1. Introduction

Due to their unique properties, nanoparticles have found many practical applications such as protective coatings, self-cleaning surfaces and gas sensors to name only a few. In all these applications the handling of the nanopowders is essential for the quality of the deposit. To understand and control the deposition process, the drag coefficient of the nanoparticles has to be known. In addition, the correct interpretation of the results from nanoparticle measuring devices which are based on the motion of the particles relative to the carrier gas such as low-pressure impactors or low-pressure differential mobility analysers requires a sound knowledge of the friction forces. Stokes derived an analytical expression for the friction force in the continuum regime at small Reynolds numbers by assuming that the gas molecules exhibit no slip at the particle surface. However, at high Knudsen numbers, this assumption does not hold anymore and the deviation from the continuum character is considered with the slip or Cunningham correction. In the present work, measurements of the separation curve of nanoparticles in a single-stage low-pressure impactor are presented to systematically investigate the disagreement of classical theory of friction resistance of nanoparticles in low-pressure flows. At the same time, the impaction process of nanoparticles is simulated with a CFD code based on the classic theory. An effective Cunningham correction is determined as a function of the Knudsen number from fitting the calculated separation curve to the measured one. Moreover, the so far unresolved finding of too low densities determined for metal nanoparticles by low-pressure impaction is explained for the first time.

Abstract

At small Knudsen numbers (continuum regime) and sufficiently small Reynolds numbers, the friction resistance of particles with the carrier gas is described by means of the Stokes formula assuming no slip of the gas molecules at the particle surface. However, at high Knudsen numbers, this assumption does not hold anymore and the deviation from the continuum character is considered with the slip or Cunningham correction. In the present work, measurements of the separation curve of nanoparticles in a single-stage low-pressure impactor are presented to systematically investigate the disagreement of classical theory of friction resistance of nanoparticles in low-pressure flows. At the same time, the impaction process of nanoparticles is simulated with a CFD code based on the classic theory. An effective Cunningham correction is determined as a function of the Knudsen number from fitting the calculated separation curve to the measured one. Moreover, the so far unresolved finding of too low densities determined for metal nanoparticles by low-pressure impaction is explained for the first time.

Keywords: nanoparticle, Cunningham correction, high Knudsen number, drag
where \( \dot{m}_a \) is the aerosol mass flow rate through the impactor, \( c_0 \) the velocity of sound and \( p \) the impaction pressure. In the classic impaction theory, the deposition process can be described by the Stokes number alone. Half of the particles will be separated at a value \( Stk_{50} \) which in turn gives a simple way of relating particle size and density as was shown by Kütz and Schmidt-Ott \(^8\):
\[
Stk_{50} = 0.178 \cdot \frac{\rho_p \cdot x \cdot \dot{m}_a \cdot c_0^3}{p_{50}^2 \cdot D_n^3} = const
\]
\( p_{50} \) is the impaction pressure at which 50% of particles are separated. Since all the other parameters in Eq. (6) are given by the geometry of the impactor and the flow rate of the carrier gas, the following ratio \( Y \) was so far assumed to be a constant:
\[
Y = \frac{p_{50}^2}{\rho_p \cdot x} \quad [\text{Pa} \cdot \text{m}^2/\text{kg}]
\]
Eq. (7) was used extensively to determine the density of nanoparticles from single-stage low-pressure impaction measurements \(^8\). However, some inconsistencies with density data obtained with other techniques remained unresolved \(^9\). It will be shown in this study that the assumption of \( Y=\text{const} \) does not hold true anymore in the high Knudsen number regime and that the reason for the deviation is related to the incorrect formulation of the Cunningham correction in this regime.

3. Experimental Set-up

The experimental set-up is represented in Fig. 1. It consists mainly of a particle generation process, charging and classification in a Differential Mobility Analyser (DMA, GRIMM model 55-40-26-Uni), particle impaction, monitoring of inlet particle concentrations and outlet aerosol charges. The metal particles were generated by spark erosion from electrodes of the required metal. The particles formed by nucleation and agglomeration were sintered completely as they passed through a downstream tube furnace to form dense spherical particles (Fig. 2). In the case of coated metal particles, the classified spherical particles passed an atmosphere saturated with Di-Ethyl-Hexyl-Sebacate (DEHS) vapour which condensed on the particles as they cooled. The coating thickness was adjusted by the temperature in the saturator. A second DMA is used to select a particle size after coating to permit determination of the coating thickness from the difference between the particle sizes before and after the coating. Pure oil droplets were generated by atomisation of DEHS with a pneumatic nebulizer (Topas model ATM 220). Because beyond the scope of this contribution.

The article starts with the theory of particle behaviour in curve-linear motion which is the basis of inertial impaction. Then the experimental set-up is outlined and the separation results are presented. By comparison with CFD results, the correction function for the drag coefficient can be determined in absolute values. Finally, after discussing the consequences for the nanoparticle density determination based on low-pressure impaction, the results are condensed into the dependence of the correction function on the Knudsen number.

2. Basis of Particle Separation by Impaction

Here, the high Knudsen number regime to deposit nanoparticles was realized in a low-pressure impactor. After being accelerated through a nozzle, particles can be deposited in the subsequent curve-linear stream if their inertia is high enough compared with the drag in the carrier gas. For small Reynolds numbers \((Re<0.25)\), the friction force on the particle is given in one dimension by:
\[
F_d = \frac{3\pi\eta \cdot x \cdot (v-w)}{Cc(Kn)}
\]
which is proportional to the difference of gas and particle velocity \((v-w)\) and inversely proportional to the Cunningham correction \(Cc\), which in classic theory is only a function of the Knudsen number \((Kn=2\lambda/x)\):
\[
Cc = 1 + Kn \cdot (1.257 + 0.4e^{-1.1/Kn})
\]
(2)
where the coefficients have been determined empirically \(^5,6\).

The mean free path \( \lambda \) is related to the absolute pressure \( p \) by:
\[
\lambda = \lambda_0 \cdot \frac{p_0}{p} \propto \frac{1}{p}
\]
(3)
where \( \lambda_0 = 65 \text{ nm} \) at ambient pressure and \( p_0=10^5 \text{ Pa} \) at room temperature.

An important parameter to describe the efficiency of low-pressure impaction is the Stokes number which represents the ratio of inertia force \( F_i \) to drag force \( F_d \):
\[
Stk = \frac{F_i}{F_d} = \frac{\rho_p \cdot x^2 \cdot u \cdot Cc}{9\eta \cdot D_n}
\]
(4)
where \( \rho_p \) is the particle density, \( u \) the outlet velocity at the nozzle exit, and \( D_n \) the nozzle diameter.

Based on continuity, the ideal gas law and the Cunningham correction (Eq. (2), de la Mora et al. \(^7\)) derived an expression for the Stokes number in a single-stage low-pressure impactor:
\[
Stk = 0.178 \cdot \frac{\rho_p \cdot x \cdot \dot{m}_a \cdot c_0^3}{p^2 \cdot D_n^3}
\]
(5)
of surface tension, the droplets remain spherical in the carrier gas. However, due to the non-vanishing vapour pressure of DEHS in ultra-high vacuum, the shapes of DEHS-coated particles and the DEHS droplets could not be observed by means of TEM analysis. Before classification in the DMA, the particles were charged with a radioactive Kr-85 source (TSI model 3077). The size-selected particles were singly charged and monodisperse and entered the Low-Pressure Impactor (LPI). The particle number concentration in the outlet aerosol was measured with a Faraday Cup Electrometer (FCE), while the inlet concentration was recorded with a Condensation Particle Counter (CPC, GRIMM model 5.403). For a given particle size, the separation probability increases with increasing particle velocity, leading to a decrease of the concentration of charged particles in the aerosol exit as measured with the FCE. The particle velocity was controlled through the chamber pressure in the impactor. The absolute pressure in the impaction chamber was varied by means of a low-pressure valve and monitored with the aid of a low-pressure gauge. The smaller the chamber pressure, the higher the gas and particle velocity.

The Low-Pressure Impactor (LPI) is shown schematically in Fig. 3. It consists of a critical orifice (150 µm in diameter), an accelerating nozzle (2 mm in diameter), an impaction plate and a pressure gauge. The aerosol enters at the top and exits from the bottom. The critical orifice keeps the inlet gas mass flow constant. To avoid interference of the gas flow through the critical orifice with the accelerating nozzle, they were separated by about 1m (as indicated in Fig. 3). The gasborne particles were accelerated in the nozzle towards the impaction plate. The particles which did not impact on the plate were measured downstream of the impaction surface with the FCE. In order to guarantee sticking of the impacting particles, the impaction plate was coated with a thin film of vacuum grease. For a given chamber pressure, the particle separation efficiency was calculated from the ratio of the FCE signal at this pressure related to the FCE signal at higher pressure where no impact occurred (e.g. in Fig. 4 for a pressure above 4500 Pa). Fluctuations of the particle concentration at the impactor inlet were measured with the CPC and taken into account for the separation curves.

4. Results and Discussions

4.1 Comparison of Y

A typical measurement of a separation curve for

![Fig. 1 Overview of the experimental set-up to investigate the separation behaviour of different particle types.](image1)

![Fig. 2 TEM micrographs of the sintered and size-selected metal particles (left: 47 nm silver; right: 47 nm platinum).](image2)
DEHS droplets with a diameter of 454 nm is reproduced in Fig. 4. With decreasing pressure in the impaction chamber, the velocity of the gas jet increases and the particles also attain higher velocities. When reducing the pressure below 4200 Pa, particles start to deposit on the impaction plate by inertia, leading to a reduction of the aerosol electrometer signal (FCE) measured downstream of the impaction plate. At a pressure of about 2500 Pa, all particles are deposited and the electrometer signal drops to zero. The single-step drop of the curve indicates that no larger doubly charged droplets are present after the classification in the DMA. The value of $p_{50}$ can be determined from such a curve as indicated in Fig. 4. According to Eq. (7), the particle size, particle density and $p_{50}$ have to be known to determine $Y$. While the particle size is given from the classification and $p_{50}$ is obtained from the separation curve, the particle density has to be estimated. For pure DEHS droplets, it is reasonable to assume the bulk density. However, since the droplets spend a few seconds in a low-pressure regime (minimum pressure for DEHS was 2000 Pa) between the critical orifice and the acceleration nozzle, their size may change due to evaporation which would lead to a decrease of the particle separation efficiency by impaction. In order to estimate this effect, the evaporation kinetics are approximated by the following equation which applies for $x < \lambda$ and includes the Kelvin effect:

$$\frac{dx}{dt} = \frac{2M(p - p_d)}{\rho_p \cdot N_a \cdot \sqrt{2\pi \cdot m k_B T}}$$

where $p$ is the partial pressure of the DEHS vapour in the carrier gas and $p_d$ is the partial pressure of DEHS vapour at the droplet surface, given by the Kelvin equation. Assuming no DEHS vapour in the carrier gas and maximum residence time and using literature values for surface tension and molar mass, a maximum size change by evaporation was obtained. Even for the smallest DEHS droplets of 124 nm, a size reduction of only a few nm was estimated. Therefore, the size change of the DEHS droplets due to evaporation in the low-pressure regime was neglected. In addition, the particle size reduction by evaporation would lead to a reduced separation efficiency in contradiction to the experimental results which show an improved separation efficiency as discussed below (e.g. Fig. 7).

For the completely sintered metal particles the bulk density was also assumed. This is explained on one hand by the TEM micrographs which show spherical dense particles and on the other hand by the sintering treatment used here which follows the procedure by Weber et al.\textsuperscript{12} and Skillas et al.\textsuperscript{10}. Using the direct mass determination of the silver aerosol particles with Inductively Coupled Plasma Spectroscopy (ICP), they showed that particles with bulk densities can be achieved by heating in a tube furnace for residence times of a few seconds. Exactly the same temperature treatment was also applied here so that the assumption of bulk density is justified. Platinum has a high melting point, so a high sinter temperature was used. Fig. 2 shows that the Pt particles also have a compact and spherical shape. So it can be assumed that the Pt particles have a bulk density, too. However, for the Ag particles coated with DEHS, an interpolation was used for the determination of the effective density. Using the diameter $x_1$ of the silver core and the diameter $x_2$ of the coated particles, the following equation was applied:

$$\rho_{eff} = \left( x_1^3 - x_2^3 \right) \cdot \rho_{Ag} + \left( 1 - x_1^3 \right) \cdot \rho_{DEHS}$$

where $\rho_{Ag}$ is the density of silver, $\rho_{DEHS}$ the density of DEHS.

In this way, the values of $Y$ were determined for the metal particles (Ag, Pt), for the pure DEHS particles and for two types of DEHS-coated silver particles, i.e. with a thin and a thick DEHS coating. The results are shown in Fig. 5. For the metal particles, there is no difference in the $Y$ values although the density of silver (10500 kg/m$^3$) is less than half of the platinum density (21400 kg/m$^3$). This indicates that the parameter $Y$ does not depend on the particle density. It also becomes obvious that $Y$ is not constant as

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**Fig. 3 Schematic of the low-pressure impactor.**
assumed so far for the interpretation of low-pressure impacter density measurements. Moreover, there is a significant difference in the behaviour of oil surfaces and solid metal surfaces. Surprisingly, the silver particles with a thin DEHS coating show an intermittent behaviour. Since the coating thickness is rather small (a few nm) compared with the dimensions of the DEHS molecules (maximum length ca. 4 nm), layers of only a few molecules will form in the case of thin coatings. Although on a macroscopic level, oils wet extended metallic surfaces rather well, the situation may be different for the deposition of a limited number of DEHS molecules on the highly curved surface of Ag nanoparticles. On one hand, DEHS layers with a thickness of only a few molecules may not develop macroscopic surface tensions. And on the other hand, the surface may be contaminated to some extent, for instance by oxide states as observed before for Ni nanoparticles\(^1\)\(^3\). Therefore, we hypothesize that the surface might rather consist of DEHS patches and of uncovered metal areas. This would support the hypothesis that the gas molecules are scattered in a different way from solid and liquid surfaces. But the exact dispersion of the thin DEHS coating on the surface of the particles is unknown. Hence reliable conclusions cannot be drawn at this state of knowledge. Once the whole surface of the silver particle is covered with DEHS, as in the case for thick coatings, the gas molecules do not differentiate between pure DEHS particles and DEHS particles with a silver core resulting in the same increase of the Y value as found in Fig. 5.

For large particles, it is expected that Y converges towards a constant value which is the same for solid and liquid surfaces. This extrapolation will be discussed in Fig. 9 on the basis of absolute values.

In order to interpret the variation of the parameter Y, we assume that the classic value for the Cunningham correction has to be adapted for the higher Knudsen number regime (\(Kn>>1\)) encountered here by multiplication with a function \(k\):

\[
Cc_{eff} = k \cdot Cc_{class}
\]  

(10)

According to Eq. (4), the function \(k\) also enters the Stokes number, changing it to a new effective value \(Stk_{50,eff}\):

\[
Stk_{50,eff} = k \cdot Cc_{class} \frac{\rho_p \cdot x^2 \cdot u}{9 \eta \cdot D_n} = k \cdot Stk_{50,class}
\]  

(11)

To obtain the relationship between \(k\) and \(Y\), the following equation is used:

\[
Stk_{50,eff} = const \cdot \frac{k}{Y}
\]  

(12)

\(Stk_{50,eff}\) is the Stokes number calculated with the classic theory at 50% of the particle separation. The classic theory is suitable for small Knudsen numbers, i.e. relatively large particles, and short mean free paths of gas molecules, then \(k\) is equal to 1. At the present experimental conditions (low-pressure impaction of small particles), \(k\) decreases towards 1 with increasing particle size for all investigated materials (DEHS, Ag, Pt). The absolute value of \(k\) will be discussed in the next section.

With Eq. (10) and (1), the effective drag force can be written as:

\[
F_{d,eff} = \frac{3 \pi \eta \cdot x \cdot (v - w)}{k \cdot Cc_{class}}
\]  

(13)

Since \(Y\) is proportional to \(k\), increasing \(Y\) means that the effective drag force of particles is less than that in the classic theory (with the classic \(C_c\)).

For the analysis here we will focus on DEHS droplets because the DEHS droplets have a definite compact spherical shape and their effective density is known. On the other hand, the atomizer supplies a variety of droplet sizes, so it is possible to investigate the particle dynamic properties over a large size range.
range.

4.2 Determination of the factor $k$

The $k$ values are unknown. But $k$ is proportional to $Y$. If a $k$ value can be found, then all the $k$ values can be calculated by means of comparison of the $Y$ values. For determining a $k$ value, a CFD method is used.

**Fig. 6** (left) shows the simulation results of the gas flow in the impactor. The brightness in flow zone indicates the gas velocities. The brighter the colour, the higher the gas velocity. As the impactor is axially symmetrical, a 2D model of half of the cross-section of the impactor is written. The gas is accelerated by the nozzle and the velocity increases. There is a velocity profile at the nozzle exit. In the centre, the gas velocity is at its maximum (37 m/s) and at the nozzle wall it is zero. Behind the accelerating nozzle the gas velocity decreases. On the surface of the impaction plate, the gas is diverted and a stagnation domain develops in the centre. According to their velocity relative to the gas, the particles are accelerated or decelerated due to the friction force. If the particle velocity is high enough, it can reach the impaction plate. In the outskirt area, the particles exhibit lower velocities and may be carried away by the gas. Because of the inertia, the particles are focused after entering the accelerating nozzle. If a particle can be separated, its track ends at the impaction plate. The separation grade can be calculated for a given particle size and chamber pressure from the particle trajectories.

A complete separation curve can be obtained by varying the pressure in the impaction chamber. The separation curve of the 521-nm DEHS droplets is shown in **Fig. 7**. Curve 1 is the simulation result by means of the classic friction theory ($k=1$). Curve 2 is the measured separation curve. There is clearly a difference between them. The measured separation efficiency is substantially larger than anticipated from the simulation, i.e. the droplets experience less friction than in theory. However, the curve shapes are similar. Assuming larger effective Cunningham corrections ($k>1$) will lead to a shift of the separation curve to the right as shown in **Fig. 7** for $k=1.0, 1.5, 2.0$ and $2.5$, respectively. In order to adapt the simulated separation curve to the measured $p_{50}$ value for the

![Simulated (broken lines) and measured (solid line) separation curves of 521-nm DEHS droplets.](image-url)
DEHS droplets of 521 nm, it is necessary to increase the Cunningham correction by a factor $k = 1.167$:

\[
C_{\text{eff}} = 1.167 \cdot C_{\text{class}}
\]

Since $k$ and $Y$ are proportional to each other, it is sufficient to relate the values of $k$ and $Y$ for a certain particle size and $\rho_{50}$ to obtain all corresponding values of $k$ and $Y$. The results for DEHS droplets are shown in Fig. 8. For comparison, $k$ was also obtained from simulation for all droplet sizes and their $\rho_{50}$ (Fig. 8 broken line). The curves for simulation and experimental results are close to each other indicating mutual confirmation of the two approaches. In addition, the measured $k$ values of DEHS thick-coated silver particles fit in between the two lines.

The factor $k$ for silver particles was calculated with the measurements and the same CFD procedure (Fig. 8). The $k$ values for silver are close to the line of DEHS. It can be argued that the lines of silver and DEHS are actually the same. The small deviations are within the uncertainties in measurements and simulation as indicated in Fig. 8. In other words, $k$ only depends on the parameter $Y$. Meaning that all the influences for this deviation from the classic theory such as surface condition and particle size are already included in this parameter $Y$. The function between $k$ and $Y$ is independent of material, particle size, etc. and can be approximated by:

\[
k = 4.35 \cdot 10^{-11} \frac{\text{kg}}{\text{Pa}^2 \text{m}^2} \cdot Y \left(\frac{\text{Pa}^2 \text{m}^2}{\text{kg}}\right)
\]

where $Y$ has the units of $\text{Pa}^2 \text{m}^2/\text{kg}$ and $k$ is dimensionless. The proportionality constant in Eq. (14) depends on the impactor geometry and on the operation conditions. However, for a given impactor geometry and the flow conditions (type of carrier gas, temperature and gas mass flow rate at atmospheric pressure), the proportionality constant of Eq. (13) applies for all experiments performed in this study. If $k = 1$ (in the area of the classic theory), the $Y$ value or $Stk_{50}$ is independent of material, particle size, pressure, etc., and is always a constant (see also broken line in Fig. 9).

4.3 Calibration of silver density by means of DEHS droplets

Important is that Fig. 5 contains the key to explain the so far unresolved phenomenon that the densities of metallic nanoparticles determined with low-pressure impaction were substantially too low. The point is that the impactor had to be calibrated in order to evaluate Eq. (6). For this purpose, spherical particles of known density were employed – usually

<table>
<thead>
<tr>
<th>Zone 1 and 2 ($k_{\text{DEHS}} &gt; 1$)</th>
<th>Zone 2 to 4 ($k_{\text{DEHS}} = 1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 3 ($k_{\text{DEHS}} &gt; 1$)</td>
<td>b) The comparison of $\rho_{\text{Ag,calculated}}$ and $\rho_{\text{Ag,eff}}$ depends on the ratio $\frac{Y_{\text{DEHS}}}{Y_{\text{Ag}}}$ and can be different.</td>
</tr>
<tr>
<td>Zone 4 ($k_{\text{DEHS}} = 1$)</td>
<td>c) $\frac{Y_{\text{DEHS}}}{Y_{\text{Ag}}} &gt; 1$, $\rho_{\text{Ag,calculated}} &lt; \rho_{\text{Ag,eff}}$</td>
</tr>
<tr>
<td></td>
<td>d) $\frac{Y_{\text{DEHS}}}{Y_{\text{Ag}}} &lt; 1$, $\rho_{\text{Ag,calculated}} &gt; \rho_{\text{Ag,eff}}$</td>
</tr>
<tr>
<td></td>
<td>e) $\frac{Y_{\text{DEHS}}}{Y_{\text{Ag}}} = 1$, $\rho_{\text{Ag,calculated}} = \rho_{\text{Ag,eff}}$ (The classic theory is valid.)</td>
</tr>
</tbody>
</table>

Fig. 8 The factor $k$ as a function of the $Y$ value.

Fig. 9 Comparing the courses of trend lines from DEHS and silver measurements.

Table 1 Calibration of the silver particle densities with DEHS droplets in different particle size ranges
oil droplets such as DEHS or DOS. However, for determination of the unknown density of the metal particles, the upper curve in Fig. 5 was used and \( Y \) was assumed to be constant, leading to apparently changed densities. The degree of underestimation or overestimation depends on the sizes of the measured particles and the ones used for calibration. A detailed case differentiation is given in Table 1. Using rather large oil droplets (of about 700 nm) for the calibration, the correct calibration factor may have been chosen by chance. Going to smaller oil droplets, the underestimation of the real density may reach a factor close to 2 for particle sizes below 100 nm.

The particle density of silver is commonly obtained by comparison of the \( S\) by impaction of silver particles and of DEHS droplets. By combining Eqs. (6), (10) and (11), one obtains:

\[
S\text{tr}_{50,eff} = \left( k_{\text{DEHS}} \cdot Y_{\text{DEHS}} \right) / \left( m_{\text{DEHS}} \cdot Y_{\text{Ag}} \right)
\]

From Eq. (15), the following expression for the silver density is obtained:

\[
\rho_{\text{Ag}} = \frac{\rho_{\text{DEHS}} \cdot S\text{tr}_{50,eff}}{S\text{tr}_{50,DEHS}} \cdot \frac{X_{\text{DEHS}}}{X_{\text{Ag}}} \cdot \frac{k_{\text{DEHS}}}{k_{\text{Ag}}}
\]

In the classic theory, \( k \) is not considered, then \( \rho_{\text{Ag}} \) will be calculated with \( k_{\text{DEHS}} / k_{\text{Ag}} = 1 \). But actually \( k_{\text{DEHS}} / k_{\text{Ag}} \) is often not equal to 1 for small particles, leading to a deviation from the correct particle density. Since \( k \) is proportional to \( Y \), Eq. (16) may alternatively be written as:

\[
\rho_{\text{Ag}} = \frac{\rho_{\text{DEHS}}^2 \cdot S\text{tr}_{50,DEHS}}{S\text{tr}_{50,DEHS}} \cdot \frac{X_{\text{DEHS}}}{X_{\text{Ag}}} \cdot \frac{Y_{\text{DEHS}}}{Y_{\text{Ag}}}
\]

Since both \( k \) and \( Y \) depend on the particle size, the following combinations may occur (Table 1 based on the zones 1 to 4 indicated in Fig. 9):

- **Case a** \( \times_{\text{DEHS}} \) in zone 1 and 2, \( \times_{\text{Ag}} \) in all zones:
  - In this situation, is \( Y_{\text{DEHS}} / Y_{\text{Ag}} > 1 \) If the \( \rho_{\text{Ag}} \) is calculated with \( Y_{\text{DEHS}} / Y_{\text{Ag}} = 1 \) as in the theory, then the calibrated \( \rho_{\text{Ag}} \) is smaller than the effective \( \rho_{\text{Ag}} \).

- **Case b** \( \times_{\text{DEHS}} \) in zone 3, \( \times_{\text{Ag}} \) in zone 1:
  - In this case, the situations are complex. If \( Y_{\text{DEHS}} / Y_{\text{Ag}} < 1 \), the calibrated \( \rho_{\text{Ag}} \) is larger than the effective \( \rho_{\text{Ag}} \). If \( Y_{\text{DEHS}} / Y_{\text{Ag}} = 1 \), the calibrated \( \rho_{\text{Ag}} \) is exactly the same as the effective \( \rho_{\text{Ag}} \). Otherwise, it is smaller.

- **Case c** \( \times_{\text{DEHS}} \) in zone 3, \( \times_{\text{Ag}} \) in zones 2 to 4:
  - In this situation, is \( k_{\text{DEHS}} = 1 \), \( k_{\text{DEHS}} > 1 \), \( Y_{\text{DEHS}} / Y_{\text{Ag}} \) is always larger than 1, then the calibrated \( \rho_{\text{Ag}} \) is smaller than the effective \( \rho_{\text{Ag}} \).

- **Case d** \( \times_{\text{DEHS}} \) in zone 4, \( \times_{\text{Ag}} \) in zone 1:
  - In this situation, is \( k_{\text{DEHS}} = 1 \), \( k_{\text{DEHS}} > 1 \), \( Y_{\text{DEHS}} / Y_{\text{Ag}} \) is always smaller than 1, then the calibrated \( \rho_{\text{Ag}} \) is larger than the effective \( \rho_{\text{Ag}} \).

- **Case e** \( \times_{\text{DEHS}} \) in zone 4, \( \times_{\text{Ag}} \) in zones 2 to 4:
  - For large particles, \( k_{\text{DEHS}} = k_{\text{DEHS}} = 1 \). In this zone, the classic theory is valid.

De la Mora et al. also found reduced densities in low-pressure impaction measurements and attributed this to contamination of the particle surface originating from the charging process with a radioactive source. However, their particles exhibited sizes of a few nanometres only (< 10 nm). In contrast, the particles investigated here were at least 20 nm or much larger, so that monolayers of contamination, when present at all, are negligible for the impaction behaviour.

### 4.4 The factor \( k \) as a function of the Knudsen number

The factor \( k \) is a function of \( Y \), i.e. it is dependent on particle size and impaction pressure. In the presented impaction research, the impaction pressure – which can change the mean free path of gas molecules – and the particle size can influence both the frequency and strength of the interaction between particles and gas molecules. The Knudsen number indicates the ratio between the mean free path, and thus the impaction pressure and particle size. Therefore, it was attempted to describe the factor \( k \) as a function of the Knudsen number \( Kn \) as shown in Fig. 10.

For both materials, there is a critical Knudsen number \( Kn_c \), above which the function \( k \) increases strongly at first and then approaches a constant value for large \( Kn \) values. The asymptotic limit was obtained from Fig. 9 by reducing the particle size \( x \rightarrow 0 \), which in turn results in \( Kn \rightarrow \infty \). For particles much smaller than the mean free path but still larger
than the gas molecules, the friction coefficient $f$ can be derived from the kinetic gas theory (formula of Epstein)\(^{15}\):

$$f = \frac{F_d}{v_{rel}} = \frac{2}{3} x^2 \rho g \left(\frac{2\pi k_B T}{m}\right)^{1/2} \left[1 + \frac{\pi \alpha}{8}\right]$$ \hspace{1cm} (18)

where $\rho$ is the gas density and $m$ is the molecular mass of the gas molecules. The accommodation coefficient $\alpha$ gives the fraction of diffusely scattered gas molecules, while $1-\alpha$ represents the fraction of specularly reflected gas molecules.

Based on Eq. (18), agreement between the measured and calculated drag forces are obtained for $\alpha = 0.09$ for 20 nm Ag particles and $\alpha = 0.34$ for 62 nm Ag particles, respectively. This indicates that even for particles as large as 62 nm, most of the gas molecules are specularly scattered in contradiction to the finding of Li and Wang \(^3\) who found that the transition from diffuse to specular reflection occurs at a particle size of a few nanometres. Therefore, we conclude that in the high Knudsen number regime, this transition can occur quite gradually, at least for the surfaces of solid particles. However, the friction coefficients observed for the DEHS droplets are out of the range of Eq. (18). The reason for this behaviour is so far unknown.

The behaviour of the function $k$ was approximated by the following fit function:

$$k(Kn) = 1 + A \cdot \left[1 - \exp\left(-B \cdot (Kn - Kn_0)\right)\right]$$ \hspace{1cm} (19)

where $A$ and $B$ are constant. By fitting the function (19) to the measurements it was found that $A$ and $Kn_0$ are dependent on the particle material or surface state while the value of $B$ is about 0.045 independent of the particle material.

The Knudsen number is only inversely proportional to the impaction pressure $p$, but $k$ is proportional to $Y$ which is a function of impaction pressure $p^2$ and particle density $\rho_p$. Therefore, $k$ is a function of $Kn$, $p$ and $\rho_p$. The influence of $p$ and $\rho_p$ is material-dependent. However, the curve progression of the relations between $k$ and $Kn$ are similar for all materials as indicated by the constant $B$ value.

### 5. Conclusions

In the free molecular regime, small particles exhibit different drag properties than in the continuum regime, which is corrected by means of the Cunningham correction. But if the particles are sufficiently small in a high Knudsen number regime, they experience less friction than in the classic theory and their drag force cannot be well described with the classic Cunningham correction. In the experiments of low-pressure impaction it was found that the Stokes number $St_{50}$ from the classic theory, which is calculated from the pressure $p_{50}$ where 50% of particles are separated, is not constant. It depends not only on particle size, but also on the surface conditions of the particles. For correction of the theory, a factor $k$ is introduced. In the free molecular regime, $k$ is proportional to $Y = p_{50}^2 / (\rho_p \cdot x)$ and greater than 1. The classic friction force reduced by the factor $k$ leads to the effective friction force.

For determination of the absolute value of $k$, a CFD method is used. The simulation result is adjusted to the measurement by means of variation of the Cunningham correction in the model. The deviation between the effective and classic Cunningham correction yields the factor $k$.

The function between $k$ and $Y$ is independent of other parameters, i.e. all interactions between gas molecules and particles are considered in the parameter $Y$. When $k=1$, different materials reach the same constant $Y$ value. Once calibrated with standard particles such as oil droplets, the density of other particles can be determined from $St_{50}$. But if calibration and measured particles have different $Y$ values, the calibration must be adjusted by $k$ to avoid incorrect results for the particle density.

$k$ is a function of particle size and impaction pressure. The impaction pressure determines the mean free path of gas molecules. Therefore, $k$ depends also on the Knudsen number, which is determined by the mean free path and the particle size. But the relation between $k$ and $Kn$ is material-dependent, in particular the upper limit of $k$ and the critical Knudsen number $Kn_0$ where $k$ starts to increase above 1. Hence, the parameter $Y$ may be more useful than the Knudsen number for interpretation of low-pressure impaction experiments since $Y$ can be directly converted into a
In the main, future work should address two issues. The drag behaviour of agglomerated nanoparticles in the high Knudsen number regime is so far largely unknown on a theoretical and experimental basis. However, agglomerates are encountered in most technical systems and a better understanding of the friction forces in a carrier gas is needed for better handling. The other issue is the fundamental explanation of the observed differences for the interaction of the gas molecules with solid and liquid surfaces. Here, molecular dynamics simulations as performed by Li and Wang\textsuperscript{16) can be employed in future work to deepen the insight into the processes at the nanoparticle surface.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>$Cc$</td>
<td>Cunningham correction</td>
<td>[-]</td>
</tr>
<tr>
<td>$c_0$</td>
<td>velocity of sound</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$D_n$</td>
<td>nozzle diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>$f$</td>
<td>friction coefficient</td>
<td>[Ns/m]</td>
</tr>
<tr>
<td>$F_d$</td>
<td>drag force</td>
<td>[N]</td>
</tr>
<tr>
<td>$F_i$</td>
<td>inertia force</td>
<td>[N]</td>
</tr>
<tr>
<td>$k$</td>
<td>correction factor for $Cc$</td>
<td>[-]</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>[J/K]</td>
</tr>
<tr>
<td>$Kn$</td>
<td>Knudsen number</td>
<td>[-]</td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass of the liquid</td>
<td>[kg/mol]</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of a vapour molecule</td>
<td>[kg]</td>
</tr>
<tr>
<td>$m_g$</td>
<td>aerosol mass flow rate</td>
<td>[kg/s]</td>
</tr>
<tr>
<td>$N_a$</td>
<td>Avogadro’s number</td>
<td>[mol$^{-1}$]</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$p_0$</td>
<td>ambient pressure</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$p_d$</td>
<td>partial pressure of vapour at the droplet surface</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$Stk$</td>
<td>Stokes number</td>
<td>[-]</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$u$</td>
<td>outlet velocity by nozzle exit</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$v$</td>
<td>gas velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$w$</td>
<td>particle velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$v_{rel}$</td>
<td>relative velocity, $v_{rel} = v - w$</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$x$</td>
<td>particle diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>$Y$</td>
<td>$p_{so}^2/(\rho_T x)$ ratio proportional to $Stk_{50}$</td>
<td>[Pa$^2$/kg]</td>
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</tbody>
</table>

**Greek letters**

<table>
<thead>
<tr>
<th>Symbol</th>
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<th>Unit</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>accommodation coefficient for the fraction of diffusely scattered gas molecules</td>
<td>[-]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>dynamic gas viscosity</td>
<td>[kg·m$^{-1}$·s$^{-1}$]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>mean free path of carrier gas molecules</td>
<td>[m]</td>
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</table>

**Subscripts**

<table>
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<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>1</td>
<td>silver core</td>
</tr>
<tr>
<td>2</td>
<td>coated particle</td>
</tr>
<tr>
<td>50</td>
<td>at which 50% of particles are separated</td>
</tr>
<tr>
<td>Ag</td>
<td>silver particle</td>
</tr>
<tr>
<td>calcul</td>
<td>calculated</td>
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<tr>
<td>classic</td>
<td>classic</td>
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<tr>
<td>DEHS</td>
<td>DEHS droplet</td>
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<tr>
<td>eff</td>
<td>effective</td>
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<tr>
<td>g</td>
<td>gas</td>
</tr>
<tr>
<td>p</td>
<td>particle</td>
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</tbody>
</table>

**References**


Author’s short biography

Alfred P. Weber

Prof. Dr. Alfred Weber studied experimental physics and obtained his PhD in aerosol physics at ETH Zurich in 1993 on the characterization of the structure of agglomerated aerosol particles. From 1993 until 1995 he worked as a visiting scholar and lecturer in the group of Prof. Sheldon Friedlander in the Chemical Engineering Department at UC Los Angeles on tailoring nanoparticle agglomerates by understanding their restructuring kinetics. In 1996 he joined the group of Prof. Gerhard Kasper at the Institute of Mechanical Engineering and Applied Mechanics in Karlsruhe where he headed the groups of nanoparticle technology and particle measuring technology. He received the Smoluchowski Award at the International Aerosol Conference in 2001 for his work on the catalytic activity of aerosol nanoparticles. Since 2005, he has been a full professor for mechanical process engineering at the Clausthal University of Technology and director of the Institute for Particle Technology. His research focuses on the gas-phase synthesis of nanoparticles, their characterization and applications in functional coatings. Alfred Weber serves as a referee for various organizations and journals and is a member of the editorial board of the Journal of Aerosol Science and Chair of the Smoluchowski Award Committee. He gives the annual Clausthal course on “Particle Measuring Technologies” which was started by Prof. Kurt Leschonski in 1963.

Tao Wu

Dipl.-Ing. Tao Wu obtained his B.Eng. in 2001 from Tongji University, Shanghai, China, and his Dipl.-Ing. (M.Eng.) degree in 2005 from Clausthal University of Technology, Clausthal-Zellerfeld, Germany with the study of environmental engineering. For his master’s thesis, he researched the optimization of pollutant emissions from a biomass thermal power plant at WULFF Deutschland GmbH (Germany). He graduated from the Institute of Mechanical Process Engineering (Particle Technology), Clausthal University of Technology in 2005 in the research groups of particle technology headed by Prof. Dr. rer. nat. Alfred P. Weber. His PhD work focuses on the characterisation of nanoparticles by means of low-pressure impaction, the fragmentation of nanoparticle agglomerates, the charging and bouncing process of nanoparticles by low-pressure impaction and their dynamic properties in low-pressure flows.