Material-dictated upper bounds for scattering response in linear systems

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The design challenge:

Lots of degrees of freedom in geometry, but what structure is best for given device & materials?

And what performance & phenomena are possible?

Limits on what is possible

Typically, we know the materials, but don't know the structure, so geometry-independent limits on engineering performance are especially useful in guiding design:

- How strongly/quickly can light be absorbed, scattered, transmitted?
- How efficiently can energy be converted from one form to another?

 e.g. between different frequencies, radiation from heat, radiation from excited electrons (spontaneous emission)
- How long can light be stored in a given volume?
- What is the interplay with bandwidth, material loss, volume?

Example: Yablonovitch limit

E. Yablonovitch, "Statistical Ray Optics" [JOSA 72, 899 (1982)]

Enhancing the absorption efficiency of a thin film (e.g. solar cell):





single-pass absorptivity $A \ll 1$ texture+mirror absorptivity $\leq 4n^2A$

Derived under very restrictive assumptions (originally ray optics!), but has been very hard to beat (and nearly tight) in practical structures.

Other examples

- Wheeler–Chu bounds on antenna quality factor Q (per volume)
- Wiener (1912), Hashin–Shtrikman (1963), Bergman (1981), Milton (1981), bounds on homogenized properties of composites
- Black-body limit on thermal radiation (in far field for linear and/or equilibrium surface)
- Manley–Rowe limits to nonlinear frequency conversion
- Speed-of-light (c) limit on energy transport

Geometry-*dependent, material-independent* limits



 Spherical scatterers: Hamam et al. PRA 75, 053801 (2007)

 Ruan & Fan APL 98, 43101 (2011)

 Generic scatterers:
 Kwon & Pozar IEEE TAP 57, 3720 (2009)

 Liberal et al. IEEE TAP 62, 4726 (2014)

scattered power $\leq O(N^2)$

where N = # multipole orders that can be excited

... depends non-trivially on shape

(N ~ diameter as size $\rightarrow \infty$) but not on the materials!

JP Hugonin et al., *PRB* 91, 180202 (2015) scattered, absorbed power $\leq \langle \mathbf{E}_{inc}, (\text{Im } \mathbf{G}_0^*)^{-1} \mathbf{E}_{inc} \rangle_{\Omega}$

where G_0 is vacuum Green's function — depends on shape Ω but not materials!

New results

[O. D. Miller et al., PRL 115, 204302 (2015) & Opt. Exp. 24, 3329 (2016)]

- Limits on scattering & absorption by particles, on the local density of states, and also on near-field thermal radiation
- Very general, simple derivations from energy conservation & optical theorem
- Independent of geometry and bandwidth, depend only on the materials
- ~Tight (within a small constant factor) in many cases ... all?



continuum, local, linear materials: 6x6 susceptibility $\chi(x,t)$ (breaks down for metals at < 10nm scales \Rightarrow nonlocal; or very strong fields \Rightarrow nonlinear)

frequency domain:
$$\frac{\partial}{\partial t} \rightarrow -i\omega$$

passive materials: $\omega \operatorname{Im} \chi(x, \omega) > 0$

i.e., polarization currents can dissipate but not supply energy

Starting Problem: Obscurant Nanoparticles



Related applications: cancer therapy solar cells





JACS 128, 2115 (2006) Nat. Phot. 9, 205 (2010)



Key question: What is the best σ_{ext} / volume? ... averaged incident angles & polarizations ... (over some bandwidth)

A rapidly growing experimental toolkit...



C. Mirkin et. al., JACS 134, 14542 (2012)



Y. Xia et. al. ACIE 48, 60 (2009)

...with only limited theoretical designs



Size $\ll \lambda$ Qiu, DeLacy Johnson, Joannopoulos, & Soljacic, Opt. Exp. 20, 18494 (2012)



Fan et. al. PRL 105, 13901 (2010) APL 98, 43101 (2011) to start with: computational exploration of non-spherical shapes

"Warmup" problem: Optimizing Ag ellipsoids



boundary-element method



nonlinear optimization



complex-w transformation Hashemi et al *PRA* 86, 013804 (2012) Liang et al *OE* 21, 30812 (2013)

angle- and pol.-averaged

+



- Disk \approx 6x better than coated sphere
- converges to min. thickness, 3nm

+

- Disk > needle
- Tuning shape > adding coatings
- Ellipsoids: 6x improvement

how about other shapes?

"Adjoint"-based optimization: Newly emerging in photonic design

Aerodynamics



NETWORK

Weights

X(t)





Y(1)

Initial Wing 40 Design Iterations A. Jameson JSC 3, 233 (1988) O. Pironneau JFM 64, 97 (1974) MB Giles & NA Pierce FTC 65, 393 (2000)

Deep Learning

ERROR

E(t)

Y(t)

FIGURE 8.3 Basic backpropagation (in pattern learning).

Werbos, "The Roots of Backpropagation" (1994)

Rumelhart et al. Nature 323, 533 (1986)

Elasticity





Photonics





Sigmund et. al. LPR 5, 308 (2011) **1** X. Liang & SG Johnson OE 21, 30812 (2013)

Fast computation of N derivatives, for any N!

Arbitrary-shape optimization: Ag nanoparticles



Optimal Structure: "Deflated Tetrahedron"





 \approx equal for all 3 polarizations!

Angle- and polarization-averaged:



Surprise: Almost exactly the same?!

General shape optimum < 3% better than ellipsoidal optimum

... hitting an upper bound?

Empirical observation:

optimum metal structure always far subwavelength

(≈ quasistatic, absorption-dominated)

surface

Surface-integral equation (SIE) version of Poisson:

$$-\int_{S} n(x) \cdot G^{E}(x, x')\sigma(x')dx' + \left(\frac{1}{2} + \frac{1}{\chi}\right)\sigma(x) = E^{\text{inc}}(x) \cdot n(x)$$
[O.D. Kellogg (1929),
Foundations of Potential Theory]
[Ammari, ..., Milton (2012)]
bounded self-adjoint operator
(for right inner product)

Eigenvalues: $\hat{K}\sigma = (L_i - 0.5)\sigma$, where $L_i \in [0, 1]$ \Rightarrow angle-averaged response:

$$\sigma_{\text{ext}} = \frac{2\pi}{3\lambda} \sum_{i} p_i \operatorname{Im} \left(\frac{1}{L_i + 1/\chi(\omega)} \right) \qquad p_i = \frac{1}{3} \sum_{\alpha} \langle x_{\alpha}, u_i \rangle \langle v_i, n_{\alpha} \rangle$$

$$\underset{\text{left/right eigenvectors}}{\text{1}}$$

Resonances (poles) at certain materials (real $\chi < -1$), for fixed ω !

Sum rules for the cross-section

$$\frac{\sigma_{ext}}{V} = \frac{2\pi}{3\lambda} \sum_{i} p_i \operatorname{Im} \left(\frac{1}{L_i + 1/\chi(\omega)} \right)$$

lossy materials:

$$\operatorname{Im}(-1/\chi) \left| \operatorname{Im} \frac{1}{L_{i} + 1/\chi} \right| \leq \frac{1}{-\operatorname{Im} \chi^{-1}} = \frac{|\chi|^{2}}{\operatorname{Im} \chi}$$

$$(1)$$

$$\operatorname{Re}(-1/\chi)$$

sum rule #1: Fuchs *PRB* 11, 1732 (1975)

$$\sum p_{i} = \frac{1}{3} \sum_{\alpha} \sum_{n} \langle x_{\alpha}, \sigma_{n} \rangle \langle \tau_{n}, s_{\alpha} \rangle = \int_{S} \hat{n} \cdot x dx = V$$

Fuchs *PRB* 14, 5521 (1976)

$$\frac{\sum p_i L_i}{\sum p_i} = \sum_{\alpha} \sum_n L_n \langle x_{\alpha}, \sigma_n \rangle \langle \tau_n, s_{\alpha} \rangle = \frac{1}{3}$$

An interesting connection

Single-particle quasistatic surface-integral equations

Composite Bounds (Milton & Bergman)

$$\sigma_{\text{ext}} = \frac{2\pi}{3\lambda} \sum_{i} p_{i} \operatorname{Im} \left(\frac{1}{L_{i} + 1/\chi(\omega)} \right) \qquad \varepsilon_{*}$$

$$_{*} = \varepsilon_{2} \prod_{i} \frac{\tau - \tau_{i}'}{\tau - \tau_{i}}$$

sum rule #1:
$$\sum_{\text{Fuchs (1975)}} p_i = \int_{S} \hat{n} \cdot x dx = V$$
 $\frac{\partial \varepsilon_*}{\partial \varepsilon_1} (\varepsilon_1, 1) = p_1$

sum rule #2: Fuchs (1976)

$$\frac{\sum p_i L_i}{\sum p_i} = \frac{1}{3}$$

$$\frac{\partial^2 \varepsilon_*}{\partial^2 \varepsilon_1}(\varepsilon_1, 1) = -\frac{2}{3}p_1p_2$$

In the dilute limit, these formulations are equivalent!

A fundamental limit



[Owen Miller et. al. Phys. Rev. Lett. 112, 123903 (2014)]

Experimental demonstration: Tailored aspect-ratio silver nanoparticles

[E. Anquillaire, Owen Miller et. al., Submitted, arXiv: 1510.01768]



Experimental Synthesis:

thermal conversion of colloidal thin-disk particles





Aspect ratios: 1.5:1 – 10:1



Emma Anquillare Soljacic group (MIT)

Now, generalize to full electrodynamics (not quasistatic)

... and other objectives besides $\sigma_{
m ext}$



the extinction is proportional to (the imaginary part of) the overlap of the incident field and the induced polarization currents, $P_{ind} = \chi E$

Bounding the induced polarization

Optical theorem: the extinguished power is proportional to the (imaginary part of) a linear functional of $P_{ind} = \chi E$



the rest is easy:

Optimize desired objective subject to absorption ≤ extinction

(typically a convex optimization problem, can be solved analytically)

General limits to optical response

[Owen Miller et. al, Opt. Exp. 24, 3329 (2016)]

By energy conservation, variational calculus $(\partial P_{abs}/\partial P_{ind} = 0, etc.)$ and standard optimization theory (optimality conditions)...

$$\frac{\sigma_{\text{abs}}}{V}, \frac{\sigma_{\text{scat}}}{V} \le \beta \frac{\omega}{c} \frac{|\chi|^2}{\operatorname{Im} \chi} \qquad \beta = \begin{cases} 1 & \text{absorption} \\ 1/4 & \text{scattering} \end{cases}$$

for more general sources and media:

(magnetic / anisotropic / chiral / inhomogeneous $\overline{\overline{\chi}}$)

 $P_{abs}, P_{scat} \leq \beta \omega (\text{incident energy inside } V) \| \bar{\chi}^{\dagger} (\text{Im } \bar{\chi})^{-1} \bar{\chi} \|$

Similar limit to power radiated by dipole at distance *d*, i.e. the local density of states (LDOS) $\frac{\rho_{rad}}{\rho_0}, \frac{\rho_{nr}}{\rho_0} \leq \frac{\beta}{8(kd)^3} \frac{|\chi|^2}{\mathrm{Im}\,\chi}$



How tight are these bounds?



plane-wave excitation: the limits are "tight" across many frequencies

for absorption and scattering

"Best" materials vs. wavelength



Resonances in Physics

Inherent to the concept of resonance is the resonant frequency





Mathematical eigen-equations:

electromagnetism $\frac{1}{\varepsilon(x)}\nabla \times \nabla \times E_n = \omega_n^2 E_n$ linear elasticity $(\lambda + \mu)\nabla \nabla \cdot u_n + \mu \nabla^2 u_n = -\rho \omega_n^2 u_n$ quantum mechanics $-\frac{\hbar^2}{2m}\nabla^2 \Psi_n + U\Psi_n = \hbar \omega_n \Psi_n$

(subject to appropriate boundary conditions)

Differential vs. integral equation formulations

Differential Equation Volume Integral Equation (VIE) $-\nabla \times \nabla \times E + \varepsilon(x) \frac{\omega^2}{c^2} E = i\mu_0 \omega J \quad E(x) - \int_V G^0(x - x')\chi(x')E(x') = E_{\text{inc}}(x)$

Eigen-equations:

$$\frac{1}{\varepsilon(x)}\nabla \times \nabla \times E_n = \omega_n^2 E_n \qquad \qquad \int_V G^0(x - x'; \omega) E_n(x') dx' = -\frac{1}{\chi_n} E_n(x)$$

fixed structure + fixed permittivity → resonant frequency fixed structure

- + fixed frequency
- \rightarrow resonant susceptibility

(assumes piecewisehomogeneous media)

frequency vs. material resonances



Back to energy-conservation: Generalizations

[O. D. Miller et al, unpublished]

Similar limits can be derived

(1) for other linear wave equations, such as the Lamé–Navier equations of elastic media:

incident shear wave $\frac{\sigma}{V}$ in isotropic medium: $\frac{V}{V}$

$$\frac{S}{r} \leq \beta k_0 \frac{|\Delta \mu|^2}{\mu_0 \operatorname{Im} \Delta \mu}_{\mu_0 = \text{ ambient shear modulus}}$$

$$\Delta \mu = \text{ difference of scatterer} - \mu_0$$

(2) for local two-dimensional materials (e.g. graphene) $\frac{\sigma_{\text{scat,abs}}}{A} \leq \beta k_0 \left(\text{Re } \sigma_{\delta}^{-1}\right)^{-1} \sigma_{\delta} = \text{surface conductivity}$

(3) for nonlocal (e.g. hydrodynamic) constitutive equations

$$\frac{1}{\chi}P = E \longrightarrow \alpha \nabla (\nabla \cdot P) + \beta P = E$$

Radiative Heat Transfer

Far-field



Kirchoff's Law: absorptivity = emissivity = 1 "blackbody" definition (ray-optical) Stefan-Boltzmann $H/A \le \int 1 \cdot \Theta(\omega, T)/\lambda^2 = \sigma T^4$

Near field

In the near field, (evanescent) thermal transport can exceed "black-body" limit

Difficulty: comp/expt progress is very recent

e.g. for future thermo-photovoltaic systems?



Nat Nano 9, 126 (2014)

Near-field radiative heat transfer: Milestones



Rytov / Polder / Van Hove (1950–1980's)

stochastic theory, plate–plate heat transfer, possibility of greater-than-blackbody transfer

J Pendry (1999): (unrealistic) theoretical bounds to plane-plane transfer



Straightforward extension of limits to near-field heat transfer?



dotted line = bounding surface

Difficulty: sources are embedded within (arbitrary-shape) scattering body

 \rightarrow no conventional optical theorem

limits: two scattering problems + reciprocity

(1) redefine "incident" and "scattered" fields:

$$E_{\text{inc}}^{1}(x) = \int_{V_{1}} G^{1}(x, x') J(x')$$

$$G^{1} = \text{Green's function in the}$$

$$F_{\text{scat}}^{1}(x) = \int_{V_{2}} G^{1}(x, x') P_{\text{ind}}(x')$$

$$F_{\text{scat}}^{1}(x) = \int_{V_{2}} G^{1}(x, x') P_{\text{ind}}(x')$$

(2) Bound absorption in body 2, from unknown field

(3) Reciprocity: switch source + measurement points

(4) Bound the energy transmitted back to V_1



Upper limits to near-field heat transfer

[Owen Miller et al, Phys. Rev. Lett. 115, 204302 (2015)]



Design rules in the near field

(1) In the absence of the absorber, V_2 , the fields emitted by V_1 into V_2 should be amplified by material enhancement ratio:



(2) With both bodies present, the currents induced in the absorber should be further enhanced by the second material enhancement ratio

Optimal-absorber condition



Are the limits achievable in known structures?

First consider simple structures and the generic limit:

$$\Phi(\omega) \leq \frac{2k^4}{\pi} \frac{\left|\chi_1(\omega)\right|^2}{\operatorname{Im}\chi_1(\omega)} \frac{\left|\chi_2(\omega)\right|^2}{\operatorname{Im}\chi_2(\omega)} \int_{V_1} \int_{V_2} \left\|\boldsymbol{G}^0(\mathbf{x}_1, \mathbf{x}_2)\right\|_F^2$$

$$\Phi(\omega)]_{\text{dipole-dipole}} \le \frac{3}{4\pi^3} \frac{|\chi_1(\omega)|^2}{\mathrm{Im}\,\chi_1(\omega)} \frac{|\chi_2(\omega)|^2}{\mathrm{Im}\,\chi_2(\omega)} \frac{V_1 V_2}{(r_1 + r_2 + d)^6}$$

sphere-sphere reaches the limit

$$[\Phi(\omega)]_{\text{dipole-to-ext}} \le \frac{1}{8\pi^2} \frac{|\chi_1(\omega)|^2}{\operatorname{Im}\chi_1(\omega)} \frac{|\chi_2(\omega)|^2}{\operatorname{Im}\chi_2(\omega)} \frac{V}{(r+d)^3}$$

sphere-plate off by 2x (pol. mismatch), correct scaling



Drude metal, plasma frequency ω_p and dissipation $\gamma = 0.1 \omega_p$

Are the limits achievable in known structures?

What about extended (planar) structures?



Are the limits achievable in known structures?

What about extended (planar) structures?



Promising avenue: periodic nanostructure interactions



arrays of dipolar spheres interacting additively (overly idealized)

to simultaneously achieve $|\chi|^2/\text{Im }\chi$ (via particles) and $1/d^2$ (via array) enhancements

Reaching the limits: new possibilities in heat transfer

Given optimal flux (and smallest bandwidth, $\Delta \omega / \omega_{res}$, for a metal):





Progress, and New Questions

New upper bounds to optical responses proportional to $|\chi|^2 / \text{Im } \chi$

Linear elasticity? QM?

Absorbing & Scattering Nanoparticles



Radiative Heat Transfer

Comp. optimized structures to reach highest-possible absorption/scattering rates



Nonlocal interactions?

[Mortensen, PNFA 11, 303 (2013)]



Single-layer absorbers?

[Geim et al. *RMP* 81, 109 (2009)]



New limits to near-field transport



What are the optimal structures?