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.

	EGR			
middle load, 1500 rpm, 50mm^3	0%	10%	20%	30%
N_{ges} [#/cm^3]	1.63E+07	2.53E+07	4.37E+07	6.33E+07
$\ln(\sigma_g)$	0.508	0.5301	0.4985	0.4861
σ_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

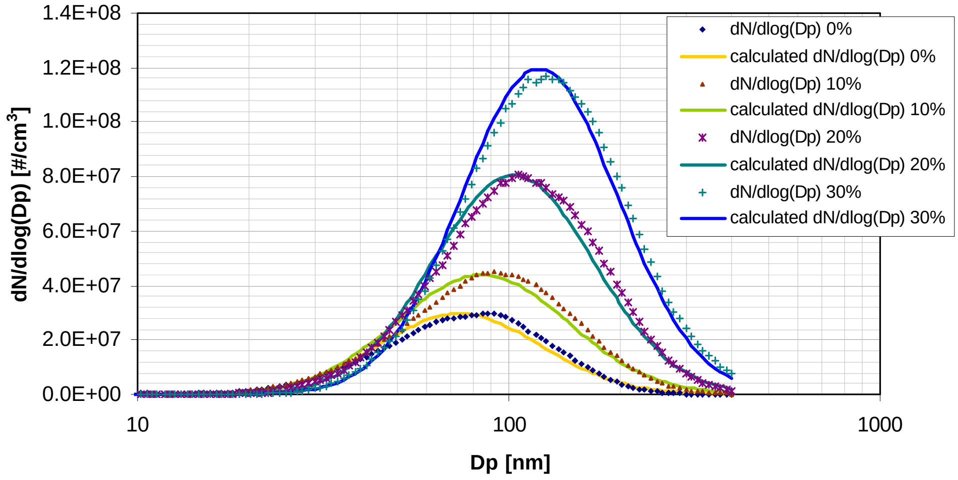

Fig. 1 Measurement of different EGR rates at a diesel engine at middle load and 1500 rpm, 50mm^3 injection amount; comparison of the calculated values of the lognormal distribution with experimental results

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

$$\beta(v_i, v_j) = \pi \cdot (d_{pi} + d_{pj})^2 \cdot \left(\frac{k \cdot T}{2 \cdot \pi}\right)^{\frac{1}{2}} \cdot \left(\frac{1}{m_i} + \frac{1}{m_j}\right)^{\frac{1}{2}} \qquad \textbf{Eq. 2}$$

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.

$$N_{pi} = \frac{v_i}{v_0} = A \cdot \left(\frac{d_{pi}}{d_{p0}}\right)^{D_f} \quad N_{pj} = \frac{v_j}{v_0} = A \cdot \left(\frac{d_{pj}}{d_{p0}}\right)^{D_f} \quad v = \frac{\pi}{6} \cdot d_p^{\,3} \qquad \textbf{Eq. 2}$$

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.

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

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 β 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.

$$v\left(dp, dp_0, D_f\right) := \frac{\pi}{6} \cdot dp_0^{3 - D_f} \cdot dp^{D_f} \qquad \textbf{Eq. 4}$$

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

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

Different variations for β_{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 β 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.

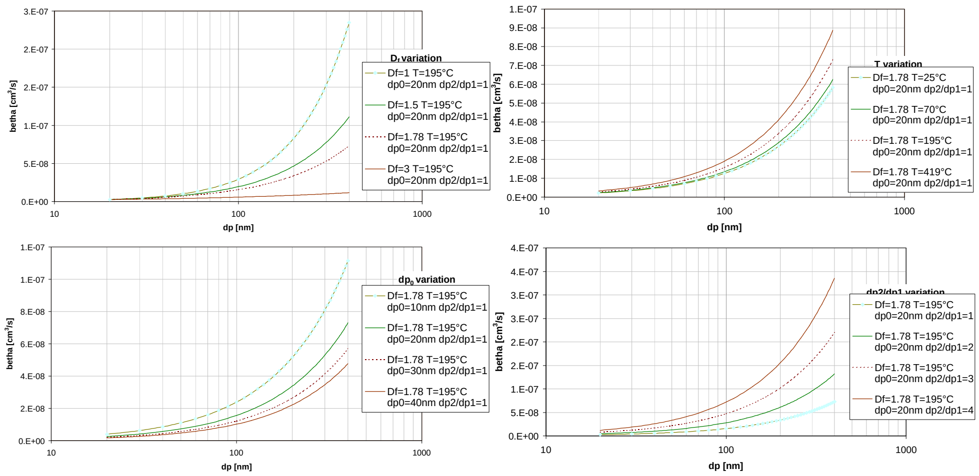

Fig. 3 betha (b) as a function of different parameters; description is given in the text

To calculate how many particles collide per time unit, especially in the observed interval, the relation between the collision frequency β and the "Stoßzahl" z is given by Eq. 7, which can be deduced out of the kinetic gas theory.

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

Combining Eq. 7 with the particle number available in the fluid per unit volume then we get the collisions happening per time unit expressed by the volumetric "Stoßzahl" Z 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 τ_{pipe} and the according volume V_{pipe}, that is between the engine 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 τ_{pipe}/τ_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. β_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 ρp_0 of 1.80E+03 [kg/m^3]. 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
%	##/(cm^3*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 Fig. 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} [#/cm^3] 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.

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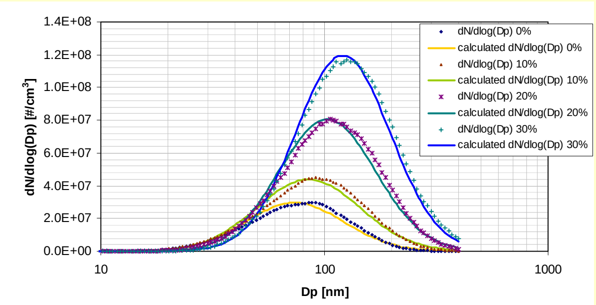

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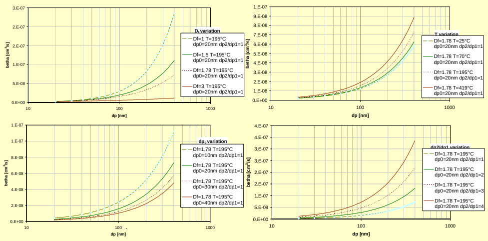

Fig. 2 betha (β) as a function of different parameters; description is given in the text

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