Making waves: Radiation damping in metallic nanostructures

Cite as: J. Chem. Phys. 151, 080901 (2019); https://doi.org/10.1063/1.5117230
Submitted: 29 June 2019 . Accepted: 02 August 2019 . Published Online: 28 August 2019

Tuphan Devkota, Brendan S. Brown, Gary Beane, Kuai Yu, and Gregory V. Hartland

COLLECTIONS

Paper published as part of the special topic on JCP Editors’ Choice 2019

This paper was selected as an Editor’s Pick

ARTICLES YOU MAY BE INTERESTED IN

Ultrafast photoelectron spectroscopy of aqueous solutions
The Journal of Chemical Physics 151, 090901 (2019); https://doi.org/10.1063/1.5098402

Energetic hot electrons from exciton-to-hot electron upconversion in Mn-doped semiconductor nanocrystals
The Journal of Chemical Physics 151, 120901 (2019); https://doi.org/10.1063/1.5119398

Platinum, gold, and silver standards of intermolecular interaction energy calculations
The Journal of Chemical Physics 151, 070901 (2019); https://doi.org/10.1063/1.5116151

Your Qubits. Measured.
Meet the next generation of quantum analyzers

- Readout for up to 64 qubits
- Operation at up to 8.5 GHz, mixer-calibration-free
- Signal optimization with minimal latency

Find out more

© 2019 Author(s).
Making waves: Radiation damping in metallic nanostructures

Tuphan Devkota, 1 Brendan S. Brown, 1 Gary Beane, 2 Kuai Yu, 3 and Gregory V. Hartland 1,a)

AFFILIATIONS
1 Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA
2 ARC Center of Excellence in Future Low-Energy Electronic Technologies, Monash University, Clayton, VIC 3800, Australia
3 College of Electronic Science and Technology, Shenzhen University, Shenzhen 518060, People’s Republic of China

a) Author to whom correspondence should be addressed: ghartlan@nd.edu

ABSTRACT
Metal nanostructures display several types of resonances. In the visible and near-IR spectral regions, there are localized surface plasmon resonances (LSPRs) that involve the coherent oscillation of the conduction electrons. Extended metal nanostructures, such as nanowires or nanoplates, also exhibit propagating surface plasmon polaritons (PSPPs), which are motions of the electrons at the surface of the structure that have a well-defined momentum. In addition, the vibrational normal modes of metal nanostructures give rise to low frequency resonances in the gigahertz to terahertz range. These different types of motions/resonances suffer energy losses from internal effects and from interactions with the environment. The goal of this perspective is to describe the part of the energy relaxation process due to the environment. Even though the plasmon resonances and acoustic vibrational modes arise from very different physics, it turns out that environmental damping is dominated by radiation of waves. The way the rates for radiation damping depend on the size of the nanostructure and the properties of the environment will be discussed for the different processes. For example, it is well known that for LSPRs, the rate of radiation damping increases with particle size. However, the radiation damping rate decreases with increasing dimensions for PSPPs and for the acoustic vibrational modes.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5117230

I. INTRODUCTION

The coherent motion of the conduction electrons in metal nanostructures gives rise to a variety of effects. The most familiar for chemists are the localized surface plasmon resonances (LSPRs) of particles, which cause the striking colors of metal nanoparticle samples 1–3 and are responsible for the field enhancements that are important in surface enhanced spectroscopies. 4–8 The frequencies and linewidths of these resonances have been extensively studied and are, in general, fairly well understood. 9–18 For example, the way the LSPR frequencies depend on the size, shape, and material of the nanostructures can be accurately calculated by solving Maxwell’s equations for the structure—either numerically 9,12,13 or (when applicable) using the analytic expressions derived by Mie for spherical particles in a homogeneous medium. 14 The linewidths (Γ) of the LSPR modes are also of interest. The linewidth is related to the T2 dephasing time of the plasmon resonance by Γ = 2h/T2, which means that linewidth measurements provide fundamental information about the electron dynamics in the particles. 15–18 For metal nanoparticles, pure dephasing effects are negligible, which means that the dephasing time is determined by the lifetime of the plasmon oscillation, T1 = T2/2. 15 When the particles are larger than a few tens of nanometers, the plasmon decay is dominated by resistive heating effects and radiation damping. 10,15–18 These two processes correspond to loss of energy from the plasmon oscillation by decay into excited electrons and holes, and through creation of a photon at the same frequency as the light field used to drive the plasmon resonance, respectively. 15,19–20

Metal nanostructures also display shape dependent resonances in the gigahertz to terahertz region of the spectrum that correspond to the vibrational normal modes of the structures. 21–29 These acoustic vibrations are excited in ultrafast pump-probe laser experiments by the rapid heating induced by the pump laser. 24,25,27–29 Like the LSPRs in the visible region of the spectrum, the lifetime of the...
acoustic resonances is determined by a combination of intrinsics/inter nal damping due to the thermoelastic effect\textsuperscript{24,25} and transfer of energy to the environment.\textsuperscript{24,25} In ultrafast pump-probe experiments, breathing mode vibrations are primarily excited, which are symmetric modes that map onto the expansion coordinate of the nanostructure.\textsuperscript{4,29,31,32} For these modes, energy transfer to the environment is controlled by radiation of sound waves.\textsuperscript{20,29,31,34} Thus, the damping mechanism for the acoustic resonances and LSPRs of metal nanostructures have analogous contributions: an intrinsic part due to the material properties of the particles, and a radiative part.

In this perspective, the factors that control radiation damping for the plasmon modes and the acoustic resonances of metal nanostructures will be explored. In addition to the LSPRs of the particles, the damping of the propagating surface plasmon polariton (SPPP) modes that exist in extended metal nanostructures, such as nanowires or nanoplates, will also be discussed. The PSPP modes are motions of the conduction electrons at the surface of the structure that have a definitive momentum.\textsuperscript{15–18,46–49} In nanowires and nanoplates, these modes can be excited by focusing a laser at the end or edge of the structure, where the break in symmetry relaxes the momentum matching conditions.\textsuperscript{15–18} The goal of this article is to provide a physical understanding of how radiation damping for the different resonances depends on the properties of the nanostructures, primarily the size of the structures, and on the environment. The discussion of the experimental results will focus on the results from single particle experiments, as ensemble measurements typically do not give precise linewidth information. Simple calculations will also be used to explain how size and environment affect radiation damping.

II. LOCALIZED SURFACE PLASMON RESONANCES

The LSPRs of nanoparticles have been extensively studied due to their importance in surface enhanced spectroscopies, principally surface enhanced Raman spectroscopy (SERS).\textsuperscript{1–8} The LSPR spectra of single metal nanoparticles can be measured using Rayleigh scattering spectroscopy,\textsuperscript{15–18,46–49} photothermal heterodyne imaging,\textsuperscript{50,51} or spatial modulation spectroscopy.\textsuperscript{11,52} Of these different techniques, Rayleigh scattering measurements are the easiest to implement. Figure 1(a) shows example Rayleigh scattering spectra of single gold nanorods from samples with different average widths but the same aspect ratio ($\xi = L/w$).\textsuperscript{17,18} The spectra are well fit by a Lorentzian function $\Gamma/((\omega - \omega_0)^2 + \Gamma^2/4)$, which allows the linewidth $\Gamma$ to be determined. For the narrow rods, the spectra are noisier and broader. The increased noise occurs because the narrower rods have smaller volumes and, thus, are less efficient light scatterers. The broadening for the narrower structures arises because these structures suffer from electron-surface scattering.\textsuperscript{17,18}

Figure 1(b) shows a plot of the average linewidth obtained from light scattering measurements for different nanorod samples plotted against the inverse of the effective pathlength $L_{\text{eff}}$, which is the parameter that characterizes electron-surface scattering.\textsuperscript{4,36} The error bars in this figure represent the standard deviations in the linewidths and dimensions. The LSPR linewidth can be written as a sum of three contributions: intrinsic relaxation processes from resistive heating ($\Gamma_{\text{res}}$), decay of the plasmon into excited electrons

![FIG. 1. (a) Example light scattering spectra of single gold nanorods from samples with average widths of 8 nm (left) and 14 nm (right). The spectra were obtained with a dark-field microscope. The dashed red lines show fits to the data using a Lorentzian function. (b) Linewidth vs $1/L_{\text{eff}}$ for gold nanorod samples with aspect ratios between 2 and 4. The error bars indicate the standard deviations. The lines show the linewidths calculated from bulk scattering (horizontal line), bulk plus electron-surface scattering (blue dashed line), and bulk plus radiation damping (orange dotted line). The solid line shows the total linewidth. Reproduced with permission from Novo et al., Phys. Chem. Chem. Phys. 8, 3540–3546 (2006). Copyright 2006 PCCP Owner Societies. (c) Analogous linewidth data for single SiO$_2$ coated Ag nanospheres. The dashed line is a fit to the data for electron-surface scattering, and the dashed-dotted line shows the expected size dependence of bulk damping. Reprinted with permission from Baida et al., Nano Lett. 9, 3463–3469 (2009). Copyright 2009 American Chemical Society.]}
and holes), electron-surface scattering ($\Gamma_{\text{surf}}$) which includes effects from surface bound ligands ("Chemical Interface Damping" or CID), and radiation damping ($\Gamma_{\text{rad}}$). These different contributions depend on particle size in different ways.

The bulk damping term is usually considered to be size independent.\cite{11,17,52} Within this approximation, it can be simply calculated from the bulk dielectric constants of the metal, although there is some debate over the exact values of the dielectric constants that should be used—especially for silver.\cite{69,70} Electron-surface scattering is inversely proportional to the dimensions of the particle and is given by $\Gamma_{\text{surf}} = A v_F/L_{\text{eff}}$, where $L_{\text{eff}} = 4 V/S$.\cite{11,52} In this expression, $v_F$ is the Fermi velocity (how quickly the conduction electrons are moving at the Fermi level) and $A$ is a proportionality constant that depends on the chemical nature of the interface.\cite{10,17,18}

The radiation damping term is proportional to the volume $V$ and is usually written as $\Gamma_{\text{rad}} = 2hV\kappa$, where $\kappa$ is a proportionality constant that can be calculated or measured from experiments.\cite{62,63} The different contributions are plotted separately and as the total linewidth in Fig. 1(b). Figure 1(c) shows analogous data for SiO$_2$ coated Ag nanospheres plotted against the inverse of the diameter, which is proportional to 1/$L_{\text{eff}}$.\cite{11,17,18} Here, each data point corresponds to a different single nanosphere, where the size was determined from single particle extinction measurements.\cite{52} The dashed line is a fit to the data using the electron-surface scattering term plus bulk damping, and the dashed-dotted line shows the bulk damping term.\cite{11,52}

The bulk damping in metals has a large contribution from electron-phonon coupling, which depends on the size of the particles.\cite{11,52,60,61} In Fig. 1(c), the measured size dependence of the electron-phonon coupling constant was used to estimate the size dependence of the bulk damping term.\cite{11,52,60,61}

The data in Figs. 1(b) and 1(c) show that the linewidths increase at small sizes (large values of 1/$L_{\text{eff}}$) due to increased electron-surface scattering and at large sizes (small values of 1/$L_{\text{eff}}$) due to increased radiation damping.\cite{11,17,18,32,53,62,65} For the gold nanorods examined in Figs. 1(a) and 1(b), a minimum in the linewidth occurs for nanorods with widths on the order of 15 nm, whereas for the Ag nanospheres in Fig. 1(c), it is at a diameter of ~25 nm. The main focus of this article is radiation damping, which becomes the dominant broadening mechanism for both the gold nanorods and the Ag spheres when the dimensions exceed 20–30 nm. It is important to note that the radiation damping contribution to the linewidth is accounted for in calculations that properly deal with retardation effects—such as discrete dipole approximation and finite element simulations—and full Mie theory calculations.\cite{9,32} In contrast, electron-surface scattering has to be added to the dielectric function of the particle—it does not naturally come out in simulations of nanoparticle spectra. This is typically done by splitting the dielectric function for the metal into interband and intraband contributions, fitting the intraband contribution to the Drude model, and adding an electron-surface scattering term to the damping constant in the Drude model—see Refs. 58 and 66–68 for details.

Figure 2(a) shows Mie theory calculations of the spectra for 25 nm radius silver nanoparticles in air, water, and glass environments (refractive indexes of 1, 1.33, and 1.5, respectively). The spectra are presented as efficiencies $Q = \sigma/\pi R^2$, where $\sigma$ is the cross section and $R$ is the radius.\cite{9,66} The dotted lines correspond to absorption, the dashed lines to scattering, and the solid lines are the total extinction efficiency (absorption plus scattering). There are a number of features to note in the spectra. First, as expected, increasing the refractive index of the medium red shifts the spectra. This effect is at the heart of refractive index sensing schemes involving plasmonic nanoparticles.\cite{6,7} Second, the spectra display a small peak to the blue of the main LSPR resonance, which is due to the quadrupole mode of the particles.\cite{12,13,72,73} This peak is more prominent in the higher refractive index environment. The quadrupole peak is more prominent in absorption and is much narrower than the main LSPR peak, which is due to the dipole mode. The reduced width arises because the quadrupole modes do not scatter light.
strongly for particles in a homogeneous environment and therefore do not suffer radiation damping.\textsuperscript{15,16,25}

The relative contributions from scattering and absorption to the main dipole mode in the extinction spectra change as the refractive index of the environment changes. For \( n_{\text{med}} = 1 \), the absorption and scattering contributions to the extinction are approximately equal, whereas at \( n_{\text{med}} = 1.5 \), scattering dominates over absorption—which is significantly reduced compared to \( n_{\text{med}} = 1 \). The reduced absolute value of the absorption efficiency at higher refractive index values occurs because the red shift of the LPSR moves the resonance away from the interband transitions of Ag and, thus, reduces the imaginary component of the dielectric constant (which gives rise to absorption).\textsuperscript{35,36,38–40} Finite element simulations of the resistive heating and electric field (which are related to the absorption and scattering of the nanoparticle, respectively) are presented in Fig. 2(b) for the nanoparticles in air and water. In each plot, the left-hand-side is air and the right-hand-side is water. The calculations were performed at the maximum of the LSPR using COMSOL Multiphysics with the Johnson and Christy dielectric constant data for Ag.\textsuperscript{9,16–20} The images illustrate the increased absorption and decreased scattering for the nanoparticles in air compared to water. The calculations also show that for a 25 nm radius Ag particle, the resistive heating is not uniform across the particle.

The increase in the scattering efficiency of the dipole LSPR with increasing medium refractive index can be understood from the polarizability. For particles much smaller than the wavelength of light (i.e., in the so-called quasistatic limit), the polarizability is given by

\[
P(\omega) = 4\pi\varepsilon_0 R^3 \left( \frac{\epsilon_1(\omega) - \varepsilon_2}{\epsilon_1(\omega) + 2\varepsilon_2} \right),
\]

where \( \epsilon_1(\omega) \) is the frequency dependent dielectric constant of the particle and \( \epsilon_2 \) is the dielectric constant of the medium. The scattering cross section is proportional to the square of the polarizability \( \sigma_{\text{sca}} \propto V^2 \left| \frac{\epsilon_1(\omega)}{\epsilon_1(\omega) + 2\varepsilon_2} \right|^2 \), and the plasmon resonance occurs when \( \text{Re}[\epsilon_1(\omega)] = -2\varepsilon_2 \).\textsuperscript{35,36,38} When this is true, \( \sigma_{\text{sca}} \propto \epsilon_1^2 \), that is, the scattering cross section increases with the dielectric constant of the medium. The increased scattering efficiency for higher medium refractive index causes an increased contribution from radiation damping to the LSPR linewidth: for the spectra in Fig. 2(a), the LSPR linewidth increases from 180 meV in air to 280 meV in glass.

A more complete analysis of how the linewidths change with size and refractive index is presented in Figs. 2(c) and 2(d). Figure 2(c) shows a plot of the relative rate of radiation damping compared to resistive heating \( \Gamma_{\text{rad}}/T_q \) for the dipole LSPR mode of different sized Ag nanoparticles in air, water, and glass. This plot was generated using the cross sections calculated by Mie theory by noting that both the cross sections and damping constants are proportional to the dissipated power so that \( \Gamma_{\text{rad}}/T_q = Q_{\text{rad}}/Q_{\text{abs}} \).\textsuperscript{41} The calculations show that radiation damping is the main contribution to the LSPR decay for Ag nanoparticles when the particle radius is greater than approximately 15 nm for glass, 17 nm for water, and 25 nm for air. Figure 2(d) shows a plot of the linewidth vs refractive index for different sized Ag nanoparticles. The increase in the linewidths with increasing size is due to radiation damping.\textsuperscript{5,15,16,25}

For the smaller nanoparticles, where radiation damping is not the dominant effect, the linewidth slightly decreases with increasing refractive index. As noted above, this is because the LSPR red shifts for larger values of the refractive index, which reduces \( \Gamma_{\text{rad}} \). For the larger 20 and 25 nm radius particles, where \( \Gamma_{\text{rad}} \) is more important, the linewidth increases with increasing refractive index, as expected from Eq. (1). This effect has been observed experimentally for Ag nanostructures by adding water to samples in dark field microscopy measurements.\textsuperscript{15,16,25,29} Similar results hold for other metals; however, the radius where radiation damping becomes dominant is typically larger because of the stronger intrinsic damping (larger \( \Gamma_{\text{rad}} \)) in other systems.

These results are well known and form a “zeroth-order” understanding of radiation damping in metal nanoparticles. A detailed discussion is included here to review the concepts of radiation damping in plasmonic systems. The main result is, of course, that \( \Gamma_{\text{rad}} \) increases with volume due to the increase in scattering efficiency.\textsuperscript{15,16,25} The size dependence of \( \Gamma_{\text{rad}} \) can be understood by noting that the rate of energy loss for the LSPR by radiation is given by \( (dU/dt) = -\Gamma_{\text{rad}} U \), where \( U \) is the electromagnetic energy stored in the particle. The rate of energy loss \( (dU/dt) \) is proportional to the scattering cross section, which is proportional to volume squared \( (\sigma_{\text{sca}} \propto V^2) \), whereas \( U \) is just proportional to the volume. Thus, \( \Gamma_{\text{rad}} = (dU/dt)/U \) is proportional to volume, as shown in Figs. 1 and 2.

III. PROPAGATING SURFACE PLASMON POLARITONS

Extended metal nanostructures, such as nanowires or nanoplates, display two types of surface plasmon polariton modes: localized resonances associated with coherent electron motion across the width or thickness dimensions of the nanowires or nanoplates (LSPRs) and modes with a definite momentum that propagate along the length of the structure.\textsuperscript{35–37,41,42} These second types of modes are known as propagating surface plasmon polaritons (PSPPs), and they have not been studied as extensively as LSPRs. As illustrated in Figs. 1 and 2, the LSPRs of nanoparticles are characterized by their resonance frequencies and linewidths. For PSPPs, the quantities of interest are the wavevectors \( k_{\text{SPP}} \) and propagation lengths \( L_{\text{SPP}} \).\textsuperscript{35–37,41,42} Furthermore, instead of recording cross section vs frequency spectra, PSPPs are better analyzed through dispersion curves—plots of the frequency vs wavevector. In particular, the slopes of these curves give the PSPP group velocity \( v_g = \partial \omega / \partial k \).\textsuperscript{35–37,41,42} Note that the lifetime of the PSPP modes can be determined from the propagation length and group velocity by \( T_1 = L_{\text{SPP}}/v_g \).\textsuperscript{35–37,41,42}

Because of their momentum, PSPP modes are more challenging to excite and detect than LSPRs. A convenient way of exciting PSPPs in metal nanostructures is to focus light at the end or edge of the structure, where the break in symmetry relaxes the momentum matching conditions.\textsuperscript{35–37,41,42} For nanowires or nanoplates on a glass surface (which is a common geometry for studying single metal nanostructures), there are two types of PSPP modes: “bound” modes that propagate at the metal-glass interface, and “leaky” modes that propagate at the metal-air interface.\textsuperscript{44–46} These modes have different effective indexes \( n_{\text{eff}} = k_{\text{SPP}}/k_0 \). The bound modes have

Published under license by AIP Publishing

151, 080901-4
an effective index that is larger than the refractive index of the substrate and, thus, cannot couple to light.\textsuperscript{41,42} These modes do not suffer radiation damping and will not be discussed further in this perspective. On the other hand, the PSPP modes that propagate at the metal-air interface have much smaller effective indexes and can couple to photons in the substrate (hence the term “leaky” mode). The effective indexes and propagation lengths of the PSPP modes can be calculated by finite element simulations. In COMSOL Multiphysics, a convenient way of doing this is to perform a two-dimensional mode analysis calculation, which yields the complex effective mode index for the system \( \tilde{n} = n_{\text{eff}} + i\alpha/k_0 \).\textsuperscript{41,42,79–86} The real part of \( \tilde{n} \) gives the PSPP wavevector \( k_{\text{SPP}} = n_{\text{eff}} k_0 \), and the imaginary part is related to the propagation length by \( L_{\text{SPP}} = 1/2\alpha \). Note that the 2D simulations effectively assume infinitely long nanostripes.

Figure 3 shows scattered light images of a Au nanostripe (a rectangular structure created by photolithography with length \( \times \) width \( \times \) height of 100 \( \mu m \) \( \times \) 4 \( \mu m \) \( \times \) 50 nm).\textsuperscript{78} A reflected light image is presented in Fig. 3(a) that shows that the nanostripes are optically smooth with uniform dimensions. A real space scattered light image of the leaky PSPP mode is shown in Fig. 3(b). This image was obtained by focusing a 760 nm laser beam at the end of the nanostripe with a high numerical aperture objective (Olympus UPlanApo, 100\( \times \), 1.35 NA) and collecting scattered photons with the same objective. The intensity of the scattered light from the leaky mode decreases down the length of the nanostripe, due to a combination of radiation damping and resistive heating processes.\textsuperscript{41,79,86}

Figure 3(c) shows a Fourier space image for the leaky PSPP mode of a Au nanostripe obtained by imaging the back-focal plane (BFP) of the objective onto the camera. These images provide information about the momentum of the leaky mode.\textsuperscript{78,81,83,85,87–93} Specifically, the PSPP wavevector appears as a horizontal line in the image. The green circle in Fig. 3(c) is the condition for total internal reflection \( (k/k_0 = 1) \), and the image has been cropped at \( k/k_0 = NA \), which is the maximum wavevector that can be detected in far-field optical experiments.\textsuperscript{81,83,85,87–92} These two features calibrate the momentum scale in the BFP images. Real-space and Fourier space images such as those in Fig. 3 can be easily generated—converting one imaging mode to the other simply involves flipping a single lens in or out of the imaging system.

Dispersion curves for the leaky mode can be obtained by recording BFP images at different excitation frequencies. An example of this analysis is shown in Fig. 3(d) for the 4 \( \mu m \) wide Au nanostripes.\textsuperscript{78} The green markers are the experimental measurements, and the red lines are the simulated dispersion curves. The simulations yield a series of leaky modes which have a different number of nodes in the width dimension. These modes suffer width and wavelength dependent cutoffs.\textsuperscript{78,92} The experimental results are in good agreement with the lowest order leaky mode, implying that the higher order modes are not detected in these measurements. This is attributed to a combination of poor overlap of the spatial profiles of the excitation beam and the higher order modes,\textsuperscript{78,92} and the shorter propagation lengths of the higher order modes.\textsuperscript{79} The slope of the dispersion curve allows the group velocity to be determined.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{(a) Reflected light image of a Au nanostripe created by photolithography. The nanostripe is 100 \( \mu m \) long, 4 \( \mu m \) wide, and 50 nm thick. (b) Real space image of the leaky PSPP mode excited by focusing a 760 nm laser at the end of the structure. (c) Corresponding Fourier space (back-focal plane) image of the leaky mode. For this image only light from the region indicated by the red rectangle in (b) was allowed to reach the detector. (d) Dispersion curve for the 4 \( \mu m \) wide Au nanostripes. The green symbols are the experimental measurements (average of three separate nanostripes), and the red solid lines are the results from finite element simulations. The different red lines correspond to different order leaky modes. The black dashed line is the light line. Reprinted with permission from Beane et al., J. Phys. Chem. C 123, 15729–15737 (2019). Copyright 2019 American Chemical Society.}
\end{figure}
For the 4 μm wide Au nanostripes in Fig. 3, $v_g = (0.89 \pm 0.01)c_0$, where $c_0$ is the speed of light in vacuum. Thus, combining the information from the real space and Fourier space experiments generates the values of $L_{SPP}$ and $v_g$ needed to calculate the lifetimes of the leaky PSPP modes.

The measured $T_1$ lifetimes are plotted in Fig. 4(a) for different width Au nanostripes, all of which are 100 μm long and 50 nm thick. The solid blue line in Fig. 4(a) shows the results from finite element simulations. The experimental and simulated lifetimes are in good agreement. This implies that the dielectric constants for the 50 nm thick Au nanostripes created by photolithography and electron beam evaporation of Au are close to the literature values, that is, there is no significant degradation in the optical properties of the structures due to surface roughness or polycrystallinity in the samples. There are two important points to note from Fig. 4(a). First, the PSPP lifetimes are almost an order of magnitude longer than the lifetime of the LSPRs of the Au nanorods in Fig. 1, which are $\ll 10$ fs. This is because the field for the leaky PSPP modes is mainly localized outside the metal, which reduces the damping from resistive heating effects.

The second point to note is that the leaky PSPP mode lifetime decreases significantly for the narrower nanostripes.

To understand the decrease in the PSPP lifetimes with decreasing width, simulations were used to investigate how $\Gamma_r$ and $\Gamma_q$ vary with dimensions for the lowest order leaky mode of the Au nanostripes. The simulations were performed for nanostripes on a glass substrate, and the results are presented in Fig. 4(b) as the attenuation constant ($\alpha$) of the lowest order leaky mode vs thickness for 2, 4, and 8 μm wide nanostripes. The solid lines in Fig. 4(b) are the total attenuation ($\alpha_{tot}$), and the dashed and dotted lines are the contributions from radiation damping ($\alpha_r$) and resistive heating ($\alpha_q$), respectively. In this analysis, the values of $\alpha_q$ were obtained by integrating the dissipated power over the volume of the nanostructure, and those of $\alpha_r$ from integrating the scattered power over a surface that surrounds the nanostructure.

These simulations show that the attenuation due to resistive heating is similar for the different sized nanostripes, however, the power radiated into the substrate increases dramatically when either the width or the thickness of the nanostripes is reduced.

The increase in $\alpha_r$ with decreasing thickness is attributed to a geometrical effect. The field for the leaky mode is primarily located at the top of the nanostructure, and the rate of radiation damping is controlled by how this field couples to the photonic modes in the

FIG. 4. (a) Lifetime of the leaky mode (red symbols) vs width for 50 nm thick Au nanostripes recorded at an excitation wavelength of 760 nm. The errors represent standard deviations calculated from at least three repeated measurements. The solid blue line shows finite element simulation results for different width Au nanostripes. (b) Simulated attenuation constants for different thickness Au nanostripes with widths of 2 (red), 4 (green), and 8 (blue) μm. The solid lines are the total attenuation, and the dashed and dotted lines are the radiation damping and resistive heating contributions, respectively. (c) Cross-sectional mode plots (norm of the electric field) for the lowest order leaky modes of Au nanostripes with widths of 2, 4, and 8 μm. The scale for the electric field is given to the right of the image, and the images have been scaled so that the nanostripes appear to have the same width. The simulations were performed at a wavelength of 800 nm. Reprinted with permission from Beane et al., J. Phys. Chem. C 123, 15729–15737 (2019). Copyright 2019 American Chemical Society. (d) Attenuation constant vs refractive index of the medium above the nanostripe ($\lambda = 800$ nm) and (e) attenuation constants vs wavelength (for air) for a 4 μm wide/50 nm thick nanostripe. The red symbols are experimental measurements. Solid lines = $\alpha_{tot}$, dashed = $\alpha_r$, and dotted = $\alpha_q$. The inset for (d) shows $k_{SPP}/k_0$ vs refractive index.
The component of the SPP wavevector: $k_{\text{SPP}}$ at a metal-dielectric interface is given by the imaginary component of $Q(k)$. This attenuation is attributed to a resonance effect. Specifically, the attenuation for SPPs in the nanostripes is large compared to substrate photons. It is important to note that the behavior of the leaky mode is opposite to what happens for the LSPRs of particles, where radiation damping is more important at larger dimensions, not smaller dimensions.

Figure 4(d) shows a plot of the calculated attenuation constant for the lowest order leaky mode of a 4 $\mu$m wide Au nanostripe. Similar to the analysis in Fig. 4(b), the attenuation constant is broken up into contributions from radiation damping and resistive heating. The inset of Fig. 4(d) shows a plot of $k_{\text{SPP}}/k_0$ for the lowest order leaky mode of a 4 $\mu$m wide Au nanostripe. The attenuation constant increases as the refractive index decreases due to increases in radiation damping. This result is similar to what happens for the LSPRs of spheres; however, the explanation is different. Increasing the refractive index of the surroundings increases $k_{\text{SPP}}/k_0$, bringing the effective index of the leaky mode closer to the refractive index of the substrate. This increases the coupling between the leaky mode and photons in the substrate.

The final issue examined for the leaky PSPP mode is how the attenuation depends on the wavelength. The plots of the calculated values of $a_{\text{rad}}$, $a_{\text{tot}}$, and $a_{\text{rad}}$, vs wavelength are presented in Fig. 4(e) for the lowest order leaky mode of a 4 $\mu$m wide Au nanostripe. Experimental measurements are shown as the red symbols (average from five separate nanostripes). The experiments and simulations are, again, in excellent agreement. The simulations show that $a_{\text{rad}}$ increases as the wavelength decreases, which is expected when the wavelength approaches the onset of the interband transitions of Au. However, there is also a large increase in the radiation damping component of the attenuation. For LSPRs, theory predicts that $\Gamma_{\text{rad}}$ should be proportional to $1/\lambda^3$. The $a_{\text{rad}}$ data in Fig. 4(e) have a stronger wavelength dependence, which is attributed to a resonance effect. Specifically, the attenuation for SPPs at a metal-dielectric interface is given by the imaginary component of the SPP wavevector: $a = k \sin \sqrt{\epsilon_1(\omega)\epsilon_2/(\epsilon_1(\omega) + \epsilon_2)}$, where $\epsilon_1(\omega)$ is the dielectric constant of the metal and $\epsilon_2$ is the dielectric constant of the surrounding medium. This simple expression predicts a large increase in attenuation when $\text{Re}[\epsilon(\omega)] \to -\epsilon_2$, which for Au occurs around the onset of the interband transitions at approximately 600 nm wavelength. A similar effect is expected for the attenuation of the leaky PSPP mode in the nanostripes.

IV. MECHANICAL RESONANCES

Metal nanoparticles also display low frequency resonances corresponding to the vibrational normal modes of the object. These modes can be conveniently studied by transient absorption spectroscopy measurements. In these experiments, excitation by an ultrafast laser pulse causes rapid lattice heating. The time scale for this process is a few picoseconds which, for particles larger than several nm, is faster than the characteristic time scale for lattice expansion. Because of this difference in time scales, the vibrational normal modes of the particle that correlate with the expansion coordinate are impulsively excited. The modes that are excited are primarily breathing modes. These modes produce a small periodic change in the volume of the particles, which creates a small shift in the position of the LPSR. This shift can be detected in transient absorption experiments when the probe laser is tuned near the LPSR.

The periods of the breathing modes can be accurately calculated by continuum mechanics, even for particles with complex shapes, and typically fall in the terahertz to gigahertz frequency range. Like the LSPRs in the visible spectral region, the dephasing times of these acoustic resonances have contributions from internal relaxation and energy transfer to the environment. For particles on or in a solid support, the measured relaxation times can be explained by radiation of sound waves into the solid. Specifically, the vibrational quality factors depend on the difference in acoustic impedance between the nanoparticle and the solid support. For small $\Delta Z$ values, the sound waves are transmitted at the nanoparticle-substrate interface, leading to rapid dissipation of acoustic energy into the environment and small quality factors. In contrast, for large values of $\Delta Z$, the sound waves are reflected at the interface, which leads to longer lifetimes and larger quality factors. The presence of these sound waves has been detected in transient absorption experiments that monitor the surface displacement of the supporting structure.

It is important to note that for the majority of single particle studies reported so far, the measured quality factors for damping by solid substrates are significantly larger than the calculated values, and there are typically large variations in the quality factors from particle to particle. Both these effects can be attributed to variable mechanical coupling between the particles and the substrate.

For particles in a liquid, it is possible that other relaxation processes can occur in addition to radiation of sound waves. In these experiments, single nanowires are suspended over trenches cut into a glass substrate. Transient absorption microscopy measurements are then performed for the suspended nanowires in air and in different liquids, and the results are subtracted to yield the damping from the liquid. Specifically, the transient absorption traces yield the lifetime $\tau_i$, and frequencies $f_i$ of the vibrational modes, which are used to calculate a quality factor $Q_i = \pi f_i \tau_i$. The quality factors have contributions from internal relaxation ($Q_{\text{int}}$), surface bound ligands ($Q_{\text{surf}}$), and the environment ($Q_{\text{env}}$), which is either air or liquid in these experiments. These different contributions add as $1/Q_{\text{tot}} = 1/Q_{\text{int}} + 1/Q_{\text{surf}} + 1/Q_{\text{env}}$. Assuming that the internal relaxation and surface bound ligand effects do not change when liquid is added, and that air has a negligible effect on damping, the damping due to the liquid can be determined by $1/Q_{\text{liq}} = 1/Q_{\text{tot}} - 1/Q_{\text{air}}$. 


Published under license by AIP Publishing
Figure 5(b) shows example transient absorption traces for a single nanowire in air and water. Chemically synthesized nanowires have pentagonal cross sections, which give rise to two breathing modes corresponding to motion at the faces and apexes of the pentagon.\textsuperscript{22} This produces the beating pattern in the transient absorption traces. The modulations from the coherently excited breathing modes of nanowires suspended over trenches on a glass substrate are strongly damped by the addition of water. The data show that the quality factors change by roughly a factor of two for water compared to glycerol, even though there are several orders of magnitude difference in the viscosity of these two liquids.\textsuperscript{21}

The solid line in Fig. 5(c) is a calculation of the quality factor expected for a circular cylinder in a homogeneous solidlike environment.\textsuperscript{24} In these calculations, the system (nanowire plus environment) is described using the Navier equation in cylindrical coordinates.\textsuperscript{22,23} The displacement fields for the breathing mode vibrations are taken to be Bessel functions and Hankel functions of the first kind for the nanowire and the environment, respectively.\textsuperscript{22,23} This choice of functions ensures that the displacement is finite at the center of the cylinder and corresponds to an outgoing cylindrical wave in the surroundings. Applying the boundary conditions of continuity in radial stress and displacement at the cylinder-medium interface yields the following eigenvalue equation:

$$
\rho_i \left( c_i^2 k_i R \frac{J_0(k_i R)}{J_1(k_i R)} - 2 c_{T,i} \right) = \rho_m \left( c_m k_m R \frac{H_0(k_m R)}{H_1(k_m R)} - 2 c_{T,m} \right),
$$

where \( \rho_i \) and \( c_i \) are the density and longitudinal and transverse speeds of sound in the cylinder (i = c) or surrounding medium (i = m), respectively, \( k_i = \omega/\sqrt{c_i^2 \rho_i} \), and \( J_n \) and \( H_n \) are the Bessel and Hankel functions, and \( R \) is the radius of the cylinder.

Equation (2) can be solved numerically to give a series of complex eigenfrequencies, with frequencies and damping rates of \( f = \text{Re}[\omega]/2\pi \) and \( \gamma = \text{Im}[\omega] \), respectively. The quality factor for damping due to the environment is thus \( Q = \pi f / \gamma = \text{Re}[\omega]/2 \text{Im}[\omega] \).\textsuperscript{28,29,32} Note that the Q values from Eq. (2) are independent of size. This is because both the frequencies and the damping constant scale with size in the same way (\( \propto 1/R \)). The 1/R size dependence of \( \gamma \) can be understood by following the analysis presented above for LSPRs, that is, the rate of energy loss is \( (dU/dt) = -\gamma U \), where \( U \) is now the acoustic energy stored in the nanostructure. For radiation of sound waves, \( dU/dt \) is proportional to the amount of the surface area of the structure in contact with the medium,\textsuperscript{31} and \( U \) is (again) proportional to the volume. Thus, \( \gamma = -(dU/dt)/U \) is proportional to the surface-to-volume ratio and goes as \( 1/R \) for a circular cylinder. The simple calculations of Eq. (2), which treat the surroundings as having a solvodynamic response, are in excellent agreement with the experimental results in Fig. 5.\textsuperscript{31} This means that in liquid environments the damping of the breathing modes of nanostructures is controlled by radiation of sound waves into the surroundings, just like for solids. This process is analogous to radiation of electromagnetic waves for the plasmon resonances of metal nanostructures.

Note that the situation is more complex for vibrational modes that produce shear waves in the liquid, such as the extensional modes of nanorods.\textsuperscript{31,32} In this case, calculations show that the shear viscosity of the liquid can play a significant role in relaxation.\textsuperscript{35} Unfortunately, single particle measurements are much harder for the extensional modes compared to the breathing modes. This is because the suspended nanostructure scheme in Fig. 5 cannot be used to study modes where there is a change in the length. Ruigrok et al. used transient absorption microscopy in combination with an optical trap to study the extensional modes of single Au nanorods in water.\textsuperscript{34} They showed significantly different quality factors for...
the extensional modes compared to the breathing modes; however, these experiments are very challenging so that it was not possible to study nanorods in different liquids—like in Fig. 5(c). Ensemble measurements in water-glycerol mixtures for Au bipyramids, which can be made with very monodisperse size distributions, have shown that solvent viscoelasticity does affect the relaxation. The results of these experiments are in good agreement with calculations that include solvent shear viscosity.

An intriguing possibility for the vibrational modes of nanostructures is to use them as mass sensors (“nanobalances”). However, very high quality factors are needed for accurate measurements, which means that radiation damping must be controlled. Recently, it has been shown that quality factors as high as 70 can be achieved by manipulating the aspect ratio of gold nanodisks on a substrate, which is over three times the typical values found for substrate supported nanodisks. This effect was attributed to hybridization between the vibrational modes of the nanoparticle and those of the substrate. For certain shapes, this creates modes that are localized on the nanoparticle but are decoupled from the substrate.

A more facile approach to reducing radiation damping for the acoustic vibrations is to simply remove the environment by either suspending the nanostructure in air (as was done in Fig. 5) or placing it on a very thin/light substrate. For nanowires, the vibrational quality factors are on the order of 30–70 for the suspended structures, which are only a factor of 2–3 higher than that for particles on the substrate. This indicates that these structures suffer fairly strong internal damping effects. In contrast, Fig. 6 shows results for a single suspended gold nanoplate where much higher quality factors have been achieved. An optical image of nanoplates suspended over trenches is presented in Fig. 6(a), and a transient absorption trace from a suspended plate is shown in Fig. 6(b). The oscillations in the trace arise from the thickness vibration of the plate, and in this case, the quality factor is ~200. Similar results have been obtained for nanoplates on lacy carbon films. The much higher quality factor for nanoplates compared to nanowires is attributed to the differences in crystal structure—chemically synthesized nanoplates are single crystals with smooth surfaces. The high quality factors for the vibrational modes of the suspended nanoplates mean that their frequencies can be accurately measured. This was recently exploited to examine vibrational coupling between overlapped nanoplates and in principle can enable mass sensing through measuring changes in the vibrational frequencies.

It is important to note that damping due to radiation of sound waves is different from heat transfer to the environment. The radiating sound waves are a coherent motion, whereas heat transfer involves incoherent phonons. Heat transfer has been extensively studied for different nanomaterials—mainly through ensemble measurements. Recent studies for particles in a solid environment have shown that the rate of heat transfer also depends on the difference in acoustic impedance between the particle and its environment, like the radiation of sound waves. For liquid environments, the heat capacity, thermal conductivity, and interface thermal conductance of the environment are also important parameters. However, heat diffusion typically occurs on a slower time scale than the dephasing times for the acoustic vibrational modes discussed above.

V. SUMMARY AND OUTLOOK

Metal nanostructures display three different spectral features: LSPRs that give rise to bands in the visible to near-IR regions of the spectrum, PSPP modes corresponding to motion of electrons at the surface of the structure, and low frequency resonances associated with the vibrational normal modes of the object. These motions are damped by internal relaxation and by radiation of waves into the surroundings. The goal of this article has been to provide an overview of the factors that control radiation damping in metal nanostructures, in particular, how the efficiency of this process depends on the properties of the environment and the size of the nanostructure.

For electromagnetic waves, the important property of the environment is the refractive index, and for sound waves, it is the acoustic impedance. In general, the rate of radiation damping increases with the magnitude of the refractive index or the acoustic impedance of the environment. However, the fundamental reason is different for different resonances. For the dipolar LSPRs, the increase in refractive index increases the polarizability of the nanoparticle, which increases the scattering efficiency and therefore, the radiation damping. For the acoustic modes, the rate of radiation damping depends on the difference in acoustic impedance $\Delta Z$ between the particle and the environment, with faster rates occurring for smaller values of $\Delta Z$. Noble metals have large acoustic impedances due
to their high densities, which means that $\Delta Z$ decreases and the rate of radiation damping rate increases with increasing acoustic impedance of the environment. The PSPP modes show a different effect. For these modes, the rate of radiation damping is determined by their effective index $n_{\text{eff}}$. For the leaky mode, increasing the refractive index of the medium above the nanostructure increases $n_{\text{eff}}$, bringing it closer to the refractive index of the substrate (usually glass). This increases the coupling to the photonic modes of the substrate.

The size of the structure is also an important effect and is the property that can be most easily controlled. For the dipolar LSPRs, radiation damping increases with size ($\Gamma_{\text{rad}} = 2\hbar n V$), again because of increases in the scattering cross section. In contrast, the rate of radiation damping for the leaky PSPP modes increases as the dimensions of the nanostructures decrease. For the thickness dimension, this is because decreasing the height of the structures increases the overlap between the leaky PSPP field (which is primarily at the metal-air interface) and the substrate photonic modes, which increases radiation damping.\(^1\) For the width dimension, the leaky PSPP modes become less confined as the width decreases, leading to stronger coupling to substrate photons.\(^2\)\(^3\)\(^4\) The rate of radiation damping for the acoustic modes also increases as the dimensions of the structure decrease. However, this is a surface-to-volume effect: a larger contact area with the surroundings leads to more efficient transfer of acoustic energy.\(^5\)

For applications such as sensing, it is desirable to have resonances with high quality factors (long lifetimes) and high frequencies, which means that radiation damping should be reduced. For the LSPR and PSPP modes, the most straightforward way of doing this is to control the size of the structures—use small structures for the LSPR and PSPP modes, the most straightforward way of doing this, which means that radiation damping should be reduced. For the LSPR and PSPP modes, the most straightforward way of doing this is to control the size of the structures—use small structures for the LSPR and PSPP modes, the most straightforward way of doing this, which means that radiation damping should be reduced.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support from the National Science Foundation through Award No. CHE-1502848. K.Y. acknowledges the support from the National Natural Science Foundation of China (NSFC Grant No. 61705133). The authors are also grateful to their collaborators, which for this work includes John Sader and Debadi Chakraborty (University of Melbourne), and Sasha Govorov (Ohio University).

REFERENCES
