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Effects of functional groups and ionization on the structure of alkanethiol coated gold nanoparticles

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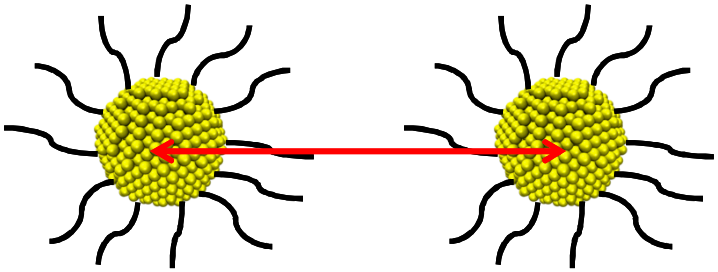
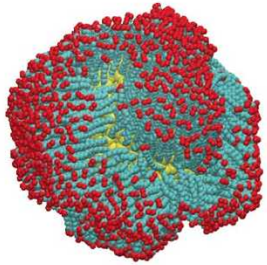
Motivation

- Understanding aggregation behavior of passivated nanoparticles vital to most applications



- Previous molecular dynamics simulations showed spontaneous coating asymmetry in solution despite spherical nature of particles



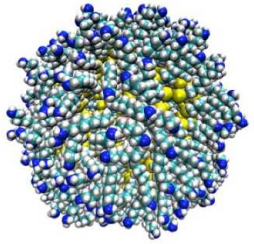
Lane and Grest, PRL 104, 235501 (2010)

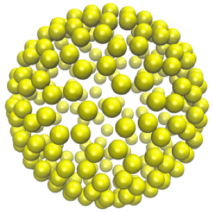
- Ionizable end groups can be used to control aggregation behavior/function, e.g. by adjusting pH

→ use MD to study structure of NP coatings with charged end groups

Systems studied

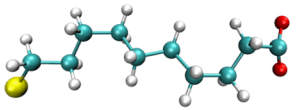
- 4 nm gold cores

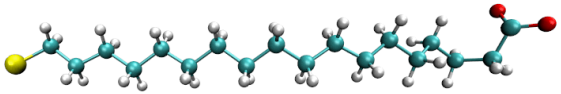




4 nm

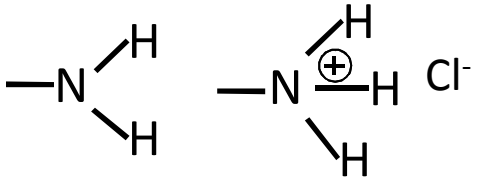
- Alkane chains are S-$(CH_2)_9$ or S-$(CH_2)_{17}$

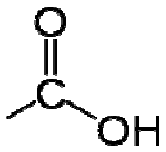


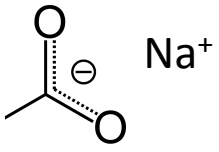


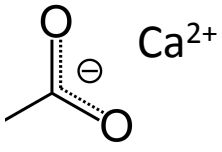
- For each alkane chain length, head groups are:

Amines (NH_2, $NH_3^+ Cl^-$) or **carboxylates** (COOH, $COO^- Na^+$ or $COO^- Ca^{2+}$)







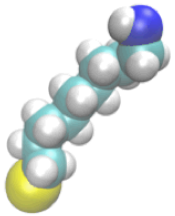
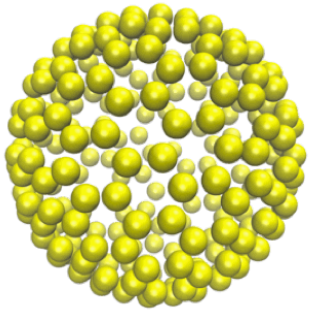
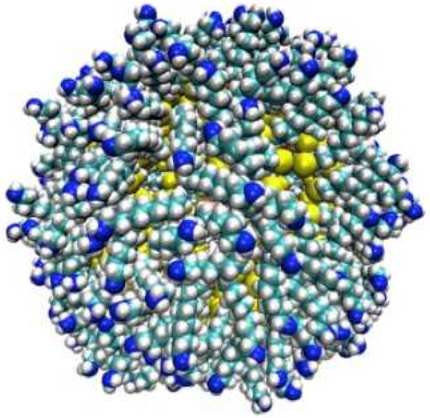


- COOH and NH_2 solvated in water and decane; others in water

Methods

System construction:

- Alkanethiol chains grafted on C-240 fullerene structure
- Sulfur atoms fixed (LAMMPS *fix rigid* command) at C-240 carbon positions, gold atoms omitted
- Large sphere placed at center of core to keep solvent out

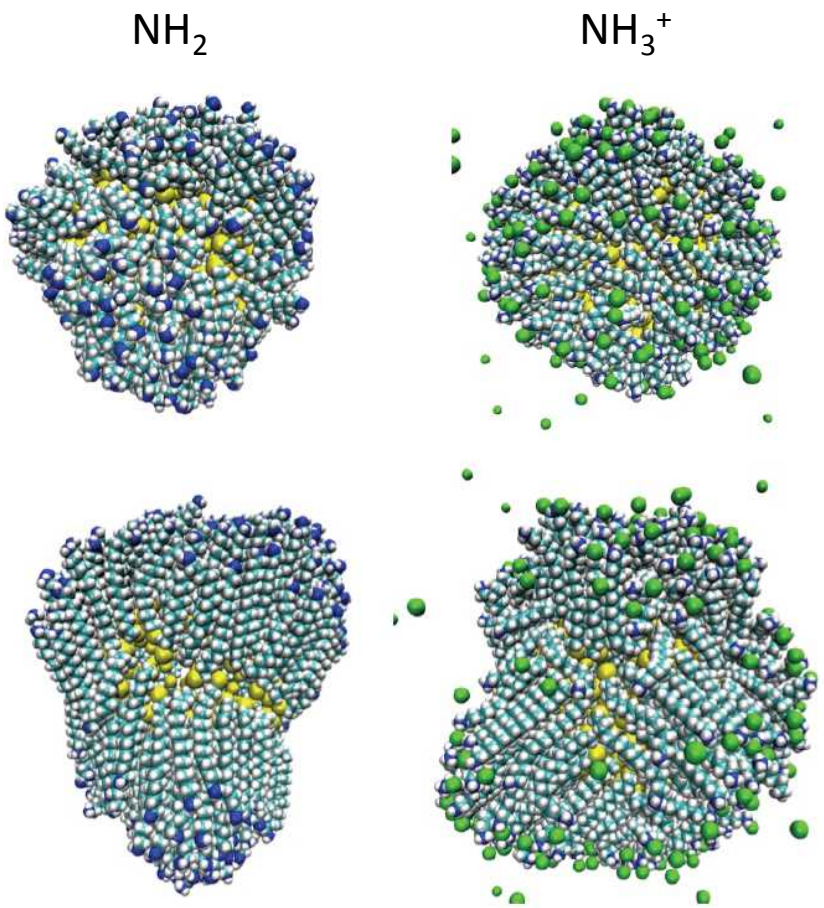
240 X  +   

Molecular dynamics simulations:

- OPLS/AA force field, TIP4P-2005 water
- LAMMPS MD code
- Short NPT runs followed by NVT production runs (300 K)

Results: bulk solution structures

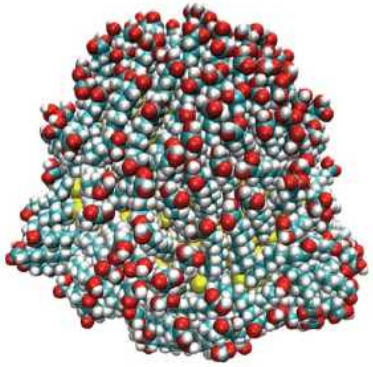
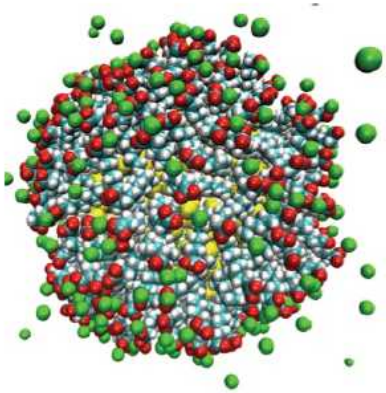
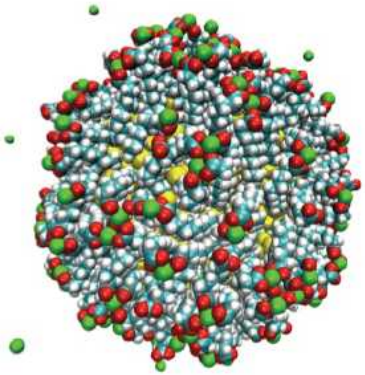
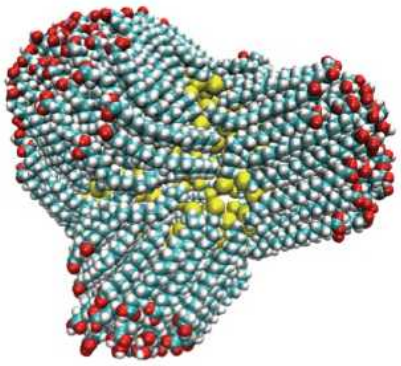
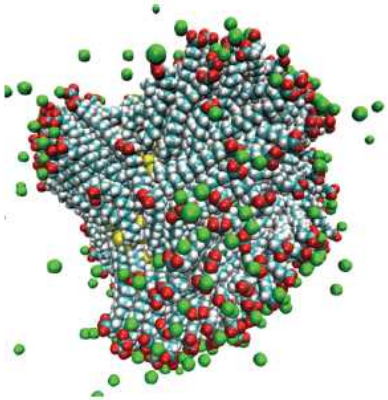
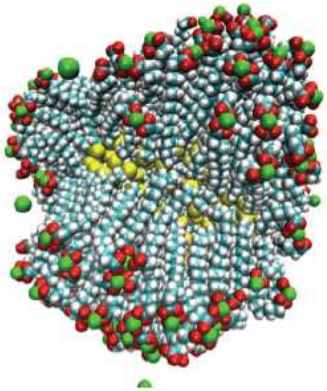
Amines



- Strong asymmetry in longer chain coatings
- Charged state attenuates asymmetry → higher solubility?

Results: bulk solution structures

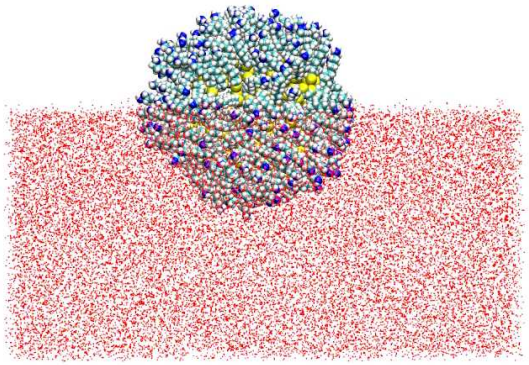
Carboxylates

	COOH	$COO^- Na^+$	$COO^- Ca^{2+}$
$S-(CH_2)_9$			
$S-(CH_2)_{17}$			

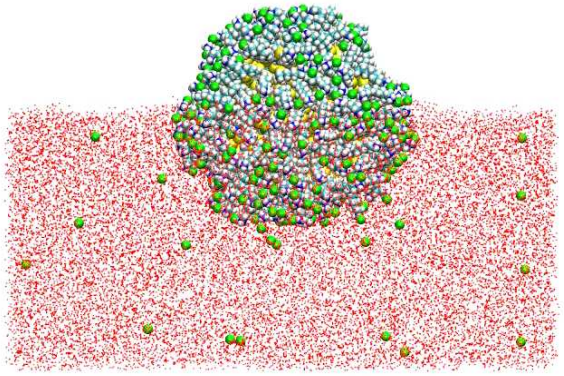
Results: simple solubility test

- Particles placed at water-air interface, followed by short equilibration

$S\text{-}(CH_2)_9\text{-}NH_2$



$S\text{-}(CH_2)_9\text{-}NH_3^+\ Cl^-$



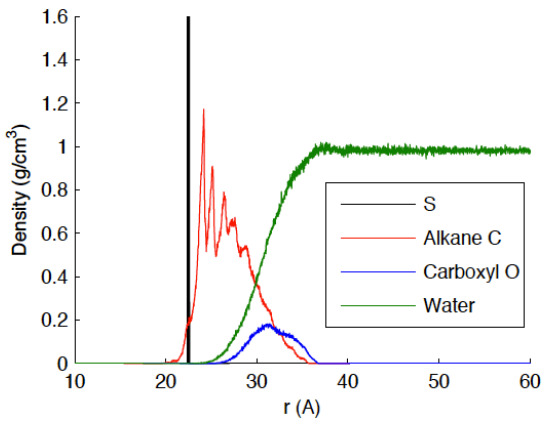
	NH_2	$NH_3^+\ Cl^-$	COOH	$COO^-\ Na^+$	$COO^-\ Ca^{2+}$
$S\text{-}(CH_2)_9$	✗	✔	✗	✔	✔
$S\text{-}(CH_2)_{17}$	✗	✔	✗	slowly	v. slowly

✔ enters water

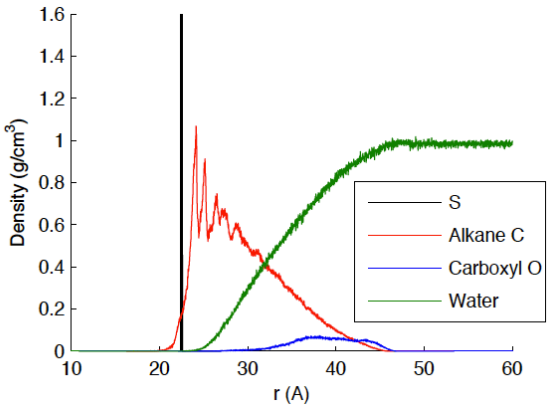
✗ does not enter water

Results: radial density profiles

S-$(CH_2)_9$-COOH

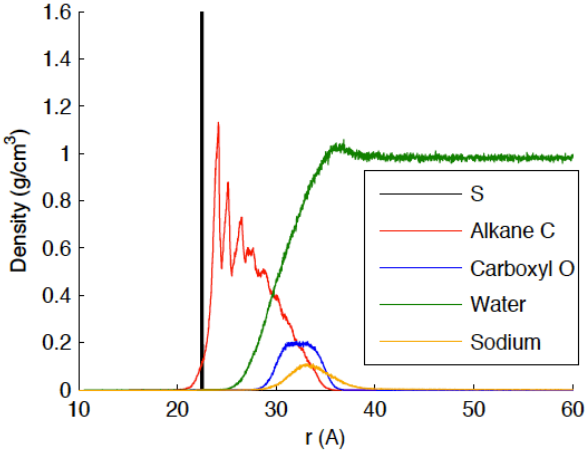


S-$(CH_2)_{17}$-COOH

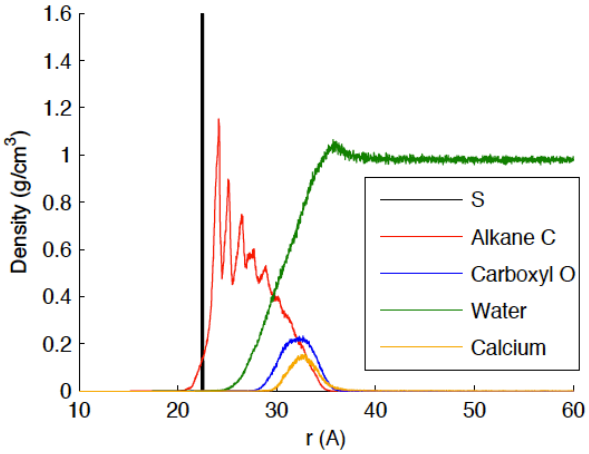


- Some packing/ordering effects in the first few layers of alkane chains, liquid beyond that
- 'Smeared' due to radial asymmetry in $(CH_2)_{17}$ alkanes

S-$(CH_2)_9$-COO^- Na^+



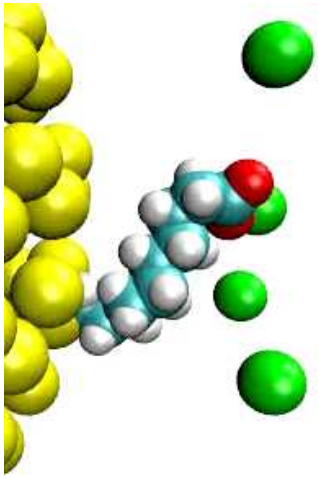
S-$(CH_2)_9$-COO^- Ca^{2+}



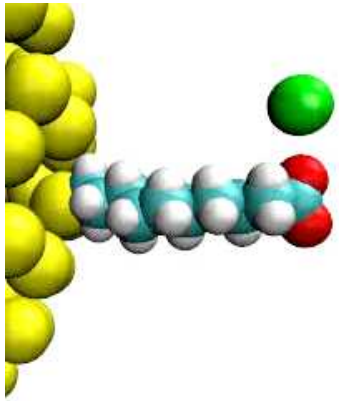
- Increased water density near interface → water coordination of counterions
- Possibly tighter ion-alkane association in divalent case

Results: ion association

Na^+

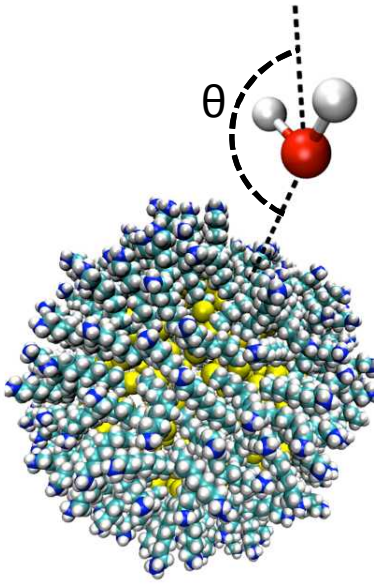


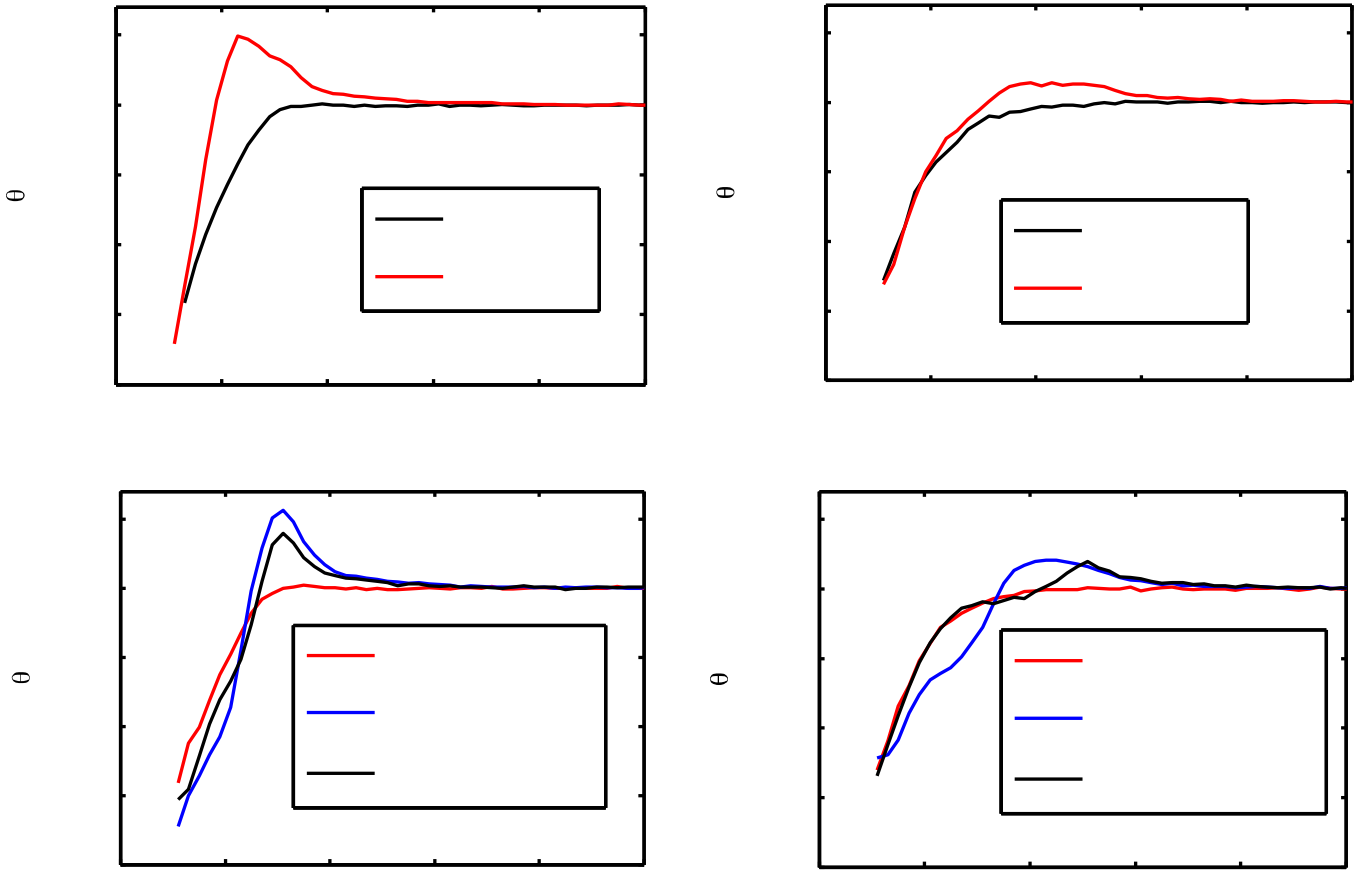
Ca^{2+}



System	Mean counterion-ion association lifetime (ps)
S-$(CH_2)_9$-NH_3^+ Cl^-	59.0
S-$(CH_2)_{17}$-NH_3^+ Cl^-	65.1
S-$(CH_2)_9$-COO^- Na^+	64.3
S-$(CH_2)_{17}$-COO^- Na^+	63.4
S-$(CH_2)_9$-COO^- Ca^{2+}	1980
S-$(CH_2)_{17}$-COO^- Ca^{2+}	1810

Results: water orientation





→ Increased ordering of water near interface for charged cases

Summary

- Functional end groups have a strong effect on nanoparticle coating structures, especially for longer chains
- Solubility enhanced in charged NP's
- Differences in local structure comparing divalent vs. monovalent counterions, but overall coating structure similar
- Solubility and aggregation determined by combination of coating structure and overall particle charge