

An experimental study of interactive forces and Hamaker constant of flame-formed carbon aerosols from AFM

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In this work, interaction forces acting between combustion-generated carbonaceous particles were studied by using atomic force microscopy (AFM). It is widely accepted that particle coagulation is a relevant step in the process of carbon nanoparticle formation. A deeper understanding of the role played by coagulation during soot formation processes can be achieved by studying the forces, particularly van der Waals interactions, acting between carbon nanoparticles. Also, the Hamaker constants for flame-formed nanoparticles have been so far mainly assumed based on particle chemical nature, since no direct experimental measurement can be found in the literature.

Carbon nanoparticles were synthesized in fuel-rich ethylene/air laminar premixed flames with different equivalent ratios Φ (from $\Phi=1.85$ to $\Phi=2.58$), and collected on mica substrates by means of a thermophoretic sampling system for AFM analysis.

Particle dimension and morphology were characterized operating the AFM in semicontact mode, showing that particles formed in the flames with equivalence ratios less than 2 have a monomodal size distribution with the mean particle size moving from 3.7 to 5 nm. The size distributions of particles sampled in richer flames are clearly bimodal with the first mode centered at about 2.5 nm and the second one which moves from 10 to 50 nm. Increasing the flame equivalent ratio, particles change from a crumpled sheet of an almost atomically thick object to thicker compounds containing stacked aromatic layers.

Interactive forces between a titanium nitride probe and sampled particles were calculated from force-distance curves acquired in AFM force spectroscopy mode (Butt *et al.*, 2005). The forces acting between the AFM tip and the surface under investigation can be recorded during approach and retract of cantilever to and from the sample, and plotted as force-distance curves. From these curves, short-range attractive and adhesive forces can be quantitatively evaluated, as reported in Figure 1.

Soot particles produced in very fuel-rich flames exhibit adhesive and attractive forces lower, but comparable, to that of highly ordered pyrolytic graphite. Whereas, carbon nanoparticles formed below the soot limit appearance have attractive and adhesive forces much lower than those of the soot particles and more similar to those characteristic of aromatic molecules.

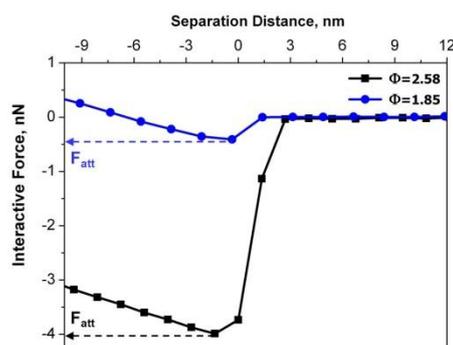


Figure 1. Experimental force-distance approach curves measured for a particle collected at $\Phi=1.85$ (blue dots) at $\Phi=2.58$ (black squares).

It is worth noting that AFM force-spectroscopy technique was employed for the first time in this work to investigate the graphitization of carbon nanoparticles in various fuel-rich flame conditions. The reported results show that this is a reliable and powerful tool to investigate the graphitization of different combustion aerosols.

From force vs. distance measurements, the Hamaker constant of the particles in each flame was also calculated, assuming that van der Waals forces are the main contribution to attractive forces (Israelachvili, 2011), and are reported in Table 1.

Table 1. Average Hamaker Constants, 10^{-19} J.

Particles at $\Phi=2.58$	3.5 ± 1.6
Particles at $\Phi=2.16$	2.2 ± 0.9
Particles at $\Phi=1.95$	1.5 ± 0.5
Particles at $\Phi=1.89$	0.98 ± 0.01
Particles at $\Phi=1.85$	0.95 ± 0.01

The trend of the Hamaker constant with the flame equivalent ratio, compared to the values of benzene and HOPG, confirm a continuous increase of particle graphitization by increasing the size and/or the three-dimensional internal ordering of the aromatic domains by increasing the flame equivalent ratios.

Butt, H. J., Cappella, B., and Kappl, M. (2005) *Surf. Sci. Rep.* **59**, 1-152.

Israelachvili, J. N. (2011) *Intermolecular and Surface Forces* (3rd ed.), Academic Press, London.