Nonlocal Optical Response of Metal Nanostructures with Arbitrary Shape

Jeffrey M. McMahon,[1,2] Stephen K. Gray,[2] and George C. Schatz[1]
[1]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, USA
[2]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA
(Received 14 April 2009; published 27 August 2009)

We present an implementation of Maxwell's equations that incorporates the spatially nonlocal response of materials, an effect necessary to describe the optical properties of structures with features less than 10 nm. For the first time it is possible to investigate the nonlocal optical response of structures without spherical or planar shape, and outside of the electrostatic limit. As an illustration, we calculate the optical properties of Au nanowires and show that nonlocal effects are particularly important in structures with apex features, even for arbitrarily large sizes.

DOI: 10.1103/PhysRevLett.103.097403 PACS numbers: 78.67.Lt, 62.23.Hj, 71.45.Lr, 78.67.Bf

Interest in metallic structures with features on the order of 10 nm or less has significantly increased as experimental techniques for their fabrication have become possible [1]. Even if the features involve many hundreds of atoms or more so that a continuum level of description is adequate, their optical response can be difficult to correctly model due to spatially nonlocal dielectric effects. In such cases, the dielectric constant $\varepsilon(\mathbf{k}, \omega)$ is a function of both the wave vector $\mathbf{k}$ and angular frequency ω (which are independent). The $\mathbf{k}$ dependence has been neglected in previous classical studies of arbitrarily shaped nanostructures (e.g., Ref. [2]). When not neglected, the constitutive relationship between the electric displacement field ($\mathbf{D}$) and the electric field ($\mathbf{E}$) is

$$\mathbf{D}(\mathbf{k}, \omega) = \varepsilon_0 \varepsilon(\mathbf{k}, \omega)\mathbf{E}(\mathbf{k}, \omega). \tag{1}$$

The $\mathbf{k}$ dependence in $\varepsilon(\mathbf{k}, \omega)$ leads to a spatially nonlocal relationship between $\mathbf{D}$ and $\mathbf{E}$ when Eq. (1) is Fourier transformed to the spatial domain [3]. This dependence has long been known necessary to describe the optical response of structures with features less than approximately 10 nm. For example, anomalous absorption is experimentally observed in thin metal films [4,5], and inclusion of $\mathbf{k}$ dependence provides an additional absorption mechanism through the excitation of longitudinal plasmons [6] (called such because they are longitudinal to $\mathbf{k}$). Since early formulations of nonlocal electromagnetics [3], treatments have been limited to planar surfaces and structures with spherical symmetry [7,8] or aggregates thereof [9–12], all within the electrostatic limit. However, it has been predicted that nonlocal effects are significant for structures with apex features [9], even for large sizes where this limit is invalid.

In this Letter, we introduce an implementation of Maxwell's equations to simulate the dynamical response of arbitrarily shaped structures that incorporates the spatially nonlocal response of the material. This allows us to describe the optical response of structures that are too large to treat using quantum mechanics, yet too small for local continuum electrodynamics to be valid. As examples, we calculate and analyze the optical response of Au nanowires, i.e., effectively 2D systems, of various shapes. (These examples allow for straightforward interpretation of our results; however, our general approach can be applied without loss of generality to 3D problems.) Our approach provides a powerful, yet simple tool to investigate the optical response of structures at the nanometer length scale.

The dielectric function of a metal like Au is well described in the classical continuum limit by three components,

$$\varepsilon(\mathbf{k}, \omega) = \varepsilon_\infty + \varepsilon_{\text{inter}}(\omega) + \varepsilon_{\text{intra}}(\mathbf{k}, \omega), \tag{2}$$

where ε_∞ is the value as $\omega \to \infty$, $\varepsilon_{\text{inter}}(\omega)$ is the contribution from d-band to conduction-band electronic transitions, and $\varepsilon_{\text{intra}}(\mathbf{k}, \omega)$ is due to excitations of the conduction electrons. [The notation in Eq. (2) highlights the $\mathbf{k}$ and ω dependencies.] The latter component is responsible for the plasmonic optical response of metals and nonlocal effects, and can be described physically by the hydrodynamic Drude model (which reduces to the local Drude expression for electron motion if $\mathbf{k} \to 0$) [13],

$$\varepsilon_{\text{intra}}(\mathbf{k}, \omega) = -\frac{\omega_D^2}{\omega(\omega + i\gamma) - \beta^2 \mathbf{k}^2}, \tag{3}$$

where ω_D is the plasma frequency, γ is the collision frequency, and $\beta = v_F/2^{1/2}$ for a free electron gas in 2D [14] with v_F being the Fermi velocity. Inserting Eqs. (1) and (2) into the Maxwell-Ampère law in $\mathbf{k}$ space for a time-harmonic field, $-i\omega\mathbf{D} = i\mathbf{k} \times \mathbf{H}$, where $\mathbf{H}$ is the magnetic field, gives

$$-i\omega\epsilon_0[\epsilon_\infty + \epsilon_{\text{inter}}(\omega)]\mathbf{E}(\mathbf{k}, \omega) + \mathbf{J}(\mathbf{k}, \omega) = i\mathbf{k} \times \mathbf{H}(\mathbf{k}, \omega), \tag{4}$$

where $\mathbf{J}$ is a nonlocal phasor polarization current associated with Eq. (3),

$$\mathbf{J}(\mathbf{k},\omega) = i\omega\epsilon_0 \frac{\omega_D^2}{\omega(\omega + i\gamma) - \beta^2\mathbf{k}^2}\mathbf{E}(\mathbf{k},\omega). \quad (5)$$

From Eq. (5), an equation of motion for $\mathbf{J}$ can be obtained by inverse Fourier transforming ($i\mathbf{k} \rightarrow \nabla$ and $-i\omega \rightarrow \partial/\partial t$),

$$\frac{\partial^2}{\partial t^2}\mathbf{J}(\mathbf{r},t) + \gamma\frac{\partial}{\partial t}\mathbf{J}(\mathbf{r},t) - \beta^2\nabla^2\mathbf{J}(\mathbf{r},t) = \varepsilon_0\omega_D^2\frac{\partial}{\partial t}\mathbf{E}(\mathbf{r},t). \quad (6)$$

For our approach, we solve Eq. (6) self-consistently with the inverse Fourier-transformed form of Eq. (4) and the Maxwell-Faraday equation, $\partial\mathbf{B}/\partial t = -\nabla \times \mathbf{E}$, where $\mathbf{B}$ is the magnetic field density, over a grid-based domain using finite differences to approximate the derivatives [15]. Note that $\varepsilon_{\text{inter}}(\omega)$ in Eq. (2) is modeled as a Lorentz oscillator, which leads to an additional polarization current. By not updating Eq. (6) outside of the nonlocal materials, we implicitly impose the Pekar additional boundary condition; i.e., the total nonlocal polarization current vanishes outside of the structure [16]. The novelty of this approach is that coupling Eq. (6) with the more standard finite-difference equations [15] allows us to describe nonlocal effects for structures with arbitrary shape.

Other analytical forms for $\varepsilon(\mathbf{k},\omega)$ could be used within our approach. In principle, quantum mechanical electronic structure theory can be used to provide rigorous estimates of $\varepsilon(\mathbf{k},\omega)$. See, for example, recent interesting work on carbon nanotubes based on time-dependent density functional theory [17]. It remains a challenge, however, to reliably apply such methods to nanostructures involving hundreds of atoms or more.

As an initial example of our formalism, we investigate the optical response of Au cylindrical nanowires. For Au, $v_F = 1.39 \times 10^6$ m/s, and we find that the hydrodynamic Drude parameters $\omega_D = 8.812$ eV and $\gamma = 0.0752$ eV provide the most accurate fit to empirically inferred bulk dielectric data [18] over the range 1–1.8 eV where Eq. (2) is determined mostly by $\varepsilon_{\text{intra}}(\mathbf{k},\omega)$. [Keeping these parameters constant, we then fit Eq. (2) over the entire optical range, 1–6 eV, while including the Lorentz oscillator model as described above.] The reduced mean free path of the conduction electrons due to electron-interface scattering is taken into consideration by using a modified collision frequency [19], $\gamma' = \gamma + Av_FP/S\pi$, where P is the perimeter of the structure, S is the surface area, and A is the proportion of such collisions that are totally inelastic, which for a metal-dielectric interface is approximately 0.1 [20].

We compare the optical response of nanowires with radii of $r = 2$–8 nm in the local and nonlocal limits by calculating extinction cross sections [21] (i.e., the amount of power absorbed or scattered relative to the incident light, which for these small systems is dominated the former) by integrating the normal component of the Poynting vector around a surface enclosing the particle [22]; Fig. 1. The

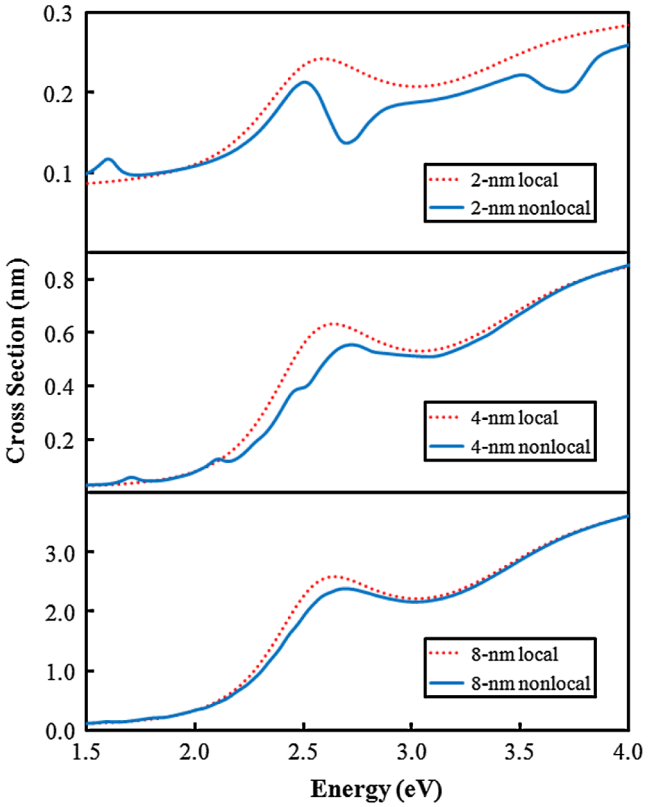

FIG. 1 (color online). Optical response of Au cylindrical nanowires with radii of 2 (top), 4 (middle), and 8 nm (bottom). Full curve is nonlocal theory; broken curve is local theory.

appearance of anomalous absorption peaks relative to local theory in Fig. 1 is similar to theoretical predictions [6] and experimental observations [4,5] on thin metal films, where they were shown to arise from the optical excitation of longitudinal plasmons that cannot be described by local electrodynamics. It is important to note that the hydrodynamic Drude model, Eq. (3), can have an effect at much higher energies than the local Drude model because of the interplay between ω and $\mathbf{k}$. In order to investigate the nature of the anomalous absorption, we look at profiles of $|\mathbf{D}|^2$ at the peak energies, which include contributions from both the incident $\mathbf{E}$ and material polarization. Figure 2 shows $|\mathbf{D}|^2$ for the $r = 2$ nm nanowire, where discrete standing longitudinal plasmon modes are seen with wavelengths $\lambda_L = 2d/n$, where $d = 2r$ and $n = 1, 3, 5, \ldots$ (i.e., odd numbers of half wavelengths that fit

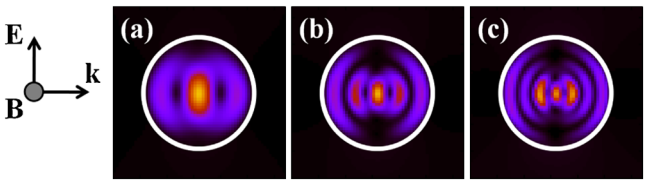

FIG. 2 (color online). Longitudinal plasmon modes inside a $r = 2$ nm Au cylindrical nanowire at energies of (a) 1.60, (b) 2.71, and (c) 3.69 eV. The polarization and direction of incident light are indicated; the nanowire is outlined in white.

into d). (Only the $n = 3$, 5, and 7 modes are explicitly shown.) This result is in sharp contrast to the local result of a relatively uniform $|\mathbf{D}|^2$, but identical to previous predictions [6] and observations [4] on analogous thin metal films. In addition to anomalous absorption, the nonlocal effects blueshift the main plasmon resonance, where, for example, at $r = 4$ nm there is a 0.014 eV blueshift. At optical energies, the discrete nature of these modes is quickly lost with increasing r (as $r \to \infty$, $n \to \infty$ and $\lambda_L \to 0$), and nonlocal effects become less important. This is seen in Fig. 1, where for $r = 4$ nm there is only minor anomalous absorption and for $r = 8$ nm it is hardly distinguishable. However, even at $r = 8$ nm there is a broadening, reduction in intensity, and a blueshift of 0.0056 eV of the main plasmon resonance due to the excitation of many closely spaced modes. While our explicit examples correspond to 2D nanowires, the $r = 4$ nm results are remarkably similar to recent experimental observations on individual Au spherical nanoparticles with similar radii [23]. For example, our results predict a 0.014 eV blueshift, while that observed is 0.011 eV. In addition, our results predict anomalous absorption at energies below the main plasmon resonance with peaks near 1.7 and 2.1 eV, and the experimental results show similar peaks near 1.8 and 1.9 eV (discrepancies that can be attributed to the differences in dimensionalities).

While cylindrical nanowires are useful because their simplicity allows us to easily understand the results, we find that nonlocal effects are particularly strong in structures with apex features, a claim previously suggested [9]. We consider the optical response of Au triangular (equilateral) nanowires, which have been thoroughly studied within local electrodynamics because of the large $|\mathbf{E}|^2$ enhancements that occur at the apices [24]. The optical responses of nanowires with side lengths of $l = 5$–40 nm are shown in Fig. 3. Strikingly, for small enough l the main plasmon resonance is hardly distinguishable from the nonlocal anomalous absorption features. In addition, for all l a significant damping and blueshift of the plasmon resonance relative to the local result is observed. This effect persists for l much larger than the analogous cylindrical nanowire dimensions, where even at $l = 40$ nm there is a 0.1 eV blueshift.

Profiles of $|\mathbf{D}|^2$ are again investigated at the anomalous absorption energies; Fig. 4. Similar to the cylindrical nanowires, longitudinal plasmon modes are excited inside the nanowires with analogous discrete wavelengths, λ_L, except in this case d is the distance between the nanowire sides along the longitudinal direction. However, comparison of Figs. 2 and 4 reveals an interesting difference. In the triangular structures, the longitudinal plasmon modes occur at discrete vertical positions, at each point where the equation for λ_L is satisfied, which increases with n. The ability of the triangular nanowires to strongly sustain these resonances over the entire structure at multiple positions (particularly near the apices where d can be arbitrarily small) explains the strength of the calculated nonlocal

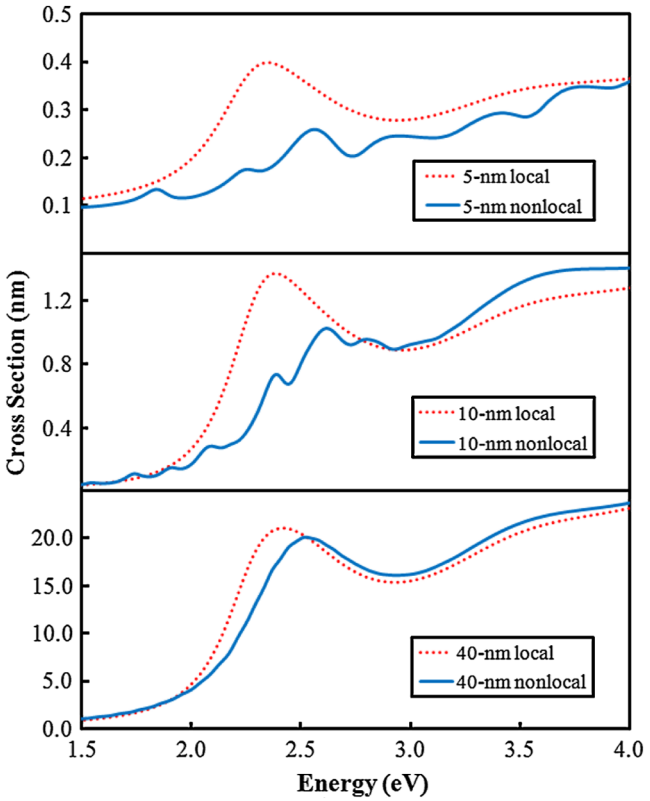

FIG. 3 (color online). Optical response of Au triangular nanowires with side lengths of 5 (top), 10 (middle), and 40 nm (bottom). Full curve is nonlocal theory; broken curve is local theory.

effects compared to the cylindrical nanowires, where the modes are only efficiently sustained along the central axis. Generalizing this result to other apex structures suggests that longitudinal plasmon modes can always be sustained (at least near the apex), causing nonlocal effects to remain important for arbitrarily large sizes.

As mentioned previously, much of the interest in apex structures is due to the high surface $|\mathbf{E}|^2$ enhancements, a quantity important for many physical processes, such as surface enhanced Raman scattering. However, in previous studies of strongly interacting metallic spheres [9,11], nonlocal effects were shown to strongly damp surface plasmons, greatly reducing $|\mathbf{E}|^2$ enhancements. It is therefore informative to compare $|\mathbf{E}|^2$ at the bottom apex of the tri-

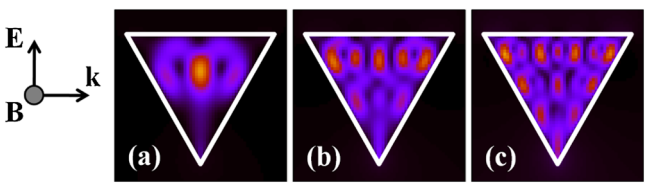

FIG. 4 (color online). Longitudinal plasmon modes inside a $l = 5$ nm Au triangular nanowire at energies of (a) 1.88, (b) 2.82, and (c) 3.71 eV. The polarization and direction of incident light are indicated; the nanowire is outlined in white.

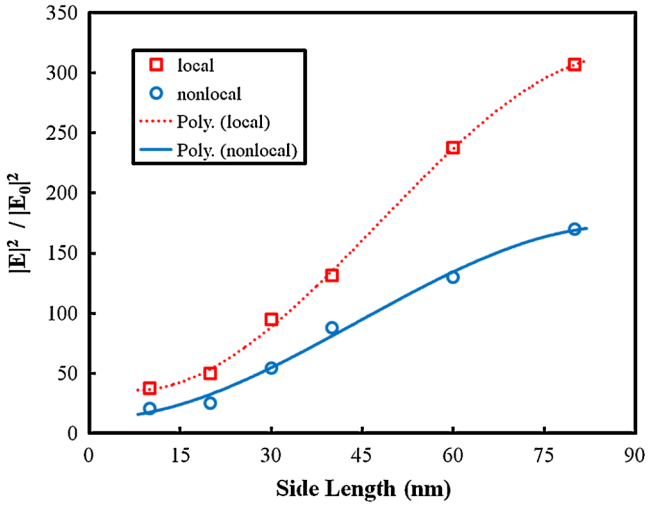

FIG. 5 (color online). $|\mathbf{E}|^2$ enhancements at the apex of Au triangular nanowires. Symbols denote the calculated points, and curves are polynomial fits to the data. The full curve with open circles represents the nonlocal theory; the broken curve with open squares represents the local theory.

angular nanowires (where for the incident light considered this is maximized) in the local and nonlocal limits. Figure 5 shows $|\mathbf{E}|^2$ enhancements at the plasmon resonances (obtained from the extinction spectra) for l values up to 80 nm. For the entire l range studied, local electrodynamics predicts enhancements greater than twice the nonlocal result, a significant difference. Furthermore, as suggested above, there seems to be no convergence of the nonlocal to the local result. Even though there appears to be no convergence of the near field properties (e.g., $|\mathbf{E}|^2$), relative convergence of those in the far field does occur; Fig. 3.

In conclusion, we presented a simple implementation of Maxwell's equations that, for the first time, can model the spatially nonlocal dielectric response of arbitrarily shaped structures. Our implementation is based on a derived equation of motion for the hydrodynamic Drude model, which is solved self-consistently with Maxwell's equations using a finite-difference approach. As an example, we calculated the optical response of Au nanowires and found strong anomalous absorption, which in some cases completely overshadowed the main plasmon resonance predicted by local electrodynamics. For structures with apex features, these effects were seen to be particularly important, where at arbitrarily large dimensions nonlocal effects significantly affected the optical spectra and surface $|\mathbf{E}|^2$ enhancements. These results clearly demonstrate the importance of including such effects when describing metal-light interactions at the nanometer length scale, especially now that experimental investigation at this scale is becoming possible. In the future, we plan to study more complex systems (including 3D structures) with our approach, which will allow for more direct comparison with experiments. We believe that our implementation will be important for many future studies, including a reconsideration of previous work based on local electrodynamics, and providing a more quantitative understanding of the optical response of structures at the nanometer length scale.

J. M. M. and G. C. S. were supported by AFOSR/DARPA Project BAA07-61 (FA9550-08-1-0221), and the NSF MRSEC (DMR-0520513) at the Materials Research Center of Northwestern University. S. K. G. was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

[1] K. A. Willets and R. P. Van Duyne, Annu. Rev. Phys. Chem. **58**, 267 (2007).
[2] M. Liu, P. Guyot-Sionnest, T.-W. Lee, and S. K. Gray, Phys. Rev. B **76**, 235428 (2007).
[3] G. S. Agarwal, D. N. Pattanayak, and E. Wolf, Phys. Rev. B **10**, 1447 (1974).
[4] M. Anderegg, B. Feuerbacher, and B. Fitton, Phys. Rev. Lett. **27**, 1565 (1971).
[5] I. Lindau and P. O. Nilsson, Phys. Lett. **31A**, 352 (1970).
[6] W. E. Jones, K. L. Kliewer, and R. Fuchs, Phys. Rev. **178**, 1201 (1969).
[7] B. B. Dasgupta and R. Fuchs, Phys. Rev. B **24**, 554 (1981).
[8] R. Chang and P. T. Leung, Phys. Rev. B **73**, 125438 (2006).
[9] F. J. García de Abajo, J. Phys. Chem. C **112**, 17 983 (2008).
[10] C. Tserkezis, G. Gantzounis, and N. Stefanou, J. Phys. Condens. Matter **20**, 075232 (2008).
[11] A. Pack, M. Hietschold, and R. Wannemacher, Opt. Commun. **194**, 277 (2001).
[12] V. Yannopapas, J. Phys. Condens. Matter **20**, 325211 (2008).
[13] A. D. Boardman, in *Electromagnetic Surface Modes*, edited by A. D. Boardman (Wiley, New York, 1982).
[14] A. L. Fetter, Ann. Phys. (N.Y.) **81**, 367 (1973).
[15] A. Taflove and S. Hagness, *Computational Electrodynamics: The Finite-Difference Time-Domain Method* (Artech House, Boston, 2005), 3rd ed.
[16] P. Halevi and R. Fuchs, J. Phys. C **17**, 3869 (1984).
[17] A. G. Marinopoulos, L. Reining, and A. Rubio, Phys. Rev. B **78**, 235428 (2008).
[18] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).
[19] E. A. Coronado and G. C. Schatz, J. Chem. Phys. **119**, 3926 (2003).
[20] M. Liu and P. Guyot-Sionnest, J. Phys. Chem. B **108**, 5882 (2004).
[21] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (John Wiley & Sons, New York, 1983).
[22] S. K. Gray and T. Kupka, Phys. Rev. B **68**, 045415 (2003).
[23] S. Palomba, L. Novotny, and R. E. Palmer, Opt. Commun. **281**, 480 (2008).
[24] J. P. Kottmann, O. J. F. Martin, D. R. Smith, and S. Schultz, Opt. Express **6**, 213 (2000).