Many-Body Effects of Substrate Supported Nanoparticles

Matthew Pham†, Alex Travesset†‡

† Department of Physics & Astronomy, Iowa State University, Ames, Iowa 50011

‡ Ames National Laboratory, Ames, Iowa 50011

U.S. DEPARTMENT OF ENERGY | Office of Science

AMES LABORATORY — Creating Materials & Energy Solutions — U.S. DEPARTMENT OF ENERGY

Introduction

Nanoparticle superlattices are commonly assembled on or transferred to solid substrate supports such as gold, silica, teflon, etc. In order to better understand nanoparticles in this context, molecular dynamics simulations were used to study substrate supported nanoparticles, nanoparticle pairs, and nanoparticle clusters to understand how the substrate may influence nanoparticle self-assembly and nanoparticle interactions.

A proposed theory dubbed the Orbifold Topological Model (OTM)[4,5] seeks to describe nanoparticle bonding via "vortex textures" and local coordination number. Although the local coordination number is usually the number of nearest neighbors for a point in a lattice, the addition of a substrate causes a nanoparticle-substrate interaction that increases the coordination number by one in contrast to interacting nanoparticles in vacuum.

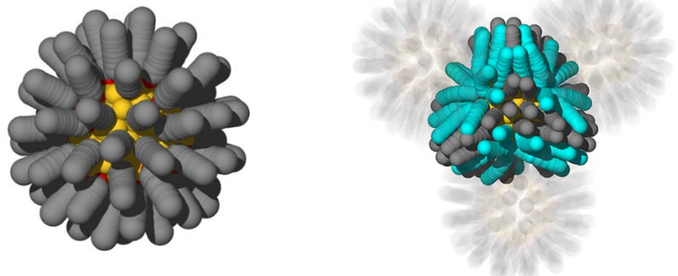

Fig 1. (Left) Non-interacting nanoparticle has coordination number of zero and forms no vortices. (Right) Nanoparticle surrounded by three other nanoparticles has coordination number of three and forms three vortices shown in cyan.

Methods

Molecular dynamics simulations were run using HOOMD-Blue[1] and HOODLT[3]. Simulations consisted of nanoparticle(s) made up of a rigid gold core grafted with hydrocarbon chains and an inert substrate support modeled as gold. Bias potentials were used to hold the nanoparticles in specific configurations to sample data along dimensions of interest. Images of simulation systems were made using OVITO[2].

1) Single Nanoparticle and Substrate
   - Adhesion Energy
   - NP-Substrate Separation

2) Nanoparticle Pair and Substrate
   - NP-NP Separation
   - Vacuum Comparison

3) Nanoparticle Cluster and Substrate
   - NP-NP Separations
   - Vacuum Comparison

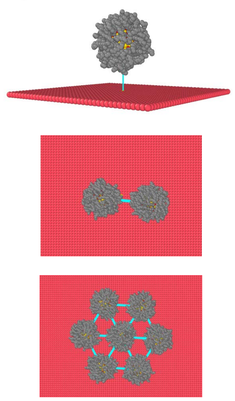

Fig 2. Example snapshots of system configurations of nanoparticles simulated.

Results

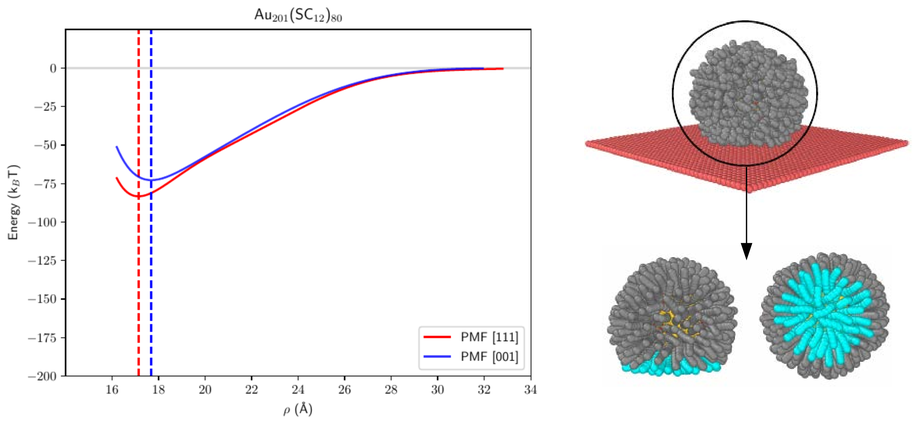

Fig 3. Potential of mean force of nanoparticle-substrate interaction as a function of nanoparticle's height above substrate.

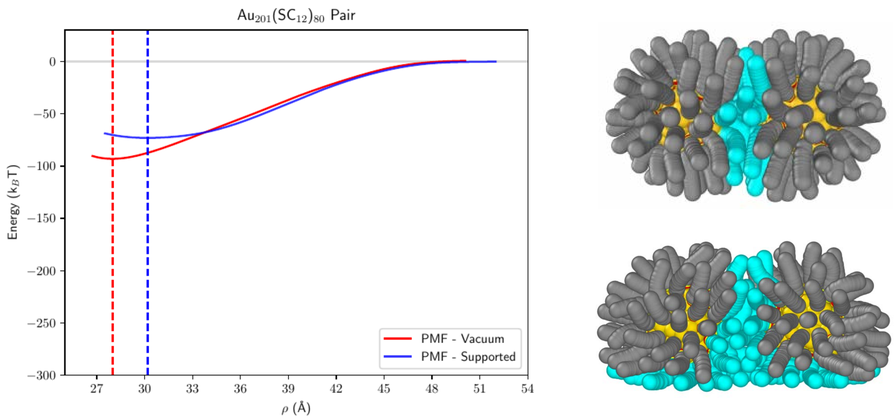

Fig 4. Potential of mean force of nanoparticle-nanoparticle interactions in a pair of nanoparticles as a function of distance between nanoparticle cores. Results for vacuum case taken from reference 6.

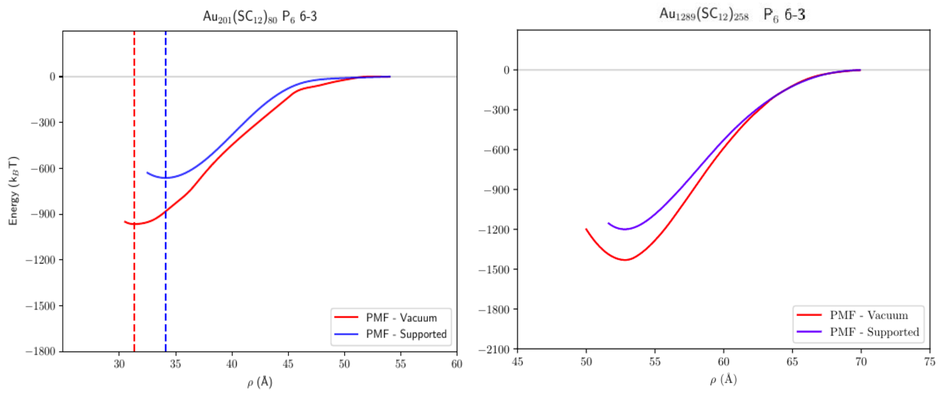

Fig 5. Potential of mean force of nanoparticle-nanoparticle interactions in a hexagonal cluster of nanoparticles as a function of distance between nanoparticle neightbors. Results for vacuum case taken from reference 7.

Conclusion

1) Like two interacting nanoparticles, a single nanoparticle also interacts with its substrate support forming a "vortex". The comparable adhesive energy indicates similarities between NP-NP and NP-Substrate vortices.

Nanoparticle	F_{min} (k_BT)	ρ (Å)
[001] $Au_{201}(SC_{12})_{80}$	73	17.7
[111] $Au_{201}(SC_{12})_{80}$	83	17.1
Half $Au_{201}(SC_{12})_{80}$ Pair[6]	57	13.6

2) Two bonded NPs form vortices at their interaction surface. Presence of a substrate forms an additional vortex that coalesces with the existing vortex. This causes a defect in the NP-NP vortex pushing the NPs further apart.

$Au_{201}(SC_{12})_{80}$ Pair	F_{min} (k_BT)	ρ (Å)
Vacuum	93	28.0
Supported	73	30.2

3) Large nanoparticles with shorter ligands experience less vortex coalescence due to the relative size of the core and vortex. Simulated nanoparticle clusters comparing supported and vacuum cases show a similar separation as the pair case for the smaller nanoparticles, but this separation is missing from the larger nanoparticles case.

Hexagonal Cluster	F_{min} (k_BT)	ρ (Å)
$Au_{201}(SC_{12})_{80}$ Vacuum[7]	965	31.3
$Au_{201}(SC_{12})_{80}$ Supported	663	34.1
$Au_{1289}(SC_{12})_{258}$ Vacuum[7]	1431	52.7
$Au_{1289}(SC_{12})_{258}$ Supported	1199	52.9

Fig 6. (Left) NP-Substrate vortex of smaller nanoparticle. (Right) NP-Substrate vortex of larger nanoparticle

Acknowledgements

Work at the Ames Laboratory was supported by the U.S. Department of Energy Office of Science, Science Undergraduate Laboratory Internships (SULI) program under its contract with Iowa State University, Contract No. DE-AC02-07CH11358. Matthew Pham is grateful to the DOE for the assistantship and opportunity to participate in the SULI program. This work used the Extreme Science and Engineering Discovery Environment (XSEDE) under allocation TG-MCB140071: Bonding Rules and Structure Prediction in Nanocrystal Clusters and Superlattices.

IOWA STATE UNIVERSITY

References

[1]Glaser, J., Nguyen, T. D., Anderson, J. A., et al.. (2015). Strong scaling of general-purpose molecular dynamics simulations on GPUs. Computer Physics Communications.
[2]Stukowski, A. (2010). Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool. Modeling and Simulation in Materials Science and Engineering.
[3]Travesset, A. (2014). Phase diagram of power law and Lennard-Jones systems: Crystal phases. Journal of Chemical Physics.
[4]Travesset, A. (2017). Soft Skyrmions, Spontaneous Valence and Selection Rules in Nanoparticle Superlattices. ACS Nano.
[5]Travesset, A. (2017). Topological structure prediction in binary nanoparticle superlattices. Soft Matter.
[6]Waltmann, C., Horst, N., & Travesset, A. (2017). Capping Ligand Vortices as "atomic Orbitals" in Nanocrystal Self-Assembly. ACS Nano.
[7]Waltmann, T., Waltmann, C., Horst, N., & Travesset, A. (2018). Many Body Effects and Icosahedral Order in Superlattice Self-Assembly. JACS.