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„Development of a versatile size analyzing nuclei counter
(vSANC) and application to ambient aerosol studies“

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To my beloved parents

Kurzfassung

In dieser Arbeit werden ein neu entwickelter Expansionskammer-Kondensationskernzähler - der versatile Size Analyzing Nuclei Counter (vSANC) - und dessen Einsatz bei der Untersuchung atmosphärischer Aerosolpartikel präsentiert.

Das Funktionsprinzip des vSANC beruht auf heterogener Nukleation von übersättigtem Dampf auf bereits existierenden Aerosolpartikeln und anschließendem Tröpfchenwachstum. Wohl definierte und uniforme Dampfübersättigung innerhalb der Expansionskammer wird durch adiabatische Expansion erreicht. Nanopartikel, die durch heterogene Nukleation aktiviert werden, wachsen an und können mittels Lichtstreuung detektiert werden. Das Messprinzip wurde vom klassischen SANC adaptiert (Preining et al. (1981); Wagner et al. (2003)).

Der vSANC wurde dahingehend entwickelt, dass er größtmögliche Flexibilität sowohl im Einsatz bei Feldstudien als auch im Einsatz bei Laborstudien bietet. Das beinhaltet große Betriebsbereiche bezüglich Temperatur und absolutem Druck, sowie hohe Flexibilität in der Wahl der kondensierenden Flüssigkeit und der Aerosoleinlassflussrate. Messungen bezüglich der Zähleffizienz zeigen, dass der vSANC 10 – 20% der Partikel oder molekularen Cluster mit einem Durchmesser von 1.5nm detektiert. Daher kann er als Partikelzähler für Cluster mit Durchmessern unterhalb von 3nm verwendet werden.

Partikelanzahlkonzentrationen und Wachstumskurven werden mit Hilfe einer optischen Detektionsmethode - der multi-angle Constant Angle Mie Scattering method (mCAMS) - gemessen. Die Tröpfchen, die in der Expansionskammer anwachsen, werden mit einem polarisierten Laserstrahl beleuchtet. Der von den anwachsenden Tröpfchen gestreute Lichtfluss wird gleichzeitig unter fünf verschiedenen Vorwärtsstreuwinkeln gemessen. Abhängig vom Streuwinkel weisen experimentelle Streulichtfluss vs. Zeit Kurven eine Serie von Maxima und Minima auf, die in guter Übereinstimmung mit theoretischen Kurven ist, die mit Hilfe der Mie Theorie (Mie, 1908) berechnet werden. Dadurch kann die Entwicklung der Tröpfchengröße als Funktion der Zeit gemessen werden (Wagner, 1985). Gleichzeitige Messungen des transmittierten Lichtflusses ermöglichen die Absolutbestimmung von Tröpfchenanzahlkonzentrationen in einem Konzentrationsbereich von 10^2 bis 10^7cm^{-3} (Szymanski and Wagner, 1990).

Darüberhinaus, kann die Abschwächung des Laserstrahls durch bereits sichtbare Teilchen berücksichtigt werden, indem eine Referenzlinie mit Hilfe eines zusätzlichen Photosensors gemessen wird.

Tröpfchenwachstumsdaten ermöglichen es die Dampfübersättigung, die eine wichtige Rolle in

der Untersuchung von Größen molekularer Cluster mittels heterogener Nukleationswahrscheinlichkeiten spielt, präzise zu bestimmen.

Der vSANC wurde während der Frühlingsmesskampagne 2014 auf der SMEAR II Messstation in Hyytiälä, Finnland, betrieben. Das Hauptziel war es, Bildung und Wachstum atmosphärischer Cluster zu untersuchen. Dafür wurde der vSANC im sogenannten *scanning* Modus, bei dem eine größenabhängige Aktivierung von Partikeln durch das Alternieren von drei unterschiedlichen Expansionsverhältnissen erreicht wird, betrieben. Folglich wurden Konzentrationsmessungen in den Partikeldurchmesserbereichen 2-5nm, 5-10nm und > 10nm nacheinander durchgeführt, wobei eine volle Messsequenz etwa sechs Minuten dauerte. Beim größten Druckabfall, nahe dem Einsetzen homogener Nukleation, können praktisch alle Cluster, die als Kondensationskerne zur Verfügung stehen, als aktiviert betrachtet werden. Atmosphärische Partikelneubildung wurde nur dann beobachtet, wenn die Betriebstemperaturen nahe der Umgebungslufttemperatur lagen. Bei höheren Betriebstemperaturen verursachten verdampfungsbedingte Partikelverluste entlang des Instrumenteneinlasses erhebliche Zählverluste. Ein weiteres interessantes Ergebnis ist, dass in Abwesenheit von Partikeln bei hoher Luftfeuchtigkeit binäre homogene Nukleation von Wasser und Betriebsflüssigkeit (n-Propanol) in der Expansionskammer beobachtet wurde. Der Tagesgang gemessener Anzahlkonzentrationen während eines atmosphärischen Partikelneubildungstages zeigt, dass Partikelkonzentrationen rund um 10^4cm^{-3} im kleinsten Durchmesserbereich 2-3 Stunden vor dem Auftreten im Signal eines Differential Mobility Particle Sizers detektiert wurden. Die Existenz kontinuierlich präsenter, hochkonzentrierter neutraler Cluster mit Durchmessern unter 3nm konnte mit diesen Feldmessungen nicht bestätigt werden.

Abstract

In this thesis a new expansion-type condensation particle counter - the versatile Size Analyzing Nuclei Counter (vSANC) - and its application to ambient aerosol studies are presented. The operation of the vSANC is based on heterogeneous nucleation of supersaturated vapor on preexisting aerosol particles and subsequent droplet growth. Well-defined uniform vapor supersaturation inside the expansion chamber is achieved by adiabatic expansion. Nanoparticles activated by heterogeneous nucleation are grown to larger sizes and can be detected by light scattering. The measuring principle was adopted from the *classical* SANC (Preining et al. (1981); Wagner et al. (2003)).

The vSANC was designed to allow maximum flexibility for its application in field as well as laboratory studies. This includes wide ranges of operating temperatures and total gas pressures, -20°C to $+40^{\circ}\text{C}$ and 0.2bar to 1.2bar, respectively, and flexibility with respect to the choice of condensing liquids and aerosol intake flowrates. Counting efficiency measurements show that the vSANC detects 10 – 20% of particles/clusters at 1.5nm in diameter. Thus it can be used as particle counter for sub-3nm clusters.

Particle number concentrations and growth curves are obtained by means of an optical detection technique - the multi-angle Constant Angle Mie Scattering method (mCAMS). The droplets growing in the expansion chamber are illuminated by a polarized laser beam. The light flux scattered by the growing droplets is monitored simultaneously at five different forward scattering angles. Depending on the scattering angle, experimental scattered light flux vs. time curves show series of maxima and minima in good agreement with theoretical curves, calculated by means of Mie theory (Mie, 1908). This way we can precisely measure the evolution of droplet size as a function of time (Wagner, 1985). Simultaneous measurement of the transmitted light flux allows to determine absolute droplet number concentrations (Szymanski and Wagner, 1990) ranging from 10^2cm^{-3} to 10^7cm^{-3} . Moreover, light attenuation by particles already visible before expansion, can be accounted for by observing a reference baseline provided by an additional photodetector monitoring the incident laser light flux.

Droplet growth data enable precision determination of vapor saturation ratios, which are key in evaluating sizes of molecular clusters down to about 1nm using heterogeneous nucleation probability curves (Winkler et al. (2008b)).

In spring 2014, the vSANC has been operated at the SMEAR II station in Hyytiälä, Finland. The main goal was to investigate the formation and growth of atmospheric clusters starting from smallest detectable sizes. To this end, the vSANC was operated in *scanning* mode,

where size-dependent particle activation is achieved by altering the expansion ratio among three different values. Accordingly, concentration measurements in the particle diameter bins 2-5nm, 5-10nm and $> 10\text{nm}$ were performed sequentially, one full measuring sequence taking about six minutes. At the highest pressure drop close to the onset of homogeneous nucleation basically all clusters capable of acting as condensation nuclei can be considered activated. Using n-propanol as working fluid, atmospheric new particle formation was observed only when operating temperatures were close to the ambient air temperature. At higher operating temperatures particle evaporation occurred along the inlet line, causing substantial counting losses. Another interesting finding was that in the absence of particles high relative humidity led to binary homogeneous nucleation of water and n-propanol in the expansion chamber. Diurnal concentration evolution during atmospheric new particle formation (NPF) events showed that particle concentrations as high as 10^4cm^{-3} were detected in the smallest size bin about 2-3 hours *before* the NPF signal appeared in a differential mobility particle sizer. A continuously present pool of highly concentrated neutral clusters in the sub-3nm size range (Kulmala et al., 2007) could not be confirmed during these measurements.

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Glossary

Greek symbols

α	Diffusion factor
α_M	Mass accommodation coefficient
α_s	Size parameter
α_T	Thermal accommodation coefficient
$\beta_{M(T)}$	Transitional correction factor
β	Expansion ratio
ϵ	Aperture
$\epsilon_r^{l/v}$	Dielectric constant of the liquid/vapor
ϵ_0	Vacuum permittivity
η	Counting efficiency
$\eta_{act/det/sam}$	Activation/Detection/Sampling efficiency
θ	Scattering angle
θ_c	Macroscopic contact angle
κ	Adiabatic index
$\kappa_{g(v)}$	Adiabatic exponent of the gas (vapor)
λ	Wavelength
λ_m	Mean free path of vapor molecules in the surrounding gas
μ	Chemical potential
μ_p	Permeability
μ_0	Vacuum permeability
ρ	Total mass concentration
ρ_{dp}	Distance between scattering droplet and lens
ρ_F	Charge density
$\rho_{g(v)}$	Partial density of the gas (vapor)
ρ_i	Total gas density before expansion
ρ_0	Total gas density at the end of expansion
σ	Conductivity
$\sigma_{l,v/l,s/s,v}$	Surface tension liquid-vapor/liquid-solid/solid-vapor

$\Phi_{i/s/t}$	Incident/Scattered/Transmitted light flux
$\tilde{\Phi}_s$	Attenuation corrected scattered light flux
$\check{\Phi}_s$	Normalized scattered light flux
χ	Electric susceptibility
ω	Angular frequency

Latin Symbols

a	Droplet radius
a_n	Scattering coefficient
A	Outer part of the expansion chamber
$\mathcal{A}$	Light attenuation
A_L	Illuminated area of the lens
A_{LB}	Cross-section of the laser beam
A_{PD}	Active area of the photo diode
A_{PMT}	Active area of the photomultiplier tube
AI	Expansion chamber inlet connector
AO	Expansion chamber outlet connector
$\vec{B}$	Magnetic induction
c	Speed of light in vacuum
$c_{v(p)}$	Specific heat capacity at constant volume (pressure)
C_c	Cunningham slip-correction
C_{EXT}	Extinction cross-section
C_{SCA}	Scattering cross-section
C_0	Droplet concentration
d_{CH}	Inner diameter of the expansion chamber
d_G	Wall thickness of the glass-ring
d_L	Diameter of the lens
d_{LB}	Laser beam diameter
d_P	Pinhole diameter
d_p	Droplet diameter
d_{PD}	Diameter of the photo-diode
d_R	Distance between the center of the expansion chamber and rectangular stop
d_{SC}	Diameter of the circular stop
d_{seed}	Diameter of the seed particle
$d_{10(50)}$	Seed particle diameter corresponding to 10(50)% counting efficiency
D	Binary diffusion coefficient
$\vec{D}$	Electric displacement
D_{CH}	Outer diameter of the expansion chamber

$\vec{E}$	Electric field
Evac	Vacuum pump generating vacuum in the subpressure vessel
Exh	Vacuum pump regulating the aerosol intake flow rate via critical orifice
EXP	Expansion chamber
f_l	Focal length
F	Polarization filter
F_M	Diffusional correction factor
F_T	Thermal correction factor
G	Gibbs free energy
G	Glass ring
h_v	specific enthalpy
$\vec{H}$	Magnetic field
HS	Half-shaded region
HUM	Humidifier
I	Total mass flux
$I_{i/s/t}$	Intensity of the incident/scattered/transmitted laser beam
$\vec{j}$	Total mass flux density
J	Nucleation rate
$\vec{J}_F$	Current density (free charges)
k	Boltzmann constant
$\vec{k}$	Wave vector
k_{PMT}	Photomultiplier tube calibration constant
K	Thermal conductivity
Kn	Knudsen number
ℓ	Extinction length
l_v	Length of the scattering light volume
L	Latent heat
L	Lens
m	Complex refractive index
$\vec{M}$	Magnetization
n_G	Refractive index of the glass ring
n_l	Number of molecules per volume in the liquid phase
$N_{c,(i/0)}$	Particle number concentration (before/at the end of expansion)
$p_{i/0}$	Total gas pressure before/at the end of expansion
$p_{v/g}$	Partial pressure of the vapor/gas
p_s	Saturation vapor pressure
Δp	Total gas pressure change inside the expansion chamber
Δp_R	Total gas pressure change inside the subpressure vessel
P	Nucleation probability
$\vec{P}$	Electric polarization

q	Total charge
$\vec{q}$	Total heat flux density
Q	Total heat flux
Q_{ae}	Aerosol flowrate
$Q_{feed/dil}$	Furnace feed/dilution flow rate
Q_{inlet}	Aerosol intake flow rate of the vSANC
r_i	Ion radius
r_k	Kelvin radius
r_{CH}	Inner radius of the expansion chamber
r_{LB}	Radius of the laser beam
r_P	Radius of the pinhole
R	Radius of seed particle
R_{CH}	Outer radius of the expansion chamber
R_G	Universal gas constant
S	Entropy
$\vec{S}$	Poynting vector
S_C	Circular stop
$S_{(i/0)}$	Vapor saturation ratio (before/at the end of expansion)
S_{onset}	Onset saturation ratio
S_R	Rectangular stop
$S_{\perp}$	Scattering matrix element
$T_{i/0}$	Temperature before/at the end of expansion
$T_{AMB/CH/HUM/INST}$	Temperature of ambient air/expansion chamber/humidifier/ instrument housing
U	Internal energy
V_{PMT}	Bias voltage photomultiplier tube
V_s	Scattering light volume
V_{1-6}	Valve
w_R	Width of the rectangular stop

Acronyms

CNC	Condensation nuclei counter
CNT	Classical nucleation theory
CPC	Condensation particle counter
DAQ	Data acquisition
DEG	Diethylene glycol
DEHS	Diethylhexyl sebacat
DMA	Differential mobility analyzer
DIO	Digital input output
DMPS	Differential mobility particle sizer
FCE	Faraday cup electrometer
FEP	Fluorinated ethylene propylene
IDE	Integrated development environment
IOA	Integrated optics assembly
LB	Laser beam
LIS	Laser inlet system
mCAMS	multi-angle constant angle Mie scattering
NPF	New particle formation
OC	Observation cone
OP	Optical plate
PCU	Process control unit
PD	Photo diode
PEEK	Polyetherether keton
PMT	Photomultiplier tube
PS	Power supply
PSM	Particle size magnifier
RH	Relative humidity
UCPC	Ultrafine condensation particle counter
vSANC	versatile Size Analyzing Nuclei Counter

1 Introduction

Atmospheric nanoparticle formation by gas-to-particle conversion is frequently observed in field measurements and is thought to be the dominant source controlling the number size distribution of atmospheric aerosol particles on global scale (Kulmala et al., 2004b). Model studies and observations have shown that these nanoparticles can grow to sizes where they act as cloud condensation nuclei (Sparcklen et al. (2008), Merikanto et al. (2009)). Thereby they contribute to the indirect radiative forcing, which ultimately affects climate (IPCC, 2007).

Regarding the initial steps of atmospheric new particle formation Kulmala et al. (2013) recently presented an observation-based framework, that confirmed that the formation of nanoparticles in the atmosphere is essentially a two-step process. This observation is in agreement with theoretical arguments (Kulmala et al. (2000); Kulmala et al. (2004a)) and laboratory experiments (Wagner and Strey, 2001). In the first step clusters between 1.2 and 1.7 nm grow predominantly by addition of sulfuric acid molecules and are stabilized by ammonia and amines, whereas in the second step the growth of clusters bigger than 1.7 nm is enhanced by condensation of oxidized organic vapors. Moreover they found that growth mechanisms of sub-2nm clusters are dominated by neutral pathways, in agreement with Hirsikko et al. (2011). Thus the key for understanding the formation of nanoparticles in the atmosphere is to explain the presence of neutral clusters (Kulmala et al., 2007). However, the mechanisms responsible for these processes remain poorly understood. Part of the difficulties associated with characterizing ambient nanoparticle formation are related to certain fundamental limits in the detection of nanoparticles by available instrumentation (McMurry, 2000b).

So far, condensation particle counters (CPCs) are the only instruments that are able to detect neutral gas-borne particles that are too small for optical observation. The operation of a CPC is based on heterogeneous nucleation of supersaturated vapor on aerosol particles or molecular clusters and subsequent droplet growth. Thereby particles grow into visible sizes where they can be detected using optical techniques.

Regarding its optical detection technique, a CPC is either a direct or an indirect detection instrument (McMurry, 2000b). If a CPC measures total particle number concentration by counting individual droplets (single-particle-counting), it is referred to as direct instrument. In single-particle-count mode CPCs measure absolute number concentrations. The upper concentration limit of this detection technique is below $10^3 - 10^5 \text{ cm}^{-3}$ depending on the instrument design. On the other hand, CPCs measuring light attenuation or light scattering

caused by a cloud of droplets are referred to as indirect instruments. Indirect measurement techniques usually require an empirical calibration. However, Szymanski and Wagner (1990) introduced an indirect measurement technique that allows absolute determination of particle number concentrations. To this end, light attenuation and the light flux scattered under a constant angle (Wagner, 1985) are measured simultaneously during droplet growth. This method allows determination of particle number concentrations ranging from $10^3 - 10^7 \text{ cm}^{-3}$. Regarding the way vapor supersaturation is achieved McMurry (2000a) categorized CPCs into two groups:

- expansion type CPCs and
- continuous flow type CPCs.

In an expansion type CPC, vapor supersaturation is achieved by means of fast adiabatic expansion of nearly saturated vapor (Metnieks and Pollak, 1959). On the other hand, in continuous flow type CPCs supersaturation is obtained either by conductive cooling (Bricard et al., 1976) or heating (Hering and Stolzenburg, 2005) of saturated sampled aerosol (laminar flow CPC), or by mixing warm and cool air streams containing the saturated vapor (mixing type CPC, Kousaka et al. (1982)).

The history of condensation particle counters spans more than a century and extends back to the work of Aitken (1888) (McMurry, 2000a). However, only recently CPCs have become available that are capable of detecting particles below 3nm in diameter.

A substantial development in the field of CPCs, which are able to detect particles down to 3nm in diameter, was the design of a butanol-based laminar-flow type ultrafine aerosol condensation nucleus counter by Stolzenburg and McMurry (1991). Hering and Stolzenburg (2005) and Hering et al. (2005) were the first to introduce water as working fluid for ultrafine laminar-flow CPCs. Iida et al. (2008) compared water- and butanol- based ultrafine CPCs. Their findings suggest, that the working fluid influences the performance of CPCs, particularly in the size range below 5nm. One of the big advantages of laminar-flow type CPCs is their stable performance during long term measurements.

Mixing type particle size magnifiers (PSM, Okuyama et al. (1984)) improved by Gamero-Gastano and Fernández de la Mora (2000), and Sgro and Fernández de la Mora (2004), which use dibutyl phtalate as condensing vapor, and Kim et al. (2000) using ethylene glycol as working fluid show great performance in detecting charged particles down to 1nm in diameter. First studies on the activation of neutral particles below 3nm in diameter using an expansion-type CPC and n-propanol as working fluid were performed by Winkler et al. (2008b). They showed, that heterogeneous nucleation on preexisting particles occurs even at sizes below the Kelvin limit, which decreases the detection limit of CPCs to considerably smaller sizes (McMurry (2000b), Kulmala et al. (2005)).

One of the limits for particle detection by means of heterogeneous nucleation in size ranges approaching 1nm is the onset of homogeneous nucleation of the vapor at high supersatura-

tions. Iida et al. (2009) solved this problem by choosing a proper working fluid. Based on theoretical and experimental analysis they identified diethylene glycol (DEG) as suitable candidate for atmospheric measurements. This idea was adopted by Vanhanen et al. (2011), who designed a mixing type PSM applicable for atmospheric measurements (Lehtipalo et al., 2014). However, recent studies (Kangasluoma et al. (2014); Kangasluoma et al. (2013); Wimmer et al. (2013)) have shown that DEG activates sub-2nm organic particles very poorly. Another approach in decreasing the smallest detectable size was made by Sipilä et al. (2009), who used pulse height analysis (Weber et al., 1998) to distinguish between homogeneously and heterogeneously formed droplets. Experiments performed by Winkler et al. (2008a) have shown that using time resolved scattered light measurements (CAMS method, Wagner (1985)) signals resulting from homogeneously formed droplets can be distinguished from heterogeneously formed droplets. Kuang et al. (2012) have shown, that the detection efficiency of laminar-flow butanol- and DEG- based CPCs in the 1nm size range can be enhanced by increasing both instrument operating temperatures and condenser flowrates. Despite substantial improvements of instrumentation by means of various sophisticated approaches, to our knowledge, no study has been published, that experimentally confirms the existence of a continuously present, large pool ($10^6 - 10^7 \text{cm}^{-3}$) of neutral clusters in the sub-3nm size range (Kulmala et al., 2007).

The objective of this study is to present a newly developed expansion-type CPC - the versatile Size Analyzing Nuclei Counter (vSANC) - and its application to atmospheric aerosol studies. The operation principle of the vSANC was adopted from the *classical* SANC (Preining et al., 1981). Using this new device clusters down to 1nm can be activated and absolute number concentrations from ranging from 10^2 to 10^7cm^{-3} can be determined both in the laboratory as well as in long-term field studies. Thus the vSANC is a promising instrument that might help solving the aerosol nucleation puzzle (Andreae, 2013).

2 Classical nucleation theory

A thermodynamic system, in which droplets are formed in a condensing vapor, undergoes a first order phase transition. The first nuclei of the new (liquid) phase appearing in a metastable mother phase (supersaturated vapor) are formed by *nucleation*. An approximate description of nucleation phenomena is given by the *classical nucleation theory* (CNT). Here the results of CNT are summarized, as far as they concern the present investigations. A more detailed description of CNT can be found e.g. in Vehkamäki (2006).

In the present study nucleation occurs at constant temperature T_0 and pressure p_0 . Furthermore the total number of molecules N_{tot} does not change during each single experiment, and only one species of molecules is used (*unary* nucleation). The free energy, corresponding to such thermodynamic systems, is the *Gibbs free energy* G , which can be expressed as

$$G = U - T_0S + p_0V = \mu N_{tot}, \quad (2.1)$$

where U , S and V are internal energy, entropy and volume of the system, respectively. μ is the chemical potential of the molecules. In equilibrium the free energy G is constant.

2.1 Unary homogeneous nucleation

In order to form nuclei in supersaturated vapor the system has to overcome the free energy barrier ΔG_{hom} .

If the initial state (referred to by subscript 0) of the investigated system is a homogeneous vapor, then the internal energy U_0 reads

$$U_0 = T_0S_0 - p_0V_0 + \mu_{v,0}N_{v,0}$$

where $N_{v,0} = N_{tot}$ and $\mu_{v,0} = \mu_v$ is the chemical potential of vapor molecules taken at initial pressure $p_0 = p_v$.

The internal energy U of the final state, where the system contains a spherical nucleus surrounded by homogeneous vapor, is

$$U = T_0S - p_vV_v - p_lV_l + \sigma_{l,v}A_l + \mu_vN_v + \mu_lN_l.$$

Subscripts v and l indicate properties of *vapor* and *liquid* phase, respectively. A_l and V_l are surface and volume of the nucleus, respectively. μ_l is the chemical potential of molecules in the liquid phase taken at pressure p_l . $\sigma_{l,v}$ is the surface tension between liquid and vapor phase.

It should be noted that in CNT, nuclei are assumed to be spherical and to have macroscopic properties, such as surface tension $\sigma_{l,v}$ and density, independent of their size. This assumption can cause discrepancies between experimental and theoretical results.

Using eq. (2.1) and $p_0 = p_v$, free energies of the initial and final state can be expressed as

$$\begin{aligned} G_0 &= U_0 - T_0 S_0 + p_0 V_0 = \mu_{v,0} N_{v,0} \\ G &= U - T_0 S + p_0 (V_l + V_v) \\ &= V_l(p_l - p_0) + \sigma A + \mu_v N_v + \mu_l N_l. \end{aligned}$$

Thus the free energy barrier $\Delta G = G - G_0$ reads

$$\Delta G_{hom} = (p_v - p_l)V_l + \sigma_{l,v}A_l + (\mu_l - \mu_v)N_l \quad \text{for} \quad \begin{cases} \mu_v = \mu_{v,0} \\ N_{v,0} = N_v + N_l \end{cases}. \quad (2.2)$$

If nuclei and surrounding vapor are in equilibrium $\mu_l = \mu_v$, the pressure p_l inside the nuclei is defined by the *Laplace* equation, which reads

$$p_l = p_v + \frac{2\sigma_{l,v}}{r}, \quad (2.3)$$

with r being the radius of a spherical nucleus.

Integrating the *Maxwell equation*

$$d\mu_l = v_l dp,$$

where v_l is the molecular volume $\frac{V_l}{N_l}$, from p_v to p_l , while keeping T constant, yields

$$\mu_l(p_l) - \mu_l(p_v) = v_l(p_l - p_v). \quad (2.4)$$

Inserting eq. (2.4) in eq. (2.2), the difference in free energy between initial and final state reads

$$\Delta G_{hom} = (\mu_l(p_v) - \mu_v(p_v)) N_l + \sigma_{l,v}A_l. \quad (2.5)$$

In equilibrium $\mu_l(p_l) = \mu_v(p_0)$, and thus

$$\Delta G_{hom} = \Delta\mu N_l + \sigma_{l,v}A_l \quad (2.6)$$

with

$$\Delta\mu = \mu_l(p_v) - \mu_v(p_v) = v_l(p_v - p_l). \quad (2.7)$$

The term $\Delta\mu_l N_l$ represents the volume contribution, $\Delta G_{hom}^V \propto r^3$, to free energy, whereas $\sigma_{l,v} A = \Delta G_{hom}^S \propto r^2$ describes the surface contribution.

Although often misleadingly interpreted as the chemical potential difference between vapor and liquid, $\Delta\mu$ is the difference in chemical potential of liquid and vapor both taken at vapor pressure p_v .

Assuming an ideal vapor ($V_v = \frac{kT}{p_v}$) and incompressible liquid, it can be shown (see e.g. Vehkamäki (2006), p. 28-30), that

$$\Delta\mu = -kT \ln S \quad (2.8)$$

where k is the *Boltzmann* constant. The vapor saturation ratio S is defined as

$$S = \frac{p_v}{p_s(T)}$$

with $p_s(T)$ being the saturation vapor pressure over a flat (liquid) surface.

Inserting (2.3) and (2.8) in (2.7) gives the *Kelvin* equation, which can be written as

$$r_k = \frac{2\sigma_{l,v}}{n_l kT \ln S}, \quad (2.9)$$

where n_l is the number of molecules per volume in the liquid phase. The radius r_k is referred to as *Kelvin* radius, and gives the size of a droplet in equilibrium with the surrounding vapor. Clearly stable clusters with radius $r_k > 0$ can only exist at supersaturated conditions, i.e. $S > 1$. A schematic diagram of ΔG as a function of r for different vapor saturation ratios S is shown in figure 2.1.

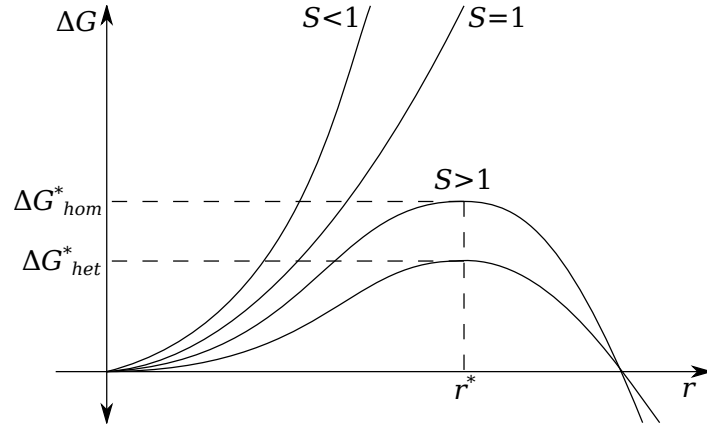


Figure 2.1: Free energy barrier ΔG as a function of cluster radius r for different vapor saturation ratios S .

For $S > 1$ the volume term is negative, whereas ΔG_{hom}^S is always positive. Since $\Delta G_{hom}^V \propto r^3$ and $\Delta G_{hom}^S \propto r^2$, the surface term, preventing formation of nuclei, dominates at small

cluster sizes (*evaporation*), whereas the volume term, that favors the formation of nuclei, dominates at large cluster sizes (*condensation*).

The free energy barrier ΔG_{hom} has a *minimum*, if $\Delta G_{hom}^V = \Delta G_{hom}^S$, which means that nuclei and vapor are in equilibrium. It can be shown (see Vehkamäki (2006)) that equilibrium occurs when the following conditions are satisfied:

$$\begin{aligned} p_l^* - p_v &= \frac{2\sigma}{r^*} \\ \mu_l^* &= \mu_v^* \end{aligned}$$

where asterisks denote equilibrium. Not surprisingly, a nucleus is in equilibrium with the supersaturated vapor if the pressure inside the nucleus satisfies the *Laplace* equation, and the chemical potential of vapor and liquid molecules are equal. Inserting the equilibrium values into (2.6) gives the *critical* free energy barrier ΔG^* , that a cluster of molecules has to overcome in order to be in equilibrium with its metastable mother phase.

$$\Delta G_{hom}^* = \frac{4}{3}\pi\sigma_{l,v}r^*, \quad (2.10)$$

with critical radius r^* being the *Kelvin* radius r_k (see eq. (2.9)).

The rate J_{hom} at which nuclei of critical size r^* are formed per unit volume and unit time can be written as (Fletcher, 1962)

$$J_{hom} = Be^{-\frac{\Delta G_{hom}^*}{kT}} \quad (2.11)$$

where B is a pre-exponential factor containing information from kinetic theory.

2.2 Unary heterogeneous nucleation

The formation of critical clusters on preexisting *seed* particles is described by the *heterogeneous nucleation theory*, which is often referred to as *Fletcher* theory (Fletcher, 1958).

Figure 2.2 illustrates the formation of a cluster on the surface of a spherical seed particle. Both seed particle and cluster cap forming on it are assumed to be spherical. In line with homogeneous nucleation, the difference in free energy between molecules in vapor and liquid phase consists of one surface and one volume term, ΔG_{het}^S and ΔG_{het}^V , respectively. Looking at fig. 2.2, it can be seen that the surface term can be expressed as

$$\Delta G_{het}^S = \sigma_{l,v}A_{l,v} + (\sigma_{l,s} - \sigma_{s,v})A_{l,s}, \quad (2.12)$$

with $A_{l,v}$ and $A_{l,s}$ being the surface areas of the (liquid) cluster against vapor and solid surface, respectively. $\sigma_{l,v}$, $\sigma_{l,s}$ and $\sigma_{s,v}$ are surface tensions between liquid and vapor, liquid and solid, and solid and vapor phase, respectively.

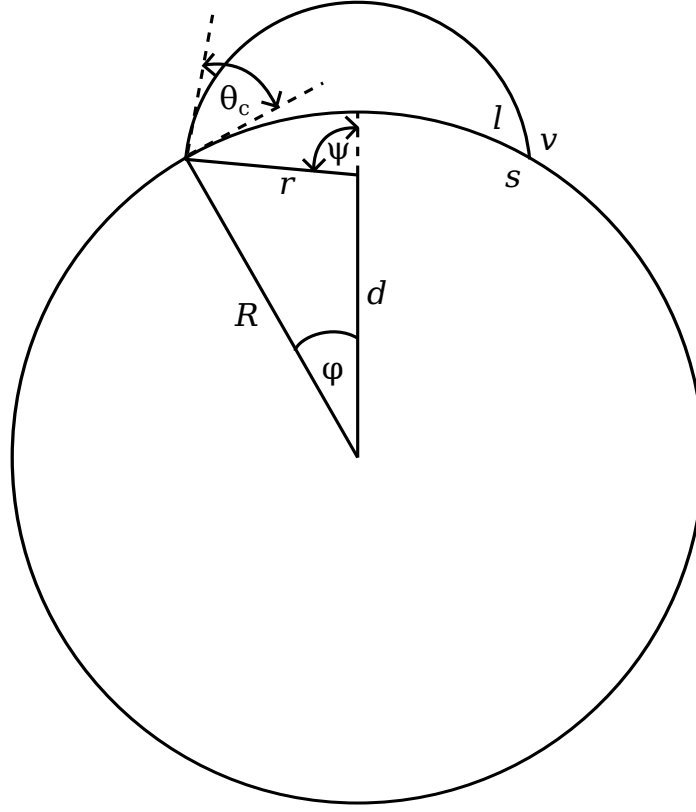


Figure 2.2: Spherical cap-shaped cluster with radius r on the surface of a spherical seed particle with radius R . Angle θ_c is the contact angle given by *Young's* equation. Distance d is the center distance between cluster and seed. ϕ and ψ define the surface area of the cluster.

Like in the homogeneous case, the volume term of free energy is given by

$$\Delta G_{het}^V = \Delta \mu_l N_l \quad (2.13)$$

In general, the relation between N_l and cluster radius r differs from the homogeneous case, because the cluster is not a complete sphere but just a cap on a preexisting particle.

Fletcher (1958) derived expressions for the surface areas $A_{l,v}$ and $A_{l,s}$ using trigonometric functions. The so obtained surface areas and the volume of the spherical cap are

$$\begin{aligned} A_{l,v} &= 2\pi r^2(1 - \cos \psi) \\ A_{l,s} &= 2\pi R^2(1 - \cos \phi) \\ V_l &= \frac{\pi}{3} (r^3(2 - 3 \cos \psi + \cos^3 \psi) - R^3(2 - 3 \cos \phi + \cos^3 \phi)). \end{aligned}$$

r and R are radii of cluster and seed particle, respectively. As can be seen from fig. 2.2 ψ and ϕ depend on r , R , distance d , and contact angle θ_c , which, in turn, is given by the *Young*

equation (Young, 1805)

$$\cos \theta_c = \frac{\sigma_{l,s} - \sigma_{s,v}}{\sigma_{l,v}}. \quad (2.14)$$

It should be noted, that above considerations are only valid for spherical seed particles and spherical caps. Furthermore, *Fletcher* theory uses macroscopic surface tension, contact angle and density values. These assumptions are questionable in the nanometer size range and might cause discrepancies between theory and experiment.

Equating the derivative of $\Delta G_{het} = \Delta G_{het}^V + \Delta G_{het}^S$ to zero yields, not surprisingly, the same equilibrium conditions as for the homogeneous case. This means, that the equilibrium radius, r^* , of a cluster equals the *Kelvin* radius r_k , and the chemical potentials in all coexisting phases are equal.

Defining the dimensionless quantities

$$\begin{aligned} x &= \frac{R}{r} \\ m &= \cos \theta_c \\ g &= \sqrt{1 + x^2 - 2xm}, \end{aligned} \quad (2.15)$$

the number of molecules in a critical cluster of radius r^* can be written as

$$N_{l,hel}^* = f(m, x) \frac{4\pi}{3} \rho_l r^{*3} = f(m, x) N_{l,hom}^* \quad (2.16)$$

where the geometric factor $f(m, x) = \frac{N_{l,hel}^*}{N_{l,hom}^*} = \frac{V_{l,hel}^*}{V_{l,hom}^*}$ can be expressed as

$$\begin{aligned} f(m, x) &= \frac{1}{4} \left\{ 2 + 3 \left(\frac{1 - xm}{g} \right) - \left(\frac{1 - xm}{g} \right)^3 \right. \\ &\quad \left. - x^3 \left[2 - 3 \left(\frac{x - m}{g} \right) + \left(\frac{x - m}{g} \right)^3 \right] \right\}. \end{aligned}$$

Since $0 < f(m, x) \leq 1$, the number of molecules in a heterogeneously formed critical cluster will never exceed the number of molecules in a homogeneously formed critical cluster. If the contact angle $\theta_c = \pi$ or the radius of the seed particle $R = 0$ (homogeneous nucleation), $N_{hom}^* = N_{het}^*$ because $f(m, x) = 1$.

Using the dimensionless quantities from eqs. (2.15), the formation energy of a critical cluster ΔG_{het}^* reads

$$\Delta G_{het}^* = \tilde{f}(m, x) \frac{4\pi r^{*2} \sigma_{l,v}}{3} = \tilde{f}(m, x) \Delta G_{hom}^*, \quad (2.17)$$

with geometric factor $\tilde{f}(m, x)$ being

$$\begin{aligned} \tilde{f}(m, x) = & \frac{1}{2} \left\{ 1 + \left(\frac{1 - xm}{g} \right)^3 + x^3 \left[1 - 3 \left(\frac{x - m}{g} \right) + \left(\frac{x - m}{g} \right)^3 \right] \right. \\ & \left. + 3mx^2 \left(\frac{x - m}{g} - 1 \right) \right\}. \end{aligned}$$

Just as for $f(m, x)$, $\tilde{f}(m, x) \in (0, 1]$, which means that the energy barrier in heterogeneous nucleation never exceeds the homogeneous one. In fact it is lower in most cases, except for $\theta_c = \pi$.

The rate J at which critical clusters are formed per seed particle and unit time can be expressed as

$$J = K4\pi R^2 e^{\frac{-\Delta G_{het}^*}{kT}}, \quad (2.18)$$

where K is a kinetic pre-factor and $4\pi R^2$ is the surface area of the seed particle. To get information about the supersaturation, at which the formation of one critical cluster per particle and second ($J = 1s^{-1}$) becomes favorable for the system, eq. (2.9) can be inserted in (2.17). This yields the following expression

$$2(\ln S)^2 = \frac{a\tilde{f}(m, x)}{\ln(bR^2)}, \quad (2.19)$$

where

$$\begin{aligned} a &= \frac{16\pi}{3} \left(\frac{\sigma_{l,v}}{kT} \right)^3 \frac{1}{n_l^2} \\ b &= \frac{4\pi K}{-\ln \frac{1}{2}}. \end{aligned} \quad (2.20)$$

Adopting the value of $10^{25} \text{cm}^{-2} \text{s}^{-1}$ for K from the original work of Fletcher (1958), the radius of the seed particle R can be calculated iteratively as a function of vapor saturation ratio S . To this end eq. (2.19) is used together with the definition of R according to (2.15) and the *Kelvin* equation (2.9). The resulting curve $R(S)$ is quite insensitive to changes in J by few orders of magnitude. Thus, although nucleation rates were not determined in the present study, experimentally obtain vapor supersaturation can still be used to obtain the radius R of a seed particle, also referred to as *Fletcher* radius.

Another experimentally determined quantity related to the nucleation rate is the nucleation probability P , which is defined as the ratio

$$P = \frac{N_{act}}{N_{tot}}, \quad (2.21)$$

where N_{act} is the number concentration of activated seed particles and N_{tot} is the total number concentration of seed particles. Assuming that only one critical cluster forms per

seed particle the following expression for P can be derived:

$$P = 1 - e^{-Jt}, \quad (2.22)$$

with t being the nucleation time.

From the *first nucleation theorem* (Kashchiev, 1981) it is known, that the number of molecules in the critical cluster N_l^* is related to the first derivative of ΔG_{het}^* with respect to the vapor supersaturation S . A formulation of this theorem might be written as

$$\left(\frac{\partial \ln J}{\partial \ln S} \right)_{T=T_0} \approx N_l^*. \quad (2.23)$$

Using the relation between nucleation rate J and nucleation probability P , an expression for N_l^* can be found, that can be calculated from experimentally obtained data. This expression reads (Vehkamäki et al., 2007)

$$N_l^* \approx \left(\frac{\partial \ln \left(\ln \frac{1}{1-P} \right)}{\partial \ln S} \right)_{T=T_0} - 1, \quad (2.24)$$

where $\left(\frac{\partial \ln K}{\partial \ln S} \right)_{T=T_0} \approx 1$ was used.

Thus experimentally obtained vapor saturation ratios and nucleation probabilities can be used to calculate not only the Fletcher radius R but also the number of molecules in the critical cluster N_l^* . However, in the present study, only the former one was determined.

2.2.1 Ion induced nucleation

Experiments were not only performed using neutral seed particles, but also charged ones. It is therefore appropriate to discuss the influence of charge on the free energy barrier, too. The so called *ion induced* nucleation is described by the classical *Thomson* theory (Thomson, 1906).

In the presence of charged seed particles or ions, electrostatic forces enhance the interaction between vapor molecules and seeds. Therefore the nucleation barrier in the *ion induced* case is not only lower than in homogeneous nucleation, but also lower than for heterogeneous nucleation on neutral seed particles.

The following derivations are based on the work of Toshev (2002).

Suppose that the initial state under consideration contains homogeneous vapor and an ion with total charge q and radius r_i . Then the electrostatic part $G_{0,es}$ of the free energy can be expressed as:

$$G_{0,es} = \int_{r_i}^{\infty} \frac{\epsilon_0 \epsilon_r^v}{2} \left(\frac{q}{4\pi \epsilon_0 \epsilon_r^v r^2} \right)^2 r^2 dr = \frac{q^2}{8\pi \epsilon_0 r_i} \quad \text{for} \quad \epsilon_r^v = 1, \quad (2.25)$$

with ϵ_r^v being the dielectric constant of the vapor. ϵ_0 is the vacuum permittivity.

The electrostatic part G_{es} of the free energy of the final state, i.e. a liquid drop with radius a formed around an ion with radius r_i , is given by

$$G_{es} = \int_a^\infty \frac{\epsilon_0}{2} \left(\frac{q^2}{4\pi\epsilon_0 r^2} \right) r^2 dr + \int_{r_i}^a \frac{\epsilon_0 \epsilon_r^l}{2} \left(\frac{q^2}{4\pi\epsilon_0 \epsilon_r^l r^2} \right)^2 r^2 dr = \frac{q^2}{8\pi\epsilon_0 a} + \frac{q^2}{8\pi\epsilon_0 \epsilon_r^l} \left(\frac{1}{r_i} - \frac{1}{a} \right), \quad (2.26)$$

where ϵ_r^l is the dielectric constant of the liquid phase.

Thus, in the ion induced case, the free energy barrier ΔG^{ii} can be written as:

$$\Delta G^{ii} = \Delta G_{hom} + \Delta G_{es} = \Delta G_{hom} + \frac{q^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_r^l} \right) \left(\frac{1}{a} - \frac{1}{r_i} \right) \quad (2.27)$$

Using $\frac{d\Delta G^{ii}}{dr} = 0$ to find equilibrium conditions, a generalization of the *Laplace* equation (2.3) is obtained. It can be expressed as

$$p_l^* - p_v = \frac{2\sigma}{r^*} - \frac{q^2}{32\pi^2\epsilon_0} \left(1 - \frac{1}{\epsilon_r^l} \right) \frac{1}{r^{*4}}. \quad (2.28)$$

Furthermore equilibrium requires

$$\mu_l(p_l)^* = \mu_v(p_v)^*. \quad (2.29)$$

Thus $\Delta\mu$ reads

$$\Delta\mu = -v_l \left[\frac{2\sigma}{r} - \frac{q^2}{32\pi^2\epsilon_0} \left(1 - \frac{1}{\epsilon_r^l} \right) \frac{1}{r^{*4}} \right] \quad (2.30)$$

with v_l being the volume of a molecule in the liquid phase.

For $\Delta\mu$ being $-kT \ln S$ (see eq. (2.8)) the vapor supersaturation is given by

$$\ln S = \frac{2\sigma_{l,v}}{n_l kT r^*} \left[1 - \frac{q^2}{64\pi^2\epsilon_0 \sigma_{l,v}} \left(1 - \frac{1}{\epsilon_r^l} \right) \frac{1}{r^{*3}} \right]. \quad (2.31)$$

For $1 < S < S_m$, where S_m is given by eq. (2.31) using $r^* = r_m$ with r_m being the droplet radius at the maximum of $p_l - p_v$ (eq. (2.28)), two equilibrium drops with radius r_s^* and r_{us}^* exist. The drop with radii r_s^* refers to a minimum of the free energy (*stable equilibrium*), whereas the drop with radius r_{us}^* is in *unstable equilibrium* with its supersaturated surrounding.

Since r_s^* refers to a minimum of the free energy, all non-equilibrium drops will spontaneously change their size until r_s^* is reached. Thus to form a critical nucleus, that will spontaneously grow, i. e. a nucleus of radius r_{us}^* , a cluster has to exceed the following free energy barrier

$$\begin{aligned} \Delta G^{ii*} &= \Delta G^{ii}(r_{us}^*) - \Delta G^{ii}(r_s^*) \\ &= \frac{4\pi\sigma_{l,v}}{3kT} (r_{us}^{*2} - r_{st}^{*2}) - \frac{q^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_r^l} \right) \left(\frac{1}{r_{st}^*} - \frac{1}{r_{us}^*} \right) \end{aligned}$$

If the cluster is forming on a charged seed particle with radius R (*Fletcher-Thomson* theory), the free energy can be expressed as

$$\Delta G_{het}^{ii} = \Delta G_{het} + \frac{q^2}{4\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_r^l}\right) \left(\frac{1}{a} - \frac{1}{R}\right) \quad (2.32)$$

and the free energy barrier to overcome reads

$$\Delta G_{het}^{ii*} = \Delta G_{het}^{ii}(r_{us}^*) - \Delta G_{het}^{ii}(r_s^*), \quad (2.33)$$

with r_{us}^* and r_s^* satisfying eq. (2.31). The *first nucleation theorem* (eq. (2.23)) is also true for heterogeneous nucleation on charged seed particles. The difference between number of molecules in a stable and an unstable cluster N_l^{ii*} can again be calculated from experimentally determined quantities S and P using eq. (2.24), see e. g. Winkler et al. (2012).

3 Theory of droplet growth

In the present study the theory of droplet growth has been used to determine the vapor supersaturation ratio S causing heterogeneous nucleation and droplet growth. A theoretical description of droplet growth in unary vapor systems has been derived by several authors, e.g. Fuchs (1959), Sednuov (1974), Preining et al. (1981) and Wagner (1982).

In general, droplet growth is determined by mass and heat transfer. Here mass and heat fluxes towards the droplet, I and Q , respectively, are assumed to be quasistationary. Consequently vapor concentration and temperature profiles always correspond to steady state solutions and changes during the growth process result in changing boundary conditions only. Furthermore, temperature profiles inside the droplets are flat and no heat flux into the droplets occurs.

Physical processes resulting in mass and heat transfer depend on the Knudsennumber

$$\text{Kn} = \frac{\lambda_m}{a} \quad (3.1)$$

where λ_m is the mean free path in the surrounding gas and a is the droplet radius. By means of Kn three different size regimes can be distinguished:

- the continuum regime ($\text{Kn} \ll 1$),
- the free molecular regime and ($\text{Kn} \gg 1$) and
- the transitional regime ($\text{Kn} \approx 1$).

In the continuum regime transport of mass and heat is diffusion controlled, whereas in the free molecular regime I and Q can be calculated from the kinetic theory. If a is in the order of λ_m mass and heat transfer are partly under diffusion control and partly under kinetic control.

The following derivations of mass and heat fluxes in different size regimes for unary vapor systems are based on the work of Preining et al. (1981) and Kulmala and Vesala (1991).

3.1 Quasistationary fluxes to a single droplet

3.1.1 Continuum regime

Assuming quasistationary droplet growth and evaporation processes, the conservation of mass in a binary mixture of carrier gas and vapor yields the following continuity equation:

$$\vec{\nabla} \cdot \vec{j} = 0 \quad (3.2)$$

where $\vec{j}$ the total mass flux density.

From the conservation of energy, on the other hand, the following continuity equation can be obtained:

$$\vec{\nabla} \cdot \vec{q} = 0 \quad (3.3)$$

where $\vec{q}$ is the energy (heat) flux density.

In order to determine density and temperature profiles, additional relations between ρ and $\vec{j}$ on the one hand, and between T and $\vec{q}$ on the other hand are required. In the case of dilute gases, these relations are phenomenological equations, that can be derived by solving the *Boltzmann* transport equation. In the present study, numerical calculations are based on the first order phenomenological equations (Hirschfelder et al. (1954), Chapman and Cowling (1970)).

In the absence of external forces and pressure gradients, assuming that the average diffusion velocity of gas molecules $\vec{v}_g$ equals zero, the following first order phenomenological equation for the mass transport of vapor molecules in a binary mixture can be obtained:

$$\vec{j}_v = -\frac{1}{1 - \frac{p_v}{p_0}} D \left(\vec{\nabla} \rho_v + \frac{\rho_v(1 + \alpha)}{T} \vec{\nabla} T \right). \quad (3.4)$$

D is the binary diffusion coefficient and T the absolute temperature. $p_0 = p_v + p_g$ is the total pressure of the binary mixture and p_v and p_g are the partial pressures of vapor and gas, respectively. $\rho = \rho_v + \rho_g$ is the total mass concentration, whereas ρ_v and ρ_g are the partial densities of the vapor and the carrier gas, respectively. Thermal diffusion factor α is usually less than 0.6.

Regarding heat transport, the first order phenomenological equation can be expressed as

$$\vec{q} = -K \vec{\nabla} T - D \left(\vec{\nabla} \rho_v + \frac{\rho_v}{T} (1 + \alpha) \vec{\nabla} T \right) \left(\frac{R_G T}{M_v} \alpha \right) \quad (3.5)$$

where R_G the universal gas constant, K the thermal conductivity and M_v the molecular weight of vapor.

It can be seen from eqs. (3.4) and (3.5) that both heat and mass flux densities, $\vec{q}$ and $\vec{j}_v$, respectively, depend on the temperature gradient as well as on the vapor concentration gradient. To separate the problem, a relation between $\vec{\nabla} T$ and $\vec{\nabla} \rho_v$ can be obtained from

the quasisteady state heat balance at the droplet surface

$$Q + LI = 0 \quad (3.6)$$

where Q is the total flux of heat and I the total mass flux, directed towards the droplet. L is the latent heat of the liquid. From eq. (3.6) the relation

$$K\vec{\nabla}T + LD\vec{\nabla}\rho_v = 0 \quad (3.7)$$

can be obtained (Preining et al., 1981). This yields the following first order phenomenological equations for $\vec{q}$ and $\vec{j}_v$:

$$\vec{q} = -KF_T\vec{\nabla}T \quad (3.8)$$

$$\vec{j}_v = -DF_M\vec{\nabla}\rho_v \quad (3.9)$$

with thermal correction factor F_T given by

$$F_T = 1 - \left(\frac{1}{L} - \frac{D\rho_v}{KT} (1 + \alpha) \right) \left(\frac{RT}{M_v} \alpha \right) \quad (3.10)$$

and diffusional correction factor F_M approximated by

$$F_M \approx 1 + \frac{p_v}{p_0} - \frac{\rho_v LD}{KT} (1 + \alpha). \quad (3.11)$$

The correction term $\frac{p_v}{p_0}$ in eq. (3.11) represents an additional mass flux caused by the center-of-mass motion of the gas-vapor mixture relative to the condensing surface (*Stefan flow*). The correction term $-\frac{\rho_v LD}{KT}$ is caused by the fact that the driving force for mass transfer is $\vec{\nabla}X_v$, not $\vec{\nabla}\rho_v$, where X_v is the mole fraction of vapor. The third correction term in eq. (3.11), i. e. $-\frac{\rho_v LD}{KT} \cdot \alpha$, describes the effect of thermal diffusion (Soret-effect). The correction term $\left(\frac{1}{L} - \frac{D\rho_v}{KT} (1 + \alpha) \right) \left(\frac{RT}{M_v} \alpha \right)$ in eq. (3.10) describes the diffusion thermo effect (Dufour-effect), which is reciprocal to the effect of thermal diffusion.

Integration of eqs. (3.8) and (3.9) over the droplet surface yields the total flux towards the droplet. Using zeroth order temperature and density profiles

$$T(r) = T_\infty + (T_a - T_\infty) \frac{a}{r} \quad (3.12)$$

$$\rho_v(r) = \rho_{v,\infty} + (\rho_{v,a} - \rho_{v,\infty}) \frac{a}{r} \quad (3.13)$$

where T_∞ and $\rho_{v,\infty}$ are temperature and vapor concentration at infinity and T_a and $\rho_{v,a}$ are temperature and vapor concentration at the droplet surface, total mass and heat fluxes, I_c

and Q_c , respectively, towards the droplet surface can be expressed as:

$$I_c = 2\pi a (D_\infty F_{M,\infty} + D_a F_{M,a}) (\rho_{v,\infty} - \rho_{v,a}) \quad (3.14)$$

$$Q_c = 2\pi a (K_\infty F_{T,\infty} + K_a F_{T,a}) (T_\infty - T_a) \quad (3.15)$$

3.1.2 Free molecule regime

For droplets, whose radii a are much smaller than the mean free path λ_m of the surrounding gas, stationary fluxes of mass and heat can be calculated using kinetic theory (Kulmala and Wagner (2001), Wagner (1982)).

Moore (1962) derived an expression for the number of moles Z_N striking a unit area per unit time which reads

$$Z_n = \frac{1}{4} N \langle v \rangle \quad (3.16)$$

where $\langle v \rangle$ is the mean velocity obtained from the *Maxwell* velocity distribution.

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}, \quad (3.17)$$

with k being the *Boltzmann* constant, T the absolute temperature and m the mass of a vapor molecule. Thus the mass flux density in the kinetic regime can be expressed as

$$j_k = \frac{\rho \langle v \rangle}{4} \quad (3.18)$$

where ρ is the vapor density. Under these conditions the total mass flux J_k to a particle of radius a is given by

$$I_k = a^2 \pi \langle v \rangle \alpha_m (\rho_\infty - \rho_a) \quad (3.19)$$

where α_m is the mass accommodation coefficient. α_m is the probability that a molecule in the gas phase striking the phase boundary, will be incorporated into the condensed phase. Using the *classical* SANC, α_m has been studied extensively by Winkler (2004). Similar expressions can be derived for the thermal accommodation coefficient α_t .

3.1.3 Transition regime

If droplet radius a is of the order of the mean free path of the surrounding gas, transport of mass and heat is partly under diffusion control and partly under kinetic control. In order to obtain growth equations for arbitrary sized droplets, a solution of the rigorous *Boltzmann* transport equation is required. Based on the work of Brock (1966) and Sahni (1966), who both used a linearization of the collision term (Bhatnagar et al., 1954), Smirnov (1971) derived expressions for mass and heat fluxes to a droplet of arbitrary size and with arbitrary

values for α_m and α_t . These expressions read

$$I_T = \beta_M \cdot I_C \quad (3.20)$$

$$Q_T = \beta_T \cdot Q_C \quad (3.21)$$

with transitional correcting factors

$$\beta_M = \left(1 + \left(\Lambda(\text{Kn}_M) - \frac{4}{3} + \frac{4}{3\alpha_m} \right) \text{Kn}_M \right)^{-1} \quad (3.22)$$

$$\beta_T = \left(1 + \left(\Lambda(\text{Kn}_T) - \frac{4}{3} + \frac{4}{3\alpha_t} \right) \text{Kn}_T \right)^{-1} \quad (3.23)$$

where Λ is the following interpolation formula proposed by Fuchs (1969)

$$\Lambda = \frac{4/3\text{Kn} + 0.71}{\text{Kn} + 1}. \quad (3.24)$$

Kn_M and Kn_T are given by

$$\text{Kn}_M = \frac{3D\sqrt{\pi M_v}}{2\sqrt{2RT_\infty}a} \quad (3.25)$$

$$\text{Kn}_T = \frac{3K_g\sqrt{\pi M_g RT_\infty}}{2\sqrt{2}p_0(C_{v,g} + R/2)a}. \quad (3.26)$$

$C_{v,g}$ is the molar heat capacity of the gas at constant volume.

For large Knudsennumber ($\text{Kn} \gg 1$) eqs. (3.22) and (3.23) become

$$\beta_M = \left(0.377 + \frac{4\text{Kn}_M}{3\alpha_m} \right)^{-1} \quad (3.27)$$

$$\beta_T = \left(0.337 + \frac{4\text{Kn}_T}{3\alpha_t} \right)^{-1}, \quad (3.28)$$

whereas for $\text{Kn} \ll 1$ they approach

$$\beta_M = \left(1 + \left(\frac{4}{3\alpha_m} - 0.623 \right) \text{Kn}_M \right)^{-1} \quad (3.29)$$

$$\beta_T = \left(1 + \left(\frac{4}{3\alpha_t} - 0.623 \right) \text{Kn}_T \right)^{-1}. \quad (3.30)$$

It can be easily seen that for very small Knudsennumber β_M and β_T approach unity. Thus heat and mass fluxes are given by I_c and Q_c , respectively, which are independent from accommodation coefficients α_m and α_t .

For very big Knudsennumbers β_M approaches $\frac{3\alpha_m}{4\text{Kn}_M}$ and first order correction terms in F_M and F_M can be neglected. Hence expression (3.19) for the mass flux in the free molecular regime is obtained from I_T .

3.2 Mass and heat balance in a monodispersed droplet aerosol

Up to this point, derivations of total mass and heat fluxes were restricted to a single droplet. However, in the present experiments up to 10^6 simultaneously growing droplets are observed per cm^3 . In order to calculate growth processes in droplet populations, taking into account the mutual interactions of droplets, the model of time dependent bulk parameters is used. First proposed by Reiss and La Mer (1951), this model assumes that steep concentration and temperature gradients only occur in the immediate vicinity of the droplets. Furthermore, vapor concentration and temperature profiles between the growing droplets are assumed to be flat. As a consequence, average bulk parameters of vapor concentration and temperature can be defined. The growth of a droplet population can be described by single droplet growth theory with time dependent bulk values for vapor concentration $\rho_{v,\infty}$, vapor pressure $p_{v,\infty}$ and temperature T_∞ . Based on that model, Wagner and Pohl (1975) calculated droplet concentration dependent growth processes in a condensation nucleus counter.

Time dependent bulk parameters are calculated by means of the balance of mass and heat in a volume V , which contains a particular amount of gas and vapor. Taking into account changes in V during the growth process Preining et al. (1981) derived following expressions for the time dependent bulk parameters

$$\rho_{v,\infty} = \frac{(T_\infty)_0}{T_\infty} \left[(\rho_{v,\infty})_0 - \rho_l \frac{4\pi}{3} C_0 (a^3 - a_0^3) \right] \quad (3.31)$$

$$p_{v,\infty} = (p_{v,\infty})_0 - \frac{R(T_\infty)_0}{M_v} \rho_l \frac{4\pi}{3} C_0 (a^3 - a_0^3) \quad (3.32)$$

$$T_\infty = (T_\infty)_0 + \frac{\rho_l L(T_a)}{(\rho_{g,\infty})_0 c_{p,g} + (\rho_{v,\infty})_0 c_{p,v}} \frac{4\pi}{3} C_0 (a^3 - a_0^3) \quad (3.33)$$

$(T_\infty)_0$, $(p_{v,\infty})_0$ and $(\rho_{v,\infty})_0$ are initial values of temperature, partial vapor pressure and partial vapor concentration at infinity, respectively. C_0 and a_0 are initial values for droplet concentration and droplet radius, respectively. ρ_l is the bulk density of the droplet.

Inserting expressions (3.31) - (3.33) in (3.20) and (3.21) the fluxes to a single droplet of the droplet population can be obtained, and the mutual interaction of droplets are taken into account.

3.3 Calculation of droplet growth

The growth rate of a single droplet of arbitrary size is determined by the total transitional mass flux $I_t = \beta_M I_c$ towards it. By taking the temperature dependence of the diffusion coefficient D into account, Preining et al. (1981) derived an expression for the first order total continuum mass flux I_c that depends on the temperature T_a at the droplet surface. In order to obtain T_a the quasisteady state heat balance equation, (3.6), has to be applied to

I_t and Q_t from eqs. (3.20) and (3.21), respectively.

$$Q_T(a, T_a) + L(T_a)I_T(a, T_a) = 0 \quad (3.34)$$

where $L(T_a)$ is the specific latent heat of condensation at droplet temperature T_a and a is the droplet radius. For different droplet radii eq. (3.34) can be solved numerically to obtain T_a . Inserting the so obtained temperature T_a into eq. (3.20) the total transitional mass flux $I_T(a)$ can be calculated. Using eqs. (3.31) - (3.33) total transitional mass and heat fluxes to a single droplet of a droplet population are obtained.

From $I_T(a)$ the droplet radius $a(t)$ as a function of growth time t can be obtained by inverting

$$t(a) = \int_{a_0}^a \frac{4\pi\rho_l r^2}{I_T(r)} dr \quad (3.35)$$

numerically. Knowing $a(t)$, bulk parameters $p_{v,\infty}, T_\infty$ and $S_\infty = \frac{p_{v,\infty}}{p_s(T_\infty)}$, with $p_s(T_\infty)$ being the equilibrium vapor pressure at temperature T_∞ , and droplet temperature T_a can be obtained as a function of time and the droplet growth calculation is completed.

4 Measuring principle

The measuring principle of the vSANC was adopted from the *classical* SANC (Preining et al., 1981). It is based on heterogeneous nucleation of supersaturated vapor on preexisting particles and subsequent droplet growth. Thereby particles, which are initially too small to be detected optically, grow into visible sizes, where they can be observed applying the multi-angle Constant Angle Mie Scattering method (see chapter 5).

4.1 Principles of operation

Before starting the actual measurement, the aerosol with initial particle number concentration $N_{c,i}$ is humidified using a diffusion type humidifier HUM with temperature T_{HUM} . The saturation ratio S_{HUM} at the exit of HUM is given by

$$S_{\text{HUM}} = \frac{p_{v,\text{HUM}}}{p_s(T_{\text{HUM}})} \quad (4.1)$$

where $p_{v,\text{HUM}}$ is the partial pressure of the vapor at the exit of HUM and $p_s(T_{\text{HUM}})$ the saturation vapor pressure at T_{HUM} . The representation of saturation vapor pressure used here reads

$$p_s(T) = e^{A_1 - \frac{A_2}{T - A_3} - A_4 \ln T + A_5 T} \quad (4.2)$$

where coefficients $A_1 - A_5$ are vapor specific constants, that can be found in Kulmala and Vesala (1991), and T is the absolute temperature in K .

For sufficiently low aerosol flow rates through HUM, S_{HUM} will be close to one.

$$S_{\text{HUM}} = 1 \quad \Leftrightarrow \quad p_{v,\text{HUM}} = p_s(T_{\text{HUM}}). \quad (4.3)$$

After humidification the aerosol enters the expansion chamber with initial temperature $T_i > T_{\text{HUM}}$ ¹ and total gas pressure

$$p_i = (p_v)_i + (p_g)_i \quad (4.4)$$

where $(p_v)_i$ and $(p_g)_i$ are initial partial pressures of vapor and carrier gas, respectively.

¹To avoid vapor condensation before expansion.

Thus the initial saturation ratio S_i inside EXP before expansion is given by

$$S_i = \frac{(p_v)_i}{p_s(T_i)} = \frac{p_{v,\text{HUM}}}{p_s(T_i)} = \frac{S_{\text{HUM}} \cdot p_s(T_{\text{HUM}})}{p_s(T_i)}. \quad (4.5)$$

By connecting EXP to a low pressure recipient R, fast expansion of the humidified aerosol is initiated. The total gas pressure p_0 at the end of expansion is given by

$$p_0 = p_i - \Delta p. \quad (4.6)$$

Since the volume of R is large compared to the chamber volume changes in total gas pressure after expansion are negligible, which makes the expansion chamber *pressured defined*.

The thermodynamic parameters at the end of the expansion process (see chapter 3), can be calculated from the conditions before expansion assuming:

- The expansion is dry-adiabatic, which means that vapor and heat exchange with chamber walls, and vapor depletion and production of latent heat due to condensational droplet growth can be neglected.

$$dQ = 0 \rightarrow dU = C_v \cdot dT = -pdV.$$

- The process is quasi-static, which means that the system is in thermal equilibrium during the expansion period (*isentropic*). Therefore,

$$pV^\kappa = \text{const.} \quad (4.7)$$

$$TV^{\kappa-1} = \text{const.} \quad (4.8)$$

with adiabatic index κ according to

$$\kappa = c_p/c_v \quad (4.9)$$

where c_p and c_v are specific heat capacities at constant pressure and volume, respectively.

- No decomposition of the gas mixture occurs during expansion.

$$\frac{(p_v)_i}{p_i} = \frac{(p_v)_0}{p_0} \quad , \quad \frac{(p_g)_i}{p_i} = \frac{(p_g)_0}{p_0}. \quad (4.10)$$

Introducing the expansion ratio β , which is defined as

$$\beta = \frac{p_i}{p_0}, \quad (4.11)$$

and using (4.5) in (4.10), the partial vapor pressure at the end of expansion can be expressed

as

$$(p_v)_0 = \frac{(p_v)_i}{\beta} = \frac{S_{\text{HUM}} \cdot p_s(T_{\text{HUM}})}{\beta}. \quad (4.12)$$

The temperature T_0 at the end of expansion can be derived from (4.7) and (4.8) using (4.11), and reads

$$T_0 = T_i \beta^{\frac{1-\kappa}{\kappa}}. \quad (4.13)$$

The adiabatic index κ of a gas mixture is given by the *Richarz* formula (Richarz, 1906), which might be written as

$$\kappa = 1 + \left[\frac{1}{\kappa_g - 1} + \frac{p_v}{p} \left(\frac{1}{\kappa_v - 1} - \frac{1}{\kappa_g - 1} \right) \right]^{-1}. \quad (4.14)$$

κ_g and κ_v are adiabatic exponents of vapor and carrier gas, respectively. Because of (4.10) κ remains constant during expansion.

In line with (4.5) the vapor saturation ratio S_0 at the end of expansion is given by

$$S_0 = \frac{(p_v)_0}{p_s(T_0)} = \frac{S_{\text{HUM}} \cdot p_s(T_{\text{HUM}})}{\beta \cdot p_s(T_0)}. \quad (4.15)$$

Due to the adiabatic temperature decrease vapor supersaturation is typically achieved at the end of the expansion process. Vapor supersaturation initiates heterogeneous nucleation of vapor molecules on aerosol particles and subsequent droplet growth. Assuming that the ratio of particle number concentration N_c and total gas density ρ is constant during droplet growth we have

$$\frac{(N_c)_i}{\rho_i} = \frac{(N_c)_0}{\rho_0}, \quad (4.16)$$

where

$$\rho_i = \frac{p_i \cdot M}{R_G \cdot T_i} \quad (4.17)$$

with molecular weight M of the gas mixture and universal gas constant R_G . Thus the particle number concentration $N_{c,i}$ before expansion can be calculated from $N_{c,0}$ according to

$$N_{c,i} = \beta N_{c,0} \frac{T_0}{T_i}. \quad (4.18)$$

Clearly number concentrations determined in the present study are droplet number concentrations after expansion. Provided that each growing droplet corresponds to just one aerosol particle, the measured droplet concentration is equal to the aerosol number concentration $N_{c,0}$ after expansion. Thus, to obtain the initial particle number concentration, the measured droplet concentration has to be corrected according to (4.18).

5 Optics

Particle number concentrations N_c and droplet growth curves $d_p(t)$ are determined applying the multi-angle Constant Angle Mie Scattering (mCAMS) method, a further development of the CAMS method introduced by Wagner (1985). Thereby droplets growing inside the measuring chamber are illuminated by a laser beam. The light flux, scattered by these droplets, is monitored at five different scattering angles. Simultaneously the total light flux transmitted through the measuring chamber is measured.

By normalizing experimental scattered light fluxes with respect to light attenuation, the influence of extinction on height and position of experimentally obtained extrema is eliminated.

Normalized (attenuation corrected) experimental scattered light flux vs. time curves show series of extrema in excellent agreement with theoretical scattered light flux vs. droplet size curves. This allows the establishment of a one-to-one correspondence between experimental and theoretical maxima and minima. Comparing position and height of experimental and theoretical extrema yields droplet diameter at specific times during growth and droplet number concentration, respectively.

5.1 Light scattering by droplets inside the expansion chamber - Mie theory

Theoretical scattered light fluxes $\Phi_s(d_p)$ as a function of droplet diameter d_p for five different scattering light angles, $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° , are calculated using Mie theory. This theory describing elastic scattering of electromagnetic waves by spherical particles was derived by Gustav Mie and Peter Debye (Mie (1908) and Debye (1909)). It is based upon Maxwell's electromagnetic theory.

Here only those results of the Mie theory are presented, which were used in the present investigation. To this end droplets growing inside the expansion chamber are described by homogeneous, isotropic, nonmagnetic spheres with radius a , relative permittivity ϵ_r and conductivity σ , being surrounded by a homogeneous, isotropic, nonabsorbing and nonmagnetic medium with relative permittivity $\epsilon_r \approx 1$. ϵ_0 is the vacuum permittivity. The droplets are illuminated by a parallel laser beam, which is polarized perpendicularly to the plane of observation. Formally, this means that a plane, linearly polarized, and time-harmonic electromagnetic wave is incident upon spherical particles. The droplets are assumed to

be randomly distributed inside the expansion chamber, the average distance between the droplets being large compared to the droplet diameter. Accordingly multiple scattering, dependent scattering and polarization field interactions can, in good approximation, be neglected.

The following derivations are based upon the Maxwell equations

$$\vec{\nabla} \cdot \vec{D} = \rho_F \quad (5.1)$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (5.2)$$

$$\vec{\nabla} \cdot \vec{B} = 0 \quad (5.3)$$

$$\vec{\nabla} \times \vec{H} = \vec{J}_F + \frac{\partial \vec{D}}{\partial t}, \quad (5.4)$$

where $\vec{E}$ and $\vec{D}$ are electric field and displacement, $\vec{H}$ and $\vec{B}$ magnetic field and induction, and ρ_F and $\vec{J}_F$ denote charge and current density associated with *free* charges.

Electric field $\vec{E}$ and displacement $\vec{D}$ are related according to

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}, \quad (5.5)$$

while magnetic field $\vec{H}$ and induction $\vec{B}$ are defined by

$$\vec{H} = \frac{\vec{B}}{\mu_0} - \vec{M}. \quad (5.6)$$

The constants ϵ_0 and μ_0 indicate vacuum permittivity and permeability, respectively. $\vec{P}$ is the electric polarization and $\vec{M}$ the magnetization of the medium.

In the absence of free charge and current densities, assuming time dependence of the form $e^{-i\omega t}$ and substituting the constitutive relations

$$\vec{J}_F = \sigma \vec{E} \quad (5.7)$$

$$\vec{B} = \mu_p \vec{H} \quad (5.8)$$

$$\vec{P} = \epsilon_0 \chi \vec{E}, \quad (5.9)$$

where σ is the conductivity, μ_p the permeability of the medium ($\mu_p = \mu_0 \cdot \mu_r$, with μ_r being the relative permeability of the medium) and χ the electric susceptibility of the medium under consideration, equations (5.1)-(5.4) become

$$\vec{\nabla} \cdot \vec{E} = 0 \quad (5.10)$$

$$\vec{\nabla} \times \vec{E} = i\omega \mu_p \vec{H} \quad (5.11)$$

$$\vec{\nabla} \cdot \vec{H} = 0 \quad (5.12)$$

$$\vec{\nabla} \times \vec{H} = -i\omega \epsilon \vec{E}. \quad (5.13)$$

In the last expression we have used

$$\epsilon = \epsilon_0(1 + \chi) + i\frac{\sigma}{\omega} \quad (5.14)$$

with ω indicating the angular frequency of the electromagnetic field. σ, μ_p and $\chi = \epsilon_r - 1$ are properties of the medium. They are independent of fields, position and direction, which is in agreement with the assumption of having a linear, homogeneous and isotropic medium. From the curl of (5.11) and (5.13), which is given by

$$\begin{aligned} \vec{\nabla} \times (\vec{\nabla} \times \vec{E}) &= \omega^2 \epsilon \mu_p \vec{E} \\ \vec{\nabla} \times (\vec{\nabla} \times \vec{H}) &= \omega^2 \epsilon \mu_p \vec{H} \end{aligned}$$

and the vector identity

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{A}) = \Delta \vec{A} - \vec{\nabla}(\vec{\nabla} \cdot \vec{A}),$$

it follows that a time-harmonic electromagnetic field in a linear, isotropic, homogeneous medium must satisfy the vector wave equations

$$\Delta \vec{E} + k^2 \vec{E} = 0 \quad (5.15)$$

$$\Delta \vec{H} + k^2 \vec{H} = 0 \quad (5.16)$$

with wave vector $\vec{k}$ fulfilling the relation

$$\vec{k} \cdot \vec{k} = \omega^2 \epsilon \mu_p \quad (5.17)$$

We emphasize, that wave vector $\vec{k}$ and frequency ω are properties of the wave, whereas ϵ and μ_p are properties of the medium in which the wave propagates.

For a homogeneous wave, $\vec{k}$ may be written as $\vec{k} = (k' + ik'')\vec{e}$, where k' and k'' are positive and $\vec{e}$ is the unit vector in the direction of propagation. It follows from eq. (5.17) that

$$k = k' + ik'' = \frac{\omega}{c} m \quad (5.18)$$

where $c = \sqrt{\frac{1}{\epsilon_0 \mu_0}}$ is the speed of light in vacuum and the *complex refractive index* m is given by

$$m = c\sqrt{\epsilon \mu_p} = \sqrt{\frac{\epsilon \mu_p}{\epsilon_0 \mu_0}}. \quad (5.19)$$

Because of eq. (5.18), the complex refractive index also may be written as

$$m = n' + in'', (n', n'' > 0) \quad (5.20)$$

where the real part n' denotes the phase velocity and the imaginary part n'' corresponds to absorption, when the electromagnetic wave propagates through a medium.

Eqs. (5.15) and (5.16) can be solved by introducing vector harmonics $\vec{M}$ and $\vec{N}$ of the form

$$\vec{M} = \vec{\nabla} \times (\vec{r}\psi) \quad (5.21)$$

$$\vec{N} = \frac{\vec{\nabla} \times \vec{M}}{k}. \quad (5.22)$$

It can be shown (see e.g. Bohren and Huffman (1983)) that $\vec{M}$ and $\vec{N}$ satisfy the vector wave equation if ψ is a solution to the scalar wave equation

$$\Delta\psi + k^2\psi = 0 \quad (5.23)$$

The scalar function ψ is called *generating function* for the *vector harmonics* $\vec{M}$ and $\vec{N}$, which are also referred to as *normal modes* and $\vec{r}$ is the *guiding vector*.

Since scattering of electromagnetic waves by a sphere is a problem of spherical symmetry it is appropriate to use spherical coordinates (r, θ, ϕ) . The scalar wave equation in spherical coordinates is given by

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} + k^2 \psi = 0. \quad (5.24)$$

Using the separation ansatz

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi\phi \quad (5.25)$$

linearly independent solutions to (5.24) are

$$\psi_{emn} = \cos(m\phi)P_n^m(\cos \theta)z_n(kr) \quad (5.26)$$

$$\psi_{omn} = \sin(m\phi)P_n^m(\cos \theta)z_n(kr) \quad (5.27)$$

where $P_n^m(\cos \theta)$ are the *associated Legendre functions* of degree n and order m , with $n = m, m+1, \dots$, subscripts e and o denote *even* and *odd*, and $z_n(kr)$ is any of the four spherical Bessel functions $j_n(kr)$, $y_n(kr)$, $h_n^{(1)}(kr)$ or $h_n^{(2)}(kr)$, where $y_n(kr)$ becomes infinite as r approaches the origin (see figure 5.1).

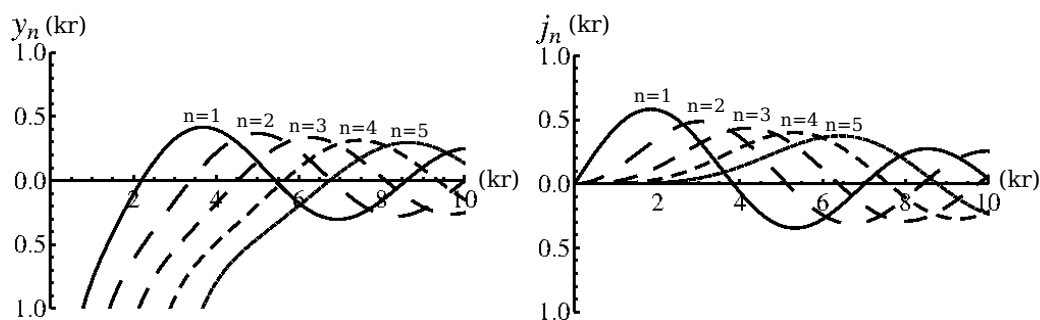


Figure 5.1: Spherical Bessel function $j_n(kr)$ and $y_n(kr)$ for $n = 1, \dots, 5$.

The spherical harmonics generated by (5.26) and (5.27) are

$$\vec{M}_{emn} = \nabla \times (\vec{r}\psi_{emn}) \quad (5.28)$$

$$\vec{M}_{omn} = \nabla \times (\vec{r}\psi_{omn}) \quad (5.29)$$

$$\vec{N}_{emn} = \frac{\vec{\nabla} \times \vec{M}_{emn}}{k} \quad (5.30)$$

$$\vec{N}_{omn} = \frac{\vec{\nabla} \times \vec{M}_{omn}}{k}. \quad (5.31)$$

Thus any solution to (5.15) can be expanded in vector spherical harmonics according to

$$\begin{aligned} \vec{E} = \sum_{m=0}^{\infty} \sum_{n=m}^{\infty} (B_{emn}\vec{M}_{emn} + B_{omn}\vec{M}_{omn} \\ + A_{emn}\vec{N}_{emn} + A_{omn}\vec{N}_{omn}). \end{aligned} \quad (5.32)$$

From now on, only the electric field component will be examined, keeping in mind that the corresponding magnetic field component can be obtained from the curl of $\vec{E}$.

Eq. (5.32) is the general solution to (5.15). However the actual electromagnetic field is a solution to (5.15), which satisfies the boundary condition of having continuous tangential field components across the droplet surface:

$$(\vec{E}_i + \vec{E}_s - \vec{E}_d) \times \vec{e}_r = (\vec{H}_i + \vec{H}_s - \vec{H}_d) \times \vec{e}_r = 0 \quad (5.33)$$

where $\vec{E}_i$ is the incident electric field, $\vec{E}_s$ the electric field scattered by the droplet and $\vec{E}_d$ the field inside the droplet. This boundary condition represents energy conservation across the boundary between droplet and surrounding medium, where ϵ and μ_p are discontinuous. The incident electromagnetic wave $\vec{E}_i$ is polarized perpendicularly to the plane of observation, which is the (x,z) plane. Moreover, the incident beam is parallel. Thus in spherical polar coordinates $\vec{E}_i$ is defined as

$$\vec{E}_i = E_0 e^{ikr \cos \theta} \vec{e}_y \quad (5.34)$$

with

$$\vec{e}_y = \sin \theta \sin \phi \vec{e}_r + \cos \theta \sin \phi \vec{e}_\theta + \cos \phi \vec{e}_\phi \quad (5.35)$$

From (5.28)-(5.31) in component form and (5.34), together with the orthogonality of sin and cos, it follows that $B_{omn} = A_{emn} = 0$ for all m and n , and that $B_{emn} = A_{omn} = 0$ for all $m \neq 1$ (see Bohren and Huffman (1983) p.90-92). For $m = 1$ one obtains

$$B_{e1n} = i^n E_0 \frac{2n+1}{n(n+1)} \quad (5.36)$$

and

$$A_{o1n} = i^{n+1} E_0 \frac{2n+1}{n(n+1)}. \quad (5.37)$$

Hence the expansion of the y-polarized incident plane wave in spherical harmonics is given by

$$\vec{E}_i = E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} \left(\vec{M}_{e1n} + i\vec{N}_{o1n} \right). \quad (5.38)$$

Since the incident wave has to be finite at the origin the radial dependence of the vector spherical harmonics is specified by $j_n(kr)$ (see fig. 5.1).

The form of (5.38), together with the orthogonality of the vector harmonics and the boundary condition (5.33) yield the form of the scattered field (see Bohren and Huffman (1983) p.93,94). The expansion of the scattered field in vector spherical harmonics can be expressed as

$$\vec{E}_s = E_0 \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} \left(a_n \vec{M}_{e1n} + i b_n \vec{N}_{o1n} \right), \quad (5.39)$$

where a_n and b_n are the *scattering coefficients*. Since both $j_n(kr)$ and $y_n(kr)$ are well behaved outside the sphere, the radial component of the scattered field can be expressed by $h_n^{(1)}$.

Introducing now the angle-dependent functions (Bohren and Huffman (1983), p. 94 ff)

$$\pi_n(\cos \theta) = \frac{P_n^1}{\sin \theta} \quad (5.40)$$

$$\tau_n(\cos \theta) = \frac{dP_n^1}{d\theta} \quad (5.41)$$

the vector spherical harmonics $\vec{M}_{e1n}$ and $\vec{N}_{o1n}$, in component form, are:

$$\vec{M}_{e1n} = -\sin \phi \pi_n(\cos \theta) z_n(kr) \vec{e}_\theta - \cos \phi \tau_n(\cos \theta) z_n(kr) \vec{e}_\phi \quad (5.42)$$

$$\begin{aligned} \vec{N}_{o1n} = & \sin \phi n(n+1) \sin \theta \pi_n(\cos \theta) \frac{z_n(kr)}{kr} \vec{e}_r \\ & + \sin \phi \tau_n(\cos \theta) \frac{1}{kr} \frac{d(kr z_n(kr))}{d(kr)} \vec{e}_\theta + \cos \phi \pi_n(\cos \theta) \frac{1}{kr} \frac{d(kr z_n(kr))}{d(kr)} \vec{e}_\phi. \end{aligned}$$

In the far field the radial component of $\vec{N}_{o1n}$ is negligible compared to the transverse component. Moreover, the *Hankel* functions $h_n^{(1)}(kr)$ are asymptotically given by

$$h_n^{(1)}(kr) \rightarrow \frac{(-i)^n e^{ikr}}{ikr}, \quad kr \gg n^2 \quad (5.43)$$

which corresponds to an outgoing spherical wave.

By further introducing the *Riccati-Bessel* functions

$$\psi_n(kr) = kr \cdot j_n(kr) \quad (5.44)$$

$$\xi_n(kr) = kr \cdot h_n^{(1)}(kr) \quad (5.45)$$

the transverse components of the scattered electric wave in the far field of the droplet is given by

$$E_s^\theta = E_0 \frac{\sin \phi}{kr} \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (ib_n \xi'_n \tau_n - a_n \xi_n \pi_n) \quad (5.46)$$

$$E_s^\phi = E_0 \frac{\cos \phi}{kr} \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} (ib_n \xi'_n \pi_n - a_n \xi_n \tau_n), \quad (5.47)$$

with scattering coefficients a_n and b_n

$$a_n(m, \alpha_s) = \frac{\psi_n(m\alpha_s)\psi'_n(\alpha_s) - m\psi_n(\alpha_s)\psi'_n(m\alpha_s)}{m\psi_n(m\alpha_s)\xi'_n(\alpha_s) - \xi_n(\alpha_s)\psi'_n(m\alpha_s)} \quad (5.48)$$

$$b_n(m, \alpha_s) = \frac{\psi_n(m\alpha_s)\psi'_n(\alpha_s) - m\psi_n(\alpha_s)\psi'_n(m\alpha_s)}{m\psi_n(m\alpha_s)\xi'_n(\alpha_s) - \xi_n(\alpha_s)\psi'_n(m\alpha_s)}. \quad (5.49)$$

Here $\alpha_s = \pi d_p / \lambda$ is the dimensionless size parameter, d_p the droplet diameter and m the refractive index of the droplet. If for a particular n the radius of the droplet is such that one of the denominators in (5.48) or (5.49) is very small, the corresponding normal mode will dominate the scattered field, which is often referred to as the *ripple structure*.

Since (5.48) and (5.49) are uniformly convergent, the series can be terminated after sufficiently large n_c , whereas n_c increases with increasing values of α_s and m .

In addition to the asymptotic behavior of $h_n^{(1)}(kr)$ shown in (5.43), the asymptotic behavior of its derivative

$$\frac{dh_n^{(1)}}{dkr} \approx \frac{(-i)^n e^{ikr}}{kr}, \quad kr \gg n^2 \quad (5.50)$$

can be substituted in (5.48) and (5.49). The resulting transverse components of the scattered electric field are

$$E_{s,\theta} = E_{s,\perp} \approx E_0 \frac{e^{ikr}}{-ikr} S_2(m, \alpha_s, \cos \theta) \sin \phi \quad (5.51)$$

$$E_{s,\phi} = E_{s,\parallel} \approx -E_0 \frac{e^{ikr}}{-ikr} S_1(m, \alpha_s, \cos \theta) \cos \phi \quad (5.52)$$

with scattering matrix elements S_1 and S_2 given by

$$S_1(m, \alpha_s, \cos \theta) = S_{\parallel} = \sum_{n=1}^{n_c} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n) \quad (5.53)$$

$$S_2(m, \alpha_s, \cos \theta) = S_{\perp} = \sum_{n=1}^{n_c} \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n). \quad (5.54)$$

Since the plane of observation is perpendicular to the incident linearly polarized wave, azimuth ϕ equals $\pi/2$. Inserting this in (5.51) and (5.52) only $E_{s,\theta}$ remains. Thus the scattered wave is polarized perpendicularly to the observation plane too.

The intensity of the scattered wave is given by the magnitude of the Poynting vector $\vec{S}$, which, in turn, reads

$$\vec{S} = \frac{1}{2} \text{Re} \left\{ \vec{E} \times \vec{H}^* \right\}. \quad (5.55)$$

If the field is homogeneous ($\vec{k} \cdot \vec{E} = 0$), eq. (5.55) can be simplified to

$$\vec{S} = \frac{1}{2\omega\mu_p} \text{Re} \left\{ \vec{k}^* (\vec{E} \vec{E}^*) \right\}. \quad (5.56)$$

The magnitude of $\vec{S}$ is proportional to $|\vec{E}|^2$, which, in the present study, equals $|E_{s,\perp}|^2$ and reads

$$|E_{s,\perp}|^2 \approx \frac{E_0^2}{k^2 r^2} |S_\perp (\cos \theta)|^2 \quad (5.57)$$

for $kr \gg n^2$ (far-field approximation).

At constant scattering angle θ , wavelength λ and refractive index m , the scattering matrix element is a function of droplet diameter d_p only

$$S_\perp = S_\perp(d_p)|_{\theta,\lambda,m=\text{const}}.$$

Thus the intensity of the scattering field, whose electric field vectors are perpendicular to the plane of observation, can be expressed as

$$I_{S,\perp} = I_i \frac{\lambda^2}{4\pi^2 r^2} |S_\perp(d_p)|^2, \quad (5.58)$$

where I_i is the intensity of the incident beam.

Figure 5.2 shows scattered light intensities at constant forward scattering angles $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° as a function of droplet diameter d_p . Droplets have real refractive index $m = 1.3875$, which refers to n-propanol at $\lambda = 488\text{nm}$ (see Moutzouris (2013)). $I_{s,\perp}$ and all other curves based on Mie theory, were calculated with **MiePlot**, a program that calculates light scattering by a sphere using Mie theory and the Debye series (Laven, 2014). **MiePlot** is based on the classic **BHMIE** algorithm for Mie scattering presented in Bohren and Huffman (1983). As can be seen from this graph, scattered light intensities show broad maxima and minima that are modulated by a *ripple structure*. Within the plotted size range, heights of broad maxima increase monotonically for all angles but 10° . Moreover, frequencies at which broad extrema occur, increase with increasing scattering angle shifting the maxima to smaller sizes, while at the same time the intensities decrease. The *ripple structure* becomes more pronounced with increasing droplet radius. This is due to the fact that for increasing values of α_s more normal modes need to be taken into account. The resonant ripple structure of light scattering curves has been experimentally observe by Szymanski et al. (1982).

The rate W_s at which energy is scattered across the surface A of an imaginary sphere

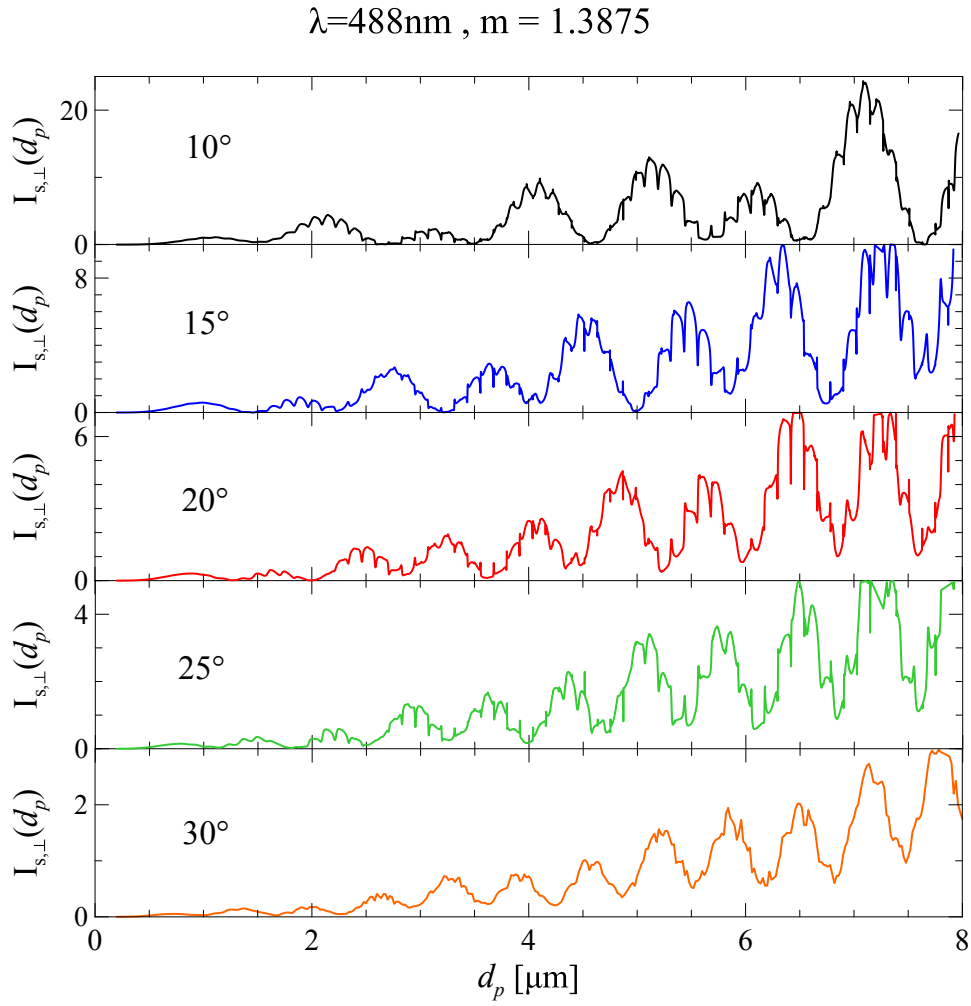


Figure 5.2: Theoretical scattered light intensities polarized perpendicularly to the plane of observation, $I_{s,\perp}$, as a function of droplet diameter d_p at constant angles $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° . The wavelength of the incident beam is 488nm and the refractive index of the droplets (n-propanol) is 1.3875 (Moutzouris, 2013).

constructed around the scattering sphere is given by:

$$W_s = \int_A \vec{S}_s \cdot \vec{e}_r dA. \quad (5.59)$$

Using eq. (5.56) together with eqs. (5.46),(5.47) and (5.48),(5.49) for large r the integral, in spherical coordinates, becomes

$$W_s = \frac{k}{2\omega\mu_p} \int_0^{2\pi} \int_0^{2\pi} (E_s^\theta E_s^{\theta*}) r^2 \sin\theta d\theta d\phi. \quad (5.60)$$

Substituting the series expansions (5.46) and (5.47) in (5.60) and integrating the resulting product series term by term, while using the relation

$$\int_0^\pi (\pi_n \pi_m + \tau_n \tau_m) \sin\theta d\theta = \delta_{nm} \frac{2n^2(n+1)^2}{2n+1}. \quad (5.61)$$

The rate at which energy is removed from the incident beam by scattering reads (see Bohren and Huffman (1983), p. 103)

$$W_s(m, \alpha_s) = \frac{\pi |E_0|^2}{k\omega\mu_p} \sum_{n=1}^{\infty} (2n+1) \text{Re}\{g_n\} (|a_n|^2 + |b_n|^2). \quad (5.62)$$

Here g_n is defined by

$$g_n = (\chi_n^* \psi'_n) - i(\psi_n^* \psi'_n + \chi_n^* \chi'_n) \quad (5.63)$$

and includes the Riccati-Bessel function $\chi_n = -kr \cdot y_n(kr)$ and therefore $\xi_n = \psi_n - i\chi_n$. Thus the scattering cross section C_{SCA} , defined as $\frac{W_s}{I_i}$, is

$$C_{\text{SCA}}(m, \alpha_s) = \frac{W_s}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2), \quad (5.64)$$

where the series expansion (5.33) was used to calculate I_i .

In general a droplet removes energy from the incident beam by *scattering* and *absorption*. However, in the present study we investigated non-absorbing droplets, thus effects related to absorption are neglected.

In forward direction ($\theta = 0^\circ$) the scattering matrix element $S_\perp(m, \alpha_s, \cos\theta)$ becomes

$$S_\perp(m, \alpha_s)|_{\cos\theta=1} = \frac{1}{2} \sum_{n=1}^{n_c} (2n+1)(a_n + b_n), \quad (5.65)$$

where the relation

$$\pi_n|_{\cos\theta=1} = \tau_n|_{\cos\theta=1} = \frac{n(n+1)}{2}. \quad (5.66)$$

was used. It can be shown (see e.g. Bohren and Huffman (1983)) that the extinction cross section can be expressed as

$$C_{\text{EXT}}(m, \alpha_s) = \frac{W_{\text{ext}}}{I_i} = \frac{4\pi}{k^2} \text{Re}\{S_{\perp}(m, \alpha_s)|_{\cos\theta=1}\}. \quad (5.67)$$

This expression is a form of the *optical theorem* (Newton, 1976). This theorem expresses that extinction depends only on the scattering amplitude in forward direction, i.e. $S_{\perp}|_{\cos\theta=1}$, although, in general, extinction results from scattering and absorption.

For a spherical droplet with radius a and using (5.67) together with (5.65) and (5.64) extinction and scattering efficiencies are given by

$$Q_{\text{SCA}}(m, \alpha_s) = \frac{C_{\text{SCA}}}{a^2\pi} = \frac{2}{\alpha_s^2} \sum_{n=1}^{n_c} (2n+1) (|a_n|^2 + |b_n|^2) \quad (5.68)$$

$$Q_{\text{EXT}}(m, \alpha_s) = \frac{C_{\text{EXT}}}{a^2\pi} = \frac{2}{\alpha_s^2} \sum_{n=1}^{n_c} (2n+1) \text{Re}(a_n + b_n). \quad (5.69)$$

The extinction efficiency for growing n-propanol droplets as a function of size parameter α_s ($\lambda = 488\text{nm}$) is shown in figure 5.3.

It can be seen that Q_{EXT} has (i) a series of regularly spaced broad maxima and minima, often referred to as *interference structure*, which approach 2 as α_s increases, and (ii) an irregular fine structure, the *ripple structure*.

The *interference structure* can be explained by the phase difference that occurs between a ray that traverses a spherical droplet and a ray that traverses the same path outside the sphere. The condition for destructive interference between these two rays yields the separation distance $\Delta = \frac{2\pi}{s(m-1)}$ between the maxima. The same condition is obtained by examining the maxima of numerators of a_n and b_n . The fact that Q_{EXT} approaches 2 is in agreement with the *extinction paradox*. This general theorem can be explained by diffraction and shadowing of incident light by a sphere (van de Hulst (1982)).

As already mentioned before the *ripple structure*, which is also referred to as morphology dependent resonances (MDRs), occurs if denominators of a_n and b_n become very small. Metz and Dettmar (1963) showed that for large α_s and real m the MDRs for one particular normal mode occur nearly at equidistant values. Moreover, they demonstrated that for higher orders of n the first MDR shifts to bigger α_s and become more pronounced. Together with the fact, that higher order n are needed for larger size parameters, this results in a sharply pronounced fast fluctuating ripple structure for sufficiently large α_s , as can be clearly seen from figure 5.3.

Up to this point only extinction by a single particle was considered. However, in the present study, extinction and light scattering measurements involve many particles. If multiple scattering can be neglected, the intensity transmitted through a collection of particles, which are assumed to be homogeneously and randomly distributed in the chamber,

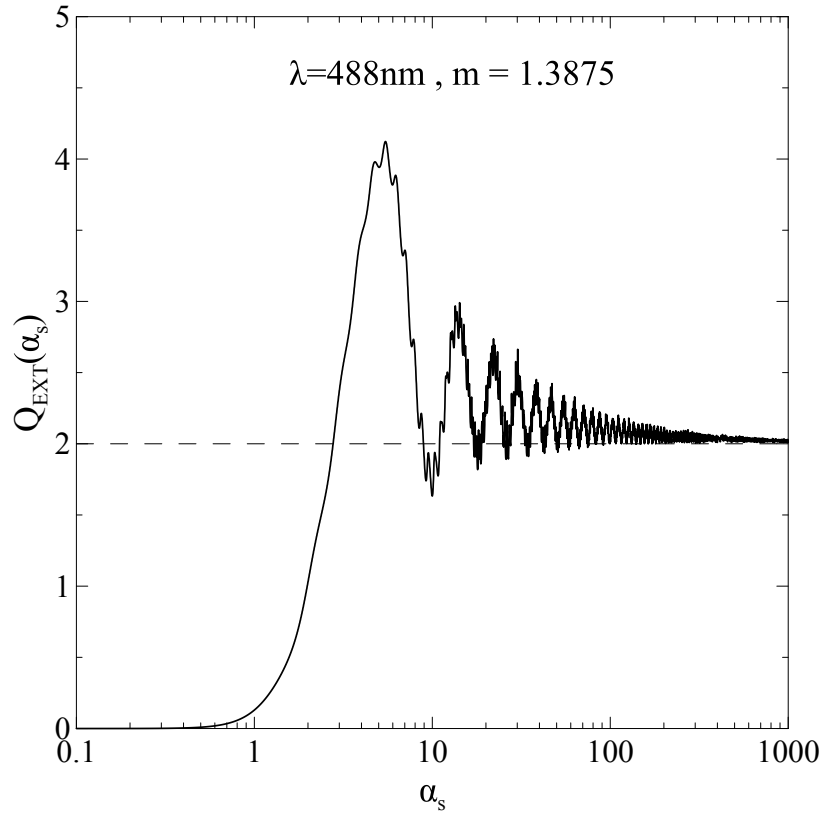


Figure 5.3: Scattering efficiency Q_{EXT} of n-propanol droplets illuminated by a blue laser beam ($\lambda = 488\text{nm}$) as a function of size parameter α_s

is given by the *Beer-Lambert* law (Beer, 1852):

$$I_t = I_i e^{-N_c C_{\text{EXT}} \ell}, \quad (5.70)$$

where I_i is the intensity of the incident beam, ℓ the distance the beam propagates through a particle collection, and N_c the number of particles per unit volume.

Obviously light attenuation does not only affect the direct laser beam transmitted through the expansion chamber but also the laser beam scattered by the growing droplets. The intensity I_s , that is scattered by a single droplet inside the expansion chamber, is determined by light scattering due to the droplet and by light extinction inside the measuring chamber. The extinction length ℓ is given by the distance the light passes from the laser entrance of the expansion chamber until the exit of the scattered wave. Applying (5.70) to (5.58) I_s is given by

$$I_s = I_i \frac{\lambda^2}{4\pi^2 r^2} |S_{\perp}(m, \alpha_s, \cos \theta)|^2 e^{-N_c C_{\text{EXT}} \ell}. \quad (5.71)$$

Division of eq. (5.71) by eq. (5.70) eliminates the influence of extinction and incident light intensity I_i on scattered light intensity I_s .

5.2 Scattering geometry

Particle number concentrations N_c and droplet growth curves $d_p(t)$ are obtained by means of the multi-angle Constant Angle Mie Scattering (mCAMS) method, which is an advancement of the CAMS method (Wagner, 1985).

Thereby droplets inside the cylindrical expansion chamber are illuminated by a parallel laser beam, polarized perpendicularly to the plane of observation. During experiments the light flux transmitted through the chamber, Φ_t , is measured with a photo diode. Simultaneously the light flux scattered by the growing droplets, Φ_s , is measured at five different light scattering angles θ using photomultiplier tubes.

Both transmitted and scattered light fluxes are monitored applying lens-pinhole detection systems (see e.g. Gumprecht and Sliepcevich (1952)). The advantage of this system is that its aperture ϵ (see figure 5.5) is exactly given by

$$\epsilon = 2 \arctan \left(\frac{r_p}{f_l} \right), \quad (5.72)$$

where $2r_p$ is the diameter of the pinhole and f_l is the focal length of the lens¹. Moreover ϵ is constant and independent of the position of the illuminated droplet. Applying this detector system practically all stray light can be excluded from detection.

Regarding measurements of Φ_t this allows to almost completely eliminate light scattered in forward direction. Thus only the attenuated light from the source is observed.

For measurements of Φ_s the use of a lens-pinhole systems allows to increase the detected scattered light flux, while at the same time system apertures can be kept negligibly small.

Figure 5.4 shows a schematic diagram of the applied optical geometry. The laser beam LB is linearly polarized by means of linear polarization filter F before it enters the expansion chamber EXP from the right. The light flux transmitted through EXP is measured with a lens-pinhole system, consisting of a circular stop S_c , a plano-convex lens L, a pinhole P and a photo diode PD, all centered at the axis of LB. To ensure total transmission of the attenuated light flux the diameter of S_c was chosen to be slightly bigger than the diameter of LB.

Detector systems for measurements of Φ_s are centered at five different light scattering angles, $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° , on both sides of the transmitted laser beam. Each lens-pinhole arrangement consists of a rectangular stop S_R , a plano-convex lens L, a pinhole P and a photomultiplier tube PMT. Position and size of S_R , L and P define the light observation cone OC for each θ . In figure 5.4 the observation cone at 15° to the right of the laser beam axis is highlighted in red. The intersection of OC with LB defines the measuring volume V_s in the central part of the cylindrical expansion chamber EXP. To ensure plane intersection between OC and LB rectangular stops were installed instead of circular ones. Only droplets

¹ f_l is actually the back focal length of a plano-convex lens. In order to minimize spherical aberrations lenses are installed so that the convex surface faces the incident beam.

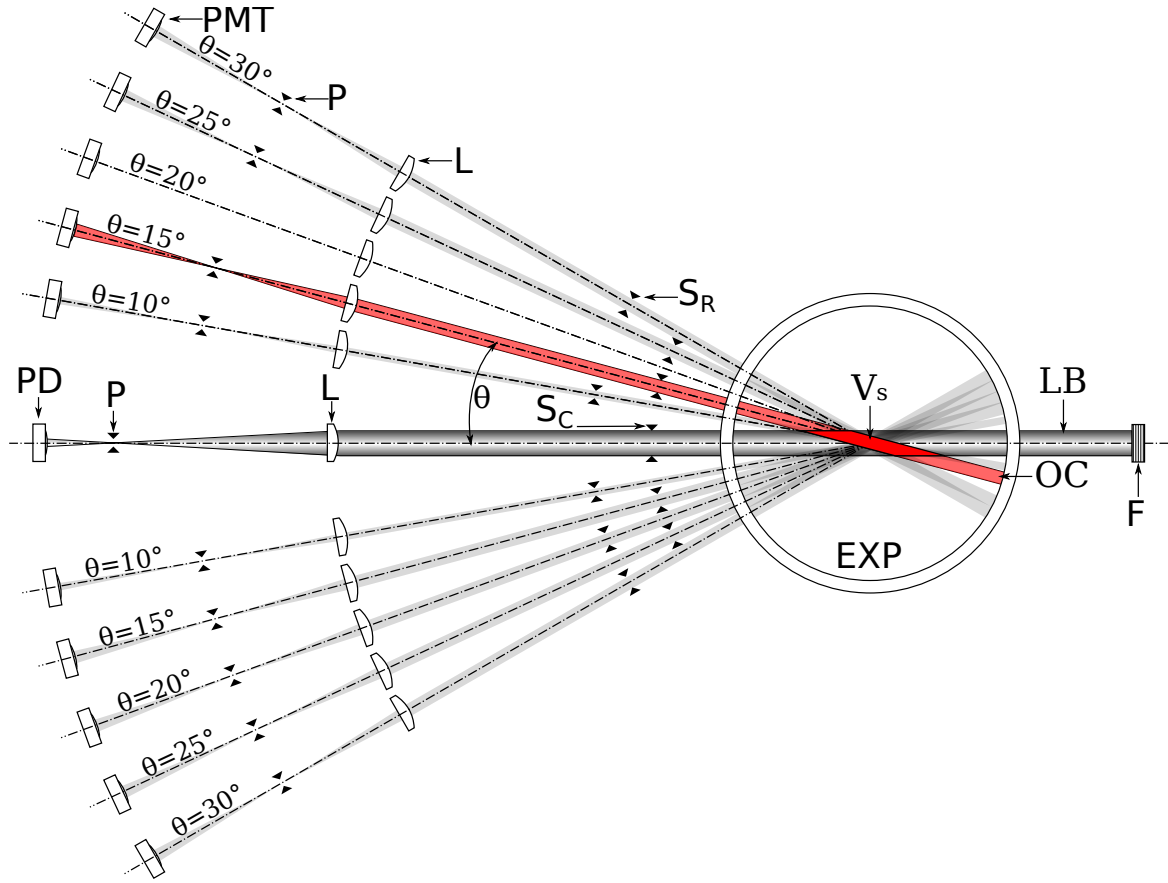


Figure 5.4: Schematic diagram of the optical geometry used for light flux measurements. Observation cones OC defined by pinhole P, lens L and rectangular stop S_R intersect with the polarized (F) laser beam LB. These intersections define light scattering volumina V_s in the central part of the expansion chamber EXP. Here OC and V_s for measurements of the light flux scattered at 15° to the right of the laser beam axis are highlighted in red. Lens-pinhole detection systems monitoring Φ_s are centered at $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° . Each detection system consists of a lens, a pinhole a rectangular stop and a photomultiplier tube PMT. Measurements of Φ_t are performed using a lens-pinhole system, consisting of P,L, circular stop S_C and photo diode PD.

inside V_s contribute to measured scattered light fluxes.

5.2.1 Transmitted light flux

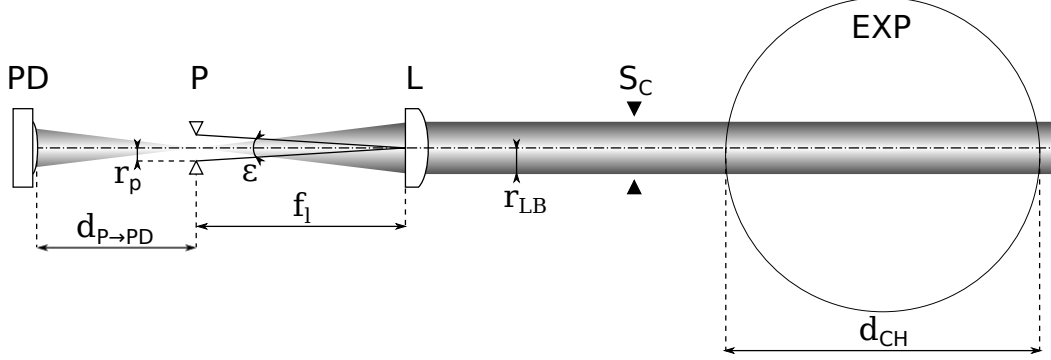


Figure 5.5: Schematic diagram of the detection cone for measurements of the transmitted light flux Φ_t . PD, P, L and S_C indicate photo diode, pinhole, lens and circular stop, respectively. Radius r_P of the pinhole and focal length f_l of the lens define the aperture ϵ . Distance $d_{P \rightarrow PD}$ between PD and P and the radius r_{LB} of the laser beam define the cross section of the laser beam when intercepting with photodiode PD.

For a Gaussian laser profile

$$I_i = I_0 e^{-\frac{r^2}{\sigma^2}} \quad (5.73)$$

where I_0 is the intensity at the center of the beam² and σ is one third of the laser radius r_{LB} , the light flux of the incident laser beam is given by

$$\Phi_i = \int_{A_{LB}} I_i dA = 2\pi I_0 \int_0^{r_{LB}} r e^{-\frac{r^2}{\sigma^2}} dr = \pi \sigma^2 I_0 \left(1 - e^{-\frac{r_{LB}^2}{\sigma^2}} \right) \quad (5.74)$$

where $A_{LB} = r_{LB}^2 \pi$ is the cross section of the incident beam.

Integration of the transmitted laser intensity I_t , which is given by (5.70), over A_{LB} yields the transmitted light flux:

$$\Phi_t = \Phi_i e^{-N_c C_{EXT} \ell} = \Phi_i e^{-N_c Q_{EXT} \frac{\pi d_p^2}{4} \ell}. \quad (5.75)$$

where N_c is the droplet number concentration, C_{EXT} the scattering cross section given by (5.67) and ℓ the extinction length, which is equal to the inner diameter d_{CH} of EXP. According to (5.69) the scattering coefficient Q_{EXT} is given by the ratio of C_{EXT} and droplet cross section $\frac{\pi d_p^2}{4}$, where d_p is the droplet diameter.

Due to the finite aperture ϵ of the the detection cone the scattering coefficient Q_{EXT} in eq.

² I_0 is assumed to be independent of z .

(5.75) needs to be replaced by Q_{EXT}^a , the apparent scattering coefficient. Using Mie theory, Q_{EXT}^a can be defined as

$$Q_{\text{EXT}}^a = Q_{\text{EXT}} - \frac{1}{\alpha_s^2} \int_{-\epsilon/2}^{+\epsilon/2} |S_{\perp}(\cos \theta)|_{m, \alpha_s}^2 \sin \theta d\theta, \quad (5.76)$$

where $\alpha_s = \frac{\pi d_p}{\lambda}$ is the dimensionless size parameter and $S_{\perp}(\cos \theta)$ the scattering matrix element according to (5.65). Gumprecht and Sliepcevich (1952) have shown that for small apertures ($\epsilon < 3^\circ$) the correction factor $R = \frac{Q_{\text{EXT}}^a}{Q_{\text{EXT}}}$ can be replaced by

$$R = \frac{1 + |J_0(\alpha_s \epsilon)|^2 + |J_1(\alpha_s \epsilon)|^2}{2}, \quad (5.77)$$

where J_0 and J_1 are *Bessel* functions of order zero and one, respectively.

For the actual dimensions of the optical arrangement ($f_l = 40.22\text{mm}$ and $r_p = 0.6\text{mm}$) the aperture reads

$$\epsilon = 2 \arctan \left(\frac{r_p}{f_l} \right) \approx 1.71^\circ. \quad (5.78)$$

Calculating R for the given ϵ and size parameters α_s ranging from 0.5 – 3.5 yields deviations from unity that are smaller than $10^{-5}\%$, which can be neglected. Thus, in the present study, $Q_{\text{EXT}}^a = Q_{\text{EXT}}$ and Φ_t can be calculated according to eq. (5.75).

Figure 5.6 shows theoretical light attenuation $\mathcal{A}(d_p) = \frac{\Phi_t(d_p)}{\Phi_i}$ as a function of droplet diameter d_p for different droplet number concentrations N_c . Numerical calculations of $\mathcal{A}(d_p)$ were performed for a relative refractive index $m = 1.3875$ (n-propanol droplets) at a wavelength of 488nm .

Another important issue regarding measurements of Φ_t is the illumination of the photo diode PD. In general non-uniformities at the edges of its active area distort the response of PD. To avoid this unwanted effect the transmitted beam incident upon PD is well centered. From fig. 5.5 it can be seen that the area $A_{\text{PD}}^{\text{LB}}$ of PD illuminated by the transmitted laser beam LB is given by

$$A_{\text{PD}}^{\text{LB}} = \left(\frac{r_{\text{LB}} d_{\text{P} \rightarrow \text{PD}}}{f_l} \right)^2 \pi, \quad (5.79)$$

where $d_{\text{P} \rightarrow \text{PD}}$ is the distance between pinhole and photo diode. Inserting the actual dimensions ($r_{\text{LB}} = 1.42\text{mm}$, $d_{\text{P} \rightarrow \text{PD}} = 2\text{mm}$ and $f_l = 40.22\text{mm}$) the illuminated area is $\approx 0.02\text{mm}^2$, which is less than 1% of the active area of PD ($A_{\text{PD}} = 2.5^2\pi\text{mm}^2$). Hence the transmitted laser beam is well centered. However, non-uniformities of the central part of the sensitive area may cause unwanted effects on measurements too. Thus it is planned to increase the illuminated area by installing a different lens-pinhole system.

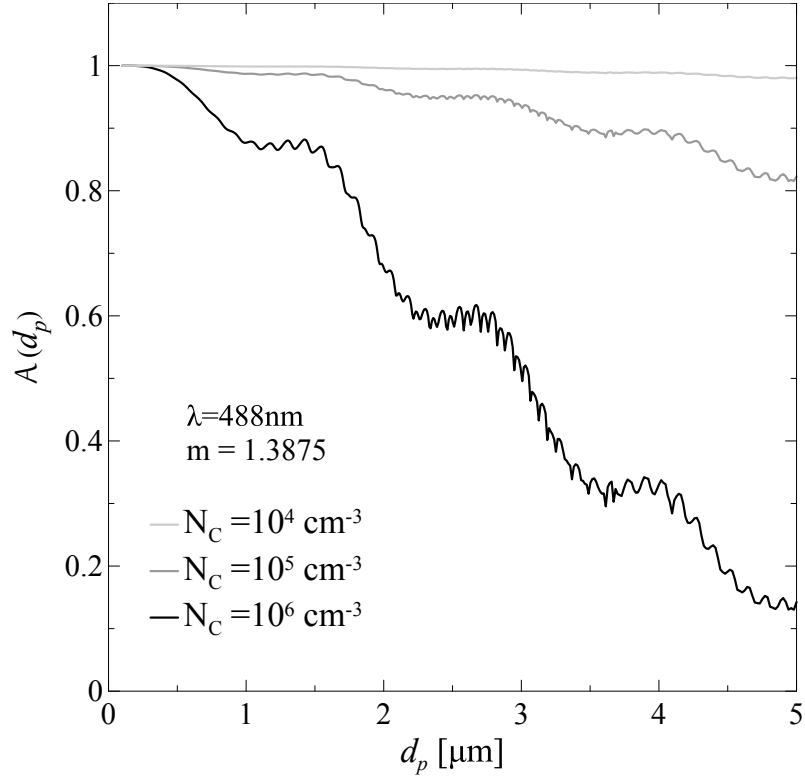


Figure 5.6: Theoretical light attenuation calculated for three different droplet number concentrations N_c as a function of droplet diameter.

5.2.2 Scattered light fluxes

The light flux scattered by a single droplet through lens L centered at scattering angle θ (see fig. 5.7) reads

$$\Phi_s^1 = I_s \cdot A_L, \quad (5.80)$$

In the last expression I_s is the scattered intensity according to eq. (5.71) and A_L is the illuminated area of the lens. A_L can be expressed as

$$A_L = \left(\rho_{dp} \cdot \tan \frac{\epsilon}{2} \right)^2 \pi. \quad (5.81)$$

where ρ_{dp} is the distance between scattering droplet and lens and ϵ the system aperture according to (5.78). Assuming that A_L is smaller than the cross section of L for all droplets scattering light within $\theta \pm \epsilon/2$ inside light scattering volume V_s , the total light flux incident upon L is given by

$$\Phi_s^{tot} = N_c \int_{V_s} \Phi_s^1 dV. \quad (5.82)$$

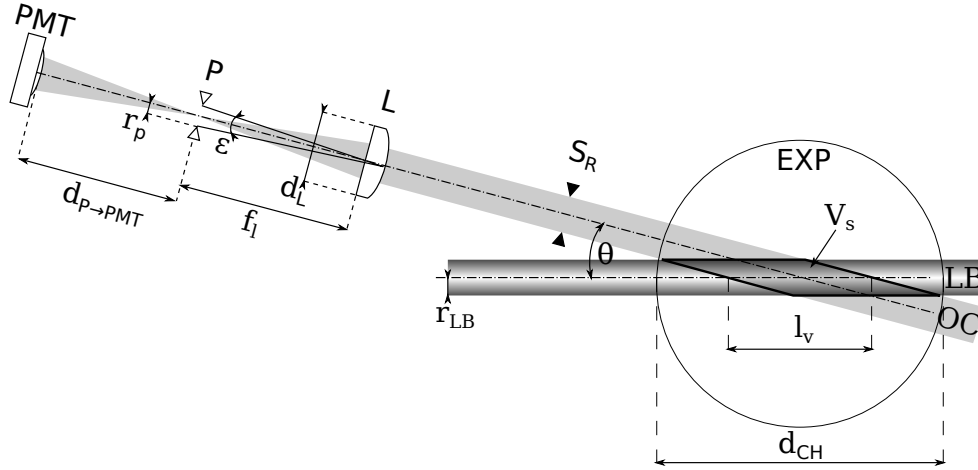


Figure 5.7: Schematic diagram of the detection geometry for light scattering measurements at constant angle θ . The cylindrical light scattering volume V_s with length l_v results from the intersection of laser beam LB having radius r_{LB} with observation cone OC. The width of OC is defined by rectangular stop S_R . Pinhole P with radius r_P and lens L with diameter d_L and focal length f_l define the aperture ϵ of the detection system. A photomultiplier tube PMT is used for light scattering measurements, the distance between PMT and P being $d_{P \rightarrow PMT}$.

After inserting (5.80) in (5.82) using (5.81) for A_L and (5.71) together with (5.73) for I_s , and assuming that ϵ is negligibly small compared to θ , the total scattered light flux reads

$$\Phi_s^{tot} = \alpha I_0 \int_{V_s} e^{-\frac{r^2}{\sigma^2}} e^{-N_c C_{EXT} \ell} dv \quad (5.83)$$

with

$$\alpha = N_c \left(\frac{r_P}{f_l} \right)^2 \frac{\lambda^2}{4\pi} |S_{\perp}(\cos \theta)|^2. \quad (5.84)$$

Due to the cylindrical shape of the laser beam LB it is useful to calculate the integral over light scattering volume V_s in cylindrical coordinates (r, ϕ, z) . To this end, the coordinate system's origin is set to the center of EXP, with $z > 0$ in forward scattering direction and $z < 0$ in backward scattering direction.

As can be seen from figure 5.8 the integral $\mathcal{I}$ in (5.83) can be expressed as

$$\mathcal{I} = \int_{-l_v/2}^{+l_v/2} \int_0^{2\pi} \int_0^{r_{LB}} e^{-\frac{r^2}{\sigma^2}} e^{-N_c C_{EXT} \ell(r,z)} r dr d\phi dz \quad (5.85)$$

where the length l_v of V_s is given by

$$l_v = \frac{w_R}{\sin \theta}, \quad (5.86)$$

For a fixed optical geometry ($r_p, f_l, l_v, \theta = \text{const.}$) and constant λ, m and Φ_i

$$\tilde{\Phi}_s^{\text{tot}} = \tilde{\Phi}_s^{\text{tot}}(d_p, N_c). \quad (5.89)$$

However, in general, $\ell(r, z) \neq d_{\text{CH}}$. For example extinction lengths of light scattered by droplets i, j and k in fig. 5.8 from the entrance of the laser beam into the cylindrical expansion chamber until the exit of the scattered wave is given by

$$\ell^i(r_{\text{LB}}, z) = d_1^i + d_2^i = d_{\text{CH}} + \beta \cdot z \quad (5.90)$$

$$\ell^j(r_{\text{LB}}, z) = d_1^j + d_2^j = d_{\text{CH}} + \beta \cdot z - \gamma \cdot r_{\text{LB}} \quad (5.91)$$

$$\ell^k(r_{\text{LB}}, z) = d_1^k + d_2^k = d_{\text{CH}} + \beta \cdot z + \gamma \cdot r_{\text{LB}} \quad (5.92)$$

with

$$\beta = 1 - \cos \theta \quad (5.93)$$

$$\gamma = \frac{\cos \theta - 1}{\sin \theta}. \quad (5.94)$$

Thus a general expression for the extinction distance can be written as

$$\ell(r, z) = d_{\text{CH}} + \beta \cdot z - \gamma \cdot r \quad \text{for } \phi \in [0, \pi] \quad (5.95)$$

$$\ell(r, z) = d_{\text{CH}} + \beta \cdot z + \gamma \cdot r \quad \text{for } \phi \in [\pi, 2\pi], \quad (5.96)$$

where azimuth $\phi \in [0, \pi]$ refers to the half of V_s facing away for the detection system.

In the following we calculate $\mathcal{I}$ from eq. (5.85) using expressions (5.95) and (5.96) for ℓ . Introducing $K = N_c C_{\text{EXT}}$, the integral can be written as

$$\mathcal{I} = e^{-K d_{\text{CH}}} \int_{-l_v/2}^{+l_v/2} e^{-K \beta \cdot z} dz \times \quad (5.97)$$

$$\begin{aligned} & \times \left(\int_0^\pi e^{-K \left(\frac{r^2}{\sigma^2} - \gamma \cdot r \right)} r dr d\phi + \int_\pi^{2\pi} e^{-K \left(\frac{r^2}{\sigma^2} + \gamma \cdot r \right)} r dr d\phi \right) \\ & = \frac{e^{-K d_{\text{CH}}}}{-K \beta} \left(e^{-K \beta \cdot l_v/2} - e^{+K \beta \cdot l_v/2} \right) \times \\ & \times \left(\int_0^\pi e^{-K \left(\frac{r^2}{\sigma^2} - \gamma \cdot r \right)} r dr d\phi + \int_\pi^{2\pi} e^{-K \left(\frac{r^2}{\sigma^2} + \gamma \cdot r \right)} r dr d\phi \right). \end{aligned} \quad (5.98)$$

Thereby the relative deviation σ_{rel} between *idealized* ($\ell = d_{\text{CH}}$) and *actual* (ℓ according to (5.95) and (5.96)) scattered light fluxes can be expressed as follows:

$$\sigma_{\text{rel}} = \frac{I_0 \mathcal{I} - l_v \Phi_t}{l_v \Phi_t}. \quad (5.99)$$

In the last expression we have used expression (5.87) for the *idealized* scattered light flux and expression (5.83) with $\mathcal{I}$ according to eq. (5.97) for the *actual* scattered light flux.

Figure 5.9 shows the relative deviation of scattered light fluxes as a function of light attenuation for different light scattering angles using the following dimensions of the actual optical arrangement:

$$r_{\text{LB}} = 1.42\text{mm}$$

$$\sigma = 0.47\text{mm}$$

$$d_{\text{CH}} = 45\text{mm}$$

θ	10°	15°	20°	25°	30°
l_v [mm]	6.91	15.45	11.70	9.46	8.00

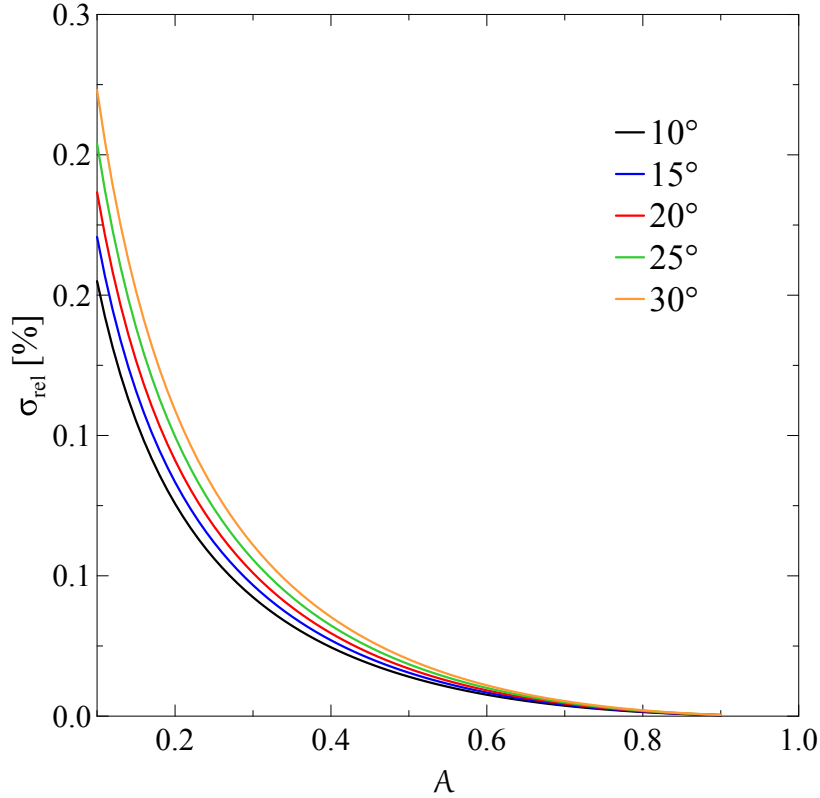


Figure 5.9: Relative deviation between *ideal* and *real* scattered light fluxes resulting from a misinterpretation of ℓ as a function of light attenuation $\mathcal{A}$.

It can be seen from figure 5.9 that the assumption of having a constant attenuation length $\ell = d_{\text{CH}}$ yields underestimation of light extinction less than 0.25% for all light scattering angles under consideration. Moreover the relative deviation σ_{rel} increases with increasing light attenuation and increasing light scattering angle. Due to the very small value of σ_{rel}

deviations of ℓ from d_{CH} can be neglected and the *idealized* scattered light flux from (5.87) can be used.

5.2.3 Half-shaded regions

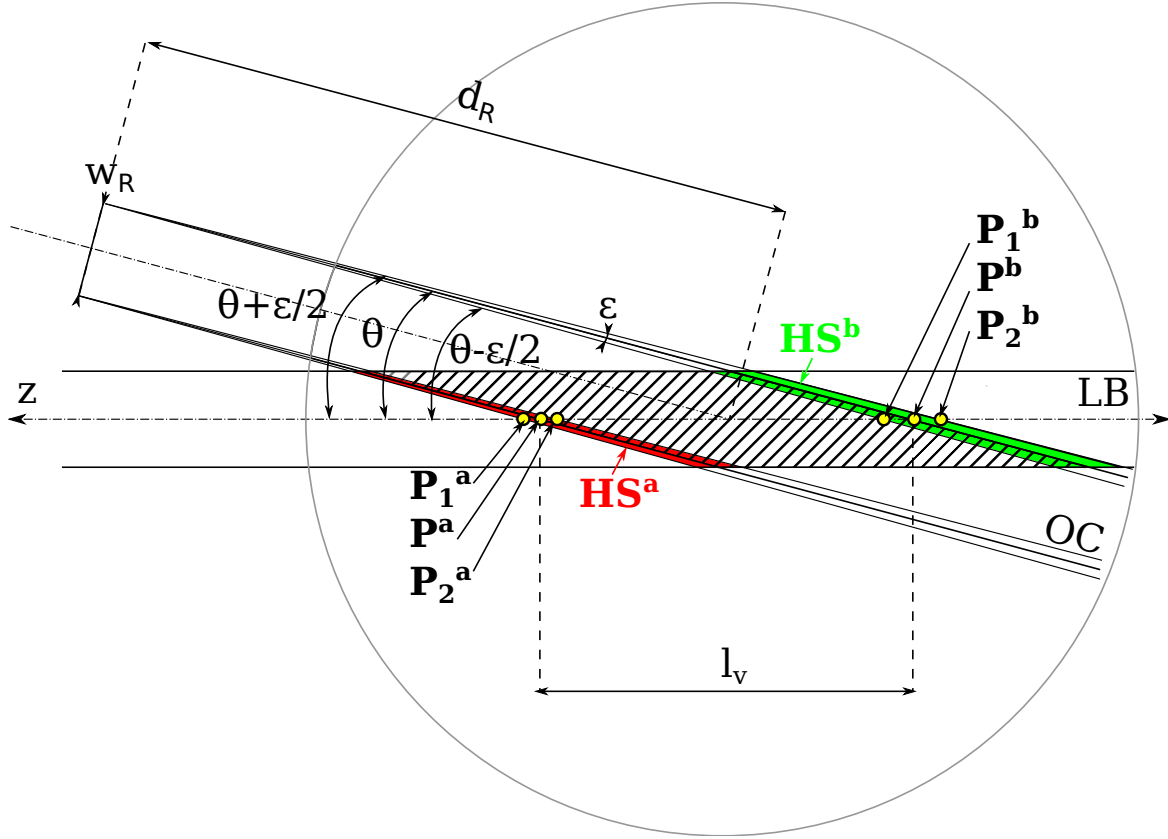


Figure 5.10: Schematic diagram of the detection geometry for measurements of Φ_s showing half-shaded regions HS^a and HS^b resulting from finite system aperture ϵ . LB and OC are laser beam and observation cone, respectively. θ is the light scattering angle, d_R the distance between rectangular stop S_R with width w_R and chamber center. l_v is the length of the light scattering volume without half-shaded regions. Points $\mathbf{P}^a$ and $\mathbf{P}^b$ refer to droplets being located inside HS^a and HS^b , respectively.

Figure 5.10 shows the two half-shaded regions HS^a (red) and HS^b (green) resulting from the finite detection system aperture ϵ . Up to this point influences of half-shaded regions on the actual scattering geometry have not been taken into account. The length of the so far considered light scattering volume V_s (shaded area) is given by the distance $\overline{P^a P^b}$ (see eq. 5.86). It can be seen that not all droplets inside V_s scatter light within the detectable angular range, i.e. $\theta \pm \epsilon/2$. In fact, droplets inside the green shaded area scatter light within $\{\theta - \epsilon/2 + \delta, \theta + \epsilon/2\}$, where $\delta \rightarrow \epsilon/2$ as $z \rightarrow -l_v/2$. On the other hand, droplets inside the red shaded area scatter within $\{\theta - \epsilon/2, \theta + \epsilon/2 - \delta\}$, with $\delta \rightarrow \epsilon/2$ as $z \rightarrow +l_v/2$. This

effect is partly eliminated by droplets inside full green and red regions. The full green region, where droplets scatter within $\{\theta - \delta, \theta - \epsilon/2\}$, and the full red region, where droplets scatter within $\{\theta + \delta, \theta + \epsilon/2\}$, for $\delta \rightarrow \epsilon/2$ as $|z| \rightarrow l_v/2$, compensate red and green shaded areas, respectively.

However this compensation is not complete since green regions are bigger than red ones. This yields overcompensation of the red shaded area and undercompensation of the green shaded area. To estimate the incomplete compensation distances $\overline{P_1^b P^a}$ and $\overline{P^a P_2^a}$ are compared with $\overline{P_1^b P^b}$ and $\overline{P^b P_2^b}$, respectively. The relative undercompensation of the green shaded area can be approximated by

$$\Delta_b \approx \frac{\overline{P_1^b P^b} - \overline{P_1^a P^a}}{\overline{P_1^b P^b}} = \frac{2(\sin(\theta + \epsilon/2) - \sin \theta)}{\sin(\theta + \epsilon/2) - \sin \theta \left(1 - 2 \frac{d_R}{w_R} \sin \epsilon/2\right)}, \quad (5.100)$$

while the relative overcompensation of the red shaded area is approximately given by

$$\Delta_a \approx \frac{\overline{P^b P_2^b} - \overline{P^a P_2^a}}{\overline{P^a P_2^a}} = \frac{2(\sin(\theta - \epsilon/2) - \sin \theta)}{\sin(\theta - \epsilon/2) - \sin \theta \left(1 + 2 \frac{d_R}{w_R} \sin \epsilon/2\right)}. \quad (5.101)$$

where the actual values of d_R , which is the center distance between V_s and rectangular stop, are

θ	10°	15°	20°	25°	30°
d_R [mm]	105	110	105	110	105

Inserting the values of w_R, r_P, f_l and d_R , all listed in appendix B.4, into eqs. (5.101) and (5.100), Δ^a and Δ^b read:

θ	10°	15°	20°	25°	30°
Δ^a [%]	6	13	10	7	6
Δ^b [%]	7	15	11	8	7

Thus asymmetric half-shaded regions yield a slight increase of the mean scattering angle $\bar{\theta}$ with respect to angle θ , where detection systems are actually centered. However an angular deviation within $\pm \epsilon/2$ does not change the position of the Mie extrema significantly. Therefore the effect of half-shaded regions on measured scattered light fluxes can be neglected.

Another measurement artifact, caused by the finite diameter of pinhole P, is the increase of observation cone OC when intercepting with photomultiplier tube PMT. However, calculations performed in appendix B.3.3 show that, including half-shaded regions, 3% of the active area A_{PMT} of installed photomultiplier tubes are illuminated at 10°, and 14% at 15° – 30°. These fractions are small enough to avoid influences of non-uniformities at the edges of A_{PMT} , which may distort measurements of Φ_s . However, as already discussed before, unwanted measurement artifacts due to non-uniformities of the central part of the sensitive

area might still influence measurements. Thus, it is planned to increase the illuminated area by using different lens-pinhole detector systems.

5.2.4 Glass ring effect

In order to have a parallel laser beam inside the expansion chamber EXP a lens system, consisting of one focusing and one defocusing cylindrical lens, L_{CF} and L_{CD} , respectively, was installed between polarization filter F and EXP (see fig. 5.11). This lens system compensates for the defocusing effect of the cylindrical glass ring.

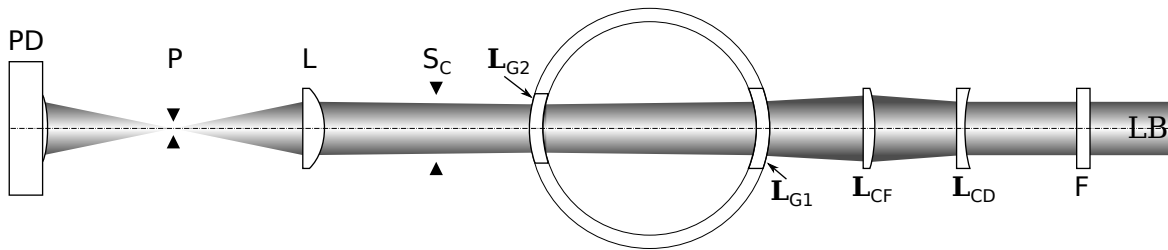


Figure 5.11: Schematic diagram of the laser beam (LB) geometry. F is the polarization filter, L_{CF} and L_{CD} are cylindrical lenses, and L_{G1} and L_{G2} cylindrical lenses representing entrance and exit window of the glass ring. S_C , L, P and PD are circular stop, lens, pinhole and photo diode of the lens-pinhole detector system, respectively.

The resulting beam geometry inside the expansion chamber was calculated using ray tracing formulae according to the matrix representation of Gaussian Optics (Halbach (1964), see appendix B.3). Calculations show that the laser beam diameter is 5.1mm after entering and 4.8mm before leaving the expansion chamber. The convergence of about -0.1° is small enough to approximate the laser with a parallel beam inside EXP.

Detection geometry for measurements of Φ_t

Regarding measurements of Φ_t the glass-ring causes divergence of the detection cone inside EXP. Only rays, that converge by -0.26° inside the expansion chamber, leave the exit window, L_{G2} , of EXP parallel. The actual convergence of the laser beam inside EXP is -0.11° . Thus LB diverges slightly (0.16°) after leaving EXP. However, the half-angle of the detection system $\epsilon/2 = 0.85^\circ$ is larger than the divergence of the transmitted laser beam, which enables measurements of the transmitted light flux ($\theta = 0^\circ$).

In order to perform quantitative measurements of light attenuation total transmission of the incident laser beam is necessary. From fig. 5.11 it can be seen that this implies following

conditions on laser beam diameters d_{LB}^i :

$$\begin{aligned} d_{LB}^{SC} &< d_{SC} \\ d_{LB}^L &< d_L \\ d_{LB}^P &< d_P \\ d_{LB}^{PD} &< d_{PD} \end{aligned}$$

where d_{SC} , d_L and d_P are diameters of circular stop, lens and pinhole, respectively. d_{PD} is the diameter of the active area of the photo diode. Clearly d_{LB}^i is increased due to the glass-ring curvature. However ray-tracing calculations performed in appendix B.3.2 prove above stated inequalities to be true.

In addition to its defocusing effect, the inclination of glass-ring G causes a shift of the transmitted beam parallel to the plane of observation. To minimize reflections inside the

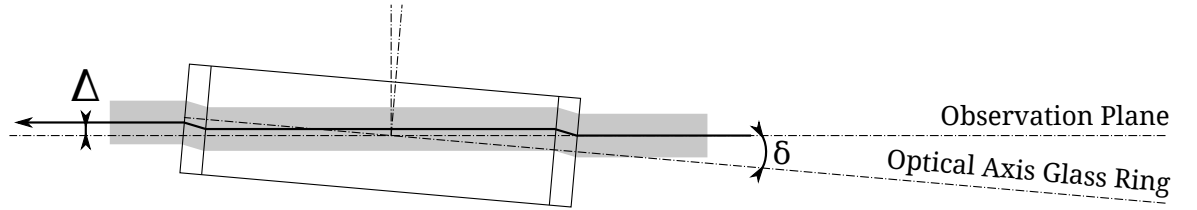


Figure 5.12: Inclination of the glass ring axis with respect to the observation plane by angle δ .

expansion chamber, G is tilted with respect to the observation plane by an angle δ . The resulting shift Δ of the beam axis parallel to the plane of observation can be expressed as

$$\Delta = 2d_G \cdot \sin\delta \left(1 - \frac{\cos\delta}{\sqrt{n_G^2 - \sin^2\delta}} \right) \quad (5.102)$$

where

$$\delta = 1.24^\circ,$$

the wall thickness of G is

$$d_G = 3.6\text{mm},$$

and its refractive index

$$n_G = 1.45.$$

Thus the parallel shift is

$$\Delta \approx 0.04\text{mm},$$

which is negligibly small.

Detection geometries for measurements of Φ_s

Clearly observation cones for measurements of Φ_s are affected by the glass-ring curvature too. The defocusing effect of glass ring G causes divergence of the observation cone OC inside the expansion chamber EXP, which increases light scattering volumina by $\approx 20\%$ and half-shaded regions up to 55%, depending on the light scattering angle.

Nevertheless, the assumption of having an extinction length ℓ equal to the inner diameter of EXP stays valid, since σ_{rel} in eq. (5.99) does not exceed 0.25% for the actual dimensions of the optical arrangement and light attenuation ranging from 0.9 to 0.1 (see appendix B.3.3). System apertures ϵ given by (5.78) increase to $\tilde{\epsilon}$ (see table 5.1). due to G. However, positions

θ	10°	15°	20°	25°	30°
ϵ	0.28°	1.01°	1.01°	1.01°	1.01°
$\tilde{\epsilon}$	0.44°	1.50°	1.50°	1.50°	1.50°

Table 5.1: *Ideal* and *real* detection system apertures, ϵ and $\tilde{\epsilon}$, respectively, for five different light scattering angles.

of Mie extrema are insensitive to small changes ($\pm\epsilon/2$) in θ (see fig. 5.13). Thus a small increase of ϵ does not affect measurements.

Apart from negligibly small angular variations and σ_{rel} , precision measurements of Φ_s require half-shaded regions, and therefore also light scattering volumina, not to intercept with chamber walls. Otherwise reflections on the glass-ring may enter light observation cones, which yields distortion of the measured scattered light fluxes.

To keep HS inside the chamber the distance r_{max} between its most distant point and the center of the chamber has to be smaller than the inner radius of the chamber, r_{CH} , (see figure 5.14).

$$r_{max} < r_{CH} = 22.5\text{mm}. \quad (5.103)$$

For individual light scattering angles, r_{max} was calculated by intersecting lines representing the outermost rays of observation cones and LB inside the expansion chamber. Lines s_a and s_b correspond to the outermost rays defining the light scattering volume (see figure 5.14). Including half-shaded regions the outermost rays become s_a^{HS} and s_b^{HS} , which correspond to half-shaded region HS^a and HS^b , respectively.

Introducing a two dimensional Cartesian coordinate system, where the x-axis is along the optical axis of the laser beam and the origin is located at the center of the chamber, lines

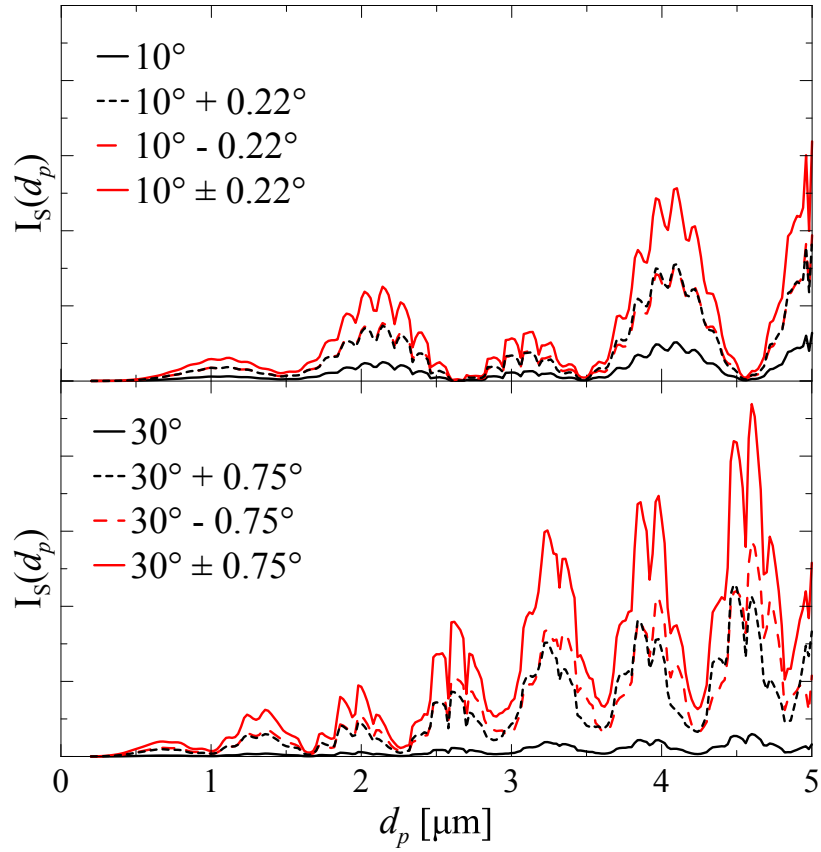


Figure 5.13: Theoretical scattered light intensities as a function of droplet diameter d_p at light scattering angles $\theta = 10^\circ$ and 30° (solid black curves). Refractive index m of the growing droplets is 1.3875, and wavelength λ of the incident laser beam is 488nm. Solid red curves correspond to light scattering within an angular range of $\theta \pm \epsilon/2$, whereas dashed red and black curves represent scattering within $\theta - \epsilon/2$ and $\theta + \epsilon/2$, respectively.

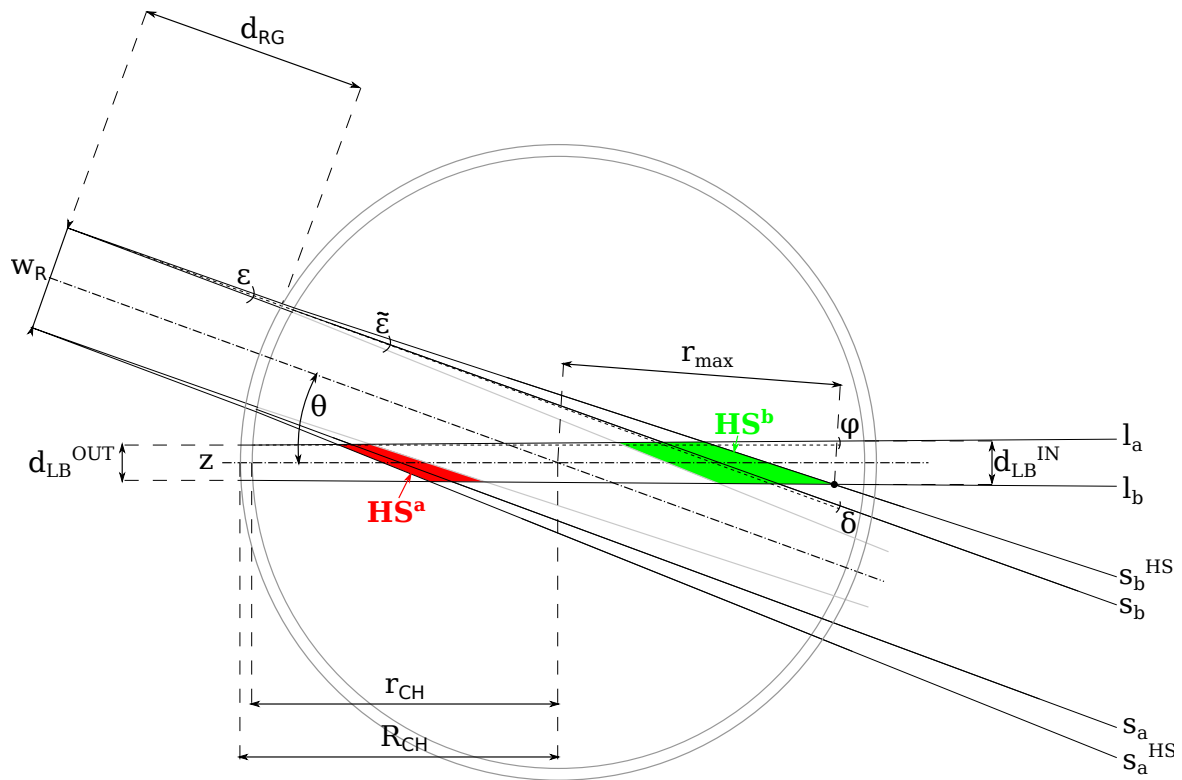


Figure 5.14: Detailed schematics of the scattering geometry showing the defocussing effect of glass ring G. $d_{\text{LB}}^{\text{IN}}$ and $d_{\text{LB}}^{\text{OUT}}$ are diameters of the laser beam LB before it enters and after it leaves expansion chamber EXP. r_{CH} and R_{CH} are inner and outer radii of EXP, respectively. ϵ and $\tilde{\epsilon}$ are *ideal* and *real* system apertures. HS^a (red) and HS^b (green) are half-shaded regions. s_b and s_a represent the outermost rays of an idealized observation cone OC, whereas s_a^{HS} and s_b^{HS} are outermost rays of OC including half-shaded regions. The distance between most distant point of the light scattering volume (including half-shaded regions) and chamber center is r_{max} . w_{R} is the width of rectangular stop S_{R} centered at light scattering angle θ and d_{RG} is the distance between S_{R} and glass ring G.

describing the laser beam are given by

$$l_a = \tan \phi \cdot x + d_{LB} \quad (5.104)$$

$$l_b = -\tan \phi \cdot x - d_{LB} \quad (5.105)$$

with

$$\tan \phi = \frac{(d_{LB}^{IN} - d_{LB}^{OUT})}{4 \cdot r_{CH}} \quad (5.106)$$

$$d_{LB} = \frac{1}{2} (d_{LB}^{IN} - r_{CH} \cdot \arctan \phi), \quad (5.107)$$

where

$$\begin{aligned} d_{LB}^{IN} &= 5.1 \text{mm} \\ d_{LB}^{OUT} &= 4.8 \text{mm} \end{aligned} \quad (5.108)$$

are diameters of the laser beam entering and leaving EXP, respectively, and $r_{CH} = 22.5 \text{mm}$ is the inner radius of EXP. Outermost rays, which correspond to observation cones defining V_s (without half-shaded regions) are given by

$$s_a = -\tan(\theta + \delta) \cdot x + d_a \quad (5.109)$$

$$s_b = -\tan(\theta - \delta) \cdot x - d_b \quad (5.110)$$

with

$$\delta = (\mathbf{L} \cdot \vec{v})_1 \quad (5.111)$$

$$d_a = \frac{(\mathbf{L} \cdot \vec{v})_2}{\cos(\theta)} + \frac{\tan(\delta)}{\cos(\theta - \delta)} r_{CH} \quad (5.112)$$

$$d_b = \frac{(\mathbf{L} \cdot \vec{v})_2}{\cos(\theta)} + \frac{\tan(\delta)}{\cos(\theta + \delta)} r_{CH}. \quad (5.113)$$

Ray-tracing vectors $\vec{v}$ in eqs. (5.111) - (5.113) are related to the width w_R of the rectangular stop S_R according to

$$\vec{v} = \begin{pmatrix} 0 \\ w_R/2 \end{pmatrix}. \quad (5.114)$$

The system matrix $\mathbf{L}$, representing beam propagation through the glass ring, can be expressed as

$$\mathbf{L} = \begin{pmatrix} 1 & -\frac{n_G - n_{air}}{-R_{CH}} \\ 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ d_G/n_G & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & -\frac{n_{air} - n_G}{-r_{CH}} \\ 0 & 1 \end{pmatrix}. \quad (5.115)$$

Actual values of refractive index n_G , wall thickness d_G , inner radius r_{CH} and outer radius R_{CH} of glass ring G can be found in appendix B.1.

Line equations s_a^{HS} and s_b^{HS} including half-shaded regions are simply formed by replacing $\vec{v}$ with

$$\vec{v}^{\text{HS}} = \begin{pmatrix} \epsilon \\ \tan(\epsilon/2) \cdot d_{\text{RG}} + \frac{w_{\text{R}}}{2} \end{pmatrix} \quad (5.116)$$

in eqs. (5.111) - (5.113), where $d_{\text{RG}} = d_{\text{R}} - r_{\text{CH}}$.

From figure 5.14 it can be seen, that the most distant point including half shaded regions is given by

$$l_b \cap s_b^{\text{HS}}, \quad (5.117)$$

and the length l_v of the light scattering volume can be approximated by

$$l_v \approx \frac{|(s_a \cap l_b)(s_b \cap l_b) + (s_a \cap l_a)(s_b \cap l_a)|}{2}. \quad (5.118)$$

For the actual dimensions of the optical arrangement the following values for r_{max} and l_v are obtained:

θ	10°	15°	20°	25°	30°
$r_{\text{max}}[\text{mm}]$	19.66	21.46	15.89	12.80	10.59
$l_v[\text{mm}]$	8.29	18.54	14.04	11.45	9.60

Hence light scattering volumina and surrounding half-shaded regions are located inside the expansion chamber.

5.2.5 Summary

The above-mentioned estimations yield following conclusions:

- Influences of light scattered in forward direction on measurements of Φ_t can be neglected, because the detector system aperture ϵ is sufficiently small.
- The assumption of having a constant light attenuation length, which equals the inner diameter of the expansion chamber, yields relative deviations from the actual attenuation length of less than 0.25% for all light scattering angles θ under consideration.
- The effect of asymmetric half-shaded regions on actual values of θ can be neglected.
- The parallel shift of the transmitted laser beam due to the inclination of the glass-ring G can be neglected.
- Although the glass ring has a defocusing effect on both laser beam and observation cones, light scattering volumina and half-shaded regions do not intercept with chamber walls.

5.3 Evaluation of experimentally obtained light fluxes

5.3.1 Determination of droplet growth curves

Droplet growth curves were determined by establishing a unique correspondence between theoretical scattered light flux vs. droplet diameter and attenuation corrected experimental scattered light flux vs. time curves, $\Phi_s(d_p)$ and $\tilde{\Phi}_s^{tot}(t)$, respectively, where

$$\tilde{\Phi}_s(t) = \frac{\Phi_s(t)}{\mathcal{A}(t)}$$

with light attenuation $\mathcal{A}$ being

$$\mathcal{A}(t) = \frac{\Phi_t(t)}{\Phi_i}.$$

Φ_i is the incident light flux³.

Since experimental scattered light fluxes $\Phi_s(t)$ are normalized with respect to light attenuation $\mathcal{A}(t)$, the influence of light attenuation on height and position of scattering extrema is eliminated.

A typical set of attenuation corrected scattered light fluxes $\tilde{\Phi}_s(t)$ is shown in figure 5.15. Measurements of $\tilde{\Phi}_s(t)$ were performed at five different forward light scattering angles $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° using ambient aerosol particles and n-propanol as condensing vapor. As can be seen from these graphs experimental curves show series of maxima and minima. The clearly pronounced *ripple structure* indicates a very narrow size distribution of the growing droplets. In fact, Syzmanski (1981) showed that a relative standard deviation of 5% already yields complete disappearance of this fine structure (see figure 5.16). Comparing fig. 5.15 with 5.2 it can be seen that, experimental scattered light flux-vs-time and theoretical scattered light flux-vs-diameter curves are in excellent agreement. This allows the establishment of a unique correspondence of experimental and theoretical extrema. Thereby droplet diameters are assigned to extrema occurring on experimental curves, which yields droplet growth data $d_p(t)$.

This method of determining $d_p(t)$ is limited to particles, which are initially smaller than the size corresponding to the first Mie maximum. Only then a clear allocation of experimental to theoretical extrema is possible.

5.3.2 Absolute determination of droplet number concentrations

In the absence of multiple scattering, dependent scattering and polarization field interactions (Wagner, 1985), the height of normalized scattered light fluxes (see equ. (5.89)) is proportional to the number concentration of particles inside the light scattering volume. In the present study number concentrations were calculated from the height of the 1st global Mie maximum only. The constant of proportionality between measured heights in Volts and

³To simplify upcoming notation Φ_s^{tot} will be abbreviated by Φ_s in the following.

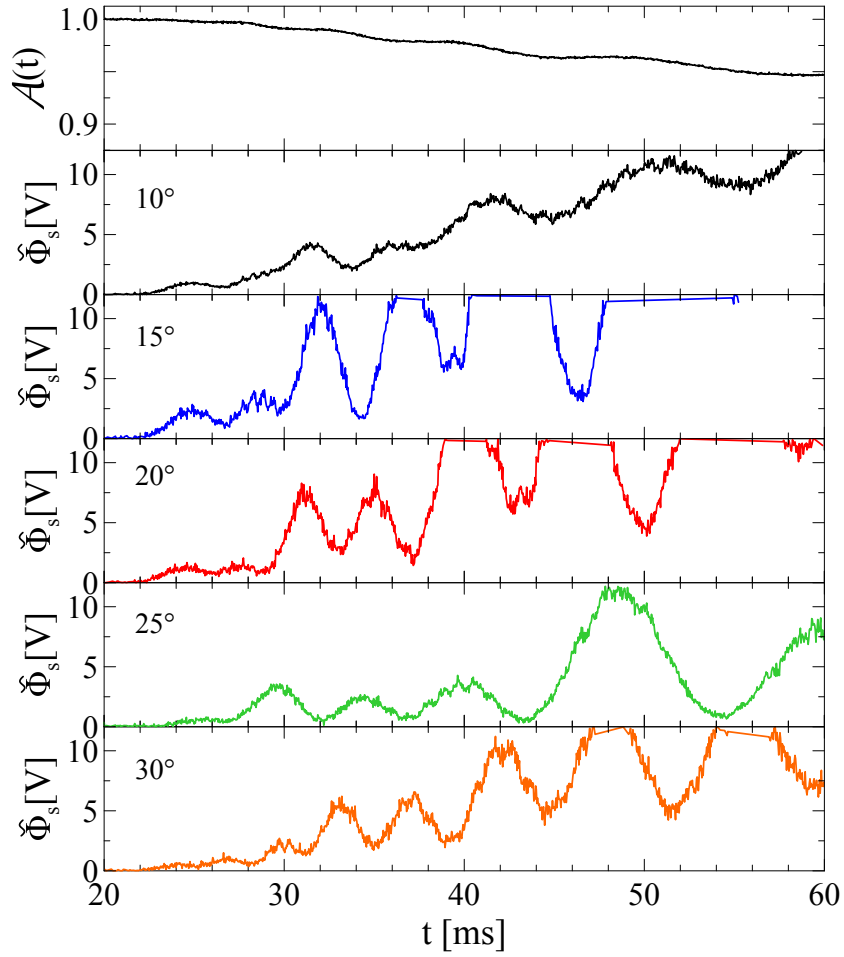


Figure 5.15: Attenuation corrected scattered light fluxes $\tilde{\Phi}_s$ and light attenuation $\mathcal{A}$. The droplet number concentration is $1.2 \cdot 10^4 \text{ cm}^{-3}$. Because the *ripple structure* can be identified the growing n-propanol droplets have a very narrow size distribution.

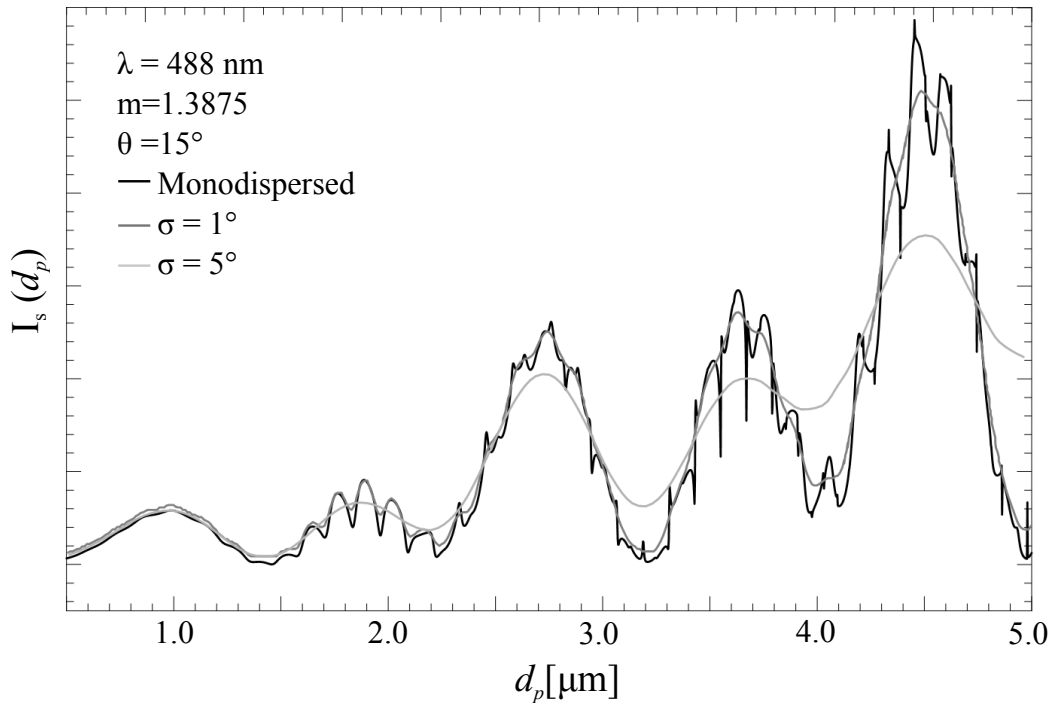


Figure 5.16: Theoretical scattered light intensity- vs-droplet diameter curves for three different log-normal size distributions. It can be seen, that the *ripple structure* vanishes completely for a relative standard deviation of 5%, in agreement with Syzmanski (1981).

droplet number concentration N_c was determined by calibrating each photomultiplier tube applying the EXT method (Szymanski and Wagner, 1990). To this end, the incident light

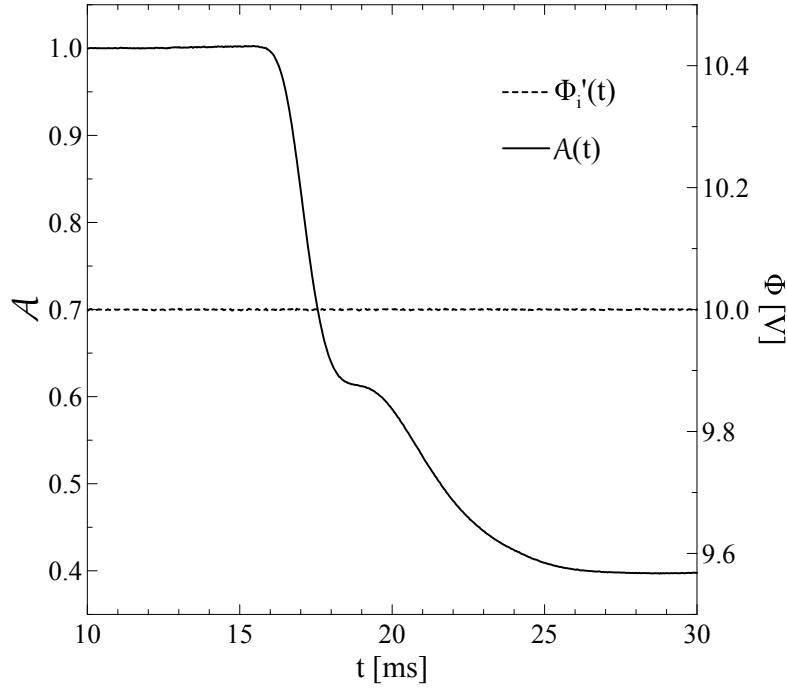


Figure 5.17: Experimental light attenuation $\mathcal{A}(t)$ and incident light flux $\Phi'_i(t)$ vs-time curves for a droplet number concentration N_c of about 10^5cm^{-3} .

flux Φ_i and transmitted light flux vs. time curves $\Phi_t(t)$ are measured to determine the light attenuation $\mathcal{A}(t)$ during particle growth quantitatively. Provided that

$$\Phi_i(t) = \text{const.} \quad \forall t$$

and particles inside the expansion chamber EXP do not attenuate light before expansion (t_{exp}),

$$\Phi_t(t_0) = \Phi_i \quad \forall t_0 < t_{exp}$$

light attenuation $\mathcal{A}$ can be expressed as

$$\mathcal{A}(t) = \frac{\Phi_t(t)}{\Phi_i} = \frac{\Phi_t(t)}{\Phi_t(t_0)} \quad \forall t_0 < t_{exp}. \quad (5.119)$$

However, if seed particles already cause some extinction before expansion then

$$\Phi_t(t_0) < \Phi_i \quad (5.120)$$

and $\mathcal{A}(t)$ can not be determined using 5.119. Therefore an additional photodetector measures the initial laser light flux Φ'_i before the laser beam enters EXP. This additional photodetector

can also be used to monitor the stability of the incident laser beam Φ_i . In fact, in the present study, Φ'_i is only used to check whether Φ_i is constant or not. However, to increase the upper size limit of detectable particles, it is planned to normalize Φ_t with respect to Φ'_i instead of $\Phi_t(t_0)$ in future studies.

Figure 5.17 shows a typical set of $\mathcal{A}(t)$ and $\Phi'_i(t)$ curves measured as a function of time. Assuming that laser beam wavelength λ , refractive index m of the droplets, length l_v of light scattering volumina and droplet number concentration N_c are constant during droplet growth, theoretical light attenuation given by the Beer-Lambert law (eq. (5.75)) is a function of droplet size only, $\mathcal{A} = \mathcal{A}(d_p)$.

The dependence of light attenuation on droplet size is given by the extinction coefficient C_{EXT} , which can be expressed as

$$C_{\text{EXT}}(d_p) = \frac{\pi d_p^2}{4} Q_{\text{EXT}}(d_p)|_{\lambda, m=\text{const.}} \quad (5.121)$$

To relate experimental and theoretical light attenuation, $\mathcal{A}(t)$ and $\mathcal{A}(d_p)$, respectively, information on the droplet size as a function of time is needed. Normalized Φ_s vs. time curves, measured simultaneously with the transmitted light flux, provide this information (see section 5.3.1).

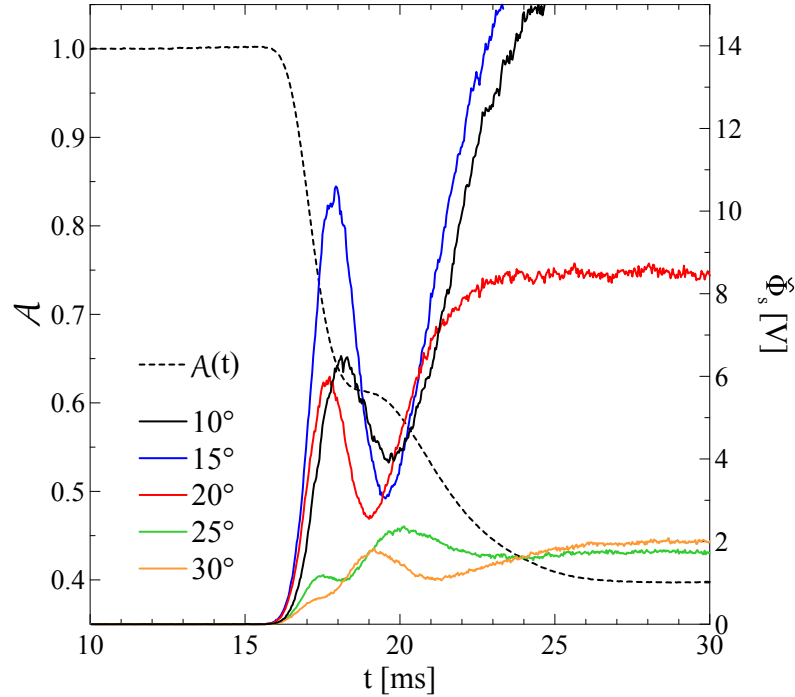


Figure 5.18: Light attenuation $\mathcal{A}(t)$ and attenuation corrected scattered light fluxes $\tilde{\Phi}_s(t)$ measured at different light scattering angles θ . The droplet concentration N_c is about 10^5cm^{-3}

Figure 5.18 shows attenuation corrected scattered light fluxes $\tilde{\Phi}_s$ corresponding to light at-

tenuation $\mathcal{A}(t)$ shown in figure 5.17. As already mentioned before only the first global Mie maximum is evaluated.

Suppose that t' is the time, where the first Mie maximum is identified at fixed angle θ . Comparison between theoretical and experimental scattered light fluxes gives the droplet diameter d_p at time t' . Furthermore light attenuation $\mathcal{A}(t')$ at time t' can easily be obtained from measured $\mathcal{A}(t)$ curves. Knowing $\mathcal{A}(t')$ and $d_p(t')$ equation (5.75) can be transformed into

$$N_c = -\ln(\mathcal{A}(t')) d_{\text{CH}} C_{\text{EXT}}(d_p(t')) \quad (5.122)$$

Thus knowledge about droplet size and light attenuation allows quantitative determination of particle number concentrations without referring to any external calibration units. However the EXT method of measuring N_c is limited to concentrations ranging from 10^4 to 10^5 cm^{-3} . Below that the signal-to-noise ratio is too low to evaluate light attenuation and above multiple scattering causes deviation from the Beer-Lambert law.

To increase the measurable concentration range scattered light signals were used to determine N_c . Assuming that the output signals of photomultiplier tubes are linearly proportional to incident scattered light fluxes, attenuation corrected signals $\tilde{\Phi}_s(t)$ depend linearly on the number concentration of droplets inside the light scattering volume. Thus N_c , determined according to eq. (5.122), can be used to calibrate photomultiplier tubes (PMTs) measuring Φ_s .

If $\tilde{\Phi}_s(t')$ is the normalized output signal corresponding to the first Mie maximum at constant angle θ , then the calibration constant k_{PMT} relating $\tilde{\Phi}_s(t')$ to N_c , is given by

$$k_{\text{PMT}} = \frac{N_c}{\tilde{\Phi}_s(t')} [\text{V}^{-1} \text{cm}^{-3}] \quad (5.123)$$

At constant light scattering angle k_{PMT} depends on sensor sensitivity, refractive index m and total incident light flux Φ_i . To have k_{PMT} being independent of Φ_i it is planned to normalize Φ_s with respect to Φ_t instead of $\mathcal{A}$ in the future. Since Mie maxima shift towards smaller droplet diameters with increasing m

$$\tilde{\Phi}_s(t'_1) \Big|_{m=m_1} < \tilde{\Phi}_s(t'_2) \Big|_{m=m_2} \quad \text{for } m_1 > m_2, t'_1 < t'_2$$

which implies that

$$k_{\text{PMT}}(m_1) > k_{\text{PMT}}(m_2),$$

because

$$N_c = \tilde{\Phi}_s(t'_1) \Big|_{m=m_1} \cdot k_{\text{PMT}}(m_1) = \tilde{\Phi}_s(t'_2) \Big|_{m=m_2} \cdot k_{\text{PMT}}(m_2).$$

Knowing $k_{\text{PMT}}(m)$, N_c can directly be obtained from the height of the first Mie maximum without referring to light attenuation measurements. Since the calibration procedure does not depend on any external standards the mCAMS method can also be regarded as an ab-

solute method for determination of particle number concentrations.

In fact, in the present study this is the only way of determining N_c at number concentrations below 10^4cm^{-3} , because in this concentration range light attenuation is too weak to be measured quantitatively.

For number concentrations higher than 10^4cm^{-3} both, EXT and mCAMS, signals can be used to determine N_c . However, Filipovicova (1996) showed that for $N_c > 2 \cdot 10^6 \text{cm}^{-3}$ influences of multiple scattering yield an increase of the transmitted light flux with respect to the Beer-Lambert law. Multiple scattering influences both scattered as well as transmitted light fluxes to approximately the same amount. Thus the influence of multiple scattering on measured scattered light fluxes can be eliminated by normalizing scattered relative to the transmitted light fluxes. This yields a linear response of the scattered light signals at concentrations up to about $3 \cdot 10^7 \text{cm}^{-3}$ (Filipovicova, 1996).

5.3.3 Advantages of measuring at different scattering angles

As already mentioned above scattered light fluxes are monitored as a function of time at five different forward scattering angles $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° . Regarding the calibration procedure described above, this yields five independent sets of $(\tilde{\Phi}_t(t'), d_p(t'))$, which result in five different calibration constants $k_{\text{PMT}}^\theta(m)$. In principle, the five calibration constants should be related to each other according to Mie theory calculations. However, the five photomultiplier tubes will have somewhat different sensitivities and observation cones have different apertures.

Once calibrated the five independently measured scattered light fluxes can be used to check the alignment of the optical system. This is accomplished by comparing the number concentrations obtained from the height of the first maxima or by checking the position and height of extrema relative to each other. From theoretical scattered light curves shown in figure 5.2 it follows that (a) the first global Mie maxima shift to smaller sizes for bigger angles, (b) the number of global maxima appearing in a fixed size range increases with increasing θ , and (c) the height of global maxima increases monotonically with increasing droplet size for all angles but 10° . (a)-(c) must also apply to experimental curves, when replacing droplet size by time. Any deviation from (a)-(c), and strong discrepancies between the five independently determined number concentrations indicate misalignment of the optical apparatus.

Another obvious feature of measuring at multiple angles is that the number of assignable extrema increases, which in turn lowers uncertainties regarding droplet growth curves. Moreover, every mCAMS measurement yields five independently determined number concentrations. Thus relative uncertainties in N_c can be reduced by simply averaging the five simultaneously measured values.

In case of very high number concentrations, droplet growth will suffer from vapor depletion. This may result in droplets not growing up to the second Mie maximum, leaving only one point (the first maximum) to be identified on the experimental curve (see fig. 5.18). How-

ever mCAMS measurements still yield five different droplet diameters, which can be used to build a droplet growth curve.

If droplet concentrations are very low ($\approx 100\text{cm}^{-3}$) experimental maxima are only weakly pronounced, which complicates their identification. If for example the first two global maxima of the 15° -curve are superimposed by the signal noise, then the third one is the first to appear on the experimental curve. This might yield misinterpretation of experimental extrema if measurements were performed at 15° only. However, in the present study especially the 10° -curve can be used to eliminate uncertainties regarding the 15° -curve. From fig. 5.2 it can be seen that the second global maximum of the 10° -curve, which has a very high intensity compared to its neighboring maxima, has to come earlier in time than the third global maximum of the 15° -curve, whereas the first global maximum at 10° appears later than the first one at 15° . Thus by checking the position of first appearing maxima relative to each other misinterpretations can be eliminated.

Summarizing, the mCAMS method enables determination of number concentrations and droplet growth curves in a larger concentration range ($10^2 - 10^7\text{cm}^{-3}$), provides information about the alignment of the optical apparatus, and includes all features of CAMS and EXT method.

6 Measuring cycle

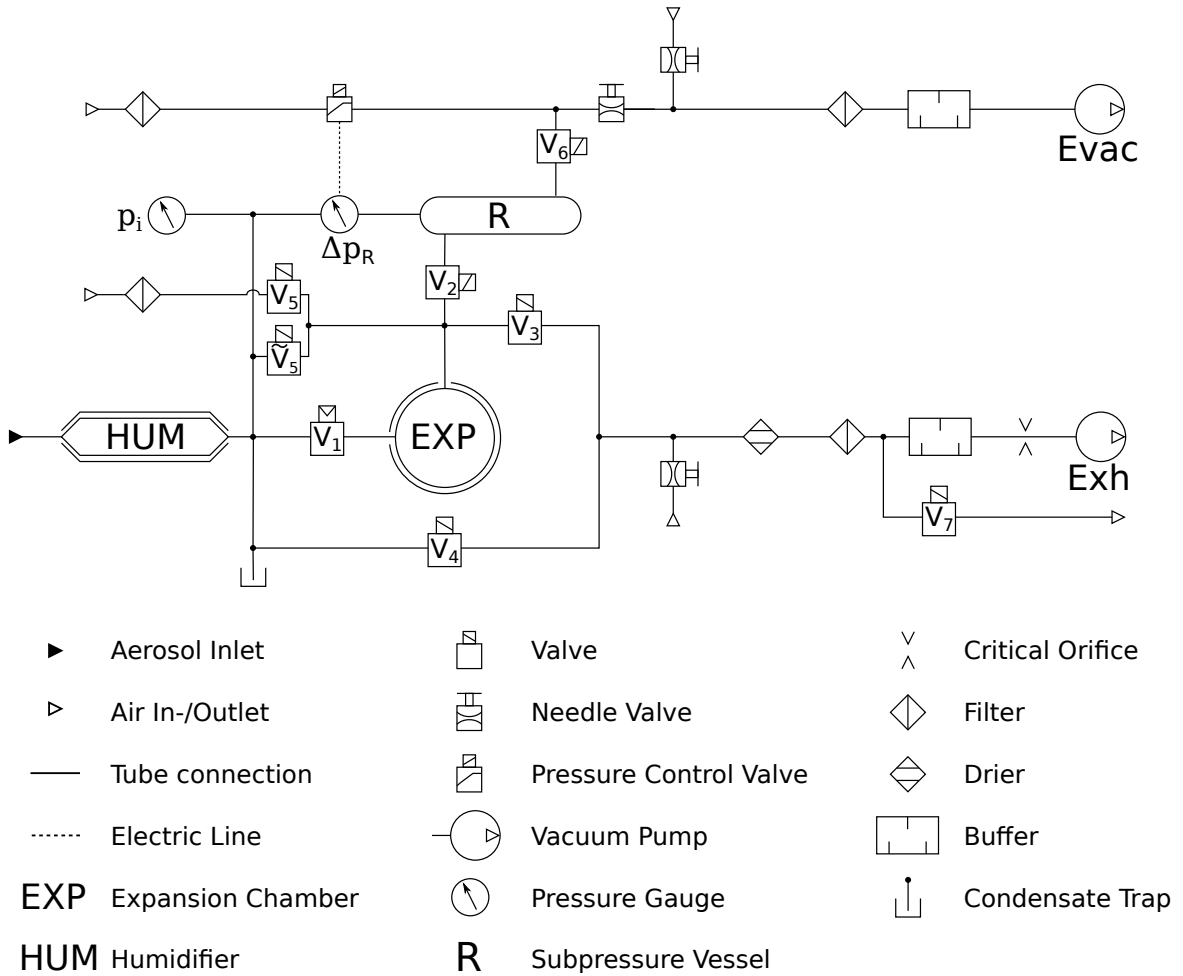


Figure 6.1: Flow diagram of vSANC

The timing of the experiment is defined by an automated measurement cycle, which consists of the following consecutive steps:

- **Flushing**

At the beginning of the cycle valves V_1 , V_3 and V_6 are opened. Aerosol entering the instrument from the left in figure 6.1 is flushed through the expansion chamber EXP. In

the present study the aerosol flow is controlled by means of a critical orifice connected to vacuum pump Exh (*active sampling mode*). However, it is also possible to operate the vSANC in *passive sampling mode* by opening V₇ and stopping Exh. In this case aerosol flow is regulated externally.

While aerosol is flushed through EXP, vacuum pump Evac generates underpressure inside the subpressure vessel R. The pressure difference Δp_R between total gas pressure p_i and vacuum inside R is monitored using a differential pressure gauge. An electrically operated pressure control valve regulates Δp_R to a preset value.

- **Delay**

After sufficient flushing V₄ is opened before V₃ and V₁ close. A short time delay between the opening of V₄ and closing of V₃ and V₁ enables continuous aerosol flow at the transition from *flushing* to *delay*.

Now aerosol inside EXP can equilibrate with its surrounding, while aerosol entering the instrument flows towards Exh via a bypass line. Before the cycle switches to *expansion* V₆ is closed.

- **Expansion**

In the next step EXP and R are connected by opening expansion valve V₂. The resulting fast expansion yields well-defined and uniform vapor supersaturation inside EXP, which, in turn, results in heterogeneous nucleation of supersaturated vapor on preexisting aerosol particles¹ and subsequent droplet growth. Thereby particles, which are too small to be detected optically, grow to visible sizes.

Data acquisition starts 500ms before the opening of V₂ and finishes when V₂ is closed.

- **Pressure Adjust**

Pressure compensation between underpressure in EXP and ambient air pressure is achieved by briefly opening V₅. In principle, it is also possible to run measurements at system pressures different from ambient air pressure. This feature is particularly useful when conducting chamber experiments, e.g. at CLOUD (CERN). In that case $\tilde{V}_5$ is briefly opened instead of V₅ and pressure compensation is achieved by connecting EXP with the aerosol inlet line. However, this results in a pressure surge, that disturbs the aerosol inlet flow, which might cause higher inlet losses.

In the present study measurements were performed at ambient pressure only.

- **Cycle Back**

To guarantee continuous aerosol flow during the whole measuring cycle valves V₁, V₃ are opened before closing V₄ and switching to *flushing*.

A complete measurement cycle takes about 35s. The measuring frequency can be tuned by decreasing *flush* and *delay* times, t_{flush} and t_{delay} . However, it is limited by the regulating

¹or homogeneous nucleation of supersaturated vapor molecules

speed of Δp_R and the equilibration rate of the aerosol inside EXP. Typical values for t_{flush} and t_{delay} are 20s and 10s.

7 Experimental apparatus

7.1 Expansion chamber

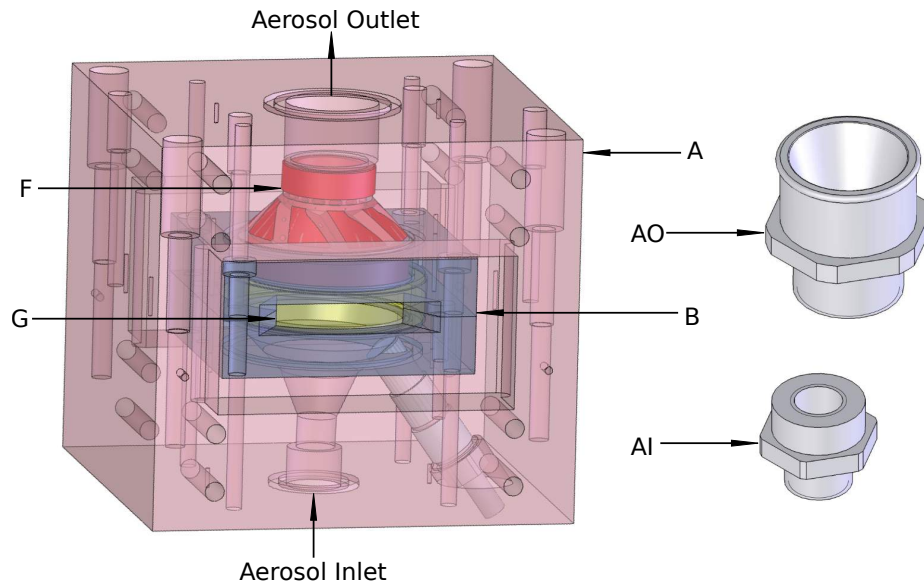


Figure 7.1: 3 dimensional drawing of expansion chamber EXP, aerosol inlet connector AI and aerosol outlet connector AO. A (light red) and B (gray) are inner and outer parts of EXP. F (red) is the flowshaper and G (yellow) the glass ring.

The expansion chamber consists of an outer part A, an inner part B, a glass ring G and a flowshaper F (see figure 7.1). All these parts are sealed from each other by FEP-sheathed Viton O-rings of various sizes. Upper and lower parts of A and B are assembled by means of screws. Central holes in parts A, B and F define the aerosol inlet ($\varnothing 10\text{mm}$), the chamber volume ($\approx 100\text{cm}^3$)¹ and the chamber outlet ($\varnothing 30\text{mm}$). To reduce reflexions inside the chamber volume A, B and F, all made from 1.4571 stainless steel, are black-oxide-finished. Additionally, G has an anti-reflective coating and is tilted against in- and outlet axes by 1.24° (see section 5.2).

Recesses in A and B expose the glass ring at two opposing sides. Here two identical optical plates OP are mounted (not shown in figure 7.1). One OP is the bearing for the support of the laser inlet system (see section 7.3.2). The other one is equipped with optical elements

¹Excluding volumina in A

for light flux measurements (see section 7.3.1).

Inner and outer parts of the expansion chamber provide holes, where a piezoelectric pressure transducer, for measurements of the total gas pressure change Δp , and a PT100 temperature sensor, for measurements of the chamber temperature T_{CH} , can be inserted (see figure 7.2). Clearly, measurements of Δp require, that the hole for the pressure transducer extends to the chamber volume. In contrast, measurements of T_{CH} can be performed in B, without disturbing the measuring volume². In fact the center distance between measuring volume and mounting hole for the temperature sensor is 36mm, whereas the radius of the measuring chamber is 22.5mm.

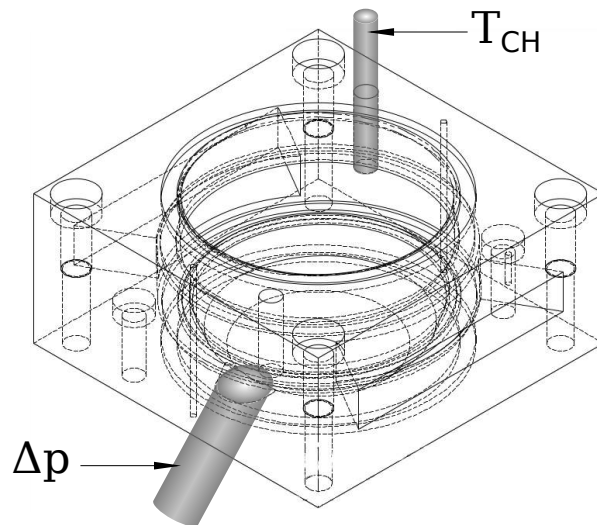


Figure 7.2: 3 dimensional drawing of the inner part B, showing the mounting holes for pressure transducer (Δp) and temperature sensor (T_{CH}).

To enable fast and complete flushing of the entire measuring volume, F is installed at the outlet of the expansion chamber (see fig. 7.1). However, measurements indicate, that this flowshaper represents a flow resistance, which slows the expansion process down (see e.g. figure 7.3). It is therefore planned to redesign F for future studies.

Part A bears threads for connection of the aerosol inlet connector AI and the aerosol outlet connector AO (see figure 7.1). The inner diameter of AI is 10mm and the inner diameter of AO 30mm. Via PVC-tubing, expansion valve V_2 is connected to AO in order to prevent mechanical vibrations of the expansion chamber during and after the opening of V_2 . On the other hand, the aerosol inlet valve V_1 is connected to AI via electropolished stainless steel tubing to minimize losses of charged particles due to electrostatic forces. However, measurements have shown that inlet losses of charged particles still exceed those of neutral particles by about 50%. This is very likely due to the fact, that V_1 is a pinch valve. Initially installed because of its very simple geometry, i.e. a tube with a length of 80mm and an

²Provided that measuring volume and B are in thermal equilibrium

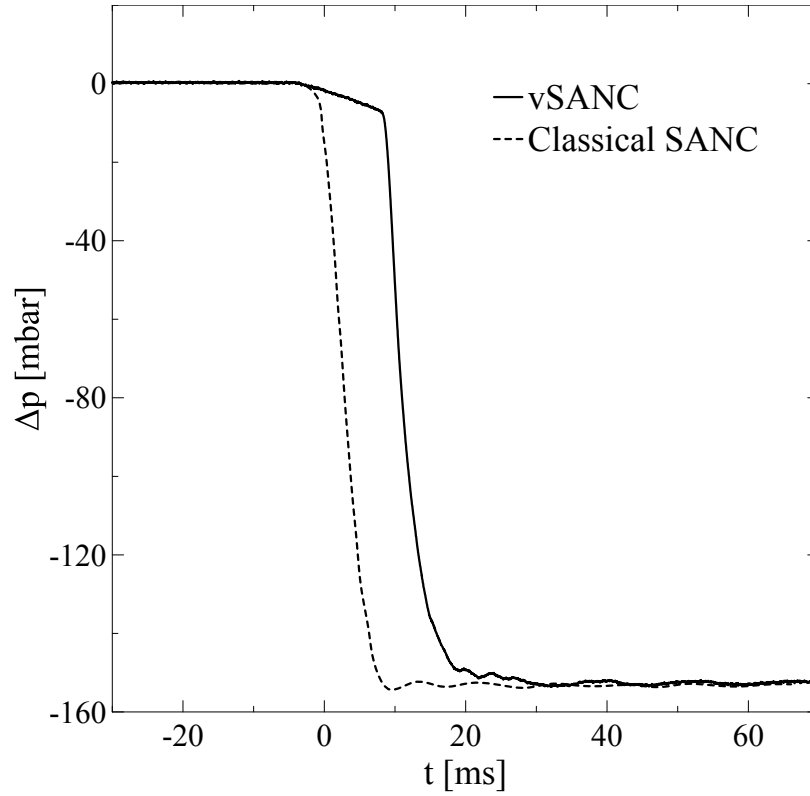


Figure 7.3: Total pressure drop Δp inside the chamber during expansion. Solid and dashed lines correspond to vSANC and *classical* SANC, respectively.

inner diameter of 10mm, V_1 turned out to act as an ion trap because of its plastic sleeve. It is therefore planned to replace it by a stainless-steel ball valve. The total volume, which is expanded during experiments, i.e. the volume between V_1 and V_2 is about 250mm^3 . Subpressure vessel R is connected to V_2 via PVC-tubing. It has a volume of about 1l, which is four times bigger than the expanded volume.

7.2 Humidifier

The humidifier HUM is connected to the expansion chamber via V_1 . It consists of a double-walled cylindrical stainless steel vessel with a length of about 30cm, an inner diameter of about 4.5cm and a total volume of approximately 480cm^3 . Tapered at both ends by 30° , the humidifier has an in-/outlet diameter of 10mm, which equals the inner diameter of V_1 , AI and A.

To keep HUM at constant temperature, thermostating liquid circulates around the outer wall. The temperature of the liquid is controlled by means of a thermostat (see section 8.2). By removing the screw mounted and O-ring sealed inlet part (red part in figure 7.4), the inside of HUM can be covered with blotting paper (VWR, SARTFT2-518580600N). This

paper is wetted with the humidification liquid (in this study n-propanol). The wet surface has a total area of approximately 425cm^2 .

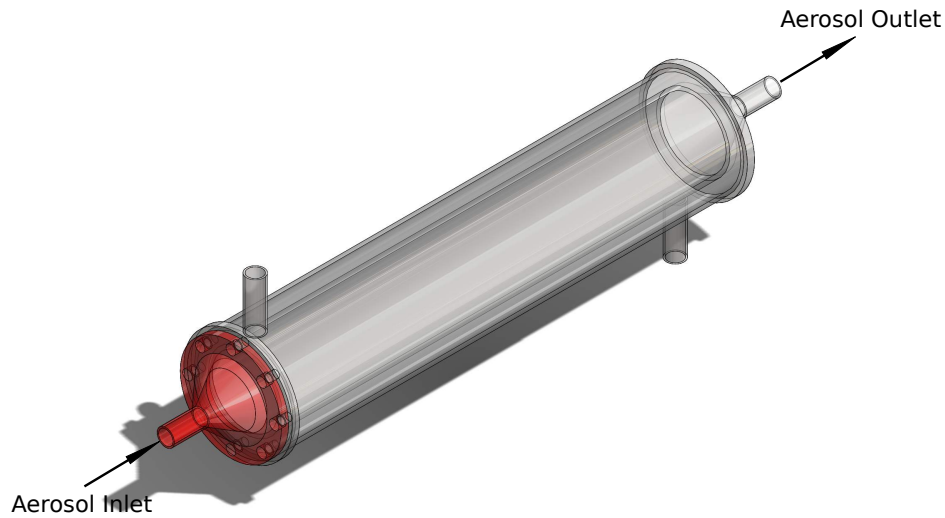


Figure 7.4: 3 dimensional drawing of the humidifier.

Flowrate dependent humidification by means of HUM has been tested using a humidity probe (Driesen + Kern Model DKRF400) with an accuracy of about 2% for relative humidities (RH) ranging from 20 to 80%. A schematic diagram of the test setup is shown in figure 7.5. Measurements of the humidity at the exit of HUM show, that a vapor saturation above 99.8%

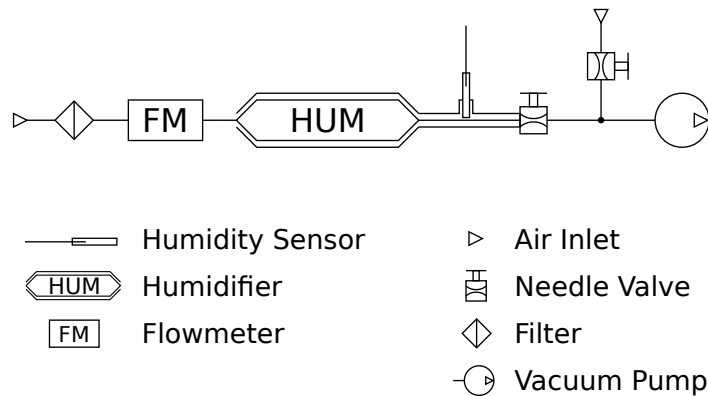


Figure 7.5: Schematic diagram of the experimental setup used to test the humidifier.

can only be achieved at flowrates below 1l/min . To increase the aerosol intake flow rate, while keeping the vapor saturation ratio at the exit of HUM close to one, we tried to install two identical humidifiers in parallel. However, it turned out, that this setup increases inlet losses. Thus, all experiments presented here, were conducted using only one humidifier. To achieve low inlet losses, the aerosol intake flow rate was set to 9l/min by means of a critical

orifice for most experiments. Clearly, the high flow rate results in undersaturated conditions at the exit of HUM. However, vapor supersaturation at the end of the expansion can still be achieved by choosing sufficiently high pressure drops.

7.3 Integrated optics assembly

Light flux measurements described in section 5.2 are performed by means of the integrated optics assembly (IOA). The IOA basically consists of two identical optical plates (OP) and the laser inlet system.

A detailed list of optical elements installed in the IOA can be found in appendix B.2.

7.3.1 Optical plates

Each OP comprises a cover (OP1) and a base (OPs) plate made from glassfibre-reinforced plastic (PEEK) with very low thermal expansion coefficient. Thus, once attached to the expansion chamber, the alignment of optical elements is not affected by differences between temperatures of chamber and surrounding air. In order to reduce reflectivity the originally yellow material was blackened using one layer of black ink (*Edding T100*) on top of one layer of graphite (*PITT Graphite Pure 2900*) on top of another layer of black ink. Since the ink left a somewhat reflecting surface the blackened plates were finally coated with a transparent top coat (*Manhattan Pro Matt Top Coat*) that produces an even matt finish. The effect achieved by the top coat is shown in Appendix A.1, figure A.1. For the same reason, rectangular and circular stops, and mounts for lenses, pinholes, polarization filter, mirrors and photo sensors, were blackened in the same way. Additionally anti-reflection coated lenses are used (VIS 0°, Edmund Optics).

The OP, which is used for measurements of transmitted and scattered light fluxes, is equipped with lenses, pinholes, rectangular stops, circular stops, deflecting mirrors and photo sensors (see section 5.2.2). As can be seen from figure 7.6 all optical elements can be inserted in rectangular recesses of OP2. To enable alignment of lenses (L2) and pinholes (P2), spring mounted pin assemblies (S) are installed below these optical components.

L2 and P2 are adjusted via fine thread screw assemblies L1 and P1, respectively, mounted in OP1. As can be seen from figure 7.7 one screw is used for lenses and two screws for pinholes. The screws press L2 and P2 against S in OP2. Thus, lenses can be adjusted vertically and pinholes both horizontally and vertically with respect to the plane of observation.

The other OP bears the support of the laser inlet system and is equipped with a polarization filter and two cylindrical lenses (see section 5.2.1). In principle, lens-pinhole detector systems are also installed here (measurements of backward scattered light fluxes). However backward scattering signals showed very low signal-to-noise ratios and were therefore not considered in the present work.

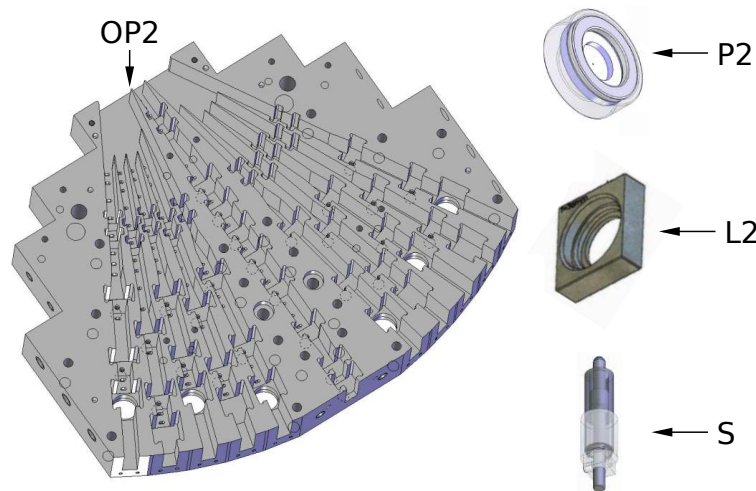


Figure 7.6: 3 dimensional drawing of bottom plate OP2, pinhole P2, lens L2 and spring mounted pin assembly S.

7.3.2 Laser inlet system

The laser inlet system (LIS), attached to OP, consists of a blue continuous-wave solid-state laser LAS, three deflecting mirrors M1-M3, a photo diode PD and a beam expander BE (4x expansion). Figure 7.8 shows a 3 dimensional drawing of the LIS. LAS is mounted on an aluminum plate with cooling fins, which can be adjusted in height using a screw with double thread. The beam leaving the laser source (JSDU, Model FCD488) has a wavelength of 488nm, a diameter of 0.71mm and a power of 20mW. Blue laser light was chosen instead of red (*classical* SANC, Preining et al. (1981)) to decrease visible droplet sizes. The laser beam is first deflected by a semi-transparent mirror (M1). Behind that mirror PD monitors Φ'_i during measurements. This provides information about the beam stability. Moreover light attenuation by particles, which already scatter light before expansion, can be accounted for by comparing Φ'_i and Φ_t , measured before and transmitted through the expansion chamber, respectively.

After M1 the beam is expanded by a factor of 4. In this way, the scattering light volume is increased, which, in turn, lowers the limit of detectable number concentrations. Then M2 and M3 direct the expanded beam towards OP attached to the laser inlet side of the expansion chamber. Pictures of the LIS can be found in figure Appendix A.1 figureA.3.

7.3.3 Alignment

The IOA is attached to the expansion chamber as shown in figure 7.9. To adjust the laser beam relative to the expansion chamber, the lens-pinhole detector system measuring Φ_t is replaced by a circular stop. Correct alignment is achieved, if the laser centrally passes the

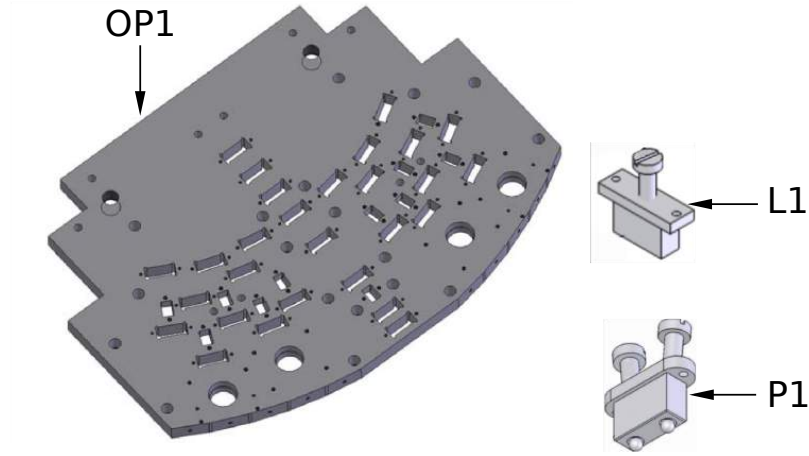


Figure 7.7: 3 dimensional drawing of cover plate OP1, and lens and pinhole alignment assemblies, L1 and P1, respectively.

circular stop.

Once the laser beam is in the right position, measuring systems for scattered light are adjusted by means of L1 and P1. To this end, the expansion chamber is continuously flushed with diethyl-hexyl-sebacat (DEHS) droplets ($d_p \approx 800\text{nm}$) using the setup shown in figure 7.10. DEHS droplets are generated by atomizing a 3.5% DEHS in isopropanol solution using a collision atomizer operated at 2.5bar. To get a more monodispersed particle size distribution, a LaMer system (La Mer et al., 1950), consisting of one heater ($T = 205^\circ\text{C}$) and one cooler ($T = 20^\circ\text{C}$) is used subsequently. Thereby DEHS droplets first evaporate in the heater, before they condense slowly and uniformly in the cooler.

After alignment, the correct angular orientation can be checked by comparing experimental and theoretical scattered light fluxes during droplet growth.

7.3.4 Calibration

Droplet number concentrations are determined optically applying the multi-angle Constant Angle Mie Scattering (mCAMS) method (see section 5.3). Thereby droplets growing inside the expansion chamber are illuminated by a polarized laser beam. The light flux Φ_s scattered by these droplets is measured at five different angles as a function of time. Simultaneously, the light flux Φ_t transmitted through the chamber is monitored. According to Mie theory the heights of experimentally obtained, normalized scattered light maxima are related to droplet number concentrations.

In order to determine the constant of proportionality k_{PMT} between measured signals in

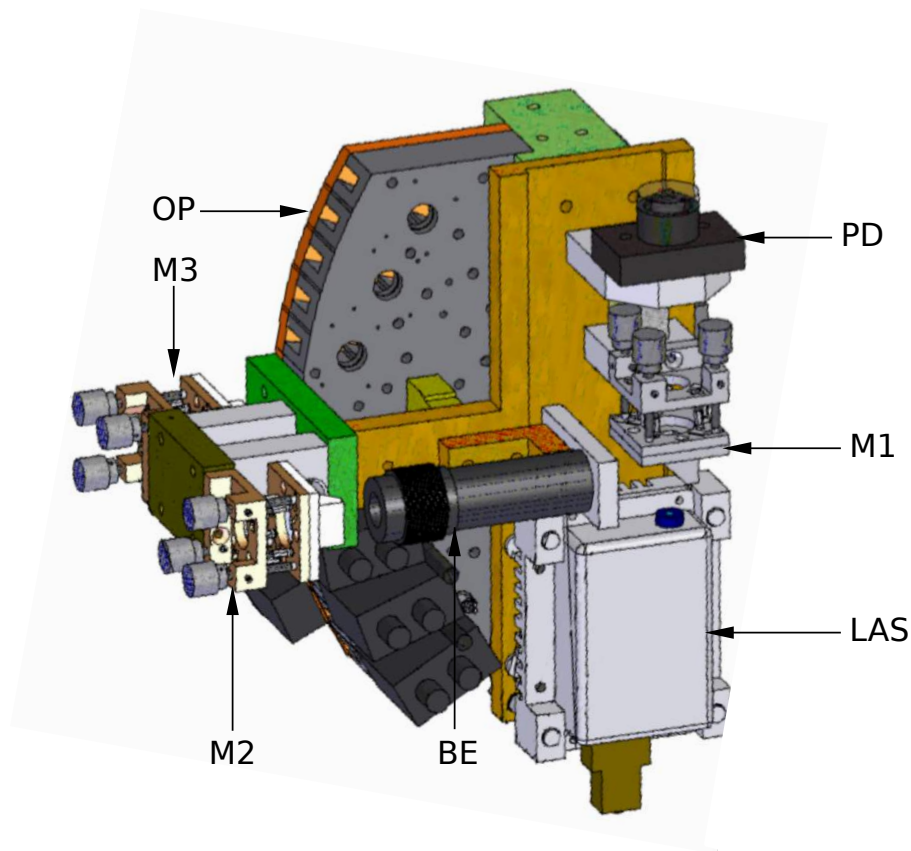


Figure 7.8: 3 dimensional drawing of the laser inlet system, consisting of a solid state laser LAS, three deflecting mirrors M1-M3, a photo diode PD and a beam expander BE, all attached to the optical plate OP.

Volts and number concentrations in cm^{-3} , photomultipliers are calibrated by means of the EXT method (see section 5.3.2). Calibration measurements have been performed using the experimental setup shown in figure 7.11. Quantitative light attenuation measurements (EXT method) require droplet number concentrations in the order of 10^5cm^{-3} . Thus the entire size distribution of particles, generated in a tube furnace, is used for calibration measurements³. A typical set of raw data obtained with silver seed particles and n-propanol vapor at a PMT control voltage of 0.7V is shown in figure 7.12. It can be seen, that the position of the first Mie maximum shifts towards earlier times, i.e. smaller droplet diameters, with increasing light scattering angle θ . This observation is in agreement with theoretical predictions, and indicates good alignment of the optical system. Moreover, for θ ranging from 15° to 30° , the height of the first Mie maximum decreases with increasing θ , which is again in agreement with theoretical predictions. The 10° curve, however, is not in line with this trend. This is

³As long as particles do not scatter light before expansion, polydispersity will not affect this kind of measurements.

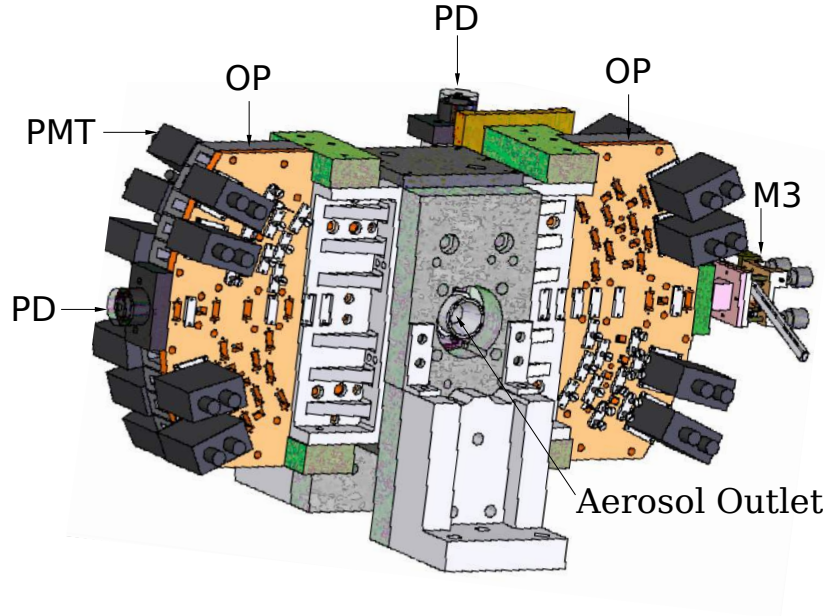


Figure 7.9: 3 dimensional drawing of the integrated optics assembly being attached to the expansion chamber. The IOA consists of two optical plates OP equipped with photomultiplier tubes PMT and photo diode PD, and the laser inlet system (not visible in that particular view).

due to the fact, that the aperture of the detector system installed at 10° is one third that of those installed at $15^\circ - 30^\circ$.

Suppose that t' is the time were the first Mie maximum appears on an experimental curve, and $\mathcal{A}(t')$ is the light attenuation measured at that time. Using Mie theory the droplet diameter d_p corresponding to the first Mie maximum can be calculated. Thus, d_p and $\mathcal{A}$ are known and the droplet number concentration N_c can be calculated from the Beer-Lambert law, which might be written as

$$N_c = -\frac{4 \ln \mathcal{A}}{\pi d_p^2 Q_{\text{EXT}} d_{\text{CH}}}. \quad (7.1)$$

Knowing N_c , the calibration constant k_{PMT} (see section 5.3.2) is obtained from

$$k_{\text{PMT}} = \frac{N_c}{\Phi_s(t')}. \quad (7.2)$$

The procedure of finding k_{PMT} has to be conducted for each photomultiplier. This yields ten different values, since light fluxes are measured to both sides (L,R) of the laser beam axis, at five different scattering angles ranging from 10° to 30° . At a PMT control voltage

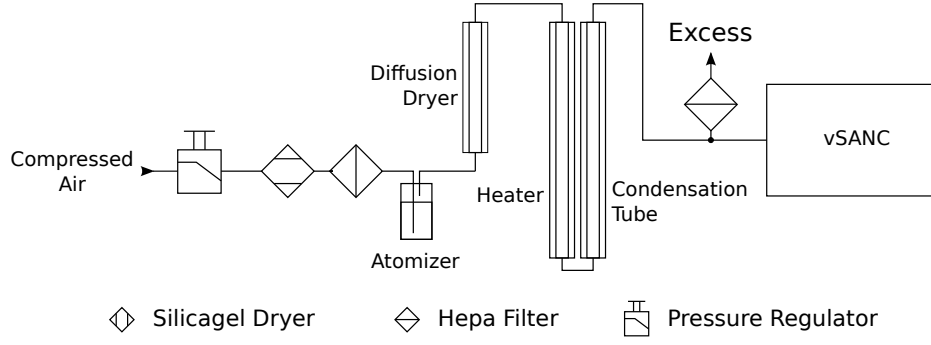


Figure 7.10: Experimental setup for the alignment of the integrated optics assembly.

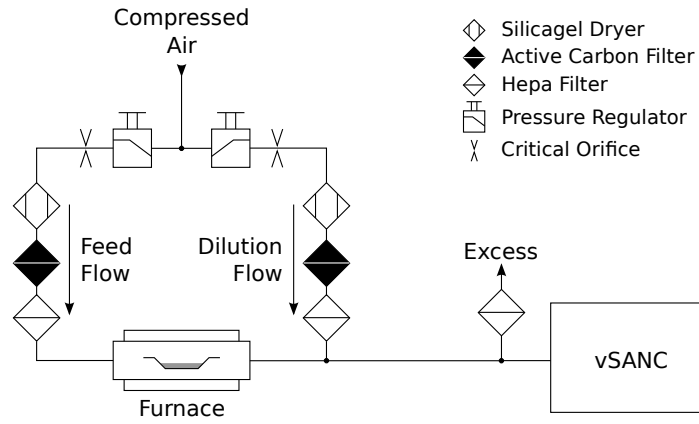


Figure 7.11: Experimental setup for PMT calibration

of 0.7V, typical values for k_{PMT} are in the order of $10^5 \text{cm}^{-3} \text{V}^{-1}$ for 10° , 15° and 20° , and $10^6 \text{cm}^{-3} \text{V}^{-1}$ for 25° and 30° .

After normalizing experimentally obtained scattered light fluxes by multiplying attenuation corrected scattered light fluxes $\tilde{\Phi}_s$ using k_{PMT} , the height of the first maximum directly gives the droplet number concentration. Figure 7.13 shows the set of normalized, attenuation corrected scattered light fluxes $\check{\Phi}_s$ corresponding to raw data shown in fig. 7.12. As can be seen from this graph, the droplet number concentration is about $4.4 \cdot 10^5 \text{cm}^{-3}$. Moreover, agreement between independently normalized scattered light fluxes underlines that the optical system is well aligned.

The mCAMS method of determining N_c has the advantage, that it can be applied to a wider range of number concentrations than the EXT method. Regarding N_c in the order of 10^4cm^{-3} , $\mathcal{A}(t')$ is above 99%, which makes its quantitative determination practically impossible (see figure 7.14). For N_c above $2 \cdot 10^6 \text{cm}^{-3}$, on the other hand, multiple scattering increases the transmitted light flux with respect to theoretical predictions based on the Beer-Lambert law. However, Filipovicova (1996) has shown, that the effect of multiple scattering on scattered light fluxes is eliminated by normalizing Φ_s with respect to Φ_t (or to $\mathcal{A}$). Thus

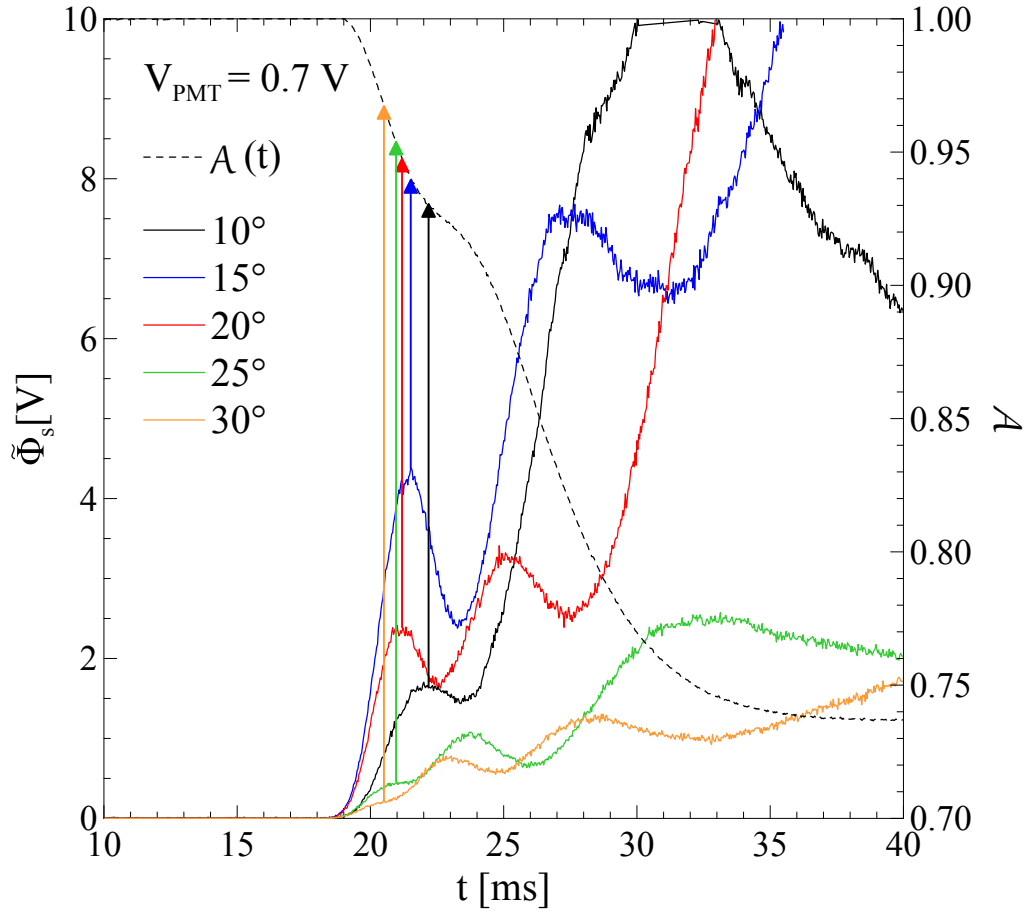


Figure 7.12: Attenuation corrected experimental scattered light fluxes $\tilde{\Phi}_s$ (solid lines) measured at a photomultiplier bias voltage V_{PMT} of 0.7V. The dashed line corresponds to experimentally determined light attenuation $\mathcal{A}$ during droplet growth. Arrows point towards $\mathcal{A}(t')$ data at different light scattering angles θ .

linear correspondence between mCAMS signal and actual number concentration is still given at comparatively high N_c . Figure 7.15 shows the reduction of EXT concentration relative to mCAMS concentration as N_c exceeds about $2 \cdot 10^6 \text{cm}^{-3}$. In the present study, PMT control voltages V_{PMT} have been adapted to actual number concentrations. The higher N_c the lower V_{PMT} was set. Thus k_{PMT} was not only determined for each photomultiplier tube, but also as a function of bias voltage V_{PMT} . Figure 7.16 shows normalized calibration constants $\tilde{k}_{\text{PMT}}$ as a function of V_{PMT} . In order to compare bias voltage dependent changes in k_{PMT} to the PMT gain given in the sensor data sheet, k_{PMT} values were normalized to achieve the same value for $\tilde{k}_{\text{PMT}}$ and PMT gain at $V_{\text{PMT}} = 0.7\text{V}$, i.e. $1.4 \cdot 10^4$. Thus normalized experimentally determined calibration constants $\tilde{k}_{\text{PMT}}$ are related to k_{PMT} as follows:

$$\tilde{k}_{\text{PMT}} = \frac{k_{\text{PMT}}}{\mathcal{K}} : \tilde{k}_{\text{PMT}} \Big|_{V_{\text{PMT}}=0.7\text{V}} = 1.4 \cdot 10^4.$$

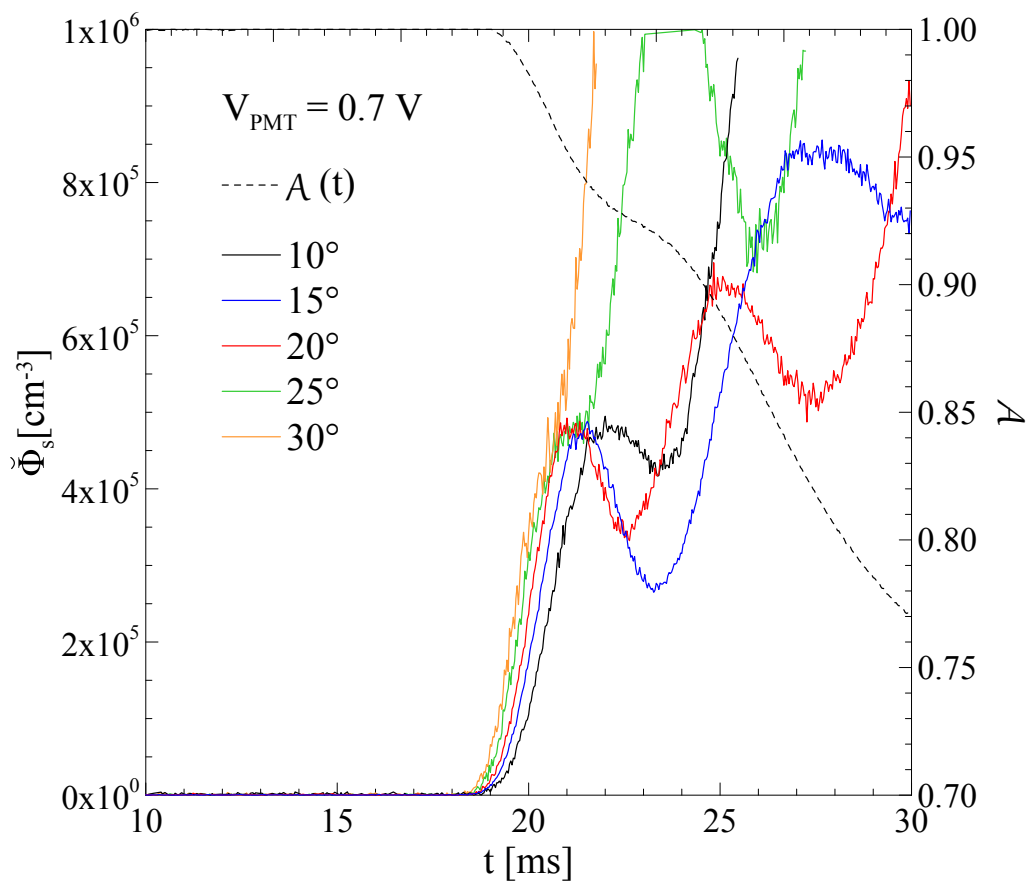


Figure 7.13: Attenuation corrected, normalized scattered light fluxes $\check{\Phi}_s$ (solid line) and corresponding light attenuation $\mathcal{A}$ (dashed line). $N_c \approx 5 \cdot 10^5 \text{cm}^{-3}$

The solid red line in figure 7.16 corresponds to the PMT gain given in the sensor data sheet. The crosses represent $\tilde{k}_{\text{PMT}}$ determined at different light scattering angles θ . As can be clearly seen from this graph, normalized calibration constants nicely agree with the PMT gain curve. Absolute values of k_{PMT} increase by about two orders of magnitude for control voltages ranging from 0.7V to 1.1V. Thus, bias voltage dependent changes of calibration constants do not have to be determined experimentally but can be calculated from PMT gains specified in the sensor data sheet.

Another issue regarding the determination of k_{PMT} is its dependency on refractive index m of the growing droplets. Suppose that $k_{\text{PMT}}(m_1)$ is the calibration constant determined for droplets with refractive index m_1 . From Mie theory, the height of the first Mie maximum for droplets with refractive index m_1 and m_2 , $\Phi_s^{\text{theory}}(m_1)$ and $\Phi_s^{\text{theory}}(m_2)$, can be calculated. Thus the calibration constant for droplets with refractive index m_2 is given by

$$k_{\text{PMT}}(m_2) = k_{\text{PMT}}(m_1) \frac{\Phi_s^{\text{theory}}(m_2)}{\Phi_s^{\text{theory}}(m_1)}.$$

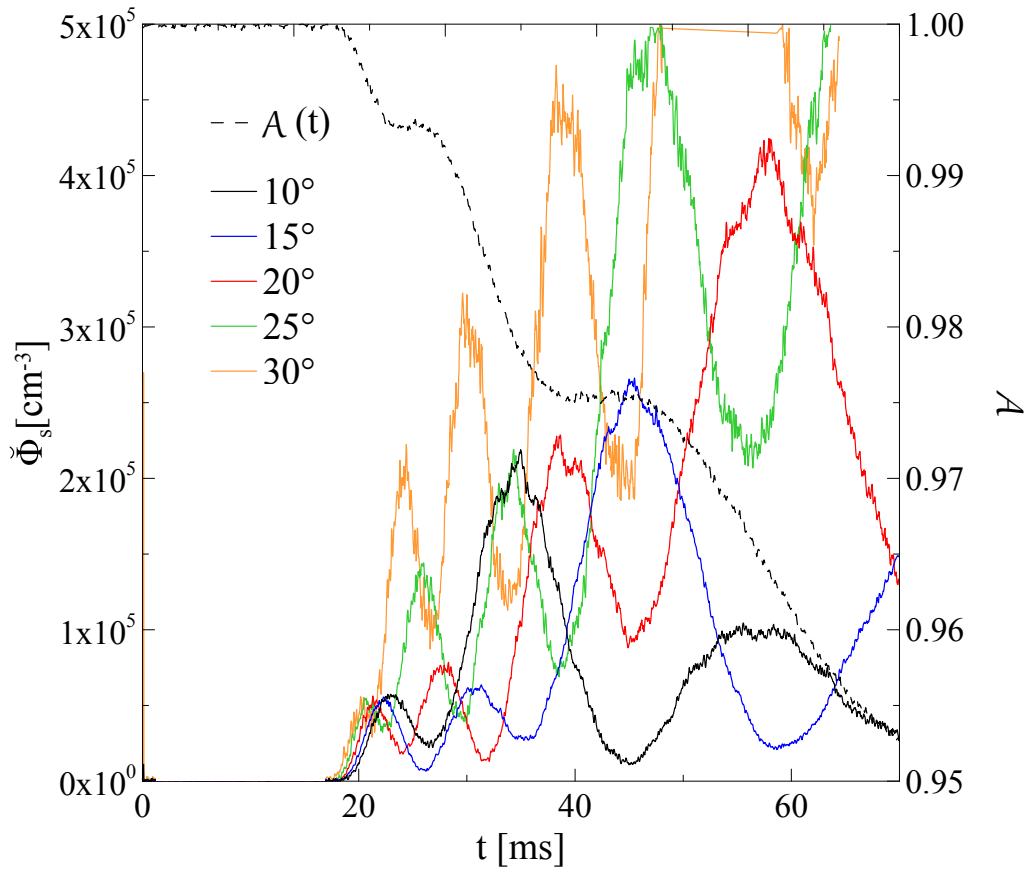


Figure 7.14: Typical set of normalized, attenuation corrected scattered light fluxes $\check{\Phi}_s$ measured at light scattering angles $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ$ and 30° for ambient aerosol particles growing in n-propanol vapor. The droplet number concentration is about $5 \cdot 10^4 \text{cm}^{-3}$.

In summary, it can be said, that the calibration k_{PMT} depends on photomultiplier tube PMT, control voltage V_{PMT} and refractive index m . $k_{\text{PMT}}(\text{PMT})$ has to be determined experimentally at known V_{PMT} and m . After that, changes in k_{PMT} resulting from changes in V_{PMT} and m can be calculated using the sensor's data sheet and Mie theory, respectively. Whenever the instrument has been moved, the optical system needs to be aligned and calibrated first before performing actual measurements. This usually takes about one week.

7.4 Instrument housing

The vSANC consists of three housings, i.e. the measuring head, the supply box and a liquid thermostat. The dimensions of these housings are listed in table 7.1. The commercially available liquid thermostat (*Lauda*, Model VC1200) is used to regulate the humidifier temperature (see section 8.2).

Located inside the supply box are vacuum pumps Exh and Evac (see section 6), a critical

	Width [cm]	Height [cm]	Depth [cm]
Measuring head	80	105	135
Supply box	80	65	60
Thermostat	45	60	55

Table 7.1: Dimensions of instrument housings

orifice regulating the aerosol intake flowrate and a compressor. On top of this housing driers and filters are mounted.

A three dimensional drawing of the measuring head is shown in figure 7.17. Expansion chamber EXP and integrated optics assembly (IOA) are centered in the measuring head. As part of the instrument inlet humidifier HUM and inlet valve V_1 are installed approximately 70cm above ground. At the outlet of EXP, expansion valve V_2 and subpressure vessel R are located. All other devices shown in figure 7.17 are discussed in the following chapter.

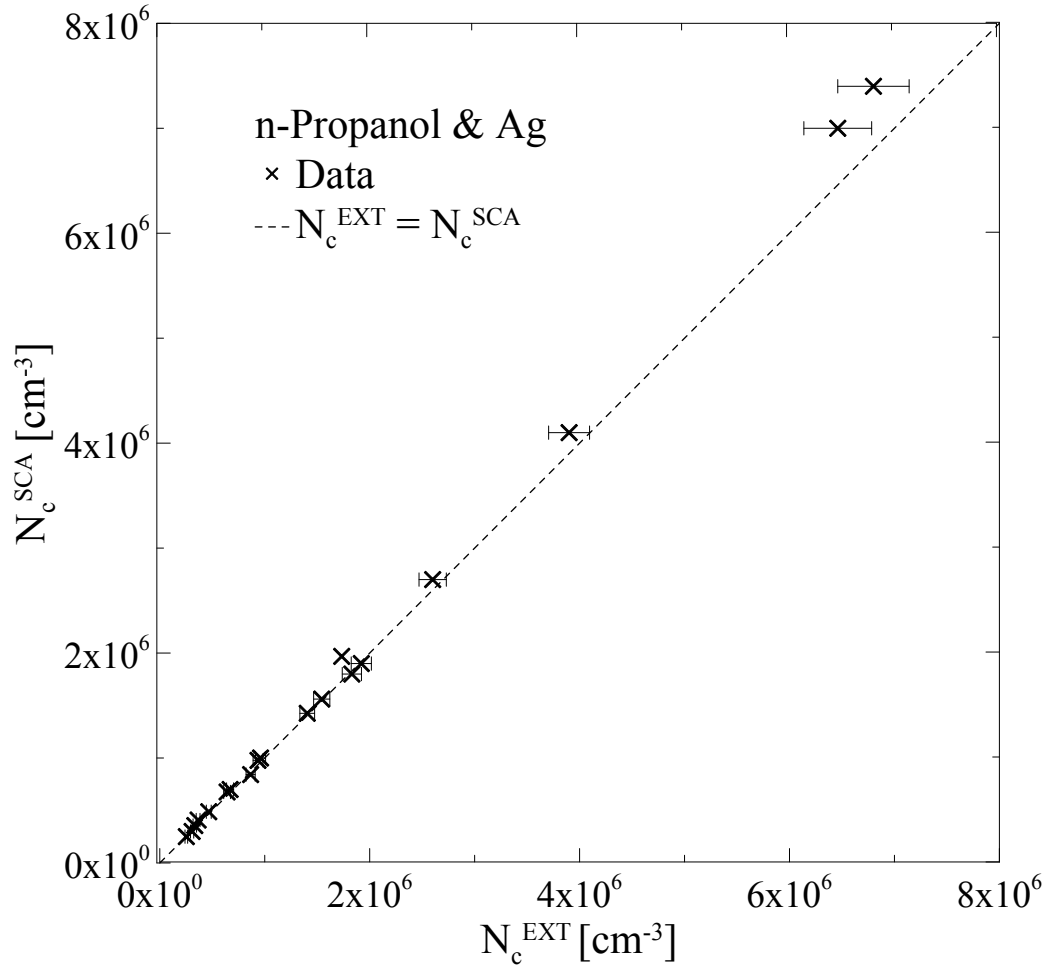


Figure 7.15: Number concentrations determined using the mCAMS method, N_c^{SCA} , vs. number concentrations determined by means of the EXT method, N_c^{EXT} . Experiments were performed with silver seed particles in n-propanol vapor. It can be seen, that for $N_c > 6 \cdot 10^6 \text{cm}^{-3}$ the number concentration determined by means of the mCAMS method, i. e. N_c^{SCA} , exceeds N_c^{EXT} , the number concentration determined using the EXT method.

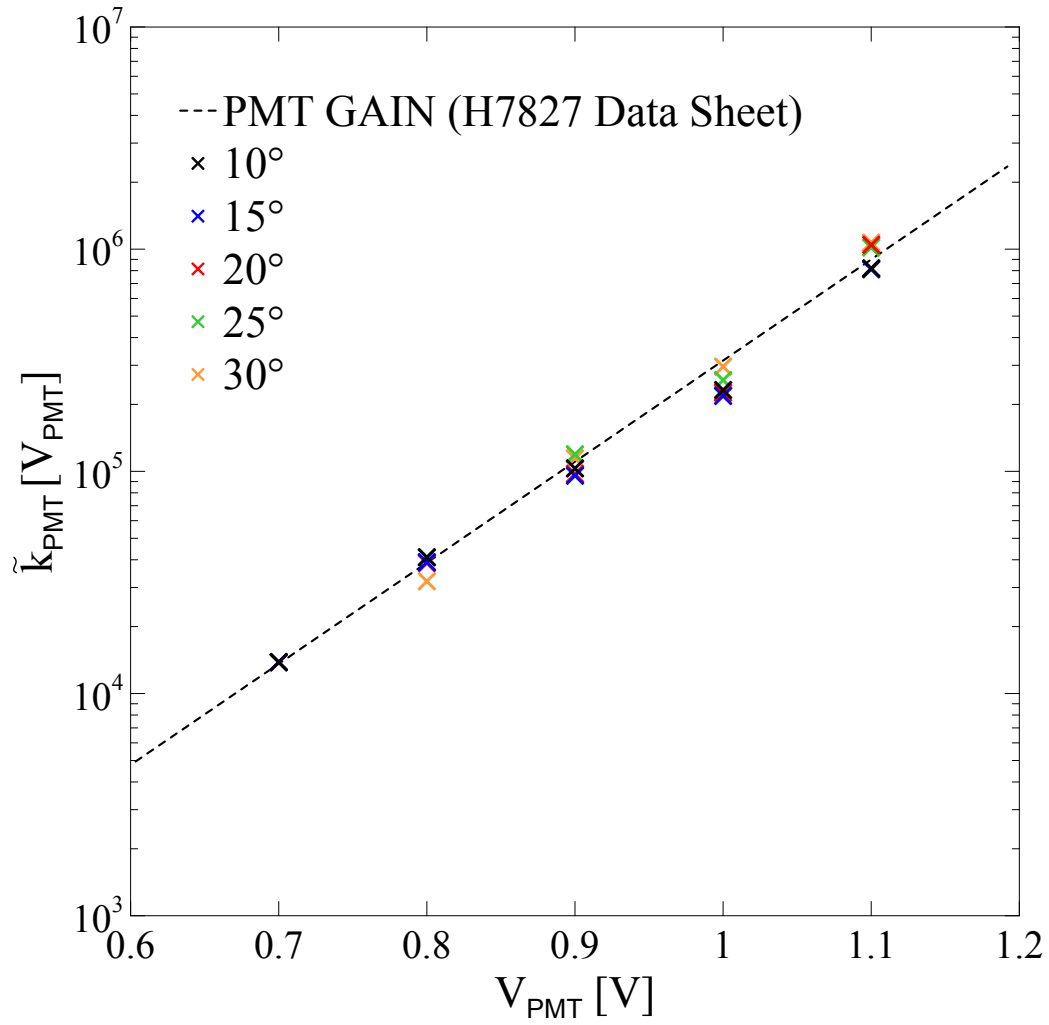


Figure 7.16: Normalized calibration constants $\tilde{k}_{\text{PMT}}$ (crosses) and photomultiplier (PMT) gain according to the H7827 data sheet (dashed line) as a function of bias voltage V_{PMT} .

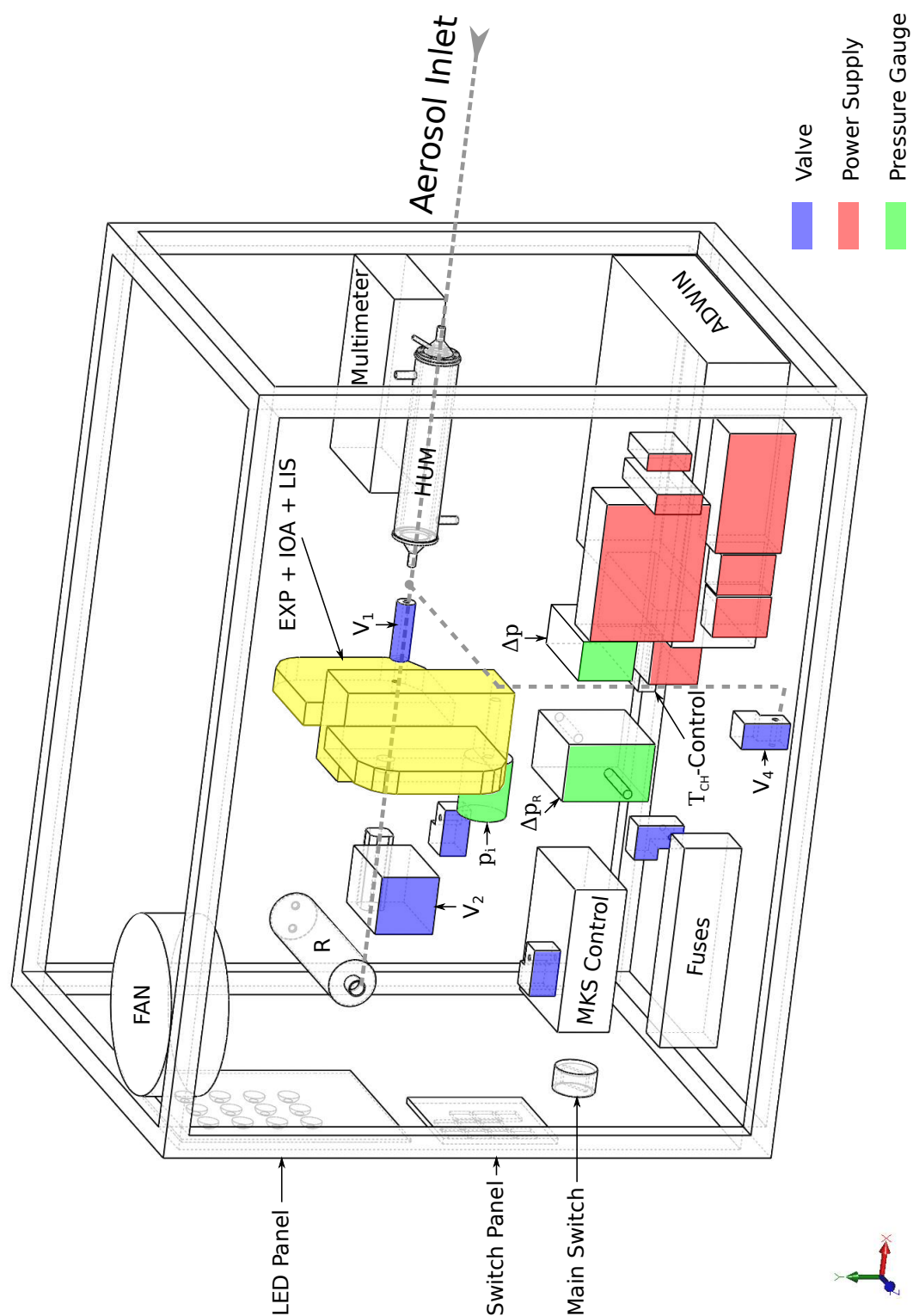


Figure 7.17: 3D drawing of the measuring head

analogue voltage. This makes accurate determination of p_i and Δp_R possible. Regarding measurements of p_i analogue signals ranging from 0V to 10V correspond to total gas pressures ranging from 0mbar to 1333mbar. Whereas the same voltage range corresponds to pressure changes Δp_R ranging from 0mbar to 1000mbar.

Since capacitance pressure transducers are too slow to measure the pressure drop during fast expansion, a Piezo sensor is used to measure Δp . It rapidly converts changes in pressure to electrical charges. The Piezo sensor is directly connected to the **charge meter**, that converts the charge displacement into an analogue voltage. The **charge meter** is configured by means of a tailor-made driver implemented in the LabView code **MAIN.vi**, which is running on the **process control unit**. To achieve high resolution of the pressure edge the entire voltage range (−10 to 0V) is set to cover pressure drops ranging from −500 to 0mbar.

Looking at figure 8.1 it can be seen that analogue pressure signals measured during data acquisition (DAQ) are digitalized in the **ADWIN** unit, before being transferred to the **process control unit**. To this end, the software **AIN.bas** runs on the **ADWIN** system. On the other hand the digital setpoint value Δp_R^{SET} , defined in **Main.vi** is DA converted by means of the software **AOUT.bas** running on the **ADWIN** too.

List of Components

- MKS Control Unit, Type 250 E
- MKS Baratron Absolute, Type 628 A ($p_i : 0 \rightarrow 10V \hat{=} 0 \rightarrow 1333\text{mbar}$)
- MKS Baratron Differential, Type 220 D ($\Delta p_R : 0 \rightarrow 10V \hat{=} 0 \rightarrow 1000\text{mbar}$)
- MKS Flow Control Valve, Type 248 A
- Kistler Quartz Pressure Sensor, Type 7031 ($\Delta p : -10 \rightarrow 0V \hat{=} -500 \rightarrow 0\text{mbar}$)
- Kister Charge Meter, Type 5015

Required Software

- **MAIN.vi**
- **AOUT.bas**
- **AIN.bas**

8.2 Temperature measurement and control

Humidifier and expansion chamber are thermostated using coolant and Peltier elements, respectively. To avoid vapor losses due to condensation along the inlet line, the humidifier temperature is always set to be at least 2°C below the chamber temperature.

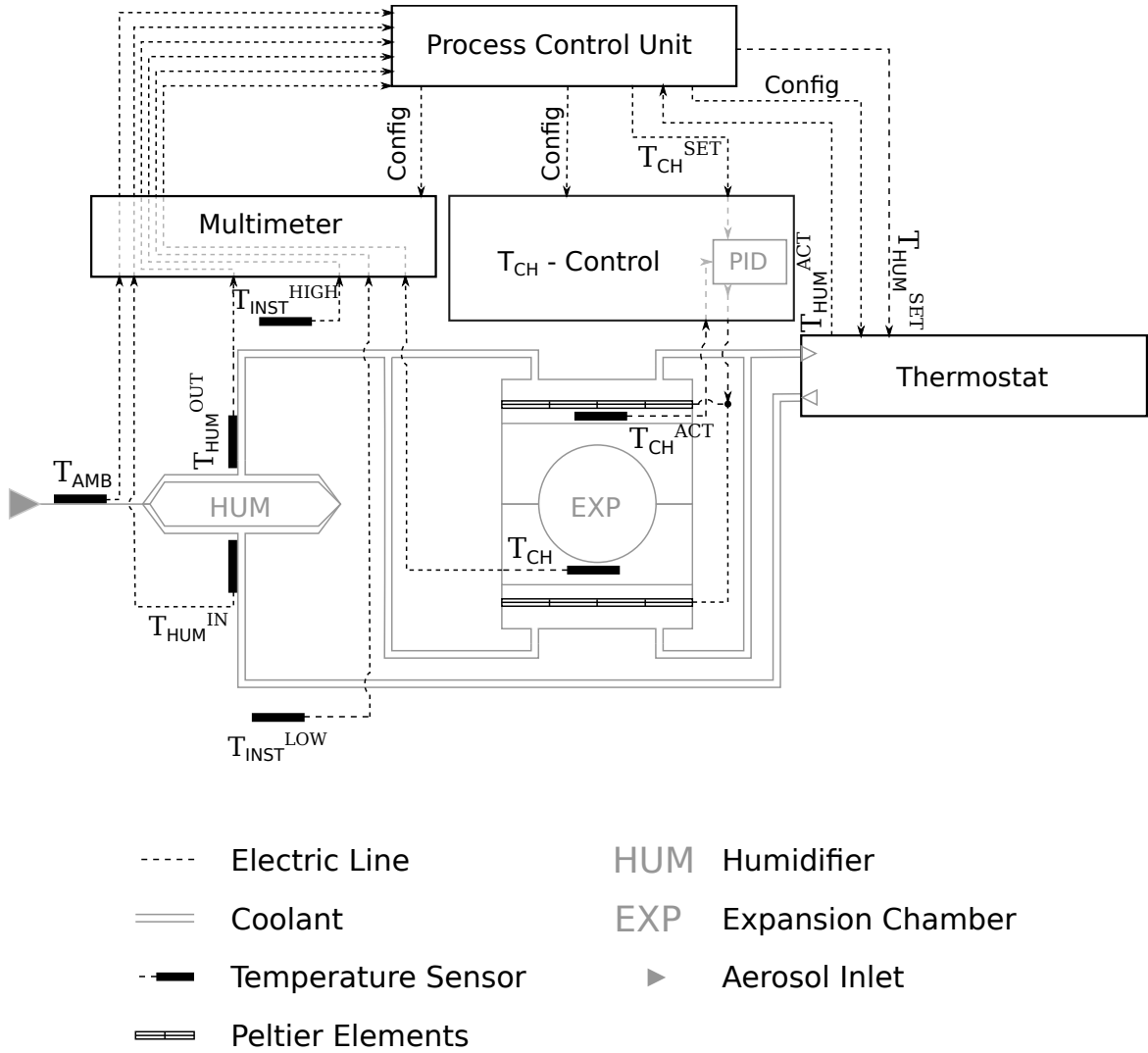


Figure 8.2: Temperature measurement and control flow chart

The temperature of the coolant, $T_{\text{HUM}}^{\text{ACT}}$, is controlled using a liquid thermostat, which is configured by means of the tailor-made LabView code `TEMP.vi`, running on the process control unit (PCU). The setpoint value, $T_{\text{HUM}}^{\text{SET}}$ for temperature regulation is set in `TEMP.vi`, too. Accurate measurements of T_{HUM} are performed using two PT100 temperature sensors. One measures the temperature of the cooling liquid before it enters the humidifier $T_{\text{HUM}}^{\text{IN}}$. The other measures $T_{\text{HUM}}^{\text{OUT}}$, the temperature of the coolant after leaving HUM. The humidifier temperature T_{HUM} is calculated as follows:

$$T_{\text{HUM}} = \frac{T_{\text{HUM}}^{\text{IN}} + T_{\text{HUM}}^{\text{OUT}}}{2}.$$

The temperature of the expansion chamber, T_{CH} , is regulated via eight Peltier elements using a temperature controller (T_{CH} -Control) with an integrated PID module. The PID module minimizes the difference between setpoint value $T_{\text{CH}}^{\text{SET}}$ and measured value $T_{\text{CH}}^{\text{ACT}}$ by regu-

lating the current through the thermoelectric coolers. PID parameters and setpoint values are defined in the `LT-interface` software of the temperature controller running on the PCU. A NTC sensor measuring $T_{\text{CH}}^{\text{ACT}}$ is installed in an aluminum block, that is placed between Peltier elements and expansion chamber. The other side of the Peltier elements (facing away from EXP) is cooled using the coolant that leaves HUM.

To calculate thermodynamic parameters at the end of the expansion (see section 4.1) accurate determination T_{CH} is required. Therefore another PT100 sensor is installed in the stainless steel block of the expansion chamber. The sensor is placed as close as possible to the actual measuring volume without disturbing it (see figure 7.2). Due to the high heat capacity of stainless steel a constant chamber temperature is reached slowly. However, this property also enables high temperature stability independent of short-term fluctuations.

Besides T_{CH} and T_{HUM} , temperatures $T_{\text{INST}}^{\text{LOW}}$ and $T_{\text{INST}}^{\text{HIGH}}$ inside the instrument, and ambient air temperature T_{AMB} are monitored with PT100 sensors.

The sensor measuring $T_{\text{INST}}^{\text{LOW}}$ is attached to the ventilation flap on the bottom side of the measuring head, whereas $T_{\text{INST}}^{\text{HIGH}}$ is measured close to the inlet valve V_1 . Thereby overheating of the instrument due to malfunction can be identified ($T_{\text{INST}}^{\text{LOW}} \ll T_{\text{INST}}^{\text{HIGH}}$). Moreover comparison between $T_{\text{INST}}^{\text{HIGH}}$ and T_{HUM} provides information about condensational losses along the unthermostated line connecting HUM and EXP.

T_{AMB} is monitored at the very beginning of the instrument inlet.

A multimeter converts changes in conductance of the PT100 sensors into digital signals, that are transferred to the PCU. The configuration of the multimeter is implemented in `TEMP.vi`, too. All system temperatures are acquired sequentially at a frequency of 1s^{-1} .

A typical set of measured temperature profiles is shown in figure 8.3. Measurements were conducted on the 6th of April 2014, during the spring measurement campaign in Hyytiälä, Finland. During this field campaign vSANC was installed in an air conditioned, ground level measurement container.

As can be seen from fig. 8.3 humidifier and expansion chamber temperatures show high stability despite fluctuations in T_{AMB} , $T_{\text{INST}}^{\text{LOW}}$ and $T_{\text{INST}}^{\text{HIGH}}$. Periodic changes of $T_{\text{INST}}^{\text{LOW}}$ and $T_{\text{INST}}^{\text{HIGH}}$ are caused by the air-condition system of the container. Not surprisingly, the temperature inside the instrument housing $T_{\text{INST}}^{\text{HIGH}}$ is slightly higher, than the temperature measured at the ventilation inlet of the housing, $T_{\text{INST}}^{\text{LOW}}$. Moreover the temperature of the coolant increases on the way from the thermostat, $T_{\text{HUM}}^{\text{ACT}}$, to the humidifier, T_{HUM} .

Whenever setpoint values for temperature control (shortly before noon in this graph) are changed, it takes less then 30 minutes for the humidifier temperature to stabilize, whereas it takes about 2 hours for T_{CH} . Thus temperature regulation should be started about 3 hours prior to actual measurements (see section 8.8).

List of Components

- Keithley Multimeter, Type

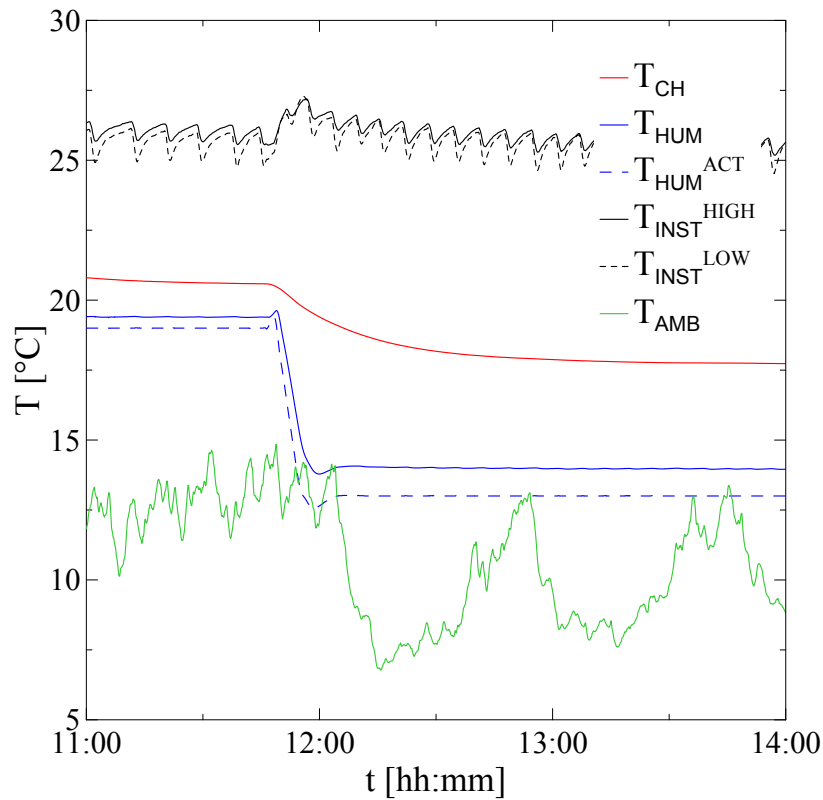


Figure 8.3: vSANC temperature profiles from 6th of April, Hyytiälä, Finland.

- Lauda Thermostat, Type
- Laird Temperature Controller(incl. NTC temperature sensor), Type
- 8 Peltier elements
- 5 PT100 temperature sensors, Type

Required Software

- TEMP.vi
- LT-Interface

8.3 Valve control

The timing of the measuring cycle described in section 6 is realized by means of a programmable microcontroller. To this end the software `VALVE.ino` is uploaded from the process control unit (PCU) using the microcontroller's `integrated development environment (IDE)`. The software assigns digital output 3-9 to valves $\tilde{V}_1 - V_6$, respectively ¹. Physically

¹ $\tilde{V}_1$ is the solenoid pilot valve of the pneumatic valve V_1

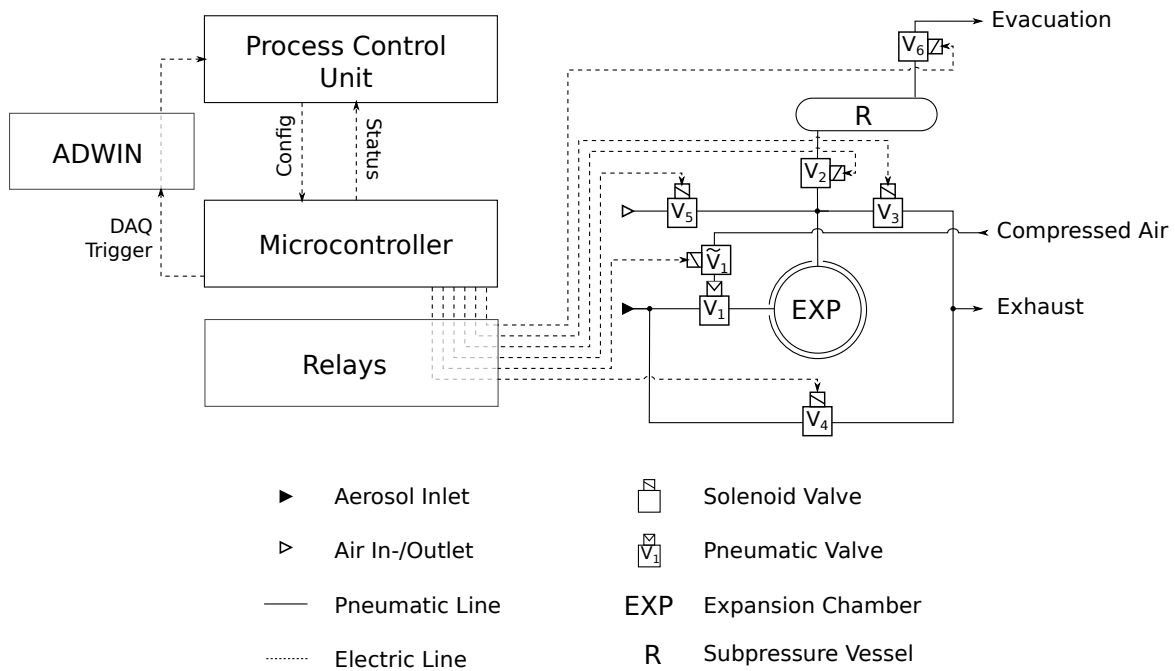


Figure 8.4: Valve control flow chart

DO3-DO9 are connected to relays, that control the power supply of the valves. In the currentless state (DO3-DO9 low) all solenoid valves are closed, whereas the pneumatic valve V_1 is open.

To avoid feedback, microcontroller and relays are electrically isolated by means of optocouplers. Tailor-made electric circuits are shown in Appendix C.3.

Besides cycle timing, `VALVE.ino` also includes the data acquisition trigger, that initiates data acquisition on the ADWIN system and on the process control unit. To this end digital output 10, which is connected to ADWIN, is set high 500ms prior to each expansion. Thus DAQ starts half a second before expansion valve V_2 is opened and lasts 1.5 seconds.

Once *flush* and *delay* times are set, the cycle is runs automatically and can be stopped after every full loop. While it is running individual cycle steps are displayed on the PCU.

List of Components

- Arduino UNO microcontroller
- 6 PCB relays, TE Connectivity Type PB114024
- 4 solenoid valves, Buschjost Type 8499498.9832.02400 ($V_3 - V_6$)
- 1 solenoid valve, Buschjost Type 8570500.8401.02400 (V_2)
- 1 pneumatic valve, Norgren Series 80 (V_1)
- 1 solenoid valve, Buschjost Type 82540 ($\tilde{V}_1 = \text{Pilot valve for } V_1$)

Required Software

- VALVE.ino

8.4 Light flux measurement and control

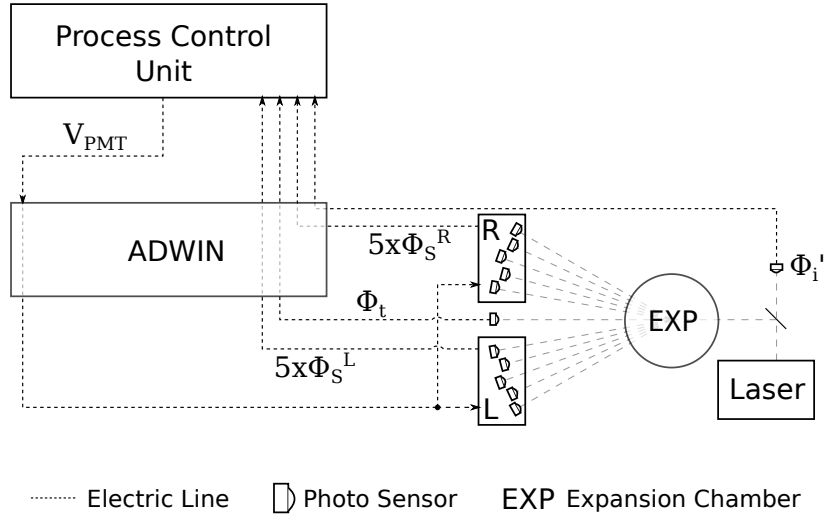


Figure 8.5: Light flux measurement and control flow chart

As already discussed in chapter 5 light fluxes scattered by the growing droplets Φ_s are measured at 5 different light scattering angles, to both sides (L and R in figure 8.5) of the laser beam axis. Simultaneously the light flux transmitted through the expansion chamber Φ_t and the incident light flux Φ_i' are monitored.

Scattered light fluxes are measured using photomultiplier modules (PMT) with integrated current-to-voltage conversion units. Depending on the droplet concentration inside EXP, the PMT sensitivities can be adjusted in `MAIN.vi` running on the process control unit (PCU). To this end, PMT control voltages, V_{PMT} , can be varied between 0.5V (low sensitivity) and 1.1V (high sensitivity). In line with the conversion of the setpoint value for pressure regulation, i.e. Δp_R^{SET} control voltages are digital-to-analogue (DA) converted by `AOUT.bas` running on the ADWIN system.

Photo diodes measuring Φ_t and Φ_i' are equipped with integrated amplifiers. The gain of those amplifiers is manually adjusted via potentiometers and stays constant during measurements. During data acquisition scattered light fluxes, the transmitted light flux and the incident light flux are measured, AD converted and acquired by the software `AIN.bas` running on the ADWIN system, before being transferred to the PCU.

A detailed list of the optical sensors can be found in B.2.

Required Software

- `MAIN.vi`
- `AOUT.bas`
- `AIN.bas`

8.5 ADWIN unit

The ADWIN Pro II unit (Jaeger Messtechnik) used for AD/DA-conversion is equipped with following modules:

- Processor module PRO-CPU-T11
- Digital-I/O module DIO-32
- Analog Output module AOut 8/16
- 2x Analog Input module AIn F-8/16.

The analog output module has 8 outputs, each providing voltages between $\pm 10\text{V}$, and DA conversion with 16 bit resolution. Outputs 1-6 are controlled by means of `AOUT.bas`, a *Basic* code running on the T11-processor. Thereby AOUT 1-5 are assigned to regulate photomultiplier sensitivities, whereas output 6 defines the setpoint for pressure regulation. The process structure of `AOUT.bas` (see Appendix C.1) enables changes in PMT sensitivities and Δp_R^{SET} anytime but during active data acquisition.

The second process `AIN.bas` running on the ADWIN system controls both analog input modules, `AIN_I` and `AIN_II`, and the digital I/O module. On `AIN_I` and `AIN_II` 16 individual signals (a detailed list of input configurations can be found in Appendix C.2), ranging from $\pm 10\text{V}$, are measured at a sampling rate of 30kHz^2 and digitalized with 16-bit resolution. The AD-conversion rate is 250ns .

Data acquisition on `AIN_I` and `AIN_II` is triggered by a digital high on bit 28 of the DIO module. Thus bit 28 is connected to DO 10 of the Arduino microcontroller (see section 8.3). On the other hand, bit 16 is configured as output, and is used to turn on the valve power supply.

Both processes, `AIN.bas` and `AOUT.bas`, are uploaded from the process control unit, whenever `Main.vi` is started. Setpoint values for AOUT 1-6 are also defined in `Main.vi`. Moreover the converted analog signals are visualized and pre-evaluated in `Main.vi`.

²This sampling rate is high enough to resolve the *ripple structure* on experimental Mie curves, while it keeps the quantity of data to be transferred to the PCU reasonably small.

8.6 Process control unit

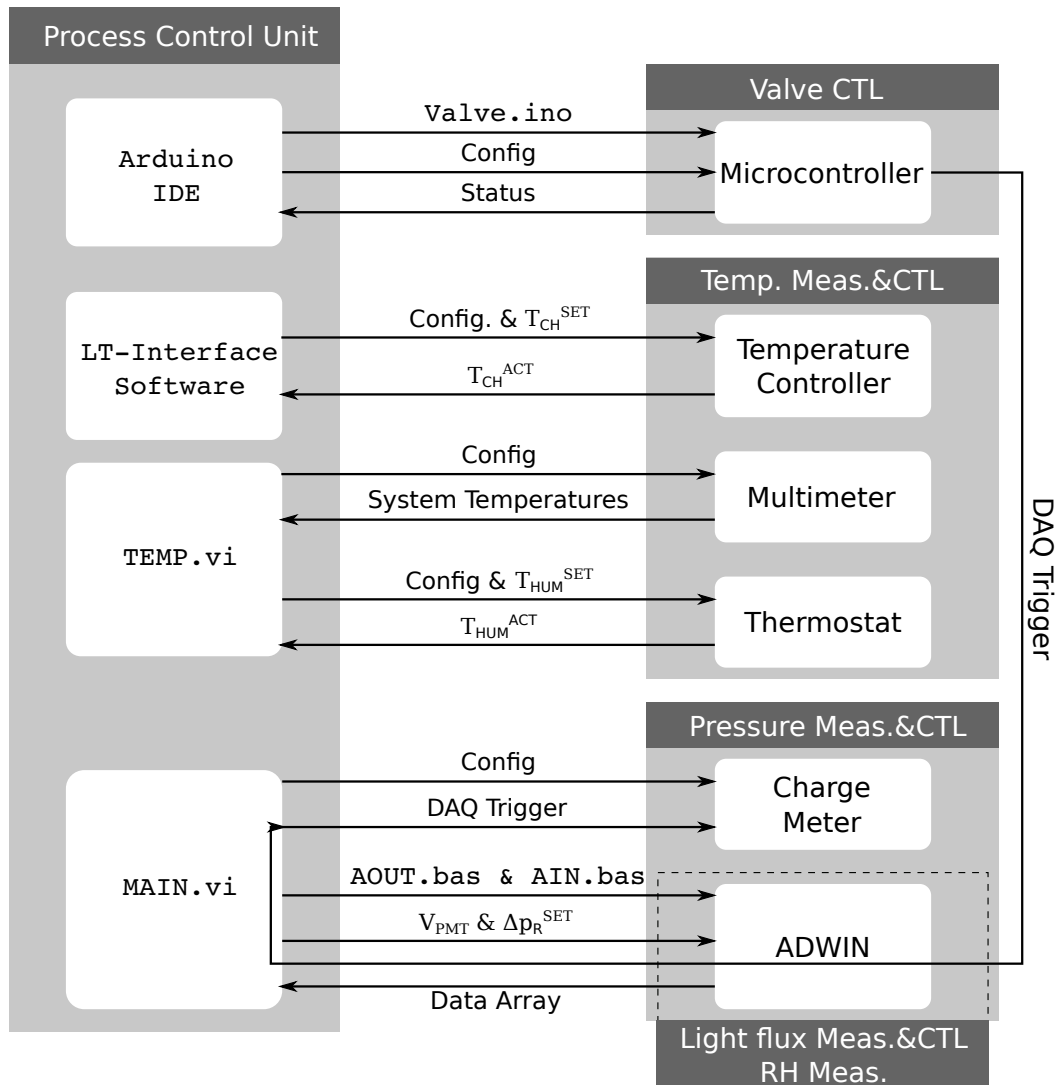


Figure 8.6: Process control flow chart

There are four programs running in parallel on the process control unit (see figure 8.6). Two of them, the Arduino's *integrated development environment* (IDE) and the LT-Interface Software, are commercially available, whereas TEMP.vi and MAIN.vi are tailor-made Lab-View codes.

Using Arduino's IDE, the software `Valve.ino`, which defines the valve cycle, is uploaded onto the microcontroller via USB (see section 8.3). Once `Valve.ino` is running, individual cycle steps (see section 6) are displayed on the IDE's built-in serial monitor. As can be seen from the `Valve.ino` source code (Appendix C.1) *flush* and *delay* time are initially set to 3s and 1.5s, respectively. These values can be changed on the serial monitor, either before

starting the cycle or after every full cycle. Typical values for *flush* and *delay* are 20s and 10s, respectively.

By means of the **LT-Interface** Software the temperature controller regulating the chamber temperature T_{CH} , is configured (see section 8.2) via RS232. Thereby PID parameters are adjusted and the setpoint value $T_{\text{CH}}^{\text{SET}}$ is defined. Typical values for (P,I,D) control are (12, 0.5, 5). Moreover $T_{\text{CH}}^{\text{ACT}}$ is displayed on a built-in graphical user interface.

The second program used for temperature measurement and control is the LabView code **TEMP.vi**. This software configures **multimeter** and **thermostat**. Thereby the **multimeter** is set to sequentially measure T_{CH} , T_{HUM} , $T_{\text{INST}}^{\text{LOW}}$, $T_{\text{INST}}^{\text{HIGH}}$ and T_{AMB} at a frequency of 1s^{-1} via GPIB. The **thermostat**, on the other hand, is connected to the PCU via RS232. The setpoint for temperature regulation of HUM is entered on the frontpanel of **TEMP.vi**. Moreover system temperature T_{CH} , T_{HUM} , $T_{\text{INST}}^{\text{LOW}}$, $T_{\text{INST}}^{\text{HIGH}}$ and T_{AMB} are displayed graphically, and saved to a buffer. When the program terminates, data from the buffer are saved in a **.txt** file, before the buffer is emptied. The created document contains system temperatures in the following order:

Column	1	2	3	4	5	6	7	8
Entry	Date	Time	$T_{\text{HUM}}^{\text{ACT}}$	T_{HUM}	$T_{\text{INST}}^{\text{HIGH}}$	T_{CH}	$T_{\text{INST}}^{\text{LOW}}$	T_{AMB}
Units	[dd/mm/yy]	[hh:mm:ss]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]

Table 8.1: Structure of a file created by **TEMP.vi**

The software **MAIN.vi** represents the core of process control. It uploads **AOUT.bas** and **AIN.bas**, the two processes defining AD/DA-conversion, onto the **ADWIN** system via Ethernet. Furthermore, a built-in instrument driver configures the **charge meter** (see Appendix C.4), that measures the total gas pressure change Δp inside **EXP**, via RS232.

On the frontpanel **PMT** control voltages V_{PMT} , sampling mode, humidification liquid and setpoints $\Delta p_{\text{R}}^{\text{SET}}$ for pressure regulation are entered. V_{PMT} can be adjusted between 0.6V and 1.1V on a virtual rotary switch.

If sampling mode *Constant* is selected, $\Delta p_{\text{R}}^{\text{SET}}$ remains constant. On the other hand, sampling mode *Scanning* causes $\Delta p_{\text{R}}^{\text{SET}}$ to alter among three different values, $\Delta p_{\text{R}}^1 < \Delta p_{\text{R}}^2 < \Delta p_{\text{R}}^3$. To improve measuring statistics, three measurements are performed at constant pressure drop, before $\Delta p_{\text{R}}^{\text{SET}}$ is changed.

It is necessary to adjust the humidification liquid on the frontpanel, because height and position of Mie extrema (see chapter 5) depend on the refractive index m of the growing droplets, too. Thus, to guarantee, that first maxima of experimental scattered light fluxes directly give the number concentration of droplets inside the expansion chamber, calibration constants k_{PMT} have to be adapted to the current refractive index m (see section 5.3).

Once V_{PMT} , $\Delta p_{\text{R}}^{\text{SET}}$, sampling mode and humidification liquid are defined, the measurement

can be started.

As soon as the data acquisition (DAQ) trigger is active (see section 8.3), `Main.vi` initiates measurements of Δp on the charge meter. Simultaneously the ADWIN system acquires the analog signals listed in Appendix C.1. Active data acquisition is visualized on the frontpanel by a virtual LED.

After 1.5s of DAQ, data acquired on the ADWIN are transferred to the process control unit via Ethernet. Here `MAIN.vi` adds a timestamp and performs the following data conversion steps:

1. Unit conversion:

$$\begin{aligned} p_i[\text{V}] \times 133.32 \left[\frac{\text{mbar}}{\text{V}} \right] &\rightarrow p_i[\text{mbar}] \\ \Delta p_{\text{R}}^{\text{ACT}}[\text{V}] \times 100 \left[\frac{\text{mbar}}{\text{V}} \right] &\rightarrow \Delta p_{\text{R}}^{\text{ACT}}[\text{mbar}] \\ -\Delta p[\text{V}] \times 50 \left[\frac{\text{mbar}}{\text{V}} \right] &\rightarrow \Delta p[\text{mbar}] \\ RH[\text{V}] \times 100[\text{V}^{-1}] &\rightarrow RH[\%] \end{aligned}$$

2. Conversion to absolute pressures:

$$\begin{aligned} \bar{p}_i &= \frac{1}{n} \sum_{n=0}^m p_i(n \cdot \Delta t) \quad (\Delta t = 1/30\text{ms}, m = 4.5 \cdot 10^4) \\ p_0 &= \bar{p}_i - \Delta p \\ p_{\text{R}} &= p_0 - \Delta p_{\text{R}}^{\text{ACT}} \end{aligned}$$

3. Normalization of light fluxes:

$$\begin{aligned} \Phi_t(t_0) &= \frac{1}{n} \sum_{n=0}^m \Phi_t(i \cdot \Delta t) \quad (\Delta t = 1/30\text{ms}, m = 1 \cdot 10^4) \\ \mathcal{A}(t) &= \frac{\Phi_t(t)}{\Phi_t(t_0)} \\ \tilde{\Phi}_s(t) &= \frac{\Phi_s(t)}{\mathcal{A}(t)} \\ \check{\Phi}_s(t)[\text{cm}^{-3}] &= \tilde{\Phi}_s(t)[\text{V}] \cdot k_{\text{PMT}}(m)[\text{V}^{-1}\text{cm}^{-3}] \\ &\rightarrow N_{c,0} = \check{\Phi}_s(t') \quad (t' = \text{1stMieMax}) \end{aligned} \tag{8.1}$$

It should be mentioned here, that by determining $\mathcal{A}(t)$ as follows

$$\mathcal{A}(t) = \frac{\Phi_t(t)}{\Phi_i'(t)} \tag{8.2}$$

where

$$\tilde{\Phi}'_i(t) = k_{\text{PD}} \Phi'_i(t) \quad (8.3)$$

with

$$k_{\text{PD}} = \frac{\Phi_t(t_0)}{\Phi'_i(t)} \quad (8.4)$$

quantitative light attenuation measurements can be performed in situations where particles already cause some extinction before expansion (see eq. 5.120). This increases the upper diameter limit of detectable particles.

After conversion, data are displayed graphically on the frontpanel. Displayed scattered light fluxes $\check{\Phi}_s(t)$ can be smoothed using a *Savitzky-Golay* filter (Savitzky and Golay, 1964). To this end, smoothing parameters such as *polynomial order* and *number of points* can be adjusted on virtual slide bars. Thereby the degree of smoothing can be adopted to actually measured Mie curves.

At the end of each measuring loop, the converted data are saved in a text file for further analysis, the first 450ms being dismissed (DAQ starts 500ms before expansion). Data files contain date (dd/mm/yy) and time (hh:mm:ss) in the first row followed by data columns listed in table 8.2.

Column #	1	2	3	4	5	6	7	8
Entry	t	$\mathcal{A}(t)$	$\Phi'_i(t)$	$\check{\Phi}_{s,L}^{10^\circ}(t)$	$\check{\Phi}_{s,L}^{15^\circ}(t)$	$\check{\Phi}_{s,L}^{20^\circ}(t)$	$\check{\Phi}_{s,L}^{25^\circ}(t)$	$\check{\Phi}_{s,L}^{30^\circ}(t)$
Units	ms	-	V	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}
Column #	9	10	11	12	13	14	15	16
Entry	$\check{\Phi}_{s,R}^{10^\circ}(t)$	$\check{\Phi}_{s,R}^{15^\circ}(t)$	$\check{\Phi}_{s,R}^{20^\circ}(t)$	$\check{\Phi}_{s,R}^{25^\circ}(t)$	$\check{\Phi}_{s,R}^{30^\circ}(t)$	$p_0(t)$	$p_R(t)$	$\bar{p}_i$
Units	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}	cm^{-3}	mbar	mbar	mbar
Column #	17							
Entry	RH (t)							
Units	%							

Table 8.2: Structure of a file created by `Main.vi`

8.7 Power supply

In order to supply the vSANC with sufficient power, connection to a 16A three-phase power source is required. Power losses in the system are minimized by taking care that all three lines (R,S,T) share approximately equivalent loads. From figure 8.7 it can be seen that the

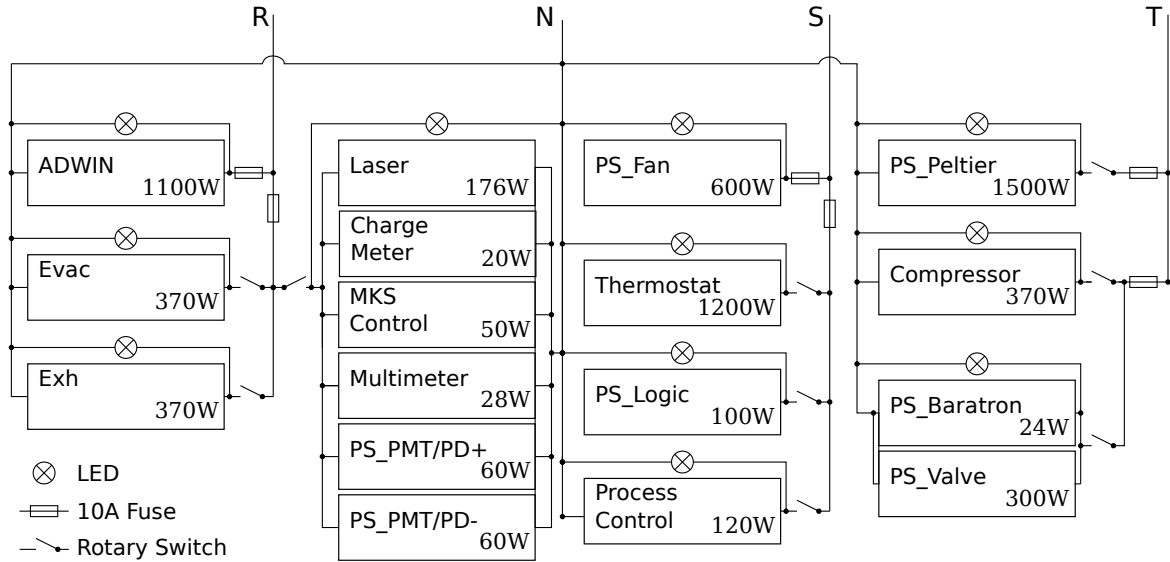


Figure 8.7: Schematic diagram of the 230VAC circuit. (PS-* indicates DC power supply)

nominal power of vSANC is approximately 6.5kW.

To ensure safe operation, wire sizes are installed according to IEC 60228. Moreover all instrument housings are grounded. Protection of individual loads is achieved by installing 10A fuses in all first generation sub-branches shown in figure 8.7. To prevent the instrument from overheating, a 100W cooling fan is installed at the top cover of the housing.

To turn the vSANC on, the main switch has to be turned clockwise first (see figure 7.17). Thereby, cooling fan and ADWIN system are directly supplied with power. After that, remaining components are turned on via nine individual rotary switches (see fig. 8.7 and 7.17). Once all components are powered, 11 green LEDs monitor the function of the instrument (fig. 8.7 and 7.17).

Components, such as photo sensors, that require direct current, are powered by means of DC power supplies, PS-* (see figure 8.7). Table 8.3 shows a detailed list of the individual DC loads. All power supplies but PS_Valve are turned on mechanically. PS_Valve, however, is powered by means of an analogue switch, that is controlled by AOUT.bas.

8.8 Timeline

Before measurements under computer control can be performed, temperatures of humidifier and expansion chamber have to stable. As already discussed in section 8.2, a stabilizing

Power supply	DC Load	DC Voltage
PS.PMT/PD+	Photomultiplier tubes, Photo diodes, Analog switches	+15V
PS.PMT/PD-	Photomultiplier tubes, Photo diodes, Analog switches	-15V
PS.Fan	Cooling fan	24V
PS.Logic	Opto couplers, analog switches	5V
PS.Peltier	Peltier elements, Temperature Controller	15V
PS.Baratron	Absolute pressure transducer	24V
PS.Valve	Valves, relays	24V

Table 8.3: List of components requiring DC supply.

period of several hours is required to obtain well-defined conditions. Particularly the expansion chamber must be turned on well in advance. Thus measurement preparation starts with the regulation of T_{CH} (see section 8.2).

After an hour, the regulation of T_{HUM} can be started by running **Temp.vi**. At that time, ADWIN system, cooling fan, process control unit, Peltier elements, temperature controller, multimeter, pressure controller, laser, charge meter and photo sensors are powered.

To remove residuals from previous experiments, the system is flushed with filtered air for about 90 minutes before starting measurements. To this end, **Valve.ino** is set to *flushing*, and vacuum pump **Exh** and power supply **PS.Valve** are switched on (see section 8.3). Thereby, **PS.Baratron** and **PS.Logic** are also powered (see section 8.7).

As can be seen from figure 8.8, measurements can be started after about three hours of measurement preparation. To start measurements, compressor and vacuum pump **Evac** are turned on. Furthermore *flush* and *delay* periods are entered on the serial monitor of the microcontroller's IDE (see section 8.3), and the valve cycle is started. Then experimental parameters are entered on the frontpanel of **Main.vi** (see section 8.6) before running the software.

After measurements, all components, except those required for valve control, are turned off. Then valves are switched to *flushing* position and the chamber is flushed for an hour. After that, the remaining components can be turned off.

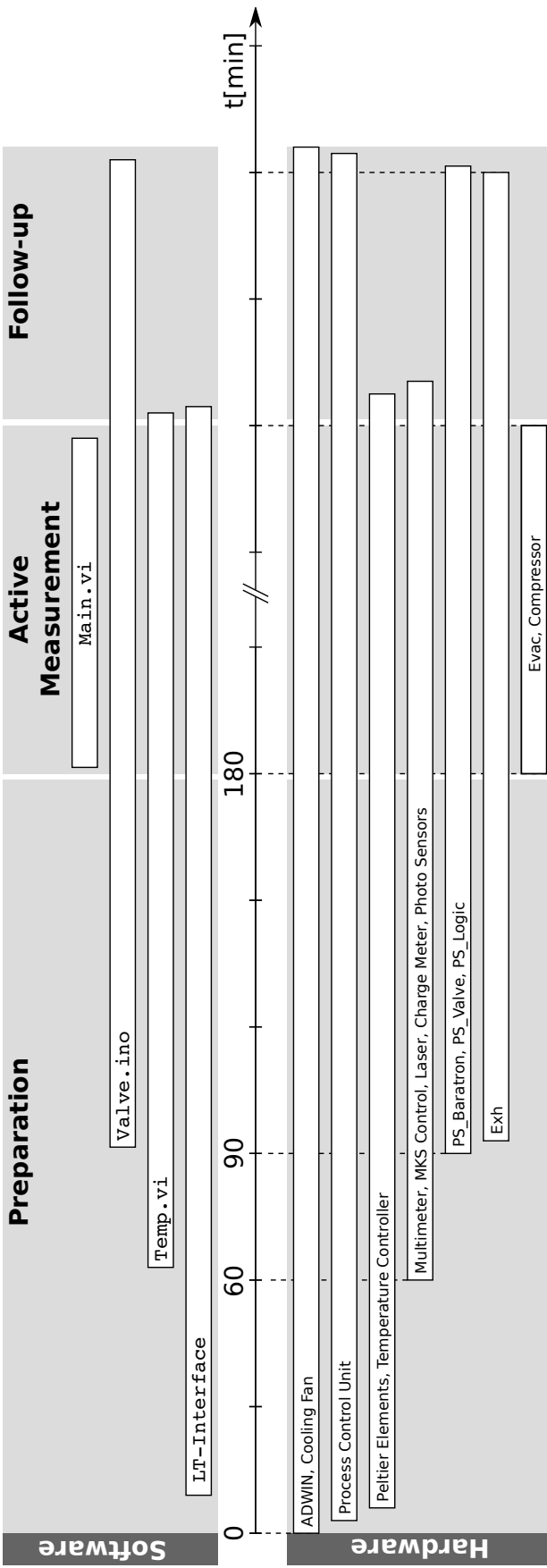


Figure 8.8: Timeline for measurements with the vSANC.

9 Data evaluation

9.1 Experimentally determined quantities

To investigate heterogeneous nucleation and droplet growth in supersaturated vapors, and to determine absolute particle number concentrations using a pressure-defined expansion chamber (see section 4.1), the following quantities are acquired:

- Normalized, attenuation corrected scattered light fluxes $\check{\Phi}_s(t)$ measured at five different light scattering angles $\theta = 10^\circ, 15^\circ, 20^\circ, 25^\circ, 30^\circ$ to both sides of the laser beam axis
- Light attenuation $\mathcal{A}(t)$
- Incident light flux $\Phi'_i(t)$
- Chamber temperature $T_{\text{CH}} = T_i$ before expansion
- Total gas pressure changes inside the expansion chamber $\Delta p(t)$
- Total gas pressure p_i before expansion
- Total gas pressure changes $\Delta p_R(t)$ inside the sub pressure vessel

By means of `Main.vi`, a text file, e.g. `'Test.txt'`, containing all quantities listed above, is created after each expansion experiment (see section 8.6). Consecutive experiments are numbered sequentially, e.g. `'Test_0000.txt'` and `'Test_0001.txt'`. For further analysis, all data files are saved to an external harddrive (*Acquisition* drive).

9.2 Automated data evaluation

9.2.1 evaluate

Automated data evaluation is performed entirely on a separate machine (Samsung RV511). This machine is connected to the same network as the process control unit (PCU) and has access to the files created during data acquisition via the SAMBA protocol. The tailor-made program `evaluate` is running interactively on the Samsung notebook and looks every 30 seconds for new data. If a new file is created, it is copied over to the Samsung machine, such that a mirror backup of the measured data is generated automatically. For three consecutive

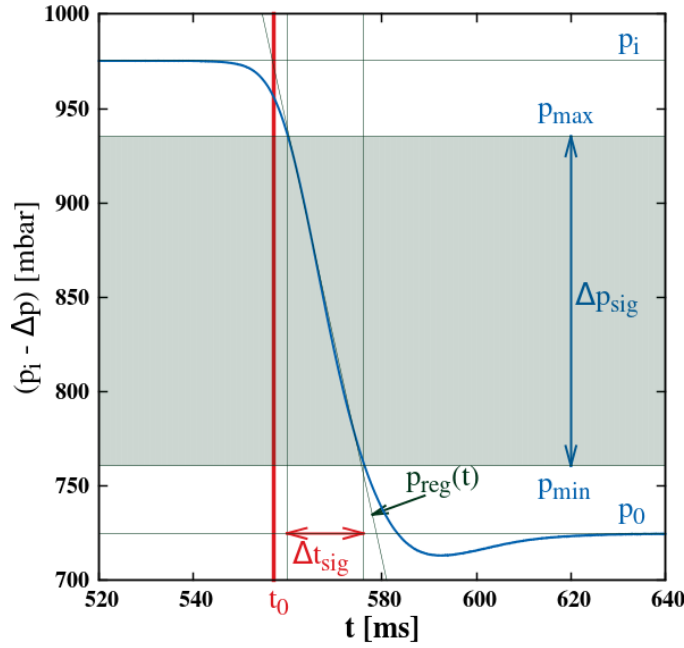


Figure 9.1: Measured pressure drop curve (blue) and determination of zero time point t_0 as crossing point of p_i and p_{reg} (green). The latter is obtained from the linear regression of the significant data Δp_{sig} lying in the blue stripe.

experiments performed at constant pressure drop, e.g. `Test_0000.txt`, `Test_0001.txt` and `Test_0002.txt`, `evaluate` shifts the time axes, so that pressure drop curves overlay exactly. This is done as follows:

First, the zero time point t_0 of each measurement `Test_000*.txt` is determined from the pressure drop curve $p_i - \Delta p(t)$ shown as blue line in Fig. 9.1. To this end significant pressure drop data $p_{\text{min}} \leq \Delta p_{\text{sig}} \leq p_{\text{max}}$, indicated by the gray shaded region and determined using $p_{\text{max}} = 0.7 \cdot p_i$ and $p_{\text{min}} = 1.3 \cdot p_0$ are fitted to a straight line on the interval Δt_{sig} to obtain $p_{\text{reg}}(t)$. The crossing point of p_i with $p_{\text{reg}}(t)$ defines the initial time point t_0 of each data set `Test_000*.txt` and makes averaging of consecutively recorded scattered light fluxes possible. Subsequently averaged curves are smoothed first by means of a Savitzky-Golay filter (Savitzky and Golay, 1964), and then using a Gauss filter. Averaged and smoothed scattered light fluxes are saved in three individual text files named e.g. `Test_mean_0-2.txt` (averaged), `Test_mean_gauss_0-2.txt` (Savitzky-Golay and Gauss filter) and `Test_mean_smoothed_0-2.txt` (Savitzky-Golay filter). Furthermore automated determination of the pressure difference $\Delta p = p_i - p_0$ yields the expansion ratio β .

To automatically determine droplet growth curves, experimental Mie extrema $(\check{\Phi}_s(t_i), t_i)$ are identified from `Test_mean_gauss_0-2.txt` by finding times t_i , where the numerical gradient $k_i = (\check{\Phi}_s(t_{i+1}) - \check{\Phi}_s(t_i)) / (t_{i+1} - t_i)$ changes its sign, i.e. satisfies

$$\text{sgn}(k_i) \text{sgn}(k_{i+1}) = -1.$$

The same is done for theoretical $\Phi_s(d_p)$ curves calculated using the BHMIE algorithm for Mie scattering from spherical droplets presented in Bohren and Huffman (1983). Thereby extremal diameters $d_{p,i}$ are obtained. Then the positions t_i of experimental extrema $\check{\Phi}_s(t_i)$ are assigned to theoretical extrema positions $d_{p,i}$ and the data pairs $(d_{p,i}, t_i)$ are saved in another text file called `output_0-2.dat`. This text file also contains parameters, such as wavelength and refractive index, used to calculate theoretical Mie curves and filter settings. A typical set of averaged and smoothed curves for scattered light fluxes measured at 15° is shown in figure 9.2. Droplet number concentrations at the end of expansion, $N_{c,0}$, are determined from

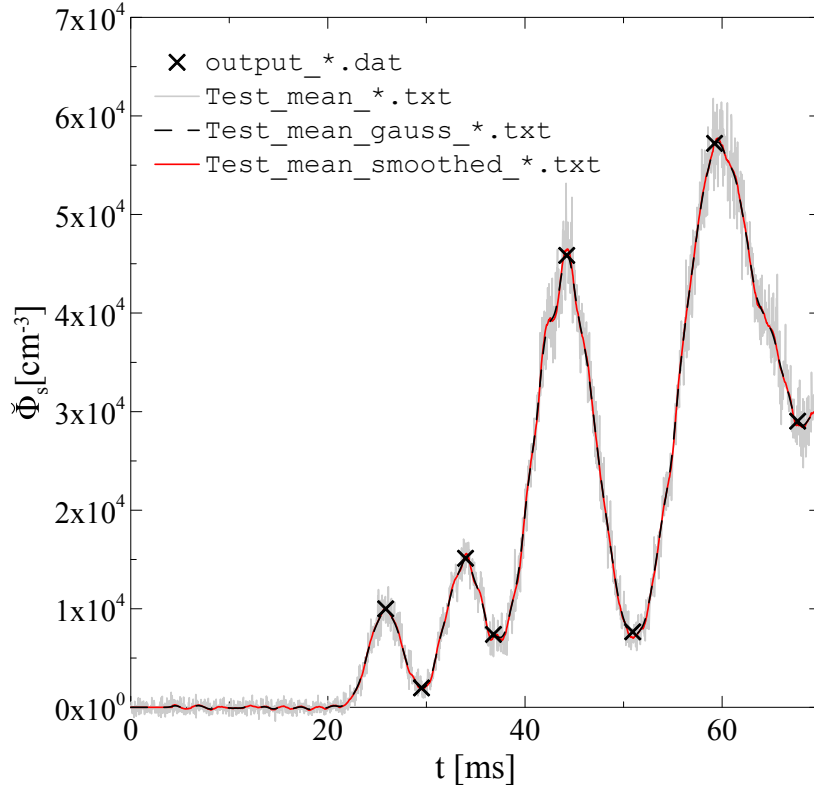


Figure 9.2: Typical set of averaged (solid gray line), and smoothed (dashed black line and solid red line) experimental scattered light fluxes measured at 15° to the right of the laser beam axis. Measurements were performed with ambient aerosol particles in n-propanol vapor. Black crosses are Mie extrema identified by `evaluate`.

heights of `Test_mean_smoothed_0-2.txt` curves. To this end, times t_i corresponding to the first Mie maximum of each light scattering angle listed in '`output_0-2.txt`' are used. This yields 10 individually determined number concentrations ($2 \times$ five light scattering angles) for each series of three consecutive measurements. Before saving these number concentrations, values measured at fixed angle but to different sides of the laser beam axis are averaged. Thus a set of five number concentrations, $N_{c,0}^\theta$, is obtained for each measurement triplet. Together with date and time, number concentrations of consecutive measurement triplets

are saved in 'summary.dat'.

9.2.2 growth

The program **growth** is based on **newalc**, which was developed by Aron Vrtala and Markku Kulmala based on theoretical droplet growth principles presented in Preining et al. (1981), Wagner (1982) and Wagner (1991).

growth calculates theoretical droplet growth curves for vapor saturation ratios S_0 ranging from S_{start} to S_{final} numerically. To this end, the following parameters are defined in the file 'input':

- Condensing vapor
- Total gas pressure p_i before expansion
- Expansion ratio β
- Temperature at the end of expansion T_0
- Droplet number concentration at the end of expansion $N_{c,0}$
- Range, S_{start} to S_{final} , and stepsize ΔS of saturation ratios

In this study only n-propanol has been used as condensing vapor. The total gas pressure p_i before expansion is measured directly (see section 8.1). The expansion ratio β is calculated from p_i and Δp according to eq. (4.11). The temperature T_0 at the end of the expansion process is determined from T_i and β according to eq. (4.13). The droplet number concentration $N_{c,0}$ at the end of expansion is determined from the height of the first Mie maximum of normalized scattered light fluxes $\check{\Phi}_s$ according to eq. (8.1).

growth compares theoretical droplet growth curves $d_p(t)$ for vapor supersaturation ratios ranging from S_{start} to S_{final} with experimental droplet growth data ($d_{p,i}(t_i)$), listed in 'exp.dat'. To this end experimental data $d_{p,i}(t_i)$ are shifted timewise until the least square error between theoretical curves and experimental data reaches a minimum. The supersaturation S_0 , which yields the best match between theory and experiment (lowest least square error), is saved in 'OPT.CLC'. The corresponding theoretical droplet growth curve can be found in 'OPT.OUT' and the time-shifted experimental data are saved to 'exp.shifted.dat'. Figure 9.3 shows a typical set of time-shifted experimental growth data and theoretical growth curves. As can be seen from this graph, droplet growth strongly depends on vapor supersaturation S_0 . This allows precision determination of S_0 within ± 0.05 provided that mass and thermal accommodation coefficients, α_m and α_t , respectively (see section 3.1.2), equal one (Winkler, 2004). Moreover, precision determination of S_0 requires, that significant droplet growth starts at the end of expansion.

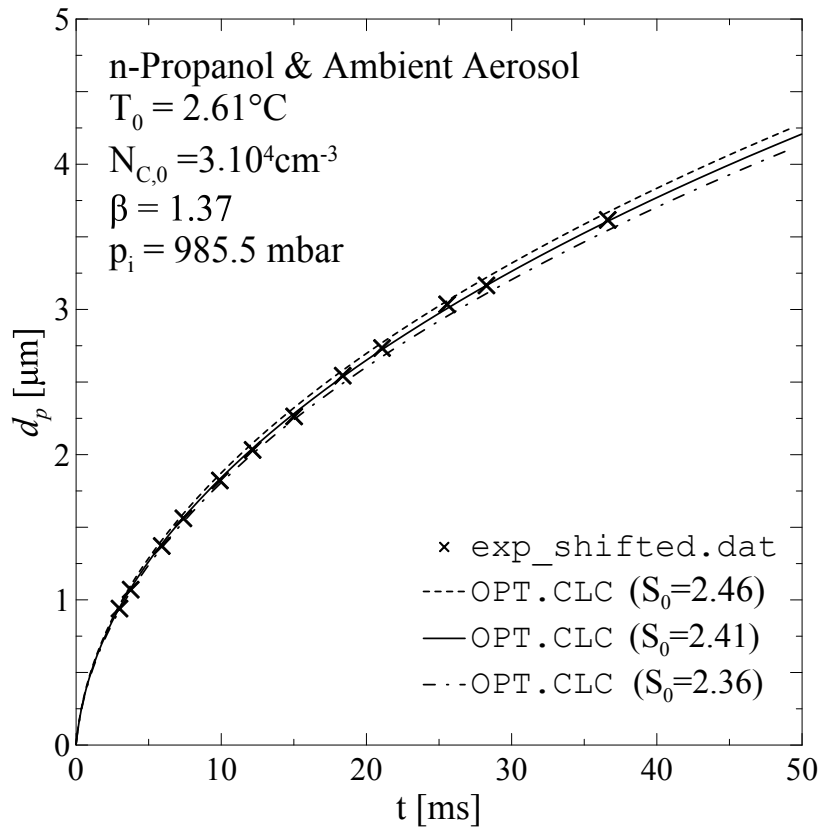


Figure 9.3: Theoretical droplet growth curves calculated for three different vapor supersaturations S_0 and manually determined droplet growth data.

9.3 Manual data evaluation

9.3.1 Growth_Eval.vi

As can be seen from figure 9.2 automated identification of experimental Mie extrema using `evaluate` might be incomplete. Particularly, sub-extrema are only rarely identified. On the other hand, accuracy in determining the vapor supersaturation at the end of expansion increases with increasing (t, d_p) data pairs. Thus the LabView code (`Growth_Eval.vi`) was developed to enable manual allocation of experimental and theoretical Mie extrema.

9.3.2 Determination of Δp

For some experiments, particularly at very high pressure drops, droplet growth might start well before the end of expansion (see e.g. figure 9.4). This behavior is partly due to the comparatively slow pressure drop (see section 7.1) and partly due to the low vapor saturation ratio S_i before expansion (see section 7.2).

In such a situation, the relevant pressure drop is not determined by the pressure difference before and at the end of expansion, i.e. $p_i - p_0$. Instead, the pressure drop Δp needs to

be identified manually by considering the moment when significant droplet growth starts. Uncertainties regarding Δp result in uncertainties of β and thus of T_0 , too.

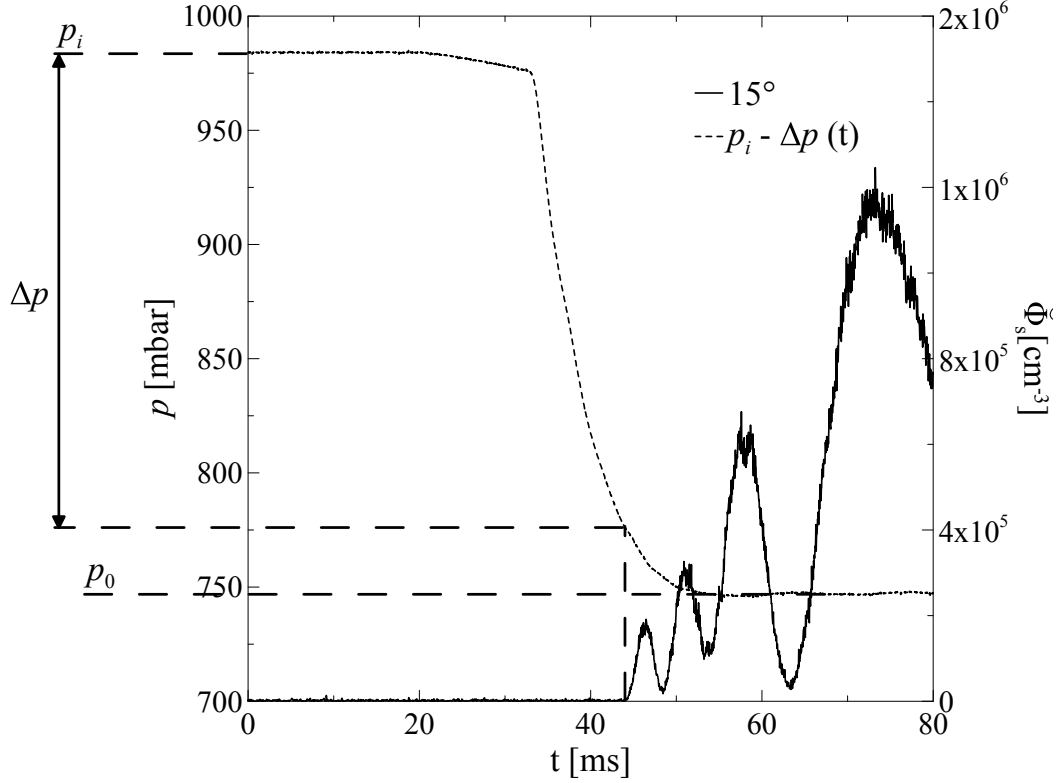


Figure 9.4: Attenuation corrected, normalized scattered light flux $\check{\Phi}_s(t)$ measured at 15° forward scattering direction and total gas pressure $p_i - \Delta p(t)$ during expansion. It can be seen that droplet growth starts before the end of expansion ($p = p_0$). In this situation the pressure drop is not calculated from $p_i - p_0$, but by manually identifying the time where significant droplet growth started.

As can be seen from fig. 9.4 the expansion process continues during droplet growth. Thus the actual vapor supersaturation corresponding to the observed growth process increases with time until $p_i - \Delta p$ equals p_0 . However, theoretical droplet growth curves describing such a process can not be calculated using **growth**. Hence the vapor supersaturation S_0 can only be estimated using input parameters β and T_0 calculated from manually identified pressure drops. This yields an estimate for the maximum vapor supersaturation S_0 initiating heterogeneous nucleation.

In order to enable precision determination of S_0 it is planned to speed up the pressure drop by (i) replacing the flowshaper at the outlet of the expansion chamber (see section 7.1) and (ii) improving the humidification system (see section 7.2).

9.3.3 Determination of the onset saturation ratio

Heterogeneous nucleation of vapor molecules on seed particles is investigated by determining nucleation probabilities P (see eq. (2.21)) as a function of vapor supersaturation S_0 experimentally. To this end S_0 is stepwise increased by increasing the expansion ratio β . Thereby an increasing fraction of particles is activated and grows to visible sizes. The onset saturation ratio S_{onset} is defined as the saturation ratio where 50% of the particles are activated.

$$P(S_{onset}) = 0.5 \quad (9.1)$$

S_{onset} can be determined by fitting experimentally determined data to a fitting function. In the following $\tanh x$ is used as fitting function. Figure 9.5 shows experimental nucleation probability data as a function of S_0 for charged silver particles ($d_{seed} = 6\text{nm}$) in n-propanol vapor. Here the onset saturation ratio is 1.43. Knowing S_{onset} , the radius R of the seed

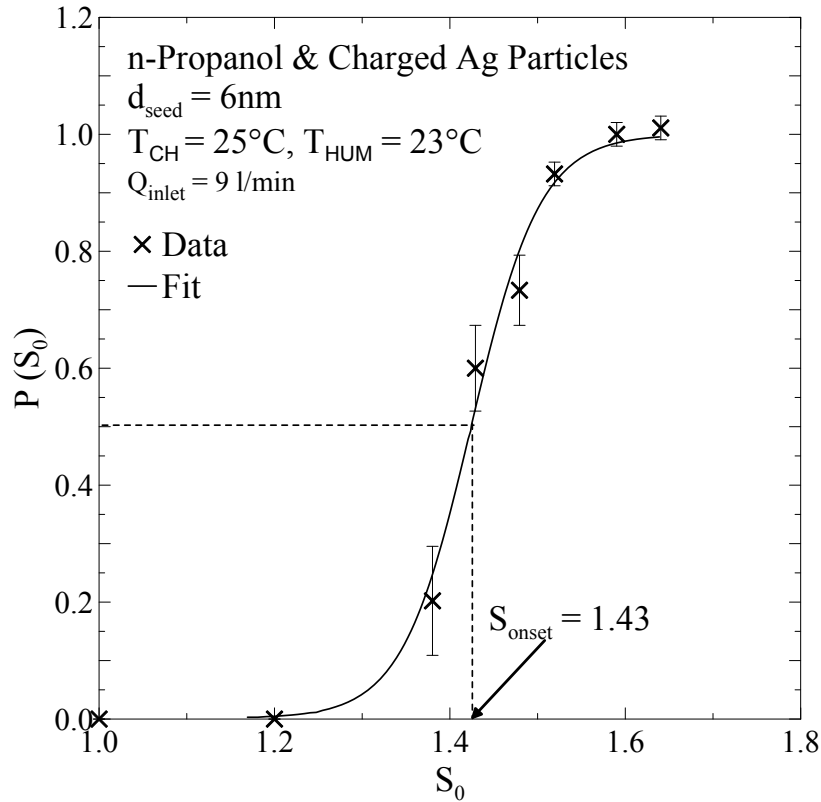


Figure 9.5: Experimentally determined nucleation probability P (black crosses) as a function of vapor saturation ratio S_0 for charged 6nm silver particles in n-propanol vapor. The onset saturation ratio S_{onset} is determined by fitting the data with a $\tanh$ (solid black line).

particle can be approximately determined using the *Fletcher* theory (see section 2.2).

10 Instrument performance

10.1 Particle generation

In this study different seed particles, such as ammonium sulfate, tungsten oxide, silver, sodium chloride and tetra-alkyl ammonium ions (Ude and Fernandez de la Mora, 2005), have been used together with n-propanol (*Merck* p.a., 99.99%) vapor to characterize the performance of vSANC, particularly in the sub-3nm size range. To guarantee constant particle number concentration and constant number size distribution during experiments particle generation techniques, such as tube furnace and hot-wire particle generation or electrospraying, have been employed. In the following the different generation procedures are discussed.

Generation of silver and sodium chloride particles

Silver and sodium chloride particles with diameters ranging from about 2nm to 10nm have been generated using a tube furnace (Scheibel and Porstendörfer, 1983). Thereby silver wool (*Merck* 1.01506.0010, > 99.95%) or crystalline sodium chloride (*Merck* 1.06404.0500, > 99.95%) is evaporated at 1300K or 920K, respectively. Together with a furnace feed flow Q_{feed} of 3.35l/min, silver or sodium chloride vapor is passed from the furnace to a cooling region. Here the vapor nucleates homogeneously. Then, newly formed particles are charged bipolarly in an Am^{241} charger (Reischl et al., 1983) and passed through a Vienna-type Differential Mobility Analyzer (DMA) (Reischl et al., 1997) using a dilution flow Q_{dil} of 3l/min. The DMA classifies the particles according to their electrical mobility. Thereby a monodispersed particle number size distribution with a geometrical mean standard deviation of typically $\sigma_g = 1.06$ is obtained. Assuming Boltzmann charge equilibrium before the aerosol enters the DMA, particles below 10nm in diameter leaving the DMA can be considered as singly charged. In the present study, only positively charged particles have been investigated. In the following these particles are referred to as *charged*.

In order to *neutralize* the singly charged particles, another Am^{241} charger is used after the DMA. Thereby the classified aerosol particles are brought back to Boltzmann charge equilibrium. In the following these particles are referred to as *neutral*.

The experimental arrangement of Ag and NaCl particle generation was adopted from Winkler (2004), a schematic diagram is shown in figure 10.1. As can be seen from this setup, cleaned air is used for furnace feed and dilution flow. Thus, although contamination of seed particles

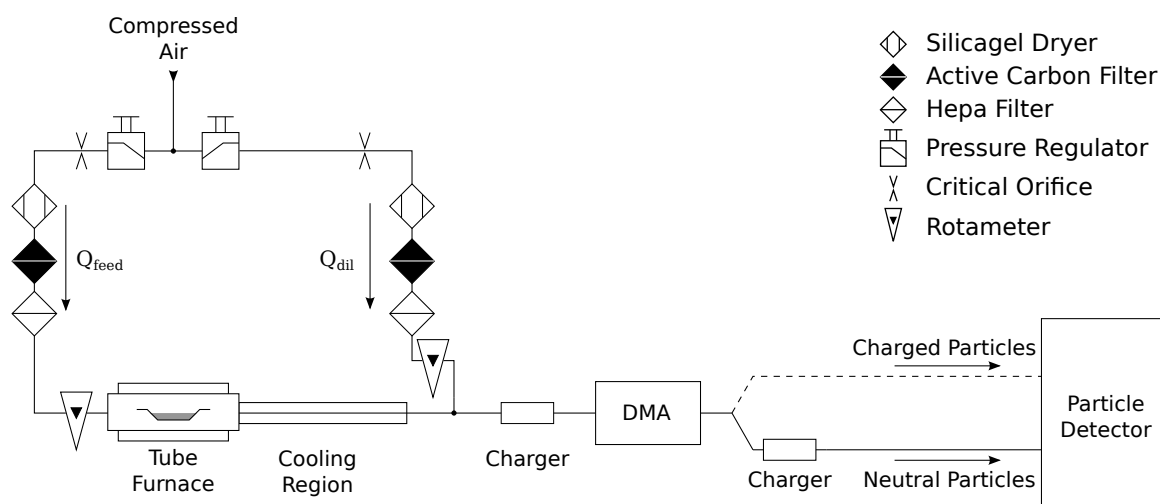


Figure 10.1: Experimental setup of silver and sodium chloride particle generation.

should not be an issue, they might oxidize.

Generation of tungsten oxide particles

Tungsten oxide particles with diameters below 2nm have been generated using a commercially available WOx generator (*Grimm Aerosoltechnik*, Model 7.860 (Steiner, 2006)). The operation of this particle generator is based on sublimation of tungsten oxide at temperatures of about 900°C . To this end, a WOx coil is surrounded by a heating wire, which provides the sublimation temperature. Immediately after WOx sublimates into a controlled fraction of carrier gas, it is diluted by means of two clean air streams, when exiting the heated zone. In the present study air streams were adjusted to yield a total aerosol flow Q_{ae} of 4.6l/min. Although Steiner (2006) mentioned, that sublimated WOx molecules are already charged, particles were classified applying the same method as mentioned above.

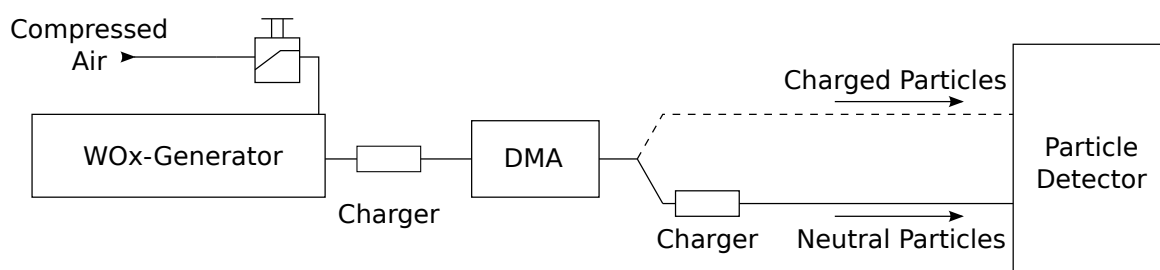


Figure 10.2: Experimental setup of tungsten oxide particle generation.

Generation of ammonium sulfate particles

Positively charged ammonium sulfate particles, ranging from about 1nm to 7nm in diameter, have been generated using a tube furnace (Carbolite MTF). Calibration measurements using these particles have been conducted at the University of Helsinki, Finland. A detailed description of the particle generation setup can be found in Kangasluoma et al. (2013). The generated particles are charged bipolarly in an Am²⁴¹ charger and subsequently classified using a Hermann-type DMA (Hermann et al., 2000) with a resolving power ($1/\text{FWHM}^1$) of about 20.

Generation of tetra-alkyl ammonium ions

Monomobile tetra-heptyl ammonium bromide ions have been generated by electrospraying solutions of their salts in methanol. To this end an electrospray designed by Michel Attoui (University of Paris, attoui@u-pec.fr) has been used. The technique of generating very small particles using an electrospray goes back to Zeleny (1917). Ude and Fernandez de la Mora (2005) have shown, that electrosprayed tetra-alkyl ammonium halide salts produce sharp ion peaks, that enable the selection of particle mobility standards from about 1nm in diameter onwards. In the present study tetra-heptyl ammonium bromide monomers, tetra-propyl ammonium iodide monomers and tetra-dodecyl ammonium bromide dimers, with mobility equivalent diameters of 1.47nm, 1.17nm and 2.04nm, respectively, have been selected using a Hermann-type DMA (see previous section). A detailed description of the experimental setup can be found in Kangasluoma et al. (2013).

10.2 Counting efficiency

The size dependent counting efficiency $\eta(d_{seed})$ of a particle counter is defined as the ratio of particle number concentration measured by the counter to the actual particle number concentration of the aerosol entering its sampling line. For condensation particle counters (CPCs) Stolzenburg and McMurry (1991) factored $\eta(d_{seed})$ into the product

$$\eta(d_{seed}) = \eta_{\text{sam}}(d_{seed}) \cdot \eta_{\text{act}}(d_{seed}) \cdot \eta_{\text{det}}(d_{seed}),$$

where η_{sam} , η_{act} and η_{det} are sampling, activation and detection efficiencies, respectively. The sampling efficiency η_{sam} is defined as the ratio of particle concentration of the aerosol exiting the sampling line to that entering it. Usually particle losses along the sampling line, particularly in the size range below 10nm, are dominated by diffusion. The activation efficiency η_{act} is defined as the fraction of particles activated by means of heterogeneous

¹Full width at half maximum of the mobility transfer function

nucleation. Clearly, η_{act} depends on the vapor supersaturation². The detection efficiency, η_{det} , is the fraction of activated particles, that grow large enough to be detected by an optical system.

Size dependent vSANC counting efficiencies have been investigated as a function of particle composition, system temperatures (T_{HUM} , T_{CH}), charging state (*charged* or *neutral*) and aerosol intake flow rate, Q_{inlet} .

In case of vSANC, η_{sam} refers to particle losses along the inlet line, consisting of a diffusion type humidifier HUM, a plastic pinch valve V_1 and stainless steel tubing. The particle number concentration detected by vSANC, i. e. N_{vSANC} , is determined by stepwise increasing the expansion ratio β and thus the vapor supersaturation S_0 at the end of expansion until further increase does not yield higher values for N_{vSANC} . Thus the activation efficiency η_{act} is, in general, close to one. However, if particles are very small, increasing S_0 might not lead to a *plateau* in N_{vSANC} . In that case, η_{act} might be smaller than one, as illustrated in figure 10.3.

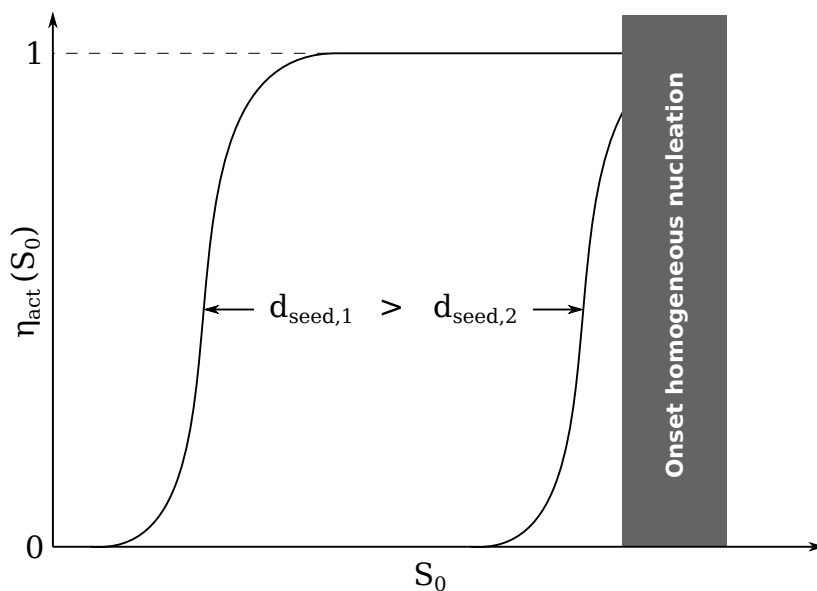


Figure 10.3: Schematic diagram of the activation efficiency η_{act} (=nucleation probability) as a function of vapor saturation ratio S_0 for seed particles with two different diameters $d_{seed,1} > d_{seed,2}$. By increasing S_0 an activation efficiency of one can be achieved for seed particles with diameter $d_{seed,1}$, whereas homogeneous nucleation hinders full activation of particles with diameter $d_{seed,2}$.

Regarding the detection efficiency η_{det} of vSANC, optical detection applying the mCAMS method indicates, that the droplets growing into visible sizes are sufficiently monodispersed. Thus either all droplets grow large enough to be detected or none of them. Experiments

²In fact, $\eta_{act}(d_{seed})$ is the nucleation probability P as a function of seed particle diameter d_{seed} . However, in the present study P is rather considered as a function of vapor saturation ratio S at fixed d_{seed} .

have shown, that despite vapor depletion particle number concentrations up to 10^7cm^{-3} can be detected. Hence, in general, the detection efficiency η_{det} is close to one, as well. Therefore the vSANC counting efficiency essentially reduces to

$$\eta(d_{\text{seed}}) \approx \eta_{\text{sam}}(d_{\text{seed}}),$$

if the *plateau* in η_{act} is reached.

In the following, d_{50} and d_{10} are seed particle diameters corresponding to 50% and 10% counting efficiency, respectively.

Counting efficiencies of charged particles have been determined using a Faraday Cup Electrometer (FCE, TSI Model 3068b) as reference instrument (Liu and Kim, 1977). The FCE consists of an electrometer and a filter inside a metal housing (Faraday cage). Charged particles deposited on the filter cause an electric current which is measured by the electrometer. In this study we assume, that the FCE has a counting efficiency of one. Thus the counting efficiency of vSANC using a FCE as reference is given by

$$\eta(d_{\text{seed}}) = \frac{N_{\text{vSANC}}(d_{\text{seed}})}{N_{\text{FCE}}(d_{\text{seed}})}.$$

For neutral particles a Particle Size Magnifier (PSM, Airmodus A09 (Vanhanen et al., 2011)) has been used as reference instrument. The operation of a PSM is based on turbulent mixing of a cooled sample flow with a heated clean air flow saturated by the working fluid. Thus the PSM is a mixing-type CPC. Since the working fluid, i. e. diethylene glycol (DEG) (Iida et al., 2009), has a very low vapor pressure, particles do not grow large enough to be detected with optical detection methods. Therefore another conventional condensation particle counter (CPC), also referred to as *booster* (Iida et al., 2009), is used to grow the DEG droplets to visible sizes. Usually a laminar flow type CPC is chosen as booster see e.g. Iida et al. (2009). In the present study either TSI Model 3776 or Airmodus Model A20, both laminar flow type CPCs with n-butanol as working fluid, have been utilized. The very high vapor supersaturation achieved in a PSM enables the activation of particles down to about 1nm in diameter. The counting efficiency of a PSM is size dependent, particularly in the size range below 3nm. Thus vSANC counting efficiencies of neutral particles can not directly be calculated from the ratio of N_{vSANC} to the particle number concentration detected by a PSM, i.e. N_{PSM} . However, PSM counting efficiency curves shown in Kangasluoma et al. (2013) indicate, that above about 2.5nm counting efficiencies are (i) size independent and (ii) independent of the charging state. Hence, vSANC counting efficiencies for neutral particles above 2.5nm in diameter can be calculated according to

$$\eta(d_{\text{seed}}) = \frac{N_{\text{vSANC}}(d_{\text{seed}})}{N_{\text{PSM}}(d_{\text{seed}})} \cdot \frac{N_{\text{PSM}}}{N_{\text{FCE}}} \Big|_{d_{\text{seed}} \geq 2.5 \text{nm}}$$

where the constant factor $\frac{N_{\text{PSM}}}{N_{\text{FCE}}}\big|_{d_{\text{seed}} \geq 2.5\text{nm}}$ depends on the chemical composition of seed particles. For silver it is 0.725 and for sodium chloride 0.6 (Kangasluoma et al., 2013).

It is important to note that vSANC counting efficiencies mainly depend on particle losses along the sampling line. Once particles reach the expansion chamber EXP and the number concentration of particles inside EXP lies above the lower detection limit of the optical arrangement, i.e. in the order of 10^2cm^{-3} , we assume that all of them can be activated³. Therefore, d_{50} and d_{10} are determined by fitting counting efficiency data $\eta(d_{\text{seed}})$ with a two parameter equation that is based on an expression for the penetration through a cylindrical tube derived by Gormley and Kennedy (1949). This expression reads

$$\eta_{\text{GK}}(\mu) = \begin{cases} 0.819e^{-11.5\mu} + 0.00975e^{-70.1\mu} & \text{for } \mu < 0.009 \\ 1 - 5.50\mu^{2/3} + 3.77\mu & \text{for } \mu > 0.009 \end{cases}$$

where the dimensionless parameter μ is given by

$$\mu = \frac{DL}{Q}$$

with L and Q being tube length and flowrate, respectively. D is the diffusion constant according to

$$D = \frac{kTC_c}{3\pi\eta_{\text{air}}d_{\text{seed}}}$$

where T is the temperature in Kelvin, η_{air} is the viscosity of air and k the Boltzmann constant. C_c is the Cunningham slip-correction and reads

$$1 + 1.55\frac{2\lambda_m}{d_{\text{seed}}} + 0.471\frac{2\lambda_m}{d_{\text{seed}}}e^{-\frac{0.596d_{\text{seed}}}{2\lambda_m}}$$

with λ_m being the mean free path in air. The fitting equation used in the present study reads

$$F(d_{\text{seed}}) = a \cdot \eta_{\text{GK}}(L, d_{\text{seed}}) \quad (10.1)$$

with free parameters a and L . L usually exceeds the actual length of the inlet line, i.e. 0.7m. This reflects the fact, that particle losses along the inlet are not only caused by diffusion. A detailed list of numerical values for fitting parameters a and L is given in Appendix D.1.

In contrast to vSANC, counting efficiencies of laminar flow or mixing type CPCs are mainly determined by η_{act} . This results in much steeper counting efficiency curves as can be seen from figure 10.4. Here counting efficiencies for positively charged ammonium sulfate particles are plotted against the particle diameter d_{seed} . The PSM (Vanhanen et al., 2011) and the modified TSI model 3025 UCPC (Iida et al., 2009) are both running with DEG as working fluid. The PSM is a mixing type CPC whereas the modified TSI 3025 is a laminar flow type

³This assumption is correct if the plateau of the $\eta_{\text{act}}(S_0)$ curve can be reached (see fig. 10.3).

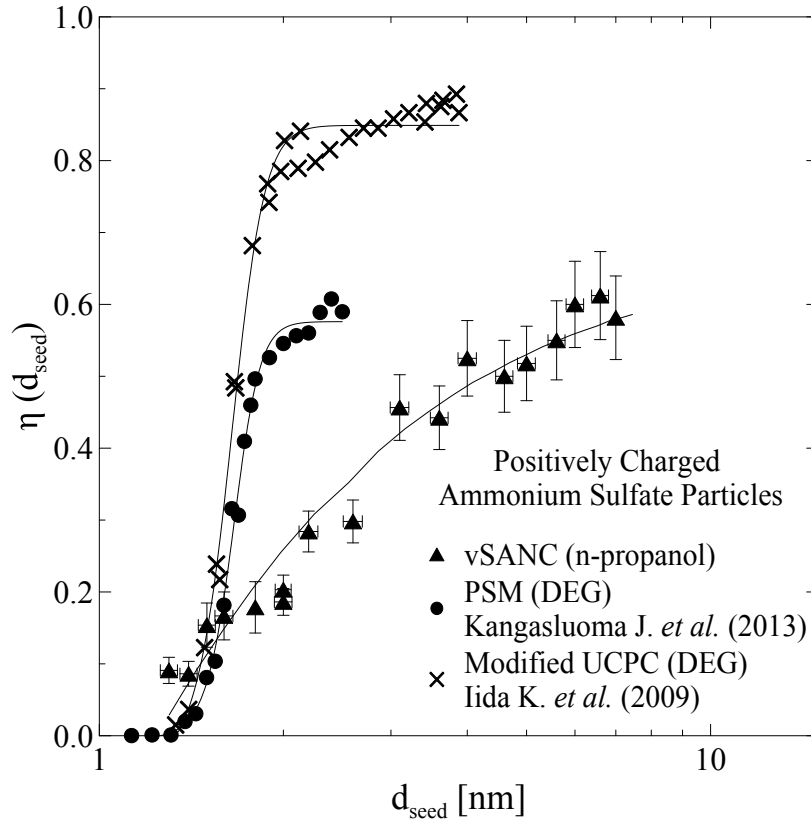


Figure 10.4: Counting efficiencies of various condensation particles counters including vSANC (black triangles). All experiments were performed with positively charged ammonium sulfate particles.

CPC (Stolzenburg and McMurry, 1991).

The cut-off diameter, d_{50} , of vSANC clearly exceeds those determined by the other instruments. However, the flat decrease of the vSANC counting efficiency curve yields a d_{10} that is comparable to those of the DEG based CPCs.

10.2.1 Counting efficiencies at different aerosol intake flow rates

vSANC inlet losses for various aerosol intake flow rates Q_{inlet} have been investigated using charged silver particles in n-propanol vapor (*Merck* 1.00997.2500, > 99.5%). Thereby Q_{inlet} was varied between 1.6 and 9 l/min by means of critical orifices. Expansion chamber and humidifier temperatures were 25°C and 23°C, respectively. At the highest flowrate, i.e. 9 l/min, the Reynolds number characterizing the flow through the inlet system does not exceed 1340. Thus it can be assumed that we have laminar flow conditions for all flowrates discussed here.

Not surprisingly, it turned out, that inlet losses decrease with increasing inlet flow rate Q_{inlet} . Therefore field measurements (see section 11) have been performed at highest Q_{inlet} , which

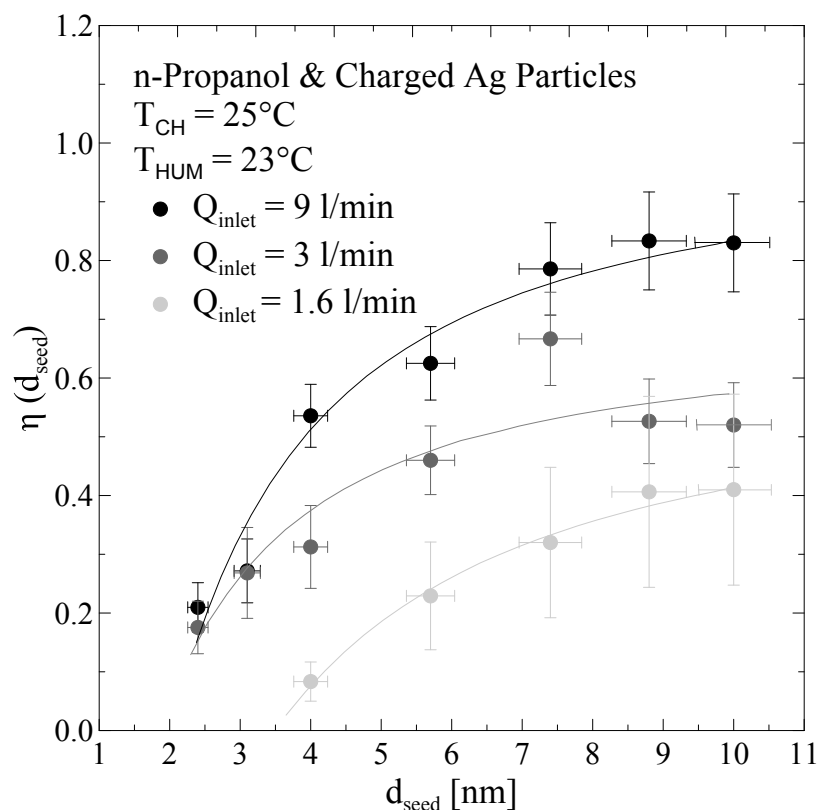


Figure 10.5: Counting efficiency of the vSANC as a function of seed particle diameter for charged silver particles in n-propanol vapor at three different intake flowrates Q_{inlet} .

is 9l/min. Figure 10.5 shows vSANC counting efficiencies η as a function of seed particle diameter for charged silver particles in n-propanol vapor. By increasing Q_{inlet} from 1.6 to 3l/min $\eta(10\text{nm})$ increases by about 40% and $\eta(4\text{nm})$ even increases by more than 450%. The next higher flowrate, i.e. 9l/min, yields further increase of $\eta(10\text{nm})$ by about 45% and of $\eta(2.5\text{nm})$ by about 12% with respect to η determined at 3l/min. The fact that the derivative of the relative change in η with respect to d_{seed} is negative when changing Q_{inlet} from 1.6 to 3l/min, while it is positive when increasing the flowrate from 3 to 9l/min, can not be explained by flowrate dependent diffusion losses of particles along the inlet line.

A detailed list of d_{50} and d_{10} corresponding to counting efficiencies shown in fig. 10.5 is given in table 10.1.

10.2.2 Counting efficiencies of particles having different chemical compositions

The effect of particle composition on vSANC counting efficiencies has been studied using charged silver and ammonium sulfate particles, and tetra-alkyl ammonium ions. Particle composition dependent counting efficiencies of neutral particles have been studied using sil-

Q_{inlet} [l/min]	d_{50} [nm]	d_{10} [nm]
9	3.95	2.26
3	6.45	2.2
1.6	-	4.2

Table 10.1: d_{50} and d_{10} corresponding to counting efficiencies of charged silver particles in n-propanol at different aerosol intake flow rates shown in figure 10.5.

ver and sodium chloride seeds. In both cases (charged/neutral) n-propanol has been used as condensing vapor. During experiments expansion chamber and humidifier temperature were 25°C and 23°C, respectively.

It can be seen from figure 10.6, that the counting efficiency of charged particles increases with increasing seed particle size. However, it does not exceed 0.85. The fact, that even for particles with diameters around 10nm, counting efficiencies do not approach one, can probably be explained by the plastic pinch valve V_1 installed along the inlet (see section 7.1), which acts as ion trap. Moreover measurements indicate that $\eta(d_{seed} < 2\text{nm})$ is approximately the same for charged ammonium sulfate particles and tetra-alkyl ammonium ions. On the other hand counting efficiencies of charged silver and ammonium sulfate particles do not match. $\eta(d_{seed} > 4\text{nm})$ is higher for silver, whereas $\eta(d_{seed} < 4\text{nm})$ is higher for ammonium-sulfate particles. In table 10.2 d_{50} and d_{10} of charged silver and ammonium sulfate particles in n-propanol vapor are listed.

Chemical composition	d_{50} [nm]	d_{10} [nm]
Ammonium Sulfate	4.28	1.47
Silver	3.95	2.26

Table 10.2: d_{50} and d_{10} corresponding to counting efficiencies of charged seed particles in n-propanol vapor shown in figure 10.6.

Figure 10.7 shows counting efficiencies obtained for neutral sodium chloride and silver particles. It can be seen from this graph, that the penetration of silver particles is about 50% higher than that of sodium chloride particles. This effect might probably be caused by V_1 , because sodium chloride (ionic crystal) has a higher polarity than silver (metallic bonding). In table 10.3 d_{50} and d_{10} corresponding to counting efficiencies shown in fig. 10.7 are listed.

10.2.3 Counting efficiencies of particles having different charging states

The negative effect of inlet valve V_1 also occurs when comparing counting efficiencies of charged and neutral particles with *identical* chemical composition. In the present study *identical* with respect to chemical composition means that particles mostly consist of the

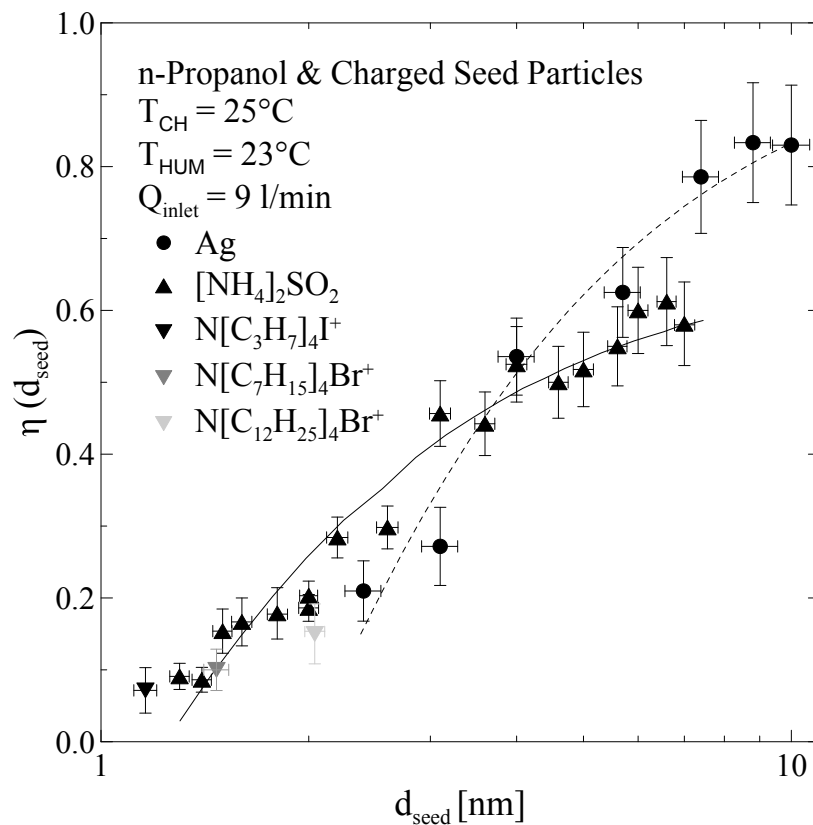


Figure 10.6: vSANC counting efficiency as a function of seed particle diameter for charged seed particles of different chemical composition in n-propanol vapor.

same material⁴. Figure 10.8 shows counting efficiencies obtained for neutral and charged silver particles in n-propanol vapor. Measurements have been performed at a chamber temperature of $25^{\circ}C$, humidifier temperature of $23^{\circ}C$ and inlet flow rate of 9l/min.

It can be seen from this graph that the smaller the particles are the larger the difference in counting efficiencies between charged and neutral seeds becomes. For seed particles with diameters around 2.5nm, the counting efficiency of neutral particles is about 50% higher than the one of charged seeds. Unfortunately, the generation of neutral particles below 2nm at sufficiently high number concentrations ($N_c \approx 10^4 \text{ cm}^{-3}$) turned out to be extremely difficult. Thus no data are available for neutral sub-2nm particles. d_{50} and d_{10} for charged and neutral silver particles in n-propanol vapor are listed in table 10.4.

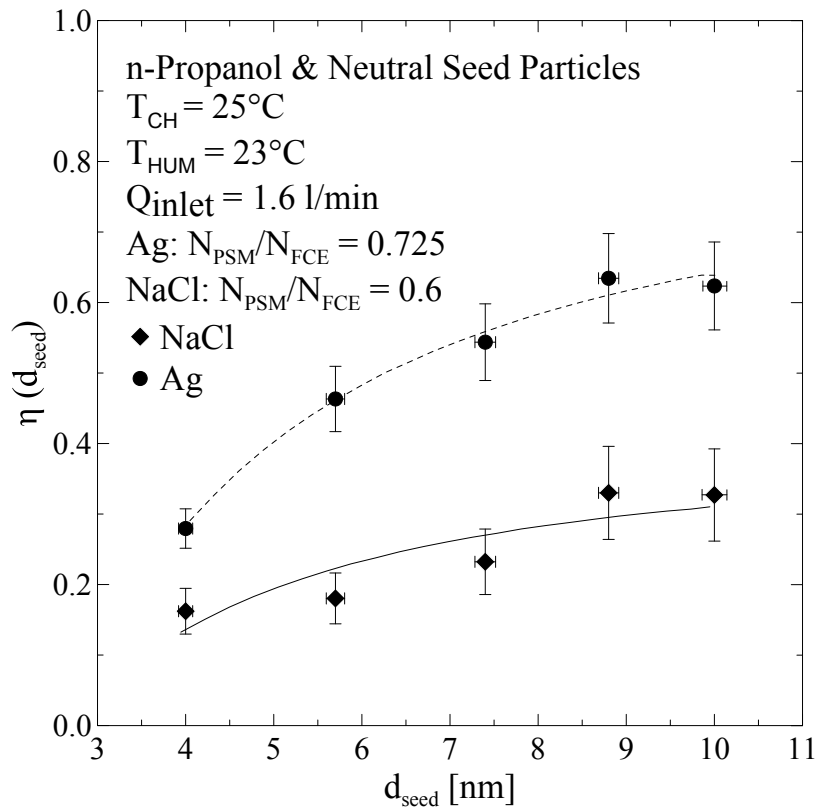


Figure 10.7: vSANC counting efficiency as a function of seed particle diameter for neutral silver and sodium chloride particles in n-propanol vapor.

10.2.4 Counting efficiencies at different system temperatures

Another interesting effect on counting efficiencies was observed when changing expansion chamber and humidifier temperatures from 25°C and 23°C, respectively, to 15°C and 13°C, respectively. It turns out, that inlet losses decrease by approximately 50%, when performing measurements at lower temperatures.

Figure 10.9 shows data obtained with charged tungsten oxide particles with diameters below 2nm in n-propanol vapor. Clearly a higher penetration of particles from the inlet to the expansion chamber is achieved at low temperature settings. Below about 1.5nm inlet losses at high temperature settings are so high, that no particles are detected by vSANC. In contrast, low temperature settings yield detectable number concentrations down to 1.2nm. For high temperature settings d_{10} is 1.25nm, whereas low temperature settings yield a d_{10} of 1.52nm. The positive effect of low temperature settings has also been observed during field measurements (see section 11).

⁴Clearly particles of different charging states can not be identical with respect to chemical composition. However, influences of charge carriers, such as charger ions, are neglected here. Charging state dependent differences in the chemical composition of ammonium sulfate particles are discussed in Kangasluoma et al. (2013).

Chemical composition	d_{50}	$d_{10}[\text{nm}]$
Sodium Chloride	-	4.95
Silver	6.33	3.05

Table 10.3: d_{50} and d_{10} corresponding to counting efficiencies of neutral seed particles in n-propanol vapor shown in figure 10.7.

Charging state	d_{50}	$d_{10}[\text{nm}]$
Neutral	3.20	1.80
Charged	3.95	2.26

Table 10.4: d_{50} and d_{10} corresponding to counting efficiencies of neutral and charged silver particles in n-propanol shown in figure 10.8.

It should be mentioned that the temperature dependence of vSANC counting efficiencies is not to be confused with the unusual temperature dependence of heterogeneous nucleation reported by Schobesberger et al. (2010) and Kupc et al. (2013). vSANC counting efficiencies shown in figure 10.9 refer to number concentrations obtained at vapor supersaturations well above the onset saturation ratio. Thus temperature effects on the onset saturation ratio are not reflected in counting efficiency data. However, if onset saturation ratios are shifted away from the limit of homogeneous nucleation by decreasing the chamber temperature, and therefore nucleation temperatures too, it becomes more likely to reach an activation efficiency close to one even for very small particles.

Summary

In summary, it can be said that vSANC counting efficiencies depend on chemical composition, charging state, chamber and humidifier temperatures and aerosol intake flowrate. Dependencies on chemical composition and charging state are probably attributed to the plastic sleeve of inlet valve V_1 , whereas influences of temperature and flowrate can be explained by particle diffusion.

vSANC counting efficiencies are comparable to those of other CPCs for particles below 1.5nm in diameter. Above that size vSANC detects less, because particle losses along the inlet line do not decrease as much as activation efficiencies of other CPCs increase. Comparatively high inlet losses are on the one hand caused by inlet valve V_1 and on the other hand by the fact, that in an expansion-type CPC particles are not activated until they reach the expansion chamber. This is a fundamental difference between expansion-type CPCs on the one hand and laminar flow- or mixing-type CPCs on the other.

However, it should be noted, that the vSANC can, in general, achieve activation efficiencies close to one. This is due to the fact, that vapor supersaturation can be increased up to the limit of homogeneous nucleation. In fact, even if homogeneous nucleation occurs in the

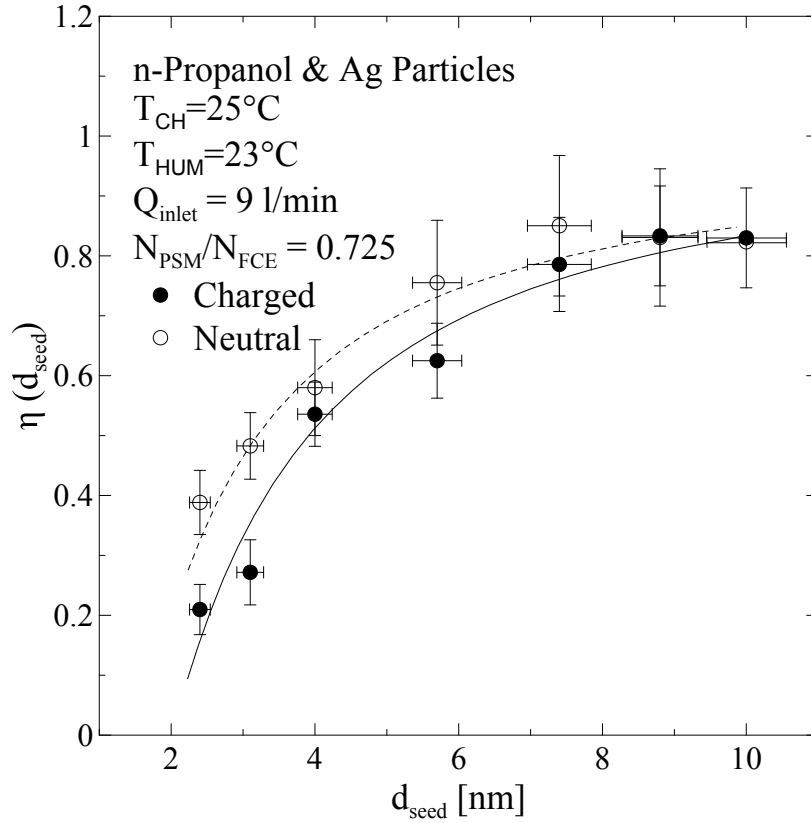


Figure 10.8: vSANC counting efficiency as a function of seed particle diameter for charged and neutral silver particles in n-propanol vapor.

expansion chamber, time resolved light flux measurements still enable to distinguish the signals of heterogeneously formed droplets from homogeneously formed ones (Winkler et al., 2008a). This distinction is possible because in the presence of seed particles supersaturation required to form critical clusters is always lower than without preexisting particles, and therefore signals from heterogeneously formed droplets will always appear earlier in time (lower supersaturation). This feature of vSANC becomes particularly useful, when sub-2nm particles are to be activated.

10.3 Comparison with theory

Instrument performance was not only characterized by checking counting efficiencies of different seed particles at various instrument settings but also by comparing experimentally determined onset saturation ratios S_{onset} with theoretical predictions. To this end, S_{onset} (see section 9.3.3) of n-propanol vapor has been determined for charged and neutral silver particles with diameters ranging from about 3nm to 10nm, and for charged sub-2nm tung-

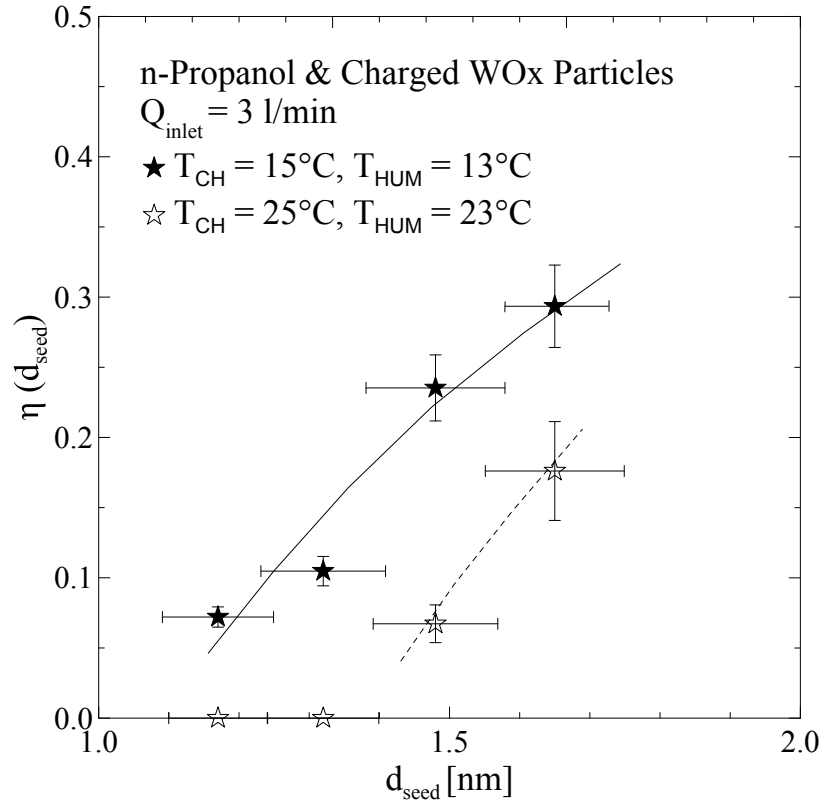


Figure 10.9: vSANC counting efficiency as a function of seed particle diameter for charged tungsten oxide particles in n-propanol vapor at different system temperatures.

sten oxide particles.

Figure 10.10 shows experimentally determined onset saturation ratios as a function of seed particle diameter. Solid lines are calculated using the *Kelvin* equation, which gives the diameter d_k of a droplet in equilibrium with the supersaturated ambient vapor (see section 2 eq. (2.9)).

It should be mentioned that *Kelvin* curves illustrated in fig. 10.10 are non-isothermal. This is due to the fact that, in the present study, an increase in vapor supersaturation was achieved by increasing the pressure drop instead of changing the initial saturation ratio before expansion and keeping the pressure drop constant. Consequently the temperature T_0 at the end of the expansion decreases with increasing supersaturation and non-isothermal *Kelvin* curves $S(d_k)$ need to be calculated by varying the expansion ratio β (see sections 2 and 4.1). Solid blue lines refer to low temperature settings (temperature before expansion $T_i = 15^\circ\text{C}$), whereas red lines correspond to high temperature setting ($T_i = 25^\circ\text{C}$). It can be seen from fig. 10.10 that at low temperature settings higher vapor supersaturation is required to form droplets in equilibrium with the supersaturated vapor.

For high temperature settings, the *Fletcher* curve (dashed red line), which describes the activation of neutral particles, was calculated. To this end eq. (2.19) from section 2 was

solved iteratively for seed particle radius $R = d_{seed}/2$ using $R = x \cdot r_k$, with r_k being the *Kelvin* radius, assuming that the contact angle θ_c is 0° . Again, calculations were performed for non-isothermal conditions.

Comparing *Kelvin* and *Fletcher* curve for high temperature settings, it can be seen that seed particles with diameters d_{seed} are already activated at sizes smaller than those predicted by the *Kelvin* equation. This is due to the fact, that in heterogeneous nucleation the critical cluster is formed on a preexisting surface, which lowers the free energy barrier of cluster formation (see section 2). It is this positive effect of seed particles on the formation of critical clusters, that makes the activation of particles below 2nm even possible. Looking at figure 10.10, it can be seen that according to *Kelvin* equation, the activation of seed particles below around 2.5nm in diameter would not be possible, because of homogeneous nucleation. However, Winkler et al. (2008b) showed, that particles well below 2.5nm can be activated, which is in agreement with *Fletcher* theory.

vSANC data (open/full red circles, blue stars in figure 10.10) are obtained from nucleation probability curves according to section 9.3.3. To this end vapor supersaturations corresponding to experimentally observed droplet growth were determined according to section 9.2.2. S_{onset} data for neutral silver particles (open red circles) are in nice agreement with the *Fletcher* curve. This indicates, that experiments are well-defined and data evaluation works fine.

Experiments with charged seed particles, result in onset saturation ratios lower than those predicted by the *Fletcher* theory. This effect is explained by the lowering of free energy barrier in the presence of charged seed particles, i.e. ion induced nucleation (see section 2). Tungsten oxide data determined with vSANC nicely agree with data obtained with the *classical* SANC (Winkler et al., 2008b). This further indicates the proper performance of vSANC.

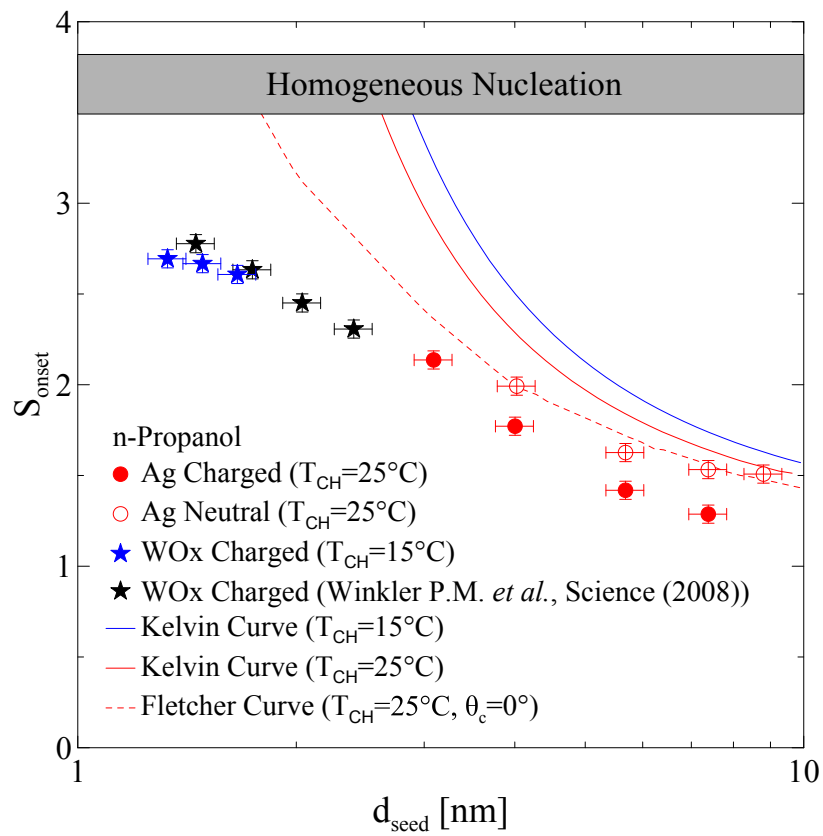


Figure 10.10: n-propanol onset saturation ratio S_{onset} as a function of seed particle diameter d_{seed} .

11 Field campaign

Field measurements with the vSANC have been conducted in spring 2014 at the boreal forest ecosystem measurement station SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations). This station is located in Hyytiälä, Finland (61°51'N, 24°17'E), in a 53-year-old Scots pine stand. A more detailed description of the measurement site can be found elsewhere, e. g. Dal Maso et al. (2005).

SMEAR II is equipped with various facilities that measure forest ecosystem-atmosphere interactions. Particle size distribution measurements are performed using two differential mobility particle sizers (DMPS) designed by Pasi Aalto (Aalto et al., 2001). A DMPS system basically consists of one DMA and one CPC. The DMA extracts a narrow electrical mobility fraction from the sample aerosol and the CPC measures the total number concentration of the extracted fraction. To obtain the size coverage of 3 – 500nm, the first DMPS measures particles between 3 and 10nm, and the second one between 10 and 500nm. In the following number concentrations measured by vSANC are compared with DMPS data.

11.1 Field configuration

During the spring 2014 field campaign the vSANC has been operated in *scanning* mode (see section 8.6) at an aerosol intake flowrate of 9l/min. Thereby the underpressure Δp_R^{SET} ¹ in vessel R is altered between three different values $\Delta p_R^1 < \Delta p_R^2 < \Delta p_R^3$. This results in three different vapor supersaturations S_0 at the end of the expansion (see figure 11.1).

Defining S_0^j as the vapor supersaturation corresponding to subpressure Δp_R^j , the three different vapor supersaturations are related to each other as follows:

$$S_0^1 < S_0^2 < S_0^3.$$

According to *Fletcher* theory (Fletcher, 1958) the diameter $d_{seed}(S)$ of particles, that can be activated by means of heterogeneous nucleation, depends on the vapor supersaturation at the end of the expansion (see e.g. figure 10.10, section 10.3). If d_{seed}^j is the diameter of a seed particle activated at S_0^j , then

$$d_{seed}^1 > d_{seed}^2 > d_{seed}^3.$$

¹To simplify upcoming notation superscript *SET* will be omitted in the following.

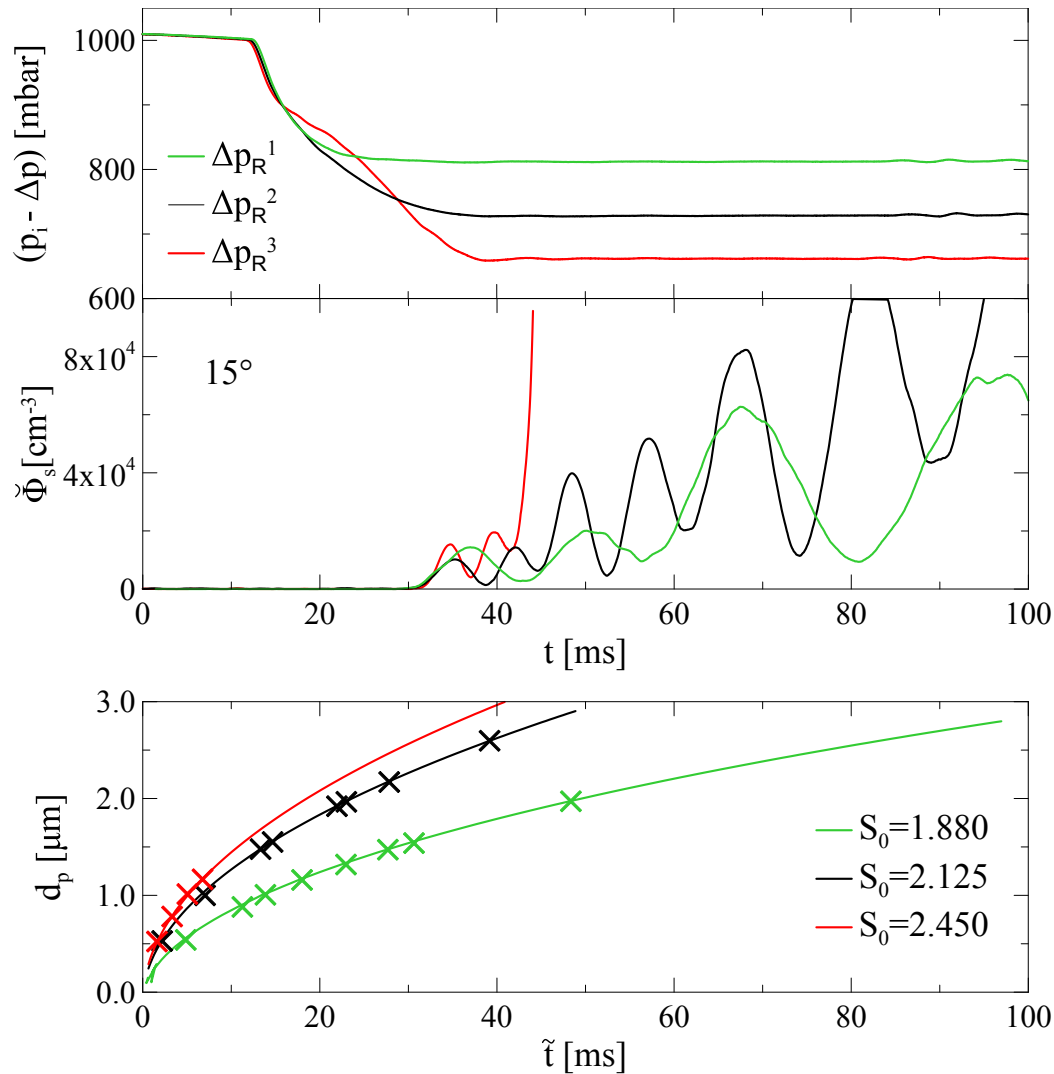


Figure 11.1: vSANC operated in *scanning* mode. The upper most graph shows the total chamber pressure $(p_i - \Delta p(t))$ during adiabatic expansion for three different underpressures $\Delta p_R^1 < \Delta p_R^2 < \Delta p_R^3$ in the subpressure vessel. The second graph shows normalized, attenuation corrected scattered light fluxes $\check{\Phi}_s(t)$ measured at 15° forward scattering direction. The green Mie curves corresponds to Δp_R^1 , the black to Δp_R^2 and the red to Δp_R^3 . Keeping the same color coding, it can be seen from the third graph, that the vapor supersaturation S_0 at the end of the expansion increases with increasing pressure drop.

Let N_c^j be the total particle number concentration measured at vapor supersaturation S_0^j . Then N_c^j refers to particles bigger or equal to d_{seed}^j in diameter. By subtracting

$$N_c^j - N_c^k \quad \text{for} \quad \begin{cases} j = \{2, 3\} \\ k = \{1, 2\} \\ j > k \end{cases},$$

the following size dependent normalized particle number concentrations are obtained:

$$\begin{aligned} \tilde{N}_c^1(d_{seed}) &= \frac{N_c^1}{d_{seed}^{max} - d_{seed}^1} \quad \text{for} \quad d_{seed} \in [d_{seed}^1, d_{seed}^{max}] \\ \tilde{N}_c^2(d_{seed}) &= \frac{N_c^2 - N_c^1}{d_{seed}^1 - d_{seed}^2} \quad \text{for} \quad d_{seed} \in [d_{seed}^2, d_{seed}^1] \\ \tilde{N}_c^3(d_{seed}) &= \frac{N_c^3 - N_c^2}{d_{seed}^2 - d_{seed}^3} \quad \text{for} \quad d_{seed} \in [d_{seed}^3, d_{seed}^2], \end{aligned}$$

Here d_{seed}^j is calculated from S_0^j for $j = \{1, 2, 3\}$ using *Fletcher* theory. It is assumed that all seed particles are perfectly wetted by n-propanol, which means that the macroscopic contact angle θ_c is 0° . Previous observations have shown, that neutral nucleation dominates in the boreal forest environment Kulmala et al. (2007), Kulmala et al. (2013). Thus, for field measurements in this environment the lowering of d_{seed} due to electric field interactions (ion-induced nucleation, see section 2.2.1) can be neglected. The particle diameter d_{seed}^{max} is assumed to be 100nm.

The *scanning* mode operation of vSANC yields information on the total particle number concentration in three different size bins. In order to be able to observe atmospheric formation and growth of nanoparticles, also referred to as new particle formation (NPF), subpressures Δp_R^1 , Δp_R^2 and Δp_R^3 were set to result in vapor supersaturations at the end of the expansion, that correspond to *Fletcher* diameters d_{seed} around 5nm, 2nm and 1nm, respectively. In fact, at the highest pressure drop, the vapor supersaturation is sufficiently high to cause homogeneous nucleation. However, as already mentioned before, time resolved scattered light flux measurements, allow to distinguish between homogeneously and heterogeneously formed droplets.

11.2 Results

11.2.1 High temperature settings

At the beginning of the measurement campaign vSANC has been operated at a chamber temperature of 25°C and a humidifier temperature of 23°C . During that period, three new particle formation (NPF) events according to Dal Maso et al. (2005) have been observed by the DMPS system.

Due to the high aerosol intake flow rate, i. e. 9l/min, it has been necessary to apply comparatively high pressure drops in order to achieve sufficiently high vapor supersaturations at the end of the expansion. Unfortunately high pressure drops, particularly in combination with polydispersed aerosols, yield heterogeneous nucleation and droplet growth to start before the end of expansion. This, in turn, makes it practically impossible to automatically determine the pressure drop Δp , that gives the vapor supersaturation S_0 initiating heterogeneous nucleation and droplet growth. Instead, Δp has to be determined manually as described in section 9.3.2. Since manual evaluation of experimental data, especially for long-term field campaigns, is very time intensive (about one hour per expansion experiment), only once every NPF day seed particle diameters defining the width of size bins have been determined from experimental Mie curves (see section 9.3.2). Averaging these values yields following particle diameter bin margins:

$$\begin{aligned} \text{Size bin 1 } d_{seed} &\in [(9.4 \pm 0.8)\text{nm}, 100\text{nm}] \\ \text{Size bin 2 } d_{seed} &\in [(3.1 \pm 0.5)\text{nm}, (9.4 \pm 0.8)\text{nm}] \\ \text{Size bin 3 } d_{seed} &\in [(2.9 \pm 0.4)\text{nm}, (3.1 \pm 0.5)\text{nm}] \end{aligned}$$

It can be seen that the margins of size bins 3 and 2 overlap. Thus effectively two size bins are left to determine particle size distributions. Moreover it can be seen that despite sufficiently high vapor supersaturations no particles below around 3nm in diameter have been activated. Figure 11.2 shows contour plots referring to vSANC (upper graph) and DMPS (lower graph) data measured on the 10th of April 2014 - a NPF day. Data from further NPF days (8th and 9th April) can be found in Appendix E. From the contour plots shown in fig. 11.2 it can be concluded that for particles above 10nm in diameter vSANC data show the same trend as DMPS data. Higher particle concentrations occur during two pollution bursts at around 2 a.m. and 6 a.m., and when newly formed particles grow above 10nm (around 1 p.m.). However, absolute normalized particle number concentrations detected by vSANC are clearly below those measured by DMPS.

Looking at size bin 2 of vSANC, i. e. particles between about 3 and 10nm, neither pollution bursts nor particle growth become visible.

Possible reasons for the disagreement between vSANC and DMPS data are:

1. Inlet losses of particles with diameters above 10nm are underestimated.
2. The size bin margins are assumed to be constant. However, the exact value of S_0^j , which is used to calculate d_{seed} , very probably varies from expansion to expansion because the exact moment, when significant droplet growth starts is rather undefined. This in turn yields unstable size bin margins, which has not been taken into account.
3. Automated determination of number concentrations overestimates actual values because the software uses the height of a higher Mie maximum instead of the height of the first one.

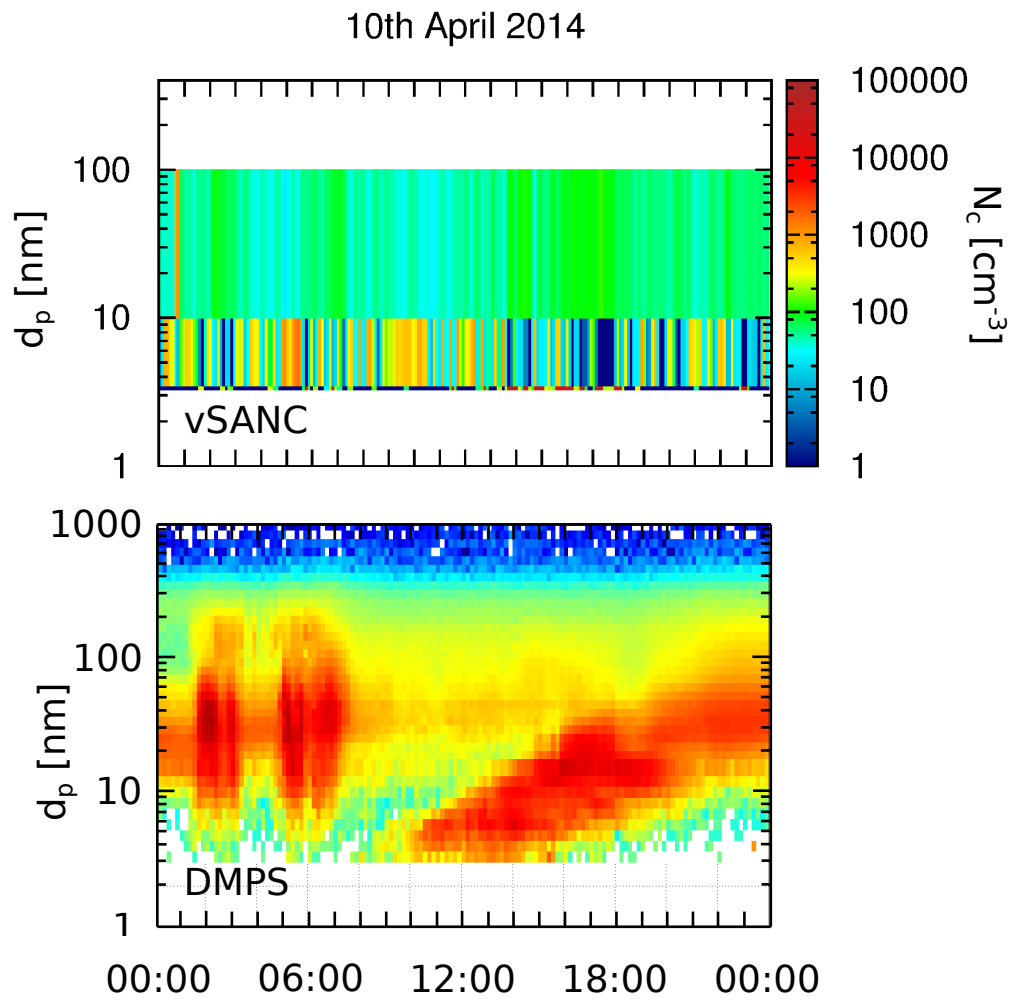


Figure 11.2: vSANC and DMPS contour plots from the 10th of April 2014.

4. Instrument temperatures higher than the ambient air temperature cause evaporation of particles along the inlet line.

Point (1) can be validated by performing laboratory measurements analogous to those presented in section 10.2 using particles above 10nm in diameter.

Problem (2) is eliminated by either manually evaluating all data, which, in particular for long term measurement campaigns, is unreasonable, or by improving the humidification system. An improved humidification system ideally results in vapor saturation ratios close to one before expansion. Then, pressure drops needed to achieve sufficiently high vapor supersaturations at the end of expansion are small enough, so that it is likely, that significant droplet growth will not start before the end of expansion. Experiments with the classical SANC have shown, that if the expansion takes about 20ms droplets will not grow during expansion.

Misinterpretations of Mie maxima might be eliminated by implementing a subroutine in `evaluate` (see section 9.2), which is comparing the relative position of Mie maxima at different light scattering angles with theoretical predictions. For example, the first Mie maximum of the 10° curve will always appear after the first maximum of the 15° curve and so on.

Evaporation losses of particles can be eliminated by decreasing system temperatures. In fact, chamber and humidifier temperatures were the only variables that could be changed during the field campaign. Thus after 3 weeks of operating the instrument at high temperature settings, chamber and humidifier temperatures were decreased to 15°C and 13°C, respectively.

11.2.2 Low temperature settings

While vSANC was operated at low temperatures, 7 NPF events have been identified. Again size bin margins had to be determined manually. The averaged values are:

$$\begin{aligned} \text{Size bin 1 } d_{seed} &\in [(8.1 \pm 1.4)\text{nm}, 100\text{nm}] \\ \text{Size bin 2 } d_{seed} &\in [(3.4 \pm 0.4)\text{nm}, (8.1 \pm 1.4)\text{nm}] \\ \text{Size bin 3 } d_{seed} &\in [(2.3 \pm 0.5)\text{nm}, (3.4 \pm 0.4)\text{nm}] \end{aligned}$$

Figure 11.3 shows contour plots from the 23rd of April 2014 - a NPF day. It can be seen that operating vSANC at lower temperatures yields a somewhat better agreement between DMPS and vSANC data. However margins of the second size bin seem to be wrong. The concentration trend of the second size bin rather refers to particles above 10nm in diameter according to the DMPS plot.

Since the agreement between vSANC and DMPS contour plots was still not satisfactory, vSANC data have been evaluated manually, for this specific day. Knowing temperature T_i before expansion and pressure drop Δp , S_0 is determined using `growth` (see section 5.3.1). After that, T_i , Δp and S_0 are used to check the saturation ratio S_i before expansion (see section 4.1). Figure 11.4 shows S_i and S_0 resulting from manually determined pressure drops.

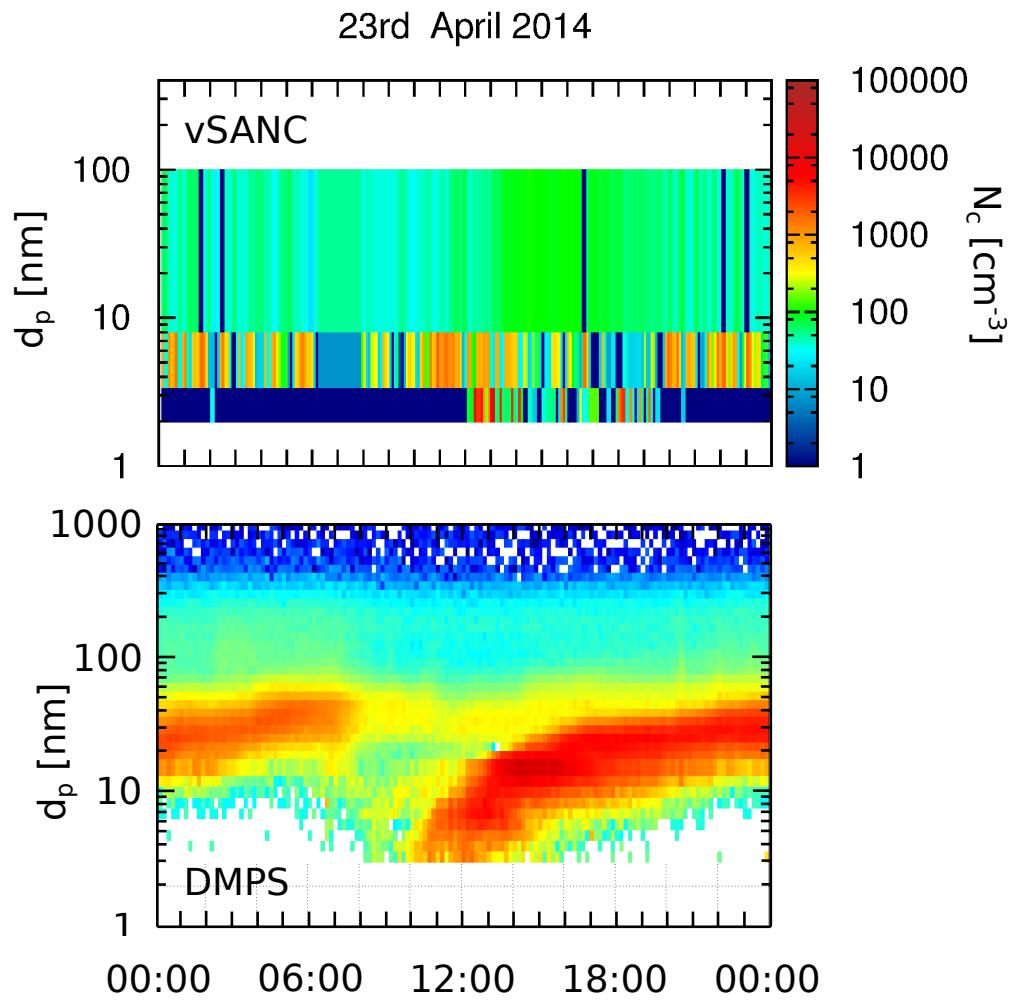


Figure 11.3: vSANC vs DMPS contour plots from the 23rd of April.

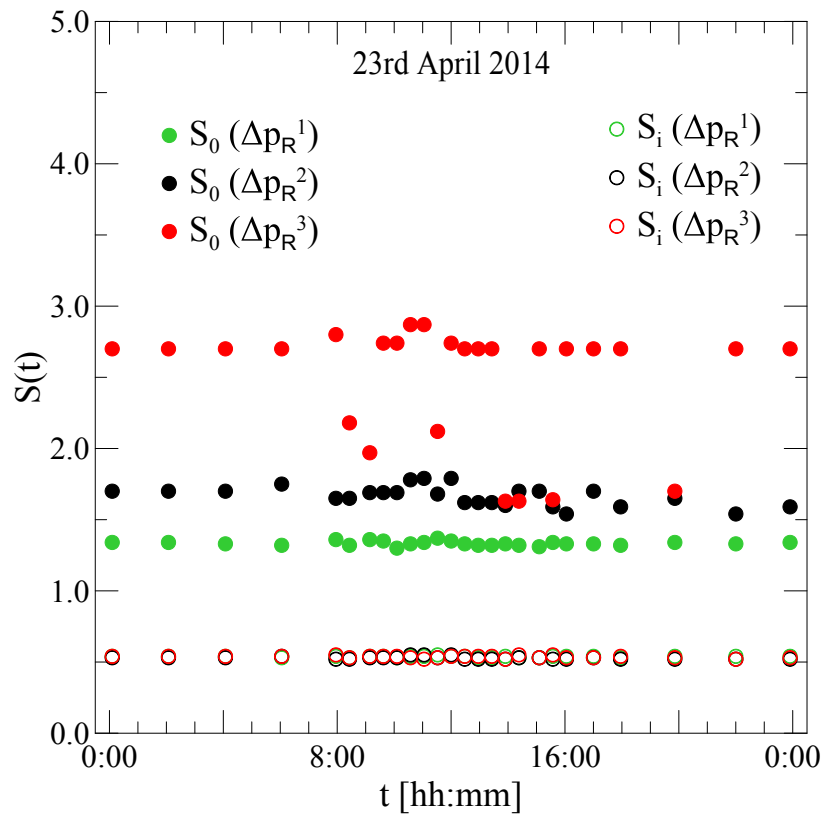


Figure 11.4: Experimentally determined n-propanol vapor saturation ratios before and at the end of expansion, S_i and S_0 , respectively.

It can be seen, that the initial vapor saturation ratio S_i^j is constant and about 0.52. Thus the humidification of the sample aerosol is stable. However, vapor supersaturations at the end of expansion fluctuate, which results in varying size bin margins. Strongest fluctuations occur at the highest pressure drop (solid red circles).

The contour plot resulting from manual data evaluation is shown in figure 11.5. Clearly,

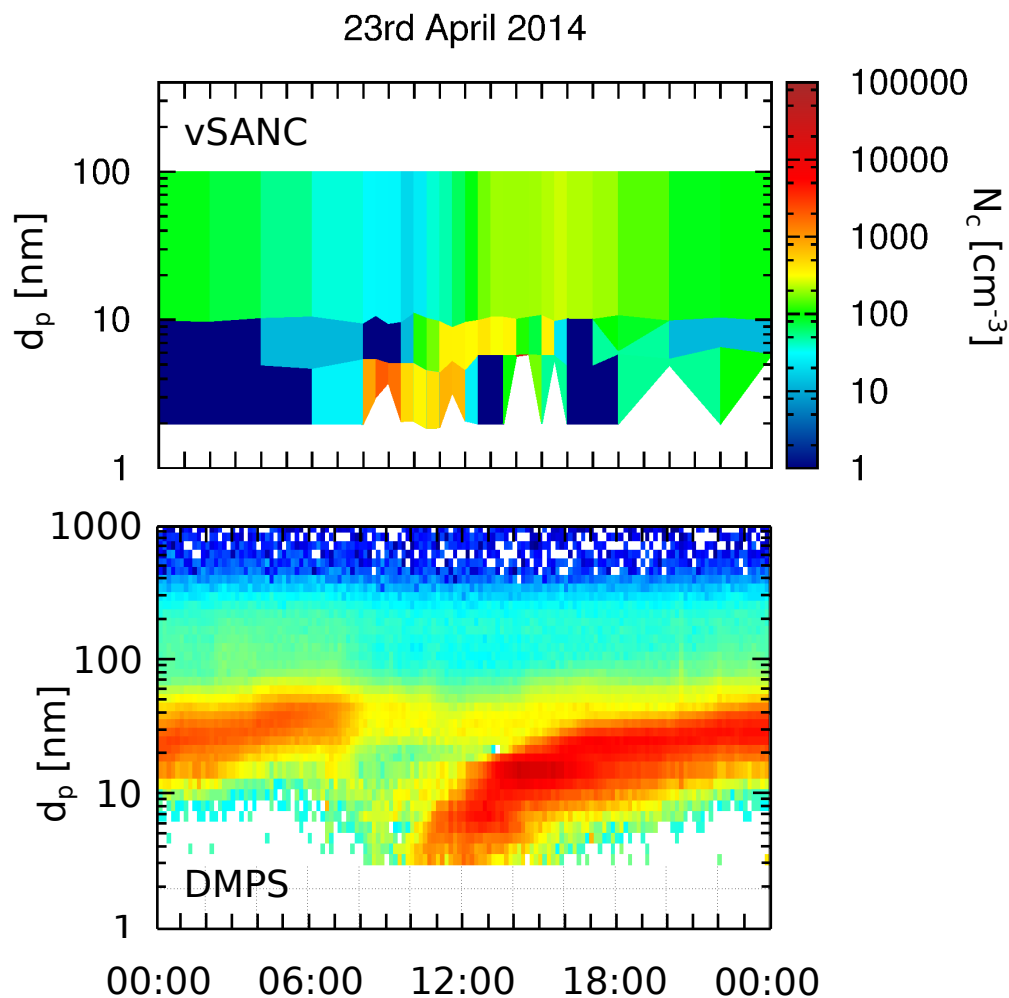


Figure 11.5: vSANC (manual data evaluation) vs DMPS contour plots from the 23rd of April.

the agreement between vSANC and DMPS data is better now. Moreover, vSANC detects particles below 3nm in diameter, where the DMPS is *blind*. Sub-3nm particles occur already around 9 a.m., which is about 3 hours prior to the observation of NPF by the DMPS. How-

ever the continuous presence of a large pool of sub-2nm particles, as suggested by Kulmala et al. (2007), could not be confirmed during these measurements.

The second day, where manual data evaluation has been performed, is the 3rd of May (see figure 11.6). Here no particles below 4nm in diameter have been detected, which is in agree-

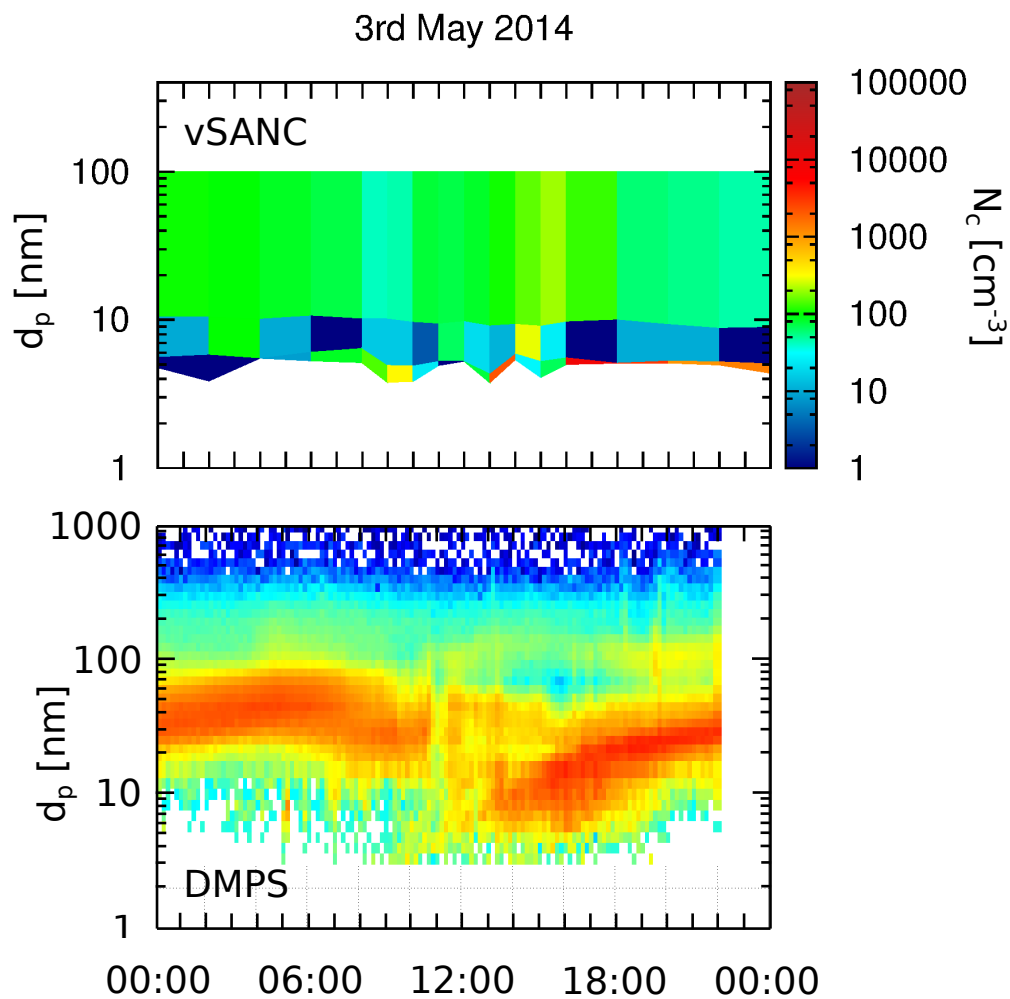


Figure 11.6: vSANC (manual data evaluation) vs DMPS contour plots from the 3rd of May.

ment with DMPS data. Further automatically evaluated vSANC campaign plots including all NPF days can be found in Appendix E.

11.2.3 Influence of relative humidity

Another interesting observation during vSANC's field deployment was the influence of relative humidity (RH) on measurements. To check the performance of vSANC, *zero* measurements have been performed in the morning and evening of each measurement day. To this end a HEPA filter was installed at the instrument inlet and the onset of homogeneous nucleation was investigated by stepwise increasing the pressure drop in the expansion chamber. All-campaign averages of Mie curves from homogeneous nucleation tests are shown in figure 11.7. Red, green and blue solid lines are normalized and averaged experimental Mie curves

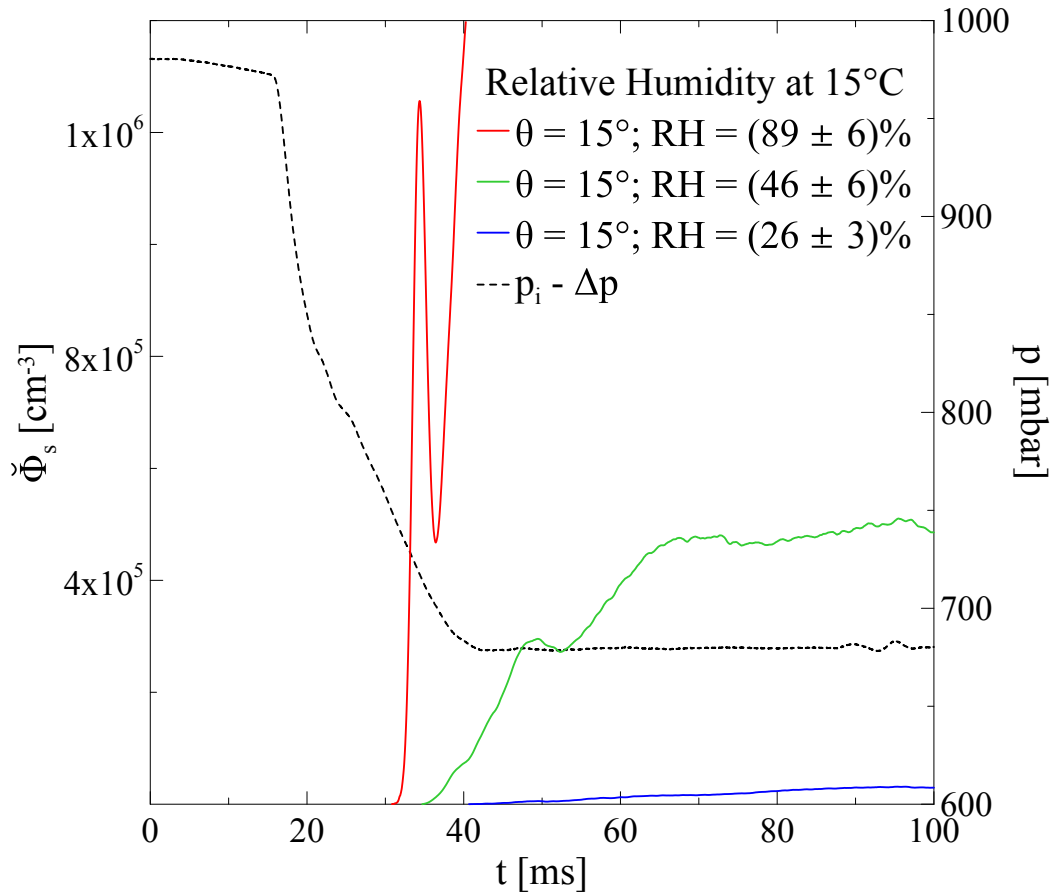


Figure 11.7: Averaged, attenuation corrected and normalized scattered light fluxes $\langle \check{\Phi}_s \rangle$ measured at 15° forward scattering direction. Red, green and blue curves represent the mean of all $\check{\Phi}_s$ measured at ambient RH $\approx 89\%$, $\approx 46\%$ and $\approx 26\%$, respectively. The dashed black line corresponds to the total gas pressure change during expansion.

measured at 15° forward scattering direction, when the relative humidity of the particle free sample air at 15°C was about 89%, 46% and 26%, respectively. It can be clearly seen, that as RH increases homogeneous nucleation starts at lower pressure drops. This is a strong indicator for binary nucleation of n-propanol and water. Fortunately, NPF events usually

occur when RH is sufficiently low, so that binary nucleation can be neglected.

11.2.4 Summary

During Spring 2014 the vSANC has been operated in *scanning* mode at an aerosol intake flowrate of 9l/min using n-propanol as nucleating and condensing liquid at the SMEAR II station in Hyytiälä, Finland. Measurements indicate, that system temperatures strongly influence the performance of the instrument. In this context, it turns out that operating the instrument at temperatures close to ambient air temperatures, yields better agreement with DMPS data.

Uncertainties about the actual vapor supersaturation ratio that initiates heterogeneous nucleation, yield uncertainties about the size of activated particles. This is mainly due to the fact, that droplet growth starts before the end of expansion, which makes manual data evaluation necessary. Ideally, significant droplet growth always starts after the end of expansion. Only then the pressure drop Δp can be determined automatically, which facilitates data evaluation significantly. To reach more favorable operating conditions, it is planned to redesign the humidification system.

Although vapor supersaturation ratios at the end of the expansion were set to be sufficiently high to activate particles down to 1nm in diameter, no such particles have been observed. This can have the following reasons:

- (i) Not enough particles in that size range are present, which would be in disagreement with predictions made by Kulmala et al. (2007).
 - (ii) The signal resulting from activated 1 – 2nm particles is superimposed by the signal of bigger particles, which are activated earlier in time.
 - (iii) Atmospheric nanoparticles below 2nm in diameter are not wetted by n-propanol.
- (i) is very unlikely, because at least during NPF events high number concentrations of sub-2nm particles have already been observed Kangasluoma et al. (2014). Also (iii) is rather unlikely, because so far the activation of all kinds of seed particles with n-propanol has been no problem. (ii) needs to be investigated in the laboratory. A possible test setup could consist of two DMAs, which are extracting different mobility fractions from an initially poly-dispersed, stable test aerosol. Combining the two mobility fractions yields a well defined bimodal number size distribution. If (ii) is true, than the number concentration detected by vSANC increases relative to the number concentration detected by a FCE, when the diameters of the two modes approach each other.

Homogeneous nucleation tests performed on every measurement day indicate, that at high relative humidity binary nucleation of water and n-propanol occurs in the expansion chamber. This effect is not only restricted to the n-propanol - water system but has also been

observed by other condensation particle counters, such as the PSM, which are operated at very high vapor supersaturations.

12 Summary

Based on our experience with the *classical* Size Analyzing Nuclei Counter (SANC, Preining et al. (1981); Wagner et al. (2003)), we developed a new expansion chamber condensation particle counter - the versatile Size Analyzing Nuclei Counter (vSANC).

The operation of vSANC is based on heterogeneous nucleation of supersaturated vapor on preexisting aerosol particles and subsequent droplet growth. Well-defined and uniform vapor supersaturation is obtained by fast adiabatic expansion of an undersaturated vapor-gas mixture. Thereby, particles down to 1nm in diameter (Winkler et al., 2008b) can be activated and grow to visible sizes.

The number concentration N_c of the growing droplets is determined applying the multi-angle Constant Angle Mie Scattering method (mCAMS), an optical detection technique. The mCAMS method is a further development of the Constant Angle Mie Scattering method (CAMS, Wagner (1985)). Droplets growing inside the expansion chamber are illuminated by a blue laser beam, which is polarized perpendicularly to the plane of observation. The light flux scattered by the growing droplets, Φ_s , is measured at five different forward scattering angles. Simultaneously the light flux incident upon and transmitted through the expansion chamber, Φ'_i and Φ_t , respectively, are monitored. Measurements of Φ_s and Φ_t allow to eliminate the influence of light attenuation on measured light scattering signals. The height of attenuation corrected scattered light fluxes, $\tilde{\Phi}_s$, is directly proportional to the number concentration of droplets. Provided that each growing droplet corresponds to just one aerosol particle, the measured droplet concentration is equal to the aerosol particle number concentration. The mCAMS method allows to determine *absolute* number concentrations ranging from 10^2 to 10^7cm^{-3} without referring to empirical calibrations by external reference standards. Moreover, measurements of Φ'_i allow to determine light attenuation in situations, where aerosol particles already scatter light before expansion and to monitor the incident beam stability. Thus the mCAMS method is not restricted to particles, which are initially small enough, that Mie scattering can be neglected.

Time resolved measurements of $\tilde{\Phi}_s(t)$ yield experimental curves, which are in good agreement with theoretical $\Phi_s(d_p)$ curves calculated using Mie theory (Mie, 1908). This enables the establishment of a unique correspondence between experimental and theoretical Mie extrema, provided that the diameter of particles scattering light is initially smaller than the diameter corresponding to the first Mie maximum. Thereby experimental droplet growth data $d_p(t)$ are determined. Measurements of $\tilde{\Phi}_s(t)$ at five different light scattering angles provide information on the alignment of the optical arrangement.

Besides light flux measurements, the temperature of the particle-vapor-gas mixture before expansion T_i , the total gas pressure p_i before expansion and the total pressure change during expansion Δp are monitored. Knowing the vapor saturation ratio S_i before expansion, vapor supersaturation S_0 at the end of the expansion process can be calculated from the above listed quantities provided that the expansion process is dry adiabatic. Since droplet growth is very sensitive to S_0 , experimentally determined $d_p(t)$ data can be used to verify S_0 . On the other hand, if S_i is unknown, S_0 can be determined by comparing experimental $d_p(t)$ data with theoretical $d_p(t)$ curves.

Knowing N_c and S_0 nucleation studies can be performed. To this end, S_0 is stepwise increased until all particles in the expansion chamber are activated. This results in experimental nucleation probability curves $P(S_0)$, which provide the fraction of activated particles as a function of S_0 . From experimental $P(S_0)$ curves, the onset saturation ratio S_{onset} , which is defined as the vapor supersaturation where 50% of particles are activated, can be determined. S_{onset} , in turn, can be used to estimate the size of seed particles that can be activated according to *Fletcher* theory (Fletcher, 1958).

In the present study, S_{onset} was determined for monodispersed neutral and positively charged silver particles and for monodispersed positively charged tungsten oxide particles of well known size in n-propanol vapor. Theoretical determination of seed particles sizes based on the *Fletcher* theory, assuming perfect wettability of the seeds (contact angle $\theta_c = 0^\circ$), yield good agreement with experimental values for neutral seed particles. Charged seeds, however, nucleate at vapor supersaturations lower than those predicted by *Fletcher* theory. This finding is in agreement with previous studies of Winkler et al. (2008b) and can be explained theoretically by the *Fletcher-Thomson* theory.

Laboratory studies on size dependent vSANC counting efficiencies $\eta(d_{seed})$ were performed with various monodispersed seed particles in n-propanol vapor. Corresponding to the particle size S_0 was properly chosen to achieve the activation of all seed particles inside the expansion chamber ($P = 1$). Thus, in good approximation, vSANC counting efficiencies are only depending on particles losses along the inlet line. The inlet line basically consists of a 30cm long humidifier, a 8cm long inlet valve and stainless steel tubing. Results show that $\eta(d_{seed})$ depends on:

- (1) aerosol intake flow rate,
- (2) expansion chamber and humidifier temperature, T_{CH} and T_{HUM} , respectively,
- (3) charging state and
- (4) chemical composition of seed particles.

With increasing aerosol flow rate, and decreasing system temperatures $\eta(d_{seed})$ increases. This indicates that (1) and (2) are mainly caused by particle diffusion losses. On the other hand, (3) and (4) very likely originate from additional electrostatic forces caused by the

plastic sleeve of the inlet valve. Neutral particles and those with weaker polarity penetrate better through the inlet. In order to achieve counting efficiencies, which are independent of chemical composition or charging state of particles, it is planned to replace the pinch valve by a stainless steel ball-valve. Compared to other condensation particle counters (CPCs) running with diethylene glycol (DEG) as condensing liquid, such as Airmodus Model A09, which is a mixing type CPC (Vanhanen et al., 2011) or the modified TSI Model 3025 (Iida et al., 2009), which is a laminar flow type CPC (Stolzenburg and McMurry, 1991), vSANC counting efficiency curves for positively charged ammonium sulfate particles show weaker size dependence. This is due to the fact that vSANC counting efficiencies are dominated by inlet losses, whereas counting efficiencies of most other CPCs are mainly determined by particle nucleation probabilities. This fundamental difference between expansion-type CPCs on the one hand and mixing- or laminar flow-type CPCs on the other, becomes clear when comparing d_{10} and d_{50} , which are the seed particle diameters corresponding to 10% and 50% counting efficiency, respectively:

	$d_{50}[\text{nm}]$	$d_{10}[\text{nm}]$
vSANC	4.3	1.5
Airmodus A09 (Vanhanen et al., 2011)	1.8	1.5
Modified TSI 3025 (Iida et al., 2009)	1.7	1.5

In spring 2014 field studies with vSANC have been conducted at the SMEAR II station in Hyytiälä, Finland. During its field deployment vSANC has been operated in *scanning* mode, where the vapor supersaturation S_0 at the end of the expansion is altered among three different values. Knowing S_0 , particle number concentrations in three different size bins, and thereby information on particle number size distributions, can be obtained. Comparison with data obtained from two differential mobility particle sizers (DMPS, Aalto et al. (2001)) yield following conclusions:

- (1) vSANC size bin margins are not constant, but rather vary from expansion to expansion and
- (2) better agreement between vSANC and DMPS data is achieved, when chamber and humidifier temperatures are closer to the ambient air temperature.

Ideally, S_0 varies between three different but constant values. This would result in constant size bin margins. Currently this is not the case, which makes manual data evaluation necessary. To achieve stable conditions regarding S_0 , it is necessary to achieve vapor saturation ratios S_i close to one before expansion. It is therefore planned to optimize the humidification system.

Another interesting observation was the fact, that although vSANC has been operated at vapor supersaturation ratios close to the onset of homogeneous nucleation, no particles below 2nm in diameter have been observed during field measurements. However, laboratory

studies showed, that, in principle, particles down to 1nm in diameter can be detected. This yields following conclusions:

- (1) either ambient aerosol particles with diameters below 2nm are not wetted by n-propanol,
- (2) or the number concentration of particles in the sub-2nm size range is below 10^4cm^{-3} ,
- (3) or the signal of activated sub-2nm particles is superimposed by the signal of bigger particles, which are activated earlier in time.

Hypothesis (1) is rather unlikely because the activation of all kinds of seed particles with n-propanol has never been a problem so far. Hypothesis (2) is in disagreement with predictions made by Kulmala et al. (2007). They hypothesized that a large pool of neutral clusters with diameters below 3nm is continuously present. Hypothesis (3) requires further laboratory tests.

13 Outlook

Based on the results of this thesis, the following modifications are recommended before performing further laboratory or field studies:

1. The humidification system should be redesigned to achieve nearly saturated vapor conditions before expansion and to decrease particle losses along the instrument inlet.
2. The inlet valve (pinch valve) should be replaced by a stainless steel ball valve to decrease inlet losses.
3. The flowshaper should be redesigned to achieve faster expansion processes.
4. To eliminate the influence of the incident laser light flux on measured scattered light signals, scattered light fluxes should be normalized with respect to the transmitted light flux.
5. To increase the upper diameter limit of detectable seed particles, the incident light flux measured before entering the expansion chamber should be used as reference for the determination of light attenuation.
6. The implementation of a critical orifice “battery” (three different critical orifices) would enable to change the vapor saturation ratio S_i before expansion by varying the aerosol flow rate through the humidifier. Then size-dependent particle activation (*scanning* mode) can be achieved by altering among three different aerosol intake flow rates without changing the expansion ratio, which results in constant temperatures at the end of expansion.
7. A subroutine comparing the position of experimental Mie extrema identified at different scattering angles with one another and with theoretical predictions, should be implemented in the data evaluation software **evaluate**. Thereby misinterpretation in corresponding experimental to theoretical extrema might be eliminated. Then the mCAMS method might enable automated interpretation of Mie extrema.

Appendices

A Pictures

A.1 Integrated optics assembly



Figure A.1: Integrated Optics Assembly. (a) shows cover and base part of one optical plate. The Cover plate (to the left) is coated with a matt top coat whereas the base plate (to the right) is not. The influence of the matt layer on the reflectance of the material is clearly visible. Lenses and pinholes installed in the base plate (b) are adjusted using fine thread screws (d) pressing the elements against spring mounted pins (c).

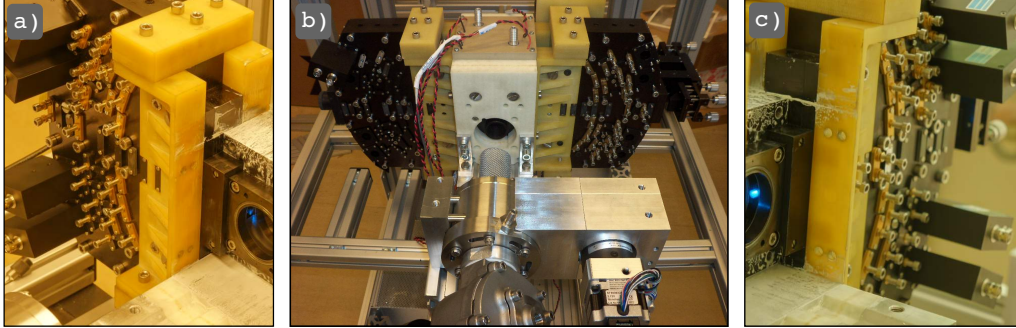


Figure A.2: Integrated Optics Assembly. Optical plates are attached to both sides of the expansion chamber (b). (a) shows the fully equipped optical plate for measurements of transmitted and scattered light fluxes. The optical plate attached to the laser inlet side is shown in (c).

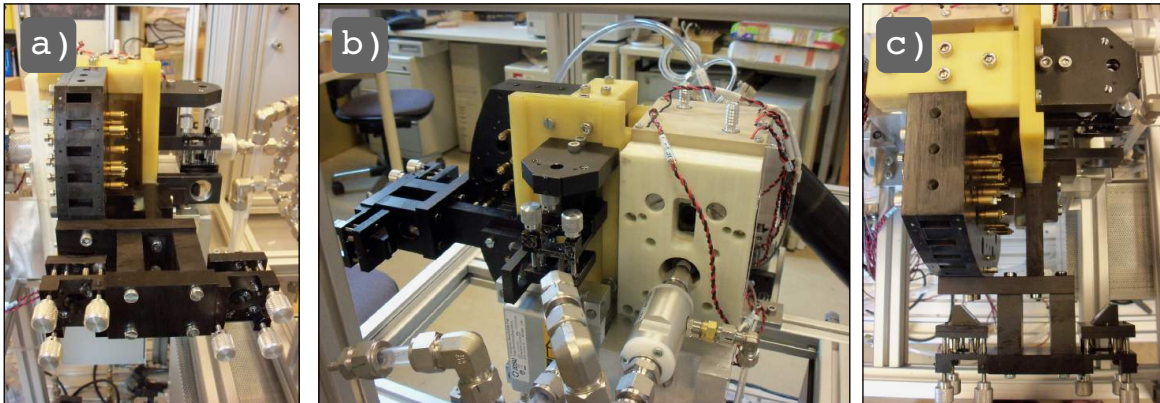


Figure A.3: Pictures of the Laser Inlet System (LIS) attached to the optical plate on the laser inlet side of the expansion chamber. (a) shows the two final deflecting mirrors, which direct the beam towards the expansion chamber. Each mirror can be adjusted using three fine thread screws. (b) shows the LIS from the aerosol inlet side and (c) from the top. The photo diode measuring Φ'_i and the beam expander were not installed yet, but their mounts can be seen on (c) and (a), respectively.

B Optics

B.1 Dimensions of the optical arrangement

Inner diameter	$d_{\text{CH}} = 2r_{\text{CH}}$	45mm
Outer diameter	$D_{\text{CH}} = 2R_{\text{CH}}$	52.2mm
Wall thickness	d_{G}	3.6mm
Refractive index	n_{G}	1.45
Angle of inclination	δ	1.24°

Table B.1: Dimension of the expansion chamber

Radius	r_{LB}	1.42mm
Half-width	$\sigma = \frac{r_{\text{LB}}}{3}$	0.47mm
Diameter after entering expansion chamber EXP	$d_{\text{LB}}^{\text{IN}}$	5.1mm
Diameter before leaving EXP	$d_{\text{LB}}^{\text{OUT}}$	4.8mm

Table B.2: Dimensions of the laser beam

Radius of pinhole P	r_{P}	0.6mm
Back focal length of lens L	f_l	40.22mm
Diameter of circular stop S_{C}	d_{SC}	6mm
Distance between P and photo diode PD	$d_{\text{P} \rightarrow \text{PD}}$	2mm
Active area of PD	A_{PD}	$2.5^2 \pi \text{mm}^2$

Table B.3: Dimensions of the lens-pinhole detector system for measurements of the transmitted light flux

B.2 Part lists

Part lists of integrated optics assembly and laser inlet system are shown in table B.5 and B.6, respectively.

Light Scattering angle	θ	10°	15°	20°	25°	30°
Width of rectangular stop S_R	$w_R[\text{mm}]$	1.2	4	4	4	4
Radius of pinhole P	$r_P[\text{mm}]$	0.1	0.3	0.3	0.3	0.3
Back focal length of lens L	$f_l[\text{mm}]$	40.22	34.07	34.07	34.07	34.07
Distance between L and scattering droplet	$\rho_{dp}[\text{mm}]$	149.5	163.5	152.5	171.5	150.5
Distance between rectangular stop S_R and expansion chamber EXP	$d_R[\text{mm}]$	105	110	105	110	105
Distance between P and deflecting mirror M	$d_{P \rightarrow M}$	42.1	34.7	34.7	34.7	34.7
Distance between M and photomultiplier tube PMT	$d_{M \rightarrow \text{PMT}}$	22	22	22	22	22
Active area of PMT	$A_{\text{PMT}}[\text{mm}^2]$	$5^2\pi$	$5^2\pi$	$5^2\pi$	$5^2\pi$	$5^2\pi$

Table B.4: Dimensions of lens-pinhole detector system for measurements of scattered light fluxes

Optical Element	Supplier (Part No.)	Specifications
8× Plano-convex lens	Edmund Optics (47-334)	$f_l = 34.07\text{mm}$
3× Plano-convex lens	Edmund Optics (47-335)	$f_l = 40.22\text{mm}$
8× Pinhole	Edmund Optics (56-284)	$r_P = 0.1\text{mm}$
2× Pinhole	Edmund Optics (56-288)	$r_P = 0.3\text{mm}$
1× Pinhole	Edmund Optics (56-291)	$r_P = 0.6\text{mm}$
1× Cylindrical plano-convex lens	Edmund Optics (68-169)	$f_l = 50\text{mm}$
1× Cylindrical plano-concave lens	Edmund Optics (69-794)	$f_l = -25\text{mm}$
1× Linear polarization filter	Edmund Optics (47-325)	Transmission $\approx 30\%$
1× Photo diode	Centronic (OSD35-5T)	$A_{PD} \approx 2.5^2\pi\text{mm}^2$
10× Photomultiplier tube	Hamamatsu (H7827-002)	$A_{\text{PMT}} \approx 5^2\pi\text{mm}^2$

Table B.5: Part list of the integrated optics assembly

B.3 Matrix representation of Gaussian optics

Ray-tracing formulae according to the matrix representation of Gaussian Optics can be used to analyze beam paths in complex optical systems.

Thereby a two dimensional column vector

$$\vec{v} = \begin{pmatrix} \alpha \\ h \end{pmatrix} \quad (\text{B.1})$$

is introduced, describing a ray at a reference plane R , which is always perpendicular to the optical axis. h is the vertical distance between the optical axis and the point where the ray intercepts with R and α is the angle between ray and optical axis.

Optical Element	Supplier (Part No.)	Specifications
2× Mirror	Edmund Optics (43-869)	Reflectance < 95%
1× Mirror	Edmund Optics (68-419)	Reflectance 80%, Transmission 20%
1× Beam expander	Qioptiq (G038658000)	4× expansion
1× Laser	JSDU (FCD488)	$\lambda = 488\text{nm}$, $P = 20\text{mW}$
1× Photo diode	Centronic (OSD35-5T)	$A_{\text{PD}} \approx 2.5^2\pi\text{mm}^2$

Table B.6: Part list of the laser inlet system

Giving first-order (Gaussian) optics, equations describing ray propagation are linear and can therefore be formulated using following matrices:

1. The transmission matrix $\mathbf{T}$:

$$\mathbf{T}(d, n) = \begin{pmatrix} 1 & 0 \\ \frac{d}{n} & 1 \end{pmatrix} \quad (\text{B.2})$$

describes the propagation of $\vec{v}$ through a homogeneous medium of length d and refractive index n .

2. The refraction matrix $\mathbf{R}$:

$$\mathbf{R}(D(n_i, n_j, r)) = \begin{pmatrix} 1 & -D(n_i, n_j, r) \\ 0 & 1 \end{pmatrix} \quad (\text{B.3})$$

with refractive power

$$D(n_i, n_j, r) = \frac{n_i - n_j}{r} \quad (\text{B.4})$$

represents the refraction of a ray at an interface with curvature r between two media with inner and outer radii r_2 and r_1 , respectively, and refractive indices n_i and n_j .

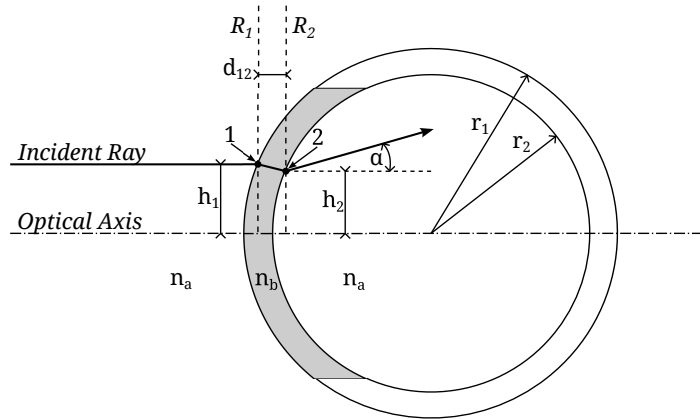


Figure B.1: Schematic diagram of ray propagation in an optical system consisting of a cylindrical ring with refractive index $n_b > n_a$.

For example a ray entering a cylindrical ring (see fig. B.1) with refractive index $n_b > n_a$, whereas n_a is the refractive index of the surrounding medium, can be described using the following ray tracing equation

$$\vec{v} = \begin{pmatrix} \alpha \\ h_2 \end{pmatrix} = \begin{pmatrix} 1 & -\frac{n_a - n_b}{r_1} \\ 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ \frac{d_{12}}{n_b} & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & -\frac{n_b - n_a}{r_2} \\ 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ h_1 \end{pmatrix}, \quad (\text{B.5})$$

where vector $\vec{v}$ represents the ray leaving reference plain R_2 at point 2 in figure B.1. r_1 and r_2 are inner and outer diameter of the ring, respectively. h_1 is the vertical distance between ray and optical axis at reference plane R_1 and d_{12} is the distance, which the ray propagates through the ring.

It follows from equation B.5 that a cylindrical glass-ring surrounded by air ($n_b > n_a$) has a defocusing effect on incident light.

B.3.1 Incident laser beam

The laser beam inside the expansion chamber is described by a two-dimensional vector $\vec{v}_{\text{LB}}^{\text{IN}}$, which is given by

$$\vec{v}_{\text{LB}}^{\text{IN}} = \mathbf{L}_{\text{G1}} \cdot \mathbf{T}_{\text{LCF} \rightarrow \text{LG1}} \cdot \mathbf{L}_{\text{CF}} \cdot \mathbf{T}_{\text{LCD} \rightarrow \text{LCF}} \cdot \mathbf{L}_{\text{CD}} \cdot \vec{v}_L^0, \quad (\text{B.6})$$

$\vec{v}_L^0$ is the ray-tracing vector corresponding to the outermost ray of LB, that enters correction lens L_{CD} from the right (see fig. B.2). Matrices $\mathbf{T}_{i \rightarrow j}$ describe ray propagation in air ($n_{\text{air}} = 1$) from i to j . Individual lenses¹, are described by matrices $\mathbf{L}_i$ given by:

$$\mathbf{L}_i = \mathbf{R}_{i,2} \cdot \mathbf{T}_{i,1 \rightarrow 2} \mathbf{R}_{i,1}, \quad (\text{B.7})$$

where $\mathbf{R}_{i,1}$ describes refraction on the side facing the incident light and $\mathbf{R}_{i,2}$ the one that is adverted from it. $\mathbf{T}_{i,1 \rightarrow 2}$ describes ray propagation inside the lens.

The ray-tracing vector leaving L_{CD} is given by

$$\begin{aligned} \mathbf{L}_{\text{CD}} \cdot \vec{v}_{\text{LB}}^0 &= \mathbf{R}(D(1, 1.517, \infty)) \cdot \mathbf{T}(2\text{mm}, 1.517) \cdot \mathbf{R}(D(1.517, 1, -129.2\text{mm})) \cdot \begin{pmatrix} 0^\circ \\ 1.41\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} 3.26^\circ \\ 1.50\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.8})$$

¹lenses $\mathbf{L}_{\text{G1}}$ and $\mathbf{L}_{\text{G2}}$ represent entrance and exit window of the glass-ring, respectively.

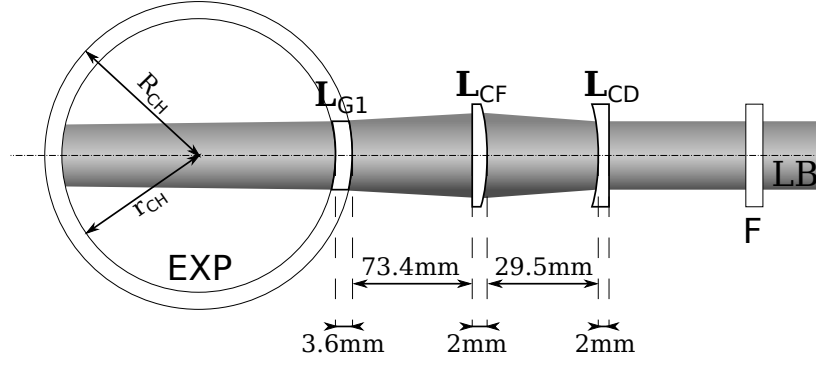


Figure B.2: Detailed schematics of the incident laser beam LB. $\mathbf{L}_{CD}$ and $\mathbf{L}_{CF}$ are cylindrical corrective lenses, F is a polarization filter and $\mathbf{L}_{G1}$ the entrance window of the expansion chamber EXP.

Before entering $\mathbf{L}_{CF}$ it becomes

$$\begin{aligned} \mathbf{T}_{LCD \rightarrow LCF} \cdot \mathbf{L}_{CD} \cdot \vec{v}_{LB}^0 &= \mathbf{T}(29.5\text{mm}, 1) \cdot \begin{pmatrix} 3.26^\circ \\ 1.50\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} 3.26^\circ \\ 3.18\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.9})$$

After passing through $\mathbf{L}_{CF}$ the ray-tracing vector is

$$\begin{aligned} \mathbf{L}_{CF} \cdot \mathbf{T}_{LCD \rightarrow LCF} \cdot \mathbf{L}_{CD} \cdot \vec{v}_{LB}^0 &= \mathbf{R}(D(1, 1.485, \infty)) \cdot \mathbf{T}(2\text{mm}, 1.485) \cdot \\ &= \mathbf{R}(D(1.485, 1, 229.3\text{mm})) \cdot \begin{pmatrix} 3.26^\circ \\ 3.18\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} -0.38^\circ \\ 3.17\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.10})$$

and becomes

$$\begin{aligned} \mathbf{T}_{LCF \rightarrow LCF} \cdot \mathbf{L}_{CF} \cdot \mathbf{T}_{LCD \rightarrow LCF} \cdot \mathbf{L}_{CD} \cdot \vec{v}_{LB}^0 &= \mathbf{T}(73.4\text{mm}, 1) \cdot \begin{pmatrix} -0.38^\circ \\ 3.17\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} -0.38^\circ \\ 2.67\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.11})$$

before entering the entrance window $\mathbf{L}_{G1}$ of the expansion chamber EXP. After passing $\mathbf{L}_{G1}$ the ray-tracing vector $\vec{v}_L^{IN}$ describing the outermost ray of laser beam LB entering EXP is given by

$$\vec{v}_{LB}^{IN} = \begin{pmatrix} -0.11^\circ \\ 2.55\text{mm} \end{pmatrix} = \mathbf{R}(D(1, 1.45, 22.5\text{mm})) \cdot \mathbf{T}(3.6\text{mm}, 1.45) \cdot \mathbf{R}(D(1.45, 1, 26.15\text{mm})) \cdot \begin{pmatrix} -0.38^\circ \\ 2.67\text{mm} \end{pmatrix}$$

Before entering the exit window $\mathbf{L}_{G2}$ of EXP it becomes $\vec{v}_{LB}^{OUT}$

$$\vec{v}_{LB}^{OUT} = \begin{pmatrix} -0.11^\circ \\ 2.38\text{mm} \end{pmatrix} = \mathbf{T}(45\text{mm}, 1) \cdot \begin{pmatrix} -0.11^\circ \\ 2.55\text{mm} \end{pmatrix}.$$

B.3.2 Transmitted laser beam

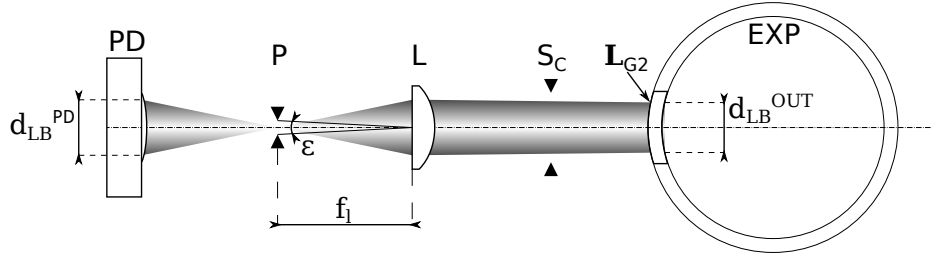


Figure B.3: Detailed schematics of the laser beam leaving expansion chamber EXP. $\mathbf{L}_{G2}$ is the exit window of EXP. PD, P, L and $\mathbf{S}_C$ are photo diode, pinhole, lens and circular stop of the lens-pinhole detector system measuring Φ_t .

The ray-tracing vector describing LB after leaving EXP is given by:

$$\begin{aligned} \mathbf{L}_{G2} \cdot \vec{v}_{LB}^{OUT} &= \mathbf{R}(D(1, 1.45, -26.15\text{mm})) \cdot \mathbf{T}(3.6\text{mm}, 1.45) \cdot \mathbf{R}(D(1.45, 1, -22.5\text{mm})) \cdot \begin{pmatrix} -0.11^\circ \\ 2.55\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} 0.16^\circ \\ 2.50\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.12})$$

and becomes

$$\begin{aligned} \mathbf{T}_{L_{G2} \rightarrow L} \cdot \mathbf{L}_{G2} \cdot \vec{v}_{LB}^{OUT} &= \mathbf{T}(171.33\text{mm}, 1) \cdot \begin{pmatrix} 0.16^\circ \\ 2.50\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} 0.16^\circ \\ 2.98\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.13})$$

before intercepting with L. After leaving the plano-convex lens it has the coordinates

$$\begin{aligned} \mathbf{L} \cdot \mathbf{T}_{L_{G2} \rightarrow L} \cdot \mathbf{L}_{G2} \cdot \vec{v}_{LB}^{OUT} &= \mathbf{R}(D(1, 1.458, \infty)) \cdot \mathbf{T}(3\text{mm}, 1.458) \cdot \mathbf{R}(D(1.458, 1, 18.83\text{mm})) \cdot \begin{pmatrix} 0.16^\circ \\ 2.98\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} -4.00^\circ \\ 2.86\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.14})$$

At the pinhole the outermost rays of LB are described by

$$\begin{aligned} \mathbf{T}_{L \rightarrow P} \cdot \mathbf{L} \cdot \mathbf{T}_{LG2 \rightarrow L} \cdot \mathbf{L}_{G2} \cdot \vec{v}_{LB}^{OUT} &= \mathbf{T}(34.07\text{mm}, 1) \cdot \begin{pmatrix} -4.00^\circ \\ 2.86\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} -4.00^\circ \\ 0.48\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.15})$$

And when intercepting with the photo diode PD it has the coordinates

$$\begin{aligned} \mathbf{T}_{L \rightarrow PD} \cdot \mathbf{L} \cdot \mathbf{T}_{LG2 \rightarrow L} \cdot \mathbf{L}_{G2} \cdot \vec{v}_{LB}^{OUT} &= \mathbf{T}(2\text{mm}, 1) \cdot \begin{pmatrix} -4.00^\circ \\ 0.48\text{mm} \end{pmatrix} \\ &= \begin{pmatrix} -4.00^\circ \\ 0.62\text{mm} \end{pmatrix} \end{aligned} \quad (\text{B.16})$$

Thus the inequalities for total transmission read

$$\begin{aligned} d_{LB}^{SC} &< 5.96\text{mm} < d_{SC} = 6\text{mm} \\ d_{LB}^L &= 5.96\text{mm} < d_L = 10\text{mm} \\ d_{LB}^P &= 0.96\text{mm} < d_P = 1.2\text{mm} \\ d_{LB}^{PD} &= 1.24\text{mm} \ll d_{PD} = 5\text{mm} \end{aligned}$$

B.3.3 Observation cones

Influence of glass-ring G on the length of light scattering volumina l_v

The divergence of the initially parallel light observation cone OC caused by glass-ring G can be expressed as

$$\vec{v}_{OC} = \mathbf{L}_{G1} \cdot \begin{pmatrix} 0^\circ \\ w_R/2 \end{pmatrix} \quad (\text{B.17})$$

where $\vec{v}_{OC}$ is the ray-tracing vector describing the outermost ray of OC inside EXP. w_R is the width of the rectangular stop S_R . If

$$\delta = \left(\mathbf{L}_{G1} \cdot \begin{pmatrix} 0^\circ \\ w_R/2 \end{pmatrix} \right)_1$$

describes the convergence of OC inside EXP, than the relative deviation σ_{rel}^{lv} between l_v given by

$$l_v = w_R / \sin \theta$$

and the length l'_v of V_s including the glass-ring effect:

$$l'_v = \frac{d_R \sin \delta + w_R/2}{\sin(\theta - \delta)} + \frac{d_R \sin \delta + w_R/2}{\sin(\theta + \delta)}$$

is given by

$$\sigma_{rel}^{lv} = \frac{l'_v - l_v}{l_v} \quad (\text{B.18})$$

Inserting the actual dimensions of the optical arrangement δ , σ_{rel}^{lv} and $\sigma_{rel}(\Phi_t/\Phi_i)$ from eq. (5.99) are:

θ	10°	15°	20°	25°	30°
δ	0.06°	0.22°	0.22°	0.22°	0.22°
σ_{rel}^{lv}	20%	21%	20%	21%	20%
$\sigma_{rel}(0.9)$	0.15%	0.17%	0.18%	0.20%	0.21%
$\sigma_{rel}(0.1)$	0.16%	0.17%	0.19%	0.21%	0.23%

Influence of glass-ring G on observation cone cross section A_{OC}^{PMT}

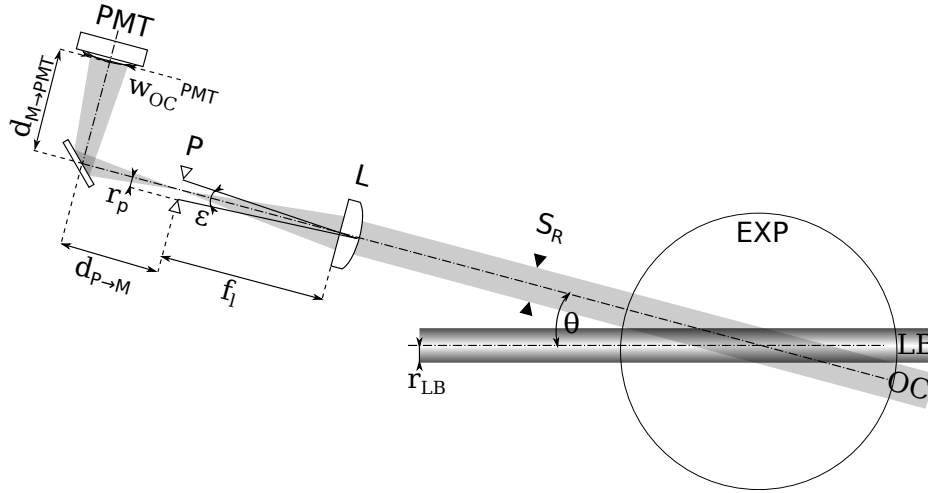


Figure B.4: Schematic diagram of the scattering geometry for calculations of the observation cone cross section A_{OC}^{PMT} when OC intercepts with photomultiplier tube PMT.

To calculate ratio of active area A_{OC}^{PMT} illuminated by observation cone OC, the width w_{OC}^{PMT} of OC can be determined according to

$$w_{OC}^{PMT}/2 = \frac{w_R/2 + r_P}{f_l} (d_{P \rightarrow M} + d_{M \rightarrow PMT}) + r_P$$

The height (normal to the plane of observation) of OC at PMT is given by

$$h_{OC}^{PMT}/2 = \frac{d_L/2 + r_P}{f_l} (d_{P \rightarrow M} + d_{M \rightarrow PMT}) + r_P$$

Inserting the actual values listed in appendix B.4 the cross section of OC $A_{OC}^{PMT} = w_{OC}^{PMT} \cdot h_{OS}^{PMT}$ when intercepting with PMT becomes

$$A_{OC}^{PMT} = \begin{cases} 2.52\text{mm}^2 & \theta = 10^\circ \\ 11.13\text{mm}^2 & \theta = 15^\circ, 20^\circ, 25^\circ, 30^\circ \end{cases},$$

which refers to 3% and 14% of the sensitive area $A_{PMT} = 7.5^2\pi\text{mm}^2$.

C Instrumentation and control

C.1 Source codes

Valve control

```

1  int incomingByte = 0;
   int incomingStop = 0;
3  char Flush[5];
   char Delay[5];
5  int i;
   int j;
7  unsigned long time;
   unsigned long time2;
9  int Flush\_time = 3000;
   int Delay\_time= 1500;
11 int V1=3;
   int V2=5;
13 int V3=6;
   int V4=7;
15 int V5=8;
   int V6=9;
17 int ADW=10;
   int counter=0;
19
   void setup()
21 {
   pinMode(V1, OUTPUT);
23 pinMode(V2, OUTPUT);
   pinMode(V3, OUTPUT);
25 pinMode(V4, OUTPUT);
   pinMode(V5, OUTPUT);
27 pinMode(V6, OUTPUT);
   pinMode(ADW, OUTPUT);

```

```
29   Serial.begin(9600);
30 }
31
32 void loop()
33 {
34     if (Serial.available() > 0)    //something came across serial
35     {
36         incomingByte = Serial.read();
37         if (incomingByte == 'P')
38         {
39             digitalWrite(V1, LOW);    //aerosol inlet open
40             digitalWrite(V2, LOW);    //expansion valve closed
41             digitalWrite(V3, HIGH);   //aerosol flow through chamber
42             digitalWrite(V4, LOW);    //bypass closed
43             digitalWrite(V5, LOW);    //pressure back closed
44             digitalWrite(V6, HIGH);   //recipient open
45             digitalWrite(ADW, LOW);   //no trigger signal
46
47             Serial.print("Cycle on flushing position – Turn the pumps ON!");
48         }
49         if (incomingByte == 'A')
50         {
51             do
52             {
53                 if (Serial.available())
54                 {
55                     Flush[i] = Serial.read();
56                     i++;
57                 }
58
59                 if(i<1)time = millis();
60             }
61             while (i<5&&(millis()-time) < 500);
62             {
63                 Flush[i] = 0;
64                 Flush\_time = atof(Flush);    //Change value from string to number
65                 i=0;
66             }
67         }
68
69         if (incomingByte == 'B')
70         {
71             do
72             {
73                 //If serial available write to data (up to 7 byte) or wait
74                 //for 0,5 seconds after first received byte.
75
76                 if (Serial.available())
```

```

77     {
78         Delay[j] = Serial.read();
79         j++;
80     }
81
82     if(j<1)time2 = millis();
83 }
84 while (j<5&&(millis()-time2) < 500);
85 {
86     //Finite zero for valid string.
87
88     Delay[j] = 0;
89     Delay\_time = atof(Delay);    //Change value from string to number
90     j=0;
91 }
92 }
93
94 if (incomingByte == 'C')
95 {
96     do
97     {
98         //Flushing
99
100         Serial.print("Flushing \n");
101
102         digitalWrite(V1, LOW); //aerosol Inlet open
103         digitalWrite(V2, LOW); //expansion valve closed
104         digitalWrite(V3, HIGH); //aerosol flow through chamber
105         digitalWrite(V4, LOW); //bypass closed
106         digitalWrite(V5, LOW); //pressure back closed
107         digitalWrite(V6, HIGH); //recipient open
108         digitalWrite(ADW, LOW); //no trigger signal
109         delay(Flush\_time);    //duration = preset flushing time
110
111         //Flushing ->Delay
112
113         Serial.print("Delay \n")
114
115         digitalWrite(V1, HIGH); //aerosol inlet closed
116         digitalWrite(V3, LOW); //aerosol through chamber closed
117         digitalWrite(V4, HIGH); //bypass open
118         digitalWrite(V6, LOW); //recipient closed
119         digitalWrite(ADW, LOW); //no trigger signal
120         delay(Delay\_time);    //aerosol in chamber equilibrating for preset
121                                //delay-time
122
123         //Expansion

```

```
125     digitalWrite(ADW, HIGH);           //trigger signal before expansion –
127                                         //otherwise initialization peak bigger
                                         //than pressure drop@Kistler

129     delay(500);                         //data acquisition starts
                                         //500ms before Expansion

131

133     Serial.print("Expansion \n");

135     digitalWrite(V2, HIGH);             //expansion valve open

137     delay(1000);                        //expansion for 1s

139     //Pressure Back

141     Serial.print("Pressure Back \n");

143     digitalWrite(V2, LOW);              //expansion valve closed
145     digitalWrite(V5, HIGH);            //pressure back open
147     digitalWrite(ADW, LOW);            //no Trigger signal

149     delay(200);

151     digitalWrite(V1, HIGH);             //aerosol inlet closed
153     digitalWrite(V6, HIGH);            //recipient open

155     delay(5000);                        //pressure back duration 3s

157     //Cycle Back

159     digitalWrite(V1, LOW);              //aerosol inlet open
161     digitalWrite(V3, HIGH);            //aerosol through chamber
163     digitalWrite(V4, LOW);             //bypass closed

165     if (Serial.available())
    {
        incomingByte = Serial.read()
    }
    while (incomingByte != 'S');

167     if (incomingByte == 'X')
    {
169         Serial.print("Flush the chamber for 30 minutes!");
        digitalWrite(V1, LOW);           //aerosol inlet open
        digitalWrite(V2, LOW);           //expansion valve closed
        digitalWrite(V3, HIGH);          //aerosol through chamber
```

```

173     digitalWrite(V4, LOW);           //bypass closed
      digitalWrite(V5, LOW);           //pressure back closed
175     digitalWrite(V6, HIGH);          //recipient open
      digitalWrite(ADW, LOW);          //no trigger signal
177 }

179 if (incomingByte == 'Y')
    {
181     Serial.print("All valves turned off – Turn the pumps OFF!");
      digitalWrite(V1, LOW);           //aerosol inlet open
183     digitalWrite(V2, LOW);           //expansion valve closed
      digitalWrite(V3, LOW);           //aerosol through chamber
185     digitalWrite(V4, LOW);           //bypass closed
      digitalWrite(V5, LOW);           //pressure back closed
187     digitalWrite(V6, LOW);           //recipient open
      digitalWrite(ADW, LOW);          //no trigger signal
189     }
    }
191 }

```

ADWIN - AOUT.bas

```

#include ADwinPro_All.inc
2
Dim data_3[16] As Long           //Array for 8 analog output
4 Dim data_2[16] As Long           //Array for 8 analog outputs

6 Init:
    P2_DAC8(1,data_3,1)           //Set analog outputs = data_3
8                                   //Initial values for analog outputs = 0V

10 Event:
    P2_DAC8(1,data_2,1)           //Set analog outputs = data_2
12                                   //PMT bias voltage and setpoint for
                                   //subpressure in vessel

14 Finish:
    P2_DAC8(1,data_3,1)           //Set analog outputs = data_3
16                                   //Reset AOUTs to 0V

```

ADWIN - AIN.bas

```

1 #include ADwinPro_All.inc

```

```
3 #Define AIN1 10 //Module address first AinF
5 #Define AIN2 11 //Module address second AinF
7 #Define LEN 720000 //Number of data acquired during one run
9 dim index as long
  dim Data_1[LEN] as long //Data_1 = Array for acquired data
11 dim Pattern as long
13 init:
  index =1
15  Pattern = shift_left(1, (AIN1 - 1)) or shift_left(1, (AIN2 - 1))
  //Generate pattern to read AIN cards
17
  Processdelay = 1010 //Measuring frequency = 30kHz
19
  par_10 = -1 //Flag for process is running
21
  P2_Sync_all(Pattern)
23
  P2_DigProg(4,1100b) //Configure DIO module with address no. 4:
25 //Bit 0-7,8-15 as Input;
  //Bit 16-23, 24-31 as Output'
27
event:
29  P2_Digout(4,16,1) //DIO module 4 bit 16 = high -> PS Valves ON
31
  If (P2_Digin_Long(4) > 0) Then
    Par_4 = 1
33    P2_Read_ADCF8(AIN1, Data_1, index)
    P2_Read_ADCF8(AIN2, Data_1, index + 8)
35    P2_Sync_all(Pattern) //Start conversion on both AIN cards
    //synchronously
37    index = index + 16
    if (index >= LEN) then end
39
  Else
41    Par_4 = 0
  Endif
43
finish:
45  par_10 = 1 //Flag for process is terminated
  Par_4 = 0 //Stop data acquisition in LabView
47  P2_Digout(4,16,0) //Turn off PS Valves
```

C.2 Pin configuration

ADWIN

Input #	1	2	3	4	5	6	7	8
Signal	Φ_t	Φ'_i	$\Phi_{10^\circ}^L$	$\Phi_{15^\circ}^L$	$\Phi_{20^\circ}^L$	$\Phi_{25^\circ}^L$	$\Phi_{30^\circ}^L$	$\Phi_{10^\circ}^R$

Table C.1: Pin configuration of analogue input module I.

Input #	9	10	11	12	13	14	15	16
Signal	$\Phi_{15^\circ}^R$	$\Phi_{20^\circ}^R$	$\Phi_{25^\circ}^R$	$\Phi_{30^\circ}^R$	Δp	Δp_R	p_i	RH

Table C.2: Pin configuration of analogue input module II.

Output #	1	2	3	4	5	6	7	8
Signal	V_{PMT}	V_{PMT}	V_{PMT}	V_{PMT}	V_{PMT}	Δp_R^{SET}	NC	NC
Pin #	19	18	17	16	15	14	13	12

Table C.3: Pin configuration of the analogue output module. NC = not connected.

Bit #	0-15	16	17-27,29-31	28
Signal	NC	PS_Valves	NC	DAQ Trigger
Pin #	12-19,30-37	11	4,6-10,22-29	5

Table C.4: Pin configuration of the digital input/output module.

C.3 Circuit diagrams

Valve control

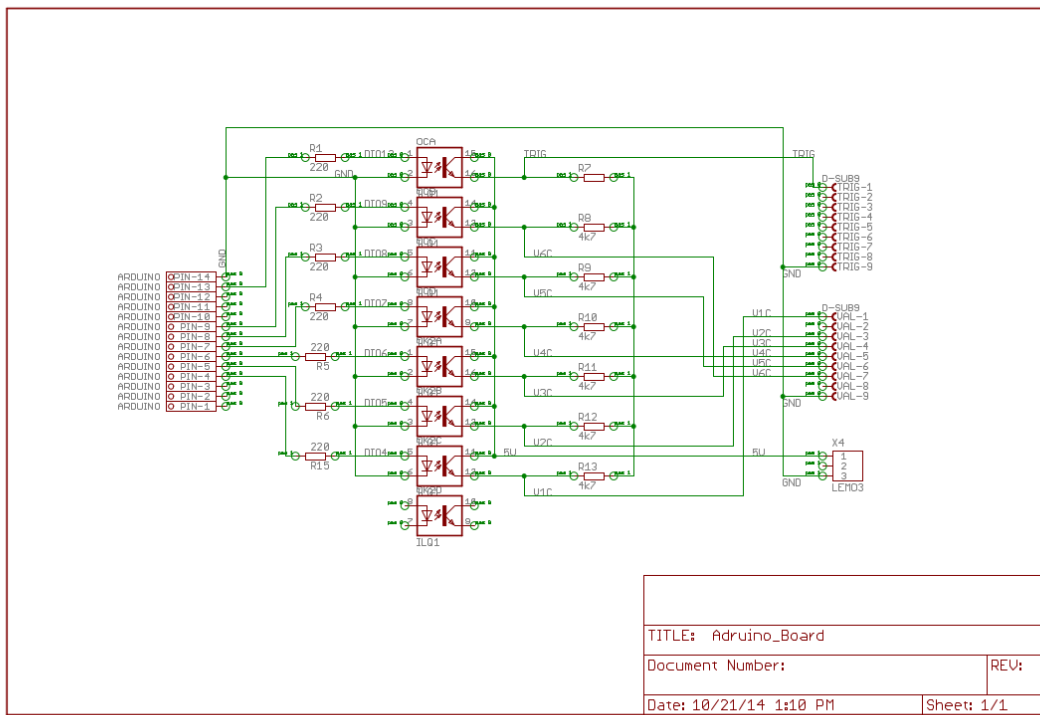


Figure C.1: Circuit diagram microcontroller board.

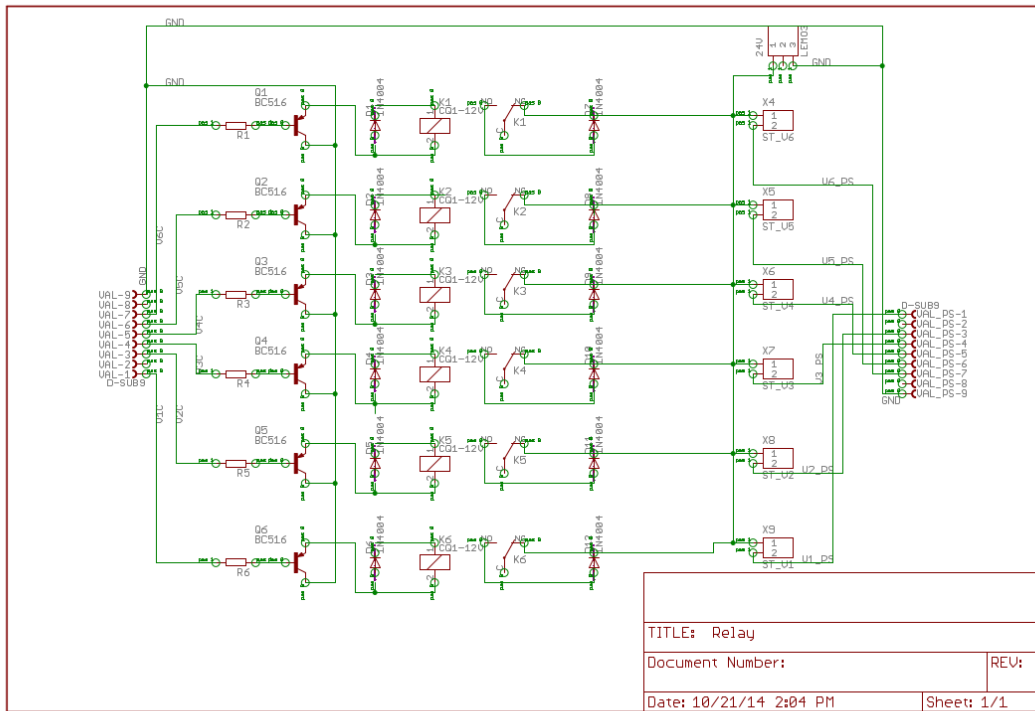


Figure C.2: Circuit diagram relay board.

C.4 Instrument configuration

Charge meter

Parameter	Value
2nd order lowpass filter	OFF
5th order lowpass filter	OFF
Highpass filter	OFF
Output voltage range	0-10V
Control mode	Remote
Mode of mechanical unit for sensor sensitivity	Metric
Mechanical unit for sensor sensitivity	pC/bar
Sensor sensitivity	58.6
Measurement range	0.5 bar

Table C.5: Configuration Parameters of the Kistler charge meter.

D Counting efficiency

D.1 Fitting parameters (table D.1)

Chemical Composition	Q_{inlet} [l/min]	Charging State	T_{CH}/T_{HUM} [°C]	a	L [m]	d_{50} [nm]	d_{10} [nm]
Ag	9.0	Charged	25/23	1.00	18.50	3.95	2.26
Ag	3.0	Charged	25/23	0.67	5.21	6.45	2.20
Ag	1.6	Charged	25/23	0.61	9.88	-	4.2
Ag	9.0	Neutral	25/23	0.97	11.63	3.20	1.80
Ag	3.0	Neutral	25/23	0.87	4.08	3.75	1.87
Ag	1.6	Neutral	25/23	0.83	5.78	6.33	3.05
[NH ₄] ₂ SO ₂	9	Charged	25/23	0.67	7.05	4.28	1.47
NaCl	1.6	Charged	25/23	0.35	10.02	-	4.95
NaCl	1.6	Neutral	25/23	0.41	5.87	-	3.57
WO _x	3	Charged	25/23	1.1365	2.9186	-	1.53
WO _x	3	Neutral	15/13	0.85	1.83	-	1.25

Table D.1: Fitting parameters a and L and corresponding particle diameters d_{50} and d_{10} for various seed particles and n-propanol vapor.

E Field campaign contour plots

High temperature settings

At high temperature settings chamber and humidifier temperatures were 25°C and 23°C, respectively. vSANC has been operated at high temperature settings from March 25 to April 18, 2014. Contour plots from this period are shown in fig. E.1, E.2, E.3, E.4 and E.5.

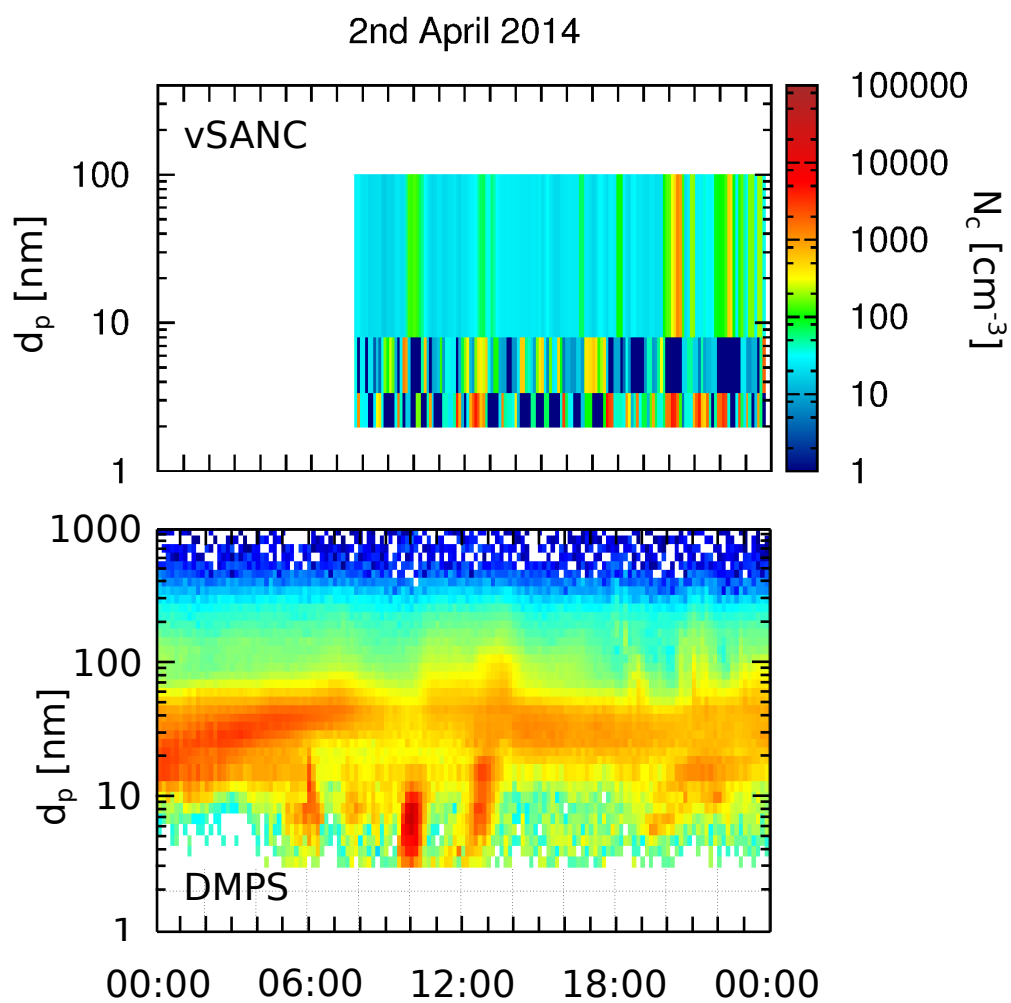


Figure E.1: vSANC and DMPS contour plots from April 2nd, 2014.

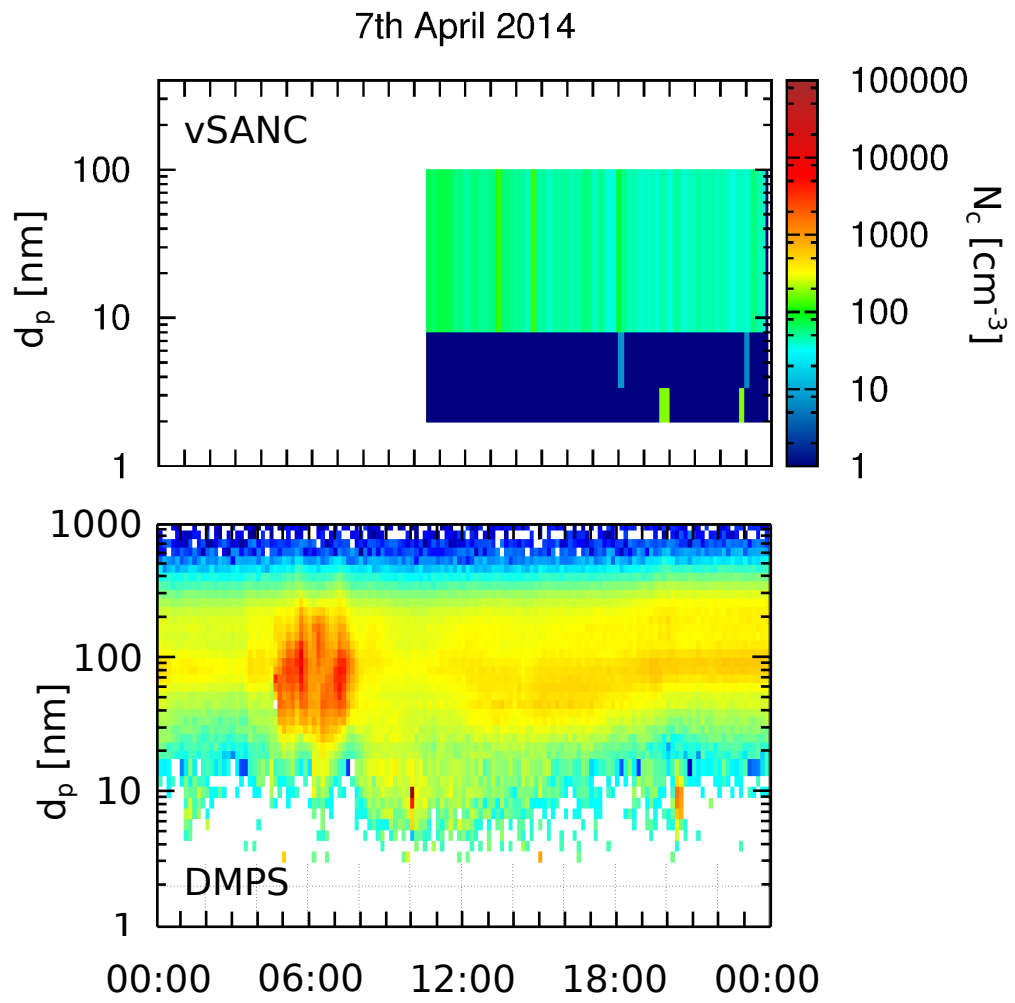


Figure E.2: vSANC and DMPS contour plots from April 7th, 2014.

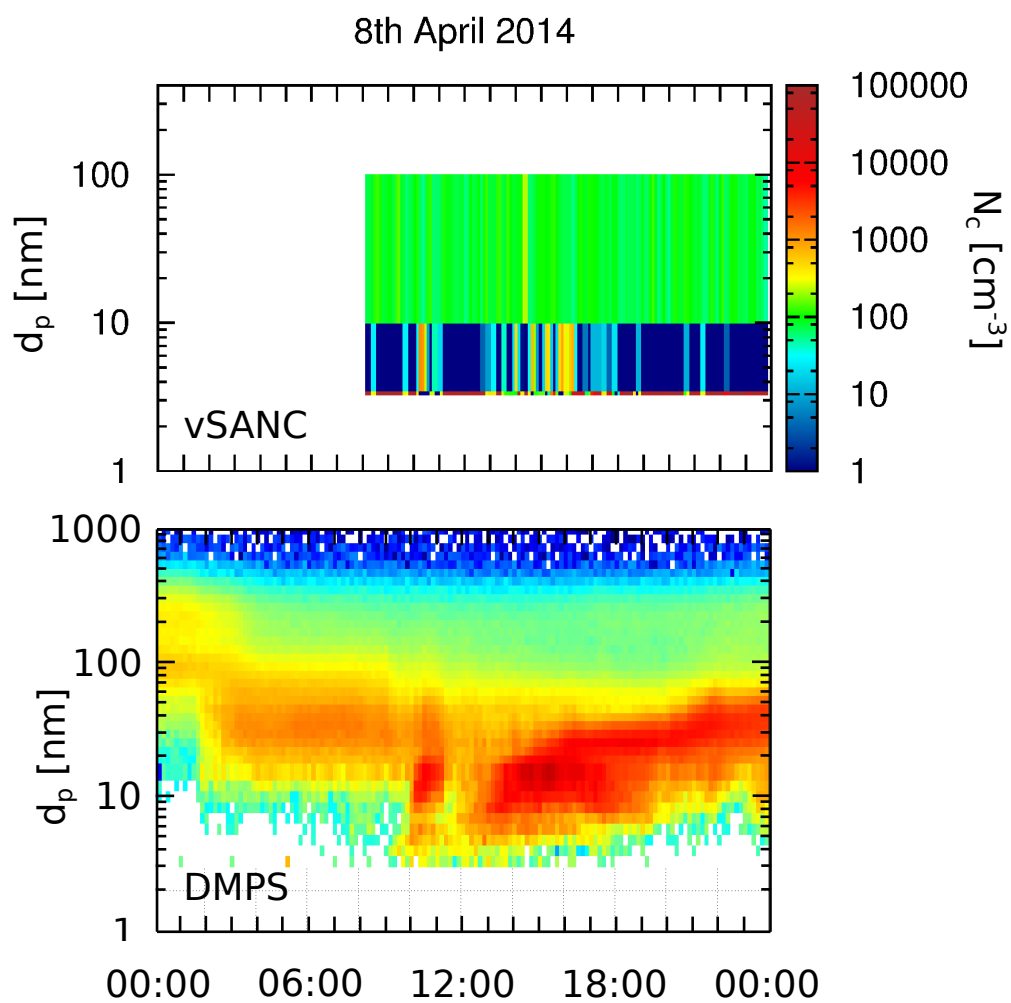


Figure E.3: vSANC and DMPS contour plots from April 8th, 2014.

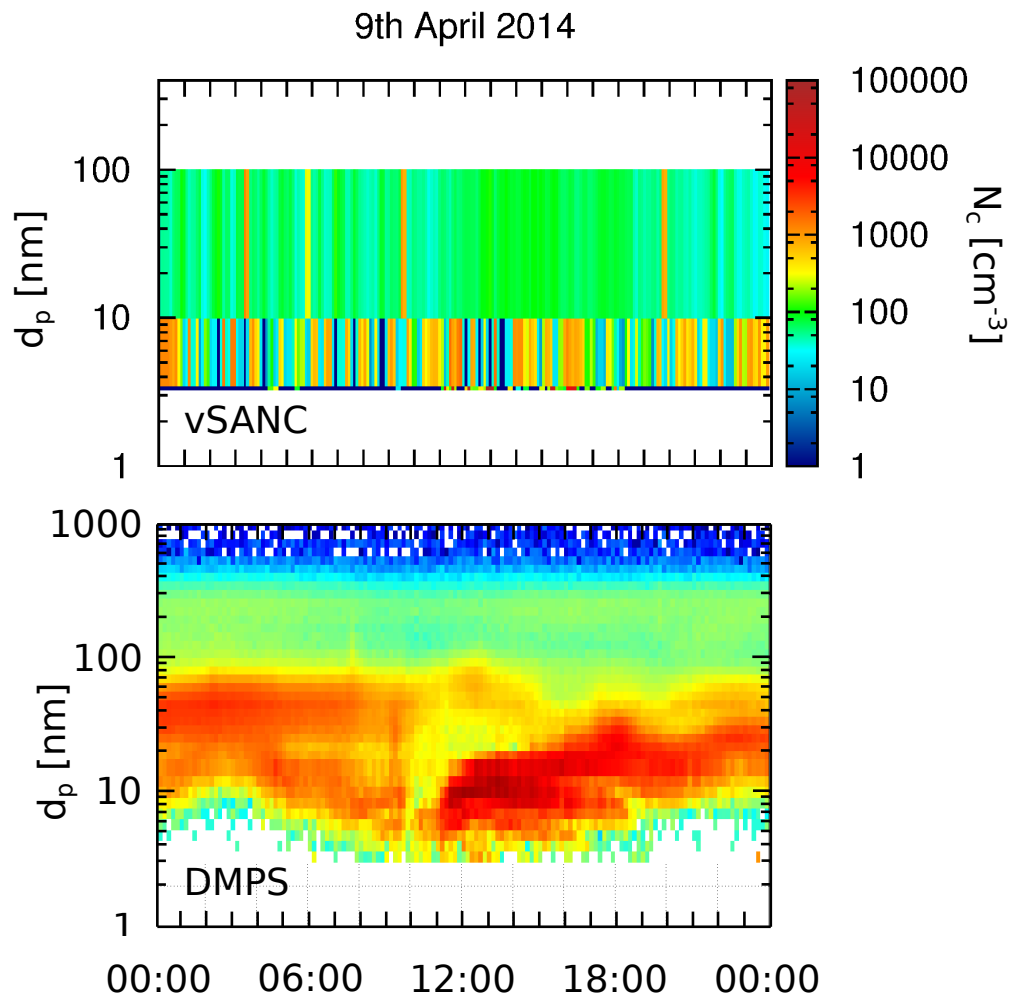


Figure E.4: vSANC and DMPS contour plots from April 9th, 2014.

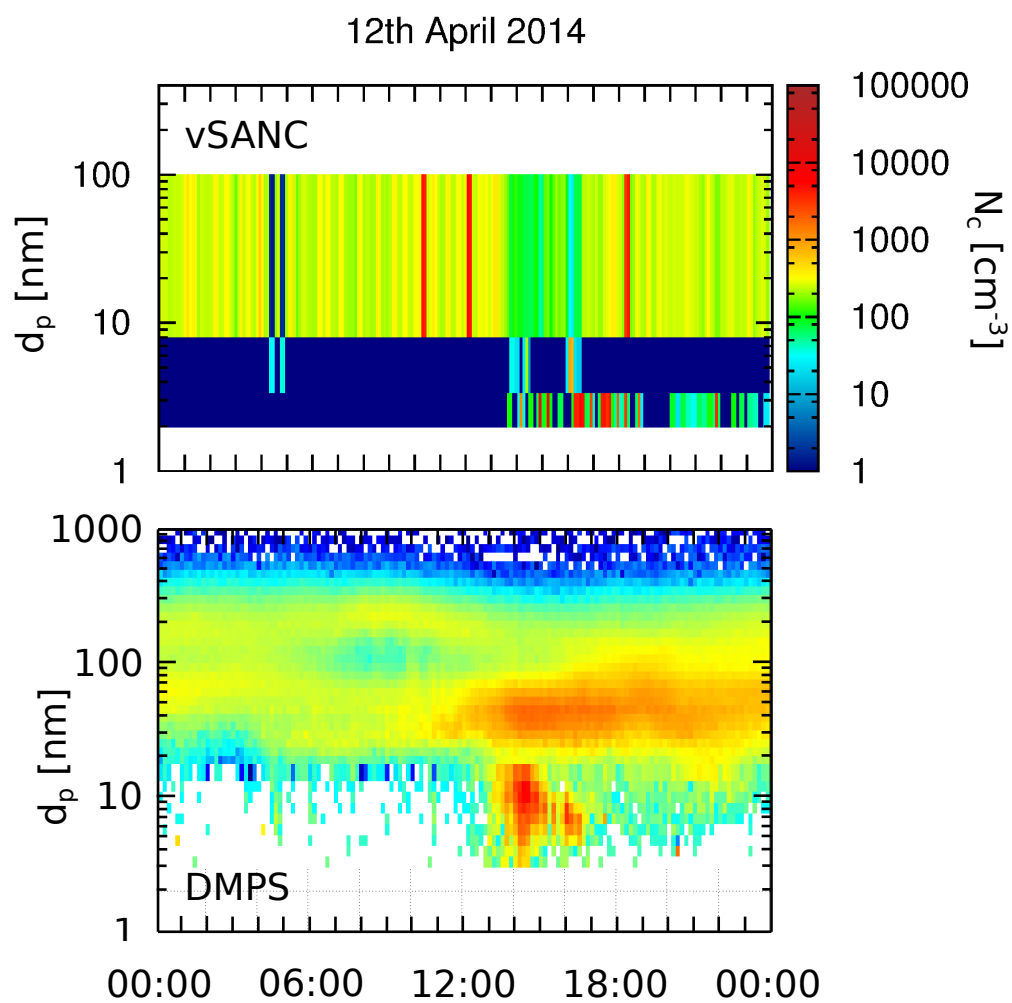


Figure E.5: vSANC and DMPS contour plots from April 12th, 2014.

Low temperature settings

Between April 20 and May 21 vSANC has been operated at low temperature settings, where chamber and humidifier temperatures were 15°C and 13°C, respectively. Contour plots corresponding to that measuring period are shown in fig. E.6, E.7, E.8, E.9, E.10, E.11 and E.12.

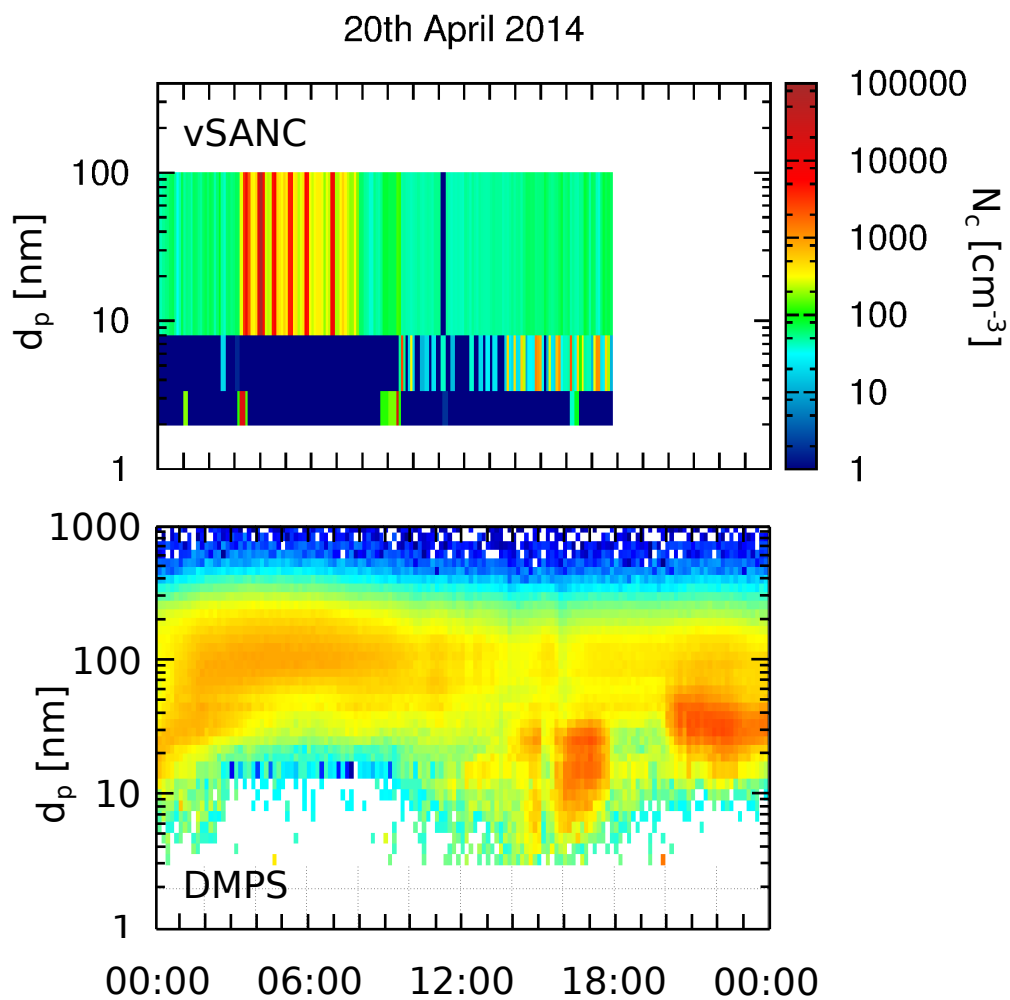


Figure E.6: vSANC and DMPS contour plots from April 20th, 2014.

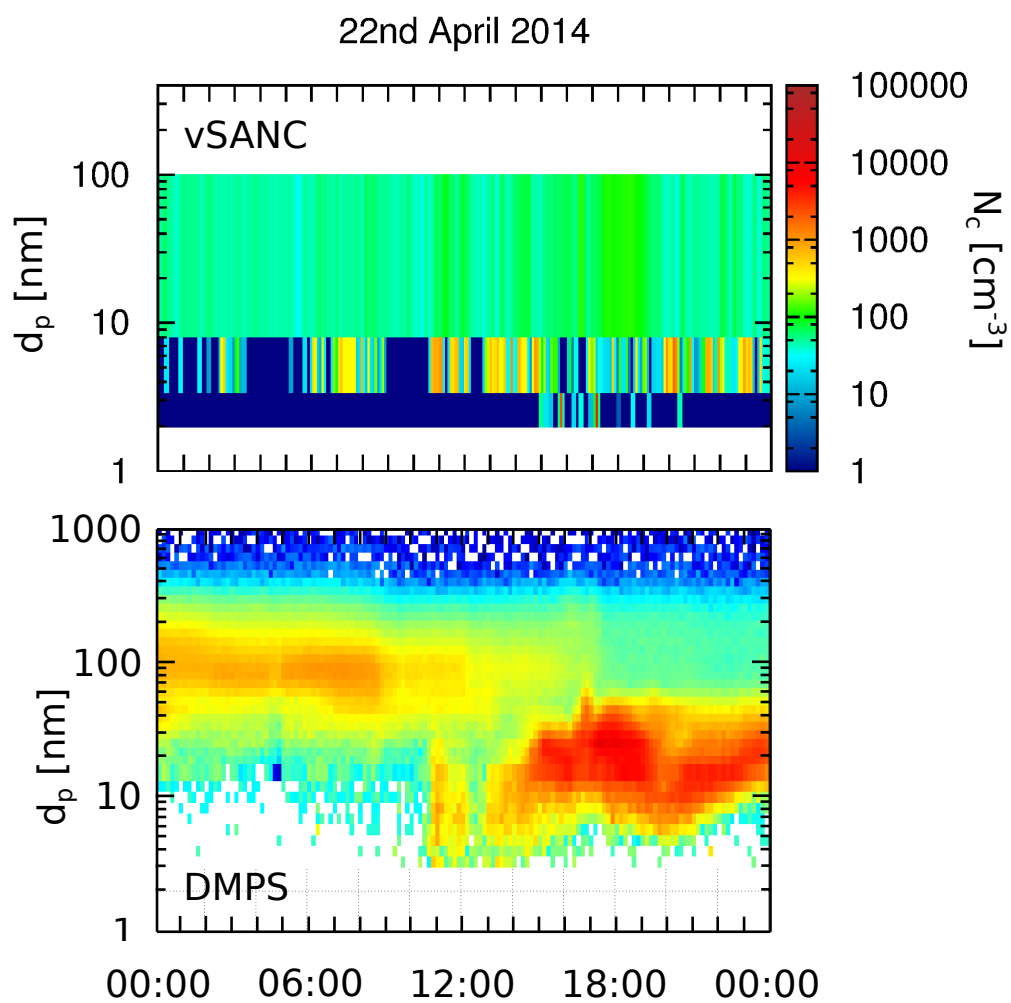


Figure E.7: vSANC and DMPS contour plots from April 22nd, 2014.

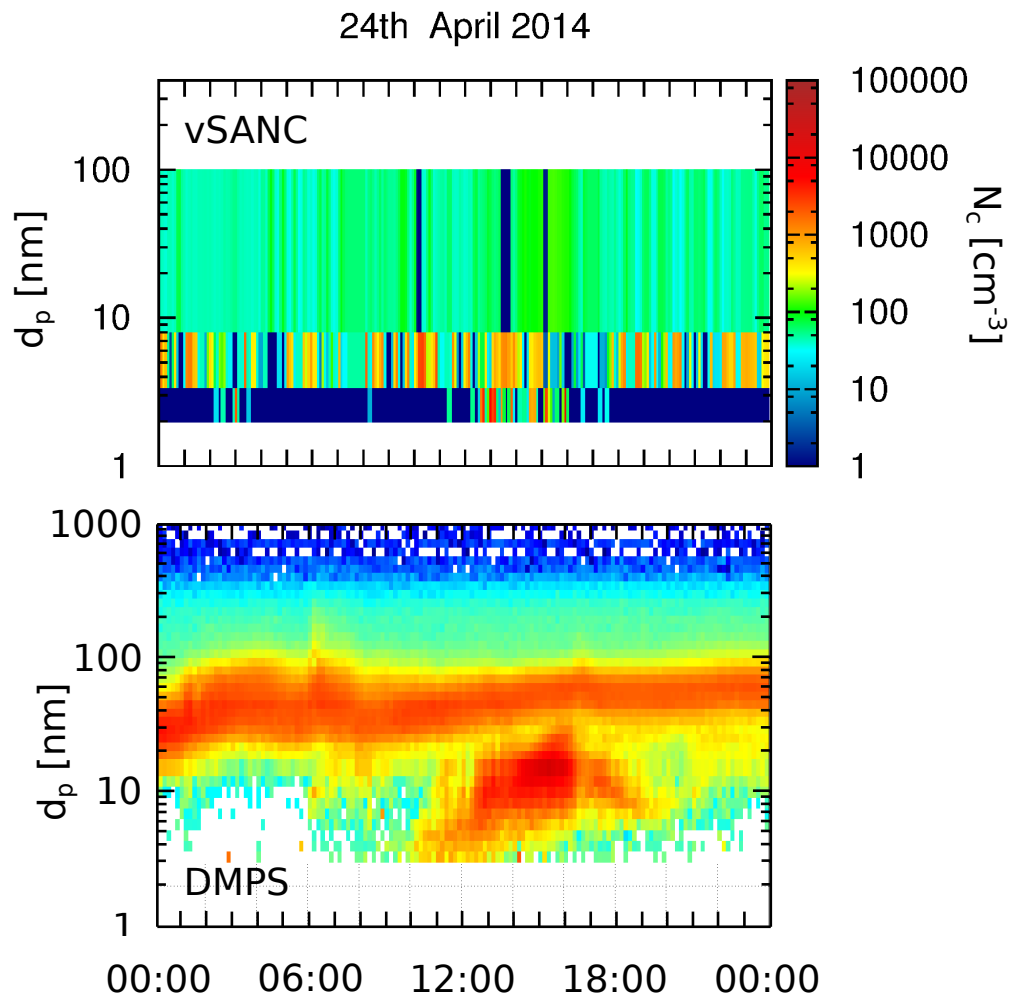


Figure E.8: vSANC and DMPS contour plots from April 24th, 2014.

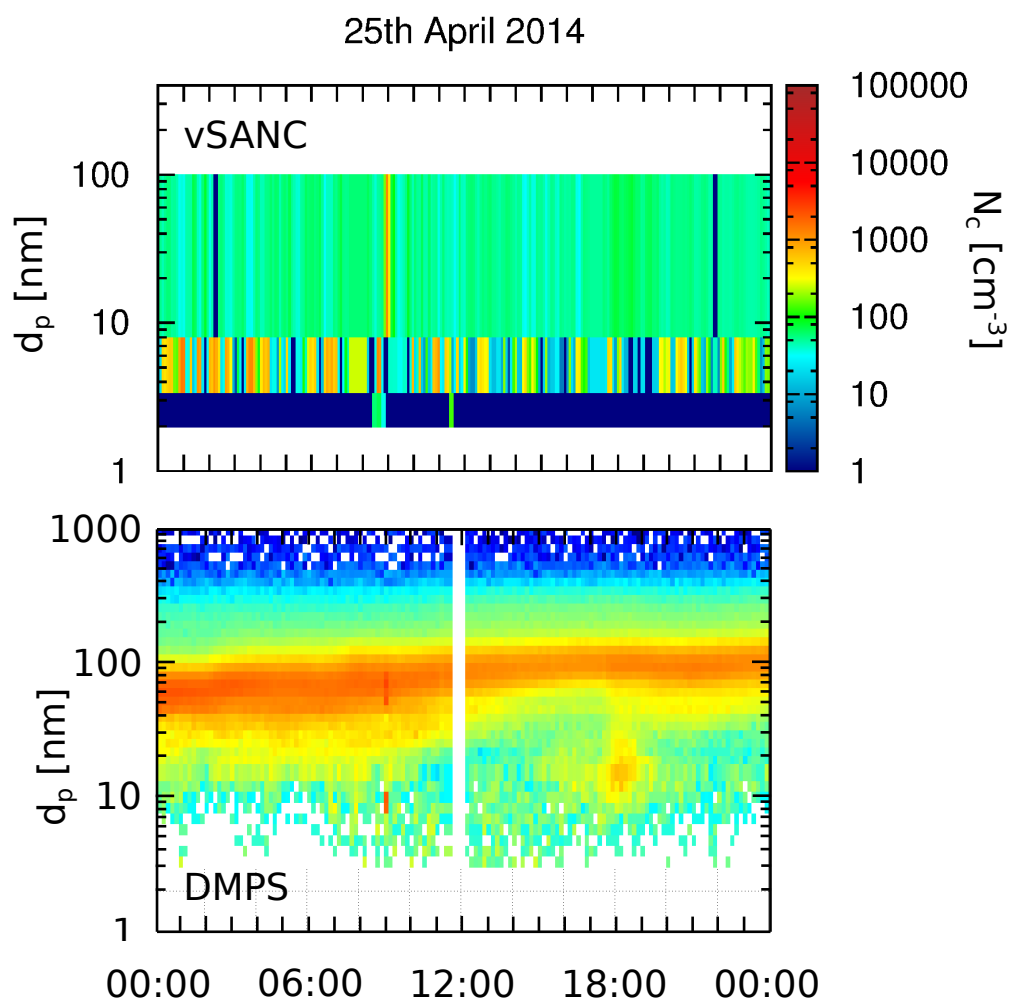


Figure E.9: vSANC and DMPS contour plots from May 25th, 2014.

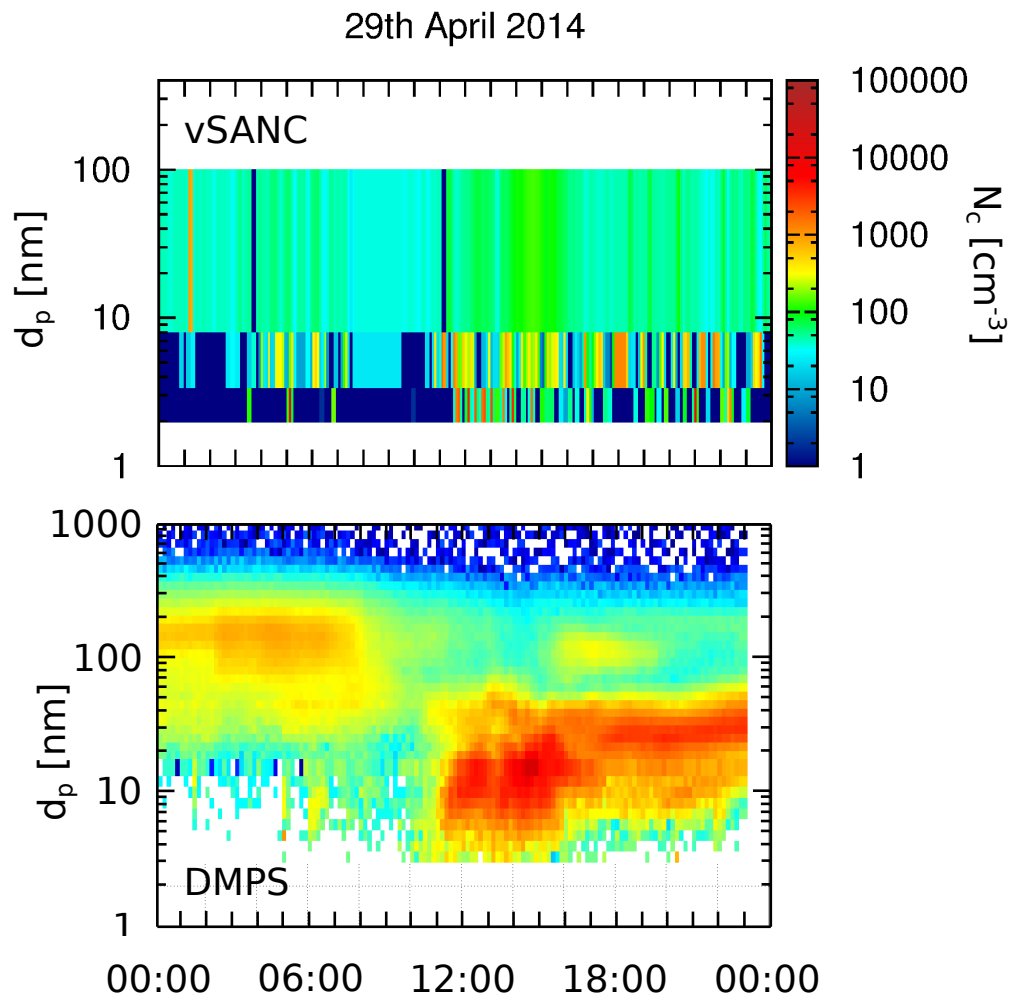


Figure E.10: vSANC and DMPS contour plots from April 29th, 2014.

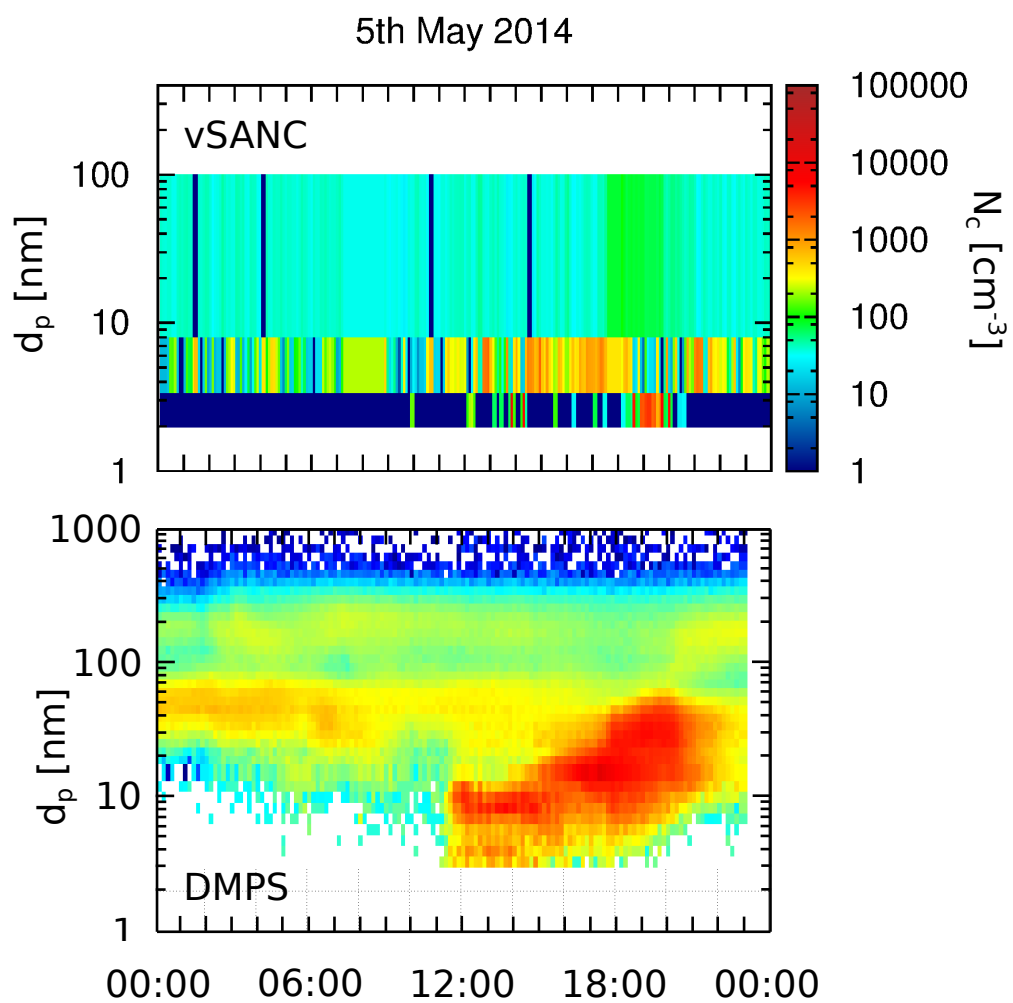


Figure E.11: vSANC and DMPS contour plots from May 5th, 2014.

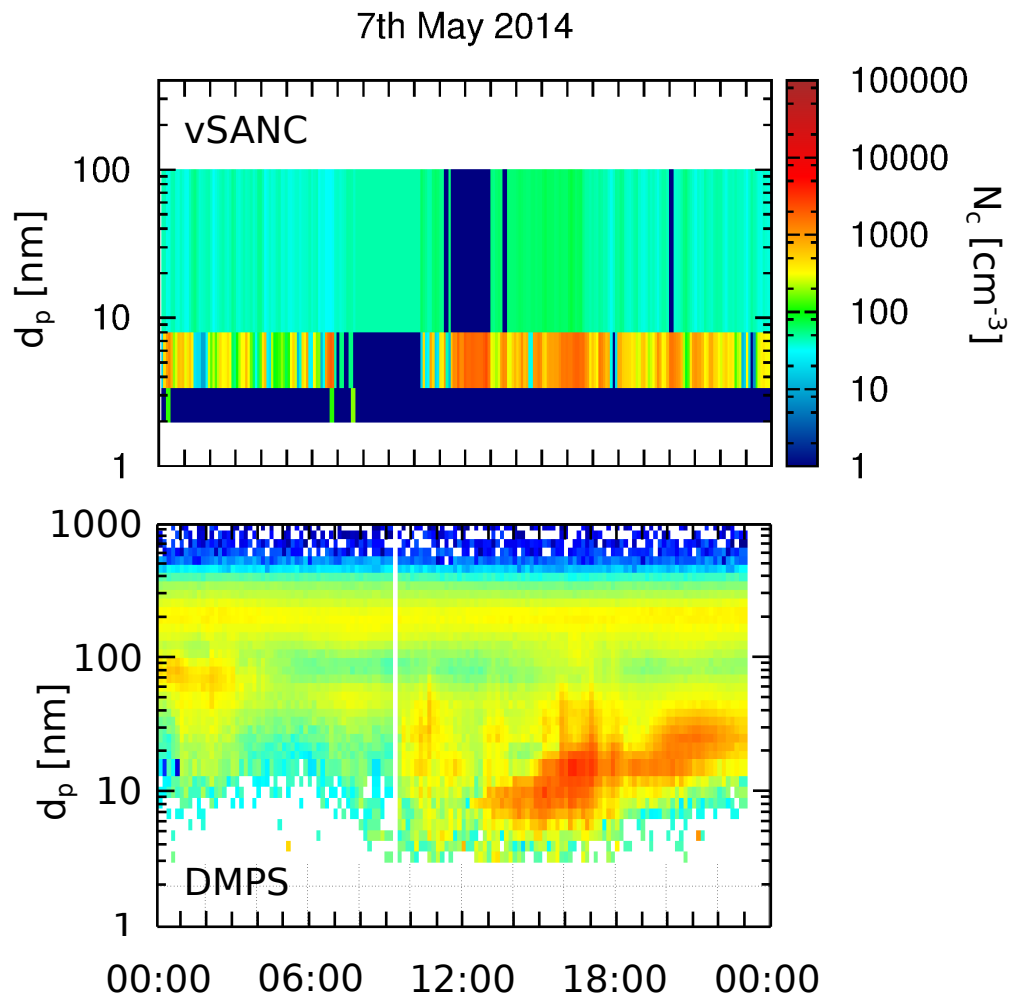


Figure E.12: vSANC and DMPS contour plots from May 7th, 2014.

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Curriculum Vitae

Tamara Pinterich

Date of birth	February 25th, 1986
Place of birth	Vienna
Nationality	Austria

Education

09/2004 - 06/2009	Master Program in Physics <i>Faculty of Physics, Aerosol- and Environmental Physics, University of Vienna, Austria.</i> Graduation with highest distinction Thesis title: "Temperature Dependence of the Contact Angle for 1-Propanol on Silver and on Sodium Chloride Substrate" Adviser: Prof. Paul E. Wagner
06/2004	High school graduation with highest distinction <i>Gymnasium Sacré-Coeur, Vienna, Austria</i>

Work Experience

10/2012 - 04/2015	PhD Scholarship <i>Department of Physics, University of Helsinki, Finland.</i>
07/2009 - 09/2012	PhD Position <i>Faculty of Physics, University of Vienna, Austria.</i>

International Experience

10/2014	CLOUD campaign at CERN, Switzerland
03/2014 - 05/2014	Spring campaign at SMEAR II in Hyytiälä, Finland.
02/2014	Research visit at the Department of Physics, University of Helsinki, Finland.

Teaching Experience (University of Vienna)

09/2009 - 06/2015	Lecturer, Methods of Experimental Physics I and II
03/2012 - 06/2012	Lecturer, Aerosol Physics Senior Lab Course
09/2011 - 06/2012	Teaching Assistant, Introduction to Physics I and II
07/2011 - 09/2011	Co-Supervision of a bachelor thesis
03/2006 - 06/2006	Tutor for entrance level class “Women in Physics”

Scholarships and Prizes

10/2012 - 04/2015	Scholarship, University of Helsinki
08/2012	1st Prize Poster Contest, Hyytiälä, Finland
06/2012	Jury Prize at FameLab Austria
10/2013 - 10/2014	6 Travel grants <i>US Department of Energy, Association for Aerosol Research, Austrian Research Association, Faculty of Physics</i> , for oral presentations at international conferences.

Skills

Computer	LabView, Eagle, Solid Works, Basic, C, MS Office, Windows and Linux, data processing and laboratory applications.
Technical	Design and development of innovative instrumental methods (optomechanics), electronic circuits, data acquisition and processing softwares, manufacturing
Language	German (native), English (fluent), Korean (basic)

Outreach activities

03/2014	Personal portrait at the TV show “Newton”, Austrian public service broadcaster (ORF)
01/2013	Participant at the physics:open, an information event for high school students at the Faculty of Physics, University of Vienna
11/2012	Role model for “Science: It’s a girl thing!” an initiative (WiST2) of the European Commission
06/2012 - 06/2014	Several invited lectures at YO!Tech an information event for high school students, Technical Museum Vienna
10/2012	Invited lecture at HighHeel@HighEnd, a project to promote women in technical professions, Vienna
11/2010	Participant at the 1st Vienna Science Slam (TV broadcast)
05/2010 - 09/2011	Demonstration of experiments at public places in Austria (“Physik Mobil”)
09/2010	Invited lecture at the Federal Ministry of Science and Research
06/2010	Finalist at FameLab Austria

Memberships

- Association for Aerosol Research (Gesellschaft für Aerosolforschung)
- Austrian Chemical-Physical Society (Chemisch Physikalische Gesellschaft)

Publications and presentations

Peer-Reviewed Papers

1. T. Pinterich, P.M. Winkler, A. Vrtala and P.E. Wagner, “Experiments on the Contact Angle of n-Propanol on Differently Prepared Silver Substrates at Various Temperatures and Implications for the Properties of Silver Nanoparticles”, *Atmos. Res.* **101**, 510 (2011).
2. S. Schobesberger, P.M. Winkler, T. Pinterich, A. Vrtala, M. Kulmala and P.E. Wagner, “Experiments on the Temperature Dependence of Heterogeneous Nucleation on Nanometer-Sized NaCl and Ag Particles”, *ChemPhysChem.* **11**, 3874 (2010).

Conference Proceedings

1. T. Pinterich, P. M. Winkler, P. E. Wagner, M. Kulmala and A. Vrtala, “The versatile Size Analyzing Nuclei Counter – vSANC”, *AIP Conf. Proc.* **1527**, 161-164 (2013).

Conference Presentations (*presenting author)

Oral

1. T. Pinterich*, P. M. Winkler, P. E. Wagner and M. Kulmala, “A new expansion chamber CPC for efficient sub 2nm particle detection”, *International Aerosol Conference*, Busan, Korea (2014)
2. T. Pinterich*, P. M. Winkler, P. E. Wagner, M. Kulmala, A. Vrtala, “The versatile Size Analyzing Nuclei Counter (vSANC)”, *European Aerosol Conference*, Prague, Czech Republic (2013).
3. T. Pinterich*, P. M. Winkler, P. E. Wagner, M. Kulmala, A. Vrtala, “The versatile Size Analyzing Nuclei Counter – vSANC”, *International Conference on Nucleation and Atmospheric Aerosols*, Fort Collins, Colorado, USA (2013).
4. T. Pinterich*, P. M. Winkler, P. E. Wagner, M. Kulmala, A. Vrtala, “The vSANC - An instrument for basic nucleation studies and ambient measurements of nanoparticles”,

31st Annual Meeting of the American Association of Aerosol Research, Minneapolis, Minnesota, USA (2012).

5. T. Pinterich*, P. M. Winkler, P. E. Wagner, M. Kulmala, A. Vrtala, “A new expansion chamber CPC applicable to atmospheric measurements”, *European Aerosol Conference*, Granada, Spain (2012).

Poster

1. T. Pinterich*, P. M. Winkler, P. E. Wagner, A. Vrtala, “Development of a versatile Size Analyzing Nuclei Counter - The vSANC”, *European Aerosol Conference*, Manchester, UK (2011).
2. T. Pinterich*, P. M. Winkler, P. E. Wagner, A. Vrtala, “Wetting of silver surfaces by n-propanol at different surface-layer thickness”, *International Aerosol Conference*, Helsinki, Finland (2010).
3. T. Pinterich*, P. M. Winkler, P. E. Wagner and A. Vrtala, “Temperature dependence of the contact angle for n-propanol on silver and on sodium chloride substrate”, *European Aerosol Conference*, Karlsruhe, Germany (2009).