Small Au nanoparticles - quantum confinement effects and atomic-scale simulations of interactions in biological environments

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Metal nanoparticles (NPs) provide new functionalities of matter at the nanoscale. Their properties can be tuned via chemical composition, size, binding strength between the core and ligand shell, overall charge, and stability in a given medium. Quantum confinement effects arise as the NP size decreases down to a few nanometers, which is reflected, e.g., in optical properties and catalytic reactivity. In this context, gold nanoparticles (AuNPs) are among the most studied systems as they have potential for applications in molecular electronics, molecular recognition, catalysis, biolabeling and sensing, and drug delivery. The enhanced stability of specific sizes of ligand-protected AuNPs of 100 gold atoms or less is due to electronic shell closing which obeys a simple formula in the spirit of the spherical jellium model [1]. However, recent experimental evidence points that the simplified model does not account for all the synthesized cluster sizes/compositions and extensions are necessary. Furthermore, the effects of the solvent environment require attention.

Despite being chemically inert as a bulk material, nanoscale gold can pose harmful side effects to living organisms. In particular, cationic Au nanoparticles ($AuNP^+$) of 2nm diameter or less permeate readily through plasma membranes and induce cell death. We report atomistic simulations of both cationic and anionic Au nanoparticles interacting with realistic membranes and explicit solvent using a model system that comprises two cellular compartments, extracellular and cytosolic, divided by two asymmetric lipid bilayers. The membrane–AuNP binding and membrane reorganization processes are governed by co-operative effects where AuNP, counterions, water, and the two membrane leaflets all contribute. The results suggest $AuNP^+$ permeation to take place through the formation of a pore together with partial nanoparticle neutralization/deprotonation, leading to membrane disruption at higher nanoparticle concentrations [2]. The negatively charged nanoparticle ($AuNP^-$) does not disturb the membrane structure and remains on the extracellular side [3].

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[2] E. Heikkilä, H. Martinez-Seara, A.A. Gurtovenko, M. Javanainen, H. Häkkinen, I. Vattulainen, and J. Akola, *Cationic Au Nanoparticle Binding with Plasma Membranelike Lipid Bilayers: Potential Mechanism for Spontaneous Permeation to Cells Revealed by Atomistic Simulations*, J. Phys. Chem. C **118**, 11131 (2014).

[3] E. Heikkilä, H. Martinez-Seara, A.A. Gurtovenko , I. Vattulainen, and J. Akola, *Atomistic simulations of anionic $Au_{144}(SR)_{60}$ nanoparticles interacting with asymmetric model lipid membranes*, Biochimica et Biophysica Acta – Biomembranes **1838**, 2852 (2014).