Hierarchical Structure of Nano-Aggregates

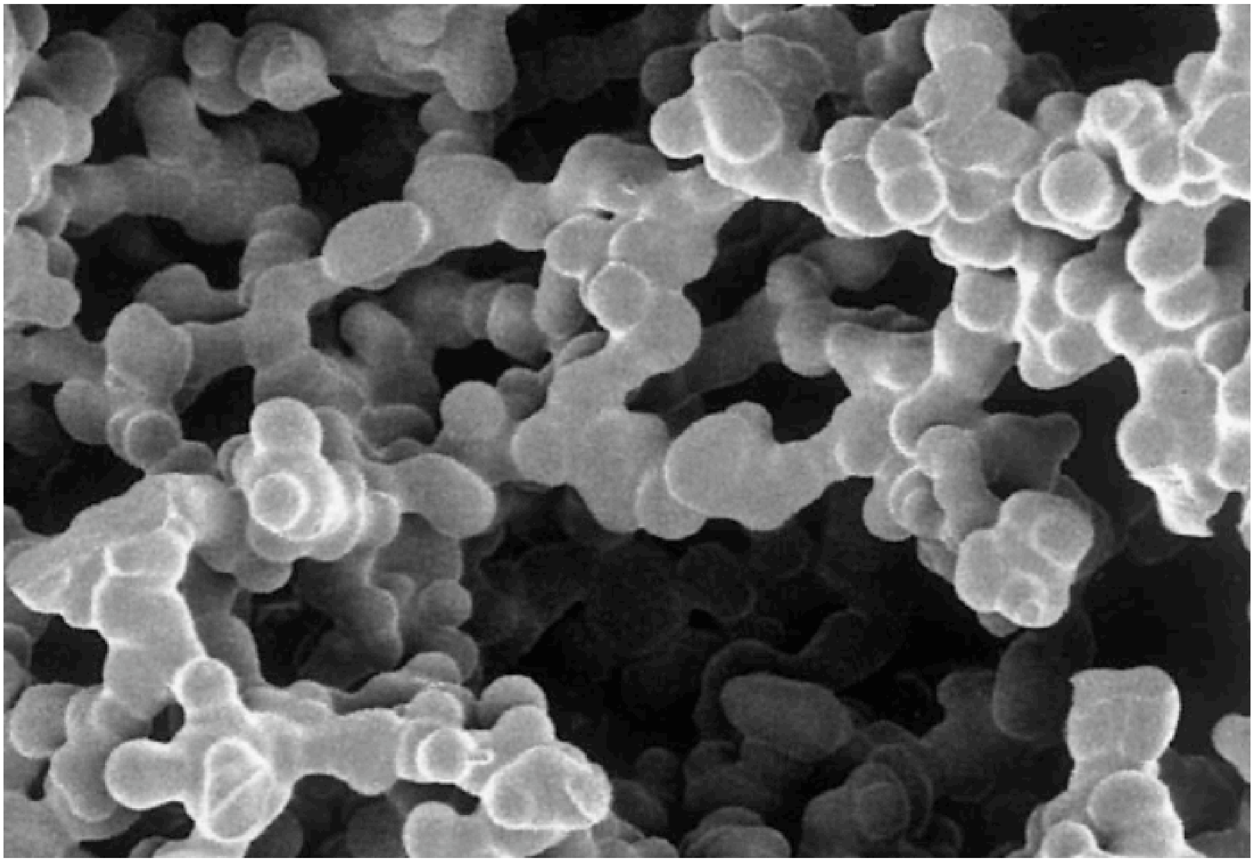


Figure 1. Hierarchical structure for a silica-siloxane hybrid material used for low density super-insulation. Guo L, Hyeon-Lee J, Beaucage G *J. Non-Cry. Solids* **243** 61-69 (1999).

Nanoaggregates are materials that are used for a variety of industrial applications. Titania and zirocnia aggregates are used as heterogeneous catalyst supports providing extremely high surface areas for chemical reactions. Carbon and silica aggregates are used as reinforcing filler for polymers and elastomers providing high surface area for interfacial contact and a large volumetric displacement due to the large hydrodynamic radius of aggregates relative the primary particle from which they are constructed. Nanoaggregates are used as food additives to add body to foods like ketchup and yoghurt, as filtration media for food, most domestic beer is filtered with colloidal silica. These nanomaterials are also used as additives to toothpaste, and other consumer produces and pharmaceuticals. Aggregates are used to prevent sticking and to assist in slip for industrial processes such as the production of plastic film. Aggregates are used as absorbents both active such as activated carbon and iron oxide nano-particulates as well as passive such as silica gel used in electronics packaging inserts. Aggregates of organic pigments, Figure 3, have a strong effect on the coloration of these plastics additives.

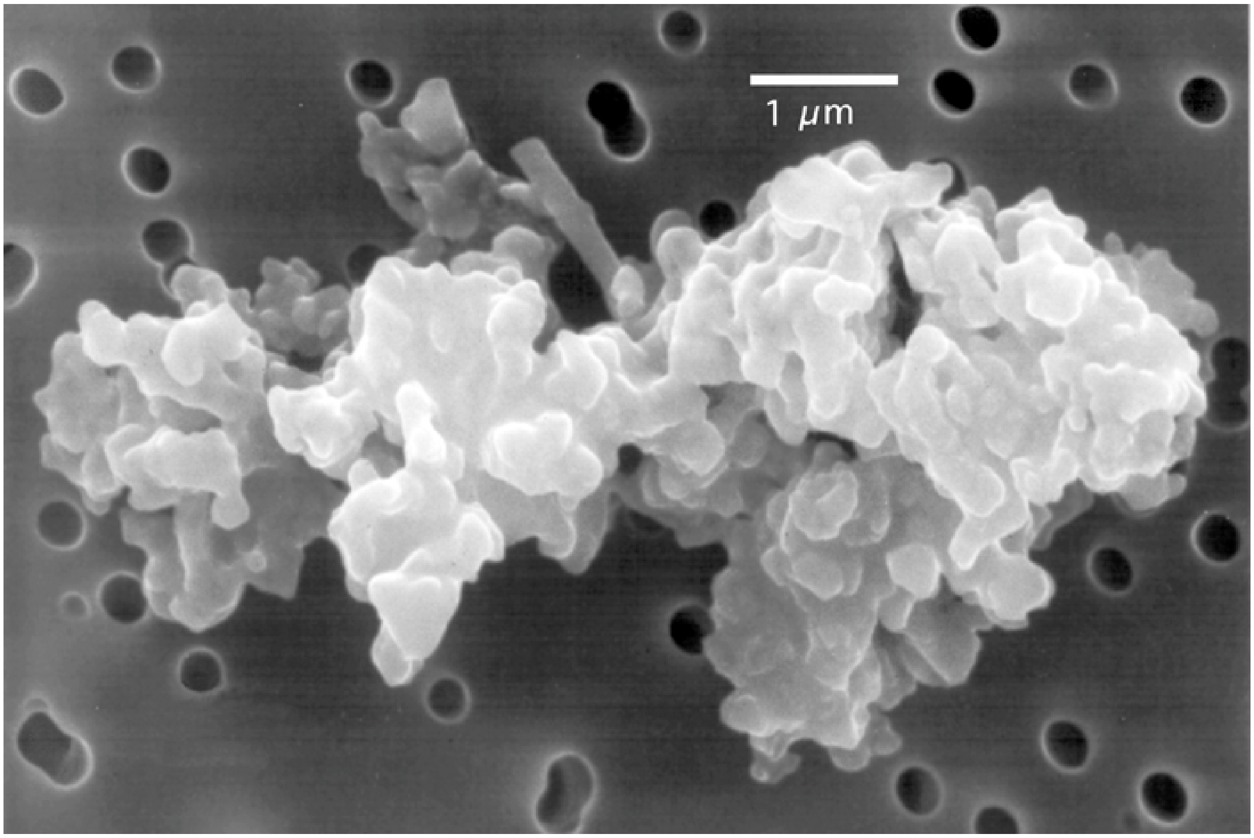
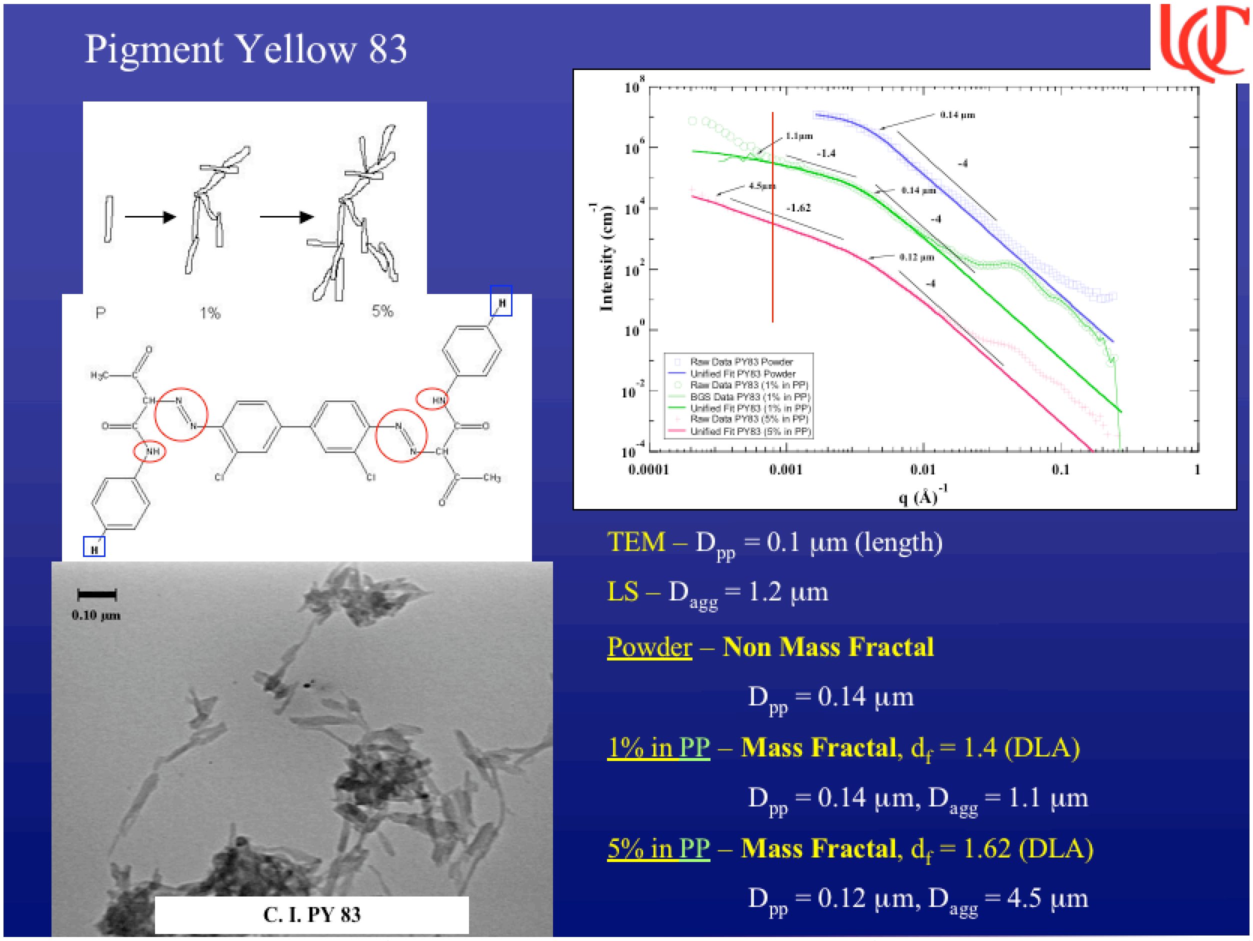


Figure 2. Space Dust. *This is a scanning electron micrscope image of an interplanetary dust particle that has roughly chondritic elemental composition and is highly rough (chondritic porous: "CP"). CP types are usually aggregates of large numbers of sub-micrometer grains, clustered in a random open order. The authors of this figure are Don Brownlee, University of Washington, Seattle, and Elmar Jessberger, Institut für Planetologie, Münster, Germany. This file is licensed under Creative Commons Attribution 2.5 License: http://creativecommons.org /licenses/by/2.5/* From http://en.wikipedia.org/wiki/Image:Porous_chondriteIDP.jpg (11/30/07).

Aggregates also occur in the natural environment for example, Figure 2 shows a kind of silica aggregate that is observed in interstellar space called "space dust". Space dust is of scientific interest since it is the material form which solar systems are constructed. It is of technical interest since these tiny ceramic aggregates moving at extremely high velocities are common to the space environment meaning that any device put into space is constantly bombarded by these nano-bullets. Space dust is one of the chief limiting factors to interplanetary space travel.

Hierarchy of Aggregates:

Aggregates as a class can be described in terms of a hierarchy of structure beginning with the primary particle or base unit of the aggreagate. Typically the primary particle can not be easily broken down either mechanically or visually, it represents the smallest structural feature that is identified in a micrograph for instance. Primary particles can be of asymmetric shape, such as in the organic pigment particles shown in Figure 3. More often primary particles are largely symmetric although they are often faceted such as the silica particles in Figure 2. Since on of the primary uses of nano-aggregates involves their high surface area a convenient means to quantify



Pigment Yellow 83

TEM – D_{pp} = 0.1 μm (length)

LS – D_{agg} = 1.2 μm

Powder – **Non Mass Fractal**

D_{pp} = 0.14 μm

1% in PP – **Mass Fractal**, d_f = 1.4 (DLA)

D_{pp} = 0.14 μm, D_{agg} = 1.1 μm

5% in PP – **Mass Fractal**, d_f = 1.62 (DLA)

D_{pp} = 0.12 μm, D_{agg} = 4.5 μm

Figure 3. Organic Pigment from Sun Chemicals. Dissertation of Nikhil Agashe University of Cincinnati.

primary particles is the Sauter mean diameter. The Sauter mean diamter is defined as diameter of a sphere that has the same surface to volume ratio as the particles. The volume of a sphere is given by $4\pi R^3$ and the surface area by $4/3 \pi R^2$ so $d_p = 2R = 6 (V/S)$. Typically we measure the specific surface area, S_V, as m^2/g. The 6000 divided by the density in g/cm^3 times S_v yields the Sauter mean diameter in nanometers.

$$d_p = \frac{6000}{\rho S_V} \qquad (1)$$

The size of primary particles is generally described by a distribution rather than a single value. The primary particle size distribution is, for the most part, a skewed distribution that reflects 1) the more rapid transport of smaller primary particles; 2) the large surface area of large primary particles and 3) The production of a large primary particle from the collision of a small primar and a large primary that is almost indistinguishable from the starting large primary particle. As particle growth progresses a broad distribution of particle size will narrow, Figrue 4. This narrowing will continue until a dynamic equilibrium is reached where the average particle size grows while the shape of the particle size distribution remains the same.

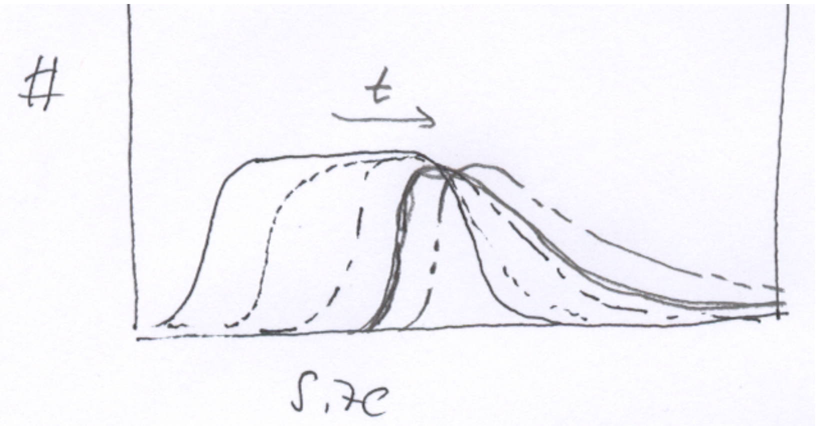


Figure 3. Typical evolution of particle size distribution with time.

The final shape of the particle size distribution becomes symmetric when the size (x-axis) is plotted on a log-scale. A bell-shaped curve on a linear log-scale is described by the log-normal distribution function;

$$f(x,\mu,\sigma) = \frac{e^{-\frac{(\ln x-\mu)}{2\sigma^2}}}{x\sigma\sqrt{2\pi}} \quad \text{where } e^{\sigma} = \sigma_g = \text{ geometric standard deviation}$$

$$e^{\mu} = m = \text{ geometric mean}$$

For the final distribution, or self-preserving distribution, the geometric standard deviation, $\sigma_g \sim 1.5$.

Aggregate Growth:

Aggregates grow by a similar mechanism to primary particles in that small aggregates and primary particles have superior transport compared to large bulky aggregates while large aggregates provide a larger profile for collision. Aggregate growth occurs at a lower temperature or under conditions where coalescence is not possible. Figure 4 shows micrographs of primary particle and aggregate growth in a flame. The initial nucleation is associated with aggregation but due to high temperatures these aggregates collapse and coalesce into larger primary particles. Higher in the flame larger primary particles again aggregate and form stable nano-aggregates due to the dropping temperature profile with height in the flame. We expect the dominant mechanism of growth for aggregates to be primary particle/large aggregate or small aggregate/large aggregate growth. Growth can be dominated by transport, diffusion limited growth (DLA), or dominate by the slow kinetics of bonding of particles into aggregates, reaction limited growth (RLA). For example, at high temperatures we expect diffusion limited growth of ceramics in flames while at low temperatures where bonding is more difficult, we expect reaction limited growth. Generally, RLA leads to dense aggregates and DLA leads to diaphanous, ramified aggregates. This is because the particle can attach and release from an aggregate during RLA probing several different bonding states and finding the state that most significantly reduces the surface area of the aggregates, that is a state with multiple bonding sites. We expect RLA to lead to highly branched aggregates while DLA will lead to lightly branched aggregates.

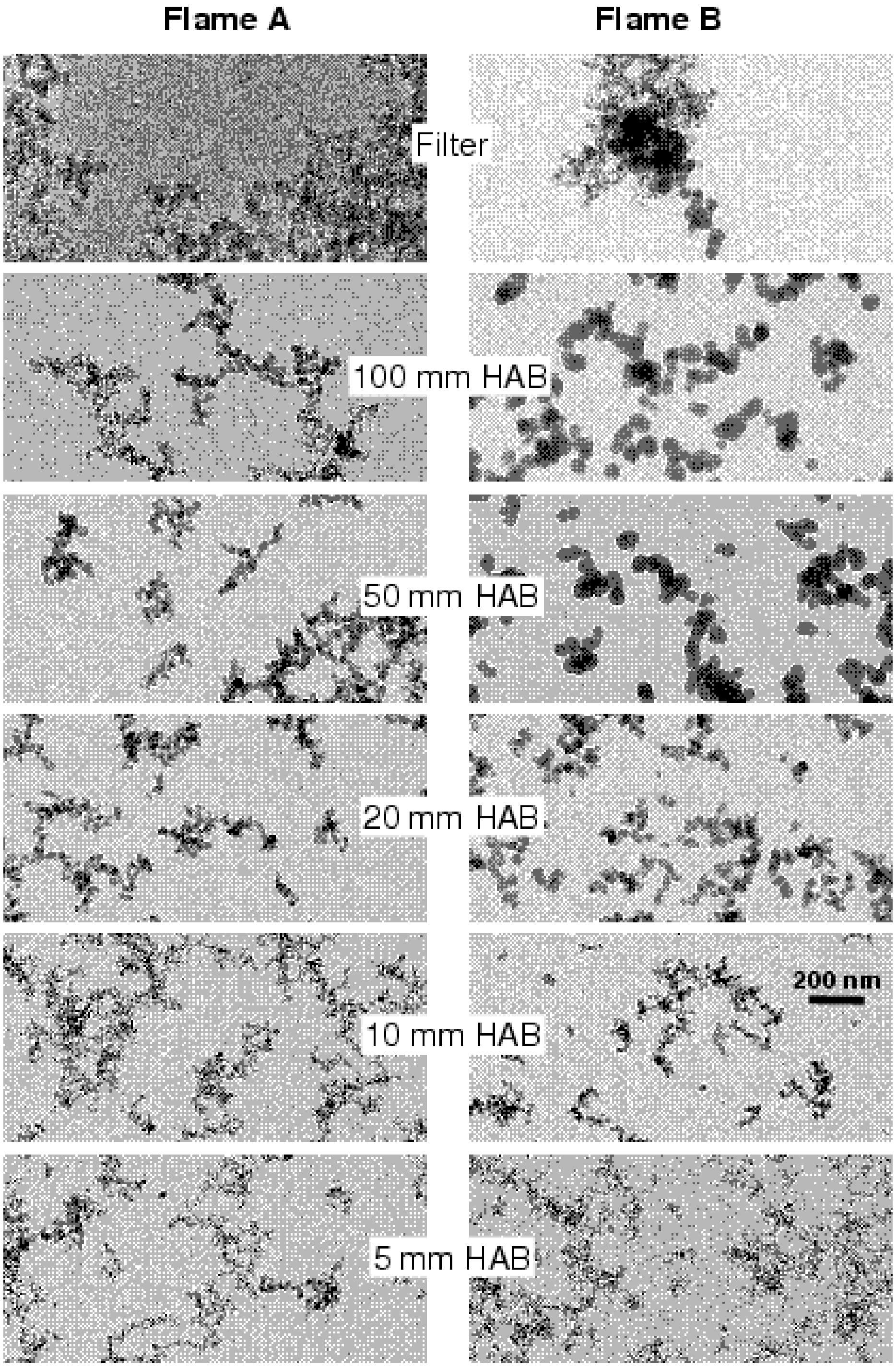
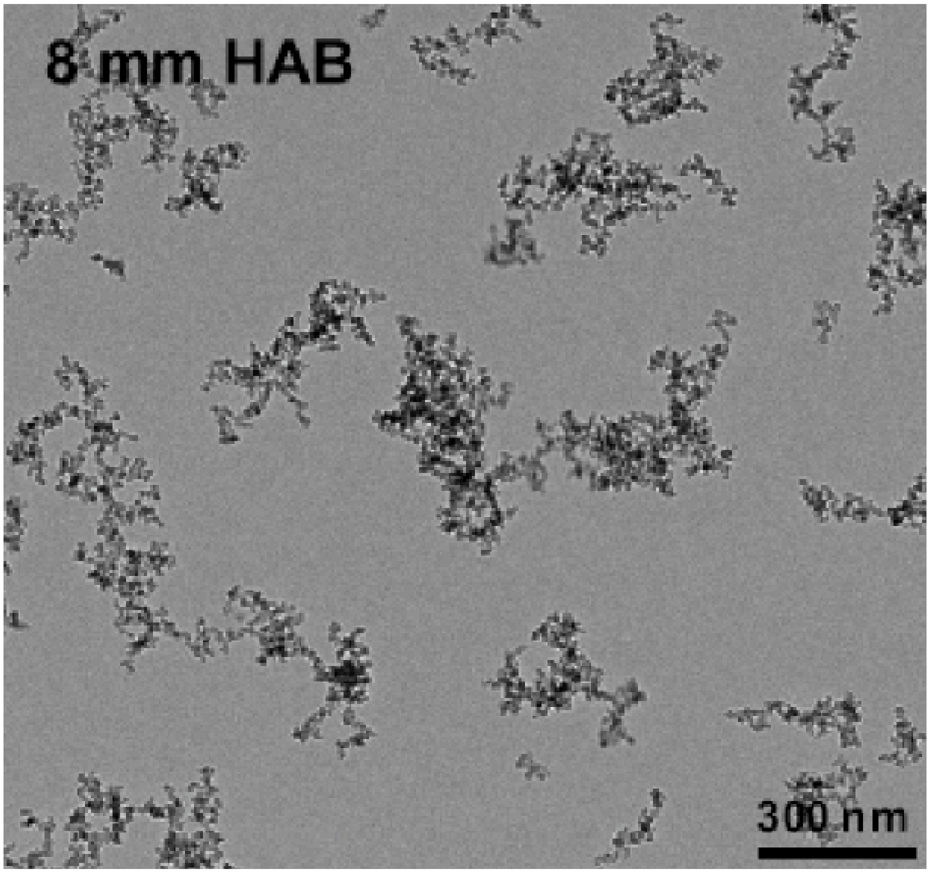


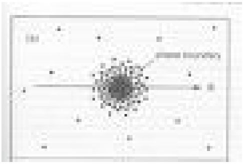
Figure 4. Primary particle and aggregate growth in two flames. Kammler HK, Beaucage G, Kohls DJ, Agashe N. Ilavsky J *J Appl. Phys.* **97**(2005) (Article 054309).


8 mm HAB
300 nm

Lower Energy Barrier for Surface Nucleation
(Lower Supersaturation is Needed)

Homogeneous Nucleation

Surface Nucleation



$$G = \Delta H r^3 + 6\gamma r^2$$

$$G = \Delta H r^3 + 4\gamma r^2$$

Figure 5. Bulk (homogeneous) versus surface (heterogeneous) nucleation.

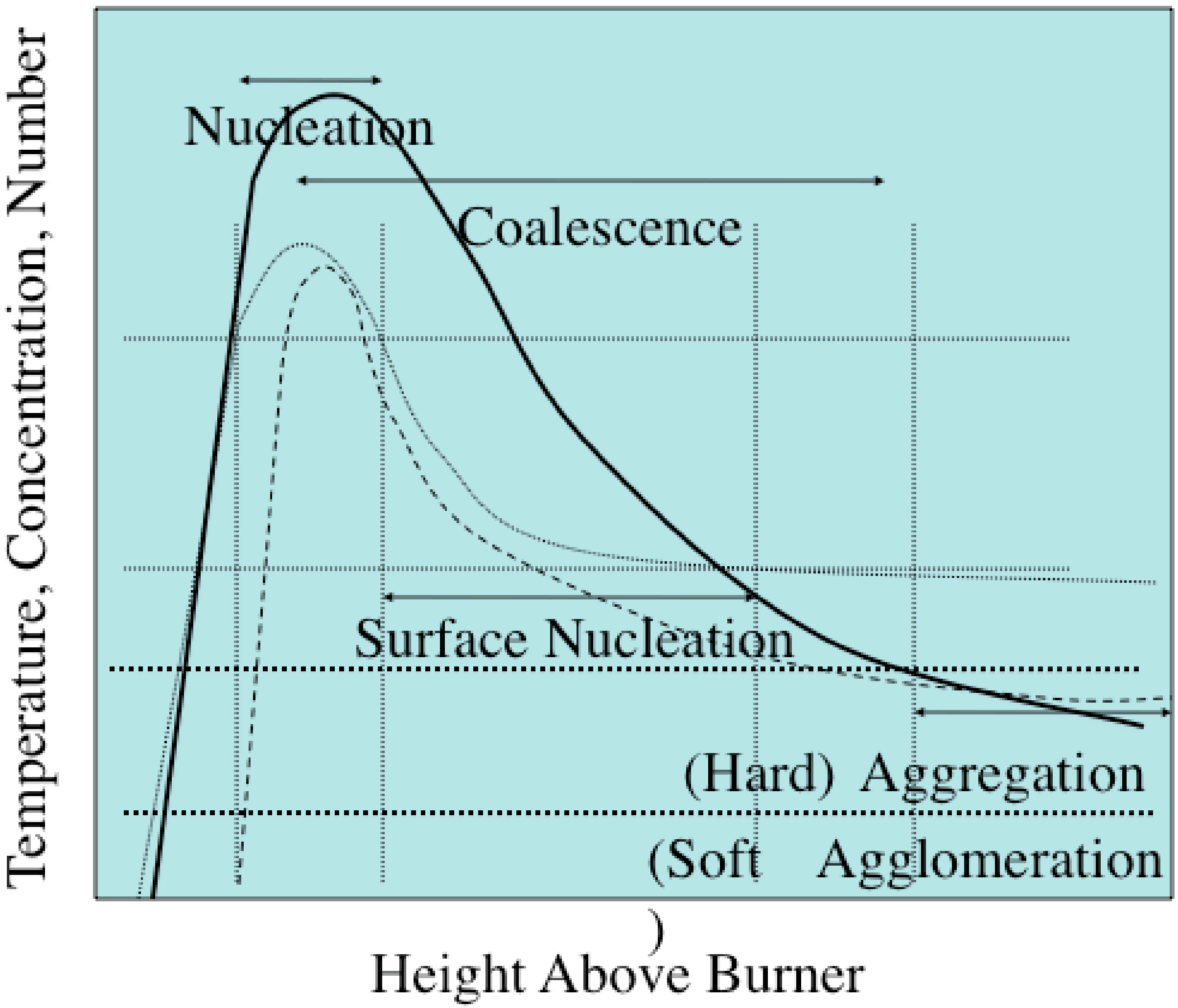


Figure 6. Regimes of Growth.

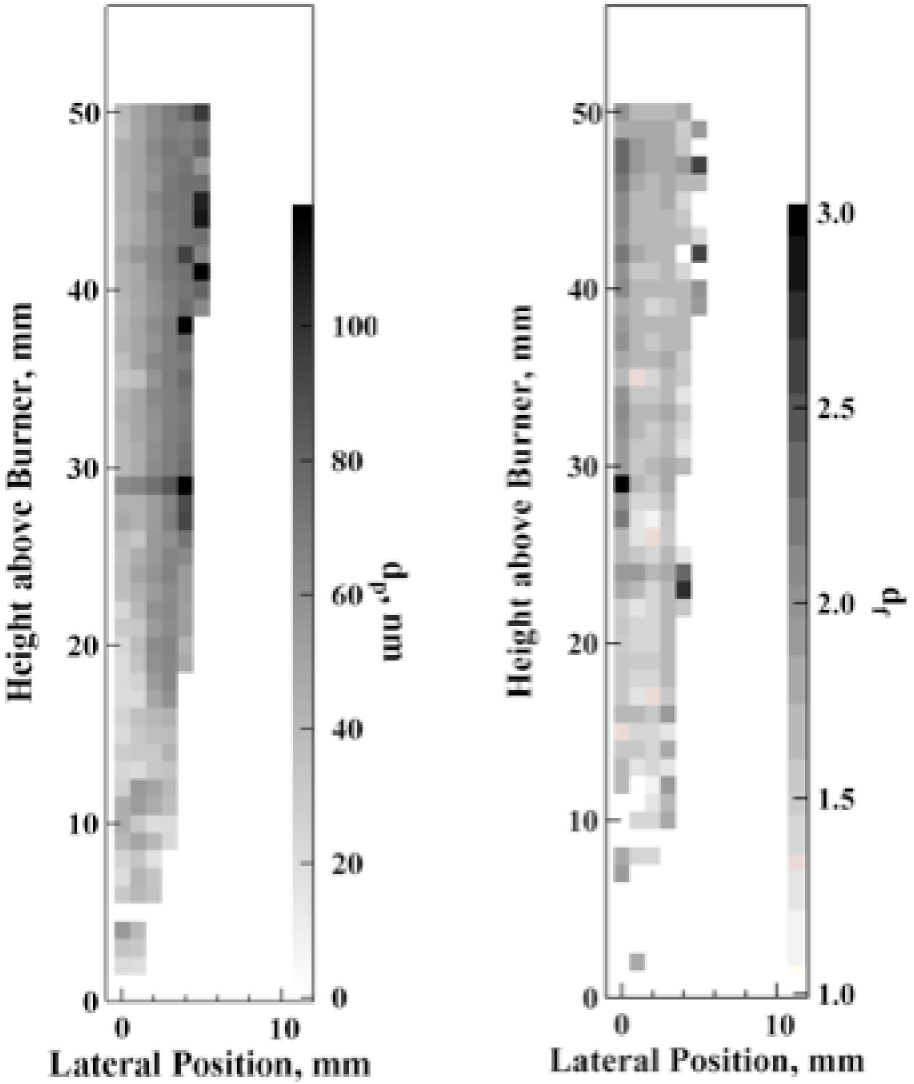
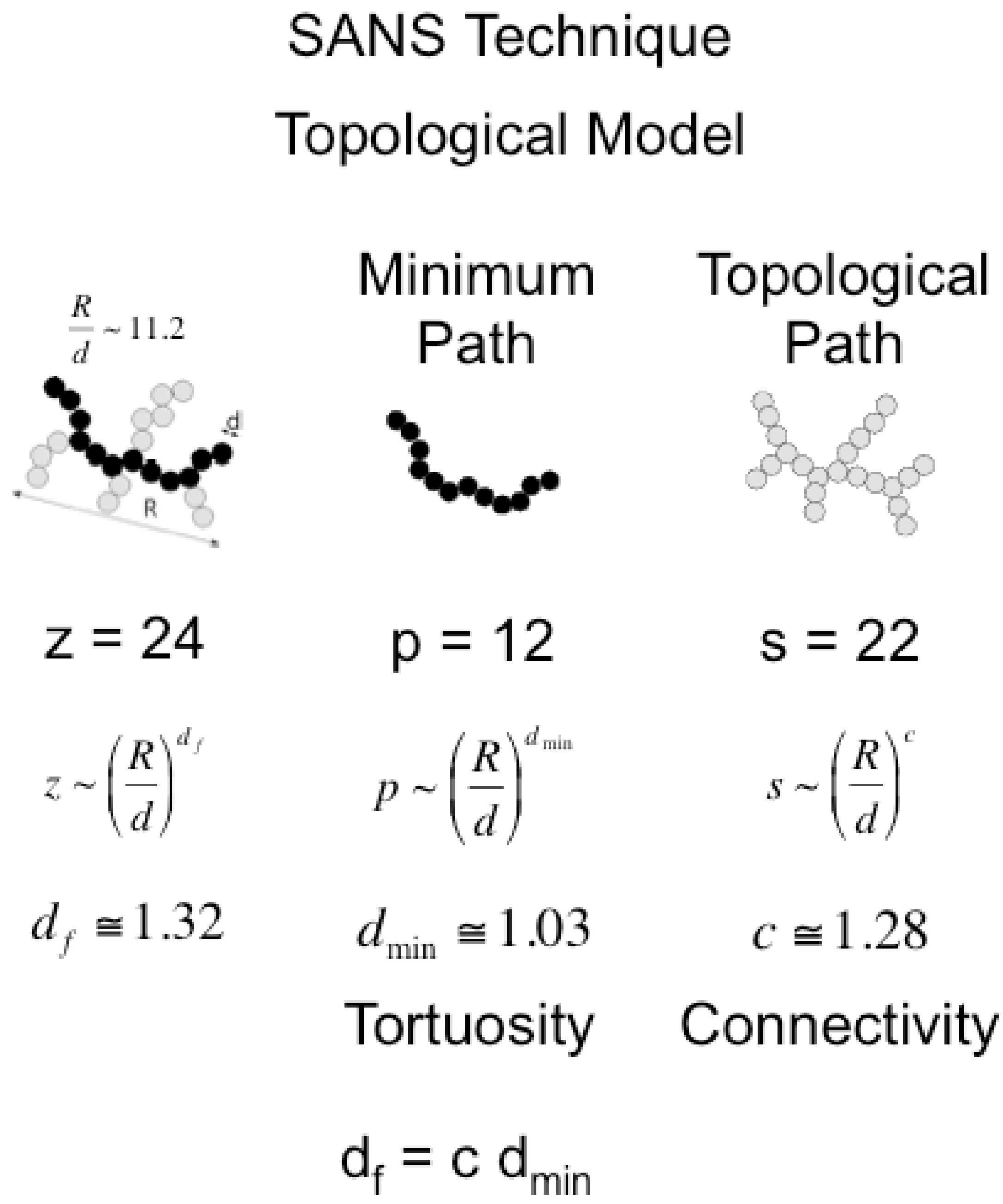


Figure 7. Aggregation versus Coalescence. (Hot part of this flame is towards the outside.)



SANS Technique

Topological Model

$\frac{R}{d} \sim 11.2$

Minimum Path

Topological Path

z = 24

p = 12

s = 22

$z \sim \left(\frac{R}{d}\right)^{d_f}$

$p \sim \left(\frac{R}{d}\right)^{d_{\min}}$

$s \sim \left(\frac{R}{d}\right)^{c}$

$d_f \cong 1.32$

$d_{\min} \cong 1.03$

$c \cong 1.28$

Tortuosity

Connectivity

$d_f = c\ d_{min}$

Figure 8. s, p, d_{min}, c, d_f, z and ϕ_{Br}.

$Modulus \sim \frac{kT}{M^{1/d_{\min}}}$ For large N $\frac{f_{agg}}{f_1} = cN^{1/c}$ $\frac{D_{agg}}{D_1} = \frac{1}{c}N^{-1/c}$

Cyclics and 4 arm stars: