Sintering Rate and Crystallinity Dynamics of Gold Nanoparticles by Atomistic Simulations

E. Goudeli and S.E. Pratsinis

Particle Technology Laboratory, Institute of Process Engineering, Department of Mechanical and Process Engineering, ETH Zürich, Sonneggstrasse 3, CH-8092 Zürich, Switzerland.

E-mail: goudeli@ptl.mavt.ethz.ch, sotiris.pratsinis@ptl.mavt.ethz.ch

Abstract

Gold nanoparticles find applications in catalysis, plasmonic biosensing, target-specific drug delivery, nanolithography and ion detection as they have unique optical, electronic, chemical and magnetic properties due to their high surface-to-volume ratio. For example, small nanoparticles are more attractive as catalysts due to their increased activity and selectivity compared to larger particles. However, their crystal structure along with particle size and morphology can affect the final product characteristics and eventually their plasmonic, photothermal or catalytic performance (Sotiriou et al., 2014). Molecular Dynamics (MD) simulations provide useful physical insight in understanding phenomena such as sintering and crystal structure changes in atomistic scale especially for very small nanoparticles (smaller than 10 nm).

Here, detailed atomistic MD simulations are used to investigate the sintering mechanism and crystallinity dynamics of gold nanoparticles of different size at various temperatures (227 – 727 °C). The method is benchmarked by calculating the melting temperature of Au nanoparticles ($d_{p,0}$ = 1.5 – 11 nm) which increases with increasing particle size and gradually approaches the bulk melting point, in excellent agreement with experimental measurements and simulations. The characteristic sintering time of pairs of Au particles is determined by tracing their surface area evolution (Buesser et al., 2011). Increasing temperature results in faster sintering, consistent with experimental observations, while for sintering temperatures near the size-dependent melting point the characteristic sintering time, τ_s, levels off at $\tau_s \approx$ 0.02 ns.

The stage of crystallinity is theoretically quantified by determining the deviation of each gold atom from a perfect face cubic centered crystal, providing an indication of the system's degree of disorder. Coalescing nanoparticles form grains of different and dynamically-changing orientation. The atoms at the grain or particle boundaries are disordered compared to the bulk atoms, especially during particle adhesion. Defects such as grain boundaries at the atomic scale can strongly affect electrical, optical and mechanical properties of 2D materials. At high temperatures and sufficiently long time these grains transform to a single crystal.

Keywords: nanocrystallinity, sintering rate, gold.

References

Buesser, B., Gröhn, A.J., Pratsinis, S.E. (2011) *J. Phys. Chem.* 115, 11030-11035.

Sotiriou, G.A., Etterlin, G.D., Spyrogianni, A., Krumeich, F., Leroux, J-C., Pratsinis ,S.E. (2014) *Chem. Commun.* 50, 13559-13562.