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Framework: How Rapid Coagulation can be for Diesel Soot ?

Very rapid coagulation may take place in exhausts and sampling system of Diesel engine. Information about the kinetics of the agglomeration process is useful to assess the design requirements of exhausts and sampling systems. On the other hand, the knowledge of the rate of coagulation can be extremely useful to infer some properties of the combustion aerosol both in the cylinder and at exhaust, like the degree of agglomeration, the temperature of the gas, the density of the particles. The investigation about agglomeration kinetics in such environments must front the inner nature of diesel combustion (high gas temperature and pressure, complex fuel composition, turbulent mixing, unsteady nature of the process), which makes difficult the recovering of clear evidence for agglomeration kinetics concepts. thus, feasibility of measurements can be usually first checked in atmospheric flames.

Soot formation verify in diesel engines at temperature between 1000 and 2800 K, at pressure of 50 to 100 atm. It is usually described in terms of soot volume fraction fv , i.e., the ratio of the volume of solid particles with respect the total volume of particles plus gas, of number of particles per unit volume N and of size of particles d with volume v. The volume fraction is obtained integrating the product of the particle volume and the number distribution over the whole probability distribution of particle number concentration vs. volume (or radius).

From measurements of mass concentration M_S at exhaust (of order of 10 mg / m^3 at low load for light-duty diesel engines) and soot density ρ_s (about 2.0 g / cm^3) it is possible to evaluate the volume fraction as $f_V = M_S / \rho_s$. Nevertheless, number density is *not* immediately *computable* lacking specific information about the agglomeration process in terms of mean number and size of elementary particles in aggregates.

Competition between Nucleation and Agglomeration

The balance between the two processes of nucleation and agglomeration is represented by the following equation (Heywood, 1988):

$$dN/dt = \dot{N}_n - \dot{N}_a \quad .$$

Thus, number density of particles peaks when the rate at which fresh nuclei appear $\dot{N}_n$ balance the rate of agglomeration $\dot{N}_A$ of spherules or particles which collide and consequently undergo *coalescence* (two particles fuse in one particle) or *sticking* (two particles form a doublet, in which each particles retains its original shape) . For $\dot{N}_n > \dot{N}_a$ the dominant mechanism is nucleation. When $\dot{N}_a > \dot{N}_n$ elementary spherules of order of less than 10 nm undergo a high number of agglomerating collisions standing number concentration of order 10^7-10^9 part / cm^3.

At $\dot{N}_a > \dot{N}_n$ the nucleation mechanism ends due to the enhanced possibility of occurring of gaseous deposition of hydrocarbon intermediates on the particle surface.

Thus, slightly on the right of the peak of $N(t)$ curve, all the subsequent increase in fv is due to the surface growth. Pure agglomeration does not contribute to the augmenting of fv , i.e., the number of cluster can be obtained as the ratio of the initial primary particles (monomers) and the mean number of monomers per cluster $N_A = N_0 / N_P$.

Free Molecular Coagulation: Smoluchowski Equation

For nearly monodispersed systems undergoing Brownian coagulation, very often the Smoluchowski equation for liquid colloids in the free molecular regime ($Kn \equiv \ell / r >> 1$) is advocated in the form (Heywood, 1988):

$$-dN/dt = K \cdot N^2$$

where K is the coagulation constant. Physically, K depends on size, shape, concentration and density of the solid particles and temperature, pressure and viscosity of the surrounding gas.

If K is retained constant, then the following equation is retained to hold true:

$$N/N_0 = 1/(1+KN_0t) \approx (KN_0t)^{-1}$$

where $\tau_{coag} \equiv (K N_0)^{-1}$ is the *coagulation time* (time requested to halve the initial number concentration). For particles from modern diesel engines is retained K in the range of 1.3×10^{-9} cm^3 s^{-1}.

Free Molecular Coagulation: constant *fv* and *T*

Prado and Lahaye (1981) for Free-Molecule Coagulation in flames of uncharged spherical particles ($d \leq 60nm$) obtain:

$$\frac{dN}{dt} = -\frac{6}{5} \kappa f_V^{1/6} N^{11/6} \qquad \text{with:} \quad \kappa \equiv \frac{5}{12}\left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6k_B T}{\rho_s}\right)^{1/2} G \alpha$$

with f_V, ρ_s equal to the particle volume fraction, particle density. G is a factor which accounts for the inter-particle dispersion forces (valued about 2 for spherical particles), and α equal to a weak function of the particle size distribution, reflecting the variation in collision rate with different particle sizes.

Integrating at constant *fv* and T, for large values of N_0 ($N_0 > 10^{18}$ $part/m^3$) the solution is:

$$N \propto \left[T^{1/2} f_V^{1/6} t\right]^{-6/5}.$$

Problematics and Working Strategy

Key point is that *neither* the coagulation constant K *nor* the coagulation time can be retained as *constant*. Moreover, surface growth and oxidation may be taking place during the agglomeration process.

Optical light scattering measurements of light scattering patterns for both co-and cross-polarized light $F_{VV}(\theta)$, $F_{HV}(\theta)$ have been performed in a ethylene diffusion flame at different heights above the burner.

The size of the primary spheroids which agglomerate has been deduced by Scanning Electron Microscopy at different heights above the burner and / or residence times. Particle density has been measured by Helium Pycnometry.

Fractal dimension, gyration radius and the kinetics properties in terms of structure, mean number of particles per aggregates, volume fraction and weight of the aggregates can be inferred as function of the residence time (di Stasio, 1998*c*).

It is worth to be stressed that no *a priori knowledge* about the physical and chemical properties of particles (like refractive index, shape, morphology, etc.) is assumed in the reduction of the experimental data.

Kinetics of Cluster Agglomeration

The evolution of the size distribution function $n(v,t)$ for coalescing droplets of volume v is described by the coagulation equation:

$$\partial n(v,t)/\partial t = 1/2 \int_0^v K(v', v-v')\, n(v',t)\, n(v-v',t)\, dv' - n(v,t) \int_0^\infty K(v,v')\, n(v',t)\, dv'$$

where $K(v,v')$ is defined as the *coagulation coefficient*.

As well known, two regimes are usually referenced in the literature in the limits of the Knudsen number with respect to unity.

The *Free Molecular* or Epstein Regime is considered for $Kn \equiv \ell / r >> 1$ and the coagulation coefficient can be written as the following (Mountain *et al.*, 1986):

$$K(v,v') = \left(\frac{3}{4\pi}\right)^{\frac{1}{6}} \left(\frac{6k_B T}{\rho_s}\right)^{\frac{1}{2}} \left(v^{\frac{1}{3}} - v'^{\frac{1}{3}}\right)^2 \left(\frac{1}{v} + \frac{1}{v'}\right)^{\frac{1}{2}}$$

where ρ_S is the density of the individual sphere. In atmospheric flames at about 1500 K the mean free path of gas molecules in the flame is evaluated about 350 nm (Sorensen *et al.*, 1992).

The *Continuum* or Stokes-Einstein Regime is reported for $Kn \equiv \ell / r << 1$ and the expression of the coagulation coefficient can be written as:

$$K(v,v') = \frac{2k_B T}{3\eta}\left(v^{\frac{1}{3}} + v'^{\frac{1}{3}}\right)\left(\frac{1}{v^{1/3}} + \frac{1}{v'^{1/3}}\right) = \frac{2k_B T}{3\eta}(r+r')\left(\frac{1}{r} + \frac{1}{r'}\right)$$

where η is the gas viscosity. Physically, the fluid is trapped in the agglomerate and the whole system (solid plus gas) moves as it were a compact sphere of radius of gyration R_g.

Coagulation Theory for Fractals

For Mass Fractals the equation between mass M, radius of gyration of the cluster R_g, radius of primary particles r_P and fractal dimension D_F it is written as:

$$M \propto \left(R_g / r_P\right)^{D_F}.$$

Standing the proportionality of mass and volume of the cluster for through of cluster density, the following relationship between radius of gyration R_g and volume v of the cluster can be easily argued:

$$R_g \propto v^{1/D_F}.$$

Substituting the above in the Eq.s for the coagulation coefficient it is possible to obtain two cases as in the following.

In the *Free Molecular* limit the coagulation coefficient can be expressed as:

$$K(v,v') \propto \left(v^{1/D_F} - v'^{1/D_F}\right)^2 \left(\frac{1}{v} + \frac{1}{v'}\right)^{1/2} \text{ and } \frac{N_0}{N(t)} \propto t^p, \qquad p \equiv \left(3/2 - 2/D_F\right)^{-1}$$

for $D_F = 3$ is $p = 6/5$ (Lai *et al.*, 1972); for $D_F = 1.80$ is $p = 2.57$.

In the *Continuum* limit the same quantity can be written as:

$$K(v,v') \propto \left(v^{1/D_F} + v'^{1/D_F}\right)\left(\frac{1}{v^{1/D_F}} + \frac{1}{v'^{1/D_F}}\right) \text{ and } \frac{N_0}{N(t)} \propto t$$

i.e., the time dependence of the number $N(t) \equiv N_0 / N_P(t)$ of clusters is the same as for a compact structure (the p enhancement arising from the increased collision radius is cancelled by the decrease in the diffusion coefficient).

The above analysis is supported by the rigorous treatment by Van Dongen and Ernst (1985), which verify the existence of similarity solution and find the following result:

$$N_0 / N(t) \propto t^Z, \quad Z \equiv 1/(1-\lambda)$$

where λ is determined by the following property of scaling:

$$K(av, av') = a^\lambda K(v,v').$$

Comparison of Experimental Results and Previsions

The experimental apparatus is described in detail elsewhere (di Stasio, 1998a; 1998b). Soot aggregates are produced by a Bunsen burner fueled with ethylene with the air inlet blocked. The light source is a Argon-Ion laser operating at 514.5 nm. Scattering volume of about 0.4 μm^3 is located at the centre of the flame. Heights above the burner are varied along the flame axis. Measurements of both the Vertical-Vertical (Scattered-Incident) light $I_{VV,}$ and depolarized light $I_{HV,}$ are performed at 30 different angles between 10 deg and 160 deg. A lock-in amplifier is used to separate light scattering signals against flame luminosity and out of band noise.

We report in the following some of the more significant results. Three different regimes for agglomeration kinetics are identified for the soot cluster number density $N_A(t)$ in term of power law as function of residence time. A complete presentation and a detailed discussion on this topic will be object of a forthcoming paper (di Stasio, 1998*c*).

Regime	$N_A(t)$ part / cm^3	power law, measured	power law, simulations (*), theory (†)	$\tau_{coag}^{measured}$	$\tau_{coag}\left(N_A \propto t^{-1}\right)$
1.	$N_A \approx 2\times10^{12}$	$N_A \sim t^{-2.9}$	$N_A \sim t^{-2.6}$ (*)	10 *ms*	30 *ms*
2.	$N_A \approx 8\times10^{10}$	$N_A \sim t^{-6/5}$	$N_A \sim t^{-6/5}$ (†)	50 *ms*	84 ms
3.	$N_A \approx 4\times10^{10}$	$N_A \sim t^{-0.8}$	$N_A \sim t^{-1.15}$ (*) $N_A \sim t^{-1.0}$ (†)	160 *ms*	153 *ms*

simulations (*) Mountain, Mulholland & Baum (1986)
theory (†) Prado & Lahaye (1981)

Some Points to Synthesize

Three *different* regimes of agglomeration kinetics have been evidenced from measurements of light scattering in the ethylene atmospheric diffusion flame. In particular:

a) in the *low residence times* (free-molecular regime) the number of clusters is proportional to $t^{-2.9}$ which is coherent with the behaviour ($N_A \propto t^{-2.6}$) predicted by the fractal agglomeration kinetics. The measured coagulation time is about a factor of three *smaller* with respect to the usually reported Smoluckowski size independent coagulation ($N_A \propto t^{-1}$). In this regime coalescing collisions are contemporary to strong surface growth;

b) in the *high residence times* (continuum regime) the number of clusters evolves as $t^{-0.8}$ instead of the t^{-1} behaviour predicted from both the Smoluckowski equation and the fractal agglomeration in continuum regime;

c) at intermediate residence times, the number of clusters depends on $t^{-6/5}$ which represents the value obtained in the free-molecular regime at constant volume fraction and temperature by Prado and Lahaye (1981). In this regime sticking (not coalescing) collisions occur at the same time with a weak surface growth.

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