Carbonaceous Nanoparticles in Combustion; a Multiscale Approach

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Particulate emissions in the nanoparticle size range are related to two pressing environmental problems - the health impact of fine particles and global warming. Airborne fine particles are either emitted *directly* in terms of elemental carbon (i.e. soot from combustion sources) or *indirectly*, through gas to particle conversion in the atmosphere or from the gas to particles evolution of volatile organic compounds, leading to the secondary formation of organic carbon particles.

Recent studies[1-2] on the mechanisms by which particles act show that the particle deposition in the epithelial cells in the lungs trigger a number of responses: cell activation leading to inflammation; production of cytokines (proteins) that stimulate the release of fibrinogens, which bind to platelets, contribute to their aggregation, and enhance their ability to clot; and stimulation of nerve cells that leads to changes in the nervous system's control of breathing and heart rate. The high number concentration and small size of nanoparticles lead to high rates of deposition deep in the lung.[3] The ultrafine particles (< 0.1 micron) have been found to promote acute pulmonary response,[4] and they impair the ability of the macrophages (the scavenger cells in lungs) to engulf and remove particles from the extracellular milieu.[5] Therefore, nanoparticles emitted by combustion sources are a very serious health concern because of both their size and the carcinogens with which they are associated.

Carbon nanoparticles have in addition an adverse impact on the environment, in terms of visibility degradation and likely contributions to global warming. Global warming is broken down into effects from gases and effects from aerosols. It is easier to compute the effect of greenhouse gases in forcing the radiative transfer of the atmosphere, i.e. mainly the CO_2 problem. However, the role of aerosols, through their albedo[6] in changing the incoming and outgoing radiative flux from the surface of the earth, is much more difficult to assess. Furthermore, the presence of aerosols is critical for the heterogeneous nucleation of water droplets and hence for the formation of clouds, which themselves have a central and not yet fully understood effect on the radiation balance on the atmosphere.

The problems of both climate change and health effects point to the question of characterizing chemical and physical properties of atmospheric particles, which is obviously related to the relative role of natural and anthropogenic processes in their formation. Combustion is the main process through which man continuously injects particles into the atmosphere. More importantly, these particles are produced at the smallest sizes physically possible in the form of clusters with nanometric dimensions.[7] Therefore, it is clear that it is not possible to give a precise answer to the environmental problems outlined above, without going deeper into the chemistry and physics of the formation of particles at high temperature during combustion processes, and following their subsequent evolution and fate at ambient temperature.

The goal of this work is to characterize organic pollutants of high molecular mass both chemically and physically, to study their fate in the environment, especially within living organisms. Size, chemical functionalities and water solubility have a decisive role in establishing the interactions of aerosol with human tissues in the lungs. The same parameters establish their optical properties relevant to direct radiative forcing and to their ability to act as cloud condensation nuclei.

The primary focus is to provide a detailed multi-scale characterization of nanoparticle formation in combustion environments, through the use of novel simulation methodologies operating across disparate (spatial/temporal) regimes. The use of atomistic models, such as the Kinetic Monte Carlo technique and Molecular Dynamics simulation, allow us to follow the transformations that occur during nanoparticle formation in a chemically specific way, thereby providing information on both the chemical structure and the configuration of the nanoparticles and their agglomeration. This approach establishes a connection between the various time scales in the nanoparticle self-assembly problem, together with an unprecedented opportunity for the understanding of the atomistic interactions underlying carbonaceous nanoparticle structures and growth. Preliminary results will also be given from atomistic-scale simulations of the nanoparticles interacting with model cell membranes.

References

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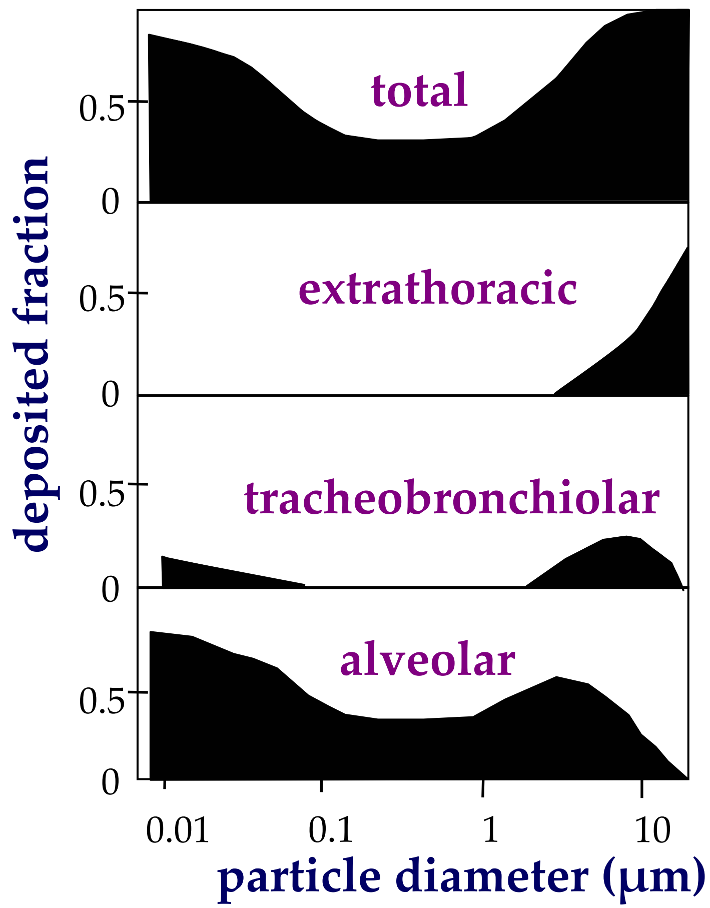
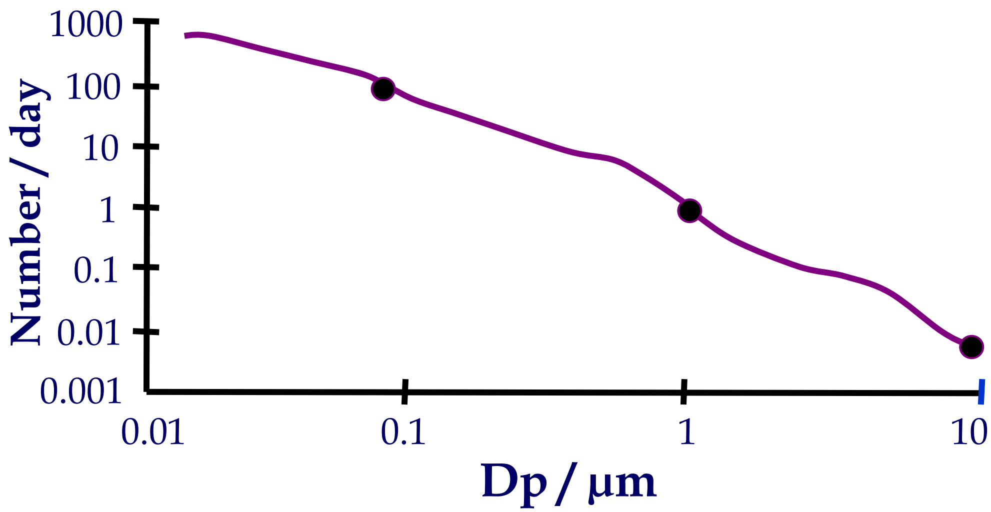
Health Impact: Why nanoparticles are bad, hence important?

Deposition of ultrafine particles



From H. Schulz et al. 2000

Average Deposition #/day/alveolus



Number deposited/Alveolus/day = 0.01 for 10μm, 1 for 1μm, 100 for 0.1μm (Oberdoester, 2001)

Health Impact: Particle Effects (HEI, 2002)

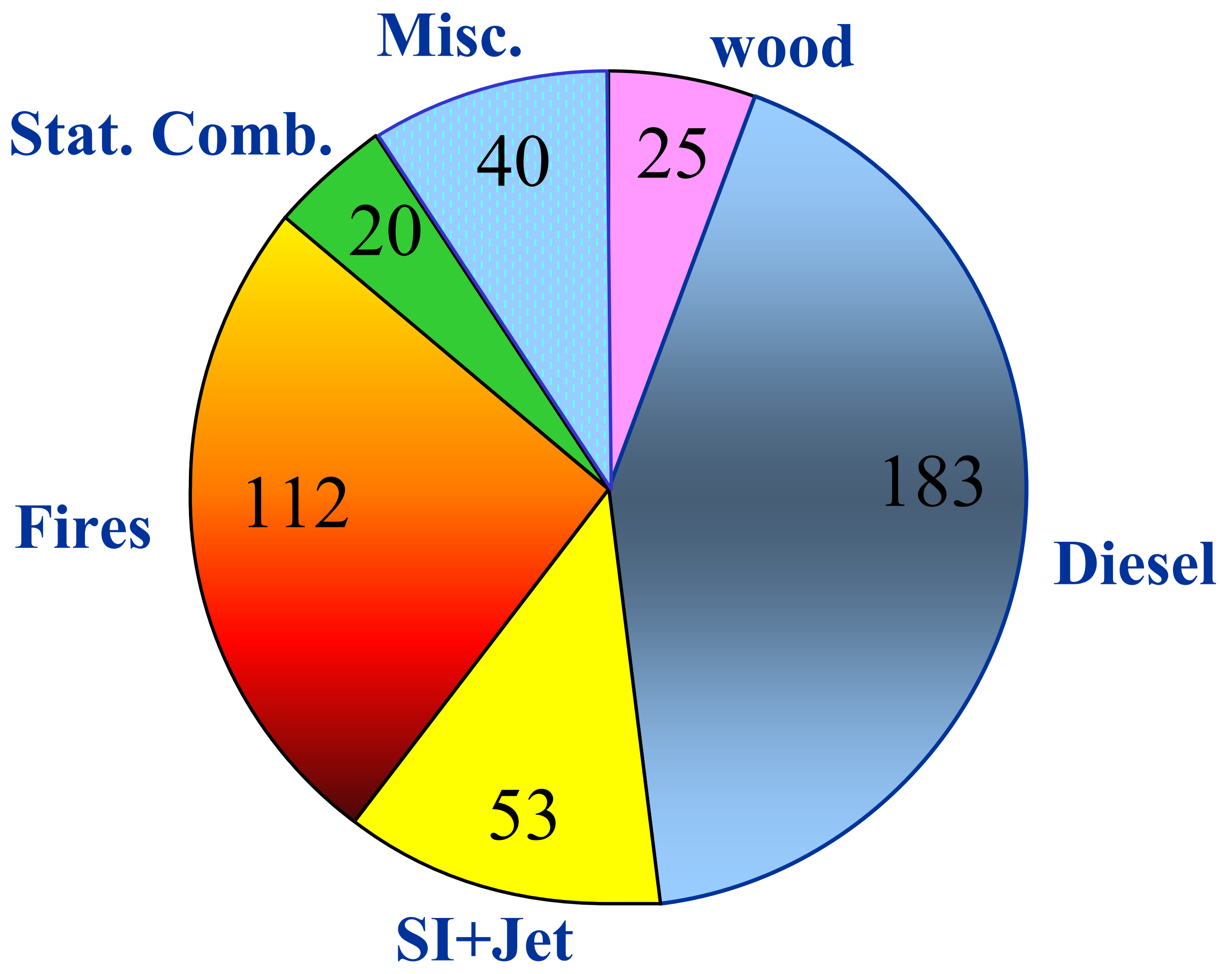
Evidence for different fate of inhaled ultrafine particles

- Passage of inhaled carbon particles in the blood circulation (Nemmar et al., 2002).
- Substancial translocation of inhaled ^{13}C-carbon particles into the liver (Oberdorster et al., 2002)
- Translocation of inahed insoluble iridium particles from lung epithelium to extrapulmonary organs (Kreyling et al., 2002)

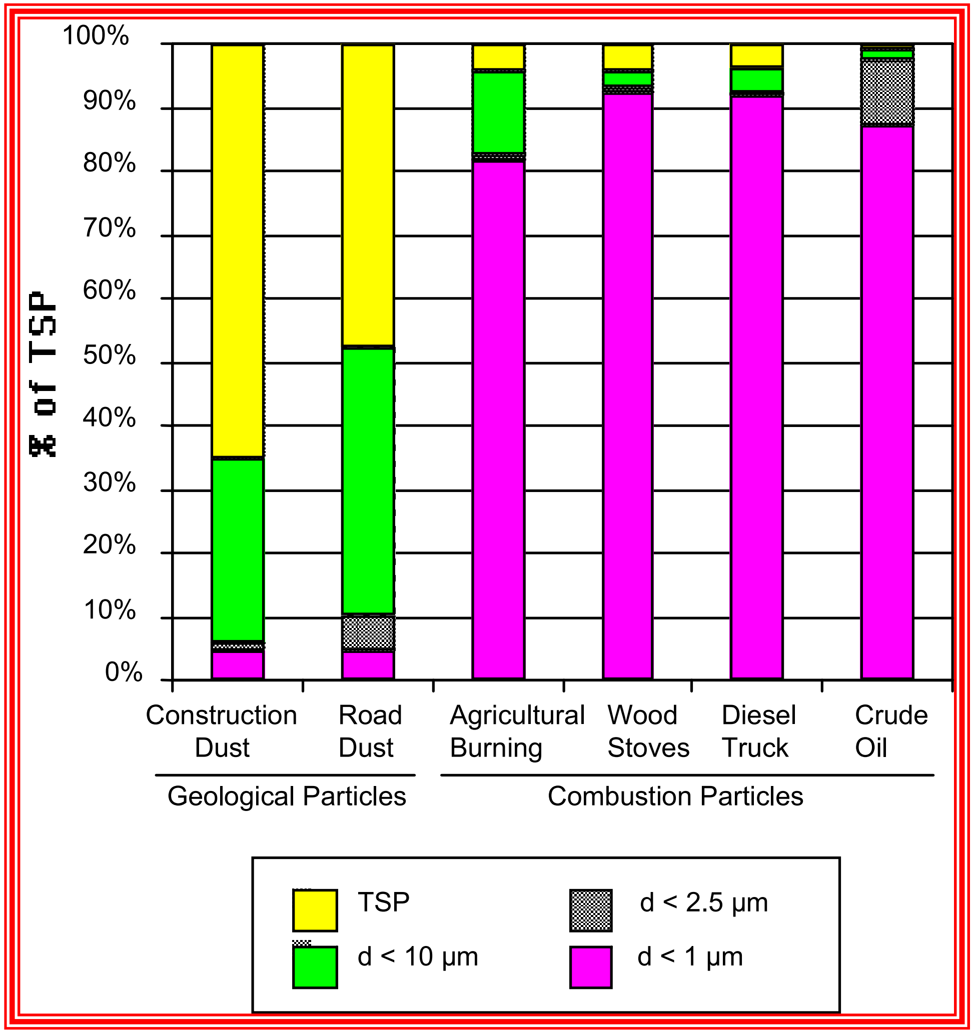
Factors are:

Solubility, chemical composition, surface area, singlet or agglomerates, etc…

Major classes of particulate matter: Carbonaceous particles dominate (Pace, EPA'01)



Major classes of particulate matter: Carbonaceous particles dominate (Pace, EPA'01)



(Watson,'99)

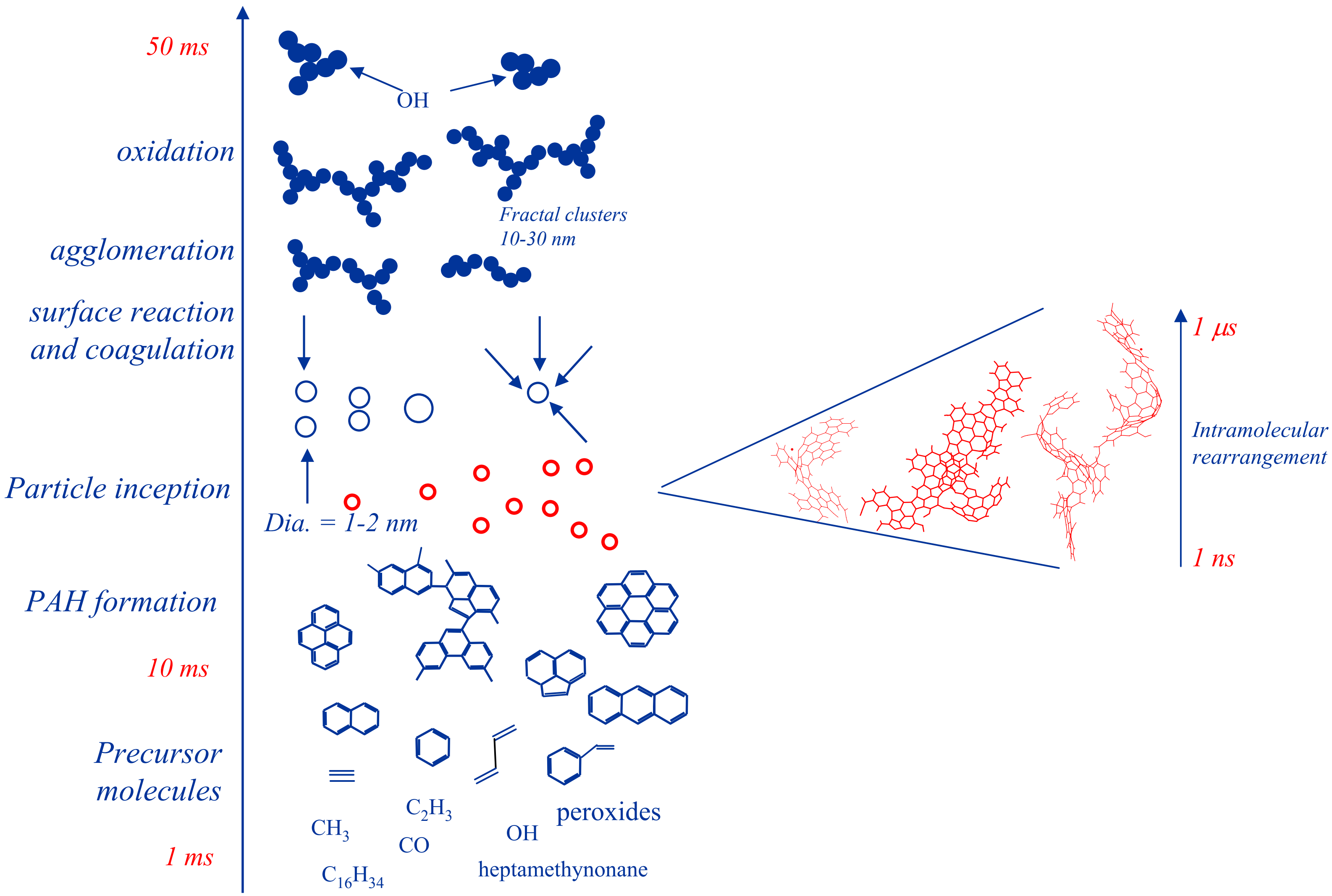
Major classes of particulate matter: Carbonaceous particles dominate (Pace, EPA’01)

… from combustion processes

combustion sources dominate *submicron* particles

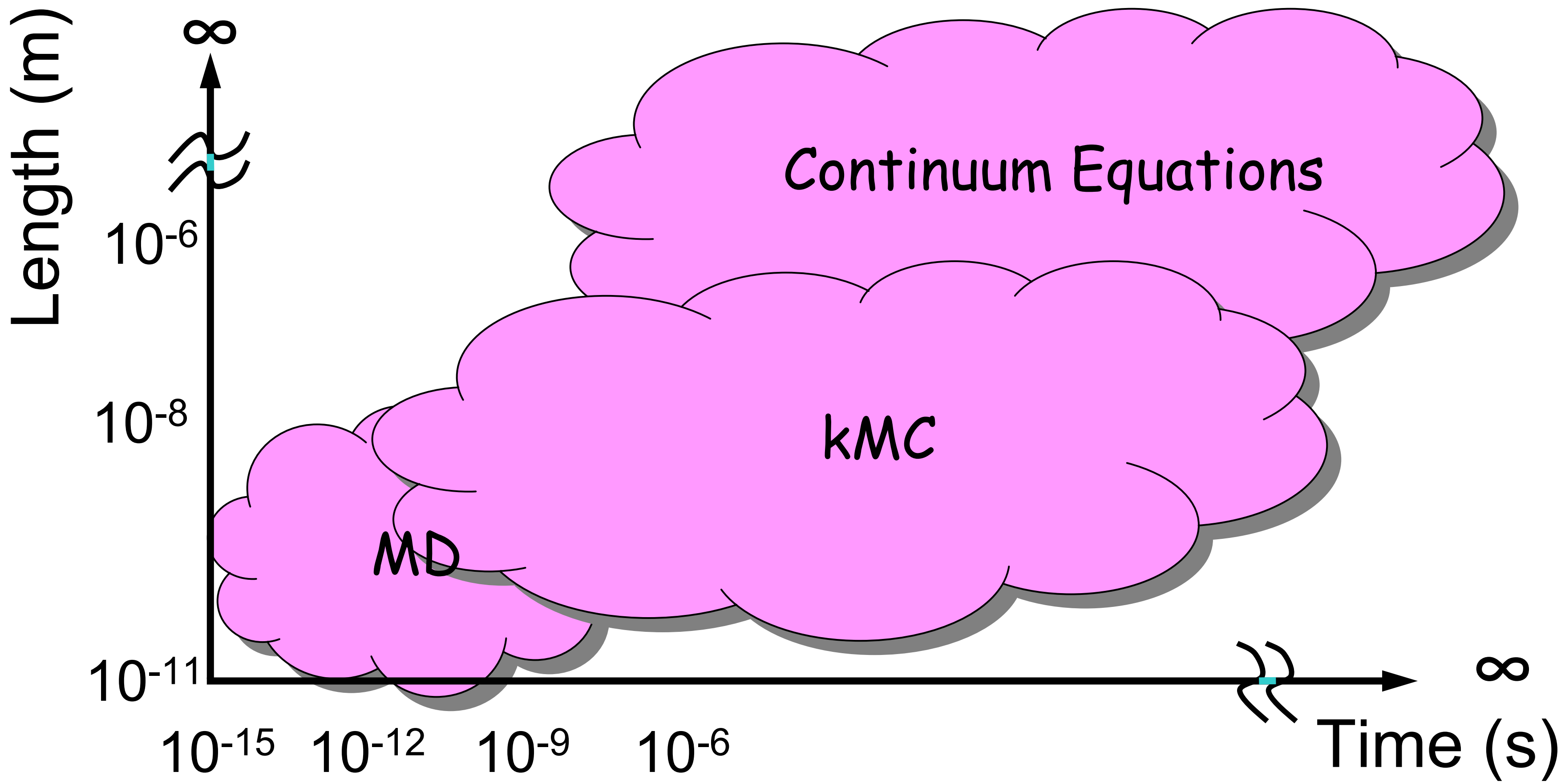
Health issues require knowledge of the chemical and physical properties of carbonaceous material, such as size, morphology, chemical composition, etc.

Particle Formation from Combustion Sources

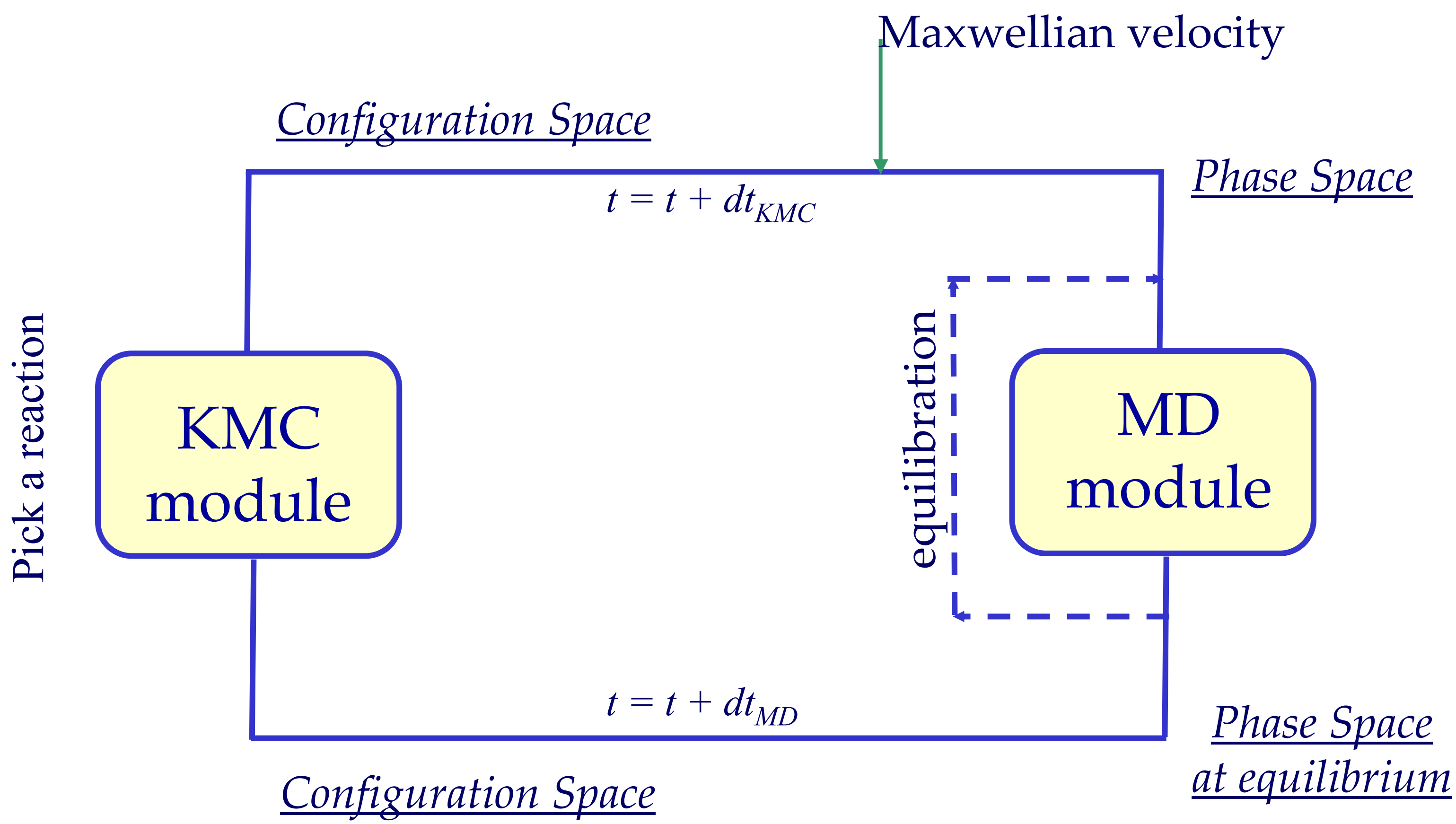


adapted from Bockhorn

A Multi-Scale Problem: Setting the stage



Atomistic Model for Particle Inception: AMPI code

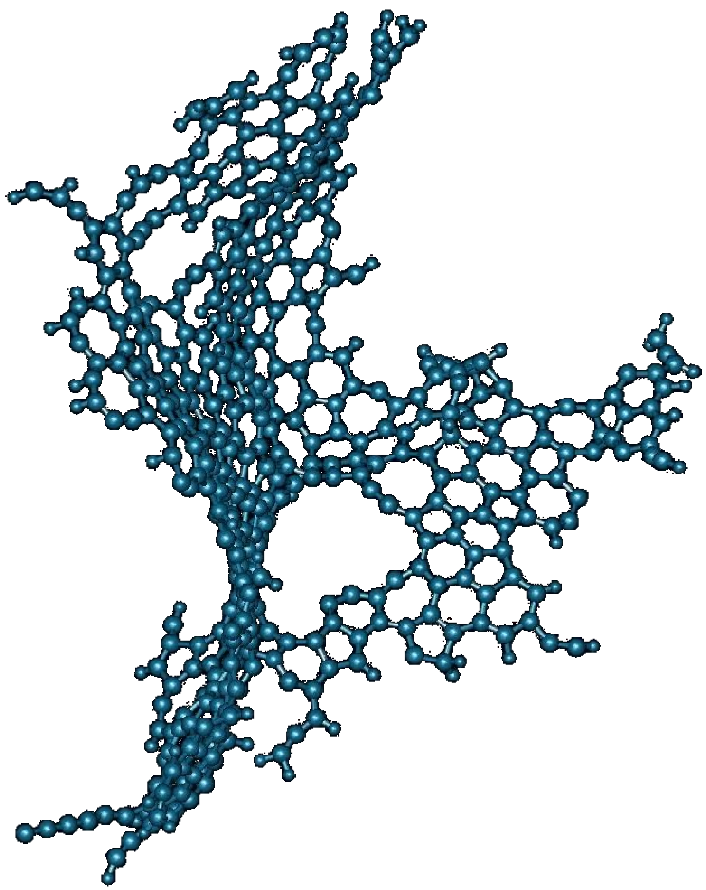


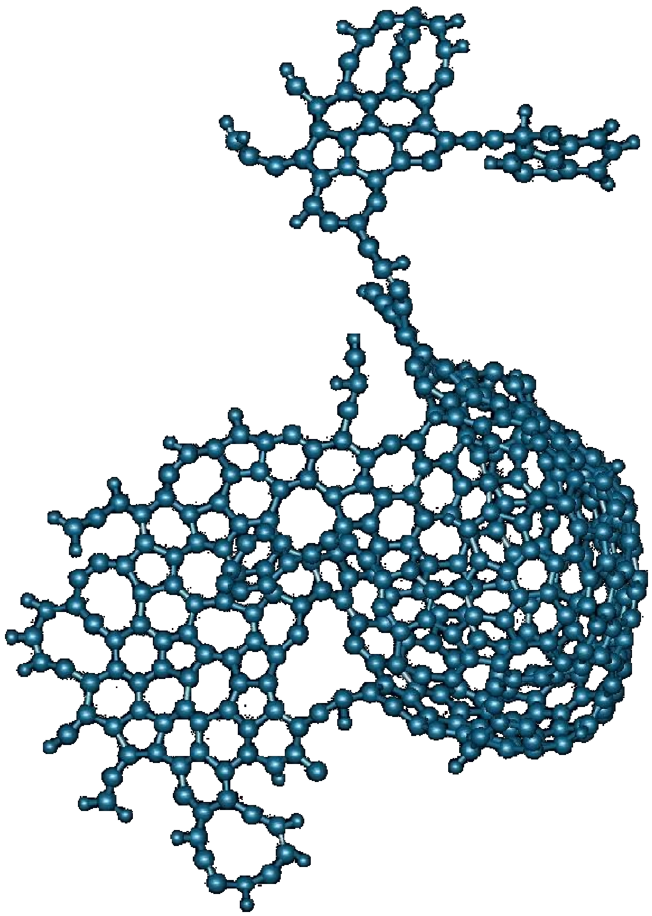
Violi, Sarofim, Voth *Comb. Sci. Tech.* 2002
Violi *Combust. Flame* 2004

Structure for chemical and physical properties

- H/C
- Free radicals concentration
- Functional group distribution
- Morphology
- Surface Reactivity
- Optical properties
- Porosity
- Surface area
- Pore Size Distribution
- Surface-Averaged Energy distribution
- Density

Influence of reaction pathways





aliphatic and aromatic flames for the sphericity

From combustion sources to living cells

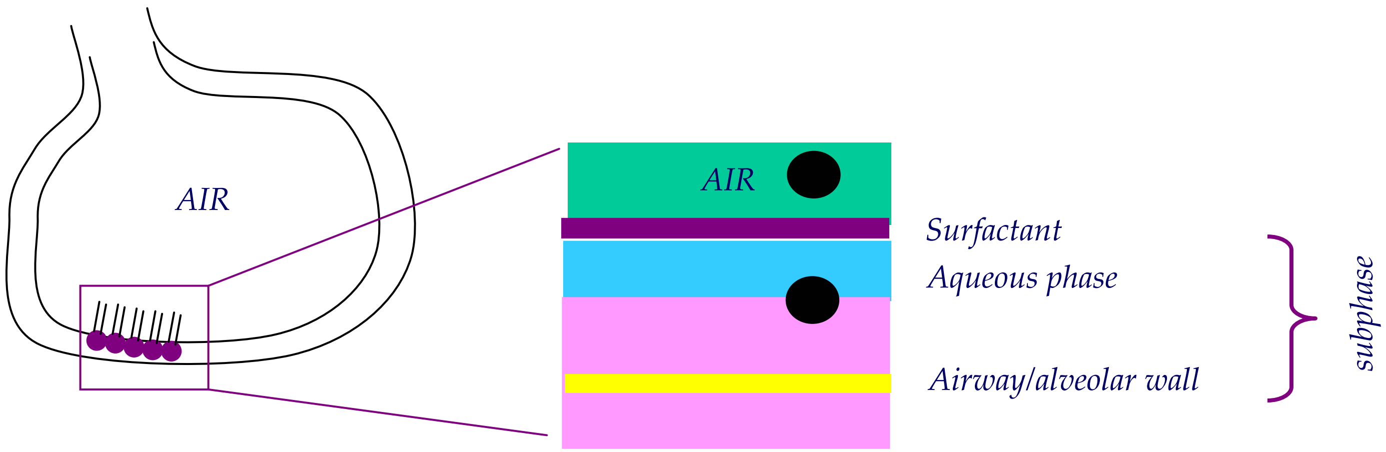
Biomedical Impact: objectives

To gain a detailed knowledge of the long term interactions of nanoparticles with self-assembled biological structures, such as lipid bilayer membranes and lung surfactant.

To elucidate the role of:

- carbon nanoparticles in changing the *morphology,* surface tension, and mechanical response of the biomolecular assemblies,
- the carbon nanoparticle *thermodynamics* of interaction with the biomolecular assemblies,
- the carbon nanoparticle *transport* through the biological assemblies.

Translocation of Nanoparticles: Lung Surfactant



Surfactant in an alveolus

By lowering and varying surface tension during breathing, lung surfactant reduces respiratory work and stabilizes alveoli against collapse and overexpansion.

DPPC is an amphiphillic molecule

Carbonaceous Nanoparticles in DMPC