DEVELOPMENT OF A NEAR-FIELD SCANNING OPTICAL MICROSCOPE
AND
ITS APPLICATION IN STUDYING THE OPTICAL MODE LOCALIZATION OF
SELF-AFFINE AG COLLOIDAL FILMS

by

Peng Zhang

A thesis submitted in conformity with the requirements
for the degree of Doctor of Philosophy
Graduate Department of Chemistry
University of Toronto

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Ph. D. 1998

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ABSTRACT

A scanning photon tunneling microscope (PSTM) combined with shear-force
atomic microscope (AFM) was designed and built, which allows the topography and the
optical response of a surface to be investigated simultaneously on a sub-microscopic scale.
The lateral resolution attained by our instrument in topographic images is 30 to 50 nm,
varying with the fiber tip. While operating in the near-field region, the optical resolution
can overcome the traditional diffraction limit, producing a resolution typically of about
100 nm. Thus, it is possible to obtain site-specific spectroscopic information. The system
was employed to study the optical behavior of fractal silver colloidal films.

Near-field microscopy with simultaneous topographic imaging show that the
electromagnetic fields excited in a self-affine film are localized in small portions of the
film. The pattern of high-field areas varies greatly with excitation wavelength and does not correlate simply with the topography.

Near-field spectroscopic study further complemented the microscopic study. Tunable CW lasers were used to excite the silver colloidal thin films. When scanning the incident laser, site specific spectra showed that distinct resonance arises from different spots apart on the same sample.

This observation validates a recent theory of the optical response of self-affine fractal objects and also indicates that the locus of optical effects, such as surface enhanced Raman, does not reside in special topographic elements such as interstices. Additionally, it is shown that the conclusions of the theory, which was based on a quasi-static approximation, are qualitatively valid for self-affine films considerably larger than the exciting optical wavelength.
Dedication

This thesis is dedicated to my wife, Hong Tang, with love.
Acknowledgement

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Chapter 1. Introduction

Clusters are objects formed when a number of objects gathered together or grow together. Over the last two decades, atomic and especially metal clusters have been objects of continuously growing interest.\textsuperscript{1,2,3,4} Because clusters are intermediate between atoms on one hand and the solid or liquid state on the other hand, basic scientific questions concerning the cluster-size effects on various material properties of the metal clusters have been considered. One is interested in how metallic behavior develops with cluster size. Questions such as "at what size do clusters start to display bulk properties" often come up, although in reality, there are different answers according to the material property interrogated. At times, it is difficult to define a definite boundary between cluster and bulk. There are other important scientific questions concerning the role of metal clusters for surface-enhanced processes like Raman scattering or chemical catalytic reactions. It is believed that a unique feature of clusters comes particularly into play for these phenomena. There is a proposal that small metal clusters may be reasonable models of metal surfaces,\textsuperscript{5} because clusters have a very high number of surface atoms compared to the atoms located inside the cluster. Thus, studies of clusters can contribute importantly to surface science.

In addition to the basic scientific questions, clusters have long been of prime technological concern. While the single cluster is the object of basic research, occurrence of clusters in nature and technology is based upon many-cluster systems containing up to $10^{20}$ single clusters. Technical and also practical applications require systems of very many clusters, forming macroscopic samples. Clusters in nature are also mostly found in macroscopic ensembles. Cluster matter is a particular case of inhomogeneous, mesoscopic, granular, or composite matter since typical clusters are usually large compared to the atomic scale. Interest in cluster matter has increased because of the possibility to artificially tailor novel materials like dielectrics with extraordinary properties, special composites of non-miscible metals, or metal-dielectric systems with or without percolation structures.
Electrical and optical responses of the clusters strongly depend on the shape and the environment. For small clusters, both theoretical and experimental studies focus on the question of how electronic and structural cluster properties, such as ionization potentials, binding energies, chemical reactivity, crystal structure, melting point, and optical properties, vary as a function of particle size and geometry. In the case of metal clusters, one is interested in how metallic behavior develops with cluster size, when the onset of bulk properties occurs, etc. For large metal clusters and cluster matter, e.g. clusters of colloidal particles, each constituent in the cluster, which consists of many atoms itself, is already metallic. Studies usually focus on the collective electronic or lattice excitations of the particles.

The experimental variety of cluster geometries (sizes and shapes) of materials, surroundings, and topology illustrates the difficulty of developing a general theory which can explain all features of their optical response. On one hand, one has to deal with very small clusters with molecule-like structures like trimers and pentamers. On the other hand, one encounters large clusters which are regarded as tiny, size-limited solids. The geometry of small clusters strongly depends on their size. Theoretical treatments usually begin at the molecular level. Large clusters are usually approximated as spheres and spheroids, or ellipsoids for free or supported clusters, respectively. For even larger clusters, such as cluster matter, colloids, where single clusters are in contact with each other in some form, electrodynamics theory can be applied using bulk optical constants. However, there is a problem that, when dealing with such densely packed cluster samples, the cluster-cluster interactions also needs to be considered, which presents a formidable calculational task. 

For clusters consisting of small metal particles (radii $R \ll \lambda$) situated in an oscillating electromagnetic field with wavelength $\lambda$, the quasi-static approximation can be applied. In the quasi-static regime the time dependence is retained, but spatially the electromagnetic field is considered to be constant. The clusters thus feel a field with spatially constant, but time dependent, phase. In this approximation, excitations due to
the magnetic field are unimportant. Only dipolar excitations, which are due to the charge displacements within the metal particles in the electric field, is considered, while effects of higher multipoles can be neglected. Well separated spherical metal clusters have long been treated by Mie theory.\textsuperscript{7,8}

The subjects that have been studied in this project are very large clusters. Their structures belong to a unique class of geometries: fractal. Thus, it would be worthwhile to briefly describe the concept of fractal first.

1.1 What is fractal?

The geometry of natural objects ranging in size from the atomic scale to the size of the universe is central to the models that are used to understand nature. Traditionally the Euclidean lines, circles, spheres and polyhedra have served as the basis for the intuitive understanding of the geometry of nature. The concept, fractal geometry, was first introduced by Benoit B. Mandelbrot,\textsuperscript{9} who first offers the following tentative definition of a fractal:

\begin{quote}
A fractal is by definition a set for which the Hausdorff-Besicovitch dimension strictly exceeds the topological dimension.
\end{quote}

He then believed this tentative definition was too restrictive, albeit correct and precise, and retracted the definition and proposed the following\textsuperscript{10}:

\begin{quote}
A fractal is a shape made of parts similar to the whole in some way.
\end{quote}

The second definition contains the essential feature seen in the experiments: A fractal looks the same whatever the scale. The fractals may be considered to be sets of points embedded in space, where the Hausdorff-Besicovitch dimension $D$ is noninteger. For example, the set of points that make up a line in ordinary Euclidean space has the
The mathematical definition of a fractal is rather complex, and can be found in textbooks.\textsuperscript{9,10} Here I would instead describe the concept in the context of physics.

In general, physical systems have a characteristic smallest length scale such as the radius of an atom or molecule. In order to apply the mathematical results of fractal theory, the sets of points are replaced by a collection of molecules or monomers. Let us consider a 3-dimensional close-packing of spherical monomers into a spherical region of radius $R$, the number of monomers is given by $N = \rho (R/R_0)^3$, where the number density is $\rho = \pi / 3\sqrt{2}$. The relation applies only in the limit $R/R_0 \gg 1$, because the circular shape of the disk perimeter and the spherical surface of the ball can only approximately be covered by the monomers. In general, if a spherical region is packed by spherical monomers, we may write the asymptotic form for the relation between the number of particles and the cluster size measured by the smallest sphere of radius $R$ containing the cluster as follows:

$$N = \rho (R/R_0)^D, N \to \infty.$$  

In this relation $D$ is the cluster dimension. The density, $\rho$, depends on how the monomers are packed. The cluster dimension, $D$, on the other hand, does not depend on the shape of the cluster, or on the way the monomers are packed: close packing, random packing or porous packing with a uniform distribution of holes. It is important to realize that the dimension $D$, defined by the above equation, may be noninteger, i.e., fractal. In general, the exponent $D$ in the number-radius relation is called the cluster fractal.
Figure 1.1 Construction of a fractal structure
dimension, or the *Hausdorff* dimension. The cluster fractal dimension is a measure of how the cluster fills the space it occupies.

The fact that a cluster is porous or random does not necessarily imply that the cluster is fractal. Fractal clusters have a density that decreases with increasing size in a way described by the exponent in the number-radius relation. The density at a radius $r$ for clusters is given by $\rho(r) \propto R_0^{-D} r^{D-d}$. This density is constant only if the fractal dimension $D$ equals the Euclidean dimension, $d$, of the space in which the cluster is embedded, in which case it is non-fractal or a trivial fractal.

The number of particles in a fractal cluster of gyration radius $R_c$ is given by $N \propto (R_c / R_0)^D$, where $R_0$ is a typical separation between nearest neighbors, and $D < d$, the dimension of the embedding space. Such a power-law dependence of $N$ on $R_c$ implies a spatial scale invariance for the system. Particle positions in fractals are correlated so that the pair correlation function $g(r) \propto r^{D-d}$, where $r$ is the distance between two points in a cluster.

Metal colloid clusters resulting from cluster-cluster aggregation are among the well-known fractal systems, and have been the subject of both theoretical and experimental studies for years.\textsuperscript{11} Figure 1.2 shows a typical fractal silver colloid cluster. The image (a) is a confocal image and (b) an AFM image. The similarity between the two images is obvious in that the fraction of the cluster occupied by empty space or holes is approximately the same in the two images despite the fact that their dimensions are very different. The scale bar in the confocal image is 25 $\mu$m, while that in the AFM image is 0.5 $\mu$m. This indicates an approximately 10:1 ratio between the two “annular” structures. Such scale-invariance is an important property of fractals.

The cluster in the above images was obtained by the cluster-cluster aggregation process, where monomers start from far away and diffuse by a random walk process. When the wandering monomers reach each other, they stick together and form dimers.
Figure 1.2 Fractality of the aggregate Ag film.
a. Confocal microscopic image, scale bar is 25 microns.
b. AFM image, scale bar is 0.5 microns.
Dimers may also move, and stick to other dimers and trimers and so on, gradually growing into clusters. The dominant combinations involve clusters of comparable sizes. Experiments and calculations show that the Hausdoff dimension $D$ for such fractals is around 1.75.\textsuperscript{13,14}

1.2 Properties of fractal clusters

Fractal structures are prevalent in composites. The emergence of fractal geometry was a significant breakthrough in the description of irregularity.\textsuperscript{15} Electromagnetic phenomena in inhomogeneous metal-insulator composites (thin films, cermets, colloidal aggregates, etc.) have been intensively studied for the last two decades.\textsuperscript{16} Nanostructured composites possess fascinating electromagnetic properties, which differ greatly from those of ordinary bulk material. For example, dipolar excitations in fractal composites are substantially different from those in other media. In a dielectric sphere, there is only one dipolar eigenstate that can be excited by a homogeneous field; the total dipole moment of all other eigenstates is zero, and therefore they can only be excited by inhomogeneous fields. In contrast, fractal aggregates possess a variety of dipolar eigenstates, distributed over a wide spectral range, which can be excited by a homogeneous field. In the case of continuous media, dipolar eigenstates are running plane waves that are eigenfunctions of the translational symmetry operator. This also holds in most cases for microscopically disordered media that are, on average, homogeneous. Dipolar modes are typically delocalized over large areas in this case, and all monomers absorb light energy with approximately equal cross-section in regions that significantly exceed the wavelength. In contrast, fractal composites possess many eigenstates that are localized in subwavelength regions. Absorption by monomers located in these "hot zones" is higher than by other monomers in a fractal composite. This is a consequence of the fact that fractals do not possess translational symmetry, and therefore cannot transmit ordinary waves.\textsuperscript{17,18} Instead, they are symmetrical with respect to scale dilation, i.e. scale invariance. Accordingly, dynamical excitations such as vibrational modes tend to be localized in fractals, because
plane running waves are not eigenfunctions of the operator of dilation symmetry characterizing fractals.

The properties of disordered systems are of considerable significance in physics. There is a wide class of mutually-related phenomena associated with disorder, among which are localization of elementary excitations (plasmons and eigenstates), fluctuations and enhancement of local fields, correlation of such fluctuations, and spatial-temporal chaos, including quantum chaos. Such localization is closely related to fluctuations and enhancement of local electromagnetic fields in disordered systems, which cause surface-enhanced Raman scattering from surfaces $^{19}$ and fractal clusters, $^{20}$ and giant enhancement of nonlinear-optical responses of such clusters. $^{21}$ This enhancement is generally associated with excitation of surface plasmon oscillations. Typically two types of surface plasmons occur: surface plasmon waves (SPW), and localized surface plasmons (LSP). SPW propagates laterally along the metal surface, while LSP are confined to metal particles that are much smaller in size than the wavelength of incident light. The localization of plasmons is of principal importance for the enhancement of optical-response because it is a near-zone analogue of focusing of electromagnetic radiation. The "focusing" of electromagnetic fields by plasmon localization occurs on a nanometer scale rather than on a micron scale as in conventional optical far-zone focusing. Such near-zone focusing creates local regions of high field intensity, causing enhancement of nonlinear photoprocesses. Similar to the conventional focusing, the stronger the nonlinear-optical enhancement due to the plasmon localization, the higher is the order of nonlinearity. $^{22}$

Theoretical studies found that eigenmodes of fractal clusters are chaotic. They change dramatically with small changes of their frequencies (eigenvalues), a signature of chaos. Also, local fields created by external waves are chaotic and highly singular. This chaos and singularity are believed to be responsible for the giant fluctuations of local fields and nonlinear-optical enhancement.
Experimental verification of these theories is not very extensive. Not until recently, when near-field scanning optical microscopy (NSOM) technique was introduced, was there an ideal approach available to study the localized plasmon on a nanometric scale. Conventional optical instruments can image, at best, on a scale of the order of the wavelength, where only the coarse optical properties of many clusters are observed. Also, the detector is usually far from the sample, which eliminates the possibility of studying the localized surface plasmons, as they are confined to the sample surface.

The introduction of the NSOM immediately offers an ideal tool to study such localization phenomena. Pohl et al. \textsuperscript{23} first reported using NSOM to investigate the optical properties of Rayleigh-size silver particles. A shift of the resonance frequency compared to the bulk material was observed. Tsai et al. \textsuperscript{24} and Bozhevolnyi et al. \textsuperscript{25} also reported using photon scanning tunneling microscopy to investigate surface plasmon of silver and gold films.

1.3 Near-field scanning optical microscopy (NSOM) and spectroscopy (NSOS)

1.3.1 What is near-field optics

In the present context, an operational definition of near-field described by Paesler and Moyer \textsuperscript{26} is adopted: near-field (NF) optics is the branch of optics that considers configurations which depends on the passage of light to, from, through, or near an element with subwavelength features and the coupling of that light to a second element located a subwavelength distance or less from the first. Near-field scanning optical microscopy (NSOM) is a general term for instruments that involve optical effects taking place in the near-field zone. Similarly, near-field optical spectroscopy (NSOS) refers to spectroscopic measurements in the near-field.
1.3.2 How NSOM differs from conventional optical microscopy

When an electromagnetic wave interacts with the object to be imaged, the wave is diffracted into two components: a propagating components with low spatial frequencies \( f < \frac{2}{\lambda} \), and an evanescent component with high spatial frequencies \( f_e ( > \frac{2}{\lambda} \). The evanescent component decays exponentially with distance from the object, and is thus confined to subwavelength distances from the object. For conventional optical microscopes, there is a fundamental limit imposed by the nature of incident light, far-field diffraction, which represents a lower bound to the spatial resolution the instrument can achieve, often called the Abbé barrier. The Abbé description of resolution in conventional optical systems can be understood from the perspective of Fourier optics. Conventional optical techniques utilize far field components to image. Effectively, no information at these high spatial frequencies reaches the remote collection optics, hence data with subwavelength spatial resolution cannot be collected. These high spatial frequencies, as well as subwavelength spatial resolution information can, however, be obtained by NSOM, when the object is either placed very close to the sensing element or is excited with the evanescent wave, i.e., either by collecting the high spatial frequency or by exciting with high spatial frequency, depending on the instrumental configuration. There are a number of different configurations for NSOM, all of which take advantage of the subwavelength spatial resolution of information inherited in near-field zone.

1.3.3 Brief history of NSOM

The theory of the operation of the NSOM was first discussed by E. H. Synge more than half a century ago, when he suggested "a method for extending microscopic resolution in the ultra-microscopic region." He discussed the scanning of a small aperture in the near field of the sample in great detail. Although he claims to have developed the theory of the instrument's operation only in the abstract, his proposed instrument is very similar in construction to modern NSOM's.
A more complete theory of NSOM was developed in varying degrees of detail ever since. In the early work, the fundamental principles behind the theory of NSOM operation were sometimes discussed without considering the experimental realization of these principles.

In 1969, Nassenstein suggested that by diffraction of evanescent waves, it would be possible to transform the high spatial frequencies of evanescent waves of the order of the wavelength into lower (propagating) frequencies. This explanation in terms of spatial frequency transformation lies at the heart of current understanding of the theory of NSOM.

The first proposals for surpassing Rayleigh's diffraction limit, where two diffraction limited lines are considered to be just resolved if the central diffraction maximum of one profile coincides with the first minimum of its neighboring profile, were made by O'Keefe in 1956. Sixteen years later Ash and Nicholls experimentally verified the concept by attaining $\lambda/60$ resolution with $\lambda = 3$ cm microwaves. Similar experiments in the optical regime of visible light were not feasible until the scanning probe technology was introduced along with the invention of scanning tunneling microscopy. Between 1983 and 1986 Massey, Pohl et al, Fischer, Betzig et al, and other groups also proposed the use of a series of superresolvent devices that work in the visible range. The experimental resolution that was obtained with near-field microscopes by optical tunneling detection was shown to be far better than the limits imposed by the Rayleigh criterion.

In the 1990s, more groups participated in this field. Commercial instruments began to appear. The technique draws more and more attention as it gets better developed.
1.3.4 How does the NSOM work?

Among the possible configurations of NSOM, whose number increased constantly since the first successful effort, there are several that dominate most of the research. Figure 1.3 illustrates the most common configurations. The signal transduction element is represented by a tapered optical fiber. Arrows indicate the light path in the different configurations.

In the collection mode, light is collected through the aperture at the fiber tip (near-field), while the incident light (far-field) can either be transmitted through (Figure 1.3a) or reflected by (Figure 1.3d) the sample. In the illumination mode, the sample is illuminated with light from the tip aperture (near-field), and collected by a far-field device in either a transmission (Figure 1.3b) or the reflection (Figure 1.3e). In Figure 1.3c, the tip acts both as a light emitter and light collector. In these five configurations, the tapered tip should be coated by an opaque layer, usually of Al (indicated as shadows in the figure), with only the aperture at the end exposed. The configuration as shown in Figure 1.3f is slightly different. The incident light is made to totally internally reflect from the substrate surface, while the signal is collected by a tapered tip placed in near-field of the sample.

This last configuration, the so-called photon scanning tunneling microscopy (PSTM), deserves more mention, since it is this configuration that was adopted to study the local optical behavior of small particles.

Optical tunneling has in fact been observed at least since Newton⁴¹, and has been successfully applied in the fields such as microscopy, spectroscopy, optical waveguide coupling and holography long before the birth of scanning tunneling microscopy (STM). Although its lateral resolution decreases almost to the traditional diffraction limit, the vertical resolution remains high. After the concept of a scanning probe was introduced along with STM, a strict optical analog to STM employing
Figure 1.3 Illustration of various NSOM configurations.
photons tunneling rather than electrons and a scanning subwavelength aperture or waveguide leads to the PSTM.

A distinct advantage of this configuration of NSOM is the elimination of background radiation. Since there is no far-field component in the second medium, a coated tip is not necessary, and an uncoated tip usually suffices. There are also disadvantages to PSTM, including the limitation of measuring only transmitting samples and the necessity of configuring the sample so that it is illuminated by total internal reflection (TIR). It should be pointed out that the use of evanescent incident waves is neither essential nor necessary for obtaining sub-Rayleigh resolution.

In NSOM instruments, if either the illuminating beam or the collected light is spectrally resolved, spectroscopic information can be obtained. This is how near-field optical spectroscopy (NSOS) experiments are done. The extremely low throughput of NSOMs, due to the nature of the tapered tip, is usually the limiting factor in NSOS. Spectroscopic measurements can include fluorescence imaging or spectrum acquisition.

Fluorescence spectroscopy is usually performed in the illumination mode of NSOM. In fluorescence imaging, the signal is projected through filters and onto the detector. Images are obtained by raster scanning the sample. Alternatively, spectra may be acquired at various points on the sample by coupling the signal into a spectrometer. Other spectroscopies, such as Raman spectroscopy and UV-vis excitation spectroscopy, can also be performed with proper design and using appropriate detectors.

1.3.5 What can NSOM do

All near-field microscopic and spectroscopic studies to date involved either chemical, solid state materials, or biological systems. Optical spectroscopy can provide useful information regarding the structure of molecule or groups of molecules. The most promising and rapid application of NSOM is in surface chemistry studies, which
includes: detection and spectroscopy of single molecules; \textsuperscript{42-45} investigations of liquid crystals and Langmuir-Blodgett films; \textsuperscript{46} and studies of polymer film fluorescence and spectroscopy. \textsuperscript{47}

Reports on single molecule studies range from straightforward detection to spectroscopic studies to time-dependent analyses. For example, Ambrose \textit{et al} \textsuperscript{42} studied the fluorescence emission of single R-6G molecules by near field techniques, showing photobleaching effects locally. Betzig and co-workers \textsuperscript{43} reported the fluorescence NSOM images of isolated single carbocyanine molecules under various polarization conditions. Xie and co-workers \textsuperscript{44} studied the molecular fluorescence lifetime of sulforhodamine 101 molecule. Trautman \textit{et al} \textsuperscript{45} analyzed the fluorescence spectroscopy of two isolated 1,1'-dioctadecyl-3,3′,3′,3′-tetramethylindocarbocyanine molecules, which were about 150 nm apart. The results demonstrated that inhomogeneous broadening of far field spectra due to the averaging effect was not observed in the near field. The successful application of NSOM to investigate liquid crystal \textsuperscript{46} and polymer films \textsuperscript{47} has also been reported.

The most commonly reported optical characterization of solids by NSOM includes photoluminescence, Raman scattering and emission spectroscopy. Photoluminescence was used to probe the defect states within the bandgap of semiconductors. Raman scattering spectroscopy can provide site-specific bonding information of solids. Spectroscopic analysis can also help to investigate optical properties of solid material on a sub-microscopic scale. Near-field luminescence spectroscopy of GaAs/AlGaAs quantum structures was reported by Grober \textit{et al} \textsuperscript{48}. Hess \textit{et al} \textsuperscript{49} studied the excitation spectroscopy of quantum structures at low temp, and found that the inhomogeneous spectral broadening caused by the large sample volume inherent in far-field experiments was not observed in the near-field. The near-field spectrum showed very narrow, isolated spectral features, in contrast to the far-field spectrum. Such investigations highlight the strengths of NSOM in subwavelength microscopy-spectroscopy investigations.
NSOM has also been proposed as a data storage technique. A number of experiments on this front have been reported, although so far no practical device has been constructed.

NSOM has yet to be widely applied in biology. However, there are some results that demonstrate the strength of NSOM imaging when applied to biological problems. A large proportion of biological spectroscopic studies involve fluorescence microscopy. NSOM can be used to monitor the migration of, say, dye molecules, within biological systems such as cells, membranes etc. The resulting fluorescence spectra can often yield information about local conditions or elemental concentrations. Betzig and co-workers first used NSOM to investigate tissue sections from the hippocampus region of the monkey brain, stained with toluidine blue as the chromophore. The spatial resolution was shown to be better than in conventional diffraction-limited images. Dunn et al applied NSOM to the fluorescence imaging single proteins and photosynthetic membranes. Nanoscale spatial resolution were achieved and lifetime measurements were made. These investigations indicate a potential for performing spectroscopic and time-dependent studies on such structures.

The near-field properties of small structures, especially of metal cluster structures, are of interest in sub-micron range generally. The nano-optical properties of such small structures have rarely been studied experimentally until NSOM was introduced. The optical regime is of particular interest for the following reasons:
1. Microscopes and fibers allow the radiation to be detected selectively from a small source, discriminating efficiently against other nearby sources.
2. Substantial field enhancement may be achieved with appropriate interface geometry and by exploiting the surface plasmon effects on a nanoscale. Such experimental results would have substantial significance in testing theories.
3. The radiation is sufficiently energetic to allow surface modification by photochemical or photo-thermal effects.
NSOM, together with other scanning probe microscopy techniques, offers new tools to exploit surface plasmons associated with individual features. For example, NSOM studies have investigated plasmons associated with individual small protrusions on a flat gold film\textsuperscript{54}, and on the edge and at the corner of a tetrahedral tip.\textsuperscript{55} PSTM was used by Goudonnet \textit{et al.}\textsuperscript{56} to study the surface plasmon propagation of some silver films, and by Tsai \textit{et al.}\textsuperscript{57} to study the optical behavior of silver fractal films. Bozhevolnyi \textit{et al.}\textsuperscript{58} also used PSTM to investigate surface plasmon of some gold and silver films.
Reference

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Chapter 2. Theoretical background

2.1 Optical properties of small particles

A metal cluster placed in an electric field will have its negative charges displaced from the positive nuclei. If treating the clusters as spheres, the internal field is

\[ E_i = E_0 \frac{3\varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \]

where \( \varepsilon_m \) is the dielectric constant of the embedding medium (which could be vacuum), \( \varepsilon(\omega) \) is the dielectric function of the clusters, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \).

The static polarizability of the sphere is

\[ \alpha = 4\pi\varepsilon_0 R^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \]

A resonance occurs when the denominator, \( |\varepsilon(\omega) + 2\varepsilon_m| \), is minimum, which can be simplified to \( \varepsilon_1(\omega) = -2\varepsilon_m \), provided that \( \varepsilon_2(\omega) \) is small or does not vary much in the vicinity of the resonance. Such resonance are described in terms of a dipolar surface plasmon.

An electrodynamic description of the optical properties of large metal particles was given a long time ago by Mie.\(^1\) Based upon Maxwell's equations, the Mie theory describes fully the optical response of a particle, including the unique Mie resonance, i.e., plasmon polaritons.

In large particles of almost free-electron metals such as the alkalis and the noble metals, the most prominent features of the optical response in absorption or scattering are the surface plasmon polaritons. They are the multipole resonances of Mie's theory.
For $R \ll \lambda$, i.e., within the quasi-static approximation, a single resonance peak, the dipolar surface-plasmon, dominates the spectrum in all of these materials.

The optical spectra of particles of almost all of the metallic elements and other materials have been intensively studied and calculated using Mie's theory and the Generalized Mie theory (GMT). Depending on the existence of an embedding material, there are two different kinds of cluster matter: fine grain materials and porphyric structures. The former includes nanoceramics and nanocrystalline materials, i.e., particles which are closely packed. The latter kind will be discussed in more details, since the sample we study belongs to this kind.

In porphyric structures, the particles can be more or less densely packed, the mean packing being described by a filling factor if the topology is statistically random. The individuality of the particles in the aggregate is preserved, if interlayers of the matrix material separate neighboring clusters. For metallic particles in dielectric matrices this means that the electrons are confined to the individual particles.

Several ways of describing this kind of colloidal particle aggregates have been developed. The first, the 'effective medium' approach, is based on statistical assumptions on the topography of the particles distributed in the matrix. An effective macroscopic dielectric function is introduced, replacing the inhomogeneous by a fictitious homogeneous material with an effective macroscopic optical properties.

The second way is to describe the optical properties of typical examples of the existing particles aggregates in detail and then to compose the macroscopic sample by multiplying their optical responses by their partial filling factors. The effect of aggregation on the optical response is a drastic one: not only intensities are changed but the structure of the spectra is strongly influenced.
A straightforward physical model to describe macroscopic aggregates is the following: A coagulation aggregate is assumed to contain a limited number, \( n \), of identical spherical particles with equal center-to-center distance between all next neighbors. All \( n \)-aggregates of similar shape contained in the sample are then replaced by one "typical" \( n \)-aggregate of regular topography (chain, triangle etc.). The optical response of these aggregates is computed from the GMT. Finally it is averaged over all aggregate orientations to describe more closely realistic samples.

In general, aggregated samples exhibit strong scattering which, within the framework of the GMT, can be computed numerically. The theoretical spectra strongly differ for different topographic structures, \(^3\) which is a fact due to the different normal modes of excitation of the aggregate as a whole. In real samples with various aggregate structures most of the calculated spectral features are smeared out in measured spectra by superimposition effects.

Over the last decade, a series of theoretical approaches have been developed to study the optical properties of large clusters using the concept of fractals. The theory suggests that, because of the unique properties of fractals, dipolar normal modes in fractal clusters are substantially different from those in other media. The fractal clusters may possess a variety of dipolar normal modes distributed over a wide spectral range, each mode being confined in sub-wavelength regions of the clusters. The theoretical treatment will be outlined below.

In brief, the theory, which is based on scale invariance, results in a dispersion law which relates the localization length of the mode excitation and a frequency parameters. The corresponding exponents are expressed in terms of the spectral and \textit{Hausdorff} dimension of the fractals. This theory will now be briefly outlined. \(^4\)
Consider a model which considers dipolar excitations only, where a cluster consisting of $N$ constituent particle (called monomers) are positioned at points $r_i$, $i = 1,...,N$. The light-induced dipole-dipole interactions between the polarizable particles in the aggregate is determined by the complex polarizability $\chi_0$ of an isolated monomer. The monomers are subjected to an external electric field oscillating at an optical frequency. The field at the site of the $i$-th monomer, $E_i^{(0)}$, is $E_i^{(0)} = E_\alpha^{(0)} \exp(-i\omega t + ik \cdot r_i)$. This field polarizes the monomers, inducing oscillating dipole moments $d_\alpha = d_\alpha \exp(-i\omega t + ik \cdot r_i)$ ($\alpha = x, y, z$), which are random quantities due to the random structure of the cluster. Defining $Z = \chi_0^{-1}$, where $\chi_0$ is the dipole polarizability of an isolated monomer, and the spectral variable $X = \Re Z$ that will be used instead of the frequency $\omega$, and a parameter $\delta = -\Im Z$ which determines the dissipation in a monomer. If the monomers are spherical particles with $\chi_0 = \frac{R_m^3(\varepsilon-1)/(\varepsilon+2)}{\varepsilon}$, then $X = -\frac{2\varepsilon+3}{(2\varepsilon+1)^2 - 9}/(4\varepsilon-1)$ and $\delta = 3R_m^{-3}E_2/|\varepsilon-1|^2$, where $\varepsilon=\varepsilon_1+i\varepsilon_2$ is the dielectric constant of the material of which the particles is comprised.

The local field at any point is a superposition of the incident wave and all secondary waves scattered by the dipoles. Thus, dipole moments interact with each other and with the incident field, and obey the coupled-dipole equations (CDE):

$$d_\alpha = \alpha_0 \left[ E_\alpha^{(0)} \exp(i\vec{k} \cdot \vec{r}_i) + \sum_{j=1}^{N} G_{\alpha\beta}(r_{ij})d_{\beta j} \right], \quad (1)$$

where the time-dependent term, $\exp(-i\omega t)$, is omitted, $r_{ij} = r_i - r_j$ and $\Sigma$ denotes the sum over all values of index $j$ except $j = i$. The interaction tensor $G_{\alpha\beta}$ is defined as:

$$G_{\alpha\beta}(r) = k^2 \left[ A(kr)\delta_{\alpha\beta} + B(kr)\frac{r_\alpha r_\beta}{r^2} \right], \quad (2)$$

$$A(x) = [x^{-1} + ix^{-2} - x^{-3}]\exp(ix), \quad (3)$$

$$B(x) = [-x^{-1} - 3ix^{-2} + 3x^{-3}]\exp(ix), \quad (4)$$
where $\alpha$ and $\beta$ denote Cartesian components. Summation over repeated Greek indices is implied.

Introducing a $3N$-dimensional vector $|d\rangle$ and $|E\rangle$ with the components $(i\alpha|d\rangle = d_\alpha$ and $(i\alpha|E\rangle = E$ (similar notations also used for other vectors), we obtain a single equation in a $3N$-dimensional space

$$(Z + V)|d\rangle = |E\rangle$$

where the dipole-dipole interaction operator $V$ is defined by its matrix elements as

$$(i\alpha|V|j\beta) = [a^* \delta_{\alpha\beta} - 3b^y n_\alpha^{(y)} n_\beta^{(y)} r_{yy}^{-3} e^{ikr_y - \bar{a}^*\bar{b}y}]_{\alpha\beta},$$

$$a^* = 1 - ikr_y - (kr_y)^2, \quad b^y = 1 - ikr_y - \frac{1}{2}(kr_y)^2, \quad r_{ij} = r_i - r_j, \quad \text{and} \quad n_{\bar{y}} = n_{\bar{y}} / r_{ij}.$$ 

Note that in $|i\alpha\rangle$ basis, $V$ has components, $(i\alpha|V|j\beta) = -G_{\alpha\beta}(r_{ij})$, where $G_{\alpha\beta}(r_{ij})$ is defined in equations (2-4).

The solution of the above equation has the form:

$$|d\rangle = \sum_{n} \frac{|n\rangle(n|E\rangle}{(n|n\rangle} \frac{1}{Z + v_n},$$

where $v_n$ are the eigenvalues of $V$ defined by $V|n\rangle = v_n|n\rangle$ and the "bar" sign denotes complex conjugation of all components of a vector. In the $|i\alpha\rangle$ basis the solution acquires the form

$$|d\rangle = \sum_{n,l} \frac{(i\alpha|n\rangle(n|E_{l\beta}\rangle|E_{l\beta}\rangle}{\sum_{l'}(n|l' \alpha'\rangle(l' \alpha'|n\rangle)} \frac{1}{Z + v_n}.$$
Once the CDE are solved for dipole moments $d$, extinction and absorption cross sections ($\sigma_e$ and $\sigma_a$ respectively) can be obtained from the optical theorem:

$$\sigma_e = 4\pi k |E^{(0)}|^2 \ \text{Im} \sum_{i=1}^{N} \vec{d}_i \cdot \vec{E}^{(0)} \ast e^{-k \rho} = 4\pi k |E^{(0)}|^2 \ \text{Im}(d \cdot E) \ , \quad (5)$$

$$\sigma_a = 4\pi k |E^{(0)}|^2 \ \eta \sum_{i=1}^{N} |d_i|^2 = 4\pi k |E^{(0)}|^2 \ \eta (d \cdot d) \ ,$$

where $\eta = -\text{Im}(Z) - \frac{2}{3} k^3$ is a non-negative constant characterizing the absorption strength.

If the clusters are much smaller than the wavelength of the incident wave and $\eta \gg 2k^3/3$, then the quasi-static approximation can be used for the dipole interaction matrix. Thus, terms $1/x$, $1/x^2$ and $\exp(i\alpha)$ in equations (3-4) can be omitted, and $\exp(\pm i k \cdot r_i) = 1$ can be put in formulas (1) and (5).

$$\sigma_e = 4\pi k N \ \text{Im} \alpha , \text{ where } \alpha = \frac{1}{3N} \sum_{i} \text{Tr}[\alpha_{\alpha\beta}^{(i)}] , \text{ and } \alpha_{\alpha\beta}^{(i)} \text{ are related to } d_{\alpha} \text{ via}$$

$$d_{\alpha} = \sum_{\beta} a_{\alpha\beta}^{(i)} E_{\beta}^{(0)} .$$

If $R_o^3 |X| \gg (R_o/\lambda)^{3-D}$ for $D < 2$ and if $R_o^3 |X| \gg (R_o/\lambda)^{N^{1-2D}}$, particles positioned at distances $r_i \sim \lambda$ and $r_i \gg \lambda$ from a given monomer, $i$, contribute negligibly to the local field acting on this monomer. Thus, the dipole-dipole interaction operator $V$ can be reduced to the near-zone dipole-dipole interaction operator $W$. 


(i\alpha | W | j\beta) = [\delta_{de} - 3 \frac{(r_y)_\alpha(r_y)_\beta}{r_y^2}] \frac{1}{r_y^3}, \text{ if } kr_y < 1, \; i \neq j; \text{ and zero otherwise.}

Defining \( |\varphi_\alpha\rangle = \frac{1}{\sqrt{N}} \sum_i |i\alpha\rangle \), where \( \alpha = x, y, z \), we can get

\[
\alpha = \left( \varphi_\alpha | \frac{1}{W + Z} | \varphi_\alpha \right) = \sum_n \frac{(\varphi_\alpha | n)(n | \varphi_\alpha)}{\alpha_0^{-1} + \omega_n}.
\]

where \( \omega_n \) is the eigenvalues of the \( W \) operator. It shows that the polarizability of a particle in a cluster is given by the sum of the eigenmodes having different eigenfrequencies, \( \omega_n \), and contributing to the polarizability with a weight given by the product of the corresponding eigenfunctions.

When fractal clusters settle onto a surface, the scaling properties in one of the canonical directions is different from those in the other two. Such clusters become self-affine clusters, i.e., the self-similarity is limited to two directions. A self-affine surface is characterized by a different scaling dimension in the \((x,y)\)-plane and in the normal direction, \( z \).

There has been discussion regarding whether self-affine objects are also characterized by localized normal modes.\(^9\) Shalaev et al. have recently considered the optical response of self-affine objects theoretically and through simulation.\(^10\) They concluded that normal-mode localization is also a characteristic of such an object, although the localization is not as strong as in a self-similar fractal.

The concept of self-affinity is of practical importance since many pseudo two-dimensional systems such as deposited thin films or surfaces roughened by evaporation or etching are self-affine.\(^11\) Assuming that the wavelength \( \lambda \) of the exciting electromagnetic radiation greatly exceeds the total size of the cluster (quasi-static limit), in a spherical particle, the surface plasmon is described by a spatially uniform
polarization extended over the whole sphere, oscillating harmonically in time. This polarization creates charges only at the surface of the particle. In contrast to the behavior of surface plasmons in regular spherical particles, the dipolar excitations of a self-affine cluster fill in the whole space of the cluster only on average. Each particular eigenmode is extremely non-uniform. Consequently, it creates charges throughout the volume of a cluster causing long-range interactions. In the rough self-affine films composed of metal nanoparticles, the eigenmodes are associated with localized surface plasmon (LSP) oscillations. The unusual morphology associated with fractional dimension results in the unique physical properties of fractals, one of which is the localization and enhancement of dynamical excitations. A number of optical phenomena are strongly enhanced on a rough metal film.\textsuperscript{12}

Numerical simulations of the optical properties of computer-generated fractal clusters, based on the above approaches, have been done by several groups. Different types of fractals were studied, including random-walk clusters and cluster-cluster aggregates.\textsuperscript{13,14} It has been shown that the dipole-dipole interactions in fractals lead to substantially large inhomogeneous broadening. The collective dipolar modes in fractals are localized, which is non-trivial since dipolar excitations in compact media (D=3) are typically delocalized. The localization is strongly dependent on the frequency and polarization of the excitation wave, and its length is usually smaller than the excitation wavelength. The localization results in high local fields in small regions of the cluster, leading to huge field enhancements. Such enhancements are believed to mainly, if not totally, account for effects, such as surface enhanced Raman scattering, degenerate for-wave mixing etc.\textsuperscript{15,16}

Experimentally, there have been reports on studying the transmission spectrum of the silver colloidal aggregates fixed in gelatin, which indirectly supports theoretical predictions of mode localization in fractals.\textsuperscript{14} The near-field technique makes it possible to investigate the isolated clusters out of the aggregates. Such experiment was first reported by Tsai \textit{et al},\textsuperscript{17} which will be discussed in the later chapter.
2.2 NSOM theory

2.2.1 General principles of NSOM

Although the concept of near-field optics has existed for almost three quarters of a century, the field progressed only in the last decade or so, after the introduction of scanning probe technology made routine NSOM feasible. Many aspects of how one should treat the theory of NSOM operation remain controversial. 18 This is not to say that important theoretical progress has not been made. On the contrary, a number of crucial studies have contributed to the understanding of how the NSOM delivers it signal and what resolution it is capable of providing.

In contrast to the conventional optical microscopes, the resolution and consequently the transfer function of the near-field microscope cannot be defined from its own characteristics only, as is the case with all local probe microscopes. It also depends on the tip-sample interaction, i.e., the probe tip itself plays an active role, and has to be taken into account when considering the resolution of the microscope. This shows that in the domain where evanescent waves are not negligible, or more generally in all tunnel devices, the detector can never be considered as separated from the sample. The fundamental reason for the extraordinary resolution that can be obtained with these devices comes from this fact.

The basic theory of NSOM can be illustrated by considering a simple configuration. 19 Models of far-field and near-field microscopes are shown in Figure 2.1. In both instruments, a subwavelength slit of width \( L \) in an opaque plane is illuminated with monochromatic plane waves of wavelength \( \lambda \) from the left, while the imaging plane is located at a macroscopic distance \( z = Z \) to the right. In the near-field model (b), a subwavelength aperture of width \( w \) is scanned across the object slit at a distance \( z = c \ll \lambda \).
Figure 2.1 Model of far-field (a) and near-field (b) microscopes.
In this two-dimensional system, the field detected at $Z$ can be written in terms of the Fourier transform of the field at $z = 0$.\(^{20}\)

$$E(x, z = Z) = \int_{-\infty}^{\infty} dk_x e^{-2\pi k_x x} E(k_x, z = 0) e^{-2\pi z \sqrt{k^2 - k_x^2}}$$

Since the only surviving spatial frequencies require propagating exponentials, limits can be placed on the range of integration, i.e.,

- $\sqrt{k^2 - k_x^2}$ is positive and real for $\sqrt{k^2 - k_x^2} > 0$, and,
- $\sqrt{k^2 - k_x^2}$ is negative and imaginary for $\sqrt{k^2 - k_x^2} < 0$.

For simplicity, assume the field at $z = 0$ to be $E(x, z = 0) = E_0 \text{rect}(x/L)$, a simple rectangular function. Consider the situation shown in Figure 2.1(a), the far-field solution becomes

$$E(x, z = Z) = \int_{-\omega / 2\pi}^{\omega / 2\pi} dk_x e^{-2\pi k_x x} \frac{\sin k_x L}{k_x} e^{-2\pi z \sqrt{k^2 - k_x^2}} \tag{1}$$

Next, consider the situation shown in Figure 2.1(b), and first express the field very close to the object at $z = c << \lambda$:

$$E(x, z = c) = \int_{-\infty}^{\infty} dk_x e^{-2\pi k_x x} E(k_x, z = 0) e^{-2\pi c \sqrt{k^2 - k_x^2}}$$

Then consider the presence of the aperture by writing the field at the aperture as $E(x, z = c) = E_0(x, z = c) \text{rect}(x/w)$. The far-field solution in this configuration takes the form:

$$E(x, z = Z) = \int_{-\omega / 2\pi}^{\omega / 2\pi} dk_x e^{-2\pi k_x x} e^{-2\pi (Z-c) \sqrt{k^2 - k_x^2}}$$

$$\times \int_{-\infty}^{\infty} dk_x' e^{-2\pi k_x' x} E(k_x', z = 0) \frac{\sin(k_x - k_x')L}{k_x - k_x'} e^{-2\pi c \sqrt{k^2 - k_x'^2}} \tag{2}$$
To examine how the two expressions for the far-field (1) and (2) behave with regard to delivering spatial information to the detector at the macroscopic distance \( z = Z \), consider just one spatial frequency \( K \). Let us examine the transmission of the Fourier coefficient:

\[
E(k_x, z = 0) = E \delta(k_x - K)
\]

From Eq. (1), the far-field for the conventional (near-field) microscope, as in Figure 2.1(a), becomes

\[
E(x, z = Z) = E_0 e^{-2\pi i K x} e^{-2\pi i \sqrt{\omega^2 c^2 - k_x^2}} \text{ for } K < \omega/c, \text{ and becomes zero for } K > \omega/c. \quad (3)
\]

Similarly from Eq. (2), the far-field solution for the near-field instrument (Figure 2.1(b)) is

\[
E(x, z = Z) = E_0 e^{-2\pi i \sqrt{k_x^2 - k^2}} \int_{-\omega/\omega c}^{\omega/\omega c} dk_x e^{-2\pi i k_x x} \frac{\sin(k_x - K) L}{k_x - K} e^{-2\pi i \sqrt{2Zc - k_x^2}} \quad (4)
\]

Equation (3) shows that the conventional microscope cannot collect the high spatial frequency information beyond the diffraction limit. Equation (4), however, behaves differently. The integrand does not vanish for spatial frequencies \( K > \omega/c \), so that these spatial frequencies would contribute to the signal that arrives in the far-field in such a near-field device. That is, high spatial frequencies that do not propagate in the conventional instrument can be detected in the far-field with the near-field device. Note that Eq. (4) reduces to Eq. (3) in the limit of large aperture \( L \), since

\[
\frac{\sin(k_x - K) L}{(k_x - K)} \xrightarrow{L \to \infty} \delta(k_x - K)
\]
This model of NSOM imaging is satisfying in describing how resolution beyond the Abbe limit is achieved. It also implies that the image obtained is not an image of the sample alone. It is a folding of the sample and the probe together, obtained in whatever feedback mode the instrument employs. This problem cannot be resolved by first determining an impulse response function of the probe and then folding the object out of the subsequently derived image, because such function would also be affected by the properties of the individual probes. Thus, the impulse response function of the device could not be uniquely defined.

The descriptions above do not model a realistic near-field microscope. Yet it does demonstrate clearly that superresolution can be obtained when a small probe is placed in the near-field of a subwavelength object. Experimentally, one can only look at images of known structures and compare to images obtained by using other techniques, if possible, to find out the limits of NSOM performance. More realistic modeling \(^{18}\) may involve more careful descriptions of near-field profiles, tip-sample interactions, device structure, and sample and tip materials.

2.2.2 Principles of PSTM

The principle behind photon scanning tunneling microscopy (PSTM) has long been understood, mainly due to the early establishment of optical tunneling microscopy (OTM), arguably the predecessor of PSTM. \(^{21}\) The contrast of images produced with OTM is a result of frustrated total internal reflection (TIR), a well-understood phenomenon, thus image interpretation is more straightforward than with an NSOM.

Consider light incident on planar interfaces, as shown in Figure 2.2. If an electromagnetic wave \(E_0\) is incident on an interface between two media with refractive indices \(n_1\) and \(n_2\), total reflection can happen when \(n_1 > n_2\) and the incident angle \(\theta\) is larger than the critical angle \(\theta_c\) \((\theta_c = \sin^{-1}(n_2/n_1))\). In this case, no energy flows through
Figure 2.2 Illustration of photon-scanning-tunneling microscope.
the interface into the second medium. However, the electric field penetrates into the second medium. This field $E$ in the second medium can be written as:

$$E = E_0 e^{-ikz} e^{-ikz \sqrt{n_2^2 - n_1^2}}$$

where $\beta = \sqrt{(n_2^2 - n_1^2) \sin^2 \theta - 1}$, and the incident spot taken as origin.

The field $E$ decays exponentially with distance from the interface, $z$, and is, therefore, termed an evanescent wave. Note that the equation also shows that $E$ propagates in the $x$ direction. Analysis on the Poynting vector shows that, all energy into the second medium is transported in the $X$ direction, but not in $z$ direction.

If a second interface exists within the region of evanescent wave, the evanescent wave will tunnel into the third medium, and a propagating field will exist in this third medium. The total reflection is thus frustrated, and the phenomenon of optical tunneling occurs, whereby a wave is partially transmitted through a region where it would be forbidden by geometrical optics. The magnitude of this propagating field will depend on the distance between two interfaces, that is, on the distance that a photon in the evanescent region must tunnel to enter a region where conditions for propagation are again satisfied.

Now if this third medium is a fine, tapered tip with the size of tip end well below the wavelength, it can, in principle, achieve the lateral resolution below the diffraction limit, while preserving the high vertical resolution that previous OTMs possess. Referring to Figure 2.2, the sample is placed on the interface between media 1 and 2, and is illuminated through total internal reflection. The presence of the taper probe, equivalent to medium 3 in Figure 2.2, frustrates the TIR, thus providing an optical signal only from the region of the sample in the near-field region, where the presence of the dielectric tip alters the conditions for TIR. Compared to the previous photon tunneling microscopes, the lateral resolution is limited by the size of tip end, rather than
the wavelength of incident light, thus could overcome the diffraction limit with a subwavelength tip.

In practice, the second medium is usually air. If optical tunneling across the air gap between two media occurs, the non-zero transmissibility is:

\[ T_{s,p} = \frac{1}{a_{s,p} \sin^2 (\frac{\theta}{l_0}) + 1} \]

where \( l_0 = \frac{\lambda}{2\pi} \left( \frac{1}{\sqrt{n^2 \sin^2 \beta - 1}} \right) \), \( a_s = \left( \frac{n^2 - 1}{2n} \right)^2 \cos^2 \beta \left( \frac{1}{\sin^2 \beta - 1} \right) \),

\( a_p = a_s [(n^2 + 1) \sin^2 \beta - 1] \), \( s \) denotes polarization normal to the plane of incidence and \( p \), parallel to the plane of incidence.

Because of the exponential dependence, the tunneling will be detected only when the air gap is very small, usually less than the wavelength of the incoming light.

In operation, PSTM resembles STM. Both exploit exponentially decaying fields, and are conceived as tunneling instruments. Both operate in a scanning mode, rather than in a lenslike imaging mode as for the conventional optical microscopes.

Numerical calculations show that the transfer function in PSTM is an intrinsic feature of the probe. PSTM images depend sharply on the competition among 3 phenomena that distort the spatial spectrum of the sample: attenuation along Z-direction, scattering by the tip apex, and coupling between the near field and fiber mode(s).
The signal transduction mechanisms to consider involve scattering in the tip and direct modal coupling into the propagating mode of the fiber. The modeling of scattering in this configuration was undertaken in a number of careful studies by Girard et al.\textsuperscript{23,24,25} who used a microscopic formalism, where the sample and the tip are discretized into a number of scattering centers that may be dipolar or even multipolar. The resulting equations are then solved self-consistently. Alternatively, a Green's function dyadic technique\textsuperscript{26} has been employed, as has an analysis of Mie scattering in this configuration\textsuperscript{27}. It has been suggested that the near field interaction between such a pointed dielectric and a sample can provide a signal that would allow for subwavelength resolution.

The smaller the tip-object distance, the better the resolution is. This arises from the exponentially decaying amplitude of the evanescent waves, which depends on the value of the spatial frequency $k$ ($k = 2\pi/\lambda$). The greater the value of $k$, i.e., the shorter the wavelength, the faster the amplitude of the corresponding component decays in the $z$ direction.

For the experiments that we set up to study the local optical behavior of small particles, the intensity of signals that are collected by the tapered tip can be expressed as three components,

$$I = I_{\text{evanescence}} + I_{\text{scattering}} + I_{\text{interference}}$$

The first term above represents the background evanesence signal; the second the scattering by the objects. The last term represents the interference due to interaction between the first two terms and particle-particle interaction. Details will be discussed in the later chapters.
2.2.3 *Shear force feedback mechanism*

Let us now briefly describe the mechanism of the shear force feedback, which is used to maintain a constant tip-sample separation distance in the near-field experiment.

Consider two bodies, $A$ and $B$, in very close proximity which are in relative motion. A friction force $F_f$ occurs along the direction of motion. The friction force is related to the applied load $F_{ext}$ between the two bodies as, $F_f = \mu F_{ext}$. If interatomic $A$-$A$ interactions are comparable in strength to $B$-$B$ interactions, and both much weaker than $A$-$B$ interactions, the relative motion between $A$ and $B$ will lead to plastic deformation and dislocation of either or both bodies, resulting in friction with wear. To avoid plastic deformations, i.e., to have friction without wear, the applied load $F_{ext}$ on the interface cannot exceed the elastic limit of both bodies. In the shear-force operation, this applied load appears to be due to viscous forces, although the physics of the interaction is still unclear.\(^{28}\)

It has been shown that the friction force depends on the direction of motion between two bodies in contact.\(^{29}\) The friction is a non-conservative process, it cannot be obtained as a derivative of a potential. Two different approaches have been used to determine atomic-scale friction. Molecular dynamics calculations with parametrized pair potentials have been used to simulate the stick-slip motion and to determine the friction force.\(^{30}\) Another approach, based on an *ab initio* density functional calculation, has also been used to determine the trajectory of an atom moving along a surface and to estimate the associated friction force.\(^{31}\) The hysteresis resulted from the dependence on the direction of motion reflects the microscopic irreversibility in the friction process. The energy dissipated in friction as heat is related to the hysteresis curve.

In the shear force feedback mechanism, the tapered tip is dithered laterally at or close to its resonance frequency. When the tip-sample separation decreases below a
certain distance, the friction force $F_f$ becomes significant enough that it damps the dithering of the tip. Thus, if the friction force is maintained constant by monitoring the change of the amplitude of the tip dithering, $F_{ex}$ can also be maintained constant, given that $\mu$ does not vary much over the scanning region. A topographic image can be recorded by recording the distance necessary to move the sample to maintain the tip oscillation amplitude constant, when the tip rasters over the sample. Actually, a “topographic” image generated by such an approach is a “constant force” image, as with other force microscopies.
Reference


3.1 Fibre tip fabrication

Tapered fiber tips are prepared by heating a single mode optical fiber while pulling it apart. A fiber splice machine was used for this purpose. Single mode fiber with a core diameter of 3.8 µm and cladding diameter of 125 µm (FS-A, Newport), which is designed for 488 nm light, was used. Typically, a portion of approximately 40 cm of a fiber was stripped of 0.5 cm of its plastic coating at the center. It was then mounted tightly in the groove on the machine, with the electrodes pointing at the bare portion of the fiber. The fiber on both sides of the electrodes was adjusted to be coaxial to ensure the straightness of the resulting tips. The fiber was then heated by an arc discharge between the electrode pair, and was pulled apart either by the contraction of the fiber itself or at a constant force by a mass attached to one end of the fiber through a pulley. The heating was carefully controlled by adjusting the discharge current, the ramping time and duration of the discharge, so that the fiber broke slowly enough to form two tapered tips on each 20 cm-long portion of the fiber. Figure 3.1 is a diagram of the scheme.
Figure 3.1 Schematic of the fabrication procedure for producing tapered fiber tips.
3.2 SEM microscopy

Scanning electron microscopy was performed on a Hitachi S-2500 microscope. Before being imaged, the tapered tips were vacuum-coated with a very thin layer of gold, using a Polaron SEM coating system. The image of a typical tip is shown in Figure 3.2, indicating a diameter of about 60 nm at tip end.
Figure 3.2 SEM image of a tapered fiber tip.
3.3 Preparation of self-affine silver colloidal films

Self-affine silver colloidal films were prepared by depositing the fractal silver clusters out of the solution onto a 2-dimensional surface, as follows:

Twenty milliliters of a 1.00 × 10⁻³ M aqueous silver nitrate solution were prepared and cooled down to 10°C. Sixty milliliters of a 2.00 × 10⁻³ M aqueous sodium borohydride was prepared and cooled in an ice-bath down to 2°C. The sodium borohydride solution was stirring constantly by a magnetic stirrer and silver nitrate solution was added dropwise to the borohydride solution. Stirring was continued for 45 minutes after the two solutions were mixed. The resulting colloid solution was bright yellow, with maximum of absorption at about 390 nm. Figure 3.3 shows a UV-visible spectrum of the solution.

Two methods that were slightly different were then employed to help colloidal particles settle onto thin films:

a) (Referred to later as the non-adsorbate method) A clean Zinc rod was used to stir the colloid solution in a petri dish for 5 minutes. The solution turned slightly reddish, darkening progressively. Clean cover slides were placed at the bottom of the dish for a certain period of time, depending on the required thickness of the samples and the colloid clusters allowed to settle onto the slide under the influence of gravity. The resulting films on the slides were rinsed carefully with distilled water, and left to dry.

b) (Referred to later as the adsorbate method) In most cases, the colloid solution was allowed to settle for one day before a small amount of adsorbate was introduced to help deposit the colloid particles into films. In one run, 2.00 ml of 0.1M aqueous phthalazine solution was mixed with 4.00 ml of the colloid solution. The solution changes from bright yellow to reddish and then slightly darker. Clean cover slides were then placed at the bottom of the solution for two hours. The slides were later taken out and rinsed with
Figure 3.3 UV-visible absorption spectrum of a colloid solution.
distilled water several times to remove any adsorbate particles that may also have deposited on the film. The colloidal thin film was formed on top of the cover slide. Different reaction conditions, including concentration of aqueous phthalazine solution, volumes of each solution and settling time, are also tried, as detailed in Table 3.1.

UV-vis absorption spectroscopy is also used to characterize the silver thin films prepared as above. Figure 3.4 shows the typical UV-vis spectra for the two types of samples. Curve a corresponds to the sample prepared by the non-adsorbate method, and curve b to the one prepared by the adsorbate method.
Figure 3.4 UV-visible absorption spectra of Ag colloidal films prepared by, a) non-adsorbate, b) adsorbate, method.
3.4 Confocal microscopy

Confocal microscopy measurements were performed on a Bio-Rad Microscience microscope, model MRC-600. Silver thin films deposited on the cover slides were imaged directly without other processing. A 488 nm laser line from an Argon ion laser was used.

Confocal microscopy was employed to check the quality of the prepared films. The morphology of the colloidal thin films changed with conditions under which the films were prepared such as the concentration of the added adsorbates and the time the deposition last. Figure 3.5 shows some confocal images of the prepared samples. The scale bar in the images indicates 25 μm. Table 3.1 lists the corresponding preparing conditions.
Figure 3.5 Various colloidal silver films prepared under the conditions listed in Tab.3.1.
Table 3.1 Preparing conditions for the self-affine Ag films shown in Figure 3.5

<table>
<thead>
<tr>
<th>Condition</th>
<th>0.1ml 0.01M phthalazine (aq)</th>
<th>0.3ml 0.01M phthalazine(aq)</th>
<th>2ml 0.1M phthalazine(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 ml colloid solution</td>
<td>6 ml colloid solution</td>
<td>4 ml colloid solution</td>
</tr>
<tr>
<td>3 hour deposition</td>
<td>7a1x2</td>
<td>7a2x2</td>
<td>7a3x2</td>
</tr>
<tr>
<td>5 hour deposition</td>
<td>7a1x4</td>
<td>7a2x4</td>
<td>7a3x4</td>
</tr>
</tbody>
</table>
3.5 AFM/PSTM system setup and operation

A schematic of the instrumental setup is shown in Figure 3.6. The near-field optical microscope consists of a piezoelectric scanning tube mounted coaxially on a Burleigh inchworm linear motor that is used for coarse approach. A micro-dovetail ATR prism is mounted at the end of the scanning tube. A Pyrex cover-slide with the sample deposited on one side is attached to the prism with index-matching fluid. The laser beam is coupled into a single mode fiber (F-SA, Newport) through a fiber coupler (F-915T, Newport). The other end of the optical fiber is fixed to the scanning tube with a collet, conducting the laser beam to the entrance surface of the prism, so that the illumination of the sample does not change as the sample is rastered. The sample is excited by the evanescent wave of a laser beam totally internally reflected inside the ATR prism. The tapered fiber tip is glued to the face of a piezoelectric bimorph, which itself is fixed to the bottom plate through a stainless steel holder. During the scanning, the tip is fixed, while the sample is scanned by means of the piezoelectric tube. Regulation of the tip-sample distance is achieved through the shear force mechanism. The bimorph, together with the sharpened tip, is excited acoustically at or near its resonant frequency (20~40 kHz). The amplitude of the tip oscillation is measured by focusing the beam of a semiconductor laser on the tapered part of the tip. The diffraction pattern of the beam is then imaged on a sectored photodetector. As the sample approaches the tip, oscillation amplitude of the tip decreases due to damping by attractive forces between the tip and the sample. The decrease of the amplitude is used as the feedback signal to regulate the tip-sample distance. Recording the voltage to the Z-control of the piezoelectric scanning tube needed to keep the tip oscillation amplitude constant as a function of lateral position approximately produces a topographic image of the sample. Simultaneously, near-field optical signals are collected by the tapered tip, whose other end is connected to a photomultiplier tube. The output of the PMT is amplified before being transferred into the controlling PC to generate the near-field optical image. The controlling electronics is a RHK unit for scanning probe microscopy.
Figure 3.6 Schematic for the shear-force AFM/PSTM system
Both topographic and optical images, as well as optical spectra, are collected by and stored in a personal computer.

The sample position is so adjusted that the tip probes the spot on the prism surface where total-internal-reflection takes place. The intensity profile of the laser beam after it passes through the illuminating fiber is shown in Figure 3.7, as collected by a beam analyzer placed less than 1 mm away from the fiber end. It is close to Gaussian, with a full width at half height of approximately 150 μm.

To improve the signal-to-noise ratio of the optical signals, lock-in detection is employed, by chopping the laser beam before it is coupled into the fiber and collecting only those signals at the same frequency as, and with a fixed phase relation to, the chopping frequency.

When optical spectroscopy is performed, the exciting CW laser is swept over a wavelength range of about 575 to 615 nm (dye laser) or about 720 to 830 nm (Ti/sapphire laser), while maintaining the fiber tip over the location of the sample of interest at a very close distance (usually 25 nm) while the laser is swept. Again, lock-in detection is adopted.
Figure 3.7 Intensity profile of a laser beam out of a fiber.
3.6 System testing and calibration.

The shear force AFM/PSTM was tested and calibrated with samples whose dimensions are known through other measurements.

Figure 3.8 is a shear force AFM image of a commercial gold cross-grating (Pelco, 607-AFM, 2160 lines/mm), with a spacing of approximately 463 nm. The grid of the gratings itself is well resolved, indicating a lateral resolution of better than 60 nm.

Figure 3.9(a) shows a thin layer of uniform latex particles deposited on a mica substrate. The same sample was also imaged with a Nanoscope II AFM microscope, as shown in Figure 3.9(b). The parameters for the piezo-scanner sensitivity can be calibrated accordingly.

Figure 3.10 shows a topographic image of a typical silver colloidal film, which is the subject of this study. The smallest feature in the image that can be resolved is approximately 25 nm.

Figure 3.11 shows the topographic and optical images of a clean cover slide, which were obtained simultaneously. The topographic image is very flat, as expected for a clean surface. The optical image, on the other hand, appears very “noisy”, which is due to the extremely weak near-field signals leading to poor signal-to-noise, when the glass surface is clean.

Figure 3.12 shows an $I \sim Z$ curve for a thick silver film (approximately 100 nm thick), prepared by vacuum evaporation at a pressure of $5 \times 10^{-6}$ Torr, where $I$ represents the intensity of collected near-field signal and $Z$ the tip-sample distance. Note that $Z$ starts at approximately 10 nm from the sample due to the precaution against breaking the tip. The zero of $Z$ is defined as the tip elevation above the surface when the tip resonance is completely damped, which was determined by carefully advancing a tip.
Figure 3.8 AFM images of a commercial gold grating, 2160 line/mm.
Figure 3.9 AFM images of latex particles on mica.
a) Shear-force AFM, b) Nanoscope II.
Figure 3.10 Shear-force AFM image of silver colloidal film.
Figure 3.11 AFM/PSTM images of clean prism surface. Laser wavelength 592 nm.
Figure 3.12 $I$ vs. $Z$ relationship. The dot line indicates an exponential fit.
to the surface until it broke. Because of the dynamic ranges of the piezoscanner and the electronics, $Z$ value was limited to about 500 nm. The curve adopts an exponential-decay profile overall, with the exception that the near-field signal seems to be depressed when tip-sample distance is closer than 80 nm. This result will be discussed in later chapters.
Chapter 4. Considerations in AFM/PSTM instrumentation

The detailed description on NSOM systems can be found in several reviews and books\textsuperscript{1,2}. Here only some details that were encountered during the design and setup of our system are discussed.

4.1 Improvement of image quality

There are several factors that have to be considered in order to improve the image, both topographical and optical, quality.

4.1.1 Vibrational isolation

Similar to other scanning probe microscopies, the exponential dependence of the evanescent signal on tip-to-sample gap distance makes vibrational isolation an extremely critical factor in the AFM/PSTM development. The basic concepts of vibration isolation have been treated in several books\textsuperscript{3,4} and papers\textsuperscript{5,6}.

There are two types of disturbance from which the AFM/PSTM system must be isolated: vibration and shock. Typically, buildings vibrate at frequencies between 10 and 100 Hz. The vibrational spectra of buildings frequently contain maxima around 15 to 20 Hz.\textsuperscript{6} Vibrational excitations due to the response of the floor to irregular motions, such as those caused by people walking and working in the laboratory, are typically in the 1-3 Hz range. The influence on the tip-to-sample distance of such external perturbations can be reduced by damping mechanisms and/or by constructing sufficient stiffness in the basic structure of the AFM/PSTM. The stiffer the structure, the less the damping needed. This can be done by maintaining compact scanners and sample mounts, and using low-mass components. In addition, the stainless steel plate that
supports the scanning module is hung by four springs. The whole system is placed on an optical table, and covered by a box with foam over the inside wall. This effectively reduces the vibrational and acoustic noise.

The desired instrument resolution determines the lengths to which one must go to achieve adequate damping. A rule of thumb is to require a stability of at least an order of magnitude better than the desired resolution. Since the shear force AFM usually has a resolution of a few tens of nanometers, the system require roughly 1.0 nm tip-sample separation stability. As seen in Figure 4.1, this corresponds to a tolerable value for noise at roughly 4 percent of the feedback signal. In practice, a noise level of 1 percent of the feedback signal is usually achieved, before starting the image scan.

Lastly, line noise from the powerline in the lab may sometimes trigger a resonance within the circuit of the controlling electronics. Thus, it is necessary to ground the system, every power supply that is involved, and shield all junctions properly.

4.1.2 Effect of dithering frequency

The dithering frequency of the tip working in the AFM mode, which is at, or in the vicinity of, the resonance frequency of the tip/bimorph module, is also an important factor affecting the noise level in the whole system. A typical curve of the signal from the diode detector vs. tip oscillation frequency is shown in Figure 4.2. If the resonance frequency of the tip is too low, the noise level of the signal from the detector will be high, which reduces the signal-to-noise ratio, and thus, the resolution of the AFM. On the other hand, too high a dithering frequency reduces the resolution too, because the increased frictional interaction between the tip and the sample, due to the higher dithering frequency, will decrease the resolution of AFM working in the shear force mode. This was reported by Paesler et al., and also observed by us. The working frequency is usually a compromise between these two factors. In our system, the
Figure 4.1 Shear-force signal vs. tip-surface distance relationship.
Figure 4.2 Resonance profile of fiber tip. Solid line is a Lorentzian fit.
resonance frequency of the tip, and thus the dithering frequency, can be adjusted by changing the relative location of the fiber on the bimorph. It is found that a resonance frequency of above 20 kHz gives a reasonably good stability of dithering, with the optimal conditions at around 30 kHz.

4.1.3 Signal-to-noise ratio of the optical signal

To improve the quality of the optical images, there are two techniques that would help to increase the signal-to-noise ratio dramatically: (1) placing the fibre coupler and the laser on the same optical bench, but different from the bench where the AFM/PSTM sits; and (2) using lock-in detection in collecting the signals. The former de-synchronizes the noise of the optical signal detected from that of the laser; and the latter ensures that only signals that are in phase with the chopper are collected.

4.2 Light excitation and detection

As in most NSOM systems, lasers are used as the light sources. A laser beam can easily and efficiently be coupled into the fiber. It also provides such benefits as polarization control, phase coherence and spectral purity, as in other conventional laser spectroscopy experiments. For PSTM, when the illuminating beam is brought to the interface directly, laser sources have advantage in that the low angular divergence of the laser results in a small range of incident angles when total internal reflection takes place. If the divergence is large, there could still be some far-field component of the incident light propagating through the interface although most far-field light are reflected. Such far-field components would easily dominate over the desired optical signal, and the near-field information would be surpressed. In cases where the illuminating beam is brought to the interface through a single mode fiber, the low angular divergence of laser sources is crucial in coupling light into the fiber.
In designs where the tip is used as a light emitter, the laser power that can be coupled into the fiber probes is dependent on the wavelength of interest, the coupling efficiency, and the probe aperture size. The light injected into the probe cannot be increased without limit, because of the inefficiency of the near-field aperture coupling. Increasing input power can contribute to probe heating resulting, eventually, in tip melting and/or sample destruction or degradation. Even at laser powers below the threshold for physical aperture damage, the thermal effects can adversely affect the experiment by transferring heat to the sample. It is believed that a laser output power of less than 1 mW at the tip end lies safely below the damage threshold, even for small apertures (~20 nm).

With near-field microscope designs where the tip is used as a light collector, as in the PSTM, probe heating problems can be reduced and a relatively higher intensity can be incident on the sample, provided that it does not damage the sample. However, the low coupling efficiency of the tip, leads to low intensity of the detected near-field signals, and only transmitting samples can be measured by PSTM.

A commonly used laser is the argon ion laser, which has six useful lines in the spectral range 458 to 514 nm. It is often used for laser imaging and spectroscopy, more specifically, emission spectroscopy, such as fluorescence spectroscopy and Raman spectroscopy. When excitation spectroscopy is required, a CW light source must be used. A CW laser is usually the first choice, as the CW dye laser and Ti/sapphire laser used in our experiments. However, such CW lasers normally cover only a portion of the UV-vis range, which limits the spectral range being studied. A potentially ideal light source for such experiment would be the optical parametric oscillator (OPO), which provides a wide range of tunability, with intense output.

Besides lasers, white light sources, such as Xenon lamp, may also be considered, providing that enough light intensity is transported through the fibre, and the detecting
device is sensitive enough. Such light sources may be useful particularly in doing spectroscopy.

One bottleneck for the all types of NSOM measurements is the extremely low light throughput through the probe aperture, e.g., about $10^{-6}$ for a 20 nm aperture. This, together with the limited exciting laser intensity, makes it quite difficult a task to improve the contrast of the image or increase the S/N ratio of the spectra. Most NSOM systems use either a photomultiplier tube (PMT), a charge-coupled device (CCD), or a photodiode. When spectroscopy is performed, a cooled CCD is the detector of choice. Its very great quantum efficiency and multiplex characteristics allow spectra to be taken much faster than with conventional photomultiplier tubes because the spectral region is dispersed across the CCD array, in contrast to having to scan the grating when using a PMT. In our spectroscopy experiment, it is the excitation spectroscopy that is being performed, i.e., the excitation laser wavelength is swept while near-field signals are collected without being dispersed by a grating. Therefore, the collected signals are strong enough to use a PMT tube only.
Reference


Chapter 5. Discussions

5.1 Near-field optical microscopic study

5.1.1 Observation

Near-field optical and topographic images of a sample prepared by the non-adsorbate method are shown in Figure 5.1. It is a 3 \( \mu m \times 3 \mu m \) portion of a self-affine silver film. The top panels are the topographic images, the bottom optical images. The laser lines used for each scanning (Ar ion laser) are indicated below each pair of images. The topographic images were very reproducible even though they were recorded minutes apart while the exciting laser wavelength was changed, and the transmission through the fiber optimized. The lower right image in the figure is a little shifted due to thermal drift of the sample; however, it is evident that it is an image of the same region of the sample. The near-field optical images excited with different wavelengths, on the other hand, differ dramatically one from the other. It is very sensitive to the excitation wavelength, and no correlation appears to exist between topographic and optical images. However, with any given wavelength they are highly reproducible even when images with other wavelengths are recorded before returning to the original wavelength, as for 458 nm excitation. This demonstrates the fact that the near-field images are not spurious. Also visible in the optical images are a series of fringes oriented perpendicularly to the incident beam, which will be discussed later. (Laser beam comes from top slightly tilted to the right).

Figure 5.2 shows a 3 \( \mu m \times 3 \mu m \) portion of another silver film, which is prepared by the adsorbate method. Similar results are observed, even for a different wavelength range. Here again one sees highly repeatable topographic images and very localized and wavelength-sensitive near-field images. The maximum and minimum intensities in the optical images approximately have a ratio of approximately 4 : 1,
Figure 5.1 AFM/PSTM images of a self-affine Ag film prepared by non-adsorbate method, illuminated with an Ar ion laser. Top series of images are topographs, the lower, optical images.
Figure 5.2 AFM/PSTM images for a Ag film prepared by adsorbate method, illuminated with a R6G dye laser. The bottom right pair is from a blank glass slide. Top series of images are topographs, the lower, optical images.
which eliminates the possibility that such patterns could be due to the random noise of the system. For comparison, a blank glass slide is also scanned in the same manner, which displays only random noise with an intensity of four orders of magnitude weaker in the optical image.

To illustrate that such localized near-field patterns are common among these self-affine films, different images on different samples using various laser lines are shown in Figures 5.3 and 5.4.

5.1.2 Discussion

Let us first analyze the signal that is collected by the tapered tip. Consider Figure 5.5. When the surface of the prism is clean, the tip collects the near-field evanescent signal $I_1$ as it tunnels through the air gap between the surface and the tip, $I_1 = I_{NF} = |E_0 e^{-kZ}|^2$, where $Z$ is the tip-surface distance, $k$ and $\beta$ are defined in Chapter 2. When the surface is flat, $I_1$ is quite uniform too, as seen in the blank glass slide images in Figure 5.2.

$I_1$ decays exponentially with $Z$, as seen in Figure 3.12. The deviation from exponential decay for tip-surface gaps less than 100 nm is due to the fact that the tip begins to remove a significant amount of energy from the evanescent field. Thus the treatment of near-field component as in Chapter 2 will not be valid without taking the tip into account. Such a deviation has been observed experimentally by other groups. It is gratifying that the $I$ vs. $Z$ curves reported in Ref. 1 are very similar to those we measure, considering the difference in system setup and samples.

When there are certain objects on the surface that are being probed by the tip, the collected signal is more complex. Taken as dipoles, these objects may absorb the incident light at the interface and scatter. Thus the signal $I_2$ that the tip collects would be, $I_2 = I_{NF} + I_{scattering} + I_{interference}$. The second term $I_{scattering}$ is due to scattering by the
Figure 5.3 AFM/PSTM images for a Ag film prepared by adsorbate method, illuminated with a Ti/sapphire laser. Top series of images are topographs, the lower, optical images.
Figure 5.4 AFM/PSTM images for a Ag film prepared by non-adsorbate method, illuminated with a R6G dye laser. Top series of images are topographs, the lower, optical images.
Figure 5.5 Illustration of the near-field signal.
objects, and the last term \( I_{\text{interference}} \) due to the interference between the field emitted by the dipolar elements on the surface and the tangential component of the near-field.

Among the three terms, \( I_{\text{NF}} \) should have a form as above, and should be quite constant throughout the scanning region, given the flat surface of the prism. Thus, it can be treated as a DC component in the images since the tip is kept approximately at a constant height above the surface. \( I_{\text{scattering}} \) is the most important term. If there is correlation between the geometry of the object and its dipole, there should be correlation between the topographic image and the optical image. Or, if there is field enhancement, as the theory suggests, it should be reflected in this term. If \( I_{\text{scattering}} \) is not very large, \( I_{\text{interference}} \) would be comparable to \( I_{\text{scattering}} \). Both \( I_{\text{scattering}} \) and \( I_{\text{interference}} \) should be observed in the optical images. These predictions are confirmed by the images in Figure 5.6, where correlation is clearly seen between the topographic and optical images. The particles in the images are aggregates of organic molecules, namely, phthalazine, which was used as adsorbate to prepare the colloidal silver films. Note that also visible clearly are interference fringes due to \( I_{\text{interference}} \).

For the sample of self-affine silver films, theoretical calculations suggest that the dipolar excitation will not be related to the sample geometrically. Instead, the excitation is localized and enhanced, and is very sensitive to the excitation light. Let us write the collected signal \( I_3 \) in the form as: \( I_3 = I_{\text{NF}} + I_{\text{scattering}} + I_{\text{interference}} \). In this case, \( I_{\text{scattering}} \) and \( I_{\text{interference}} \) can be expressed as: \( I_{\text{scattering}} = |E_0 Q|^2 \) and \( I_{\text{interference}} = |E_0|^2 e^{-i\delta} Q e^{i\delta} e^{-i\delta} \), where \( Q \) is the \( Q \)-factor for the resonance enhancement of the normal mode.\(^2\) With a large \( Q \), \( I_3 \) is dominated by \( I_{\text{scattering}} \). Although it is difficult to calculate \( Q \) quantitatively, based on an overall intensity difference of four orders of magnitude between \( I_3 \) and \( I_1 \), the average intensity can be estimated to be approximately 100-fold enhanced. For some modes that are in resonance, \( Q \) can be significantly higher than the average. The enhancement also seems to vary greatly from sample to sample and from mode to mode. For example, in the optical images in Figures 5.2 and 5.3, the interference fringes are much less pronounced than those of Figures 5.1 and 5.4. This indicates that a higher
Figure 5.6 AFM/PSTM images of a particle consisting of adsorbate molecules. Top series of images are topographs, the lower, optical images.
enhancement $Q$ factor for the samples in Figures 5.2 and 5.3 and in that spectral ranges, which leads to $I_{\text{scattering}}$ completely overshadowing $I_{\text{interference}}$. Within each optical image, the observed intensity at the "hot spots" is measured to be 3-4 times greater than that at the lowest intensity portions of the samples. This is less than what is predicted by theory. The result probably reflects the limitations of some of the approximations assumed in the theory.

Because the (tangential) component of the near-field propagates unidirectionally (in the plane of the image) while the dipolar field emitted by the structural elements of the rough surface propagates cylindrically from each element, the superposition is asymmetrical with strong fringes along the propagation direction of the exciting field and weak fringes in the opposite direction. The observed fringes possess these properties.

The evanescent-wave configuration reduces the role of the incident light in the near-field images. Although all wavelengths are collected (including Raman-shifted components and other inelastic emissions) the near-field images are formed predominantly by the Rayleigh (i.e. elastically) scattered light originating from the aggregated colloidal particles. The normal mode images shown in the figures correspond roughly to the single normal mode centered at zero frequency shift plus whatever contribution arises from the tail of inelastically excited modes close in frequency to the unshifted mode.

The results vindicate the major predictions of the optical theory of self-affine surfaces. The optical images bear similarity with those simulated numerically. Specifically, the excitation is localized. The square modulus of the local electric field strength is intense at only a small portion of the surface at a given frequency. Such localized "hot spots" are extremely sensitive both in space and to the external field. Some of the "hot spots" are smaller than the exciting wavelength, with the smallest localization length $l_x$ around 100 nm, which justifies the assumption of $l_x < \lambda$ in the
theoretical treatment. Finally, there does not appear to be any obvious correlation between the film morphology and the pattern of excitation in a given normal mode. That is, for some normal modes, the hot spots correspond to valleys while for others they coincide with peaks. In some images both topographical high and low portions of the film correspond to high field or low field regions simultaneously. Furthermore, the observation of field localization over regions of the sample substantially exceeding the wavelength, suggests that the results of Ref. 3, obtained within the quasi-static approximation requiring the sample to be smaller than the exciting wavelength, are qualitatively valid over linear dimensions substantially larger than the wavelength.

5.1.3 Non-fractal samples

As a comparative study, similar imaging was also carried out some non-fractal silver clusters. Such non-fractal samples were prepared by a different method. In brief, interfacial silver colloid-adsorbate films were prepared by vigorous shaking of a two-phase system consisting of silver colloid (aqueous phase) and a solution of an adsorbate in a suitable water-immiscible solvent (e.g. CH2Cl2, organic phase). The films formed at the interface were then deposited on glass slides for imaging. Depending on the nature of the adsorbate, the resulting 2-D silver films can be either fractal or non-fractal objects. Figure 5.7 is an SEM image of such a silver cluster film. The single cluster size is between 5 nm to 10 nm. The fractal dimension (D) of the sample, according to the procedure described in detail in Ref. 4, was determined to be D = 1.97, which indicates that the 2-D film is a trivial fractal, i.e. a non-fractal object.

The topographic and optical images collected on this sample are shown in Figure 5.8. Unlike those self-affine silver films, there appears no self-similar pattern.

Several laser lines (Ar ion laser) were used to illuminate the sample. However, the strong inhomogeneous pattern that appears so frequently in the optical images for the self-affine films does not appear in these images. Interestingly, a correlation
Figure 5.8 AFM/PSTM images of a non-fractal Ag film.
between topographic and optical images is observed. Note that there are two large particles in the upper right portion of the scanning region. In the optical images, there are corresponding features at the same locations. This correlation does not change with different wavelengths, although the features become less distinguishable for some laser lines. These large particles are aggregates of the organic molecules used as adsorbate to prepare such films, as can also be seen in the SEM image, Figure 5.7. Such adsorbates are not expected to have optical enhancement. Thus, it is not surprising to see the correlation between topographic and optical images. The $Q$-value, in the previous context, would be $\approx 1$, or $< 1$ (when absorption is strong at some wavelengths). For example, if taking the signal intensity at the bright feature in the optical image of Figure 5.8 (514 nm) as $I_a$, $I_a = I_{NF} + I_{scattering} + I_{interference}$, and that of the fringes as $I_b$, $I_b = I_{NF} + I_{interference}$, neglecting $I_{NF}$, we can get $I_{scattering} / I_{interference} \approx 2 \approx Q$. It is obvious that $I_a$ varies with the wavelength, for some wavelengths, $I_a \approx I_b$, and $Q \approx 1$. This confirms that there is no enhancement phenomenon involved for non-fractal samples.

The results from the non-fractal samples in turn support that the pattern observed in the optical images for those self-affine films are indeed due to the unusual optical properties of those samples, and not artifacts due to the system configurations, as some may question.

5.1.4 Optical intensity vs. $Z$-distance relationship

The optical intensity vs. tip-surface distance relationship was also investigated for the self-affine films. Figure 5.9 shows some $I$ vs. $Z$ curves, which were collected at the same spot, but with different excitation wavelengths. Note that the relative intensity scale for different curves are different. Interestingly, the exponential decay pattern, as seen in Figure 3.12, is no longer observed. At 604 nm excitation, the detected signal still decays with $Z$-distance (curve a), but almost linearly instead of exponentially. At the other two excitations (592nm and 587nm), the detected signals remain almost constant over the scanning $Z$-distance range. This could be explained as follows: When
Figure 5.9 Near-field signal vs. tip-surface distance.

Laser wavelength: a) 604nm, b) 587nm, c) 592nm.

Different curves have different scales.
the tip is close to the surface, only the few silver monomers right under the tip contribute to the detected signals. The surrounding monomers give an insignificant input. When the tip moves farther from the surface, the sampling “cross section”, i.e., the portion of the film that contributes to the detected signals, becomes larger. The relative input of the monomers that are far from the tip to the detected signals increases. It is quite different from the situation where Figure 3.12 was obtained. Therefore, it should not be surprising to observe that intensity of the detected signal does not decay exponentially with Z-distance.

5.1.5 Comparison with the experiments of others

Bozhevolnyi et al. have reported a series of near-field studies on the optical fields of surface plasmon polaritons (SPPs) excited at surfaces of rough silver films, using a similar instrumental setup as ours. Their observations were explained in terms of interference between the excited and multiple scattered SPPs. They also related the phenomenon to weak localization of SPPs caused by multiple SPP scattering in the surface plane.

The main difference between Bozhevolnyi's group's experiments and ours lies in the samples. The samples that were studied in their experiments were prepared by thermal evaporation in vacuum, which are non-fractal. The images showed that the films were rather smooth, with µm-sized bumps separated on average 5 - 7 µm. Also, in their experiments, the incident beams were angularly adjusted so as to ensure resonant SPP excitation at the interface. As they reported, the average optical signal was more than 20 times weaker if the angle of incidence was out of resonance by about 2°.

The observations for the self-affine silver films are very different from the smooth films. The field localization, and thus enhancement, is stronger, including various patterns. The contrast between the patterns in the optical images is very pronounced. No attempts were made in our experiments to angularly adjust the incident
beam to ensure resonant SPP excitation at the interface. Although SPP excitation at the interface cannot be excluded from the signals being collected, we believe it is the localized dipolar normal modes that are in resonant, and mostly account for the 'hot spots', which are often dominant of the images.

As a matter of fact, the images collected on the non-fractal silver films are quite similar to the observation by Bozhevolnyi et al, although the samples were prepared in quite different ways. For those non-fractal samples, interference fringes are more pronounced, and no localized/enhanced 'hot spots' are observed. This supports the view that 'hot spots' are indeed due to the fractality of the self-affine films.

Previous work had also been done by Tsai et al, to investigate the optical behavior of such self-affine silver films. An early model of PSTM was used for those measurements, where no independent mechanism was employed to monitor the tip-surface distance. The tapered fiber tip collects the near-field signal, and compares it with a pre-set value. The difference between the two was used as a feedback signal to the electronics to maintain a constant local field intensity during the rastering of the tip. Thus the contour of the local field is mapped out as an image. Their results did indicate the localization and enhancement of the optical field, with the localization length lying in the range from 60 nm to 140 nm and a typical $Q$ factor believed to be 125 for the mode enhancement.

What was missing in Tsai's experiment was that, the topography of the sample was not clear. No evidence was given on whether or not there is a correlation between the sample topography and its optical behavior. There are arguments in that, without knowledge of the surface profile, the interpretation of the optical images is cumbersome and could be ambiguous.
5.2 Near-field optical spectroscopic study

5.2.1 Observation

In this section we report near-field excitation spectra taken on self-affine silver samples. In order to use the near-field microscope to perform spectroscopy, the AFM/PSTM setup was modified somewhat. A CW laser was used as a light source and the spectrum is collected with the tapered tip fixed in a pre-selected position within the near-field of the self-affine silver sample. The laser line is scanned.

Optical spectra are shown in Figure 5.10, the inset indicating the positions of each spot where the spectrum was taken. A Ti:sapphire laser with wavelengths from 723 to 832 nm was used for this measurement. The tip was maintained approximately 25 nm above the surface. As seen, distinct spectra arise from different spots, even though they are only a few microns apart.

Similar results can be seen in Figure 5.11, which were collected for a 3 μm x 3 μm portion of another sample and in a different wavelength range (R6G dye laser, 575 - 615 nm). Again one sees very distinct spectra for different spots, even within such a small wavelength range.

5.2.2 Discussion

The UV-vis absorption spectra (far-field) of the colloid aggregate films are shown in Figure 3.4. It displayed two very broad bands in the visible range. The UV-vis absorption spectrum (far-field) of the colloid solution before it is aggregated is also shown in Figure 3.3, which contains a major peak around 400 nm. Such a colloid solution consists mainly of colloidal monomers, plus a few dimers and trimers. The development of broad red-shifted band upon aggregation is a well known phenomenon. Limitation of the mean free path by the particle boundary broadens and decreases the
Figure 5.10 Near-field optical spectra at different spots on a self-affine Ag film excited by a Ti/sapphire laser.
Figure 5.11 Near-field optical spectra of different spots on a self-affine Ag film excited by R6G dye laser.
peak absorption for very small particles, while at larger sizes the peak shifts to longer wavelengths and broadens as higher-order modes are excited. The two peak structure of the plasmon is typical for aggregated clusters, their relative intensity indicating the degree of aggregation. The more intense the peak around 500 nm, the more the colloid aggregated into clusters.

The peak around 400 nm in the spectrum of colloid solution has a full width at half maximum (FWHM) of about 25 nm. The broad bands in the far-field spectra of the aggregate film can be attributed to inhomogeneous broadening, since the cross section in the far-field spectrum would span over a large portion of sample, thus it may be composed of a large number of overlapping normal modes localized in a small region. The peaks in Figures 5.10 and 5.11 are about 7 to 15 nm, significantly narrower than the far-field spectra. More interestingly, although most peaks in the near-field spectra still show inhomogeneous broadening, there are a few peaks that appear Lorentzian line shape, e.g. peaks a and b in Figure 5.10, as shown in Figure 5.12. We may argue that this homogeneous form of line broadening suggests such peaks are due to excitation of a single normal mode. If this is the case, the Lorentzian fitting in Figure 5.12 indicates a lifetime of 30 fs for the mode corresponding to peak a. Similar analysis gives a lifetime of 36 fs for the mode corresponding to peak b. The surprisingly close values between the two peaks in turn support the argument of the observation of a single normal mode.

It should be pointed out that most of the observed peaks are probably still made up of superposition of single normal modes. Yet the fact that they are much narrower than those in the far-field spectra suggests that the superposition, if any, is composed of much fewer modes. This observation is justified, in line with the inhomogeneous localization scenario of polar excitations in large self-affine clusters.

The observed results are also pertinent to surface-enhanced Raman spectroscopy (SERS). Our measurements indicate that for fractal objects, which constitute by far the largest set of SERS-active substrates including aggregated colloids and cold-deposited
Figure 5.12 Expansion of peak a in Figure 5.10. The red curve is a Lorentzian line fitting.
films, there is no simple correlation between the high local electric-field strength which is predominantly responsible for SERS and sample topography, in contrast to the suggestion by calculations on periodic structures\textsuperscript{12} or on very small aggregates,\textsuperscript{13} that the most effective SERS-active regions are the interstices between particles.\textsuperscript{14} For example, for a 600 nm excitation of the sample whose spectra are shown in Figure 5.11, the local field would be much stronger at spot \( C \) which is a flatter area than spot \( B \), an interstice. Thus, molecules binding to \( C \) would very well contribute more, per molecule, to the total SERS signal observed, compared to those binding to \( B \). Of course some portions of the surface, perhaps interstices like \( B \), may still be chemically more favorable for molecular binding. Also, the portion of the surface excited is sufficiently large to encompass all types of surface features simultaneously for all excitation wavelengths, despite the localization. Hence for SERS collected from macroscopic portions of the surface, the SERS intensity would be characteristic of the mean field strength excited by a chosen laser wavelength rather than of any statistical fluctuations in the types of surface morphology excited. Further investigation can be made by collecting SERS signals with a near-field probe, which should result in highly variable SERS intensities according to the portion of the surface interrogated and the excitation wavelength used.

As seen in Figures 5.10 and 5.11, there are different resonance peaks for different spots, even within a small wavelength range. Marvel \textit{et al.} recently studied computationally a similar problem by simulating the surface of a 10,000-particle 3D cluster-cluster aggregate of silver.\textsuperscript{15} The calculation used exact interaction formulae between monomers and the dielectric function of silver reported by Johnson \textit{et al.}\textsuperscript{16} The results show that resonances exist in the visible spectral range, and vary with the spot on surface which is interrogated, with the widths on the order of 50-100 nm. The discrepancy in peak width could be due to the approximation made in the theoretical treatment and/or the parameters chosen for the simulations. Further computational studies are underway.
We note that caution should be taken in the interpretation of near field microscopic and spectroscopic results. Pohl et al pointed out recently that the motion of the tip normal to the sample surface (z-motion) caused by the gap-width control can give rise to undesired crosstalk in the near-field optical images. The z-motion artifact generates features in the optical image that are highly correlated with the structures in the topographic image. Thus an optical image showing only topographic features can be a genuine near-field optical picture as well as a pure z-motion artifact image, or a superposition of both. In our experiment, there appears no phenomenon, i.e., correlation between topographic and optical images of self-affine silver films, that usually exist when the near field optical image is believed to be an artifact due to the z-motion of the fiber tip. Thus we believe such artifact, if any at all, is not an important factor for our imaging. On the other hand, there do appear some modulations upon the peaks in the optical spectra (Figure 5.11) when the dye laser was used, which turns out to be the consequence of the folded cavity geometry of the dye laser, as confirmed by the controlled experiment. Such modulations do not appear when a Ti/sapphire laser is used.

We therefore conclude that the major elements relating to field localization and enhancement of the predicted optical properties of self-affine surfaces have been demonstrated microscopically and spectroscopically.

5.3 Some related technical issues

5.3.1 Formation of colloidal films by cluster-cluster aggregation

In the silver soles prepared by the reduction of silver nitrate (AgNO₃) with sodium borohydride (NaBH₄), the colloidal silver particles are surrounded by an electrical double layer, arising from adsorbed nitrate and borohydrate ions and the cations attracted to them. This results in a Coulombic repulsion between the particles which decays approximately as the inverse interparticle distance. The weak minimum in
the potential energy at moderate interparticle distances defines a stable arrangement for the colloidal particles, which can be easily disrupted by medium effects and the thermal motion of the particles. The electric repulsion associated with the charged double layer is sufficiently high to prevent particle agglomeration. Thus the colloidal solution can be kept stable for a long time. It also explains why the reacting solutions have to be cooled before mixing, which helps to reduce the thermal motion of the particles.

The stabilized sol can be coagulated if the surface charge on the particles is reduced by the displacement of adsorbed anions by a more strongly binding neutral adsorbate. The colloidal particles then collide and agglomerate under the influence of the van der Waals attractive forces. This phenomenon has previously been demonstrated by the addition of pyridine to a gold sol. The method has been widely used to prepare colloidal films for SERS studies.

The color of silver sol, and the relationship of the color to particle size have been the subject of research for a long time. Silver colloid, as well as colloids of gold and copper, have characteristic colors, resulting from strong absorption in the visible region of the spectrum. These absorptions are a manifestation of the electronic structures of the metallic particles and are due to the excitation of plasmon resonances in the confined electron gas of the particles. The absorption spectrum is related to the particle size and relative dielectric properties compared to the surrounding medium.

The wavelength of the absorption maximum is dependent on the size and shape of the particles and to their proximity to each other. As the particle size increases due to colloid aggregation, the absorption maximum splits into two peaks, one corresponding to the transverse resonance which remains at the wavelength of the spherical particles, and a second corresponding to the longitudinal resonance which shifts to about 500 nm (Figure 3.4). This allows the use of UV-visible absorption spectra to estimate the degree of aggregation.
5.3.2 Shear force response of the fiber tip

The shear force AFM is based on the fact that there is a tangential friction force microscopically between the tip and the sample when the tip is close enough to the sample. The nature of the shear force is still open to research. The van der Waals force does not start to make a significant contribution until the tip-surface distance is down to a few Angstroms, thus it cannot account for the shear force interaction, which usually starts to take effect in the nanometer range. It is known that distance, viscosity, type of material etc. are some of the factors affecting the shear force. The fact that such a shear force depends on the nature of the sample could explain the discrepancy between different reports on the tip-surface distance that the shear force starts to be felt. Several research groups claim that the shear force starts to decrease the dithering magnitude of tapered tip when the distance is down to a few tens of nanometer. One group\(^1\) found the value to be around 140 nm for liquid glycerol as a sample, while another report showed the value to be 25 nm under ambient conditions.\(^{22}\)

To clarify the situation, or at least to understand such behavior for the sample we studied, the shear force response was measured with different tips for different samples or different spots on the same sample of colloidal silver films. The results are shown in Figure 5.13. Curves \(a\) and \(b\) are collected with the same tip on different spots of the same sample, while curve \(c\) is collected with a different tip on another sample. The \(Z\) value is defined as zero, when the dithering magnitude of a tapered tip is first completely damped as the tip moves towards the surface. Several tapered tips were purposely broken in this manner. The absolute tip-surface value is then determined by the z-direction sensitivity of the piezoelectric tube.

The results show that, for the samples we studied, the dithering magnitude of tapered tips remains constant for tip-surface gaps above 28 nm. When tip-surface distance decreases below 28 nm, the signal, and thus the magnitude of tip dithering,
Figure 5.13 Shear-force signal vs. tip-surface distance.

Curves a and b are on different spots of the same sample with the same tip; curve c is on another sample with a different tip. Both samples were prepared by adsorbate methods.
decreases almost linearly, until the tip crashes into the surface and the signal goes to zero (Fig. 4.1).

Note that different curves in Figure 5.13 represent different locations of the different silver samples. Their similarity implies that, for the samples studied and the given configuration, the shear force interaction is quite uniform.

It should be noted that the signal vs. tip-surface distance curves are obtained by monitoring the amplitude times \( \cos \beta \), where \( \beta \) is the phase angle between the driving voltage applied to the bimorph and the oscillation of the tip. Upon interaction with the surface of the sample, the resonance is damped, reducing the amplitude of tip oscillation. In addition, the phase difference between the driving signal and the actual motion of the tip also changes as a function of interaction force. Thus, the product of the two signals is more sensitive to small forces than either of the signals alone. This product of the two signals is easily processed by a lock-in amplifier, and used as feedback to control tip-surface distance.

Most of the imaging was done when the tip dithering amplitude was damped by 10 per cent. This corresponds to a tip-surface distance \( Z \) of approximately 25 nm (Figure 3.7). To see whether different \( Z \) values may affect the results, imaging was also done at other \( Z \) distances. Figure 5.14 shows two pairs of topographic/optical images of the same region scanned at different tip-surface distances. (a) were collected at 30 per cent damping (20 nm away from surface), while (b) collected at 10 percent damping (25 nm).

There appears no distinct differences between the topographic and optical images. The resolution for the topographic image in (a) is slightly better than in (b). The optical images have almost identical patterns. This result is understandable. Because the characteristic decay length of the evanescent wave is in the order of \( 0.5 \lambda \), a small change from 25 nm to 20 nm should not have much impact.
Figure 5.14 Imagining at two different tip-surface distances. a) 20 nm; b) 25 nm. Top series of images are topographs, the lower, optical images.
The operating load for the shear-force is inversely correlated to the tip-surface distance. Its range is limited in two ways. If the applied load on the tip is too small, modulations on the tip resonance will be too weak, and the signal-to-noise ratio of the image will be low. On the other hand, if the load is too large, the sample and/or the tip may be destroyed by the friction force, which was observed on a gold grating image, where the tip-surface distance is approximately 14 nm (Figure 5.15). Since the above observation (Figure 5.14) suggests that the resolution, in both topographic and optical images, does not improve much over the available range of tip-surface distance, images are mostly collected with an approximate tip-surface distance of 25 nm, which seems to have little damage on either sample or tip.

5.3.3 Dithering amplitude of the tip

Consider the geometry of shear force mechanism, as shown in Figure 5.16. The fiber tip is glued to the bimorph, and is caused to dither when the bimorph oscillates. At resonance, the tip amplitude is given by \( A = aQ \), where \( Q \) is the quality factor of the resonance, and \( a \) is the displacement of bimorph. The displacement \( a \) is given as:

\[
a = \frac{d_{31}}{8} \cdot U \cdot \frac{3}{\varepsilon} \cdot \left( \frac{l}{h} \right)^2,
\]

where \( d_{31} \) is the relevant piezoelectric coefficient, typically 1 \( \text{Å/V} \); \( l \) and \( h \) are the length and thickness of bimorph, respectively.\(^\text{23}\) In our configuration, \( l \) and \( h \) are 7 mm and 0.52 mm, respectively. \( U \) is usually 40 mv and \( Q \) is typically 50 (Figure 4.2). Thus \( A \approx 136 \text{ Å} \). This indicates the lower limit of the lateral resolution, regardless of the sharpness of the tip. It also shows that, in contrast to the usual non-contact AFM, where a high quality factor \( Q \) is preferred to achieve better sensitivity, shear force AFM prefers a lower \( Q \) for improved lateral resolution.

Shear force AFM is similar to non-contact AFM, with the significant difference that the tip dithers laterally in shear force AFM and vertically in non-contact AFM. Therefore, the resolution of shear force AFM not only depends on the sharpness of the probing tip, but also on the dithering amplitude of the tip, which makes it difficult to
Figure 5.15 Shear-force AFM image of a gold grating. Tip-surface distance is approximately 14nm.
Figure 5.16 Scheme of tip/bimorph dithering.
achieve atomic resolution. Nevertheless, its resolution is usually good enough for NSOM, which does not achieve atomic resolution.

One modification was invented to improve the lateral resolution of shear force detection. Considering the two geometries in Figure 5.17, normally, the tip is positioned vertically to the surface as in (a). In this case, the force that modulates the tip dithering amplitude takes effect over the whole range of \( A \), thus the lateral resolution is limited by \( A \). If the tip is positioned, instead of vertically, at an angle \( \beta \) to the surface, as in (b), the "effective contact", between the tip and surface is reduced. This should in principle improve the lateral resolution to some degree, although care should be taken to avoid the tip approaching the surface by laterally.

Such a configuration is somewhat similar to the tapping-mode AFM, where the tip dithers normal to the surface. In practice, such a modification is easily realized by using an oblique holder that supports the bimorph and the tip. The improvement is illustrated further in Figure 5.18, where (a) is obtained with an oblique holder and (b) with a flat holder.

5.3.4 Effect of beam spreading

Because there is divergence for the laser beam coming out of the fiber that transports light from the laser to the prism, the incident light will not be uniform across the scanning area. Let us consider the effect of this intrinsic inhomogeneity of the incident beam across the scanning area.

Assuming a Gaussian profile of the incident beam, its beam waist, which is determined by the fiber specifications and the system configurations, will describe the beam divergence. The single mode fiber has a numerical aperture (NA) of 0.11. The fiber is placed at approximately 1.5 mm away from the interface where total internal
Figure 5.17 Different orientations of tip approach.
Figure 5.18 AFM images of commercial Au gratings
Tip approaches in a) oblique; b) normal direction.
reflection takes place. This gives a beam waist of the beam at the interface \( w = 0.11 \times 1500 = 165 \ \mu m \). Compare to Figure 3.7, where the Gaussian profile of the laser beam out of the fiber has a beam waist of approximately 75 \( \mu m \). The difference in beam spreading is due to the fact that the fiber was placed much closer to the detector of the beam analyzer when the measurement shown in Figure 3.7 was done.

Experimentally, a typical scanning area is 3 \( \mu m \times 3 \ \mu m \). Although the exact position of this area within the profile cannot be accurately determined, we may assume it is within ±80 \( \mu m \) around the center, since the tip is usually probing the brightest part at the interface where total internal reflection happens. Based on these numbers, simple calculations reveal that the possible maximum difference in the intensity of incident beam is only about 3% between the two ends of the 3 \( \mu m \times 3 \ \mu m \) area. This shows that the effect due to beam spreading is negligible.
Reference

15. V.A. Markel (private communication).
Chapter 6. Conclusions

A scanning photon tunneling microscope (PSTM) combined with shear-force atomic microscope (AFM) was designed and built. It allowed us to study the topography of the surface and its optical response simultaneously on a sub-microscopic scale. The lateral resolution in the topographic images, 30 to 50 nm, varied with different fiber tips prepared. While operating in the near field region, the optical resolution which overcomes the diffraction limit with a fine tip, is typically about 100 nm. Thus, it is possible to obtain site-specific spectroscopic information. The system was employed to study the optical behavior of fractal and non-fractal silver colloidal films.

Near-field microscopy with simultaneous topographic imaging shows that the electromagnetic fields excited in self-affine silver colloidal thin films are localized in very small portions of the films. There is no simple correlation between the topographic and optical images. The pattern of high-field areas varies greatly with excitation wavelength. In comparison, similar imaging on non-fractal silver films displays correlation between the topographic and optical images, which persists for different excitation wavelengths.

Near-field spectroscopic study complemented further the microscopic study. A tunable CW laser was used to excite the silver colloidal thin films. When scanning the incident laser site specific spectra showed that distinct resonance arises from different spots on the same sample.

This observation validates a recent theory of the optical response of self-affine fractal objects and also indicates that the locus of optical effects such as surface enhanced Raman does not reside in special topographic elements such as interstices. Additionally, it is shown that the conclusions of the theory, which was based on a quasi-
static approximation, are qualitatively valid for self-affine films considerably larger than the exciting optical wavelength.