Role of Capillarity on Field Enhancement in Tip-enhanced Raman Spectroscopy

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Introduction

Capillarity interactions are found on solid surfaces under ambient conditions. It can exist due to water condensation, between two solid surfaces, the meniscus distance intact with the condensation of steam in liquid phase, given that the gap between the sample. The next work shows the simulation of the effect of water films in Electric Field Enhancement under different humidity conditions and tip-sample distances.

Methods and Models

The capillary interaction decomposes into two different terms: Laplace pressure force and surface tension. Meniscus will grow until mechanical equilibrium is reached, and pressure inside the meniscus has a stable value which is determined by Relative Humidity (RH), tip-sample distance, contact angles and tip radius. If thermodynamic equilibrium is assumed, we can use to describe the meniscus shape formed between the AFM tip and the sample the Kelvin equation which relates meniscus curvature and relative humidity [9].

Kelvin Equation:

\[ \frac{1}{a} + \frac{1}{b} + \frac{1}{c} = \frac{1}{\gamma} \frac{ln(h/m)}{100} \]

Where \( \gamma \) = \( \frac{2 \pi \gamma_{r, l, a} T}{\text{mol}^{-1} \cdot K^{-1}} \) Molar gas constant

\( T \) = 298 K Absolute system temperature

\( \gamma_{r, l, a} = 8.31 \text{ J mol}^{-1} \cdot \text{K}^{-1} \) Water liquid-vapor interface tension

\( V_{mol} = 1.8 \cdot 10^{-5} \text{ mol} \cdot \text{m}^{-3} \) Molar volume of water

RH = 70% Relative humidity

Using equation system given in [5]:

- Outer radius of meniscus

\[ R = l \cdot \pi \cdot (\cos(\theta - \alpha) - \cos(\beta - \alpha)) / \sin(\theta - \alpha) \]

- Inner radius of meniscus

\[ l = R \cdot \pi \cdot (\sin(\theta - \alpha) + 1 - \sin(\theta - \alpha)) / \sin(\theta - \alpha) \]

- Capillary Force

\[ F = \frac{\pi \cdot \gamma_{l, r, a} \cdot \sin(\theta - \alpha) + 1 - \sin(\theta - \alpha) + \gamma_{l, r, a} \cdot 2 \cdot \sin(\theta - \alpha) + \gamma_{l, r, a} \cdot 2 \cdot \sin(\theta - \alpha)}{\sin(\theta - \alpha)} \]

\[ \alpha = 1.8 \cdot 10^{-5} \text{ mol} \cdot \text{m}^{-3} \]

The results are used to model the geometry in ANSYS®, and so to study the effect of the meniscus in the electric field enhancement.

Simulation Parameters

Values of the Geometry for RH = 70%

<table>
<thead>
<tr>
<th>Distance</th>
<th>0.5</th>
<th>177</th>
<th>133.41</th>
</tr>
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Simulation 70% RH Electric Field Enhancement

In the simulations it was observed the change of the electric field enhancement due to the presence of water bridge. The decrease in the EFE is about 24%.

Simulation and Results

Relation between Capillary Force and distance between the Tip and surface at different RH

ANSYS with RH = 70%

Cross section of 3D simulations of silver tip and SiO, Si surface (tip-sample distance of 0.5 nm) excited by a laser beam at 532.8 nm.

ANSYS simulations were performed for no meniscus and meniscus given by 70% RH, 0.5nm tip-sample distance. Electric field enhancement decreased in 24% for this parameters. This would suggest a shift in the Plasmon resonance frequency.

Summary

- The formation meniscus is strongly related to RH. Simulations were performed for different values of humidity 35%, 60% and 70%.
- Capillary forces were calculated to verify the presence of meniscus. It is observed that for 35% RH the meniscus forms at 0.4 nm tip-sample distance, for 60% RH the meniscus forms at 0.8 nm tip-sample distance and for 70% RH the meniscus forms at 1.095 nm tip-sample distance.
- ANSYS simulations were performed for no meniscus and meniscus given by 70% RH, 0.5nm tip-sample distance. Electric field enhancement decreased in 24% for this parameters. This would suggest a shift in the Plasmon resonance frequency.

References: