fields (or, equivalently, currents), the design problem can be written

$$\begin{aligned} &\text{maximize } f(\mathbf{E}) \\ &\text{subject to } P_{\text{abs}}(\mathbf{E}) \leq P_{\text{ext}}(\mathbf{E}) \end{aligned} \quad (2)$$

Thanks to the convex nature of the constraint $P_{\text{abs}} \leq P_{\text{ext}}$ and the simple expressions for P_{abs} and P_{ext} , eq 2 can often be solved

analytically, unlike the highly nonconvex Maxwell equations, thereby providing general upper-bound expressions without approximation.

To find bounds that solve eq 2, we must specify a relationship between the field \mathbf{E} and the induced current \mathbf{K} . To maintain generality, we assume only that they are related by a linear operator \mathcal{L} ,

$$\mathcal{L}\mathbf{K} = \mathbf{E} \quad (3)$$

where in different size, material, and parameter regimes, \mathcal{L} may represent anything from a density-functional-theory operator⁴⁶ or a hydrodynamic model^{43,47} to a simple scalar conductivity. For a scalar conductivity σ , $\mathcal{L} = 1/\sigma$. Given this current–field relation, the quadratic dependence of absorption on induced current, per eq 1a, is made explicit: $P_{\text{abs}} = (1/2) \text{Re} \int_A \mathbf{K}^* \cdot \mathcal{L}\mathbf{K} \, dA$. If we choose the figure of merit to be the absorbed or scattered power, then straightforward variational calculus (see Supporting Information) from eq 2 yields the bounds

$$P_{\alpha} \leq \frac{1}{2} \beta_{\alpha} \int_A \mathbf{E}_{\text{inc}}^* \cdot (\text{Re } \mathcal{L})^{-1} \mathbf{E}_{\text{inc}} \, dA \quad (4)$$

where α denotes absorption, scattering, or extinction. The variable β takes the values

$$\beta_{\alpha} = \begin{cases} 1, & \alpha = \text{absorption or extinction} \\ \frac{1}{4}, & \alpha = \text{scattering} \end{cases} \quad (5)$$

which represent a power-balance asymmetry: absorption and extinction are maximized when $P_{\text{abs}} = P_{\text{ext}}$, whereas scattering is maximized when $P_{\text{scat}} = P_{\text{abs}} = P_{\text{ext}}/2$, akin to conjugate-matching conditions in circuit theory.⁴⁸ Equation 4 sets a general bound at any frequency given only the incident field and the (material-driven) field–current relationship, dictated by the operator \mathcal{L} . The bounds apply in the far field, where \mathbf{E}_{inc} might be a plane wave or Bessel beam, as well as the near field, where \mathbf{E}_{inc} might be the field emanating from dipolar sources. Further below, we show that $(\text{Re } \mathcal{L})^{-1}$ can be considerably simplified in the case when \mathcal{L} is the differential operator arising in nonlocal hydrodynamic models. First, however, we simplify eq 4 for the important case of a spatially local conductivity.

A local conductivity σ , relating currents at any point on the surface to fields at the same point, by $\mathbf{K} = \sigma\mathbf{E}$, is the primary response model employed in the study of optical and plasmonic phenomena, in two as well as three dimensions. In 2D materials, it is common to have off-diagonal contributions to the conductivity (e.g., through magnetic-field biasing), and thus we allow σ to be a general 2×2 matrix (implicitly restricting \mathbf{E} to its two components locally tangential to the 2D surface). Given that $\mathcal{L} = \sigma^{-1}$, the term involving \mathcal{L} in the bound of eq 4 can be written: $(\text{Re } \mathcal{L})^{-1} = \sigma^{\dagger} (\text{Re } \sigma)^{-1} \sigma$. In far-field scattering, the quantity of interest is typically not the total absorbed or scattered power, but rather the cross-section, defined as the ratio of the power to the average beam intensity. The scattering cross-section, for example, is given by $\sigma_{\text{scat}} = P_{\text{scat}}/I_{\text{inc}}$, where $I_{\text{inc}} = |\mathbf{E}_{\text{inc}}|_{\text{avg}}^2/2Z_0$. Then, the bound of eq 4 simplifies for the absorption, scattering, and extinction cross sections to

$$\frac{\sigma_{\alpha}}{A} \leq \beta_{\alpha} Z_0 \left\| \sigma^{\dagger} (\text{Re } \sigma)^{-1} \sigma \right\|_2 \quad (6)$$

where Z_0 is the impedance of free space, β_α is defined above in eq 5, and $\|\cdot\|_2$ denotes the induced matrix 2-norm⁴⁹ (which is the largest singular value of the matrix). The power of eq 6 is its simplicity—the scattering efficiency of any 2D scatterer, whether it is a periodic array of circles,⁵ a spherical coating,⁵⁰ an isolated strip,³⁷ or in any other configuration, has an upper bound defined solely by its material conductivity. We show below that simple ellipses can approach within $\approx 10\%$ of the bounds, and that structures with two additional degrees of freedom can approach within $< 1\%$ of the bounds.

A key feature of the approach outlined here is that the optical response of a 2D material of interest can be cleanly delineated (without approximation) from the response of any “background” structures. Our formulation relies on the passivity constraints $P_{\text{scat}}, P_{\text{abs}} > 0$, and yet the choice of “incident” and “scattered” fields is arbitrary, as long as they sum to the total fields. As an example, there is significant interest in integrating 2D materials with photonic crystals;^{6,7} we can define the incident field that controls the bounds in eqs 4 and 6 as the field in the presence of only the photonic crystal, and the scattered field as arising only from the addition of the 2D layer above it. The limits of eqs 4 and 6, as well as the limits derived below, then capture the maximum achievable enhancement due to the 2D material itself, subject to its inhomogeneous environment. Throughout this Letter, we focus on free-standing graphene to understand its unique optical response, noting that generalization involving substrates and more complex surrounding structures can follow precisely this prescription.

Near-field optical response in the presence of nearby emitters is at least as important as far-field response. Here we find bounds to two important near-field quantities: (i) the local density of states (LDOS), which is a measure of the spontaneous-emission rate of a single excited dipole near the scatterer, and (ii) near-field radiative heat transfer, which is a measure of the radiation exchange between two bodies at different temperatures. The (electric) LDOS at a point \mathbf{x} is proportional to the power radiated by an (orientation-averaged) electric dipole at that point and is given by the expression $\rho = (1/\pi\omega)\text{Im}\sum_j \mathbf{p}_j \cdot \mathbf{E}_j(\mathbf{x})$, where \mathbf{E}_j is the electric field excited by the dipole with moment \mathbf{p}_j , and where the sum over $j = x, y, z$ accounts for orientation averaging.¹⁶ The expression for ρ shows that LDOS is dictated by a causal amplitude (not a squared amplitude), exhibiting similar mathematical structure to extinction. The source of the similarity is that both extinction and LDOS can be decomposed into radiative and nonradiative components, which for the LDOS we denote by ρ_{rad} and ρ_{nr} , respectively. The nonradiative part of the LDOS is given by the absorption in the scattering body (which is often an antenna), and per eq 1a is quadratic in the induced currents. Unlike far-field scattering, in the near field the incident field increases rapidly at smaller distances ($|\mathbf{E}| \sim 1/d^3$). Thus, the same convex-optimization problem laid out in eq 2 leads to distance-dependent LDOS bounds via the replacements $P_{\text{ext}} \rightarrow \rho$ and $P_{\text{abs}} \rightarrow \rho_{\text{nr}}$. For an arbitrarily shaped 2D surface separated from the emitter by some minimum distance d , the bounds are (Supporting Information)

$$\frac{\rho_\alpha}{\rho_0} \leq \frac{3\beta_\alpha}{8(k_0d)^4} Z_0^2 \left\| \sigma^\dagger (\text{Re } \sigma)^{-1} \sigma \right\|_2 \quad (7)$$

where α in this context denotes the total, radiative, or nonradiative component of the LDOS, $k_0 = \omega/c$, and ρ_0 is the free-space electric-dipole LDOS, $\rho_0 = \omega^2/2\pi^2c^3$. Again β_α

represents a power-balance (conjugate-matching) condition and takes the value 1 for nonradiative or total LDOS and 1/4 for the radiative LDOS. Equation 7 includes the highest-order ($\sim 1/d^3$) term from the incident electric field; lower-order terms ($\sim 1/d^2, 1/d$) are generally negligible in the high-enhancement regimes of interest, as discussed quantitatively in ref 15. The 3/8 coefficient in eq 7 is for the common case in which the surface is separated from the emitter by a separating plane; if the scattering body surrounds the emitter across a solid angle Ω , the bound in eq 7 is multiplied by 4Ω . Equation 7 provides a general answer to the question of how efficient and effective a 2D optical antenna can be.

Radiative heat transfer (RHT), in which a warm body transfers energy to a colder one via photon exchange, is also subject to optical-response bounds. It has long been known^{21–23} that near-field RHT can surpass the blackbody limit, as evanescent tunneling can outpace radiative exchange. Yet general limits to the process in conventional 3D materials had been unknown until our recent work.⁵¹ The total RHT rate, H , is given by the net flux from one body at temperature T_1 to another at temperature T_2 , typically expressed as (ref 25) $H_{1 \rightarrow 2} = \int_0^\infty \Phi(\omega) [\Theta(\omega, T_1) - \Theta(\omega, T_2)] d\omega$, where $\Phi(\omega)$ is a temperature-independent energy flux and Θ is the Planck spectrum. The flux Φ is the power absorbed by the second body, having been emitted from the first, such that it is similar to the scattering problem bounded by eq 6. A key distinction is that the (incoherent) sources are in the interior of one of the scattering bodies, invalidating the conventional optical theorem. This difficulty can be circumvented by breaking the flux transfer into two scattering problems, connected by a generalized⁵² reciprocity relation (the material conductivity does not need to be reciprocal), as outlined in ref 51. The key distinction in the case of 2D materials is the dimensionality of the domain over which the field intensities are evaluated, which for bodies with identical conductivities σ leads to the bound

$$\frac{\Phi}{\Phi_{\text{BB}}} \leq \frac{3}{2(k_0d)^4} Z_0^2 \left\| \sigma^\dagger (\text{Re } \sigma)^{-1} \sigma \right\|_2^2 \quad (8)$$

where d is the minimum separation distance between the arbitrarily shaped bodies, $\Phi_{\text{BB}} = k_0^2 A / 4\pi^2$ is the blackbody limit (for infinite area A),²⁵ and the conductivity term is squared due to potential contributions from each body (see Supporting Information). As for the LDOS bounds, eq 8 assumes a separating plane between the bodies; corrugated surfaces that are interlaced (but nontouching) have bounds of the same functional form but with different numerical prefactors. An interesting 2D-specific aspect of eqs 7 and 8 is that they exhibit identical $1/d^4$ distance dependencies, whereas for 3D bodies, RHT increases more slowly for smaller separations ($\sim 1/d^2$) than does the LDOS ($\sim 1/d^3$).

The fundamental limits of eqs 6–8 share a common dimensionless material “figure of merit” (FOM), $Z_0 \|\sigma^\dagger (\text{Re } \sigma)^{-1} \sigma\|_2$. The FOM, which simplifies to $Z_0 \sigma^2 / \text{Re } \sigma$ for a scalar conductivity, captures the intrinsic trade-offs between high conductivity for large response and high losses that dissipate enhancement, and can be used to identify optimal materials. In Figure 1, we plot the FOM across a range of frequencies, using experimentally measured or analytically modeled material data for common 2D materials of interest: graphene, for various Fermi levels,⁵³ magnetic biasing,⁵⁴ and AA-type bilayer stacking⁵⁵ (at 300 K), hBN,⁵⁶ MoS₂,⁵⁷ black phosphorous (BP),¹¹ Bi₂Se₃ (at THz frequencies⁵⁸), and

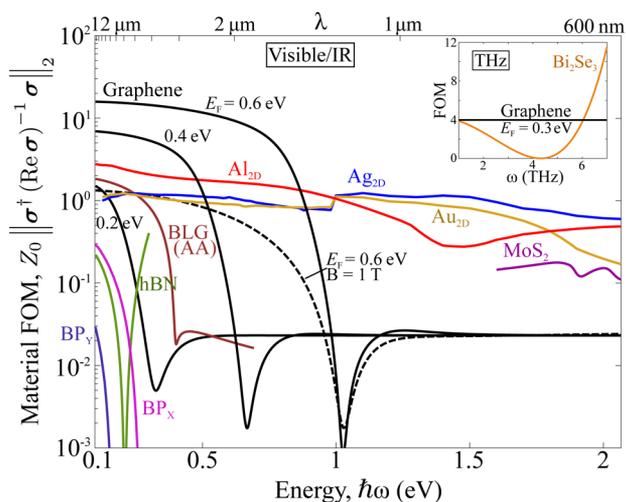


Figure 1. A simple material FOM, $Z_0 \|\sigma^\dagger(\text{Re } \sigma)^{-1} \sigma\|_2$ for conductivity σ , dictates the maximum optical response that can be generated in 2D materials. Experimentally tabulated or analytically modeled optical data can be compared to assess optimal materials as they emerge. Here, we compare: graphene at different Fermi levels (solid black lines) and magnetic-biasing (dashed black line), AA-stacked bilayer graphene (dark red), hBN (green), MoS₂ (purple), the anisotropic conductivity components of black phosphorus (BP, pink and dark purple), and three 2D metals, Al (red), Ag (blue), and Au (gold). High-Fermi-level graphene and 2D silver offer the largest possible responses at infrared and visible wavelengths, respectively. The inset compares graphene at THz frequencies to the topological insulator Bi₂Se₃, which can have a surprisingly large FOM.

metals Ag, Al, and Au, all taken to have 2D conductivities dictated by a combination³⁹ of their bulk properties and their interlayer atomic spacing. Strongly doped graphene ($E_F = 0.6$ eV) offers the largest possible response across the infrared, whereas 2D Ag tends to be better in the visible. At terahertz (THz) frequencies, where graphene's potential is well-understood,^{59–61} the topological insulator Bi₂Se₃ shows promise for even larger response. More broadly, the simple material FOM, $\|\sigma^\dagger(\text{Re } \sigma)^{-1} \sigma\|_2$ or its anisotropic generalization $\|\sigma^\dagger(\text{Re } \sigma)^{-1} \sigma\|_2$, offers a metric for evaluating emerging (e.g., silicene,⁶² phosphorene^{63,64}) and yet-to-be-discovered 2D materials.

In the following we specialize our considerations to graphene, the standard-bearer for 2D materials, to examine the degree to which the bounds of eqs 6–8 can be attained in specific structures. We adopt the conventional local description, including intra- and interband dispersion. Appropriate modifications^{37,53} are included to account for a finite intrinsic damping rate, $\gamma = 1/\tau = (10^{12} \text{ eV/s})/E_F$, which is taken as Fermi-level-dependent (corresponding to a Fermi-level-independent mobility), with a magnitude mirroring that which was adopted in ref 37. Figure 2 shows the cross-section bounds (dashed lines), per eq 6, alongside graphene disks (with $E_F = 0.4$ eV) that approach the bounds at frequencies across the infrared. For simplicity, we fix the aspect ratio of the disks at 2:1 and simply reduce their size to increase their resonant frequency; each disk achieves $\approx 85\%$ of its extinction cross-section bound. The disk diameters are kept greater than 10 nm to ensure the validity of our local description. We employ a fast quasistatic solver⁶⁵ to compute the response of the ellipses, which is verified with a free-software implementation⁶⁶ of the boundary element method (BEM)⁶⁷ for the full electrodynamic problem with the surface conductivity incorporated as a

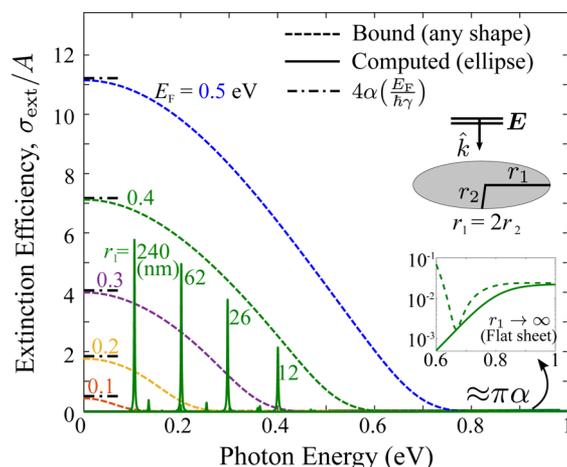


Figure 2. Upper limits (dashed lines) to the extinction cross-section of graphene scatterers of varying Fermi level, patterned into any shape, alongside the computed response of elliptical graphene disks of varying sizes for $E_F = 0.4$ eV (green, solid). The bounds, per eq 6, depend on graphene's 2D conductivity and incorporate the extent to which losses can be overcome. The disks reach within $\approx 85\%$ of the bounds, and in the Supporting Information we show that slightly more exotic shapes can reach $>99\%$ of the bounds. Simple asymptotic expressions for the bounds emerge at low (dash-dot lines) and high frequencies. In the high-frequency limit, the limits converge to $\pi\alpha$ and are thereby reached with a simple flat sheet (inset).

modified boundary condition.⁴⁵ If edge scattering, or any other defect, were to increase the damping rate, such an increase could be seamlessly incorporated in the bounds of eqs 6–8 through direct modification of the conductivity. In the Supporting Information, we show that with two extra geometrical degrees of freedom (e.g., a “pinched ellipse”), one can reach $>99.6\%$ of the bound. The cross-section bounds can also be used as bounds on the fill fraction of graphene required for perfect absorption in a planar arrangement, and they suggest the potential for an order-of-magnitude reduction relative to the best known results.⁵ Conversely, such room for improvement could be used to significantly increase the perfect-absorption bandwidth beyond the modern state-of-the-art.

The bounds simplify analytically at the low- and high-frequency extremes. In these regimes, graphene's isotropic conductivity is real-valued and comprises simple material and fundamental constants, such that the material FOM is approximatel

$$Z_0 \|\sigma^\dagger(\text{Re } \sigma)^{-1} \sigma\|_2 \approx Z_0 \sigma \approx \begin{cases} 4\alpha \left(\frac{E_F}{\hbar\gamma} \right) & \omega \ll \gamma \\ \pi\alpha & \omega \gg 2E_F/\hbar \end{cases} \quad (9)$$

The low-frequency proportionality to $E_F/\hbar\gamma$ arises as a consequence of the intraband contributions to the conductivity in contrast to the interband dominance at high frequencies. Interband contributions to the conductivity are often ignored at energies below the Fermi level, but even at those energies they are responsible for a sizable fraction of the loss rate, thus causing the quadratic roll-off (derived in Supporting Information) of the maximum efficiency seen on the left-hand side of Figure 2.

Famously, at high frequencies a uniform sheet of graphene has a scattering efficiency $\sigma/A \approx \pi\alpha$ (refs 68–70). Interestingly,

Figure 2 and eq 9 reveal that $\pi\alpha$ is the *largest possible* scattering efficiency for *any* shape or configuration of graphene at those frequencies. Per the incident-field discussion above, it is possible to increase the absolute absorption of a plane wave at those frequencies by structuring the background (e.g., with a photonic-crystal slab supporting the graphene), but the percentage of the background field intensity that can be absorbed by the graphene is necessarily $\leq \pi\alpha$, no matter how the graphene is structured. The right-hand side of Figure 2 shows the bounds for each Fermi level converging to $\pi\alpha$, with the inset magnifying the high-energy region and showing that the response of a flat sheet indeed reaches the bound.

The near-field LDOS and RHT limits are more challenging to attain. We study the LDOS near a flat sheet of graphene, the most common 2D platform for spontaneous-emission enhancements to date,^{9,71,72} and show that there is a large performance gap between the flat-sheet response and the fundamental limits of eq 7. There are two key factors that control the near-field bounds (for both LDOS and RHT): the material FOM $|\sigma|^2/\text{Re } \sigma$, and a “near-field enhancement factor” $1/d^4$, for emitter–sheet distance d . The $1/d^4$ near-field enhancement factor is particularly interesting, because it increases more rapidly than in 3D materials (for which the LDOS¹⁵ and RHT⁵¹ bounds scale as $1/d^3$ and $1/d^2$, respectively). In Figure 3, we show the

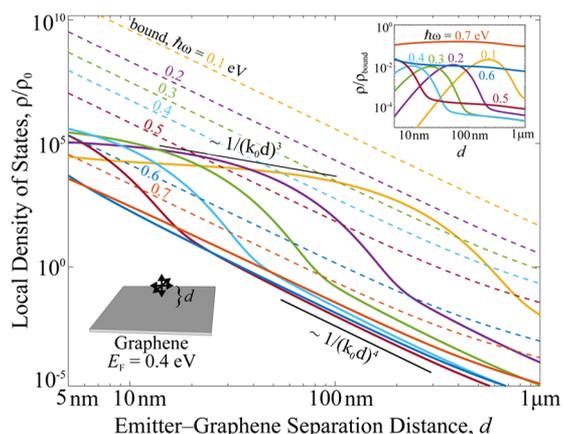


Figure 3. Comparison of the LDOS above a flat graphene sheet (dashed lines) to the LDOS bounds for any structure (solid lines), for multiple frequencies (colored lines) and as a function of the emitter–graphene separation distance d (with $E_F = 0.4$ eV). For larger separations and higher frequencies, the LDOS above a flat sheet follows the ideal $\sim 1/d^4$ scaling, but at shorter separations and lower frequencies (where the response is potentially largest), the optimal-frequency response follows a $\sim 1/d^3$ envelope. The inset shows the ratio of the flat-sheet LDOS to the upper bound, showing that there is the potential for 1–2 orders of magnitude improvement.

LDOS as a function of the emitter–graphene separation, for a fixed Fermi level $E_F = 0.4$ eV and a range of frequencies (colored solid lines). The bounds for each frequency are shown in the colored dashed lines, and the ratio of the LDOS ρ to the LDOS bound ρ_{bound} is shown in the inset. For low and moderate frequencies, there is an ideal distance at which the LDOS most closely approaches its frequency-dependent bound, whereas the high-frequency regime (e.g., $\hbar\omega = 0.7$ eV) is almost distance-insensitive due to high losses.

Figure 3 shows two asymptotic distance-scaling trends. First, at high frequencies and/or large separations (50 nm to 1 μm), the LDOS enhancement scales as $1/(k_0d)^4$. We show in the

Supporting Information that in this regime the LDOS further exhibits the material-enhancement factor $|\sigma|^2/\text{Re } \sigma$, falling short of the bound only by a factor of 2. In this regime, the LDOS is dominated by a “lossy-background” contribution,⁷¹ which is insensitive to details of the plasmonic mode, and due instead predominantly to interband absorption in graphene (permitted even below $2E_F$ for nonzero temperatures). Of more interest may be the opposite regime, higher frequencies at smaller separations, which are known⁷³ to have reduced distance dependencies. It is crucial to note that the bounds presented in this Letter are not scaling laws; instead, at each frequency and distance they represent independent response limits. We see in Figure 3 that for each individual frequency, ρ/ρ_0 flattens toward a constant value at very small distances, because the corresponding plasmon surface-parallel wavenumber is smaller than $1/d$ and does not change; however, the envelope formed over many frequencies (for a given separation d) shows a $1/(k_0d)^3$ dependence as higher-wavenumber plasmons are accessed at smaller distances. This suggests a simple potential approach to reach the bound: instead of finding a geometrical configuration that approaches the bound at all frequencies and separations, concentrate on finding a structure that reaches the bound at a single frequency and separation of interest. A “family” of structures that combine to approach the bounds over a large parameter regime may then naturally emerge.

Near-field RHT shows similar characteristics, in which the bounds may be approached with flat graphene sheets at specific energy, Fermi-level, and separation-distance parameter combinations. As a counterpart to the LDOS representation of Figure 3, in Figure 4 we fix the separation distance at 10 nm and plot

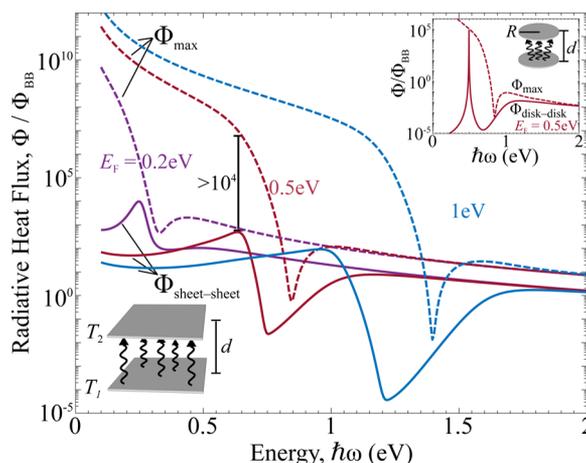


Figure 4. Radiative heat flux between two graphene structures (at $T = 300$ K and $d = 10$ nm) for flat sheets (solid lines) and for the arbitrary-shape analytical bounds (dotted lines). For a Fermi level 0.5 eV, the flat sheets fall short of the bounds by 10^4 at their peak due to near-field interference effects between the sheets. The interference effects do not arise between dipolar circles (inset), whereby the bound is nearly achieved (for $R = 5$ nm and $d = 30$ nm). The discrepancy between the disk and flat-sheet RHT rates suggests the possibility of significant improvement via patterning.

the frequency-dependent RHT⁷⁴ for three Fermi levels. The respective bounds, from eq 8, show the same “dip” as seen in the inset of Figure 2, which occurs at the frequency where the imaginary part of the conductivity crosses zero. At these frequencies, the RHT between flat sheets can approach the bounds. However, at other frequencies where the potential

RHT is significantly larger, the flat sheets fall short by orders of magnitude, as depicted in Figure 4 at $E_F = 0.5$ eV. The flat-sheet case falls short due to near-field interference effects: as the sheets approach each other, the plasmonic modes at each interface interact with each other, creating a level-splitting effect that reduces their maximum transmission to only a narrow band of wavevectors.¹⁵ By contrast, for two dipolar circles in a quasistatic approximation (Figure 4 inset), the RHT between the two bodies can approach its respective bound. These examples suggest that patterned graphene sheets, designed to control and optimize their two-body interference patterns, represent a promising approach toward reaching the bounds and thereby unprecedented levels of radiative heat transfer. In the Supporting Information, we show that achieving RHT at the level of the bound, even over the narrow bandwidths associated with plasmonic resonances, would enable radiative transfer to be greater than conductive transfer through air at separations of almost 1 μm , significantly larger than is currently possible.¹⁵

Having examined the response of graphene structures in the local-conductivity approximation, we now reconsider nonlocal conductivity models. For structures in the 2–10 nm size range, below the local-conductivity regime but large enough to not necessitate fully quantum-mechanical models, hydrodynamic conductivity equations,^{42,43,47} or similar gradient-based models of nonlocality,^{54,75} can provide an improved account of the optical response. In a hydrodynamic model, the currents behave akin to fluids with a diffusion constant D and convection constant β (both real-valued) with a current–field relation given by⁴³

$$\underbrace{\left[\frac{-i}{\epsilon_0 \omega \omega_p^2} (\beta^2 + D(\gamma - i\omega)) \nabla \nabla \cdot + \sigma_{\text{loc}}^{-1} \right]}_{\mathcal{L}} \mathbf{K} = \mathbf{E} \quad (10)$$

where σ_{loc} , ω_p , and γ are the local conductivity, plasma frequency, and damping rate of the 2D material, respectively. Per eq 4, the 2D-material response bounds depend only on the Hermitian part of the \mathcal{L} operator, denoted by an underline in eq 10. Before deriving bounds dependent on the hydrodynamic parameters, we note that the grad–div hydrodynamic term in eq 10 cannot increase the maximum optical response. The operator $-\nabla \nabla \cdot$ is a positive semidefinite Hermitian operator (for the usual L^2 -space overlap-integral inner product), shown by integration by parts in conjunction with the no-spillover boundary condition. The Hermiticity of the grad–div operator means that the Hermitian part of \mathcal{L} is given by $\text{Re } \mathcal{L} = (\mathcal{L} + \mathcal{L}^\dagger)/2 = -\frac{D}{\omega_p^2} \nabla \nabla \cdot + \text{Re } \sigma_{\text{loc}}^{-1}$. Because $-\nabla \nabla \cdot$ is a positive-semidefinite addition to the positive-semidefinite term $\text{Re } \sigma_{\text{loc}}^{-1}$, $\|(\text{Re } \mathcal{L})^{-1}\| \leq (\text{Re } \sigma_{\text{loc}}^{-1})^{-1} = |\sigma_{\text{loc}}|^2 / \text{Re } \sigma_{\text{loc}}$. Thus, the nonlocal response is subject to the bound imposed by the underlying local conductivity, demonstrating that nonlocal effects of this type cannot surpass the local-conductivity response explored in depth above.

We can further show that hydrodynamic nonlocality necessarily reduces the maximum achievable optical response in a given 2D material, by exploiting the quasistatic nature of electromagnetic interactions at the length scales for which nonlocal effects manifest. The key insight required to derive bounds subject to the nonlocal current–field relation, eq 10, is that the absorbed power can be written as a quadratic form of

both the currents \mathbf{K} as well as $\nabla \cdot \mathbf{K}$ (proportional to the induced charge): $P_{\text{abs}} = (1/2) \text{Re} \int_A \mathbf{K}^* \cdot \mathbf{E} = 1/2 \int_A [a (\nabla \cdot \mathbf{K}^*) (\nabla \cdot \mathbf{K}) + b \mathbf{K}^* \cdot \mathbf{K}]$, where $a = D/\omega_p^2$ and $b = \text{Re}(\sigma_{\text{loc}}^{-1})$. Similarly, the extinction can be written as a linear function of either \mathbf{K} or $\nabla \cdot \mathbf{K}$ (exploiting the quasistatic nature of the fields), such that $P_{\text{abs}} \leq P_{\text{ext}}$ offers two convex constraints for the generalized nonlocal-conductivity problem. We defer to the Supporting Information for a detailed derivation of general figures of merit under this constraint, and state a simplified version of the result for the extinction cross-section. The additional $\nabla \cdot \mathbf{K}$ constraint introduces a size dependence in the bound, in the form of a “radius” r that is the smallest bounding sphere of the scatterer along the direction of the incident-field polarization. Defining a plasmonic “diffusion” length $l_D = \sqrt{cD/\omega_p^2}$ (for speed of light c), the variational-calculus approach outlined above yields an analogue of eq 6 in the presence of a hydrodynamic nonlocality

$$\frac{\sigma_{\text{ext}}}{A} \leq \left[\left(Z_0 \frac{|\sigma_{\text{loc}}|^2}{\text{Re } \sigma_{\text{loc}}} \right)^{-1} + \left(\frac{r^2}{l_D^2} \right)^{-1} \right]^{-1} \quad (11)$$

Equation 11 has an appealing, intuitive interpretation: the cross-section of a scatterer is bounded above by a combination of the local-conductivity bound and a nonlocal contribution proportional to the square of the ratio of the size of the scatterer to the “diffusion” length. Thus, as the size of the particle approaches l_D , and goes below it, there must be a significant reduction in the maximal attainable optical response. There is ambiguity as to what the exact value of D , or equivalently l_D , should be in 2D materials such as graphene; the bounds developed serve as an impetus for future measurement or simulation, to delineate the sizes at which the local/nonlocal transition occurs. Conversely, because the bound shows a dramatic reduction at sizes below l_D , eq 11 can serve as a means to extract this nonlocal property of any 2D material from experimental measurements.

General limits serve to contextualize a large design space, pointing toward phenomena and performance levels that may be possible and clarifying basic limiting factors. Here we have presented a set of optical-response bounds for 2D materials, generalizing recent 3D-material bounds^{15,51} to incorporate both local and nonlocal models of 2D conductivities. We further studied the response of standard graphene structures, ellipses and sheets, relative to their respective bounds, showing that the far-field absorption efficiency bounds can be reliably approached within 10%, but that the near-field bounds are approached only in specific parameter regimes, suggesting the possibility for design to enable new levels of response. The figure of merit $\|\sigma^\dagger (\text{Re } \sigma)^{-1} \sigma\|$ can serve to evaluate new 2D materials as they are discovered, and their optical properties are measured. Our results point to a few directions where future work may further clarify the landscape for 2D-material optics. One topic of current interest is in patterned gain and loss^{76,77} (esp. \mathcal{PT} -symmetry^{78–80}), which exhibits a variety of novel behaviors, from exceptional points to loss-induced transparency. Our bounds depend on passivity, which excludes gain materials, but in fact the bounds only require passivity on average, that is, averaged over the structure. Thus, eqs 4–8 should be extensible to patterned gain–loss structures. A second area for future work is in exploration of quantum models of the \mathcal{L} operator. We have shown here explicit bounds for the cases of local and hydrodynamic conductivities, but there is also significant interest in quantum descriptions of the

response. Through, for example, density functional theory,⁸¹ analytical bounds in such cases may lead to a continuum of optical-response limits across classical, semiclassical, and quantum regimes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b02007.

Optimized structure to reach within 1% of extinction bound; optimal conductive heat transfer through graphene; graphene material gure of merit: second-order approximation; variational-calculus derivation of upper bounds; bounds in the presence of hydrodynamic nonlocality; LDOS above a planar conducting sheet (PDF)

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Notes

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