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Introduction

Surface enhanced Raman spectroscopy (SERS) is a powerful technique that uses metal nanostructures (Au, Ag, Cu) to gain in the best case single molecule sensitivity [1]. Most of the enhancement is attributed to the enhancement of the electric field near the surface of the metal, because the Raman signal in this case scales approximately proportional to the fourth power of the electric field strength [2]. A combination of AFM and the discrete dipole approximation (DDA) is a promising approach for a better understanding of solid SERS substrates. Using the AFM the geometry of a nanostructure on a flat substrate or a structured surface can be measured very accurately and the DDA is a well-established method for solving scattering problems for arbitrary shapes, which makes few assumptions about the sample other than the target geometry [3]. With our own MATLAB implementation of the DDA that calculates the nearfield from a given AFM image we are trying to predict the SERS enhancement factors of sputtered thin films.

From AFM measurements to the final results

1. filtered (to avoid spike like features, discontinuities between lines and „nano-roughness due to noise“)
2. corrected (median plane subtracting, setting zero point, flattening substrate regions ...)
3. cut (region of interested is selected)

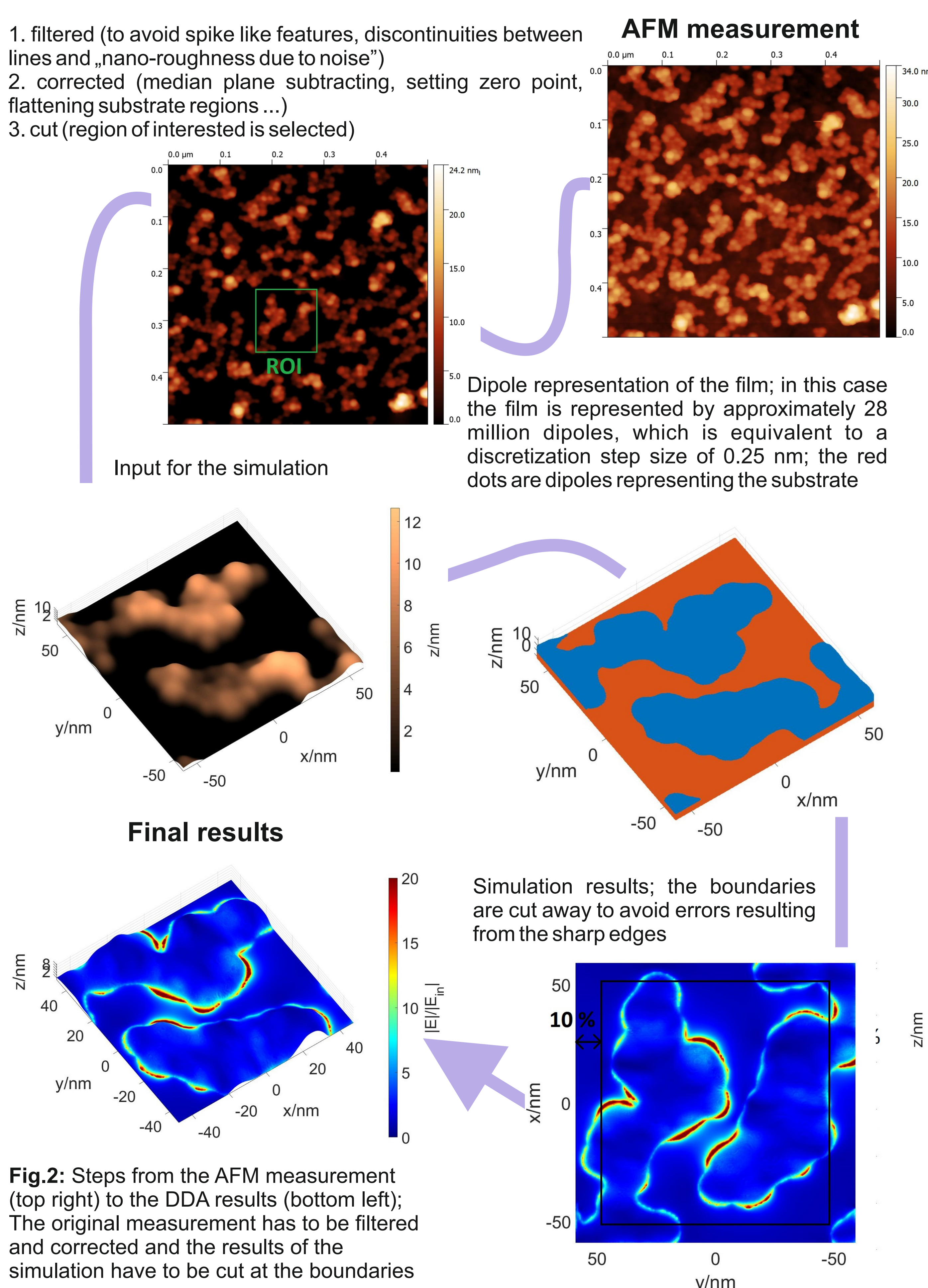


Fig.2: Steps from the AFM measurement (top right) to the DDA results (bottom left); The original measurement has to be filtered and corrected and the results of the simulation have to be cut at the boundaries

Conclusion

We have developed a MATLAB based implementation of the DDA, which can perform simulations of electric fields from an AFM image, with a discretization step size comparable to the resolution of an AFM. The qualitative simulations of sputtered Au thin films (currently used as SERS substrates at our institute) allow us to predict the positions of hot spots (which are responsible for the bulk of the enhancement) on large substrate areas. Quantitative simulations of the hot spots predict enhancement factors of some 10^3 , which is in agreement with our measurements. However, in order to make a true comparison between simulation and experiment, we need to go beyond the crude E^4 -approximation that is often used to analyze SERS substrates. We have outlined the mathematical ground works to accurately connect the simulations to the measurements. Unfortunately additional simulations that are not yet available are necessary to do so.

References/ Literature

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- [2] Garcia-Vidal, F.J. and Pendry, J.B. (1996), Collective Theory for Surface Enhanced Raman Scattering, *Phys. Rev. Lett.* 77, 1163
- [3] Yurking, M.A. and Hoekstra, A.G. (2007), The discrete dipole approximation: an overview and recent developments, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 106(1), 558-589

Acknowledgements

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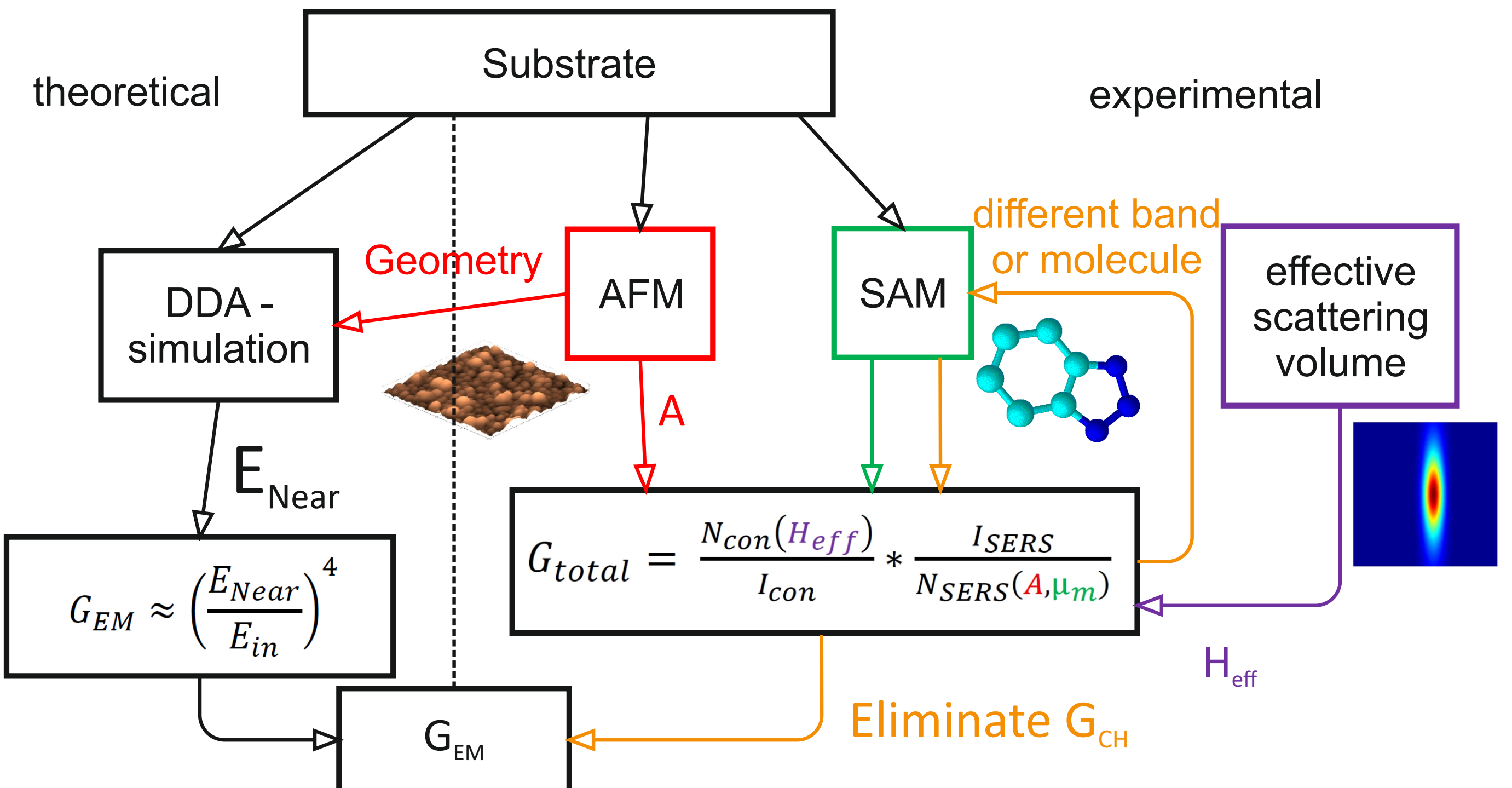


Fig.1: Flow chart of our approach to predict SERS enhancement factors; this poster focuses on the theoretical (left) part

Results for sputtered Au films (E^4 -approximation)

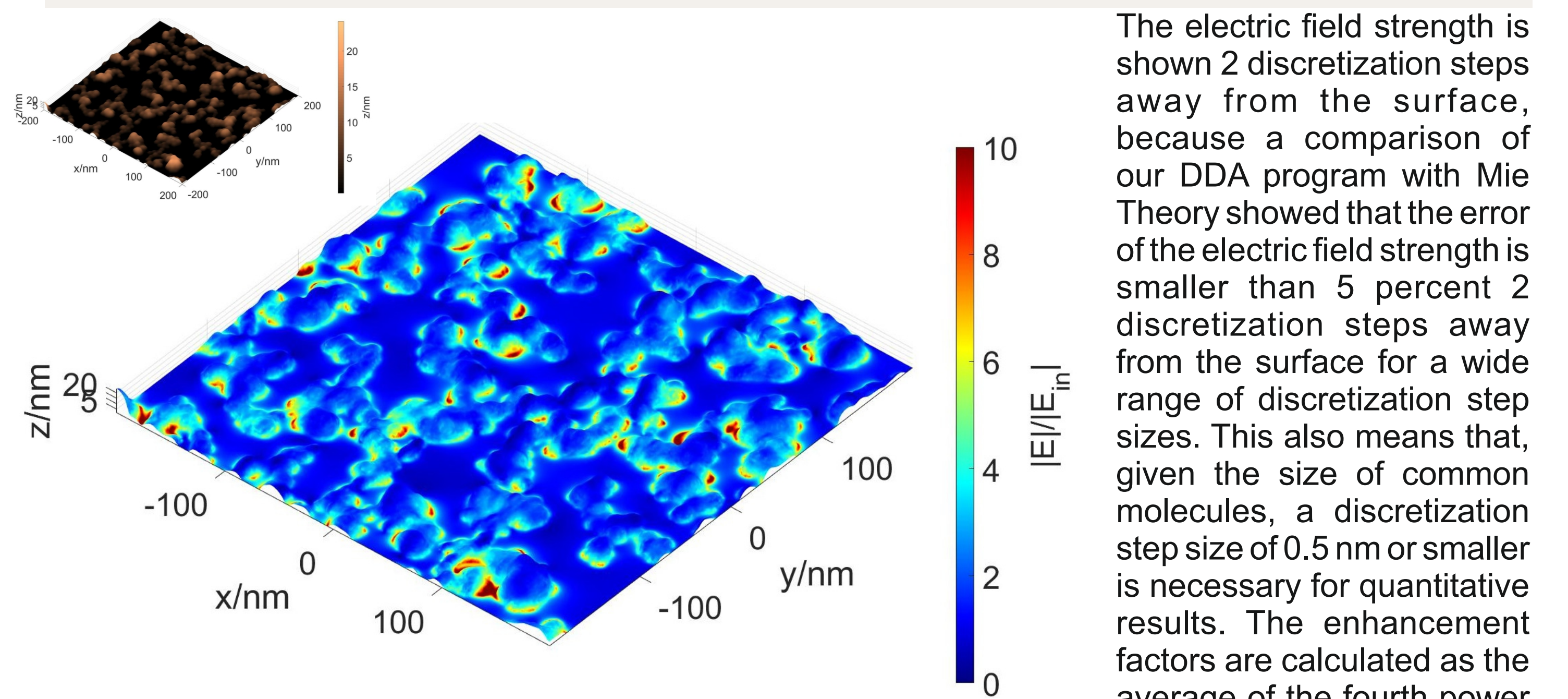


Fig.3: Large scale simulation of a substrate; the discretization step size is 1 nm, which is too large for quantitative predictions, but the locations of the hotspots are visible

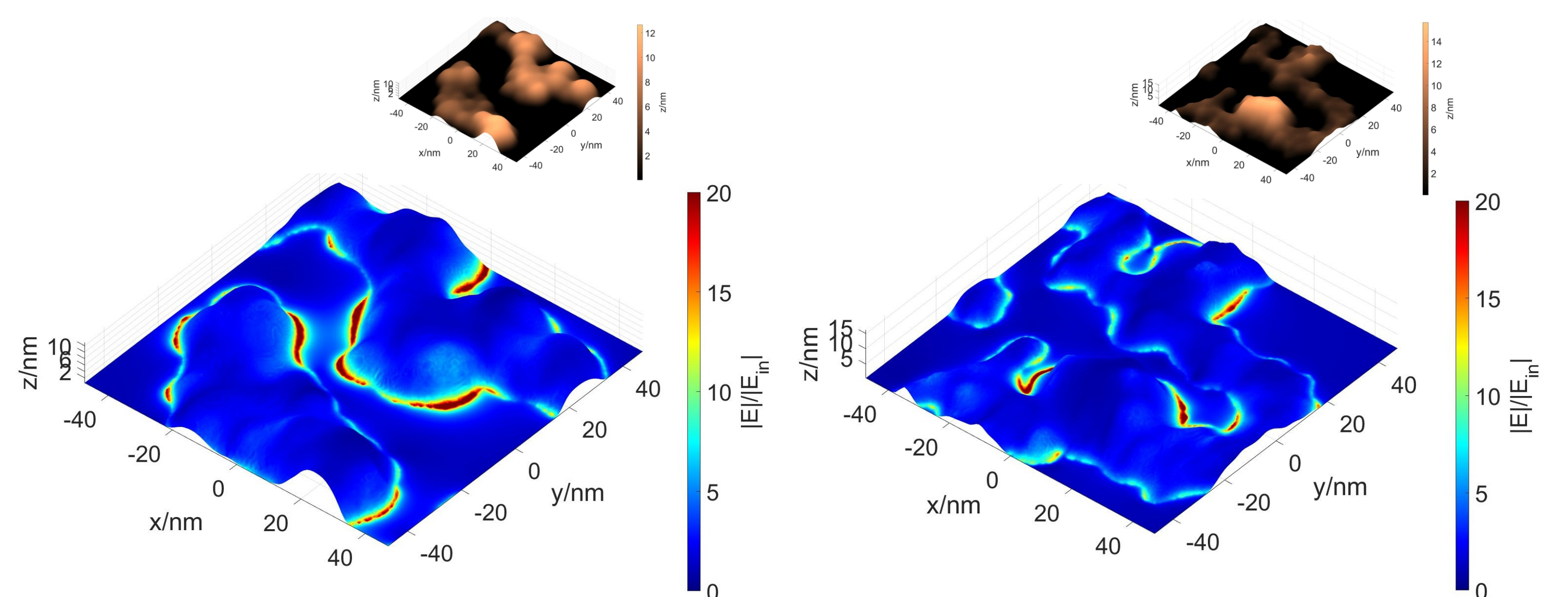


Fig.4: Detailed simulation of two substrates; In both cases the E^4 -approximation predicts the correct order of magnitude of the enhancement, but for precise predictions the E^4 -approximation is inadequate

Beyond the E^4 -approximation

$$G_{total}(\omega_R, \vec{d}) = \frac{\sum_{i=\perp, \parallel} \langle |\vec{E}_i(\omega_R) * \vec{\alpha}_{SERS}(\omega_R, \vec{d}) * \vec{E}(\omega_L)|^2 \rangle}{|E_0|^4 \sum_{k=\perp, \parallel} \langle |\vec{e}_k * \vec{\alpha}_{SOL}(\omega_R) * \vec{e}_L|^2 \rangle}$$

G_{total} ... total enhancement factor of the Raman band
 E_{\parallel} ... electric field strength parallel/perpendicular to the excitation laser
 E_0 ... electric field strength of the excitation laser
 ω_R ... frequency of the Raman band
 ω_L ... frequency of the excitation laser
 \vec{d} ... orientation of the molecule
 α_{SERS} ... Raman tensor of the molecule on the surface
 α_{SOL} ... Raman tensor of the molecule in solution
 $\rho_{SOLSERS}$... depolarization ratio of the Raman band in solution/ on the surface

Smart experimental choices:

- Raman band has a diagonal tensor ($\rho_{SOLSERS} \approx 0$)
- Raman tensor does not change significantly on the surface ($\omega_{SERS} \approx \omega_{SOL}$)

$$G_{total}(\omega_R) \approx \sum_{i=\perp, \parallel} \langle |\vec{E}_i(\omega_R) * \vec{E}(\omega_L)|^2 \rangle$$

$$\rho_{SERS}(\omega_R) \approx \frac{\langle |\vec{E}_{\perp}(\omega_R) * \vec{E}(\omega_L)|^2 \rangle}{\langle |\vec{E}_{\parallel}(\omega_R) * \vec{E}(\omega_L)|^2 \rangle}$$

measurable variable
 calculable variable
 unknown variable

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