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Optical image contrast enhancement in near-field optics induced by water condensation

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ABSTRACT

In surface science, water adsorption on hydrophilic samples is usually invoked, addressing their nanoscale experimental effects in scanning probe microscopy, especially when water condensates between tip and sample. Here we study by means of a numerical hybrid method the effect of water bridge formation in near field imaging. We show how this nanometric water neck plays an important role not only in the optical image, producing a high contrast at hydrophilic patches, but also in the tip–sample distance control. This work contributes with a new methodology able to retrieve the original application of SNOM, using it as an instrument to study the optical properties of matter overcoming the diffraction limit. It extends the application of SNOM to study the hydrophilic character of polymeric and biological samples, taking advantage of ubiquitous effect of humidity when operating in ambient condition.

1. Introduction

Similar to the Atomic Force Microscope (AFM), SNOM forms part of the vast family of scanning probe microscopes (SPM) and so, it is affected by the similar issues [1]. In AFM, sample images are obtained by measurement of the local forces created on a probe (sharp tip) while in proximity to the surface of the sample. The accurate measurement of small forces between the tip and the sample using sophisticated feedback mechanisms allows a full characterization of the tip–sample interaction [2]. For near field microscopes, images are obtained from the analysis of local interaction of the incoming light with the probe–sample system. Depending on the experiment a wide variety of probes have been used [3], ranging from AFM tips to fiber tapered tips (uncovered or with different coatings). SNOM apertureless probes (AFM tips like) configuration along with the feedback mechanism provide working distances between tip and substrate in the range of angstroms, allowing, for example, the tip interaction with the near field at the surface and the far field coming from the illuminating light. Other probes, like those based on tapered optical fibers, have been used as illuminating light sources, or as light collectors of scattered radiation coming from the surface. In this case, tip–surface distance may be controlled using feedback systems based on the lateral interaction between tip and sample, known as shear force. Very small shear forces between the tip and sample could induce a resonance shift large enough to cause substantial changes in the amplitude and phase of the probe oscillation [4], as measured using tunning fork or optical lever configurations [5,6]. Perhaps, the most important limiting factor in SNOM imaging interpretation is the poor determination of the actual distance between tip and sample [3,7,8]. Although many improvements have been introduced, the effective control of the tip–sample distance is a major unresolved issue [9].

It is well established that, when working in air conditions using AFM probes, the humidity presence causes characteristic jump-to-contact events, in a first approach, due to spontaneous formation of water meniscus between tip and sample [10]. Unfortunately, the origin of shear force is still unknown, and some authors argue that it may be somehow affected by environmental humidity [8,11–13]. Consequently humidity has been treated as a problem for SNOM, as it obscures the proper operating conditions for shear force control mechanism [12,13]. For that reason, a large amount of studies ignore the optical image information focusing only on the topographic or spectroscopic interpretation [14–16]. Authors [17] who have been able to study the optical signal under a variable environmental humidity have shown the conditional increase in the optical signal with environmental humidity depending on the hydrophobic character of the sample. Recently, Kaupp [17] suggested that the inclusion of the water neck concept should be

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considered for any modeling or simulation of the experimentally secured enhancement effect.

Since, ubiquitous water presence at relatively high humidity experimental conditions will modify the dielectric properties of the medium between tip and substrate, optical images could be altered by humidity and water condensation. Actually, hydrophilic SNOM tips condense some water layers, leading to the formation of a water bridge (meniscus) between the tip and a hydrophilic sample for small tip–sample distances. The shape of such meniscus will depend on the geometry of both surfaces, their separation, and environmental conditions (temperature, relative humidity).

In this article we aim to include the effect of the environmental humidity and water bridge formation on the SNOM-acquired images as an optofluidic application tool of both imaging and, chemical and biological surfaces detection [18]. We used two-dimensional (2D) hybrid simulations that combine two different computational methods: on one hand, a Monte Carlo (MC) description of the water condensation between tip and sample and, on the other hand, a state-of-the-art method for describing the light propagation through the tip-water neck-sample systems.

2. Methods

The 2D-like SNOM system studied is sketched in Fig. 1, based on a geometry previously described by Wang et al. [19]. A tapered optical fiber probe coated with a perfect conducting metal layer is placed at a variable distance *h* from a non-homogeneous dielectric substrate. The 2D tip apex is represented by a trapezoidal structure with an aperture of 100 nm and an angle of 18.4°. We have considered a flat substrate formed by a dielectric material with a 10 nm thickness, where a dielectric patch with a different diffraction index and the same thickness has been embedded. The resulting system does not present topographic contrast.

Water meniscus formation between tip and sample is studied using a 2D lattice gas model that successfully describes the gas–liquid transition in water [20]. This model has been extensively used to study structural and thermodynamic properties of water as well as the formation conditions and geometry of the water meniscus formed between an AFM tip and a substrate [21]. The fluid is represented by a 2D square lattice with a spacing of 3 Å. In the model, we assume thermal and phase equilibrium with a bulk reservoir, specified by a temperature *T* and a chemical potential μ, directly related to the relative humidity $Rh = e^{(\mu-\mu_c)/k_B T}$, being k_B the Boltzmann constant and μ_c the critical chemical potential (if $\mu = \mu_c$ then $Rh = 100\%$).

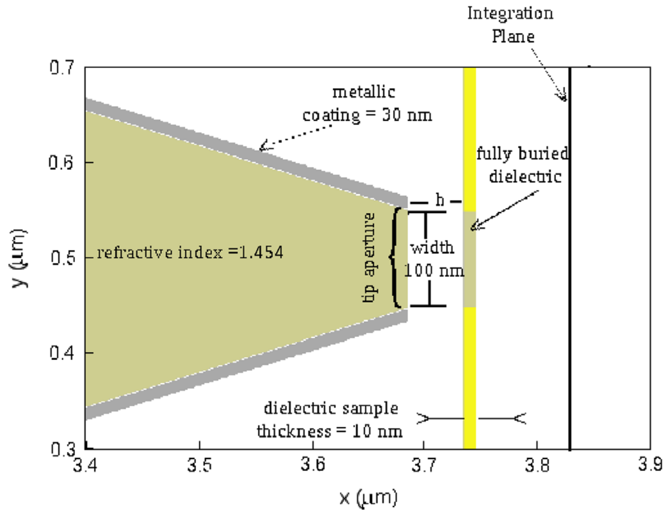

Fig. 1. Schematic representation of the region of interest for the simulated tapered coated optical fiber tip. The tip is used for illuminating the region under the aperture, while transmitted signal is detected at a sample distance of 100 nm (integration plane).

We have performed a (*V*,*T*,μ) Monte Carlo (MC) numerical simulation at laboratory conditions, $T = 293$ K, using a Hamiltonian that describes the interaction between water molecules and between water molecules and different surfaces [22]. This model assumes that each site (i,j) of our lattice is either occupied with a water molecule $\rho(i,j) = 1$ (liquid phase) or empty $\rho(i,j) = 0$ (gas phase).

The Hamiltonian reads as

$$H = -\varepsilon \sum_{\langle (i,j)(i',j')\rangle} \rho(i,j)\cdot\rho(i',j') - \mu \sum_{(i,j)} \rho(i,j) + b_S \sum_{(i,j)\in Susbstrate} \rho(i,j) + b_t \sum_{(i,j)\in tip} \rho(i,j)$$

This Hamiltonian is very similar to the Ising-like model used to describe many physical systems. The first two terms describe the water–water interaction and the water–chemical potential interaction correspondingly. Each water occupied site interacts with its (occupied) neighbor sites with an attractive energy $\varepsilon = 9$ kJ/mol. This value has been chosen to reproduce the critical temperature of real water ($T_c = 647$ K). Conditions considered correspond to equilibrium bulk evaporation. The third and fourth terms describe the interaction of water molecules with the sample and tip surfaces, respectively. Tip and sample surface sites feel an interaction energy with water of value $b_T = -56$ kJ/mol and $|b_s| = 46$ kJ/mol, respectively. Two kind of water surface interaction constant (b_s) were considered for the water sites close to the dielectrics surface regions in the substrate, $b_s < 0$ (implying a negative contribution to the total energy of the system when water and surface interact) for the hydrophilic surfaces and $b_s > 0$ (implying a positive contribution to the total energy of the system when water and surface interact) for the hydrophobic surfaces [22].

Water density average at each lattice site $(0 < \langle \rho(i,j) \rangle < 1)$ was calculated after system thermalization and considering 20,000 different microstates. Once $\langle \rho(i,j) \rangle$ was known for every site in our lattice, the effective refractive index $n(i,j)$ at a given site (i,j) is calculated assuming that for $\langle \rho(i,j) \rangle = 0$ the refractive index is $n = 1$, for $\langle \rho(i,j) \rangle = 1$ the refractive index is $n = 1.33$ (water refractive index for the temperature considered), and that for intermediate $\langle \rho(i,j) \rangle$ values there is a linear dependence $(n(i,j) = 1 + 0.33\langle \rho(i,j) \rangle)$ between the refractive index and the average water density [23].

The propagation of the electromagnetic (EM) radiation in our system was studied by means of a 2D Finite Difference Time Domain (FDTD) simulation, based on Yee algorithm [23], with a Perfect Matching Layer (PML) as boundary condition for perfect absorption [24]. TM_z fundamental mode is propagated through the dielectric coated fiber guide with frequency $\omega = 3.77 \times 10^{15}$ Hz ($\lambda = 500$ nm), when radiation gets to the tapered region, the geometrical condition for propagation changes from the fundamental mode to the evanescent field. Radiated intensity, at transmission, is integrated at a plane surface located at a distance $D = 100$ nm from the sample surface as shown in Fig. 1. For completeness, also far-field integration surfaces, situated at several wavelengths from the substrate, have been considered but the overall trend was maintained, except for the expected decay in the intensity values with distance. In our study all intensities were normalized to the one collected without any substrate, I_0. In order to match FDTD lattice constant with the one used in the lattice-gas simulation, a lattice step of 9 Å was considered for the FDTD. In this way, the refractive index for each FDTD node was calculated as the average of those values corresponding to nine water lattice nodes included within the FDTD cell. General assumptions were taken into account for the simulation. Indeed, all water necks calculated at equilibrium were considered to be stable during the