CHAPTER 1

General Introduction

Abstract

A brief introduction of glass is given in this chapter. Sol-gel processing which is one of the major and common glass fabrication methods is discussed here. The process is known for its low temperature preparation and since the precursors are in the form of solution a high homogeneity and purity could be promised. A relatively high dopant concentration is possible through sol-gel process which promotes our major interest to dope the glassy matrices with rare-earth ions and nanoparticles. A brief introduction of holmium rare-earth is provided. Judd-ofelt theory is discussed, since using this quantum mechanical theory an estimation of electric dipole transition strength between the energy levels are possible for analyzing its spectroscopic properties. Also a discussion of impedance spectroscopy is provided, as holmium doped glassy matrices with and without silver-nanoparticle co-doping is a good dielectric material. A brief account of the surface plasmons brought about by silver nanoparticle doping is also discussed.
1.1 Glass

Glass is one of the most ancient materials known to mankind. There are many different methods by which we can produce amorphous solids, which we cannot classify as glass. On defining the glassy state, two different approaches are taken by glass scientists. One definition is based on the concept of disorder. By disorder we mean mainly that the spatial arrangement of atoms, ions and molecules do not exhibit three dimensional periodicity (translational symmetry) and the long range order of the crystalline state is destroyed. We can define the glassy state as a state with short range order and long range disorder. The short range order is of great significance to the optical and spectroscopic properties as all the electronic movements take place in the short range region within or among the atoms or ions. The second definition is based on the internal stability of the materials. Classic glasses are characterized not only by the absence of crystallinity but above all by their ability to pass progressively and reversibly to a more and more fluid state as the temperature is increased. In the course of this change, there is modification of properties at a point called the glass transition. Gradual softening with increasing temperature is moreover, extremely important in technical applications and constitutes one of the fundamental properties of a glass material. Based on these conditions Zarzyki [1] adopted the definition “A glass is a noncrystalline solid exhibiting the phenomenon of glass transition.” He named the corresponding physical state as vitreous state originating from the Latin word *vitrum*. Varshneya [2] adopted
the definition glass as a ‘solid with liquid like structure’, ‘a noncrystalline solid’ or simply an amorphous solid’. Zachariasen [3] postulated that, as in crystals, the atoms in glass must form extended three dimensional networks. However, Hagg [4] pointed out that an infinite three dimensional network may not be a necessary condition for glass formation. He concluded: ‘it seems as if a melt contains atomic groups which are kept together with strong forces and if these groups are so large and irregular that their direct addition to the crystal lattice is difficult, such a melt will show a tendency to supercooling and glass formation”. According to Smekal [5] mixed chemical bonding in a material is necessary for glass formation. Sun [6] showed that bond strengths in glass forming oxides are particularly high. Turnbull [7] pointed out that bond type, cooling rate, density of nuclei and various material properties like crystal-liquid surface tension and entropy of fusion are significant factors which affect tendency of different liquids to form glasses. The sol-gel process of making a glass avoids the normally high temperature employed for fusion of glass.

1.2 Sol-Gel Processing

Sol-gel processing is a wet-chemical technique mainly for the production of glasses, ceramics, crystals, powders, thin films etc. The technique dates back to mid 1800s with Ebelman[8,9] and Graham’s[10] studies on silica gels, a time when they found that the hydrolysis of tetraethylorthosilicate (TEOS) under acidic conditions yielded SiO₂ in the form of a glass like material. But to avoid fracture of the glasses, extremely long drying time of 1 year or more were
necessary and hence was of little technological interest. From a period of later 1800 through 1920 this process developed with the contributions directly and indirectly from many noted chemists including Ostwald[11], Lord Rayleigh[12], Iler[13], Strober[14] et al. The prime motivation for sol-gel processing is its potentially higher purity, homogeneity, high doping concentrations and the lower processing temperatures compared with traditional glass melting or ceramic powder methods. Presently the process has developed to a more versatile regime with many end products like bulk glasses, ceramics, thin films, colloids, fibers, coatings, powders etc, having diverse applications in luminescent solar concentrators [15,16], photochromic, electrochromic and gasochromic plates for smart windows [17–19], sensors for environmental and biological impurities [20,21], solid state lasers tunable in the visible spectral range [22–26], active waveguides [27], materials for linear and nonlinear optics [28], semiconductor quantum dots [29–33] and complexes of rare earth ions that can be used for diagnostics and biological markers [34–37].etc. The many areas of interest are best summarized in the solgel tree of Dislich [38] as shown in figure 1.1. This sol-gel tree was proposed by Helmut Dislich from a poll by Battelle Columbus Laboratories, Columbus, Ohio, U.S. The tree is impressive due to its somewhat different standpoint and Dislich concludes with a wish that "1000 flowers may bloom" in the sol-gel area depending on whether we are found ourselves in a forest. The sol-gel area of research is quite new, and consequently the problem of extrapolation is quite a difficult one, but nevertheless an interesting challenge - if bravely faced. It is safe to assume that the sol-gel
technology will continue to expand strongly, and the circle of researchers interested in this field will grow.

1.3 Sol-Gel Chemistry

As the name indicates, the principle of the sol-gel technique consists of converting the sol which is a suspension of colloidal or polymeric particles in a solvent, into a semisolid phase known as gel. Commonly, the most preferred starting reagents are metal alkoxides, with general formula \( M(OR)_n \), where \( M = \) metal, \( R = \) alkyl group, \( n = \) the valence of the metal atom (\( n \) is usually 4). The transition from sol to gel involves two key steps, hydrolysis and condensation [39-42]. Hydrolysis occurs by introducing water in the sol. In this process, the alkoxide groups (OR) are replaced stepwise...
by hydroxyl groups (OH) as summarized in equation 1.1 and 1.2. The hydrolysis rate was found to depend upon many factors, the reaction can favorably be promoted by an increase in the charge density on the metal, the number of metal ions bridged by an hydroxo- or oxo-ligand, and the size of the alkyl groups. Conversely, inhibition occurs as the number of hydroxo-ligand coordinating M increases or when the pH, temperature, or water and solvent concentration tend to favour the reverse reaction (esterification).

\[
M(OR)_n + H_2O \rightarrow M(OH)(OR)_{n-1} + ROH \quad \text{(1.1)}
\]

or

\[
M(OR)_n + H_2O \rightarrow M(OH)(OR)_{n-x} + xROH \quad (1 \leq x \leq n) \quad \text{(1.2)}
\]

The hydrolysation of the metal alkoxide particles is usually catalyzed by addition of an acid or base. In acidic solution, the hydrolysis reaction proceeds by the mechanism of electrophilic attack [39]. As illustrated in figure 1.2 for tetra-alkylorthosilicate precursors, this mechanism features the attraction of a protonated water molecule (H$_3$O$^+$) to the negatively charged oxygen in the more basic alkoxide groups resulting in the substitution of an alkoxide group (OR) by a hydroxide group (OH). In basic solutions the hydrolysis mechanism occurs by nucleophilic substitution. In this case, the positively charged metal (M$^+$) is preferentially attacked by a negatively charged hydroxide (OH$^-$) leading to the deprotonation of a hydroxo ligand as shown in figure 1.3.
Once partially or totally hydrolyzed, the metal hydroxides undergo a stepwise polycondensation summarized as follows:

\[
2M(OR)_n OH \rightarrow H_2O + n(OR)M - O - M(OR)_n
\]

The condensation reaction involves hydroxyl groups and results in M-O-M linkages which, in turn, yields a three-dimensional network (called gel) upon a polymeric weight and cross-linking degree. The gel state is then best described as a viscoelastic material composed of interpenetrating solid and liquid phases. Its structure is strongly dependent on the water content in the system and whether acid or base was used as hydrolysis catalyst. In acidic solution or for low...
water concentration, weakly crosslinked linear chains are produced, resulting in a soft gel which can be readily redispersed in solution. On the other hand, in base-catalyzed solutions, branched clusters are preferentially formed and their propensity to coalesce is responsible for the gelation of the solution. However, the gel itself is not an end product. To obtain coatings, ceramic powders or monolithic shapes, the amorphous gel must be dried at high temperatures. Most difficulties arise during the drying stage and are mainly caused by the removal of large amounts of solvent trapped in the polymeric network [39]. Indeed, the gel is prone to shrink by a large amount and capillary forces induce the formation of cracks. To minimize these effects, gels are normally dried by slow evaporation and for coatings, the thickness usually must not exceed 10 µm [42].

The hydrated silica tetrahedra interact in a condensation reaction (eq 1.4), forming $≡\text{Si-O-Si}≡$ bonds.

$$\text{HO} - \text{Si} - \text{OH} + \text{HO} - \text{Si} - \text{OH} \rightarrow \text{HO} - \text{Si} - \text{O} - \text{Si} - \text{OH} + \text{H}_2\text{O}$$  \hspace{1cm} \text{(1.4)}

Linkage of additional $≡\text{Si-OH}$ tetrahedra occurs as a polycondensation reaction (eq 1.5) and eventually results in a SiO$_2$ network. The H$_2$O and alcohol expelled from the reaction remains in the pores of the network. When sufficient interconnected Si-O-Si bonds are formed in a region, they respond cooperatively as colloidal (submicrometer) particles or a sol. The size of the sol particles and the cross-linking
within the particles (i.e., density) depend upon the pH and r value \( r = [H_2O]/[Si(OR)_4] \) among other variables.

\[
\text{HO-Si-O-Si-OH + 6Si(OH)_4} \rightarrow
\]

1.3.1 Processing Steps

The processing involved in making sol-gel-derived silica monoliths comprises of seven steps: (Figure 1.4)

**Step 1: Mixing.** A liquid alkoxide precursor, such as Si(OR), where R is most commonly CH3, C2H5, or C3H7, is hydrolyzed by mixing with water. Since the mixing takes place at a molecular level, the homogenity of the sol-gel process is achieved at the very first step.

**Step 2: Casting.** The sol is a low-viscous liquid, it can be cast into a mold. The mold must be carefully selected to avoid adhesion of the gel.

**Step 3: Gelation.** With time the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend greatly upon the size of particles and extent of cross-linking prior to gelation. At
gelation, the viscosity increases sharply, and a solid object results in the shape of the mold. With appropriate control of the time-dependent change of viscosity of the sol, fibers can be pulled or spun as gelation occurs.

**Step 4: Aging.** Aging of a gel, also called as syneresis[39], involves maintaining the cast object for a period of time, hours to days. During aging, polycondensation continues along with localized solution and reprecipitation of the gel network, which increases the thickness of interparticle necks and decreases the porosity. The strength of the gel thereby increases with aging. An aged gel must develop sufficient strength to resist cracking during drying.

**Step 5: Drying.** During drying the liquid is removed from the interconnected pore network. Large capillary stresses can develop during drying when the pores are small (<20 nm). These stresses will cause the gels to crack catastrophically unless the drying process is done in a controlled manner.

**Step 6: Dehydration or Chemical Stabilization.** The removal of surface silanol (Si-OH) bonds from the pore network which results in a chemically stable ultraporous solid.
Step 7: Densification. Heating the porous gel at high temperatures causes densification to occur. The pores are eliminated, and the density ultimately becomes equivalent to fused quartz or fused silica. The densification temperature depends considerably on the dimensions of the pore network, the connectivity of the pores, and surface area etc.

1.4 Advantages of Sol-Gel Processing

- Can easily shape materials into complex geometries in gel state
- Can have low temperature sintering capability
- Can produce high purity products
- Can provide a simple, economic and effective method to produce high quality materials.
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• Allows higher doping levels for rare-earth ions, transition metals etc without the common clustering effect found in other glass making techniques.

1.5 Rare Earth Ions

Rare earth elements are a collection of seventeen chemical elements in the periodic table, namely scandium, yttrium, and the fifteen lanthanoids (lanthanides). The lanthanoid series comprises the fifteen elements with atomic numbers 57 through 71, from lanthanum to lutetium. All lanthanoids are f-block elements, corresponding to the filling of the 4f electron shell, except for lutetium, which is a d-block lanthanoid. The general property of rare earth is greatly determined by their 4f electrons. The electrons at the inner shell are shielded by the 5s, p, d electrons. So the effect of ligand field becomes weak. The energy levels of rare earth ions depend on, firstly, the static electric interaction between electrons ($H_e$) and secondly on the interaction between spin and orbital ($H_{so}$). $4f^N$ electronic configuration forms the energy levels denoted with LSJ under the effect of the above two interactions. The energy levels of rare earth ions in glass are similar to those of free ions. Energy level of a system of state such as atom or ion is usually calculated by determining the Hamiltonian of the system. In many particle systems like rare earths the most common method is to apply the central field approximation [43] method to calculate the Hamiltonian of the system. Hamiltonian of optically active electron is composed of several terms. The interaction of electron with nucleus represents the central field Hamiltonian ($H_0$), the interaction between the
electrons represents the coulomb field ($H_c$), the interaction between the spin and orbital motion of the electrons represents the spin orbit field ($H_{so}$) and the crystal field ($H_{cf}$) which represents the interaction of electron with the crystal field from the surrounding ion in the solid. Therefore the total Hamiltonian of the system can be written as

$$H_{4f} = H_0 + H_c + H_{so} + H_{cf}$$

Since the optical transition of interest in rare earth involves the 4f-electrons, the magnitude of the different interaction terms is different in each rare earth ions. The other three terms give rise to a set of states labeled by total spin $S$, total orbital angular momentum $L$ and total angular momentum $J$. Spin-orbit interaction has considerable effect, so the resultant total angular momentum $J$ is considered to be a good quantum number in almost all circumstances. The effect of other interactions such as those with nucleus or crystal fields is to lift the (2$J+1$) degeneracy of the level and the small splitting produced may be treated as perturbation.

The rare earth ion in a crystalline salt is situated in a potential $V(r)$ in the crystalline field, which arises from charge $Ze$ on neighboring ions

![Figure 1.5](image)

**Figure 1.5.** Schematic diagram of the splitting of energy levels of rare earth ions
at positive $R_i$ with a potential term of $V(r) = \sum_i eZ_i |r - R_i|$. This potential lifts the $(2J+1)$ degeneracy [44]. From susceptibility measurements it is clear that these splittings due to $V(r)$ are much smaller than the multiplet separation. So that mixing of different multiplet can usually be neglected. In the absence of any magnetic field the levels of an ion with odd number of $4f$ electrons can at most be split into levels which are doubly degenerate. This is applied to rare earths with half-integral 'J' ground states e.g. Ce$^{3+}$. The environment of an ion with a degenerate ground state spontaneously distorts to a lower symmetry so as to remove the degeneracy. It implies that ions with an even number of $4f$- electrons always have singlet ground state e.g. Pr$^{3+}$. This rule doesn't apply to excited state. Riseberg and Weber [45] describe the splitting of energy levels of rare earth in schematic fashion as shown in Figure 1.5. Typical separation due to coulomb interaction is $\geq 10^4 \text{ cm}^{-1}$ and it is $\approx 10^3 \text{ cm}^{-1}$ for spin-orbit interaction, which splits the 'L' terms into 'J' states. The crystal field interaction breaks the spherical symmetry of the Hamiltonian and remove $(2J+1)$ degeneracy of the levels. The so-called Stark splitting is generally a few hundred cm$^{-1}$ in magnitude. Radiative transition can occur from any Stark component of one $\{L S J\}$ multiplet. As an example of the energy level splitting in rare earth, a schematic diagram of the splitting in $4f^6$ electronic configuration is given in Figure 1.6.
Because of the extreme complexity of the splitting, only a part of the diagram is shown here. In crystal spectra, Zeeman and polarisation studies have made it possible to characterise the J manifolds to which many of the lower lying crystal levels belong. At higher levels this becomes more and more difficult [46].

The basic energy levels of free ions are those of the configurations, which are $2(2l_1+1)$ $2(2l_2+1)$ ..... $2(2l_n+1)$ degenerate, and have separation $\sim 5 \times 10^4$ cm$^{-1}$. The detailed energy structure arises from the splitting of these levels by interaction between electrons. Here the interaction is between $4f$-electrons involved and also between electrons and nucleus. In the case of rare earths three main interactions are dominant in order of magnitude.

(i)  Coulomb repulsion between electrons
(ii) Spin orbit interaction
(iii) Nuclear hyperfine and quadrupole interaction

The advantages of glass over crystal in the contest of laser materials can be summarised as follows. The laser glass can be made in a variety of sizes and shapes, with excellent homogeneously and low birefringence; it is less expensive than
crystals and it has good coupling to broad band pump sources such as flash lamps and is thus capable of high stored energy density. Glass by its nature has a variety of sites that differ from each other in the number and position of the surrounding anions. Thus transitions in glass are inhomogeneous and relatively broad. The broader emission lines and generally lower cross sections of glass are compensated by its broader absorption bands, which allow glass to couple more efficiently to broad band pump sources than do crystals. Laser glass can store large amounts of energy because it can be produced in large sizes and due to its low cross section. Laser glass has an additional advantage over laser crystals in lasers operating in the picosecond and femtosecond regime. The broad fluorescence line width of glass allows for shorter transform limited pulses. In addition to rare earth ions, the glass serves as a host for numerous other luminescent species. Solid state tunable dye lasers were developed by doping dye molecules in various sol-gel derived glasses and organically modified silicons (ORMOSILS)[47-50].

1.6 Holmium ion

A trivalent metallic rare earth element, holmium has the highest magnetic moment (10.6 \( \mu_B \)) of any naturally occurring element and possesses other unusual magnetic properties. When combined with yttrium, it forms highly magnetic compounds. The 4f electrons provide holmium ion with specific spectral energy levels that lead to some specialized luminescent uses. Holmium ion show well defined absorption and emission peaks in the visible and IR regions. Much of the studies in Holmium are connected with the
upconversion mechanisms involved in Ho$^{3+}$ doped matrices and such a property can be used in storage and other photonic applications. Holmium doped materials whose absorption and emission features are in the eye sensitive green spectral region [51]. Holmium is used in yttrium-iron-garnet (YIG)- and yttrium-lanthanum-fluride (YLF) solid-state lasers found in microwave equipment (which are in turn found in a variety of medical and dental settings). Holmium lasers emit at 2.08 microns, and therefore are safe to eyes. They are used in medical, dental, and fiber-optic applications.[52]. Holmium is one of the colorants used for cubic zirconia and glass, providing yellow or red colouring. Glass containing holmium oxide and holmium oxide solutions (usually in perchloric acid) have sharp optical absorption peaks in the spectral range 200–900 nm. They are therefore used as a calibration standard for optical spectrophotometers.[53]. Ho$^{3+}$ doped gallium lanthanum sulphide (GLS) glasses have first been reported 20 years ago by Reisfield and coworkers with emphasis on visible and near-infrared emission [54-56]. Since then the qualities of the glasses has improved considerably, in particular due to the reduction of lanthanum oxide and hydroxyl impurities. The infrared emission bands have been observed at 1.2, 1.25, 1.67, 2, 2.2, 2.9, 3.9 and 4.9$\mu$m, some of which have not been reported in glass or other rare-earth host materials before. Figure 1.7 shows the energy level diagram of Ho$^{3+}$ ions.
Figure 1.7 shows the energy level diagram of Ho$^{3+}$ ions.

1.7 Judd-Ofelt Theory

The rare earths are usually doped into solid state host in the trivalent state. The absorption spectra of these ions in the optical region arise from the transition within 4f$^n$ configuration mainly. Origin of these levels and its location are determined by Coulomb, spin-orbit and crystal field interactions. Each of these interaction has typical terms and energy separation values. Direct measurement of radiative transition rates between excited levels is extremely difficult to perform. In 1960 Judd [57] and Ofelt [58], developed a quantum
mechanical theory of rare earth ion doped solid state media which allowed estimates to be made of the electric dipole transition strengths between any pair of LSJ manifolds. Judd-Ofelt analysis of a rare earth ion doped material essentially involves using the line strengths of all the observable transitions from the ground state to the excited manifolds, which can be determined from white light absorption measurements, and using these line strengths to estimate line strengths of transition between pairs of excited levels. The theory has been applied to rare earth ions in a variety of glass hosts in the past with a considerable degree of success.

Judd-Ofelt analysis is accurate to 10-15% and is particularly valuable for obtaining strengths of transitions for which direct measurements are difficult or impossible.

1.8 Impedance (Dielectric) Spectroscopy

Impedance Spectroscopy (IS) is a very versatile electrochemical tool to characterize intrinsic electrical properties of any material and its interface. In this thesis we have studied the IS of holmium doped silica matrix with and without silver nanoparticle co-doping. The presences of nanoparticles are known for the enhancement in permittivity for glassy matrices. The basis of IS is the analysis of the impedance (resistance of alternating current) of the observed system in subject to the applied frequency and exciting signal. This analysis provides quantitative information about the conductance, the dielectric constant, the static properties of the interfaces of a system, and its dynamic change due to adsorption or charge-transfer-phenomena. Impedance spectroscopy measures the
dielectric properties of a medium as a function of frequency and temperature. The frequency range extends over nearly 18 orders in magnitude from the micro Hz to the terra Hz range close to the infrared region. IS is sensitive to dipolar species as well as localized charges in a material. It determines their strength, their kinetics and their interactions [59]. Thus, dielectric spectroscopy is a powerful tool for the electrical characterization of nonconducting or semiconducting materials in relation to their structure and also of electronic or sensor devices.

There are different types of electrical stimuli which are used in IS. The most common and standard one is to measure impedance directly in the frequency domain by applying a single frequency voltage to the interface and measuring the phase shift and amplitude, or real and imaginary parts, of the resulting current at that frequency. These frequency dependent measurements have been recognized as an important tool for the electrical characterization of materials [60-62]. Commercial instruments are available which measure the impedance as a function of frequency automatically in the frequency ranges of about 1 mHz to 1 MHz and which are easily interfaced to laboratory microcomputers. The advantages of this approach are the availability of these instruments and the ease of their use, as well as the fact that the experimentalist can control the frequency range.

1.9 Surface Plasmons and van der Waals Energy

It is now recognized that surface plasmons can be present on particulate, smooth, or corrugated metallic surfaces. They have
enormous potential in the fields of optical computing, novel optical devices, and—more recently—biological and medical research [63]. These emerging applications are the result of the unique properties of surface plasmons, which are confined in a two-dimensional surface and can have dimensions considerably smaller than optical wavelengths. Surface plasmons can be, to a reasonable extent, controlled in two dimensions, trapping and transporting optical energy in nanoscale structures[64]. The two-dimensional nature of plasmonic structures makes them compatible with modern lithographic methods used for preparation of integrated circuits. The applications and understanding of plasmonics are now being facilitated by modern nanofabrication technologies. These technologies allow preparation of numerous metallic nanostructures, in particular regular patterns of particles, holes, or other features. These metallic nanostructures are already known to display unusual and unexpected optical properties [65]. The plasmonic fields generated in such structures provide opportunities for new experimental capabilities such as subwavelength optical imaging.

Plasmonics of nanoparticles is an integrated bottom-up technique to fabricate the advanced devices and materials using the surface plasmon resonance (SPR) of nanostructured metals. In this technique, the nanoparticles are mainly used as building blocks. The character and performance of the fabricated devices and materials are largely dependent on composition, dimension (size and shape), and arrangement of the nanoparticles[66] Nanoparticles (NPs) of Ag and Au exhibit plasmon absorption bands in the visible wavelength
region. The absorption spectrum is sensitive to various factors such as particle size and shape, the electron density on particle, the dielectric properties of the surrounding medium, aggregation state and interparticle interaction. In the case of core–shell nanoparticles, Mie scattering theory predicts that the plasmon resonance can be shifted between the ultraviolet (UV) to the midinfrared (IR) region by varying the shell thickness ratio to the overall size. Gold (Au), silver (Ag), and copper (Cu) nanoparticles display well-known surface plasmon resonance (SPR) bands as a result of the coherent oscillations of the conduction band electrons induced by the interacting electromagnetic field [67]. The underlying theory behind SPR is defined by the Mie solutions to Maxwell’s equations by Stern and Ferrell [68], which showed that an interface plasmon mode can exist at the boundary between two metals. For the case of a bimetallic particle, the two different metals have different electron densities and, therefore, two different plasma frequencies. [69]. To account for bimetallic structures, the dielectric function used is a weighted linear combination of dielectric constants of the constituent metals. Theoretical simulations were compared to experimentally produced Au/Ag nanoparticles and the data revealed relatively high correlation [67]. This correlation is consistent when the particle sizes are above 5 nm, for which Mie theory holds. Cottancin et al. have developed a theory that combines the classical Mie theory with quantum effects that play an enhanced role at this size regime [68, 69]. Probably the most interesting property of metallic nanoparticles is the ability to tune their plasmon resonances across a wide range. The properties of localized plasmons and, thus, the optical response
of the nanoparticle depends critically on their material shape, and size. For example, optical forces between silver nanoparticle aggregates are known to be enhanced by exciting plasmon resonances conveniently [70]. This interaction is mediated not by a photon field but by the electromagnetic vacuum fluctuations and is particularly interesting for the design of control mechanisms of the adherence of nanoparticles among each other or on to a surface.

The SPR of AgNPs with high symmetry, like spheres or ellipsoids, can be calculated with good accuracy by analytical expressions developed in the frame of the Mie theory. For instance, Mie theory can be used to obtain a good fitting of experimental UV–visible spectra of spherical gold and silver nanoparticles in solution and to evaluate the average size of the nanoparticles. However, when particle’s symmetry is lowered, the exact solution of the electromagnetic problem is not possible, and numerical approaches are necessary. One of the most frequently used numerical methods for the calculation of the SPR in metal nanoparticles is the discrete dipole approximation (DDA). In DDA, each object is approximated with a cubic array of dipoles each having a definite polarizability. The result of DDA calculations is considered reliable if the nanoparticles are described with an adequate number of dipoles and with the adequate size-corrected dielectric function. To describe the van der Waals interactions between a nanoparticle and a surface, usually a dipole approximation is used, which is valid only for large enough distances between the particle and the surface. Recently, van der Waals forces between a spherical particle and planar substrate have
been considered with the help of expansion of electromagnetic fields over usual spherical harmonics[71]. The van der Waals energy between realistic metallic surfaces was shown to be dominated by surface plasmon oscillations for small distances.

Reference


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