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

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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, $\alpha$, 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. \cite{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 $\alpha$ 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, $\alpha$ is found through Monte Carlo integration over all incident gas molecular trajectories.

This approach was initially used to characterize $\alpha$ 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.