Nanoparticles & light and matter interaction

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Nanoparticles

Nanoparticles are inorganic materials particles whose linear dimensions range between 1 nm and 1 µm. Since the atom average diameter is one third of a nanometer ($10^{-9}$m), a 5 nm solid nanoparticle will be made of a few thousand atoms and a 50 nm one will count a few millions of them.

The term nanoparticle doesn’t imply a particular system or substance and it may be used for a wide range of systems which greatly vary in dimension and composition. There are metal nanoparticles (Au, Ag, etc.), semiconductor ones (Si, SeCd, ecc.), etc. Some nanoparticles are actually made of different parts each one of a different material. For instance recently CdSe nanoparticles covered with an ultrathin CsS coating have been synthetized. Last but not least, since shape is an extremely important factor too, as we will soon see, spherical, cylindrical, hollow or even branched nanoparticles have all been manufactured.

Two main characteristics of nanoparticles are particularly worth of notice:

- Their properties depend not only on the composition but also on their shape and dimension. For instance the light absorbed by gold and silver nanoparticles, which is one of the features addressed in these background reading notes, may depend on their diameter and shape (whether they are more or less pronouncedly round).

Since shape and dimension can be controlled within certain limits, it is therefore possible to manufacture nanoparticles with pre-designed properties. For instance such particles may be tuned to absorb only light of a fixed color.

Fig. 1 The left vial contains gold colloid with nanoparticles of 3 to 30 nm diameter: their color is ruby red. On the right end blue-purple is characteristic of gold nanoparticles with approx. one hundred nanometers diameter.
- Owing to their small dimensions, nanoparticles have an extremely high surface to volume ratio \( S/V \). Take a sphere: its surface is proportional to the radius squared while the volume to the radius cubed. As a consequence the \( S/V \) ratio progressively increases as the nanoparticle dimensions decrease. This is a very important fact since nanoparticles interact with the external environment through their surface atoms. For instance, if the nanoparticles are used as a gas sensor they will result much more efficient than a sensor made out of the bulk material.

- Considering the experiments that will be proposed in the module, we will focus here on how nanoparticles interact with electromagnetic radiation, which ultimately means color. For some kind of nanoparticles color depends on both dimension and shape. What happens is exactly as if the color of a ball was determined by its dimension rather than the material it is made of. If nanoscale laws were applicable at the macroscale a deflated basketball would appear red but then pumping air inside it would progressively take on a more rounded shape and the color would change accordingly. An unusual effect indeed!

**Solutions, colloids, suspensions**

Nanoparticles are often dispersed in a colloidal solution. A *colloid* is a finely dispersed substance in an intermediate state between an homogeneous solution and an etherogeneous dispersion. In other words it consists of a substance of microscopic dimensions (diameter from 1 to 1000 nm) dispersed within a continuum phase. *Solutions* on the contrary are homogeneous systems in which everything is in the same phase, while *suspensions* contain particles of larger dimensions (and therefore much more influenced by gravitational force) which will finally sink to the bottom.

As a rule solutions are clear while as colloids often look a bit murky. However this can’t be considered as absolutely true: gold colloids in fact look really clear while silver ones exhibit “muddy” colors.

Many common substances are colloids, among them jelly, mayonnaise, fog, smoke. In these last two examples liquid or solid particles respectively are suspended within a gas.

An effective way to discern between colloids and solutions is represented by the *Tyndall effect*. When a light beam passes through a sheer liquid or a solution the path is not visible whatever the viewing angle, since the particles are too small to scatter light and in the sheer liquid case there are no particles whatever. The particles average diameter is in fact smaller than the wavelength of visible light (approx. 400-700 nm), therefore the matter-radiation interaction is minimal or even null. In colloidal systems however particles dimensions are comparable to light wavelength and this causes scattering, therefore the luminous path can be easily observed looking perpendicularly to the beam. As particles dimensions increase this becomes even more and more evident: the light beam “opens up”, producing a thicker but less clearly outlined path owing to the
increased scattering at 360°. Finally, for bigger particles there will be just a diffused light and no path will be perceived any longer. The intensity of this phenomenon is proportional to both the concentration and the cubed radius of the suspended particles.

Evidence of such an effect in everyday life can be observed when light beams cross suspended or dispersed particle systems, no matter whether solid or liquid, such as dust or water droplets in air. Car lights in a foggy day are a typical example too. Tyndall effect is exploited in the instruments measuring turbidity in liquids (such as wine) called turbidimeters or nephelometers.

<table>
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<th>Summary table</th>
<th>Sinks?</th>
<th>Tyndall Effect</th>
<th>Particles Diameter</th>
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<tr>
<td>Solution</td>
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<td>&lt; 1nm</td>
</tr>
<tr>
<td>Colloid</td>
<td>No</td>
<td>Yes</td>
<td>1 nm ÷ 1000 nm</td>
</tr>
<tr>
<td>Suspension</td>
<td>Yes</td>
<td>Yes</td>
<td>&gt; 1000 nm</td>
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Fig. 2 Tyndall effect in everyday life. Wiki imagine

Fig. 3 The laser beam is visible as it crosses the second glass (colloid) but not the first one (water).

Color

What our eyes commonly perceive as the color of an object or substance, actually is the result of a quite complicated process. Electromagnetic radiation coming from a light source interacts with a substance and is partially absorbed and/or scattered before it finally reaches our eyes. Physics of matter experiments often outline the radiation/matter interaction as one of the major features since such interaction strongly depends on the intrinsic properties of the material and is therefore apt to reveal its inner nature. In experiments, however, a spectrophotometer takes the place of the human eye as detector and it can measure the exact intensity of the scattered radiation covering a large frequency range. In many cases it is quite usual to use a monochromatic radiation such as the one emitted by a laser or a synchrotron.

In most cases light sources emit with characteristic spectra which can greatly vary according to the specific source. As a consequence the color of an object observed in the sunlight (emitting over
the whole range of visible light frequencies) will be perceived very differently than it would be in LED light (which emits at certain selected frequencies), or in incandescence light (weakly emitting in the highest visible frequencies and therefore giving the objects a yellowish tint, a phenomenon well known to photographers).

The perceived color and the corresponding spectrum also depend on how light is absorbed or/and scattered by objects before it finally reaches either the eye or the spectrophotometer. In most cases this is strongly determined by the substances and components of the bodies, namely on what part of light their atoms and molecules absorb. It must be very clear that what is actually seen is the light that has not been absorbed, that is to say the light either transmitted or scattered by the observed objects.

In most cases color does not depend on pigments but rather on structure (structural colors). Surface patterns at the micro or nano scale exhibiting dimensions typically comparable to the wavelength of visible radiation, may induce interference between incident and reflected light, thus producing different colours. Examples of such structural colors can be found in many natural systems, from soap bubbles to some plants as Selaginella Willdenowii (see picture), from bird feathers to some beetles armor or butterfly wings. In more recent times photonic crystals have been specifically designed to stop some frequencies and enhance the reflection or transmission of the other ones.

Fig. 4 From left to right. The wings of the Morpho butterfly derive their blue color from an honeycombed microstructure similar to the photonic crystals one (Wiki picture). A tungsten nanostructured photonic crystal. An example of structural color in a plant Selaginella Willdenowii. Photo courtesy Daniela Rambaldini.

Fig. 5 The color wheel with complementary colors: from the absorbed color it is possible to infer the reflected one and vice versa.
If a material absorbs in a limited range of frequencies corresponding to a single color of the visible spectrum, a very easy and practical way to predict which color will reach the observer eye is the use of the **color wheel**. The material will reflect, scatter and transmit most efficiently the frequencies corresponding to the color on the opposite side of the wheel (and the two are called complementary colors). For instance, if blue is absorbed then the material will look orange. However when more colors are absorbed at the same time, prediction by the color wheel will be much more complex and sometimes may result incorrect.

**Metals color**

There are many microscopic mechanisms through which light and matter interact. Which will be the dominant one strongly depends on both the material composition and the radiation frequency. In any case, the color of a macroscopic object is characteristic of its substance. Of course as a rule it depends only on the surface upper layer; we must however consider that this is still very thick when considered at the nanometer sized scale).

In the specific case of metals being exposed to both visible and UV frequencies, the material response to electromagnetic radiation is mostly related to the metal valence electrons. Differently from insulators or semiconductors, in fact, in metals valence electrons are weekly bound to ions therefore they can respond easily to the fluctuating electric field. Such electrons are able to bear collective oscillations in which all electrons move in phase at their own specific frequency, called **plasma frequency**, see

\[ \omega_p = \left( \frac{e^2 N_e}{\hbar m_e} \right)^{1/2} \]

\( m_e \) the electron mass, is identical for all metals, therefore plasma frequency essentially depends on valence electron density \( N_e \).

The swinging movement of the electrons to which an oscillating electric field has been applied can be imagined as the movement of a mass subject to an elastic pulling back force due, in this specific case, to ions. This is a well known phenomenon in classical physics: the mass-spring system exhibits its own specific frequency, called **resonant frequency**, and in order to transfer energy to the system efficiently it is necessary to apply a force depending on it. The swinging movement of electrons following the sinus mode of the electric field is called plasmonic mode or just **plasmon**.\(^1\)

\(^1\) The term **plasmon** highlights the fact that this oscillating modality, however accountable in terms of waves according to classical physics, can interact with other charged particles exchanging quanta of energy. In quite a similar way, the electromagnetic radiation, which can be described as a classical wave when it propagates freely, interacts with
In the specific case of radiation, the applied force is represented by the varying electric field of the radiation (the magnetic component can be overlooked at the optical frequencies). The electromagnetic field can propagate efficiently in a metal only at the plasma frequency, since in this case the swinging electric field and plasma oscillation are at 90° and no dissipation occurs. At lower frequency however, there’s little or even null propagation, therefore the metal totally reflects the incident light. Since plasma frequency usually falls within the UV region, visible light can’t propagate within the metal. Actually this is what we experience in our daily life, where metals often look like mirrors reflecting almost all the incident light.

In gold specific case, the metal absorbs mainly the purple and nearby frequencies: consequently gold objects look yellow to us.

It may be quite interesting to estimate the order of plasma frequency in a specific example. If a glass sheet (light speed propagation $v = 2 \times 10^8$ m/s) absorbs blue light with wavelength $\lambda = 450$ nm, the natural frequency of the electrons in the material will be $f = v/\lambda = (2 \times 10^8 \text{ m/s})/450 \times 10^{-9} \text{ m} = 7 \times 10^{14} \text{Hz} = 700$ THz.

**Color at the nanoscale**

In metal nanoparticles too, absorbed light (and therefore color) is related to the collective oscillations of valence electrons (plasmons) just as in the microscopic case. However at the nanoscale these oscillations depend not only on the material, but also on the dimensions of the objects interacting with the electromagnetic radiation and last but not least also on the surrounding environment in which nanoparticles are immersed. This allows for the use of nanoparticles as highly sensitive molecular sensors.

When the electromagnetic radiation hits the atoms exchanging energy quanta called photons.
nanoparticles, it induces an instantaneous electric shifting along the field action line of the valence electrons, which in a metal can be considered as almost free. As a result a net negative charge is produced at one of the extremities of the nanoparticles surface, and an equivalent positive charge, due to ions, on the opposite one.

This charge shift induces a pullback force on the electrons, as in a mass-spring system in full analogy with the volume case. However here the intensity of the pullback force depends on the surface charge density and therefore by both surface shape and dimensions. It also depends on the substance in which the particles are immersed, namely the dielectric constant. According to the analogy with the spring-mass system a dielectric medium surrounding the nanoparticle can be represented by a highly viscous substance such as oil. Similarly to what it happens with the plasmonic oscillations, a spring in vacuum will oscillate with a much higher frequency than in oil.

These collective excitations of the electron charges are called Localized Surface Plasmon Resonances (LSPR) to highlight the fact that this collective motions take place near the material surface and are localized in a reduced volume, the nanoparticle one. These excitations are in fact possible only if the light wavelength is much greater than the particle diameter. Since visible light wavelength is a few hundreds of nanometers, the particle as well should exhibit a nanometer sized diameter, otherwise no excitations will be possible. On the other hand if the electromagnetic radiation has a resonant frequency matching these oscillation, the interaction between radiation and nanoparticle is extremely intense.

Nanoparticles LSPR have a lower energy than in the bulk gold and usually they fall in the range of visible light. Therefore nanoparticles give a specific color to the matrix in which they are immersed. As nanoparticles dimension increases, the absorbed frequency decreases exhibiting a red shift. Even more sensitive is the dependence of the absorbed frequency from the refraction index (dielectric constant) of the medium. A higher absorption constant induces a decrease in the plasmonic frequency (and thus in the absorption one) with an increasing red shift.

The light - nanoparticles interaction is quite simple to describe from a theoretical point of view when the particles are spherical. Such a theory was first proposed in 1908 by G. Mie, and its most known applications are found in the physics of atmosphere. The theory, consisting in an exact solution of Maxwell equations for an homogeneous spherical particle in a dielectric, is able to predict how much light is absorbed or scattered and in which direction, depending on the incident radiation frequency. Particles of approximately 10 nm diameter illuminated by visible light, almost totally absorb radiation. However larger particles, approx. 100 nm diameters, scatter a large amount of the radiation. The fraction of absorbed radiation added to the scattered one is called extinction coefficient and depends on frequency. On the web many simulations based on this theory can be found: through them it is possible to make predictions about the extinction spectrum of nanoparticles with different diameters and dielectric environment.
As already seen, at the nanoscale even the shape of objects has a strong influence on the absorbed frequencies of incident light. The same happens with the color of colloidal solutions containing nanoparticles. For instance it is possible to synthetize hollow nanoparticles whose absorbed frequencies are lower than similar but massive nanoparticles. Such a phenomena is due to the interaction between the oscillating charge on the particle inner surface and the one on the outer surface. An elongated particle, such as a nano-cylinder, instead, will exhibit two main oscillation modes: the first along the main ax at lower frequency and the second along the transversal ax with higher frequency. Similarly if one or more nanoparticles get very near to each other, a very common occurrence in colloidal solutions due to aggregation, they may develop electrons oscillating modalities which are common to the two nanoparticles. In other words, from an optical point of view, many aggregated nanoparticles will appear as one bigger nanoparticle and therefore exhibit a lower absorbed frequency.

A most important characteristic of nanoparticles is that they enhance the electric field of the incident radiation in the surface proximity. The smaller the bending radium and the more intense the field enhancement. This may be interpreted as due to electrons concentration near the tips. The electric field generated in the nanoparticles immediate neighborhood can be very high, and allows for enhancement of other processes depending on radiation. For instance, if a molecule is near a nanoparticle its answer to the electromagnetic field can be strongly augmented. By localizing a molecule between two near sharply pointed nanoparticles it is possible to detect the light either absorbed or emitted even by a single molecule!

**Gold and silver nanoparticles applications**

*Functionalization and colorimetric sensors*

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2 Here are reported in extreme synthesis some examples of cutting edge applications of metal nanoparticles. If you want more details have a look to the links at the bottom of this document.
The high degree of interaction of nanoparticles with visible light, due to the LSPR phenomenon, and the high sensitivity to both nanoparticle shape and surrounding dielectric changes, may be exploited in using sets of nanoparticles as platforms for chemical or biological sensors which may be so sensitive as to detect even single target molecules. The basic idea is to make the nanoparticle sensitive to specific molecules or tissues which we want to detect. As a rule in order to reach this goal some molecular system which is able to recognize and bind the targeted molecule or tissue is attached to the nanoparticle by chemical means. Most often this is an antibody which is able to recognize and dock specific biological targets. This process is often indicated as functionalization.

One of the most widely known examples of colorimetric sensor are pregnancy tests. In some cases the strip that turns pink in case of a positive pregnancy test, is made out of gold colloid whose nanoparticles bind to antibodies linked to the HCG hormone (Human Chorionic Gonadotropin) in urine. Nanoparticles and the linked hormone are captured by other antibodies in the reactive region of the test strip which turns bright pink.\(^3\)

In other applications, the gold nanoparticles may be functionalized attaching DNA sequences which are able to detect other complementary DNA sequences. These are attached to other nanoparticles and as the two sequences come together the nanoparticles get nearer and the suspension changes its color since the absorbed light frequency changes upon aggregation. The test result is a positive response to the presence of a specific DNA sequence.

In order to reveal the presence in a solution of specific molecules with high sensitivity, it is also possible to functionalize the nanoparticles with molecules to which the target molecules can directly attach. As a consequence of the docking, the dielectric constant of the surrounding medium will slightly change, thus causing a shifting in the light absorption and in the colloidal solution perceived color.

\(^3\) http://www.accutest.net/products/pdf/pf52a250_labmanual.pdf
Last but not least functionalization of nanoparticles with different molecules may also allow for detection within the electrolyte of different molecular systems at the same time (multiparametric detection).

**Glass and enamel coloring**

Since the IVth b.c. century craftsmen used to add gold salts to the glass mixture to obtain a brilliant red colour. As the glass mixture heated up the gold ions from the salts transformed into gold atoms which aggregated forming nanoparticles which were dispersed into a silicon oxide matrix. The resulting material absorbed all visible light frequencies except red. The stained glass windows can still be admired in many Middle Age churches. This was the first, although unconscious, attempt of nanotechnology application.

In Italy, during the XVth and XVIth century, craftsmen used nanoparticles to decorate vases. Such a technique originally dates back to muslims in the Middle East during the IXth century, then extended to Spain in the Middle Ages, and finally arrived in Italy. The vases exhibited an iridescent golden red brilliancy. The effect was obtained by mixing silver and gold salts with vinegar, ocre and clay. Such a mixture was then applied to the already enameled vase surface. As a consequence of the heating in the oven the metal ions in the mixture got reduced to metal nanoparticles of 5-100 nm in diameter. The red color came from copper. Of course only nowadays people are able to fully appreciate the 'nano' origin of these colors.

Another well-known example of nanotechnology ante litteram is the so called Licurgo’s cup, made out of dichroic glass. The cup appears green in reflection and red in transmission. It is not just a chance that the two colors are complementary ones.

**Nano-medicine**

One of the most up to date and interesting applications of gold nanoparticles in nanomedicine is their use in cancer fight. Among other techniques, phototherapy specifically exploits the strong light absorption of gold colloids. Such substances can be considered chemically and biologically inactive and once conveniently functionalized they are able to recognize receptors present only in ill tissues, then they gather and accumulate in such tissues. As they absorb light and convert it into thermal energy, they are able to destroy selectively the damaged cells simply by heating. Nowadays it is possible to produce gold hollow nanoparticles with resonance frequency in the Near InfraRed (NIR). This means that when irradiated with this light frequency such nanoparticles are able to harvest a huge amount of luminous energy converting it into heat. Since water and most of biomolecules do not absorb in this region of the electromagnetic spectrum (biological
tissues are highly transmitting for frequencies in the 650 - 900 nm range) it is possible to irradiate with a NIR laser the tissue at a certain depth, thus inducing through resonance the heating up of the gold nanoparticles and producing necrosis in the cancer tissue with no damage altogether for healthy cells.

**Nano-materials growth**

Metal nanoparticles may be used to favor the growth of other nano materials such as for instance through CVD, Chemical Vapor Deposition. This actually is an example of bottom up approach. Usually CVD stands for a class of processes where solids are manufactured starting from a gas phase. In this case gold nanoparticles are first being deposited on a substrate and act as catalyzers attracting the gas molecules. Afterwards the substrate is put into a room filled with a gas containing all the necessary chemical elements, like silicon, that will preferentially attach under the nanoparticles ultimately bringing to the growth of nanowires under the nanoparticle “hat” whose diameter can be controlled.

**Silver nanoparticles as antimicrobial.**

The antimicrobial effect of silver is well known since ancient times. Nowadays on the market is possible to find many products based on silver nanoparticles (clothes, tooth brushes, bandages, filters, etc...). In spite of their undeniable advantages (silver nano filters to use for water sterilization in first aid and emergency cases, low temperature linen sterilization in hospitals, etc...), there are still concerns about the possibility of silver particles getting into pipes and sewage where they may destroy also the “good” bacteria employed to remove ammonia in water treatment plants. In some countries there’s actually a lot of debate about this. For instance the commercialization of a nanosilver based washing machine produced in the USA has been forbidden in Europe till further research on the topic will ensure it is totally harmless for the environment.

**Concerns on possible harmful effects for both people and environment**

The use on an industrial scale of nanoparticles in many areas of everyday life and in many health related applications, rises the issue about the safeness of such systems. The nano dimension of particles may bring to overcoming natural defense barriers bringing to potential biological damage. Actually nanoparticles are much smaller than the well-known pm10, whose rate in the atmosphere is used as a pollution detection parameter. However as it has been already clearly shown, the term nanoparticles is used to describe systems which may be extremely different from each other. Some nano systems are used just because of their biocompatibility in diagnostics as a substitute...
for many molecules previously used and whose toxicity is actually well established.

It doesn’t make much sense to worry about nanoparticles in a general way just because of their dimensions: many kinds of nanoparticles are in fact produced spontaneously in Nature and are already present in the air we breath or, as shown above, have been used for centuries. The properties of nanoparticles may depend on many details: dimensions, exposed surface, combination with other systems, etc. and not only by the substance they are made of. It is therefore very important to take great care that any new system or technology (not just in nano) undergoes safety test targeting the specific applications. If we plan to use some kind of nanoparticles in everyday products, from motorways to clothes (such as super hydrophobic or antibacterial textiles), we should have reached a reasonable certainty that these specific particles are not noxious to either people or environment according to predictable exposure.

Further research

- Alternative modalities for nanoparticles production (at research level)
  - A video on nanoparticles generation in a liquid through laser ablation. [www.youtube.com/watch?v=kOv0YuWpUzU](http://www.youtube.com/watch?v=kOv0YuWpUzU)
  - There are many “green chemistry” recipes for nanoparticles synthesis; one of them is a room temperature process with the aid of tea or coffee essence. Mallikarjuna N. Nadagouda and Rajender S. Varma [Green Chem., 2008, 10, 859-862](http://www.epa.gov/ord/gems/scinews_tea-nano.htm)
  - Synthesis of nanoparticles in different shapes and dimensions [www.nhn.ou.edu/\~bumm/NanoLab/ppt/nanogold.ppt](http://www.nhn.ou.edu/\~bumm/NanoLab/ppt/nanogold.ppt)

- Potential risks coming from nanoparticles use
  - Antimicrobial properties of silver nanoparticles and possible harmful effects on the bacteria in sewage and water treatment plants [http://www.sciencedaily.com/releases/2008/04/080429135502.htm](http://www.sciencedaily.com/releases/2008/04/080429135502.htm)

- Gold nanoparticles applications in medicine
  - A video on the use of gold nanoparticles in cancer treatment [http://www.youtube.com/watch?v=RBjWlnq3cA&NR=1](http://www.youtube.com/watch?v=RBjWlnq3cA&NR=1)
  - and an article [http://www.sciencedaily.com/releases/2010/02/100216140402.htm](http://www.sciencedaily.com/releases/2010/02/100216140402.htm)
- **Background reading**

  - phototherapy against cancer
    
  
  - silver nanoparticles as blood anticoagulant
    

- **Other applications**

  - Importance of shape and geometry of nanoparticles, use as colorimetric sensor
    
    [http://www.sciencedaily.com/releases/2010/06/100623085841.htm#.TmU5jwTfGnM](http://www.sciencedaily.com/releases/2010/06/100623085841.htm#.TmU5jwTfGnM)
  
  - “Nanoscale origami’ enables the creation of 3D nanostructured devices for optics and bio-sensing”
    
  
  - Nanowires from gold colloid
    
    [http://science.howstuffworks.com/nanowire3.htm](http://science.howstuffworks.com/nanowire3.htm)
  
  - Nanoparticles use in solar cells
    
  
  - Plasmonic tuning of optical fibers for biosensing
    

- About Lycurgus cup and the **stained glass windows with gold nanoparticles**.
  
  - “Nanoplasmonics: the physics behind the applications “ in physics today. Download at
    
  
  - [http://master-mc.u-strasbg.fr/IMG/pdf/lycurgus.pdf](http://master-mc.u-strasbg.fr/IMG/pdf/lycurgus.pdf)