**Model for the Photoluminescence of Gold Nanoparticles**

The following paragraph explains the model of relaxation of optical excitation we use to understand photoluminescence from gold nanoparticles. The different steps taking place between absorption of light and re-emission of photoluminescence are described sequentially.

1. Plasmon absorption: We assume the incoming optical wave to be reduced to a single monochromatic photon. Under this incoming wave, the gas of conduction electrons oscillates collectively, giving rise to a scattered wave and to extinction of the incoming wave according to the optical theorem. This scattered field is simultaneous with the excitation and has nearly the same spectrum (neglecting Brillouin and Raman scattering). It is obviously cut off by the notch filter.

2. The coherence of the collective oscillation is broken by decoherence processes, due to collision with the particle’s surfaces and to the interaction with baths. The responsible baths can be the many degrees of freedom of all conduction electrons, coupled to the plasmon oscillation by electron-electron interactions, the bath of phonons coupled by electron-phonon coupling, and the bath of photons coupled via spontaneous emission. This decoherence process is extremely efficient and rapid. The decoherence time  as measured in pulsed experiments or deduced from the inverse linewidth of the plasmon resonance is of the order of 6 fs or shorter. After the phases between electron states have been lost, the state of the system can be described as a statistical superposition of hot electron and hole states (1 electron and 1 hole per photon). We now examine how these 2 hot carriers relax from their initial state with given energy and momentum.

3. The hot electron and hole cool down by exchanging energy with the lattice on a timescale of ≈ 1 ps, as can be measured in time-resolved experiments (Vallée, Hartland). Much before this, however, electron and hole have a small\* probability of recombining radiatively again, and thereby re-emitting their high electronic energy as a photoluminescence photon. Some tens of fs after excitation, the wavevectors of electron and hole are decorrelated, either because of interactions with phonons, or because of scattering at surfaces (the time to reach the surfaces is the particle size divided by the Fermi velocity, about 40 fs). To recombine radiatively, electron and hole must meet at the same position and match their wavevectors, . If they interacted only with static surfaces, their energy is not changed and the recombination photon will have the same energy as the laser, . It will not contribute to the measured photoluminescence. Alternatively, if they have interacted with phonons, they have lost or acquired a phonon energy and momentum quantum before recombining. They can also interact with phonons (with creation or destruction of a phonon) upon recombination. In that case they will obey ,  being the wavevector of the phonon created or annihilated upon recombination. In both cases, the energy available upon recombination cannot exceed, but can be much lower because electron and hole may have performed (much) more than one interaction with phonons. Note that, in the hypothesis of a single-photon absorption (linear or low-power regime), the temperature  is that of the bath before absorption, i.e. the particle (room) temperature. In pulsed experiments, the electron gas temperature can be orders of magnitude higher than room temperature, giving rise to two- or multi-photon-excited photoluminescence. This latter case is not considered here.

4. Radiative recombination gives thus rise to weakly emitting sources distributed in space throughout the particle, and distributed spectrally over a broad frequency band (with an exponential cutoff at about ). This intrinsically weak recombination emission can be considerably enhanced by the surface plasmon resonance of the particle acting as an antenna. Again, the collective coupling of all electrons of the particle becomes crucial for interaction with photons.

The model above predicts the following properties of the photoluminescence:

- emission spectrum: because it is considerably plasmon-enhanced, the PL spectrum must follow the plasmon spectrum if the excitation laser is well above the plasmon resonance (Yorulmaz et al.). If the excitation frequency falls within the plasmon resonance, the spectrum is expected to follow the plasmon spectrum, multiplied by a Bose-Einstein statistics factor arising from phonon population, proportional to  for anti-Stokes, and to  for Stokes processes. The average phonon population is .

- polarization: the PL should be essentially polarized as the plasmon (a small depolarization due to the distribution of sources within the particle is possible, but this effect should be very weak)

- lifetime: the lifetime should be determined by the lifetime of hot electrons and holes (actually by the shortest of the two lifetimes). This time should be significantly shorter than the thermalization time of the carriers, as a few interactions with phonons suffice to significantly reduce the carrier energy. After these few interactions, the electron and hole energies are too low to produce an optical photon.

- excitation spectrum: In this model, only the presence of hot carriers is required to create recombination and PL. As the wavevectors are randomly distributed at all times, the probability of recombination remains the same at all stages of the relaxation. Therefore, excitation well above the plasmon resonance should excite PL with roughly the same efficiency as just above the plasmon resonance. The special case of interband transitions in gold add another channel for the population of hot carriers, possibly with their own radiative recombination channels in addition to the relaxation of d-band carriers to (s,p) band carriers.

\* *Because of the necessary wavevector matching between electron and hole, with possibly absorption or creation of a phonon, the probability for radiative recombination is extremely weak, because it competes with extremely fast relaxation of the carriers to different wavevectors and lower energies. The wavevector matching may be helped by the spatial confinement in small particles, compared to bulk ().*



Figure1: Schematic view in real space (left) and energy-momentum diagram (right) of the relaxation steps described above.