Mapping plasmons at the nanometer scale in an electron microscope

Mathieu Kociak* and Odile Stéphan

In this tutorial review, we present the use of electron energy loss spectroscopy (EELS) and cathodoluminescence (CL) spectroscopy for surface plasmon mapping within metallic nanoparticles. We put a special emphasis on particles that are much smaller than the wavelength of visible light. We start by introducing the concept of surface plasmons, keeping the formalism as simple as possible by focusing on the quasi-static approximation. We then make a link between optical cross-sections, EELS and CL probabilities, and the surface plasmons' physical properties. A short survey of simulation tools is given. We then present typical experimental set-ups and describe some problems frequently encountered with spectrometers. Experimental conditions for improved signal to noise ratio are discussed. Analysis techniques are discussed, especially those related to the spectral imaging mode, which is extremely useful in EELS and CL experiments. Finally, the specific range of applications of EELS and CL with respect to other nano-optic techniques is discussed, as well as the strengths and weaknesses of EELS as compared with CL.

Key learning points
- What is a surface plasmon in a nanoparticle?
- Why EELS and CL are good at mapping surface plasmons?
- When EELS and CL are worth using instead of other tools to study surface plasmons?
- How to perform optimised EELS and CL experiments for surface plasmon mapping?

1 Introduction

Chemical and nanofabrication engineering have created a panoply of new nanoobjects with properties that strongly depart from those of their bulk counterparts. Among them, noble metal nanoparticles (NPs), with sizes close to or smaller than the typical wavelength of light in the visible range, are of special interest. Their optical properties are dominated by the absorption and scattering of light by confined electromagnetic waves called surface plasmons (SPs). SPs are, in small NPs, mostly oscillations of the surface charge density. As the note sounded by a bell entirely depends on its shape and size, because acoustic waves are confined at its surface, the colour of an NP depends on its shape and size because of SP confinement at its surface. Similarly, as acoustic energy density in a bell concentrates at antinodes of acoustic waves, SP energy density concentrates at antinodes of SP waves in small volumes close to the surface of the NP.

Chemists’ ingenuity has made engineering the electromagnetic field at a distance much smaller than the wavelength of light (the so-called “sub-wavelength scale”) readily possible, opening a large and fascinating field of investigation for physicists. In addition, the SP energy value heavily depends on the immediate local environment of the NP. For example, a change in the local dielectric properties induces easily detectable energy shifts. All these properties hold great promise for applications ranging from biological and chemical sensors to enhanced photovoltaic devices.

However, SP phenomena appear at scales that are inaccessible to standard optical techniques. Indeed, sub-wavelength phenomena are by definition not observable using common optical microscopes, whose resolution is diffraction-limited to around half the wavelength of light—not better than typically 200 nm. Various strategies have been developed in the past twenty five years to overcome this limit, leading to experimental and theoretical breakthroughs in the field of SP and beyond. Among these, the use of fast electrons such as those produced in an electron microscope (EM) has proved extremely well adapted to the study of SPs in NPs.
In their pioneering work, thirteen years ago, Yamamoto et al.\(^1\) showed for the first time that it is possible to access information on SPs in the visible range at sub-wavelength scales by detecting the photons emitted under electron irradiation (cathodoluminescence spectroscopy, CL) in a scanning transmission electron microscope (STEM). This observation was supported by accurate simulations based on well-established theories.\(^2\) This led to the improvement of CL systems on the one hand, essentially in scanning electron microscopes (SEMs), and the use of other spectroscopic signals generated by the interaction between the electron and the SP on the other hand. Indeed, after decades of experimental and theoretical developments for the study of materials optical properties,\(^3\)\(^–\)\(^5\) electron energy loss spectroscopy (EELS) has gained recently\(^6\)\(^,\)\(^7\) a huge interest for SP mapping in the infrared to ultraviolet (IR-vis-UV) range. An example of an EELS experiment\(^6\) is presented in Fig. 1 for a triangular silver prism which is much smaller than the wavelength of light. It shows that it is possible to measure the nanometric spatial distributions of SP arising over the IR-vis-UV range. Different energy peaks appear at different locations over the prism (Fig. 1a). The location where an EELS spectrum is acquired can be identified with high precision because the normal image is taken in parallel (inset of Fig. 1a). The energy value of a given peak does not change over the prism (Fig. 1b). However, a strikingly different and characteristic intensity pattern over the prism, with rapid changes at the nanometer scale (Fig. 1c–e), is associated with each energy.

Such kind of experimental findings\(^1\)\(^,\)\(^6\)\(^–\)\(^8\) indicate that EELS and CL are good at “mapping surface plasmons”. Despite the existence of firmly established theoretical and simulation tools,\(^4\)\(^,\)\(^5\) there is a clear need to understand to which extent the maps and spectra measured in EELS and CL are related to SPs’ physical properties and more generally to optical measurements. The precise interpretation of such experiments in terms of plasmons’ eigenmode mapping\(^9\)\(^–\)\(^11\) has definitely promoted EELS and CL as relevant nanooptical tools for studying SPs in NPs. The present tutorial aims at introducing the interpretation and use of EELS and CL for mapping the SPs’ physical properties. It starts with a description of SPs in small NPs. Considering mainly small particles will help to simplify the formalism, but will furnish interpretations that can be qualitatively extended to larger ones. Keeping the same formalism, we introduce the calculation of experimental optical, EELS and CL cross-sections. This highlights the link between photon- and electron-based optical studies. We then switch to the description of experimental apparatus and data analysis. EELS and CL set-ups are still rather rare and expensive. This part is intended to indicate the key aspects to be checked when visiting facilities equipped with such systems or when planning to acquire new equipment. We start by describing typical EM set-ups, emphasising key aspects of EELS and CL spectrometers and acquisition conditions. We then switch to the analysis of EELS and CL data, insisting on the wealth of information contained in the huge set of spectra (called “spectral-images”, SI) usually acquired in EELS and CL experiments. We finish with a general description of the strength and weaknesses of EELS and CL experiments as well as their related applications.

In doing so, we leave many of the difficulties untreated. On the theoretical side, we suggest to the interested reader the excellent and comprehensive theoretical discussions in the review of J. Garcia de Abajo\(^12\) and references therein (especially...
the review of Rivacoba et al.15). Comprehensive discussions of
the approximations and interpretations used in the first section
of this tutorial can be found in more recent studies.11,13 On
the experimental and analysis side, information on STEM, EELS
and SI can be found in ref. 14 and 15. Technical aspects of
modern CL systems, especially concerning the use of CL for SP
mapping, have not been reviewed recently to the best of our
knowledge. The reader may find it fruitful to read the well-
known book of Yacobi.16 Recent applications of EELS and CL
knowledge. The reader may find it fruitful to read the well-
modern CL systems, especially concerning the use of CL for SP
experimental and analysis side, information on STEM, EELS
for the study of the optical properties of small nanoparticles,
both metallic and semi-conducting, have been reviewed in
depth in ref. 17. Finally, we have concentrated our study on
small NPs—essentially bottom-up structures. CL has been
shown to be of very great value for studying larger, essentially
top-down, structures, and the interested reader is invited to
consult ref. 18 and references therein for further information.

2 What is a surface plasmon?

2.1 Quasi-static descriptions of plasmons in metallic nanoobjects

Surface plasmons are most generally described as a mixture of
photons and electrons. Formally, they are solutions of the
Maxwell equations. However, when the size of the object of
interest is smaller than the typical wavelength of light (let us
recall that the visible range extends from typically 400 nm—
violet—to 700 nm—red), electromagnetic phenomena are well
described within the so-called quasi-static (QS) approximation.
In the QS approximation, only the Poisson equation plus
relevant boundary equations are necessary:12

\[ \nabla \cdot \varepsilon(\vec{r}, \omega) \nabla \phi(\vec{r}, \omega) = 0 \]  
(1)

\[ \vec{D}_1 \vec{n} = \vec{D}_2 \vec{n} \]  
(2)

where \( \varepsilon(\vec{r}, \omega) \) is the space- and energy-dependent dielectric
constant linking the electric displacement \( \vec{D}(\vec{r}) \) to the electric
field \( \vec{E}(\vec{r}) \) through \( \vec{D}(\vec{r}) = \varepsilon(\vec{r}) \vec{E}(\vec{r}) \), and \( \phi(\vec{r}, \omega) \) is the electric
potential at energy \( \hbar \omega \). \( \vec{D}_1 \vec{n} \) (resp. \( \vec{D}_2 \vec{n} \)) is the component of
the electric displacement at the interface between medium 1
and 2 and perpendicular to it in medium 1 (resp. 2).

These equations are much easier to manipulate than the
Maxwell equations. In frequency space, they are, for each individu-
also describes the potential and
charges of the system. In this context, plasmons are then simply
described as self-sustained charge oscillations. The solutions are
very accurate for the description of SPs in small metallic NPs, and
give very relevant first order physical approximations for most
larger ones. Finally, the plasmons measured by fast electrons, such
as those delivered by an electron microscope, are often well
described in this approximation. The QS approximation will be
used mostly in this tutorial, for the sake of simplicity and without
much loss in generality. For phenomena that are not well
described in the QS approximation—so-called retarded, relativistic,
or propagative phenomena—we will give a short description of the
departures. For interested readers, an enlightening discussion on
retarded phenomena, especially in the context of EELS, is given in
the introduction of ref. 19.

In eqn (1) and (2), the nanoobject(s) of interest and their
environment are hidden in the description of \( \varepsilon(\vec{r}, \omega) \). Unless
otherwise specified, we will consider the dielectric constant to be
\( \varepsilon(\omega) \) within the nanoobject(s) and 1 in the surrounding
medium (thus supposed to be the vacuum). The effects of other
kinds of surrounding media will be discussed when necessary.

There are multiple possible descriptions of dielectric func-
tions. For metals, a useful description is that given by the
Drude model, where

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + \gamma)} \]  
(3)

with \( \omega_p \), the so-called bulk plasmon frequency and \( \gamma \) a damping
term. Although imprecise, the Drude model, when introduced
in eqn (1) and (2), is simple and gives most of the salient
information when dealing with SPs in metals. SPs always occur
at energies lower than the bulk plasmon energy, in a region
where the dielectric constant is negative.

Surface plasmons are expected to arise in most materials, be
they metals, semi-conductors or insulators. However, only in a
few metals with dielectric constant barely resembling that of
Drude models do SPs arise in the IR-vis-UV range. The most
common ones are Ag (bulk plasmon around 3.8 eV), Au (bulk
plasmon around 2.6 eV) and Al (bulk plasmon around 15 eV).

Finally, surface plasmons are highly dissipative excitations.
This means that the full width at half maximum (FWHM) of an SP
peak is quite large, typically around one to a few hundreds of meV.

2.2 Plasmons in infinite slabs and cylinders

To start with, it is interesting to consider infinite and highly
symmetric systems instead of more realistic ones. Indeed, the
former allow for simple analytical expressions,5 and many inter-
esting NPs (such as nanorods or nanoprisms) can be at least
conceptually built from these simple objects, as we will see.

NP plasmons can be usefully characterised using conceptual
tools known as response functions. The simplest way of doing
so is to impose (in a thought experiment) an electric field
(varying at frequency \( \omega \)) and to measure the induced electric
field at the same frequency. The ratio between them will
characterise the electromagnetic response of the system, in
the present case, the plasmons. Plasmon energies will be
defined as the poles of the response functions. These functions
may take different names and have a symmetry-dependent
definition depending on the object under consideration: Fres-
nel coefficient for planar structures, polarizability or multipolar
polarizability for spheres and cylinders.5,12 The important
point is that the response functions will depend uniquely on
the geometry of the system and the dielectric constant, and will
show resonances characteristic of the plasmon energies.

In the case of infinite slabs and cylinders, the systems being
invariant with respect to translation along one or two axes, it is
possible to define a wavevector \( \vec{q} \) along this (these) axis (axes).
The electric potential of the plasmon of wavevector \( \vec{q} \) will
oscillate along the direction(s) with a wavelength \( \lambda = 2\pi/|q| \).

In the case of a cylinder of diameter \( d \) or a slab of thickness
\( d \), a convenient way of representing these response functions is
to plot their maxima as a function of the energy and the wavevector. The resulting so-called dispersion relations, which give the energy and wavevector relations for all the plasmons of the systems, are presented in Fig. 2 for a cylinder (Fig. 2a) and a slab (Fig. 2b). One notes that in the QS case, the dispersion relation has a universal behaviour. The energy does not depend on the wavevector alone, but on the wavevector multiplied by $d$. This will have interesting consequences discussed below. The dispersion relations exhibit similar behaviours for both geometries. They exhibit a low energy branch that strongly disperses from 0 to an energy $\omega_{\text{sp}}$, somewhat confusingly called surface plasmon energy. This energy corresponds to the maximum of the response function for an infinite plane \( \tilde{E}(\omega_0) \), which arises for $d(\omega_0) = -1$. The symmetry of the modes of this branch is the same for both the cylinder and the slab. They are symmetric in charge (see insets in Fig. 2). For the cylinder, this corresponds to an "$m = 0$" mode, with $m$ being an integer giving the number of nodes of the surface charge density along the perimeter of the cylinder. Of course, along the cylinder length, the charge density associated with an $m = 0$ SP oscillates according to its associated wavevector. Other modes are present at higher energy. They barely disperse in a narrow energy window around $\omega_{\text{sp}}$ (blue and green modes in Fig. 2). They correspond to other charge symmetries and will be ignored here for the sake of simplicity. Studying the low energy branch allows one to understand in simple terms what happens in two popular NP systems: nanoprisms and nanorods (nanoantennas). It is worth noting that in a retarded treatment, high order modes have a much higher dispersion at small wavevectors than in the QS approximation.\(^{14}\)

Finally, we note that the polarizability depends on the medium in which the object is embedded. For a medium of dielectric constant $\varepsilon_m$, the condition for a surface plasmon to arise becomes $\varepsilon(\omega_0) = -\varepsilon_m$. Due to the fact that $\varepsilon$ increases monotonically with $\omega$, and because $-\varepsilon_m < -1$, this leads to a red-shift of the plasmon energy. For example, in the Drude model and for an infinite plane, it corresponds to $\omega_{\text{sp}} = \frac{\omega_p}{\sqrt{1 + \varepsilon_m}}$. A red-shift is always expected when a metallic object, whatever its shape and size, is placed in or close to an insulating medium. The higher the medium dielectric constant, the higher the shift.

### 2.3 Plasmons in prisms and rods

A very simple way of understanding the formation of SPs in 2D prisms and nanorods is to start from a 2D slab or an infinite cylinder, which we cut to form a prism or a nanorod, and see the effect on the dispersion relations. It is easier to consider the effect on a rod of length $L$. Truncating a cylinder, we would impose new boundary conditions at its ends, restricting the number of possible wavevectors (typically, integer multiples of $1/2L$) and corresponding energies for the plasmons (for example $\omega_0$ and $\omega_2$ for the two first modes as shown in Fig. 2). This will induce the creation of stationary charge density waves (plasmon waves) of well defined energy and symmetry—the result is shown in the case of a nanorod in Fig. 2 and 3. In the case of the $m = 0$ modes of nanorods, there appear modes of increasing orders (number of oscillations), wavevectors (decreasing wavelengths), and energy, which are either symmetric or antisymmetric with respect to the rod mid-plane, but of course axially symmetric in charges.

Such a simple model makes it possible to draw simple conclusions on the energy of the modes. Indeed, as already mentioned, the dispersion relation depends on $qd$ in the QS approximation. In a nanoparticle, this means that the energy of a
mode of given order will depend only on the aspect ratio \( d/L \), irrespective of the actual size of the nanoparticle. The plasmons’ properties are thus to first order driven by the geometry of the nanoparticle rather than its actual size. This approximation, of course, becomes increasingly invalid as the NP size increases and as retardation effects come into play. Still, this approach explains most of the physics of small (less than a few hundreds of nm) nanoparticles and especially flat or elongated ones.

The lowest energy modes, known as dipolar modes, presenting a \(+|−\) charge distribution (see Fig. 2 or 3) are ubiquitous. As they strongly interact with light, they occupy a special place and will be discussed in more detail later.

### 2.4 Surface plasmons in a sphere

Finally, an important class of nanoparticles must be discussed: spheres. Contrary to the former case of nanorods or prisms, it is indeed one of the few NP geometries (with ellipsoids) yielding analytical expressions for most physical properties and experimentally relevant quantities (like, for example, optical cross sections or EELS and CL probabilities). These expressions clarify the link between photon- and electron-based optical techniques.

Plasmon modes in a sphere are usually classified with respect to their angular momentum \( l \), for which a polarizability \( \alpha_l(\omega) \propto \frac{l(l + 1)}{\varepsilon_0 + l + 1} \) can be defined. With each different \( l \) value is associated, in the QS approximation, a given charge distribution. Here, \( l \) plays the role of \( qd \) in the preceding examples. Once again in the QS approximation, the plasmon energies do not depend on the size. The redshift of the dipolar plasmon as a function of the sphere’s size is a well-known retarded effect.

The dipolar plasmon of a sphere has an energy given by the low energy pole of the response function. This corresponds to the condition \( \varepsilon = -2 \) and to a plasmon energy \( \omega_p = \frac{\omega_0}{\sqrt{3}} \) in the Drude model. The associated charge distribution is given by an accumulation of positive and negative charges on opposite poles of the sphere. This is the same symmetry as other dipolar modes, such as that of a nanorod (Fig. 3).

### 2.5 Plasmon in arbitrary nanoparticles

In all the above theoretical examples, SP modes in NPs were characterised by an energy \( \omega \) associated with a given charge density distribution. Both the energy and the spatial distribution result from the confinement of the SP at the surface of the NPs, and are thus intimately linked to their morphology. In the retarded case, the situation is too complex to describe in terms of charge density alone, but other quantities (such as the electric field) can be used. In any case, experimental facts such as those presented in Fig. 1 clearly highlight the need to get a description that links the morphology of NPs to the energy and spatial variation of the SPs.

---

\( \dagger \) Similar retarded effects arise in many geometries especially for the dipolar plasmon, see e.g. ref. 21.

\( \ddagger \) In the presence of dissipation (for example \( \gamma \neq 0 \) in the Drude model), the energy is not real but contains an imaginary part describing the damping of the mode.

---

#### 2.5.1 A generic description: the EMLDOS

A description in terms of modes, accounting for both spatial and spectral variations, thus seems appropriate for representing SPs in NPs. One useful concept achieving this goal is the electromagnetic local density of states (EMLDOS). This quantity gives, at a given point in space, and for a given energy, the density of electromagnetic modes. It helps to pinpoint where the electromagnetic energy is concentrated in the vicinity of NPs. Note that it is a vectorial quantity, as each electric mode has three components.

Following the EMLDOS spatial variation at a particular mode energy gives the spatial variation of that mode, while looking at the spectral information contained in the spatially integrated EMLDOS gives all the plasmon energies. As we will see, EELS and CL are closely related to this quantity projected along the electron beam direction. Unfortunately, there is in general no simple representation of the EMLDOS. In the QS approximation however, where modes can more generally be defined, as we will see in the following section, a simple representation of the EMLDOS can be given.

#### 2.5.2 A convenient modal description for the quasi-static case: the boundary element method solution

It can be shown that the Poisson equation and boundary conditions (eqn (1) and (2)) can be elegantly rewritten in the form of an eigen-equation for the surface charges. The solution of this equation is a set of surface charge distributions \( \sigma_i(\vec{r}) \) and associated (real) eigenvalues \( \lambda_i \) indexing the modes. Associated with these modes, one can also define eigenpotentials \( \psi_i(\vec{r}) \) or eigen-electric fields \( E_i(\vec{r}) \). All these quantities can be calculated within the boundary element method (BEM) framework (see Section 4.4). As an example, Fig. 3 presents the three first solutions \( \varepsilon = -0.89, -0.72, -0.56 \) for a nanorod with an aspect ratio (length/diameter) of 5. The surface eigencharges (Fig. 3a) as well as the square of the eigenpotentials (Fig. 3b) and the z component of the electric eigenfield (Fig. 3b)—in a given plane close to the nanorod surface—are all shown. One clearly sees the standing wave oscillations for each of these quantities associated with the confinement of the SP eigencharge.

We note that none of these quantities explicitly depend on the energy, which is a specificity of the QS approximation. Of course, when one wishes to describe real modes, energy has to come into play. In fact, once the eigenvalues \( \lambda_i \) are calculated, the plasmon energies \( \omega_i \) can be retrieved as the solution of the following equation:

\[
A(\omega_i) = \frac{1 + e(\omega_i)}{1 - e(\omega_i)} = \lambda_i
\]

This scheme is a generalisation of the above-mentioned formalisms developed for slabs or spheres. Indeed, the case of a plane \( \varepsilon = -1 \) is trivially retrieved for \( \lambda_i = 0 \), while the case of the dipolar mode of a sphere \( \varepsilon = -2 \) is retrieved for \( \lambda_i = -1/3 \). Similarly, in the case of the Drude model with a vanishing \( \gamma \), one can retrieve the mode energies as a function of \( \lambda_i \) : \( \omega_i = \frac{\omega_0}{\sqrt{1 + \lambda_i}} \).

\( \ddagger \) Definitions differing by a factor of 2\( \pi \) can be found in the literature. Here, we follow ref. 11, but use a capital \( A \) to differentiate from a wavelength \( \lambda \).
More generally, this method allows us to describe any quasistatic mode, as shown for example in the case of the first few modes of a nanorod in Fig. 3.

This formalism also gives an explicit and intuitive modal representation for the EMLDOS. Most generally, the EMLDOS is a vectorial quantity. Without loss of generality, it can be projected along an arbitrary axis \( z \) (zEMLDOS):

\[
p_z(\mathbf{r}, \omega) = \frac{1}{2\pi^2 \omega} \sum_i \Im[f_i(\omega)] |\hat{E}_i(\mathbf{r})|^2
\]

with \( f_i(\omega) = \frac{A_i + 1}{A_i - A(\omega)} \). Here, we directly see that the spectral properties of the EMLDOS are given by \( f_i(\omega) \), while for a given mode, the zEMLDOS varies in space just like the square of the \( z \) component of the electric field associated with that mode.

To illustrate this clearly, we can rewrite the EMLDOS in the case where the NP is described by a Drude model with a vanishing dissipation \( \gamma \rightarrow 0 \). In that case, \( f_i(\omega) \propto \delta(\omega - \omega_i) \), and exactly peaks at the plasmon eigenenergies.

In the quasi-static approximation, the above-mentioned theory is thus particularly useful for describing the optical properties of NPs at the nanoscale. In Section 4.2, we will see how it is related with the interpretation of EELS and CL.

As a final comment, it is worth mentioning the spatial extent of SP modes. Seen as a charge density (Fig. 3a), an SP mode is obviously confined at the surface of the object of interest. However, the associated eigenfields and eigenpotentials spread over distances that are a good fraction of the typical object size (see Fig. 3b and c). Because the fields are confined relatively close (much less than a wavelength) to the surfaces, techniques that are able to probe them are often called “near-field” techniques. The spatial extent of the electric-field outside of the NP is at the origin of many important properties of SPs. It explains how SPs of different particles can couple efficiently when they are close enough. It also explains how a fast electron can couple to the SP and why the EMLDOS is a relevant quantity for studying SPs.

### 2.6 General retarded case

We have already said that the QS approximation holds for “small” NPs. It is not always easy to define what “small” is and what difference it makes not to consider the retarded approximation. In general, going beyond the QS approximation means that magnetic fields and propagating electromagnetic waves have to be considered. The most notable retarded effects are redshifts in the SP energies, coupling of light to modes other than dipolar (see below), and higher dispersion for high energy SP mode branches. Also, while in the QS approximation the SP properties depend only on the geometry of the NP, and not its actual size, this is not true in the retarded regime. In the literature, it is often considered that “small” means less than half the typical wavelength of light, i.e. around 200 to 400 nm. However, this statement holds only for anisotropic objects, with only one or two dimensions comparable to the typical wavelength of light while the other one(s) is (are) much smaller, i.e. for flat or nanorod-like NPs [see discussion in ref. 20]. Indeed, a case in which a NP is already in the retarded regime for a typical diameter of 50 nm is the sphere. Depending on the constituting material, strong retarded effects including red-shifts arise in this range of diameters. However, the QS approximation is quite an interesting limit for at least two reasons. Firstly, highly anisotropic NPs are among the most widely studied nanostructures, in particular because they appear frequently in colloidal synthesis and are easily synthesised via lithographic techniques. Secondly, most of the physical effects described rely on the fact that the SPs are confined waves at the surface of the NPs. This statement holds in the retarded regime, and many predictions of the QS description can be qualitatively extrapolated to the retarded regime. For example, in a nanorod, even though the nature of the SP changes in the retarded regime (they can no longer be described as pure charge density waves), the most interesting plasmons are still \( m = 0 \) modes confined in the longitudinal direction with a very similar type of dispersion relation.

### 3 Measuring plasmons in far-field optics

Before introducing the link between EELS or CL and plasmon optical properties, let us recall some results for the case of far-field optical measurements with light, which might be more familiar to the reader. By far-field, we mean a measurement in which light is directed onto the sample of interest, the optical properties of which are detected far (in terms of light wavelength) from it. In a typical far field experiment, the spatial resolution is limited by the so-called optical diffraction limit to around half the wavelength of light. The desire to overcome this limit explains the development of innovative all-optical “near-field” techniques24 (e.g. scanning near-field optical microscopy, SNOM), which are not the subject of this tutorial paper but which share many similarities with EELS and CL.

#### 3.1 Cross sections

In a typical classical and linear far-field experiment, there are three important cross-sections to be discussed (see ref. 26 for an in-depth discussion). When one sends an optical plane wave onto a NP of interest, the NP can absorb and/or scatter part of the incoming radiation. This leads to the definition of (wavelength-dependent) absorption and scattering cross-sections. These are useful, as absorption and scattering are dominated by SPs. Another very important quantity is the so-called extinction cross section, which is the sum of the former two cross sections and thus accounts for all interaction phenomena of the light beam with the SPs. It can be measured

---

*For the sake of simplicity, the expression given here excludes points which are within the NP. Full expression can be found in ref. 11.*
through the decrease of intensity of a light beam along its trajectory through a sample.

It is worth stressing here that, for small enough particles (i.e. in the quasistatic approximation), the electric field of an optical plane wave will only interact with dipolar modes. This is because in the QS limit, the exciting electric field is static (no spatial variation) over the entire NP; thus, it can only couple to a $\pi$-sequence of charges.

### 3.2 Linking cross-sections and polarisabilities

At the time of writing, there are no generic formulas for arbitrary NPs that link these cross-sections to the quantity described in the preceding sections.

One important exception is the case of the sphere, which does clearly show the link between the polarisabilities—and thus the plasmon properties—and the cross-sections, even in the full retarded theory. It will also elucidate the link between optical and EELS/CL measurements, as presented later in the text. Also, the results for the dipolar mode of a sphere can simply be applied to any other kind of dipolar modes. We give a brief description of the cross-section properties of the sphere. As always, we will remain, for simplicity, within the QS limit here, letting the reader explore the sphere’s more general optical properties in ref. 4 and 26.

For a sphere of diameter $a$, the extinction cross-section in the QS limit can be written as

$$\sigma_{\text{ex}}(\omega) \propto a^2 \Im[z_{2;1}(\omega)]$$

while the QS scattering cross-section is

$$\sigma_{\text{sca}}(\omega) \propto a^4 |z_{2;1}(\omega)|^2$$

and the absorption cross-section is then equal to $\sigma_{\text{abs}} = \sigma_{\text{ex}} - \sigma_{\text{sca}}$.

Several observations can be made. Firstly, as $z_{2;1}(\omega)$ has a pole at the dipolar plasmon energy, the three cross-sections will have peaks at almost the same energy.** Secondly, in the QS approximation, only the dipolar mode is detected, as already stressed. When the sphere becomes larger and reaches the retarded regime, other multipoles can be excited but with a lower efficiency. Modes that can be detected through optical means are often called “bright” and the others “dark”. Finally, the cross-sections behave quite differently as a function of sphere size, the ratio between the extinction and the scattering cross-section varying as $1/a^3$. Very small NPs scatter very weakly and thus exhibit mostly absorption, while the opposite holds for large particles.

Despite its specificity, the sphere model can be used to understand many other NP optical properties. Indeed, because of the above-mentioned symmetry issues, only dipolar modes can be studied, in the QS limit and by optical means, whatever the geometry of the object. Thus, any NP presenting a dipolar mode will roughly be described by the dipolar cross-section of a sphere, and all the above-mentioned generalities should hold.

** The differences in energy positions are usually small and theoretically vanish for non-dissipating NPs; e.g. $\Im[z_{2;1}(\omega)]$ and $|z_{2;1}(\omega)|^2$ peak at the exact same energy when $\gamma = 0$ in the Drude model.

### 4 A theoretical description of EELS and CL for plasmon measurements

#### 4.1 Generalities and the case of the sphere

The starting equations to describe EELS and CL can be found in ref. 12. The EELS probability is

$$\Gamma_{\text{EELS}}(\mathbf{R}, \omega) = \frac{e}{\pi \rho_0} \int \Re \left\{ e^{-i\mathbf{k}_0 \cdot \mathbf{R}} \tilde{E}^{\text{ind}}(\mathbf{r}, \omega) \right\} d\mathbf{t}$$

with $\mathbf{r}(t) = (\mathbf{R}, \mathbf{k}_0 \cdot \mathbf{r})$ the position of the electron traveling along $z$ at speed $v = |\mathbf{v}|$ and $\tilde{E}^{\text{ind}}$ the electric field induced by the electron polarizing the object of interest. The CL probability is

$$\Gamma_{\text{CL}}(\mathbf{R}, \omega) = \frac{e}{4\pi^2 \rho_0} \lim_{\mathbf{r} \to -\infty} \left\{ |\mathbf{I}|^2 \Re \left\{ \bar{u}_\nu \cdot (\tilde{E}^{\text{ind}}(\mathbf{r}, \omega) \wedge \tilde{H}^{\text{ind}}(\mathbf{r}, \omega)) \right\} \right\}$$

with $\bar{u}_\nu$ the unit vector along the radial direction, and $\tilde{E}^{\text{ind}}(\mathbf{r}, \omega)$ and $\tilde{H}^{\text{ind}}(\mathbf{r}, \omega)$ the induced electric and magnetic fields, respectively.

These expressions are much too specific to be useful as they stand. It is however instructive to understand how an EELS or a CL calculation is performed. In both calculations, the approximation is made that a point electric charge with constant speed impinges on the sample of interest. The electron carries an electromagnetic field (an electric field in the QS approximation) that polarises the NP of interest, which itself generates an induced field.

EELS is computed by estimating the work done by the electron in the induced field it has itself generated. CL is computed by estimating the energy carried by the induced field and propagating to the far-field. It is clear that EELS and CL are efficient only if the induced electric field is oriented along the electron beam path. Although it is not obvious from eqn (9), the same applies to the CL, because no light emission exists if no energy has been previously transferred from the electron to the NP through an energy loss.

It is also worth noting that the electric field here is the induced electric field, which is different from the eigen-electric fields associated with the distribution of eigencharges that we discussed before. An expression of EELS as a function of eigenfields is given below.

Finally, there is a common misunderstanding in interpreting eqn (8). EELS (and CL) can only occur when the electron beam path is parallel to the induced electric field lines. This does not mean that EELS or CL will not be able to measure the optical property of a dipole (such as the dipolar mode of a nanorod, see Fig. 3) that may lie in a plane perpendicular to the electron beam axis. While the dipole orientation is perpendicular to the e-beam direction, this is not true for the induced field lines, so energy loss can occur. However, this constraint explains why certain modes, having part of their induced field lines perpendicular to the e-beam trajectory, may not be easy to map directly; see comprehensive discussions in ref. 5 and 17.

The case of sphere will help in understanding the relationship between EELS and CL, on the one hand, and extinction and scattering, on the other hand. Although given here in the
Q1 case, the remarks below can be generalised to the retarded case. Beyond the example of the sphere, no general expression linking electron and photon based spectroscopy has been yet established, even in the Q1 approximation.

For an electron travelling at a distance \(b\) from the surface of a sphere of diameter \(a\), the EELS probability of losing an energy \(\hbar \omega\) can be expressed as

\[
\Gamma_{\text{EELS}}^{\text{sphere}}(R, \omega) = \frac{4e^2 a}{\pi \hbar v} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{(a \omega)^{2l}}{(l+m)!(l-m)!} K_m(\frac{\omega R}{v}) 3\left\{ x_l(\omega) \right\}
\]

which reduces for the dipolar term to

\[
\Gamma_{\text{EELS}}^{\text{sphere}}(\omega, R) \propto a^6 \left\{ x_{l=1}(\omega) \right\} \left[ K_1^2(\omega R / v) + K_0^2(\omega R / v) \right]
\]

Here, \(K_m\) are modified Bessel functions of the second kind. A similar expression can be deduced from the CL probability of detecting a photon of energy \(\hbar \omega\),

\[
\Gamma_{\text{CL}}^{\text{sphere}}(\omega, R) \propto a^6 \left\{ x_{l=1}(\omega) \right\} \left[ K_1^2(\omega R / v) + K_0^2(\omega R / v) \right]
\]

It is obvious that for the dipolar mode, EELS (CL) (eqn (12) and (13)) shares great similarities with the extinction (scattering) cross sections (eqn (6) and (7)). These similarities remain for the retarded expressions. This is because the electron field looks very similar to a plane wave of white light. Indeed, from the point of view of the NP, the electric field carried by the electron is large only when the electron is close to it. At that time, the electric field pointing from the electron towards the NP is essentially perpendicular to the electron trajectory. As it follows the electron, the electromagnetic wave packet resembles strongly a plane wave travelling in the direction of the electron path. As the electron speed is very high (approximately half the speed of light at 100 keV), it stays only a few tenths of a fs close to the NP. The NP thus sees a pulse containing a large spectrum of frequency. These considerations mean that the electromagnetic field carried by the electron resembles a very local, white, plane wave. It is this field which is scattered in the case of CL. All the energy absorbed or scattered by the NP has to be provided by the electron. Thus, although to the best of our knowledge it has never been proved, EELS should naturally reflect the extinction suffered by the field the electron carries.

There are two differences, however, between electronic and photonic excitations. Firstly, in the case of EELS, all modes are measured, not only the dipolar modes, which dramatically departs from the far field optical experiments in the Q1 approximation. This is because the electric field generated by the incoming electron, in contrast with that of a plane wave, varies very rapidly at the scale of the nanoparticle, and can thus easily excite non-dipolar modes. However, within the QS approximation, the CL cannot detect non-dipolar modes, although they are excited, because the non-dipolar part of the induced field is vanishing in the far-field. Secondly, both EELS and CL have a position-dependent probability, a feature which is obviously absent in far-field optical experiments.

We note that the general structure of eqn (10), giving the EELS spectrum as the sum over all modes of a product of two terms, one being the imaginary part of the polarisability, and the other a monotonically decreasing function of the beam position, applies for all highly symmetric cases (slabs, cylinders and multilayer versions of these). Of course, in such cases, the definitions of the polarisations are different, and the spatial dependency of the second term is different. However, for large values of the impact parameter, the latter behaves roughly as \(\exp(-\omega R / v)\). This illustrates the near-field behaviour of EELS (and CL), as the typical decreasing length is \(b = v / \omega\) which is of the order of a few nanometers.

These equations give thus precise insights into the relationship between the plasmonic response of EELS, CL, extinction and scattering (basically, all quantities have peaks at the plasmon energy), but they do not give clear hints on how EELS and CL can be used to map the plasmon variations. This is what will be discussed in the following sub-sections.

4.2 Modal description of EELS in the QS limit

We have seen in Section 2.5 that a description of optical quantities in terms of modes was desirable. Also, EELS experimental data, as presented in Fig. 1, clearly show a series of energy peaks, the intensity of which follows patterns that resemble standing-wave behaviour. The question is thus to determine whether the energy peaks are related to SP energies, but they do not give clear hints on how EELS and CL can be used to map the plasmon variations, which is what will be discussed in the following sub-sections.

From this, a modal decomposition in terms of SP properties can be deduced to answer the above-mentioned questions. For an electron travelling at speed \(v\) along the z axis, the EELS probability at point \(x, y\) is

\[
\Gamma_{\text{EELS}}(\vec{R}, \omega) = \frac{e^2}{\pi \hbar v} \sum_{i} \left| \mathcal{F}(f_i(\omega)) \right|^2 \phi_i(\vec{R}, \omega / v)^2
\]

where \(\phi_i(\vec{R}, q_z = \omega / v)\) is the Fourier transform along the path direction \(z\) of \(\phi_i(\vec{R}, \omega)\) at point \(\vec{R} = (x, y)\) in real space and \(q_z = \omega / v\) in reciprocal space.

Eqn (14) has a very clear meaning. It states that the EELS spectrum is a sum over all the modes of the product of two quantities. One represents the spectral properties of that mode \(\mathcal{F}(f_i(\omega))\), and the other its spatial variation.

The physical meaning of the first term is straightforward. \(\mathcal{F}(f_i(\omega))\), which can be understood as a generalized polarizability, peaks at the plasmon energy of mode \(i\). This clearly points to the fact that EELS spectra directly probe surface plasmons.

To make clear the physical content of the second term, let us assume that the particle of interest is very thin. Let us also assume that we are interested only in the low energy modes which are symmetric in charge, an important case in practice.
(see Section 2.3). In such a case, one can assume that $\hbar \omega / v = 0$. 13
Then, $\langle \hat{\phi}_i (\mathbf{R} - \mathbf{q}_i, \omega) \rangle = \langle \hat{\phi}_i (\mathbf{R}) \rangle$ where $\langle \hat{\phi}_i (\mathbf{R}) \rangle$ is the average of the eigenpotential $i$ along the $z$ direction. One can thus understand the second term as the spatial variations of the square of the (averaged) eigenpotential of the mode. The EELS spatial variations at a given plasmon energy thus reflect the plasmon spatial distribution through the variations in the associated eigenpotential. This also explains in simple terms why the EELS signal spreads outside the particle (see Fig. 1). A comparison of the eigencharges, the square of the eigenpotential and the EELS for a nanorod is given in Fig. 3. Even if the agreement is not quantitative, the node and antinode positions in EELS and the square of the eigenpotential are very close.

One would, of course, also be very interested in mapping the spatial distribution of plasmon eigencharges. However, this is not directly possible14 and requires a complex reconstruction scheme. 13

### 4.3 Linking EELS, CL and the EMLDOS

We have just seen that EELS can be shown to map, at a given eigenenergy, the plasmon modes through the mapping of the square modulus of the eigenpotential at the associated energy. This is clearly reminiscent of what happens in a totally different field, namely scanning tunnelling microscopy (STM) and spectroscopy. In that technique, one maps, at a given energy, the square modulus of the electronic wavefunction. There is thus a clear analogy between the two techniques: STM maps spectrally and spatially the solutions of the Schrödinger equation, while STEM-EELS maps spectrally and spatially the solutions of the Maxwell equations. Usually, the STM is supposed to map the electronic local density of states. Here, the EELS can be shown to be very closely related to the $z$EMLDOS (eqn (5)), as defined in Section 2. In the QS approximation, the link can be made clearer. Rewriting eqn (14) as a function of the eigen-electric field rather than the eigenpotential, one finds

$$\Gamma_{\text{EELS}} (\mathbf{R}_z, \omega) = \frac{e^2}{\pi \hbar \omega} \sum_i |\mathcal{f}_i (\omega)|^2 |\mathcal{E}_i (\mathbf{R}_z, \omega)|^2$$

(15)

Within a Fourier transform along the $z$-axis and an $\omega$ prefactor, EELS thus is clearly equal to the $z$EMLDOS. It is worth noting that this Fourier transform has some annoying importance in trying to make quantitative comparisons between EELS and the $z$EMLDOS. 10 This can be seen in Fig. 3, where the EELS and the square of the $z$-component of the electric eigen-field are shown for the three first modes of a nanorod. As in the case of the eigenpotential, the EELS and $z$-electric eigen-field variations, although not quantitatively comparable, have nodes and antinodes very close in positions. Note that this is definitely not the case for other polarizations of the eigen-field (not shown).

Although no comprehensive modal decomposition exists in the general retarded case, a $z$EMLDOS can be rigorously defined. It has been shown15 that the preceding link between EELS and the $z$EMLDOS still holds in this case. This is exemplified in the case of a silver disk presented in Fig. 4. The $z$EMLDOS, together with the EELS, is displayed. There is a quantitative agreement between $z$EMLDOS and EELS peak energies and a qualitative agreement with the positions of the maxima and minima.

The link between CL and the $z$EMLDOS has also been partly established. For small nanoparticles, such as the nanorod shown in Fig. 3, the EELS and CL have very similar spatial distributions (and energies, not shown). However, as expected from the discussion of Section 4.1, the non-dipolar modes are clearly darker than the dipolar ones. In the case of purely photonics, non-dissipative, modes (such as guided modes), EELS and CL are exactly equal, and thus CL also maps the $z$EMLDOS (again, within a Fourier transform along the $z$ axis). However, it is obvious that this situation, for plasmons, can only hold for bright modes. This is exemplified in Fig. 4, where the CL signal resembles that of the EELS and the $z$EMLDOS only for the dipolar mode. Despite obvious similarities between the EMLDOS and the CL, a formal link in the case of plasmons is still to be established.

Finally, it is worth noting that the EMLDOS is a vectorial quantity. By mapping only one of its components (that along the beam trajectory axis), one is likely to miss some information. This is particularly true for modes that have portions of their eigen-field distributions polarized perpendicular to the beam axis. Such modes must be studied at points where the eigen-field has a $z$ component, or through a rotation of the NP. 13

### 4.4 Simulation tools

We have seen how EELS and, to a lesser extent, CL can be precisely related to the plasmon properties (eigenenergies, eigenpotentials, eigenfields . . .) of nanoparticles. The preceding discussion can help us to understand the physics behind EELS
and CL; it also helps in interpreting simple cases based on symmetry arguments. However, in many practical cases, it of course lacks predictability: for a given set of nanoparticles in a given environment, how to interpret the maps and spectra that we acquire as described in Section 5? How should we compare the EELS and CL results to optical measurements? And how might one deduce from EELS and CL experiments quantities that are not directly measured (for example the phase).

To tackle these questions, we have to use simulations that must solve the Maxwell equations for a given nanoparticle/environment geometry and electron beam position, and then compute the resulting EELS or CL spectrum. There are two main classes of methods for performing such simulations. Any method, however, relies on the a priori knowledge of the dielectric constants of the different materials under consideration. These have to be retrieved from an external source (tables, experiments on bulk material...). The first class concerns computations requiring a solution of the frequency dependent Maxwell equations. At the time of writing, these are by far the most widely used techniques. There exist essentially two different ways of performing such calculations. The first technique is called the discrete dipole approximation (DDA), which is extensively used in optics, and was adapted to EELS first for carbonaceous material and later for metallic systems. It has been more recently extended to CL. In this framework, the objects are discretized into small cubes to which a dipole moment is attributed. The dipole moments are calculated using the dielectric constant of the material. The second technique is called the boundary element methods (BEM). Its quasi-static implementation is based on a finite element solution of the equations presented in Section 2.5.2 and 4.2, and can be extended to the retarded case. In this case, only the surface has to be discretized. DDA and BEM free access implementations are now available for EELS and CL applications.

The second class concerns computations that are performed by solving the Maxwell equations in the time domain. They are much less widespread than the former. Finite-difference time-domain (FDTD) solutions of the Maxwell equations have been developed for CL, while a discontinuous Galerkin time-domain method has been also used for EELS.

5 Practical EELS and CL in the electron microscope

5.1 Experimental set-up: the S(T)EM microscope and its detectors

Very generally, the main difference between a SEM and a STEM is that electrons are transmitted through the sample in the latter. As concerns the present tutorial, CL can be performed in both microscopes, while EELS is performed only in STEMs. Usually, SEMs operate at rather low-accelerating voltages (typically 1 keV to 30 keV) while STEMs operate at higher voltages (typically 60 keV up to 300 keV)—higher voltages enabling electrons to go through a given sample. SEM designs are also usually somewhat simpler than those of STEMs. These considerations of course make SEMs typically an order of magnitude cheaper than STEMs. Conceptually, however, the STEM and the SEM are rather similar instruments, and some modern STEMs working at very low accelerating voltages would have been classed as SEMs a few years ago, while SEMs with a small gap, symmetric objective lenses (see below) could have been considered as STEMs. We will therefore describe the most complete set-up, pointing out when differences are worth noting.

The primary role of a S(T)EM is to form an electron probe that will be scanned over the sample to record various signals of interest. As such, the probe size—which gives the best spatial resolution that can be expected—and probe currents—which determine the maximum amount of information that can be gained during the acquisition—are of prime importance. As a rule of thumb, the smallest probe sizes are achieved at the highest accelerating voltages and smallest intensities, which results in compromises in practical experiments. It is worth noting here that electron optics can be viewed analogously with photon optics, with a similar set of elements (lenses, spectrometers, etc.). Electron optical lenses are most often of the magnetic type (some might be electrostatic). They produce a magnetic field with a strong component along the electron path. Some might be weak and a more weak one, which serves to focus the electron beam. Electron lenses are composed of magnetic coils producing the field and conical magnetic metal parts (pole pieces) concentrating it over small distances. At least on paper, they behave similar to optical lenses (for which focal planes, focal length, etc. can be defined) with extremely high spherical aberrations and higher order aberrations. These aberrations are limiting the range of focussable angles. As in photon optics, the higher the angles, the smaller the achievable probe size. In practice, the aberrations thus limit the size of the electron probe.

With current technologies, SEMs can typically achieve probe sizes of a few angströms or nanometers, while STEMs nowadays achieve probe sizes lower than an angstrom. For nanometric probe sizes (which are sufficient to probe most of the plasmonic properties), nA or tens of nA are typical, while for angstrom-sized probes, tens of pA to hundreds of pA are more typical.

A schematized STEM, depicted in Fig. 5, can be described as follows:

- **An electron gun.** This is composed of a tip from which electrons are extracted and then accelerated to the required high voltage. Two main properties are worth considering: brightness and energy spread. Brightness is a measure of the current that can be put into a small area: a brighter gun allows one to generate a sharper electron beam with a high current in it. Energy spread determines the energy resolution in EELS (see below) and can limit spatial resolution in SEM and modern STEM. Different technologies exist for the guns. The most common are, in the order of increasing brightness and decreasing energy spread (increasing energy resolution), thermionic, W or LaB6, Schottky field emission gun (FEG), made up of ZrO coated W tips, and cold FEG (cFEG) with W tips. Only FEG and
cFEG will be considered here, the former having a typical native energy spread of $>0.7\,eV$ and the latter $<0.3\,eV$.$^\dagger$†

- **A monochromator.** This is an option essentially used in STEM for EELS applications. Monochromation decreases the natural energy spread of the gun, at the expense of losing intensity (at least linearly with the improvement of spectral resolution). It usually consists of a combination of magnetic and/or electric fields spatially separating the electrons as a function of their energies in a so-called dispersive plane. A slit is usually placed in this plane to select the electrons of a given energy. Different designs exist with pros and cons,$^{32}$ 100 meV energy spreads are commonly reported, but at the time of writing performances are rapidly improving, with reports around 50, 30 and less than 20 meV (ref. 32) now appearing.

- **A set of condenser lenses.** Condenser lenses are used to gather the beam from the electron source, and their role can be safely ignored here. A condenser aperture is used to define the angular size of the beam.

- **Scanning coils.** These are magnetic and/or electrostatic deflectors used to scan the beam across the sample. Symmetrically with respect to the sample on the transmitted side, descan coils can be used (see Section 5.3).

- **Aberration corrector.** (Not shown) Electrons, like photons, are waves, and the size of a spot that can be formed by a lens is ultimately limited by the diffraction and is proportional to the inverse of the condenser aperture size. Increasing this size increases the available angles to form a sharper probe. However, the spherical aberration typically limits the practical angles to a few mrd. This not only limits the electron probe size, but also decreases the available current for a given probe size. For technological reasons, the development of aberration correctors in electron optics has taken a long time, but they are now routinely available in STEMs, allowing the use of angles of several tens of mrd. This enables very small electron probe size formation (better than half an angstrom, depending on the acceleration voltage) and relatively high currents in small probes.

- **Objective lens.** As in an optical microscope, the objective lens is the most critical part, as it forms the image. In a scanning microscope, the image quality depends on the probe size, which requires high angles. In an EM, this is achieved with lenses of short focal, which have relatively short working distances (a few mm). In typical STEM configurations, the objective lens is symmetrical, with two pole-pieces separated by a short distance (the pole-piece gap), which can be as small as 1 mm. The magnetic field in the gap can be higher than 1 T.

- **A sample holder.** Due to space restriction in a STEM, the sample holders are often very thin (less than one mm).

- **A cathodoluminescence system.** See details below.

- **Secondary electron detector (SE).**

- **A set of projector lenses** (not shown in the diagram) that enable one to control the angular range of transmitted beams impinging on different detectors.

- **High angle dark field (HAADF) detector and bright field (BF) detector.** (the latter being removed when EELS is operated)

- **An EELS detection system.** See details below. Of course, the EELS and CL system are of particular interest.

The EELS system consists of a magnetic prism that disperses the electrons as a function of their energy. With the help of several magnetic multipoles, the resulting beam is sent onto a scintillator, which is imaged onto a CCD camera.

The CL system is usually made up of a concave mirror (typically a paraboloid), which transmits the detected light onto an optical spectrometer, fitted with a CCD camera and/or a photomultiplier.

### 5.2 Spectromicroscopy

When the beam is focused on a sample, several signals can be recorded. SE, HAADF and BF are signals related to the presence of matter under the electron beam. In particular, SE and HAADF will give rise to an increasing signal when the matter content increases, and this is roughly the opposite for the BF signal. When the beam is scanned over the sample, one can record images made up of the SE, HAADF or BF signals. These images, to first order, give information on the morphology of the sample (see for example Fig. 1a inset and Fig. 7a).

Also, with the beam at a fixed position, an EELS or a CL spectrum can be recorded on their respective CCD cameras. In certain cases, only an integrated range of the CL spectrum is recorded directly on a serial detector (a photomultiplier, for example). In this configuration, a spectrum can be optionally acquired by changing sequentially the part of the spectrum that is sent to the serial detector.

CL spectra resemble standard optical spectra and are not worth commenting here. However, an EELS spectrum, such as that shown in Fig. 6, has typical features that are worth discussing.

Three main parts can be distinguished. Around the zero energy loss position arises an intense peak, called the zero loss peak (ZLP). It is constituted by all the electrons that have not (up to the spectral resolution of the apparatus) interacted inelastically with the...
can be extracted at locations precisely determined due to the parallel acquisition of a morphological signal (HAADF for EELS SI, inset of Fig. 1a, and SE for CL SI, Fig. 7a). This operation can be applied to each position in the SI, yielding maps of the SPs (Fig. 1c, d, e and 7c).

Alternatively, in CL, filtered images can be produced if, at each scan position, only a limited range of the spectrum is integrated on a serial detector (a conceptually similar possibility exists in EELS but it will not be discussed further; see ref. 33 for more information).

The advantages of SI over filtered imaging will be exemplified in Section 5.4.

5.3 Practical issues in performing nanoplasmonic experiments in a S(T)EM

5.3.1 Understanding basic spectrometer optics. EELS and CL spectrometers, although based on the use of dissimilar waves (electrons and photons), are conceptually identical. As they are crucial for successful experiments, it is worth spending some time on how they work. We cannot of course describe the precise alignment procedures here; however, these basic hints should serve as a general guide when using such equipment.

In order to understand the performances and limitations of a spectrometer, it is worth noting that it has two different functions. Of course, it disperses a beam into components of different wavelengths. But, at the same time, it also acts as an imaging optical element. This is illustrated in the schematic spectrometer design in Fig. 8. The imaging function of a spectrometer is best exemplified in the case of a monochromatic beam. In this case, a spectrometer acts basically as a set of lenses projecting the object plane onto the dispersion plane (the plane where spectra are recorded when the beam is not monochromatic). For EELS, the dispersion plane is the scintillator plane while in CL it is directly the CCD plane. In the case of a monochromatic beam, an object $O_1$ thus produces an image $D_{1,1}$ in the dispersive plane. In both spectroscopy methods, the object plane is the plane in which the electron probe hits the sample. Therefore, the optical object in EELS will be the electron probe in the sample plane, usually slightly broadened after interaction with the sample. In CL, it will be the point source formed at the emission location, which is usually the nanoparticle as a whole.

If the overall magnification of the spectrometer is large enough, then the size of $D_{1,1}$ might spread over several CCD pixels, degrading the energy or wavelength resolution of the experiment. That is why the object for the spectrometer (which is in the microscope image plane) has to be small enough so that once magnified, it is not larger than a CCD pixel size. The magnification of the spectrometer depends on the actual energy or wavelength dispersion that is targeted. In regular CL spectrometers, the dependence of the spectral resolution as a function of the spot size at the entrance of the spectrometer...
can be a limit. Thus, in CL, a slit in the image plane (‘entrance slit’ in Fig. 8) can be used to decrease the incoming beam size and increase the spectral resolution. We see here that increasing the spectral resolution has to be done at the price of decreasing the available signal. On the opposite for EELS, at the time of writing, even at high dispersion (small eV per channel), the magnification is not large enough in EELS to be a problem. There is no need for such a slit in EELS.

An additional cause of broadening of the image of a monochromatic image is the presence of geometric aberrations in the spectrometer. As these aberrations increase quickly with the angle, one has to keep only rather small angles. That is why optical spectrometers have relatively low numerical apertures. The lower the numerical aperture, the higher the ultimate spectral resolution. Again, if the different numerical apertures along the path of the photons or electrons are not adapted, there is a loss of signal. In the case of CL spectrometers, it is very common to introduce an aperture (entrance aperture in Fig. 8) at the entrance of the spectrometer (a plane conjugated with the focal plane of the objective lens, where angles are well defined) to cut off a large range of angles. In parallel to the development of monochromated instruments, aberration-corrected EELS spectrometers have been developed, enabling an increase of the acceptance angle (and thus the available signal) of the spectrometers. Surprisingly, aberration correction in optical spectrometers is less common. When considering the performances of an EELS or CL spectrometer, it is thus important to consider the available spectral resolution and available signal at the same time, as high spectral resolution may be promised at the cost of a drastic reduction of detected signal, which may prevent practical experiments from being performed.

In addition to the issue of the spectrometer’s object size degrading the spectral resolution, the displacement of the electron probe on the sample can be a problem. In the absence of any entrance slit, an object far from the optical axis, will produce an image which will be shifted with respect to it. Consequently, the spectrum will shift on the dispersive plane (I2 being imaged as D2,E1 on Fig. 8). This effect can be corrected in several ways. The displacement can be calibrated and then automatically corrected on the CCD camera. In EELS, at the dispersions required for plasmon studies, this can be an important effect. The so-called descan-coils can also be used to cancel the known shift during acquisition. Alternatively, post

Fig. 8 Schematic representation of a spectrometer. The schematic ignores all details including the bent trajectories in an EELS spectrometer. The top stripe lists the main elements in a CL (optical) spectrometer, while the bottom one lists those of an EELS (electron) spectrometer. Trajectories are exemplified for two different object points,  and , shifted perpendicular to the optical axis. They give rise to two image points I1 and I2 in an image plane which serves as an object plane for the spectrometer. For one arbitrary energy E1, they are imaged in the dispersive plane as D1,E1 and D2,E1 (trajectories for D2,E1 not shown for simplicity). An image of I1 at another energy E2, D1,E2, is also shown.

§§ The numerical aperture is defined as $NA = n \sin(\theta)$, with $n$ being the medium optical index and $\theta$ the semi-angle of incidence. The numerical aperture thus serves at defining how much signal can enter a specific optical device.
acquisition realignment can be done if the ZLP is not saturated (see below). In CL, however, this effect will most generally reduce the attainable field-of-view for a given spectral resolution. Indeed, as shown in Fig. 8, the image (which is the object for the spectrometer) $I_2$ of $O_2$ is stopped by the slit defining the spectral resolution. Typically, for a realistic high efficiency collecting system (a large numerical aperture mirror for example), a roughly 5 µm field of view is available at a resolution of 10 meV in the visible range. Such a limitation can be removed through the use of optical fiber bundles preserving both the spectral resolution and field of view.14 If the sample can be moved independently from the collection optics (the mirror), this limitation may not be so drastic, as NP sizes are usually less than a micron. However, this effect certainly precludes the use of a system in which the sample and the mirror cannot be moved independently (i.e. for a CL system fitted into a sample holder), because then the part of the sample that can be studied is extremely small.

A final issue affecting spectrometer performances is the quality of the alignments of the electron or photon paths with respect to the spectrometer entrance aperture. In the case of electrons, all the optics can be controlled through electric currents which makes it relatively easy. In the case of photons, every alignment has to be achieved mechanically. One of the most important alignments is the positioning of the collection optics (usually a concave mirror) with respect to the object. Usually, the collection optics is designed to collect high angles. In typical SEMs, the pole piece gap is large, and this can be done by using large mirrors. However, for high spatial resolution SEMs, or in STEMs, the pole-piece gaps are small (only a few mm are available for inserting a mirror). Thus, mirrors have very small focal lengths (about a few mm). In contrast, the CL spectrometer accepts relatively low angles and thus, if considered as a convergent lens, has relatively large focal lengths (of the order of a few hundred mm). The magnification is basically proportional to the ratio of these focal lengths, and is of the order of a hundred. As a typical slit entrance aperture will be about 100 µm wide, the mirror positioning with respect to the sample typically has to be better than a micron in the three spatial dimensions in a STEM or high resolution SEM. This requires at least micrometric screws34 or piezo driven actuators.35 The collecting optics being in vacuum and in a tight environment, it introduces stringent mechanical conditions. If one has to use a system that cannot be aligned with such a precision, then a trade-off in terms of available signal and spectral resolution has to be made.

5.3.2 Samples. The choice of a spectroscopic technique (EELS or CL) and relevant microscope (SEM or STEM) will depend on the kind of samples to be studied. EELS and related STEM based imaging (HAADF and BF) requires electron-transparent samples. Indeed, thicker samples can seriously degrade the quality of EELS (and imaging) data in two main ways. Firstly, there can be multiple inelastic scattering.14 In this case, the EELS spectrum becomes the convolution of a single scattering spectrum with itself, broadening the information in such a way that it can rapidly become uninterpretable. Secondly, a strong elastic scattering can deflect a large part of the signal out of the spectrometer entrance aperture (see Fig. 8). This leads to the absence of signal within the object of interest if it is too thick. Both effects are material-dependent; the second is, for example, extremely important in gold. The definition of a “thin” electron transparent sample is somewhat arbitrary, and will depend on the accelerating voltage: the higher the voltage the more transparent the sample (this is because the higher the voltage the lower the interaction). At 100 keV, a thickness of a few tens of nanometers usually lets most of the electrons get through to the EELS spectrometer. It thus allows for getting an SP signal even when the beam hits the bulk of the NPs of interest. For thicker objects, it is possible that most of the signal is lost outside the spectrometer when the beam hits the bulk of the (thick) NP. In that case, it is still possible to study the SP when the electron beam is outside, but close to, the NP.

The choice of a relevant support is thus important, as it must be as thin as possible. Regular carbon grids can be used for supporting nanoparticles. Note, however, that the carbon support may couple to the plasmons, shift them in energy and damp them. Insulating (optically transparent) supports may also shift the plasmon energy but will not damp it. Also, there exist now several types of semi-conductors and insulating supports (Si or Si₃N₄) that fit the regular 3.05 mm diameter holes of the STEM sample holders. Some of them consist of Si frames a few hundred microns thick, with either Si or Si₃N₄ suspended membranes of a few tens of nanometers. These samples are ideal for studying lithographic nanostructures.26

In the case of CL, the sample can be a priori arbitrary thick. In this case, however, if the sample is partly insulating, one can face the problem of sample charging. This can be avoided or at least diminished by increasing the accelerating voltage, decreasing the current intensity and sample thickness, and metalizing the surface of the sample for charge evacuation. In the latter case, of course, care has to be taken so that the metalization does not affect the plasmon properties of the object of interest.

The interaction of the beam with the sample can also be a problem. In the case where the quality of the vacuum is bad, or the sample itself contains carbonaceous material, the e-beam is able to crack residual hydrocarbons and lay down some soot (known as “contamination”) at the observation point. In the worst situations, it can be so thick that it prevents observation. However, a more subtle effect is that the contamination can electromagnetically couple to the plasmons and change their properties (see for example Fig. 9). Fixes are not always easy, but can range from sample improvement (e.g. ligand removal for colloidal NPs) to the use of cold stages that efficiently trap hydrocarbons preventing them from being cracked under the beam.

5.3.3 Signal-to-noise ratio. In order to get the best signal to noise ratio (SNR), it would seem natural to increase the current intensity. Increasing the current intensity might involve increasing the beam size. However, for most plasmonic works, a probe size of a few nanometers is usually sufficient. With such probe sizes, currents of the order of several nA can be produced. They are ideally suited for CL works.

The situation for EELS is more subtle and requires a much more sophisticated strategy. Indeed, several contradictory requirements have to be fulfilled at the same time. Of course, the detected EELS intensity has to be optimised in the SP region. However, at beam positions where a typical SP signal is
maximum, it is at least three orders of magnitude smaller than the ZLP. The SP signal intensity then decreases roughly exponentially with the distance from the interface (see Section 4.2). Now, the ZLP has to be recorded without saturation. Indeed, it is typically limited to 16 bits (approx. 60,000 counts) in each pixel. If one can get finer control of the CCD camera, its dynamics can be further increased at the expense of longer readout times, see ref. 6.

Thus, the best strategy (an “align-and-sum” strategy) is to rapidly acquire a large set of unsaturated spectra that will be recorded individually. Then, each spectrum can be realigned automatically based on the ZLP position, and all spectra summed, drastically increasing the dynamic range of the experiment. In this way, the issues in spectral resolution and SNR can be solved at the same time; both the SNR and FWHM are optimised. The best is to acquire a set of spectra at each pixel position, a mode called ChronoSI. However, this mode is not available commercially at the time of writing (only the sum without alignment is possible). An alternative approach is to oversample the SI: if one targets say 1 nm spatial resolution and to sum 100 spectra per pixel position, one can acquire an SI with a step of 0.1 nm. After the SI acquisition and ZLP realignment, one can then construct an SI with ten times fewer pixels for each direction (a binned SI), with the spectrum in a given pixel being the sum of 100 pixels of the previous SI.

A last specificity of EELS is the optimisation of the energy resolution. This quantity is determined by the intrinsic FWHM of the ZLP, which depends on the physics of gun emission, which itself depends on the emission current and accelerating voltage, or on the slit width and settings of the monochromator. The instabilities of the high voltage, especially at high frequency, then broaden further the ZLP width. Finally, the spectrometer might degrade the resolution, either by adding electronic instabilities or by adding geometric aberrations. Geometric aberrations arise when the spectrometer is fed with high-angle. The easiest way to remove them is by putting a very small aperture at the entrance of the spectrometer which leads to redshift of the plasmon energies. (e) EELS intensity images generated by fitting the SI in the energy region of the corners. After ref. 21.
channel dispersion is already a small dispersion value for CL, it is the best that can be delivered by cutting edge EELS spectrometers. As already mentioned, a typical SP FWHM is of the order of 100–200 meV. Depending on the goal of the experiment, 2 to 10 pixels might be necessary to sample a peak. The high dispersions obtained with standard optical spectrometers (in the meV range) may thus not be necessary. In a CL experiment, it might thus be interesting to change the dispersion. This requires a change in the gratings of the spectrometer, which is not always possible. Thus, in CL, the best is often to bin the pixels, i.e. to sum adjacent pixels, preferably during the acquisition (this decreases the so-called read-out noise) to degrade the energy resolution but gain SNR. In an EELS experiment, where dispersion can be changed easily, a typical 20 to 50 meV dispersion is typically used.

Let us conclude on the choice of STEMs that can handle high-quality EELS experiments for plasmon mapping. The gun must be at least a cFEG one or some gun fitted with a monochromator. Although the best spectral resolutions are clearly required, one has to keep in mind that typical incident current of the order of a few tens of pA and a sufficiently high acceptance angle (ideally a few tens of mrad) are needed to get an acceptable amount of signal arriving at the spectrometer detector. A new generation, 3rd order aberration-corrected spectrometer, as well as fitted with a fast (1–10 ms acquisition time) camera, is thus a suitable set-up. Such spectrometers, now being produced, also have the ability to provide a better electronics stability that will naturally go hand-in-hand with a stable high voltage microscope. While a Cs-corrected machine is not mandatory (it might however help in getting higher currents for sub-nanometer beams if required), last generation guns and/or monochromators fitted with the state-of-the-art spectrometers and CCD cameras are crucial. This means that currently, although plasmon mapping in EELS is getting more widespread, probably less than a hundred machines worldwide are likely to be usable for that purpose.

5.4 Data analysis

Before describing data analysis methods specific to the SI technique, let us give two specific remarks for EELS and CL data treatments.

In an EELS experiment, one generally wants to minimise the influence of the ZLP, which is two-fold: first, its width determines the spectral resolution of the experiment and, second, its tail can be of the order of or even much larger than the SP signal of interest. The best way to decrease these effects is to use monochromation. When it is impossible or not sufficient, one can use deconvolution techniques. The idea behind these processing techniques is the following. A measured EELS spectrum can be conceptually described as being the result of the convolution of an ideal spectrum with no ZLP by the impulse function of the EELS system. This impulse function is nothing else than the ZLP itself. Knowing the ZLP from the vacuum, one could theoretically deconvolve it from the experimental spectrum to get an ideal spectrum. Several deconvolution strategies exist, the best ones for EELS being described in ref. 37. They require the acquisition of a ZLP in the vacuum with minimum noise (so an align-and-sum strategy for the acquisition, as described above, is likely to be used), and a close following of the guidance given in ref. 6 and 37. The effect of a complete sum-and-align plus deconvolution strategy is described in ref. 6 and 15.

In both EELS and CL, various defects in the CCD cameras may appear as shadow signals. Sometimes, these signals may be higher than a typical signal of interest. It can be useful to record a spectrum when no beam hits the sample. This signal can then be subtracted from all other spectra in the SI.

Finally, in a CL experiment, spectra can contain glitches that arise for example due to cosmic rays. Such events have typical aspects (high intensity in a single pixel) which make them very different from the physical signal of interest; several algorithms exist for their automatic removal.

The zero order data treatment in the SI is to produce filtered images, i.e. images where, in each pixel, the sum over a given energy range of the intensity of the spectra acquired at this pixel is computed. In Fig. 9, we show an SI taken on a silver nanocube (HAADF shown in Fig. 9a). Nanocubes have many modes, but we focus here on the mode localised at the corners. An intensity map (Fig. 9b) has been produced by filtering the SI around the corner-modes energy (spectra presented in Fig. 9c). Such treatment is very easy, but can be extremely dangerous in the results it gives. In particular, slight energy shifts or FWHM changes from pixels to pixels can be missed, or interpreted as intensity changes and vice versa. This is the case for the nanocube under consideration here, where the presence of contamination (see Section 8) at two corners shifts and damps these corner modes SP. This might lead to erroneous conclusions on the physics of the objects probed. Also, especially due to the presence of the ZLP tail in EELS, but more generally due to the presence of multiple and overlapping peaks, the local change of an intense peak may artificially drive an effective change in the energy position and intensity of a lower intensity one. Such issues are commonplace for example in serial detection experiments and can be fixed by a proper understanding of the wealth of information contained in the SI.

A better solution is thus to perform fits to each spectrum with a certain number of peaks. The nature of the peaks (Gaussian, Lorentzian, Voigt...) is best selected on a case-by-case basis (see ref. 39 for example). An automatic detection of the number of peaks can be used. At the end of the fit, one can then generate for each peak a series of different maps (Energy, Intensity, FWHM). Such maps can be used to retrieve the physical origin of different modes. Consider the nanocube as an example. In Fig. 9d is presented a map of the corner peak energy position, which clearly shows the general redshift of the two bottom corners SP energy. The corresponding fitted intensity map (Fig. 9e) demonstrates that the intensity of the bottom modes is also slightly lower than that at the top.

Moreover, a specificity of the SI approach is that it directly entangles both the spectral and spatial information. Instead of thinking in terms of images or spectra separately, it is usually useful to try to identify a specific feature directly in the combined spectrum/position space. It is simpler to understand this for a 1D system, because in this case the spectrum/position space can be represented as a map (see Fig. 10). In such a map, one can for example follow how the spatial variations of the SP modes are
dependent on their energy. In the case of a simple nanorod in Fig. 10, it is clear that multipolar modes have specific features appearing as islands in this space. For more involved cases, where modes overlap spatially and/or spectrally, physical information can be extracted by directly fitting peaks in this combined spectrum/position space. Simple extensions to the 2D (position) + 1D (spectrum) case can be represented graphically. However, much more powerful techniques allow one to retrieve automatically the relevant information in this combined space. Such methods, known as multivariate analysis techniques, have various forms. One of the best known is the principal component analysis. This analysis enables the extraction of a limited set of representative spectra and/or images in the SI, from which all experimental spectra can be deduced through a linear combination. Such representative spectra do not in general have a physical meaning, and care has to be taken when interpreting the results. However, it can be a very efficient technique for reducing the noise in experimental data, as a kind of generalised average. Although commonly used in EELS in the core loss regime, it has been only sparsely used in low loss EELS and CL. A freeware called Hyperspy (hyperspy.org) dedicated to multivariate analysis is available.

6 Applications

As for any relatively new technique, one has to find the applications that make it really worth using and justify its development. Indeed, it has to compete with diffraction limited techniques (like confocal microscopy), i.e. having a bare 200 nm spatial resolution, as well as sub-diffraction techniques such as photoelectron emission microscopy (PEEM) or various flavours of scanning near optical microscopy (SNOM), STM based approaches or innovative far-field optical microscopy techniques such as stimulated-emission-depletion (STED). Compared to these techniques, EELS and CL lack many physical aspects, such as time resolution or measurement of the phase of the plasmons or the polarization (for EELS). On the other hand, they benefit from the best spatial resolution for plasmon measurements (STED has even better spatial resolution but does not apply to plasmons) with spectral imaging capabilities, a broad energy range (especially for EELS), and a direct comparison with morphological characterisation. Also, the theory behind EELS and CL is quite well understood now. The use of an electron probe does not generate artefact such as for example SNOM probes do. They are thus very versatile techniques for a broad range of applications in plasmonics, although other methods may have better performances in specific cases. However, it is also worth remembering that EELS and CL give a partial view on SP modes through the measurement of the component of the electric field parallel to the electron axis only; care has to be taken in interpreting the experiments.

When operated in a SEM, CL will always be cheaper than EELS in a TEM. Also, CL in a S(T)EM will easily offer a much better spectral resolution despite the impressive recent developments in monochromator technology. However, one has to keep in mind that plasmon-wise, a resolution of 100 meV is probably enough in many cases, and is available in regular monochromators or through deconvolution. CL is also able to offer information on the polarization of the emission which is nowadays not currently possible via EELS. Finally, SP variations within thick objects are difficult to track (see Section 5.3.3) in EELS while totally compatible with CL. On the other hand, EELS can be recorded over an energy range which is much broader than for CL, with SP energies now as low as 170 meV (deep IR) right up to the deep UV and beyond. For small NPs, the CL signal is vanishing which is not the case for EELS; moreover, all the emitted energy in CL comes from the incoming electron, and thus is already detected in EELS. If the CL emission is directional, it can be missed by the collection optics, while EELS spectrometers usually gather nearly all the signal. Altogether, a much higher signal is expected in the EELS experiments, especially for small NPs. Finally, EELS senses all modes, radiative or not, whereas CL is only sensitive to radiative ones. For particles larger than a typical wavelength of light, CL is extremely useful (see ref. 18).

A very broad range of applications has appeared for both techniques in the study of small NPs. A comprehensive survey is given in ref. 17. One can however summarise when EELS and/or CL have a definite interest:

- When the spatial and spectral aspects are entangled, such as in the case of nanoantennas (Fig. 2) or very localized plasmons (Fig. 9)
- When spatial resolution matters
- When accessing dark modes matters (for EELS)
- When one needs to go outside the visible range (for EELS)

Fig. 10 Combined spatial and spectral information in a 1D SI. Top: HAADF image of a silver nanorod. Bottom: EELS intensity as a function of beam position along the rod and the EELS energy. Clear lobes appear exemplifying the entangled character of the information in the SI. Courtesy of D. Rossouw and G. Botton.
7 Conclusions

In this tutorial review, we have tried to provide a general description of SPs in NPs. We have shown why and how EELS and CL are theoretically linked to these SPs, stressing the analogy with and differences from conventional optical quantities. Besides the theoretical descriptions, we have directed the reader to specific simulation tools. We have also presented the instrumentation which is needed to perform EELS and CL in the context of the spectral imaging technique. We have tried to give practical hints about its important features. We finally ended this tutorial by pointing out the relative strengths and weaknesses of EELS and CL as compared to other techniques.

We hope we have helped the reader to better understand how and why a particular EELS and CL experiment is successful or not, and how to interpret it. We have just scratched the surface of a field which has been exploding over the last few years, and the reader is encouraged to get a better view of the field via the listed references.

Acknowledgements

This tutorial is the result of many of our discussions and collaborations. We would like to thank all our collaborators, amongst the Orsay STEM group: C. Colliex, M. Tencé, and A. Gloter, amongst our former students and post docs: J. Nelayah, G. Boudarham, A. Losquin, Z. Mahfoud, and L. F. Zagonel; and worldwide: L. Henrard (Namur Univ., Belgium), J. Garcia de Abajo (ICFO, Spain) and team, L. Liz-Marzán (Vigo Univ., Spain) and team, and M. Wegener (KIT, Karlsruhe, Germany) and team. We want to thank M. G. Walls for his reading of the manuscript. We want to acknowledge G. Botton (Hamilton Univ., Canada) and A. Polman (Amolf, the Netherlands) for permission to reproduce their work. MK acknowledges U. Hohenester (UNIGRAZ, Austria), A. Losquin and Z. Mahfoud for setting up the MNPBEM code used in this paper. This work has received support from the National Agency for Research under the program of future investment TEMPOS-CHROMATEM with the Reference No. ANR-10-EQPX-50. The research leading to these results has received funding from the European Union Seventh Framework Programme [No. FP7/2007-2013] under Grant Agreement No. n312483 (ESTEEM2).

References

12 F. J. Garcia de Abajo, Rev. Mod. Phys., 2010, 82, 209–275.


