NANOPHOTONICS

Plasmon quantum limit exposed

Confinement of light in subnanometre gaps encounters a fundamental limit in the quantum tunnelling regime.

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Plasmons are collective oscillations of free electrons in the conduction band of metals. Their optical properties are readily derived from Maxwell's equations by plugging in bulk metal-optics parameters. Yet, it is intuitive that the classical picture must go wrong at the atomic scale, and indeed recent advances in nanofabrication have pushed Maxwell's description to the limit, although direct observations of quantum effects in plasmonic nanostructures have remained elusive. Now, writing in *Nature*, Jeremy Baumberg at the Cavendish Laboratory in Cambridge, UK and co-workers from the Material Physics Center in San Sebastian, Spain and the Université Paris Sud, France, describe an elegant experiment that captures the quantum regime in plasmonic nanostructures and shows that quantum tunnelling is the limit for charge and field confinement in metal nanostructures[1].

In the classical electrodynamic description, free electrons follow the oscillation of an externally applied electric field, as long as the frequency of the field is below the so-called plasmon frequency, which governs the dielectric dispersion of the metal. Yet, in this regime of optical frequencies, metals are not perfect and the finite conductivity causes the charges to extend into the metal, rather than being confined to the surface. Particularly when coupling plasmonic nanoparticles the tiny gaps between them can concentrate a large amount of light with huge electric field enhancement — a favourable condition for applications requiring light focusing, such as surface-enhanced Raman scattering and higher harmonic generation.

Soon after the invention of scanning tunnelling microscopy, weak emission of light was observed from the tunnelling gap between the tip and the surface, and it did not take long to attribute the spectral features to tip-induced plasmon modes on the metal surface[2]. However, these early tunnelling efforts, made using a nanometre-size tip and subnanometre gaps, did not allow investigations to be extended to larger dimensions and bridge to the classical regime of dispersion of plasmon modes.

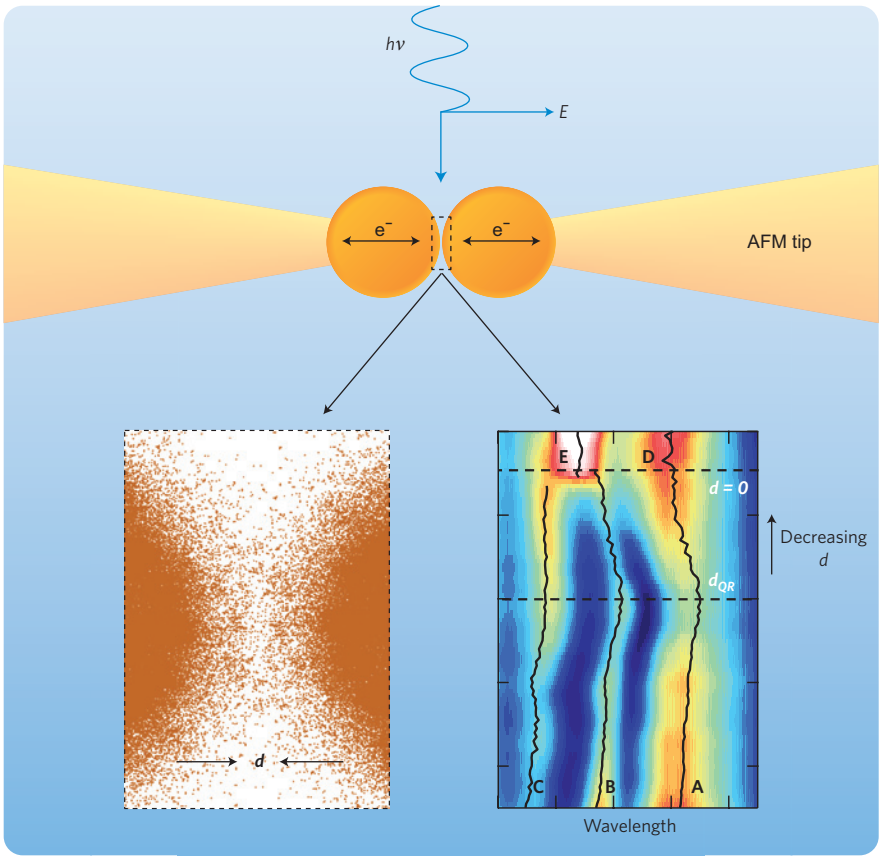

Figure 1 | The colour of light in the quantum tunnelling regime. Two metal nanoparticles (orange) are brought into close proximity by moving the AFM tips onto which they are attached (below left). Simultaneously, the light-scattering spectra of the gap-zone is acquired. Bottom right: Data show that the classical plasmonic modes (A, B and C) collapse as the distance approaches the onset of the quantum regime (d_{QR}) and new modes (D and E) appear as the particles touch ($d = 0$). This is in agreement with quantum theoretical modelling of the nanogap. The experiment captures the transition of the plasmon coupling from the classical down to the quantum regime. The colours describe the scattering signal where red and blue indicate high and low intensity, respectively. Image adapted with permission from: bottom left, © Shaun O'Kane; bottom right, ref. 1, © 2012 NPG.

Owing to tremendous progress in nanofabrication over the past decade through both top-down and self-assembly approaches, a huge variety of plasmonic structures (generally termed nanoantennas) have been described in the literature, with single-molecule sensitivity and strong metal-enhanced fluorescence being the main driving forces for pursuing studies on nanogaps between nanoparticles[3]. In essence, when two plasmonic nanostructures approach each other, interparticle coupling causes a large pile up of charges in the interparticle junction[4]. New symmetric and anti-symmetric modes arise in the coupled system ('plasmon hybridization'). The energy of the hybridized modes depends critically on the gap size: the allowed modes shift to the red as the interparticle gap decreases[4,5]. On touching, however, a distinct new mode that is markedly different from the modes of the separated nanoparticles appears (charge-

transfer mode). Clearly, when passing from non-touching to touching, the non-classical regime is crossed.

It was recently confirmed that for gaps smaller than 1 nm, the energy modes' redshift is less than what would be expected from classical electrodynamics[6]. The hypothesis is that some charge distribution spreads over a tiny zone around the metallic surface and counteracts the plasmon coupling causing slight blueshifts and resonance linewidth broadening[7]. Although this type of nonlinear effect already puts a fundamental limit on the field enhancement that is attainable in nanogaps, there is no need to invoke quantum theory, so experimentalists have kept pushing towards the observation of a real quantum coupling regime.

Very-high-resolution electron-beam lithography allows for the fabrication of particle pairs separated by gaps as small as 0.5 nm; yet, despite efforts, the optical response still obeys Maxwell's theory[5]. Self-assembly allows the side-by-side alignment of atomically flat nanorod pairs with gaps as small as 0.3 nm, but also in this case classical theory can explain essentially all observations[8] — although, it should be noted, that some subtle optical scattering did indicate the onset of either non-local effects or quantum effects that would confirm recent quantum-based modelling of the nanogap, hinting at the fact that maximum field enhancement is achieved around a 0.3-nm gap, just before quantum tunnelling sets in[9,10].

The work by Baumberg and co-workers[1] takes a different experimental approach. They mount a 300-nm-diameter gold sphere at the end of an atomic force microscope tip. Two of these particle-bearing tips are then oriented tip-to-tip (Fig. 1). They then simultaneously measure the current between the particles using electron tunnelling microscopy and the optical field enhancement by dark-field plasmon spectroscopy as the gap between the particles is decreased. Measuring the conductance allows the researchers to finely control the distance between the particles and correlate it with the optical response. As the nanogap approaches 1 nm, the characteristic redshift of plasmonic modes (spectral lines A, B and C in Fig. 1) is observed. Pushing on to 0.3 nm, the modes gradually collapse, as expected by blueshift nonlinear effects. Finally, moving into the quantum regime, where the gap between the particles is smaller than 0.3 nm, new charge-transfer modes are brought to light (lines D and E in Fig. 1) as the tunnelling pushes the field from the centre towards the outside of the gap area. The full dispersion of the plasmon is therefore traced from the classical through to the quantum regime, before conductive contact is reached and the particles touch each other.

Observing the plasmonic quantum regime for the first time is conceptually elegant, but from a practical point of view, the work by Baumberg and co-workers means that the plasmon resonance does indeed collapse when the gap is smaller than 0.3 nm. The lower volumetric limit for the plasmonic field confinement is set to $\sim 10^{-8}\ \lambda^3$ for the optical regime. This insight prompts a rethink of the impact of quantum tunnelling on single-molecule sensing in nanogaps and the field enhancements observed in surface-enhanced Raman scattering and higher harmonic generation. But for now Maxwell's theory is still perfectly valid for most practical devices, at least until the accuracy of nanofabrication techniques moves from the nanometre to the ångström scale. ❐

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