Are there novel resonances in nanoplasmonic structures due to nonlocal response?

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We study the nonlocal response of a confined electron gas within the hydrodynamical Drude model. We address the question whether plasmonic nanostructures exhibit nonlocal resonances that have no counterpart in the local-response Drude model. Avoiding the usual quasi-static approximation, we find that such resonances do indeed occur, but not in the visible spectrum. Thus the recently found nonlocal resonances at optical frequencies for very small structures, obtained within quasi-static approximation, are unphysical. As a specific example we consider nanosized metallic cylinders, for which extinction cross sections and field distributions can be calculated analytically.

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Nanoplasmonics [1, 2] is presently entering an exciting era where the metallic structures offer nano-scale features that will eventually allow both photons and electrons exhibit their full wave nature. This regime challenges the existing theoretical framework resting on a local-response picture using bulk-material parameters. In tiny metallic nanostructures, quantum confinement [3–7] and nonlocal response [8–18] are believed to change the collective plasmonic behaviour with resulting strong optical fingerprints and far-reaching consequences for e.g. field-enhancement and extinction cross sections. Within nonlocal response, Maxwell's constitutive relation between the displacement and the electric fields reads

$$\boldsymbol{D}(\boldsymbol{r},\omega) = \varepsilon_0 \int d\boldsymbol{r}'\, \boldsymbol{\varepsilon}(\boldsymbol{r},\boldsymbol{r}',\omega)\cdot \boldsymbol{E}(\boldsymbol{r}',\omega). \qquad (1)$$

The dielectric tensor $\boldsymbol{\varepsilon}(\boldsymbol{r},\boldsymbol{r}',\omega)$ reduces to $\varepsilon(\boldsymbol{r},\omega)\delta(\boldsymbol{r}-\boldsymbol{r}')$ in the local-response limit. Historically, there has been a strong emphasis on nonlocal response in extended systems with translational invariance (TI) [10], where a k-space representation is useful. However, for the present problem of metallic nanostructures, TI is broken and a real-space description is called for.

Recent theoretical studies of nanoscale plasmonic structures have predicted considerable differences in the field distributions and scattering cross sections between local and nonlocal response theories, both in numerical implementations of a simplified hydrodynamic Drude model [14–18], and in corresponding analytical calculations [15]. Surprisingly, new resonances of the free-electron plasma were found, also at optical frequencies, which have no counterparts in local-response theories. Such novel resonances have already gained interest both from a fundamental perspective [7] and in the context of engineering ultrasmall plasmonic structures with new functionalities [19], especially since their monodisperse fabrication gets within reach [20, 21]. However, in Ref. 13 the same nonlocal model was used as in Refs. 14–17, and yet no corresponding new modes were found at visible frequencies. In this Letter we clarify the important issue whether novel resonances exist in nanoplasmonic structures due to nonlocal response. Anticipating that different implementations of the common quasi-static approximation [9, 11] are the reason for the conflicting results in [14, 15] and [13], we refrain from making this approximation altogether. This allows us to analyze the validity and implementation of the quasi-static approximation in the hydrodynamic model. We state our main conclusion: there are indeed novel (and observable) resonances due to the nonlocal response, but they do not occur in the visible part of the spectrum.

The hydrodynamic model. We express the collective motion of electrons in an inhomogeneous medium in terms of the electron density $n(\boldsymbol{r},t)$ and the hydrodynamical velocity $\boldsymbol{v}(\boldsymbol{r},t)$ [8]. Under the influence of macroscopic electromagnetic fields $\boldsymbol{E}(\boldsymbol{r},t)$ and $\boldsymbol{B}(\boldsymbol{r},t)$, the hydrodynamic model is defined via [10]

$$\left[\partial_t + \boldsymbol{v}\cdot\boldsymbol{\nabla}\right]\boldsymbol{v} = -\gamma\boldsymbol{v} - \frac{e}{m}\left[\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{B}\right] - \frac{\beta^2}{n}\boldsymbol{\nabla}n, \qquad (2)$$

along with the continuity equation $\partial_t n = -\boldsymbol{\nabla}\cdot(n\boldsymbol{v})$, expressing charge conservation. In the right-hand side of Eq. (2), the γ-term represents damping, the second term is the Lorentz force, while the third term is due to the internal kinetic energy of the electron gas, here described within the Thomas–Fermi model, with β proportional to the Fermi velocity v_{F}. In analogy with hydrodynamics, the third term represents a pressure that gives rise to a nonlocal dielectric tensor, since energy may be transported by other mechanisms than electromagnetic waves.

We follow the usual approach [11] to solve Eq. (2) and the continuity equation, by expanding the physical fields in a zeroth-order static term, where (e.g., n_0 is the homogeneous static electron density), and a small (by assumption) first-order dynamic term, thereby linearizing the equations. In the frequency domain, we obtain

$$\beta^2\boldsymbol{\nabla}\left[\boldsymbol{\nabla}\cdot\boldsymbol{J}\right] + \omega\left(\omega+i\gamma\right)\boldsymbol{J} = i\omega\omega_{\mathrm{p}}^2\varepsilon_0\boldsymbol{E}, \qquad (3a)$$

for a homogeneous medium, where $\boldsymbol{J}(\boldsymbol{r}) = -en_0\boldsymbol{v}(\boldsymbol{r})$ is the current density, and ω_{p} is the plasma frequency which also enters the Drude local-response function $\varepsilon(\omega) = 1 - \omega_{\rm p}^2/[\omega(\omega+i\gamma)]$. We focus on the plasma, leaving out bulk intra-band effects present in real metals that could easily be taken into account [14, 22], as well as band-bending effects at the metal surface.

The electromagnetic wave equation. The retarded linearized hydrodynamic model is then fully described by Eq. (3a) together with the Maxwell wave equation

$$\boldsymbol{\nabla}\times\boldsymbol{\nabla}\times\boldsymbol{E} = \frac{\omega^2}{c^2}\boldsymbol{E} + i\omega\mu_0\boldsymbol{J}. \tag{3b}$$

In order to see that these coupled equations (3) indeed describe nonlocal dielectric response, one can in Eq. (3b) rewrite the current density $\boldsymbol{J}$ as an integral over the Green tensor of Eq. (3a) and the electric field, whereby the nonlocal dielectric tensor of Eq. (1) can be identified.

In a local-response description it is commonplace to introduce the quasi-static or curl-free assumption that $\boldsymbol{\nabla}\times\boldsymbol{E} = 0$ [23]. This well-established approximation lies at the heart of most treatments and interpretations of electromagnetic wave interactions with sub-wavelength structures. Intuitively, one might expect that it can be extended to the nonlocal case and indeed several nonlocal treatments use this assumption [9, 11, 13–17]. However, as we shall demonstrate, one should proceed with care.

Three models. In this work we solve the Eqs. (3) directly, without further assumptions or approximations. We also compare the *nonlocal model* with two other models obtained by further assumptions. The *curl-free nonlocal model* enforces the condition $\boldsymbol{\nabla}\times\boldsymbol{E} = 0$, which with Eq. (3a) implies that also $\boldsymbol{\nabla}\times\boldsymbol{J} = 0$ in the medium. For the differential-operator term in Eq. (3a), from now on denoted $\hat{L}_J$, this has the consequence that $\boldsymbol{\nabla}[\boldsymbol{\nabla}\cdot]$ simplifies to the Laplace operator $\boldsymbol{\nabla}^2$, which gives the model used by Ruppin in the context of exciton physics in [24], and recently in plasmonics by McMahon *et al.* [14–17] and also by ourselves [18]. Finally, by assuming $\hat{L}_J = 0$ in the hydrodynamic treatment (3a), the familiar *local model* is obtained, with $\boldsymbol{J}$ and $\boldsymbol{E}$ related by Ohm's law.

We assume that the static density of electrons n_0 vanishes outside the metal of volume V, while it is constant and equal to the bulk value inside V, thus neglecting tunneling effects and inhomogeneous electron distributions associated with quantum confinement [3, 6]. As a consequence, $\boldsymbol{J} = 0$ outside V for all three models.

Boundary conditions. In the local model the current $\boldsymbol{J}$ has the same the spatial dependence as the $\boldsymbol{E}$–field. Thus, in this case there are no additional boundary conditions (ABC) to those already used in Maxwell's equations. For the nonlocal-response models on the other hand, ABCs are in general needed [10, 25–27]. From discussions in the literature it might appear that the number of necessary ABCs is a subtle issue, but we emphasize that there should be no ambiguity. The crucial point is that the required number of ABCs depends on the assumed static electron density profile at the boundaries [27]. For the present problem with the electron density vanishing identically outside the metal, only one ABC is needed in the nonlocal model to obtain unique solutions [27], and it is readily found from the continuity equation and Gauss' theorem: $\hat{\boldsymbol{n}}\cdot\boldsymbol{J} = 0$ on the boundary, where $\hat{\boldsymbol{n}}$ is a normal vector to the surface, i.e. the normal-component of the current vanishes [10, 25, 27], for all three models. On the other hand, in general the tangential current $\hat{\boldsymbol{n}}\times\boldsymbol{J}$ is non-zero. This 'slip' of the current is not surprising, since the hydrodynamic equation (2) describes the plasma as a non-viscous fluid.

Likewise, in several implementations of the quasi-static approximation, no further ABCs are needed to uniquely determine the electric field and current density [11, 13]. In contrast, in the curl-free nonlocal model of Refs. [14–18, 24] one more ABC *is* needed. Assumed is that the tangential components of $\boldsymbol{J}$ vanish at the boundary ($\hat{\boldsymbol{n}}\times\boldsymbol{J} = 0$), so that both normal and tangential components of the current field vanish on the boundary. In the different context of exciton physics [24] these are often referred to as Pekar's additional boundary conditions. There, the vanishing of the tangential boundary currents is motivated by the physical assumption that exciton wave functions vanish on the boundary [24, 28]. Instead, in the hydrodynamical theory of metals, the ABC $\hat{\boldsymbol{n}}\times\boldsymbol{J} = 0$ seems more *ad hoc*: not a direct consequence of the quasi-static approximation, and not correct if that approximation is not made. The different boundary conditions are summarized in Table I.

	$\boldsymbol{r}\in V$		$\boldsymbol{r}\in\partial V$		$\boldsymbol{r}\notin V$
	$\boldsymbol{\nabla}\times\boldsymbol{J}$	$\hat{L}_J$	$\hat{\boldsymbol{n}}\cdot\boldsymbol{J}$	$\hat{\boldsymbol{n}}\times\boldsymbol{J}$	$\boldsymbol{J}$
local	$\neq 0$	0	0	$\neq 0$	0
nonlocal	$\neq 0$	$\beta^2\boldsymbol{\nabla}[\boldsymbol{\nabla}\cdot]$	0	$\neq 0$	0
nonlocal (curl-free)	0	$\beta^2\boldsymbol{\nabla}^2$	0	0	0

TABLE I: Summary of the three different response models. V is the volume of the nanostructure, and ∂V its boundary.

Extinction cross section of metallic nanowires. To illustrate the surprisingly different physical consequences of the three models, we consider light scattering by a nanowire. Rather than solving Eqs. (3) numerically for a general cross-sectional geometry, we here limit our analysis to cylindrical wires whereby significant analytical progress is possible. We use an extended Mie theory, developed by Ruppin [24, 29], to calculate the extinction cross section $\sigma_{\rm ext}$ of an infinitely long spatially dispersive cylindrical metal nanowire in vacuum. Outside the wire there are incoming and scattered fields (both divergence-free), whereas inside the wire both divergence-free and curl-free modes can be excited, the latter type only in case of nonlocal response. The cross section is [30]

$$\sigma_{\rm ext} = -\frac{2}{k_0 a}\sum_{n=-\infty}^{\infty}{\rm Re}\{a_n\}, \tag{4}$$

where a is the radius, $k_0 = \omega/c$ is the vacuum wave vector, and a_n is a cylindrical Bessel-function expansion coefficient for the scattered fields. We consider a normally incident plane wave with the electric-field polarization perpendicular to the cylinder axis (TM). The expression for the coefficients a_n depends on the particular response model and the associated ABCs. For the curl-free nonlocal model, the a_n are known [24]. For the full hydrodynamic model we follow the approach of Ref. 29, where the ABC of Ref. 26 is employed. This ABC is for metals in free space equivalent to $\hat{\boldsymbol{n}} \cdot \boldsymbol{J} = 0$. We obtain

$$a_n = -\frac{\left[d_n + J_n'(\kappa_t a)\right] J_n(k_0 a) - \sqrt{\varepsilon} J_n(\kappa_t a) J_n'(k_0 a)}{\left[d_n + J_n'(\kappa_t a)\right] H_n(k_0 a) - \sqrt{\varepsilon} J_n(\kappa_t a) H_n'(k_0 a)}, \tag{5}$$

where J_n and H_n are Bessel and Hankel functions of the first kind and $\kappa_t^2 = \varepsilon(\omega) k_0^2$. The d_n coefficients are

$$d_n = \frac{n^2}{\kappa_l a} \frac{J_n(\kappa_l a)}{J_n'(\kappa_l a)} \frac{J_n(\kappa_t a)}{\kappa_t a} \left[\varepsilon(\omega) - 1\right], \tag{6}$$

where $\kappa_l^2 = (\omega^2 + i\omega\gamma - \omega_p^2)/\beta^2$. In the limit $\beta \to 0$, the d_n vanish and the a_n of Eq. (5) reduce to the local Drude scattering coefficients [30], which confirms that nonlocal response in our model requires moving charges.

Are there nonlocal resonances? Figure 1 depicts the extinction cross section of Eq. (4) for two cylinder radii, comparing the nonlocal models with the local Drude model. The main surface-plasmon resonance peak at $\omega_p/\sqrt{2}$ is blueshifted as compared to the local model, and more so for smaller radii. Similar blueshifts have been reported for other geometries [12] and in the curl-free nonlocal model [14, 24].

Figure 1 provides the answer to the question posed in the title of this paper: additional peaks *do* appear in the nonlocal theory but only for frequencies *above* the plasmon frequency ω_p ($\hbar\omega_p = 8.9\,\text{eV}$ for Ag and Au; 1.5 to 3 eV is visible). These peaks (such as P2 in Fig. 1) are due to the excitation of confined longitudinal modes, which are bulk-plasmon states with discrete energies above $\hbar\omega_p$ due to confinement in the cylinder [13]. These peaks are analogous to discrete absorption lines above the band gap in quantum-confined semiconductor structures. Interestingly, contrary to the common belief that light does not scatter off bulk plasmons, which is correct in the local theory (*i.e.* no peak around ω_p in Fig. 1), here in the nonlocal model we do find such a coupling to longitudinal modes. The new resonances could therefore be observed with electron loss spectroscopy but also with extreme UV light. The curl-free model also exhibits these resonances.

The striking difference between the two nonlocal-response models is that the curl-free nonlocal model shows additional stronger resonances, both above and below the plasma frequency, such as P1 in Fig. 1, in particular also at optical frequencies. These peaks do not show up in the full hydrodynamical model, and thus originate from a mathematical approximation rather than

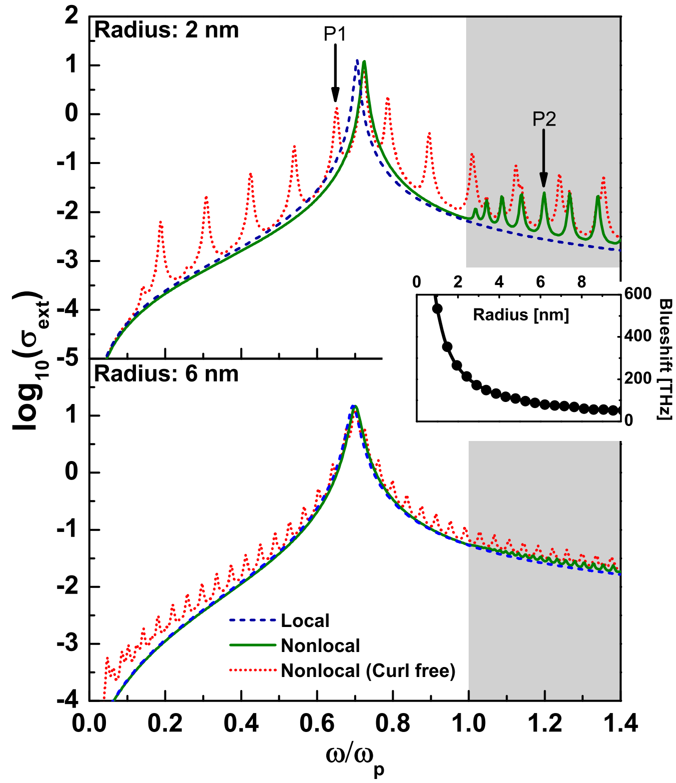

FIG. 1: (Color online) Extinction cross sections σ_{ext} as a function of frequency for TM-polarized light normally incident on a metallic cylinder in vacuum. Parameters for Au as in Ref. 14: $\hbar\omega_p = 8.812\,\text{eV}$, $\hbar\gamma = 0.0752\,\text{eV}$, and $v_F = 1.39 * 10^6\,\text{m/s}$. Inset: frequency shift of the maximum $\sigma_{\text{ext}}(\omega)$ for nonlocal against local response, as a function of radius.

a physical mechanism. It would however be premature to conclude that the quasi-static approximation breaks down, because in Ref. 13 the modes of cylinders in the hydrodynamical Drude model were found after making the quasi-static approximation, and the only novel modes found were the confined bulk plasmon modes above ω_p. Fig. 1 also illustrates that for increasing radii, σ_{ext} in the two nonlocal models converges towards the local-response value. This convergence is slower for the curl-free model.

In Figure 2(a) we depict the scaled *displacement*-field distributions for the three models at the frequency marked P1 in Fig. 1, where only the curl-free nonlocal model has a (spurious) resonance. Correspondingly, in Fig. 2(a) we find a standing-wave pattern only in that model. Its appearance in the displacement field illustrates that the spurious resonance is a transverse resonance, *i.e.* occurring in the divergence-free components of $\boldsymbol{E}$ and $\boldsymbol{J}$. Fig. 2(b) on the other hand shows the normalized *electric*-field intensity for a true resonant mode at the frequency P2 of Fig. 1. Only the two nonlocal models give rise to resonant electric-field patterns. These confined bulk plasmon modes are longitudinal and would not produce standing waves in the displacement field.

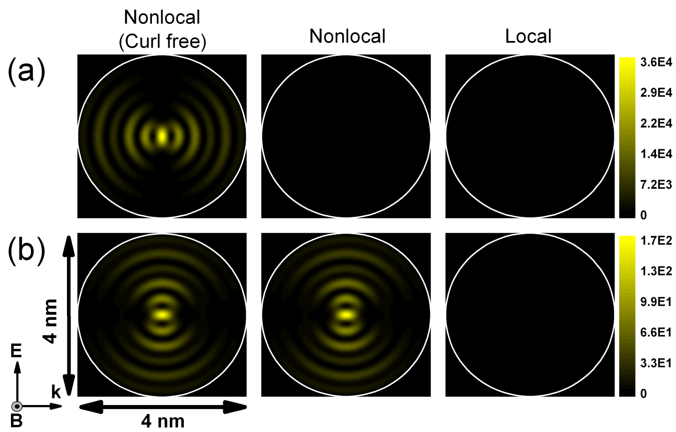

FIG. 2: (Color online) Field distributions in the three different models, for TM-polarized light normally incident on a cylinder of radius $a = 2\,\mathrm{nm}$. (a) Normalized displacement field $|\boldsymbol{D}|^2/|\boldsymbol{D}_{\rm in}|^2$ at the frequency $\omega = 0.6503\omega_{\rm p}$ (P1 in Fig. 1). $\boldsymbol{D}_{\rm in} = \varepsilon_0\boldsymbol{E}_{\rm in}$ and $\boldsymbol{E}_{\rm in}$ is the incident electric field. (b) Analogous plots of $|\boldsymbol{E}|^2/|\boldsymbol{E}_{\rm in}|^2$ for $\omega = 1.1963\omega_{\rm p}$ (P2 in Fig. 1).

Origin of spurious resonances. By eliminating the electric field from Eqs. (3), it follows that the exact hydrodynamic current satisfies the pair of third-order equations

$$\left(\beta^2\nabla^2 + \omega^2 + i\omega\gamma - \omega_{\rm p}^2\right)\boldsymbol{\nabla}\cdot\boldsymbol{J} = 0 \qquad (7a)$$

$$\left(c^2\nabla^2 + \omega^2\varepsilon(\omega)\right)\boldsymbol{\nabla}\times\boldsymbol{J} = 0, \qquad (7b)$$

which reduce to the more symmetric Boardman equations [31] in the absence of damping. For arbitrary geometry, Eq. (7a) has damped solutions of $\boldsymbol{\nabla}\cdot\boldsymbol{J}$ for $\omega < \omega_{\rm p}$ and finite-width resonances for $\omega > \omega_{\rm p}$, as seen in Fig. 1. Both solutions can be consistent with the quasi-static approximation $\boldsymbol{\nabla}\times\boldsymbol{J} = 0$ that trivially solves Eq. (7b). On the other hand, we find that the spurious resonances have resonant divergence-free components of $\mathbf{E}$ and $\mathbf{J}$. However, these cannot at the same time be curl-free. Thus the curl-free nonlocal model has resonant solutions with nonvanishing curl, which is logically inconsistent. But how could this arise? Once the $\boldsymbol{\nabla}\times\boldsymbol{J} = 0$ assumption has been invoked to simplify the differential operator into $\hat{L}_J = \beta^2\nabla^2$, the resulting Laplacian equation analogous to (3a) carries no information that the resulting solution should also be curl-free. Thus, the solutions found for this equation are not necessarily self-consistent.

Conclusions. We have shown that in the hydrodynamic Drude model plasmonic nanostructures exhibit novel resonances due to nonlocal response, but only above the plasma frequency. The recently reported nonlocal resonances in the visible [14–18] are a surprisingly pronounced consequence of an implementation of the quasi-static approximation that is not self-consistent. For nanowires, we find extinction resonances without making the quasi-static approximation that agree with the quasi-static modes of Ref. 13, so we do not claim a general breakdown of the approximation itself. Even though there are no nonlocal resonances in the visible, plasmonic field enhancements are affected by nonlocal response. For arbitrary geometries, numerical methods must be used to quantitatively assess their importance. Self-consistent versions of the versatile time- [14–17] and frequency-domain [18] implementations of the hydrodynamical model can do just that.

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