

MATRL 265 Class 5: Gold nanoparticles

Nanoscope gold, much prized for its brilliant colors, has been used for a long time as a pigment for stained glass and elsewhere. For example, Andreas Cassius published in 1685, a recipe for making a purple pigment through the reduction of gold salts by Sn metal; a pigment called *purple of cassius*.

The first systematic studies of gold nanoparticles in solution were carried by Sir Humphrey Davy in the Royal Institution. These studies were continued by Davy's protégé Faraday, whose Bakerian Lecture in 1857 is particularly important (no need to print):

M. Faraday, The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light, *Philos. Trans. R. Soc. Lond.* **147** (1857) 145-181. [JSTOR](#).

The origin of color in sols of small particles is due usually to Rayleigh scattering, which is the wavelength dependent scattering of light by particles much smaller than (typically $d < \frac{\lambda}{10}$) wavelength of the radiation. The scattering species need not be a "particle" it could be an inhomogeneity in the refractive index (a density fluctuation). The intensity of Rayleigh scattering is proportional to the inverse fourth power ($\sim 1/\lambda^4$) of the wavelength. The sky is blue because of Rayleigh scattering.

If the particles are larger than λ , the scattering is called Mie scattering, and is characterized by its being only very weakly dependent on the wavelength.

The colors of small metal particles do not arise from Rayleigh or Mie scattering as much as they do from plasmons. Plasmons are quanta of a plasma oscillation: the collective longitudinal excitation of the conduction electron gas. Please read a book like Kittel for more information, and see the handout. In most metals, visible light is of lower energy than the plasmon levels, so it is reflected. In copper and gold there are electronic processes in the visible (the $3d$ to $4s$ transition of electrons) that make the materials absorb in the visible and hence the color.

Small metal particles (and thin films) have in addition, to the *volume* plasmon described above, a *surface* plasmon which is a charge density oscillation (coupled to an oscillation of an electromagnetic field) that propagates in a transverse mode along interfaces between media. The different colors of gold particles arise from surface plasmons, and their confinement. For more on plasmons in small particles, see:

M. A. El-Sayed, Some Interesting Properties of Metals Confined in Time and Nanometer Space of Different Shapes, *Acc. Chem. Res.* **34** (2001) 257-264. [DOI](#).

Modern research into stable gold nanoparticles has exploded since the synthetic route developed by Brust and coworkers:

M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid-liquid system, *J. Chem. Soc. Chem. Commun.* (1994) 810-812. [LINK](#).

This has led to the formation highly monodisperse nanoparticles being made in quantity, and their surfaces being functionalized. Also superlattices:

R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke, and Uzi Landman, Nanocrystal gold molecules, *Adv. Mater.* **8** (1996) 428-433. [LINK](#).

The best preparative methods for gold colloids involve *digestive ripening*:

S. Stoeva, K. J. Klabunde, C. M. Sorensen, and I. Dragieva, Gram-Scale Synthesis of Monodisperse Gold Colloids by the Solvated Metal Atom Dispersion Method and Digestive Ripening and Their Organization into Two- and Three-Dimensional Structures, *J. Am. Chem. Soc.* **124** (2002) 2305-2311. [DOI](#).