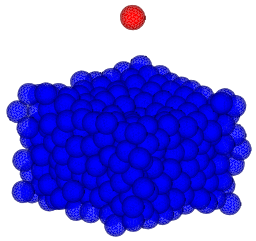
Extending Time-Resolved LII to Metal Nanoparticles: Simulating the Thermal Accommodation Coefficient

K. J. Daun[a*], J. T. Titantah[b], M. Karttunen[a] and T. A. Sipkens[a]

[a]*University of Waterloo, Waterloo ON Canada*
[b]*University of Western Ontario, London ON Canada*
Corresponding Author,* ***kjdaun@uwaterloo.ca*

There is growing interest in adapting time-resolved laser-induced incandescence (TiRe-LII) to size metal nanoparticles, owing to their emerging applications in materials science. Extending TiRe-LII to new aerosols requires a model for the heat transfer between the laser-energized nanoparticles and the surrounding gas. Unfortunately, the thermal accommodation coefficient, α, which defines the energy transferred when a gas molecule scatters from the particle surface, is rarely available. This parameter can sometimes be obtained from LII measurements made on a reference aerosol sized using electron micrography, but this process is notoriously time-consuming, and thermophoretic sampling of metal nanoparticles is often problematic. These challenges have precluded interpretation of data from several pioneering TiRe-LII studies on metal nanoparticles, including one by Murakami et al. [1] that intended to determine how the bath gas influences the growth of molybdenum nanoparticles formed through laser-induced photolysis of $Mo(CO)_6$.

Alternatively, it is sometimes possible to estimate α using molecular dynamics (MD). In this technique, a pairwise potential between the gas molecule and metal atoms is derived from ab initio (generalized gradient approximations of density functional theory, GGA-DFT) calculations of the gas/surface potential. The potentials then differentiated to obtain forces, and Newton's equations of motion are time-integrated to obtain atomic trajectories during a gas/surface scattering event. Finally, α is found through Monte Carlo integration over all incident gas molecular trajectories.



MD simulation of an argon molecule scattering from a laser-energized iron nanoparticle

This approach was initially used to characterize α between soot and various gases, and is presently being extended to metal nanoparticles. Preliminary results show that MD-derived accommodation coefficients are highly sensitive to the potential well depth. Unfortunately, a well-known limitation of GGA-DFT is that they cannot describe the long-range electron correlations responsible for van der Waals (vdW) forces, which contribute to the potential well. While the Ni/Ar interaction is dominated by a strong Casimir force, vdW forces are thought to play a major role in other systems. Accordingly, true accommodation coefficients are probably larger compared to ones found using ab initio derived gas-surface potentials with no vdW correction. Current research is focused on identifying an appropriate heuristic correction that can account for the dispersive forces.

Preliminary thermal accommodation coefficients for metal nanoparticles

	α_{MD}	α_{exp}
Ni/Ar	0.20±0.02	
Fe/He	0.07±0.01	0.01 [2]
Fe/Ar	0.04±0.01	0.1 [2], 0.13 [3]
Mo/He	0.006±0.002	
Mo/Ar	0.04±0.01	

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[2] A. Eremin, E. Gurentsov, C. Schulz, J. Phys D: App. Phys, 41 (2008) 055203.
[3] B. F. Kock, C. Kayan, J. Knipping, H. R. Orthner, P. Roth, Proc. Comb. Inst., 30 (2005) 1689.