Solvation Behavior of Gold Nanorods in Water: A Monte Carlo Simulation Study

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Abstract: Gold nanoparticles have become common in many applications of biotechnology due to their specific properties. Shape and size are important attributes which affect their solubility in water. In this study, the outcomes of Monte Carlo Simulation for the solvation of gold nanorods in aqueous solution with the different radii, in terms of solvation free energy, are discussed. Simulation results show a negative solvation free energy for all the samples with radii of 4 to 9 Å. The results show that the absolute values of solvation free energy for gold nanorods with smaller radii are larger, which indicate the dependency between the gold nanorods solvation and their radius.

Keywords: Gold Nanorod, Monte Carlo Simulation, Solvation, Free energy.

1. INTRODUCTION

Over the last decades, gold nanoparticles (GNPs) applications have become a focal center of interest [1]. Various properties such as biocompatibility, non-cytotoxic effects, optical and electrical properties, which are basically stems from their availability in different sizes and forms (rod, tube, sphere, shell, cage, etc.); have made GNPs appropriate candidate for many applications [2]. Rendering high surface area at nanoscale leads to utilizing GNPs in cancer therapy [3, 4], drug transportation [5, 6], imaging [7, 8], and biological disclosure and diagnosis [9, 10]. Previous studies showed that surface adsorption of GNP has direct effect on both dynamic behavior of the nanoparticles and the configuration of the molecules which are adsorbed on the surface of GNP [11]. In this case, solubility limitation has been one of the most controversial threats for all nanomaterials. Among all possible alternatives for GNPs, gold nanorods (GNRs) have caught special attention because of their vast surface area [12].

Restrictions of experimental studies on nanoparticles especially in such small-scale begets using computational simulation as an feasible approach to study these systems [13]. One of the enthralling subjects is investigation of the adsorption mechanism of water molecules on the spherical gold nanoparticles by means of molecular dynamic (MD) simulation. Recent reported studies revealed that decreasing the diameter of GNPs not only increases the water adsorption, but also decreases average interaction energy per a water molecule. Moreover, oxygen and hydrogen atom distribution patterns showed that the adsorption of water molecules arises in two water shell-like structures close to the GNPs surface [14]. Additionally, arrangement and self-diffusion coefficient of water molecules confined between two gold plates of (001) planes separated by different gap sizes and the arrangement of water molecules inside gold nanotubes of various diameters have been studied via MD simulation. According to their research, the interaction energy between water molecule and Au nanotube enlarges as the nanotube diameter reduces and the diffusing ability of water molecules is enhanced when they are contained within smaller Au nanotubes [15, 16].

In this study, the solubility of GNRs with
different radii has been investigated to evaluate the size effect on solvation. Monte Carlo simulation and perturbation methods are used to calculate solvation free energies and compare solubility of these nanorods. In addition arrangement of water molecules surrounding GNRs is studied through reduced density profile of water molecules to compare GNRs’ solvation.

2. COMPUTATIONAL DETAILS

Monte Carlo (MC) simulation is carried out for six GNRs in water media using standard procedure of Metropolis sampling including 107 configurations [17]. To scale the temperature of the water molecules and the Au atoms to equilibrium temperature of 298 K in the course of the simulation Canonical ensemble is utilized. The simulation box was defined with 40×40×56 Å³ dimensions and periodic boundary conditions imposed in x, y and z directions, and a relative cutoff of 12 Å. The box contains about 1000 water molecule surrounding gold nanorods of 72, 168, 200, 296, 360 and 488 Au atoms which radii vary from 4 to 9Å with the same length of 32Å. Dimensions of GNRs is chosen in accordance to the periodicity of a fcc gold with the lattice constant of 4.07Å, and the Au atoms are cut from a fcc Au crystalline so that the axis of the GNRs is parallel to the [100] direction (Fig. 1). Using a dilute solution; one molecule of GNR is merged in a rectangular box of water. The simulation data should be properly analyzed to extract applicable properties. To verify accuracy of Monte Carlo calculations, statistical fluctuations of ensemble averages are calculated. The statistical errors which reported as standard deviations are under 1%.

The intermolecular interaction energy (E_xxx) encompasses two parts of water–water and gold–water potentials. The transferable intermolecular potential function (TIP3) [17,18] is applied for modeling water molecules. The interactions between GNRs and the water molecules are characterized by site-site interaction potential with parameters \( c_i \) and \( \sigma_i \) for each atom:

\[
E_{ij}^{AB} = 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^12 - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 + \frac{q_i q_j e^2}{r_{ij}}
\]  

(1)

\( c_{ij} \) and \( \sigma_i \) are calculated based on the Lorentz–Berthelot combining rules [19]. The LJ parameters for the Au atoms are derived from the universal force field (UFF) [20] with the quantity of 0.039 kcal/molÅ and 2.934 Å (\( \sigma \)).

Free Energy Perturbation (FEP) approach is used to investigate the solvation free energies of GNRs in water. The free-energy difference between two states 0 and 1 can be given by [21].

\[
\Delta A_{0-1} = A_1 - A_0 = -k_B T \ln \left[ \exp \left( \frac{\Delta H_1 - \Delta H_0}{k_B T} \right) \right]
\]  

(2)

where \( k_B \) is the Boltzmann constant and \( \Delta H_1 - \Delta H_0 \) is the difference in the Hamiltonian of systems 0

Fig.1. Schematic diagram of the simulation box with periodic boundary condition imposed in all directions.
and 1. Since the kinetic energy contributions is possible to be integrated out in the Helmholtz free energies calculation, the difference in the Hamiltonian can be resulted from potential energy [22]. Hence, the FEP formula for the Helmholtz free-energy difference between two systems 0 and 1 is as follows:

\[ \Delta A_{0,1} = A_1 - A_0 = -k_B T \ln\left(\exp\left(-\frac{(U_1 - U_0)}{k_B T}\right)\right) \]  

(3)

Therefore \( U_1 - U_0 \) represents difference in the potential energy of states 0 and 1. It must be considered that if the two states of 0 and 1 do not overlap in phase space, the energy differences between the two states will be much larger than \( k_B T \), so the value of the potential energy variations between the two states will not be very accurate. In this case, a coupling parameter \( \lambda \) is introduced to divide the intervals 0-1 into \( n \) subintervals. Then, a combination of solute and solvent’s LJ parameters in the intermediate states between 0 (\( \lambda = 0 \)) and 1 (\( \lambda = 1 \)) can be written by

\[ \varepsilon_i = \lambda \varepsilon_i + (1 - \lambda) \varepsilon_0 \]  

(4)

\[ \sigma_i = \lambda \sigma_i + (1 - \lambda) \sigma_0 \]  

(5)

In this work, both \( \varepsilon_0 = 0 \) and \( \sigma_0 = 0 \) correspond to the initial state, where there is no interaction between solute and solvent. Then, the total Helmholtz free-energy difference between 0 and 1 states can be obtained through taking a summation of these averages,

\[ \Delta A_{0,1} = \sum_{i=0}^{1} \Delta A_i = \sum_{i=0}^{1} -k_B T \ln\left(\exp\left(-\frac{(U_i - U_0)}{k_B T}\right)\right) \]  

(6)

The solvation free energy stands for the needed free energy to transfer one mole of solute (B) from an ideal gas state to an infinitely dilute solution. This free energy is the difference between the free energies of solute B in the aforementioned two phases:

\[ \Delta A_{solv}(B) = A_{sol}(B) - A_{gas}(B) \]  

(7)

Using FEP method, the solvation free energy of the species B (which in this investigation is GNR), can be interpreted in terms of perturbations where the species approaches to zero in the gas phase and in solution.

\[ \Delta A_{solv}(B) = \Delta A_{0,1} - \Delta A_{0,sol}(B) \]  

(8)

3. RESULTS AND DISCUSSION

Water molecules arrangement surrounding GNRs affected by water-gold interaction is shown via reduced density profile of oxygen atoms. In addition variation of solvation free energy with alteration of radius of GNRs is investigated.

Radial distribution functions (RDF), \( g(r) \), measure the probability of finding a particle as a function of distance from GNRs (local density) relative to that expected from a completely uniform distribution.

Local density for solvent atom type \( x \), \( \rho_x(r) \) is obtained from the frequency histogram using:

\[ \rho_x(r) = \frac{n_x(r)}{\Delta v} \]  

(9)

where, \( n_x(r) \) is the frequency of finding an atom of type \( x \) (oxygen or hydrogen) between \( r \) and \( r + \Delta r \) of the central axis of GNRs [23].

Fig. 2 shows the reduced density profiles of oxygen atoms surrounding GNRs. Since the mass center for water molecule is located close to its oxygen atom. Oxygen reduced density profile is used to represent water molecule reduced density profile. The vertical axis indicates the reduced density (\( \rho_{local} / \rho_{bulk} \)). \( \rho_{local} \) stands for number of oxygen that their center forms a cylindrical shell with the same axis of the GNRs, divided by the shell volume, where the horizontal axis represents distance of oxygen atoms from the surface of GNRs. To clarify the influence of GNRs radius on water molecules distribution, reduced density profiles are shown for different radii. It can be seen that all of the density profiles are showing peaks corresponding with the shell-like formations of water molecules around the surface of GNRs.
As it is shown in Fig. 2, the first peak takes place within 3Å of the GNRs surface, in which the potential energy, caused by the intermolecular interactions between the water molecules and the Au atoms, has the lowest value. By increasing the distance from the GNRs surface, this potential energy first escalates and forms an energetically unfavorable region for the accommodation of water molecules in the distance between the first two peaks. The second peak, appearing at approximately 4Å from the GNRs surface, is caused by increasing the appealing part of the potential energy. From this point onwards, broad and connected peaks are provided due to the hydrogen bonding of some water molecules within the shells. In all samples, adopting the water molecules to a bulk structure at distances greater than 8Å from the GNRs surface demonstrates the limit of bulk behavior for water. To have an analogy of water arrangement around GNR, a snapshot issued from the simulation GNR with radius of 8 Å is given in Fig. 3. This top view picture shows the arrangement of the first layer of water molecules around the GNR which presents a cylindrical symmetry of the water environment near to the GNR.

Variation of first peak height of oxygen reduced densities as its maximum value, and local density of water molecules within 4 Å (plocal 0-4) with GNRs’ radius are compared in
Table 1. plocal 0-4 is calculated by dividing the number of water molecules within 4 Å of the GNRs surface by volume of this area. In other words, plocal 0-4 is equal to area below the first peak of the reduced density profiles. Regarding to Table 1, plocal 0-4 and the first peak height rises as GNRs’ radius become smaller, which means configuration of water molecules around narrower GNRs is more packed. This may also be concluded from Fig. 2, that with increasing radius of GNR, the first peak becomes shorter and wider.

Table 2. shows the list the intermolecular interaction energies (Einter) of all samples as the radius of GNRs, respectively. Einter is explained previously as sum of the energy contributions from water–gold and water–water interactions. Since the LJ parameters for hydrogen atoms in TIP3 model are zero, the water–gold interaction includes only vander Waals interaction between gold and oxygen atoms. Moreover, portion of water–water interaction does not change with GNRs radius, so the difference between Einter values stems from only change of water–gold interaction. The results affirm that absolute value of Einter decreases with increasing the GNRs radius, which is in agreement with the plocal 0-4 and reduced density values of Table 1. In fact, greater water–gold interaction energy for smaller GNRs results in a more packed arrangement of water molecules in the rods’ vicinity.

Solubility of spherical gold nanoparticles

Table 1. Variation of first peak height of oxygen reduced densities and water molecules local density within 4Å (plocal 0-4) with GNRs’ radius.

<table>
<thead>
<tr>
<th>GNRs radius (Å)</th>
<th>Einter(kcal/mol)</th>
<th>ΔAsolv (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-17.876</td>
<td>-86.653</td>
</tr>
<tr>
<td>5</td>
<td>-16.990</td>
<td>-72.786</td>
</tr>
<tr>
<td>6</td>
<td>-14.337</td>
<td>-48.046</td>
</tr>
<tr>
<td>7</td>
<td>-11.339</td>
<td>-25.176</td>
</tr>
<tr>
<td>8</td>
<td>-11.235</td>
<td>-23.292</td>
</tr>
<tr>
<td>9</td>
<td>-11.190</td>
<td>-21.446</td>
</tr>
</tbody>
</table>
agrees with the present results [13]. Based on this
consequence, smaller gold nanoparticles have
stronger interaction with surrounding water
molecules, which the lower cohesive energy of
surface Au atoms for smaller particles is
considered to be the main reason. The ratio of
number of surface atoms and bulk atoms in Au
nanoparticles of smaller size is greater than ratio in
larger nanoparticles. Hence, cohesive energy is
reduced and a more unstable structure occurs.
Accordingly, these surface atoms have a greater
tendency to absorb water molecules to increase
their cohesive energy. Results also show that
the influence of cohesive energy becomes less
significant as nanoparticle diameter increases. As it
is shown in Table 2, $E_{int}$ values do not decrease
monotonically, and the radius 7Å is a critical size
from which the declining trend levels off.

Solvation-free energy ($\Delta \lambda_{solv}$) is computed as
aforementioned discussion in computational
details. The fluctuation of solvation-free energies
with GNRs radius is presented in Table 2. $\Delta \lambda_{solv}$
value is negative for all the GNRs, which
conveys the hydrophilic nature of gold particles.
In addition, its absolute value decreases as the
radius of GNR increases, which indicates the
higher solubility potential for the narrower
GNRs. It can be seen in Tables 1 and 2 that the
variations of $\Delta \lambda_{solv}$ and $E_{int}$ values with GNRs
radius are the same and their declining trend
levels off after 7Å for radius. Actually from this
radius onwards, influence of increasing the radius
on degree of solubility is not significant and this
comes from the change in hydrogen bonding
structures.

The trend of decreasing of solvation free
energy with growing of nanorod's radius will be
reversed if the structure is hallowed. It has been
shown that solvation free energies of Multi-
Walled Carbon Nanotube (MWCNTs) in water
environment increase with growing the
MWCNTs diameter [24]. In fact, unlike solid
structures like rod, in a hallow structure such as
(MWCNTs) with constant number of walls; the
ratio of atoms presenting at the surface to the
bulk atoms is constant. Therefore the cohesive
energy of surface atoms on MWCNTs doesn't
altered with MWCNTs size and so the greater
solubility of larger MWCNTs (in diameter or
length) stems from their larger interacting surface
area with solvent.

4. CONCLUSION

In this study, Monte Carlo Simulation method
is utilized to investigate the solubility of GNRs
with radii in a range of 4 to 9 Å. Results affirm
that water molecules arrange in a shell-like
structure around the GNRs, and greater
gold-water attraction energy for narrower GNRs leads
to a more packed water distribution around their
surface.

Variation of solvation free energy ($\Delta \lambda_{solv}$) with
GNRs radius showed that hydrophilicity and
solubility potential declines as the radius grows.
This is caused by cohesive energy change of
surface atoms. Furthermore, the trend of
solvation free energy ($\Delta \lambda_{solv}$) of GNRs with
increasing the diameter is opposite to that of
previous studies for hallow nanostructures like
CNTs, due to variation of interacting surface
area. According to the results, narrower GNRs
represent higher solvation potential and build
more stable particles in water. The matter of
stability is a main concern in bio or non-
biomedical applications for nanomaterials.

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