Gold nanoparticle influence on SPC/E water structure and dynamics

Nina Albouy[a], Nicolas Lamoureux[a], Yilin Ye[a], Axel Gomez[b]

[a]Département de Chimie, Ecole Normale Supérieure, PSL University, 75005 Paris, France

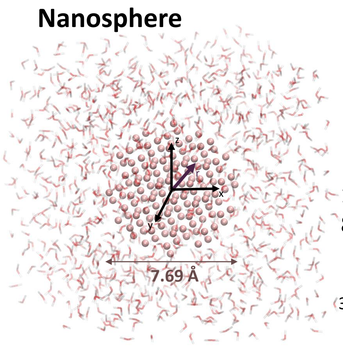
[b]PASTEUR, Département de Chimie, Ecole Normale Supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France

Introduction

Colloidal gold nanoparticles give a renewed potential to gold uses as they are of key importance for imaging, diagnostics, drug delivery or radiotherapy. Optical properties of gold nanoparticles are the most investigated, much less is their behaviour in solution[1].
Here, we study two shapes of gold nanoparticles in SPC/E water[2] to check out the effects of its presence on the dynamics and the structure of the solvent.

Methodology

Nanosphere



141 gold atoms
805 water molecules

31.65 Å x 31.65 Å x 31.65 Å box

Two systems: **nanosphere** and **nanorod** of same external surface

Force field

Lennard-Jones potential: $V_{LJ}(r) = \epsilon \left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$

Non-zero pair coefficients[2,3] :

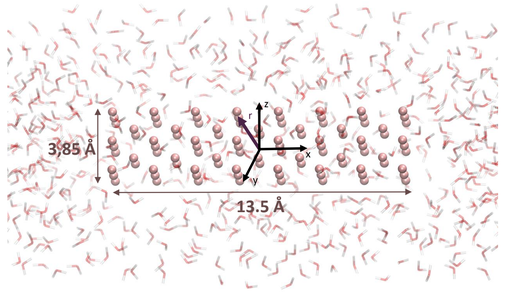
Au – O : $\epsilon_{Au-O} = 3.80\ \mathrm{kJ.mol^{-1}}$; $r_{Au-O} = 3.25$ Å

O – O : $\epsilon_{O-O} = 0.650\ \mathrm{kJ.mol^{-1}}$; $r_{O-O} = 3.55$ Å

Simulation time: 1 ns / 10 fs steps, 5 trajectories

Nanorod

100 gold atoms
380 water molecules



20.83 Å x 20.83 Å x 57.54 Å box

Results

Residence time in the first solvation shell of the nanoparticles

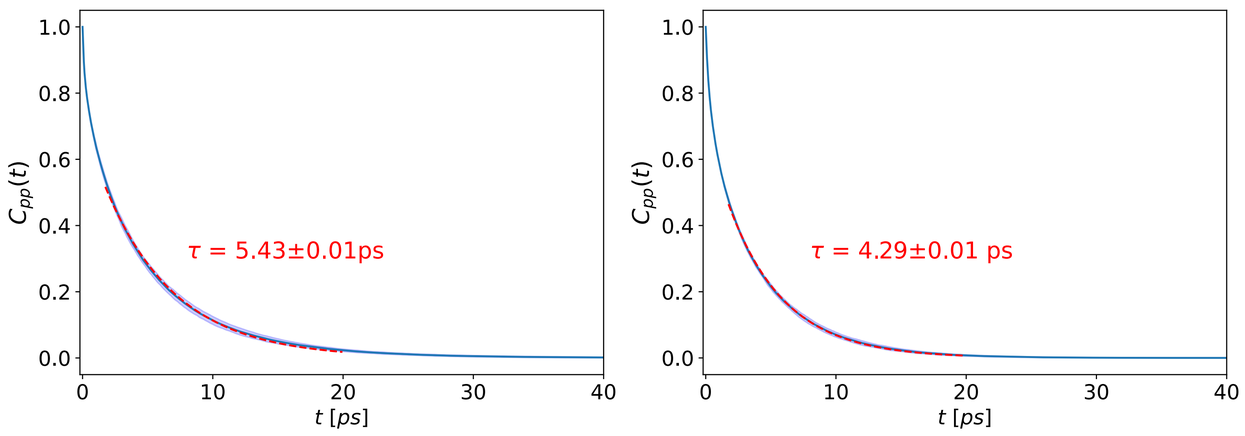
What are the characteristic residence times of water molecules in the first solvation shell?

Probability to be in the solvation sphere: $p_i(t) = \begin{cases} 1 \text{ if the water molecule i is in the first solvation shell at time t} \\ 0 \text{ otherwise} \end{cases}$

Definition of a time correlation function of this probability:

$$C_{pp}(t) = < p_i(0)p_i(t) > = \frac{1}{N_{mol}} \sum_{i=1}^{N_{mol}} \frac{1}{N_{step}} \sum_{j=1}^{N_{step}} p_i(t_j)p_i(t_j + t)$$ with: N_{mol}: number of water molecules, N_{step}: number of time steps

Time correlation function and exponential fit (red) for the system with the nanosphere (left) and the nanorod (right)

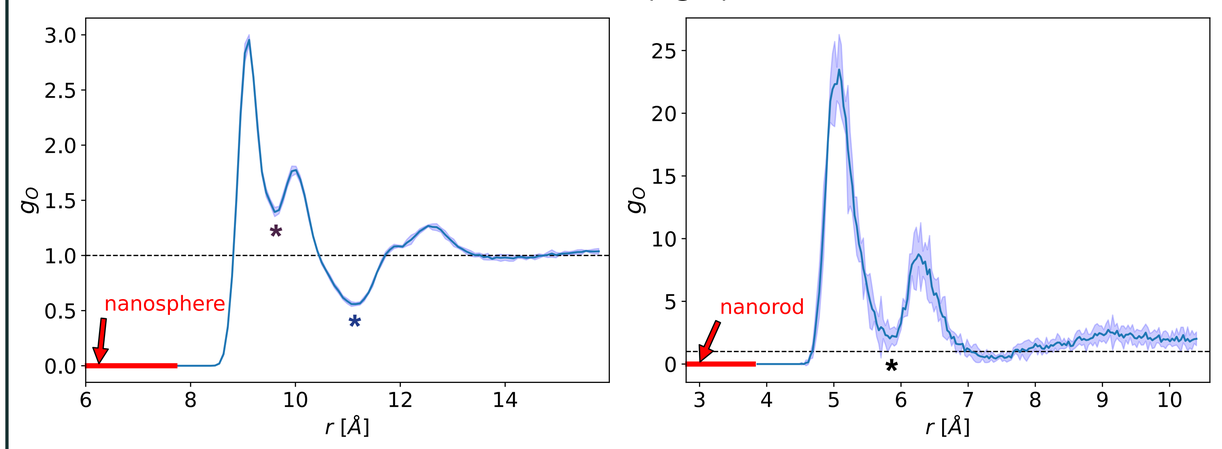


$V^{nanosphere}_{solvation\ sphere} = 1812\ \text{Å}^3 > V^{nanorod}_{solvation\ sphere} = 820.3\ \text{Å}^3$: more time is spent in the first shell of the nanophere and so its characteristic residence time is higher.

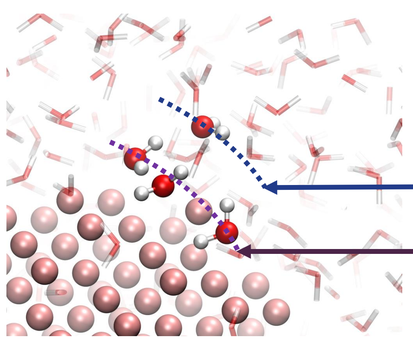
Radial distribution function of oxygen atoms

What are the differences between the solvation sphere of the nanorod and the nanosphere?

Radial distribution function of oxygen atoms around the nanosphere (left) and the nanorod (right)



The first solvation spheres are found for a radius of **1.92 Å** and **3.46 Å** around the nanosphere and **1.98 Å** around the nanorod.



The first and second solvation spheres around the nanosphere are mixed due to the shape of the nanosphere that is not perfectly round.

Second solvation sphere: H_2O on top of an Au atom

First solvation sphere: H_2O between two Au atoms

Diffusion coefficient of SPC/E water

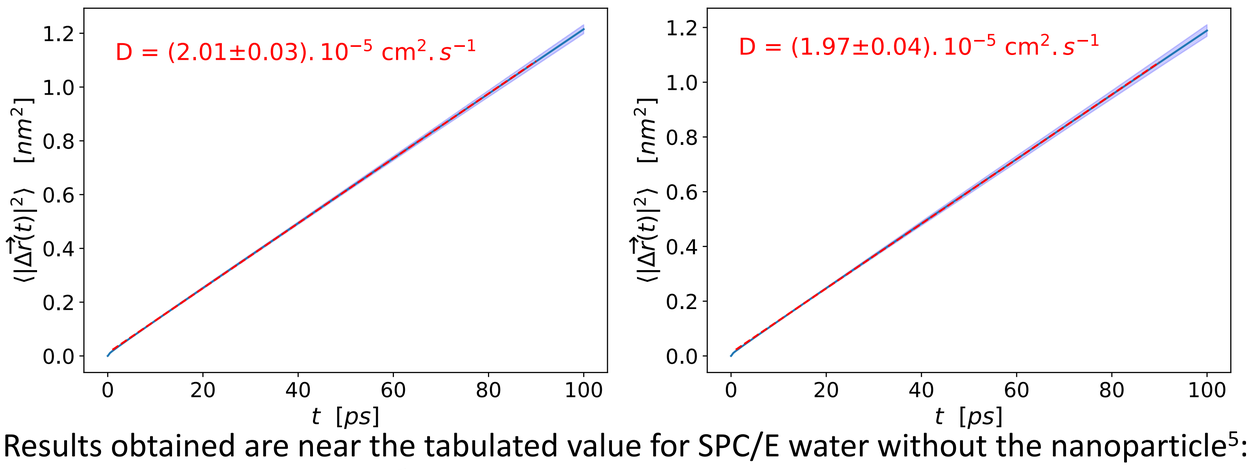
Are water dynamical properties affected by the presence of the nanoparticule?

Water self-diffusion coefficient computed for water molecules:

In the diffusive regime: $\langle |\Delta\vec{r}(t)|^2 \rangle = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle = 6D_{PBC}t$

Correction of the periodic boundary conditions[4,5] applied: $D = D_{PBC} + 2.83729 \frac{k_B T}{6\pi\eta L}$

Mean square displacement (blue), linear regression (red) and corrected self-diffusion coefficient for water in the system with the nanosphere (left) and the nanorod (right)



Results obtained are near the tabulated value for SPC/E water without the nanoparticle[5]: $D_{SPC/E} = 2.85 \pm 0{,}02\ .10^{-5}$ cm².s^{-1}

However it is a bit lower, indicating a possible effect of the nanoparticles slowing down the diffusion of water molecules. A study focused on the molecules near the nanoparticle might reveal an effect quantitatively.

Conclusion

In this work, we studied some dynamical properties of SPC/E water and its structure around two types of gold nanoparticles: a nanorod and a nanosphere.
While we showed that the general dynamic is not affected by the presence of gold nanoparticles, we found some structural differences due to the organisation of the solvent around the nanoparticle. Their difference in terms of organisation around the nanoparticles explain those results even though the solvent properties are the same.
To go further, a study of the dynamic of the solvent can be done around the nanoparticle, which might give different results for the solvent properties as the diffusion coefficient and density. Moreover a study of the partial solvation sphere can also be performed, and how it impacts the residence time in the first solvation sphere. The model can also be perfected by taking into account interactions between gold atoms or using a better force field for gold nanoparticles.

References and Acknowledgment

[1] C. Louis & O. Pluchery (Eds), 2nd edition, *World Scientific*, **2017** ISBN 978-1-78634-124-2
[2] P. Mark & L. Nilsson, *J. Phys. Chem. A*, **2001**, *105* (43), 9954–9960
[3] A. Berg, C. Peter & K. Johnston, **2017**, *J. Chem. Theory Comput., 13* (11), 5610-5623
[4] I.-C. Yeh & G. Hummer, **2004,** *J. Phys. Chem. B*, *108* (40), 15873–15879
[5] Z. A. Piskulich & W. H. Thompson, **2021,** *J. Chem. Theory Comput.,* 17 (5), 2659-2671

The authors would like to thank Damien Laage for his help and advice for the analysis of the results obtained in this study and Rolf David for his hints on the creation of this poster.