# Supporting Information for “Enhancement and Confinement Analysis of The Electromagnetic Fields Inside Hot Spots”

Eduardo M. Perassi,[†] Luis R. Canali,[‡] and Eduardo A. Coronado [*,†]

*INFIQC, CLCM, Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba (5000), Argentina, and CIII, Universidad Tecnológica Nacional, Facultad Regional Córdoba, Córdoba (5000), Argentina*

E-mail: coronado@mail.fcq.unc.edu.ar

## Details of the VTV approach using DDA

Here we show our own implementation of the DDSCAT 6.1 [1] program in order to compute the electric field enhancement ($\Gamma$) as well as the trapped volumes ($V_T$). As it is standard in this approach, the target is replaced by a cubic array (with lattice parameter $d$) of $N$ polarizable point dipoles. Each dipole $j$ is characterized by a polarizability tensor $\alpha_j$ whose complex dipole moment $\mathbf{P}_j$ is given by:

$$\mathbf{P}_j = \alpha_j \mathbf{E}_{ext,j} \tag{5}$$

where $\mathbf{E}_{ext,j}$ is the electric field at position $j$ due to the contributions of all the other sources including the rest of the dipoles and the incident field. In our implementation the electric field in

[†]INFIQC
[‡]CIII

the vicinity of the NP was calculated by transposing eq 5

$$\mathbf{E}_{ext,j} = \alpha_j^{-1}\mathbf{P}_j \tag{6}$$

Then by adding probe dipoles of almost zero polarizability (setting their dielectric constant to $\varepsilon \approx 1.001$) outside the NP, the electric field at any position $j$ can be calculated using eq 6. An scheme of the material dipoles and the probe dipoles is shown in Figure 5. The material dipoles and the probe dipoles must fulfill the usual lattice dispersion relation.[2]

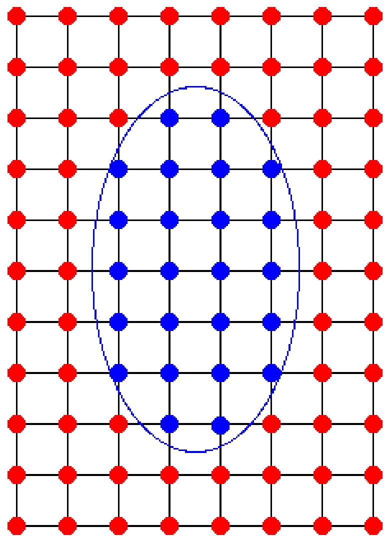

Figure 5: Scheme of the material dipoles (red) and probe dipoles (blue) used to compute the electric field

Since each probe dipole of the array occupies a volume fraction equal to $d^3$, the calculation of $V_T$ for a given $\Gamma$, if $d$ is small enough, can be approximated quite well considering the number of dipoles ($N$) where the enhancement is equal to or greater than $\Gamma$, then $V_T = N.d^3$. Although this procedure is quite simple and very easy to implement there could be some degree of inaccuracy, specially for small values of $V_T$. Other methods more appropriate to calculate volumes can be implemented but we found that due to the relatively small values of $d$ used in this work the error introduced by applying the present approximation is very small. We have not computed $V_T$ for very small volumes since this is the regime where more uncertainties on the field enhancement are expected.

# Comparison of the VTV approach with exact electrodynamic solutions for a prolate gold spheroid

In this section we compare the enhancement obtained using our VTV approach with exact electrodynamic calculations performed by Calandera *et al.*[3] for a prolate gold spheroid with $ar = 3$ and major axis 63.3 $nm$ illuminated at $\lambda = 633$ $nm$ with $\varepsilon = -10.84 + 0.762i$. The converged VTV curve for this target is depicted in Figure 6 bellow as well as the result of fitting this curve to eq 1 with the parameters indicated in Table 3. The maximum enhancement computed by these authors corresponds to values very close to the NP surface, so in order to make the comparison we take the volume of a gold atom ($V_T = 0.0125nm^3$) and compute the field. We obtained a value of $\sqrt{\Gamma} = 42$ which is in excellent agreement with the exact result $\Gamma = 47$ taken from Figure 2b of the same reference.

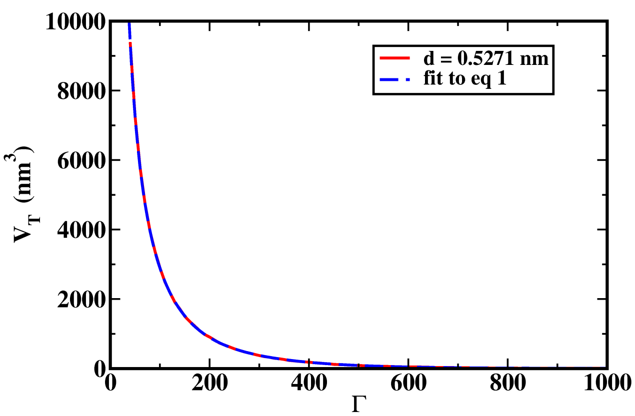


Figure 6: Comparison between the converged VTV curve resulting from DDA calculations and the curve fitted to eq 1 whose parameters are shown in Table 3, for the prolate gold spheroid considered in this section

Table 3: Parameters resulting after fitting the converged VTV curve to eq 1 for the prolate gold spheroid whose dimensions are indicated in the text at $\lambda = 633$ *nm*.

| parameters | spheroid |
|---|---|
| $\Gamma_{V_T=0}$ | 6598 |
| $A_0$ $(nm^3)$ | 0.434 |
| $k_0$ | 146.7 |
| $A_1$ $(nm^3)$ | 1.634 |
| $k_1$ | 49.2 |
| $A_2$ $(nm^3)$ | 4.262 |
| $k_2$ | 16.5 |
| *RMS per cent error* | 0.2 |
| *Correlation coefficient* | 0.999 |

# References


(1) Draine, B. T.; Flatau, P. J. *User Guide for the Discrete Dipole Approximation Code DDSCAT.6.1, "http://arXiv.or/abs/astro-ph/ArXiv/0409262"* **2004**.

(2) Draine, B. T.; Goodman, J. *Astrophys. J.* **1992**, *405(2)*, 685–697.

(3) Calandera, N.; Willander, M. *J. Appl. Phys.* **2002**, *92(9)*, 4878–4884.