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***NANOPARTICLE FORMATION AS A FUNCTION OF DIFFERENT CONCENTRATIONS***


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## INTRODUCTION

Exhaust particle sampling and conditioning have become a major issue over the last years as the characterization of exhaust particles is more and more sophisticated. There are two main reasons that led to the need for a detailed characterization of exhaust aerosol. Firstly, more information on the properties of the emitted particles is necessary to understand their origin and formation in order to regulate their exhaust concentration more effectively. Secondly, studies of particle health effects request more particle dimensions to better associate observations with emissions. The main goal of this work is to make evidence of the statistical thermodynamics considerations and their application to aspects of particle agglomeration, regarding soot particle number concentration distributions.

## EXPERIMENTAL

The experimental part represents a partial flow sampling system for the characterization of airborne exhaust particle emissions (Ntziachristos et al.(2004)). The sampled aerosol is first conditioned in a porous dilutor and then subsequent ejector dilutors are used to decrease its concentration to the range of the instrumentation used. Several quality characteristics are then discussed, such as the repeatability and reproducibility of the measurements and the potential to derive total emission rate with a partial flow sampling system. For the experimental investigation a diesel engine with open application was used. The size distribution was measured with a SMPS from TSI (DMA 3080 and CNC 3010).

## THEORETICAL

The collision frequency as a function of fractal dimension is known from Friedlander (2000). These results were transformed to determine a general two particle collision frequency dependent mainly on particle diameter, fractal dimension and primary particle diameter. Assuming a quasi diffusion limited aggregation mechanism (DLA) the Markov chain was built using rate equations which describe a Poisson distributed aggregation and an exponential distributed particle decomposition time (compare also Durrett (1999)). Thus a simplified model for particle growth describes the system reasonable well for a specific time interval, specified by the experimental set up.

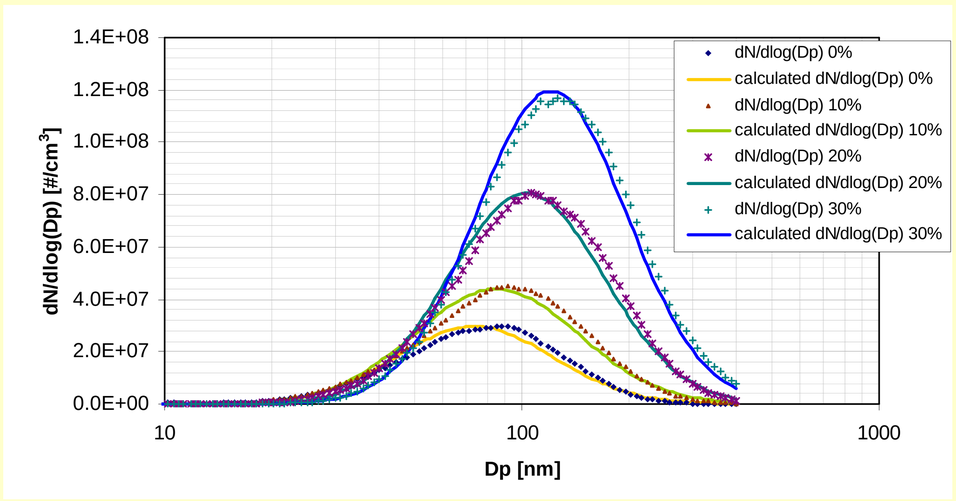


**Fig. 1 Measurement of different EGR rates at a diesel engine at middle load and 1500 rpm, 50mm³ injection amount; comparison of the calculated values of the lognormal distribution with experimental results**

| | EGR | | | |
|---|---|---|---|---|
| middle load, 1500 rpm, 50mm³ | 0% | 10% | 20% | 30% |
| $N_{ges}$ [#/cm³] | 1.63E+07 | 2.53E+07 | 4.37E+07 | 6.33E+07 |
| $\ln(\sigma_g)$ | 0.508 | 0.5301 | 0.4985 | 0.4861 |
| $\sigma_g$ | 1.662 | 1.699 | 1.646 | 1.626 |
| $dp_g$ [nm] | 75 | 86 | 105 | 123 |

**Tab. 1 Experimental results for the lognormal distribution of Fig. 1**

## FRACTAL DEPENDENCY OF THE COLLISION FREQUENCY

The collision frequency as a measure is the frequency by which two particles collide with each other in a fluid. Concerning the kinetic gas theory two molecules of gas molecules are regarded, concerning particle agglomeration, two particles are regarded which collide with each other. The collision of a particle and a gas molecule is regarded as to be reversible, that is, they do not stick together whereas two particles stick together by each collision in the investigated model. According to (Friedlander 2000) p. 231 the collision frequency is

$$\beta(v_i,v_j)=\pi\cdot(d_{pi}+d_{pj})^2\cdot\left(\frac{k\cdot T}{2\cdot\pi}\right)^{\frac{1}{2}}\cdot\left(\frac{1}{m_i}+\frac{1}{m_j}\right)^{\frac{1}{2}} \quad \text{Eq. 1} \qquad N_{pi}=\frac{v_i}{v_0}=A\cdot\left(\frac{d_{pi}}{d_{p0}}\right)^{D_f} \qquad v=\frac{\pi}{6}\cdot d_p^{\,3} \quad \text{Eq. 2}$$

which is valid for the free molecular regime. That means the particle diameter is much smaller then the mean free path of the particles. In our case we apply this up to the transition regime, that is we extend the calculation of the diameter up to the order of the mean free path. Otherwise we would have to take a interpolation formula for the collision frequency, valid for the transition regime, first considered by N. A. Fuchs. This definition can be deduced out of the kinetic gas theory (compare (Atkins 1990) p.666 eq. (26.2-2)). When we introduce now the fractal dependency of each colliding particle defined by Eq. 2 we can calculate the collision frequency dependent of the $v_i$, $v_j$ and the two fractal parameters the fractal dimension $D_f$ and the lacunarity A (Mandelbrot 1987) p. 327.

$$\beta(v_i,v_j)=\left(\frac{6\cdot k\cdot T}{\rho_{p0}}\right)^{\frac{1}{2}}\cdot\left(\frac{3}{4\cdot\pi}\right)^{\frac{2}{D_f}-\frac{1}{2}}\cdot\left(\frac{d_{p0}}{2}\right)^{2-\frac{6}{D_f}}\cdot\left(\frac{1}{v_i}+\frac{1}{v_j}\right)^{\frac{1}{2}}\cdot\left(\frac{1}{v_i^{\frac{1}{D_f}}}+v_j^{\frac{1}{D_f}}\right)^2 \quad \text{Eq. 3}$$

A is set to 1 mainly to simplify the analysis, as is also done in (Friedlander 2000). This is especially true when the particle diameter is much larger then the primary particle diameter. Eq. 1-2 result in Eq. 3 which may not be valid for collisions with very large and very small particles. This is not the case in the following calculations, as only particle-particle interactions are considered in a defined scale from approximately 10nm to 100nm. The reason are the theoretical assumptions of a mean mass in the kinetic gas theory. This could be avoided by a better model for the probability of particle interaction taking into account the properties of fractal particles instead of spherical particles.

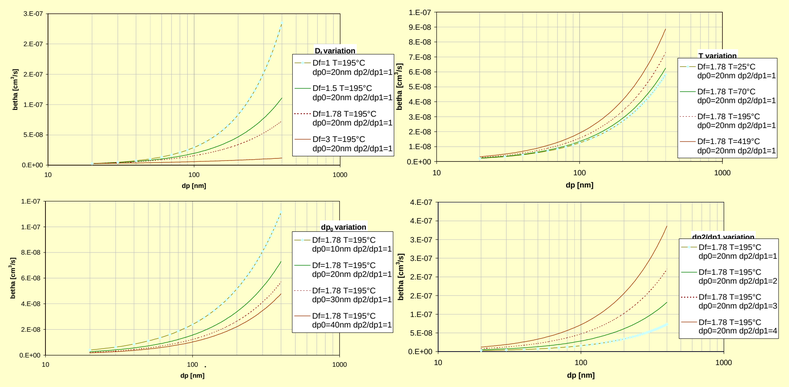


**Fig. 2 betha (b) as a function of different parameters; description is given in the text**

With the definition of $v(dp,dp_0,D_f)$ in Eq. 4, which is a result of the definition of the fractal dimension and A set to 1, we can gain the collision rate b as a function of diameter $dp_i$, $dp_j$, primary diameter $dp_0$ and fractal dimension $D_f$ in Eq. 5 and Eq. 6 for the same diameter.

$$v(dp,dp_0,D_f):=\frac{\pi}{6}\cdot dp_0^{\,3-D_f}\cdot dp^{D_f} \quad \text{Eq. 4}$$

$$\beta_{ij}(dp_i,dp_j,dp_0,D_f)=\left(\frac{3\cdot k\cdot T}{\rho p_0\cdot dp_0^{\,3-D_f}}\right)^{\frac{1}{2}}\cdot\left(\frac{1}{dp_j^{D_f}}+\frac{1}{dp_i^{D_f}}\right)^{\frac{1}{2}}\cdot(dp_i+dp_j)^2 \quad \text{Eq. 5}$$

$$\beta(dp,dp_0,D_f)=\left(\frac{96\cdot k\cdot T}{\rho p_0\cdot dp_0^{\,3-D_f}}\right)^{\frac{1}{2}}\cdot dp^{2-\frac{D_f}{2}} \quad \text{Eq. 6}$$

Different variations for $b_{ij}$ are given in Fig. 3 for the fractal dimension $D_f$, the temperature T, the primary diameter $dp_0$, and the ratio $dp_2/dp_1$. In the last case the reference diameter $dp_1$ refers to the abscissa. It can be seen that the collision frequency b is increasing with decreasing $dp_0$ and $D_f$ and with increasing T, $dp_2/dp_1$ and $dp/dp_0$. The ratio $dp_2/dp_1$ is the ratio of the two fractal particles colliding with each other, having both the same primary spherical particle diameter $dp_0$. To calculate how many particles collide per time unit, especially in the observed interval, the relation between the collision frequency b and the "Stoßzahl" z is given by Eq. 7, which can be deduced out of the kinetic gas theory.

$$z=2\cdot\beta\cdot\frac{N}{V}=2\cdot\beta\cdot c \qquad Z=z\cdot\frac{1}{2}\cdot\frac{N}{V}=\beta\cdot c^2 \quad \text{Eq. 7} \qquad K=\beta_m c^2\cdot V_{pipe}\tau_{pipe} \quad \text{Eq. 8}$$

Combining Eq. 7 with the particle number available in the fluid per unit volume we get the collisions happening per time unit expressed by the volumetric "Stoßzahl" Z also in Eq. 7 (collisions/(time*volume)). To make a rough estimation of the collisions K in the above experiment Eq. 7 is multiplied with the time interval in which the coagulation is assumed to take place $t_{pipe}$ and the according volume $V_{pipe}$, that is between the engine site and the measurement site, resulting in Eq. 8. This can be assumed, as the residence time is much larger in the exhaust pipe than in the engine and $t_{pipe}/t_E$ is at about 20, and the assumption that the fuel oxidation reaction and hence the chemical particle formation is restricted to the combustion engine. The calculated values from Eq. 7-8 are shown in Tab. 2 for the experimental set up. The logarithmic mean value of the temperature is chosen with 468 [K] for the exhaust pipe and with 692 [K] for the combustion engine. $b_m$ is calculated for the geometric mean value of the measurement site, the fractal dimension $D_f$ is 1.78 as is typical for soot particles and the primary particle diameter $dp_0$ is 20 [nm] with a density $\rho p_0$ of 1.80E+03 [kg/m³]. The ratio $K_{pipe}/K_E$>255, that means that the particle particle collisions are much higher then in the combustion engine.

| EGR - calculated | Z | $K_{pipe}$ | $K_E$ | $K_{pipe}/K_E$ |
|---|---|---|---|---|
| % | ##/(cm³*s) | ## | ## | |
| 0.0 | 2.91E+06 | 5.31E+09 | 2.08E+07 | 255 |
| 8.8 | 8.65E+06 | 1.73E+10 | 6.18E+07 | 280 |
| 20.6 | 3.55E+07 | 8.15E+10 | 2.54E+08 | 321 |
| 31.0 | 9.69E+07 | 2.56E+11 | 6.92E+08 | 370 |

**Tab. 2 collisions per residence time in the exhaust pipe and in the engine**

## RESULTS

Nanoparticle formation in a diesel engine has been investigated as a function of EGR rate. A significant increase of particle number concentration as a function of EGR can be observed. In Figure 1 the experimental result can be seen. As the EGR rate is increased also particle geometric mean diameter $dp_g$ [nm] and total particle number concentration $N_{ges}$ [#/cm³] is increasing. The applied lognormal distribution fits very well. The engine acting as a particle generator with specific residence times of sampling and combustion can be regarded as mainly determining the number size distribution. The engine out number size distribution was then simulated using variations of particle number concentrations as of parameters for the collision frequency. The quality of the simulation depends on parameters as e.g. the fractal dimension or temperature. They change significantly the agglomeration (collision) rate when increasing the residence time. Therefore a further investigation of these parameters in the nanometer range needs to take place.

## ACKNOWLEDGEMENTS


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