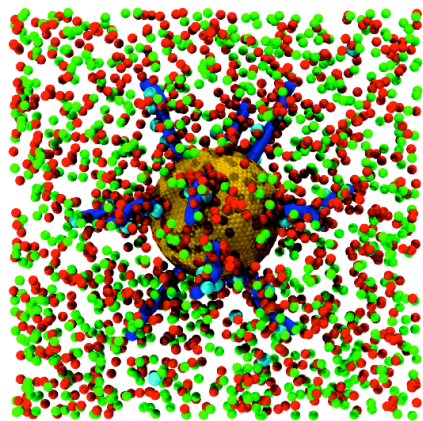
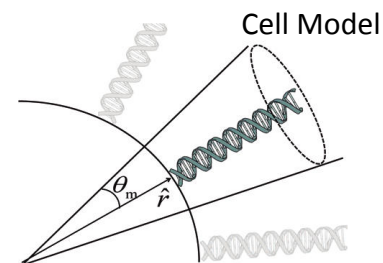


# Local Ionic Environment around Polyvalent Nucleic Acid-Functionalized Nanoparticles

Jos W. Zwanikken, Peijun Guo, Chad A. Mirkin, and Monica Olvera de la Cruz

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Polyvalent oligonucleotide-functionalized gold nanoparticles are remarkably stable against degradation by nucleases. We investigate the composition of the ion cloud around spherical nanoparticles that are functionalized by stiff, highly charged polyelectrolyte chains by means of classical density functional theory and molecular dynamics simulations, and present a cell model that includes ligands explicitly. The ion cloud for varying oligonucleotide grafting densities and bulk ionic concentrations was studied, as well as different sizes of nanoparticles and chains, and distinguish a parameter regime where many-body interactions between the ligands have a dominant effect on the local environment.



Simulation snapshot: Na<sup>+</sup> (red), Cl<sup>-</sup> (green), Ca<sup>2+</sup> (cyan), with DNA (blue), on a small nanoparticle.

## For small particles with high oligonucleotide surface densities, we find:

- Strongly enhanced local salt concentrations
- A large radial component of the electric field between the ligands
- A pronounced localization of divalent ions near the surface of the nanoparticle.
- Close quantitative agreement found up to unrealistically high grafting densities
- For increasing grafting densities Ca<sup>2+</sup> ions replace Na<sup>+</sup> ions especially close to the nanoparticle surface.
- The strong cloud of Na<sup>+</sup> and Ca<sup>2+</sup> ions stabilizes the gold-DNA particles in blood by preventing DNA-specific enzymes from digesting the DNA attached to the nanoparticle.
- This supports recent attribution of the stability against degradation to the local high concentration of mono- and divalent ions
- Such DNA functionalized particles have applications in disease detection. For instance, once inside a cell, mRNA from a diseased gene replaces the ssDNA which activates a fluorescent marker for detection.

MD simulations (symbols) and Theory (curves) of the mean number of compensating charges per nanometer for distances  $r$ , for low (red dashed curves) and high (black continuous curves) grafting densities, for Ca<sup>2+</sup> ions and counterions.

